Explorations of *N-C* Atropisomerism in Indigo Diimines and Related Complexes

by

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B.Sc., University of New Brunswick, 2013

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Supervisory Committee

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Abstract

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This study focused on the preparation and characterization of new indigo diimine (Nindigo) derivatives as a new atropisomeric scaffold. *Trans*- and *cis*- indigo diimines were studied and structure-property relationships were investigated regarding *N*-*C* atropisomerism using variable temperature ^{1}H NMR studies and density functional theory calculations.

Neutral *trans*- and protonated *cis*-Nindigos were prepared featuring a variety of mono *ortho*-substituted aryl imine groups with varying levels of steric bulk. The neutral *trans*-Nindigo derivatives generally have smaller *N*-*C* rotational energy barriers than their protonated *cis*-congeners. This finding is consistent with the latter having closer proximity of the *N*-aryl groups to each other, leading to steric repulsions between the two groups. The *N*-*C* rotational energy barriers are substituent dependent; the *N*-*C* rotational energy barriers of mono *ortho* substituted *trans*-Nindigos were in the range of 6.0 – 16.4 kcal/mol and can be classified as predominantly "*Class 1*' atropisomers as defined by LaPlante, while the mono *ortho* substituted protonated *cis*-Nindigo analogs have *N*-*C* rotational barriers between 12.3 – 25.5 kcal/mol and are classified as "*Class 1"* and "*Class 2"* atropisomers. The introduction of additional substituents onto the other *ortho* position of

the aryl imine subunit has significant consequences for the *N-C* rotational energy barriers of both the neutral *trans*- and protonated *cis*-Nindigos making them stable, or close to being, *'Class 3*' atropisomers, having *N-C* rotational energy barriers between 31.5 – 276.9 kcal/mol and 29.3 – 32.6 kcal/mol respectively.

Recognizing that the protonation state induced *trans*- to *cis*-isomerization process could have significant consequences regarding the potential applicability of these atropisomeric Nindigo derivatives, *cis*-Nindigo derivatives were synthesized that contained a tether (oxalyl or palladium (II) acetylacetonate) between the two indole type nitrogens of the Nindigo, which prevent the central -C=C- from isomerizing. The *N-C* rotational barriers of the tethered *cis*-Nindigos also displayed substituent dependent *N-C* rotational energy barriers. The protonation state of the *N, N'*-oxalyl bridged *cis*-Nindigos has a significant impact (higher in energy by a minimum of 5.1 kcal/mol) on the *N-C* rotational barriers; the neutral *N, N'*-oxalyl bridged *cis*-Nindigos have *N-C* rotational energy barriers ranging between 11.8 – 14.9 kcal/mol, classifying them as "*Class 1"* atropisomers, while their protonated congeners have *N-C* rotational energy barriers between 16.9 – 19.8 kcal/mol, which classifies them as "*Class 1*" atropisomers but are on the cusp of being "*Class 2*" atropisomers. The size of the tether influences the N-C rotational energy barriers of *cis*-Nindigos; the one-atom bridged palladium (II) acetylacetonate complexes have generally lower N-C rotational energy barriers than their protonated *N, N'*-oxalyl bridged *cis*-Nindigo congeners. The palladium acetylacetonate tethered *cis*-Nindigo complexes displayed substituent *N-C* rotational energy barrier dependence and the mono *ortho* substituted analogs have *N-C* rotational energy barriers between 12.4 – 20.2 kcal/mol and are predominantly *"Class 1"* atropisomers, while the

bulkier analogs are "*Class 2"* atropisomers. The palladium (II) acetylacetonate *cis*-Nindigo complexes that have aryl imine groups with a 2,6-disubstitution pattern have *N*-*C* rotational energy barriers greater than 19.7 and 20.2 kcal/mol and are presumed to be stable *"Class 3"* atropisomers like their unbridged neutral *trans*- and protonated *cis*-Nindigo counterparts.

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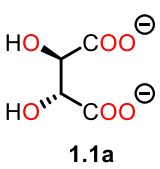
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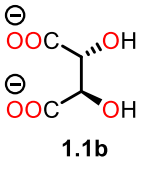
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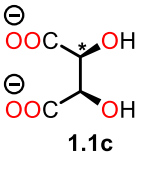
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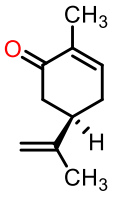
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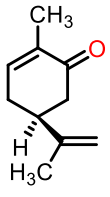
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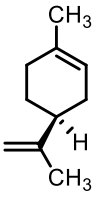
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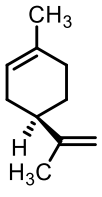
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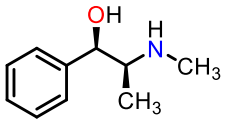
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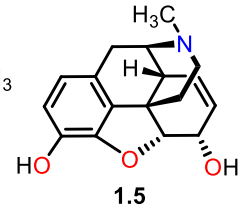
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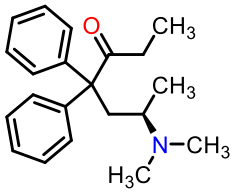
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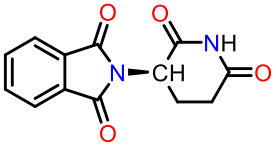
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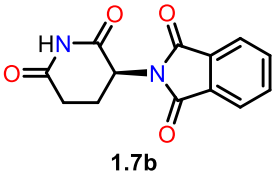
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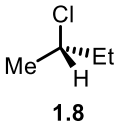
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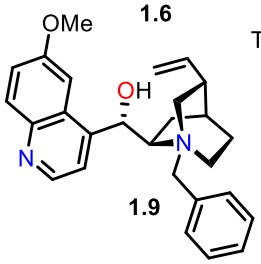
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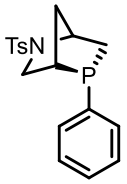
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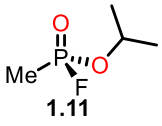
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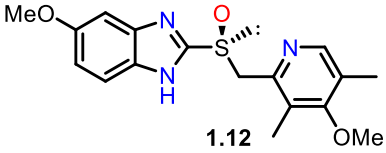
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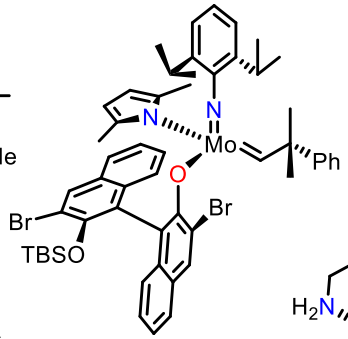
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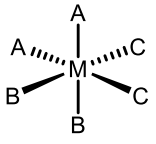
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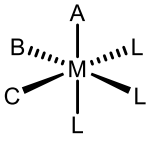
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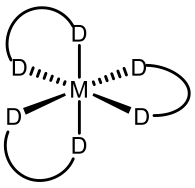
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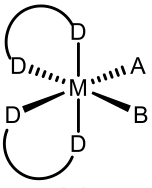
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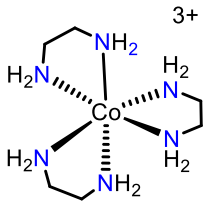
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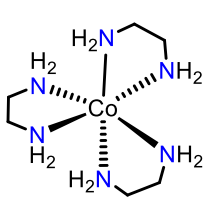
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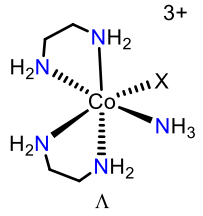
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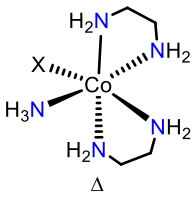
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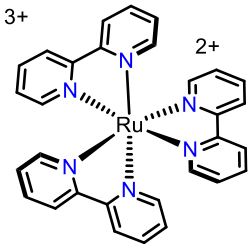
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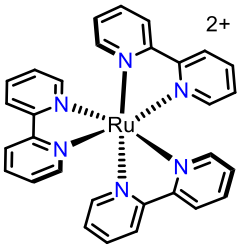
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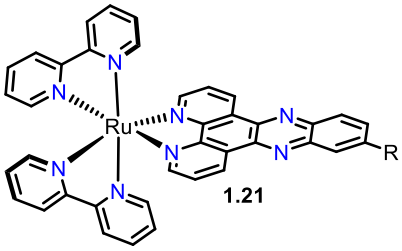
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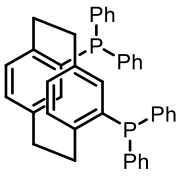
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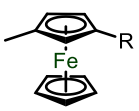
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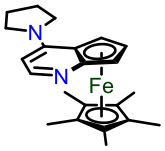
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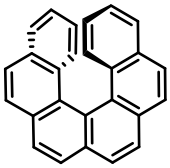
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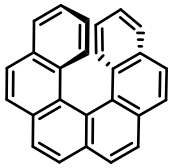


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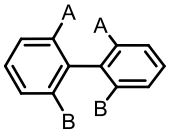
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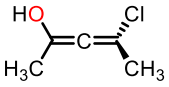


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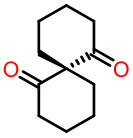
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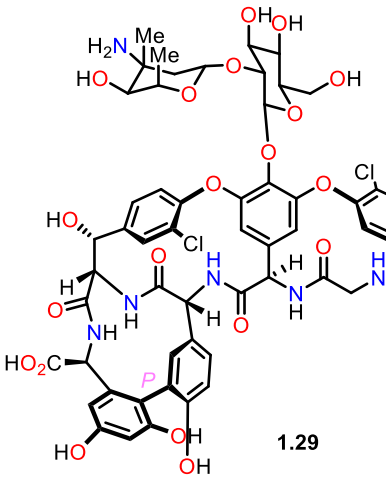
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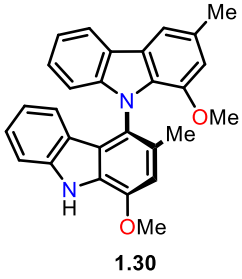
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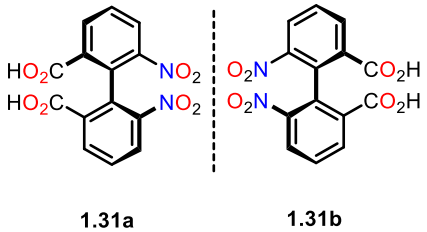
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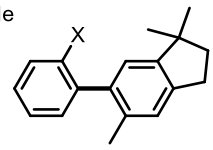
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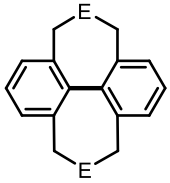
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1.31a **1.31b**

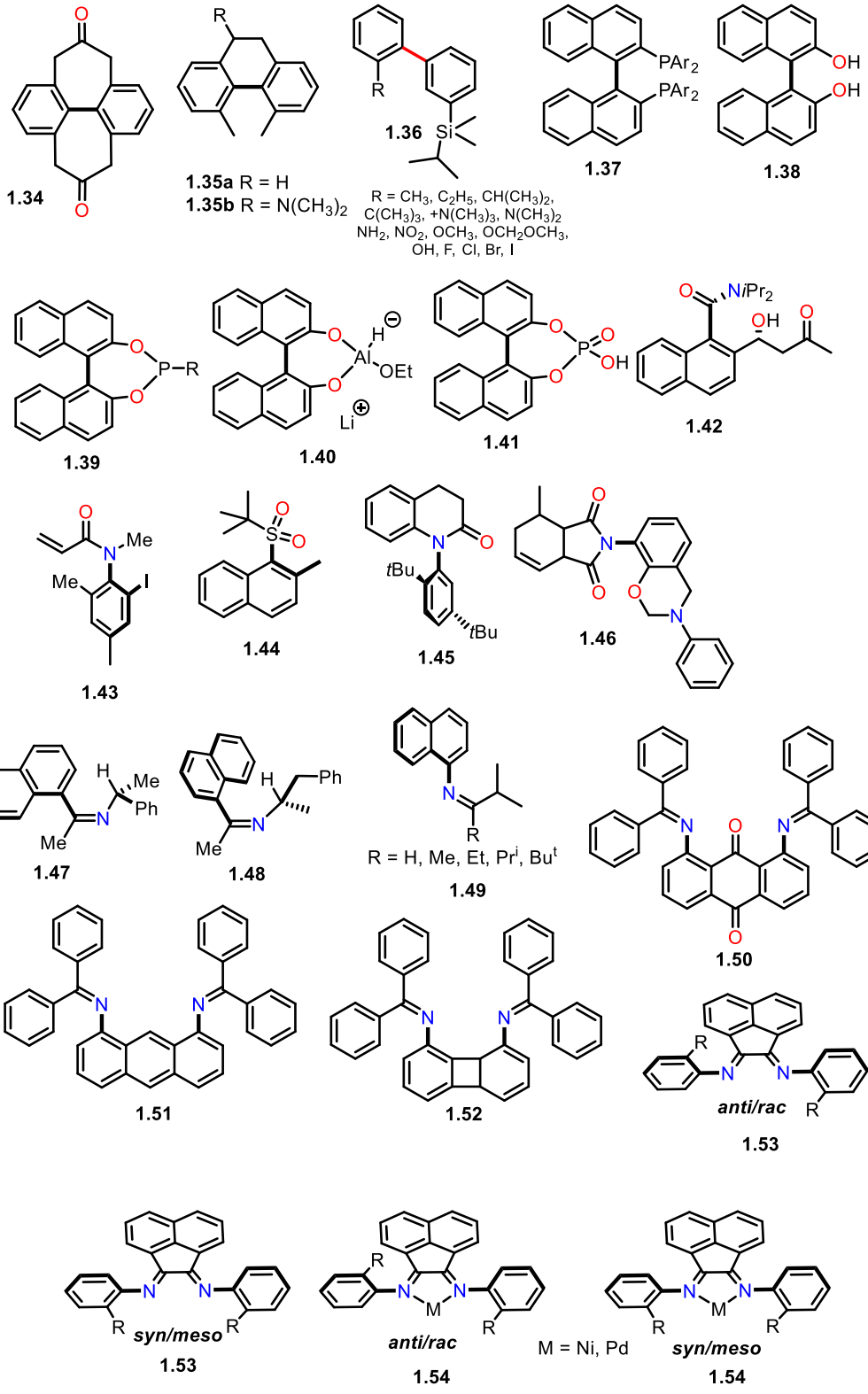


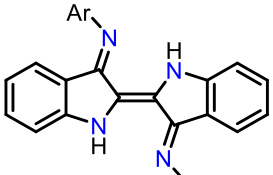
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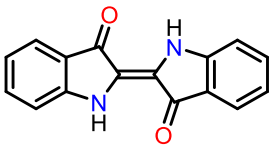
1.33a, E= O
1.33b, E= S

X = F, Cl, Br, I, CH_3, OCH_3, OH, OAc, COOMe, $COCH_3$, Ph, CH_2Ohc $CH(CH_3)_2$, CF_3, NO_2, NH_2 $NHCH_3$, $N(CH_3)_2$, $N(CH_3)_3^+$, $NHCOCH_3$, $Si(CH_3)_3$ SH, SCH_3, CN, HgCl

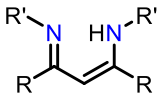

1.34
1.35a R = H
1.35b R = N(CH3)2
1.36
R = CH3, C2H5, CH(CH3)2, C(CH3)3, +N(CH3)3, N(CH3)2 NH2, NO2, OCH3, OCH2OCH3, OH, F, Cl, Br, I
1.37
1.38
1.39
1.40
1.41
1.42
1.43
1.44
1.45
1.46
1.47
1.48
R = H, Me, Et, Pri, But
1.49
1.50
1.51
1.52
anti/rac
1.53
syn/meso
1.53
anti/rac
1.54
M = Ni, Pd
syn/meso
1.54



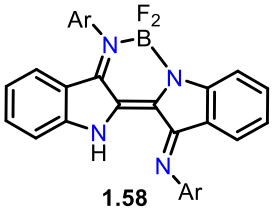
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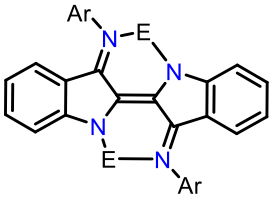
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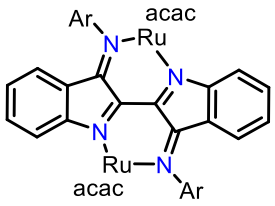
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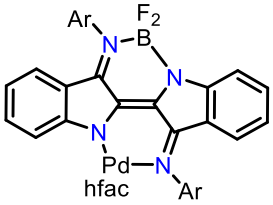
1.58



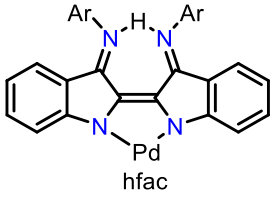
E= BF_2 **(1.59),** Pd(hfac) **(1.60),** and $Co(N(SiMe_3)_2)$ **(1.61)**



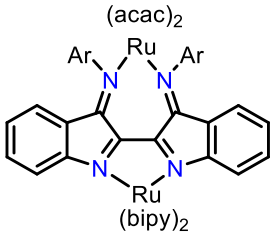
1.62



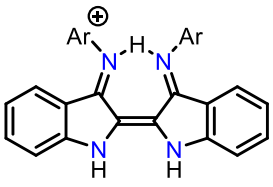
1.63



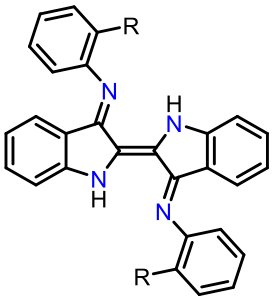
1.64



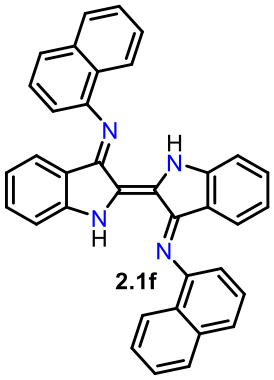
1.65



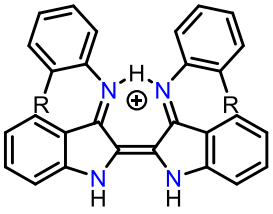
1.66



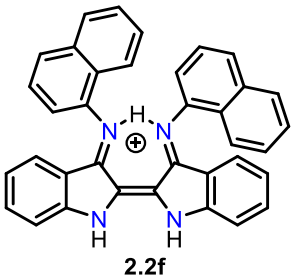
2.1
(a) R = Me, (b) R = iPr
(c) R = Ph, (d) R = tBu
(e) R = Et, (g) R = F



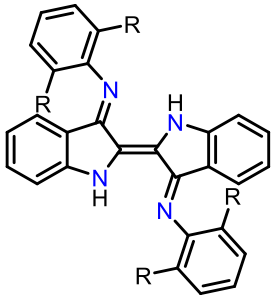
2.1f



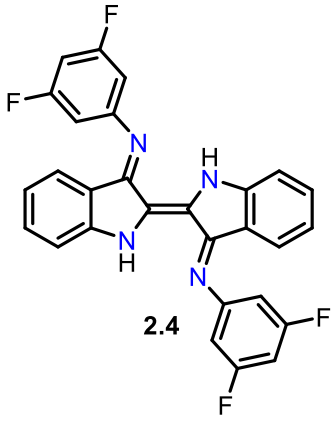
2.2
(a) R = Me, (b) R = iPr
(c) R = Ph, (d) R = tBu
(e) R = Et, (g) R = F



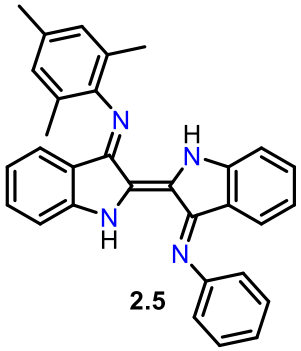
2.2f



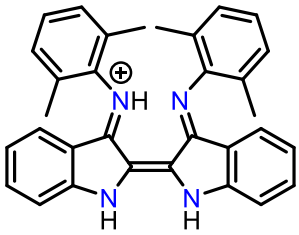
2.3a R = Me
2.3b R = iPr



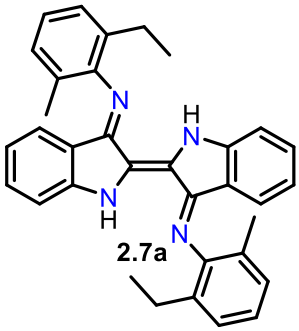
2.4



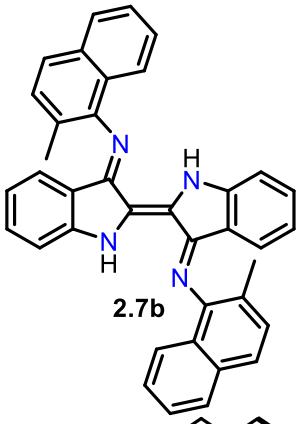
2.5



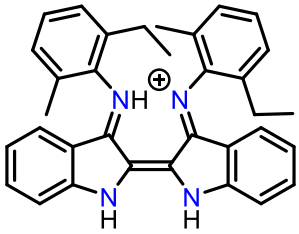
2.6



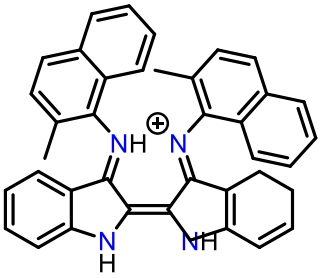
2.7a



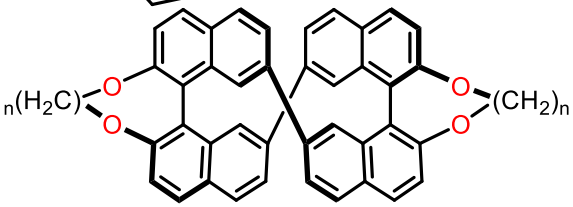
2.7b



2.8a

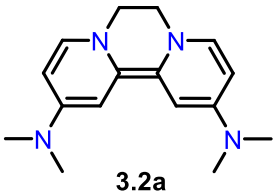


2.8b

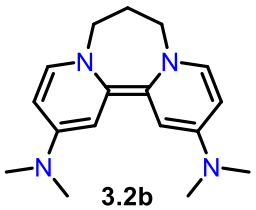


3.1

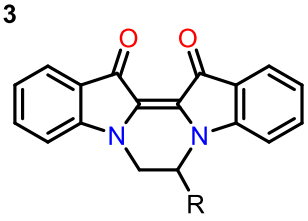
n = 1, 2, 3



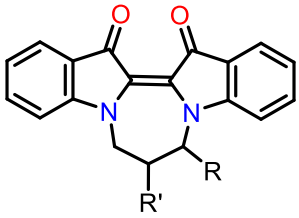
3.2a



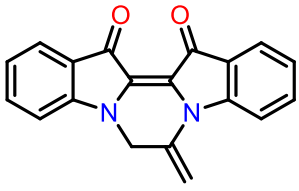
3.2b



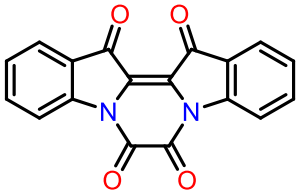
R = H (**3.3a**), CH_2OH (**3.3b**),
CH_2NHTs (**3.3c**)



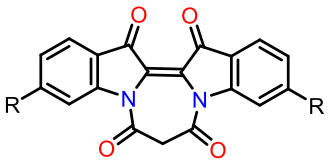
R = H, R' = H (**3.4a**),
R = CH_2NHTs, R' = NHTs (**3.4b**)



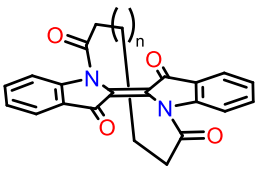
3.5



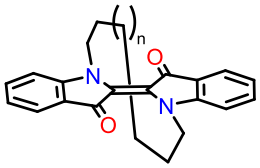
3.6



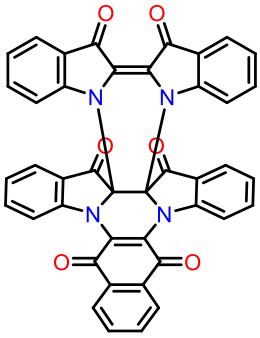
3.7a, R = H
3.7b, R = tBu



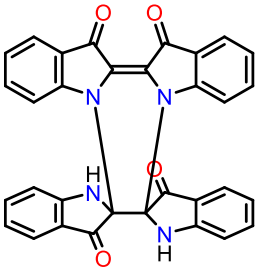
3.8a, n = 4
3.8b, n = 5



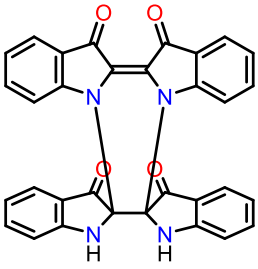
3.9a n = 3; 3.9b n = 5; 3.9c n = 7
3.9d n = 9; 3.9e n = 11



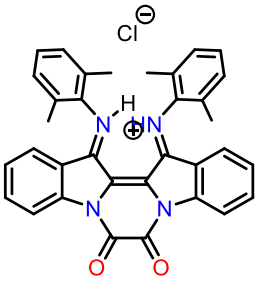
3.10



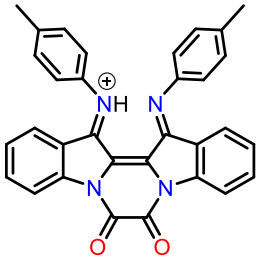
3.11



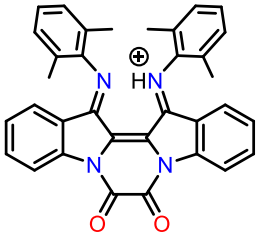
3.12



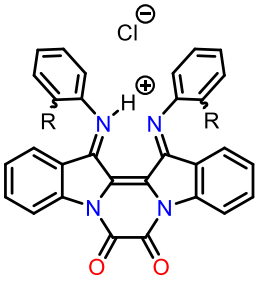
3.13a



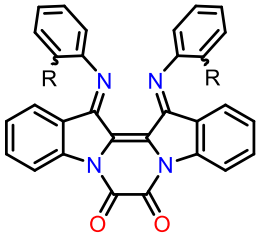
3.13b



3.14

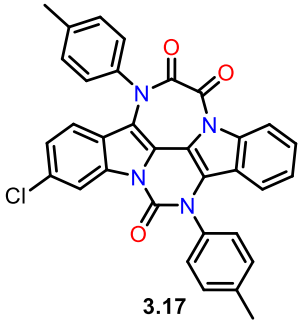


3.15a - 3.15e

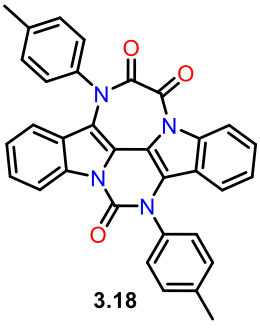


3.16a - 3.16e

R = Me (a), R = iPr (b), R = tBu (c)
R = Ph (d), R = Et (e)



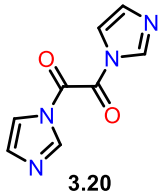
3.17



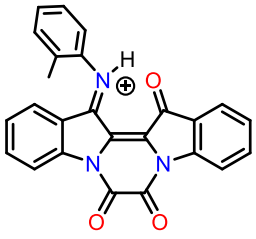
3.18



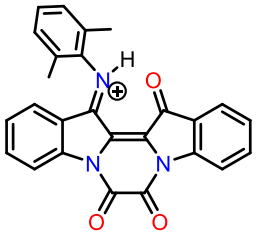
3.19



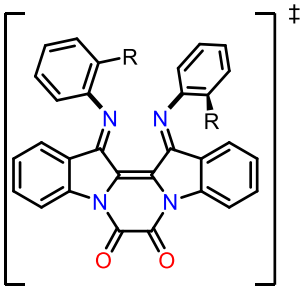
3.20



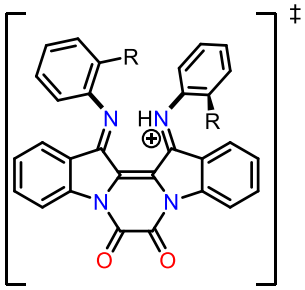
3.21



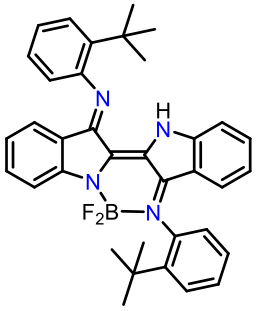
3.22



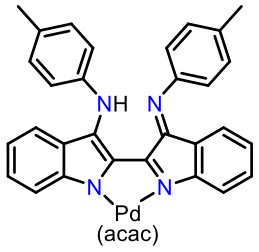
TS-3.16



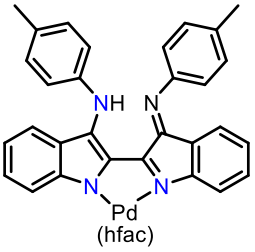
TS-3.15



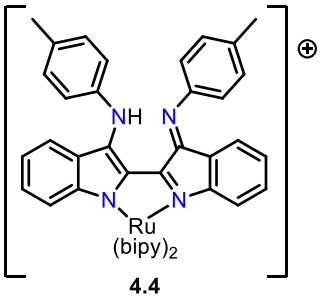
4.1



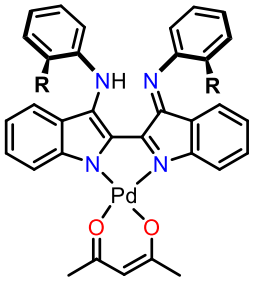
4.2



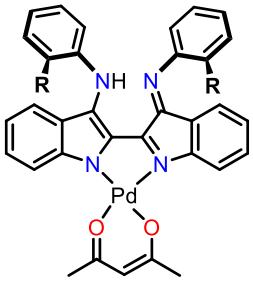
4.3



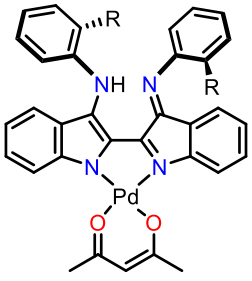
4.4



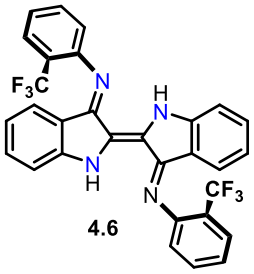
4.5



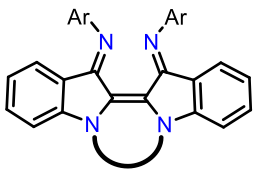
syn-4.5



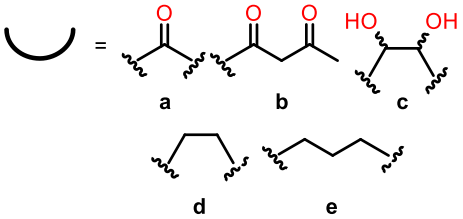
anti-4.5



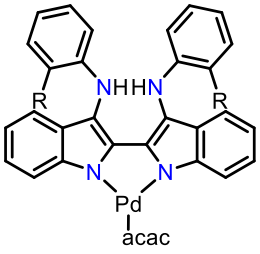
4.6



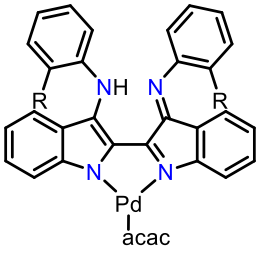
5.1



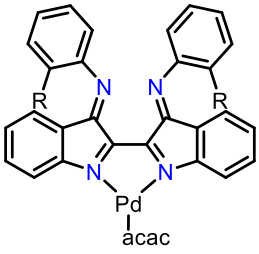
a b c d e



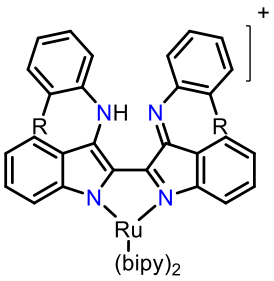
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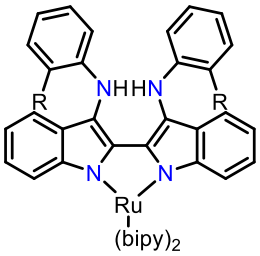
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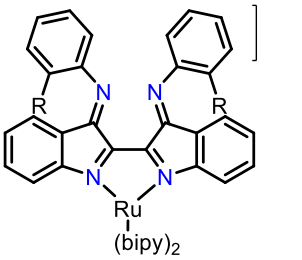
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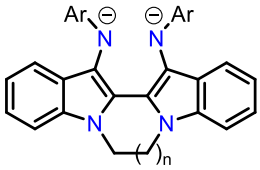
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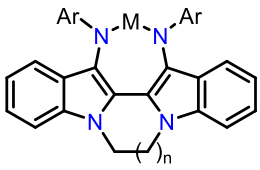
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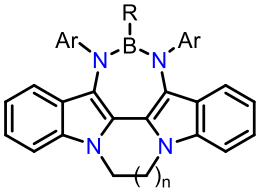
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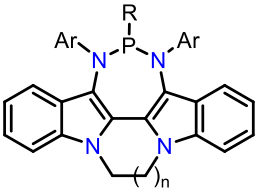
5.4 or **5.5**



5.6



5.7



5.8

List of Symbols, Nomenclature or Abbreviations

ACN	Acetonitrile
Acac	Acetylacetonate
Å	Angstrom
Ar	Aryl
bipy	2,2'-Bipyridine
br	Broad
δ	Chemical shift
TC	Coalescence temperature
CPCM	Conductor-like polarizable continuum model
COSY	Correlation spectroscopy
D3BJ	D3 version of Grimme's dispersion with Becke-Johnson damping
DFT	Density functional theory
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicycloundec-7-ene
DCM	Dichloromethane
Et_2O	Diethyl ether
θ	Dihedral/torsional angle
DMAP	4-Dimethylaminopyridine
d	Doublet
dd	Doublet of doublets
ddd	Doublet of doublet of doublets
EDG	Electron donating group
ESI	Electrospray ionization
EWG	Electron withdrawing group
$\Delta H^{\ddagger}$	Enthalpy of activation
$\Delta S^{\ddagger}$	Entropy of activation
eq	Equivalents
Et	Ethyl
ε	Extinction coefficient

FT	Fourier transform
FID	Free induction decay
FMO	Frontier molecular orbitals
R	Gas constant
$\Delta G^{\ddagger}$	Gibbs free energy of activation
$t_{1/2}$	Half life
Hz	Hertz
HMBC	Heteronuclear multiple-bond correlation
HSQC	Heteronuclear single quantum coherence
hfac	hexafluroacetylacetonate
HOMO	Highest occupied molecular orbital
HRMS	High resolution mass spectrometry
h	Hour
^{i}Pr	Isopropyl
IR	Infrared
K	Kelvin
kcal	Kilocalorie
L	Ligand
LUMO	Lowest unoccupied molecular orbital
MHz	Megahertz
mp	Melting point
m	Meta
M	Metal
Me	Methyl
m	Multiplet
M	Molarity
M	Minus
msec	Millisecond
mol	Mole
MO	Molecular orbital
nm	Nanometer

nsec	Nanosecond
NEB	Nudged elastic band
NMR	Nuclear magnetic resonance
NOESY	Nuclear Overhauser effect spectroscopy
o-	Ortho
ppm	Parts per million
Ph	Phenyl
P	Plus
PCM	Polarizable continuum model
Rac	Racemic
k	Rate constant
R	Rectus
RT	Room temperature
sec	Second
SCF	Self consistent field
s	Singlet
S	Sinister
R	Substituent or group
T	Temperature
^{t}Bu	*Tert*-butyl
tert	Tertiary
THF	Tetrahydrofuran
TD-DFT	Time dependent density functional theory
Tol	Toluene
τ	Torsional angle
TS	Transition-state
UV-Vis	Ultraviolet-visible
SMD	Universal solvation model
VT	Variable temperature
λ	Wavelength
cm^{-1}	Wavenumber

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I would like to first thank Dr. Robin Hicks for giving me the opportunity to pursue PhD studies in his group and for being a great supervisor and mentor. He gave me significant intellectual independence while keeping me focused on my projects, while on my path towards becoming a physical organic chemist. I would also like to graciously thank the wonderful teaching staff at the University of Victoria. In particular, Dr. Dave Berry and Kelli Fawkes who have been the best teaching supervisors I could ever ask for and I would not have my current passion for teaching chemistry if it were not for their support and guidance on my TA journey during my PhD studies.

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Dedication

To my family and friends, without you this would not have been possible.

Chapter 1: Introduction

1.1 Chirality

Chirality originates from the Greek word for hand *cheir*. The term was first coined by Sir William Thomson as being "any geometrical figure, or group of points, that if its image in a mirror, ideally realized, cannot be brought to coincide with itself."[1–3] Chiral molecules and objects belong to the C_n and D_n symmetry point groups.[1,4] It was not until the nineteenth century that chirality began to be studied in the physical sciences. Jean-Baptiste Biot observed that plane-polarized light was rotated by solutions of tartaric acid and sugar.[5] Louis Pasteur discovered that crystals of sodium ammonium tartrate **1.1** (**Figure 1.1**), which were physically mirror-images of one another, rotated plane-polarized light in equal and opposite directions.[6–8] The findings of Biot and Pasteur showed that the three-dimensional orientation a chemical adopts can influence its properties.

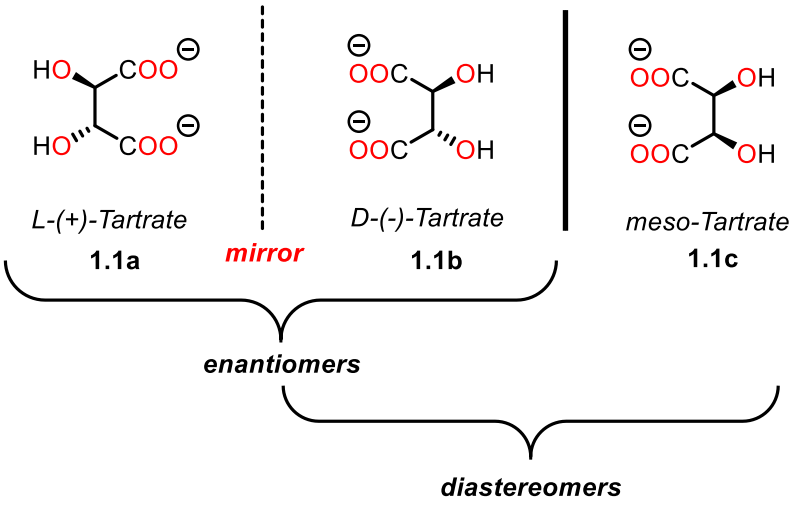
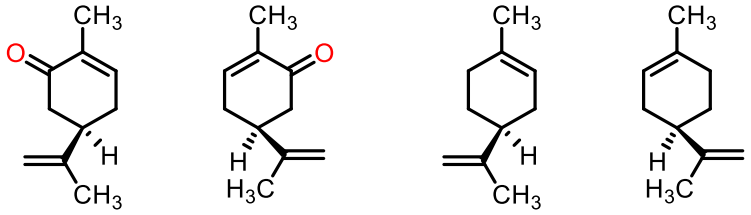


Figure 1.1 Enantiomers and diastereomers of tartrate

Chiral molecules often have different bioactivities. All naturally occurring amino acids are *L*-amino acids as opposed to *D*-amino acids.[9] Enantiomers can have different smells and tastes (e.g., *R/S* carvone[10,11] **1.2a**/**1.2b** and *R/S* limonene[12] **1.3a**/**1.3b**). The differences in bioactivities that are the result of the three-dimensional orientation a chemical adopts have been of interest for over 100 years.

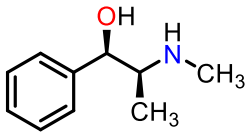


1.2a **1.2b** **1.3a** **1.3a**

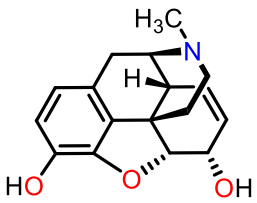
1.2 Importance of chirality

Therapeutics used historically, such as ephedrine (**1.4**), morphine (**1.5**), and quinine (**1.6**), are now known to be chiral.[13] People who were prescribing/ingesting these medications were unaware of the three-dimensional orientation of the compounds they were ingesting. This ignorance later proved deadly/disabling when more sophisticated medications were developed.

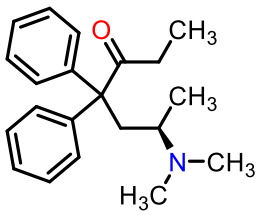
After the thalidomide disaster of the late 1950s and early 1960s,[14,15] the three-dimensional orientation molecules adopt was brought to the attention of the general population. The *R* (**1.7a**) and *S* (**1.7b**) enantiomers of thalidomide have different bioactivities.[15] The *R* enantiomer has sedative effects, while the *S* enantiomer is teratogenic. The differences in bioactivities alongside the in vivo racemization of **1.7a** and **1.7b** caused the creation of legislation by the U.S. Food and Drug Administration, requiring the evaluation of the bioactivity of each enantiomer of a chiral drug before approval.[16–18] The legislation still has consequences today, and the prevalence of single enantiomer drugs has steadily risen year by year.[19,20] The requirements enforced by the legislation has led to advancements in the understanding of stereochemistry and the development of the methodologies used to prepare enantiomerically pure chemicals. The study of chirality and its applications has culminated in several Nobel prizes for research on conformational analysis,[21–23] the stereochemistry of enzymatic and organic reactions,[24] catalytic asymmetric hydrogenation and epoxidation reactions,[25–27] and in asymmetric organocatalysis.[28–31]



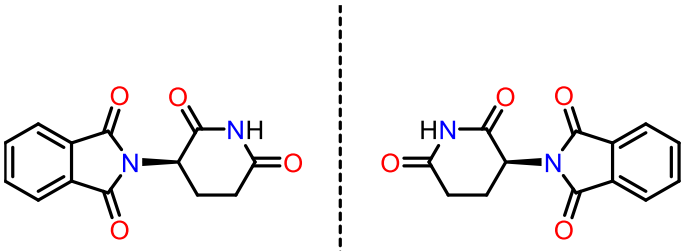
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1.5



1.6

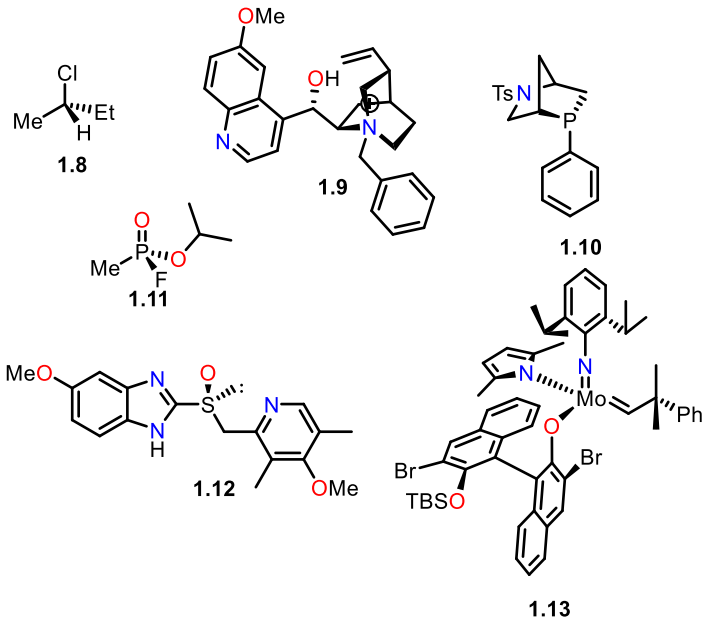


1.7a **1.7b**

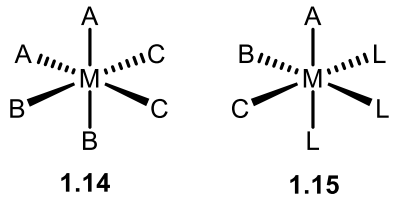
1.3 Types of chirality

1.3.1 Point chirality

Chirality is introduced in the discussion of handedness (left and right hands are non-superimposable mirror images) and subsequently in the topic of point chirality.[32] Point chirality is most commonly found at tetrahedral atoms that have four different substituents, such as 2-chlorobutane (**1.8**). This type of chirality is present in numerous chemicals, which include ammonium salts (**1.9**),[33] phosphines (**1.10**),[34] phosphine oxides (**1.11**),[35] sulfoxides (**1.12**),[36] and the highly catalytically active molybdenum complex (**1.13**), among others.[37]



Elements or atoms in octahedral environments also display point chirality. Octahedral complexes, like their tetrahedral congeners, can have all unique ligands. The presence of six different ligands results in fifteen different pairs of enantiomers.[38] Chiral complexes do not require six different ligands; a minimum of three different types of ligands is sufficient.[38] Examples include complexes of types **1.14** and **1.15**. Chiral complexes that have monodentate ligands have challenges associated with their synthesis/isolation. Challenges arise from the complexes' capacity for interconversion and possible ligand redistribution, either through associative or dissociative processes.



1.3.2 Planar chirality

Planar chirality arises in molecules that have four atoms (A, B, C, and D with A≠B) in a plane (**Figure 1.2**), alongside an atom E, referred to as the "pilot atom," which is above/below the plane.[39] The absolute configuration of molecules that have planar chirality is defined by the order of the first encounter from the pilot atom. In **Figure 1.2**, the order of the first encounter is from atom E to A, and next to the branching atom B; after atom B, the Cahn-Ingold-Prelog rules[24,40–43] are used to assign the priority of the atoms C and D. If the order of the first encounter has a clockwise or counterclockwise twist, the absolute configuration is *pR* or *pS*, respectively.

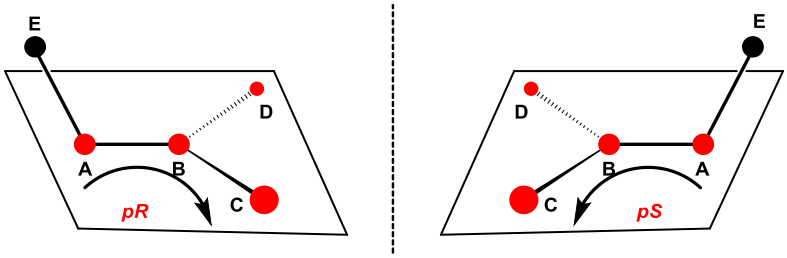
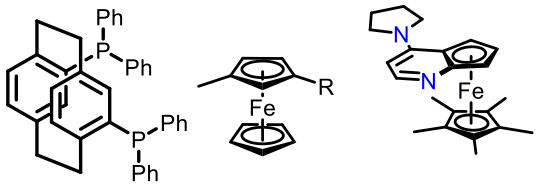


Figure 1.2 Absolute configuration assignment in systems with planar chirality

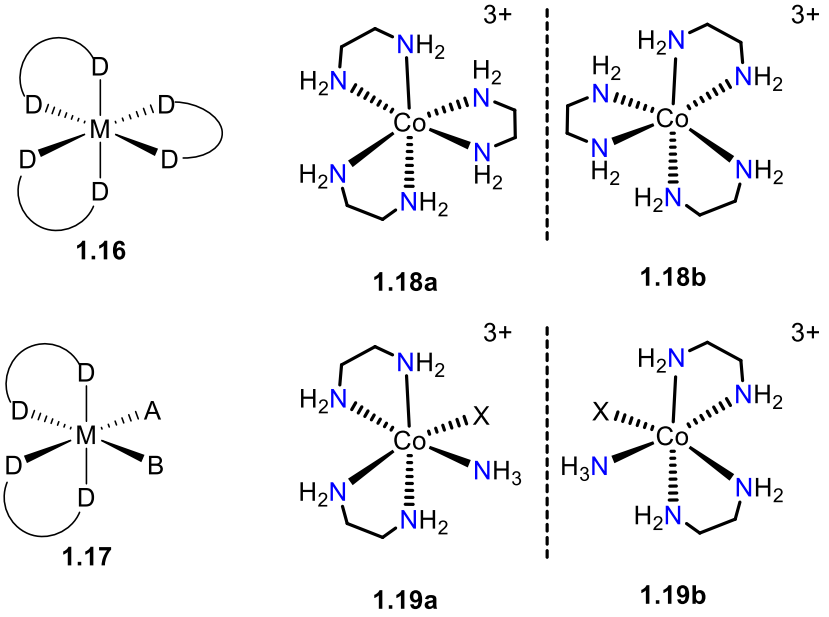
Planar chirality is present in paracyclophanes (**1.22**) and metallocenes (**1.23** and **1.24**). Paracyclophanes are used as ligands in transition metal-mediated asymmetric hydrogenations,[44–46] the asymmetric oxidation of 1,3-keto esters,[47] and in the asymmetric addition of alkyl[48,49] and alkynyl[48,50,51] zinc reagents to carbonyl compounds. Chiral metallocenes are used as ligands in numerous asymmetric transformations,[52] which include asymmetric allylic alkylation,[53–55] allylic amination,[53–55] and hydrogenation reactions,[56,57] and as asymmetric organocatalysts, among others.[58,59]



1.22 **1.23** **1.24**

1.3.3 Helical chirality

Helical chirality arises from a twisting/turning present within a molecule and is present in helicenes (**1.25a/1.25b**)[60] and metal complexes of type 1.16 and 1.17. (**Figure 1.3**).[61] A clockwise twist is referred to as **P** in organic molecules or **Δ** in metal complexes,[62] while a counter clockwise twist is **M** or **Λ**. Werner reported the first chiral metal complexes, which exhibit helical chirality, in his disclosure of cobalt complexes **1.18a**/**1.18b** and **1.19a/1.19b.** [63–68] Numerous chiral chelate complexes exist and include the ruthenium complexes used in photoredox catalysis (**1.20**)[69] and photodynamic therapy (**1.21**).[70]



1.16 **1.18a** **1.18b**

1.17 **1.19a** **1.19b**

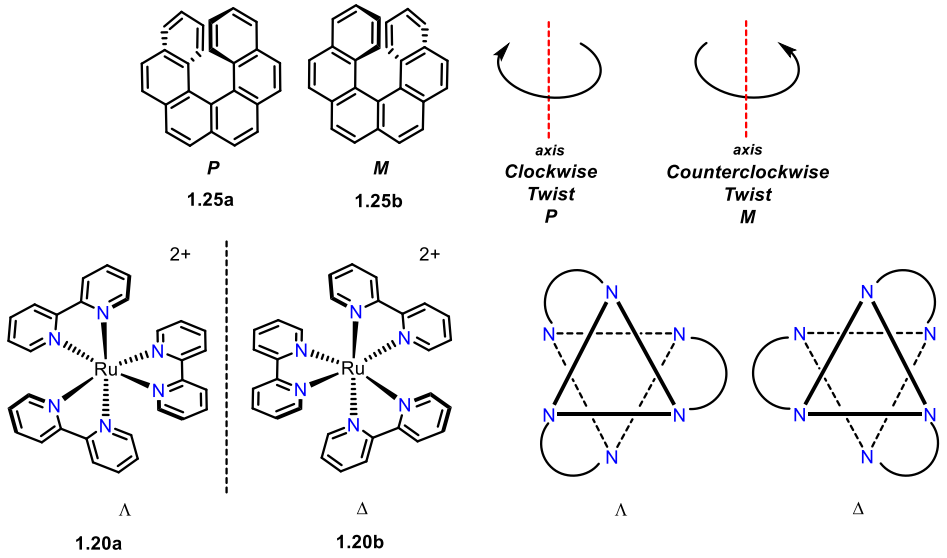
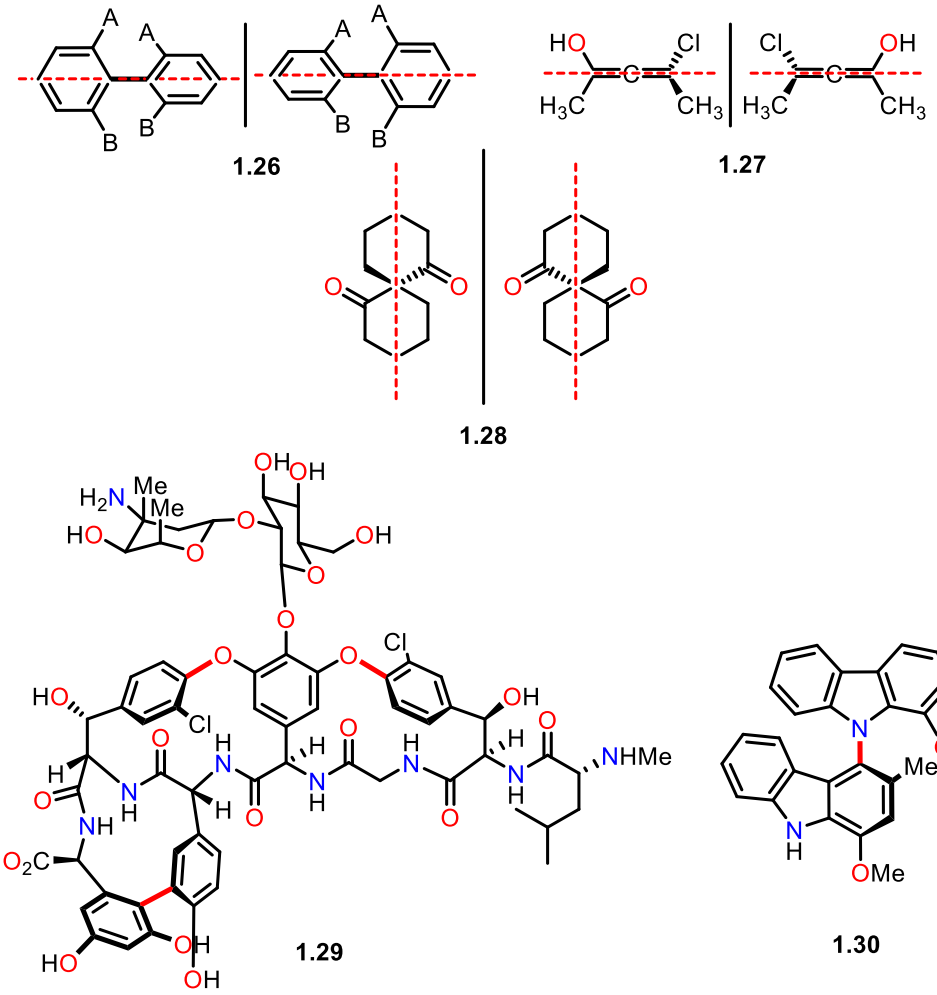


Figure 1.3 Examples of helical chirality

1.3.4 Axial chirality

Axial chirality arises from a stereogenic axis (highlighted in red) in a molecule.[39] The axis can be composed of a bond, a series of bonds, or a series of atoms not consecutively bonded. This type of chirality is present in biaryls (**1.26**),[71–73] allenes (**1.27**),[74] and spiranes (**1.28**).[39,75] The four substituents attached to the chiral axis do not have to be distinct. It is sufficient for the two substituents at each end of the axis to be unique.[4] Axial chirality is present in the natural products vancomycin B (**1.29**)[76,77] and murrastifoline-F (**1.30**).[78] Axial chirality is widespread in drug discovery, medicinal chemistry, and ligand design.[79,80]



1.4 Atropisomerism

Any stereoisomer that is related by the rotation about a bond is known as an atropisomer[72,81] and is commonly observed in axial chiral biaryls, whose enantiomers are related by the rotation about the central carbon-carbon bond. The term atropisomer originates from the Greek word for "without turn" atropos.[82] The racemization of atropisomers is called atropisomerization. Atropisomerization differs from the racemization processes of other types of chirality because of the absence of the making or breaking of chemical bonds. The first report of atropisomers was by Christie and

Kenner in their study on biaryl carboxylic acids (**1.31a** and **1.31b**, **Figure 1.4**).[83] Atropisomeric biaryl systems are now ubiquitous in asymmetric catalysis and synthesis.

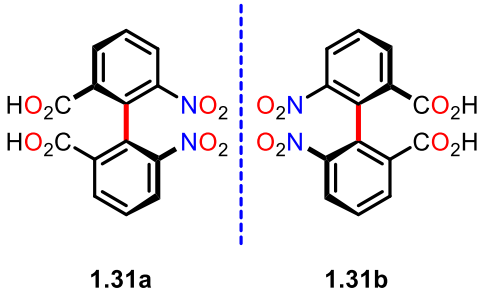


Figure 1.4 First example of atropisomeric biaryls by Christie and Kenner[83]

Oki defined atropisomers as "stereoisomers related by the rotation about a bond that can be isolated and have a half-life of at least 1000 seconds at any given temperature."[84] Oki's definition requires atropisomerization barriers of 93 kJ/mol (22 kcal/mol) at 300 K (27 °C). [84,85] LaPlante and Hucke[79] defined classes of atropisomers based on their rotational energy barriers (**Figure 1.5**). "*Class 1*" atropisomers have rotational energy barriers below 20 kcal/mol and are challenging to isolate under ambient conditions. "*Class 2*" atropisomers have rotational energy barriers between 20 and 30 kcal/mol and have rates of interconversion in the range of minutes to months and can be separated. "*Class 3*" atropisomers have rotational energy barriers greater than 30 kcal/mol, have interconversion rates on the order of years, and are conformationally stable.

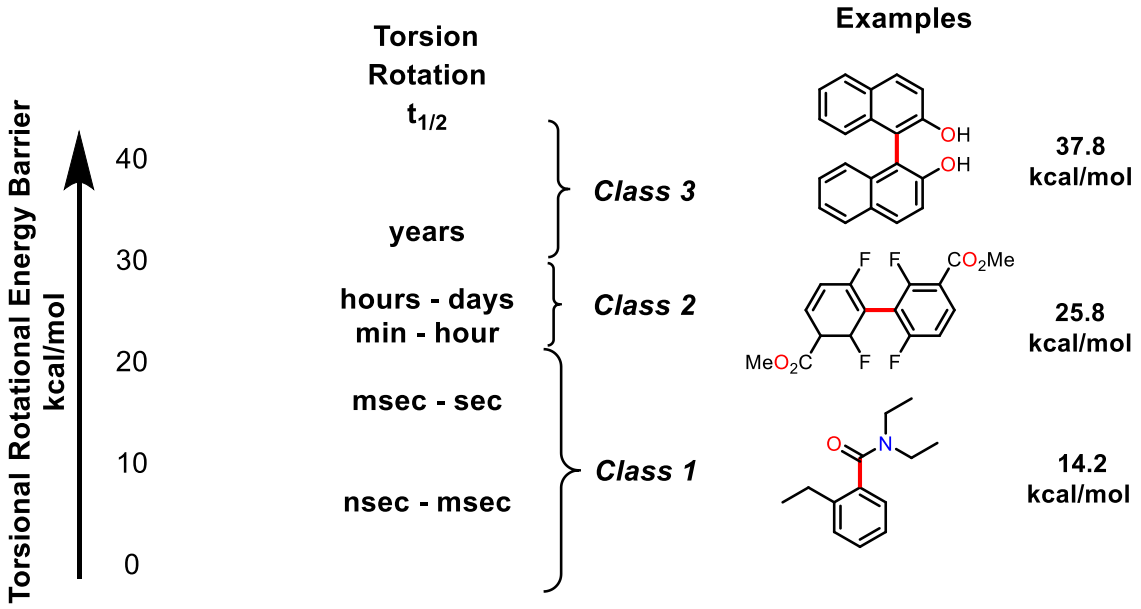
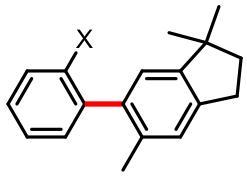


Figure 1.5 Classes of atropisomers defined by Laplante and Hecke[79]

1.4.1 Steric influence on atropisomerism

Atropisomerism is dependent on the steric bulk of the substituents adjacent to the pivot bond. Sternhell reported exhaustive studies on how substituents attached to biaryl **1.32** affected the atropisomerization barriers,[86] and culminated in the defining steric parameter referred to as the "interference value."

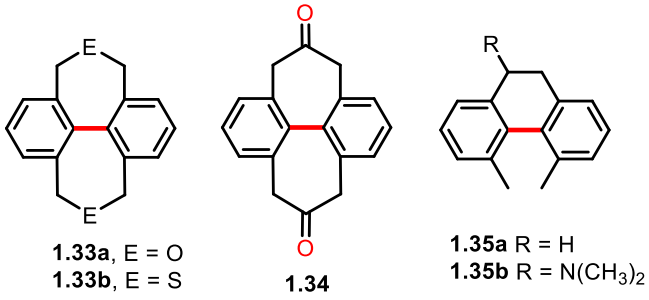


1.32

X = F, Cl, Br, I, CH_3, OCH_3, OH, OAc, COOMe,
$COCH_3$, Ph, CH_2Ohc $CH(CH_3)_2$, CF_3, NO_2, NH_2
$NHCH_3$, $N(CH_3)_2$, $N(CH_3)_3^+$, $NHCOCH_3$, $Si(CH_3)_3$
SH, SCH_3, CN, HgCl

The effect that bridging substituents have on the atropisomerization barriers of biaryls (**1.33-1.35**) was studied by Mislow.[87] The barriers were dependent on the degree

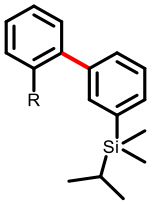
of ring strain present between the aryl rings. Steric parameters such as the *"B values"* of Ruzzoconi originate from the atropisomerization barriers of biaryls of type **1.36**.[88] These parameters allow for the rational design of molecules that have rotational energy barriers of sufficient magnitude to preclude atropisomerization and have implications for chiral ligand design and the development of new atropisomers.



1.33a, E = O
1.33b, E = S

1.34

1.35a R = H
1.35b R = $N(CH_3)_2$



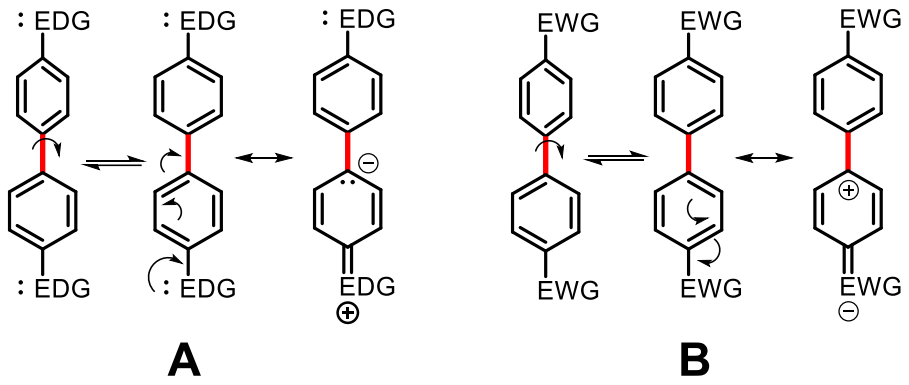
1.36

R = CH_3, C_2H_5, $CH(CH_3)_2$, $C(CH_3)_3$, $+N(CH_3)_3$, $N(CH_3)_2$
NH_2, NO_2, OCH_3, OCH_2OCH_3, OH, F, Cl, Br, I

1.4.2 Electronic effects of substituents on atropisomerism

A substituent's electronic effects can influence the atropisomerization[89,90] barriers and are more subtle than steric effects. When electron-donating or electron-withdrawing substituents are attached to biaryls, the atropisomerization barriers decrease and increase, respectively. The decrease and increase of the atropisomerization barriers are because of the increase/decrease of electron density at the pivot bond, respectively (**Scheme 1.1**). An increase in electron density at the pivot bond causes an increase in the sp^3 character of the carbon atoms. The increased sp^3 character at the pivot bond causes a release of strain in

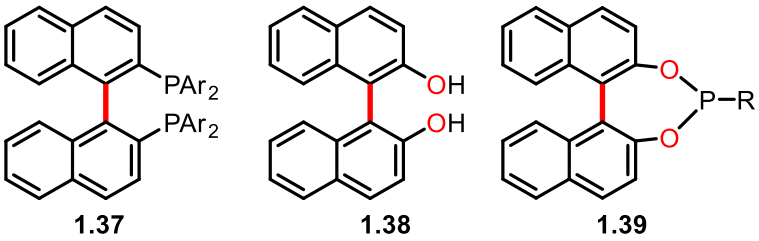
the transition state via an increase in out-of-plane bending and lowers the rotational energy barrier.[92] The opposite is true for electron-withdrawing substituents.[91] The electronic influence on atropisomerization allows for additional ways in which to tune atropisomerization barriers.[89–91]



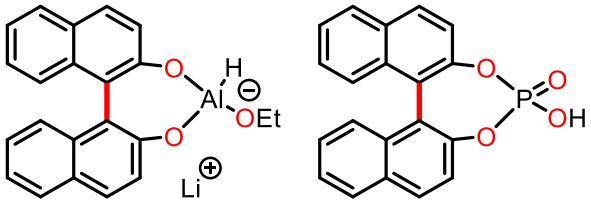
Scheme 1.1 Influence of electronic effects on transition-state stabilization; (**A**) stabilization of the transition-state by electron-donating substituents; (**B**) destabilization of the transition-state by electron-withdrawing substituents

1.5 Applications of biaryl atropisomers

The biaryl motif is widespread in ligand and organocatalyst design. The 1,1′-binaphthyl motif is common in asymmetric catalysis, most notably in the development of 2,2'-bis(diarylphosphino)-1,1'-binaphthyl, BINAP (**1.37**) class of ligands.[92] The use of BINAP, and its analogs, has resulted in advancements in asymmetric hydrogenation chemistry culminating in Noyori's Nobel prize.[26] BINAP's diol congener, BINOL (**1.37**),[93] is used in asymmetric organocatalysis and as a precursor to numerous phosphines (**1.39**),[94] aluminum-based reducing agents (**1.40**),[95] and chiral phosphoric acids (**1.41**).[96,97]



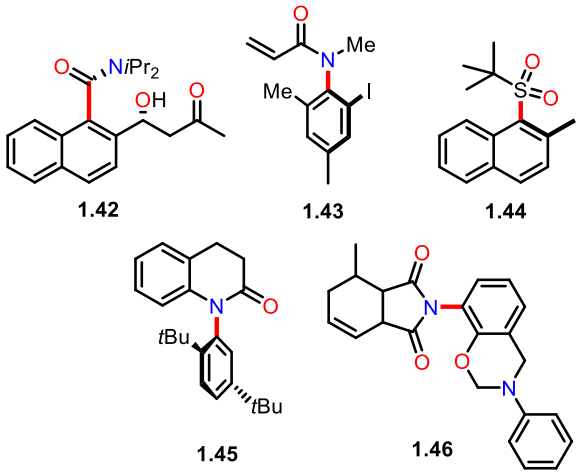
1.37 **1.38** **1.39**



1.40 **1.41**

1.6 Non-biaryl atropisomerism

Atropisomeric systems that have hindered rotation about *N*-*C*, *O*-*C*, and *S*-*C* bonds, among others, exist. Examples include hindered amides (**1.42**),[98] anilides (**1.43**),[99] sulfones (**1.44**),[100] lactams (**1.45**),[101] and imides (**1.46**),[102] among others.[103] Non-biaryl atropisomers do not have as many applications as their biaryl counterparts. Nevertheless, the disclosures of Curran[104,105] and Clayden[106,107] found that non-biaryl atropisomers can have stereodirecting abilities, act as chiral auxiliaries, and can participate in asymmetric induction. Applications of non-biaryl atropisomers now include various asymmetric transformations, such as asymmetric allyl alkylation reactions,[108,109] cross-couplings (Grignard,[110] Heck,[111] and Suzuki-Miyaura[112]), Stetter/Benzoin condensations,[113] and enantioselective allylic arylation reactions,[114] among others.[103]



1.6.1 Atropisomeric imines

Atropisomeric imines are an interesting class of non-biaryl atropisomers because of the potential for atropisomeric N-R (**red bond**), C-R' (**green bond**), and C-R'' (**blue bond**) bonds (**Figure 1.6**). The presence of one substituent on the imine nitrogen and the remoteness of the two substituents attached to the N=C carbon, from the chiral bond, creates potential challenges in achieving a rotational energy barrier of sufficient magnitude for there to be stable atropisomers. The possibility of having three different atropisomeric axes (**Figure 1.6**) allows for a lot of structural diversity.

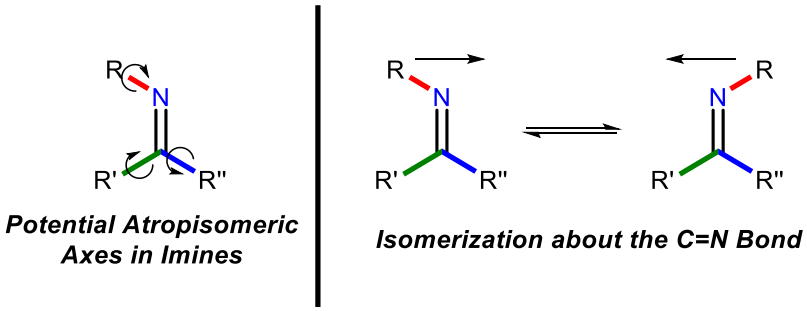
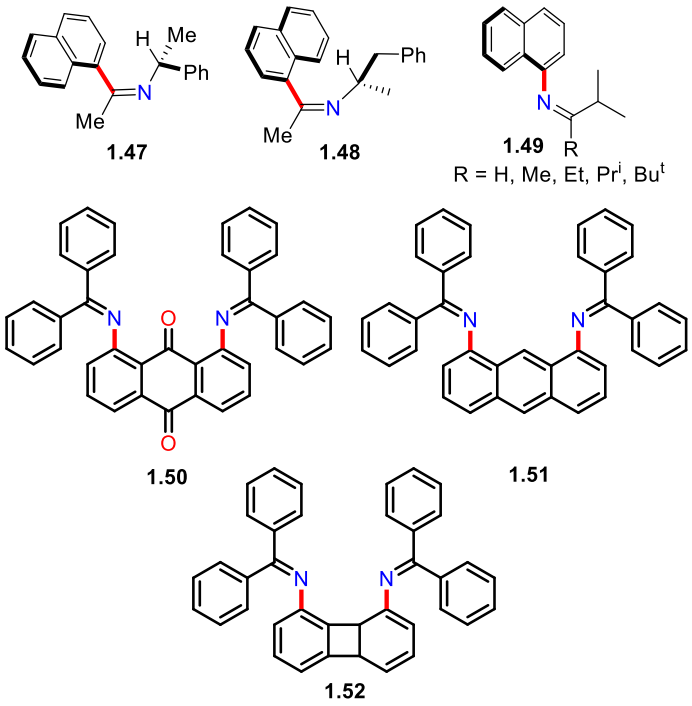


Figure 1.6 Potential avenues for imine isomerization

Studies on the atropisomerization barriers of imines have focused on naphthylimines, which feature atropisomeric C-C (**1.47** and **1.48**)[115–117] and N-C (**1.49**)[118] bonds. Further complexity can be introduced via the inclusion of multiple imine groups. Mazzanti and co-workers studied the atropisomeric behavior of anthraquinone (**1.50**), anthracene (**1.51**), or biphenylene (**1.52**) diimine systems.[119]



Mono *ortho*-substituted α-diimines can adopt two diastereotopic conformations, *anti* and *syn* (**Figure 1.7**). The atropisomeric conformations are related to each other by the rotation of one N-C bond;[120,121] the *syn* conformation is non-chiral and has C_S symmetry, while the *anti* conformation is chiral and has C_2 symmetry. The conformation that the α-diimine ligand (**1.53**) adopts in Brookhart complexes (**1.54**) has a significant influence on the properties of the polymers produced in olefin polymerization.[121]

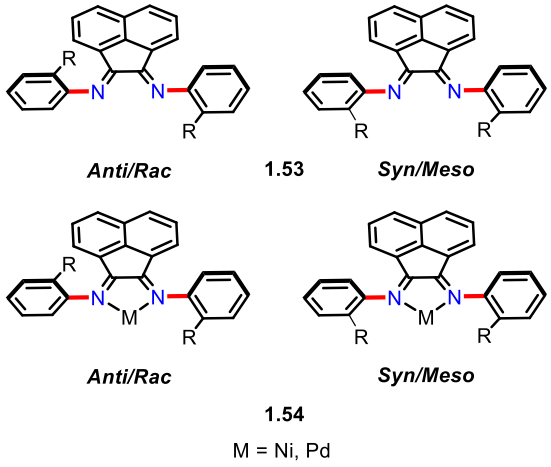
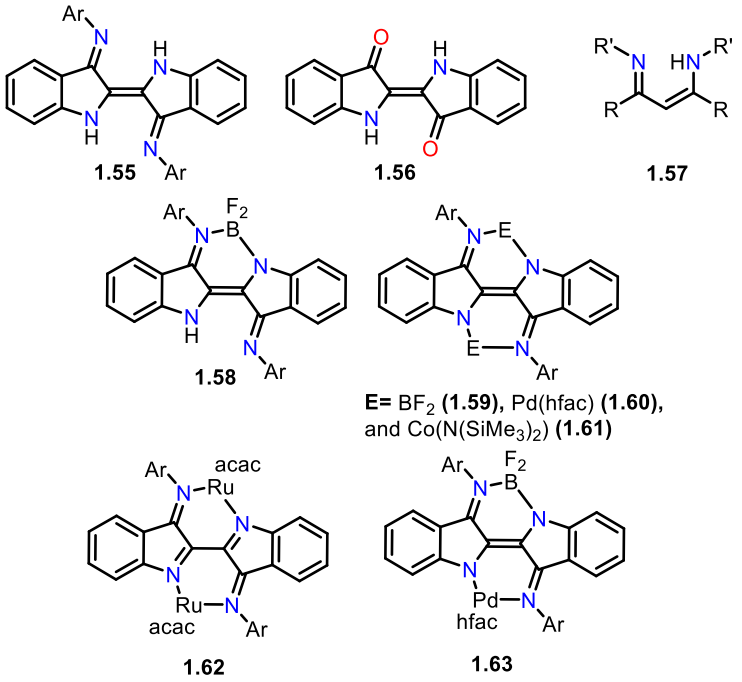


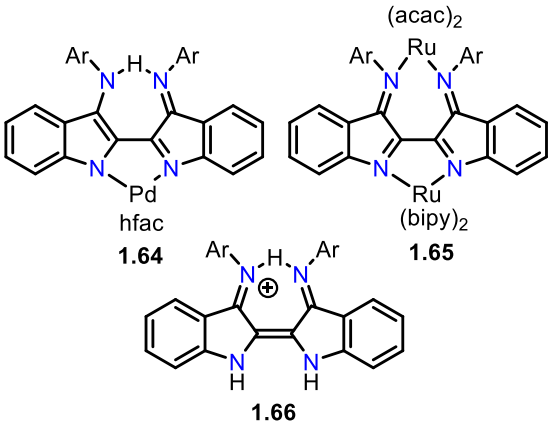
Figure 1.7 Conformations of α-diimine ligands and their corresponding metal complexes

1.7 Indigo diimines ("Nindigo")

In 2010, the Hicks group reported the synthesis of indigo diimines (Nindigo, **1.55**).[122] Nindigo derivatives retain the vibrant color of indigo (**1.56**) but have greater solubility in organic solvents. In its native *trans*- geometry, Nindigo has two β-diketiminate binding sites and as such is reminiscent of the NacNac class of ligands (**1.57**).[123,124] Nindigo and its related complexes have been explored in applications as single molecular magnets,[125,126] redox-active near-infrared dyes,[127,128] and non-innocent bridging ligands.[122,125,126,128–130] Metal complexes of *trans*-Nindigo derivatives include the boron (**1.58** and **1.59**),[127,128] palladium (**1.60**),[122,127,129] cobalt (**1.61**),[125,126] ruthenium (**1.62**),[130] and heterobimetallic boron/palladium (**1.63**) complexes.[127]



In addition to the aforementioned *trans*-Nindigo complexes, palladium (**1.64**) and ruthenium (**1.65**) complexes that have Nindigo in a *cis*-geometry have been reported.[129] In 2015, the Hicks group reported the *trans*- to *cis*-isomerization of Nindigo using a strong acid termed "protoisomerization."[131] The protonated *cis*-Nindigos were the first reports of Nindigo being in the *cis*- geometry in the absence of metal coordination.



1.8 Goals of this dissertation

Indigo diimines are an excellent scaffold on which to study *N*-*C* bond rotation and to develop an understanding of how *N*-aryl substituents affect atropisomerization barriers. The presence of two aryl imines makes Nindigo analogous to α-diimines **1.52**. To date, the aryl imines present in Nindigos have been symmetrical; only two examples have had mono *ortho*-substituted (mono *ortho*-substituted) aryl imines. When a mono *ortho*-substituted aryl imine is present, there are two conformations the aryl imine unit can adopt relative to the indigoid backbone (**Figure 1.8**); the achiral *anti* and chiral *syn* conformations of *trans*-Nindigos have C_i and C_2 symmetry, respectively. For *cis*-Nindigos, the *anti* conformation is chiral and has C_2 symmetry, while the *syn* conformation is not chiral and has C_s symmetry (**Figure 1.8**).

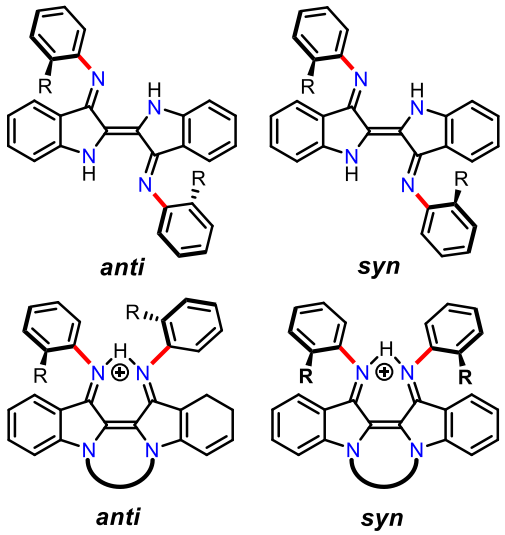
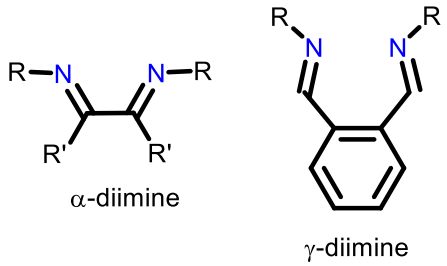


Figure 1.8 Conformations of mono *ortho*-substituted *trans*- and *cis*-Nindigos

C*is*-Nindigo derivatives are *γ*-diimines. The *γ*-diimine class of ligands has been explored much less than *α*-diimines. A Google Scholar search (search term: *α*-diimine) of

α-diimines yielded greater than 7000 results compared to γ-diimines (search term: γ-diimines), which had 27 results. The formation of a larger, less favorable seven-membered chelate in γ-diimine complexes in comparison to the five-membered chelate of α-diimines is likely the reason for the limited use of γ-diimines. In addition, γ-diimines are prone to intramolecular cyclization reactions, making their synthesis challenging.[132–134] Metal complexes featuring γ-diimine ligands have found utility in the polymerization of methyl methacrylate[135] and the oxidation of cysteine.[136,137] No intramolecular rearrangements have been observed in Nindigo; furthermore, there are examples of Nindigo complexes in which the metal chelates in the γ-diimine pocket (**1.65**).[138]



Due to the established structural diversity of Nindigo, if it were to be made atropisomeric, Nindigo has the potential to be quite versatile. The ease in which the aryl imine of Nindigo can be modified (via the choice of aniline precursor), the inexpensive nature of indigo (Aldrich: 1.65$/g), and a single-step synthesis make Nindigo an attractive scaffold to study. Nindigo has the potential to be an alternative ligand family to α-diimines and a new addition to the γ-diimines class of ligands (**Figure 1.9**).

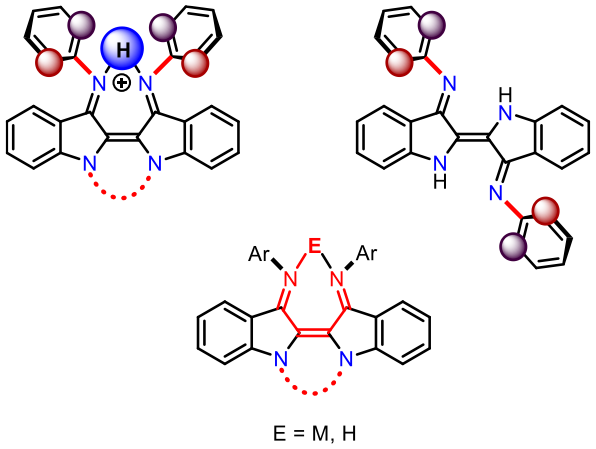


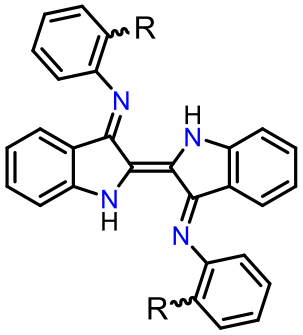
Figure 1.9 Areas of structural modifications studied in this dissertation

The goal of this dissertation is to explore how substituents attached to the aryl imine subunits affect the atropisomerism of Nindigo. The development of a fundamental understanding of how substituents affect the rotational barriers between Nindigo atropisomers is important and allows for the rational design of new and improved Nindigos that have sufficiently large rotational barriers that will allow for their isolation. This understanding can ultimately lead to a new class of ligand or reagent/catalyst that could find utility in asymmetric synthesis. **Chapter 2** focuses on exploratory/proof of principle studies into whether atropisomers of *trans*- and *cis*-Nindigo can be prepared and more fundamentally studying how aryl imine substituents influence the atropisomerization barriers. Chapters three and four focus on the study of how different tethers between the indole nitrogens of *cis*-Nindigo affect the barriers to atropisomerization. Chapter three pertains to how organic tethers and the protonation state of the *cis*-Nindigo derivatives affect the atropisomerization barriers. Chapter four explores how palladium (II) acetylacetonate tethers affect the energy barriers to atropisomerization.

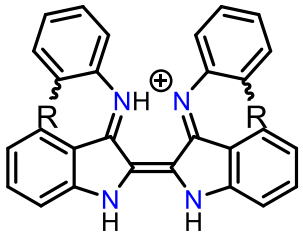
Chapter 2: Investigations of the N-C atropisomerism of neutral *trans*- and protonated *cis*-Nindigo derivatives

2.0 Preface

Preliminary studies of some of the molecules reported in this chapter were undertaken by a former undergraduate student in the Hicks group, Tyler Tuck (BSc 2015), under the supervision of Dr. Emma Davy (Ph.D. 2015). Tyler prepared the *trans*- (**2.1a - 2.1d**) and protonated *cis*- (**2.2a - 2.2d**) derivatives and obtained their ^{1}H NMR, ^{13}C NMR, electronic spectra, and X-ray crystal structures.



2.1

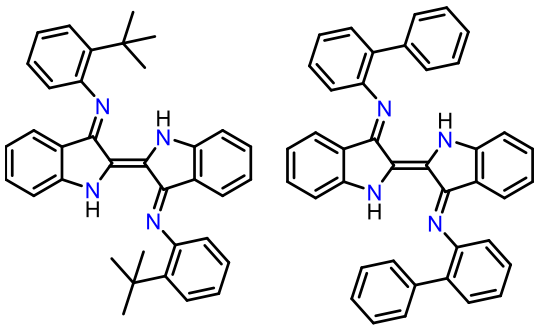


2.2

2.1/2.2a, R = Me
2.1/2.2b, R = iPr
2.1/2.2c, R = tBu
2.1/2.2d, R = Ph

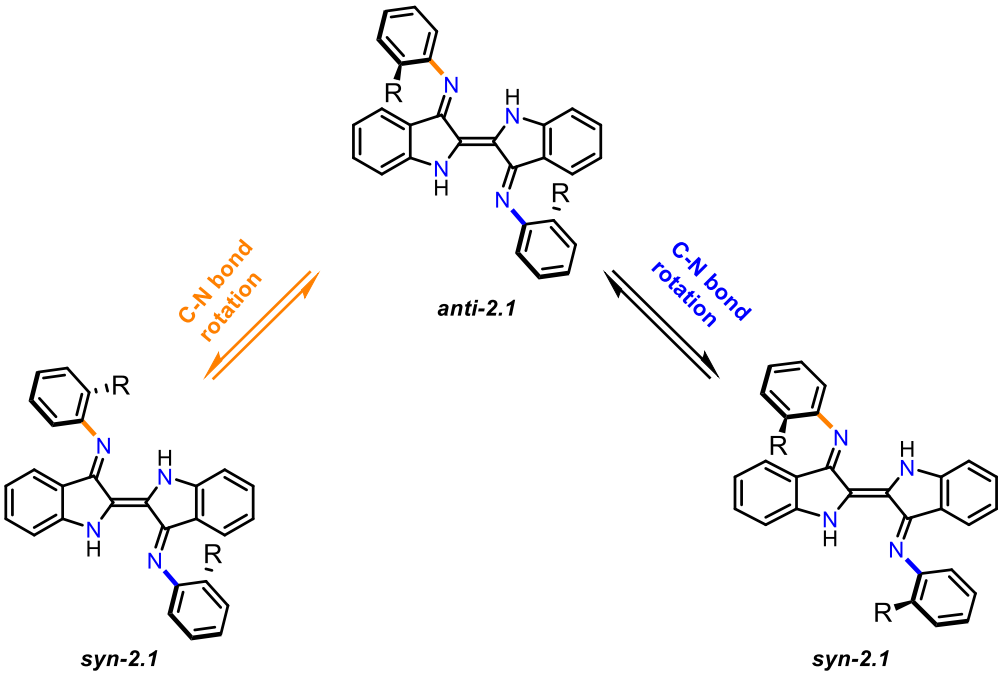
2.1 Introduction

Most of the known Nindigo derivatives have symmetrically substituted aryl imine substituents.[122,129] Two examples of mono *ortho*-substituted *trans*-Nindigo derivatives exist and have aryl imine units derived from 2-*tert*-butylaniline (**2.1c**) and 1-aminobiphenyl (**2.1d**).[129] These molecules were initially of interest as tools to explore the structural diversity of the Nindigo scaffold alongside their electronic spectra, which have wavelengths of maximum absorption of 600 and 603 nm, respectively.

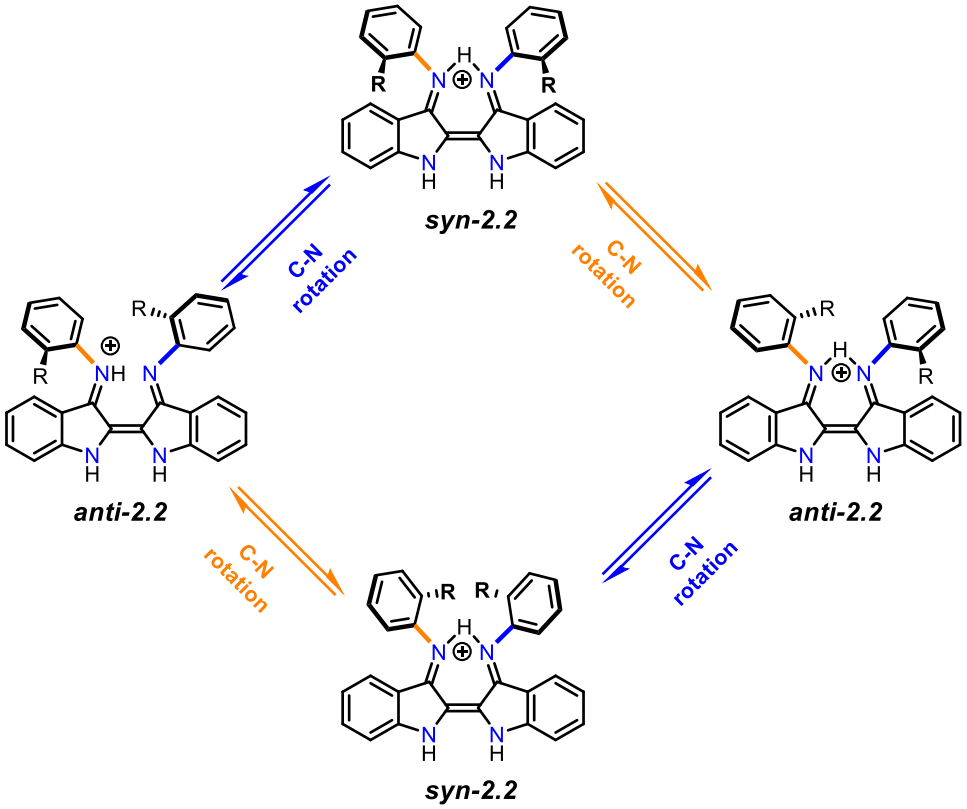


2.1c 2.1d

As outlined in **Chapter 1**, there are two atropisomeric conformations (*anti* and *syn*) mono *ortho*-substituted Nindigos can adopt. To interconvert between the *anti* and *syn* Nindigo atropisomers **2.1** and **2.2**, a rotation about a single *N*-*C* bond must occur (**Scheme 2.1** and **Scheme 2.2**, respectively). In this chapter, the preparation and characterization of a series of mono *ortho*-substituted *trans*- (**2.1a – 2.1g**) and *cis*- (**2.2a – 2.2g**) Nindigos is described. The principal objective is to explore structure-property relationships within the context of the *N*-*C* atropisomerism.



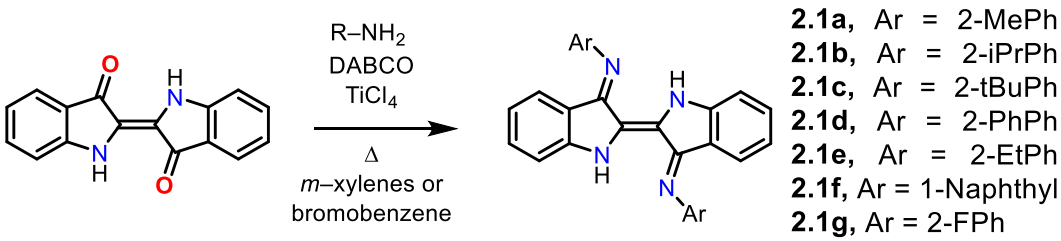
Scheme 2.1 Interconversion of *trans*-Nindigo atropisomers



Scheme 2.2 Interconversion of *cis*-Nindigo atropisomers

2.2 Synthesis of mono *ortho*-substituted *trans*-Nindigos

The *trans*-Nindigo derivatives (**2.1a – 2.1d**), previously prepared by Tyler, were synthesized following modified literature procedures (**Scheme 2.3**),[122,129] alongside new derivatives **2.1e**, **2.1f** (1-naphthyl), and **2.1g** (*o*-fluorophenyl)[122,129,131] in yields between 6 – 71%. The low yield of 6% for **2.1d** agreed well with the previously published yield of 8%.[129]



Scheme 2.3 Synthesis of mono *ortho*-substituted *trans*-Nindigos **2.1a – 2.1g**

2.3 Electronic spectroscopy of Nindigo derivatives 2.1a - 2.1g

The *trans*-Nindigo derivatives are strongly colored, like indigo and the previously reported diimine congeners (**1.54**) and have absorption wavelength maxima between 588 and 603 nm (**Table 2.1**). The narrow range (15 nm) of the absorption wavelength maxima of **2.1a – 2.1g** indicates an insensitivity to the *ortho* substituents and is consistent with the previously reported data for Nindigo derivatives.[122,129]

Table 2.1 Summary of electronic spectra of **2.1a - 2.1g**

Compound	λ_{max}	Molar Extinction Coefficient (ε) $A/mol^{-1}L^{-1}cm^{-1}$
2.1a	588	16 000
2.1b	592	16 000
2.1c[129]	600	20 500
2.1d[129]	603	10 700
2.1e	590	15 600
2.1f	601	26 000
2.1g	601	19 000

The absorption (wavelength) maximum indigo and Nindigo derivatives is because of a π to π* transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).[129] Inspection of the frontier molecular orbitals (FMOs) reveals the reasons for the lack of sensitivity of the wavelengths of

maximum absorption. The structure of Nindigo (**1.54**, Ar = Ph) was optimized with density functional theory (DFT) using the B3LYP functional. The HOMO and the LUMO are primarily localized on the indigoid core and contain small amounts (qualitatively) of orbital density on the aryl imine substituents (**Figure 2.1**). The lack of sensitivity of the absorption wavelength maxima to the substituents is consistent with the high degree of twisting between the aryl imine group and the Nindigo core. The degree of twisting results in less conjugation/delocalization of electron density from the indigoid backbone to the aryl imine subunit.

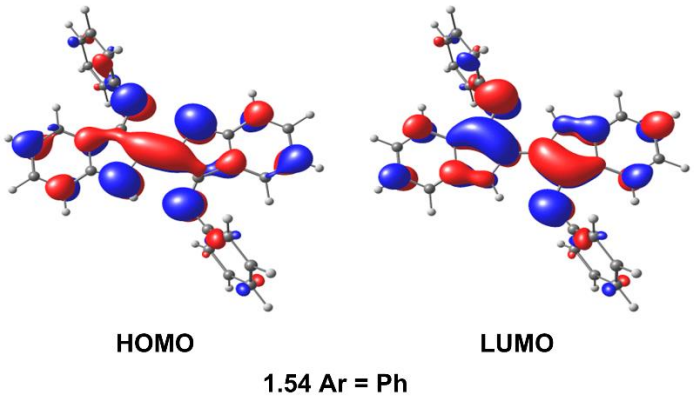


Figure 2.1 Frontier molecular orbitals of **1.54** (Ar = Ph)

2.4 Time-dependent density functional theory study of 1.54 and 2.1a - 2.1g

A time-dependent density functional theory (TD-DFT) study was done to gain insight into the absorption spectra of **2.1a – 2.1g**. Furthermore, whether there are appreciable differences in the predicted absorption wavelength maxima of *anti* and *syn* diastereomers of **2.1a – 2.1g** is of interest. The *anti* and *syn* conformations of **2.1a – 2.1g**

were first optimized in the gas state in Gaussian 16 using B3LYP/6-311G(d,p) and Grimme's D3 dispersion correction with the Becke-Johnson Damping function (D3BJ) (these structures will be used later on in this chapter in determining the atropisomerization barriers) and subsequently using solvation in dichloromethane (SMD model).[139] The optimized geometries of the *anti* and *syn* conformations of **2.1a – 2.1g** have a range of torsional angles with respect to the indigoid core and the aryl imine subunit (**Table 2.2**). The torsional angles are between 30.7 to 85.9° and support the limited sensitivity of the electronic spectra to aryl imine substituents because of the limited p-orbital overlap between the *N*-aryl subunits and the indigoid backbone.

Table 2.2 Torsional angles from the optimized geometries of **2.1a – 2.1g**

Compound	***Anti*** **torsional angle** [a] **(*syn* torsional angle)**	***Anti*** **torsional angle**[b] **(*syn* torsion angle)**
2.1a	82.3 (82.3)	62.9 (64.6)
2.1b	69.5 (70.2)	65.0 (66.5)
2.1c	67.0 (67.3)	64.5 (64.7)
2.1d	30.7 (65.7)	36.2 (44.3)
2.1e	85.9 (70.7)	70.7 (66.2)
2.1f	51.3 (51.4)	51.9 (51.7)
2.1g	46.5 (46.2)	48.4 (49.2)

[a]Torsional angle from optimized geometry in the gas phase; [b] torsional angle from optimized geometry in dichloromethane

The electronic spectra of **2.1a – 2.1g** were computed using B3LYP (**Table 2.3**) and two different basis sets (6-311G(d,p) and Def2TZVPP). The TD-DFT results for B3LYP/6-311G(d,p) and B3LYP/Def2TZVPP agreed well for **1.54**, whose predicted absorption wavelength maxima were within 11 and 14 nm of experimental values, respectively. The alkyl-substituted derivatives (**2.1a – 2.1c** and **2.1e**) have good agreement (0.3 – 19 nm) between their experimental and predicted absorption wavelength

maxima; the *anti* and *syn* conformations of **2.1a – 2.1c** and **2.1e** have predicted absorption wavelength maxima within 0.3 – 16 nm and 7 – 19 nm of experimental values using B3LYP/6-311G(d,p) and B3LYP/Def2TZVPP, respectively. The calculations are less accurate for the phenyl (**2.1d**), naphthyl (**2.1f**), and fluoro (**2.1g**) substituted Nindigo derivatives; the predicted absorption wavelength maxima were red-shifted by between 31 – 88 nm and 34 – 92 nm using B3LYP/6-311G(d,p) and B3LYP/Def2TZVPP, respectively. The lower accuracy in these derivatives is presumed to be caused by the calculations taking into account the additional conjugation of the aromatic substituents. The predicted wavelengths for Nindigo **2.1g** differed by between 31 – 42 nm for B3LYP/6-311G(d,p) and B3LYP/Def2TZVPP. The large differences in the predicted absorption wavelength maxima are likely a combination of two things: (1) the computation overcompensating the additional conjugation of the fluoro substituent and (2) a strong influence from the electron-withdrawing nature of fluoro substituent. Another takeaway from this study is that only the Ph substituted Nindigo had significant differences between the predicted electronic spectra between the *anti* and *syn* conformations. The large differences come from the significant differences in the optimized geometries. The *syn* conformation of **2.1d** is bowed across the indigo backbone, while the *anti* conformation has the expected planar geometry (**Figure 2.2**).

Table 2.3 TD-DFT results of atropisomeric Nindigos **1.54** and **2.1a** – **2.1g**

Compound	Exp. λ (nm)[a]	Predicted λ[b]	Δλ (nm)[c]	Predicted λ[b]	Δλ (nm)[c]
1.54	597[122,129]	608	11	611	14
***Anti*-2.1a**	588	603	16	607	19
***Syn*-2.1a**		602	14	605	17
***Anti*-2.1b**	592	599	7	603	11
***Syn*-2.1b**		598	6	602	10
***Anti*-2.1c**	600	602	2	607	7
***Syn*-2.1c**		604	4	609	9
***Anti*-2.1d**	603	691	88	695	92
***Syn*-2.1d**		668	65	672	69
***Anti*-2.1e**	590	590	0.3	593	3
***Syn*-2.1e**		598	8	602	12
***Anti*-2.1f**	601	657	56	661	60
***Syn*-2.1f**		661	60	665	64
***Anti*-2.1g**	601	639	38	643	42
***Syn*-2.1g**		632	31	635	34

[a] Wavelengths of maximum absorbance in dichloromethane; [b] predicted wavelength of maximum absorption using B3LYP/6-311G(d,p); [c] predicted wavelength of maximum absorption – experimental wavelength of maximum absorption; [d] predicted wavelength of maximum absorption using B3LYP/Def2TZVPP

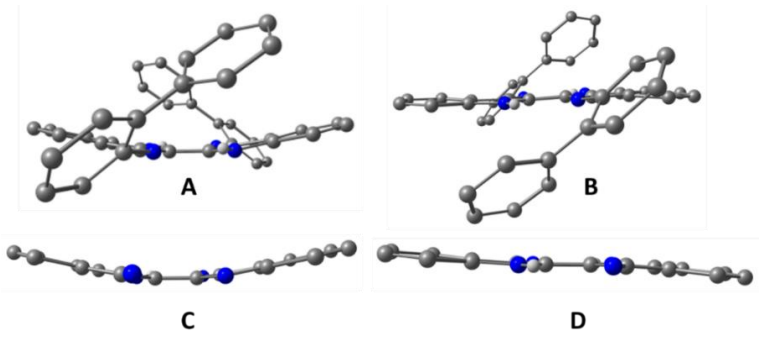


Figure 2.2 Optimized geometries of ***syn*-2.1d** (**A**), ***anti*-2.1d** (**B**), the indigoid core of ***syn*-2.1d** (**C**), and indigoid core of ***anti*-2.1d** (**D**); hydrogen atoms attached to carbons have been omitted for clarity; aryl imine groups removed for clarity in **C** and **D**

2.5 Solid-state structures of atropisomeric *trans*-Nindigo derivatives

X-ray structures of **2.1a**, **2.1c**, and **2.1e** were obtained, all of which feature the Nindigo substituents in the *anti* conformation (**Figure 2.3** and **Figure 2.4**). The structure of **2.1a** has two molecules (**2.1a** and **2.1a'**) in the asymmetric unit; the molecules have torsional angles between the indigoid backbone and aryl-imine substituent of 78.7 and 96.4°, respectively. The discrepancies between the torsional angles are attributed to packing effects. The structures of **2.1b** and **2.1e** (**Figure 2.4**) have torsional angles with respect to the indigoid backbone of 66.9 and 87.9°, respectively. The torsional angles between the indigoid backbone with respect to the substituents of the aryl imine subunit are substituent-dependent and qualitatively correlated with the size of the substituents.

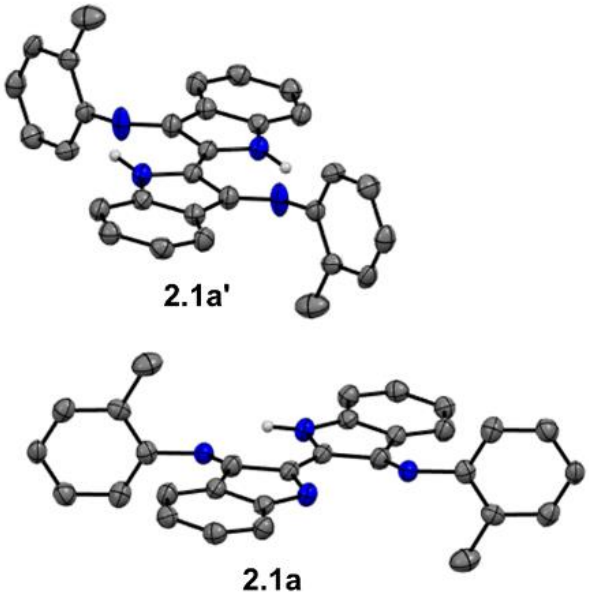


Figure 2.3 Solid-state structure of **2.1a**; thermal ellipsoids set at 50% probability level; hydrogen atoms other than N-H hydrogens have been omitted for clarity; structural disorder of one of the N-aryl rings of 2.1a and 2.1a' have been omitted for clarity

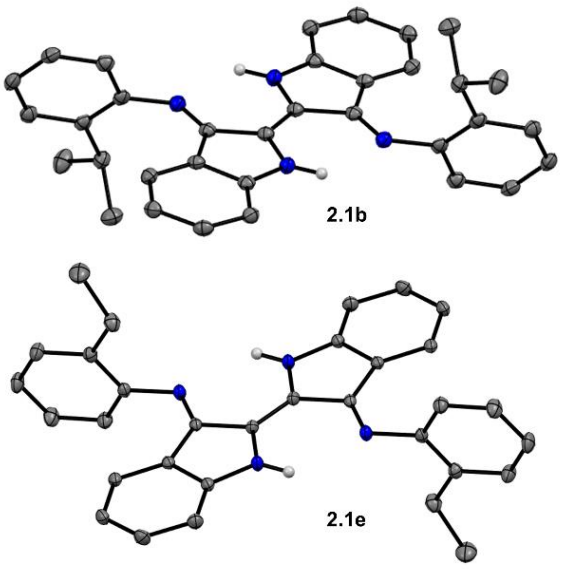


Figure 2.4 Solid-state structures of **2.1b** and **2.1c**; thermal ellipsoids set at the 50% probability level; hydrogen atoms other than N-H hydrogens have been omitted for clarity

2.6 Variable temperature ^{1}H NMR studies of 2.1a – 2.1c

The ^{1}H NMR spectra of **2.1a** – **2.1g** at 298 K all have one set of resonances. This could indicate either that only one atropisomer is present or that the barrier between the atropisomers of **2.1a** – **2.1g** is too low to observe the diastereotopic atropisomers at 298 K and the atropisomers are rapidly interconverting (**Scheme 2.4**). Nindigos **2.1a**, **2.1b**, and **2.1c** were studied using variable temperature (VT) ^{1}H NMR between 298 and 185 K.

The ^{1}H NMR spectra at low temperatures do not indicate multiple species being present for **2.1a** and **2.1b**. For **2.1c** (**Figure 2.5**), the indole NH singlet at 10 ppm splits into two broad singlets at 190 K at 10 ppm, which supports the presence of two atropisomers. The absence of distinct ^{1}H NMR resonances at low temperatures for the *anti* and *syn* conformations of **2.1a** and **2.1b** and only observing a slight separation of the

NH signal into two broad singlets for **2.1c** is because of two potential causes. The first is that the barriers between the atropisomers are small enough that the interconversion remains rapid on the NMR timescale at depressed temperatures. Alternatively, the barriers may be high enough to observe the two atropisomers, but the remoteness of the aryl imine subunits to one another may cause the spectra of the *anti* and *syn* diastereomers to be effectively identical. The separation of the *NH* signal into two peaks is the result of the *NH*s being in a sufficiently different magnetic environment in the *anti* and *syn* diastereomers of **2.1c** at low temperatures. Even at 190 K, no other ^{1}H NMR signals show any appreciable changes.

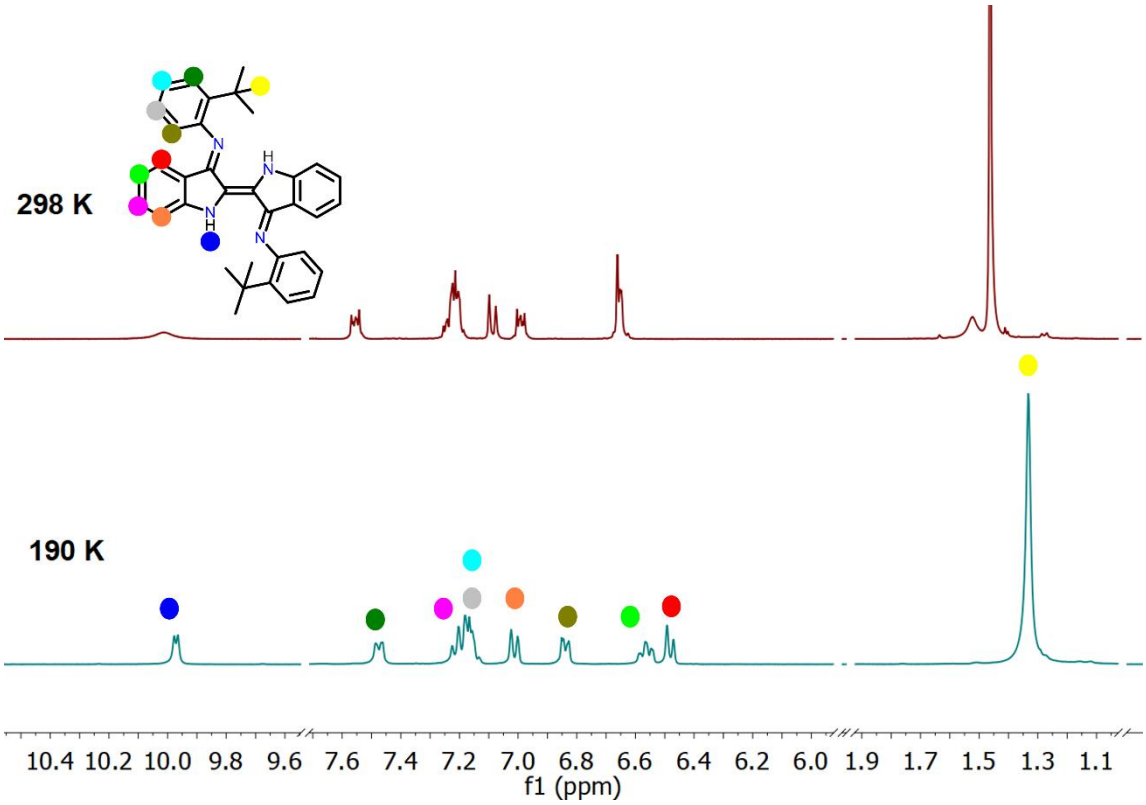
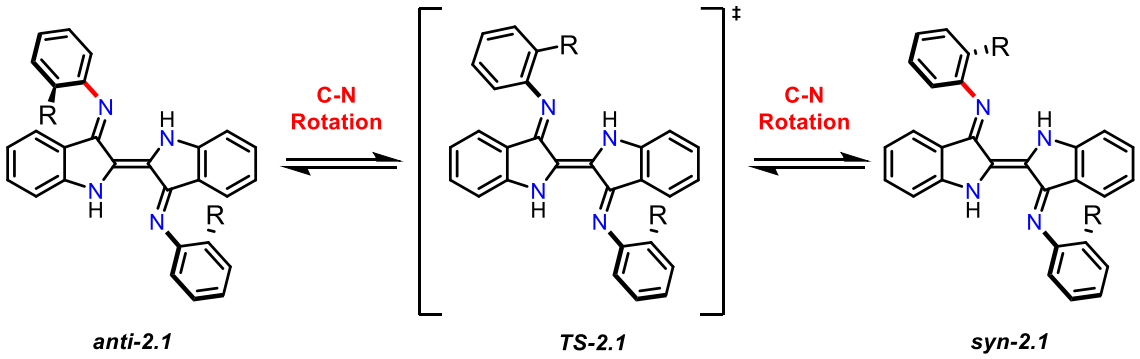


Figure 2.5 ^{1}H NMR of **2.1c** (Ar = *o-tert*butylphenyl)) at 298 K (top) and 190 K (bottom) in CD_2Cl_2

2.7 Evaluation of N-C rotational barriers using density functional theory calculations

The lack of clear separation of the ^{1}H NMR signals at low temperatures (in the absence of exchange) makes the evaluation of the *N-C* rotational energy barriers of **2.1** impossible using ^{1}H NMR spectroscopy. Determining the rotational barriers of atropisomeric systems is commonly done using DFT.[140–142] To this extent, the optimized gas-phase structures of *anti* and *syn* **2.1a** – **2.1g**, **1.54**, and their corresponding transition state (**Scheme 2.4**) for the single *N-C* bond rotation process were computed using B3LYP/6-311G(d,p).



Scheme 2.4 Pathway to interconversion between **2.1** atropisomers

The transition state geometry of **1.54** (**Figure 2.7**) has an almost perfectly coplanar aryl imine group with respect to the indigoid backbone (θ = 179.8°). The torsional angles for the transition states of **2.1a – 2.1g** ranged between 164.3 to 179.9° (**Table 2.4**); the biggest deviation from planarity was found in the ^{t}Bu substituted Nindigo **2.1c**. The computed *N-C* rotational energy barrier of **1.54** was 9.0 kcal/mol, while the barriers for **2.1a – 2.1g** ranged between 6.0 and 16.4 kcal/mol (**Table 2.4**). In general, the *N-C*

rotational energy barriers of **2.1a – 2.1g** and **1.54** are not very sensitive to the steric bulk of the *ortho* substituents. The main outlier is the ^{t}Bu derivative **2.1c**, which has a *N-C* rotational energy barrier of 16.4 kcal/mol.

From an experimental perspective, energy barriers as low as 4.1 kcal/mol[143] can be determined using VT-NMR.[143–145] The key requirement for being able to observe two interconverting species in ^{1}H NMR, is to have a sufficient difference between the peak frequencies and the rate constant of interconversion ($\Delta\nu >> k$) ; if this criterion is not met a single sharp (e.g. $\Delta\nu << k$) or broad ($\Delta\nu \approx k$) will be observed. Given that computed *N-C* rotational barriers have historically agreed well with experimental results, the absence of any separation of the ^{1}H NMR signals at low temperatures further supports the hypothesis that the ^{1}H NMR spectra of the *anti* and *syn trans*-Nindigo conformations are not sufficiently different to be distinguishable from one another. The low energy barriers computed indicate that derivatives of **2.1** belong to the "*Class 1*" or the non-atropisomer class of LaPlante's and have *N-C* rotational energy barriers below 20 kcal/mol.[79]

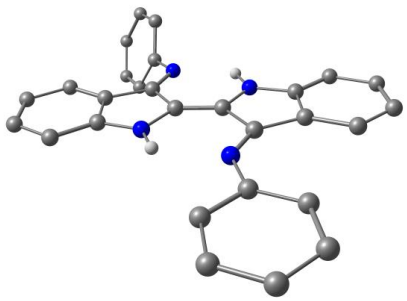


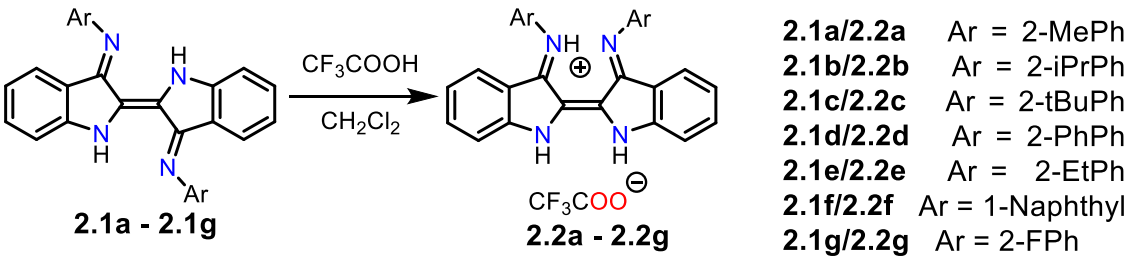
Figure 2.6 Representative optimized transition state geometry of *trans*-Nindigo **1.54**; hydrogen atoms attached to carbon have been omitted for clarity

Table 2.4 Rotational barriers and torsional angles of **1.54** and **2.1a – 2.1g**

Compound	Substituent	Calculated C-N-C-C torsional angle (°)	Calculated rotational energy barrier (kcal/mol)
1.55	H	179.8	9.0
2.1a	Me	179.9	10.5
2.1b	iPr	178.3	11.5
2.1c	tBu	164.3	16.4
2.1d	Ph	175.5	10.5
2.1e	Et	179.4	10.5
2.1f	Ar = 1-Nap	175.6	12.0
2.1g	F	179.3	6.0

2.8 Preparation of protonated *cis*-Nindigos 2.2a – 2.2g

Protonated *cis*-Nindigos (**2.2a – 2.2g**) were prepared using modified literature procedures (**Scheme 2.5**).[131] *Trans*-Nindigos, **2.1a – 2.1g**, were protonated using trifluoroacetic acid in dichloromethane to produce **2.2a – 2.2g** in yields between 64 and 83% after recrystallization from dichloromethane/hexanes. The solutions of neutral *trans*-Nindigos of **2.1a – 2.1g** immediately turned from dark blue solutions to teal upon treatment with trifluoroacetic acid; protonated species were also confirmed to be prepared by the presence of an iminium *NH* signal in their corresponding ^{1}H NMR spectra between 15 – 17 ppm.



Scheme 2.5 Synthesis of protonated *cis*-Nindigos **2.2a – 2.2g**

Like the previously protonated Nindigos **1.65** (Ar = 2,6-dimethylphenyl and Ar = 2,4,6-trimethylphenyl),[131] **2.2a – 2.2g** are strongly colored and have absorption wavelength maxima between 660 and 685 nm. The structure of the non-*ortho*-substituted protonated *cis*-Nindigo, **1.65** (Ar = phenyl), was computed using DFT. As seen in **Figure 2.8**, the FMOs of **1.65**, like **1.54** (**Figure 2.7**), are primarily delocalized over the indigo backbone with some delocalization onto the aryl imine subunits. The experimental absorption wavelength maxima of **2.2a – 2.2g** have a range of 25 nm (660 – 685 nm) (**Table 2.5**), which is a slightly larger range than in **2.1a – 2.1g**. The protonated *cis*-Nindigos, **2.2a – 2.2g** are slightly more sensitive to the nature of the *ortho* substituents; electron-withdrawing and conjugated groups such as fluorine and phenyl resulted in the most red-shifted absorption wavelength maxima (**Table 2.5**).

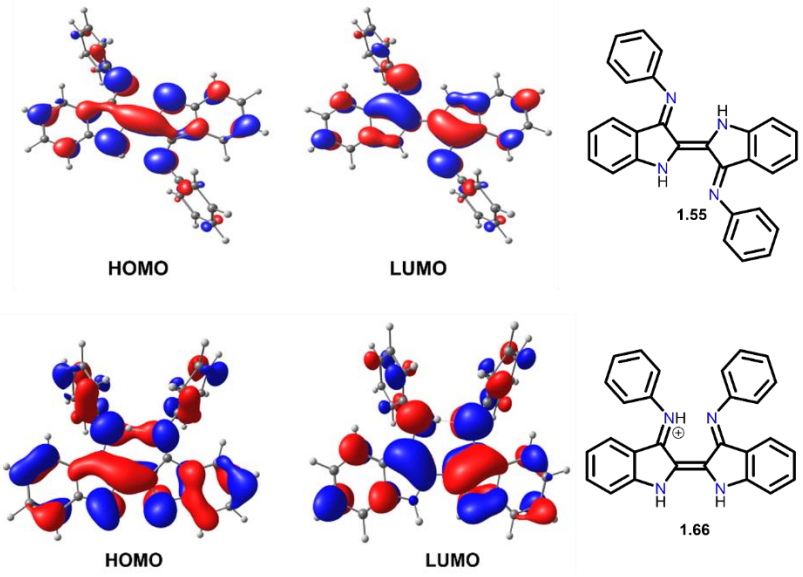


Figure 2.7 Comparison of frontier molecular orbitals of **1.55**and 1.**66** (Ar = Ph)

Table 2.5 Summary of electronic spectra of protonated *cis*-Nindigos **2.2a – 2.2g**

`Compound	Substituent	λ_{max} (nm)	Molar extinction coefficient (ε) $A/mol^{-1}L^{-1}cm^{-1}$
2.2a	H	660	19 700
2.2b	Me	660	19 800
2.2c	iPr	661	18 300
2.2d	tBu	685	16 600
2.2e	Ph	674	17 800
2.2f	Et	675	16 100
2.2g	Ar = 1-Nap F	683	13 700

2.9 Time-dependent density functional theory study of protonated *cis*-Nindigos 2.2a – 2.2g

The *anti* and *syn* conformations of **2.2a – 2.2g** were first optimized in the gas phase and subsequently optimized accounting for solvation effects.[139] The optimized geometries of the *anti* and *syn* conformations of **2.2a – 2.2g** have different torsional angles with

respect to the indigoid core and the aryl imine subunit. The torsional angles ranged between 31.1 – 75.2° and 36.0 – 86.3° for the gas phase and solvated geometries, respectively (**Table 2.6**). The non-planarity of the aryl imine subunits supports the limited sensitivity of the experimental absorption wavelength maxima to the aryl imine substituents.

Table 2.6 Torsional angles of optimized geometries of **2.2a – 2.2g**

Compound	Substituent	Gas-phase structure torsional angles (θ) [a]	Solvated structure torsional angles[b]
***Anti*-2.2a**	Me	50.5 and 46.5	53.2 and 45.1
Syn-2.2a	Me	70.5 and 44.6	86.3 and 45.2
***Anti*-2.2b**	iPr	44.1 and 53.9	51.5 and 53.8
Syn-2.2b	iPr	75.1 and 48.0	78.1 and 48.5
***Anti*-2.2c**	tBu	63.8 and 73.2	66.8 and 70.5
Syn-2.2c	tBu	63.2 and 81.8	64.5 and 85.1
***Anti*-2.2d**	Ph	59.9 and 59.3	67.5 and 60.4
Syn-2.2d	Ph	44.6 and 54.1	45.0 and 55.1
***Anti*-2.2e**	Et	51.6 and 70.8	51.2 and 70.5
Syn-2.2e	Et	63.7 and 74.0	70.3 and 76.0
***Anti*-2.2f**	Ar = 1-Nap	38.6 and 36.1	44.0 and 51.1
Syn-2.2f	Ar = 1-Nap	32.0 and 53.3	60.3 and 36.0
***Anti*-2.2g**	F	53.4 and 53.4	56.3 and 53.4
Syn-2.2g	F	38.0 and 53.5	42.0 and 51.8
Anti-2.1a	Me	82.3	62.9
Syn-2.1a	Me	82.2	64.6
Anti-2.1b	iPr	69.5	65.0
Syn-2.1b	iPr	70.2 and 70.6	66.5 and 67.5
Anti-2.1c	tBu	67.0	64.8
Syn-2.1c	tBu	67.3	64.6
Anti-2.1d	Ph	30.7	36.2
Syn-2.1d	Ph	65.7 and 65.8	44.7 and 44.3
Anti-2.1e	Et	94.1 and 84.9	70.7
Syn-2.1e	Et	70.7	66.2
Anti-2.1f	Ar = 1-Nap	51.3	51.9
Syn-2.1f	Ar = 1-Nap	51.4 and 78.1	51.7
Anti-2.1g	F	46.5	48.4
Syn-2.1g	F	46.2 and 59.9	49.2 and 60.4

[a] torsional angle from optimized geometry B3LYP/6-311G(d,p) in the gas phase; [b] torsional angle from optimized geometry B3LYP/6-311G(d,p)/SMD(dichloromethane)

The TD-DFT spectra were computed for **2.2a – 2.2g**. The calculated absorption wavelength maxima were different than the experimentally determined values for **2.2a –**

2.2g by -13.3 – 65.6 nm and -11.9 – 64.6 nm using B3LYP/6-311G(d,p) and B3LYP/Def2TZVPP, respectively (**Table 2.7**). The differences in the predicted absorption wavelength maxima for the alkyl-substituted congeners are slightly larger for **2.2a – 2.2c** and **2.2e** in comparison to the predicted wavelengths of **2.1a – 2.1c** and **2.1e**, whereas for the more conjugated analogs **2.2d**, **2.2f**, and **2.2g**, the difference between the predicted and experimental values are smaller than for **2.1d**, **2.1f**, and **2.1g**.

Table 2.7 TD-DFT study of atropisomeric Nindigos **1.65** and **2.2a – 2.2g**

Compound	Substituent	Exp. λ (nm)[a]	Predicted λ (nm)[b]	Δλ (nm)[c]	Predicted λ (nm)[d]	Δλ (nm)[c]
1.65	H	N/A	627	-	629	-
***Anti*-2.2a**	Me	660	639	-21	640	-20
***Syn*-2.2a**	Me		614	-46	615	-45
***Anti*-2.2b**	iPr	661	648	-13	649	-12
***Syn*-2.2b**	iPr		623	-38	624	-37
***Anti*-2.2c**	tBu	674	624	-50	624	-50
***Syn*-2.2c**	tBu		623	-51	624	-50
***Anti*-2.2d**	Ph	685	630	-55	631	-54
***Syn*-2.2d**	Ph		664	-21	665	-20
***Anti*-2.2e**	Et	660	616	-44.4	617	-43
***Syn*-2.2e**	Et		594	65.6	595	-64.6
***Anti*-2.2f**	Ar = 1-Nap	675	744	69	747	72
***Syn*-2.2f**	Ar = 1-Nap		693	17.9	694	19
***Anti*-2.2g**	F	683	645	-38.2	647	-36.5
***Syn*-2.2g**	F		655	-28	657	-25.7

[a] Wavelengths of maximum absorbance in dichloromethane; [b] predicted absorption wavelength maximum using B3LYP/6-311G(d,p); [c] difference between predicted and experimental absorption wavelength maximum; [d] predicted wavelength of maximum absorption using B3LYP/Def2TZVPP

2.10 Solid-state structures of protonated *cis*-Nindigo derivatives

The structure of **2.2a** has both the *anti* and *syn* conformations in the same asymmetric unit (**Figure 2.8**). The torsion angles of the indigoid backbone and the methyl substituent for ***anti*-2.2a** and ***syn*-2.2a** were 51.9/46.1°, and 55.7/81.8°, respectively.

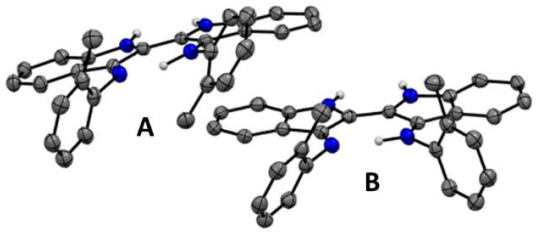


Figure 2.8 Solid-state structure of ***anti*-2.2a** (**A**) and ***syn*-2.2a** (**B**); Ar = *o*-methylphenyl; thermal ellipsoids are at the 50% probability level; hydrogen atoms other than *NH* hydrogens, trifluoroacetate counterions, and residual dichloromethane are omitted for clarity

The solid-state structures of **2.2b – 2.2d** (**Figure 2.9**) are all in the *anti* conformation and have torsional angles of 41.5 and 88.2°; 34.9 and 53.6°; and 70.6 and 64.6°, respectively. The structure of **2.2f** is the *syn* conformer and has torsional angles of 74.3 and 89.3° (**Figure 2.9**).

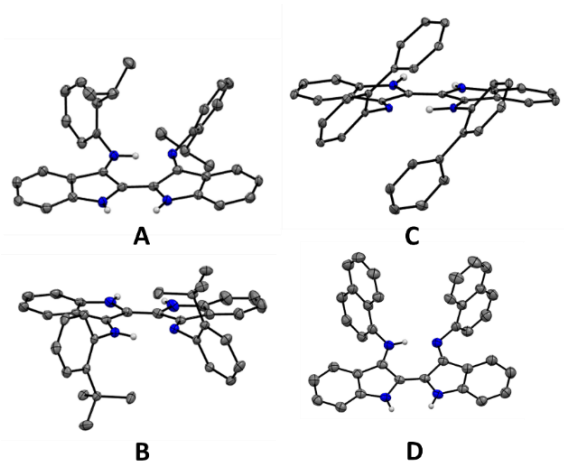


Figure 2.9 Solid-state structure of **2.2b** (**A**, Ar = *o*-isopropylphenyl), **2.2c** (**B**, Ar = *o*-tertbutylphenyl), **2.2d** (**C**, Ar = *o*-phenylphenyl), and **2.2f** (**D**, Ar = 1-naphthyl); thermal ellipsoids are at the 50% probability level; hydrogen atoms other than NH hydrogens, trifluoroacetate counterions, and dichloromethane are omitted for clarity

The solid-state structure of **2.2e** (**Figure 2.10**) was predominantly the *syn* conformer; structural disorder was modeled based on minor amounts of the *anti*-conformation being present (15 %). The torsional angles of **2.2e** substituents and the indigoid backbone are 89.6 and 73.2°, respectively.

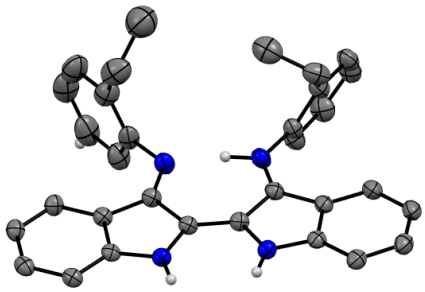


Figure 2.10 Solid-state structure of **2.2e** (Ar = *o*-ethylphenyl); thermal ellipsoids set at 50% probability level; hydrogen atoms other than NH hydrogens and trifluoroacetate counterions were omitted for clarity

The solid-state structure of **2.2g** (**Figure 2.11**) was also modeled with a mixture of *anti* and *syn* atropisomers (75% *anti*); in addition, the *ortho*-fluoro substituent also displayed positional disorder across both *ortho* positions of the aryl imine subunit.

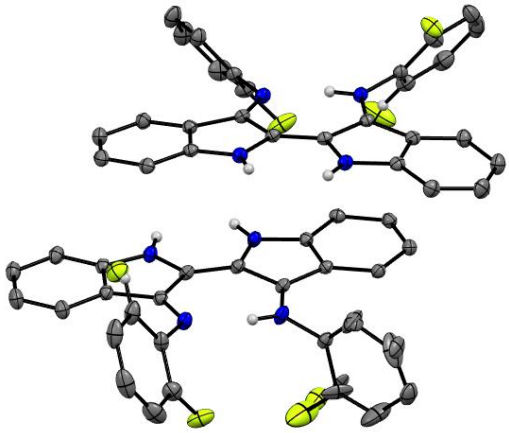


Figure 2.11 Solid-state structure of **2.2g** (Ar = *o*-flurophenyl); thermal ellipsoids set at 50% probability level; hydrogen atoms other than NH hydrogens and trifluoroacetate counterions are omitted for clarity

2.11 Room temperature ^{1}H NMR spectra of 2.2a – 2.2g

The ^{1}H NMR spectra of **2.2a**, **2.2b**, and **2.2d - 2.2f** at 298 K all have two sets of resonances (see **Figure 2.12** for a representative example of **2.2b**), which is ascribed to the presence of *anti* and *syn* conformations. The doubling is most evident in the alkyl region of the ^{1}H NMR of **2.2b**, which has two sets of two doublets for the isopropyl methyl groups at ~1.0 ppm and two septets centered at 3.1 ppm for the methine groups of the *syn* and *anti* conformers in differing ratios; the aromatic region also displays a doubling of some resonances (doublets at ~6.5 and 7.1 ppm), while two sets of iminium and indole *NH* protons are present centered at 16.5 and 13.0 ppm. In contrast, only one set of resonances is present in the spectra of the ^{t}Bu (**2.2c)** and F (**2.2g**) derivatives. The relative proportions of the *anti* and *syn* conformations in the ^{1}H NMR spectra were substituent dependent; the ratios of the *anti* and *syn* conformations (as determined by the relative integration of the iminium resonances) for **2.2a**, **2.2b**, **2.2d**, **2.2e**, and **2.2f** are 1.3, 2.5, 10, 1.8, and 1.1 to 1, respectively. In these ratios, it is assumed that as the size of the substituent increases, the *syn* conformation becomes less stable relative to the *anti* conformer because of the increase in steric interactions between the aryl imine subunits across the diimine pocket; this hypothesis is supported by computational results (*vide infra*).

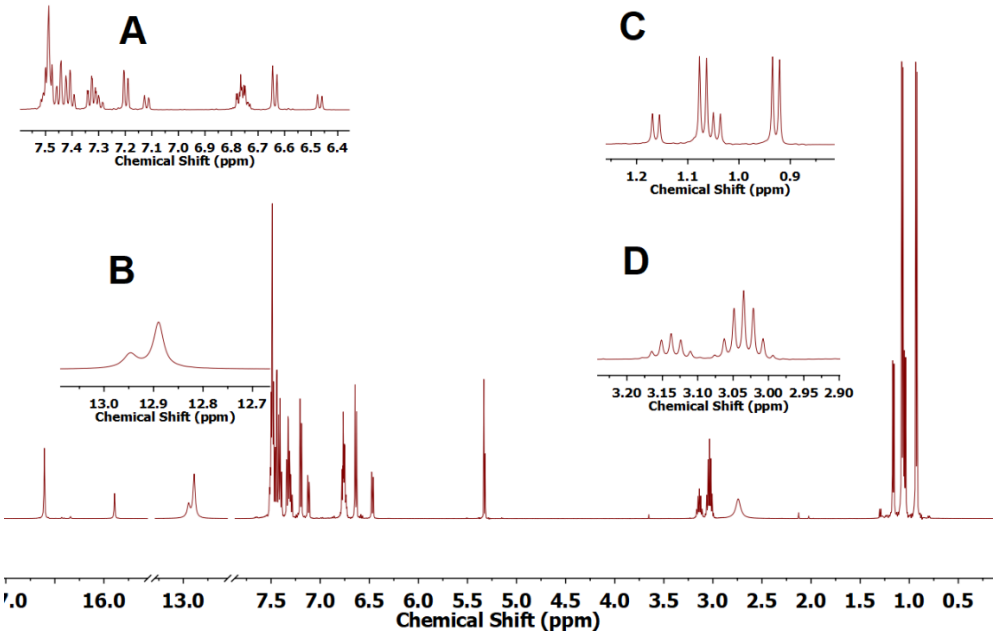


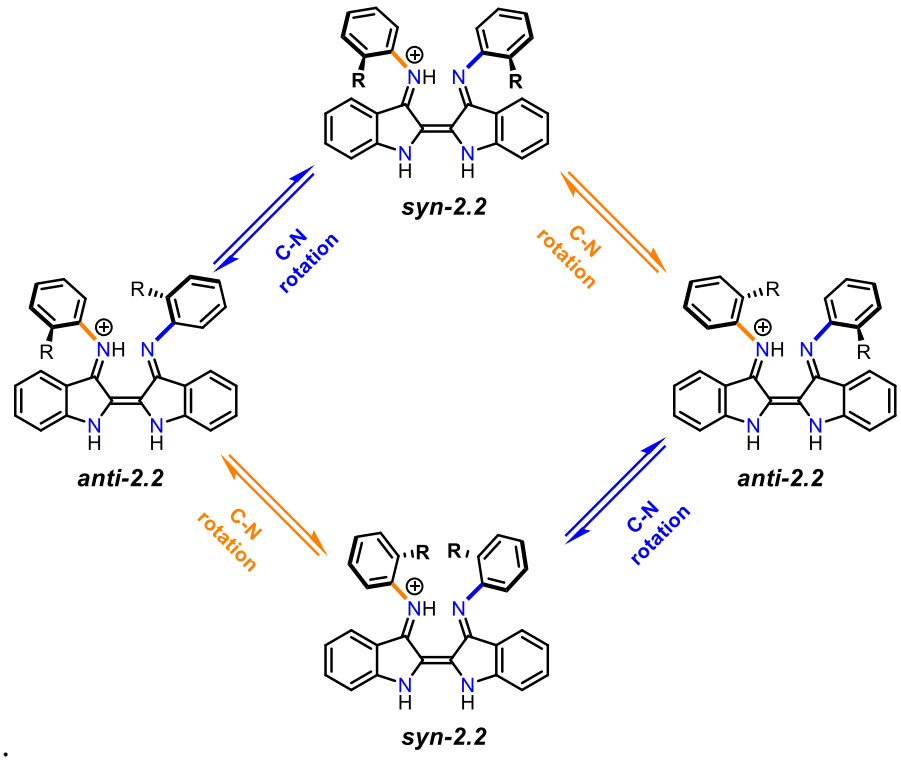
Figure 2.12 ^{1}H NMR spectrum of **2.2b**; **inset A**: aromatic region; **inset B**: indole NH region; **inset C**: alkyl region 1; inset D: alkyl region 2

The observation of a single set of resonances in the spectra of **2.2c** (Ar = *o*-tertbutylphenyl) and **2.2g** (Ar = *o*-fluorophenyl) are believed to have different origins. For **2.2c** the lone set of resonances is attributed to the *anti* conformer being the sole conformer. In contrast, the presence of one set of resonances for **2.2g** (*vide infra)* is attributed to the rapid interconversion of the *anti* and *syn* conformers and is supported by computational studies.

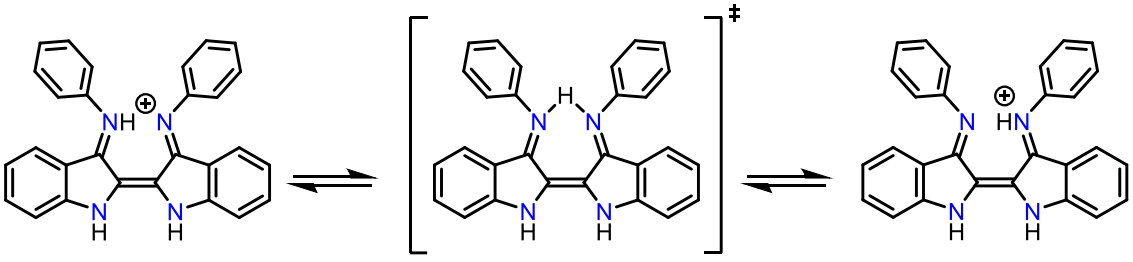
2.12 Variable temperature ^{1}H NMR studies of 2.2a – 2.2g

The presence of distinct signals due to *anti* and *syn* conformers in the ^{1}H NMR spectra for **2.2a**, **2.2b**, **2.2d**, and **2.2f** led to a series of VT-NMR experiments to study the *N-C* rotational barriers. The interconversion process could involve either the rotation of

the *N*-Ar bond or the *HN*-Ar bond (**Scheme 2.7**). To this extent, the energy for the intramolecular proton transfer of Nindigo across the diimine was also computed (**Scheme 2.7)**



Scheme 2.6 Interconversion of *cis*-Nindigo atropisomers via *N*-*C* and *C*-(*NH*) bond rotation



Scheme 2.7 Proposed intramolecular proton transfer of **1.65**

The energy barrier for the shuttling of a proton across the diimine pocket was calculated for **1.65** (Ar = Ph) using B3LYP/6-311G(d,p) to be 0.7 kcal/mol in the gas phase. The transition state geometry of the intramolecular proton transfer has the proton midway between both imine units (**Figure 2.13**). The energy barriers for the intramolecular proton transfer are very low (**Table 2.8**) which means that the proton is shuttling across the *cis*-diimine pocket rapidly at any temperature relevant to the occurrence of atropisomerization. The low barriers to proton shuttling will not influence the bond rotation process if the barriers to atropisomerization are sufficiently high. If the barriers are significantly greater for the bond rotation process relative to the proton shuttling, the bond rotation process is only dictated by whatever *N*-*C* bond rotation process is lower in energy.

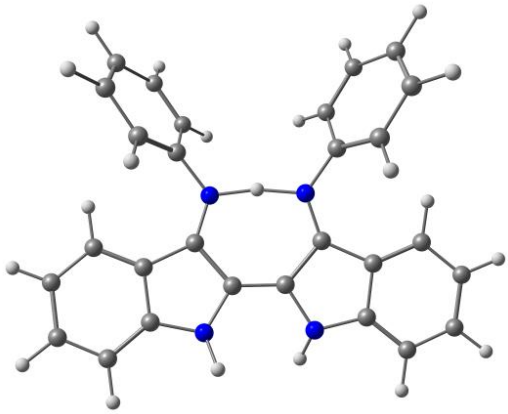


Figure 2.13 Optimized transition state geometry for intramolecular proton transfer in **1.65**

Table 2.8 Energy barriers of the intramolecular proton transfer across the diimine pocket

Compound	Substituent	Gas phase energy barrier (kcal/mol)	Compound	Substituent	Gas phase energy barrier (kcal/mol)
1.65	H	0.66	-		-
***Anti*-2.2a**	Me	0.52	***Syn*-2.2a**	Me	0.51
***Anti*-2.2b**	iPr	0.27	***Syn*-2.2b**	iPr	0.92
***Anti*-2.2c**	tBu	1.99	***Syn*-2.2c**	tBu	0.59
***Anti*-2.2d**	Ph	-0.09	***Syn*-2.2d**	Ph	1.16
***Anti*-2.2e**	Et	0.79	***Syn*-2.2e**	Et	0.74
***Anti*-2.2f**	Ar = 1-naphthyl	0.14	***Syn*-2.2f**	Ar = 1-naphthyl	-0.04
***Anti*-2.2g**	F	0.54	***Syn*-2.2g**	F	1.28

At 298 K, the signals of the CH_3 groups for each conformation of **2.2a** in toluene-d_8 appear at 1.88 and 1.84 ppm and have appreciable broadening (**Figure 2.14**). At higher temperatures, these singlets coalesce at 310 K, and an increasingly sharp singlet is present up to 378 K. When the temperature is lowered to 270 K, the signals of the CH_3 groups for the *anti* and *syn* conformers are sharp and well resolved, and have no/limited broadening from exchange.

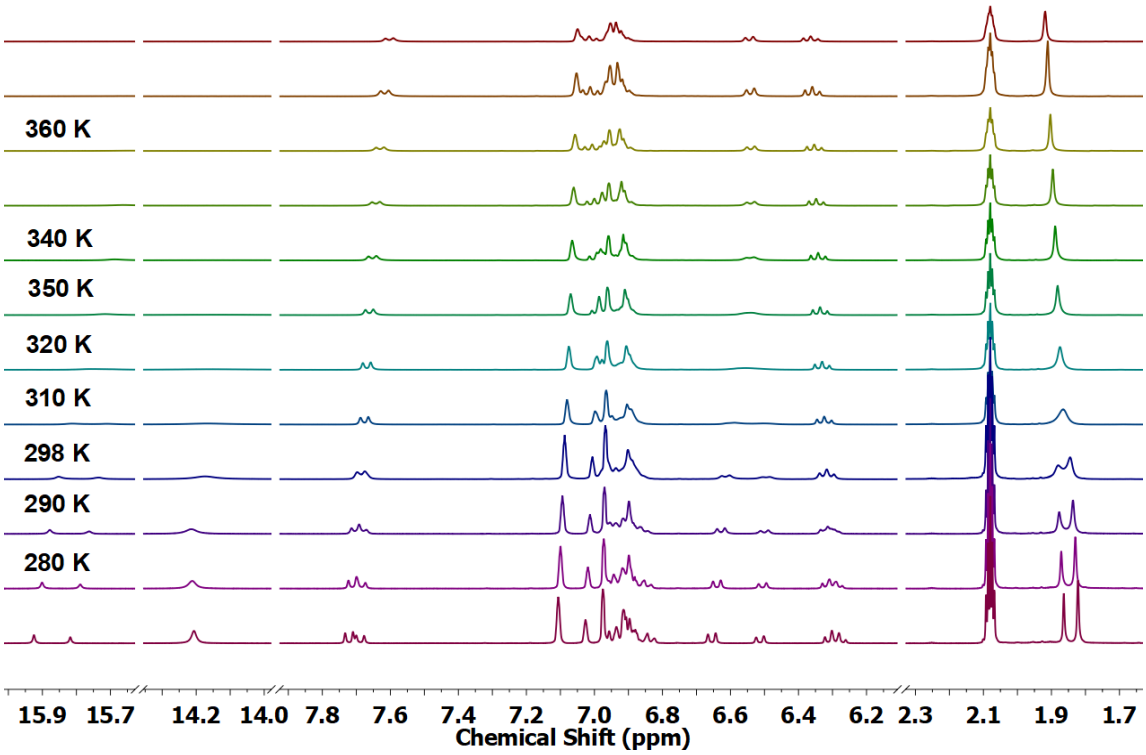


Figure 2.14 Variable temperature ^{1}H NMR study of **2.2a** (Ar = *o*-methylphenyl)

The rate constants for the interconversion of the *anti* and *syn* conformers of **2.2a** were evaluated using lineshape analysis using WinDNMR and are summarized in **Figure 2.15**.[146] The Gibbs free energy of activation ($\mathbf{\Delta G^{\ddagger}}$) for the *N*-*C* bond rotation at 298 K and at the coalescence temperature of 310 K for **2.2a** were determined to be 15.9 and 16.0 ± 0.7 kcal/mol, respectively, using the Eyring equation.[147] The barrier computed at the coalescence temperature can be directly compared to the N-C rotational energy barrier evaluated using the maximum peak separation in Hz and the coalescence temperature.

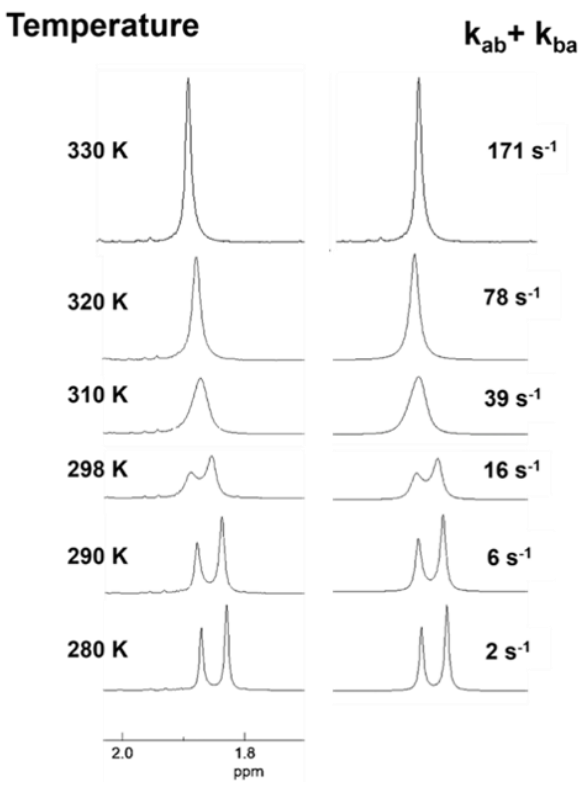


Figure 2.15 Variable temperature ^{1}H NMR and lineshape analysis of **2.2a** (Ar = *o*-methylphenyl)

The ambient temperature ^{1}H NMR spectra of **2.2b** (Ar = *o*-isopropylphenyl) and **2.2e** (Ar = *o*-ethylphenyl) suggest the presence of both the *anti* and *syn* conformations and the peaks are slightly broadened. When the temperature of the samples of **2.2b** and **2.2e** is increased, the signals coalesce at 350 (doublets centered at 6.45 ppm) and 330 K (doublets centered at 6.47 ppm), respectively. As the temperature is increased more, the signals regain resolution at 360 and 350 K for **2.2b** and **2.2e**, respectively, and continue to sharpen up to 378 K. Upon cooling **2.2e** to 290 K, the signals in the ^{1}H NMR have no line broadening because of the interconversion of *anti* and *syn* conformations (See **Figure 2.16** and **Figure 2.17** for the VT ^{1}H NMR of both **2.2b** and **2.2e**, respectively).

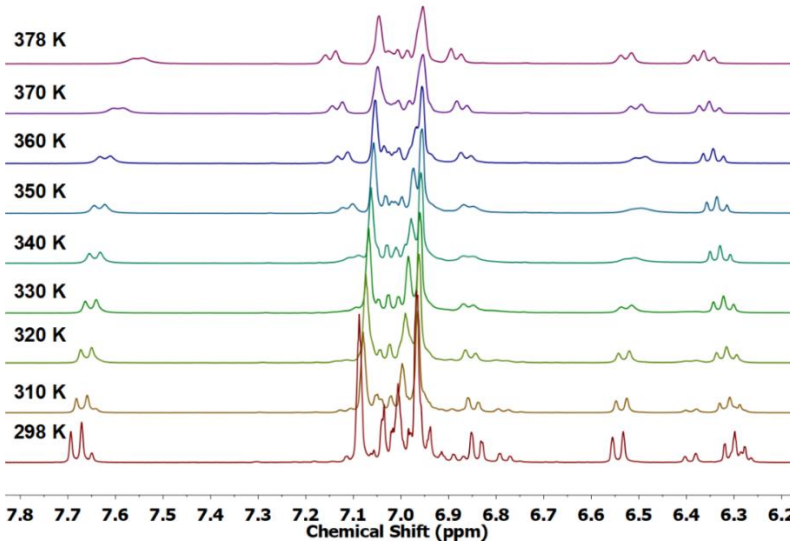


Figure 2.16 Variable temperature ^{1}H NMR study of **2.2b** (Ar = *o*-isopropylphenyl) in toluene-d_8 (aromatic region)

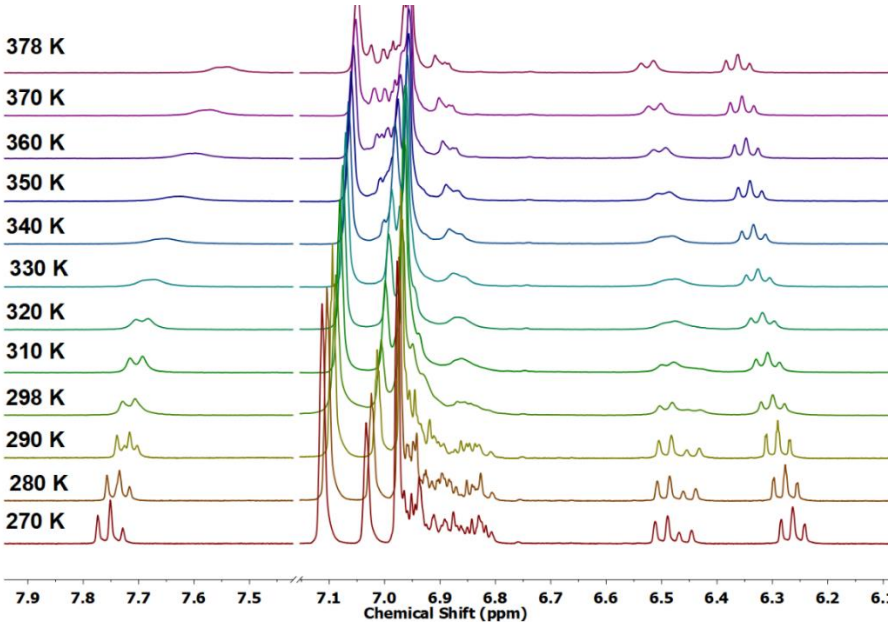


Figure 2.17 Variable temperature ^{1}H NMR study of **2.2e** (Ar = *o*-ethylphenyl) in toluene-d_8 (aromatic region)

The ambient temperature ^{1}H NMR spectra of **2.2c** (Ar = *o*-tertbutylphenyl) and **2.2d** (Ar = *o*-phenylphenyl) in toluene-d_8 are sharp and well resolved. The aromatic region

of the ^{1}H NMR spectrum of **2.2d** (**Figure 2.18**) at 298 K was challenging to interpret because of the large difference in relative abundance between the *anti* and *syn* conformations; the main support for the presence of both conformations is the two iminium resonances at 15.8 and 15.7 ppm (**Figure 2.18** inset).

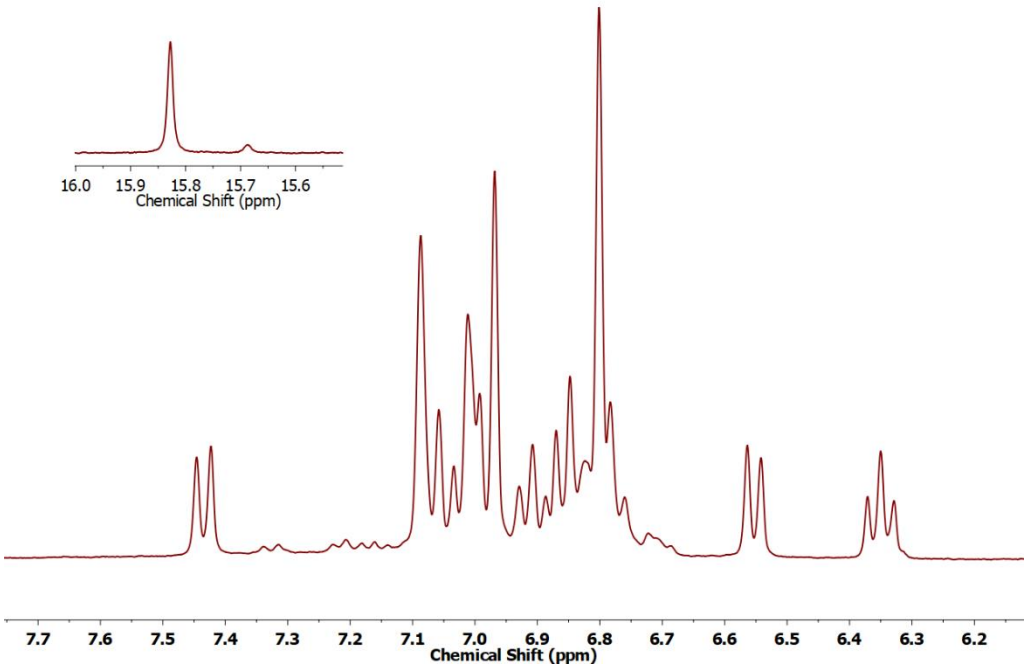


Figure 2.18 ^{1}H NMR of **2.2d** (Ar = *o*-phenylphenyl) in toluene-d_8 at 298 K

Nindigo **2.2d** was subjected to high temperature ^{1}H NMR studies (**Figure 2.19**). As the temperature is increased, the resonances at ~6.55 and 7.45 ppm are the most diagnostic for observing the interconversion between the *anti* and *syn* conformers, and significant broadening occurs at 355 K. The doublet at 6.55 ppm became unresolved at 360 K, and upon further heating, to 378 K, no further changes were observed. Only signals for the major conformation are seen broadening in the VT-NMR study, and the lack of clear signals for the minor conformation broadening makes the interpretation of the

spectra challenging. The ambiguous behavior of the signals in the ^{1}H NMR makes the use of lineshape analysis not feasible. The ambient temperature ^{1}H NMR spectrum of **2.2c** has one set of signals, which suggests that the steric bulk of the ^{t}Bu substituent is sufficient to preclude the formation of the *syn* conformer; this conclusion is supported by computational studies (*vide infra*).

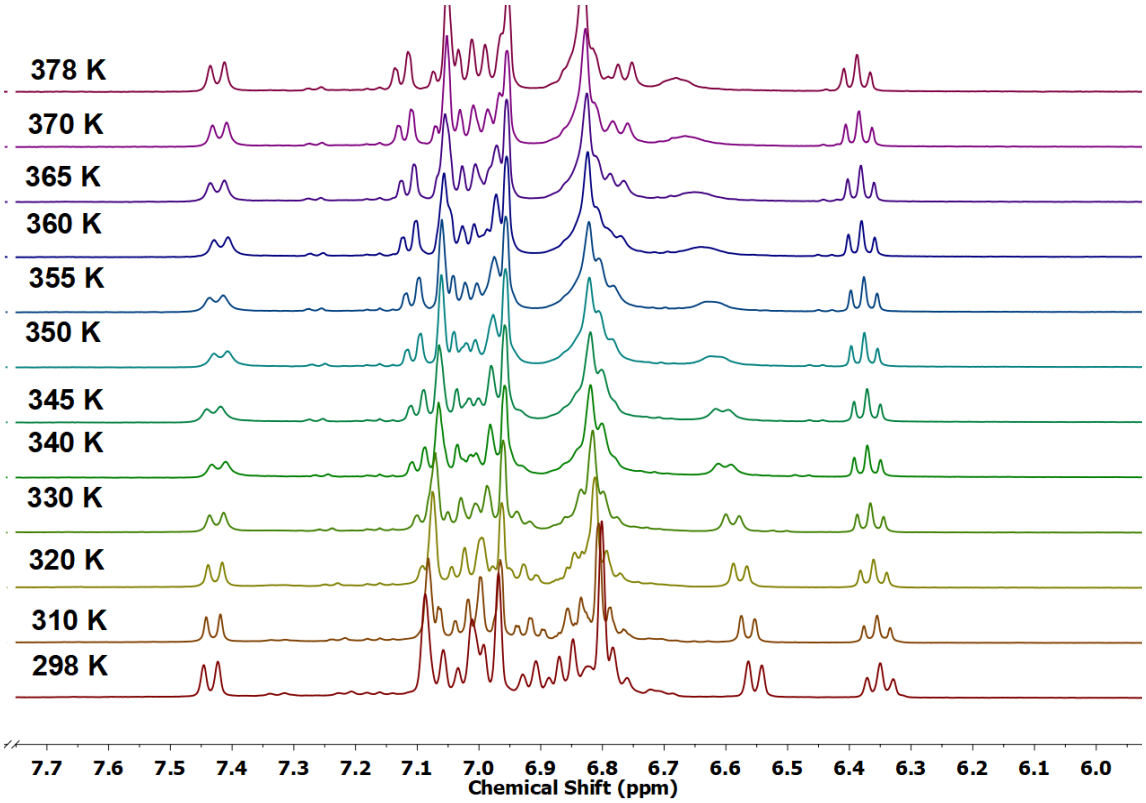


Figure 2.19 Variable temperature ^{1}H NMR study of **2.2d** (Ar = *o*-phenylphenyl) in toluene-d_8

At 298 K, the aromatic region of the ^{1}H NMR of **2.2f** (Ar = 1-naphthyl) in bromobenzene-d_5 is unresolved and broad from the interconversion of the *anti* and *syn* conformers (**Figure 2.20**). The imine resonances also have appreciable broadening from the interconversion of the conformations. Upon cooling **2.2f** to 280 K, the broad signals

at 8.1 and 7.8 ppm sharpen, and upon reaching 260 K, two sharp doublets are present (**Figure 2.21**). As the temperature of **2.2f** is increased, the resonances coalesce at 320 K and continue to sharpen up to 390 K.

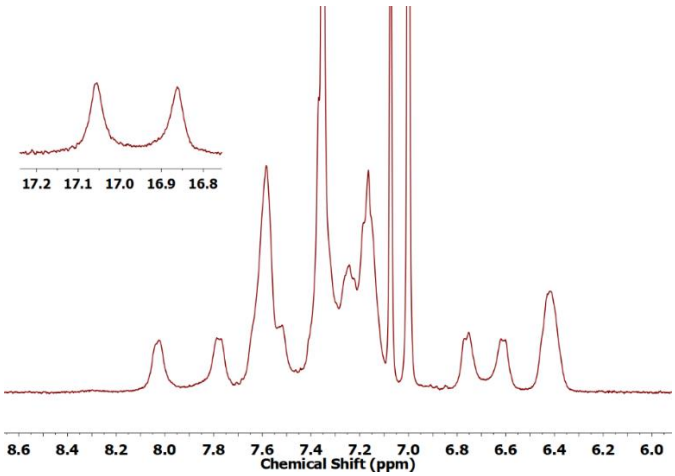


Figure 2.20 ^{1}H NMR of **2.2f** (Ar = 1-naphthyl) in bromobenzene-d_5 at 298 K

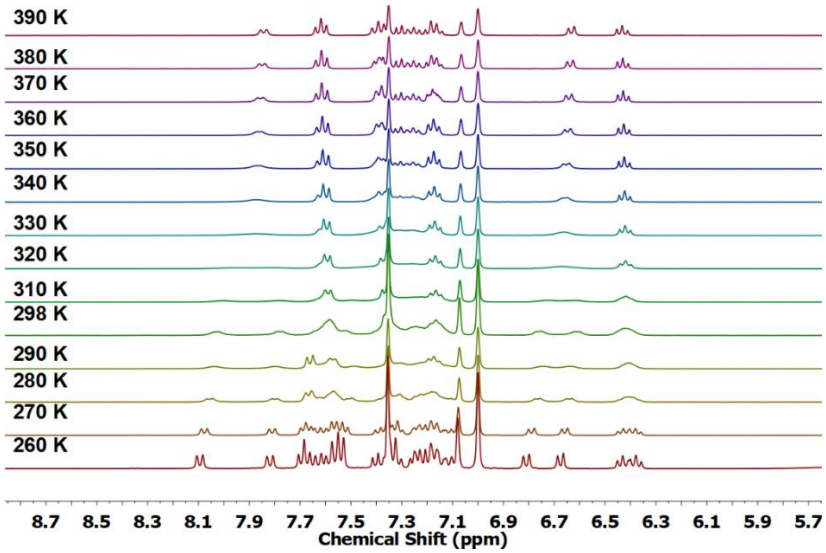


Figure 2.21 Variable temperature ^{1}H NMR study of **2.2f** (Ar = 1-naphthyl) in bromobenzene-d_5

The ^{1}H NMR spectrum of **2.2g** (Ar = *o*-fluorophenyl) at 298 K consists of a single set of resonances. The *anti* and *syn* conformations of **2.2g** were presumed to be in a rapid

equilibrium at 298 K because of the small size of the fluoro substituent. At lower temperatures, the doublet at 7.5 ppm, broadened at 260 K and subsequently separated into two doublets at 7.5 and 7.4 ppm at 200 K (**Figure 2.22**). The iminium and indole NH resonances separated into two singlets at approximately 16.4 and 12 ppm, respectively. The doubling of the resonances at low temperatures confirms the hypothesis that the *anti* and *syn* conformations are in rapid equilibrium at 298 K. The temperature of **2.2g** was lowered to 183 K, and the ratio between the *anti/syn* conformations is 1.5 to 1 as determined by the integration of the two doublets at ~7.5 ppm.

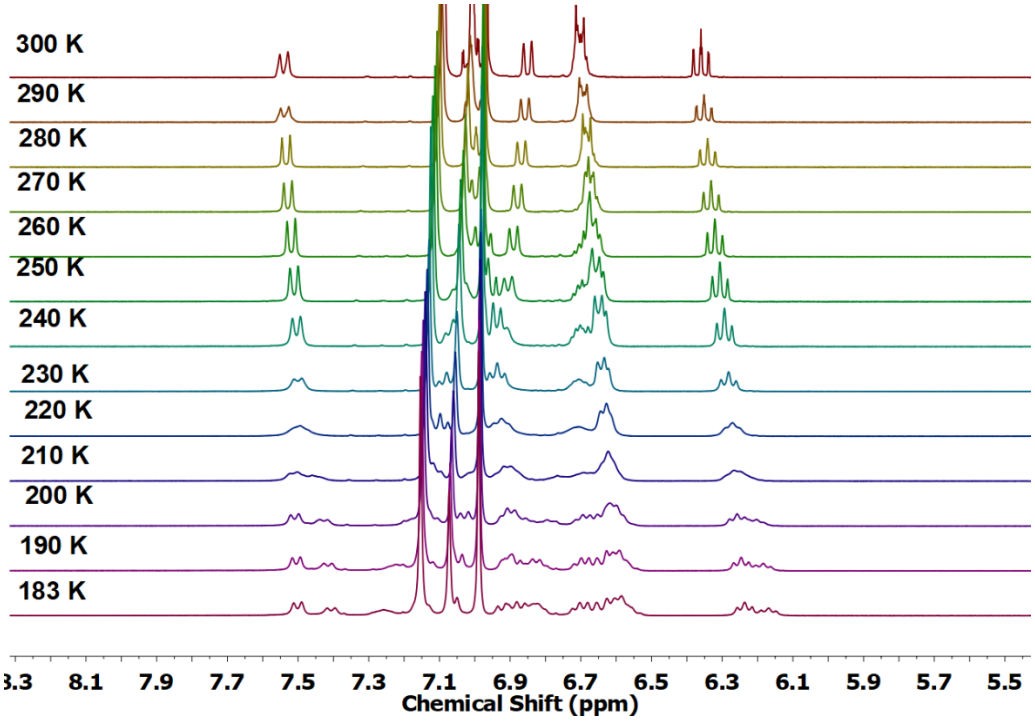


Figure 2.22 Variable temperature ^{1}H NMR study of **2.2g** (Ar = *o*-fluorophenyl) in toluene-d_8

2.13 Determination of the N-C rotational energy barriers of protonated *cis*-Nindigos 2.2b, 2.2e, 2.2f, and 2.2g

Using lineshape analysis, the rate constants for the interconversion of the *anti* and *syn* conformers (**Scheme 2.6**, *vide supra*) of **2.2b**, **2.2e**, **2.2f**, and **2.2g** were determined at 298 K and at their corresponding coalescence temperature. The doublets centered at 6.5, 7.7, 8.3, and 7.4 ppm were simulated for **2.2b**, **2.2e**, **2.2f**, and **2.2g**, respectively (See Appendix for lineshape analysis of **2.2b**, **2.2e**, **2.2f**, and **2.2g**). The barriers at 298 K are 17.1 ± 1.4, 16.3 ± 0.8 , 15.2 ± 0.5, and 12.3 ± 3 kcal/mol for **2.2b**, **2.2e**, **2.2f**, and **2.2g**, respectively; the rotational barriers determined using lineshape analysis at their coalescence temperature ($\Delta G_{TC}^{\ddagger}$) for **2.2b**, **2.2e**, **2.2f**, and **2.2g** are 17.7, 16.2, 15.7, and 10.7, respectively. This data supports the hypothesis that the rotational energy barrier should increase as the steric bulk of the substituent increases. These values also agree well with the rotational energy barriers obtained using the maximum peak separation in the absence of exchange and the coalescence temperature (**Table 2.9**), which have energy barriers of 17.3, 16.5, 15.8, and 10.9 kcal/mol, respectively.

Table 2.9 N-C rotational energy barriers of **2.2a**, **2.2b**, and **2.2e – 2.2g**

Compound	Substituent	T_c (K)	$\Delta G_{298}^{\ddagger}$ lineshape (kcal/mol)	$\Delta G_{TC}^{\ddagger}$ lineshape (kcal/mol)	$\Delta G^{\ddagger}$ coalescence (kcal/mol)
2.2a	Me	310	15.9	16.0	15.9
2.2b	iPr	350	17.1	17.7	17.3
2.2e	Et	320	16.3	16.2	16.5
2.2f	Ar = 1-naphthyl	330	15.2	15.7	15.8
2.2g	F	220	12.3	10.7	10.9

2.14 Computational evaluation of the N-C rotational energy barriers

The barriers between the conformations of **2.2a – 2.2g** and **1.65** were computed using DFT. The transition state geometries will be identical regardless of if it is the *syn* or *anti* conformation interconverting to the *anti* or *syn* conformation because the interconversion process only involves the rotation about a single *N*-*C* bond and the transition state will always have one *N*-Aryl substituent approaching coplanarity with the indigo backbone. The computational study also focused on determining whether the lowest energy *N*-*C* rotation process was either the imine or iminium *N*-*C* bond rotation (**Scheme 2.7**). The *anti* conformation was lower in energy for all except **2.2d** and **2.2g**. The differences in energy for the *anti* and *syn* conformations of **2.2a – 2.2g** ranged from 0.2 to 3.7 kcal/mol, which is reminiscent of the results for the neutral *trans*-Nindigos **2.1a – 2.1g**. No trend can be drawn from the differences in energy between the *anti* and *syn* conformations of **2.2a – 2.2g**. It was initially thought that as the steric bulk of the substituents increases, the differences in the energy between the two conformations would increase; from the data presented in **Table 2.10**, the isopropyl substituted derivative **2.2b** has a smaller difference in energy than the ethyl substituted derivative **2.2e**, while the 1-naphthyl derivative, **2.2f**, whose experimental ratio is comparable to that of **2.2a**, has a difference in energy of 1.6 kcal/mol which is 1.2 kcal/mol greater than **2.2a**. From the differences in energy between the *anti* and *syn* conformations, the ratios between the *anti* and *syn* conformations of **2.2a – 2.2g** are predicted to be (**Table 2.10**) 2.1, 3.8, 509.2, 147.7, 29.5, 2.1, and 15.2 to 1, which other than for **2.2c** do no agree well with experimental results.

Table 2.10 Experimental and theoretical ratios of *anti* and *syn* atropisomers of **2.2a – 2.2g**

Compound	Substituent	Experimental ratio of *cis*-Nindigo conformations	Theoretical ΔG between *syn* and *anti* conformations (kcal/mol)	Theoretical ratio of *cis*-Nindigo conformations
2.2a	Me	1.3:1	0.4	2:1
2.2b	iPr	2.5:1	0.8	4:1
2.2c	tBu	Only anti	3.7	509:1
2.2d	Ph	10:1	3.0	148:1
2.2e	Et	1.8:1	2.0	30:1
2.2f	Ar = 1-naphthyl	1.1:1	0.4	2:1
2.2g	F	1.5:1	1.6	15:1

The transition state geometries for the imine *N-C* (TS, **A Scheme 2.23**) and the iminium *N-C* (TS', **B Scheme 2.23**) rotation, for **2.2a – 2.2g** and **1.65**, all have one of the aryl rings of the imine/iminium subunit nearly coplanar with the indigoid backbone (**Figure 2.23**). The torsional angles of the aryl imine and aryl iminium subunits and the indigoid backbone ranged between 157 and 180° and 136 to 174°, respectively (**Table 2.11**). Interestingly, the biphenyl derivative **2.2d** has torsion angles closest to planarity for the imine and iminium *N-C* rotations, which were 180 and 170°, respectively. The closeness to planarity was surprising given the size of a phenyl substituent relative to a hydrogen (**1.65**) or fluoride (**2.2g**) substituent.

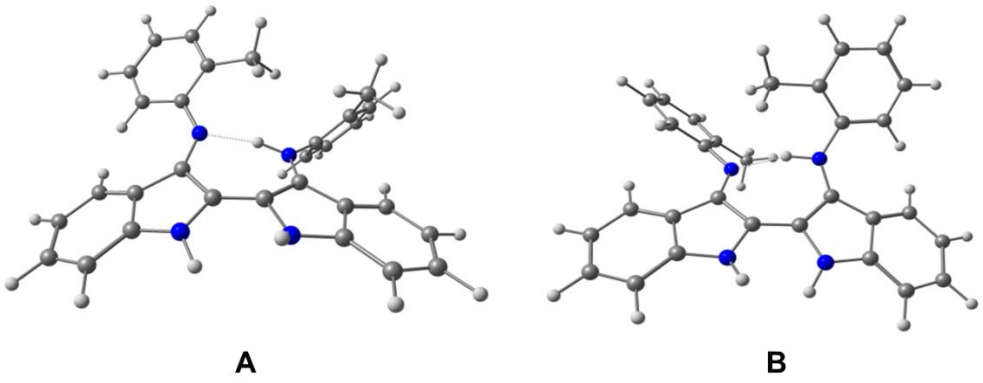


Figure 2.23 Optimized transition state geometries of **2.2a** (Ar = *o*-methylphenyl); TS (**A**) and TS' (**B**)

Table 2.11 Pertinent torsional angles of Nindigos **1.65** and **2.2a – 2.2g**

Compound	Substituent	θ for TS (°)[a]	θ for TS' (°)[b]
1.65	H	167.2	174.2
2.2a	Me	163.7	144.8
2.2b	iPr	169.1	140.9
2.2c	tBu	157.0	136.0
2.2d	Ph	180.0	169.6
2.2e	Et	162.5	149.3
2.2f	Ar = 1-naphthyl	178.7	155.1
2.2g	F	164.1	152.0

[a] Torsional angle between the indigoid backbone and aryl imine substituent for transition state for imine N-C rotation; [b] torsional angle between the indigoid backbone and aryl imine substituent for transition state for iminium N-C rotation

No trend can be drawn from the dihedral angles between the aryl imine subunit size and the indigoid backbone in the transition states (TS and TS'). Compound **2.2c** has the greatest deviation from coplanarity (torsion angles of 157 and 136° for TS and TS', respectively). The transition state torsional angle of **2.2b**, in TS, was 169°, which is closer to co-planarity than **1.65**, **2.2a**, and **2.2e**. When the transition state geometries are looked at in a qualitative sense, as the steric bulk of the substituent increases, the *cis*-imine pocket becomes increasingly distorted. The distortion is most exemplified in the extremely bowed structure obtained for **TS-2.2c** (**Figure 2.24**), which is a result from the increased

steric bulk of the "co-planar" *o-(tertbutyl)*phenylimine group pushing the other *o-(tertbutyl)*phenylimine group more out and away from itself, culminating in a severely bowed geometry.

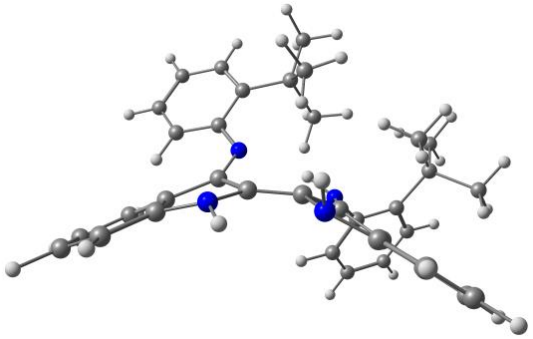


Figure 2.24 Transition state geometry of **2.2c**

The calculated energy barriers for **2.2a – 2.2g** are between 9.3 and 25.5 kcal/mol for the imine *N-C* rotation. These computed barriers agree well with experimentally determined values (**Table 2.11**). The computed barriers for the iminium *N-C* bond rotation are between 9.8 and 145 kcal/mol (**Table 2.12**) and are greater than the imine *N-C* bond rotation barriers. From the computed barriers it can be concluded that the interconversion process between the *anti* and *syn cis*-Nindigos proceeds via an imine *N-C* bond rotation. Furthermore, because the experimental and theoretically determined energy barriers ($\Delta G^{\ddagger}$) are greater than the energy required for the intramolecular proton transfer, atropisomerization is dictated by whichever bond rotation process is lower in energy. The agreement between the computationally and experimentally determined rotational bond energies means that it should be viable to use DFT methods to design Nindigo derivatives with sufficiently high rotational barriers to preclude atropisomerization.

Table 2.12 Rotational energy barriers of *cis*-Nindigo **2.2a – 2.2g** and **1.65**

Compound	Substituent	Calculated TS $\Delta G^{\ddagger}$ (kcal/mol)	Calculated TS' $\Delta G^{\ddagger}$ (kcal/mol)	Lineshape analysis $\Delta G^{\ddagger}$ (kcal/mol)	$\Delta G^{\ddagger}$ using T_c (kcal/mol)
1.65	H	9.7	9.8	-	-
2.2a	Me	15.4	16.5	15.9	15.9
2.2b	iPr	16.0	17.0	17.1	17.3
2.2c	tBu	25.5	27.0	-	-
2.2d	Ph	21.8	144.9	-	-
2.2e	Et	15.3	19.0	16.3	16.5
2.2f	Ar = 1-naphthyl	15.3	15.6	15.2	15.8
2.2g	F	9.3	13.3	12.3	10.9

The B3LYP functional is often used to optimize molecular geometries. A benchmark study was performed on the rotational energy barriers of **2.2a**, **2.2b**, and **2.2e – 2.2g** using the optimized coordinates (B3LYP/6-311G(d,p)) of the *anti*, *syn*, and TS, and performing single point energy calculations to evaluate what DFT method is best suited for evaluating the thermochemistry of the atropisomerization process. A variety of hybrid (B3LYP, B3P86, B3PW91, PBE0, TPSSH, O3LYP, M06-2X, M15, MPW1PW91), meta-GGA (TPSSTPSS), the range-separated hybrid (M11), hybrid meta exchange-correlation (Pw6B95D3) and long-range corrected (CAM-B3LYP, ωB97XD, and LC-ωHPBE) functionals were used to evaluate the rotational energy barriers (**Table 2.13**). Of the functionals studied the best performing functionals were CAM-B3LYP, wB97XD, LC-ωHPBE, M06-2X, and M11, which had mean differences between the theoretically determined barriers and the experimentally determined barriers via lineshape analysis and coalescence temperature ranging between 0.4 – 0.8 kcal/mol. Of the five top-performing functionals at replicating experimental results the M11 functional had the highest accuracy and was used to evaluate the barriers of **2.2c** and **2.2d**.

Table 2.13 Benchmark study on rotational energy barriers of **2.2a**, **2.2b**, and **2.2e – 2.2g**

Compound	Experimental barrier lineshape analysis (Tc) (kcal/mol)	B3LYP	B3P86	B3PW91	B97D3	CAM-B3LYP	LC-wHPBE	M06-2X	M11
2.2a	15.9 (15.9)	15.4	15.2	15.4	15.3	15.7	16.9	15.7	15.7
2.2b	17.1 (17.3)	16.0	15.8	16.2	16.7	17.1	16.8	17.4	18.9
2.2e	16.3 (16.5)	15.3	15.0	15.3	15.3	15.8	17.3	15.2	16.6
2.2f	15.2 (15.8)	15.3	14.7	12.8	13.1	15.1	16.4	14.1	16.0
2.2g	12.3 (10.9)	9.3	9.0	9.8	10.2	9.5	10.7	10.3	10.9
Compound	**Experimental barrier lineshape analysis (Tc) (kcal/mol)**	**M15**	**mPW1PW91**	**O3LYP**	**PBE1PBE**	**Pw6B95D3**	**TPSSTPSS**	**TPSSH**	**wB97XD**
2.2a	15.9 (15.9)	12.5	15.5	15.3	15.1	14.6	14.1	13.7	15.6
2.2b	17.1 (17.3)	16.6	16.0	14.4	16.3	15.0	15.9	13.6	17.8
2.2e	16.3 (16.5)	14.5	15.4	16.5	15.2	14.3	15.3	16.2	15.6
2.2f	15.2 (15.8)	14.4	15.1	16.4	14.0	15.0	11.0	16.0	15.1
2.2g	12.3 (10.9)	9.5	9.2	9.3	9.4	9.8	7.2	7.6	10.31

2.15 Linear free energy relationships of energy barriers of *trans*- and *cis*-Nindigos

The investigation of linear free energy relationships of various systems has been commonplace in chemistry since Hammett's initial disclosures in the 1900s.[148–150] Numerous parameters to describe substituents' electronic and steric effects exist. The steric parameters investigated for correlations with the computed and experimentally determined barriers of Nindigos of type **2.1** and **2.2** were: the interference values,[86] the "A values" developed by Winstein and Holness,[151] Charton's steric parameters,[152,153] Taft's (E_s) parameter,[154] and the "*B values*" (both experimental and theoretical).[88] Correlations between the respective steric parameters and the barriers determined computationally for **2.1** are summarized in **Table 2.13**, while correlations for barriers determined via lineshape analysis, coalescence temperature, and computationally for Nindigos of type **2.2** are summarized in **Table 2.14**. The correlations between the experimentally determined *N*-*C* rotational barriers for compounds of type **2.2** may have some limitations due to these correlations being made up of limited data sets of three (B and interference values) and four (A values, Charton and Taft parameters) data points, and a greater subset of analogs should be investigated before any significant conclusions can be drawn. For the *trans*-Nindigos, the strongest correlation was between the computed barriers and the "Charton's steric parameters," which have an R^2 of 0.94873. Moderate correlations were observed for the other parameters and have R^2 values ranging between 0.75871 and 0.94486 (See appendices for all raw data and analysis).

Table 2.14 Correlations for theoretical rotational barriers of *trans*-Nindigo **2.1a – 2.1g** and steric parameters

	A values	B values exp. [b]	B values theo.[c]	Interference values[d]	Charton's parameters	Taft parameter Es
Computed rotational barrier	0.90713	0.91676	0.86154	0.75871	0.94873	0.31271

Linear free energy relationship analysis was also conducted on the series of protonated *cis*-Nindigos **2.2a – 2.2g** (See **Table 2.14**) for a summary of correlation coefficients). The strongest correlations (R^2 = 0.9996 and R^2 = 0.9971) are between the experimentally determined energy barriers (via lineshape analysis) and the "experimental B values" and "A values", respectively. The other parameters have correlations (R^2) between 0.8986 – 0.9840 for the barriers from lineshape analysis. The *N*-*C* rotational energy barriers determined using the coalescence temperature had correlation coefficients between 0.8710 **–** 0.9939. The correlations between the computed rotational barriers for the imine *N*-*C* rotation were very strong for the "A values" (0.9951) and are between 0.6798 and 0.9274 for the other parameters. The linear free energy relationships for the iminium N-C rotation have weaker correlations relative to their imine N-C congeners and have R^2 values between 0.2366 and 0.8150. The lower correlations are the result of the very large rotational energy barrier calculated for **2.2c** of 144.9 kcal/mol. Given that there is a good relationship between the experimental and theoretical rotational barriers and that there are strong correlations between these barriers and the parameters, it should be feasible to use tables of parameters to design atropisomeric Nindigos with tailor-made

rotational barriers. Furthermore, the correlations for the protonated *cis*-Nindigos are better than for their *trans*-Nindigo counterparts.

Table 2.15 Correlations for rotational energy barriers of *cis*-Nindigos **2.2** and various steric parameters

		A values	B values exp.	B values theo.	Interference values	Charton's parameters	Taft parameters
Method used to determine barrier	**Lineshape analysis**	0.9971[a]	0.9996[b]	0.9338[b]	0.9840 [b]	0.9021[a]	0.8986[a]
	Coalescence temperature	0.9939 [a]	0.9381[b]	0.9165[b]	0.9747 [b]	0.8731[a]	0.8710[a]
	TS barrier	0.9951[c]	0.8550[a]	0.9274[d]	0.6798[c]	0.7069[c]	0.7926[c]
	TS' barrier	0.7916[c]	0.8150[a]	0.6392[d]	0.6125[c]	0.7933[c]	0.2366[c]

[a]Correlation using four available data points; [b] correlation using three data points; [c] correlation using six data points; correlation using five data points.

2.16 "Second generation" atropisomeric Nindigos

Most of the atropisomeric Nindigos studied are classified as "*Class 1*" atropisomers (**2.1a – 2.1g**, **2.2a**, **2.2b**, **2.2e**, **2.2f**, and **2.2g**); exceptions are **2.2c** and **2.2d**, which are classified as "*Class 2*." In order to have a chance at separating Nindigo atropisomers in a practical manner (e.g at room temperature), rotational energy barriers that are greater than 25 kcal/mol are are necessary. In Nindigo derivatives **2.1a – 2.1g** and **2.2a – 2.2g**, there is only one *ortho* substituent attached to the aryl imine subunit (**Figure 2.25**). An additional *ortho* substituent at the six position of the aryl imine subunit may significantly increase the atropisomerization barriers.

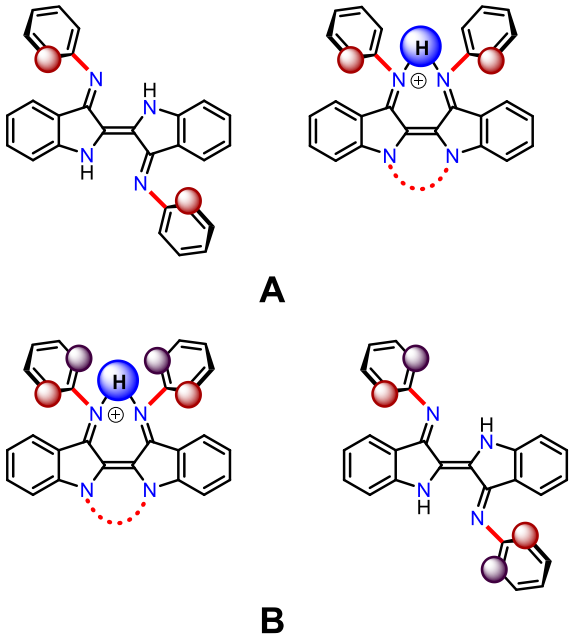
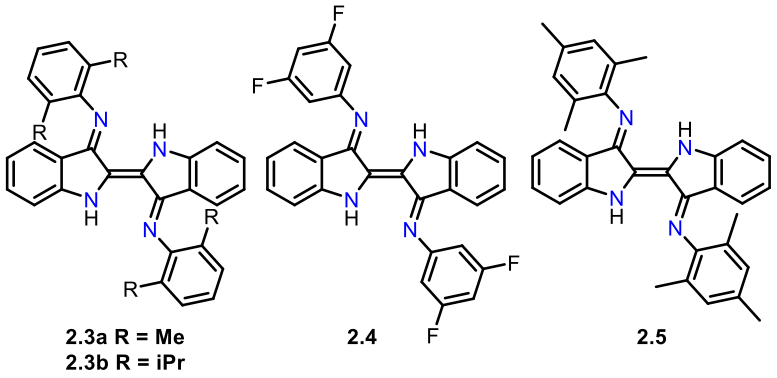
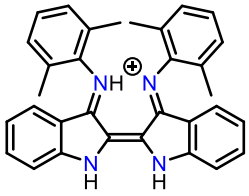


Figure 2.25 First (**A**) and second (**B**) generations of atropisomeric Nindigos

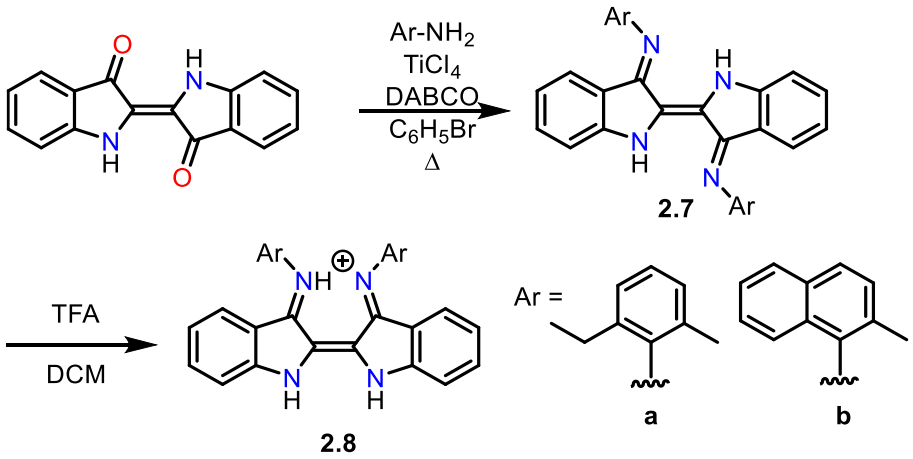
Symmetrically disubstituted *trans*-Nindigo derivatives have been reported in the literature, which includes the 2,6 (Ar = dimethylphenyl (**2.3a**) and diisopropylphenyl (**2.3b**)), the 3,5-disubstituted derivative (Ar = 3,5-difluorophenyl, **2.4**), and the trisubstituted 2,4,6-trimethylphenyl (**2.5**) derivatives; the protonated *cis*- symmetrically dimethylphenyl Nindigo has also been reported. No asymmetrically disubstituted examples have been reported and are of interest in the context of atropisomeric Nindigos.





2.17 Synthesis of asymmetrically disubstituted Nindigos

One 2,6-disubstituted and one 2,5,6-trisubstituted Nindigo were prepared using 2-ethyl-6-methylaniline and 2-methylnaphthylamine as the aniline precursors. The *trans*-Nindigos **2.7a/2.7b** were first prepared in identical 57 % yields, followed by treatment with trifluoroacetic acid to produce protonated *cis*-Nindigos of type **2.8a/2.8b** (**Scheme 2.9**) in 69 and 57 % yields.



Scheme 2.8 Synthesis of the second generation of atropisomeric Nindigos **2.7** and **2.8**

The room temperature ^{1}H NMR spectra of *trans*- **2.7a** and **2.7b** in toluene-d_8, show two sets of resonances. The introduction of additional substituents onto the aryl imine subunit is sufficient to cause the *anti* and *syn trans*-Nindigo atropisomers to be different enough (magnetically) to allow for the observation of the *anti* and *syn* atropisomers in the ^{1}H NMR (**Figure 2.26**, at 298 K). Furthermore, the presence of both conformations at room temperature supports our hypothesis that additional substituents can increase the rotational energy barriers.

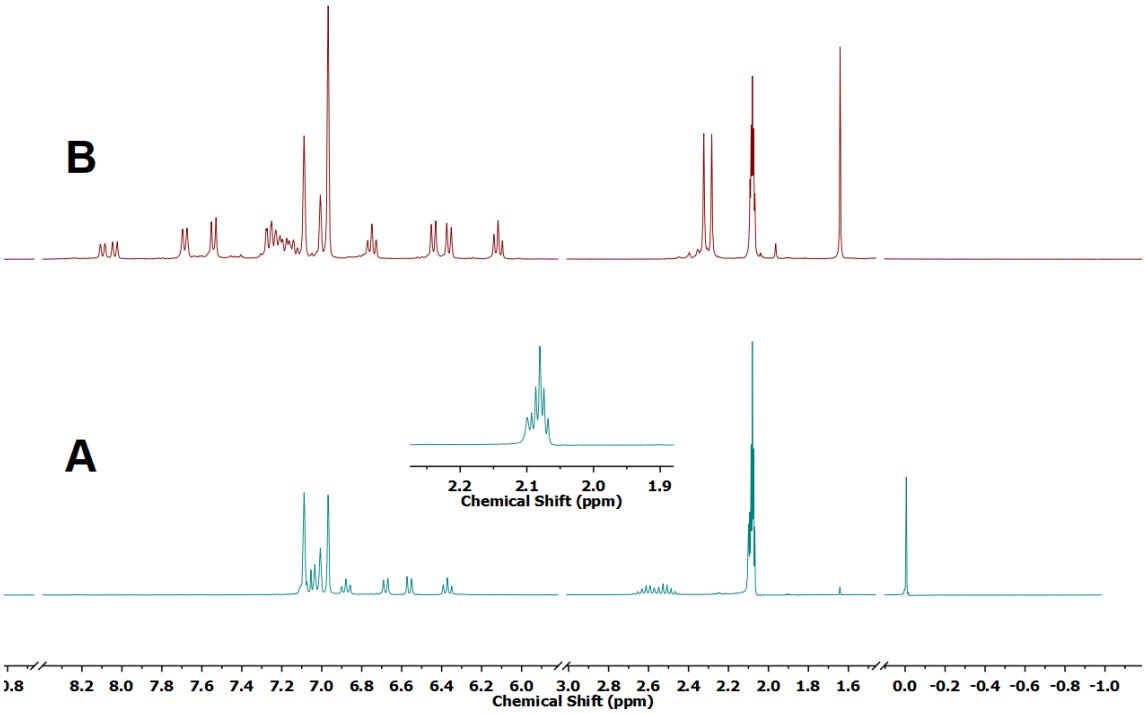


Figure 2.26 Room temperature ^{1}H NMR spectra of **2.7a** (**A**) and **2.7b** (**B**); inset: zoom in expansion of showing methyl resonances overlapping with residual solvent protons of toluene-d_8

2.18 Variable temperature ^{1}H NMR studies of *trans*- disubstituted Nindigos 2.7a and 2.7b

Samples of **2.7a** and **2.7b** were studied using VT ^{1}H NMR (**Figure 2.27** and **Figure 2.28**). As the temperature is raised, the signals in the spectrum remain sharp, and no coalescence between the *anti* and *syn* conformations for either **2.7a** or **2.7b** occurs. The doublets at ~6.6/6.75 and 6.35/6.4 ppm for **2.7a** and **2.7b**, respectively, have a temperature dependence at higher temperatures and "swap places," though no coalescence is seen. The rotational barrier of **2.7a** is estimated to be at least 19.3 kcal/mol based on the maximum peak separation of the doublets at 6.6 and 6.75 ppm (at 298 K) and an assumed "coalescence" temperature of 378 K. The rotational barrier of **2.7b** is estimated to be at least 19.7 kcal/mol based on the maximum peak separation of the methyl resonances at 2.32 and 2.28 ppm (at 298 K) and an assumed "coalescence" temperature of 378 K.

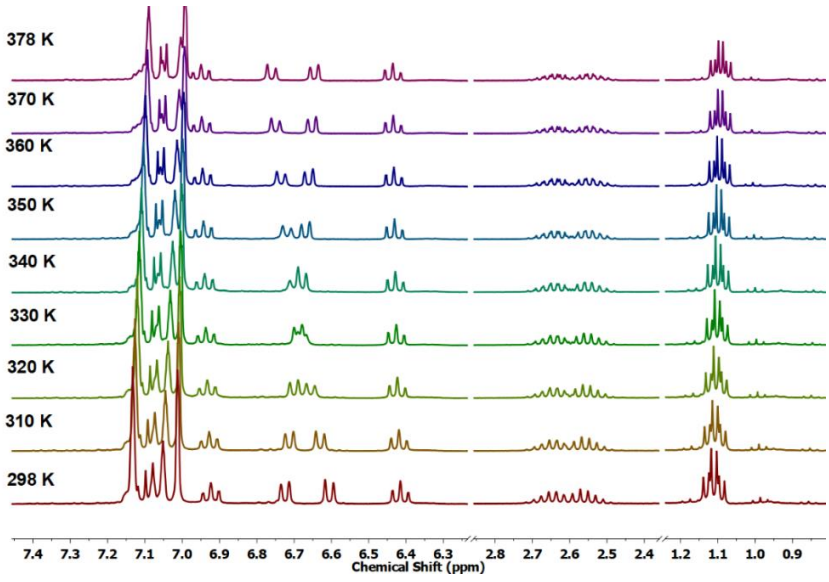


Figure 2.27 Variable temperature ^{1}H NMR study of **2.7a** (Ar = 2-ethyl-6-methylphenyl) in toluene-d_8

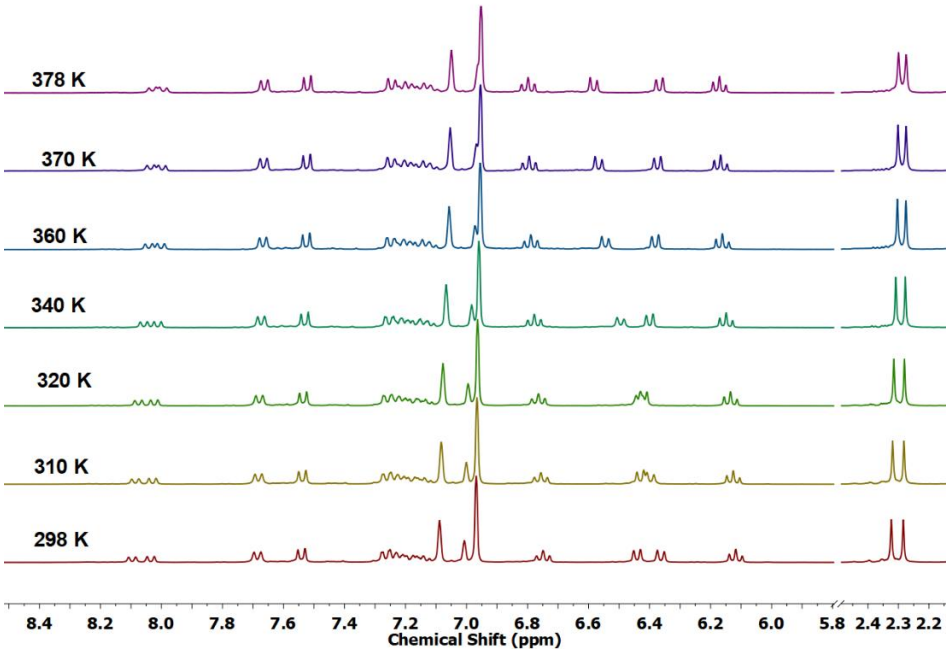


Figure 2.28 Variable temperature ^{1}H NMR study of **2.7b** (Ar = 2-methylnaphthyl) in toluene-d_8

2.19 Density functional theory studies on disubstituted *trans*-Nindigos 2.7a and 2.7b

The rotational energy barriers for **2.7a** and **2.7b** were evaluated using B3LYP/6-311G(d,p). The *anti* conformations, of **2.7a** and **2.7b** are 0.9 and 0.05 kcal/mol higher in energy than the *syn* conformation, respectively. The transition state geometries of **2.7a** and **2.7b** (**Figure 2.30**) resemble **2.1a** – **2.1g**. The transition state geometries of **2.7b** undergoing *N-C* bond rotation via the methyl (**TS**) or the naphthyl (**TS'**) substituent passing the indigoid backbone were computed. The largest difference between the transition states of **2.7a** and **2.7b** and **2.1a – 2.1g** is the imine CNC angle of the aryl imine unit that is rotating. The CNC angle of the transition states of **2.7a** and **2.7b** are 143.6° and 148.4/151.9° (**TS/TS'**), which are almost 10° greater than in **2.1a – 2.1g** (**Table 2.15**).

The atropisomerization barriers of **2.7a** and **2.7b** are 31.5 and 276.9/279.5 kcal/mol (**TS/TS'**), respectively. The introduction of an additional methyl substituent has increased the atropisomerization barrier by 21.0 and 264.9/267.5 kcal/mol for **2.1e** and **2.1f**, respectively. The computational study determined that the rotation of the methyl substituent towards the indigoid backbone is more preferred than the rotation of the naphthyl unit. These first examples of the second generation of atropisomeric Nindigos are "Class 3" atropisomers and are conformationally stable.

Table 2.15 Imine CNC angles of the transition states of **1.55, 2.1a – 2.1g**, **2.7a**, and **2.7b**

Compound	Substituent	Angle
1.55	H	134.5
2.1a	Me	133.7
2.1b	iPr	133.3
2.1c	tBu	131.7
2.1d	Ph	132.6
2.1e	Et	133.7
2.1f	Ar = 1-naphthyl	133.7
2.1g	F	135.3
2.7a	Ar = 2-Et-6-Me	143.6
2.7b	Ar = 2-methylnaphthyl	148.4 (151.9)

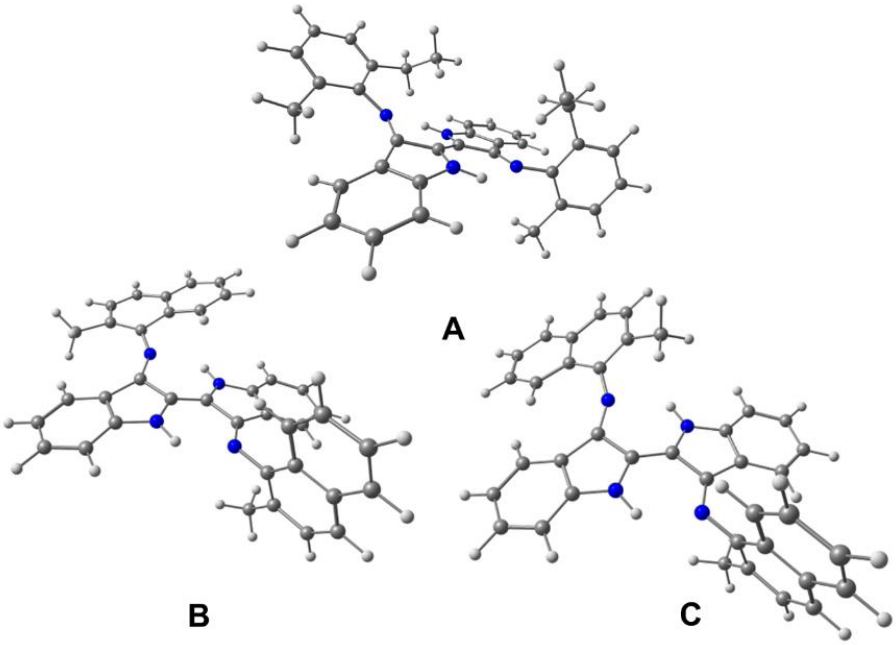


Figure 2.29 Transition state geometries of **2.7a** (**A**, Ar = 2-ethyl-6-methylphenyl) and **TS-2.7b**/**TS'-2.7b** (**B/C**, Ar = 2-methylnaphthyl)

2.20 Variable temperature ^{1}H NMR studies of protonated *cis*-Nindigos 2.8a and 2.8b

The room temperature ^{1}H NMR spectra of **2.8a** and **2.8b** have two sets of signals corresponding to the two atropisomers (**Figure 2.31**). High-temperature VT ^{1}H NMR studies were performed on **2.8a** and **2.8b** (**Figure 2.32** and **Figure 2.33**). Like their *trans*-congeners, no coalescence was observed up to 378 K for **2.8a** and up to 390 K for **2.8b**. The minimum estimated rotational barriers, using the maximum peak separation and an assumed coalescence temperature of 378 and 390 K for **2.8a** and **2.8b**, are 19.3 and 21.5 kcal/mol, respectively.

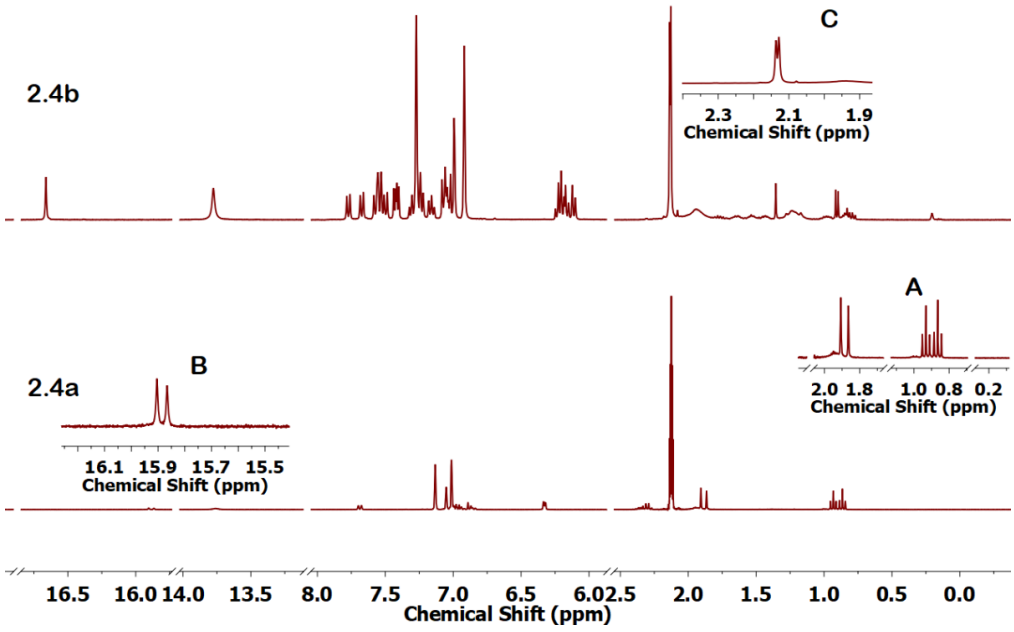


Figure 2.30 Room temperature ^{1}H NMR spectra of **2.8a** (bottom) and **2.8b** (top); **inset A**: alkyl region of **2.8a**; **inset B**: imine NH region of **2.8a**; **inset C**: alkyl region of **2.8b**

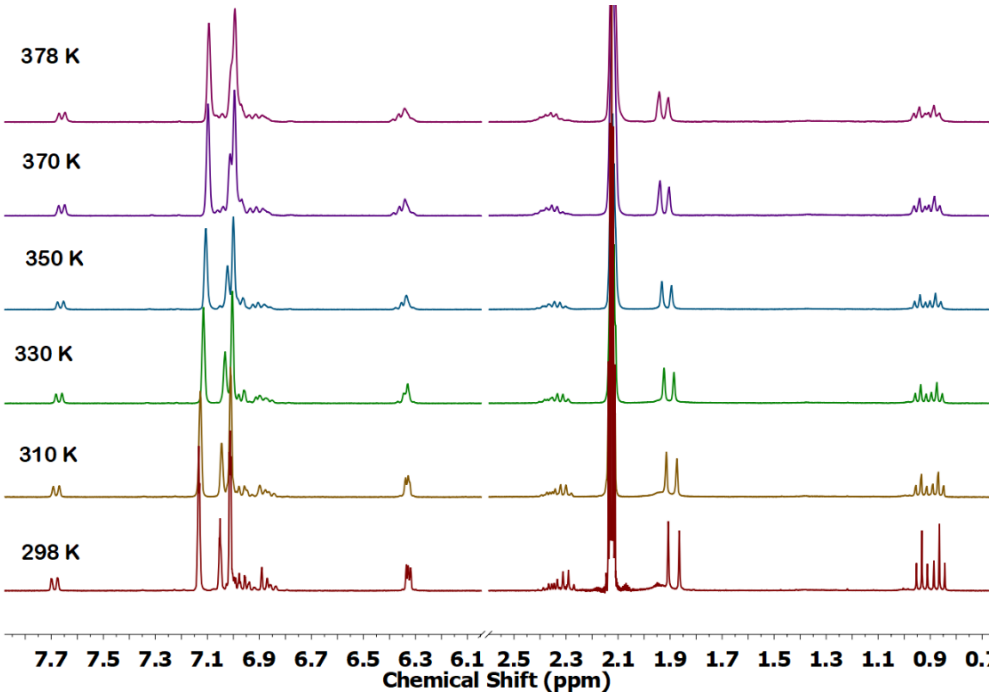


Figure 2.31 Variable temperature ^{1}H NMR study of **2.8a** (Ar = 2-ethyl-6-methylphenyl) in toluene-d_8

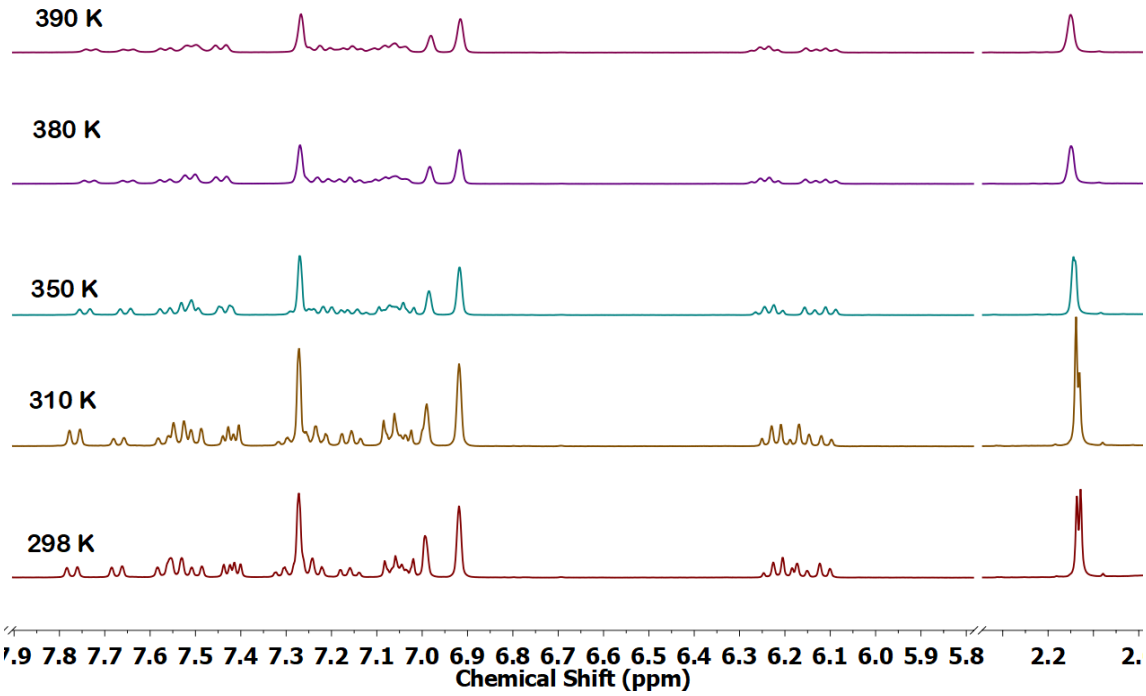


Figure 2.32 Variable temperature ^{1}H NMR study of **2.8b** (Ar = 2-methylnaphthyl) in bromobenzene-d_5

The lack of coalescence and broadening because of the interconversion between the conformations means that the rotational barriers cannot be determined using variable temperature NMR because the *N-C* rotational energy barriers are too high. The barriers were therefore calculated using DFT. For **2.8a**, the *anti* conformation is higher in energy by 0.3 kcal/mol, and the calculated rotational barrier is 29.3 kcal/mol for the imine *N-C* bond rotation (**Figure 2.32**). In contrast for **2.8b**, the *anti* conformer is 0.05 kcal/mol higher in energy, and the calculated rotational barriers are 149.1 and 32.6 kcal/mol for the *N-C* bond rotation having the methyl (**TS**) and naphthyl groups (**TS'**) rotating past the indigoid backbone, respectively (**Figure 2.32**). From the DFT calculations, the lowest energy path for the *N-C* rotation of **2.8b** is via the naphthyl part of the aryl imine subunit

rotating past the indigoid unit and not the methyl group. The simple introduction of an additional substituent on the aryl imine subunit resulted in an increase of at least 13.4 and 17.4 kcal/mol, for **2.8a** and **2.8b**, respectively, relative to **2.2e** and **2.2f.** These high rotational energy barriers put this "third" class of atropisomeric indigo diimine derivatives on the cusp of being a "*Class 3*" atropisomer as defined by LaPlante and coworkers and have the potential to be readily resolved and find use as chiral Bronsted acids upon resolution.

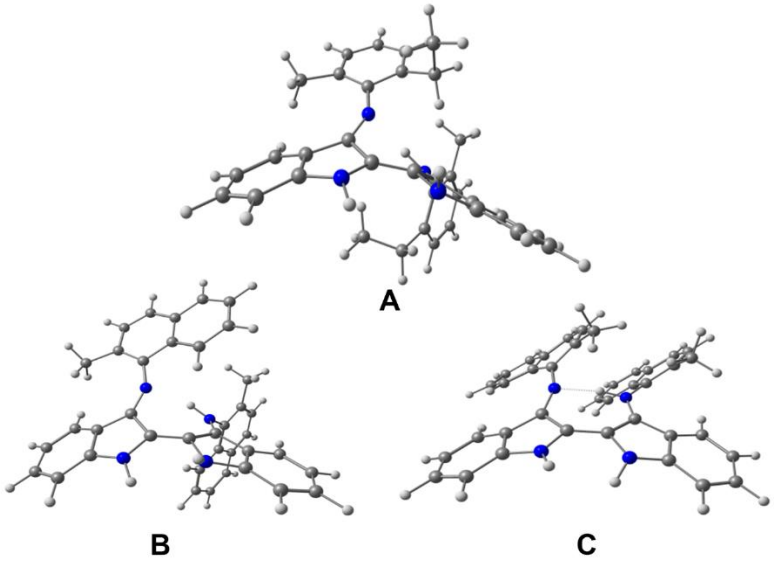


Figure 2.33 Transition state geometries of the second generation of protonated *cis*-Nindigos **TS-2.8a** (A) and **TS-2.8b**/**TS'-2.8b** (B/C)

2.21 Conclusions

This chapter presented the first investigation into the atropisomerism of compounds based on *trans*- and *cis*-Nindigos. A series of mono *ortho*-substituted neutral

trans- (**2.1a – 2.1g**) and protonated *cis*- (**2.2a – 2.2g**) Nindigo derivatives were synthesized and characterized using UV-Visible spectroscopy, X-ray crystallography, and NMR spectroscopy (room temperature and variable temperature NMR).

The electronic spectroscopy of the neutral *trans*- and protonated *cis*-Nindigo derivatives were also studied using TD-DFT and the alkyl-substituted derivatives **2.1a** – **2.1c**, **2.1e**, **2.2a – 2.2c**, and **2.2e** showed great agreement between experimental and theoretical results, while the calculations for the more conjugated derivatives showed less agreement between the experimental and theoretical results.

The atropisomerization barriers for the *N-C* rotation were determined both experimentally and computationally. The rotational barriers of the *trans*-Nindigo derivatives are generally very low in comparison to their protonated *cis*-Nindigo congeners. The atropisomerization process for the protonated *cis*-Nindigo derivatives was determined to proceed via an imine *N-C* bond rotation preferentially to of the rotation of an iminium *N-C* bond rotation. It was determined that the atropisomerization barriers for both the *trans*- and *cis*-Nindigo can be dramatically increased via the introduction of additional substituents at the other *ortho* position of the aryl imine subunit.

Lastly, linear free energy relationships between the rotational energy barriers of the neutral *trans*- and protonated *cis*-Nindigo derivatives were evaluated, and moderate correlations were observed between various steric parameters and the theoretically determined rotational energy barriers of the *trans*-Nindigos. Moderate to great correlations were found for experimental and theoretically determined imine N-C rotation in the protonated *cis*-Nindigos, while poor correlations were observed for the iminium *N*-

C rotation in the protonated *cis*-Nindigos. These correlations make it possible to rationally design new atropisomeric *trans*- and *cis*-Nindigo derivatives using tables of substituent parameters.

2.22 Experimental details

2.22.1 General experimental methods

All *trans*-Nindigo derivatives (**2.1a – 2.1g**) were synthesized under an anaerobic N_2 atmosphere in 500 mL round-bottomed Schlenk flasks following modified literature procedures.[122,129] Protonated *cis*-Nindigos (**2.2a – 2.2g**) were prepared in air in 20 mL vials following modified literature procedures.[131] 1,4-diazabicyclo[2.2.2]octane (DBU) was sublimed before use. Bromobenzene was dried by passing it through a column of activated alumina before being stored over 4 Å molecular sieves for a minimum of 24 hours. *O*-toluidine was distilled from calcium hydride before use. All other reagents and solvents were purchased from Sigma Aldrich, Alfa Aesar, or Combi-Blocks and used as received. NMR spectra that were recorded at room temperature were recorded on either a Bruker AVANCE III 300, AV360, or a Bruker AV I 500 instrument and are referenced to residual solvent signals.[155] Electronic spectra were recorded on an Agilent 8453 spectrometer in dichloromethane. High-resolution mass spectra were obtained by the University of British Columbia Mass Spectrometry Centre or at the Mass Spectrometry Facility at the University of Victoria. Melting points were obtained on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded for potassium bromide pellets using a Perkin-Elmer Spectrum One instrument.

2.22.2 Variable temperature ^{1}H NMR and lineshape analysis

Variable temperature NMR studies were performed on a Bruker AVANCE II 360 or the Bruker AVANCE 500 instrument and are referenced to residual solvent. The temperature calibration was performed as described by Braun, Kalinowski, and Berger,[156] using methanol (for temperatures less than 300 K) and 1,2-ethanediol (for temperatures greater than or equal to 300 K). The uncertainty associated with the temperature calibration for the high and low temperature variable ^{1}H NMR experiments is 2.8 K. Variable temperature ^{1}H NMR experiments were performed in toluene-d_8, dichloromethane-d_2, or bromobenzene-d_5 that was purchased from Sigma-Aldrich. The FID files for the VT-NMR experiments were converted into .nuts files using the NUTS software from Acorn NMR to be modeled using WinDNMR Pro 7.1. Line-shape analysis of the obtained spectra was performed using WinDNMR Pro 7.1.[157] The rate constants for the interconversion of the *anti* and *syn* conformations of atropisomeric Nindigo derivatives were divided by 2 to account for the two potential *N*-*C* bonds that can rotate as has been done by Mazzanti and co-workers previously.[158–160] The corresponding activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$) for the *N*-*C* bond rotation process were obtained using the rate constants from the line-shape analysis by using an Eyring plot of ln(k/T) vs 1/T. The slope of the Eyring plot was used to calculate the enthalpy of activation ($\Delta H^{\ddagger}$) using **Equation 2.1**, where R is the gas constant 1.9872 calories/mol. The entropy of activation ($\Delta S^{\ddagger}$) for the N-C bond rotation process was calculated with **Equation 2.2** using the y-intercept, where k_b is the Boltzmann constant, *h* is Planck's constant, and R is the gas constant. The Gibbs free energy of activation at 298 K was calculated using the enthalpy and entropy of activation using **Equation 2.2**. The Gibbs free energy of

activation was estimated using the coalescence temperature and maximum peak separation using **Equation 2.4**.[161]

$$\Delta H^{\ddagger} = -slope\ x\ R \qquad \textbf{(Eq. 2.1)}$$

$$\Delta S^{\ddagger} = \left(intercept - ln\left(\frac{k_B}{h}\right)\right) x\ R \ \textbf{(Eq. 2.2)}$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \ \textbf{(Eq. 2.3)}$$

$$\Delta G^{\ddagger} = \mathrm{aT}_c\left[9.972 + log\left(\frac{T_c}{\Delta v}\right)\right] \ \textbf{(Eq. 2.4)}$$

The error associated with the computed obtained enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) of activation were computed using the below equations as determined by Girolami and coworkers.[162]. The error of the Gibbs free energies of activation for 2.2a – 2.2g were determined through propagating the errors calculated for the enthalpies and entropies of activation.

$$(\sigma\Delta H^{\ddagger})^2 = \frac{R^2 T_{max}^{\ 2} T_{min}^{\ 2}}{\Delta T^2}\left\{\left(\frac{\sigma T}{T}\right)^2\left[\left(1 + T_{min}\frac{\Delta L}{\Delta T}\right)^2 + \left(1 + T_{max}\frac{\Delta L}{\Delta T}\right)^2\right] + 2\left(\frac{\sigma k}{k}\right)^2\right\}$$

$$(\sigma\Delta S^{\ddagger})^2 = \frac{R^2}{\Delta T^2}\left\{\left(\frac{\sigma T}{T}\right)^2\left[T_{max}^{\ 2}\left(1 + T_{min}\frac{\Delta L}{\Delta T}\right)^2 + T_{min}^{\ 2}\left(1 + T_{max}\frac{\Delta L}{\Delta T}\right)^2\right] + \left(\frac{\sigma k}{k}\right)^2\left(T_{max}^{\ 2} + T_{min}^{\ 2}\right)\right\}$$

where $\Delta T = (T_{max} - T_{min})$ and $\Delta L = [\ln(k_{max}/T_{max}) - \ln(k_{min}/T_{min})]$.

2.22.3 Computational chemistry

All density functional theory calculations were performed on either the Cedar or Graham clusters of Compute Canada. Molecules were built in Gaussview 5.0.[163] All

ground state and transition state geometries were optimized using Gaussian 16[164] using DFT with the B3LYP functional[165] and 6-311G(d,p) in the gas phase and using the SMD solvation model[166] in either dichloromethane or toluene. Tight optimization and SCF convergence criteria were used in the optimizations and frequency calculations. Initial transition state guesses for **2.1a – 2.1g** and **2.2a – 2.2g** were constructed by forcing the aryl imine subunit to be coplanar with the indigoid backbone. Initial guesses of the transition state geometries for **2.7a**, **2.7b**, **2.8a**, and **2.8b** were found using the nudged elastic band method (NEB)[167–169] in ORCA 4.2.1[170,171] and were subsequently reoptimized and confirmed to be transition states in Gaussian 16. Energy minima were confirmed by vibrational analysis, by the presence of no imaginary frequencies, transition state geometries were confirmed by the presence of a single imaginary frequency. Time-dependent density functional theory calculations were completed using Gaussian 16 using B3LYP and either 6-311G(d,p) or Def2TZVPP with the SMD solvation model (solvent=dichloromethane). Molecular orbital surfaces were computed using ORCA 4.2.1 and visualized using ChemCraft.[172]

2.22.4 X-ray crystallography

Single X-ray quality crystals were grown by either layering a concentrated solution of **2.1** or **2.2** in dichloromethane with hexanes or via slow evaporation of dichloromethane/hexanes or dichloromethane/ether solutions. X-ray single crystals were analyzed on either a Bruker APEX DUP equipped with a Mo or Cu source or a Bruker X8 APEX equipped with a Mo source. The data was collected by Dr. Brian O. Patrick at the university of British Columbia's X-ray Crystallography facility. The data was solved

by either Dr. Corey A Sanz (Ph.D. 2017) or Dr. Dillon T. Hofsommer (Ph.D. 2019) using OLEX-2.[173]

2.22.4 Experimental procedures

Indigo-*N, N*'bis(2-methylphenyl)diimine (2.1a): In a 500 mL Schlenk flask, 1.0 M $TiCl_4$ in toluene (15.0 mL, 15.0 mmol) was added dropwise to a solution of DABCO (3.88 g, 34.6 mmol), and *o*-toluidine (1.5 mL, 14 mmol) in *m*-xylenes (200 mL), resulting in a brown mixture. Next, indigo (1.50 g, 5.76 mmol) was added to the flask and the mixture was refluxed for 72 hours. The reaction mixture was filtered hot, and the collected solids were washed with diethyl ether (500 mL). The filtrate was evaporated, and the crude solid was taken up in ethyl acetate (1 L). The ethyl acetate solution was sequentially extracted with 1.0 M HCl (3x 100mL), 0.5 M KOH (4x 100 mL), distilled water (3x 100 mL), and brine (1x 100 mL) and dried with magnesium sulfate. Ethyl acetate was removed in *vacuo*, yielding a dark solid, which was recrystallized from boiling 1-butanol (12 mL). Nindigo **2.1a** was isolated using vacuum filtration, washed with hexanes (15 mL) and subsequently dried in *vacuo*, yielding 2.1a as a dark purple solid (1.34 g, 53 %). Mp: 239 – 241 °C; HRMS (ESI+): m/z calculated for $C_{30}H_{25}N_4^+$: 441.2074 [M+H] found: 441.2082; UV-Vis (CH_2Cl_2): λ_{max} 588 nm (ε = 16 000); FT-IR (KBr): 3358, 3305, 3061, 3006, 2974, 2927, 2871, 1774, 1612, 1572, 1544, 1479, 1467, 1456, 1418, 1304, 1185, 1139, 1111, 1074, 1049, 1013, 876, 747, 728, 670 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 9.99 (br s, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 7.7, 1.2 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.77 – 6.71 (m, 2H), 2.32 (s,

6H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 154.0, 150.2, 146.7, 133.6, 131.2, 131.1, 128.6, 127.1, 125.1, 124.6, 121.2, 119.3, 115.2, 18.2

Indigo-N, N'bis(2-isopropylphenyl)diimine (2.1b): In a 500 mL Schlenk flask, 1.0 M $TiCl_4$ (14.4 mL, 14.4 mmol) was added to a solution of DABCO (3.90 g, 34.8 mmol), and 2-isopropylaniline (2.1 mL, 15 mmol) in *m*-xylenes (250 mL). Indigo (1.508 g, 5.75 mmol) was added to the flask and the mixture was refluxed for 72 hours. The reaction mixture was filtered hot, and the collected solids were washed with diethyl ether (600 mL). The filtrate was evaporated, and the crude solid was taken up in ethyl acetate (1 L). The ethyl acetate solution was sequentially extracted with 1.0 M HCl (3x 100mL), 0.5 M KOH (4x 100 mL), distilled water (3x 100 mL), and brine (1x 100 mL) and dried with magnesium sulfate. Ethyl acetate was removed in *vacuo*, and the resulting dark solid was recrystallized from boiling *n*-butanol (15 mL). Nindigo **2.1b** was collected by vacuum filtration and was washed with hexanes (50 mL); residual volatiles were removed in *vacuo*, yielding **2.1b** as a dark purple solid (1.916 g, 67 %); mp: 202 – 204 °C; HRMS (ESI+): m/z calculated for $C_{34}H_{33}N_4^+$: 497.2700 [M+H] found: 497.2707; UV-Vis (CH_2Cl_2): λ_{max} 592 nm (ε = 16 000); FT-IR (KBr) 3392, 3331, 3060, 3018, 2960, 2926, 2866, 1611, 1577, 1564, 1547, 1478, 1453, 1413, 1319, 1302, 1201, 1172, 1136, 1112, 1075, 1032, 1016, 748, 676 cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.01 (s, 2H), 7.45 (m, 2H), 7.28 – 7.22 (m, 6H), 7.19 (d, *J* = 8.0, 2H), 7.08 (m, 2H), 6.79 (d, *J* = 7.9, 2H), 6.71 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 2H), 3.31 (hept, *J* = 6.9 Hz, 2H), 1.26 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 154.9, 150.3, 145.9, 139.6, 132.7, 131.3, 126.8, 126.4, 125.5, 125.3, 120.9, 120.0, 119.0, 114.8, 29.0, 23.4

Indigo-N, N'bis(2-tert-butylphenyl)diimine (2.1c): Prepared following modified literature procedures.[129] In a 500 mL Schlenk flask 1.0 M $TiCl_4$ in toluene (14.5 mL, 14.5 mmol) was added to a solution of DABCO (3.93 g, 35.0 mmol), and 2-*tert*-butylaniline (2.1 mL, 14 mmol) in *m*-xylenes (210 mL). Indigo (1.51 g, 5.76 mmol) was added to the flask and the dark mixture was refluxed for 72 hours. The reaction mixture was filtered hot, and the collected solids were washed with diethyl ether (300 mL). The filtrate was evaporated yielding a dark solid, which was taken up in dichloromethane (300 mL). The dichloromethane solution was extracted with 1.0 M HCl (3x 100 mL), 0.5 M KOH (4x 100 mL), distilled water (3x 100 mL), and brine (1x 100 mL) and dried with magnesium sulfate. Dichloromethane was removed in *vacuo* and the resulting dark purple solid was recrystallized from boiling *n*-butanol (15 mL). The resulting solid was collected by filtration and was washed with hexanes (15 mL), and volatiles were removed in *vacuo*, yielding **2.1c** as a dark purple solid (2.03 g, 67 %). mp: 280 – 282 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.03 (s, 1H), 7.59 – 7.52 (m, 2H), 7.25 – 7.19 (m, 6H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.03 – 6.98 (m, 2H), 6.68 – 6.64 (m, *4*H), 1.47 (s, 18H); ^{13}C NMR (125.8 MHz, CD_2Cl_2) δ 155.9, 150.3, 148.0, 141.5, 131.5, 130.9, 127.3, 127.2, 126.0, 125.2, 122.2, 120.4, 119.0, 114.0, 35.7, 30.5

Indigo-N, N'bis(2-biphenyl)diimine (2.1d): Prepared following modified literature procedures.[129] In a 500 mL Schlenk flask a solution of $TiCl_4$ (1.0 M in toluene, 36.5 mL, 36.5 mmol) was added to a solution of DABCO (9.57 g, 85.3 mmol), and 2-aminobiphenyl (6.02 g, 35.6 mmol) in *m*-xylenes (300 mL). Indigo (3.68 g, 14.0 mmol) was added to the flask, and the mixture was refluxed for 72 hours. The reaction mixture was filtered hot, and the collected solids were washed with diethyl ether (500 mL). The filtrate was

evaporated and the resulting dark mixture, was taken up in ethyl acetate (800 mL). The ethyl acetate solution was sequentially extracted with 1.0 M HCl (3x 100mL), 0.5 M KOH (4x 100 mL), water (3x 100 mL), and brine (1x 100 mL) and dried with magnesium sulfate. The ethyl acetate was removed in *vacuo* and the resulting dark purple solid was recrystallized from boiling *n*-butanol (20 mL). The solid was collected by vacuum filtration and was washed with hexanes (20 mL); residual volatiles were removed in *vacuo*, yielding **2.1d** as a dark purple solid (0.49 g, 6.2 %); mp: 237 – 238 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.72 (s, 2H), 7.50 – 7.45 (m, 6H), 7.39 – 7.31 (m, 6H), 7.30 – 7.19 (m, 8H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.82 – 6.72 (m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 150.0, 145.0, 139.8, 133.6, 131.1, 131.0, 129.8, 128.6, 128.5, 127.6, 125.2, 124.8, 121.2, 119.6, 119.4, 115.2

Indigo-N, N'bis(2-ethylphenyl)diimine (2.1e): In a 500 mL Schenk flask, a solution of $TiCl_4$ (1.0 M in toluene, 14.6 mL, 14.6 mmol) was added to a solution of DABCO (4.18 g, 37.2 mmol), and 2-ethylaniline (1.8 mL, 15 mmol) in *m*-xylenes (250 mL). Indigo (1.4929 g, 5.6924 mmol) was added, and the mixture was refluxed for 72 hours. The mixture was filtered hot, and the collected solids were washed with diethyl ether (300 mL). The filtrate was removed *in vacuo* yielding a dark solid, which was taken up in ethyl acetate (500 mL). The ethyl acetate solution was sequentially extracted with 1.0 M HCl (3x 100mL), 0.5 M KOH (3x 100 mL), water (1x 100 mL), and brine (1x 100 mL) and dried with magnesium sulfate. Volatiles were removed in *vacuo* and the resulting dark solid was recrystallized from boiling *n*-butanol (20 mL). The solid was collected by vacuum filtration and washed with hexanes (15 mL); residual volatiles were removed in *vacuo*, yielding **2.1e** as a purple solid (1.89 g, 71 %); mp: 177 – 179 °C; HRMS (ESI+):

m/z calculated for $C_{32}H_{29}N_4^+$: 469.2387 [M+H] found: 469.2397; UV-Vis (CH_2Cl_2): λ_{max} 590 nm (ε = 16 000); FT-IR (KBr) 3327, 2963, 2932, 2872, 1741, 1605, 1578, 1566, 1549, 1478, 1457, 1409, 1320, 1304, 1195, 1135, 1108, 1018, 753, 677, 591 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2): δ 10.03 (s, 2H), 7.39 (d, *J* = 7.1 Hz, 2H), 7.31 – 7.24 (m, 4H), 7.24 – 7.18 (m, 4H), 7.12 (dd, *J* = 7.7, 0.8 Hz, 2H), 6.85 (d, *J* = 7.9 Hz, 2H), 6.77 – 6.70 (m, 2H), 2.74 (d, *J* = 7.5 Hz, 4H), 1.26 (d, *J* = 7.8 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 154.2, 150.3, 146.1, 134.9, 133.5, 131.2, 129.5, 127.0, 125.3, 125.0, 121.1, 119.7, 119.2, 115.1, 25.4, 14.9

Indigo N, N'bis(1-napthyl)diimine (2.1f): In a 500 mL Schlenk flask, $TiCl_4$ (1.0 M in toluene, 5.0 mL, 5.0 mmol) was added to a mixture of DABCO (1.54 g, 13.75 mmol), 1-napthylamine 0.70 g, 4.87 mmol) and indigo (0.51 g, 1.929 mmol) in toluene (100 mL) and refluxed for 24 hours. The mixture was filtered hot, and the collected solids were washed with diethyl ether (600 mL). The volatiles were removed in *vacuo* yielding a dark solid; the residue was taken up in ethyl acetate (600 mL) and sequentially extracted with 1.0 M HCl (5x 100 mL), 0.5 M KOH (5x 100 mL), water (3x 100 mL) and brine (2x 100 mL) and dried with magnesium sulfate. Ethyl acetate was removed in *vacuo* and the dark residue was recrystallized from boiling n-butanol (5 mL). Nindigo **2.1f** was collected by vacuum filtration and was washed with hexanes (4x 5 mL); residual volatiles were removed in *vacuo*, yielding **2.1f** as a dark solid (0.36 g, 36 %) mp: 218-220 °C; HRMS (ESI+): calculated for $C_{36}H_{25}N_4+$: 513.20737 [M+H] found: 513.20745; UV-Vis (CH_2Cl_2): λ_{max} 601 nm (ε = 26 000); FT-IR (KBr): 3338, 3051, 2965, 2926, 2877, 1587, 1560, 1548, 1464, 1423, 1405, 1337, 1313, 1291, 1246, 1184, 1137, 1122, 1094, 1040, 1014, 780, 736, 671 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.96

(d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.52 (m, 4H), 7.49 (t, *J* = 7.6 Hz, 4H), 7.29 (dd, *J* = 7.3, 1.1 Hz, 2H), 7.23 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 7.9 Hz, 2H), 6.61 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 156.2, 150.1, 145.2, 134.9, 131.7, 128.5, 126.9, 126.8, 126.8, 126.3, 125.5, 124.7, 123.7, 120.8, 118.9, 114.9, 114.5

Indigo-N, N'bis(2-fluorophenyl)diimine (2.1g): A solution of $TiCl_4$ (1.0 M in toluene, 15.0 mL, 15.0 mmol) was added to a solution of DABCO (3.90 g, 35.2 mmol), and 2-fluoroaniline (1.4 mL, 15 mmol) in *m*-xylenes (200 mL), in a 500 mL Schlenk flask, resulting in a murky brown slurry. Next, indigo (1.51 g, 5.76 mmol) was added, and the mixture was refluxed for 24 hours, yielding a dark blue mixture. The reaction mixture was filtered hot, and the collected solids were washed with diethyl ether (500 mL), the filtrate was next removed in *vacuo* yielding a dark solid. The dark solid was taken up in ethyl acetate (500 mL) and extracted with 1.0 M HCl (3x 100 mL), 0.5 M KOH (3x 100 mL), water (3x 100 mL) and brine (1x 100 mL) and dried with magnesium sulfate. Ethyl acetate was removed in *vacuo* and the resulting dark solid was recrystallized from boiling 1-butanol (10 mL). **2.1g** was collected by vacuum filtration and was washed with hexanes (10 mL). Volatiles were next removed in *vacuo*, yielding **2.1g** as a dark purple solid (0.72 g, 28 %); mp: 264 – 266 °C; HRMS (ESI+): m/z calculated for $C_{28}H_{19}N_4F_2^+$: 449.1572 [M+H] found: 449.1571; UV-Vis (CH_2Cl_2): λ_{max} 601 nm (ε = 19 000); FT-IR (KBr): 3344, 3058, 3035, 2965, 2936, 2871, 1611, 1571, 1483, 1459, 1415, 1323, 1305, 1250, 1206, 1178, 1139, 1112, 881, 748, 674, 562 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.89 (s, 2H), 7.31 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 2H), 7.22 (m, 10H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.78 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ 155.4, 151.1 (d, *J* = 322.5 Hz),

131.9, 125.4 (d, *J* = 7.3 Hz), 125.1, 125.0, 122.0 (d, *J* = 2.3 Hz), 121.2, 119.3, 116.5 (d, *J* = 19.7 Hz), 114.7; Due to poor solubility not all ^{13}C resonances were found; ^{19}F NMR (282 MHz, CH_2Cl_2): δ -126.1

General procedure A for the preparation of protonated *cis*-Nindigos 2.2

In a 10 mL vial, trifluoroacetic acid (6 eq) was added to a solution of **2.1** in acetonitrile (10 mL) and stirred for 15 minutes. The resulting teal solution was next added to 100 mL of distilled water and the resulting precipitate was collected by vacuum filtration. Residual volatiles were removed in vacuo, yielding protonated *cis*-Nindigos as dark purple solids.

General procedure B for the preparation of protonated *cis*-Nindigos 2.2

In a 10 mL vial, trifluoroacetic acid (6 equivalents) was added to a solution of **2.1** in dichloromethane (10 mL) and stirred for 15 minutes. The resulting teal solution was concentrated to 2 mL and hexanes was added, before the solution being stored overnight in the freezer. Crystals of **2.2** were collected by vacuum filtration and the resulting shiny crystalline solids were washed with hexanes. Residual volatiles were removed *in vacuo*, yielding pure **2.2** shiny dark solids.

Indigo N, N'bis(2-methylphenyl)iminium trifluoroacetate (2.2a): In a 50 mL round bottomed flask, trifluoroacetic acid (0.60 mL, 7.8 mmol) was added to a suspension of **2.1a** (0.200 g, 0.45 mmol) in acetonitrile (25 mL), and stirred for 1.5 hours, resulting in a teal solution. The reaction mixture was filtered, and the teal solution was concentrated to 5 mL and added to distilled water (95 mL), precipitating **2.2a**. Protonated *cis*-Nindigo **2.2a** was collected by vacuum filtration and washed with distilled water (100 mL); residual water and acetonitrile were removed in vacuo, yielding **2.2a** as a dark purple solid (0.186 g, 74 %). mp: 220 – 221 °C (decomposition); HRMS (ESI+): calculated for

$C_{30}H_{25}N_4^+$: 441.2074 [M+] found 441.2080; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 16.40 (s, 1H, major), 16.20 (s, 1H, minor), 12.88 (s, 4H), 7.53 – 7.46 (m, 8H), 7.43 – 7.32 (m, 12H), 7.30 – 7.21 (m, 4H), 6.81 – 6.75 (m, 4H), 6.71 (d, *J* = 8.2 Hz, 2H, major), 6.60 (d, *J* = 8.2 Hz, 2H, minor), 2.20 (s, 6H, minor), 2.16 (s, 6H, major); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 162.4 (q, *J* = 35.3 Hz), 158.1 (minor), 157.9 (major), 149.5 (major), 149.4 (minor), 141.8 (minor), 141.6 (major), 135.7, 132.0, 131.4, 131.2, 131.0, 128.3, 127.9, 126.5 (major), 126.4 (minor), 123.1 (minor), 122.8 (major), 121.8 (minor), 121.7 (major), 117.3 (d, *J* = 293.2 Hz), 117.1 (minor), 117.0 (major), 114.2, 17.9; ^{19}F NMR (283 MHz, $CDCl_3$) δ -75.5

Indigo N, N'bis(2-isopropylphenyl)iminium trifluoroacetate (2.2b): In a 50 mL round bottomed flask, trifluoroacetic acid (0.60 mL, 7.8 mmol) was added to a suspension of **2.1b** (0.200 g, 0.4 mmol) in acetonitrile (25 mL), and stirred for 3 hours. The resulting teal solution was concentrated to ~5 mL and added to 95 mL of distilled water, precipitating **2.2b**. Protonated *cis*-Nindigo **2.2b** was collected by vacuum filtration and washed with distilled water (100 mL); residual water and acetonitrile were removed in vacuo, yielding **2.2b** as a dark purple solid (0.2069 g, 84 %). mp: 210 – 212 °C (decomposition); HRMS (ESI+): calculated for $C_{34}H_{33}N_4^+$: 497.2700 [M+] found 497.2697;^{1}H NMR (500 MHz, CD_2Cl_2): δ 16.61 (s, 1H, major), 15.89 (s, 1H, minor), 12.95 (s, 2H, minor), 12.89 (s, 2H, major), 7.56 – 7.37 (m, 12H), 7.34 – 7.28 (m, 3H), 7.20 (d, J = 7.8 Hz, 2H, major), 7.12 (d, *J* = 7.9, 2H, minor), 6.79 – 6.72 (m, 3H), 6.64 (d, *J* = 8.1 Hz, 2H, major), 6.47 (d, *J* = 8.1 Hz, 2H, minor), 3.13 (heptet, *J* = 6.8 Hz, 1H, minor), 3.03 (hepet, *J* = 6.9 Hz, 1H, major), 1.16 (d, *J* = 6.8 Hz, 6H, minor), 1.07 (d, *J* = 6.9 Hz, 6H, major), 1.04 (d, *J* = 6.8 Hz, 6H, minor), 0.93 (d, *J* = 6.9 Hz, 6H, major). ^{13}C

NMR (126 MHz, CD_2Cl_2) δ 162.4 (q, J_{CF} = 35.3 Hz), 158.5 (minor), 158.3 (major), 149.6 (major), 149.4 (minor), 142.0 (minor), 141.7 (major), 141.1 (minor), 140.5 (major), 135.7 (major), 135.6 (minor), 131.4 (minor), 131.3 (major), 128.8, 127.8 (minor), 127.7 (major), 127.4 (major), 127.3_5 (minor), 126.8 (minor), 126.7 (major), 123.3_1 (major), 123.2_7 (minor), 121.7 (minor), 121.6 (major), 118.5, 117.2 (minor), 117.0 (major), 116.2, 114.3, 29.3 (minor), 29.2 (major), 24.2 (minor), 23.6 (major), 23.2 (minor), 23.1 (major); ^{19}F NMR (283 MHz, $CDCl_3$): δ -75.5

Indigo N, N'bis(2-isopropylphenyl)iminium trifluoroacetate (2.2b): In a 50 mL round-bottomed flask, trifluoroacetic acid (0.05 mL, 0.7 mmol) was added to a solution of **2.1b** (0.052 g, 0.104 mmol) in dichloromethane (10 mL), and stirred for 15 minutes. The solution was concentrated to ~2 mL and hexanes (10 mL) was added. The mixture was stored at -10 °C for 18 hours and protonated *cis*-Nindigo **2.2b** was collected by vacuum filtration. The dark solid was washed with hexanes (4x 5 mL) and residual solvent was removed in *vacuo*, yielding **2.2b** as a dark purple solid (0.017 g, 26 %)

Indigo N, N'bis(2-tertbutylphenyl)iminium trifluoroacetate (2.2c): In a 50 mL round bottomed flask, trifluoroacetic acid (0.70 mL, 9.1 mmol) was added to a suspension of **2.1c** (0.213 g, 0.405 mmol) in acetonitrile (20 mL), and stirred overnight. The resulting teal solution was concentrated to ~5 mL and added to distilled water (100 mL), precipitating **2.2c**. Protonated *cis*-Nindigo **2.2c** was collected by vacuum filtration and washed with distilled water (200 mL); residual volatiles were removed in vacuo, yielding **2.2b** as a dark purple solid (0.201 g, 78 %). mp: 230 – 232 °C (decomposition); HRMS (ESI+) calculated for $C_{36}H_{37}N_4^+$: 525.3013 [M+] found 525.3010; ^1H NMR (300 MHz, $CDCl_3$) δ 15.99 (s, 1H), 12.70 (m, 2H), 7.47 (dd, J = 7.9, 1.6 Hz, 2H), 7.40 (d, J = 7.6 Hz,

2H), 7.37 (dd, *J* = 6.8, 1.2 Hz, 2H), 7.34 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.28 (td, *J* = 7.6, 1.7 Hz, 2H), 7.23 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.93 (dd, *J* = 7.6, 1.7 Hz, 2H), 6.61 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 2H), 6.15 (d, *J* = 8.2 Hz, 2H), 1.15 (s, 18H); ^{13}C NMR (76 MHz, $CDCl_3$): δ 158.3, 149.4, 143.1, 142.0, 135.6, 131.0, 128.1, 128.1, 127.9, 127.0, 125.9, 121.5, 117.0, 114.4, 35.6, 31.2; ^{19}F NMR (283 MHz): δ -75.5

Indigo N, N'bis(2-phenylphenyl)iminium trifluoroacetate (2.2d): In a 20 mL vial, trifluoroacetic acid (0.60 mL, 7.8 mmol) was added to a suspension of **2.1d** (0.204 g, 0.36 mmol) in acetonitrile (20 mL), resulting in a teal solution. The teal solution was concentrated to 5 mL and added to 200 mL of distilled water. The dark solid was collected using vacuum filtration and washes with distilled water (200 mL); residual volatiles were removed in vacuo, yielding **2.2d** as a dark purple solid (0.174 g, 71 %). mp: 200 – 202 °C (decomposition); HRMS (ESI) calculated for $C_{40}H_{29}N_4^+$: 565.2387 [M+] found 565.2388;^{1}H NMR (500 MHz, CD_2Cl_2): δ 16.22 (s, 1H, major), 15.88 (s, 1H, minor), 12.85 (s, 2H), 7.52 – 7.42 (m, 9H), 7.37 – 7.32 (m, 2H), 7.24 (d, *J* = 7.4 Hz, 2H, minor), 7.11 (t, J = 7.2 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 6H), 7.00 (t, *J* = 8.3 Hz, 4H), 6.86 (d, *J* = 7.9 Hz, 2H), 6.79 (t, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2) 162.8 (q, $^2J_{CF}$ = 34.7 Hz), 157.5 (minor), 156.7 (major), 149.5 (major), 149.1 (minor), 140.4 (minor), 139.6 (major), 138.2 (minor), 138.0 (major), 136.5_2 (major), 134.4_9 (minor), 131.80 (minor), 131.6 (major), 130.9, 129.3 (major), 129.2 (minor), 128.8 (major), 128.6 (minor), 128.4 (major), 128.1 (major), 126.37 (major), 124.2 (major), 123.8 (minor), 121.6 (minor), 121.4 (major), 117.5 (q, $^1J_{CF}$ = 294 Hz), 117.2 (minor), 116.9 (major), 114.3 (major), 114.1 (minor); ^{19}F NMR (283 MHz): δ -77.6

Indigo N, N'bis(2-phenylphenyl)iminium trifluoroacetate (2.2d): In a 50 mL round-bottomed flask, trifluoroacetic acid (0.05 mL, 0.7 mmol) was added to a solution of **2.1d** (0.042 g, mmol) in dichloromethane (10 mL) and stirred for 12 hours resulting in a teal solution. The resulting teal solution was diluted was concentrated to 2 mL and hexanes (10 mL) was added; the resulting mixture was stored at -10 Celsius for 18 hours and was subsequently filtered using vacuum filtration. Protonated Nindigo 2.2d, was washed with hexanes (4x 2 mL) and residual volatiles were removed in vacuo, yielding **2.2d** as a dark solid (0.025 g, 49 %).

Indigo N, N'bis(2-ethylphenyl)iminium trifluoroacetate (2.2e): In a 50 mL round bottomed flask, trifluoroacetic acid (1.5 mL, 20 mmol) was added to a suspension of **2.1e** (0.310 g, 0.67 mmol) in acetonitrile (40 mL), and stirred for two hours resulting in a teal solution. The solution was concentrated to 5 mL and poured into distilled water (450 mL). Residual volatiles were removed in vacuo, yielding **2.2e** as a shiny dark solid (0.307 g, 80 %) mp: 221 –223 °C (decomposition); HRMS (ESI+) calculated for $C_{32}H_{29}N_4^+$: 469.2387 [M+] found 469.2385; ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.18 (s, 1H, major), 15.82 (s, 1H, minor), 13.02 (s, 2H, minor) 12.99 (s, 1H, major), 7.45 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H) 7.35 – 7.21 (m, 8H), 7.13 – 7.02 (m, 2H), 6.65 (td, *J* = 7.6, 1.2 Hz, 2H), 6.44 (d, *J* = 8.2 Hz, 2H, major), 6.40 (d, *J* = 8.9 Hz, 2H, minor), 2.59 – 2.33 (m, 4H, major and minor), 1.00 (t, *J* = 7.6 Hz, 6H, minor), 0.93 (t, *J* = 7.5 Hz, 6H, major). ^{13}C NMR (76 MHz, $CDCl_3$) δ 158.1, 149.4 (major), 149.3 (minor), 141.3 (minor), 141.2 (major), 137.0 (major), 136.8 (minor), 135.6, 131.2, 130.3, 129.9, 128.4, 127.8_2 (major), 127.7_7 (minor) 126.3 (major), 126.2 (minor), 123.1 (minor), 123.0_6 (major) 121.6_2 (minor), 121.5_8

(major) 116.8 (minor), 116.7 (major), 114.6, 25.0, (major) 24.6 (minor), 14.9 (major), 14.6 (minor). ^{19}F NMR (283 MHz, $CDCl_3$) δ -75.4

Indigo N, N'bis(2-ethylphenyl)iminium trifluoroacetate (2.2e): In a 20 mL vial, trifluoroacetic acid (0.5 mL, 6.5 mmol) was added to a solution of **2.1e** (0.107 g, mmol) in dichloromethane (10 mL) resulting in a teal solution. The reaction was stirred for 12 hours and subsequently diluted with dichloromethane (50 mL). The dichloromethane solution was extracted with distilled water (3x 10 mL) and dried with magnesium sulfate. Volatiles were removed in vacuo, yielding **2.2e** as a dark solid (0.063 g, 49 %).

Indigo N, N'bis(1-naphthyl)iminium trifluoroacetate (2.2f): In 50 mL round bottomed flask, trifluoroacetic acid (0.20 mL, 2.6 mmol) was added to a solution of **2.1f** (0.063 g, 0.12 mmol) in dichloromethane (10 mL), resulting in a teal solution. The teal solution was concentrated to 2 mL and layered with hexanes (20 mL). The resulting mixture was vacuum filtered and the dark solid was washed with hexanes (4x 5 mL). Residual volatiles were removed in vacuo, yielding **2.2f** as a dark purple solid (0.057, 74 %) mp: 188 – 190 °C (decomposition); HRMS (ESI): calculated for $C_{36}H_{25}N_4^+$ 513.20737 [M+] found 513.20743; ^{1}H NMR (500 MHz, CD_2Cl_2): δ 17.10 (s, 1H, minor), 16.89 (s, 1H, major), 11.86 (s, 4H), 7.99 (d, J = 8.0 Hz, 2H), 7.91 (m, 2H), 7.89 (d, J = 9.1 Hz, 4H), 7.79 (d, J = 8.5 Hz, 2H), 7.60 – 7.42 (m, 10H), 7.30 (ddd, J = 8.5, 7.0, 1.0 Hz, 4H), 6.74 – 6.58 (m, 4H); ^{13}C NMR (91 MHz, CD_2Cl_2): δ 161.2 (q, J_{CF} = 38.7 Hz), 158.5, 149.1, 138.9, 136.1, 134.8, 131.6, 128.9, 128.7, 127.7, 127.6, 127.3 (minor), 127.2 (major), 126.7, 126.1, 122.4 (major), 122.2 (minor), 122.0, 119.8 (major), 119.7 (minor), 116.9, .04, 114.1; ^{19}F NMR (283 MHz): δ -76.1

Indigo N, N'bis(2-fluorophenyl)iminium trifluoroacetate (2.2g): In a 25 mL round bottomed flask, trifluoroacetic acid (0.1 mL, 2.3 mmol) was added to a solution of **2.1g** (0.052, 0.117 mmol) in dichloromethane (5 mL) and stirred for 30 minutes. The resulting teal solution was concentrated to 2 mL, layered with hexanes (20 mL), and subsequently stored at -10 Celsius for 18 hours. The mixture was filtered using vacuum filtration and the resulting dark solid was washed with hexanes (4x 10 mL). Residual volatiles were removed in vacuo, yielding **2.2g** as a shiny black solid (0.055 g, 83 %) mp: 158 – 160 °C (decomposition); HRMS (ESI+) calculated for $C_{28}H_{19}F_2N_4^+$: 449.15723 [M+] found: 449.15722;^{1}H NMR (500 MHz, CD_2Cl_2): δ 16.25 (s, 1H), 12.19 (s, 2H), 7.55 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 2H), 7.49 – 7.40 (m, 6H), 7.34 – 7.26 (m, 4H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.88 (ddd, *J* = 8.1, 7.1, 0.9 Hz, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ 157.7, 155.2 (d, J_{CF} = 250.1 Hz), 149.2, 136.3, 132.0, 130.1 (d, J_{CF} = 12.4 Hz), 129.9 (d, J_{CF} = 7.5 Hz), 126.2, 125.7 (d, J_{CF} = 2.5 Hz), 125.2, 122.2, 117.40 (d, *J* = 18.9 Hz), 116.9, 114.2; ^{19}F NMR (471 MHz, CD_2Cl_2) δ -76.1, -123.1

Indigo-N, N'bis(2-ethyl-6-methylphenyl)diimine (2.7a): In a flame dried 250 mL Schlenk flask, a solution of $TiCl_4$ (1.0 M in toluene, 15.0 mL, 15.0 mmol) was added to a solution of DABCO (4.03 g, 35.9 mmol), and 2-ethyl-6-methylaniline (2.2 mL, 16 mmol) in bromobenzene (200 mL), resulting in an olive-green mixture. Next, indigo (1.502 g, 5.725 mmol) was added, and the mixture was refluxed for two days. The resulting mixture was filtered hot, and the collected solids were washed with diethyl ether (600 mL). The filtrate was next evaporated yielding a dark solid. The residue was taken up in ethyl acetate (500 mL) and sequentially extracted with 1.0 M HCl (3x 100 mL), 0.5 M KOH (3x 100 mL), water (3x 100 mL), and brine (100 mL) and subsequently dried with magnesium

sulfate. The ethyl acetate was removed in *vacuo* and the resulting dark solid was recrystallized from boiling *n*-butanol (20 mL). Nindigo **2.7a** was collected by vacuum filtration and washed with hexanes (10 mL). Residual volatiles were removed in vacuo, yielding **2.7a** as a dark purple solid (1.63 g, 57 %). mp: 268 – 270 C; HRMS (ESI+) calculated for $C_{35}H_{33}N_4^+$ 497.2700 [M+H] found: 497.2694; ^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.92 (s, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.14 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.61 (d, *J* = 7.2 Hz, 2H), 6.46 (d, *J* = 7.9 Hz, 2H) 2.64 (m, 4H), 2.55 (m, 4H), 2.16_4 (s, 6H), 2.15_9 (s, 6H). 1.14_1 (t, *J* = 7.5 Hz, 6H), 1.13_7 (t, *J* = 7.7 Hz, 6H) ; ^{13}C NMR (126 MHz, CD_2Cl_2) : δ 158.4, 149.8, 147.0, 134.8, 132.0, 128.7, 128.5, 126.9, 125.0, 124.9, 120.5, 119.3, 113.4, 25.3, 18.4, 14.7

Indigo-N, N'bis(2-methyl-1-naphthyl)diimine (2.7b): In a flame dried 250 mL Schlenk flask, a solution of $TiCl_4$ (1.0 M in toluene, 7.6 mL, 7.6 mmol) was added to a solution of DABCO (2.58 g, 23.0 mmol), and 2-methyl-1-naphthylamine (1.1 mL, 16 mmol) in bromobenzene (200 mL), resulting in an olive-green mixture. Next, indigo (1.50 g, 5.725 mmol) was added, and the mixture was refluxed for two days. The resulting mixture was filtered hot, and the collected solids were washed with diethyl ether (600 mL). The filtrate was next evaporated yielding a dark solid, and the residue was taken up in ethyl acetate (500 mL). The ethyl acetate solution was sequentially extracted with 1.0 M HCl (3x 100 mL), 0.5 M KOH (3x 100 mL), water (3x 100 mL), and brine (100 mL) and subsequently dried with magnesium sulfate. The ethyl acetate was removed in *vacuo* and the resulting dark solid was recrystallized from boiling *n*-butanol (20 mL). Nindigo **2.7a** was collected by vacuum filtration and washed with hexanes (10 mL). Residual volatiles were removed in vacuo, yielding **2.7b** as a dark purple solid (1.63 g, 57 %). mp: 314 – 316 °C; HRMS

(ESI+) calculated for $C_{38}H_{29}N_4^+$: 541.23867 [M+H] found: 541.23849; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.13 (s, 2H), 7.93 (d, *J* = 6.3 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.46 (td, *J* = 6.8, 3.5 Hz, 2H), 7.42 – 7.35 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.44 (t, *J* = 7.6 Hz, 2H), 6.21 (d, *J* = 8.0 Hz, 2H), 2.39 (2 s, 6H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 160.2, 149.7, 144.6, 133.4, 132.4, 129.6, 128.2, 127.4, 126.6, 126.2, 125.8, 125.2, 124.4, 123.7, 123.4, 120.3, 119.1, 113.0, 18.3

Indigo N, N'bis(2-ethyl-6-methylphenyl)iminium trifluoroacetate (2.8a): In a 100 mL round bottomed flask, trifluoroacetic acid (0.06 mL, 0.8 mmol) was added to a solution of **2.7a** (0.050 g, 0.10 mmol) in dichloromethane (5 mL), resulting in a teal solution and stirred for 15 minutes. The reaction mixture was filtered, and volatiles were removed in vacuo. The resulting solid was washed with hexanes (10 mL), and residual volatiles were removed in *vacuo* yielding **2.8a** as a dark purple solid (0.0435, 69%); HRMS (ESI+): calculated for $C_{34}H_{33}N_4^+$: 497.2699 [M+] found: 497.2704; ^{1}H (300 MHz, $CDCl_3$) δ 16.12 (s, 1H, minor), 16.08 (s, 1H, major), 11.99 (s, 9H), 7.54 – 7.41 (m, 17H), 7.37 – 7.14 (m, 1261H), 6.73 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 8H), 6.31 (d, *J* = 8.1 Hz, 2H, minor), 6.30 (d, *J* = 8.1 Hz, 2H, major), 2.59 – 2.39 (m, 4H), 2.11 (s, 6H, minor), 2.10 (s, 6H, major), 1.05 (t, *J* = 7.7 Hz, 6H, major), 1.02 (t, *J* = 7.6 Hz, 6H, minor). ^{13}C NMR (76 MHz, $CDCl_3$) δ 158.9, 148.7, 140.0 (major), 139.9 (minor), 136.5_2 (major), 136.4_8 (minor), 136.1, 130.5, 130.4, 130.3, 129.3, 128.1, 127.5 (minor), 127.4 (major), 125.6, 122.2, 117.0, 114.1 (major), 114.0 (minor), 24.8 (minor), 24.6 (major), 18.3 (major), 18.2 (minor), 14.7 (minor), 14.5 (major); ^{19}F NMR ($CDCl_3$, 283 MHz): δ -75.7

Indigo N, N'bis(2-methyl-1-naphthyl)iminium trifluoroacetate (2.8b): In a 100 mL round bottomed flask, trifluoroacetic acid (0.10 mL, 1.3 mmol) was added to a solution of **2.7b** (0.050 g, 0.0923 mmol) in dichloromethane (10 mL), resulting in a teal solution and stirred for 30 minutes. The reaction mixture was concentrated to 2 mL, layered with hexanes (30 mL) and stored in the freezer overnight. The resulting mixture was filtered using vacuum filtration and the collected solids were washed with hexanes (4x 10 mL). Residual volatiles were removed in vacuo yielding **2.8b** as a dark purple solid (0.035, 57 %); mp: 230 °C (decomposition); HRMS (ESI+): calculated for $C_{38}H_{29}N_4^+$: 541.23867 [M+] found 541.23847^{1}H NMR (500 MHz, CD_2Cl_2) δ 16.80 (s, 1H), 12.96 (s, 2H), 7.89 (d, *J* = 7.8 Hz, 2H minor), 7.85 (d, *J* = 8.3 Hz, 2H, major), 7.80 (d, *J* = 8.5 Hz, 2H, major + minor), 7.78 (d, *J* = 8.4 Hz, 2H, major), 7.71 (d, *J* = 8.4Hz, 2H, minor), 7.53 – 7.39 (m, 10H), 7.35 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 6.63 – 6.56 (m, 2H), 6.20 (d, *J* = 8.2 Hz, 2H, major), 6.15 (d, *J* = 8.1 Hz, 2H, minor), 2.33 (s, 6H, major), 2.32 (s, 6H, minor); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 159.8 (minor), 159.7 (major), 149.5$_8$ (minor), 149.5$_7$ (major), 136.7$_0$ (minor), 136.6$_8$ (major) , 136.1, 133.3 (minor), 133.2$_6$ (major), 131.2$_4$ (major), 131.2$_1$ (minor), 129.4 (minor), 129.3 (major), 128.7 (minor), 128.6 (major), 128.0 (minor), 127.9$_6$ (major), 127.9$_3$ (minor), 127.9$_1$ (major), 127.7 (minor), 127.6 (major), 127.5$_7$ (minor), 127.4$_9$ (major), 126.6, 126.1 (minor), 126.0 (major), 122.2 (major), 122.1$_4$ (major), 122.1$_2$ (minor), 122.0$_5$ (minor), 117.3$_3$ (major), 117.2$_9$ (minor), 114.2$_4$ (major), 114.2$_2$ (minor), 18.3$_4$ (minor), 18.3$_0$ (major); ^{19}F NMR ($CDCl_3$, 283 MHz): -75.7

Chapter 3: Atropisomeric N, N'-oxalyl bridged Nindigo derivatives

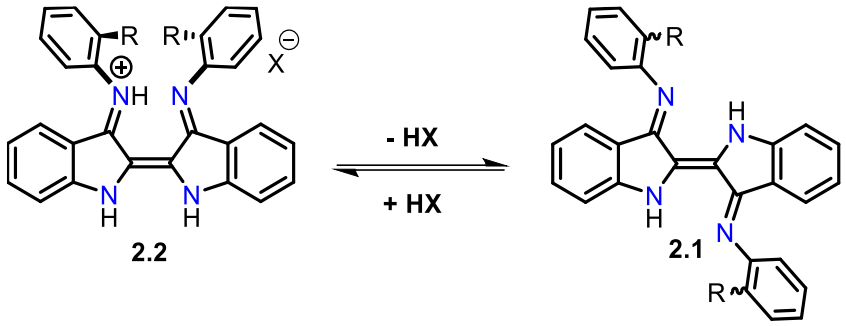
3.0 Preface

The synthetic protocols for achiral analogs of the oxalyl bridged *cis*-indigo diimines described in this chapter were developed by Dr. Hyejin (Erica) Hong (Ph.D., 2021).[174] The optimization of the synthetic protocols of the mono-*ortho* substituted oxalyl bridged indigo diimines (specifically, **3.15c/3.16c**) were performed with the assistance of undergraduate student Kyle Moodley (BSc, 2019).

3.1 Introduction

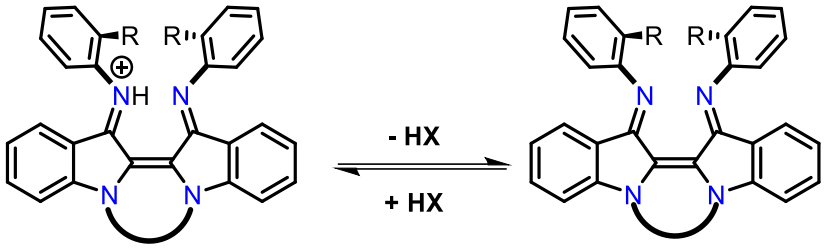
In **Chapter 2**, the synthesis and study of the conformational behavior of atropisomeric neutral *trans*- and protonated *cis*-Nindigos were described. The initial studies were focused on understanding how structure influences the atropisomerization barriers of the neutral *trans*- and protonated *cis*-Nindigos. One consequence of the protoisomerization process is that the chiral environment of protonated *cis*-Nindigo derivatives, no matter how high the atropisomerization barrier is, cannot be maintained because of proton transfer. The resulting *trans*-Nindigos, formed upon deprotonation have significantly (~5.0 kcal/mol) lower atropisomerization barriers than their *cis*-counterparts. The lower atropisomerization barriers of the *trans*-Nindigos leads the *cis*- to *trans*- isomerization process that occurs upon proton loss to scramble any chirality imparted upon the initial *trans*- to *cis*- protoisomerization. Proton transfer can therefore be regarded as a racemization process (**Scheme 3.1**). If protonated *cis*-Nindigos are ever

to be used as chiral agents, the reversible *trans*- to *cis*- isomerization upon the removal/addition of a proton must be addressed.

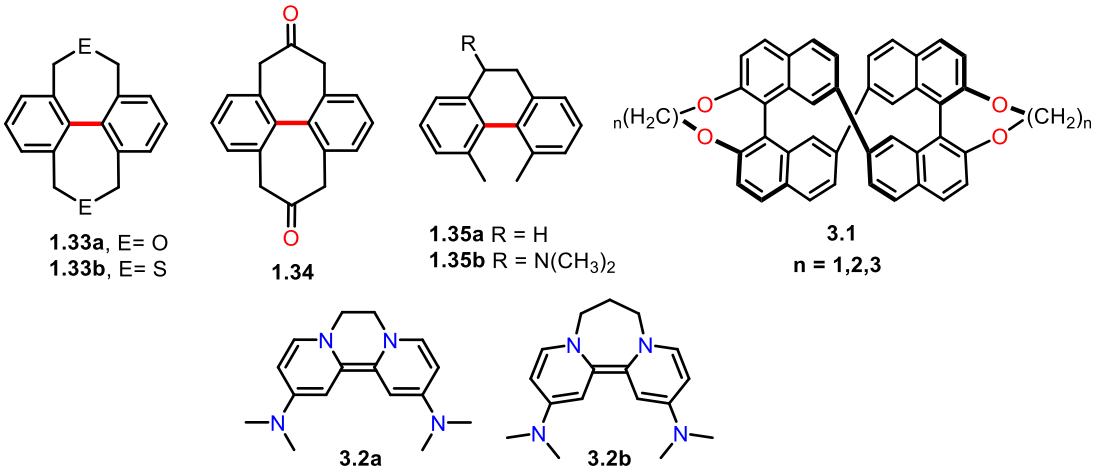


Scheme 3.1 Scrambling of protonated *cis*-Nindigo atropisomers via proton transfer

To address this problem, a conformational constraint/tether can be introduced between the indole nitrogens in **2.2** to lock the indigoid backbone in the *cis*- configuration. The atropisomerism of the permanently *cis*-Nindigos should be retained upon deprotonation/protonation (**Scheme 3.2**). The strategy of introducing geometrical constraints across parts of molecules has been studied in atropisomeric systems and was discussed in the context of biaryls in **Chapter 1**. The introduction of geometrical constraints in molecules is widespread in chemistry and is utilized in, for example, modifying the circularly polarized luminescence of binaphthyls (**3.1**)[175] and the reduction potentials of bispyridinylidene based organic reducing agents (**3.2a** and **3.2b**),[176] among others.



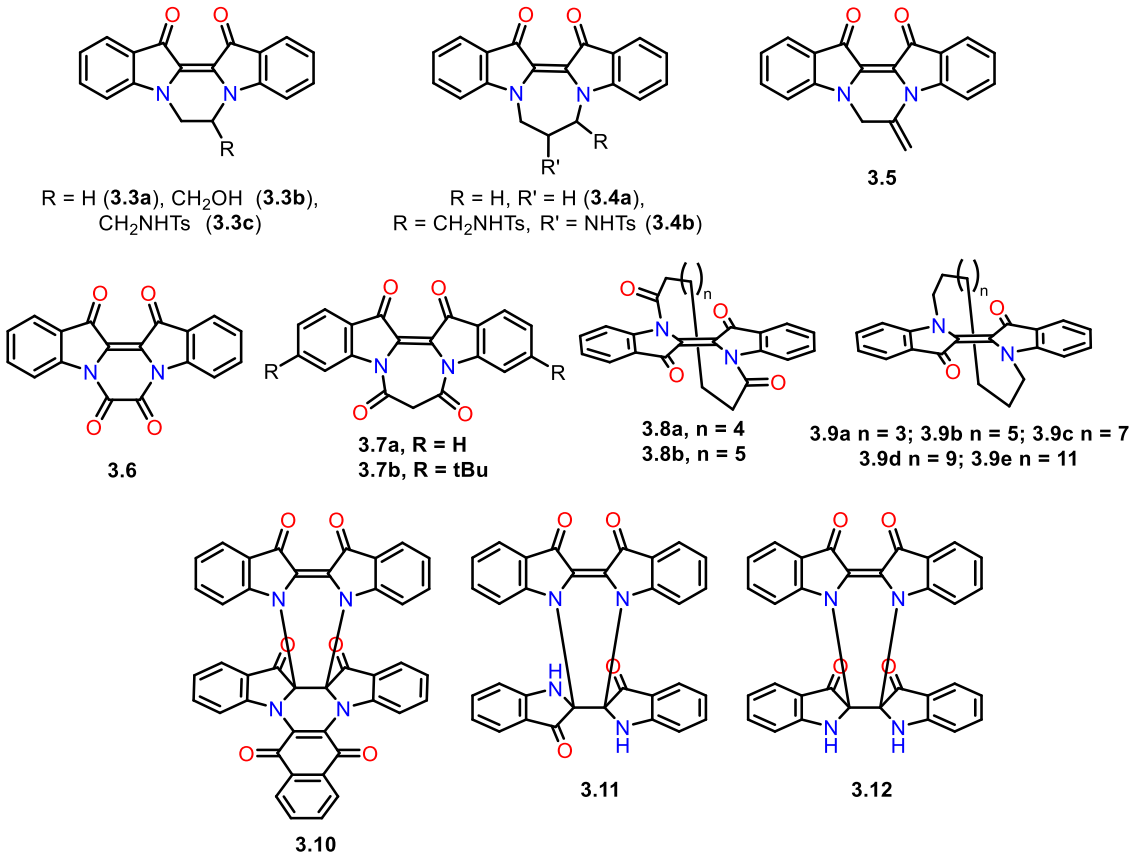
Scheme 3.2 Retention of *N*-*C* atropisomerism upon the deprotonation/protonation of *N*, *N'*-tethered *cis*-Nindigos



3.1.1 Tethered *cis*-indigoids

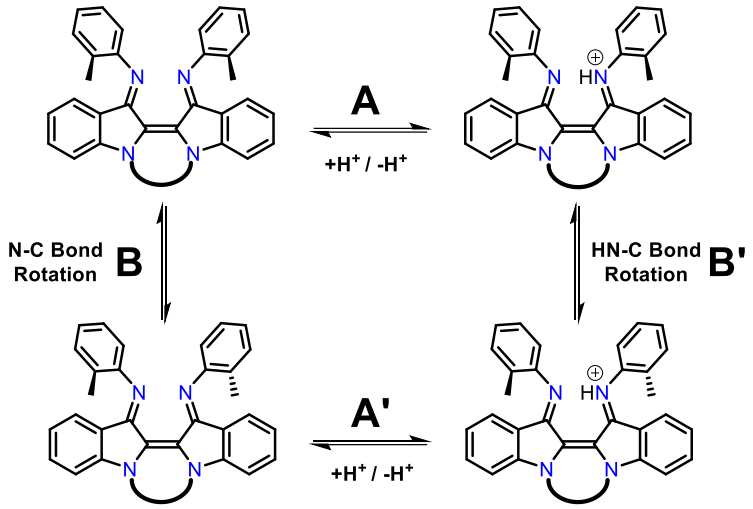
One of the first structural modifications of the indigo scaffold was the introduction of tethers between the indole nitrogens. Examples include ethylene (-CH_2CH_2-) (**3.3a – 3.3c**),[177,178] propylene (-$CH_2CH_2CH_2$-) (**3.4a** and **3.4b**),[177–180] alkene (**3.5**),[181,182] and acyl bridges (**3.6** and **3.7a**/**3.7b**).[183–187] When the tether between the indole nitrogens is sufficiently long, the tethered indigos adopt a *trans*- configuration as reported by groups led by Omote[186] and Tsubaki,[188] who studied tethered indigos that have extended acyl (**3.8a** and **3.8b**)[186] and alkyl bridges (**3.9a – 3.9e**).[188] Recently, naphthoquinone (**3.10**)[174,189] and indigoid-derived (**3.11** and **3.12**)[174,189] bridges have been introduced. The

variety of known organic tethers in *cis*-indigoids provides an excellent starting point to produce tethered *cis*-Nindigos (**3.13**/**3.14**).



Previously, Dr. Erica Hong determined that an oxalyl tether can be installed between the indole nitrogens of Nindigo (Ar = dimethylphenyl, **3.13** and **3.14**).[187,190–192] The ease of the synthesis of **3.13** and **3.14** inspired the investigation of atropisomeric *cis*-Nindigos featuring an oxalyl tether. Like their protonated *cis*- and neutral *trans*- unbridged congeners, there are two potential conformations (*anti* and *syn*) that the *N*, *N'*-oxalyl bridged *cis*-Nindigos can adopt (**Scheme 3.3**), but only one configuration of the central indigoid carbon-carbon double bond is possible. In this chapter, the preparation and characterization of mono *ortho*-substituted neutral and protonated *N*, *N'*-oxalyl bridged

cis-Nindigos is described. The principal objective is to explore how the introduction of a tether and the protonation state affects the atropisomerism of the *cis*-Nindigos.

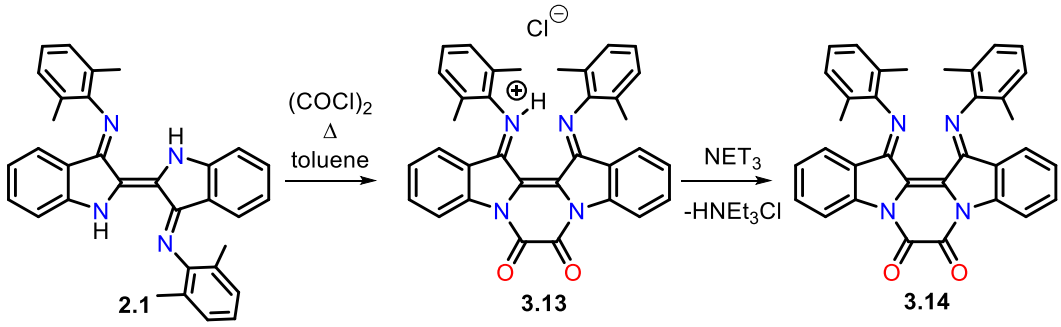


Scheme 3.3 Retention of chirality upon the protonation of tethered *syn cis*-Nindigo (**A**); retention of chirality upon protonation of tethered *anti cis*-Nindigo (**A'**); *N-C* atropisomerization of tethered *cis*-Nindigos (**B**); *HN-C* atropisomerization of tethered *cis*-Nindigos (**B'**)

3.2 Previously prepared tethered *cis*-Nindigos 3.13 and 3.14

Dr. Erica Hong prepared symmetrically substituted *N, N'*-oxalyl bridged *cis*-Nindigos (**3.13** and **3.14**), **Scheme 3.4** following a modified literature procedure for the preparation of *N, N'*-oxalyl bridged *cis*-indigo.[174] These derivatives displayed protonation state-based spectral properties; absorption wavelength maxima of 496 and 419 nm are observed for **3.13** and **3.14**, respectively. The absorption wavelength maxima of the *N, N'*-oxalyl bridged *cis*-Nindigos are blue-shifted relative to their unbridged neutral *trans*-

and protonated *cis*- counterparts. The blue shift of the absorption wavelength maxima is the result of the electron-withdrawing effects imparted by the oxalyl tether, which is in direct conjugation with the indigoid chromophore.



Scheme 3.4 Synthesis of *N, N'*-oxalyl bridged *cis*-Nindigos

The solid-state structures (**Figure 3.1**) of **3.13** and **3.14** have very different diimine pocket sizes. The neutral and protonated species have *N*-*N* distances of 2.899 and 2.618 Å, respectively (**Figure 3.2**).[174] The space-filling diagrams of the protonated (**A**) and neutral (**B**) oxalyl bridged *cis*-Nindigos show that the diimine pocket of **3.13** is more crowded than **3.14** (**Figure 3.1**). The large differences in the *N*-*N* distances are expected to have a significant influence on the *N*-*C* rotational barriers of the neutral and protonated oxalyl bridged *cis*-Nindigos.

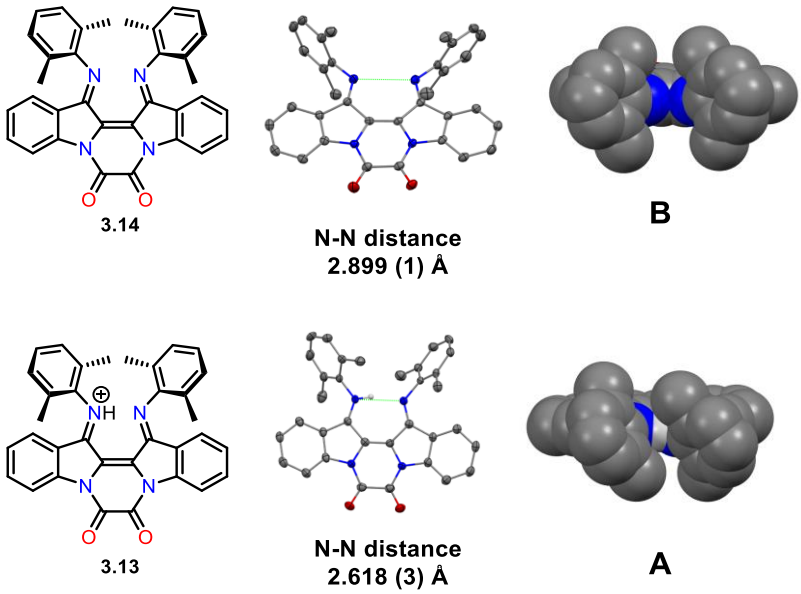
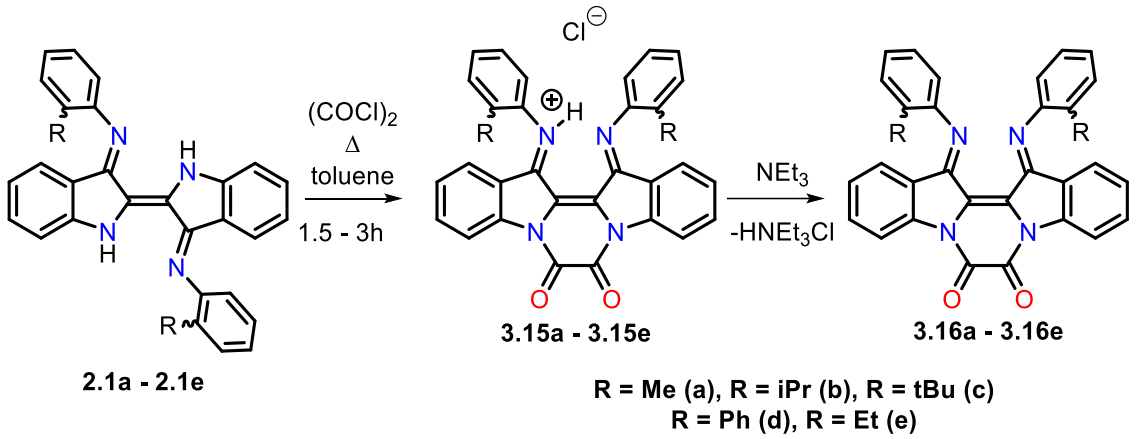


Figure 3.1 Solid-state structures of **3.13** and **3.14**;[174] space-filling diagrams of **3.13** (**A**) and **3.14** (**B**) showing the crowded nature of the diimine pocket

3.3 Synthesis of neutral atropisomeric *N, N'*-oxalyl bridged *cis*-Nindigos 3.16a – 3.16e

The previously prepared *trans*-Nindigos **2.1a – 2.1g** were reacted with oxalyl chloride in refluxing toluene for a minimum of one hour (**Scheme 3.5**). The extension of the synthetic protocols to derivatives that have a single *ortho* substituent was successful for the bulkier analogs **3.15b/3.16b – 3.15d/3.16d** but did not proceed as expected for the less bulky derivatives (e.g., methyl and ethyl), which formed intractable mixtures.



Scheme 3.5 Synthesis of *N, N'*-oxalyl bridged *cis*-Nindigos **3.15a – 3.15e** and **3.16a – 3.16d**

The ^{1}H NMR spectra of the mixtures contain resonances at approximately 5.5 ppm, implying that there may be alkene proton resonances; alkene type resonances in the ^{1}H NMR spectra of **3.15a** and **3.15e** are not expected. Intractable mixtures were also produced by an undergraduate student, Madeline Kuiper, supervised by Dr. Erica Hong in the attempted synthesis of the 4-methylphenyl *N, N'*-oxalyl bridged *cis*-Nindigo derivatives (**3.15b/3.16b**, **Scheme 3.6**). They obtained X-ray quality crystals, analysis of which revealed minor products to be rearrangement products (**3.17** and **3.18**). It should be stated that the products found using X-ray crystallography would not display any alkene type ^{1}H NMR resonances and thus should be considered as very minor components of the mixture and at this point, the structures that produce the alkene type resonances are unknown. The rearrangement products, isolated in trace amounts and confirmed by X-ray crystallography, have a Nindigo core which is reduced by two electrons in the *trans*-geometry; between one of the indole nitrogens and one of the now amine type nitrogens, there is an *N, N'*-oxalyl bridge, while there is a C=O fragment attached to the other indole

nitrogen and the other amine type nitrogen. The only difference between **3.17** and **3.18** is the presence of a chlorine atom at the six position of one side of the reduced indigoid core in **3.17**, while the six position is unsubstituted in **3.18**. The presence of several extra resonances in the ^{1}H NMR spectra, coupled with the potential alkene type resonances in the less sterically bulky derivatives means that an alternative strategy should be sought to access these less encumbered derivatives.

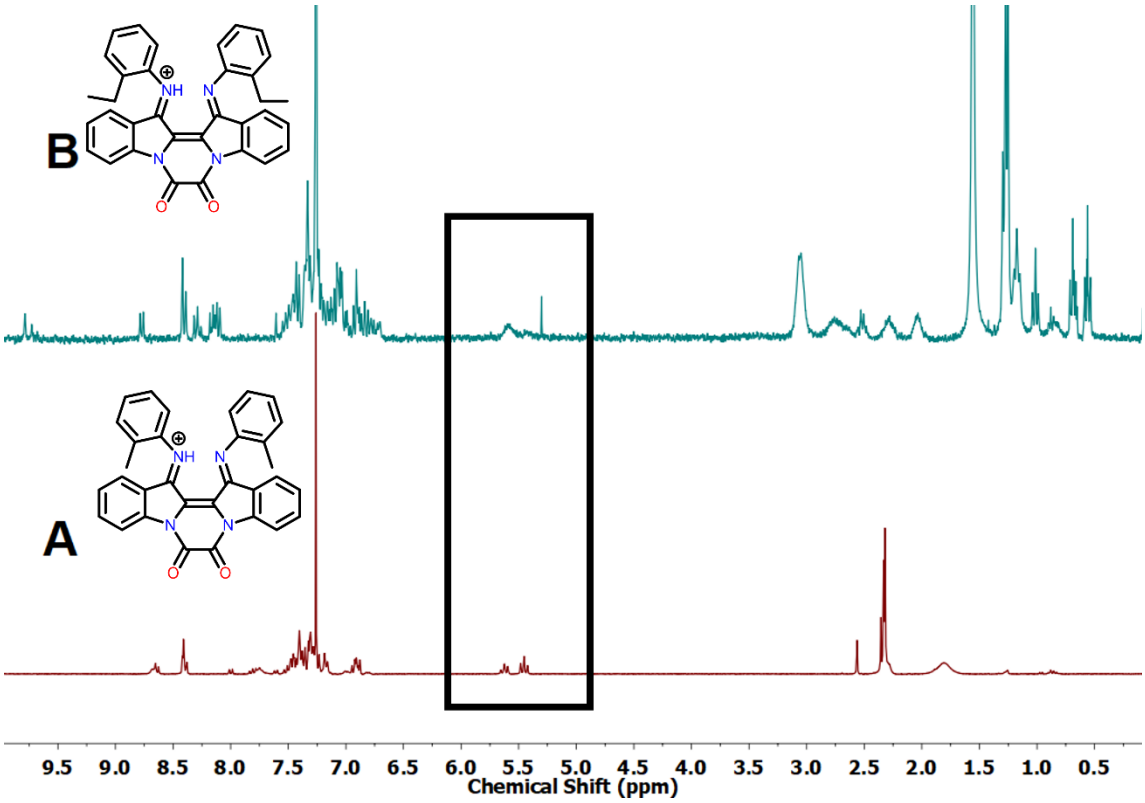
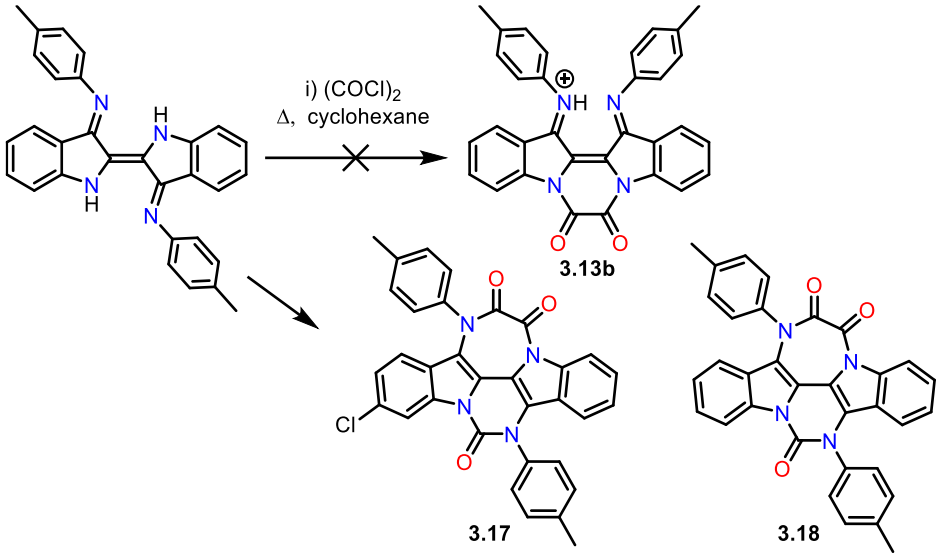
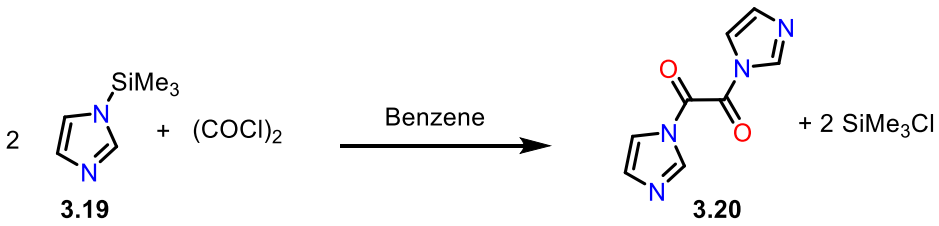


Figure 3.2 ^{1}H NMR spectra of the isolated solids from the attempted synthesis of **3.16a** (**A**) and **3.16e** (**B**); black box highlights alkene type protons in decomposed material



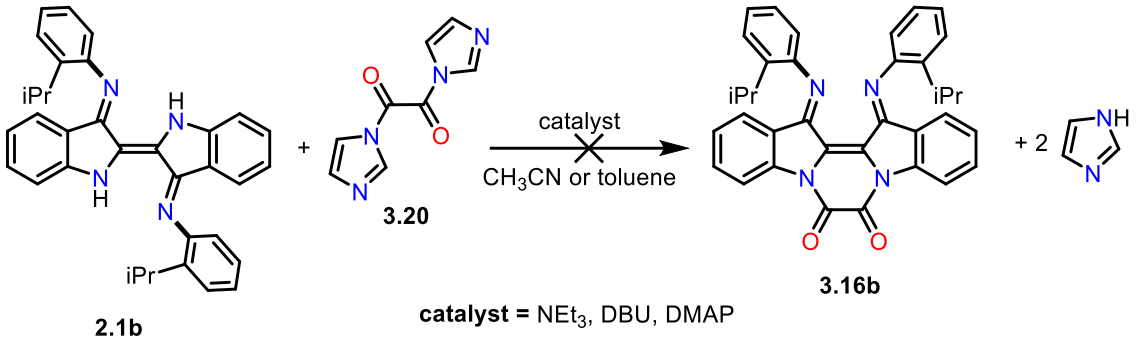
Scheme 3.6 Attempted synthesis of *N, N'*-oxalyl tethered *cis*-Nindigo **3.13b** and its decomposition products

An alternative strategy that yields neutral *N, N'*-oxalyl bridged *cis*-Nindigo analogs in one step is attractive because of the less reactive substrate produced (neutral analogs are less susceptible to hydrolysis than their protonated congeners). The use of oxalyl diimidazole (**3.20**) as an oxalyl chloride synthon was explored for the preparation of neutral *N, N'*-oxalyl bridged *cis*-Nindigos.[193–195] The high cost (80$ per gram, Fisher) of **3.20** led to it being prepared from oxalyl chloride and 1-trimethylsilylimidazole (**3.19**, **Scheme 3.7**).[196]



Scheme 3.7 Synthesis of 1,1'-oxalyldiimidazole

The attempted synthesis of neutral *N, N'*-oxalyl bridged *cis*-Nindigos using oxalyl diimidazole was performed using **2.1b** as the *trans*-Nindigo starting material in acetonitrile or toluene. Nucleophilic Lewis bases triethylamine (NEt_3), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), and 4-dimethylaminopyridine (DMAP) were used as nucleophilic organocatalysts (**Scheme 3.8**). No reaction was observed for any of the attempted reactions to access **3.16b** using oxalyl diimidazole.



Scheme 3.8 Attempted synthesis of **3.16b** using oxalyl diimidazole

The original synthetic protocols for the synthesis of **3.14** involved a minimum of a 1.5 hour reflux. As soon as the reaction mixture reaches reflux, it changes from dark green to dark red/brown and shows no further changes upon extended heating. The shortening of the reaction time (**Scheme 3.5**) from one hour to 15 minutes led to the clean formation of the mono *ortho*-substituted *N, N'*-oxalyl bridged *cis*-Nindigos **3.16a** – **3.16e** in yields between 43 and 67%.

3.4 Computational studies of *cis*-indigos 3.3a, 3.6, and *N, N'*-oxalyl 2,6-dimethylphenyl Nindigo derivatives 3.13 and 3.14

3.4.1 Computational studies of *N, N'*-bridged indigos

There have been numerous computational studies of indigo reported in the literature.[197–202] Of the tethered *cis*-indigos in the literature, only semi-empirical calculations have been reported for *N, N'*-oxalyl bridged *cis*-indigo,[203] and DFT geometry optimizations of the *N, N'*-propano bridged *cis*-indigo have recently been reported.[179] No discussion of the electronic structure and the FMOs of these *cis*-indigos has been reported. Due to the limited amount of computational work on bridged *cis*-(N)indigos, it is of interest to investigate how the tethers perturb the electronic structure of *cis*-indigoids relative to their parent indigo.

The geometries of *cis*-indigos **3.3a** and **3.6** were optimized using B3LYP/Def2TZVPP. The nature of the bridge has a significant influence on the electronic structure of the indigoids. The HOMO and LUMO (**Figure 3.3**) of the ethano bridged *cis*-indigo, **3.3a**, are essentially identical to those of indigo (**Figure 3.3**) if the central carbon-carbon double bond is isomerized from *trans*- to *cis*-. In contrast to **3.3a**, the HOMO of **3.6** (**Figure 3.3**) has a significant amount of orbital density on the strongly π-withdrawing oxalyl bridge, while the LUMO has essentially no orbital density on the oxalyl bridge. The limited orbital contributions, from the tether, in **3.3a** suggests that the tether does not have a significant effect on the corresponding electronic spectra, while significant effects are expected/predicted in **3.6** from the oxalyl bridge. The experimental absorption wavelength maxima agree with the predictions made based on the analysis of the FMOs;

cis-indigos **3.3a** and **3.6** have absorption wavelength maxima of 591 and 428 nm, respectively and the significant blue shift of the absorption wavelength maxima of **3.6** is from the electron-withdrawing nature of the oxalyl bridge.

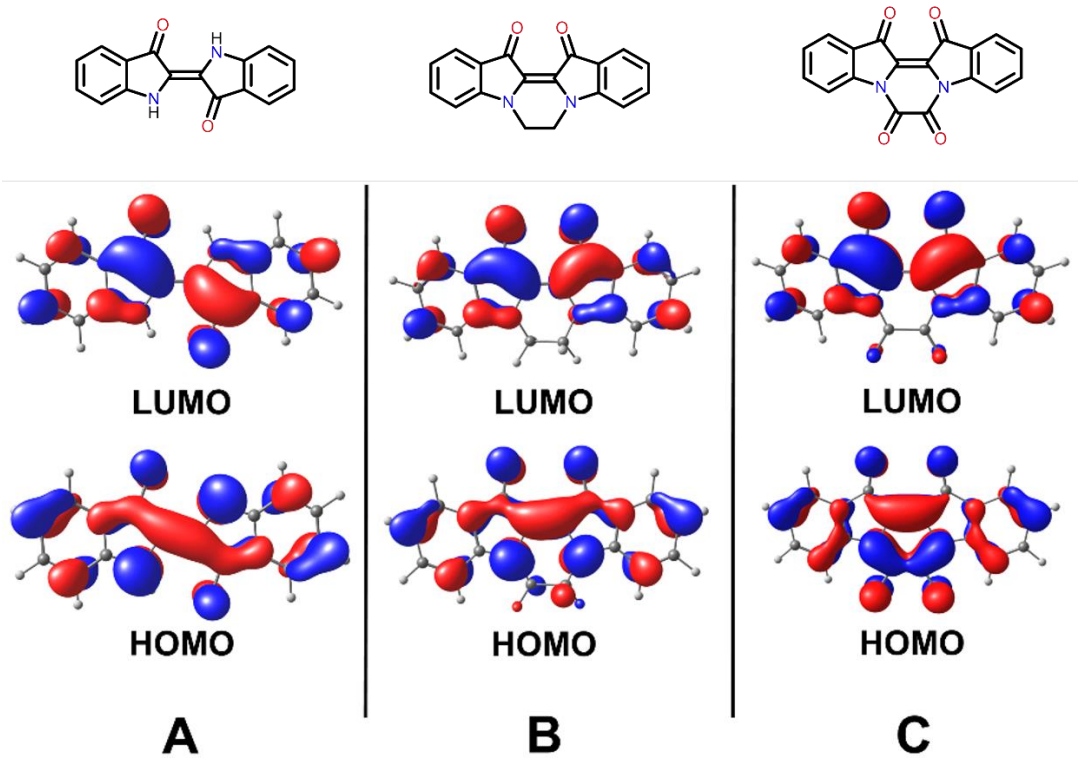


Figure 3.3 Frontier molecular orbitals of indigo (**A**), **3.3a** (**B**), **3.6** (**C**)

3.4.2 Time-dependent DFT study of *cis*-indigos 3.3a and 3.6

The prediction of the absorption wavelength maxima was performed via a benchmark study using four commonly used functionals B3LYP, CAM-B3LYP, PBE0, and wB97XD. The geometries of **3.3a** and **3.6** were first reoptimized using B3LYP/Def2TZVPP[204] in acetonitrile (can), while the predicted electronic spectra were computed using the four different functionals separately using the 6-311++G(d,p)[205–208] and Def2TZVPP[204] basis sets. Of the functionals used for the TD-DFT studies for **3.3a**,

B3LYP and 6-311++G(d,p) performed the best, having a predicted absorption wavelength maximum within one nm of experimental results (**Table 3.1**). The TD-DFT calculations indicate that the low energy absorption wavelength maximum of **3.3a** is based on a HOMO to LUMO transition. For **3.6**, the best performing functional is PBE0, which predicted the absorption wavelength maxima to within four nm of the experimentally determined wavelength for both 6-311++G(d,p) and Def2TZVPP (**Table 3.1**). The TD-DFT results indicate that the absorption wavelength maximum of **3.6**, like **3.3a**, is the result of a HOMO to LUMO transition.

Table 3.1 Benchmark TD-DFT study of *cis*-indigos **3.3a** and **3.6**

3.3				
Predicted absorption wavelength maxima 6-311++G(d,p) (Def2TZVPP)[b]				
Experimental wavelength (nm)[a]	**B3LYP**	**CAM-B3LYP**	**PBE0**	**wB97XD**
585	584 (581)	519 (517)	568 (566)	515 (513)

3.6				
Predicted Absorption Wavelength Maxima 6-311++G(d,p) (Def2TZVPP)[b]				
Experimental wavelength (nm)[a]	**B3LYP**	**CAM-B3LYP**	**PBE0**	**wB97XD**
429	451 (453)	376 (376)	425 (425)	372 (373)

[a]Experimental electronic spectra were obtained in acetonitrile; [b]predicted absorption wavelength maxima were computed in acetonitrile

3.4.3 Computational studies of neutral and protonated *N, N'*-oxalyl-bridged dimethylphenyl *cis*-Nindigo 3.13 and 3.14

To get an understanding of how substituents may affect the electronic spectra of the atropisomeric *N, N'*-oxalyl bridged Nindigo derivatives, the geometries of the protonated (**3.13**) and neutral (**3.14**) species, previously prepared by Dr. Erica Hong, were optimized (**Figure 3.4**), and their frontier molecular orbitals were visualized (**Figure 3.5**).

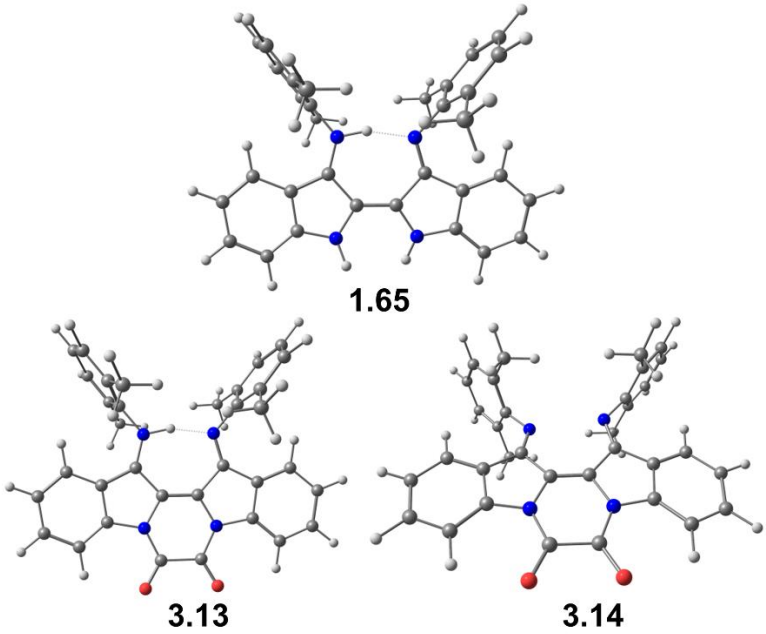


Figure 3.4 Optimized geometries of **1.65**, **3.13**, and **3.14**

The optimized geometry of **3.13** (**Figure 3.4**) is reminiscent of the structures of the protonated *cis*-Nindigos (**1.65** and **2.2**) and has a very similar distance across the diimine pocket (2.670 Å vs 2.652 Å for **3.13** vs **1.65** Ar = 2,6-dimethylphenyl).[174] In contrast, the optimized geometry of **3.14** (**Figure 3.6**) has the aryl imine units twisted out of the plane from each other because of electron-pair repulsion between the two imine groups. The distance between the imine nitrogens is larger in **3.14** (*N*-*N* distance of 2.900 Å) than for all the protonated *cis*-Nindigos in **Chapter 2** (Average *N*-*N* distance of 2.677 Å).

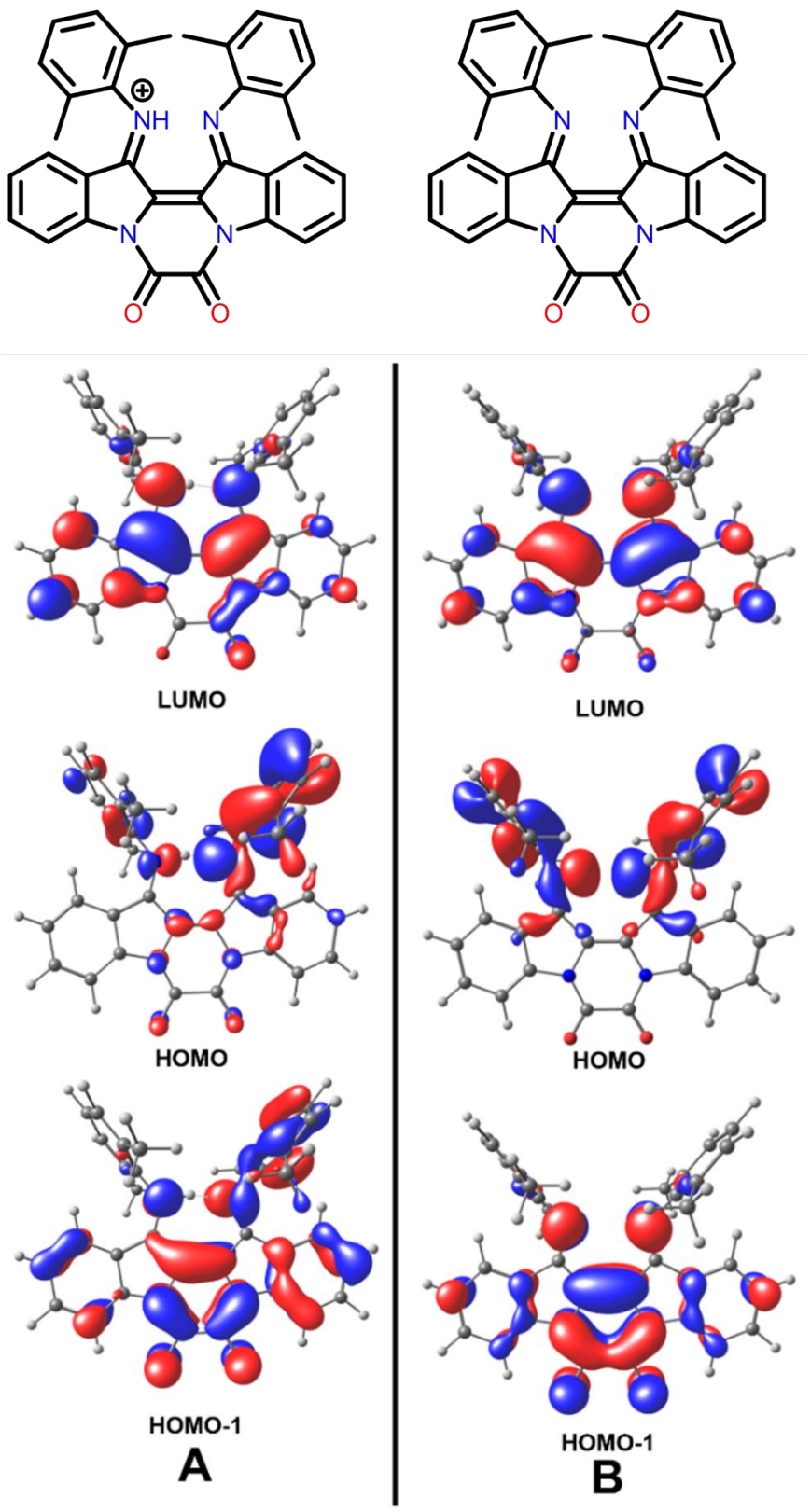


Figure 3.5 Frontier molecular orbitals of 3.13 (A), 3.14 (B)

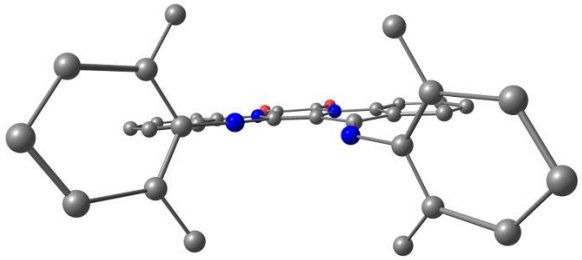


Figure 3.6 Front on view of **3.14** showing the distortion of the aryl imine units from electron-electron repulsion; hydrogen atoms have been omitted for clarity

In contrast to their unbridged neutral *trans*- and protonated *cis*- congeners, the HOMOs of **3.13** and **3.14** (**Figure 3.5**) are localized on the aryl imine subunits and have very little orbital density on the indigoid core. The HOMOs of **3.13** and **3.14** look similar to the HOMO-2 of **3.6** (**Figure 3.7**) and have some slight delocalization onto the oxalyl bridge and indigoid backbone, alongside significant orbital density on the indigoid carbonyl groups. The HOMO-1 of **3.13** and **3.14** are similar to the HOMO of **3.6** and are primarily delocalized on the indigoid backbone and oxalyl group. The HOMO-1 of **3.13** has significant delocalization onto the aryl iminium group (**Figure 3.5**), while there is no appreciable orbital density on the aryl imine groups of **3.14** (**Figure 3.6**). The fact that the HOMO is localized on the aryl imine subunit suggests that the low energy electronic transitions are not because of a HOMO to LUMO transition and are instead potentially the result of a transition between the HOMO-1 and the LUMO.

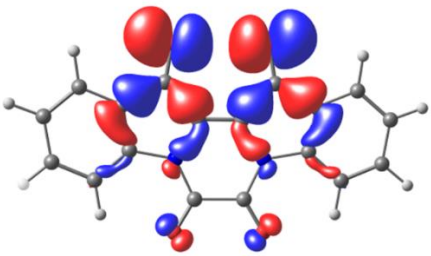


Figure 3.7 HOMO-2 of **3.6**

3.4.4 Time-dependent DFT study of *N, N'*-oxalyl bridged *cis*-Nindigos 3.13 and 3.14

The same functionals that were used to study the bridged *cis*-indigos were used to investigate the electronic spectra of the *N, N'*-oxalyl bridged *cis*-Nindigos. The functionals B3LYP and PBE0 have the strongest agreement with the experimental absorption wavelength maxima, while CAM-B3LYP and ωB97XD performed poorly. The B3LYP functional produced absorption wavelength maxima within 14 – 16 nm and 11 – 12 nm for the neutral and protonated *N, N'*-oxalyl bridged *cis*-Nindigos, respectively; while PBE0 yielded predicted absorption wavelength maxima values within 2 – 5 nm and 31 – 24 nm for the neutral and protonated *N, N'*-oxalyl bridged *cis*-Nindigos, respectively. For the long-range corrected functionals, the differences between the predicted and experimental absorption wavelength maxima ranged between 95 – 97 and 83 – 89 nm for CAM-B3LYP and ωB97XD, respectively, and are not suitable for accurately predicting the absorption wavelength maxima of *N, N'*-oxalyl bridged *cis*-Nindigos. The agreement between the predicted absorption wavelength maxima from B3LYP and PBE0 for the neutral, **3.16**, and B3LYP for the protonated, **3.15**, *N, N'*-oxalyl bridged *cis*-Nindigo

species, and their corresponding experimental values means that these methods are appropriate to use for the prediction of the absorption wavelength maxima of their atropisomeric congeners. The TD-DFT results also indicated that the absorption wavelength maxima for **3.13** and **3.14** are the result of a HOMO-1 to LUMO transition as opposed to the HOMO to LUMO transition found for their unbridged neutral *trans*-, **2.1**, and protonated *cis*-Nindigo, **2.2**, counterparts.

Table 3.2 TD-DFT predicted absorption wavelength maxima of **3.13** in acetonitrile

3.13 Experimental = 505 nm				
Method	**λ (nm)[a]**	**Difference**	**λ (nm)[b]**	**Difference**
B3LYP	494	11	493	12
PBE0	474	31	481	24
CAM-B3LYP	420	85	422	83
wB97XD	416	89	418	87

[a] computed using the 6-311++G(d,p) basis set [b]computed using Def2TZVPP basis set

Table 3.3 TD-DFT predicted absorption wavelength maxima of **3.14** in acetonitrile

3.14 Experimental = 417 nm				
Method	**λ (nm)[a]**	**Difference**	**λ (nm)[b]**	**Difference**
B3LYP	431	14	433	16
PBE0	419	2	422	5
CAM-B3LYP	322	95	322	95
wB97XD	320	97	320	97

[a] computed using the 6-311++G(d,p) basis set [b]computed using Def2TZVPP basis set

3.5 Electronic spectroscopy and time-dependent density functional theory study of 3.16a – 3.16e

The electronic spectra of the atropisomeric neutral *N, N'*-oxalyl bridged *cis*-Nindigo derivatives **3.16a – 3.16e** are like their symmetrically substituted counterparts (**3.14**) and have absorption wavelength maxima between 414 and 424 nm (**Table 3.4**).

The neutral *N*, *N*-oxalyl bridged *cis*-Nindigos are blue-shifted relative to Nindigos of types **2.1** and **2.2**. The narrow range (10 nm) of the absorption wavelength maxima of **3.16a – 3.16e** is consistent with the lack of sensitivity of the absorption wavelength maxima of other Nindigo derivatives in **Chapter 2** to substituents and because of the almost negligible orbital density on the non-coplanar aryl imine substituents.

Table 3.4 Absorption wavelength maxima of **3.16a – 3.16e**

Compound	Substituent	λ_{max}	Molar extinction coefficient (ε) $A/mol^{-1}L^{-1}cm^{-1}$
3.16a	Me	415	14500
3.16b	iPr	417	14400
3.16c	tBu	422	12300
3.16d	Ph	424	14400
3.16e	Et	414	13800

The geometries of the *anti* and *syn* conformations of *N, N'*-oxalyl bridged *cis*-Nindigos **3.16a – 3.16e** were optimized using B3LYP/Def2TZVPP in dichloromethane using the SMD solvation model, while the electronic spectra were predicted using TD-DFT with both B3LYP and PBE0, which were shown to perform well at predicting the absorption wavelength maxima of **3.14**. The PBE0 functional outperformed B3LYP at predicting the wavelength maxima and had predicted absorption wavelength maxima for **3.16a** to **3.16e** were within 1 – 12 nm of the experimental results, while the absorption wavelength maxima predicted using B3LYP were within 9 – 24 nm (**Table 3.5**). The agreement between the theoretical and experimental results is consistent with what was determined for the symmetrically substituted analogs and the PBE0 functional should in principle be able to predict the absorption wavelength maxima of other *N, N'*-oxalyl bridged *cis*-Nindigos containing different aryl imine groups. From the TD-DFT results, the absorption wavelength maxima of **3.16a – 3.16e** are the result of several transitions

and are not solely caused by the HOMO-1 to LUMO, which was determined to be the sole transition for **3.14**. The TD-DFT study of *N, N'*-oxalyl bridged *cis*-Nindigos further showed the added complexity in the corresponding electronic spectra that is caused by the introduction of a conjugated bridge to the indigoid scaffold; the absorption wavelength maximum of **3.16a – 3.16e** in all cases is the result of at least two transitions.

Table 3.5 TD-DFT predicted absorption wavelength maxima of **3.16a – 3.16e** in dichloromethane

Compound	Substituent	Exp. Λ (nm)[a]	Method	Predicted λ[a] *anti* (*syn*)	Δλ (nm)[c] *anti* (*syn*)	Predicted λ[b] *anti* (*syn*)	Δλ (nm)[c] *anti* (*syn*)
3.16a	Me	415	B3LYP	429 (426)	14 (11)	432 (426)	17 (11)
			PBE0	417 (411)	2 (4)	420 (413)	5 (2)
3.16b	iPr	417	B3LYP	431 (433)	14 (16)	434 (435)	17 (18)
			PBE0	420 (420)	3 (3)	423 (423)	6 (6)
3.16c	tBu	422	B3LYP	435 (433)	13 (11)	437 (435)	15 (13)
			PBE0	423 (421)	1 (1)	426 (423)	4 (1)
3.16d	Ph	424	B3LYP	433 (446)	9 (22)	436 (448)	12 (24)
			PBE0	421 (433)	3 (9)	424 (436)	0 (12)
3.16e	Et	414	B3LYP	432 (434)	18 (20)	431 (437)	17 (23)
			PBE0	415 (422)	1 (8)	417 (425)	3 (11)

[a] Wavelengths of maximum absorbance in dichloromethane; [b] predicted wavelength of maximum absorption using B3LYP/6-311++G(d,p); [c] predicted wavelength of maximum absorption – experimental wavelength of maximum absorption; [d] predicted wavelength of maximum absorption using B3LYP/Def2TZVPP

3.6 Room temperature ^{1}H NMR spectra of neutral N, N'-oxalyl bridged *cis*-Nindigos 3.16a – 3.16e

All the mono *ortho*-substituted neutral *N, N'*-oxalyl bridged *cis*-Nindigos displayed a single set of resonances in their room temperature ^{1}H NMR spectra (**Figure 3.8**). The single set of resonances is attributed to the *anti* and *syn* conformations being in rapid equilibrium; the permanently *cis*- geometries of the *N, N'*-oxalyl bridged Nindigos, and the closer proximity of the aryl imine subunits to each other, are expected to cause

the *anti* and *syn* conformations to not be effectively identical in the ^{1}H NMR spectra like **2.1a** – **2.1g**. As the steric bulk of the substituents increases, the broadness in the ^{1}H NMR spectra increases (**Figure 3.8**); the ^{1}H NMR spectra of the methyl (**3.16a**, **red trace**) and ethyl (**3.16e**, **green trace**) derivatives appear very sharp (**Figure 3.8**); the isopropyl substituted derivative (**3.16b**, **pink trace**) has significant broadening and has unresolved resonances for the isopropyl substituents and is either at its coalescence temperature or very close to it; the biphenyl analog (**3.16d**, **blue trace**) has significant broadening due to interconversion of the *anti* and *syn* conformations and the minor conformation is approaching coalescence. The *tert*-butyl analog **3.16c** has one set of resonances in its ambient temperature ^{1}H NMR spectrum, which is attributed to the *syn* conformation being higher in energy than the *anti* conformation that the *syn* conformation does not form under the experimental conditions (the relative energies between the *anti* and *syn* conformations of **3.16** will be discussed later in this chapter) and is consistent with what was found for **2.2c**.

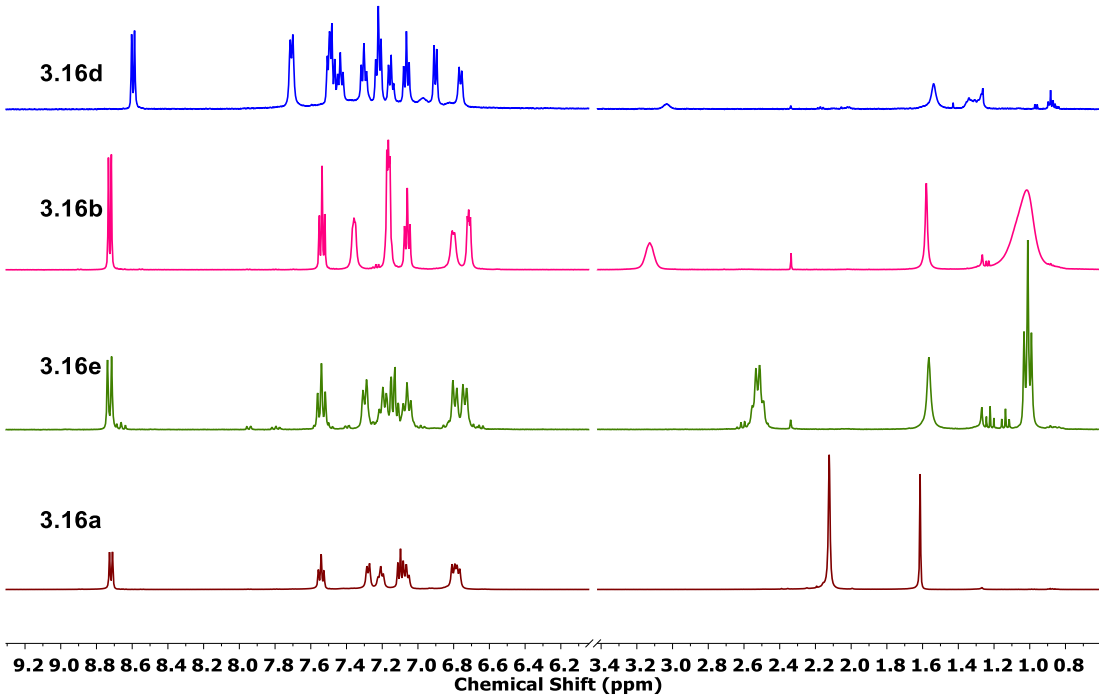


Figure 3.8 Room temperature ^{1}H NMR spectra of 3.16a, 3.16b, 3.16d, and 3.16e

3.7 Variable temperature ^{1}H NMR studies of 3.16a, 3.16b, 3.16d, and 3.16e

The presence of only one set of resonances at room temperature for the neutral *N, N'*-oxalyl bridged *cis*-Nindigos is reminiscent of their unbridged neutral *trans*-counterparts **2.1**a **– 2.1g**. Therefore, *N, N'*-oxalyl bridged *cis*-Nindigos **3.16a**, **3.16b**, **3.16d**, and **3.16e** were subjected to low temperature ^{1}H NMR studies in dichloromethane-d_2 or toluene-d_8 to assess their dynamic behavior.

For **3.16a**, the sharp singlet at ~2.1 ppm broadened as the temperature was lowered, began to separate at 243 K and split into two overlapping singlets at 2.10 and 2.05 ppm beginning at 240 K; as the temperature was further lowered the two singlets continued to sharpen down to 210 K; below 210 K the signals begin to broaden, which is attributed to **3.16a** precipitating out of solution at low temperatures (**Figure 3.9**). The only other diagnostic signal in the aromatic region with respect to the dynamic behavior of **3.16a** is the resonance at 8.65 ppm, which also begins to separate into two separate doublets beginning at 240 K.

From the low temperature ^{1}H NMR spectra (**Figure 3.9**), it is difficult to assess the ratio between the *anti* and *syn* conformations of **3.16a**; a line-fitting was done in MNOVA 12 to assess the relative integrations between the two conformations (**Figure 3.10**) at 210 K. From the area output of the line-fitting the relative integration between the major and minor conformations is 3 to 1. Using lineshape analysis the rotational energy barriers were determined to be 14.4 ± 1.3 kcal/mol (at 298 K) and 13.1 kcal/mol (at 245 K, T_c); the rotational energy barrier was determined using the coalescence temperature and maximum peak separation was determined to be 13.0 kcal/mol (at 245 K).

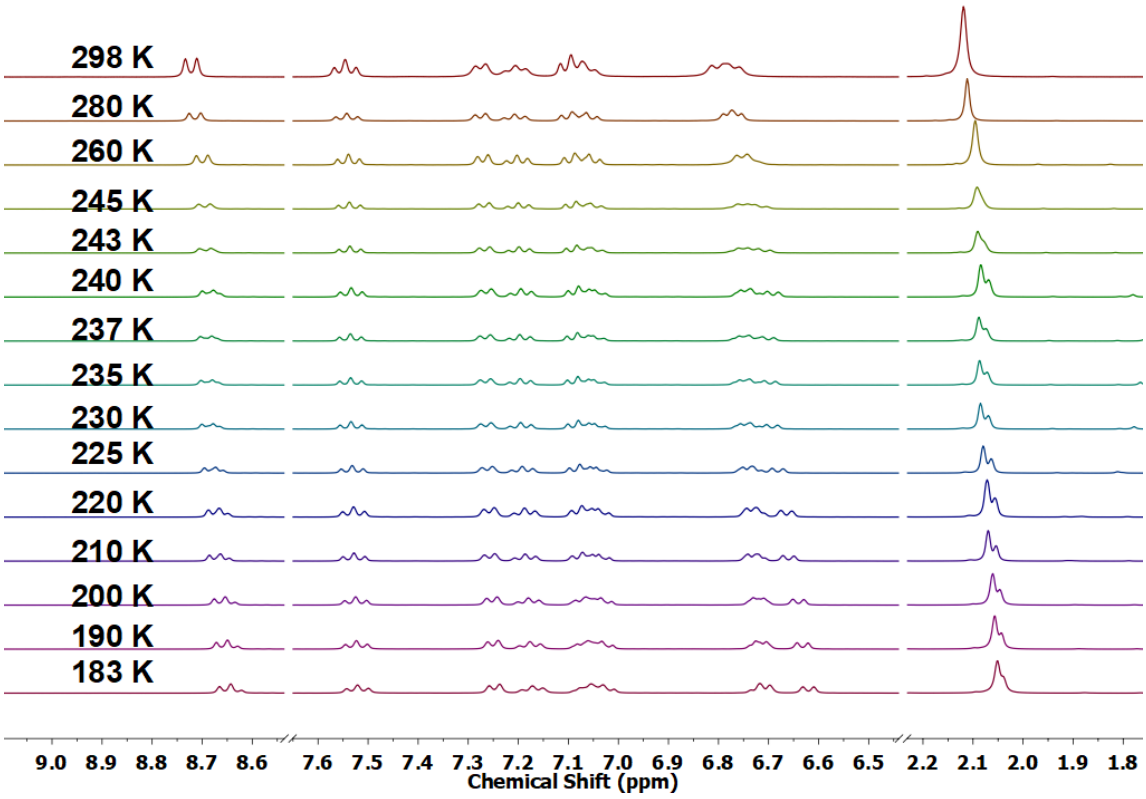


Figure 3.9 Low-temperature variable temperature ^{1}H NMR of **3.16a** (Ar = *o*-methylphenyl)

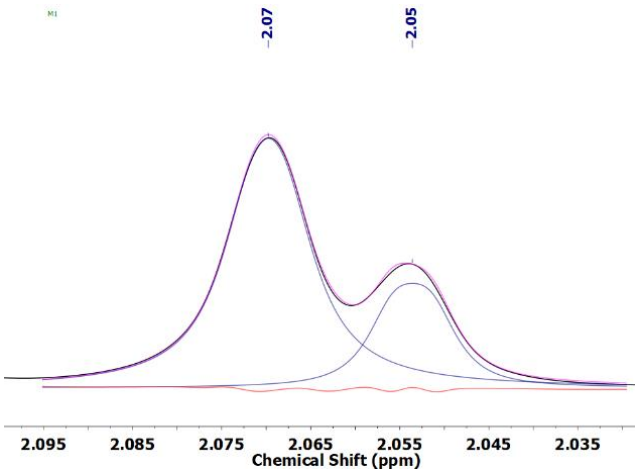


Figure 3.10 Line-fitting of **3.16a** in MNOVA12 (**Black** = experimental peaks, **red** = residual, **navy** = simulated peaks, **magenta** = sum of the navy traces)

For **3.16b**, both low (**Figure 3.11**) and high temperature (**Figure 3.12**) ^{1}H NMR studies were done because the ^{1}H NMR at 298 K appears to be at, or close to, the coalescence temperature for the alkyl resonances 3.5 ppm for the isopropyl methine protons and 1.25 and 1.35 ppm for the isopropyl methyl protons. As the sample of **3.16b** is cooled the resonances for the isopropyl methyl groups immediately start to sharpen and gain structure at 288 K (still at the original chemical shifts) and continue to sharpen down to 208 K, after which the ^{1}H NMR resonances begin to broaden. The broadening of the ^{1}H NMR resonances at low temperatures is again attributed to the low solubility of **3.16b** at low temperatures. The most diagnostic part of the spectrum that supports the presence of two atropisomers at low temperatures is the splitting of the isopropyl methine proton into two distinct septets. At 268 K, the broad septet starts to sharpen, and beginning at 258 K starts to separate into two septets, which is most evident beginning at 248 K and continues down to 188 K. At 228 K, the ratio between the *anti* and *syn* conformations is 1:1 (based on the integration between the isopropyl doublets).

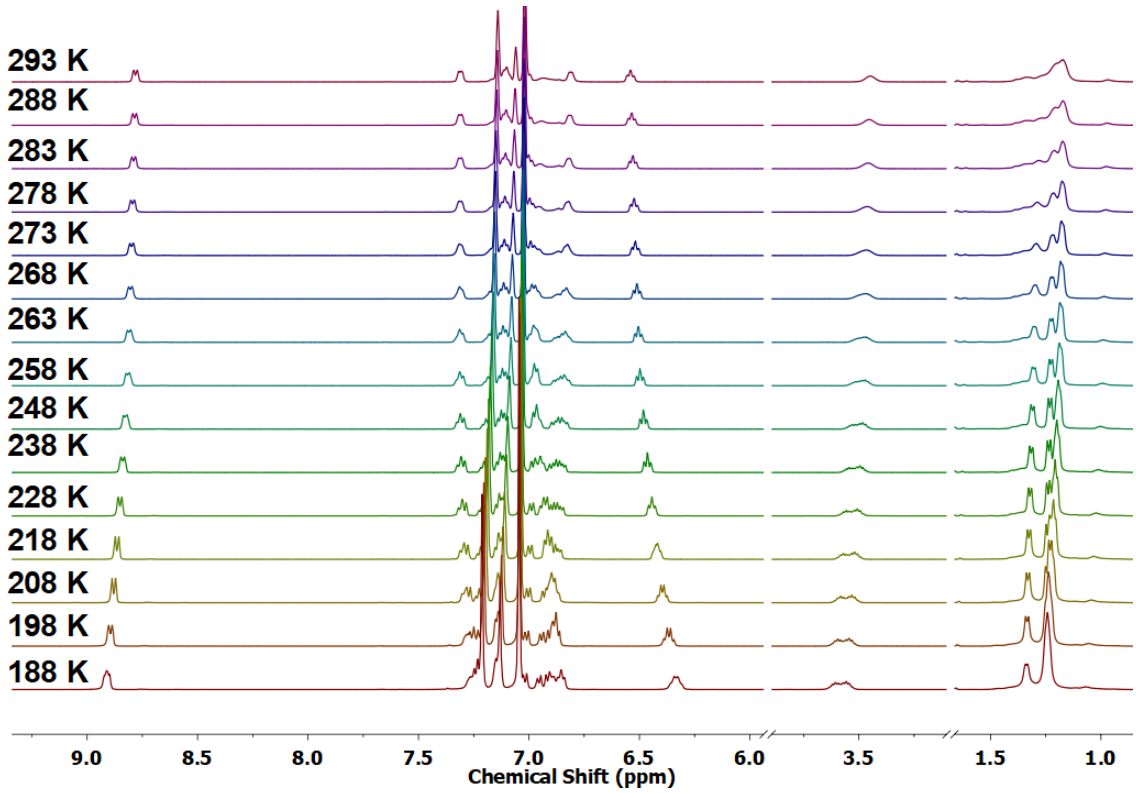


Figure 3.11 Low-temperature variable temperature ^{1}H NMR study of **3.16b** (Ar = *o*-isopropylphenyl)

As the temperature sample of **3.16b** is increased, the resonances for the methyl and methine protons of the isopropyl substituents sharpen and become fully resolved at 320 K and 298 K, respectively. The rotational energy barrier was evaluated using the maximum peak separation and the coalescence temperature (273 K) and was determined to be 13.7 kcal/mol. Lineshape analysis was not performed because there were no suitable resonances in the spectrum to simulate using WinDNMR.

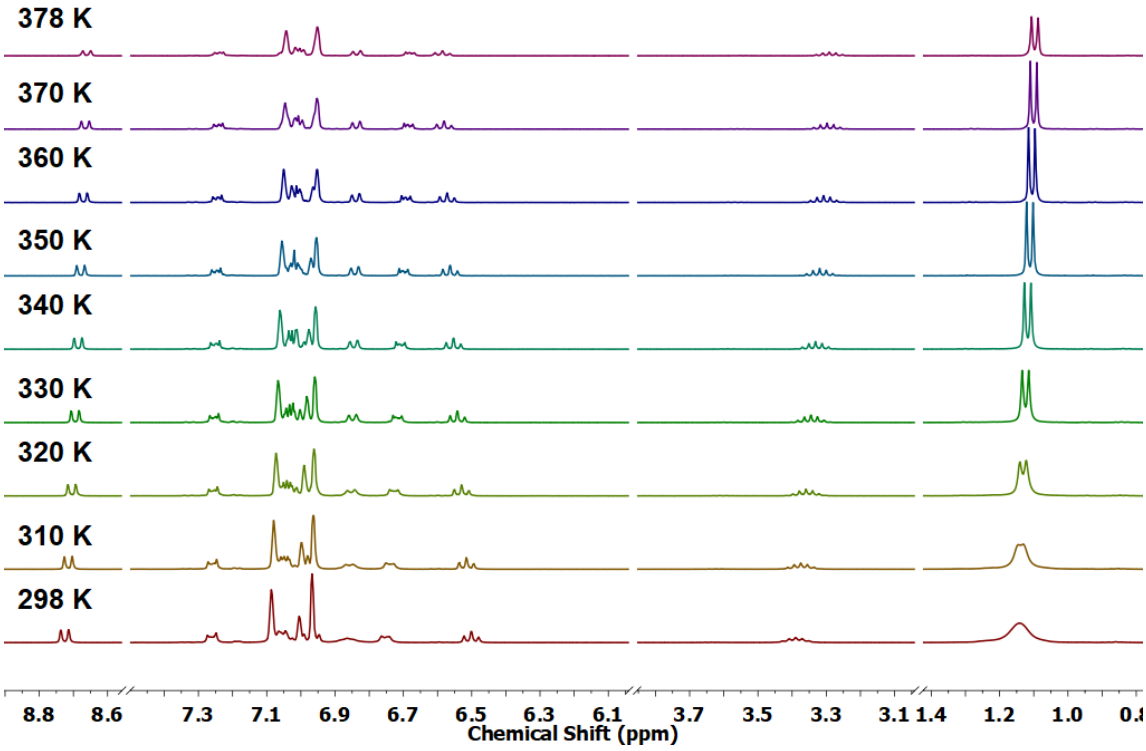


Figure 3.12 High-temperature variable temperature ^{1}H NMR study of **3.16b** (Ar = *o*-isopropylphenyl)

In the case of **3.16d**, at 298 K the ^{1}H NMR resonances for the minor conformation are broad and are approaching coalescence with the major conformer. The significant peak broadening at room temperature led to chloroform-*d* being used for the variable temperature ^{1}H NMR study as it can be cooled down and can be heated to higher temperatures than dichloromethane-d_2. As the temperature of the sample is lowered, the broadness decreases and at 270 K the signals for the minor conformation are clear and resolved. The most diagnostic ^{1}H NMR resonances for the minor conformation of **3.16d** are the doublets centered at 6.6 and 8.6 ppm. As the temperature is raised from room

temperature the doublet at 6.6 ppm broadens up to 315 K and begins to sharpen upon further heating to 330 K. In the variable temperature ^{1}H NMR study of **3.16d** there is no "pure coalescence" temperature observed for the doublet at 6.6 ppm as the doublet always retains some sort of coupling information; the signal for the minor conformation (at 6.8 ppm) disappears and merges with the doublet at 6.6 ppm at 298 K, the signal continues to broaden until 315 K. The coalescence temperature is estimated to be 298 K because of the complete disappearance of the signals of the minor conformation into the major signal. At 214 K, the ratio between the *anti* and *syn* conformations of **3.16d** was determined using the integration of the doublets at 6.6 and 6.8 ppm and is 5.7 to 1. Using the estimated coalescence temperature of 298 K and the maximum peak separation between the two doublets of the major and minor conformations the rotational energy barrier of **3.16d** is estimated to be 14.7 kcal/mol and is comparable to **2.2a**. The *N*-*C* rotational energy barrier determined using lineshape analysis was determined to be 14.9 ± 3.1 kcal/mol at 298 K.

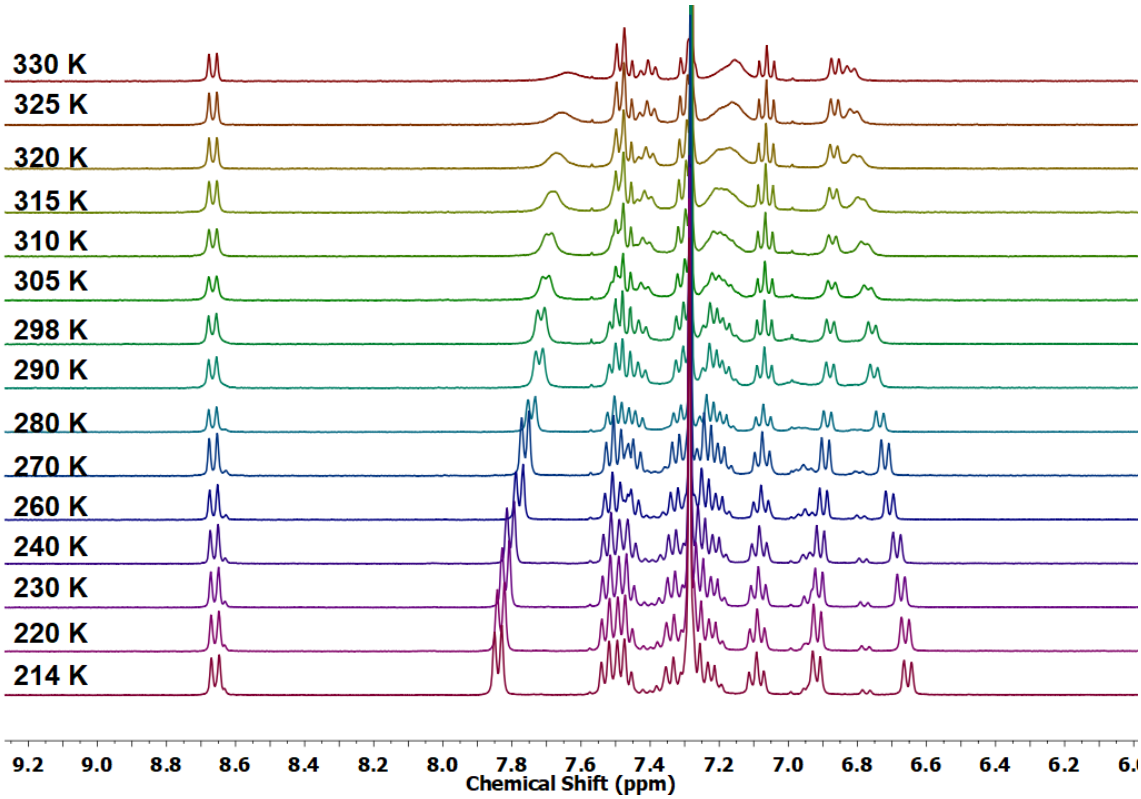


Figure 3.13 High and low-temperature variable temperature ^{1}H NMR study of **3.16d** (Ar = *o*-phenylphenyl)

For **3.16e**, at 298 K the ^{1}H NMR spectrum is very sharp and only one set of resonances is present. Like **3.16a**, this is attributed to the rapid interconversion between the *anti* and *syn* conformations. As the sample was cooled, the most diagnostic signals displaying that a dynamic process was happening were the ethyl resonances (triplet at 0.8 ppm and quartet at 2.5 ppm); the quartet for the CH_2 of the ethyl group begins to broaden significantly at 270 K, before splitting into two separate resonances at 250 K (one quartet and one ABX_3 multiplet); as the sample is cooled to 200 K the peaks continue to sharpen and separate. The methyl resonance of the ethyl substituent split into two overlapping

triplets (centered at 0.8 ppm) starting at 230 K. In the aromatic region of the spectrum, the most diagnostic signal for monitoring the atropisomerization process is the doublet at 7.29 ppm, which separates into two doublets (centered at 7.30 ppm) beginning at 250 K. At 200 K, the ratio between the *anti* and *syn* conformations of **3.16e**, was determined by the relative integrations of the two doublets centered at 7.30 ppm, to be 1.5 to 1. The two doublets centered at 7.26 ppm and the two distinctive resonances of the methylene of the ethyl group coalesce at 255 K. The rotational energy barrier between the *anti* and *syn* conformations using the maximum peak separation and the coalescence temperature of the signals centered at 7.26 ppm is 13.2 kcal/mol. The doublets at 7.26 ppm were chosen to model using lineshape analysis and the rotational energy barrier was determined to be 13.5 ± 0.8 kcal/mol and 12.6 kcal/mol at 298 and 255 K, respectively.

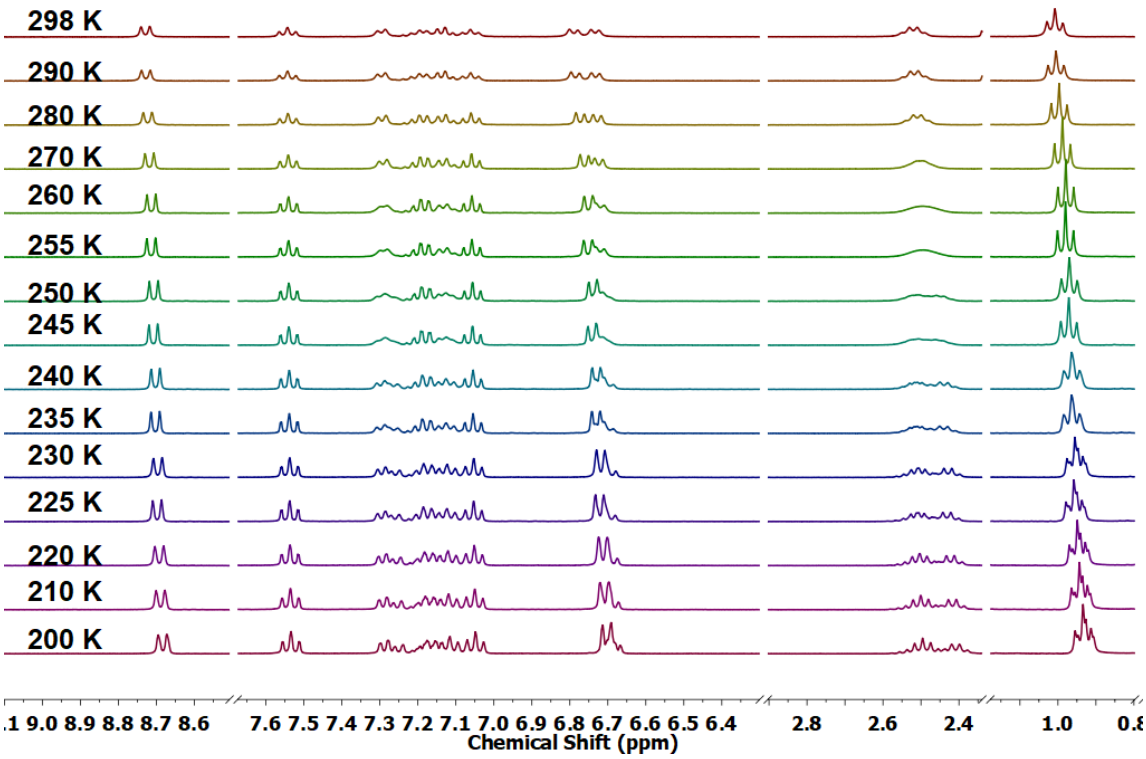


Figure 3.14 Variable temperature ^{1}H NMR of **3.16e** (Ar = *o*-ethylphenyl)

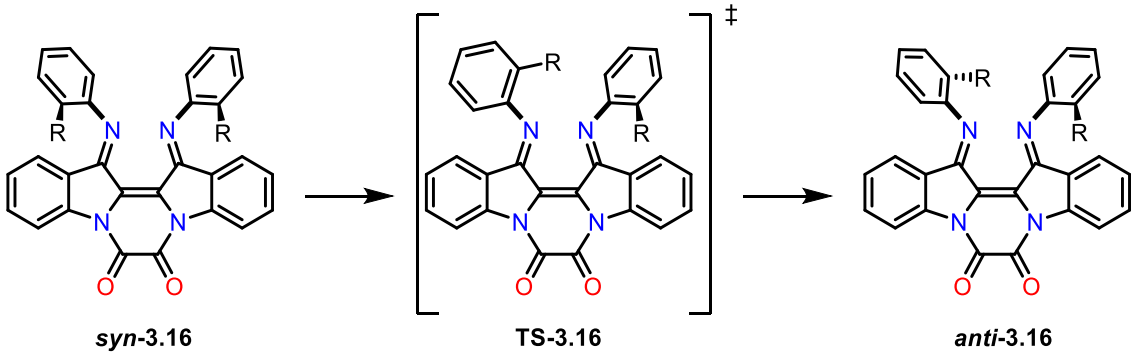
The variable temperature ^{1}H NMR studies of the neutral oxalyl bridged *cis*-Nindigos, **3.16a** – **3.16e**, show that the size of the diimine pocket has a significant influence on the rotational barriers. In all cases, the experimentally determined rotational barriers of the neutral oxalyl bridged *cis*-Nindigos are lower than their protonated unbridged *cis*-Nindigo congeners.

Table 3.6 Experimentally determined rotational energy barriers of **3.16a**, **3.16b**, **3.16d**, and **3.16e**

Compound	Substituent	Rotational energy barrier from lineshape analysis at 298 K (kcal/mol)	Rotational energy barriers from T_c (kcal/mol)
3.16a	Me	14.4	13.0
3.16b	iPr	-	13.7
3.16d	Ph	14.9	14.7
3.16e	Et	13.5	13.1

3.8 Computational determination of the *N-C* atropisomerization barriers of neutral *N, N'*-oxalyl bridged *cis*-Nindigos 3.16a – 3.16e

The barriers for the *N-C* rotation (**Scheme 3.9**) between the *anti* and *syn* conformations of **3.16a – 3.16e** were computed using DFT, similarly to **2.1a – 2.1g** and **2.2a – 2.2g**. The *syn* conformer, in all cases, is the highest energy conformation. The difference in the energy (**Table 3.6**) between the *anti* and *syn* conformations of **3.16a** – **3.16e**, using B3LYP/Def2TZVPP, ranges between 0.7 – 4.0 kcal/mol for gas-phase geometries and 0.0 – 4.0 kcal/mol for geometries computed using the SMD solvation model and dichloromethane. When the *anti* and *syn* conformations of **3.16a – 3.16e** were optimized using Def2SVP in the gas phase and using the SMD solvation model, the energy differences between the *anti* and *syn* conformations are between 0 – 4.4 kcal/mol and 0.8 – 4.5 kcal/mol, respectively.



Scheme 3.9 Interconversion between *anti* and *syn* atropisomers of **3.16**

Table 3.7 Differences in the computed Gibbs free energies of *anti* and *syn* neutral *N*, *N'*-oxalyl bridged *cis*-Nindigos in kcal/mol

		Gas-phase		SMD (dichloromethane)	
Compound	**Substituent**	**B3LYP Def2SVP**	**B3LYP Def2TZVPP**	**B3LYP Def2SVP**	**B3LYP Def2TZVPP**
3.16a	Me	0.6	0.2	1.3	0.3
3.16b	iPr	3.4	3.0	2.8	2.4
3.16c	tBu	4.4	4.0	4.4	4.0
3.16d	Ph	0	0.01	0.8	0.7
3.16e	Et	2.2	1.9	3.1	1.9

It was initially thought that as the steric bulk of the substituents increases, the differences in the energy between the *anti* and *syn* conformations would increase. This hypothesis is true for the gas-phase geometries of **3.16a** – **3.16c**, and **3.16e**; however, from the data presented in **Table 3.7**, in the gas phase the difference in energy between the *anti* and *syn* conformations of the biphenyl substituted derivative **3.16d** is 0 kcal/mol using B3LYP/Def2SVP and B3LYP/Def2TZVPP, which was surprising given the size of a phenyl substituent relative to a methyl group. When accounting for solvation the difference in energy between the *anti* and *syn* conformations of the ethyl substituted analog, **3.16e**, is 3.1 kcal/mol, which is slightly greater than the difference determined for

the isopropyl substituted analog, **3.16b**, whose difference in energy between the *anti* and *syn* conformers is 2.8 kcal/mol using B3LYP/Def2SVP; the expected trend of the *anti* conformation being lower in energy than the *syn* conformation is true for **3.16e** when accounting for solvation using B3LYP/Def2TZVPP. The ratios between the *anti* and *syn* conformations, as determined from the Boltzmann distribution equation, of **3.16a** – **3.16e** are predicted to be from 1 to 1 up to 1686 to 1 (**Table 3.8**). None of the predicted ratios of the *anti* and *syn* conformations agree with experimentally observed results.

Table 3.8 Predicted ratios between the *anti* and *syn* conformations of **3.16a – 3.16e**

		Gas-phase		SMD(dichloromethane)	
Compound	**Substituent**	**B3LYP Def2SVP**	**B3LYP Def2TZVPP**	**B3LYP Def2SVP**	**B3LYP Def2TZVPP**
3.16a	Me	2.8:1	1.4:1	9.0:1	1.7:1
3.16b	iPr	312:1	159:1	113:1	58:1
3.16c	tBu	1686:1	858:1	1686:1	858:1
3.16d	Ph	1:1	1:1	3.9:1	3.3:1
3.16e	Et	41:1	25:1	188:1	25:1

The gas-phase transition state geometries for the *N*-*C* rotation of **3.16a** – **3.16e** all displayed significant distortions across the indigoid backbone relative to the optimized *anti* and *syn* geometries (**Figure 3.15**). The distortions of the indigoid backbone were measured by the angle between two planes that are composed of the indole units of the indigoid backbone (**Figure 3.16**, highlighted as the **green** and **purple** planes in **A**). The angle between the planes (**Table 3.9**) ranged between 21.5 and 39.6°; the smallest distortion of the indigoid backbone is in **3.16b**, while the largest distortion was in the biphenyl derivative **3.16d**. Surprisingly, the *tert*-butyl analog, **3.16c**, had comparable angles between the planes to the ethyl substituted analog, **3.16e**, (31.9 vs 28.5°), which was surprising given the differences in the size of the substituents.

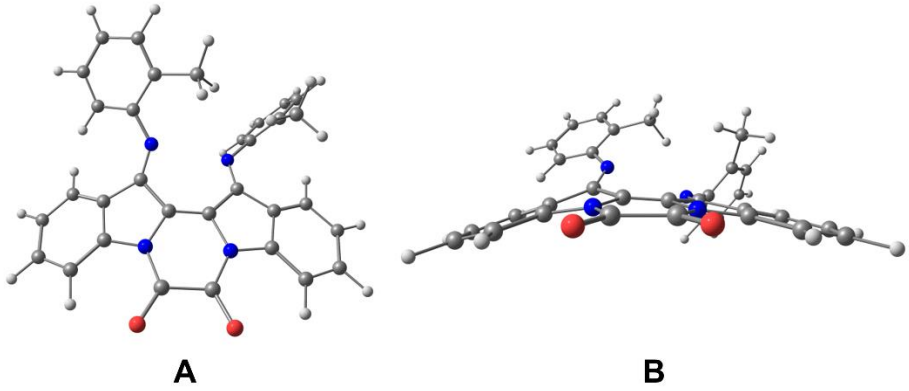


Figure 3.15 Transition state geometry of **3.16a** (Ar = *o*-methylphenyl); Overhead view **A**; Face-on view **B**

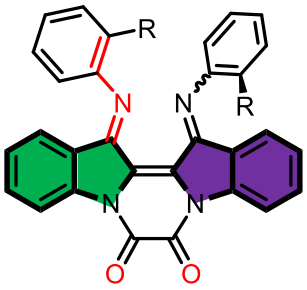


Figure 3.16 Distorted planes (**green** and **purple**) and torsional angles (**red**) measured in the transition state of neutral *N*, *N'*-oxalyl bridged *cis*-Nindigos (**3.16a – 3.16e**)

No trend can be drawn from the dihedral angles between the aryl imine subunit substituents and the indigoid backbone in the transition state (**Figure 3.16**, highlighted as the red bonds). The torsional angles ranged between 163 and 175°. Like its unbridged protonated *cis*-Nindigo congener **2.2d**, **3.16d** has torsional angles closest to planarity (θ = 175°). The ethyl derivative, **3.16e**, displayed the greatest deviation from planarity (θ = 163°), while the torsional angles in the methyl (**3.16a**), isopropyl (**3.16b**), and *tert*-butyl

(**3.16c**) substituted derivatives have comparable torsional angles of 166.6, 166.3, and 165.7°, respectively.

Table 3.9 Pertinent angles and torsional angles of neutral *N*, *N'*-oxalyl bridged *cis*-Nindigos **TS-3.16a – TS-3.16e** from gas-phase geometries optimized using B3LYP/Def2TZVPP

Compound	Substituent	∠ between planes for TS (°)[a]	θ for TS' (°)[b]
3.16a	Me	24.3	166.6
3.16b	iPr	21.5	166.3
3.16c	tBu	31.9	165.7
3.16d	Ph	39.6	175.9
3.16e	Et	28.5	163.0

[a] Angle between the two defined planes in **Figure 3.16** in transition state**;** [b] torsional angle between the indigoid backbone and aryl imine substituent for transition state for iminium N-C rotation [a]

The calculated energy barriers for the N-C rotation of **3.16a – 3.16e** are between 9.3 and 20.2 kcal/mol and 8.9 and 19.7 kcal/mol using B3LYP/Def2TZVPP and B3LYP/Def2SVP, respectively. These computed barriers using B3LYP are within 1.9 – 4.6 kcal/mol and 1.2 – 4.8 kcal/mol of the experimentally determined barriers using B3LYP/Def2TZVPP and B3LYP/Def2SVP, respectively. The rotational energy barriers of **3.16a**, **3.16d**, and **3.16e** were all predicted to be approximately 2 – 3 kcal/mol higher in energy than their experimentally determined values. The computed barrier of **3.16b** was predicted to be 3 kcal/mol lower in energy than the experimentally determined barrier. Interestingly, Def2SVP performed better than Def2TZVPP at predicting the rotational energy barriers of neutral oxalyl bridged *cis*-Nindigos.

Table 3.10 Energy barriers of neutral *N, N'*-oxalyl bridged *cis*-Nindigos **3.16a – 3.16e**

Compound	Coalescence temperature (K)	Calculated TS $\Delta G^{\ddagger}$ (kcal/mol)[a] [(b)]	Lineshape analysis $\Delta G_{298K}^{\ddagger}$ (kcal/mol)	Lineshape analysis $\Delta G_{TC}^{\ddagger}$ (kcal/mol)	$\Delta G^{\ddagger}$ using T_c (kcal/mol)
3.16a	245	14.9 (14.3)	14.4	12.7	13.0
3.16b	273	9.3 (8.9)	-	-	13.7
3.16c	-	14.9 (14.2)	-	-	-
3.16d	315	20.2 (19.7)	14.9	14.9	14.7
3.16e	255	16.3 (15.4)	13.5	12.6	13.1

[a] Rotational energy barrier computed using B3LYP/Def2TZVPP; [b] rotational energy barrier computed using B3LYP/Def2SVP; barriers are computed at 298 K

3.9 Benchmark study on *N-C* rotational energy barriers of neutral *N, N'*-oxalyl bridged *cis*-Nindigos 3.16a – 3.16e

A single point energy benchmark study was undertaken to investigate if other DFT functionals are more suited to predicting the rotational energy barriers of **3.16a – 3.16e**. The functionals chosen were: CAM-B3LYP, LC-ωHPBE, M06, M06-2X, M11, M15, TPSSh, and ωB97XD; Def2SVP was chosen over Def2TZVPP because of their comparable accuracy in modeling the *N-C* rotational energy barriers and drastically shorter computation times. In **Chapter 2**, it was shown that the M11 functional was the most accurate functional at modeling the *N-C* rotational energy barriers of protonated unbridged *cis*-Nindigos **2.2a – 2.2g**. No functional outperformed the others in the benchmark study of **3.16a – 3.16e**. The M15 and TPSSh functionals performed well in modeling the rotational energy barrier of **3.16a**, however performed very poorly for the other analogs, while M11 and ωB97XD performed well in modeling the energy barrier of **3.16b** while performing poorly for the other analogs.

Table 3.11 Calculated *N-C* rotational energy barriers of **3.16a – 3.16e**

Compound	Substituent	B3LYP	CAM-B3LYP	ωB97XD	M11	M15	M06	M06-2X	LC-ωHPBE	TPSSh
3.16a	Me	14.3	14.9	15.5	16.1	13.4	15.2	14.3	17.0	12.4
3.16b	iPr	8.9	10.6	13.2	14.2	10.0	11.1	11.3	10.6	7.9
3.16c	tBu	14.2	15.2	16.5	17.4	15.0	15.7	14.1	14.9	12.9
3.16d	Ph	19.7	18.7	21.1	21.5	22.9	18.7	18.7	19.5	21.9
3.16e	Et	15.4	16.3	17.1	18.0	15.5	16.3	15.9	17.3	14.6

3.9.1 N-C rotational energy barriers of neutral *N, N'*-oxalyl Nindigos 3.16a – 3.16e using solvation models

Accounting for solvent effects may enable the DFT calculations to better model the rotational energy barriers of **3.16a – 3.16e**. Given that B3LYP/Def2SVP performed better at predicting the *N-C* rotational energy barriers than B3LYP/Def2TZVPP, the former was used to evaluate whether accounting for solvation improves the accuracy of the computed *N-C* rotational energy barriers of **3.16a – 3.16e**. Three different solvation models, SMD,[166] the polarizable continuum (PCM),[209–213] and the conductor-like polarizable continuum (CPCM) solvation models,[214,215] were chosen to calculate the N-C rotational energy barriers. All three of the solvation models that were chosen are implicit solvation models and are commonplace in molecular modelling; the PCM model was chosen as it has previously been used as the solvation model when modelling indigoids computationally and treats the solvation as a continuum modeled using the solvents dielectric constant; CPCM was chosen because of its slight differences to the PCM solvation model in which the bulk solvent is treated as a conductor like polarizable continuum using the solvents refractive index and the dielectric constant to define the medium; the SMD solvation model was chosen as it uses several experimentally defined parameters (dielectric constant, refractive index, H-bond acidity, H-bond basicity, surface

tension at interface, carbon aromaticity, and electronegative/halogenicity) in its definition of the continuum used to define the solvation environment, There is an improvement in the accuracy of the predicted rotational energy barriers when solvation models are used (**Table 3.12**). In the case of modeling the transition states using the SMD solvent model the rotational energy barriers ranged between 7.8 to 19.4 kcal/mol; in the case of the methyl (**3.16a**), biphenyl (**3.16d**), and ethyl (**3.16e**) derivatives, the difference between the experimental and theoretical *N-C* rotational barriers decreased slightly from the previous study done in the gas-phase; the difference between the predicted and experimental *N-C* rotational barriers for the isopropyl (**3.16b)** analog increased and the SMD solvent model did not accurately model the *N-C* rotational energy barrier. The PCM and CPCM solvent models performed similarly and were less effective at modeling the rotational energy barriers. The *N-C* rotational energy barriers calculated using the PCM and CPCM solvation models ranged between 9.0 – 20.0 kcal/mol and 9.5 – 19.9 kcal/mol, respectively.

Table 3.12 Study of the effect of solvation models on the *N-C* rotational energy barriers of **3.16a – 3.16e** using B3LYP/Def2SVP

Compound	Substituent	Calculated TS $\Delta G^{\ddagger}$ (kcal/mol) SMD	Calculated TS $\Delta G^{\ddagger}$ (kcal/mol) PCM	Calculated TS $\Delta G^{\ddagger}$ (kcal/mol) CPCM	Lineshape Analysis $\Delta G_{298}^{\ddagger}$ ($\Delta G_{Tc}^{\ddagger}$) (kcal/mol)	$\Delta G^{\ddagger}$ Using T_c (kcal/mol)
3.16a	Me	13.7	14.0	14.2	14.4 (12.7)	13.0
3.16b	iPr	7.8	9.0	9.5	-	13.7
3.16c	tBu	14.2	14.2	14.4	-	-
3.16d	Ph	19.4	20.0	19.9	14.9 (14.9)	14.7
3.16e	Et	13.9	15.6	15.8	13.5 (12.6)	13.1

The success of SMD at modeling the *N-C* rotational energy barriers and the increased accuracy of other DFT functionals at modeling the rotational energy barriers

makes the next most obvious extension of this computational study to be coupling the two strategies together. Therefore, a combined benchmark study was performed to further model the *N*-*C* rotational energy barriers. From the benchmark study accounting for solvation, the highest performing functional was MN15, which displayed differences in rotational energy barriers for **3.16a**, **3.16b**, **3.16d**, and **3.16e** of 0.2, 4.6, 1.5, and 0.9 kcal/mol, respectively; the originally used method B3LYP had differences between the computed and experimental rotational energy barriers of 0.7, 5.9, 3.8, and 0.8, kcal/mol, respectively.

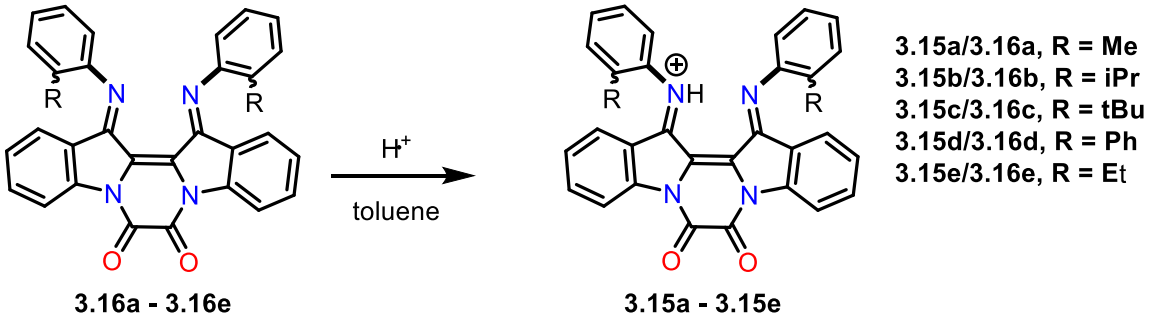
Table 3.13 Benchmark study on rotational energy barriers of **3.16a** – **3.16e** using SMD

Compound	Subsituent	B3LYP	CAM-B3LYP	ωB97XD	M11	M15	M06	M06-2X	LC-ωHPBE	TPSSh
3.16a	Me	13.7	12.3	13.0	13.7	12.8	11.0	11.9	13.7	8.7
3.16b	iPr	7.8	9.1	10.3	10.9	9.1	9.5	9.5	8.1	5.3
3.16c	tBu	14.2	11.9	15.7	17.9	14.3	15.5	14.9	14.3	12.1
3.16d	Ph	19.4	18.2	20.5	20.5	17.1	18.5	19.8	18.8	21.1
3.16e	Et	13.9	13.4	13.4	16.7	14.0	11.8	14.5	14.8	11.5

3.10 Synthesis of protonated *N, N'*-oxalyl bridged *cis*-Nindigos 3.15a – 3.15e

Neutral *N, N'*-oxalyl bridged *cis*-Nindigos **3.16a – 3.16e** were protonated using either trifluoroacetic acid or tetrafluoroboric acid diethyl etherate in toluene (**Scheme 3.10**) to prepare **3.15a – 3.15e** in yields between 57 and 96%. A dramatic color change from the brown/yellow solution of the neutral species to a vibrant red is observed upon protonation. The room temperature ^{1}H NMR spectra of **3.15a – 3.15e** are dramatically different from their neutral counterparts. In all cases, except the *tert*-butyl derivative, a doubling of resonances is observed (**Figure 3.18**). The doubling of the resonances

supports the hypothesis that the size of the diimine pocket has a strong influence on the *N-C* rotational energy barriers of *cis*-Nindigos and the protonation state of the tethered *cis*-Nindigos has a significant impact on the *N-C* rotational energy barriers of *N, N'*-oxalyl bridged *cis*-Nindigos. The similarity between the N-N distances of **2.2** and **3.13**, and by inferring a comparable N-N distance for the atropisomeric *N, N'*-oxalyl bridged *cis*-Nindigos, and it is expected that **3.15a – 3.15e** will have comparable *N-C* rotational energy barriers to their unbridged counterparts. The comparable *N-N* distances of **3.15** and **2.2** allow for the quantification of what degree of influence the conjugated electron-withdrawing oxalyl bridge has on the *N-C* rotational energy barriers. Variable temperature ^{1}H NMR studies of **3.15c** were not undertaken because of the presence of a single set of resonances in the room temperature ^{1}H NMR spectra.



Scheme 3.10 Synthesis of protonated *N, N'*-oxalyl bridged *cis*-Nindigos **3.15a – 3.15e**

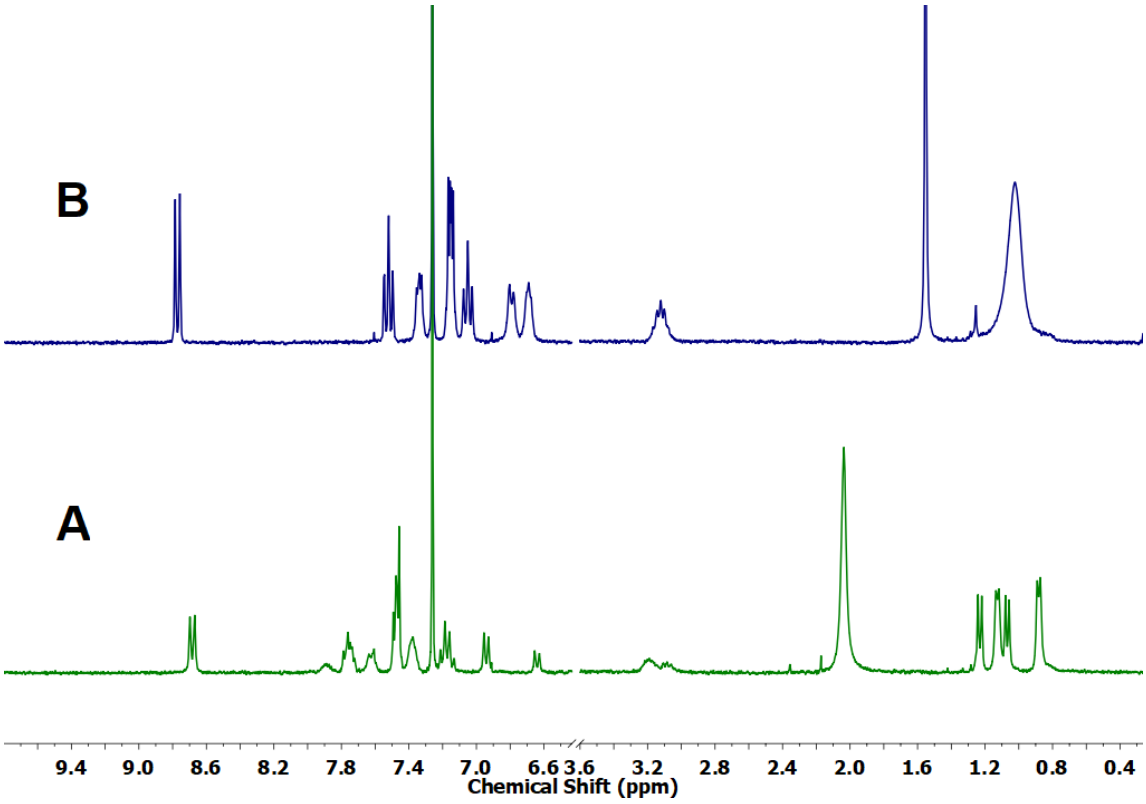


Figure 3.17 Comparison of the room temperature ^{1}H NMR spectra of neutral (**3.16b**, **B**) and protonated (**3.15b**, **A**) *N, N'*-oxalyl bridged *cis*-Nindigos (Ar = *o*-isopropylphenyl)

3.11 Electronic spectroscopy of protonated *N, N'*-oxalyl bridged Nindigos 3.15a – 3.15e

The electronic spectra of the atropisomeric protonated *N, N'*-oxalyl bridged *cis*-Nindigo derivatives **3.15a – 3.15e** are very similar to their symmetrically substituted counterparts (**3.13**) and have absorption wavelength maxima between 489 and 504 nm (**Table 3.14**). The absorption wavelength maxima of **3.15a – 3.15e** are red-shifted by 89, 82, 82, 65, and 75 nm from their neutral counterparts **3.16a – 3.16e**, respectively. The change in the absorption wavelength maxima upon protonation mirrors what is observed

for the protonation of unbridged Nindigos, where the absorption wavelength maximum of 2,6-dimethylphenyl Nindigo undergoes a red-shift of 71 nm upon protonation.[174] The range of absorption wavelength maxima of the **3.15a – 3.15e** is 18 nm, which is slightly larger than the 10 nm range observed for **3.16a – 3.16e**, but still is consistent with the lack of sensitivity to aryl imine substituents that is inherent to Nindigo derivatives. Interestingly, the only derivative with an aromatic substituent, **3.15d** is the most blue-shifted of the series **3.15a – 3.15e**.

Table 3.14 Absorption wavelength maxima of **3.15a – 3.15e**

Compound	Substituent	λ_{max}	Molar Extinction Coefficient (ε) $A/mol^{-1}L^{-1}cm^{-1}$
3.15a	Me	504	8800[a]
3.15b	iPr	499	26600[a]
3.15c	*t*Bu	503	5200[b]
3.15d	Ph	489	7240[a]
3.15e	Et	500	11900[a]

[a]tetrafluroborate salt [b]Trifluoroacetate salt

3.12 Time-dependent DFT calculations of protonated *N, N'*-oxalyl bridged Nindigos 3.15a – 3.15e

Like **3.16a – 3.16e**, the geometries of the *anti* and *syn* conformations of **3.15a – 3.15e** were optimized using B3LYP/Def2TZVPP and the SMD solvation model (solvent = dichloromethane). The success of B3LYP at predicting the absorption wavelength maxima of **3.13**, led to it being used for the atropisomeric analogs (**Table 3.15**) using 6-311++G(d,p) and Def2TZVPP; PBE0 was also used for consistency because it was used previously in this chapter for **3.16a – 3.16e**. In some instances, B3LYP or PBE0 are more appropriate for predicting the absorption wavelength maxima of **3.15a – 3.15e**; the B3LYP functional was more successful at predicting the absorption wavelength maxima

of the *anti* conformation of **3.15a**, **3.15b**, **3.15c**, and the *syn* conformation of **3.15b**, **3.15c**, **3.15d**; the PBE0 functional was more successful at predicting the *syn* conformation of **3.15a**, **3.15e**. Like **3.16a – 3.16e**, the TD-DFT calculations indicate that the absorption wavelength maxima of **3.15a - 3.15e** are the result of several transitions and are not solely from a transition between the HOMO-1 to LUMO.

Table 3.15 Absorption wavelength maxima of **3.15a – 3.15e** determined using TD-DFT

Compound	**Substituent**	**Exp. λ (nm)[a]**	**Method**	**Predicted λ[a] *Anti* (*Syn*)**	**Δλ (nm) *Anti (Syn)***	**Predicted λ[b] *Anti* (*Syn*)**	**Δλ (nm) *Anti* (*Syn*)**
3.15a	Me	504	B3LYP	490 (516)	14 (12)	491 (517)	13 (13)
			PBE0	475 (498)	29 (6)	477 (500)	27 (4)
3.15e	Et	500	B3LYP	491 (532)	9 (32)	492 (533)	8 (33)
			PBE0	474 (514)	26 (14)	475 (515)	25 (15)
3.15b	iPr	499	B3LYP	495 (491)	4 (8)	496 (492)	3 (7)
			PBE0	480 (475)	19 (24)	481 (477)	18 (22)
3.15d	Ph	489	B3LYP	615, 483 (647, 492)	126,6 (158, 3)	614, 483 (646, 493)	125,6 (157,4)
			PBE0	585, 479 (617, 473)	96,10 (128, 16)	585 , 477 (617, 474)	96,12 (128,15)
3.15c	tBu	503	B3LYP	497 (492)	7 (12)	498 (493)	6 (11)
			PBE0	481 (477)	23 (27)	482 (478)	22 (26)

[a]TD DFT computed using 6-311++G(d,p) basis set [b]TD DFT computed using Def2TZVPP basis set

3.13 High-temperature variable temperature ^{1}H NMR studies of protonated *N, N'*-oxalyl bridged Nindigos 3.15a, 3.15b, 3.15d, and 3.15e

The presence of two sets of resonances in the room temperature ^{1}H NMR spectra enabled the evaluation of the rotational energy barriers of **3.15a**, **3.15b**, **3.15d**, and **3.15e** using variable temperature ^{1}H NMR experiments at elevated temperatures. Protonated N, N'-oxalyl bridged *cis*-Nindigos **3.15** are insoluble in arene solvents, therefore the deuterated solvents used for the high-temperature studies used in **Chapter 2** could not be

used; tetrachloroethane-d_2 was used for the variable temperature studies because of its wide temperature range and because of it being able to dissolve **3.15a – 3.15e**.

At room temperature, the ^{1}H NMR spectrum of **3.15a** has a ratio of the *anti* and *syn* conformations of 1.3 to 1 ratio (based on the integrations between the two CH_3 singlets at 2.34 and 2.25 ppm). As the temperature of the sample is raised the methyl resonances coalesce at 340 K and continue to sharpen up to 380 K (**Figure 3.18**). Decomposition to the corresponding indigo monoimine of type **3.21** begins to occur at 370 K as evidenced by the appearance of an additional doublet at 8.69 ppm (**Figure 3.19)** and was inferred based on Dr. Erica Hong's previous synthesis of *N, N'*-oxalyl bridged dimethylphenyl *cis*-indigo monoimine **3.22**.

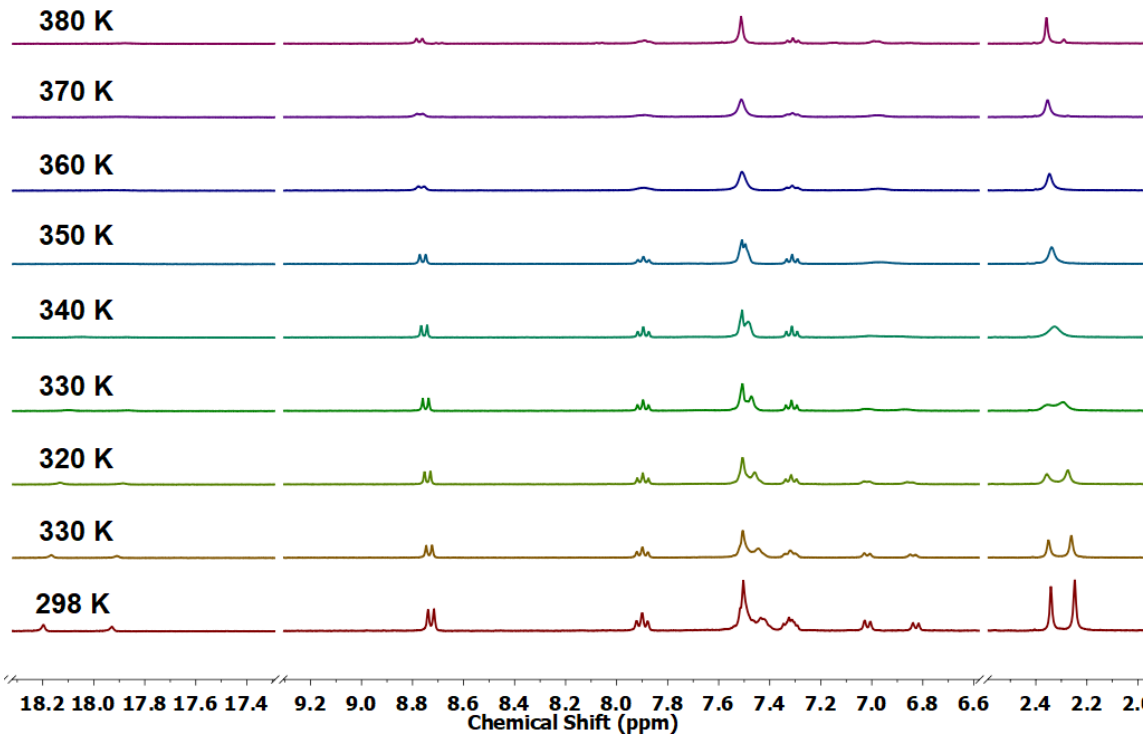


Figure 3.18 High-temperature variable temperature ^{1}H NMR study of **3.15a** (Ar = *o*-methylphenyl)

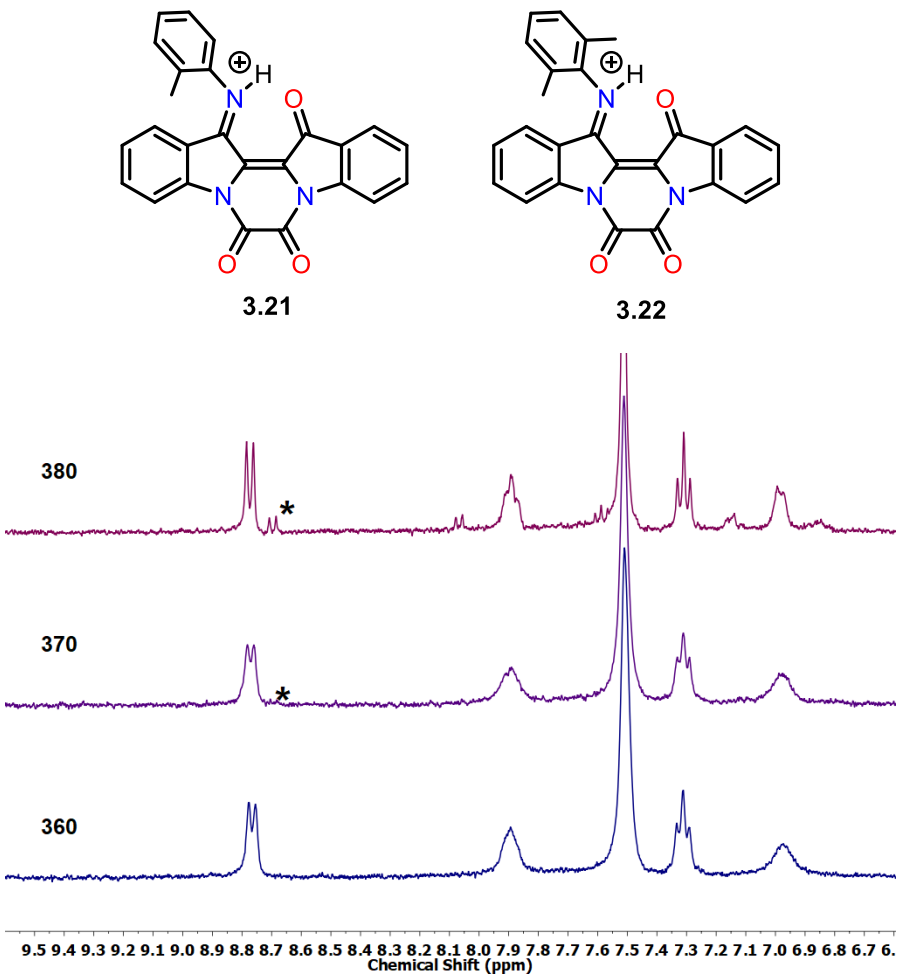


Figure 3.19 Aromatic region of the variable temperature ^{1}H NMR spectra of **3.15a** (Ar = *o*-methylphenyl) in tetrachloroethane-d_2 showing decomposition to **3.21**

As discussed in **Chapter 1**, electron-withdrawing substituents cause an increase in the N-C rotational energy barriers of biaryls; the number of bonds between the electron-withdrawing substituents in biaryls is the same as in oxalyl bridged *cis*-Nindigos (**Figure 3.20**). It is expected that the N-C rotational energy barriers will be affected by the electron-withdrawing nature of the bridge. The rotational energy barrier of **3.15a** was determined to be 16.9 ± 1.3 kcal/mol (at 298 K) and 17.0 kcal/mol (at 340 K) using lineshape analysis, while the *N-C* rotational energy barrier was determined to be 17.1 kcal/mol using the

maximum peak separation and the coalescence temperature of 340 K. The electron-withdrawing nature of the oxalyl bridge resulted in an increase of 1 kcal/mol relative to **2.2a**, while the presence of a proton in the *cis*-diimine pocket increased the barrier by 4 – 5 kcal/mol, relative to **3.16a**, showing that the protonation state of *N, N'*-oxalyl bridged *cis*-Nindigos has a significant influence on the rotational energy barriers of *cis*-Nindigo based atropisomers. The similarity in the rotational energy barriers of **3.15a** to **2.2a** further supports that the *N, N* distance across the pocket has a significant influence on the corresponding atropisomerization barriers, and the hypothesis that compounds of type **3.15** should have similar rotational barriers to **2.2** is true.

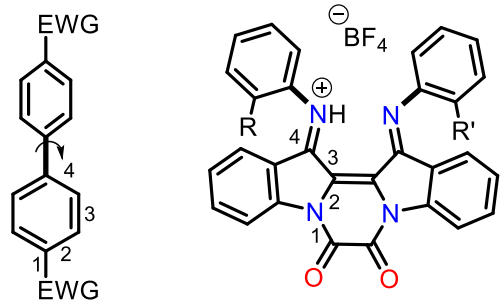


Figure 3.20 Comparison of the number of bonds between the electron-withdrawing substituents in biaryls and N, N'-oxalyl-bridged *cis*-Nindigos

The room temperature ^{1}H NMR spectrum of **3.15b** shows a ratio between the *anti* and *syn* conformations of 2.1 to 1 (based on the integrations of the doublets at 6.66 and 7.01 ppm). As the temperature of the sample is raised the doublets at 6.66 and 7.01 ppm coalesce at approximately 390 K and continue to sharpen up to 400 K (**Figure 3.21**). The rotational energy barrier of **3.15b** determined using lineshape analysis is 19.8 ± 3.3 kcal/mol at 298 K and 18.8 kcal/mol at 390 K; the rotational energy barrier using the

maximum peak separation and the coalescence temperature agreed with the lineshape analysis data and was determined to be 18.7 kcal/mol at 390 K, which is 3.1 kcal/mol greater than the N-C rotational energy barrier of **2.2b** of 16.7 kcal/mol.

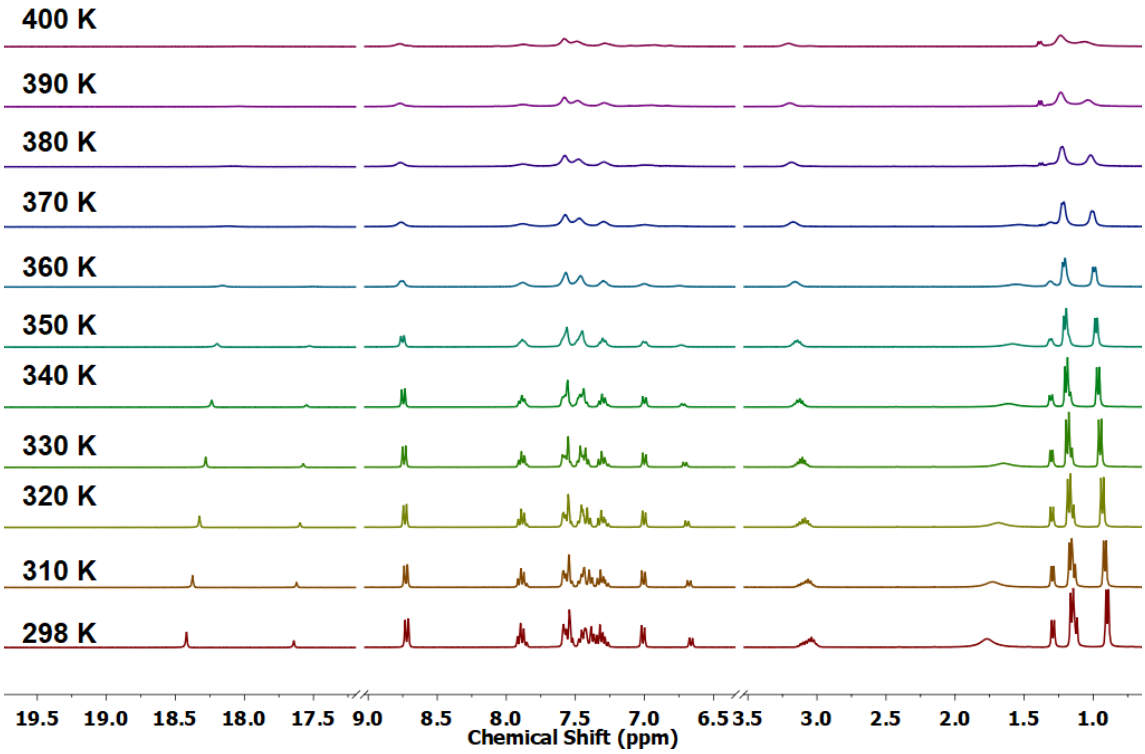


Figure 3.21 High-temperature ^{1}H NMR study of **3.15b** (Ar = *o*-isopropylphenyl)

The degradation of **3.15b** to the corresponding indigo monoimine at elevated temperatures is observed beginning at 380 K (**Figure 3.22**). This degradation should not interfere with the estimation of the coalescence temperature or in the lineshape analysis because of the sharpness of the resonances associated with the indigo monoimine decomposition product relative to the exchanging oxalyl bridged *cis*-Nindigo system.

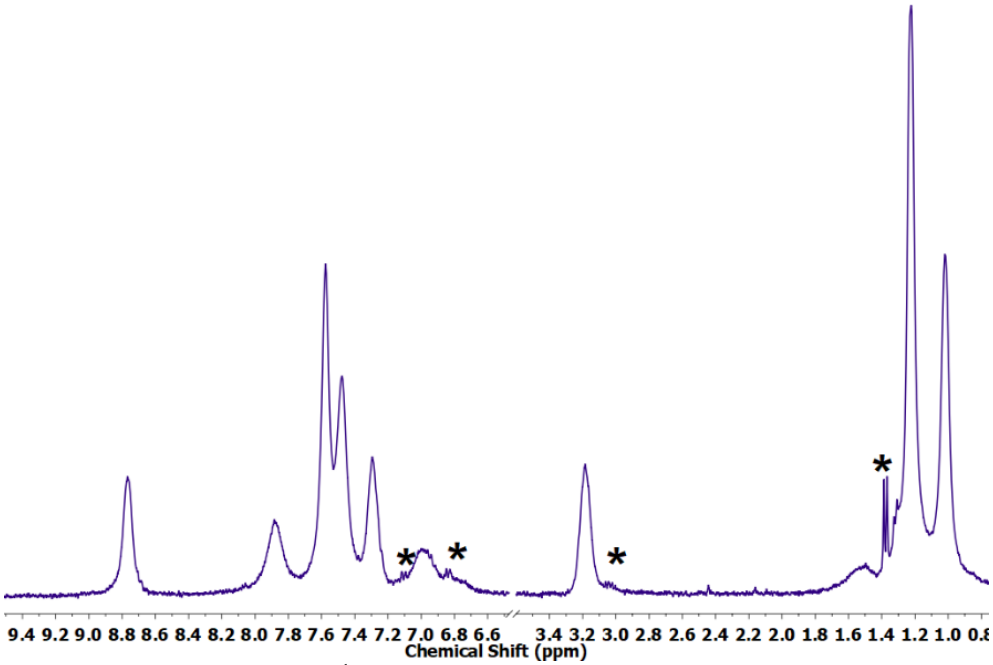


Figure 3.22 ^{1}H NMR spectrum of **3.15b** at 380 K

At room temperature, the ^{1}H NMR spectrum of **3.15d** displays resonances of the *anti* and *syn* conformations in a 17 to 1 ratio (based on the relative integrations of the doublets at 8.73 and 8.57 ppm). The large difference in the abundance between the *anti* and *syn* conformations is consistent with what was determined for **2.2d**. The crowded nature of the aromatic region of **3.15d** resulted in only the doublets at 8.73 and 8.57 ppm being chosen to estimate the *N*-*C* rotational energy barriers. As the temperature of the sample is raised the doublets at 8.73 and 8.57 ppm broaden beginning at 340 K and coalesce at approximately 390 K. Degradation of **3.15d** to its corresponding oxalyl bridged *cis*-indigo monoimine begins at 370 K. The coalescence temperature of 390 K is supported when the triplets centered at 7.85 ppm and the doublets centered at 6.91 ppm are followed during the high-temperature variable temperature ^{1}H NMR experiments. The triplets and doublets coalesce at approximately 370 and 380 K, respectively; they too

suffer from overlap with indigo monoimine degradation products. Using the estimated coalescence temperature and the maximum peak separation of the doublets at 8.65 ppm, the rotational energy barrier of **3.15d** was estimated to be 19.3 kcal/mol at 390 K and agrees well with the rotational energy barrier determined using lineshape analysis which is 19.5 ± 2.7 kcal/mol (at 298 K) and 18.2 kcal/mol (at 390 K).

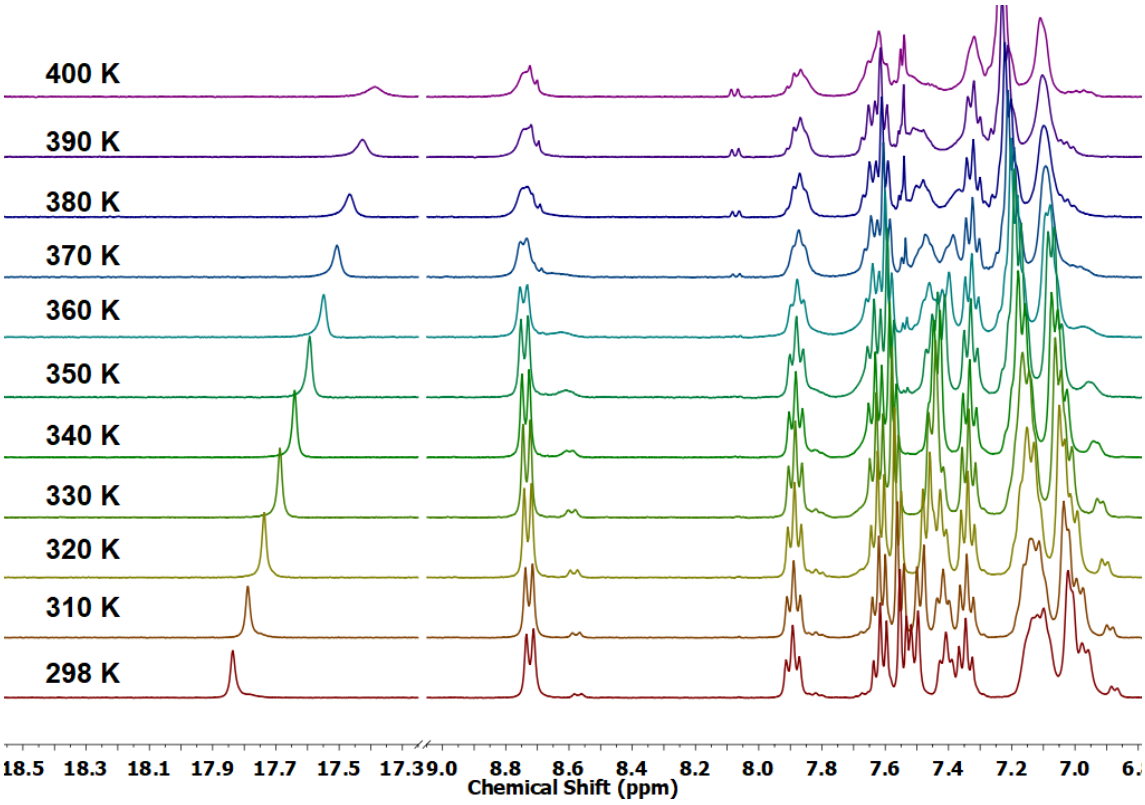


Figure 3.23 Variable temperature ^{1}H NMR study of **3.15d** (Ar = *o*-phenylphenyl)

The ^{1}H NMR spectrum of **3.15e** displays resonances of the *anti* and *syn* conformations in a 1.5 to 1 ratio (based on the integrations of the doublets at 6.89 and 6.76 ppm). As the temperature of the sample is raised the doublets at 6.89 and 6.76 ppm begin to broaden at 320 K; the doublets centered at 6.82 ppm and the CH_3 signal of the ethyl group coalesce at approximately 370 K, while the CH_2 signal of the ethyl group

displays a coalescence temperature of 350 K. The rotational energy barrier of **3.15e** evaluated using the coalescence temperature was determined to be 18.4, 17.7, and 17.3 kcal/mol using the doublets centered around 6.82, the quartets of the CH_2, and the triplets of the CH_3, respectively. The doublets centered around 6.82 ppm were chosen to model using lineshape analysis and the N-C rotational energy barrier was determined to be 18.1 ± 1.6 kcal/mol (at 298 K) and 18.0 kcal/mol at (370 K), which agrees very well with the *N-C* rotational energy barrier determined using the coalescence temperature.

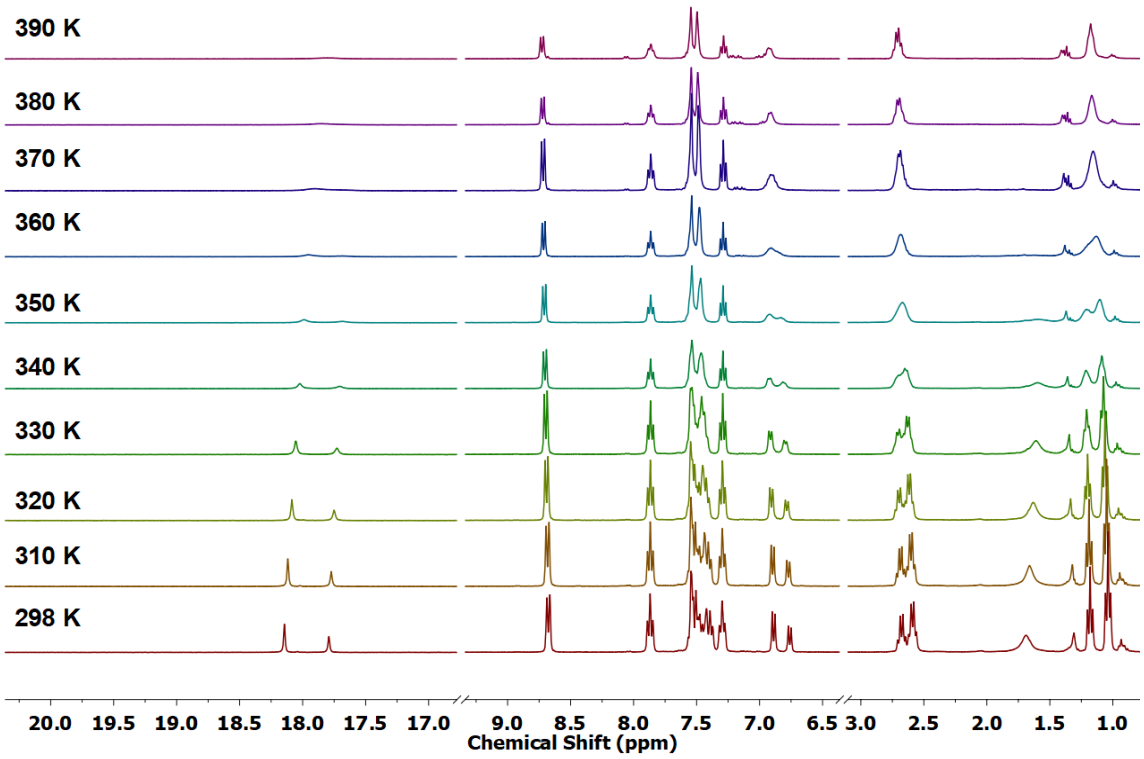


Figure 3.24 Variable temperature ^{1}H NMR study of **3.15e** (Ar = *o*-ethylphenyl)

This study also displayed the influence that the oxalyl bridge has on the rotational energy barrier and all derivatives studied have slightly greater rotational energy barriers than their unbridged congeners and the increase in the rotational energy barrier is

concluded to be the result of the influence of the electron-withdrawing oxalyl tether. This study further shows that the rotational energy barrier is affected by electronic effects.

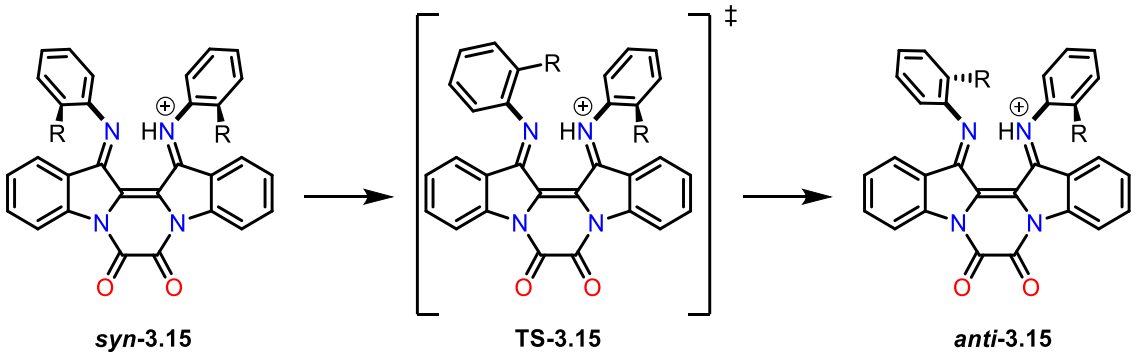
Table 3.16 Experimentally determined rotational energy barriers of **3.15a**, **3.15b**, **3.15d**, and **3.15e**

Compound	Substituent	Rotational Energy Barrier from Lineshape Analysis at 298 K (at T_c) (kcal/mol)	Rotational Energy Barriers from T_c (kcal/mol)
3.15a	Me	16.9 (17.1)	17.1
3.15b	iPr	19.8 (18.8)	18.7
3.15d	Ph	19.5 (18.2)	19.3
3.15e	Et	18.1 (18.0)	18.4

3.14 Computational investigation into the *N-C* rotational energy barriers of protonated *N, N'*-oxalyl-bridged *cis*-Nindigos 3.15a – 3.15e

The barriers for the *N-C* rotation (**Scheme 3.11**) between the *anti* and *syn* conformations of **3.15a – 3.15e** were computed using DFT. The comparable results between the predicted rotational energy barriers using B3LYP/Def2TZVPP and B3LYP/Def2SVP for **3.16a – 3.16e**, led to the rotational energy barriers of **3.15a – 3.15e** to be evaluated using B3LYP/Def2SVP in the gas phase and using the SMD solvation model. The *syn* conformer, in all cases except **3.15a,** is the highest energy conformation. The difference in the energies (**Table 3.16**) between the *anti* and *syn* conformations of **3.15a** – **3.15e** range between 0.06 – 4.9 kcal/mol and result in predicted ratios between the *anti* and *syn* conformations to be between 1.1 – 4057 to 1 (**Table 3.16**) The expected trend of the difference in energy between the *anti* and *syn* conformations increasing as the steric bulk of the substituents increases is observed for **3.15a** – **3.15c.** The smallest difference in energy was for the biphenyl analog and is consistent with what was found

for **3.16d**. The largest difference in energy for the protonated oxalyl bridged *cis*-Nindigos is found in **3.15b** and is not consistent with its neutral congener **3.16b**. It was presumed that the greatest difference in energy for **3.15a – 3.15e** would be for **3.15c** because of the *tert*-butyl substituent.



Scheme 3.11 Interconversion between *syn* and *anti* atropisomers of **3.15**

Table 3.17 Difference in the Gibbs free energy and the predicted ratios between the *anti* and *syn* conformations of **3.15a – 3.15e**

		ΔΔG of *syn* and *anti* conformations (kcal/mol)	**Ratio**
Compound	**Substituent**	**B3LYP/Def2SVP**	
3.15a	Me	0.4	2.0:1
3.15b	iPr	4.9	4057:1
3.15c	tBu	4.1	1033:1
3.15d	Ph	0.06	1.1:1
3.15e	Et	1.1	6.9:1

The transition state geometries for the *N*-*C* rotation of **3.15a** – **3.15e** were all reminiscent of the transition state geometries of **2.2a – 2.2g** and had the aryl ring of the imine substituent nearly coplanar with the indigoid backbone (**Figure 3.25**). The torsional angles of the aryl imine/iminium subunit and the indigoid backbone ranged between 154.8 and 178.2° and 140.7 and 172.2° for the *N*-*C* imine and *N*-*C* iminium rotation of **3.15a – 3.15e**, respectively (**Table 3.15**). The biphenyl derivative, **3.13d**, had the torsional angles

closest to planarity for the imine and iminium *N-C* bond rotations, which were 178.2 and 172.2°, respectively. Other than for **3.13d**, the trend of the transition states that have smaller substituents having torsional angles closer to planarity is true for both the imine and iminium rotations, which is in direct contrast to what was observed for **2.2a – 2.2g**.

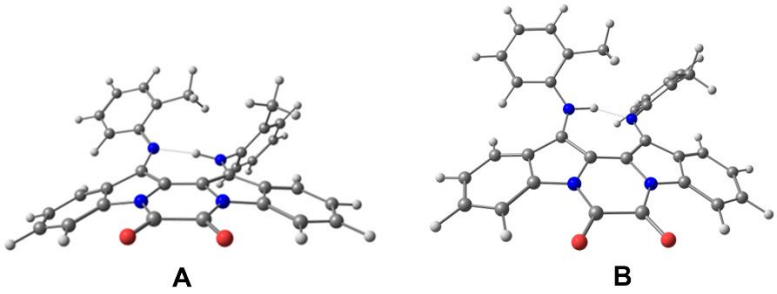


Figure 3.25 Transition state geometries (B3LYP/Def2SVP) of the imine (**A**, **TS**) and iminium (**B**, **TS'**) *N-C* of **3.15a** (Ar = *o*-methylphenyl)

Table 3.18 Pertinent torsional angles of the transition state geometries of **3.15a – 3.15e**

Compound	Substituent	θ for TS (°)[a]	θ for TS' (°)[b]
3.15a	Me	161.9	152.3
3.15b	iPr	157.7	148.6
3.15c	tBu	154.8	140.7
3.15d	Ph	178.2	172.2
3.15e	Et	161.5	151.8

[a] Torsional angle between the indigoid backbone and aryl imine substituent for transition state for imine N-C rotation; [b] torsional angle between the indigoid backbone and aryl imine substituent for transition state for iminium N-C rotation [a]

The calculated energy barriers for **3.15a** – **3.15e** are between 10.2 and 21.4 kcal/mol for the imine *N-C* rotation and 11.4 to 23.8 kcal/mol for the iminium *N-C* rotation, respectively (**Table 3.16**). The trend of the *N-C* iminium bond rotation being larger than the *N-C* imine rotation is consistent with what was found for **2.2a – 2.2g.**

Therefore, moving forward the evaluation of the rotational energy barrier for the *HN-C* rotation will be excluded in any benchmarking studies presented later in this chapter.

Table 3.19 N-C rotational energy barriers of protonated *N, N'*-oxalyl bridged *cis*-Nindigo **3.15a – 3.15e** for imine/iminium N-C bond rotation

Compound	Substituent	Calculated TS $\Delta G^{\ddagger}$ (kcal/mol)	Calculated TS' $\Delta G^{\ddagger}$ (kcal/mol)	$\Delta G^{\ddagger}$ using T_c (kcal/mol)	$\Delta G^{\ddagger}$ using lineshape analysis at 298 K (kcal/mol)	$\Delta G^{\ddagger}$ using lineshape analysis at T_c (kcal/mol
3.15a	Me	15.7	17.7	17.1	16.9	17.1
3.15b	iPr	10.2	11.4	18.7	19.8	18.8
3.15c	tBu	20.3	23.0	-	-	-
3.15d	Ph	21.4	23.8	19.3	19.5	18.2
3.15e	Et	17.4	19.2	18.4	18.1	19.0

3.15 Combined benchmark study of protonated *N, N'*-oxalyl bridged *cis*-Nindigos 3.15a – 3.15e

Previously in this chapter, a combined benchmark study was undertaken to study the rotational energy barriers of the neutral oxalyl bridged Nindigos **3.16a – 3.16e**. Given that the SMD solvation model outperformed the PCM and CPCM solvation models, the latter two will not be studied in any benchmarking of **3.15a – 3.15e**. The benchmark study will be undertaken via first optimizing the geometries of the *anti*, *syn*, and TS (imine *N-C* rotation) structures using B3LYP/Def2SVP and the SMD solvation model before doing the thermochemical frequency analysis using the different functionals. As opposed to studying the rotational barriers in 1,1,2,2-tetrachloroethane computationally, the solvent 1,1,2-trichloroethane was chosen because of precedent in the literature in using this solvent as a model for 1,1,2,2-tetrachloroethane and the lack of parameterization of 1,1,2,2-tetrachloroethane in SMD.

From the benchmark study (**Table 3.20**), a number of the functionals performed better at modeling the rotational energy barrier of **3.15a – 3.15e**, than B3LYP. There is no functional that outperforms the other functionals to an astonishing degree. The functionals, wB97XD, M11, M06-2X, and M15, were the best at predicting the *N-C* rotational barriers of **3.15a**, **3.15b**, **3.15d**, and **3.15e**, respectively. Like **3.16b**, no functional was great at modeling the experimental *N-C* rotational barrier of **3.15b** and the predicted barriers were off by 2.6 to 5.6 kcal/mol. The best performing functional at predicting all the N-C rotational barriers of **3.15a**, **3.15b**, **3.15d**, and **3.15e**, is wB97XD, which has an average percent difference between the predicted and experimental *N-C* rotational energy barriers of 10.0 percent. Functionals B3LYP, CAM-B3LYP, M11, M06, M06-2X, M15, LC-ωHPBE, and TPSSh, have average percent differences between the experimental and predicted *N-C* rotational energy barriers (at 298 K) of 12.6, 11.4, 10.4, 13.5, 10.7, 12.8, 12.0, and 16.1 kcal/mol. The comparable accuracies of wB97XD, M11, and M06-2X mean that any of the functionals are more suitable than B3LYP at predicting the experimentally determined *N-C* rotational energy barriers of **3.15a**, **3.15b**, **3.15d**, and **3.15e**.

Table 3.20 Calculated N-C rotational energy barriers of **3.15a – 3.15e**

Compound	B3LYP	CAM-B3LYP	ωB97XD	M11	M15	M06	M06-2X	LC-ωHPBE	TPSSh
3.15a	14.6	16.5	17.0	16.4	14.4	13.7	15.3	17.1	16.3
3.15b	15.7	15.2	16.0	17.2	15.6	14.5	14.7	16.5	14.2
3.15c	20.4	18.8	21.1	19.7	18.4	18.7	20.1	21.4	18.1
3.15d	21.3	21.3	21.2	22.7	21.3	21.0	19.9	22.6	24.4
3.15e	19.3	19.9	20.0	19.7	17.8	17.9	19.0	20.6	19.3

3.16 Conclusions

This chapter presented the extension of the atropisomerism of *cis*-Nindigos into the realm of analogs that cannot undergo *trans*- to *cis*- protoisomerization. Using mono *ortho*-substituted precursors presented in **Chapter 2**, a series of mono *ortho*-substituted neutral (**3.16a – 3.16e**) and protonated (**3.15a – 3.15e**) oxalyl bridged *cis*-Nindigo derivatives were synthesized and comprehensively characterized using UV-Visible spectroscopy, NMR spectroscopy (room and variable temperature), and computational chemistry (DFT and TD-DFT).

Like **2.1** and **2.2**, **3.15** and **3.16**, the absorption wavelength maxima show limited sensitivity to the substituents attached to the aryl imine subunit. The electronic spectroscopy of the neutral and protonated symmetrical (**3.13** and **3.14**) and atropisomeric *N, N'*-oxalyl bridged *cis*-Nindigo derivatives (**3.15** and **3.16**), along with the ethano (**3.3**) and oxalyl bridged *cis*-indigos (**3.6**) were studied using TD-DFT and showed good agreement between experimental and theoretical results. The absorption wavelength maxima of **3.3** and **3.6** were determined to be from HOMO to LUMO transitions, which contrasts with what was computed for their oxalyl bridged *cis*-Nindigo counterparts **3.13 – 3.16**, whose absorption wavelength maxima are primarily the result of HOMO-1 to LUMO transitions, among others. This is the first case of any density functional theory studies on oxalyl bridged *cis*-indigoids of any kind and the strong agreement between theoretical and experimental absorption wavelength maxima means that B3LYP and PBE0 are promising density functionals for the design of new types of oxalyl bridged *cis*-Nindigos.

The *N*-*C* rotational barriers of the neutral oxalyl bridged *cis*-Nindigo derivatives are generally lower (2.5 – 4.9 kcal/mol) than their protonated congeners and are primarily the result of the size of the diimine pocket size. The protonated oxalyl bridged *cis*-Nindigo analogs, which have comparable diimine pocket sizes to their unbridged protonated congeners, and in all cases have slightly larger (1.0 – 2.7 kcal/mol) rotational energy barriers than their unbridged congeners. The slight increase in the *N*-*C* rotational barriers of the oxalyl bridged *cis*-Nindigos relative to their unbridged congeners is attributed to the electron-withdrawing nature of the oxalyl bridge.

The density functional theory calculations presented in this chapter for the neutral oxalyl bridged *cis*-Nindigo derivatives showed that calculations performed modeling the *N*-*C* rotational energy barriers of **3.16a – 3.16e** using Def2SVP have comparable accuracy to those computed with the larger basis set Def2TZVPP (difference of computed vs experimental values of 0.1 – 4.8 kcal/mol vs 0.5 – 5.3 kcal/mol). It was determined that the incorporation of solvation models improves the accuracy of DFT at modeling the experimental rotational energy barriers of **3.15a – 3.15e** and **3.16a – 3.16e**; in the case of **3.16a – 3.16e**, the SMD solvation model (differences in energy of theo vs exp rotational energy barriers of 0.4 – 4.5 kcal/mol) outperformed the PCM (0.4 – 5.1 kcal/mol) and CPCM (0.2 – 5.0 kcal/mol) solvation models. Due to the success of the SMD solvation model at modeling **3.16a – 3.16e**, it was the sole solvation model used in modeling **3.15a – 3.15e.** Benchmark studies were performed on **3.15a – 3.15e** and **3.16a – 3.16e** and it was determined that the best functional for replicating experimentally determined *N*-*C* rotational barriers of **3.15a – 3.15e was** M06-2X with the SMD solvation, while for **3.16a – 3.16e** functionals ωB97XD and MN15, were determined to be the highest performing

for modeling the N-C rotational energy barriers in the gas phase and using SMD solvation, respectively. The density functional theory calculations presented in this chapter provide a means by which one can confidently predict the *N*-*C* rotational energy barriers of mono *ortho*-substituted *N. N'*-oxalyl bridged *cis*-Nindigos.

3.17.1 General experimental information

All *trans*-Nindigo derivatives (**2.1a – 2.1g**) used in this chapter were synthesized following the protocols disclosed in Chapter 2. All syntheses were conducted under nitrogen in 100 mL round-bottomed flasks. Toluene was dried by first passing it through a column of activated alumina and storing it over 4 Å molecular sieves for a minimum of 24 hours before use. Triethylamine was dried by distilling it from calcium hydride before use. Dichloromethane was dried by storing over 4 Å molecular sieves for a minimum of 24 hours before use. Oxalyl chloride, trifluoroacetic acid, and tetrafluoroboric acid diethyletherate were purchased from Sigma Aldrich and used as received.

3.17.2 Computational chemistry

All density functional theory calculations were performed on either the Cedar or Graham clusters of Compute Canada in an identical fashion to **Chapter 2**. All ground state and transition state geometries were optimized using Gaussian 16[164] using DFT with the B3LYP functional[165] and the Def2SVP or Def2TZVPP basis sets) in the gas phase and using either the PCM, CPCM, or SMD solvation model[166] in either dichloromethane or 1,1,2-trichloroethane. Time-dependent density functional theory calculations were completed using Gaussian 16 using B3LYP, PBE0, CAM-B3LYP, or wB97XD and either

6-311++G(d,p) or Def2TZVPP with the SMD solvation model (solvent = dichloromethane).

3.17.3 Experimental procedures

N, N′-(1,2-dioxoethano)indigo 3,3′-bis(2-methylphenylimine) HBF_4 (3.15a)

In a 50 mL round bottomed flask, tetrafluoroboric acid diethyl etherate (0.10 mL, 0.73 mmol) was added to a solution of **3.16a** (0.049 g, 0.099 mmol) in toluene (10 mL) and the resulting red mixture was stirred for 10 minutes. Diethyl ether (10 mL) was added to the reaction mixture and the red precipitate was collected by vacuum filtration and was triturated with diethyl ether (10 mL) and washed with hexanes (3x 3 mL). The red solid was recrystallized from dichloromethane/hexanes and collected by vacuum filtration. Residual volatiles were removed in vacuo, yielding **3.15a** as a bright red solid (0.037g, 64%). mp > 260; HRMS (ESI+): calculated for $C_{32}H_{23}N_4O_2^+$:495.18155 [M+] found: 495.18130; UV-Vis (λ,max, CH_2Cl_2): 504 nm (8800 mol^{-1},M^{-1}); IR (ATR, cm^{-1}): 1712, 1656, 1602,1463, 1386, 1328, 1305 1226, 1203, 1160, 1111, 1055, 920, 876, 776, 752, 689, 482; ^{1}H NMR (500 MHz, CD_3CN) δ 18.12 (s, 1H, major), 17.88 (s, 1H, minor), 8.64 (d, 2H *J* = 8.5 Hz, major), 8.63 (d, 2H, *J* = 8.5 Hz, minor), 7.93 (t, *J* = 7.9 Hz, 2H), 7.57 – 7.41 (m, 8H), 7.39 – 7.32 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H, major), 6.97 (d, *J* = 8.1 Hz, 2H, minor), 2.26 (s, 6H, minor), 2.20 (s, 6H, major).; ^{13}C NMR (126 MHz, CD_3CN) δ 160.3 (minor), 160.0 (major), 152.3, 146.6 (minor), 146.3 (major), 140.3 (minor), 140.0 , 139.5, 133.1, 131.8, 130.8 (major), 130.6 (minor), 129.9, 129.1 (major), 128.9 (minor), 128.6 (major), 128.5 (minor), 128.4 (minor) 128.3 (major), 123.1 (minor), 122.9 (major), 119.0, 17.8; ^{19}F NMR ($CDCl_3$, 283 MHz): -153.7

N, N′-(1,2-dioxoethano)indigo 3,3′-bis(2-isopropylphenylimine) HBF_4 (3.15b)

Tetrafluoroboric acid diethyletherate (0.1 mL, 0.7 mmol) was added to a solution of 3.16b (0.050 g, 0.0908 mmol) in toluene (10 mL). The resulting red mixture was filtered using vacuum filtration and residual volatiles were removed in vacuo yielding **3.15b** as a bright red solid (0.047g, 57%); HRMS (ESI+): calculated for $C_{36}H_{31}N_3O_2^+$: 551.24415 [M+] found; 551.2435; UV-Vis (λ_{max}, CH_2Cl_2): 499 nm (26600 mol^{-1},M^{-1}); IR (KBr cm^{-1}): 3425, 2966, 2935, 2871, 1719, 1638, 1603, 1482, 1463, 1385, 1304, 1225, 1084, 1055, 753; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 18.35 (s, 1H, major), 17.60 (s, 1H, (minor)), 8.64 (dd *J* = 8.4, 2H), 7.81 (ddd, *J* = 8.5, 7.5, 1.2 Hz, 2H), 7.58 – 7.47 (m, 6H), 7.44 – 7.36 (m, 2H), 7.36 – 7.32 (m, 3H), 7.24 (ddd, *J* = 8.3, 7.5, 1.0 Hz, 2H), 7.20 (d, 2H), 6.97 (d, *J* = 8.0, Hz, 2H, major), 6.71 – 6.63 (d, *J* = 7.6 Hz, 2H, minor), 3.11 (sept, *J* = 7.2 Hz, 2H, minor), 3.04 (sept, *J* = 6.7 Hz, 2H), 1.24 (d, *J* = 6.8 Hz, 2H, minor), 1.09 (d, *J* = 6.8 Hz, 6H, major), 1.07 (d, *J* = 6.8 Hz, 6H, minor), 0.86 (d, *J* = 6.8 Hz, 6H, major); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 159.8, 151.4 (major), 151.3 (minor), 146.0, 141.9, 139.3, 138.4_4 (minor), 138.4_2 (major), 138.3, 130.5 (major), 130.4 (minor), 128.7, 128.4 (major), 128.5 (minor), 128.1_2 (minor), 128.0_6 (major), 128.0_4 (minor), 127.9_8 (major), 127.6, 123.1 (minor), 122.7 (major), 120.0 (minor), 119.6 (major), 118.9 (major), 118.8 (minor), 29.8 (minor), 29.5 (major), 24.6 (minor), 23.9)major), 23.2 (minor), 22.8 (major). ^{19}F NMR ($CDCl_3$, 283 MHz): -154.0

N, N′-(1,2-dioxoethano)indigo 3,3′-bis(2-tertbutylphenylimine) HTFA (3.15c)

Trifluoroacetic acid (0.1 mL, 1 mmol) was added to a solution of **3.16c** (0.011 g, 0.020 mmol) in $CDCl_3$. The resulting deep red solution was layered with 10 mL of hexanes and the red precipitate was collected by vacuum filtration. Residual volatiles were removed in

vacuo, yielding **3.15c** as a bright red solid (0.009 g, 66 %). FT-IR (NaCl, thin film): 3067, 2962, 2923, 2852, 1777, 1716, 1633, 1603, 2584, 1482, 1462, 1381, 1207, 1160, 1095, 1014, 790, 752, 704 cm^{-1}; HRMS (ESI+): calculated for $C_{38}H_{35}N_4O_2^+$: 579.27545 [M+] found 579.27554; UV-Vis (λ,max, CH_2Cl_2): 503 nm (5200 $mol^{-1}M^{-1}$); ^1H NMR (500 MHz, CD_3CN) δ 17.78 (s, 1H), 8.61 (d, *J* = 8.3, 2H), 7.89 (ddd, *J* = 8.5, 7.5, 1.2 Hz, 2H), 7.70 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.52 (td, *J* = 7.8, 1.5 Hz, 2H), 7.42 (td, *J* = 7.6, 1.4 Hz, 2H), 7.28 (ddd, *J* = 8.3, 7.5, 1.0 Hz, 2H), 7.23 (dd, *J* = 7.9, 1.5 Hz, 2H), 6.62 (dt, *J* = 8.0 Hz, 2H), 1.23 (s, 18H). ^{13}C NMR (126 MHz, CD_3CN) δ 160.9, 152.1, 146.5, 143.6, 140.7, 139.6, 130.7, 129.6, 129.5, 129.0, 128.5, 125.5, 120.4, 119.1, 36.2, 31.2; ^{19}F NMR ($CDCl_3$, 283 MHz): -76.1

***N, N′*-(1,2-dioxoethano)indigo 3,3′-bis(2-phenylphenylimine) HBF_4 (3.15d)**

In a 100 mL round bottomed flask, tetrafluoroboric acid diethyletherate (0.1 mL, 0.7 mmol) was added to a solution of **3.16d** (0.056 g, 0.090 mmol) in toluene (20 mL). The resulting red mixture was stirred for 5 minutes before **3.15d** was collected by vacuum filtration and washed with diethyl ether (3x 10 mL). Residual volatiles were removed in vacuo, yielding 3.15d as a dark red solid (0.061 g, 96 %); mp = 288 – 290 C; HRMS (ESI+): calculated for $C_{42}H_{27}N_4O_2^+$: 619.21285 [M+] found 619.21291; UV-Vis (λ,max, CH_2Cl_2): 489 nm (7240 $mol^{-1}M^{-1}$); FT-IR(ATR): 3060, 1708, 1602, 1462, 1372, 1339, 1304, 1246, 1214, 1090, 1049, 740, 701, 588, 480 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 17.77 (s, 1H), 17.70 (s, 1H), 8.59 (d, *J* = 8.4 Hz, 2H), 8.45 (d, *J* = 8.2 Hz, 2H), 7.90 (t, *J* = 7.9 Hz, 2H), 7.84 (t, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.56 – 7.48 (m, 5H), 7.46 – 7.38 (m, 3H), 7.38 – 7.32 (m, 2H), 7.17 – 7.11 (m, 2H), 7.04 (d, *J* = 5.3 Hz, 9H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (126

MHz, CD_3CN) δ 158.3, 152.0, 146.1, 139.3, 137.6, 137.2, 137.1, 131.8, 131.2, 129.9, 129.8, 129.4, 129.3, 128.7, 128.4, 128.3, 124.4, 120.1, 118.9 ^{19}F NMR ($CDCl_3$, 283 MHz): -153.7

***N, N′*-(1,2-dioxoethano)indigo 3,3′-bis(2-ethylphenylimine) HBF_4 (3.15e)**

In a 50 mL round bottomed flask, tetrafluoroboric acid (0.1 mL, 0.73 mmol) was added to a solution of **3.16e** (0.024 g, mmol) in toluene (10 mL). The resulting red mixture was stirred for 5 minutes and **3.15e** was collected by vacuum filtration. The collected solids were washed with diethylether (3x 5mL) and residual volatiles were removed in vacuo yielding 3.15e as a bright red solid (0.024 g, 85%); mp >260; HRMS (ESI+): calculated for $C_{34}H_{27}N_4O_2^+$: 523.21285 [M+] found 523.21272; UV-Vis (λ,max, CH_2Cl_2): 500 nm (11900 mol^{-1},M^{-1}); FT-IR(ATR): 3012, 2971, 2942, 2875, 1716, 1635, 1602, 1591, 1481, 1462, 1386, 1276, 1260, 1054, 1037, 964, 751 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 18.09 (s, 1H), 17.72 (s, 1H), 8.62 (d, *J* = 8.3 Hz, 3H), 7.91 (ddd, *J* = 8.6, 7.4, 1.3 Hz, 3H), 7.60 – 7.49 (m, 6H), 7.50 – 7.44 (m, 2H), 7.44 – 7.39 (m, 3H), 7.36 – 7.29 (m, 4H), 6.99 – 6.94 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 2.63 (d, *J* = 7.6 Hz, 2H), 2.55 (dq, *J* = 9.7, 7.3 Hz, 4H), 1.06 (t, *J* = 7.5 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 160.5, 152.2, 146.4, 139.6_2 (minor), 139.5_8(major), 137.6 (major), 137.3 (minor), 131.7 (major), 131.4 (minor), 131.0 (major), 130.9 (minor), 129.2 (major), 129.1 (minor), 129.1 (minor), 129.0 (major), 128.8 (major), 128.7 (minor), 128.4 (major), 128.32 (minor), 123.2 (minor), 123.1 (major), 120.3 (minor), 120.1 (major), 119.1, 25.3 (major), 25.0 (minor), 15.2 (major), 14.9 (minor); ^{19}F NMR ($CDCl_3$, 283 MHz): -153.8

***N, N′*-(1,2-dioxoethano)indigo 3,3′-bis(2-methylphenylimine) (3.16a)**

In a 100 mL round bottomed flask, oxalyl chloride (0.20 mL, 2.3 mmol) was added to a solution of **2.1a** (0.114 g, mmol) in dry toluene (10 mL) resulting in a dark green solution. The dark green solution was refluxed under nitrogen for 15 minutes and turned to a red/yellow/brown mixture. The mixture was cooled to room temperature, hexanes (10 mL) was added, and the mixture was stored at -10 degrees Celsius for 30 minutes. The mixture was subsequently filtered using vacuum filtration and the collected dark red solid was washed with hexanes (10 mL). The crude solid was taken up in dichloromethane (50 mL) and triethylamine (0.40 mL, 2.9 mmol) was added and the reaction mixture was stirred for five minutes. Volatiles were removed in vacuo, and the residue was taken up in toluene (30 mL) and triethylammonium chloride salts were separated by vacuum filtration. Toluene was removed in vacuo yielding and the residue was recrystallized from dichloromethane/hexanes (1/10); residual volatiles were removed in vacuo, yielding **3.16a** as a dark red solid (0.069 g, 54%); mp: >260 C ; HRMS (ESI+): calculated for $C_{32}H_{23}N_4O_2^+$: 495.18155 [M+H] found 495.18132; UV-Vis (CH_2Cl_2, $M^{-1}cm^{-1}$): 415 nm (14500); FT-IR(ATR): 3006, 1703, 1678, 1615, 1588, 1458, 1377, 1326, 1299, 1276, 1261, 1200, 1107, 1038, 926, 751, 473 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 8.72 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.10 (q, *J* = 7.7, 7.0 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 3H), 6.77 (s, 2H), 2.12 (s, 6H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 152.8, 152.4, 150.1, 143.1, 133.3, 131.3, 127.2, 126.2, 126.2, 124.6, 124.2, 122.7, 118.4, 116.1, 17.9

***N,N′*-(1,2-dioxoethano)indigo 3,3′-bis(2-isopropylphenylimine) (3.16b)**

In a 100 mL round bottomed flask, oxalyl chloride (0.30 mL, 3.5 mmol) was added to a solution of **2.1b** (0.229 g, 0.4615 mmol) in dry toluene (10 mL) resulting in a dark green solution. The dark green solution was refluxed for 30 minutes and turned to a red/yellow/brown mixture. The mixture was cooled to room temperature, hexanes (50 mL) was added, and the mixture was stored at -10 degrees Celsius for 12 hours. The mixture was subsequently filtered using vacuum filtration and the collected dark red solid was washed with hexanes (10 mL). The crude solid was taken up in dichloromethane (50 mL) and washed sequentially with an 0.1 M aqueous solution of triethylamine (3x 5 mL) and distilled water (3x 5 mL) producing a yellow brown solution and subsequently dried with magnesium sulfate. The dichloromethane was removed in vacuo yielding **3.15b** as a dark solid (0.131 g, 52 %); HRMS (ESI+): calculated for $C_{36}H_{31}N_4O_2^+$: 551.24415 [M+H] found 551.24402; IR (KBr cm^{-1}); 3061, 2958, 2865, 1707, 1590, 1460, 1382, 1325, 1300, 1206, 934, 755; UV-Vis (CH_2Cl_2, $M^{-1}cm^{-1}$): 417 nm (14400); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.76 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.49 (m, 1H), 7.40 (t, *J* = 4.6 Hz, 2H), 7.24 – 7.17 (m, 4H), 7.10 (t, *J* = 7.7 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.78 – 6.73 (m, 2H), 3.17 (s, 2H), 1.06 (s, 13H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 152.6, 149.4, 143.4, 137.4, 133.3, 129.5, 128.7, 127.2, 127.1, 126.7, 125.1, 124.3, 122.7, 118.6, 116.4, 29.2, 23.0

***N,N′*-(1,2-dioxoethano)indigo 3,3′-bis(2-tertbutylphenylimine) (3.16c)**

In a 100 mL round bottomed flask oxalyl chloride (0.24 mL, 2.8 mmol) was added to a solution of **2.1c** (0.202 g, 0.3840 mmol) in dry toluene (15 mL). The resulting green solution was refluxed for 45 minutes, cooled to room temperature and hexanes (50 mL) was added to the solution before being stored at -10 degrees Celsius for 18 hours. The

mixture was filtered using vacuum filtration and the dark red solid was washed with hexanes (50 mL). The red solid was dissolved in dry dichloromethane (10 mL) and dry triethylamine (0.2 mL, 1.4 mmol) was added before the dichloromethane was evaporated. The resulting solid was taken up in toluene (50 mL) and filtered before the toluene was removed in vacuo; the crude mixture was next recrystalized using dichloromethane/hexanes (10 mL/90mL) and the solid was collected using vacuum filtration. The solid was washed with hexanes (10 mL) and residual volatiles were removed in vacuo, yielding **3.16c** as a dark green solid (0.149 g, 67 %); HRMS (ESI+): calculated for $C_{38}H_{35}N_4O_2^+$: 579.2755 [M+H] found 579.2757; FT-IR(ATR, cm^{-1}): 3071, 2953, 2901, 2861, 1705, 2663, 1590, 1480, 1459, 1434, 1383, 1325, 1300, 1199, 1157, 1093,934, 773, 754, 654, 480; UV-Vis (CH_2Cl_2, $M^{-1}cm^{-1}$): 422 nm (12300); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.75 (d, *J* = 8.6 Hz, 2H), 7.54 (ddd, *J* = 8.4, 7.5, 1.3 Hz, 2H), 7.42 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.09 (m, 6H), 6.80 (d, *J* = 7.8 Hz, 2H), 6.65 (dd, *J* = 7.4, 1.9 Hz, 2H), 1.21 (s, 18H); ^{13}C NMR (76 MHz, CD_2Cl_2) δ 151.7, 150.0, 143.4, 138.4, 133.1, 127.1, 127.0, 126.7, 124.5, 122.8, 118. 5, 118.1, 35.5, 29.8

***N,N′*-(1,2-dioxoethano)indigo 3,3′-bis(2-phenylphenylimine) (3.16d)**

In a 100 mL round bottomed flask, oxalyl chloride (0.50 mL, 6 mmol) was added to a solution of **2.1d** (0.326 g, 0.5778 mmol) in dry toluene (20 mL). The resulting green solution was refluxed for 15 minutes, cooled to room temperature, and hexanes (50 mL) was added. The mixture was next vacuum filtered, and the collected solid was washed with hexanes (3x 10 mL). Without further purification, crude **3.15d** was dissolved in dichloromethane (50 mL) and dry triethylamine (1 mL) was added and the reaction mixture was stirred for 15 minutes before all volatiles were removed in vacuo. The residue

was taken up in toluene (100 mL) and the triethylammonium chloride was separated by gravity filtration. The toluene filtrate was rotovaped to dryness and crude **3.16d** was recrystallized from dichloromethane/hexanes and collected by vacuum filtration; residual volatiles were removed in vacuo yielding **3.16d** as a dark solid (0.153 g, 43 %); mp: 300 – 302 C; HRMS (ESI+): calculated for $C_{42}H_{27}N_4O_2^+$: 619.21285 [M+H] found 619.2128; IR(ATR, cm^{-1}): 3067, 3007, 1799, 2633, 2601, 2590, 1463, 1385, 1305, 1260, 1213, 1049, 764, 751, 698, 482; UV-Vis (CH_2Cl_2, $M^{-1}cm^{-1}$): 424 nm (14400); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.59 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 7.6 Hz, 2H), 7.49 (q, J = 7.9, 7.3 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 7.06 (t, J = 7.7 Hz, 1H), 6.97 (s, 0H), 6.90 (d, J = 7.8 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 152.9, 149.3, 139.5, 133.4, 131.3, 130.7, 129.9, 129.3, 128.4, 127.4, 127.3, 126.4, 125.3, 122.7, 118.5, 117.0

***N,N′*-(1,2-dioxoethano)indigo 3,3′-bis(2-ethylphenylimine) (3.16e)**

In a 100 mL round bottomed flask under nitrogen, oxalyl chloride (0.2 mL, 2.4 mmol) was added to a solution of **2.1e** (0.776 g, 1.65 mmol) in toluene (10 mL). The resulting green solution was reduced for 15 minutes yielding a dark red mixture. Hexanes (15 mL) was added to the reaction mixture, and it was stored in the freezer for 20 minutes. Crude **3.15e** was collected by vacuum filtration and washed with hexanes (3x 5 mL). Crude 3.15e was taken up in dichloromethane and triethylamine (1 mL, mmol) was added and the reaction mixture was stirred for 5 minutes. Volatiles were removed in vacuo and the residue was extracted with toluene (3x 20 mL). Toluene and residual volatiles were removed in vacuo yielding **3.16e** as a dark solid (0.0432 g, 50 %); mp: 239 – 241 C; HRMS (ESI+): calculated for $C_{34}H_{27}N_4O_2^+$ [M+H]: 523.2185 found 523.21277; IR(ATR,

cm^{-1}): 2966, 2921.5, 1694, 1652, 1600, 1460, 1382, 1326, 1276, 1197, 1113, 926, 751, 673, 479; UV-Vis (CH_2Cl_2, $M^{-1}cm^{-1}$): 414 nm (13800) ^{1}H NMR (360 MHz, CD_2Cl_2) δ 8.76 (d, *J* = 8.2 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.1 Hz, 2H), 7.23 (d, *J* = 7.0 Hz, 3H), 7.17 (t, *J* = 6.8 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 3H), 6.83 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 7.5 Hz, 2H), 2.56 (q, *J* = 7.1 Hz, 5H), 1.05 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 153.0, 152.6, 149.9, 143.3, 133.4, 132.7, 129.8, 127.3, 127.3, 126.6, 125.0, 124.3, 122.7, 118.6, 116.4, 25.3, 14.8

Preparation of oxalyl diimidazole

Prepared following a preparation reported by Murata and coworkers[196]

A solution of oxalyl chloride (2.0 mL, 24 mmol) in benzene (30 mL) was added dropwise to a solution of TMS-imidazole (7.3 mL, 50 mmol) in benzene (80 mL) under a nitrogen atmosphere in a flame-dried Schlenk flask (250 mL) over a one-hour period. The resulting orange mixture was stirred overnight, and the resulting yellow solid was collected by vacuum filtration. Residual volatiles were removed in vacuo, yielding oxalyl diimidazole as a yellow solid (3.8587 g).

Chapter 4: Atropisomeric cis-Nindigo palladium (II) acetylacetonate complexes

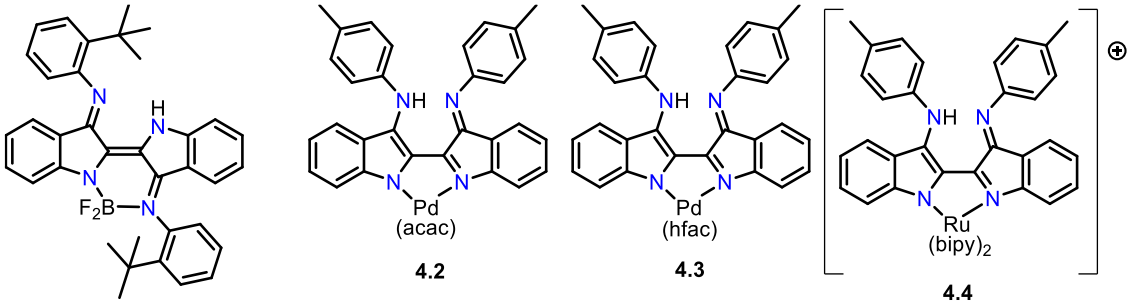
4.0 Preface

Preliminary work on some of the atropisomeric *cis*-Nindigo complexes in this chapter was performed by an undergraduate student, Ethan Sauvé, under the mentorship of Dr. Dillon T. Hofsommer (Ph.D., 2019). Ethan prepared palladium (II) hexafluroacetylacetonate complexes using mono *ortho*-substituted *trans*-Nindigos **2.1** as the ligands and showed that *cis*-Nindigo palladium complexes can adopt multiple conformations using variable temperature ^{1}H NMR. The initial syntheses of the palladium (II) acetylacetonate complexes reported in this chapter were done in collaboration with Dr. Hofsommer.

4.1 Introduction

Even though indigo has been known for millennia, its coordination chemistry has not been a primary focus of study. In the 1920s complexes of indigo featuring zinc[216,217] and copper[218] were reported by Kuhn and Kunz, albeit the complexes had limited characterization. Complexes of palladium,[219,220] platinum,[220] gold,.[221] and rhenium[222] were reported by groups led by Beck and Lu between 1989 and 2008. Since 2008 there has been a resurgence in the coordination chemistry of indigoids, alongside the "rediscovery" of indigo diimines (Nindigo) by Hicks and co-workers.[122] Since the resurgence of indigoid coordination chemistry in 2008, a variety of indigo complexes have been reported which have ruthenium,[223,224] chromium,[225] gadolinium,[226] dysprosium,[226]

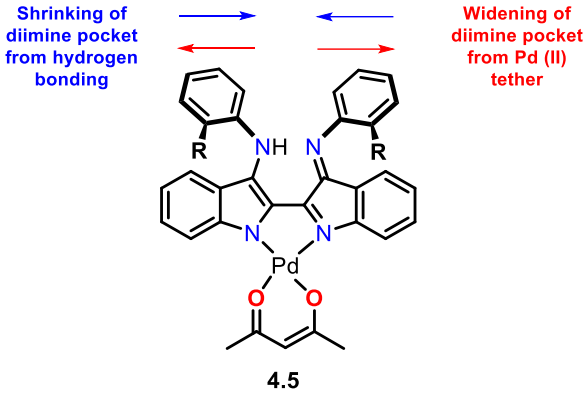
titanium, [227] and iridium.[228] The initial investigations into the coordination chemistry of Nindigo by the Hicks group focused on the study of *trans*- mono (**1.57**)[128] and bis-boron (**1.58**) complexes,[127] *trans*- bimetallic palladium (**1.59**),[122] *trans*-hetero-bimetallic palladium/boron complexes (**1.62**),[127] and monometallic palladium complexes (**1.63**).[129] More recently, Dr. Dillon Hofsommer disclosed the synthesis of *cis*-palladium (II) acetylacetonate (**4.2**), *cis*-palladium (II) hexafluoroacetylacetonate (**4.3**) and *cis*-ruthenium (II) bipyridine (bipy) Nindigo complexes (**4.4**) featuring less bulky 4-methylphenyl aryl imine subunits.[229]



4.1 **4.2** **4.3** **4.4**

In **Chapter 3**, the introduction of a tether between the indole nitrogens of Nindigo was shown to prevent the *cis*- to *trans*- isomerization upon deprotonation, and thus, in principle, prevents the loss of chiral information imparted from the initial *trans*- to *cis*-isomerization. The *cis*-Nindigo metal complexes are another type of tethered *cis*-Nindigo which have distinctive structural and electronic properties. With regard to structure, the tether between the two indole nitrogens is one-atom in length for *cis*-Nindigo metal complexes in comparison to the two-atom bridge present in *N, N'*-oxalyl bridged *cis*-Nindigos **3.15/3.16**. A one-atom tether may result in greater structural distortions by pulling the diimine pocket apart more than a two-atom tether. The widening of the diimine pocket may be countered to some degree by the internal hydrogen bonding between the

imine nitrogen and the amine *NH* present in the diimine pocket (**4.5**, **Figure 4.1**). The other difference between the *N, N'*-oxalyl bridged *cis*-Nindigos and the *cis*-Nindigo metal complexes is the charges of the Nindigo ligand and the tether; the Nindigo core in **3.15/3.16** is formally neutral, while in the *cis*-Nindigo palladium and ruthenium complexes it has a formal charge of -1. The -1 charge of the *cis*-Nindigo ligand in **4.5** may have a significant impact on the stabilization of the transition state resulting in lower N-C rotational barriers. The charge of the tether in **3.15/3.16** does not contribute any additional charge to the final structure, while in the metal complexes the charge of the tether is formally +1 and +2 for the palladium (II) and ruthenium (II) complexes **4.2** and **4.3**, respectively. The differences between the metal-based tethers and their organic counterparts make the mononuclear *cis*-Nindigo palladium complexes (**4.5**) an interesting system for studying their *N-C* atropisomerism.

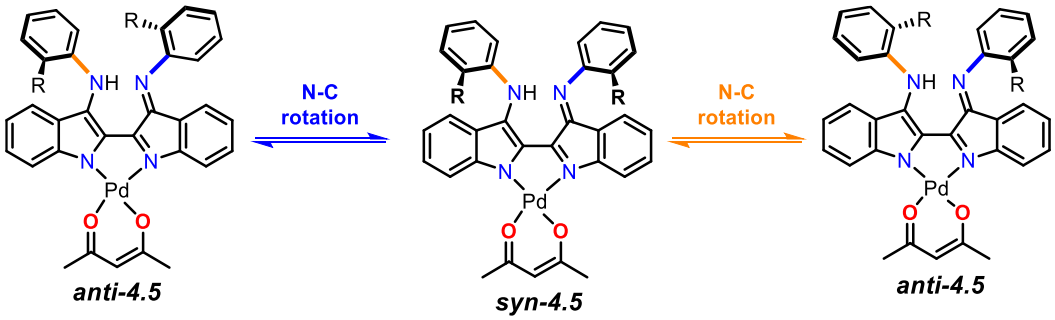


4.5

Figure 4.1 Effects of palladium (II) tether and internal hydrogen bonding on diimine pocket size

4.2 Atropisomerism of *cis*-Nindigo palladium (II) acetylacetonate complexes

In the context of the atropisomerism of *cis*-Nindigo, *anti* and *syn* conformations are possible for the *cis*-Nindigo palladium complexes of type **4.5** (**Scheme 4.1**). In comparing the X-ray crystal structures of the *N, N'*-oxalyl bridged *cis*-Nindigos and *cis*-Nindigo palladium (II) acetylacetonate complex **4.2**, the diimine pocket (*N, N*) distance of the *cis*-Nindigo palladium complex, falls between that of the neutral (**3.14)** and protonated (**3.13**) *N, N'*-oxalyl bridged *cis*-Nindigo derivatives (**Figure 4.2**). It should be stated that in this comparison the aryl imine subunits of **4.2**, 4-methylphenyl, are less sterically encumbered than the 2,6-dimethylphenyl groups in **3.13** and **3.14**. The different *N*-Ar substituent sizes could influence the diimine pocket size. Having said that, this observation supports the idea of the "tug-of-war" between the pulling of the *cis*-diimine pocket apart by the tether and the tightening of the pocket induced by the internal hydrogen bonding. It is hypothesized that these types of complexes will have *N-C* rotational energy barriers between those of the neutral (**3.16**) and protonated (**3.15**) *N, N'*-oxalyl bridged *cis*-Nindigo derivatives.



Scheme 4.1 Atropisomeric conformations of *cis*-Nindigo palladium (II) acetylacetonate complexes **4.5**

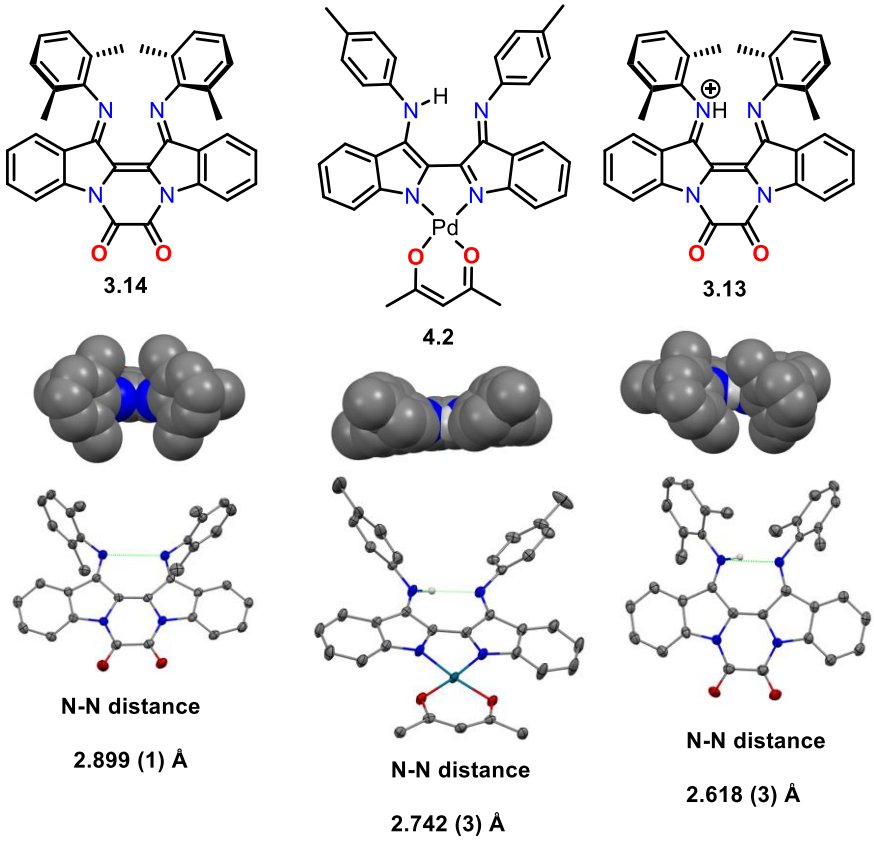
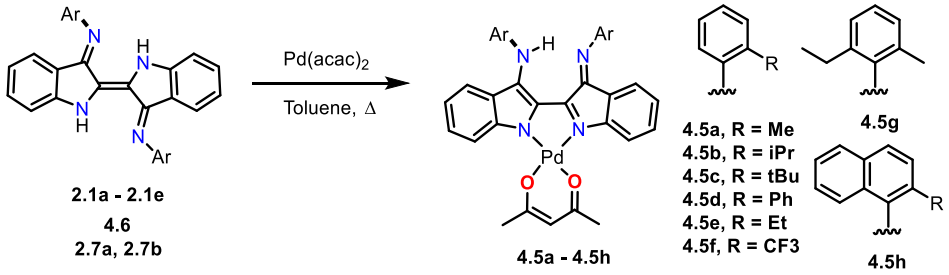


Figure 4.2 Comparison of the *N, N* distances between neutral (**3.14**) and protonated (**3.13**) *N, N'*-oxalyl bridged *cis*-Nindigos and ***c**is*-Nindigo palladium (II) acetylacetonate complex **4.2**

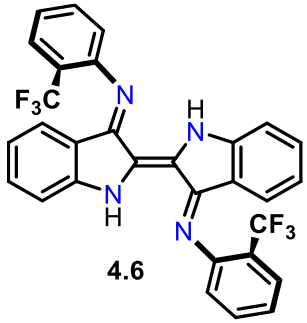
This chapter describes the synthesis and characterization of *cis*-palladium (II) acetylacetonate complexes (**4.5**) based on mono *ortho*-substituted *cis*-Nindigo ligands. The principal objective is to explore the impact of a different tether on the atropisomerism of *cis*-Nindigos.

4.3 Synthesis of *cis*-Nindigo palladium (II) acetylacetonate complexes 4.5a – 4.5h

The palladium (II) acetylacetonate precursor was prepared following literature procedures.[230] All *cis*-palladium (II) acetylacetonate Nindigo complexes **4.5a – 4.5h** were prepared in yields ranging from 40 – 61% by mixing the corresponding *trans*-Nindigos (**2.1a – 2.1e**, **2.7a**, **2.7b**, and **4.6**) and palladium (II) acetylacetonate in boiling toluene (**Scheme 4.2**).[229] The compounds were crystallized directly from the reaction mixture by the addition of acetonitrile yielding dark microcrystalline powders. The *ortho* trifluoromethyl Nindigo complex (**4.5f**) was synthesized from Nindigo **4.6**, which was prepared following standard Nindigo synthetic protocols[122,129] using 2-trifluoromethylaniline as the aniline precursor. The synthesis of the less bulky 2-methylphenyl substituted palladium acetylacetonate complex using Nindigo **2.1a** yielded an intractable mixture of compounds.



Scheme 4.2 Synthesis of atropisomeric *cis*-palladium (II) acetylacetonate complexes **4.5b – 4.5h**



4.4 Room temperature ^{1}H NMR spectra of *cis*-Nindigo palladium (II) acetylacetonate complexes 4.5b – 4.5h

The integration ratios of the aromatic aryl imine resonances and the acetylacetonate resonances confirm the formation of mononuclear (as opposed to binuclear) complexes nature of the complexes. Mononuclear *trans*- complexes are not observed; these complexes would have spectra comprised of a doubling of the aromatic resonances, alongside a signal for the indole *NH*. The *NH* resonances of these complexes, of type **4.5** (Ar = 4-methylphenyl), are found at ~12 ppm, broadly consistent with the chemical shifts of the NH resonances for **4.2** and **4.3**, which are 12.5 and 12.3 ppm, respectively.[229] The *NH* resonances of the *cis*-Nindigo palladium complexes are more

upfield than their protonated *cis*-Nindigo counterparts, **2.2** and **3.15**, which are found between 15 – 17 ppm and 17 – 18 ppm, respectively.

The ^{1}H NMR spectra of the palladium complexes (**4.5b**, **4.6c**, **4.5e**, and **4.5f**) all have one set of aromatic and acetylacetonate ligand (CH_3 and CH) resonances, which could be interpreted as being consistent with the idea that the *anti* and *syn* conformations are in rapid equilibrium. Alternatively, it may be that the acetylacetone unit is sufficiently removed from the diimine pocket that the resonances for the *anti* and *syn* conformations are effectively identical, analogous to that observed for the *trans*-Nindigos **2.1.** The room temperature ^{1}H NMR spectra (**Figure 4.4**) of the less bulky Nindigo palladium (II) acetylacetonate complexes (**4.5b**, **4.5e** and **4.5f**) display only one set of resonances at room temperature – analogous to what was observed in the atropisomeric neutral *N, N'*-oxalyl bridged *cis*-Nindigos in **Chapter 3**. The isopropyl derivative **4.5b** appears to be at its coalescence temperature, or slightly above it, as evidenced by the lack of fine structure in the isopropyl resonances; the less bulky ethyl analog (**4.5e**) has sharp resonances in its ^{1}H NMR spectrum and is above its coalescence temperature. The biphenyl analog (**4.5d**) has some broad resonances at approximately 6.7 ppm, which indicates that the mixture is approaching its coalescence temperature. I trifluoromethyl analog (**4.5f**) appears to be one set of resonances and is above its coalescence temperature. The 2-*tert*-butyl substituted complex **4.5c** also only displays one set of resonances, however, this is presumed to be due to only one conformation being present, as was the case for the other 2-*tert*-butyl substituted analogs (**2.2c**, **3.15c**, and **3.16c**). The disubstituted analogs **4.5g** and **4.5h** both displayed the presence of two conformations in their room temperature ^{1}H NMR spectra. The observed behaviour of **4.5g** and **4.5h** is consistent with the results

presented in **Chapter 2**, which show that the introduction of a substituent at the six position of the aryl imine subunit precluded *N-C* bond rotation.

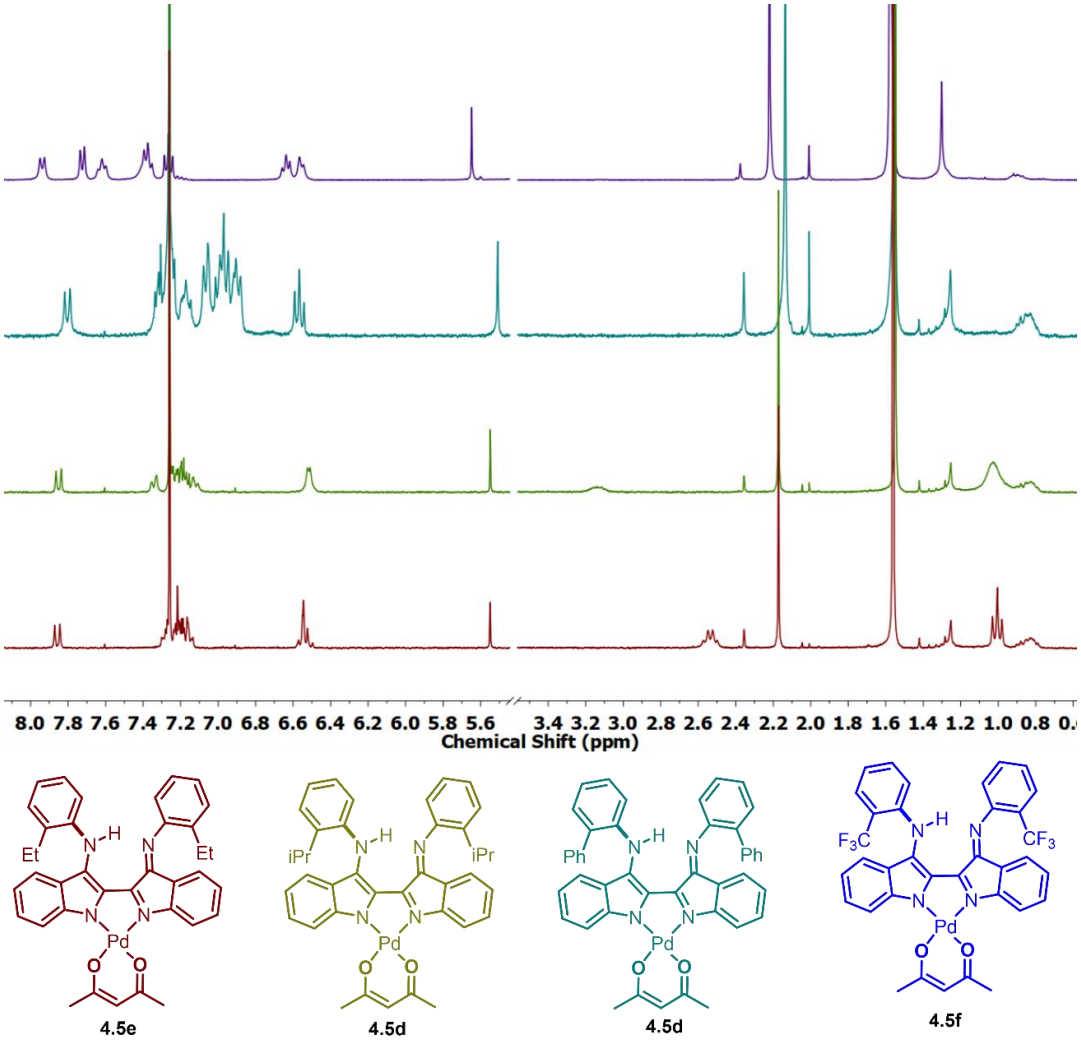


Figure 4.3 Room temperature ^{1}H NMR spectra of **4.5e** (red), **4.5b** (Green), **4.5d** (teal), and **4.5f** (Blue)

Our hypothesis that the *N-C* rotational energy barriers for the palladium complexes would be between that of the neutral (**3.16**) and protonated (**3.15**) *N, N'*-oxalyl bridged *cis*-Nindigos is supported when the room temperature ^{1}H NMR spectra of **4.5b**, **3.16b**, and **3.15b** are compared (**Figure 4.3**). The isopropyl CH and CH_3 resonances at

3.1 and 1.0 ppm of **4.5b** are significantly broader than the corresponding resonances for **3.16b**, which has some fine structure in its ^{1}H NMR spectrum because the *anti* and *syn* conformations are in rapid equilibrium. The increased broadness at room temperature suggests that the *N-C* rotational energy barrier of **4.5b** is greater than **3.16b**. The *N-C* rotational energy barriers **4.5b** are lower than for the protonated *N, N'*-oxalyl bridged *cis*-Nindigo **3.15b**, which has the presence of sharp resonances for both the *anti* and *syn* conformations at room temperature in its room temperature ^{1}H NMR spectrum. This further supports the hypothesis that the size of the diimine pocket has an influence on the *N-C* rotational energy barriers of *cis*-Nindigo.

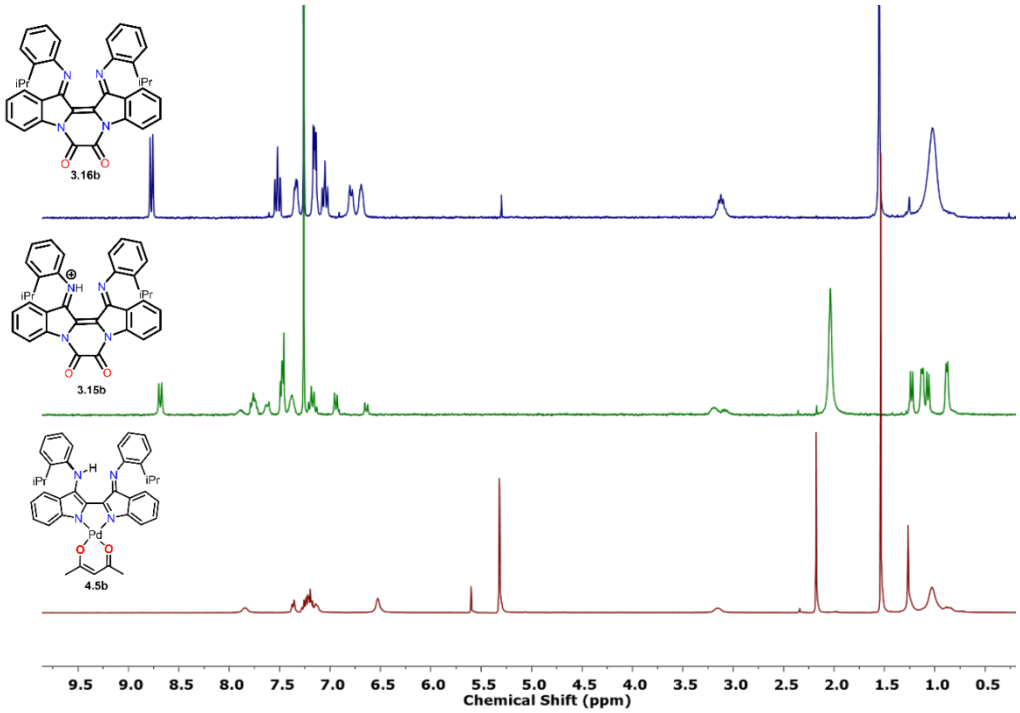


Figure 4.4 Comparison of the room temperature ^{1}H NMR spectra of neutral (**3.16b**, **blue trace**), protonated (**3.15b**, **green trace**) *N, N'*-oxalyl *cis*-Nindigos, and palladium (II) acetylacetonate *cis*-Nindigo complex (**4.5b**, **red trace**)

4.5 Variable temperature ^{1}H NMR studies of palladium (II) acetylacetonate *cis*-Nindigo complexes 4.5b - 4.5h

The *N*-*C* rotational energy barriers of **4.5b – 4.5f** were determined using variable temperature ^{1}H NMR experiments in dichloromethane-d_2, chloroform-*d*, or toluene-d_8. The *NH* region of the spectrum in all cases is diagnostic for identifying the presence of two conformations of these complexes. The *N*-*C* rotational energy barriers were evaluated using both the coalescence temperature and lineshape analysis as was done previously in **Chapter 2** and **Chapter 3**, either using the NH resonances or another suitable resonance.

Upon cooling a sample of **4.5b** (Ar = *o*-isopropylphenyl) to 270 K, the presence of two conformations is confirmed by the doubling of the resonances in the *NH* region at 11.9 and 12.5 ppm of the ^{1}H NMR spectrum. At lower temperatures, a doubling of other resonances is seen throughout the spectrum. The NH resonances continue to sharpen down to 183 K (**Figure 4.5**). Based on the relative integration between the two *NH* resonances at 183 K, the ratio between the *anti* and *syn* conformations of **4.5b** is determined to be 1.9 to 1. The signals for each conformation coalesce at 280 K. The *N*-*C* rotational energy barrier of **4.5b** was evaluated using lineshape analysis and using the coalescence temperature and maximum peak separation and were determined to be 13.9 and 12.9 kcal/mol, respectively. The *N*-*C* rotational energy barrier of 13.9 ± 0.3 kcal/mol (at 280 K) for **4.5b** is slightly greater than the *N*-*C* rotational energy barrier of **3.16b** ($\Delta G_{273K}^{\ddagger}$ = 13.9 kcal/mol) and significantly lower (6.1 kcal/mol) than the *N*-*C* rotational barrier of **3.15b** ($\Delta G_{390K}^{\ddagger}$ = 19.8 kcal/mol).

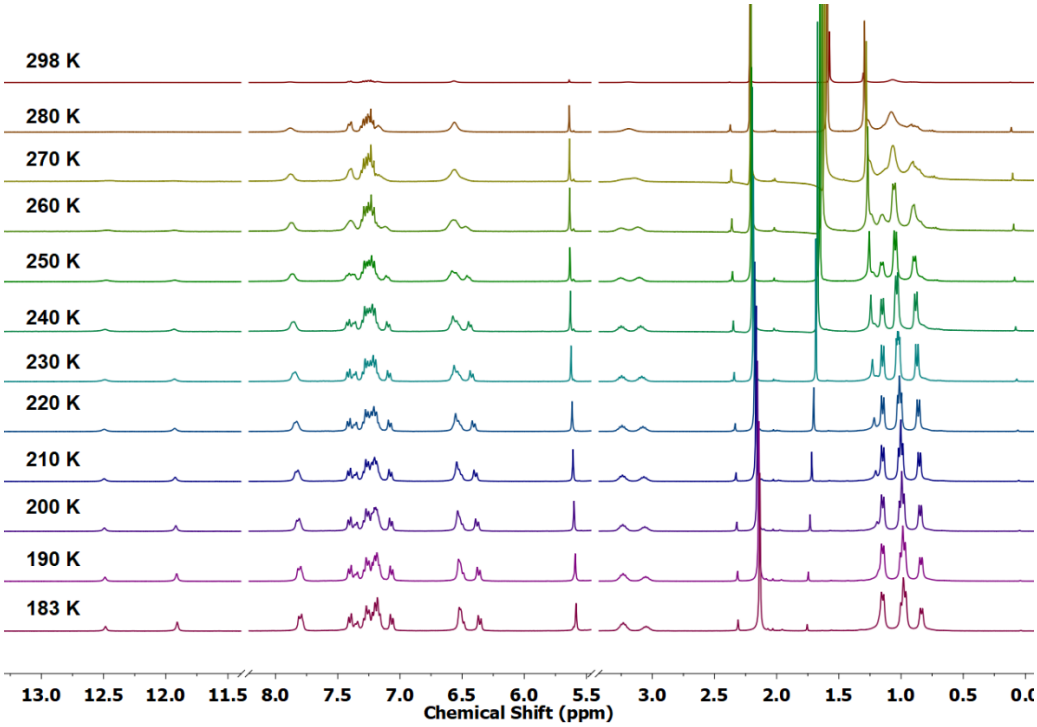


Figure 4.5 Variable temperature ^{1}H NMR study of **4.5b** (Ar = *o*-isopropylphenyl)

Upon cooling **4.5c** (Ar = *o*-tertbutylpropylphenyl) to 193 K (**Figure 4.6**), the presence of two conformations (*anti* and *syn*) is not observed. This behavior is consistent with *cis*-Nindigos **2.2c**, **3.15c**, and **3.16b**. From the low temperature ^{1}H NMR experiments, the hypothesis that only one conformation is present is confirmed. As such, no evaluation of the *N*-*C* rotational energy barriers has been performed for **4.5c**. The expected trend from the computational results disclosed in **Chapter 2** and **Chapter 3**, is that the *N*-*C* rotational energy barrier for **4.4c** is greater than its other mono-*ortho*-substituted congeners.

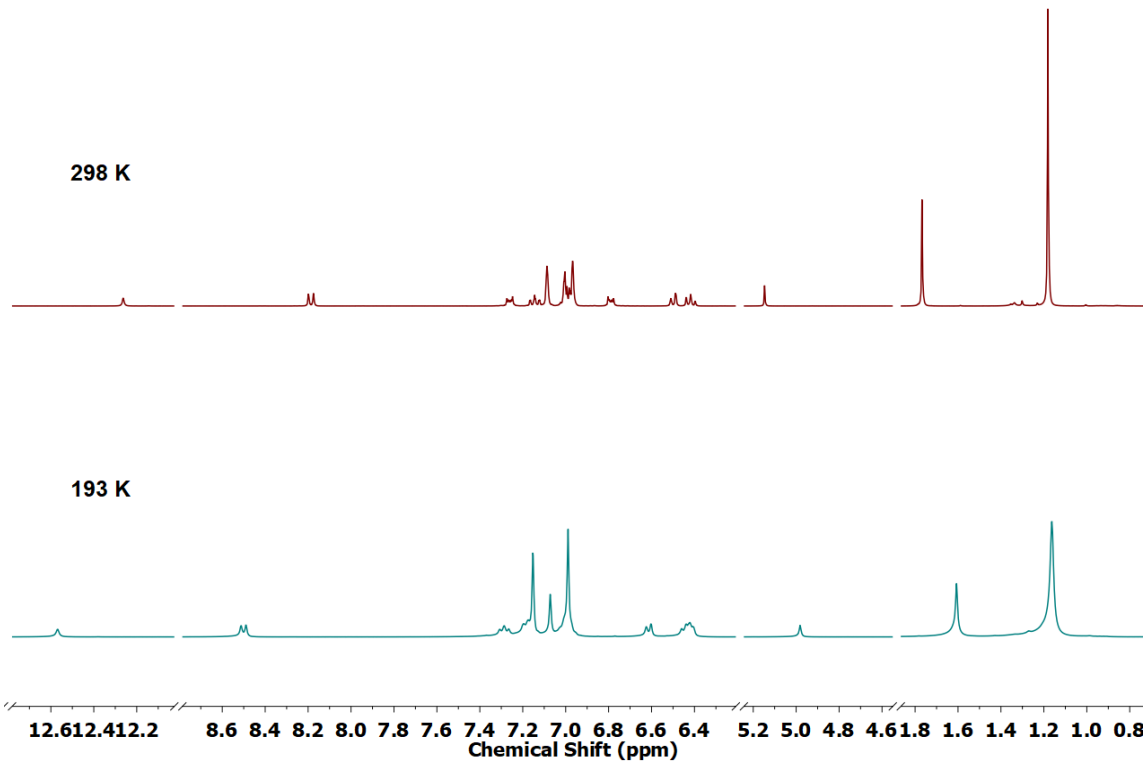


Figure 4.6 Room temperature ^{1}H NMR of **4.5c** (Ar = *o*-tertbutylphenyl) (top, **red trace**); ^{1}H NMR spectrum of **4.5c** at 193 K (bottom, **blue trace**)

The presence of broad resonances (the doublet at 6.8 ppm) for the minor conformation of **4.5d** (Ar = *o*-phenylphenyl) that is approaching coalescence with the major conformer in the room temperature ^{1}H NMR spectrum of **4.5d** led to the use of chloroform-d being chosen as the solvent for variable temperature ^{1}H NMR study (**Figure 4.7**) because of its higher boiling point relative to dichloromethane-d_2. Upon cooling the sample to 290 K, both conformations are present as evidenced by the sharpening of the minor broad resonance at 6.75 ppm and the appearance of a second *NH* resonance at ~11.5 ppm (**Figure 4.7**). The ^{1}H NMR signals continued to sharpen down to 250 K, where the

ratio between the *anti* and *syn* conformations is determined to be 7.2 to 1. Upon heating the sample, the *NH* singlets at 11.5 and 12 ppm coalesce at approximately 315 K (this is inferred based on the complete disappearance of the resonance at 12 ppm). This is also supported by the doublet for the minor conformation at ~6.75 ppm merging with the doublet at 6.9 ppm at 330 K as well.. The *N*-*C* rotational energy barrier of **4.5d** evaluated using the lineshape analysis of the two doublets centered at 7.8 ppm was determined to be 15.8 ± 1.4 kcal/mol (at 298 K). The *N*-*C* rotational energy barriers determined using the coalescence temperature agreed with the values determined using lineshape analysis and were 16.0 kcal/mol at 315 K.

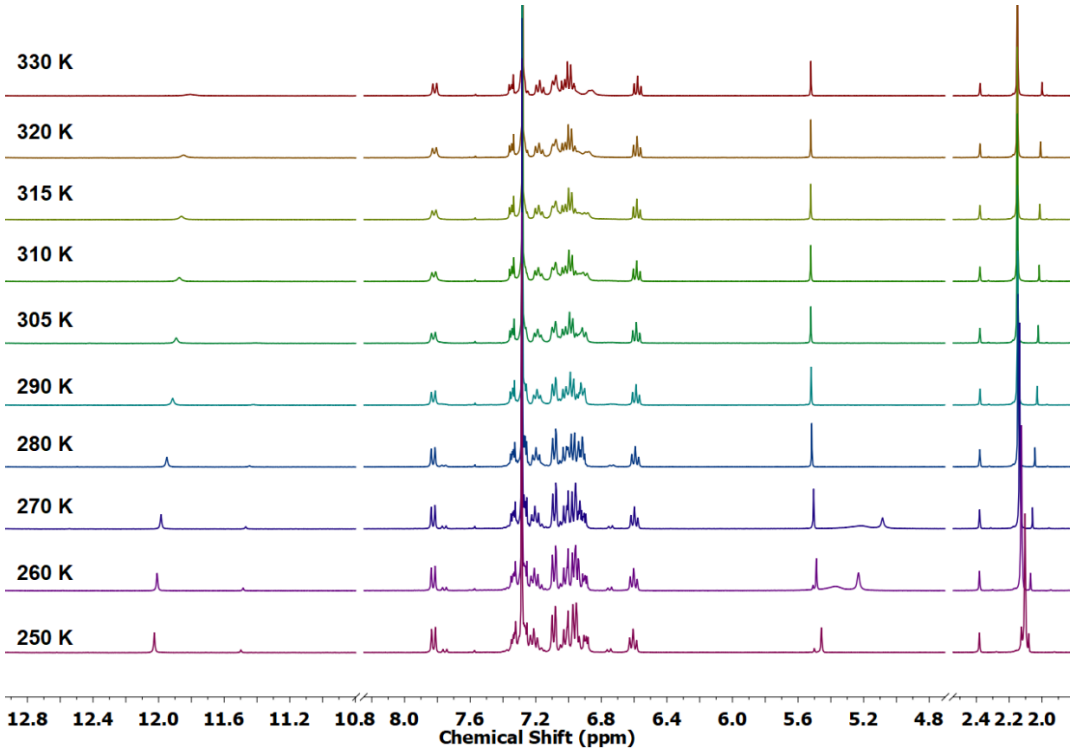


Figure 4.7 Variable temperature ^{1}H NMR study of **4.5d** (Ar = *o*-phenylphenyl)

As the temperature of the sample of **4.5e** (Ar = *o*-ethylphenyl) was lowered, ^{1}H NMR resonances corresponding to the two conformations become visible at 260 K, as evidenced by the two broad NH resonances at 11.9 and 12.3 ppm and the splitting of the ethyl CH_3 triplet into two distinct triplets at 0.9 and 1.0 ppm (**Figure 4.8**). The coalescence temperature for the interconversion of the *anti* and *syn* conformations is estimated to be 265 K. As the temperature of the sample was further lowered the *NH* and CH_3 resonances continue to sharpen and are well resolved below 240 K, while the other resonances remain broad. The ratio between the *anti* and *syn* conformations of **4.5e** is determined to be 1.3 to 1 based on the integration of the *NH* resonances and the two triplets at 190 K. The *N-C* rotational energy barrier between the *anti* and *syn* conformations of **4.5e** was determined using lineshape analysis to be 13.7 ± 0.2 kcal/mol (at 298 K) by modeling the *NH* singlets. Using the coalescence temperature of 265 K and the maximum peak separation of the *NH* singlets, the *N-C* rotational energy barrier was estimated to be 12.4 kcal/mol.

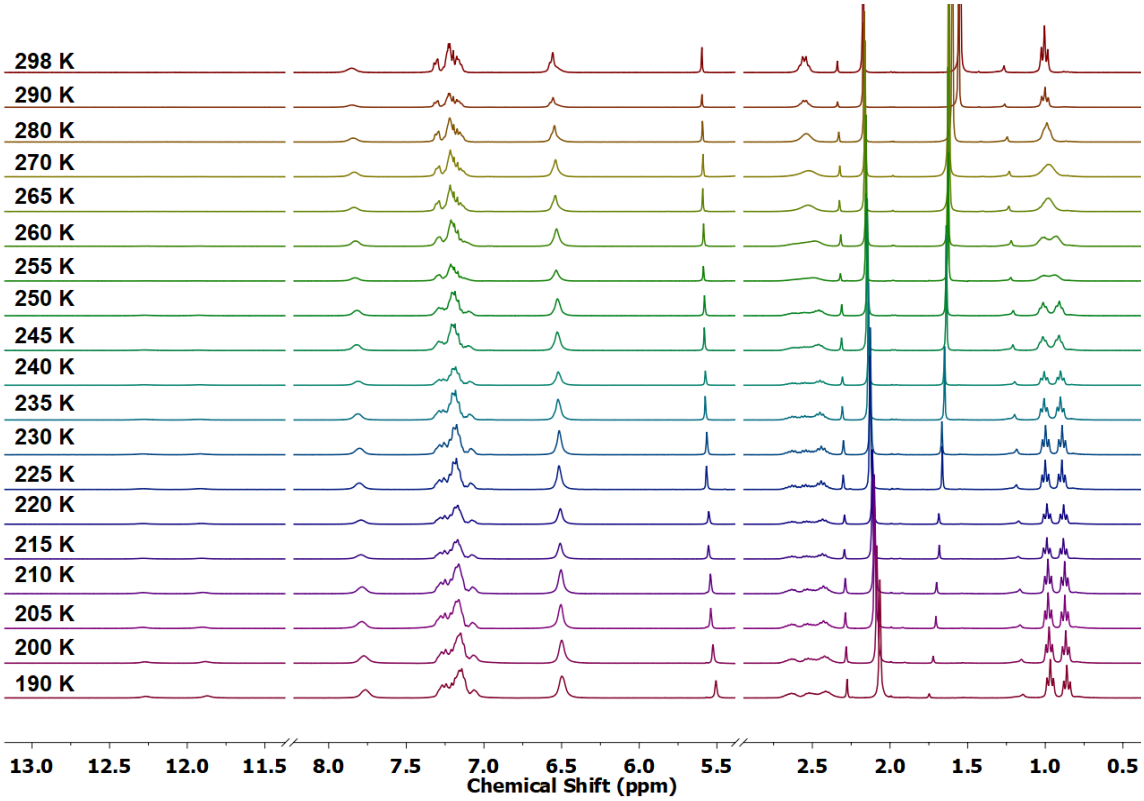


Figure 4.8 Variable temperature ^{1}H NMR study of **4.5e** (Ar = *o*-ethylphenyl) in dichloromethane-d_2

Upon cooling the sample of **4.5f** (Ar = *o*-trifluorophenylphenyl) to 270 K the presence of both conformations is observed in the ^{1}H NMR spectrum, as evidenced by the splitting of the *NH* resonance at 11.5 ppm into two separate resonances at 11.5 and 10.8 ppm (**Figure 4.9**). The coalescence temperature is estimated to be 290 K. At lower temperatures, the acetylacetonate *CH* proton also displayed some separation. As the sample is further cooled the signals continue to sharpen, albeit the minor conformation is in very low abundance and at 220 K the ratio between the *anti* and *syn* conformations is 7.2 to 1. The *N-C* rotational energy barrier between the *anti* and *syn* conformations determined using lineshape analysis is 13.5 ± 1.9 kcal/mol (at 298 K) and 13.6 kcal/mol (at 290 K). The *N-C* rotational energy barrier of **4.5f** determined using the coalescence

temperature and maximum peak separation is 13.3 kcal/mol and agrees well with the *N-C* rotational energy barrier determined using lineshape analysis.

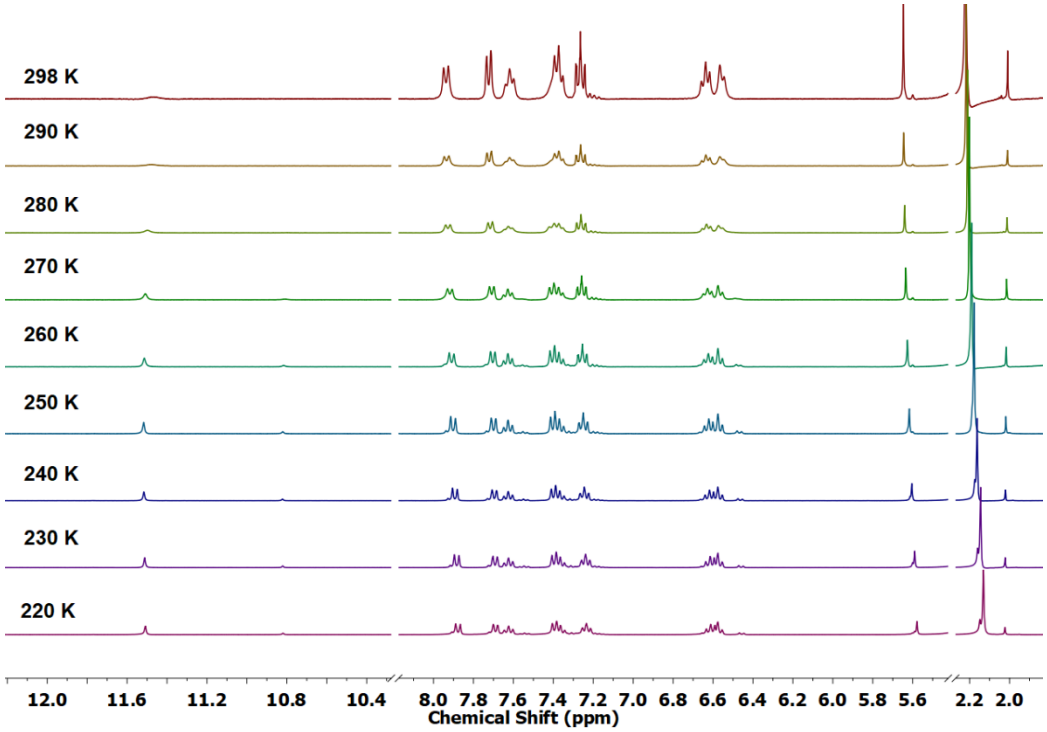


Figure 4.9 Variable temperature ^{1}H NMR study of **4.5f** (Ar = *o*-trifluoromethylphenyl)

At room temperature, the ^{1}H NMR spectrum of the 2-ethyl-6-methyl disubstituted analog (**4.5g** (Ar = 2-ethyl-6-methylphenyl)) indicates that two conformations are present, as evidenced by the presence of two distinct *NH* resonances at 12.4 ppm, and a doubling of the resonances of the methyl (at 2.1 ppm) and ethyl (at 1 ppm or CH_3 and 2.5 ppm for CH_2) substituents. The ratio between the *anti* and *syn* conformations is 1.2 to 1 based on the relative integrations between the *NH* resonances. Upon heating the sample to 378 K, none of the signals in the spectrum coalesce (**Figure 4.10**). This further supports the idea that the disubstitution of the aryl imine subunits has dramatic consequences for Nindigo

N-C rotational energy barriers. Using the maximum peak separation of the two *NH* signals centered at 12.45 ppm and a theoretical minimum "coalescence temperature" of 378 K, the *N-C* rotational energy barrier of **4.5g** is predicted to have a lower limit of 19.7 kcal/mol.

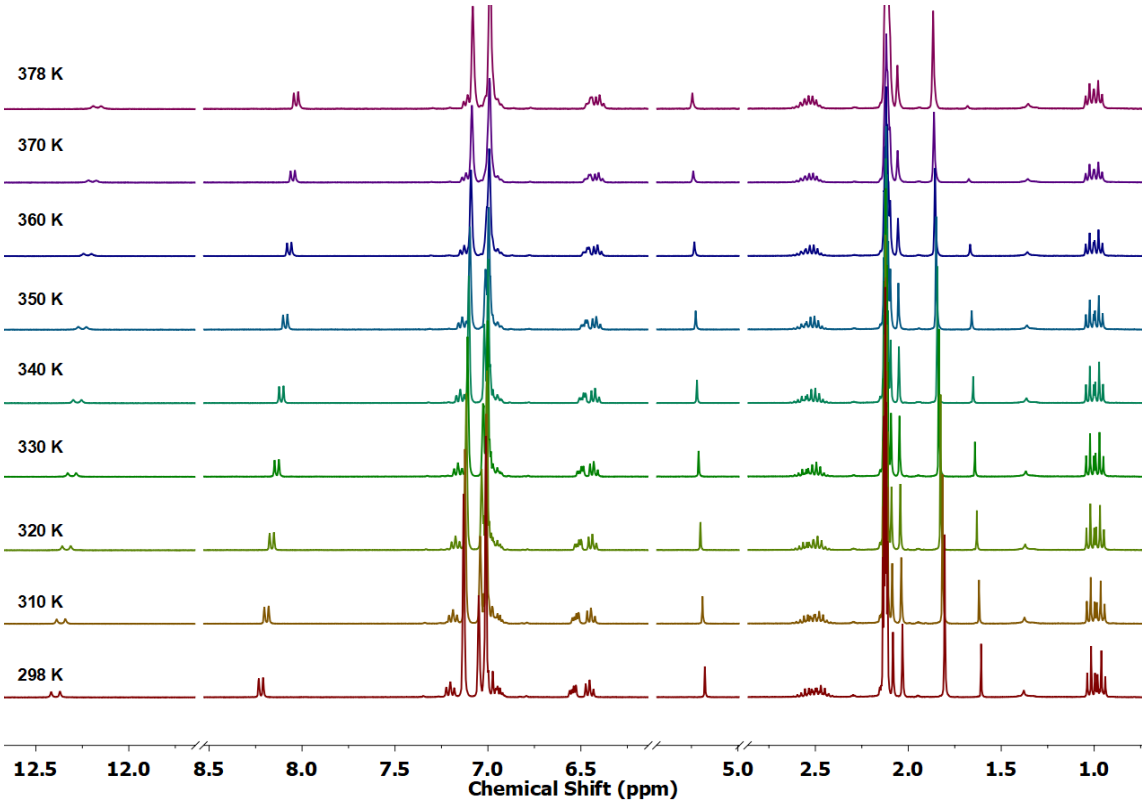


Figure 4.10 Variable temperature ^{1}H NMR study of **4.5g** (Ar = 2-ethyl-6-methylphenyl)

Like **4.5g**, at room temperature, the ^{1}H NMR spectrum of **4.5h** (Ar = 2-methyl-1-naphthyl) indicates that two conformations are present (**Figure 4.11**). The ratio between the *anti* and *syn* conformations of **4.5h** is 2 to 1 based on the integration between the doublets centered around 6.35 ppm. Upon heating the sample to 378 K, no coalescence is observed, again providing more support that disubstitution has a great impact on the *N-C*

rotational energy barriers of Nindigo derivatives. Using the maximum peak separation of the *NH* resonances at 12.98 ppm and a theoretical minimum "coalescence temperature" of 378 K, the *N-C* rotational energy barrier of **4.5h** is predicted to have a theoretical lower limit of 20.2 kcal/mol.

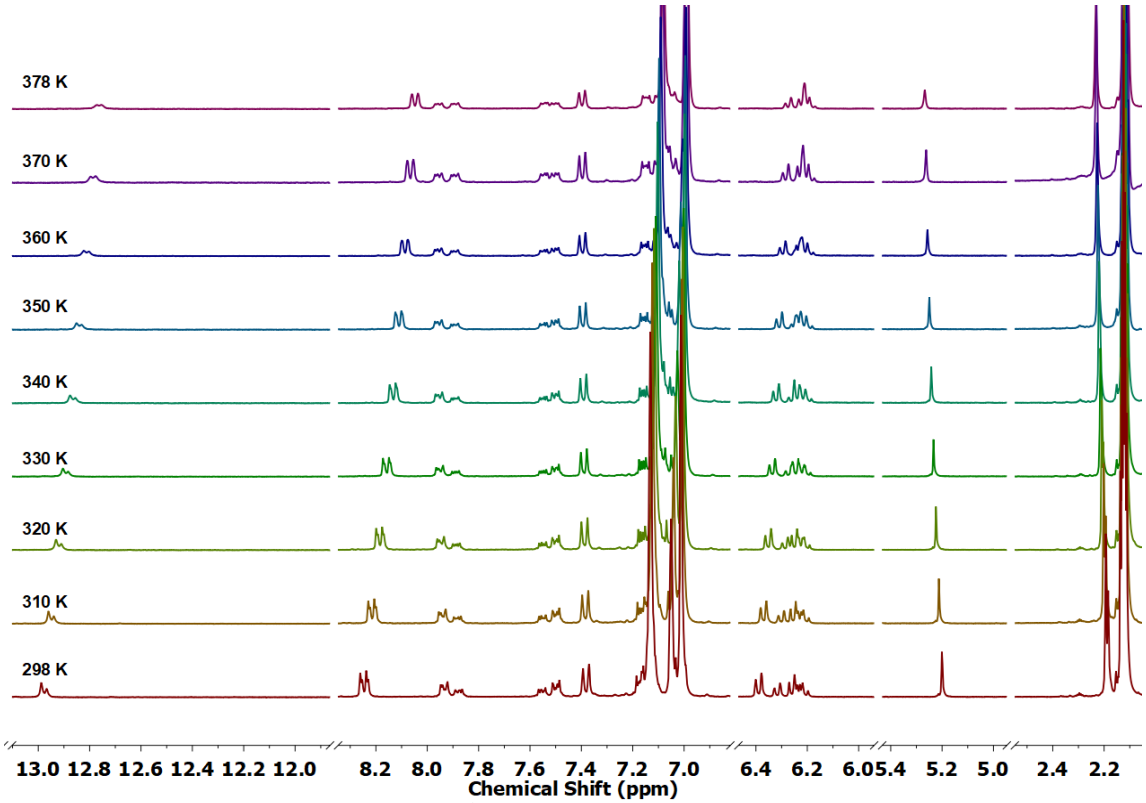


Figure 4.11 Variable temperature ^{1}H NMR study of **4.5h** (Ar = 2-methyl-1-naphthyl)

4.6 Discussion

As mentioned in **Chapter 1**, in general electronic effects have a more subtle influence on atropisomerization barriers than steric effects. It can be assumed that the electron-withdrawing nature of the tether's effect on the *N-C* rotational energy barrier will be smaller than the effect of the diimine pocket (i.e, steric considerations) has on the said

barrier. The comparison of the *N-C* rotational energy barriers, for **4.5b**, **4.5d**, and **4.5e** with those of analogs **3.15b**, **3.15d**, and **3.15e**, should provide a better understanding of how the type of tether influences the *N-C* rotational barriers while keeping the protonation state constant (**Table 4.1)**.

Table 4.21 *N-C* rotational energy barriers of *cis*-Nindigos **3.15** and **4.5**

Compound	Substituent	$\Delta G^{\ddagger a}$ (kcal/mol)	$\Delta G^{\ddagger b}$ (kcal/mol)	Compound	$\Delta G^{\ddagger a}$ (kcal/mol)	$\Delta G^{\ddagger b}$ (kcal/mol)
4.5b	iPr	13.9	12.9	**3.15b**	18.8	18.7
4.5d	Ph	15.8	16.0	**3.15d**	18.2	19.3
4.5e	Et	13.7	12.4	**3.15e**	18.0	18.4

[a]determined using lineshape analysis; [b] determined using coalescence temperature and maximum peak separation.

From the data presented in **Table 4.1** the difference in the *N-C* rotational energy barriers between **3.15** and **4.5** ranges between 2.4 to 6.0 kcal/mol; the *N-C* rotational barriers of the palladium (II) acetylacetonate complexes are always smaller than their protonated *N, N'*-oxalyl bridged *cis*-Nindigo congeners. These differences in the *N-C* rotational energy barriers provide more support for the size of the diimine pocket having an influence on the *N-C* rotational energy barriers of *cis*-Nindigo derivatives. *Cis*-Nindigo complexes **4.5b**, **4.5d**, and **4.5e** all have *N-C* rotational energy barriers in between that of their protonated and neutral *N, N'*-oxalyl Nindigo counterparts. The differences between the *N-C* rotational energy barriers of the protonated *N, N'*-oxalyl bridged *cis*-Nindigos, **3.15**, and the *cis*-Nindigo palladium acetylacetonate complexes **4.5** is the result of a combination of two differences, the steric influence dictating the size of the diimine pocket and the combination of the subtle electronic influences of the charge of the ligand

and tether. Experimentally, it is difficult to separate how the electronic effects of the tether influence the rotational energy barrier from the influence of steric effects.

4.7 Summary and conclusions

A series of *cis*-Nindigo palladium (II) acetylacetonate complexes were prepared from their mono *ortho*-substituted *trans*-Nindigo counterparts in yields ranging from 40 – 60% and spectroscopically characterized. Variable temperature ^{1}H NMR studies showed that the *N-C* rotational energy barriers of these *cis*-Nindigo complexes were in between the *N-C* rotational barriers of neutral and protonated *N, N'*-oxalyl bridged *cis*-Nindigos and complexes **4.5b, 4.5d – 4.5f** are Class 1 atropisomers, while **4.5g** and **4.5h** are predicted to be Class 2 atropisomers. The work presented in this chapter provides more evidence to support that the size of the diimine pocket has an impact on the *N-C* rotational energy barriers of *cis*-Nindigos.

The palladium (II) acetylacetonate Nindigo complexes are the first instances of Nindigo complexes that exhibit hindered *N-C* bond rotation. It offers a glimpse at the potential future development of more chiral atropisomeric complexes and in principle, the bimetallic ruthenium systems should also be accessible using similar synthetic protocols. The di-substitution strategy of stopping the *N-C* bond rotation has been validated to be an effective strategy in increasing the *N-C* rotational energy barriers of atropisomeric Nindigos and should be a central design strategy for future Nindigo analogs. Lastly, this chapter has also further showcased that with subtle changes to a remote part of the *cis*-Nindigo scaffold that dramatic differences in *N-C* bond rotation properties can be achieved.

4.8.1 General experimental procedures

All Nindigos **2.1**, were synthesized following protocols reported in Chapter 2. Palladium acetylacetonate was prepared following literature procedures and initial reactions were conducted using samples provided by the Chem 362 teaching lab at the University of Victoria. Toluene and acetonitrile were purchased from either Sigma Aldrich or Thermo-Fisher and used without further purification.

4.8.2 Experimental procedures

Acetylaceonato[*cis*-1*H*-indigo-bis(2-isopropylphenylimine)] palladium (4.5b)

A solution of **2.1b** (0.094 g, 0.19 mmol) and palladium (II) acetylacetonate (0.058 g, 0.19 mmol) were boiled in toluene (10 mL) in a 50 mL Erlenmeyer flask, open to air, for two hours resulting in a dark green solution. After cooling the solution to room temperature, acetonitrile (25 mL) was added, and the reaction mixture was stored at -20 °C for 12 hours. A dark microcrystalline solid was obtained by vacuum filtration and volatiles were removed in vacuo, yielding **4.5b** (0.053 g, 40%). mp: 278 – 279 °C; FT-IR (ATR) 3069, 2958, 2922, 2867, 1617, 1579, 1523, 1440, 1351, 1296, 1189, 1116, 1076, 937, 744, 587, 461 cm^{-1} ; HRMS (ESI+): calculated for $C_{39}H_{38}N_4O_2Pd^+$ 700.20241 [M-H, -2e +] found 700.20207; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.34 (dd, *J* = 7.1, 2.1 Hz, 2H), 7.30 – 7.08 (m, 12H), 6.52 (d, *J* = 3.6 Hz, 4H), 5.54 (s, 1H), 3.14 (s, 2H), 2.17 (s, 6H), 1.03 (s, 12H). ^{13}C NMR (91 MHz, CD_2Cl_2) δ 186.4, 157.0, 153.3, 145.4, 144.5, 143.3, 132.4, 129.4, 128.6, 127.4, 126.7, 126.4, 126.1, 119.4, 118.8, 115.2, 101.1, 35.6, 30.9, 25.9

Acetylaceonato[*cis*-1*H*-indigo-bis(2-tertbutylphenylimine)] palladium (4.5c)

A solution of **2.1c** (0.092 g, 0.18 mmol) and palladium (II) acetylacetonate (0.054 g, 0.18 mmol) were boiled in toluene (10 mL) in a 50 mL Erlenmeyer flask, open to air, for two hours resulting in a dark green solution. After cooling the solution to room temperature, acetonitrile (25 mL) was added, and the reaction mixture was stored at -20 °C for three hours. A dark microcrystalline solid was obtained by vacuum filtration and volatiles were removed in vacuo, yielding **4.5c** (0.082 g, 60 %). mp: 284 – 285 °C; IR(ATR): 3063, 2998, 2926, 2869, 1576, 1523, 1469, 1433, 1349, 1274, 1195, 1115, 1076, 1050, 938, 751, 577, 460 cm^{-1}; HRMS (ESI+): calculated for $C_{41}H_{42}N_4O_2Pd^+$ 728.23371 [M-H, -2e +] found 728.23449; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 12.21 (s, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.27 – 7.19 (m, 6H), 7.16 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 2H), 7.08 – 7.01 (m, 2H), 6.46 (t, *J* = 7.6 Hz, 2H), 6.25 (dt, *J* = 7.9, 1.0 Hz, 2H), 5.59 (s, 1H), 2.16 (s, 6H), 1.22 (s, 18H); ^{13}C NMR (91 MHz, CD_2Cl_2) δ 186.4, 157.0, 153.3, 145.4, 144.5, 143.3, 132.4, 127.4, 126.7, 126.3, 126.1, 119.4, 118.8, 115.2, 101.1, 35.6, 30.9, 25.9

Acetylaceonato[*cis*-1*H*-indigo-bis(2-phenylphenylimine)] palladium (4.5d)

A solution of **2.1d** (0.098 g, 0.17 mmol) and palladium (II) acetylacetonate (0.053 g, 0.17 mmol) were boiled in toluene (10 mL) in a 100 mL Erlenmeyer flask, open to air, for two hours resulting in a dark green solution. After cooling the solution to room temperature, acetonitrile (25 mL) was added, and the reaction mixture was stored at -20 °C for 12 hours. A dark microcrystalline solid was obtained by vacuum filtration and volatiles were removed in vacuo, yielding **4.5d** (0.079 g, 60%). mp: > 260 C; IR (ATR, cm^{-1}): 3057, 3024, 1559, 1517, 1470, 1435, 1372, 1355, 1297, 1274, 1190. 1176, 1126, 1108, 1092, 1008, 942, 767, 742, 699, 592, 462 cm-1; HRMS (ESI+): calculated for $C_{45}H_{34}N_4O_2Pd^+$ 768.17111 [M-H, -2e +] found 768.17163; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.91 (br s,

1H, major), 11.5 (br s, 1H minor) 7.79 (br s, 2H), 7.41 – 7.26 (m, 3H), 7.24 (t, *J* =7.5 Hz, 2H, minor) 7.18 (t, *J* = 7.7 Hz, 2H, major), 7.10 (d, *J* = 7.5 Hz, 2H), 7.07 – 6.96 (m, 4H), 6.93 (br s, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.71 (br s, 2H, minor), 6.57 (br s, 2H, major), 5.55 (s, 1H), 2.13 (s, 6H); ^{13}C NMR (126 MHz, CD_2Cl_2): 187.4, 138.6, 138.0, 131.8, 130.2, 129.1, 128.0, 127.9, 127.2, 125.9, 125.2, 100.9, 25.6 (not all 13C resonances obtained due to dynamic exchange between *anti* and *syn* conformations)

Acetylaceonato[*cis*-1*H*-indigo-bis(2-ethylphenylimine)] palladium (4.5e)

A solution of **2.1e** (0.217 g, 0.477 mmol) and palladium (II) acetylacetonate (0.141 g, 0.464 mmol) were boiled in toluene (20 mL) in a 100 mL Erlenmeyer flask, open to air, for two hours resulting in a dark green solution. After cooling the solution to room temperature, acetonitrile (50 mL) was added, and the reaction mixture was stored at -20 °C for 12 hours. A dark microcrystalline solid was obtained by vacuum filtration and volatiles were removed in vacuo, yielding **4.5e** (0.166 g, 55 %). mp > 260 °C; HRMS (ESI+): calculated for $C_{37}H_{34}N_4O_2Pd^+$ 672.17111 [M-H, -2e +] found 672.17139; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.08 (s, 1H), 7.86 (dt, *J* = 8.4, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.13 (m, 8H), 6.56 (d, *J* = 7.3 Hz, 2H), 6.52 (ddd, *J* = 8.0, 6.8, 1.0 Hz, 2H), 5.54 (s, 1H), 2.54 (br q, *J* = 7.3 Hz, 4H), 2.17 (s, 6H), 1.01 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.9, 156.5, 152.2, 145.3, 143.2, 132.1, 129.2, 128.4, 126.9, 126.10 125.3, 122.5, 119.0, 118.7, 115.2, 101.0, 25.9, 24.7, 14.5

Acetylaceonato[*cis*-1*H*-indigo-bis(2-trifluoromethylphenylimine)]palladium (4.5f)

In a 50 mL Erlenmeyer flask, a solution of **4.6** (0.097 g, 0.18 mmol) and palladium (II) acetylacetonate (0.054 g, 0.18 mmol) were boiled in toluene (10 mL) in a 50 mL Erlenmeyer flask, open to air, for two hours resulting in a dark green solution. After

cooling the solution to room temperature, acetonitrile (25 mL) was added, and the reaction mixture was stored at -20 °C for 12 hours. A dark microcrystalline solid was obtained by vacuum filtration and volatiles were removed in vacuo, yielding **4.5f** (0.072 g, 54 %). mp: 280 – 282 °C; FT-IR (ATR,): 3045, 3008, 2920, 1598, 1562, 1519, 1482, 1436, 1386, 1314, 1274, 1194, 1158, 1107, 1054, 1033, 936, 866, 753, 734, 648, 592 463 cm^{-1}; HRMS (ESI+): calculated for $C_{39}H_{38}N_4O_2Pd^+$ 752.08328 [M-H, -2e +] found 752.08337; ^1H NMR (360 MHz, CD_2Cl_2) δ 11.44 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 3H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 3H), 7.23 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 3H), 6.60 (t, *J* = 7.5 Hz, 2H), 6.52 (d, *J* = 8.0 Hz, 3H), 5.61 (s, 1H), 2.18 (s, 7H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ 187.8, 138.2, 133.2, 132.7, 127.0, 125.6, 125.5_8, 101.2, 25.8 (not all ^{13}C signals were obtained due to poor solubility); ^{19}F NMR (283 MHz, CD_2Cl_2) δ -61.3;

Acetylaceonato[*cis*-1*H*-indigo-bis(2-ethyl-6-methylphenylimine)]palladium (4.5g)

In a 50 mL Erlenmeyer flask, a solution of **2.7a** (0.088 g, 0.18 mmol) and palladium (II) acetylacetonate (0.059 g, 0.18 mmol) were boiled in toluene (10 mL), open to air, for two hours resulting in a dark green solution. After cooling the solution to room temperature, acetonitrile (25 mL) was added, and the reaction mixture was stored at -20 °C for 12 hours. A dark microcrystalline solid was obtained by vacuum filtration and volatiles were removed in vacuo, yielding **4.5g** (0.075 g, 61%). mp: 267 – 268 °C; IR(ATR, cm^{-1}): 3061, 2962, 2918, 2853, 1575, 1524, 1467, 1440, 1362, 1293, 1192, 1114, 1088, 1010, 939, 876, 769, 746, 702, 590, 461 cm^{-1}; HRMS (ESI+): calculated for $C_{39}H_{38}N_4O_2Pd^+$ 700.20241 [M-H, -2e +] found 700.20265; ^1H NMR (500 MHz, CD_2Cl_2) δ 12.15 (s, 1H, major), 12.11 (s, 1H, minor), 7.81 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.11 (m, 16H), 6.47 (t, *J* = 8.0 Hz, 4H),

6.23 (d, *J* = 7.9 Hz, 2H, major), 6.22 (d, *J* = 7.9 Hz, 2H, minor), 5.59 (s, 1H), 2.64 – 2.44 (m, 4H), 2.16 (s, 6H), 2.12 (s, 6H, major), 2.10 (s, 6H, minor), 1.05 (t, *J* = 7.6 Hz, 6H, minor), 1.01 (t, *J* = 7.5 Hz, 6H, major); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 186.4, 156.7, 154.0, 144.6, 142.3 (minor), 142.2 (major), 137.6 (major), 137.5 (minor), 132.6_8 (major), 132.6_7 (minor), 131.7 (minor), 131.5 (major), 128.9 (major), 128.8 (minor), 127.2 (major), 127.0 (minor), 126.8, 124.7_2 (minor), 124.7_0 (major), 119.6, 119.1 (major), 119.0_5 (minor), 115.1, 101.1, 25.9, 25.3 (major), 25.1 (minor), 18.4_3 (minor), 18.3_6 (major), 15.0 (major), 14.8 (minor)

Acetylaceonato[*cis*-1*H*-indigo-bis(2-ethyl-6-methylphenylimine)] palladium (4.5h):

In a 50 mL Erlenmeyer flask, a solution of **2.7b** (0.095 g, 0.17 mmol) and palladium (II) acetylacetonate (0.052 g, 0.170 mmol) were boiled in toluene (10 mL), open to air, for two hours resulting in a dark green solution. After cooling the solution to room temperature, acetonitrile (25 mL) was added, and the reaction mixture was stored at -20 °C for 12 hours. A dark microcrystalline solid was obtained by vacuum filtration and volatiles were removed in vacuo, yielding **4.5h** (0.055 g, 43%). mp: 290 – 292 °C; FT-IR (NaCl, thin film): 3052, 2965, 2918, 2846, 1567, 1517, 1440, 1360, 1296, 1262, 1200, 1120, 1100, 1071, 1026, 940, 808, 793, 741 cm^{-1}; HRMS (ESI+): calculated for $C_{43}H_{34}N_4O_2Pd^+$ 744.17111 [M-H, -2e +] found 744.17218; ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 12.68 (s, 1H, minor conformation), 12.67 (s, 1H, major conformation), 7.90 (d, *J* = 8.4 Hz, 2H, minor conformation), 7.83 (d, *J* = 8.4 Hz, 2H, major conformation), 7.80 (d, *J* = 8.4 Hz, 2H, minor conformation), 7.72 (d, *J* = 8.4 Hz, 2H, major conformation), 7.46 – 7.30 (m, 6H), 7.24 (m, 2H minor conformation), 7.15 (m, 10H, major conformation), 6.34 (m, 2H), 6.06 (d, *J* = 8.0 Hz, 2H, minor

conformation), 6.02 (d, *J* = 7.9 Hz, 5H, major conformation), 5.61 (s, 1H), 2.33 (s, 25H), 2.18 (s, 21H).^{13}C NMR (126 MHz, CD_2Cl_2) δ 186.5, 157.0, 154.6, 138.9 (major), 138.8 (minor), 133.2, 132.8, 129.4 (minor), 129.30 (major), 128.5_8 (major), 128.5_6 (minor), 128.3 (major), 128.2 (minor), 128.2 (major), 128.1 (minor), 126.9 (major), 126.88 (minor), 126.5, 126.0, 124.9 (major), 124.8 (minor), 123.2 (minor), 123.1 (major), 119.5 (minor), 119.49 (major), 119.1_4 (minor), 119.1_1 (major), 115.2, 101.2, 25.9, 18.5 (major), 18.4 (minor)

Indigo-N, N'bis(2-trifluoromethylphenyl)diimine (4.6): In a 500 mL Schlenk flask, 1.0 M $TiCl_4$ (37.0 mL, 37.0 mmol) was added to a solution of DABCO (8.18 g, 72.9 mmol), and 2-trifluoromethylaniline (4.6 mL, 36.6 mmol) in *m*-xylenes (250 mL). Indigo (3.184 g, 12.14 mmol) was added to the flask and the mixture was refluxed for 72 hours. The reaction mixture was filtered hot, and the collected solids were washed with diethyl ether (600 mL). The filtrate was evaporated, and the crude solid was taken up in ethyl acetate (1 L). The ethyl acetate solution was sequentially extracted with 1.0 M HCl (3x 100mL), 0.5 M KOH (4x 100 mL), distilled water (3x 100 mL), and brine (1x 100 mL) and dried with magnesium sulfate. Ethyl acetate was removed in *vacuo*, and the resulting dark solid was recrystallized from boiling *n*-butanol (15 mL). Nindigo **4.6** was collected by vacuum filtration and was washed with hexanes (50 mL); residual volatiles were removed in *vacuo*, yielding **4.6** as a shiny purple solid (1.11 g, 35%); HRMS (ESI+): calculated for $C_{30}H_{19}F_6N_4^+$: 549.15084 [M+H] found: 549.1502 ; FT-IR (KBr): 3396, 3324, 3067, 2970, 2873, 1615, 1569, 1480, 1458, 1451, 1416, 1321, 1206, 1109, 1053, 1033, 863, 760, 745, 676 cm^{-1} ; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.83 (dt, *J* =

7.9, 1.0 Hz, 2H), 6.71 (ddd, J = 8.0, 7.2, 1.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 149.6, 147.9, 132.8, 132.2, 128.9, 126.9 (q, J_{CF} = 5.4 Hz), 125.6, 124.6 (q, J_{CF} = 273.9 Hz), 123.81, 121.1 (q, J_{CF} = 29.6 Hz), 120.4, 120.2, 118.0, 113.5.

Chapter 5: Summary and Future Directions

5.1 Summary

As outlined in **Chapter 1**, one of the central areas of focus in the development of atropisomeric systems has been understanding how the steric influence of substituents alters atropisomerization barriers. The tuning of the steric properties of atropisomeric systems is primarily geared towards designing new ligands and frameworks for applications in asymmetric catalysis (organo and metal-mediated) and synthesis and adds additional tools (e.g potential new or complimentary reactivity to current state of the art systems) to the already diverse organic chemist's toolbox.

The work presented in this dissertation introduces a new atropisomeric architecture derived from the readily synthesized diimine congener of indigo, Nindigo. Atropisomeric Nindigos, in all cases (**Chapter 2 – Chapter 4**) have two *N*-*C* bondsthat have restricted rotation, and their *N*-*C* rotational energy barriers are influenced by the geometry of the central -C=C- indigoid double bond, the substitution pattern of the aryl imine subunit, and the nature of the diimine pocket (size and protonation state).

A series of mono *ortho*-substituted Nindigo derivatives were synthesized to assess how the steric bulk of the *N*-aryl substituents influences the *N*-*C* rotational energy barriers of neutral *trans*- (**Chapter 2**) and protonated *cis*-Nindigo (**Chapter 2 – Chapter 4**) analogs. The geometry of the central indigoid carbon-carbon double bond was determined to have significant influence (a minimum of 5 kcal/mol lower $\Delta G^{\ddagger}$ for *trans*-Nindigo relative to their *cis*-congeners) on the *N*-*C* rotational barriers; Nindigos in the *cis*-configuration typically have larger *N*-*C* rotational energy barriers than their *trans*-

counterparts (**2.1**) because of the closer proximity of the aryl imine subunits. The first generation of mono *ortho*-substituted Nindigos (**2.1a – 2.1g** and **2.2a – 2.2g**) had low to moderate *N-C* rotational energy barriers and are classified as either "*Class 1*" or "*Class 2*" atropisomers as defined by LaPlante.[79] Additional structural modifications to the *N*-aryl subunits were explored to further study how structure influences the atropisomerism of Nindigos (**Chapter 2**). By installing an additional substituent at the other *ortho* position of the aryl imine groups in neutral *trans*- (**2.7a** and **2.7b**) and protonated (**2.8a** and **2.8b**) *cis*-Nindigo derivatives the *N-C* rotational energy barriers increased dramatically. The installation of additional substituents onto the aryl imine subunit is an effective strategy for increasing the *N-C* rotational energy barriers of Nindigo derivatives.

The second area of study in this dissertation was the study of Nindigo analogs that do not undergo reversible *cis*- to *trans*- protoisomerization. The installation of organic and metal-containing tethers between the indole nitrogens was studied in **Chapter 3** and **Chapter 4**, respectively. **Chapter 3** presented the study of atropisomeric *N, N'*-oxalyl bridged *cis*-Nindigo analogs in both neutral (**3.16a – 3.16e**) and protonated (**3.15a – 3.15e**) states; the *N, N'*-oxalyl bridged *cis*-Nindigo derivatives showed protonation state-dependent *N-C* rotational energy barriers and absorption wavelength maxima. *N, N'*-oxalyl bridged *cis*-Nindigos exhibited substituent-based *N-C* rotational barrier differences similar to the N-C rotational barriers reported in **Chapter 2** for the neutral *trans*- (**2.1a – 2.1g**) and protonated *cis*-Nindigos (**2.2a – 2.2g**). The protonated *N, N'*-oxalyl tethered analogs, **3.15a – 3.15e**, all displayed larger *N-C* rotational energy barriers and longer absorption wavelength maxima relative to their neutral counterparts **3.16a – 3.16e**. **Chapter 4** presented the study of a series of palladium (II) acetylacetonate tethered *cis*-

Nindigo derivatives (**4.5b – 4.5h**). *Cis*-Nindigo palladium acetylacetonate complexes have an NH present in the diimine pocket and formally have a -1 charge on the Nindigo ligand. Previously, Dr. Dillon Hofsommer attempted to deprotonate complexes of type **4.5** (Ar = 4-methylphenyl), and determined that they cannot be reversibly deprotonated and result in intractable mixtures upon treatment with bases such as sodium hydride and benzyl potassium.[229] The formation of intractable mixtures upon treatment of **4.5** (Ar = 4-methylphenyl) with strong bases contrasts with the acid/base characteristics of **3.15/3.16**, which can be readily protonated/deprotonated and have a formally neutral charge state of the *N, N'*-oxalyl bridged Nindigo core. Thus, *cis*-Nindigo palladium (II) acetylacetonate complexes allow for the direct comparison of different types of tethers (oxalyl vs Pd(acac)) between the indole nitrogens. The one atom tether of the *cis*-Nindigo palladium complexes (**4.5**) widens the diimine pocket more than the two atom oxalyl tether, yielding lower *N*-*C* rotational energy barriers relative to their protonated *N, N'*-oxalyl tethered *cis*-Nindigo counterparts **3.15**. **Chapter 4** also provided further support that the introduction of additional substituents onto the aryl imine subunit has a influence on Nindigo *N*-*C* atropisomerism and no interconversion between the *anti* and *syn* conformations of **4.5g** and **4.5h** were observed even with the presumed larger diimine pocket-size relative to their unbridged protonated *cis*-Nindigo counterparts **2.8a** and **2.8b**. **Chapter 3** and **Chapter 4** showed that simple structural modifications can further modulate the atropisomerism of *cis*-Nindigo derivative; differing tether lengths and protonation states have significant consequences for the *N*-*C* rotational energy barriers of Nindigo and is an effective strategy for further modulating the *N*-*C* rotational energy barriers of *cis*-Nindigos.

This dissertation is the first report on atropisomeric Nindigos and provides insights into how structural modifications can alter their corresponding *N*-*C* atropisomerization barriers. The nature of the aryl imine subunits, the geometry of the central indigo double bond, and the installation of a tether between the indole nitrogens all have significant consequences regarding Nindigo *N*-*C* atropisomerism. The structural modifications presented in this dissertation provide initial road maps for future directions that this research can go, as will be discussed in the subsequent section. The overarching implications of the research presented in this dissertation are that a new atropisomeric scaffold has been developed, derived from Nindigo, that contains two *N*-*C* bonds that have restricted rotation and has the potential to offer different/alternative reactivity that could be complementary to the ubiquitously used biaryls (one C-C bond with restricted rotation) based systems that are commonplace in organo and transition metal mediated catalysis.

5.2 Future directions

This work is the first instance of indigoids that exhibit atropisomerism . There is significant potential for the development of these systems, to potentially be used as chiral Lewis bases or Brønsted acids. The presence of two chiral *N*-*C* bonds in the diimine pocket has the potential to offer a different chiral environment than the commonly biaryl-derived organocatalysts and ligands, which only have one chiral bond/axis.

One possible avenue to explore is to investigate more deeply how the nature of the tether influences the *N*-*C* atropisomerism of *cis*-Nindigos. By altering the nature of the tether, it should not only be possible to modulate the size of the diimine pocket, but also alter the electron richness of the diimine pocket and thus alter the acidity/basicity of the

protonated/neutral forms of *cis*-Nindigos. Several types of tethers are possible to insert between the two indole nitrogens. A series of analogs, featuring organic bridges of varying length and conjugation (**5.1** – **5.5**) are proposed. It has been shown by Dr. Erica Hong that the rigidity of the bridge between the indole nitrogens has the potential for significant structural distortions of the indigo backbone. By altering the length of the tether (one carbon to three carbons) the understanding of how the length of acyl/alkyl bridges influences the N-C rotational barriers of *cis*-Nindigos can be understood comprehensively.

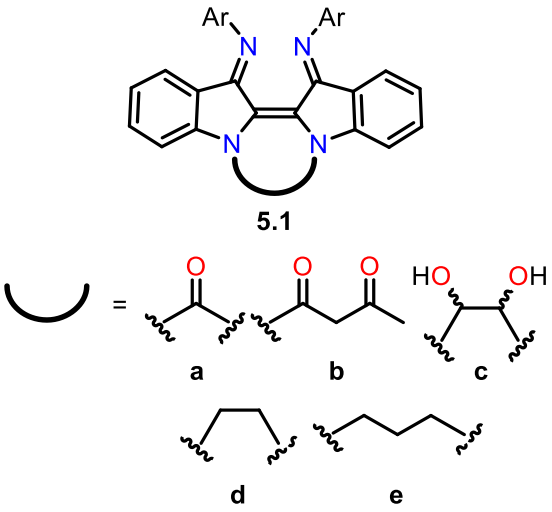
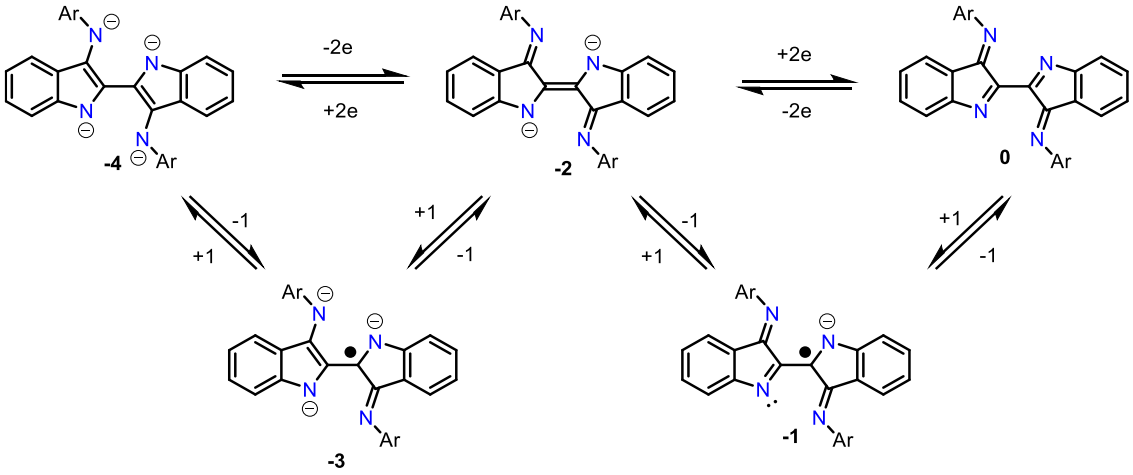


Figure 5.1 Proposed new tethered *cis*-Nindigo analogs

One of the initial focuses of investigations into Nindigo chemistry was its redox activity.[122,128,129] Deprotonated Nindigo has five accessible redox states (**Scheme 5.1**) as a free species and particularly when coordinated to a metal. *Cis*-Nindigos, which are oxidized or reduced by two electrons may have significantly different *N-C* rotational energy barriers than the unoxidized/reduced congeners. In *cis*-Nindigo metal complexes

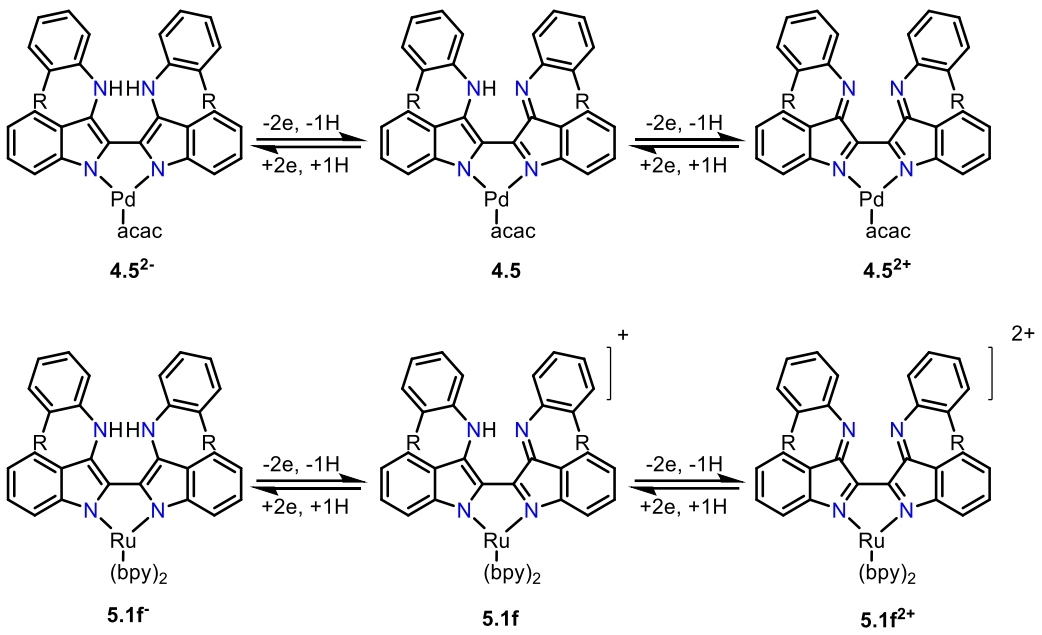
the acidity of the *NH* in the diimine pocket can be modulated via exploiting its redox chemistry; Dr. Dillon Hofsommer previously explored the acid/base properties of oxidized palladium and ruthenium *cis*-Nindigo complexes. Dr. Dillon Hofsommer reported a change of six pKa (in THF) units going from one electron to two electron oxidized palladium acetylacetonate and ruthenium bipyridine complexes.[229] The significant alteration of the *NH* acidity/basicity of *cis*-Nindigo opens up opportunities for *cis*-Nindigo metal complexes to be used as potential redox-state triggered chiral acid catalysts. The ability to tune the *N-C* rotational energy barriers of *cis*-Nindigos, or any system, via the change in the oxidation state, is of interest and to my knowledge not reported anywhere in the literature.



Scheme 5.1 Redox states of deprotonated Nindigo

Another potential area of future investigation is to study the effect that metal-containing bridges have on the *N-C* rotational barriers in more detail, in conjunction with investigating the redox state influence on said barriers. Potential complexes that could be targeted are those that feature a $Ru(bipy)_2^{2+}$ tether **5.1f**. Analogs of type **5.1f** would be

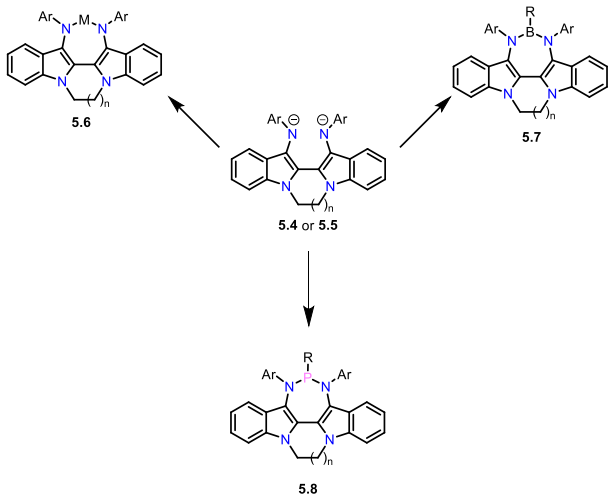
targeted using synthetic protocols developed by Lahiri and Kaim[231] and previously in the Hicks group by Dr. Dillon Hofsommer.[229] Nindigo complexes of type **5.1f** would offer additional insight into how the charge of the tether influences the *N*-*C* rotational energy barriers of *cis*-Nindigos. Another interesting aspect of the metal bridged species **5.1f** and complexes of type **4.5** is the exploitation of the redox-active nature of these complexes to modulate the *N*-*C* atropisomerism. Like their organic tethered congeners, they can be oxidized and reduced by two electrons. Unlike their organic bridged congeners, it has been shown by Dr, Dillon Hofsommer that the deprotonation of the diimine pocket of *cis*-Nindigo complexes is very challenging and leads to intractable mixtures. The effect that the redox state of the Nindigo in its complexes exudes on the *N*-*C* rotational energy barriers is of interest and will provide greater insight into how the electronics of *cis*-Nindigos influence their related *N*-*C* rotational energy barriers. To this extent, the oxidized and reduced species of the palladium (II) and the ruthenium (II) complexes are proposed to be investigated for redox state-based *N*-*C* atropisomerism. The *N*-*C* atropisomerism of the reduced species will provide insight into the experimental metrics of the NH bond rotation, while the *N*-*C* rotational energy barriers of the oxidized species will gain valuable insight into how much of an influence internal hydrogen bonding has on the *N*-*C* rotational energy barriers. To date, there have been no instances reported in which the study of the redox state of a ligand has on to atropisomerism of any metal complexes reported and is therefore of interest.



Scheme 5.2 Targeted reduced and oxidized palladium and ruthenium *cis*-Nindigo complexes

The redox activity of *cis*-Nindigo has the potential to be exploited for the development of new *cis*-Nindigo analogs, which incorporate the functionalization of the diamine pocket, via utilizing the corresponding reduced diamido species (**5.4/5.5**). The exploitation of the redox activity of tethered *cis*-Nindigos will allow for tethered *cis*-Nindigos to not only be a new class of atropisomeric ligands, but also be a synthon for other *cis*-Nindigo analogs. *Cis*-Nindigo in its fully reduced form could be used to produce diamido type species **5.4/5.5** (**Scheme 5.3**), which would then potentially be able to be used as a ligand in the preparation of new atropisomeric *cis*-Nindigo metal complexes **5.6** or as a precursor to *cis*-Nindigo derived boranes (**5.7**) and phosphines (**5.8**), **Scheme 5.3**. The functionalization of the diamine pocket of reduced *cis*-Nindigos raises the

opportunity to produce a new class of atropisomers that have potential applications in numerous asymmetric transformations.



Scheme 5.3 Synthesis of leuco *cis*-Nindigo derivatives

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Appendix A: NMR Spectra

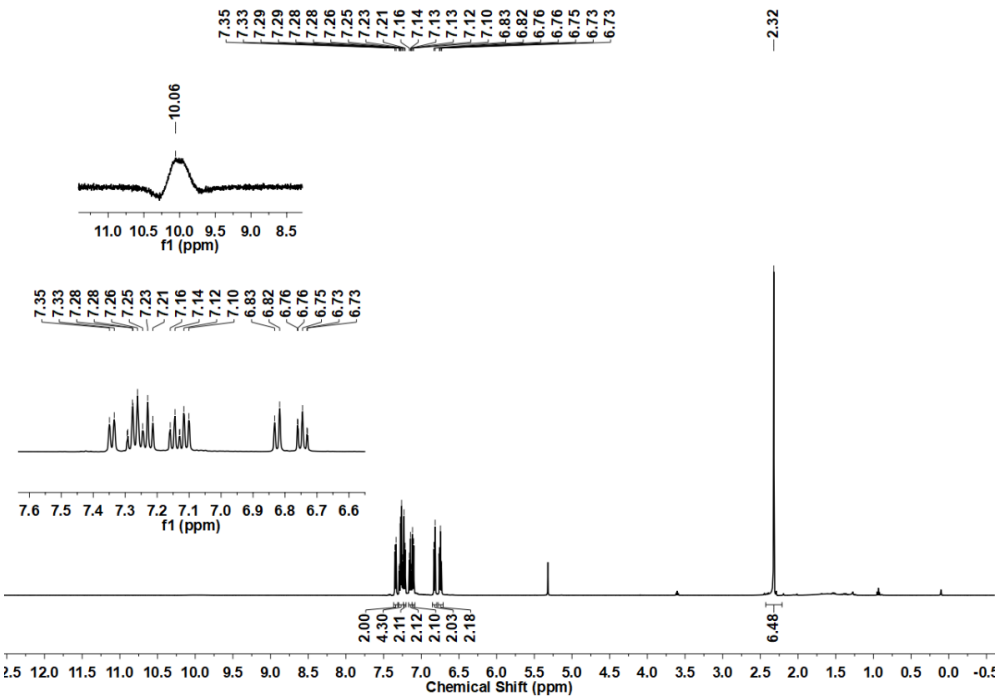


Figure A1 ^{1}H NMR (500 MHz, CD_2Cl_2) of 2.1a at 298 K

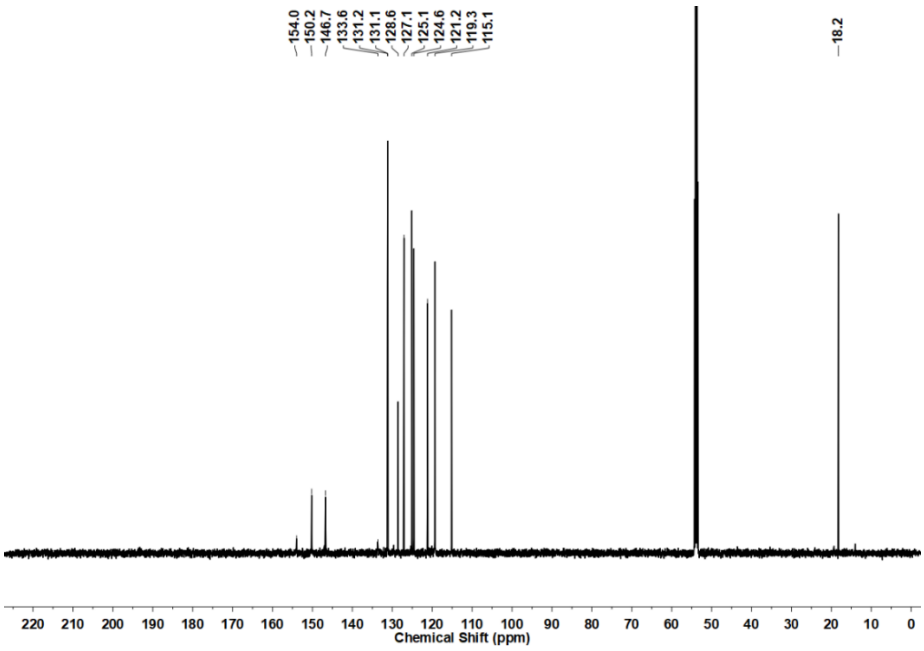


Figure A2 ^{13}C NMR (126 MHz, CD_2Cl_2) of 2.1a at 298 K

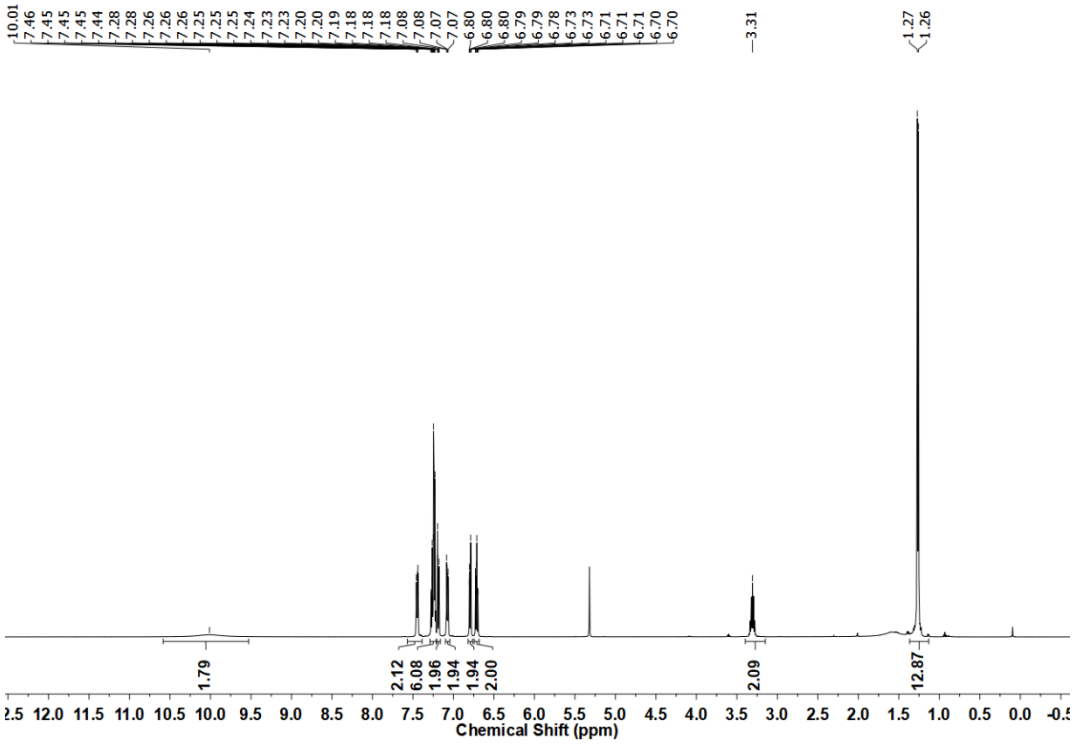


Figure A3 ^{1}H NMR (500 MHz, CD_2Cl_2) of 2.1b at 298 K

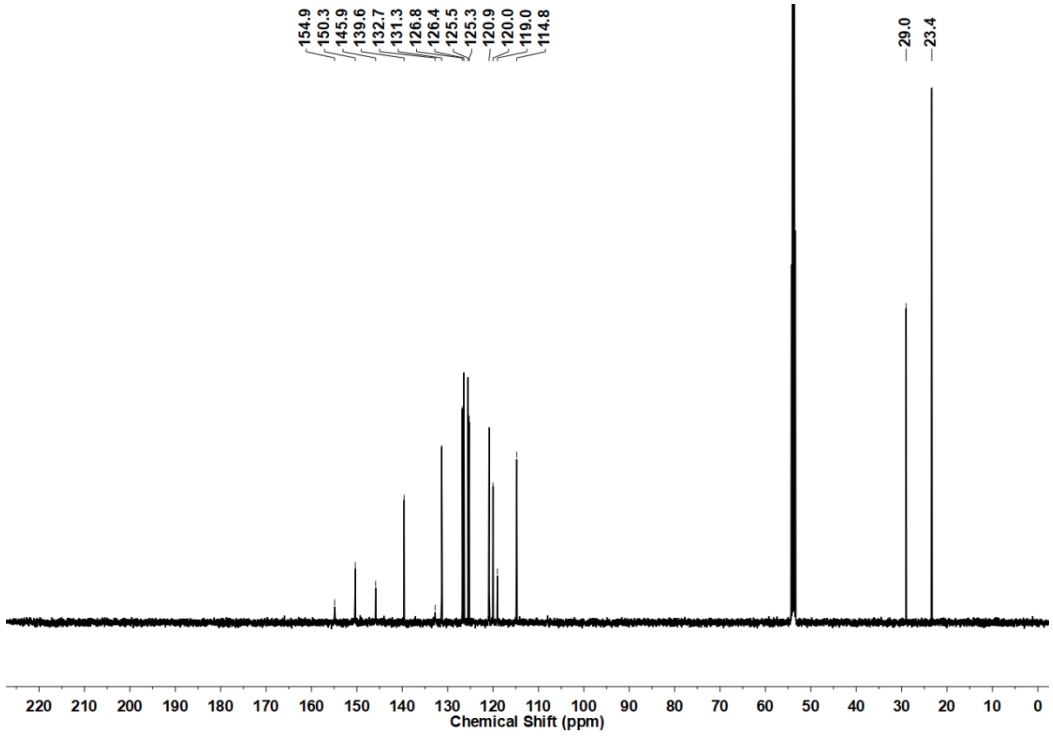


Figure A4 ^{13}C NMR (126 MHz, CD_2Cl_2) of 2.1b at 298 K

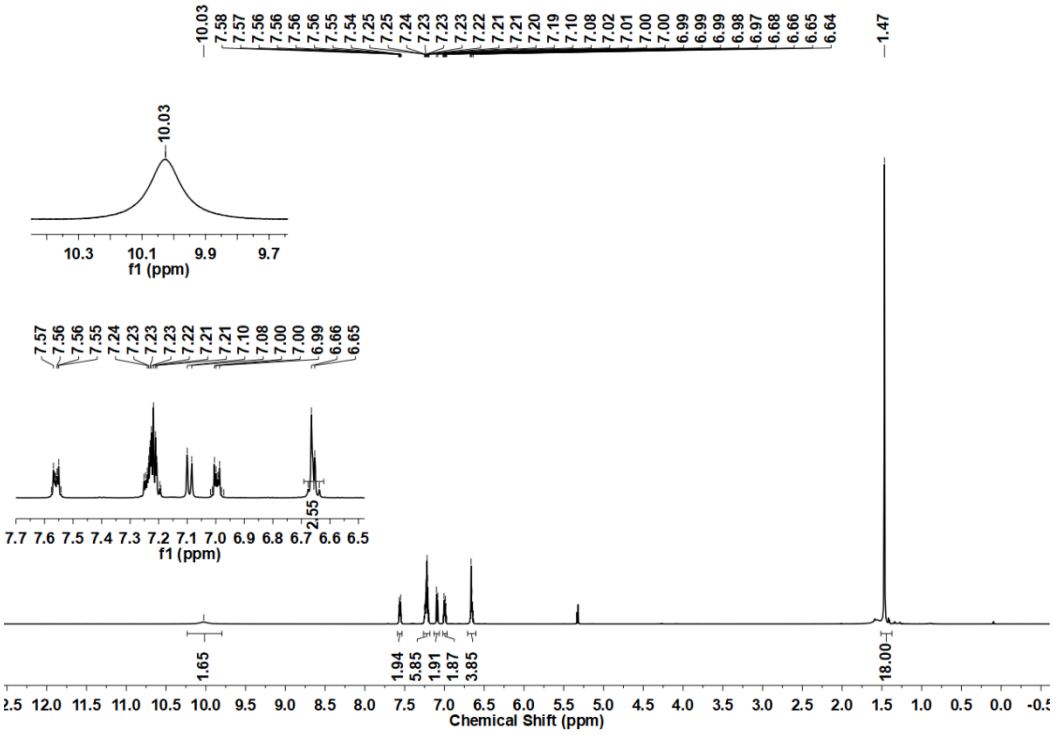


Figure A5 ^{1}H NMR (500 MHz, CD_2Cl_2) of 2.1c at 298 K

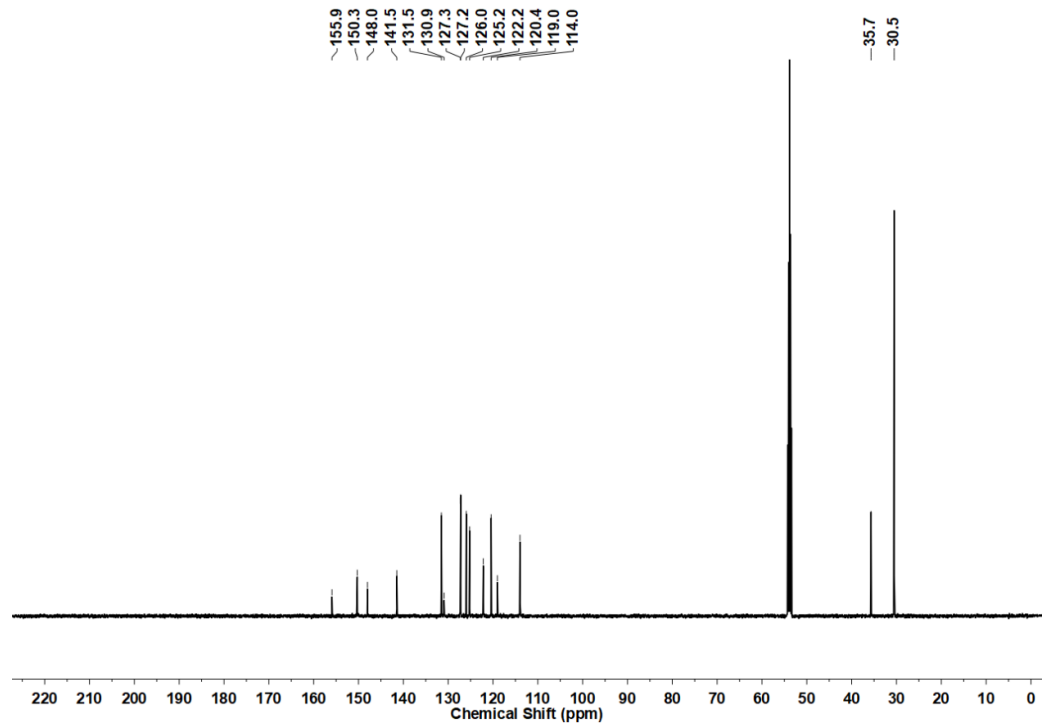


Figure A6 ^{13}C NMR (126 MHz, CD_2Cl_2) of 2.1c at 298 K

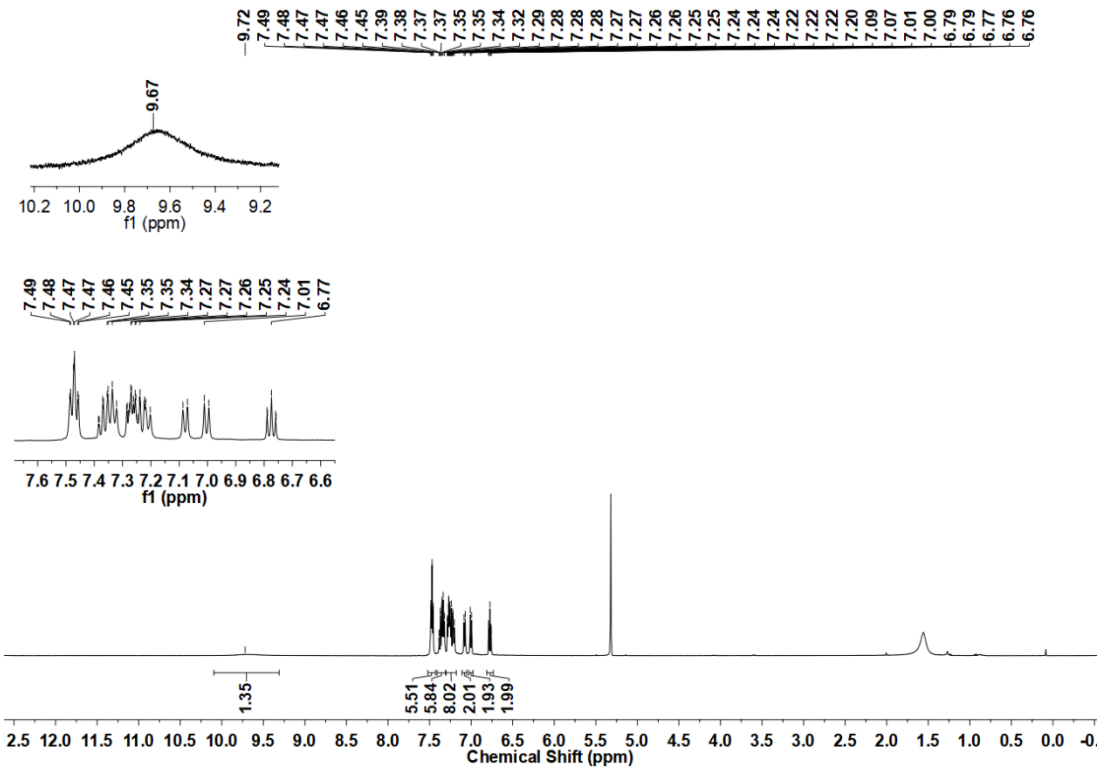


Figure A7 ^{1}H NMR (500 MHz, CD_2Cl_2) of 2.1d at 298 K

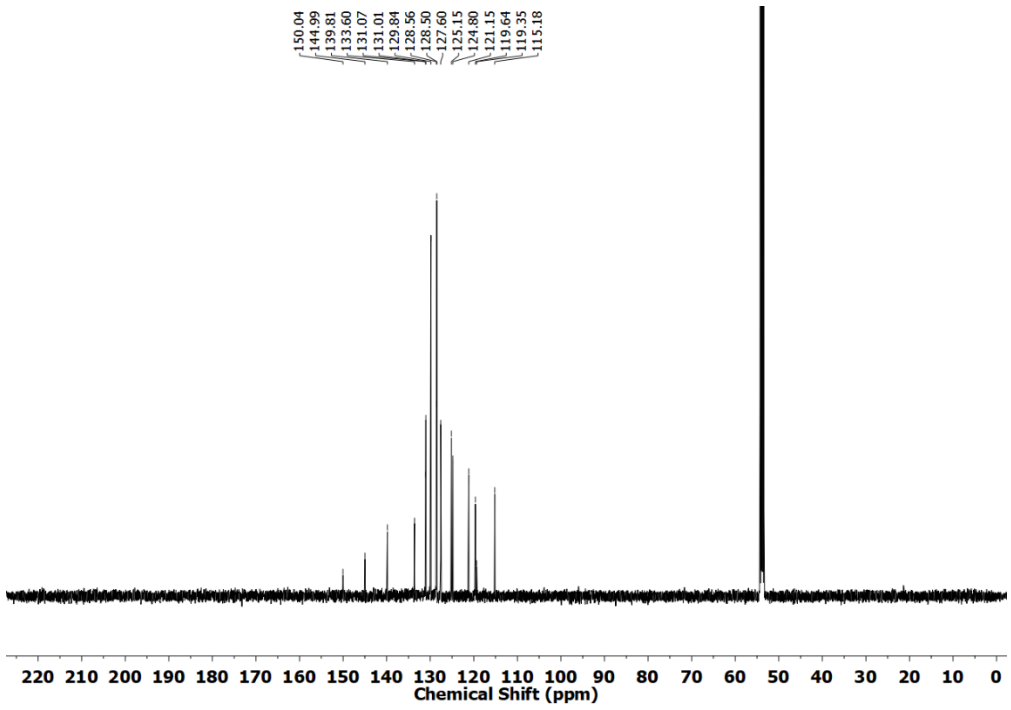


Figure A8 ^{13}C NMR (126 MHz, CD_2Cl_2) of 2.1d at 298 K

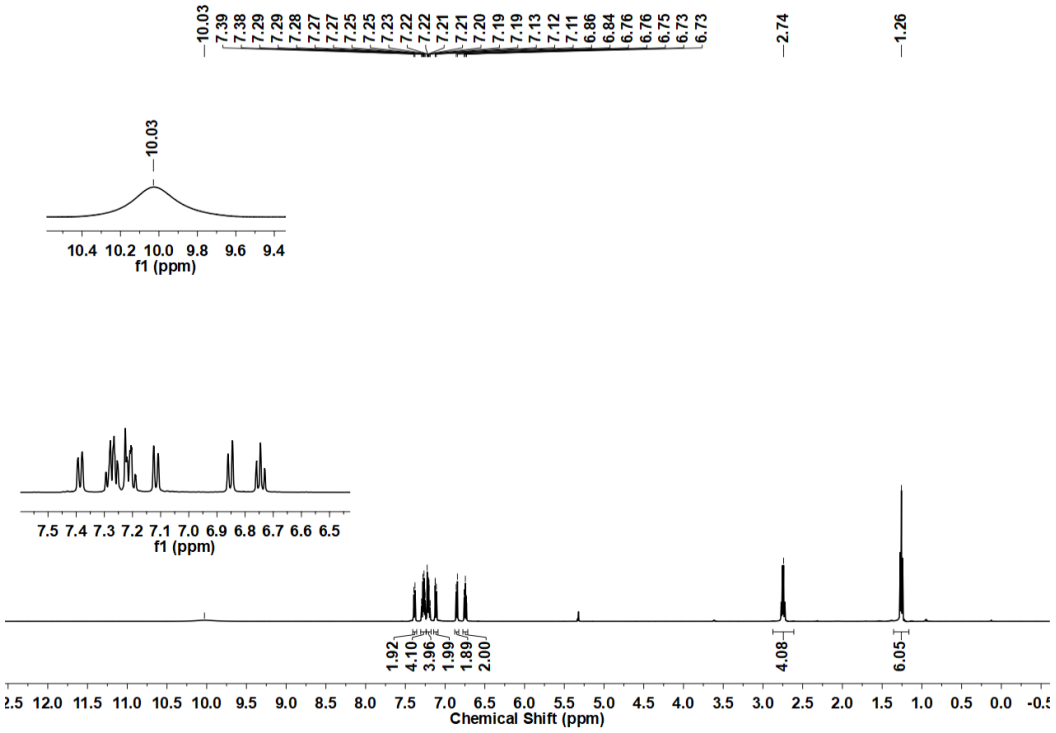


Figure A9 ^{1}H NMR (500 MHz, CD_2Cl_2) of 2.1e at 298 K

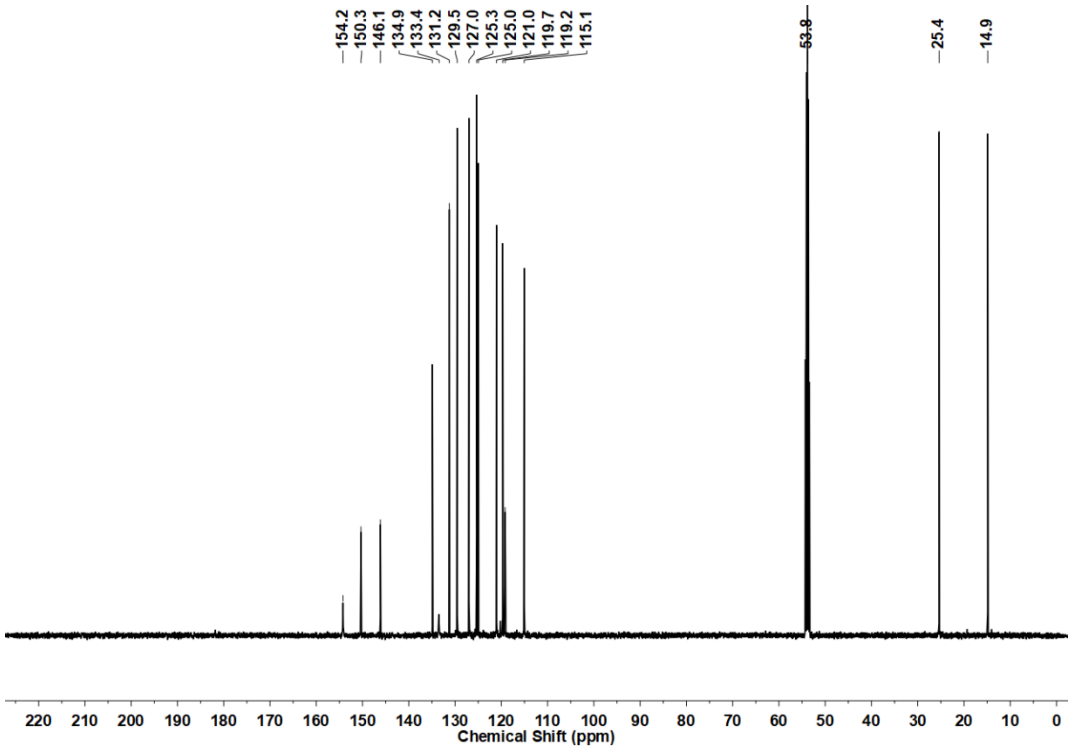


Figure A10 ^{13}C NMR (126 MHz, CD_2Cl_2) of 2.1e at 298 K

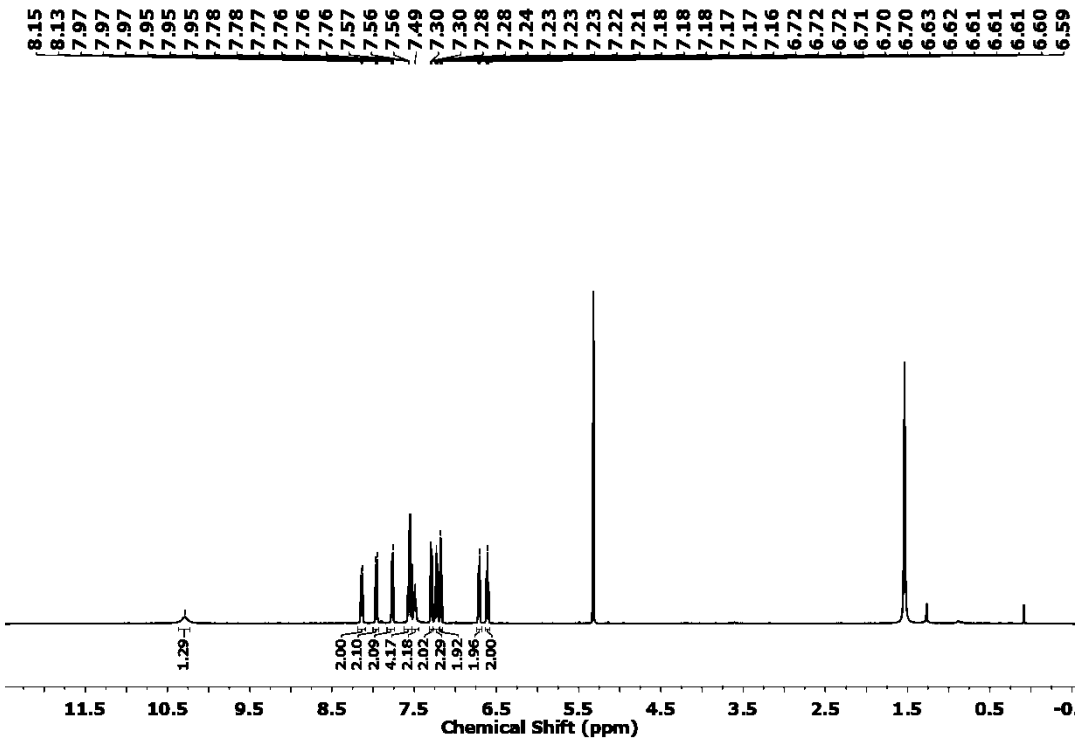


Figure A11 ^{1}H NMR (500 MHz, CD_2Cl_2) of 2.1f at 298 K

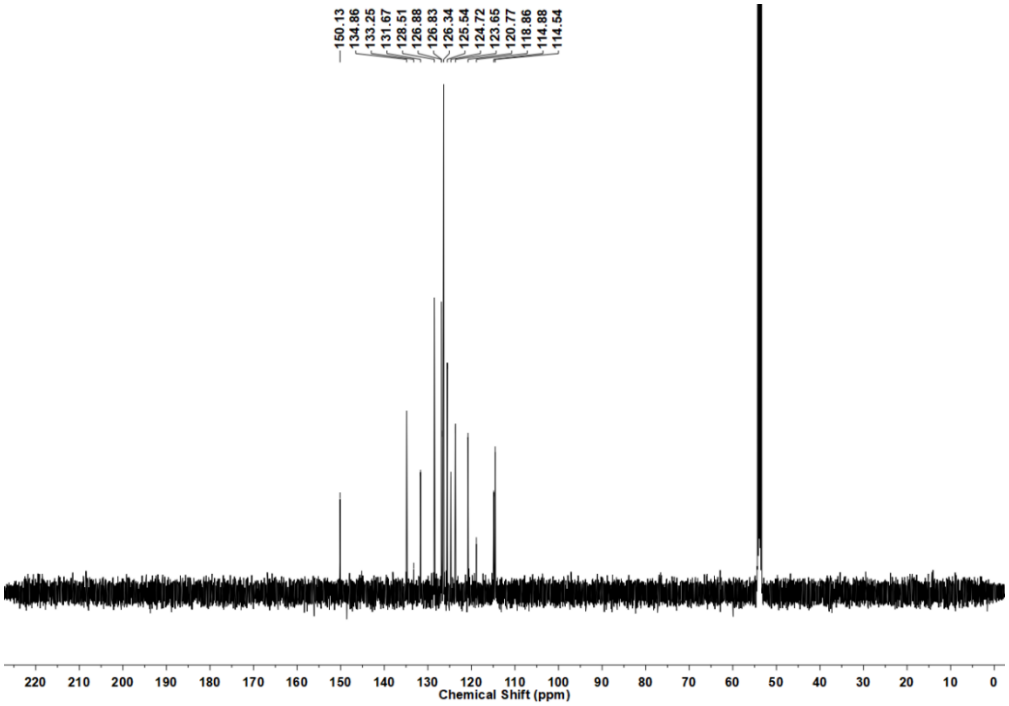


Figure A12 ^{13}C NMR (126 MHz, CD_2Cl_2) of 2.1f in CD_2Cl_2

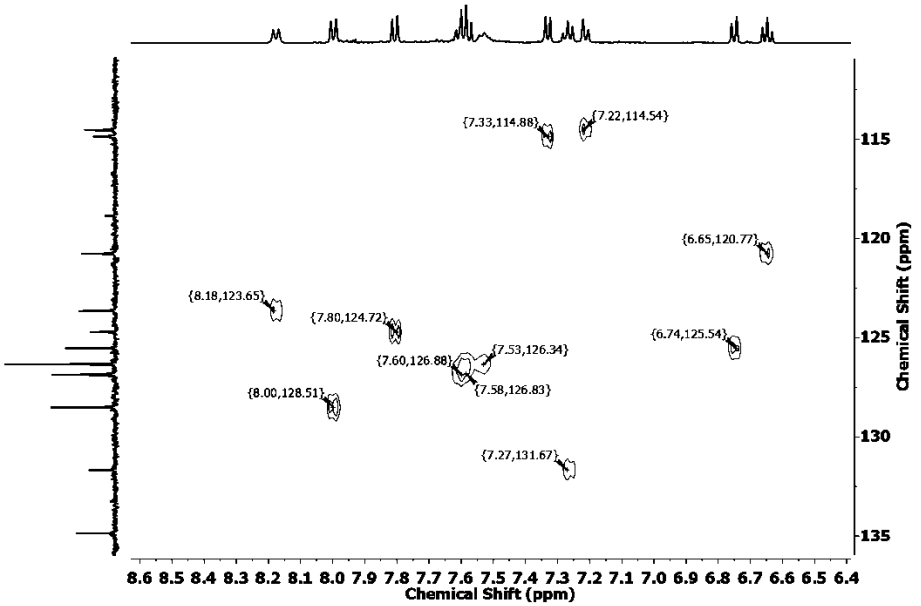


Figure A13 HSQC (500 MHz, 126 MHz) of 2.1f in CD_2Cl_2

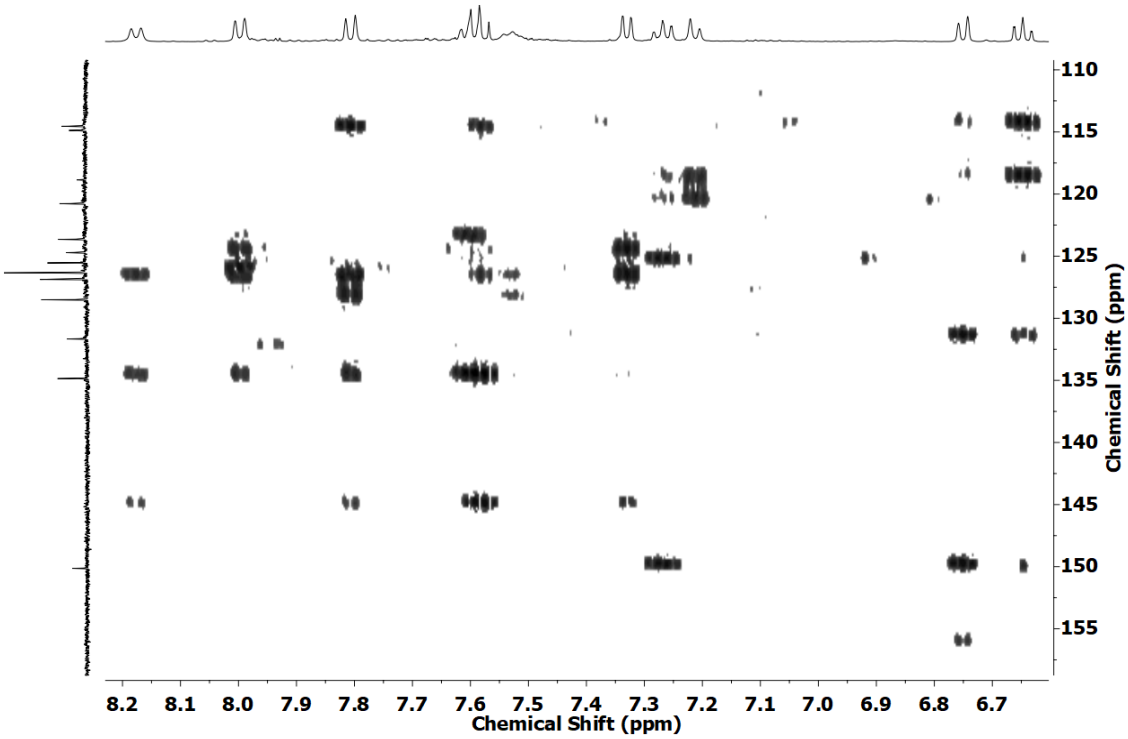


Figure A14 HMBC (500 MHz, 126 MHz) of 2.1f in CD_2Cl_2 at 298 K

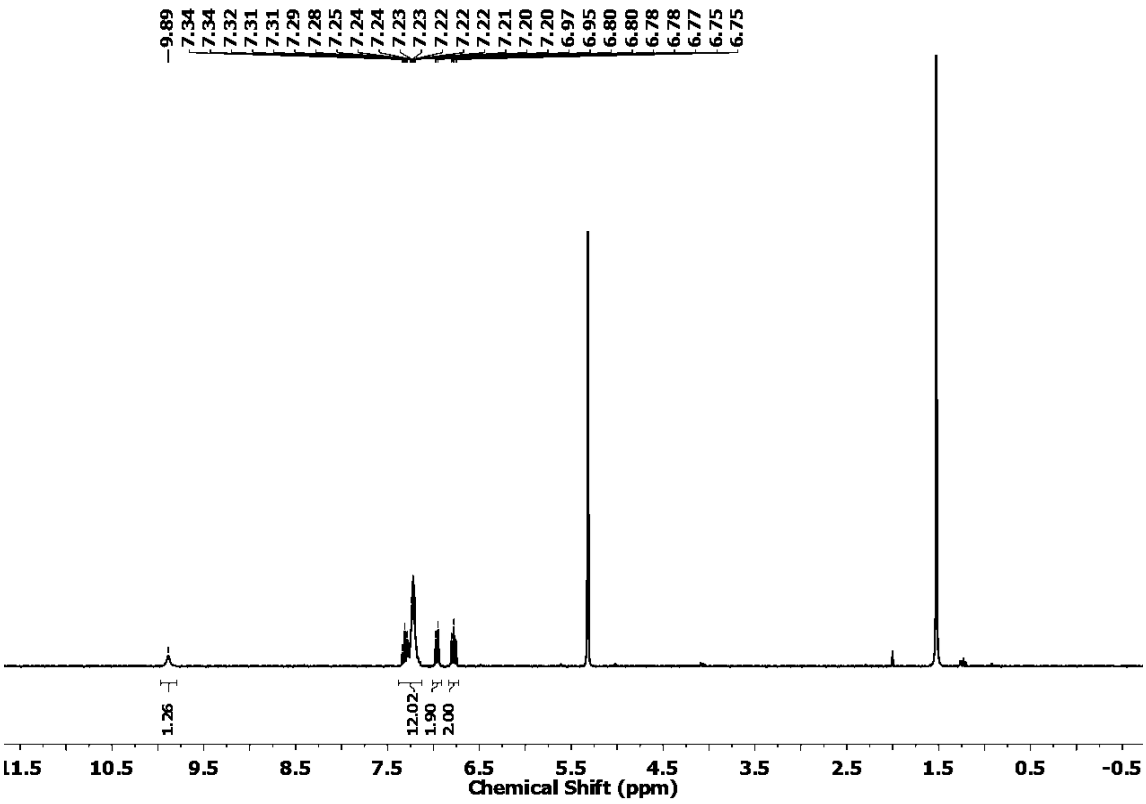


Figure A15 ^{1}H NMR (300 MHz) of 2.1g in CD_2Cl_2 at 298 K

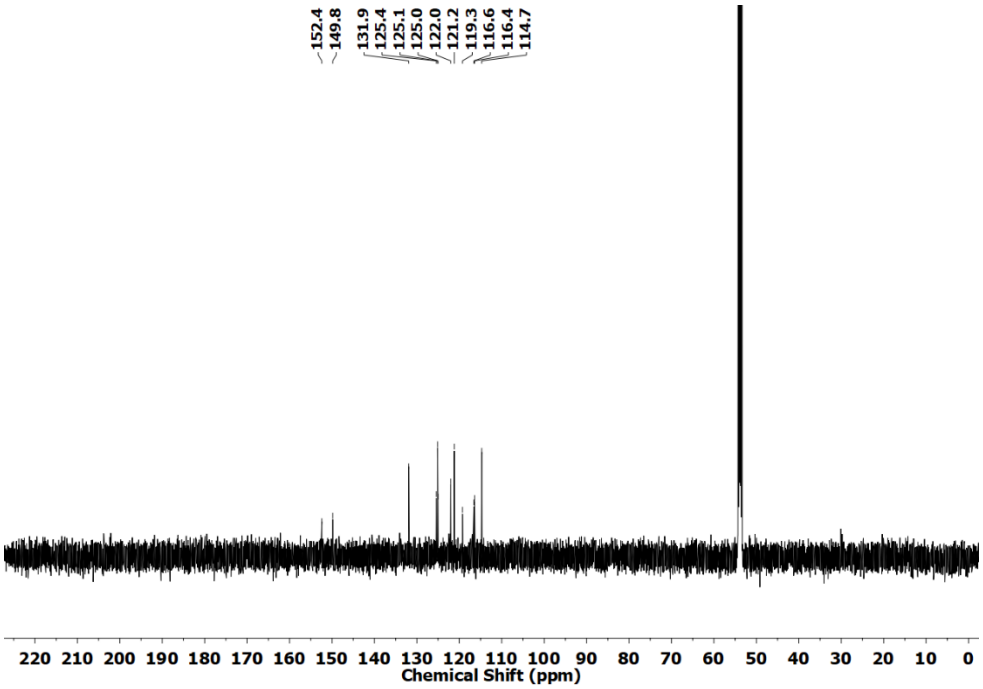


Figure A16 ^{13}C NMR (126 MHz) of 2.1g in CD_2Cl_2 at 298 K

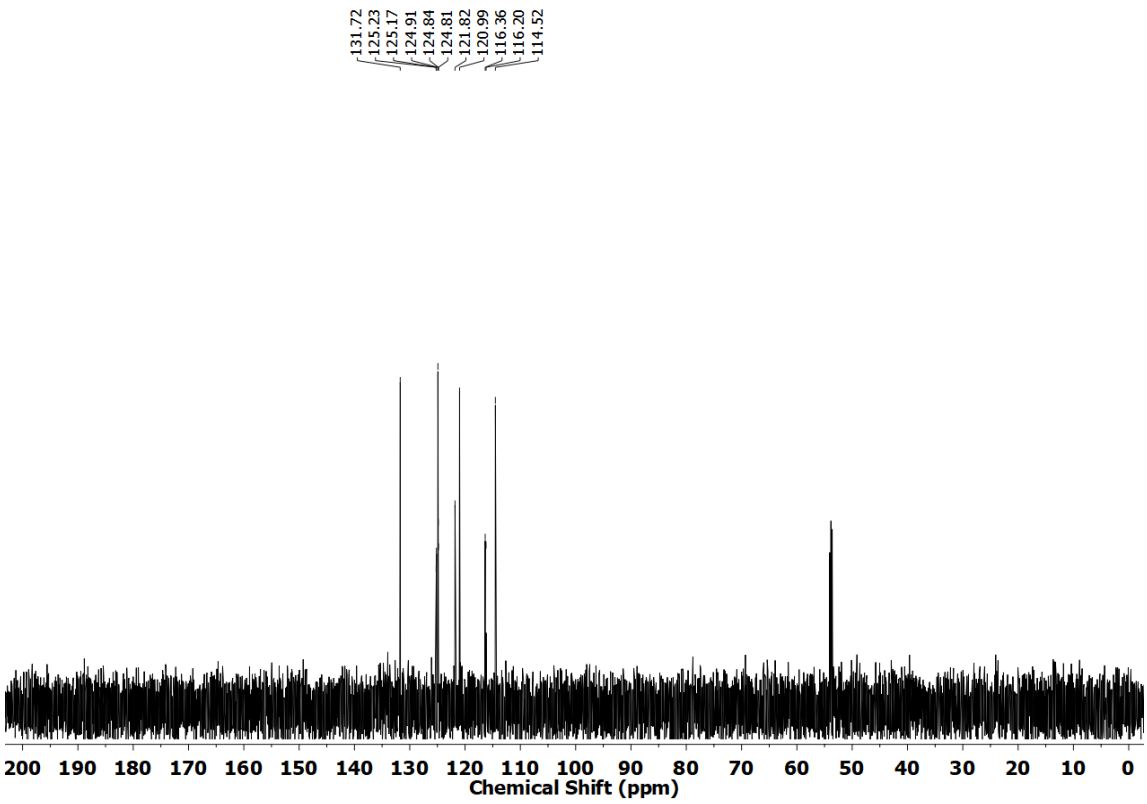


Figure A17 DEPT-135 (126 MHz) of 2.1g in CD_2Cl_2 at 298 K

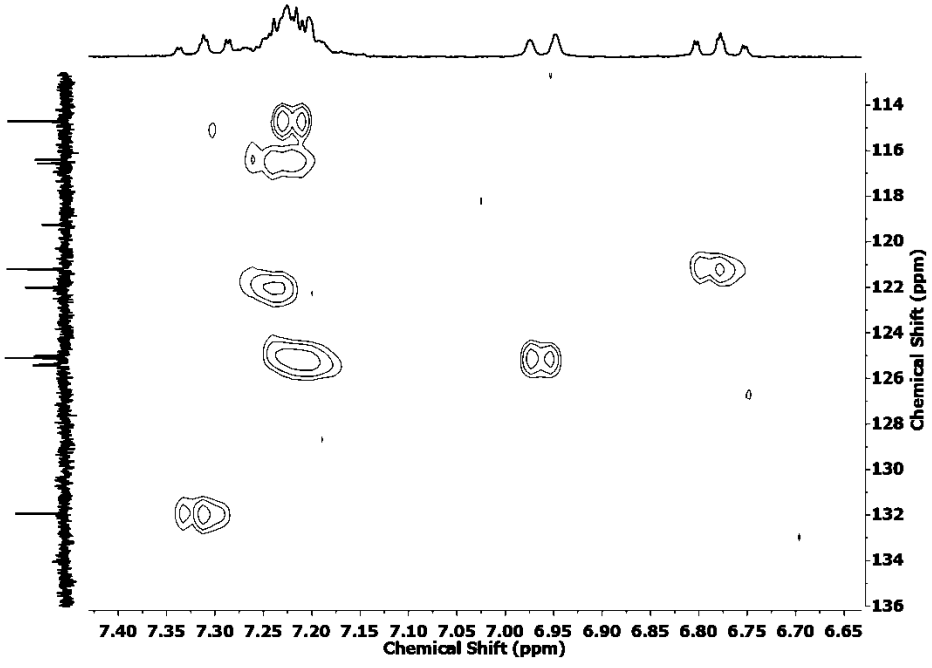


Figure A18 HSQC (500 MHz, 126 MHz) of 2.1g in CD_2Cl_2

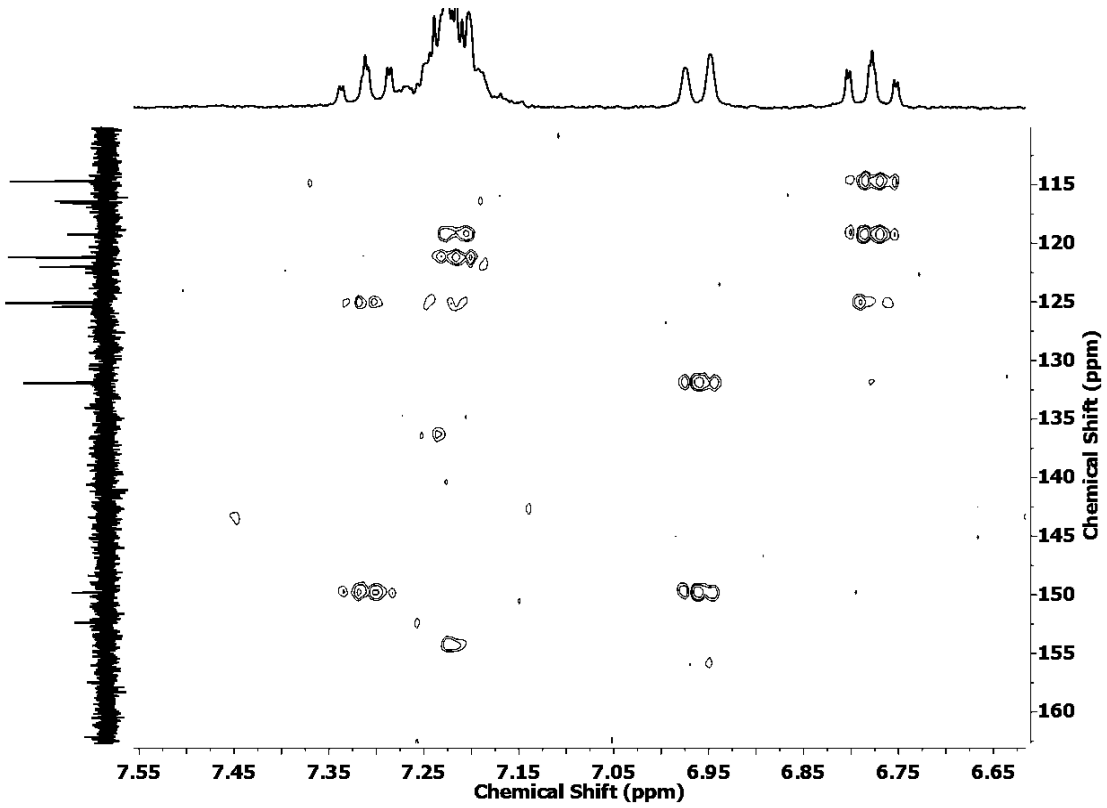


Figure A19 HMBC (500 MHz, 126 MHz) of 2.1g in CD_2Cl_2

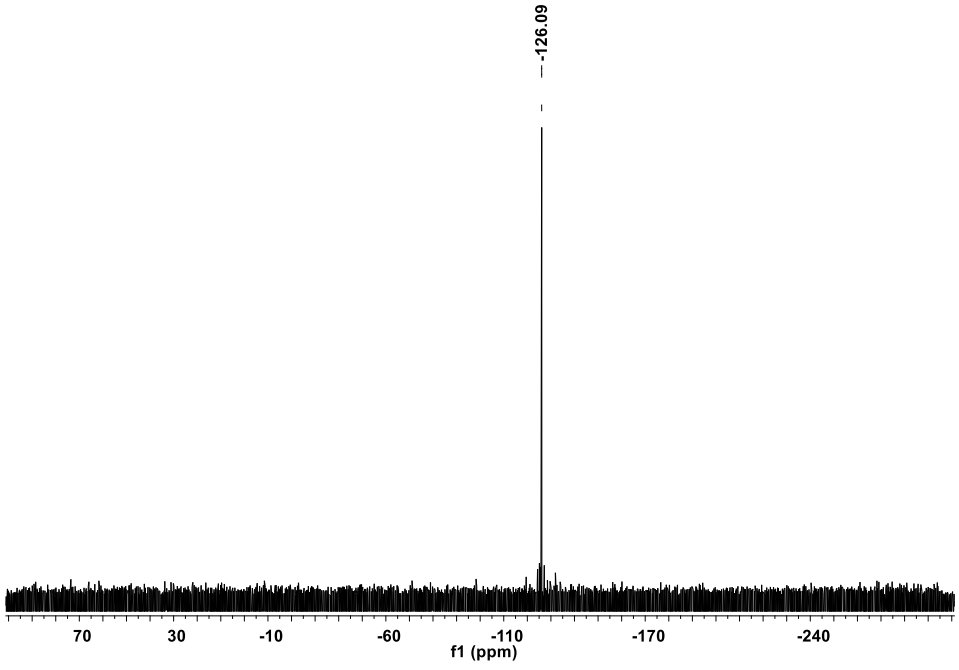


Figure A20 ^{19}F NMR (283 MHz) of 2.1g in CD_2Cl_2 at 298 K

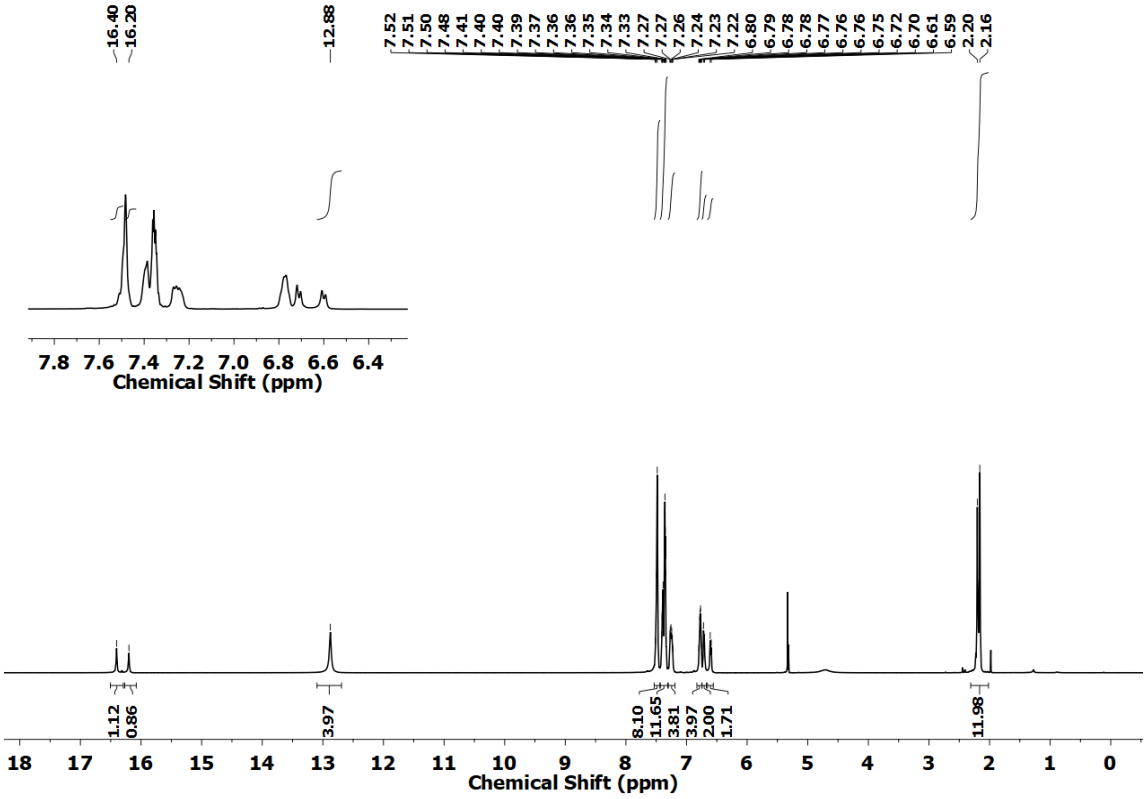


Figure A21 ^{1}H NMR (500 MHz) of 2.2a in CD_2Cl_2 at 298 K

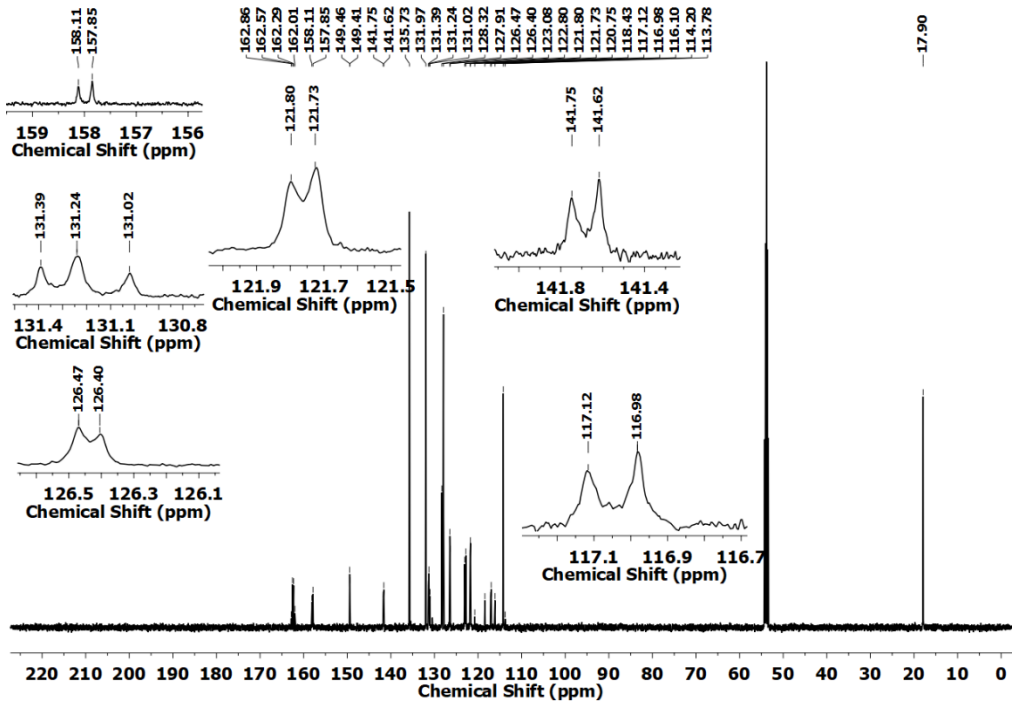


Figure A22 ^{13}C NMR (126 MHz) of 2.2a in CD_2Cl_2 at 298 K

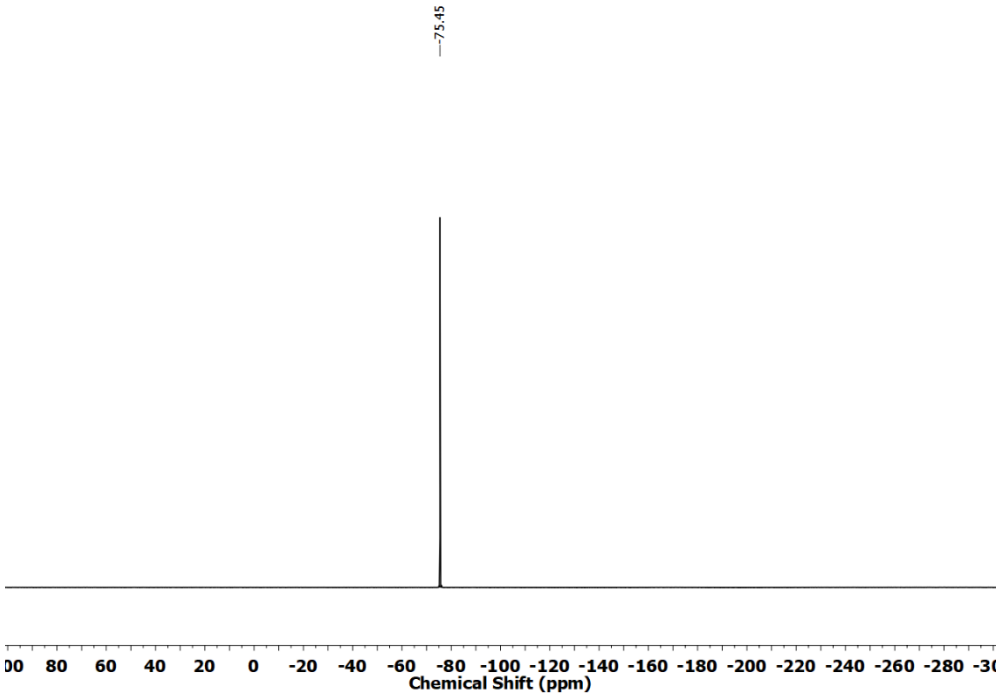


Figure A23 ^{19}F NMR (282 MHz) of 2.2a in $CDCl_3$ at 298 K

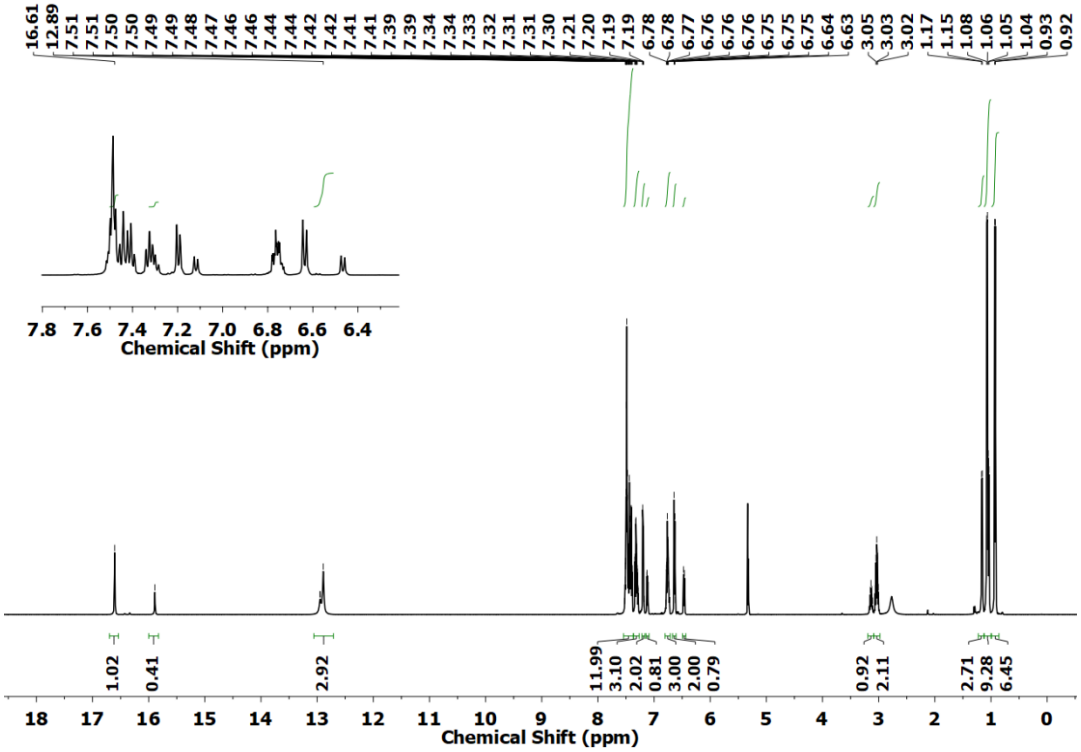


Figure A24 ^{1}H NMR (500 MHz) of 2.2b in CD_2Cl_2 at 298 K

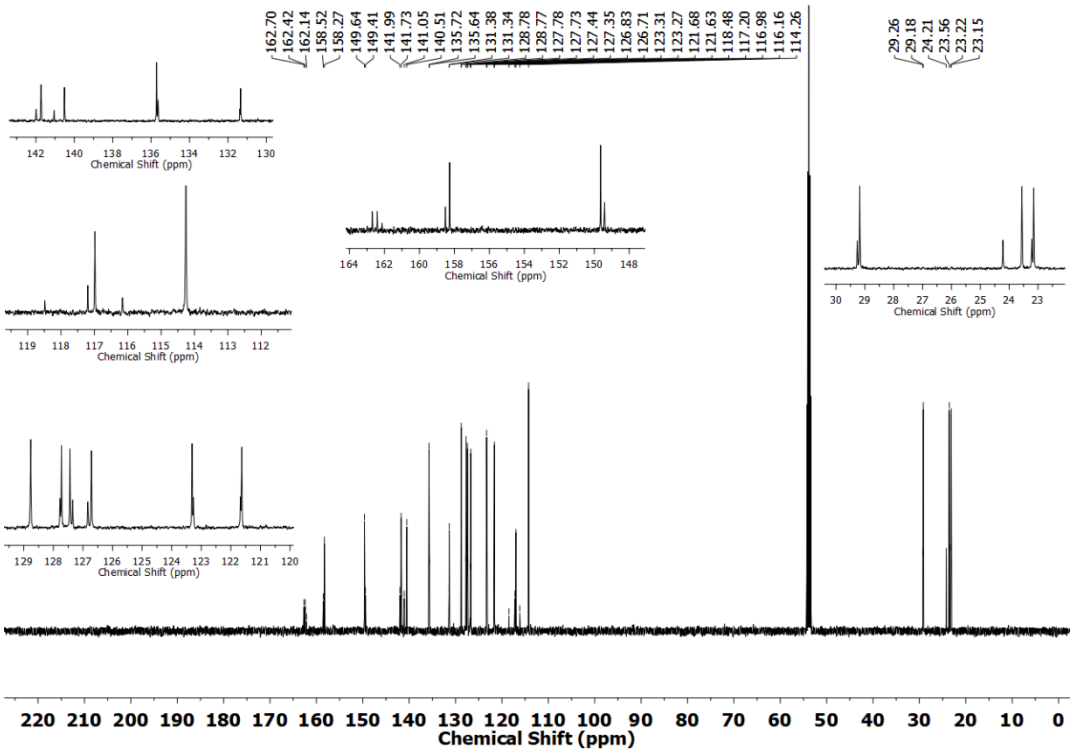


Figure A25 ^{13}C NMR (126 MHz) of 2.2b in CD_2Cl_2 at 298 K

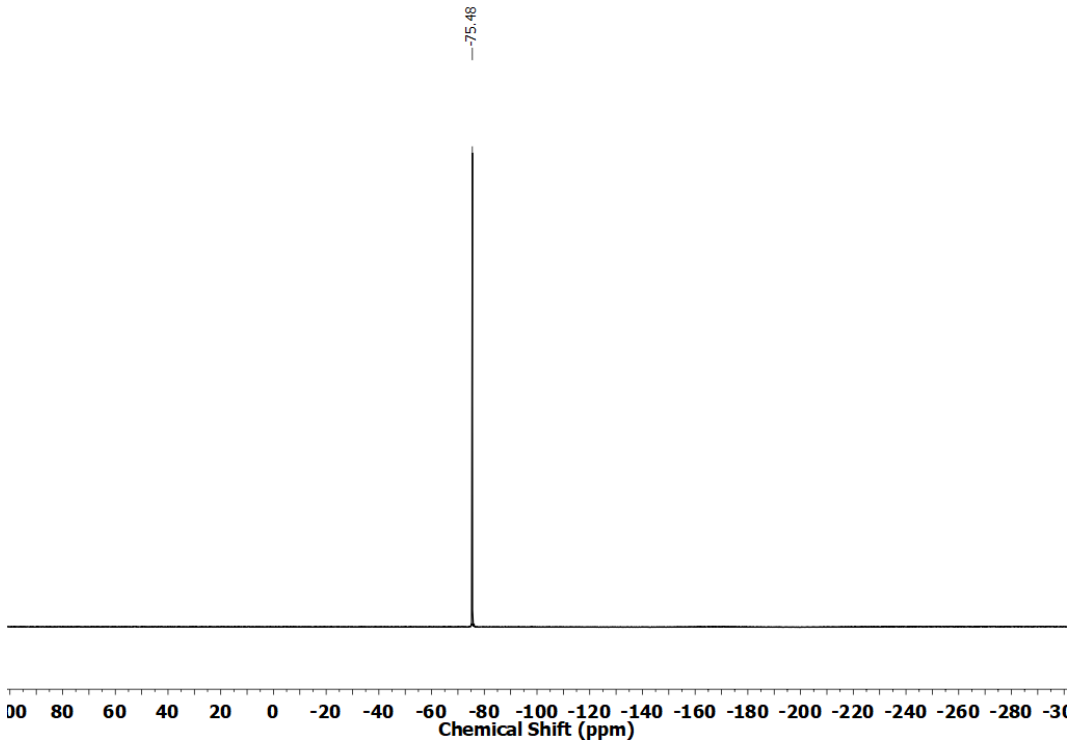


Figure A26 ^{19}F NMR (282 MHz) of 2.2b in CD_2Cl_2 at 298 K

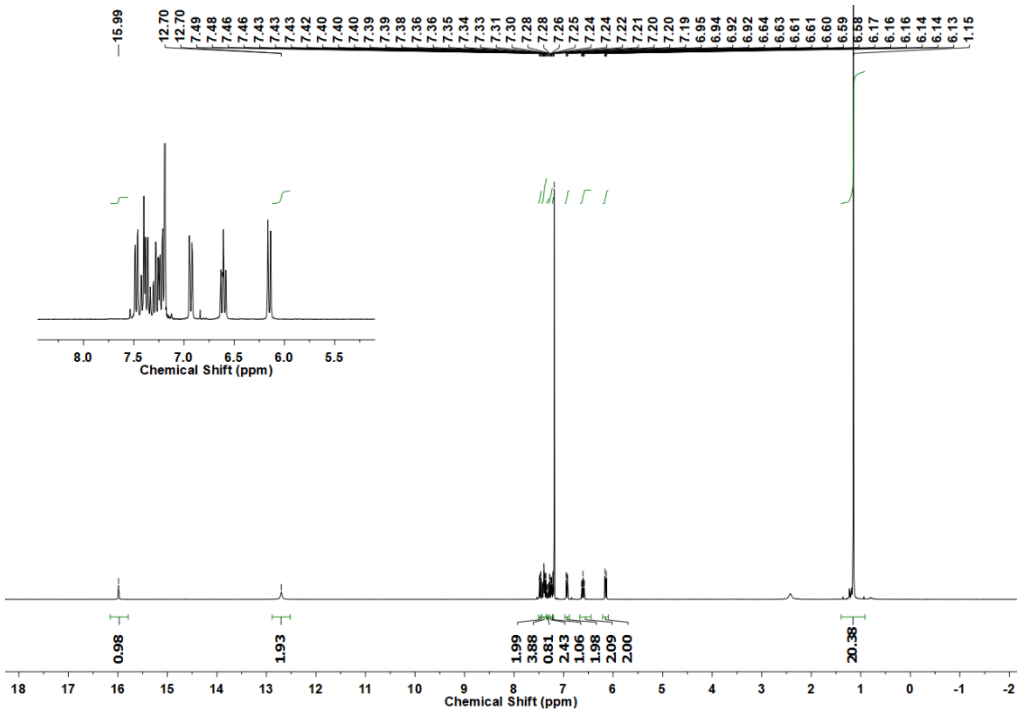


Figure A27 ^{1}H NMR (300 MHz) of 2.2c in $CDCl_3$ at 298 K

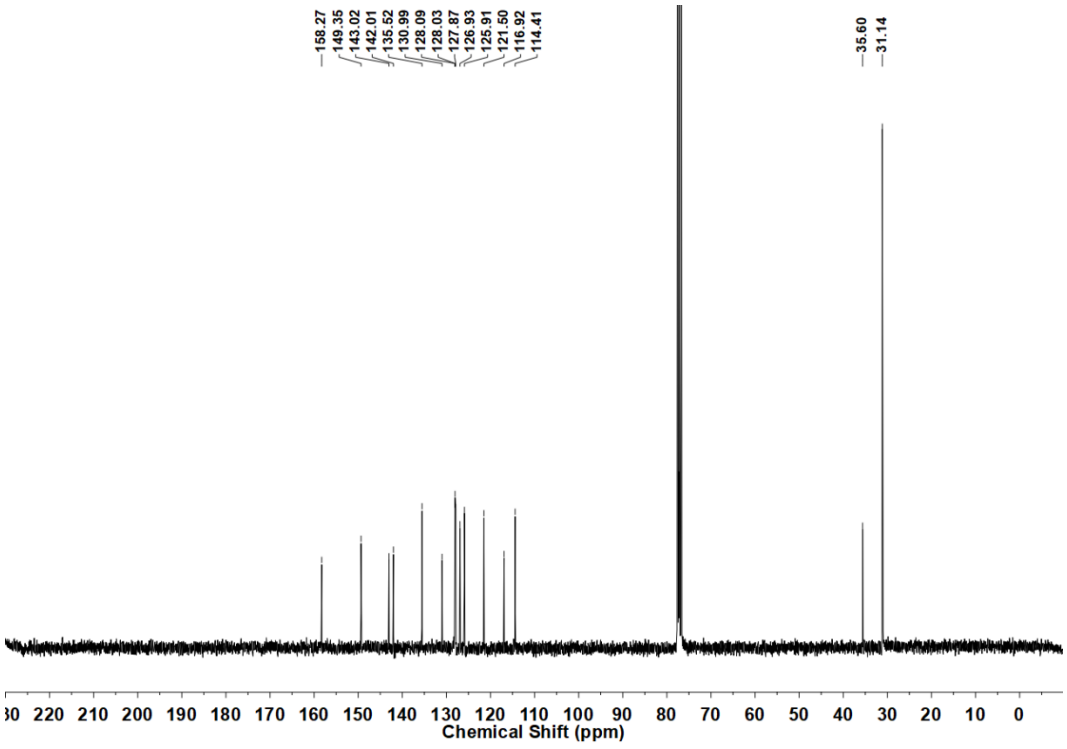


Figure A28 ^{13}C NMR (75 MHz) of 2.2c in $CDCl_3$ at 298 K

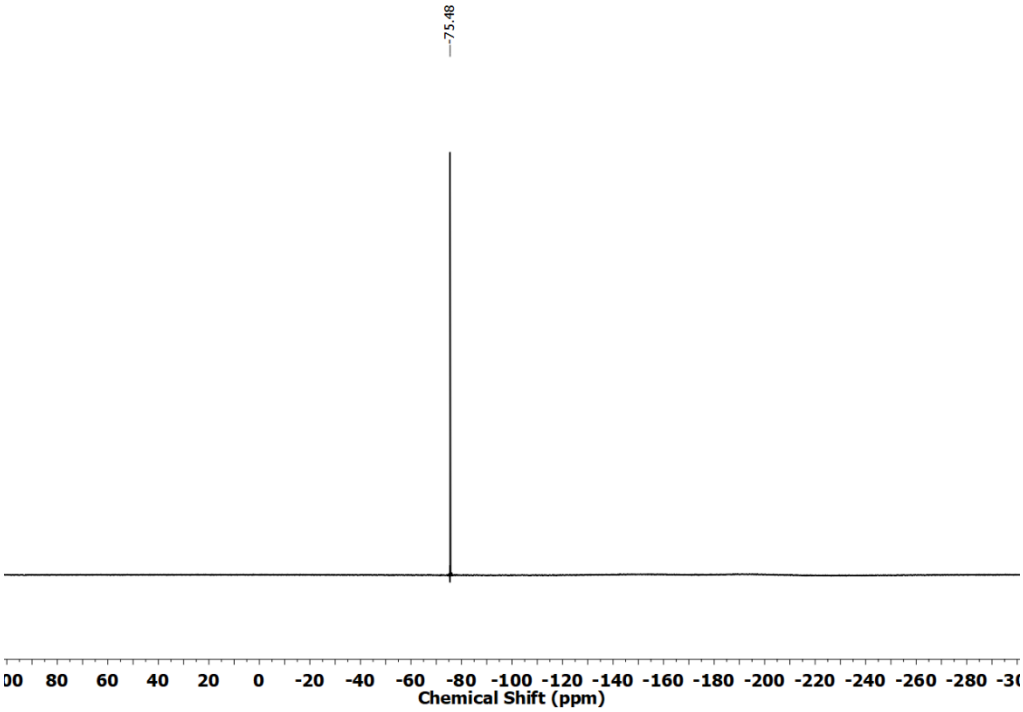


Figure A29 ^{19}F NMR (282 MHz) of 2.2c in CD_2Cl_2 at 298 K

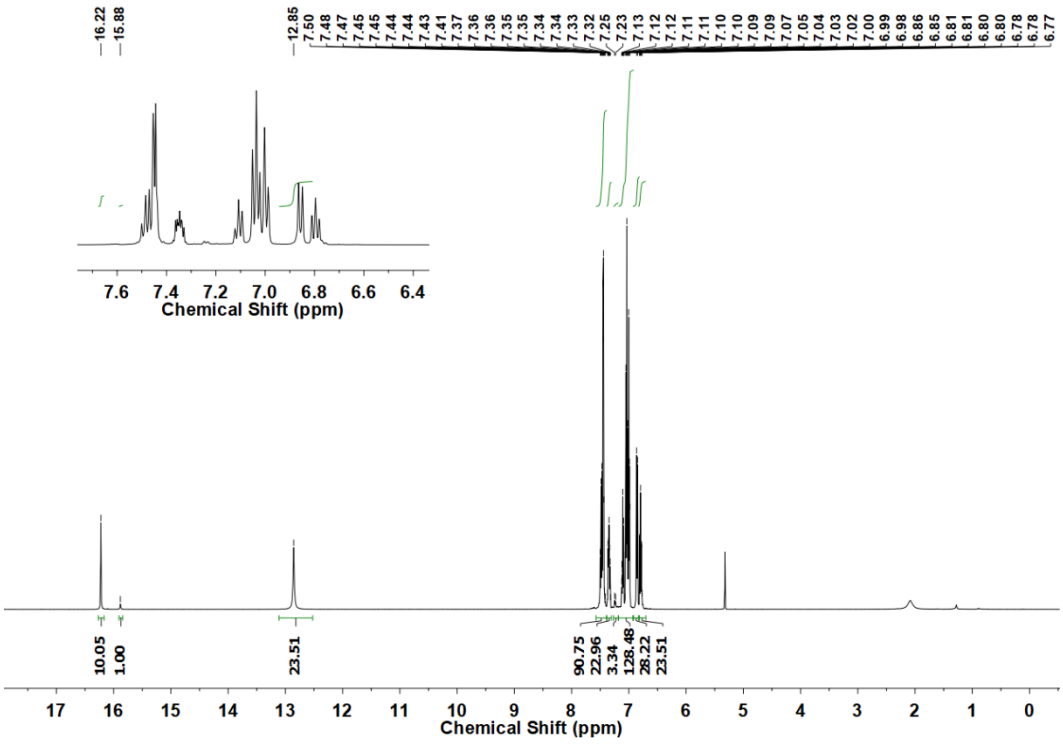


Figure A30 ^{1}H NMR (500 MHz) of 2.2d in CD_2Cl_2 at 298 K

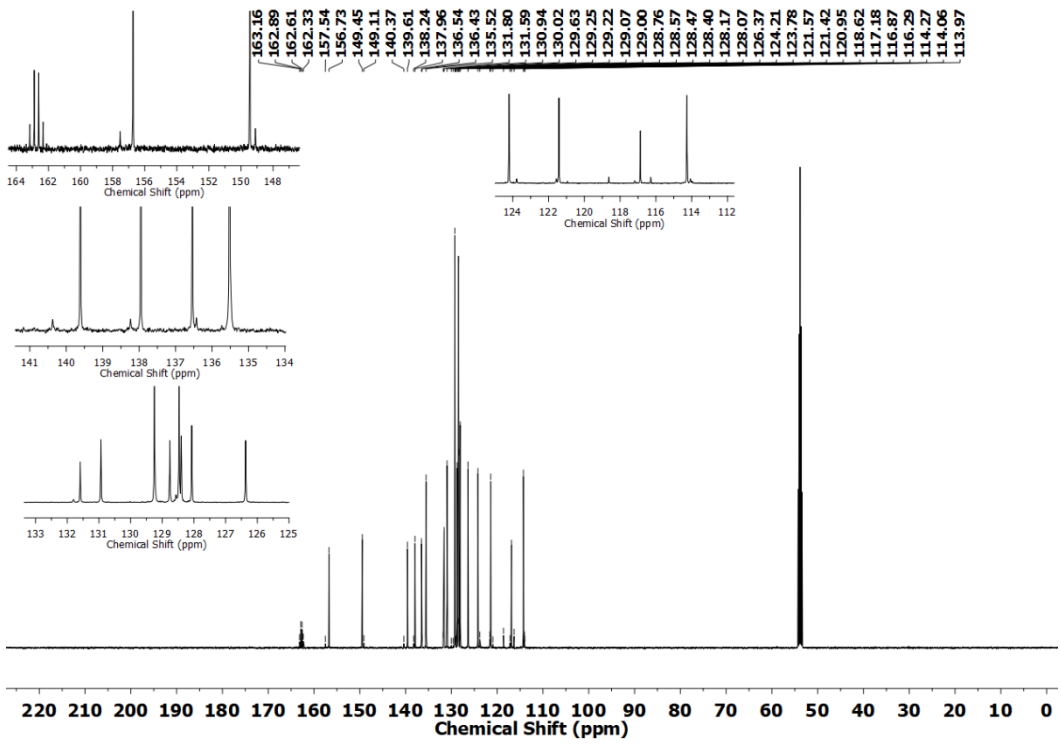


Figure A31 ^{13}C NMR (126 MHz) of 2.2d in CD_2Cl_2 at 298 K

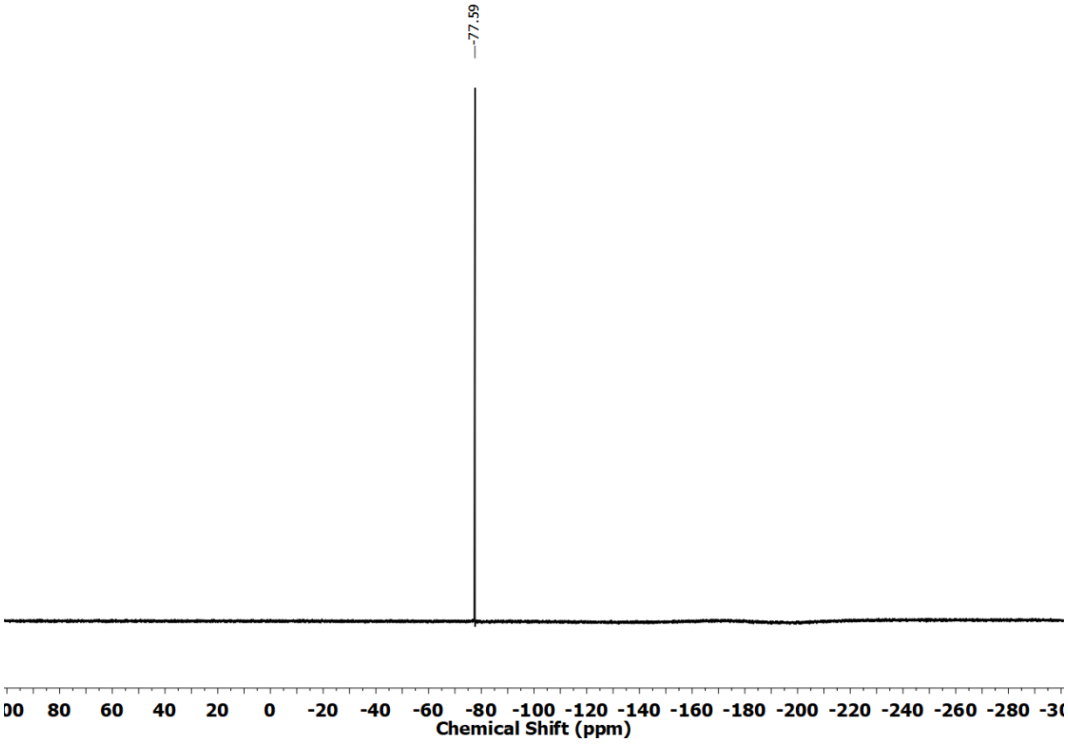


Figure A32 ^{19}F NMR (283 MHz) of 2.2d in CD_2Cl_2 at 298 K

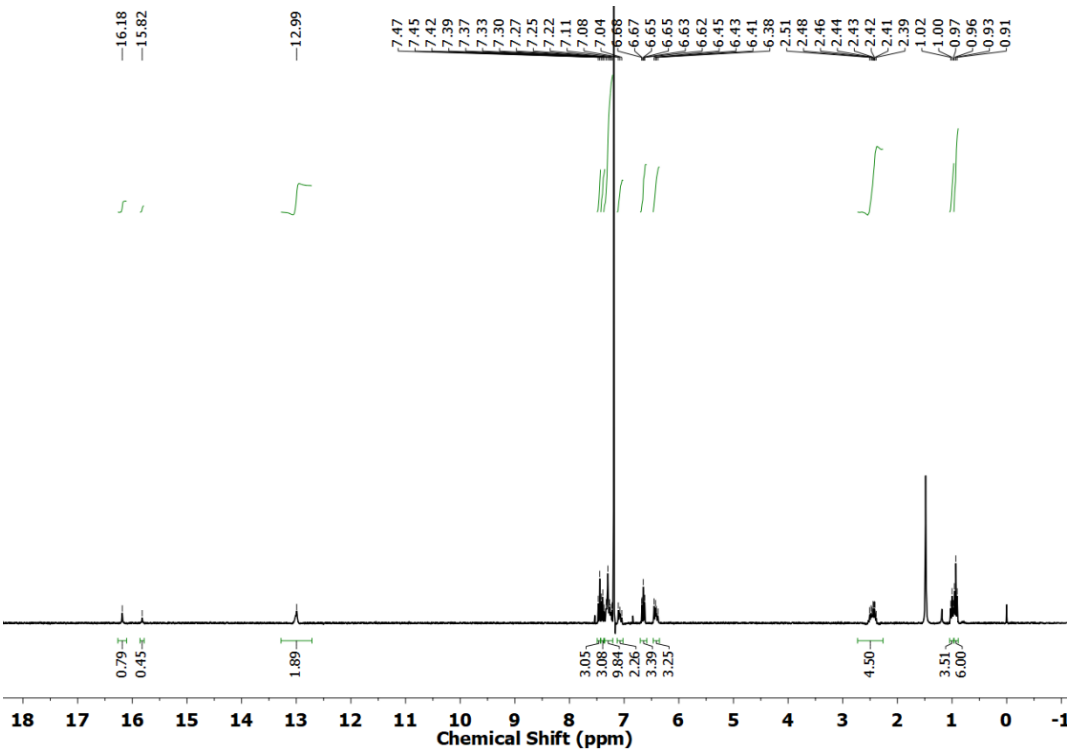


Figure A33 ^{1}H NMR (300 MHz) of 2.2e in $CDCl_3$ at 298 K

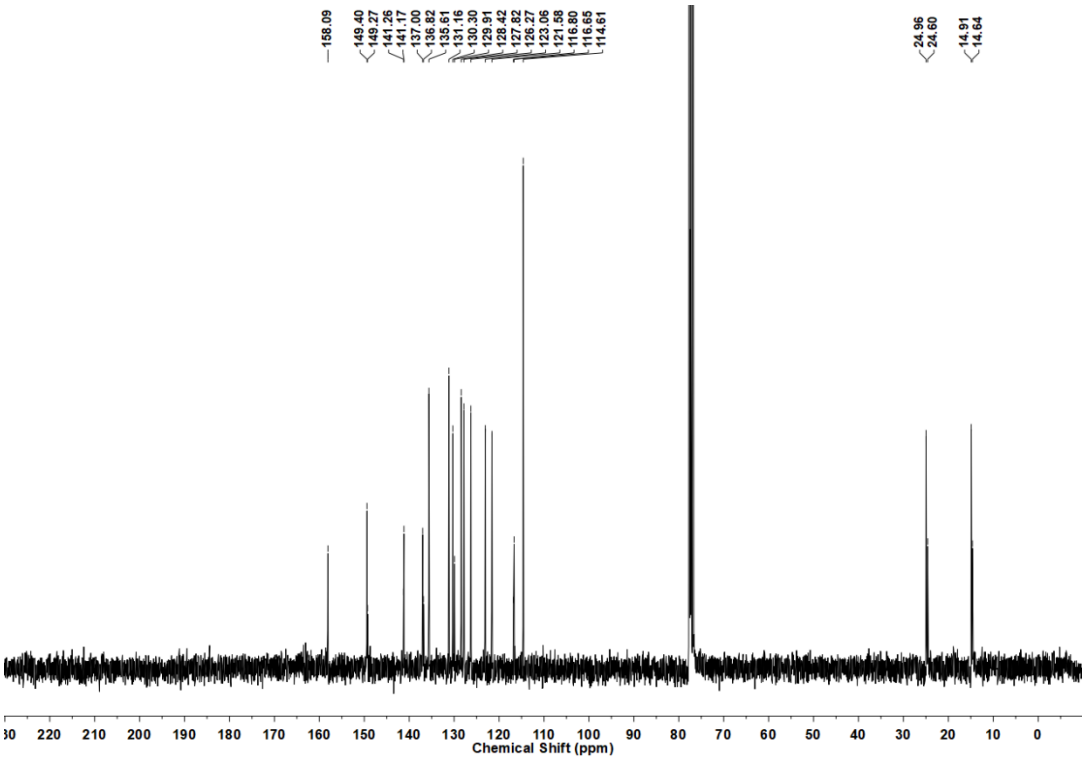


Figure A34 ^{13}C NMR (76 MHz) of 2.2e in $CDCl_3$ at 298 K

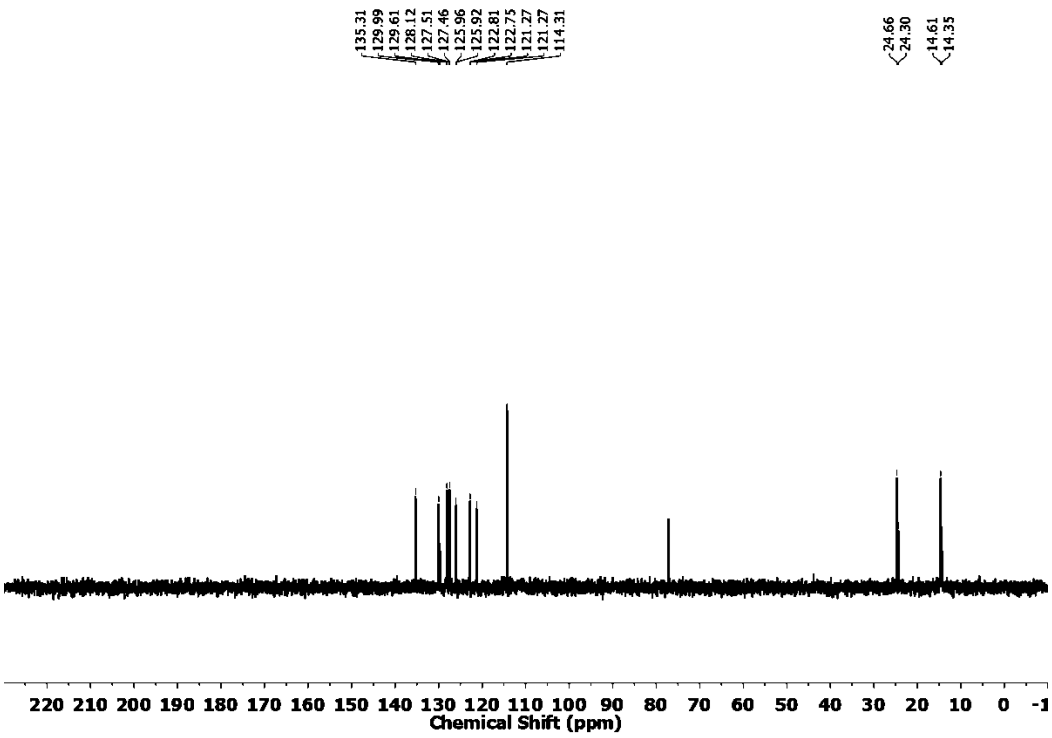


Figure A35 DEPT 135 (76 MHz) of 2.2e in $CDCl_3$ at 298 K

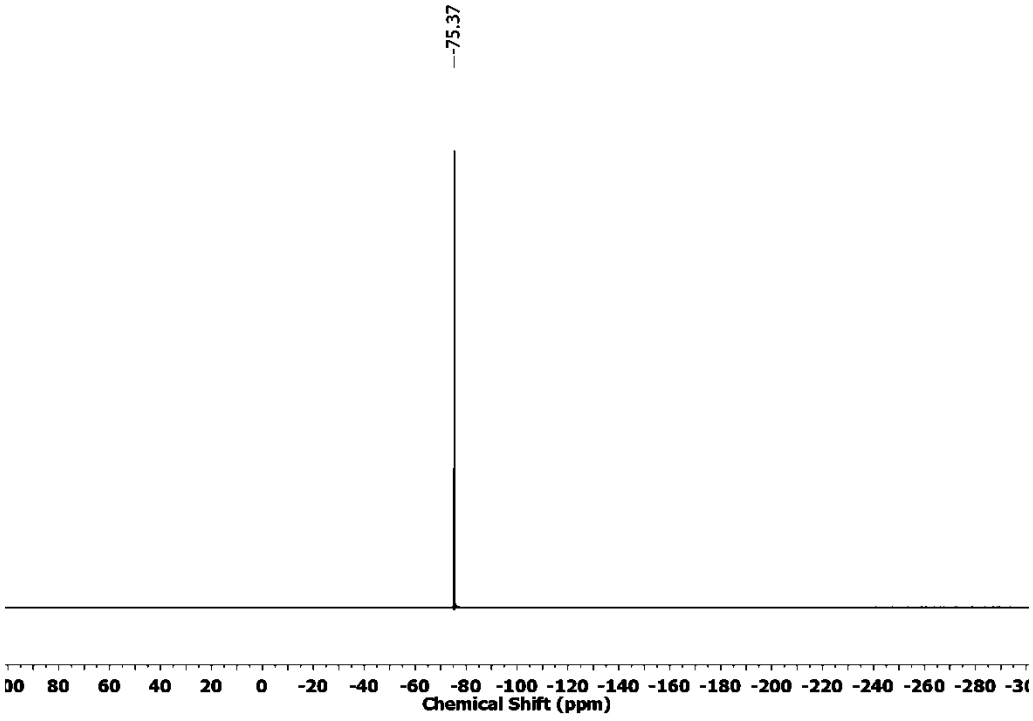


Figure A36 ^{19}F NMR (283 MHz) of 2.2e in $CDCl_3$ at 298 K

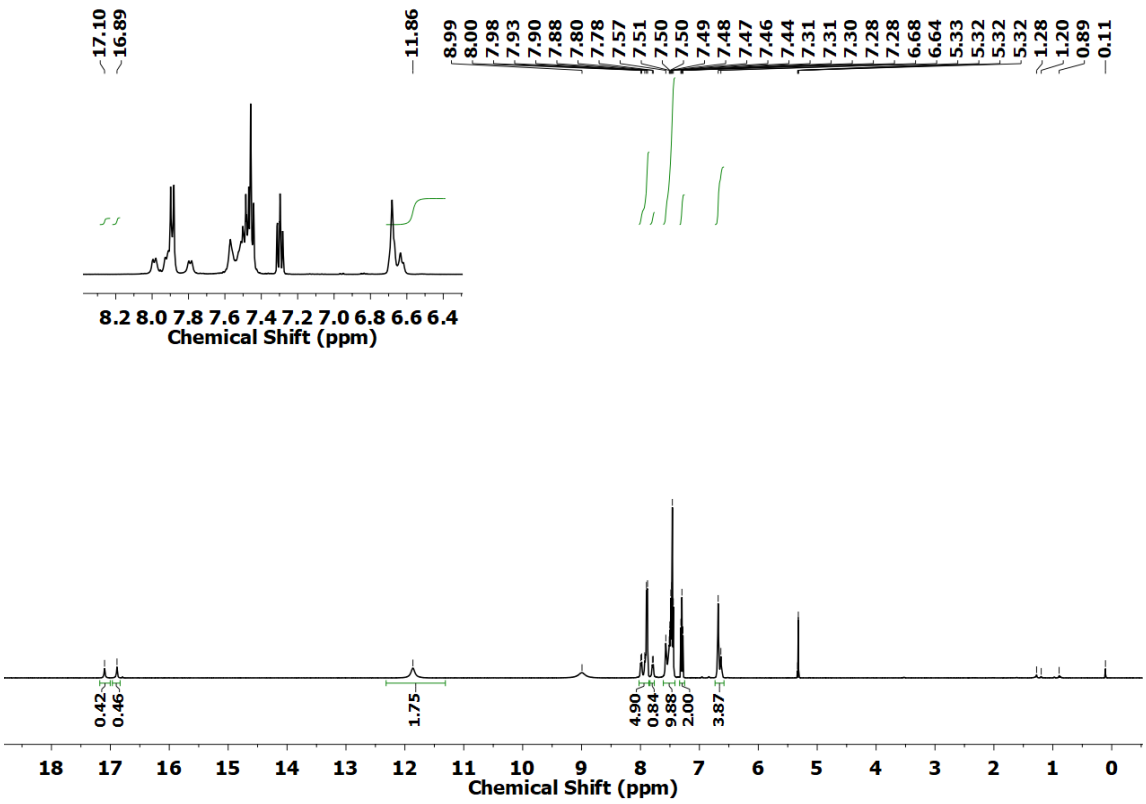


Figure A37 ^{1}H NMR (500 MHz) of 2.2f in CD_2Cl_2 at 298 K

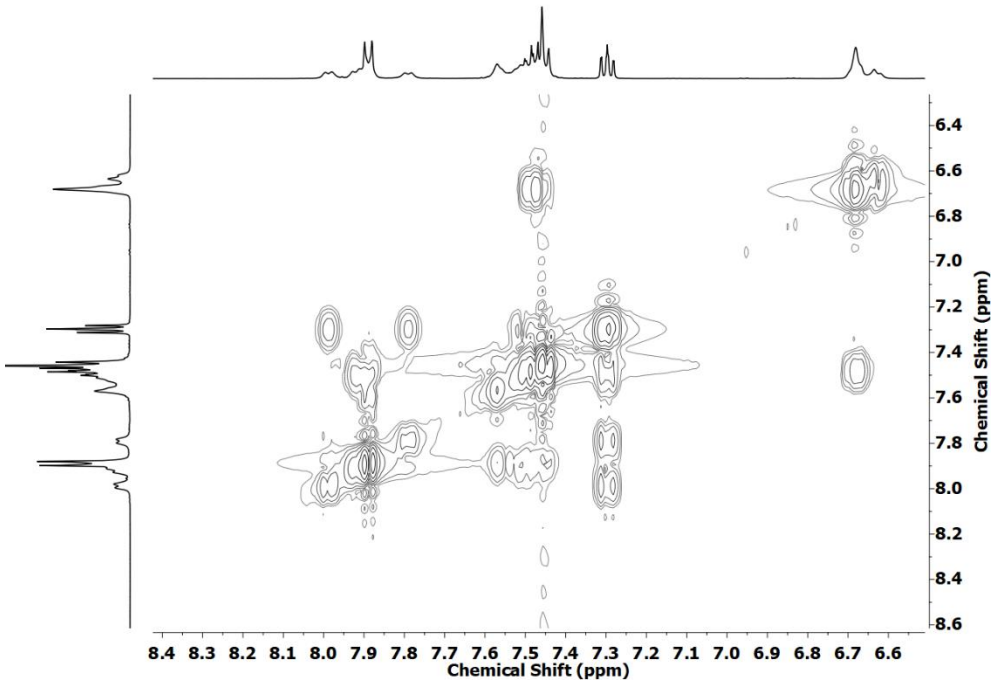


Figure A38 COSY (500 MHz, 500 MHz) of 2.2f in CD_2Cl_2 at 298 K

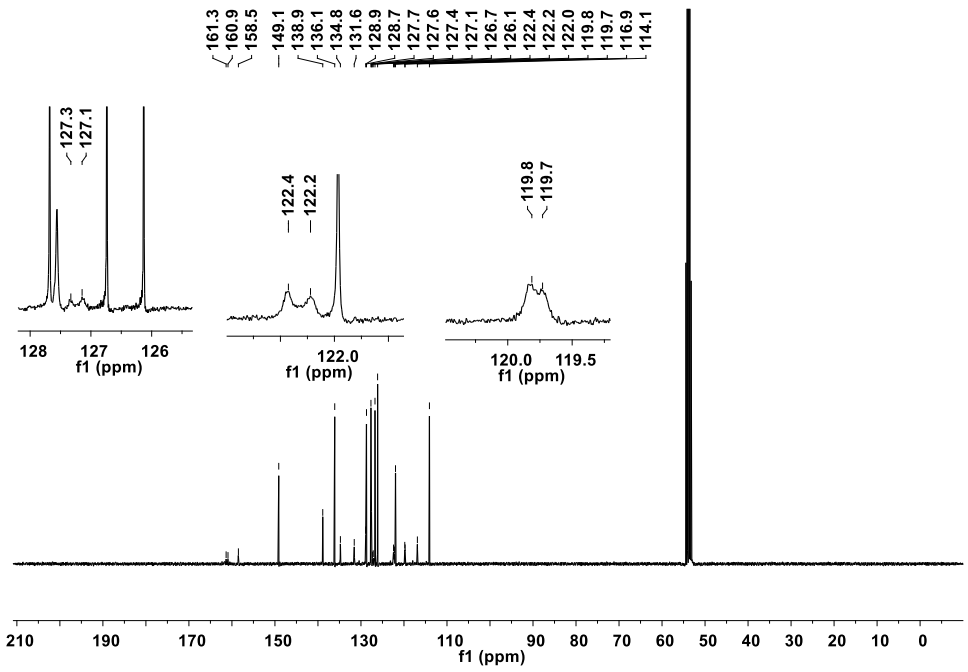


Figure A39 ^{13}C NMR (91 MHz) of 2.2f in CD_2Cl_2 at 298 K

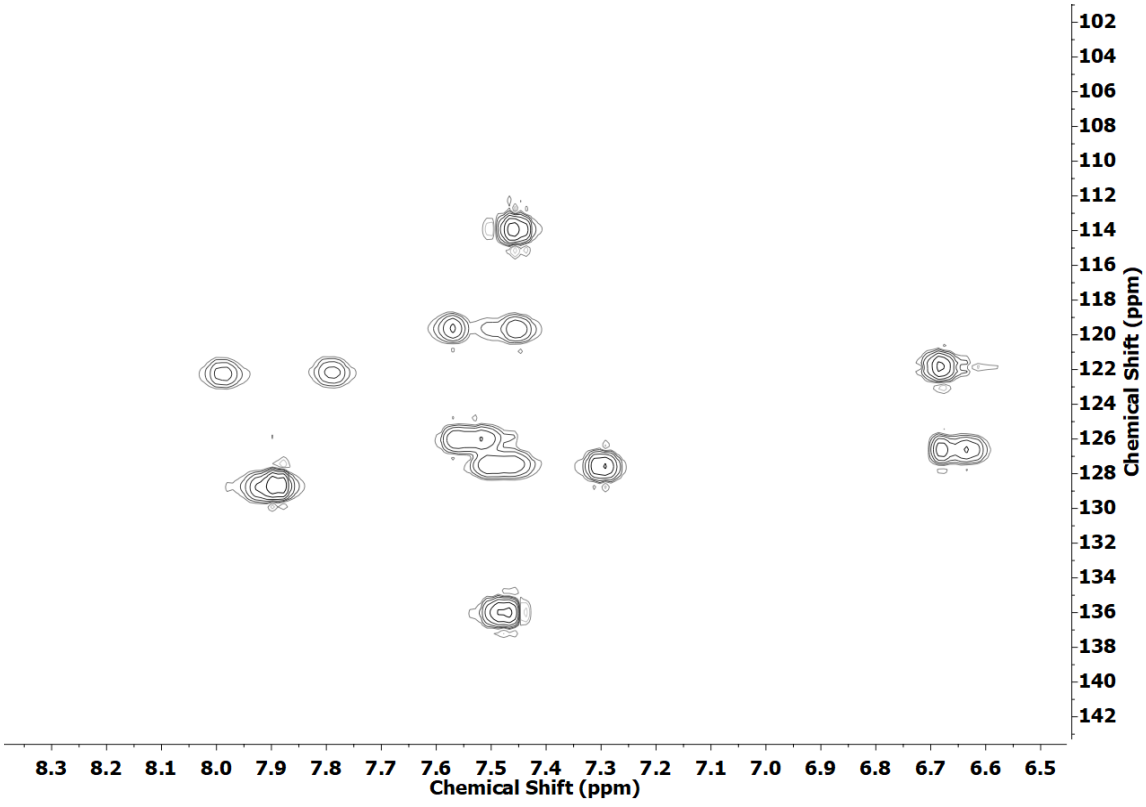


Figure A40 HSQC (500 MHz, 126 MHz) of 2.2f in CD_2Cl_2

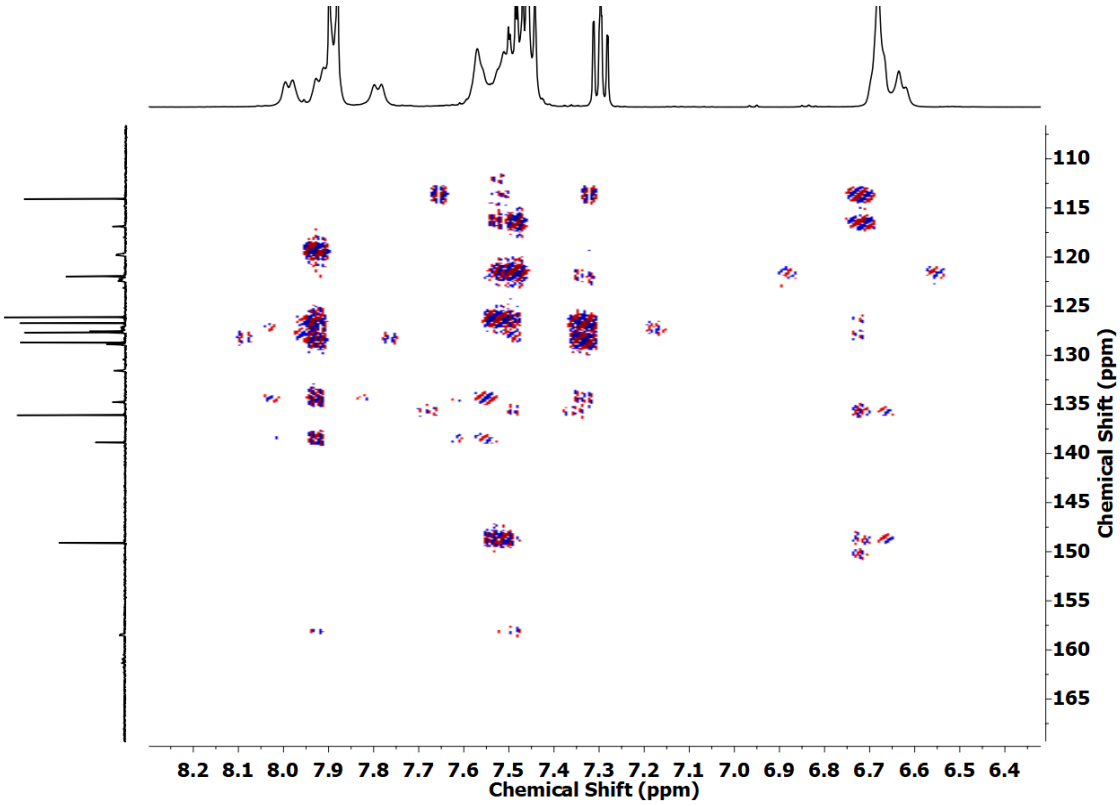


Figure A41 HMBC (500 MHz, 126 MHz) of 2.2f in CD_2Cl_2 at 298 K

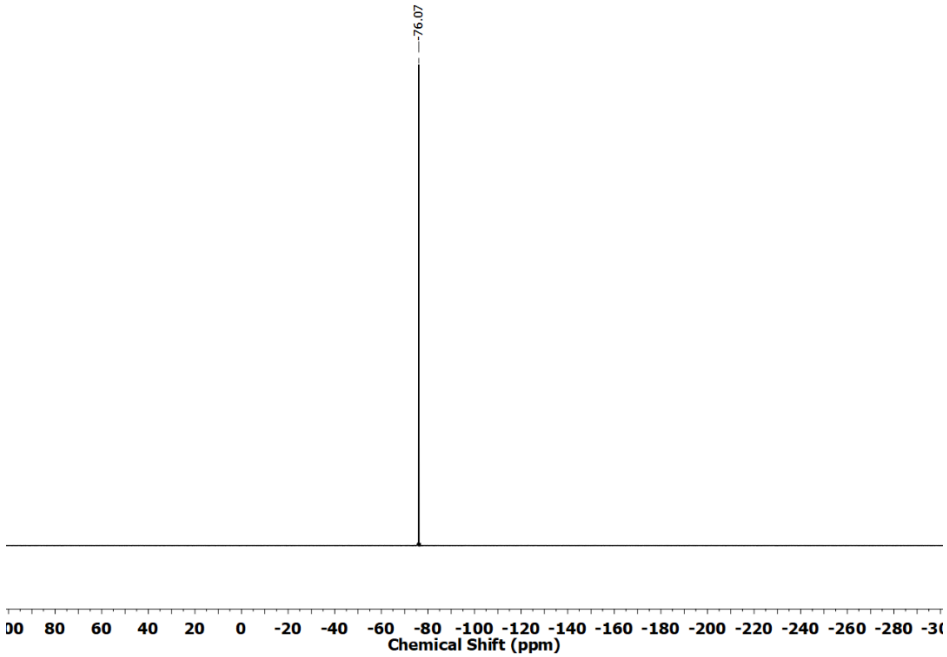


Figure A42 ^{19}F NMR (283 MHz) of 2.2f in CD_2Cl_2 at 298 K

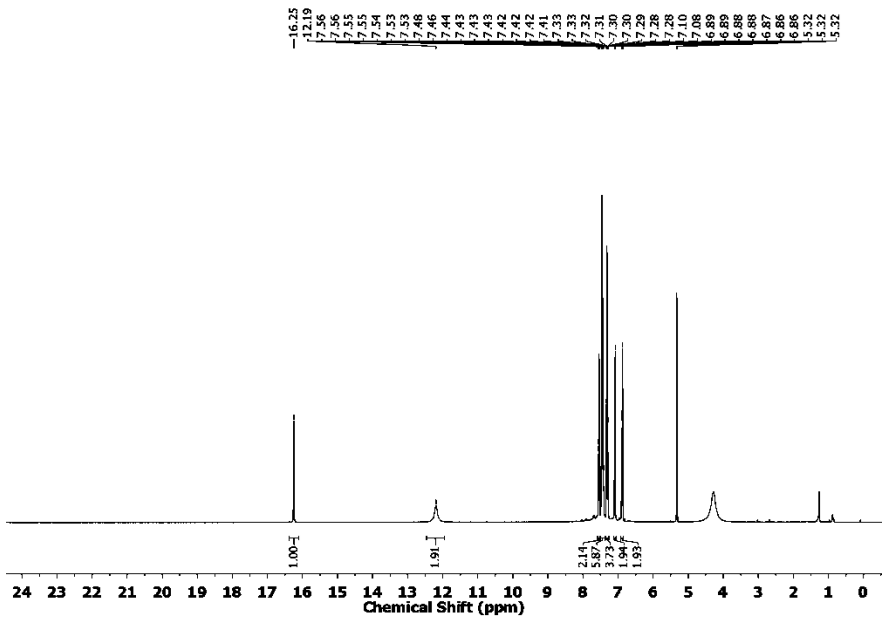


Figure A43 ^{1}H NMR (500 MHz) of 2.2g in CD2Cl2 at 298 K

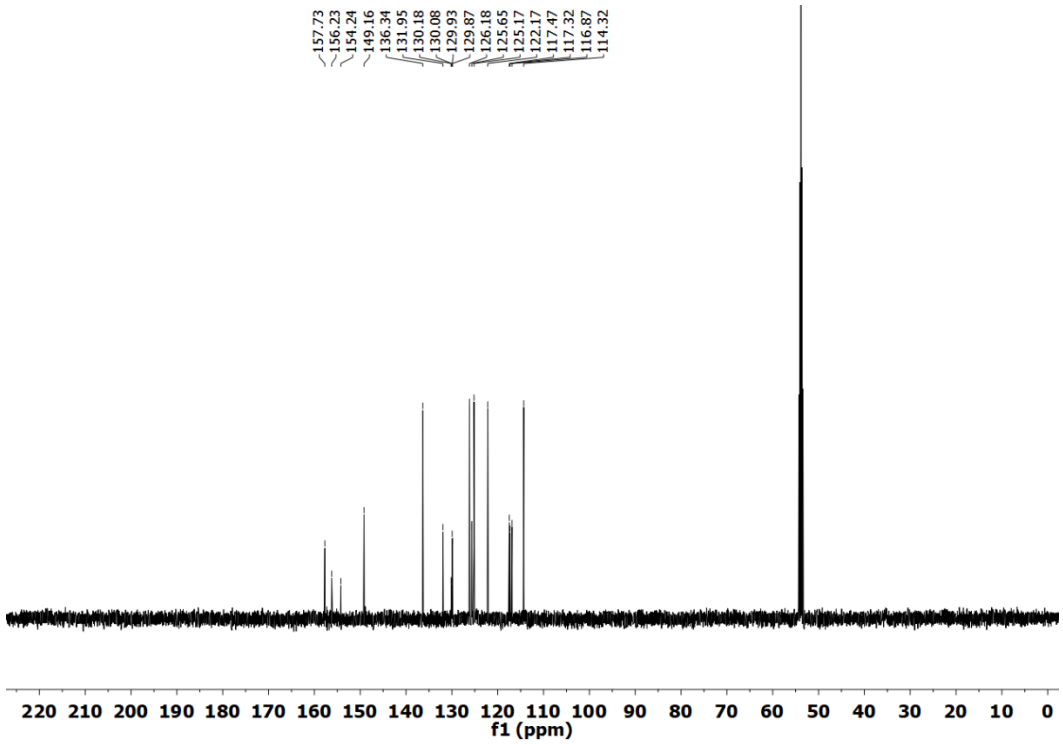


Figure A44 ^{13}C NMR (126 MHz) of 2.2g in CD_2Cl_2 at 298 K

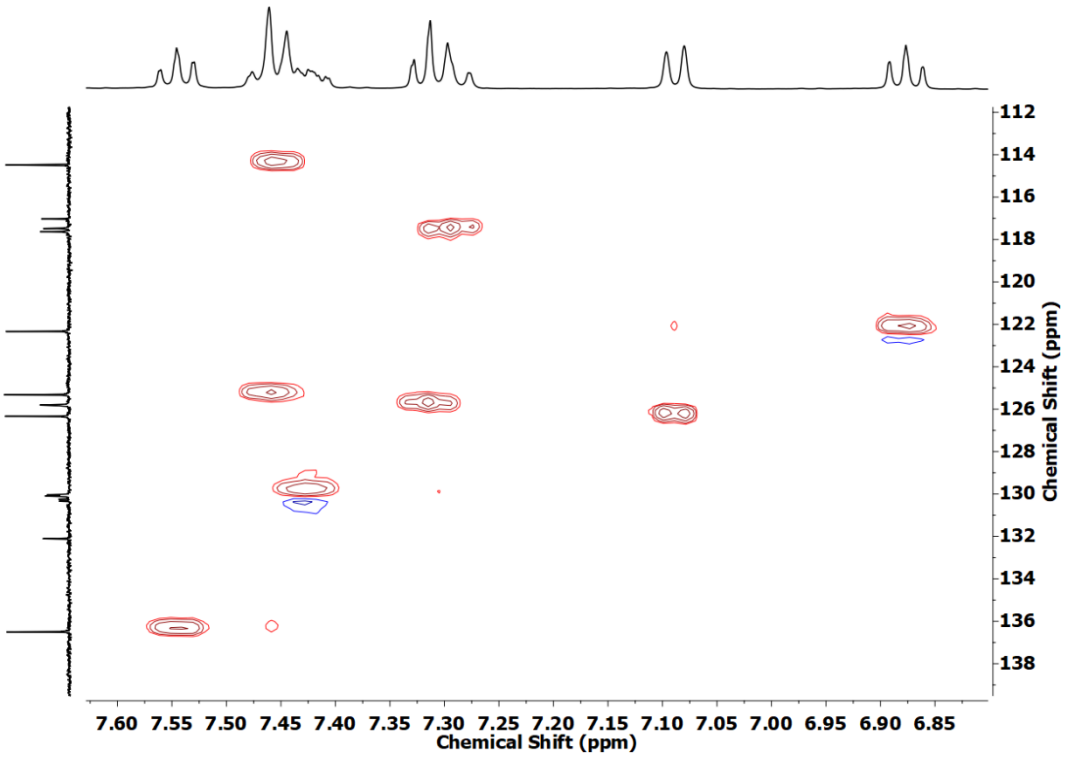


Figure A45 HSQC (500 MHz, 126 MHz) of 2.2g in CD_2Cl_2 at 298 K

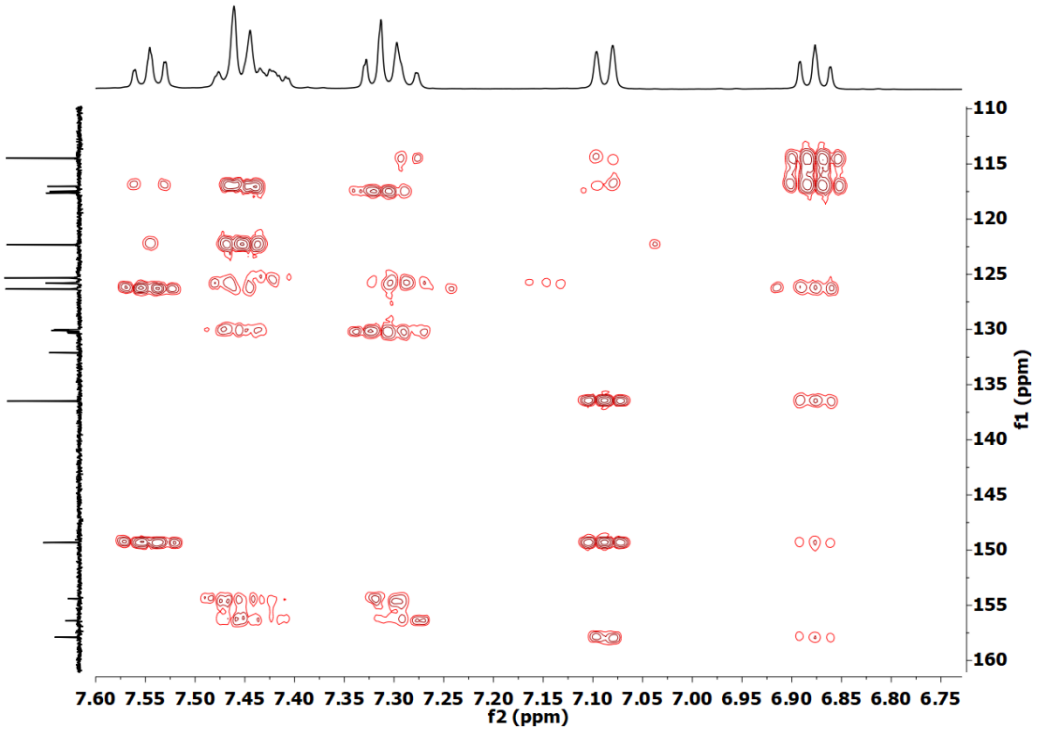


Figure A46 HMBC (500 MHz, 126 MHz) of 2.2g in CD_2Cl_2 at 298 K

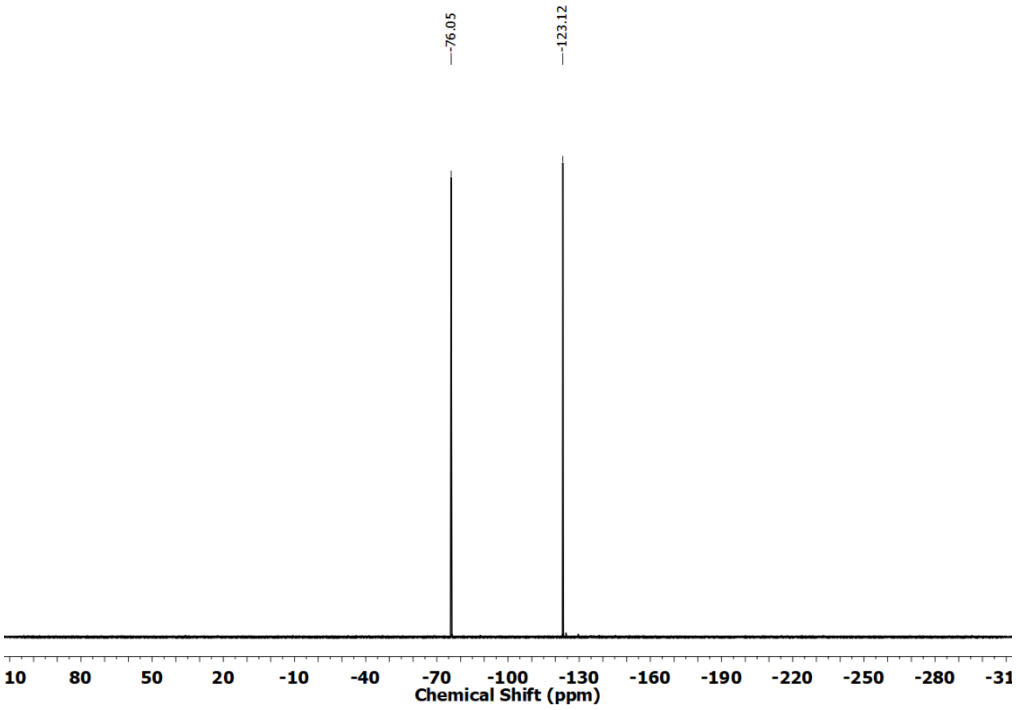


Figure A47 ^{19}F NMR (283 MHz) of 2.2g in CD_2Cl_2 at 298 K

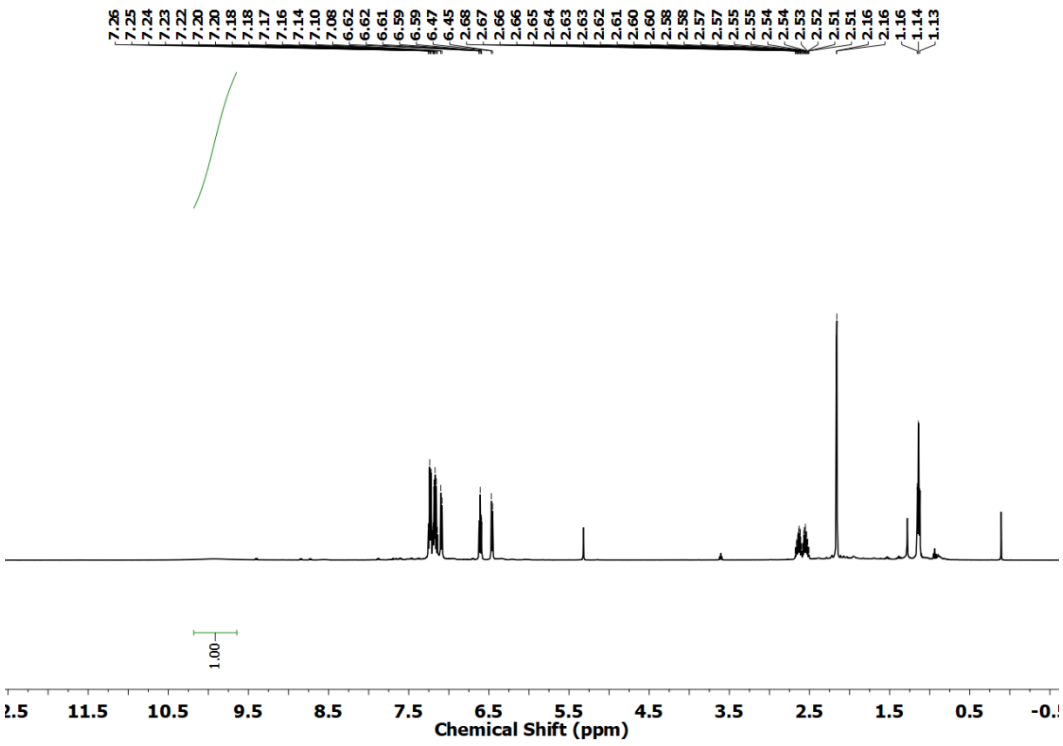


Figure A48 ^{1}H NMR (500 MHz) of 2.7a in CD_2Cl_2 at 298 K

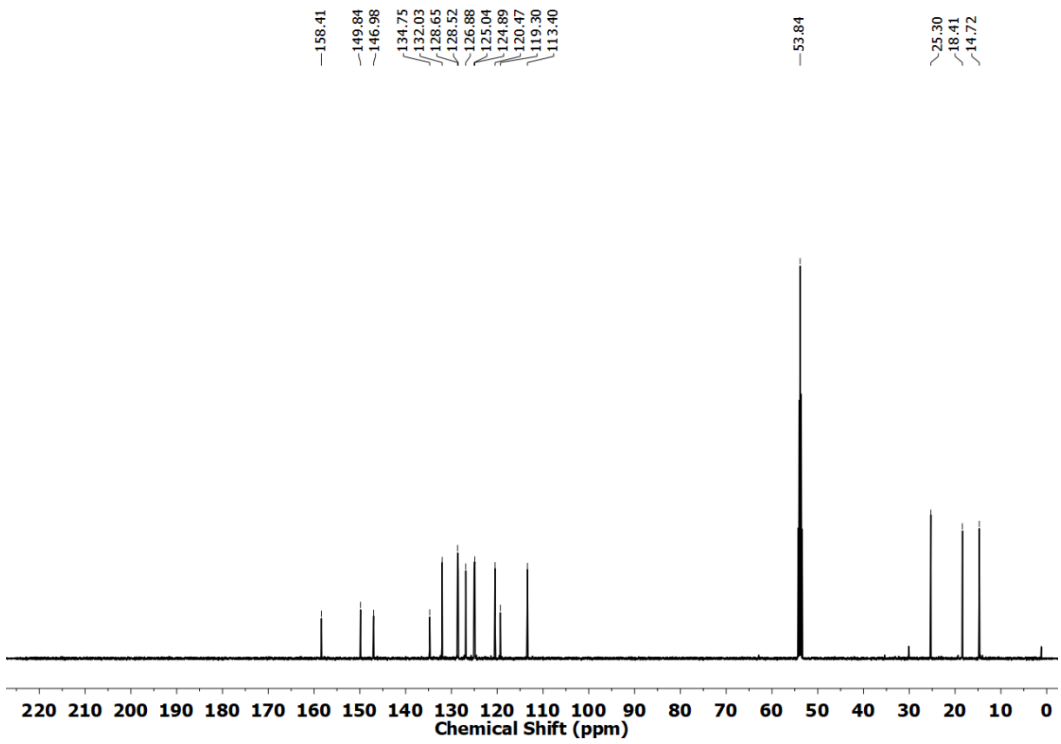


Figure A49 ^{13}C NMR (126 MHz) of 2.7a in CD_2Cl_2 at 298 K

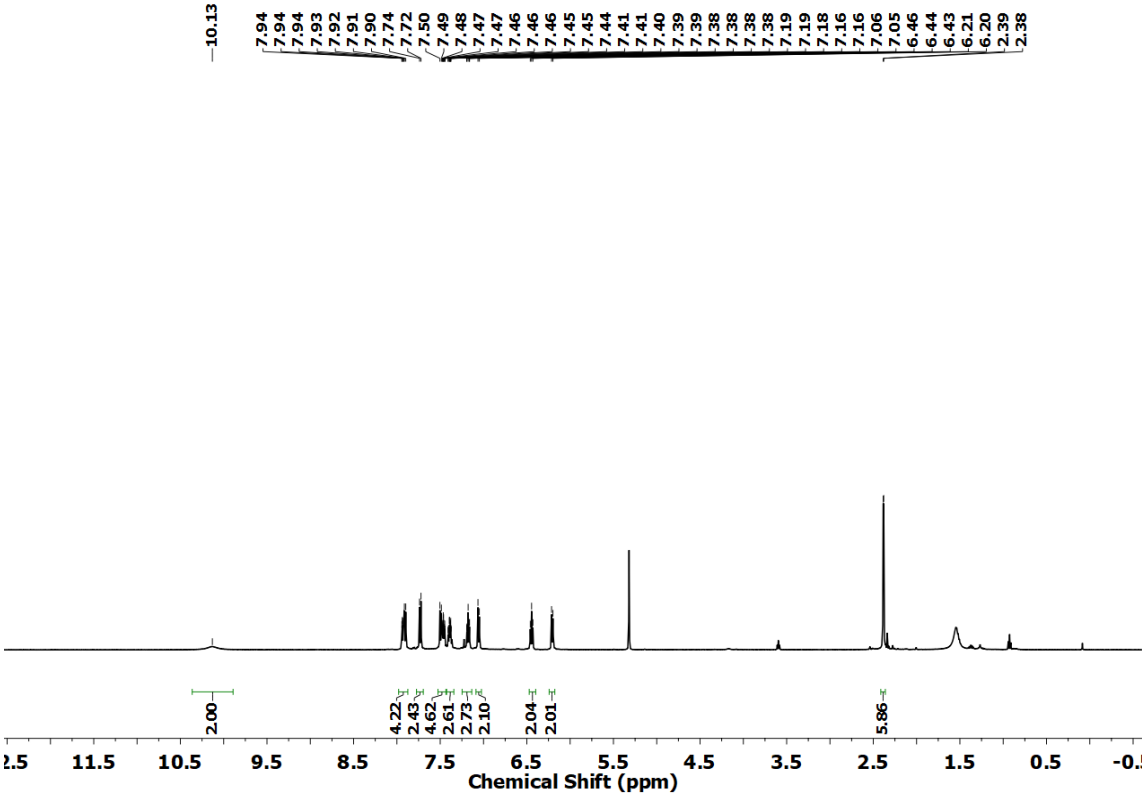


Figure A50 ^{1}H NMR (500 MHz) of 2.7b in CD_2Cl_2 at 298 K

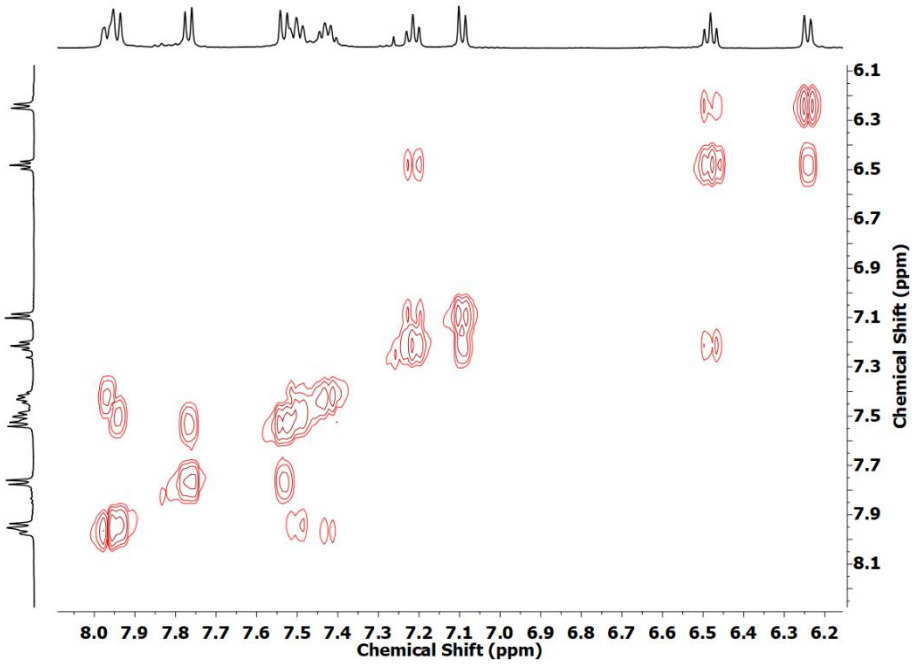


Figure A51 COSY (500 MHz, 500 MHz) of 2.7b at 298 K

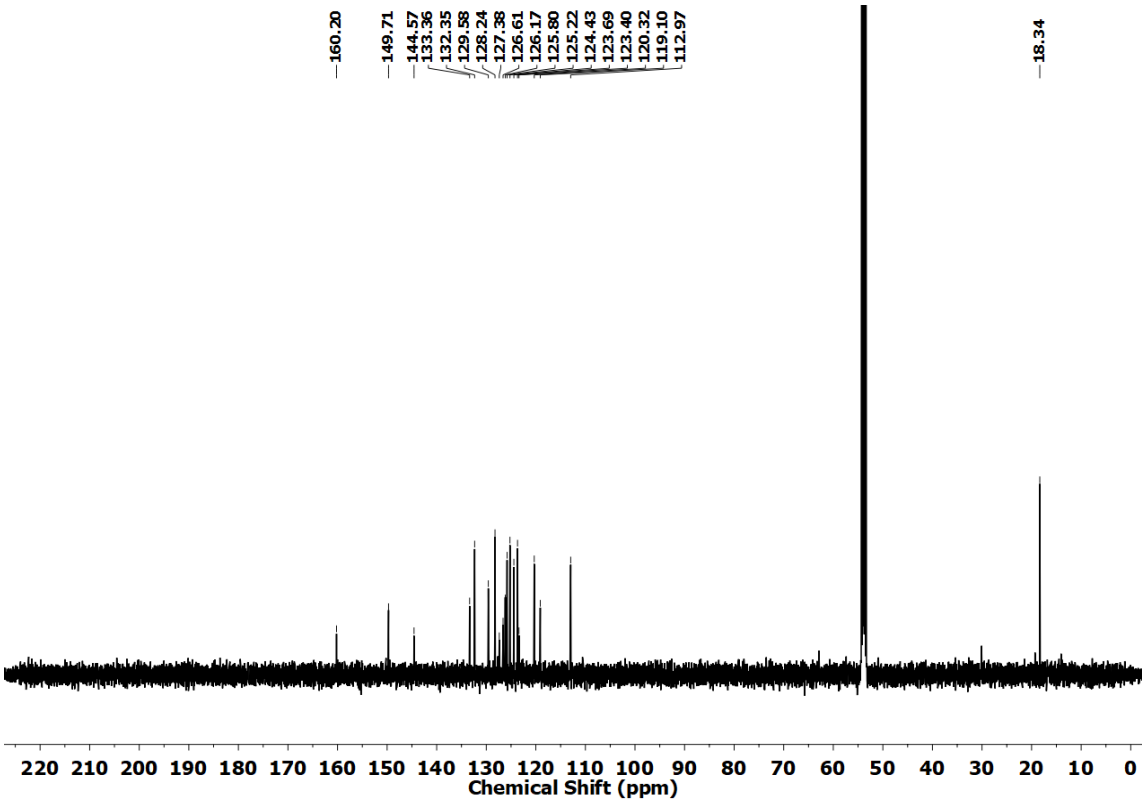


Figure A52 ^{13}C NMR (126 MHz) of 2.7b in CD_2Cl_2 at 298 K

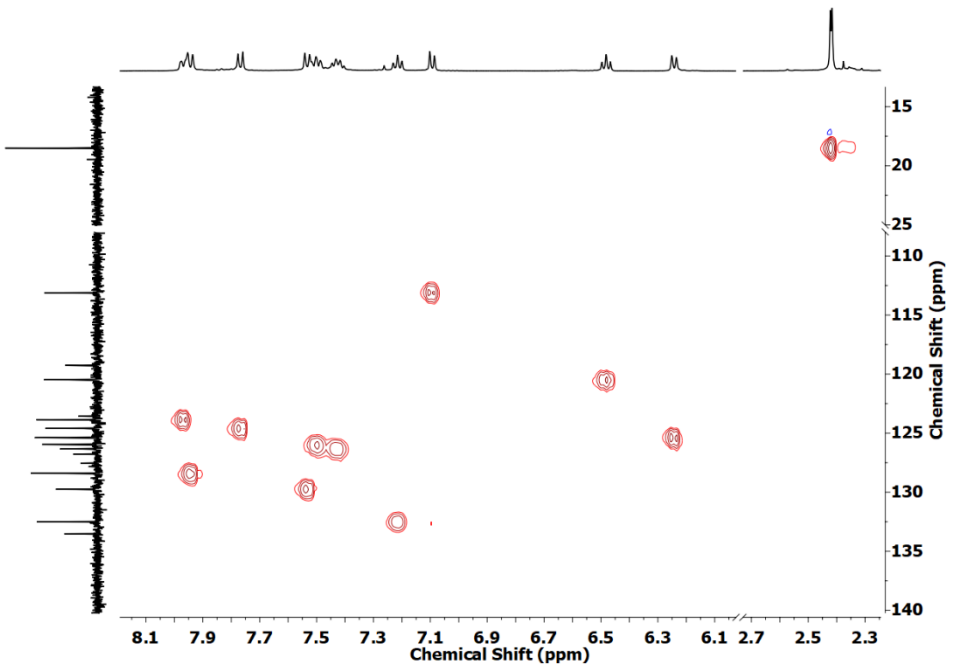


Figure A53 HSQC (500 MHz, 126 MHz) of 2.7b in CD_2Cl_2 at 298 K

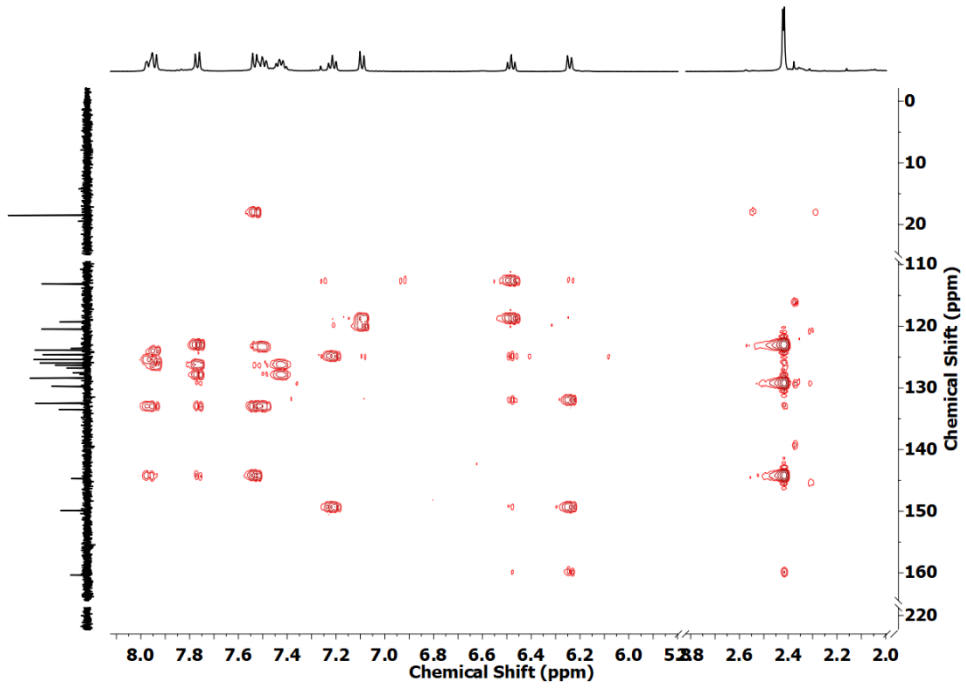


Figure A54 HMBC (500 MHz, 126 MHz) of 2.7b in CD_2Cl_2 at 298 K

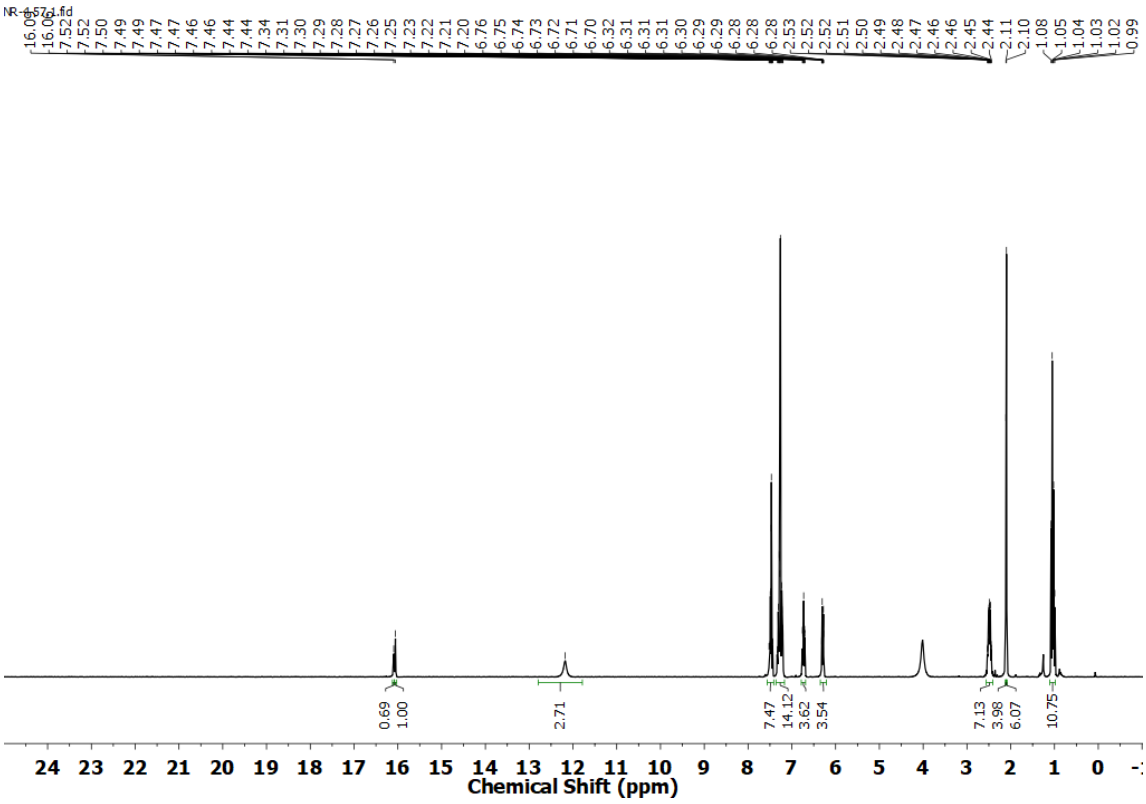


Figure A55 ^{1}H NMR (300 MHz) of 2.8a in $CDCl_3$ at 298 K

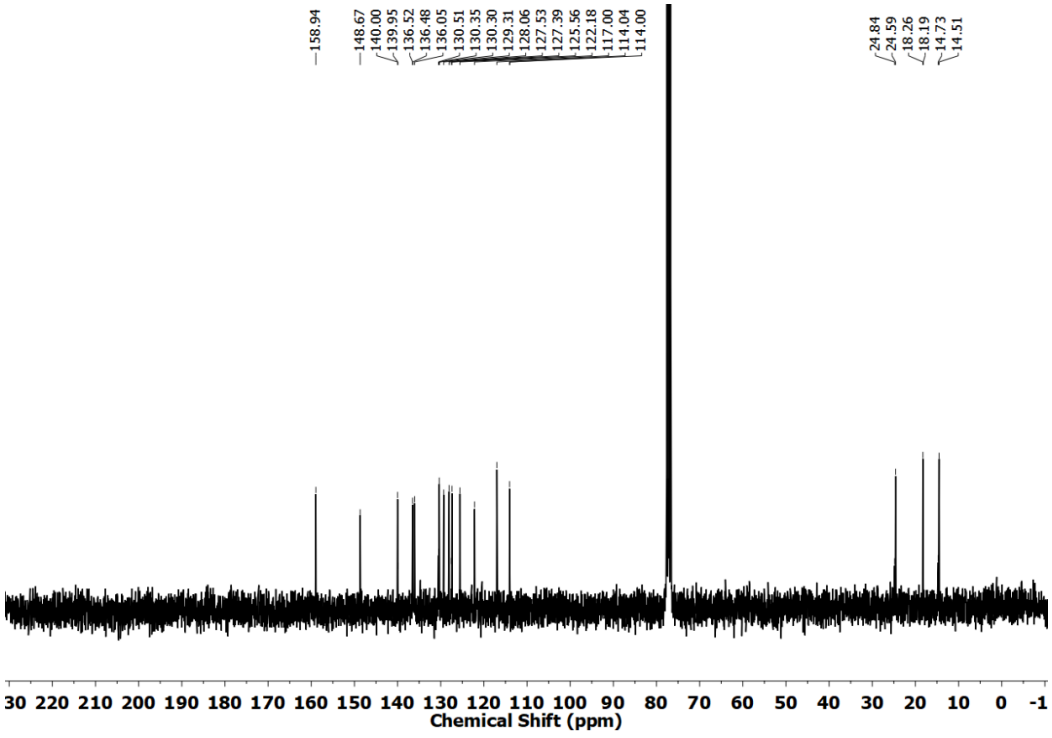


Figure A56 ^{13}C NMR (76 MHz) of 2.8a in $CDCl_3$ at 298 K

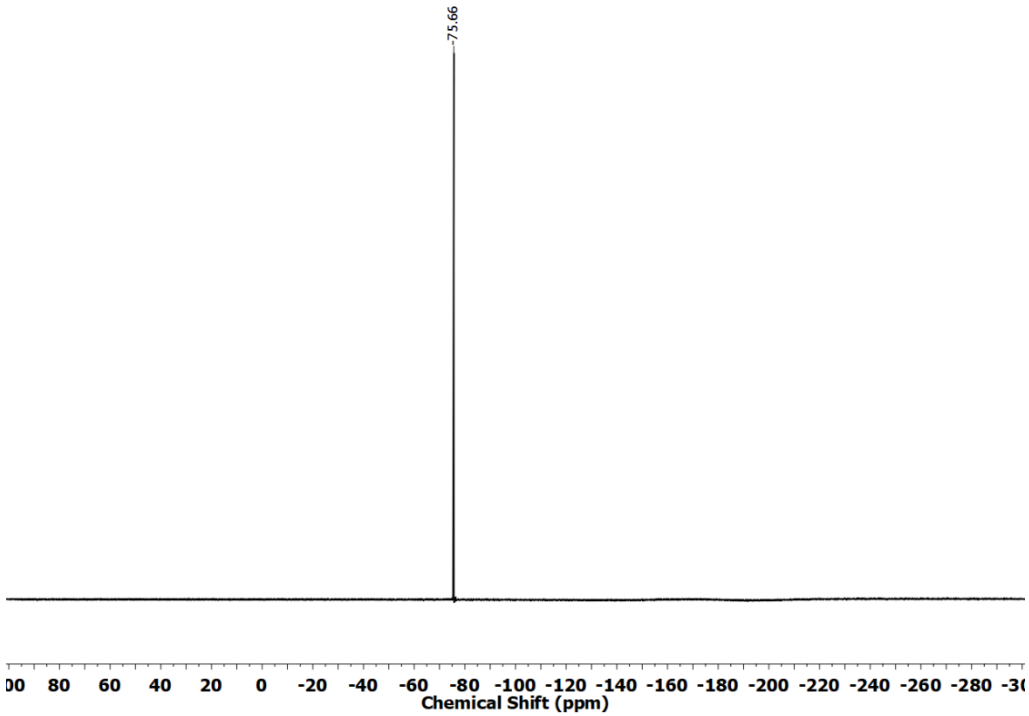


Figure A57 ^{19}F NMR (283 MHz) of 2.8a in $CDCl_3$ at 298 K

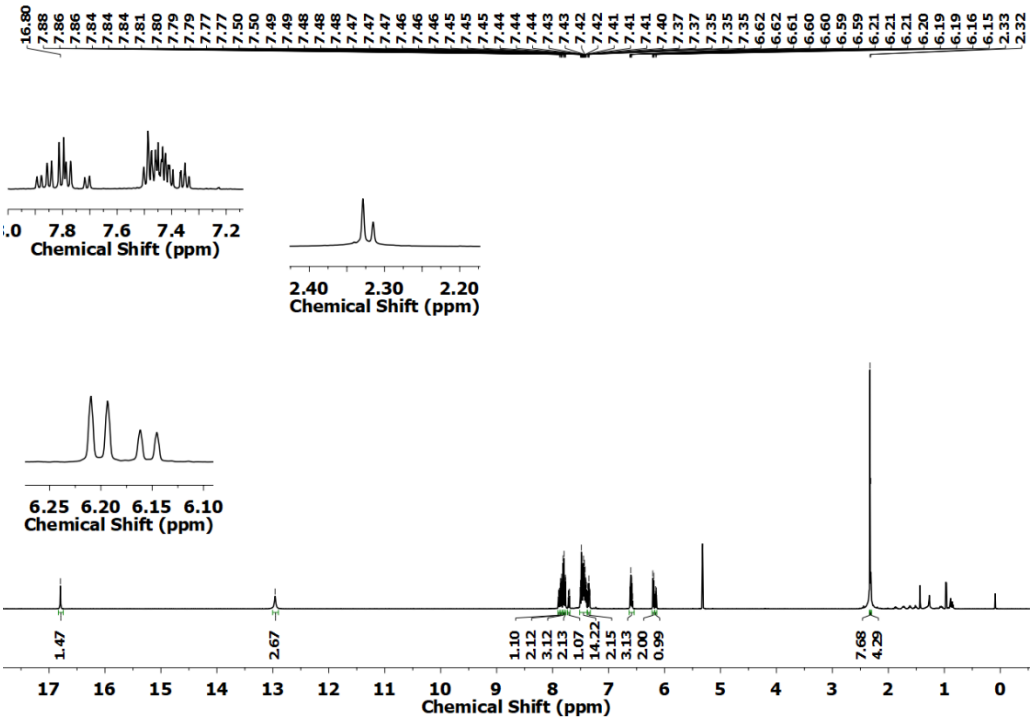


Figure A58 ^{1}H NMR (500 MHz) of 2.8b in CD_2Cl_2 at 298 K

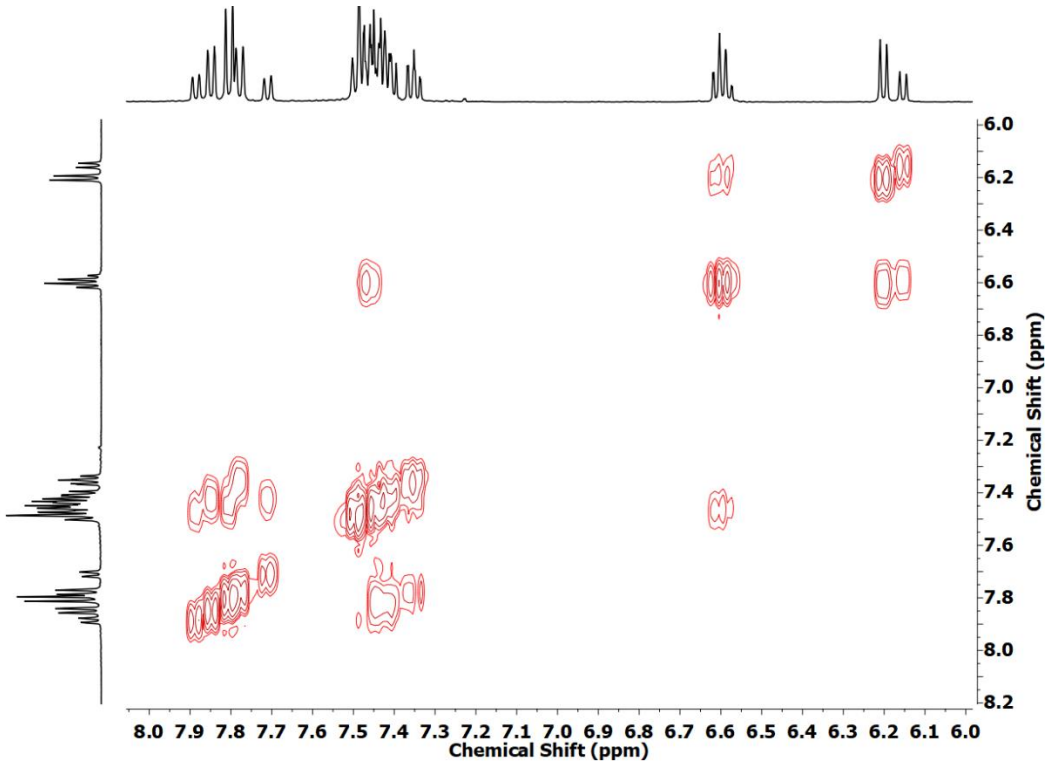


Figure A59 COSY (500 MHz, 500 MHz) of 2.8b in CD_2Cl_2 at 298 K

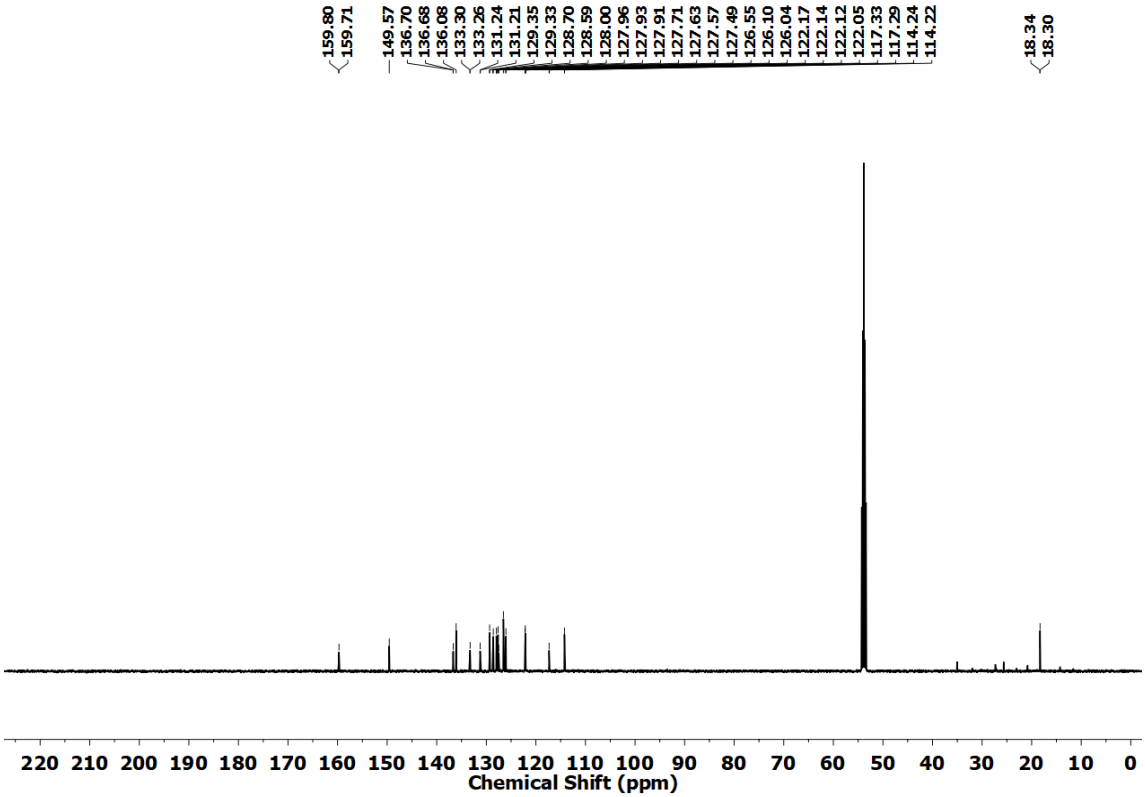


Figure A60 ^{13}C NMR (126 MHz) of 2.8b in CD_2Cl_2 at 298 K

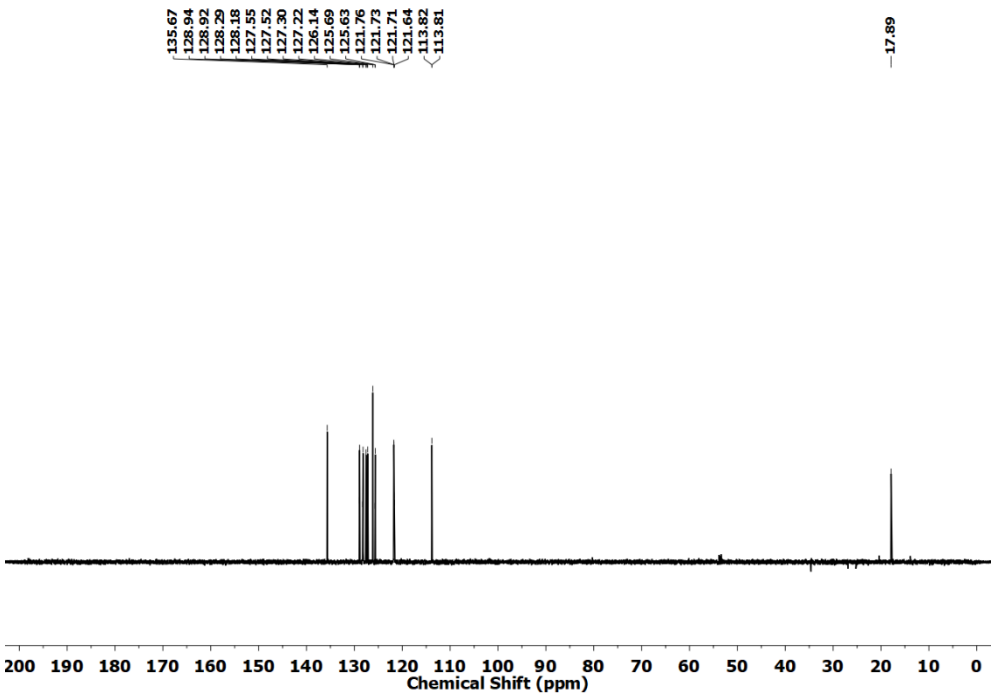


Figure A61 DEPT-135 (126 MHz) of 2.8b in CD_2Cl_2 at 298 K

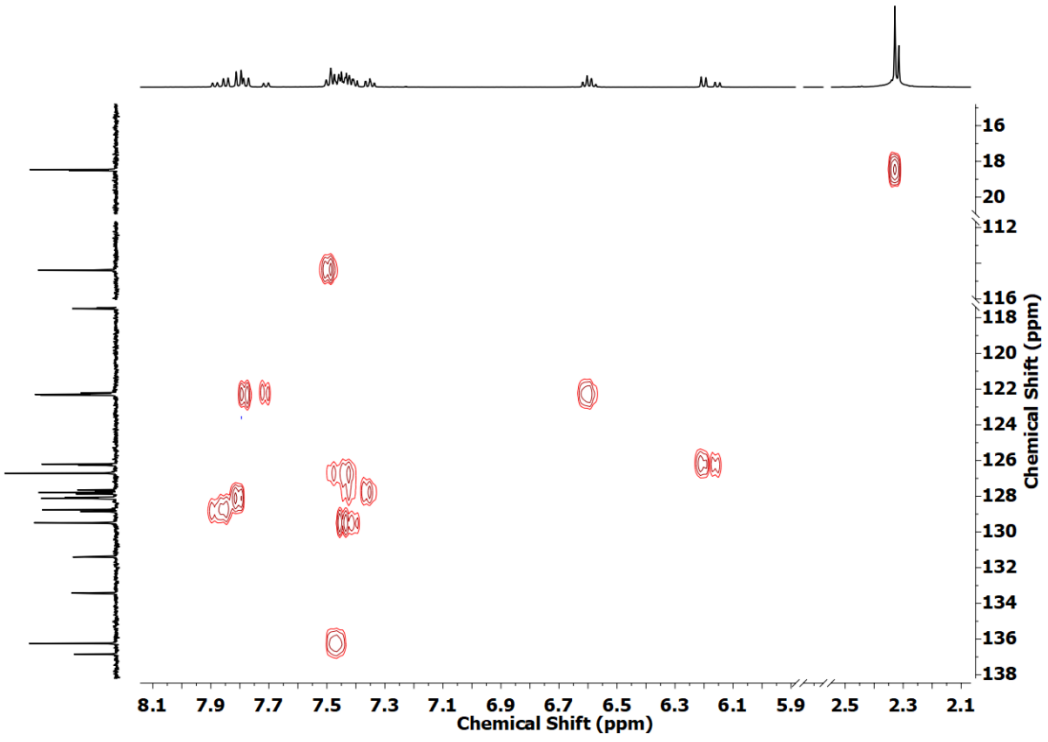


Figure A62 HSQC (500 MHz, 126 MHz) of 2.8b in CD_2Cl_2 at 298 K

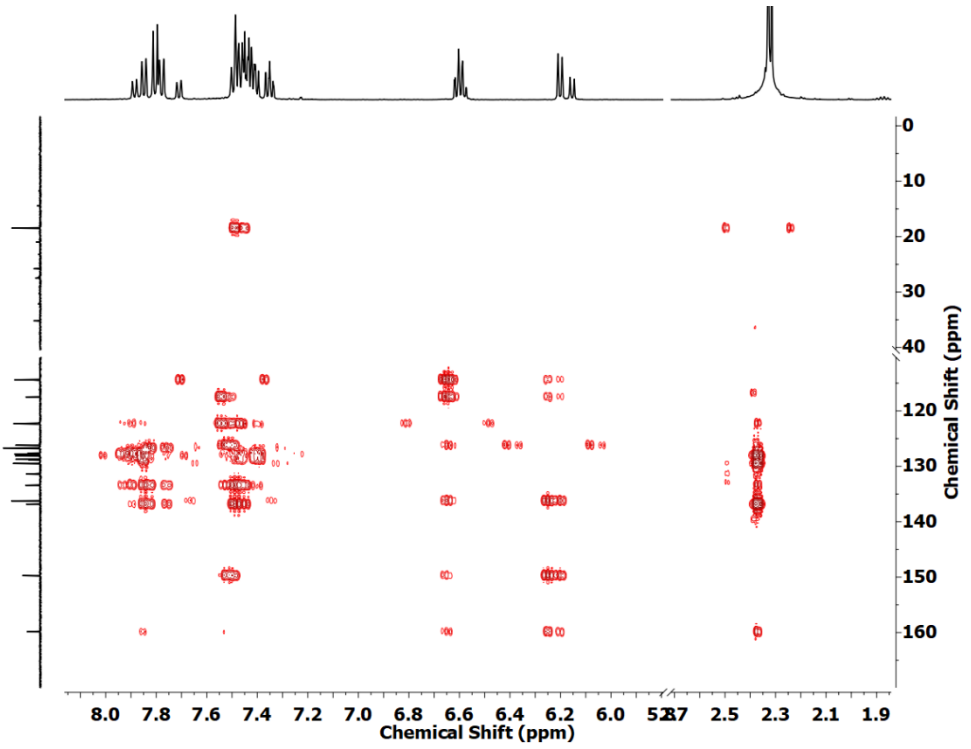


Figure A63 HMBC (500 MHz, 126 MHz) of 2.8b in CD_2Cl_2 at 298 K

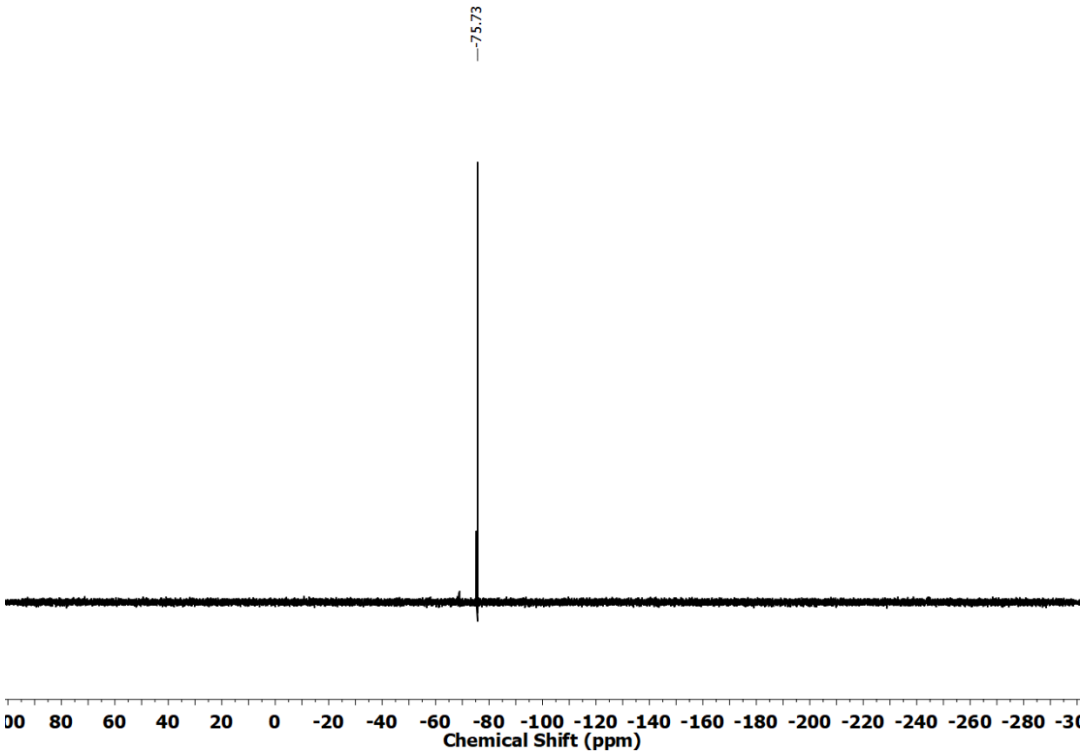


Figure A64 ^{19}F NMR (283 MHz) of 2.8b in $CDCl_3$ at 298 K

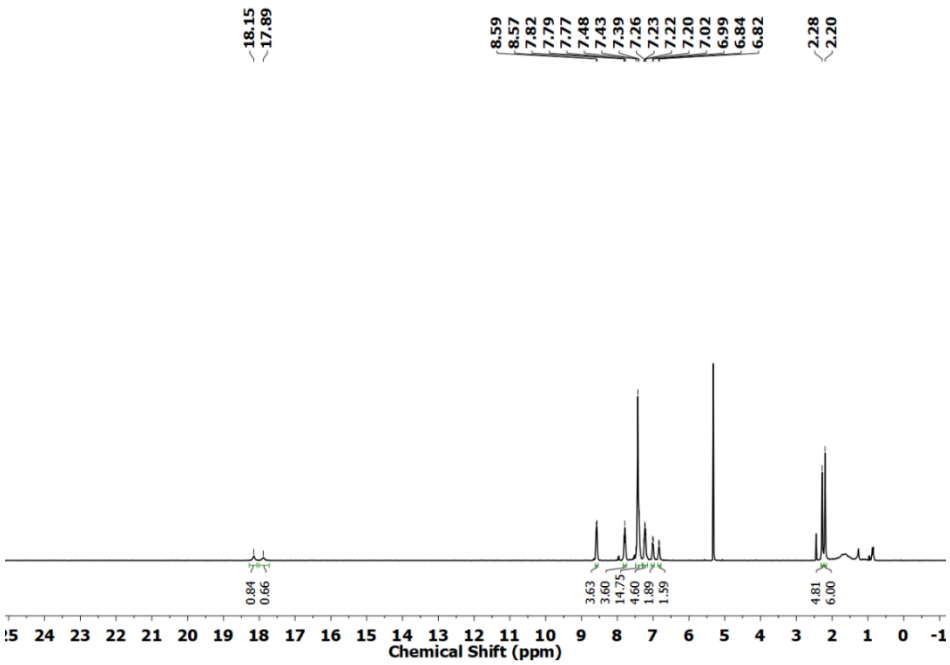


Figure A65 ^{1}H NMR (360 MHz) of 3.15a in CD_2Cl_2 at 298 K

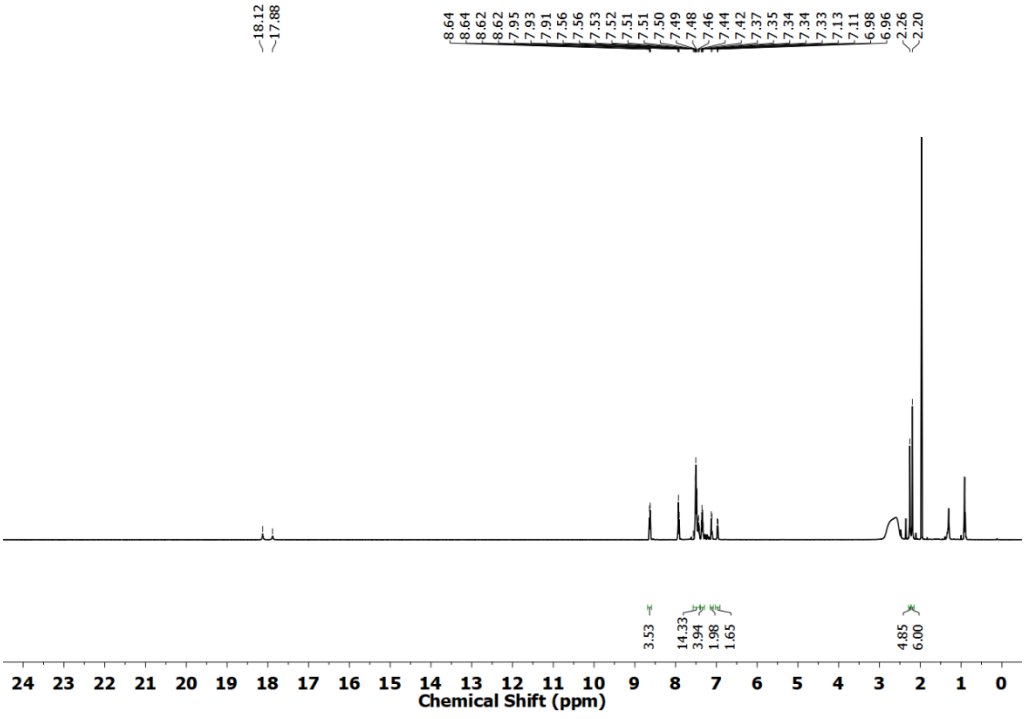


Figure A66 ^{1}H NMR (500 MHz) of 3.15a in CD_3CN at 298 K

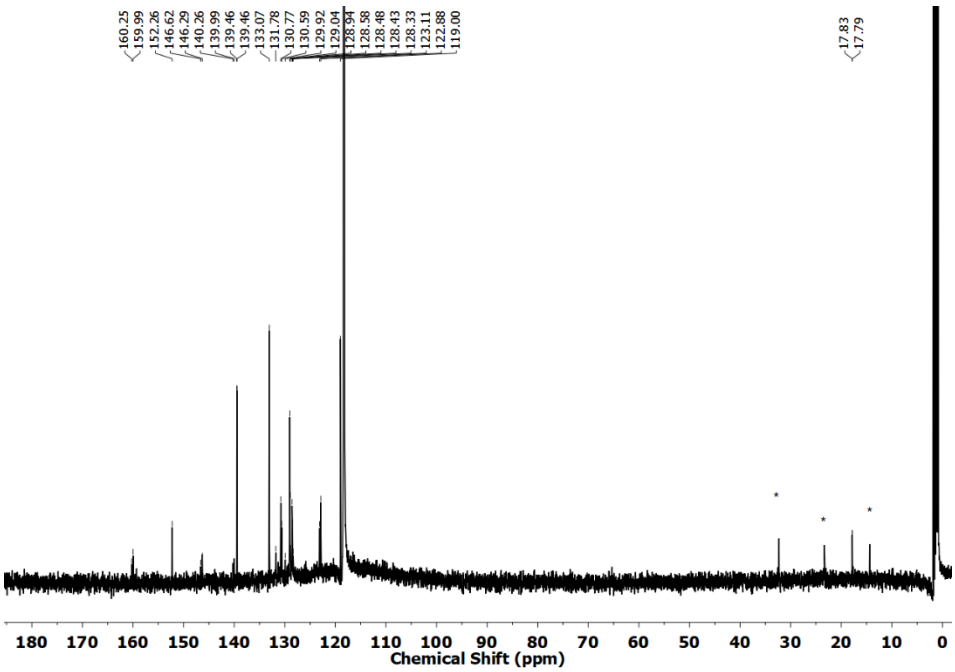


Figure A67 UDEFT (126 MHz) of 3.15a in CD_3CN at 298 K

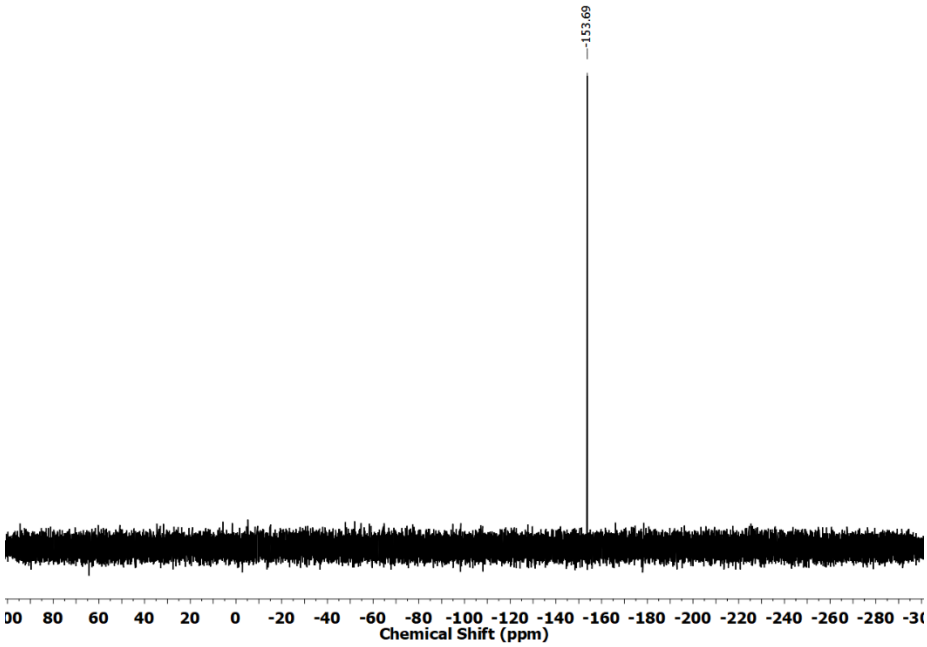


Figure A68 ^{19}F NMR (283 MHz) of 3.15a in $CDCl_3$ at 298 K

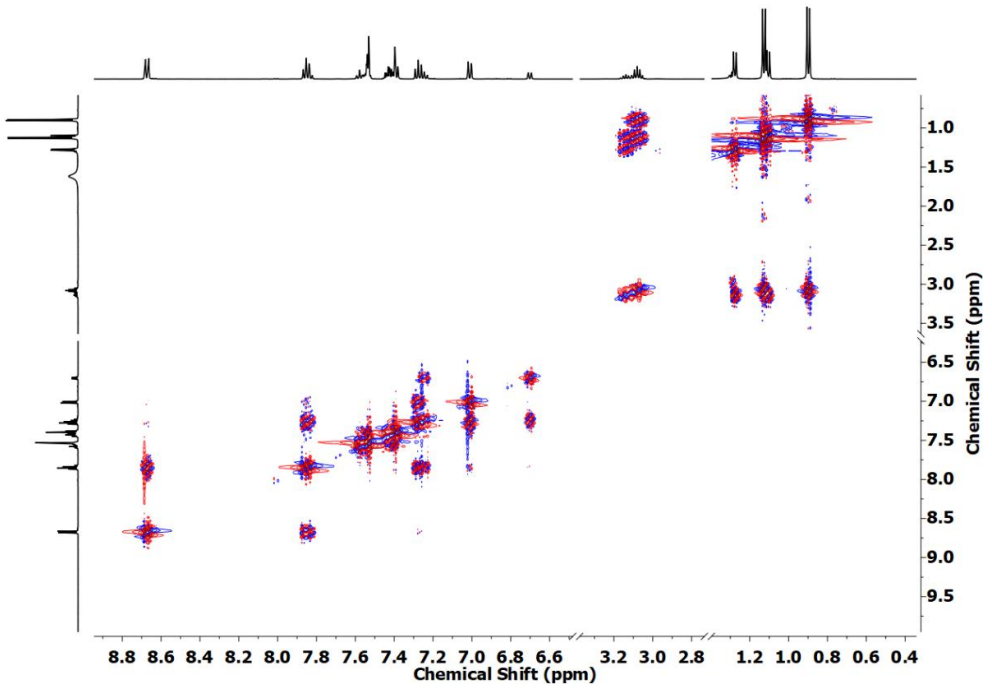


Figure A69 3.15b COSY (500 MHz, 500 MHz) of 3.15b in CD_2Cl_2 at 298 K

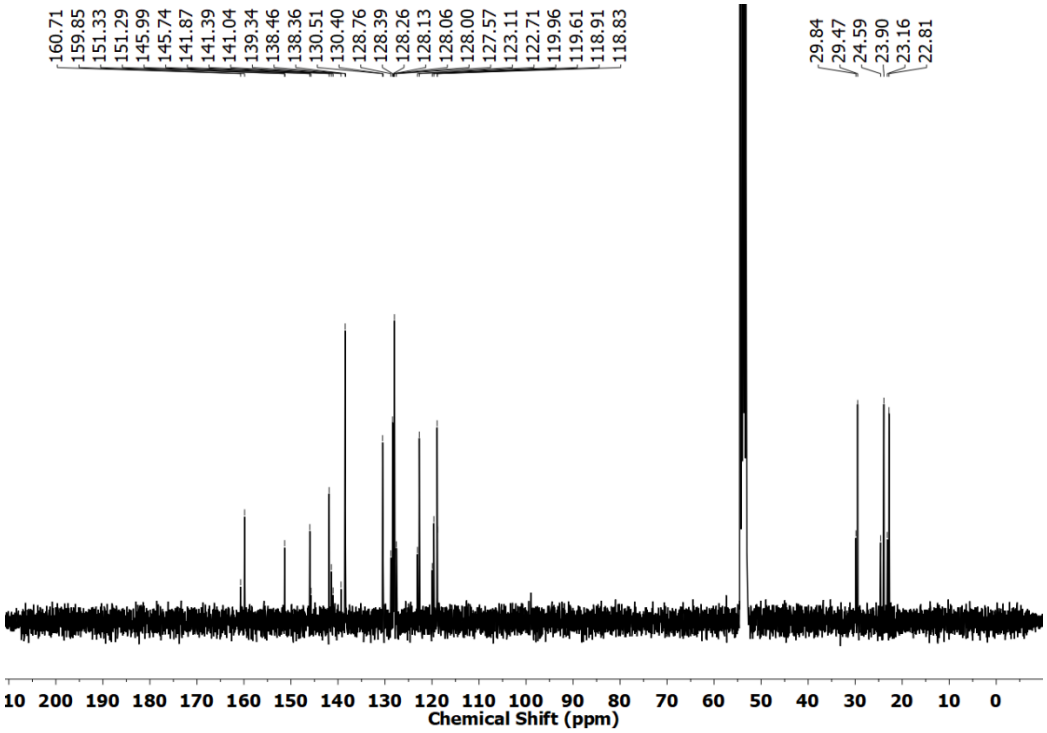


Figure A70 13 C NMR (126 MHz) of 3.15b in CD_2Cl_2 at 298 K

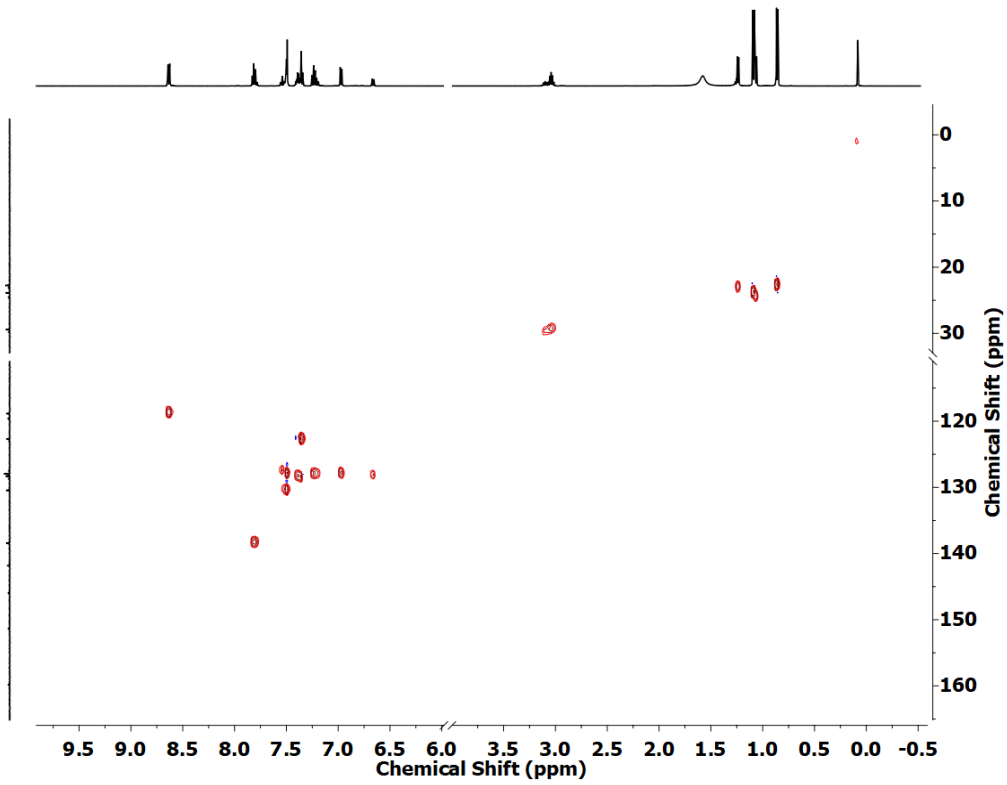


Figure A71 HSQC (500 MHz, 126 MHz) of 3.15b in CD_2Cl_2 at 298 K

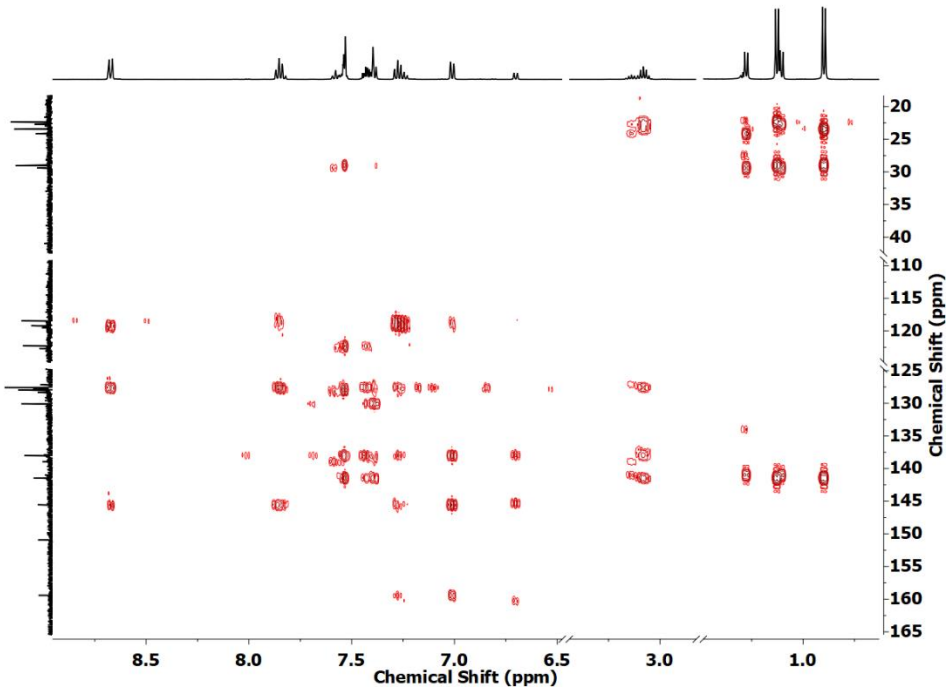


Figure A72 HMBC (500 MHz, 126 MHz) of 3.15b in CD_2Cl_2 at 298 K

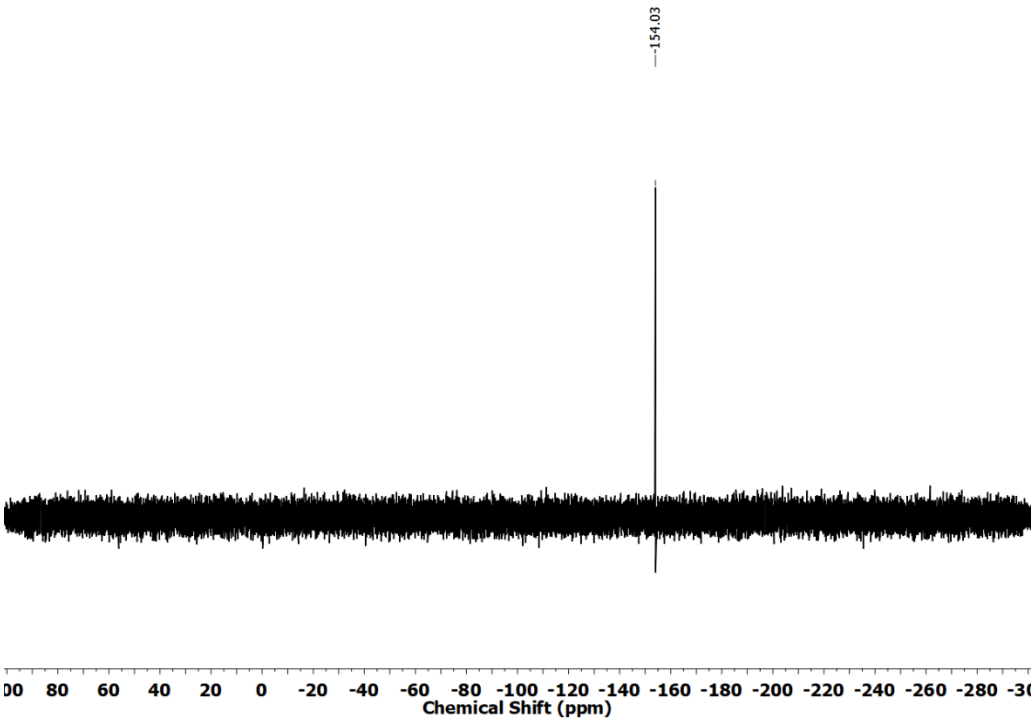


Figure A73 ^{19}F NMR (283 MHz) of 3.15b in CD_2Cl_2 at 298 K

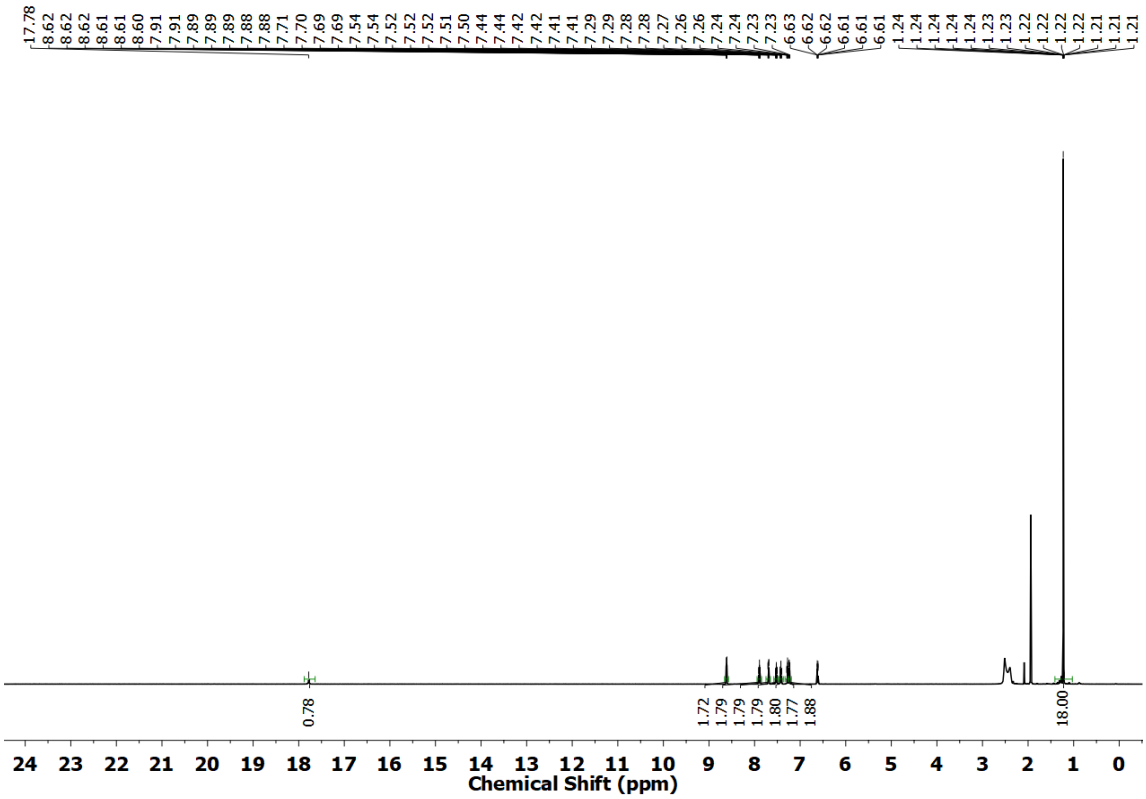


Figure A74 ^{1}H NMR (500 MHz) of 3.15c in CD_3CN at 298K

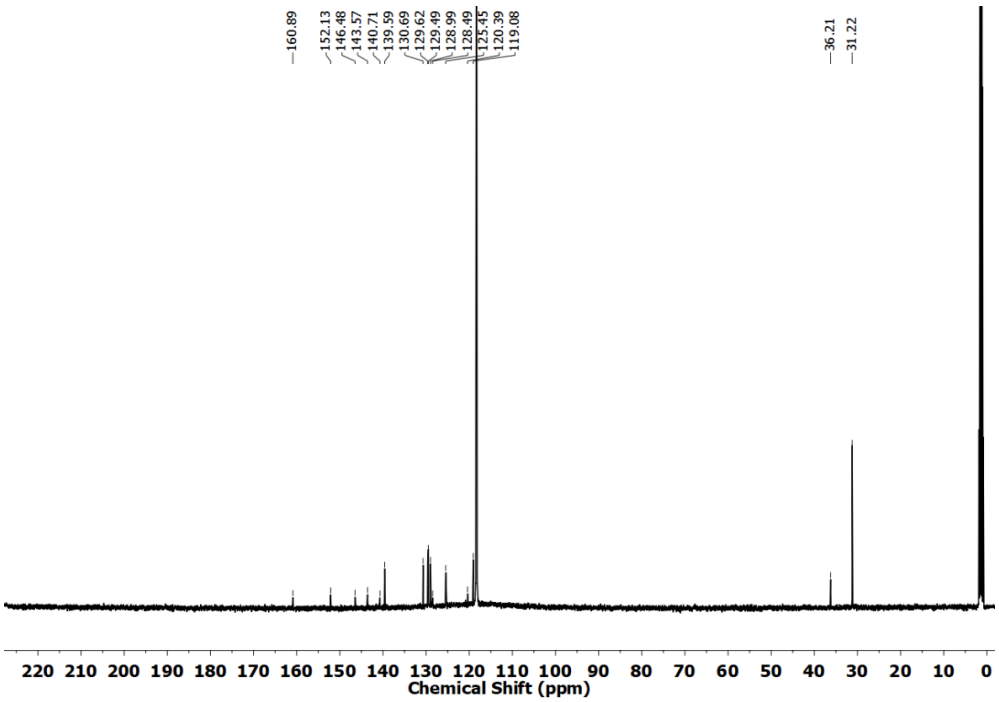


Figure A75 UDEFT (126 MHz) of 3.15c in CD_3CN at 298 K

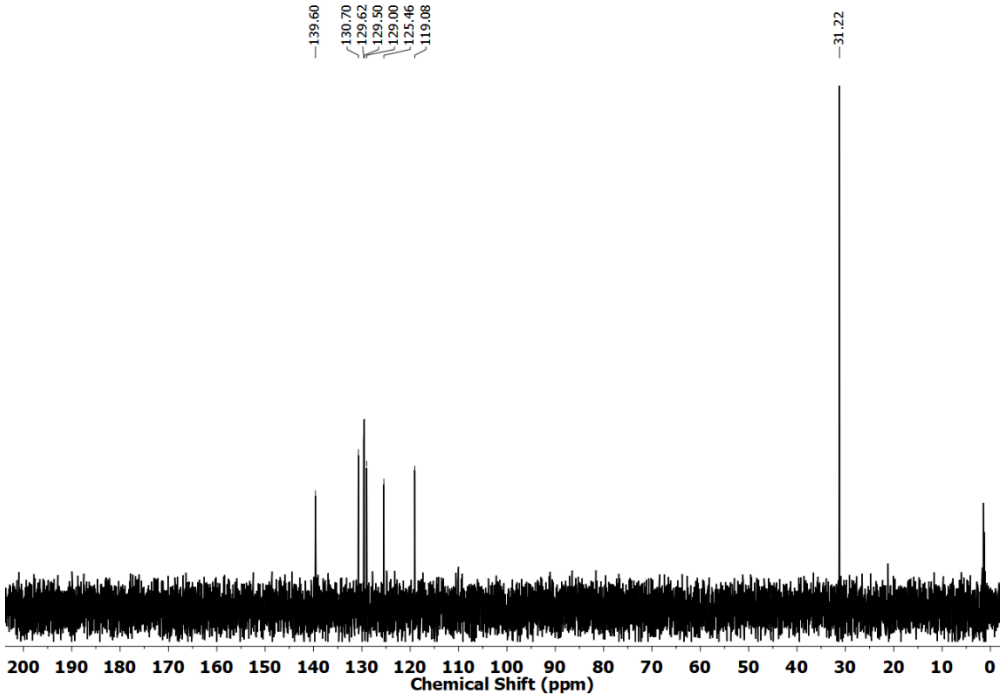


Figure A76 DEPT135 (126 MHz) of 3.15c in CD_3CN at 298 K

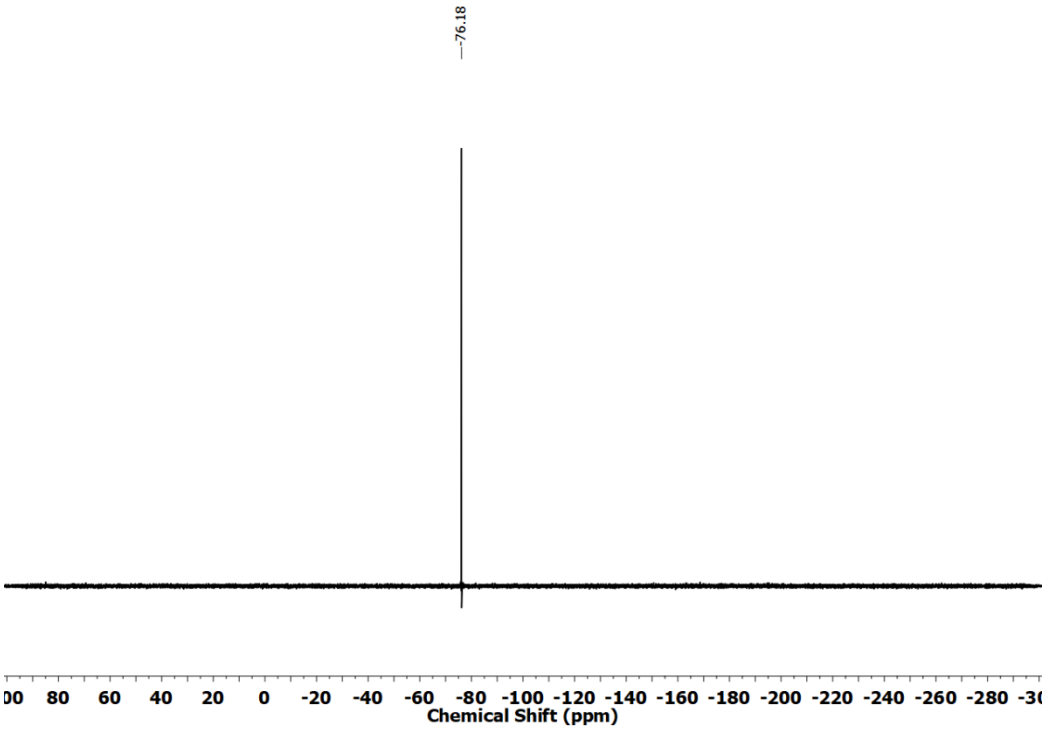


Figure A77 ^{19}F NMR (283 MHz) of 3.15c in $CDCl_3$

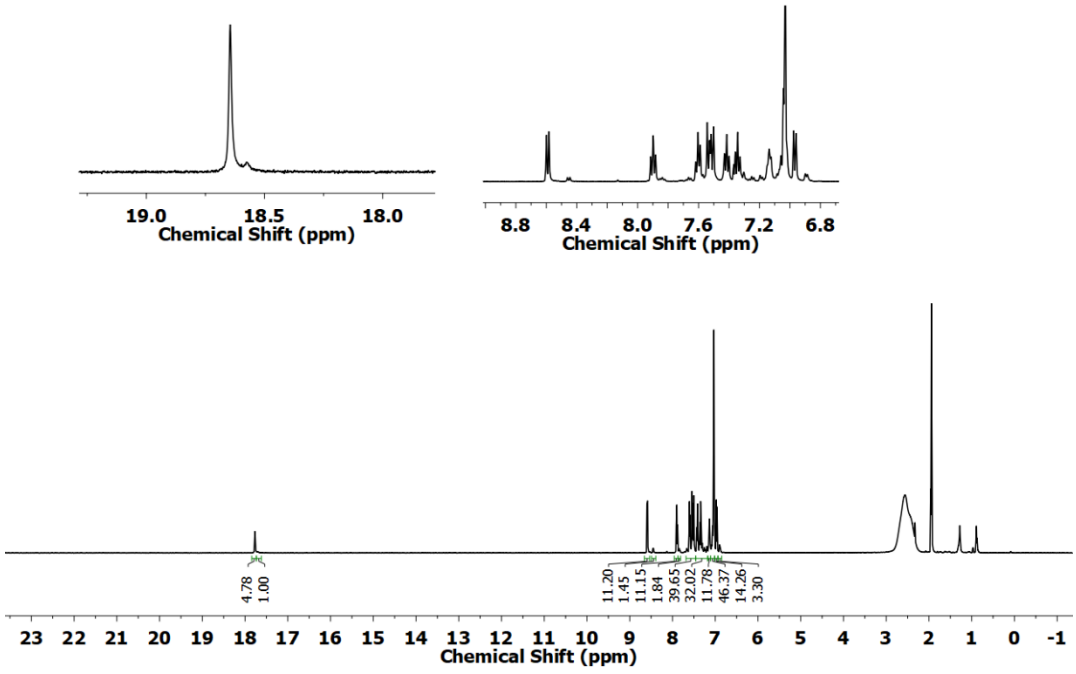


Figure A78 ^{1}H NMR (500 MHz) of 3.15d in CD3CN 3.15d at 298 K

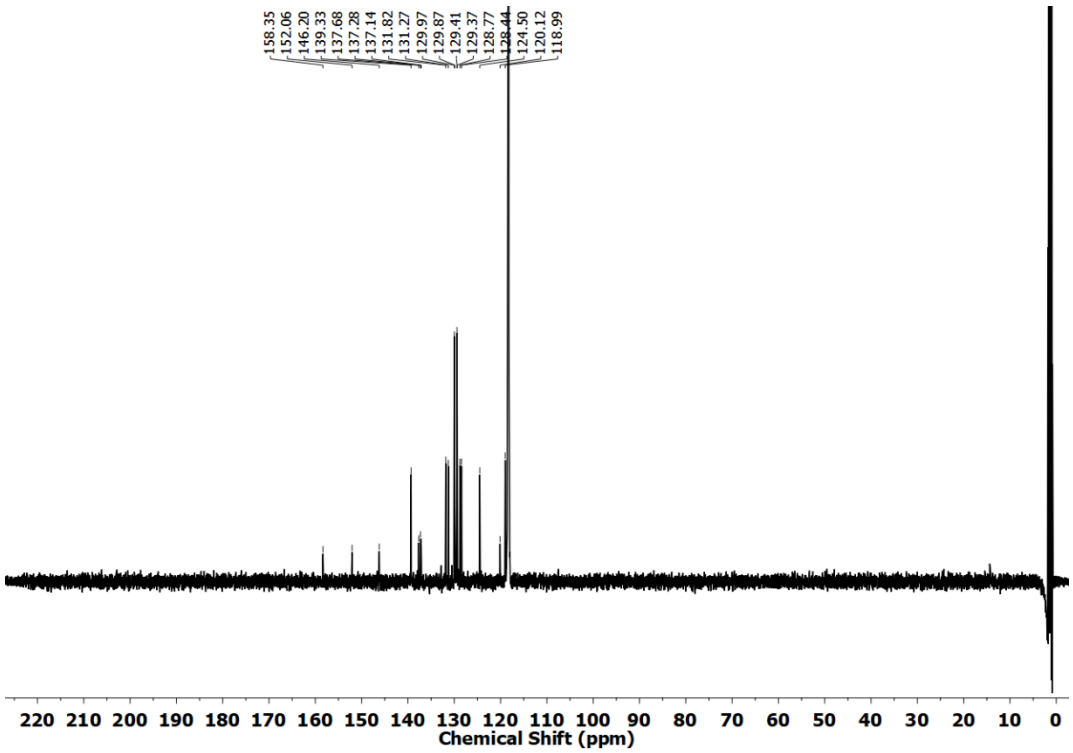


Figure A79 UDEFT (126 MHz) of 3.15d in CD3CN at 298 K

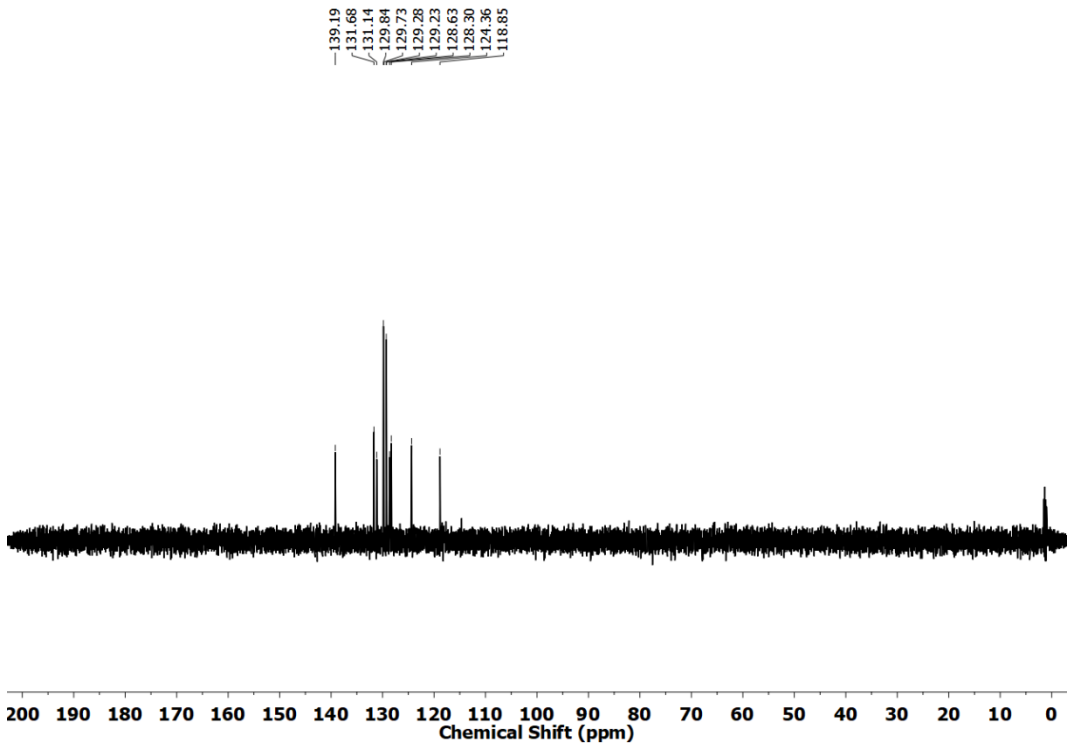


Figure A80 DEPT135 (126 MHz) of 3.15d in CD3CN at 298 K

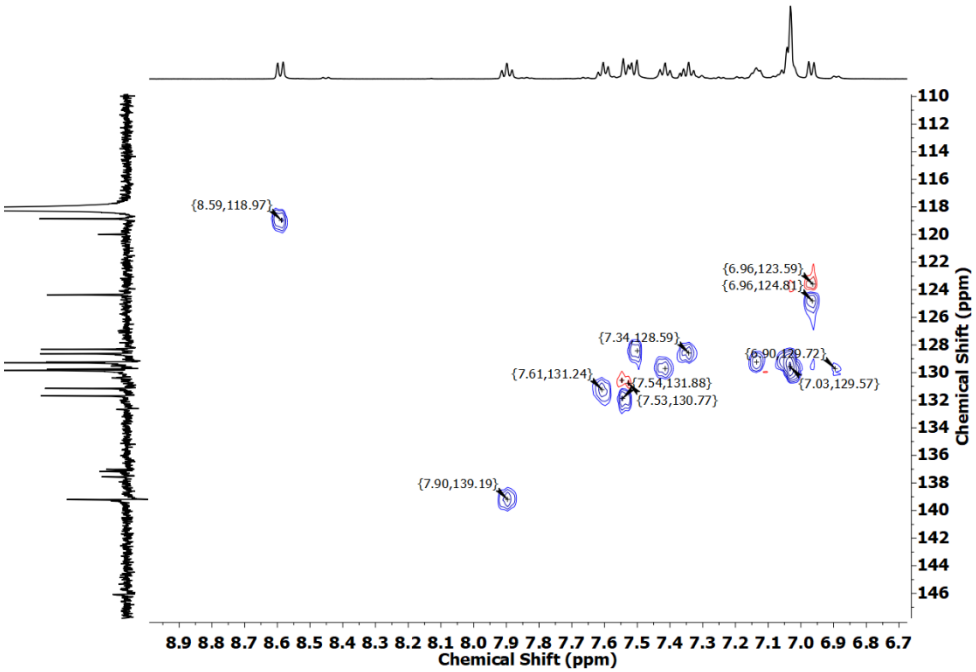


Figure A81 HSQC (500 MHz, 126 MHz) of 3.15d in CD3CN at 298 K

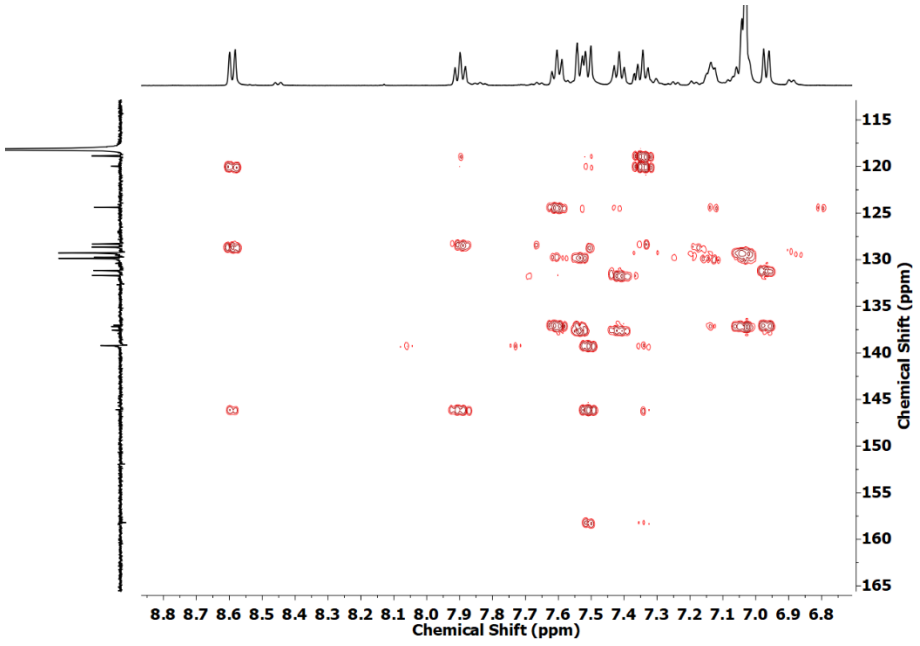


Figure A82 HMBC (500 MHz, 126 MHz) of 3.15d in CD3CN at 298 K

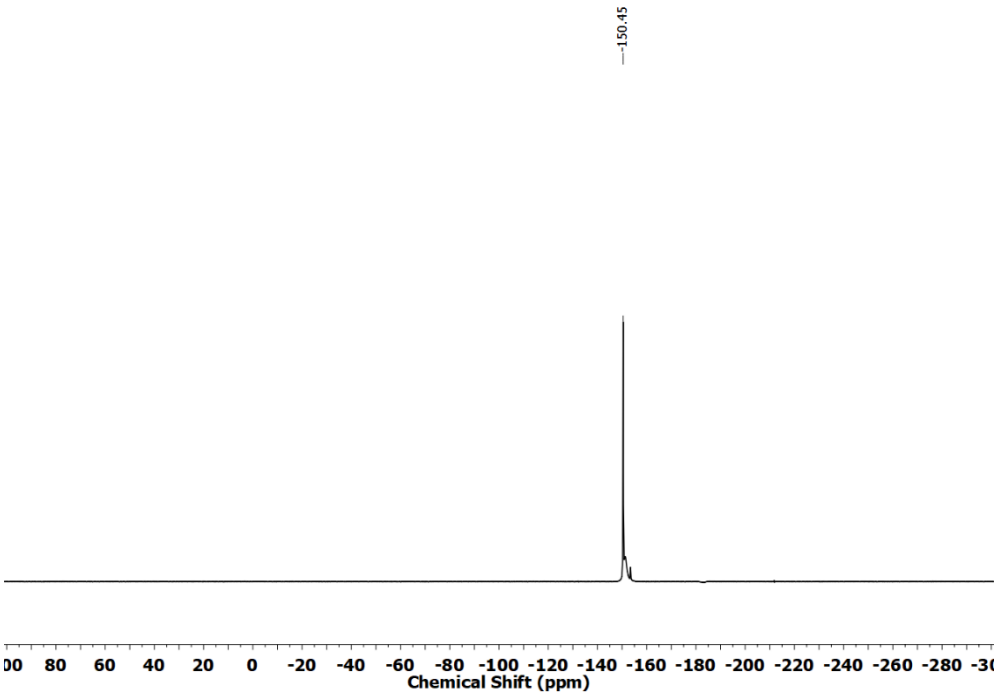


Figure A83 ^{19}F NMR (283 MHz) of 3.15d in $CDCl_3$ at 298 K

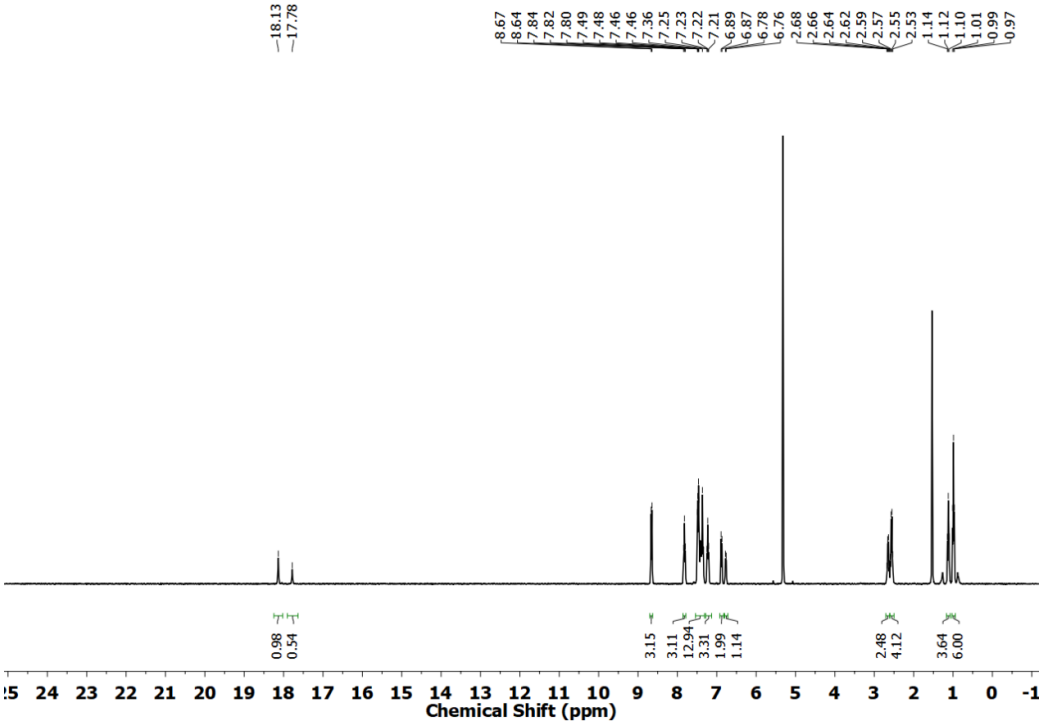


Figure A84 ^{1}H NMR (360 MHz) of 3.15e in CD_2Cl_2

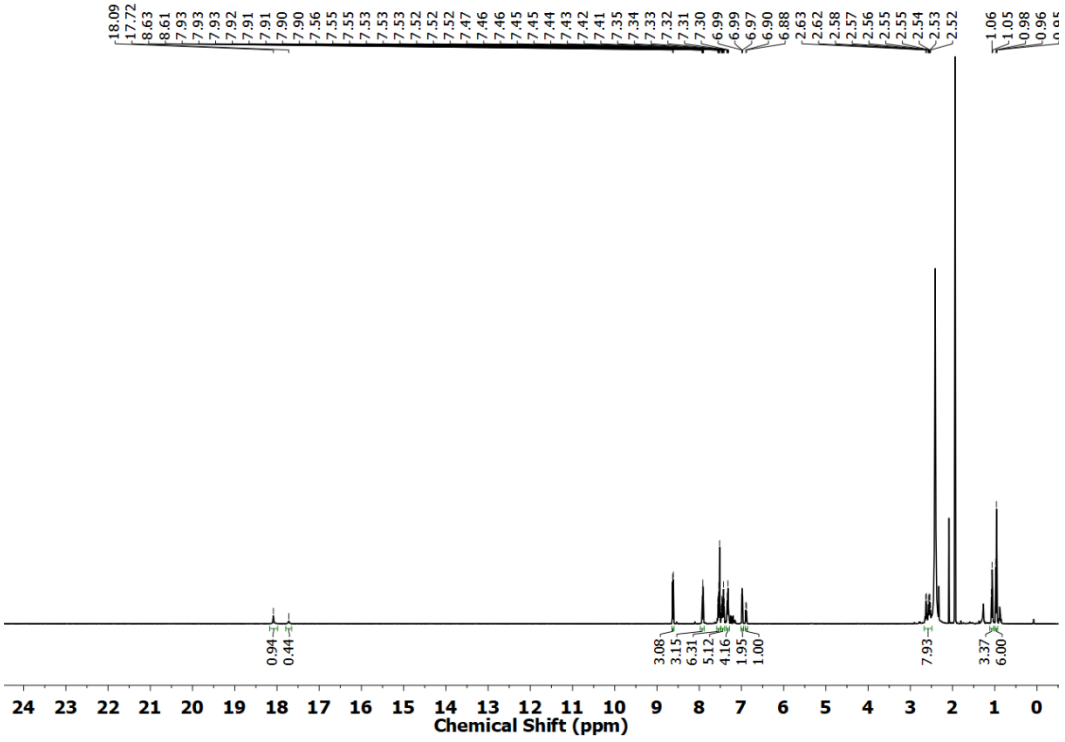


Figure A85 ^{1}H NMR (500 MHz) of 3.15e in CD_2Cl_2

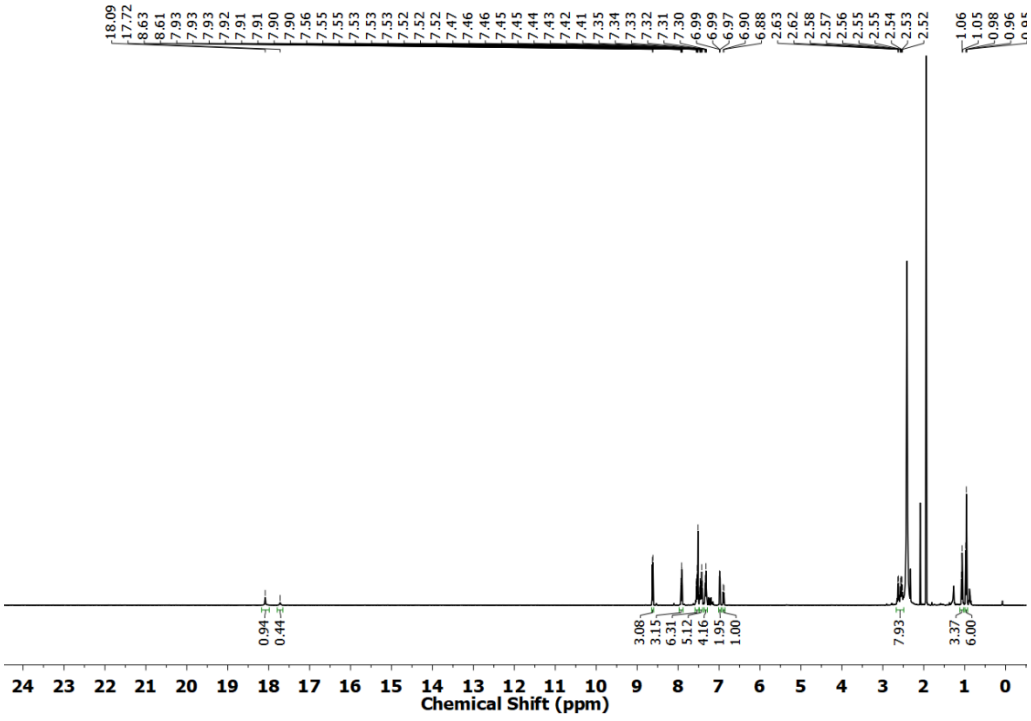


Figure A86 ^{1}H NMR (500 MHz) of 3.15e in CD_3CN

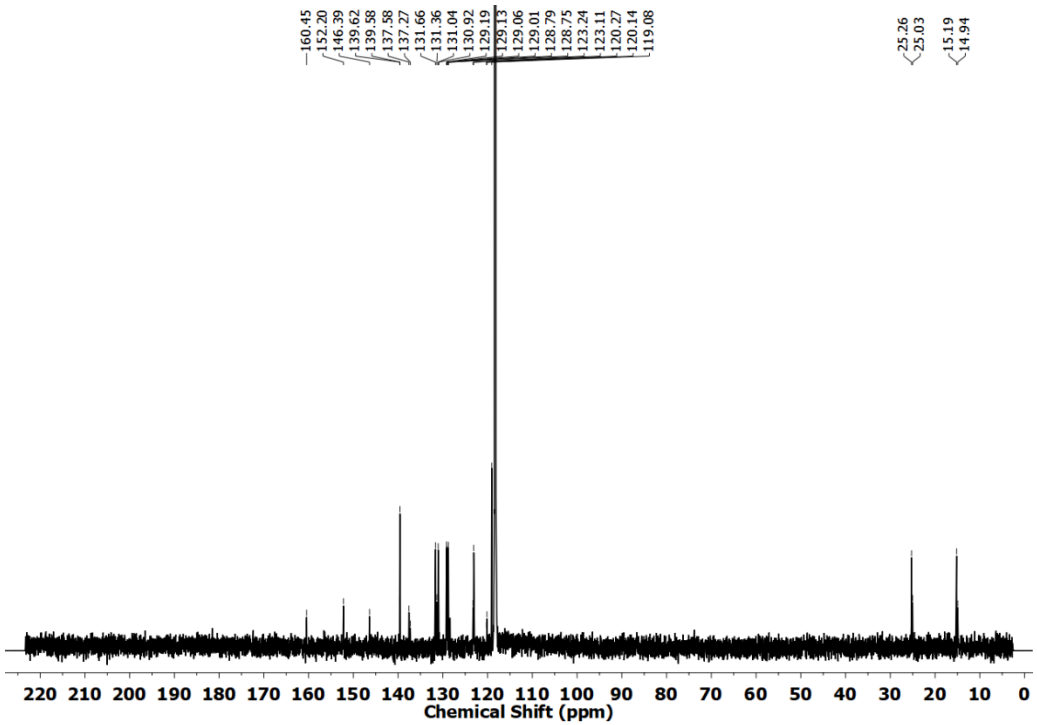


Figure A87 UDEFT (126 MHz) of 3.15e in CD_3CN at 298 K

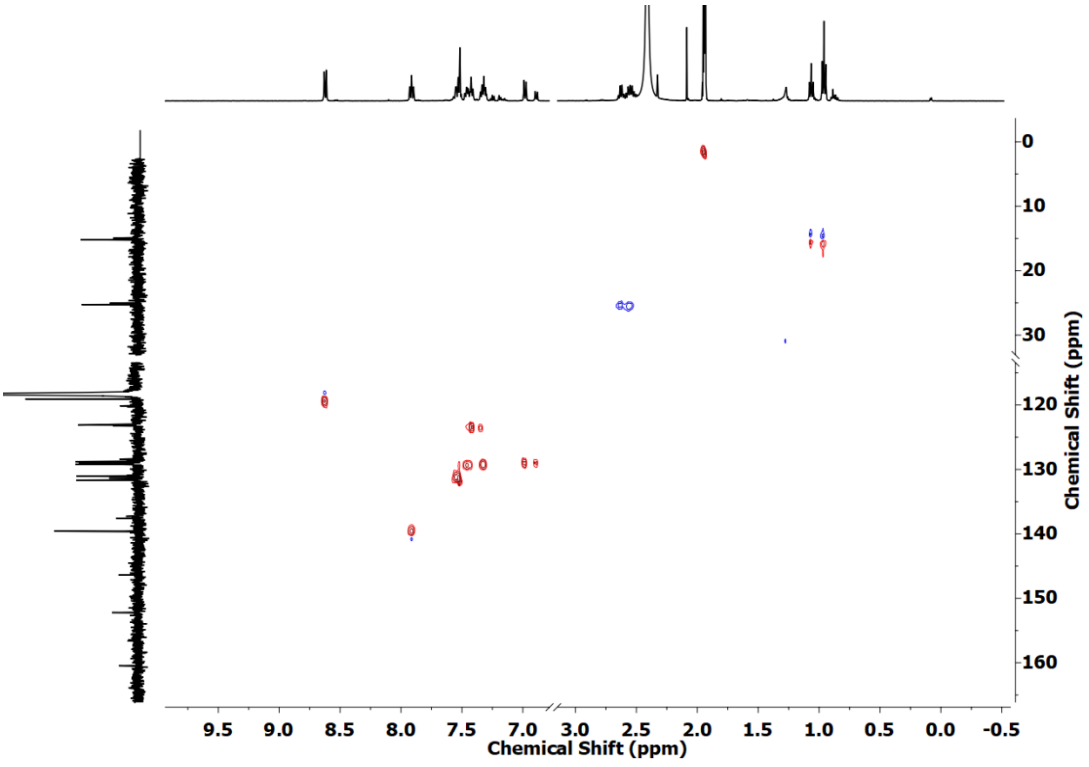


Figure A88 HSQC (500 MHz, 126 MHz) of 3.15e in CD_3CN at 298 K

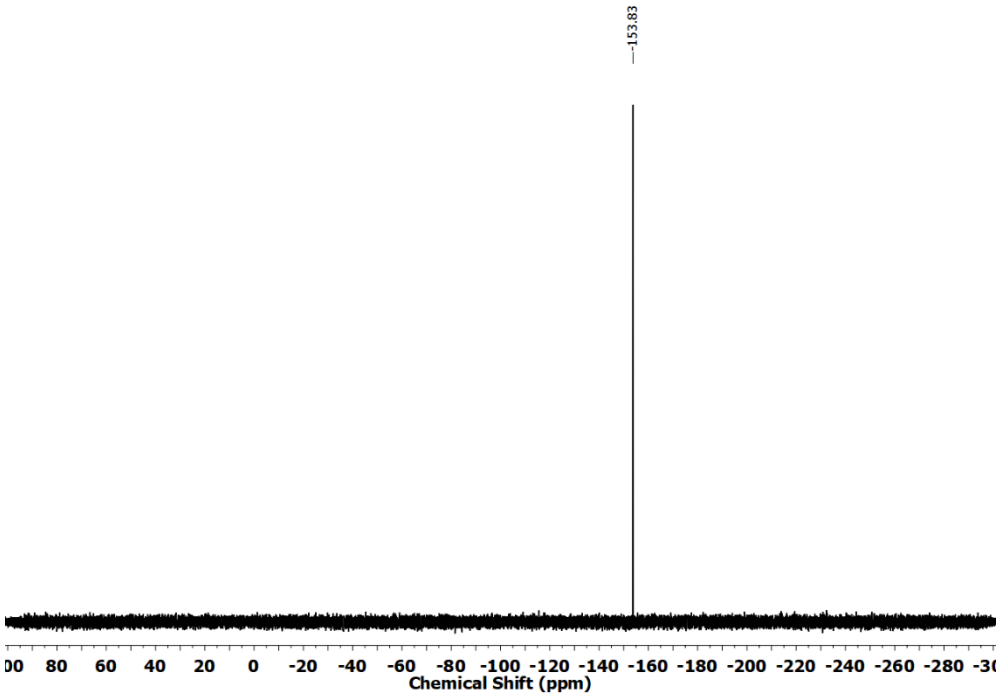


Figure A90 ^{19}F NMR (283 MHz): of 3.15e in $CDCl_3$ at 298 K

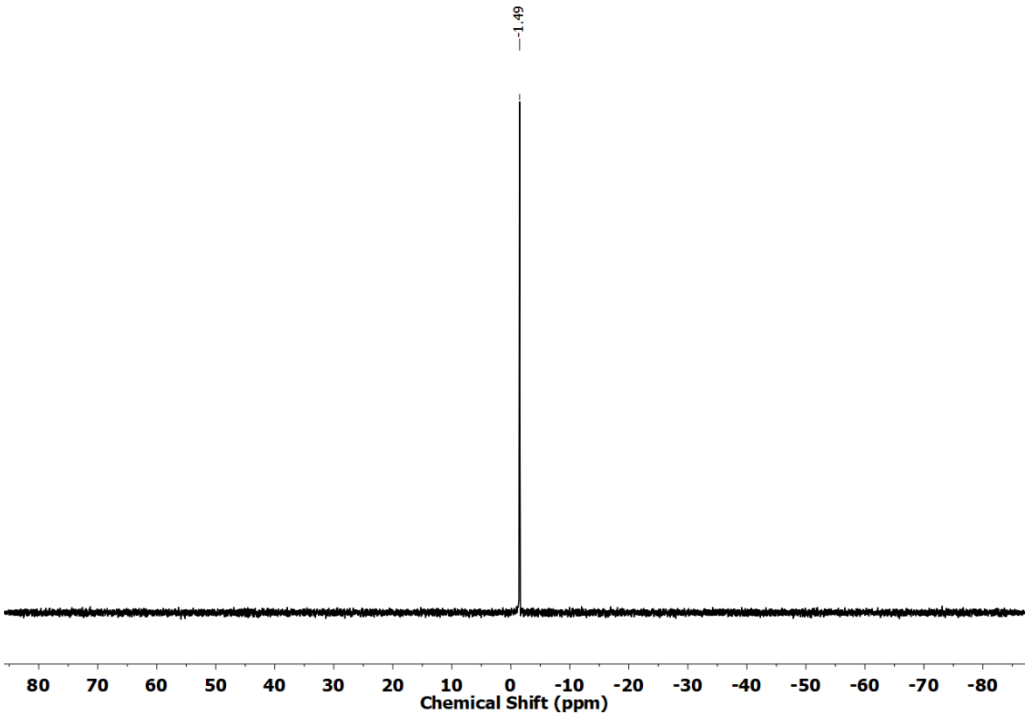


Figure A91 ^{11}B NMR (116 MHz) of 3.15e in CD_2Cl_2

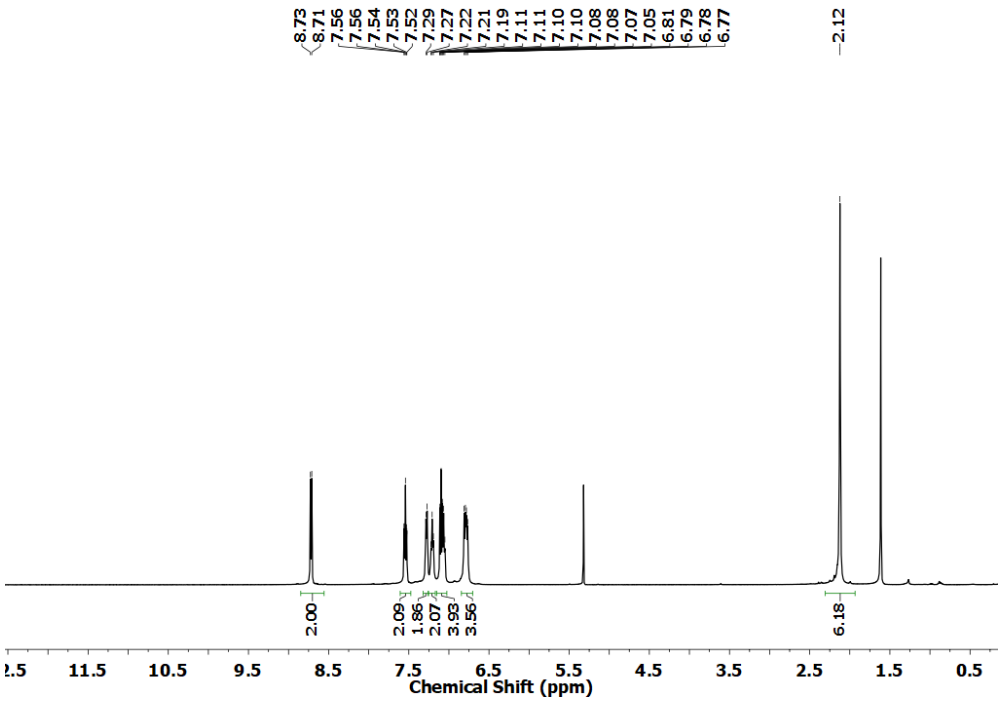


Figure A92 ^{1}H NMR (500 MHz) of 3.16a in CD_2Cl_2 at 298 K

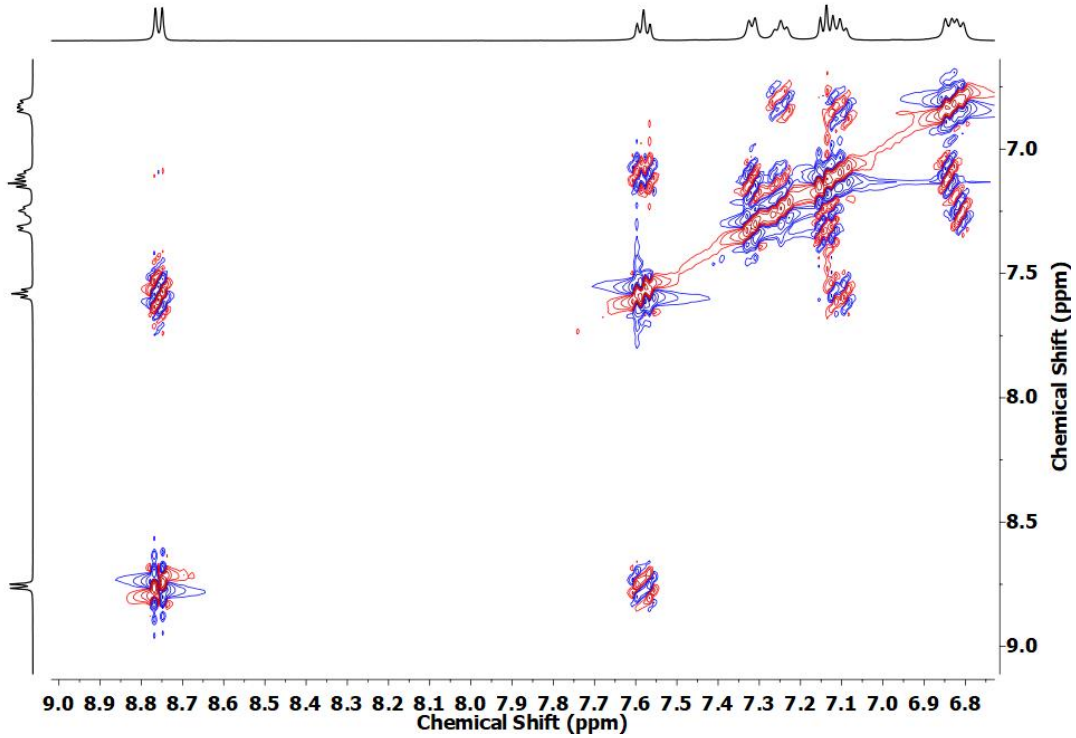


Figure A93 COSY (500 MHz, 500 MHz) of 3.16a in CD_2Cl_2 at 298 K

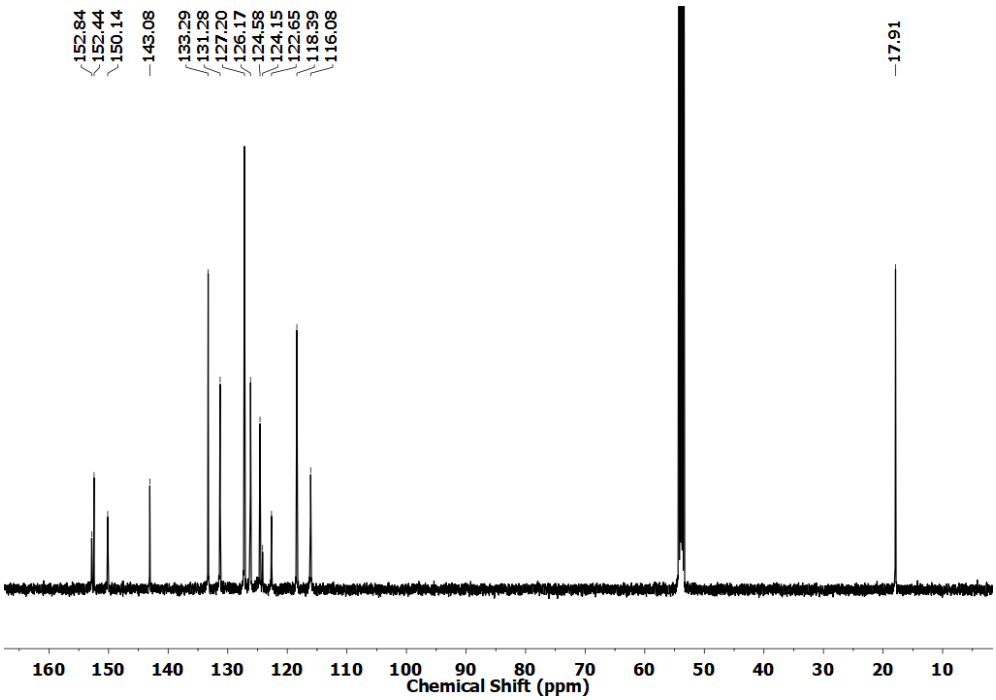


Figure A94 13C NMR (126 MHz) of 3.16a in CD_2Cl_2 at 298 K

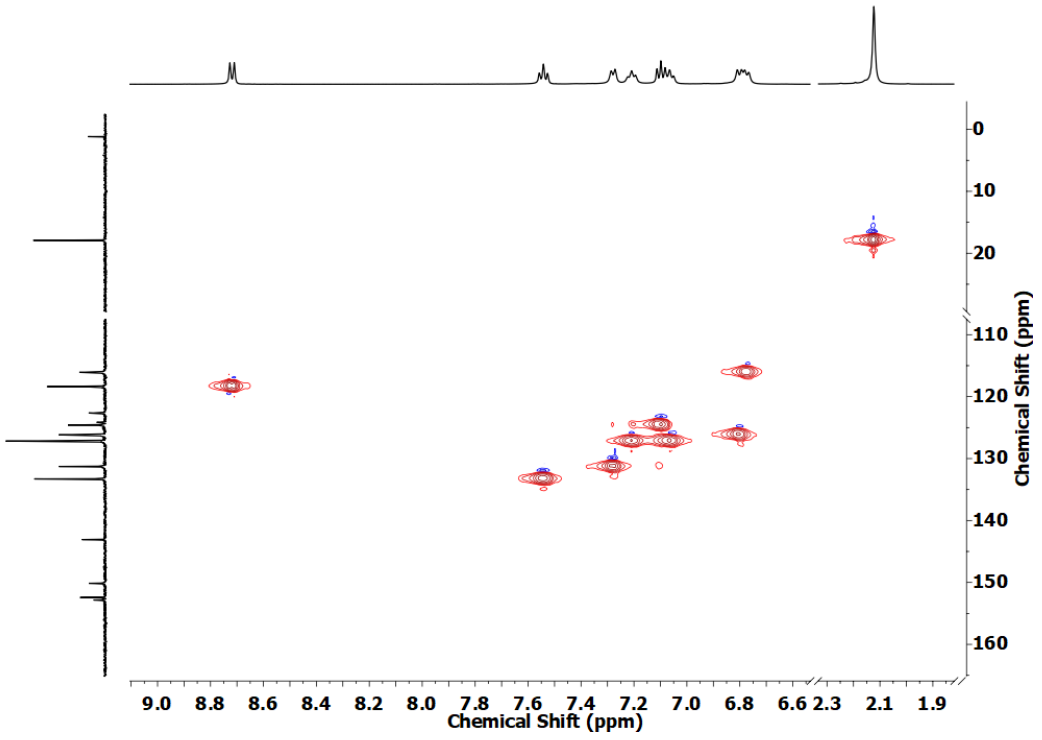


Figure A95 HSQC (500 MHz, 126 MHz) of 3.16a in CD_2Cl_2 at 298 K

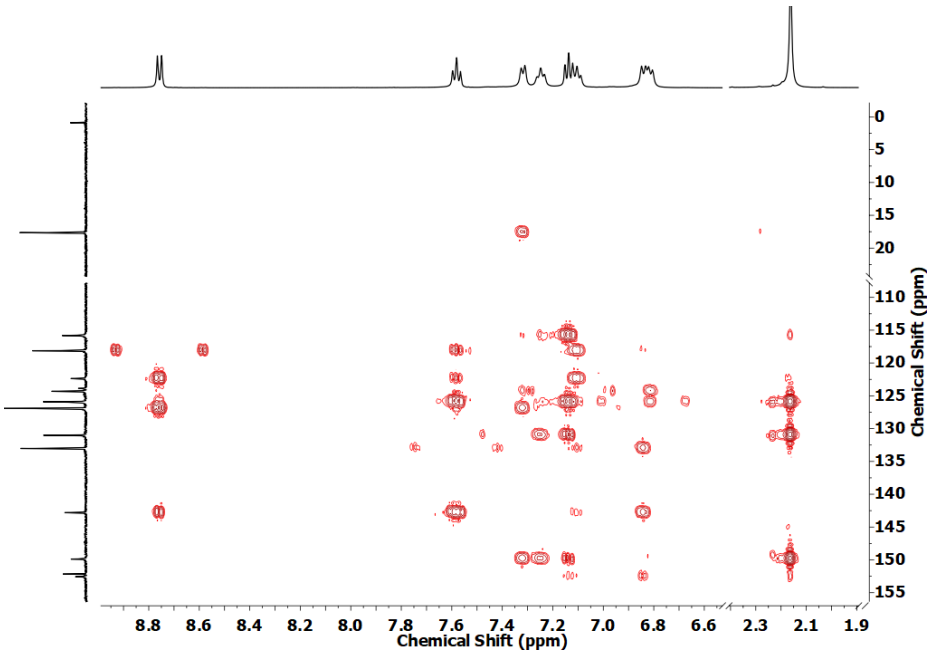


Figure A96 HMBC (500 MHz, 126 MHz) of 3.16a in CD_2Cl_2 at 298 K

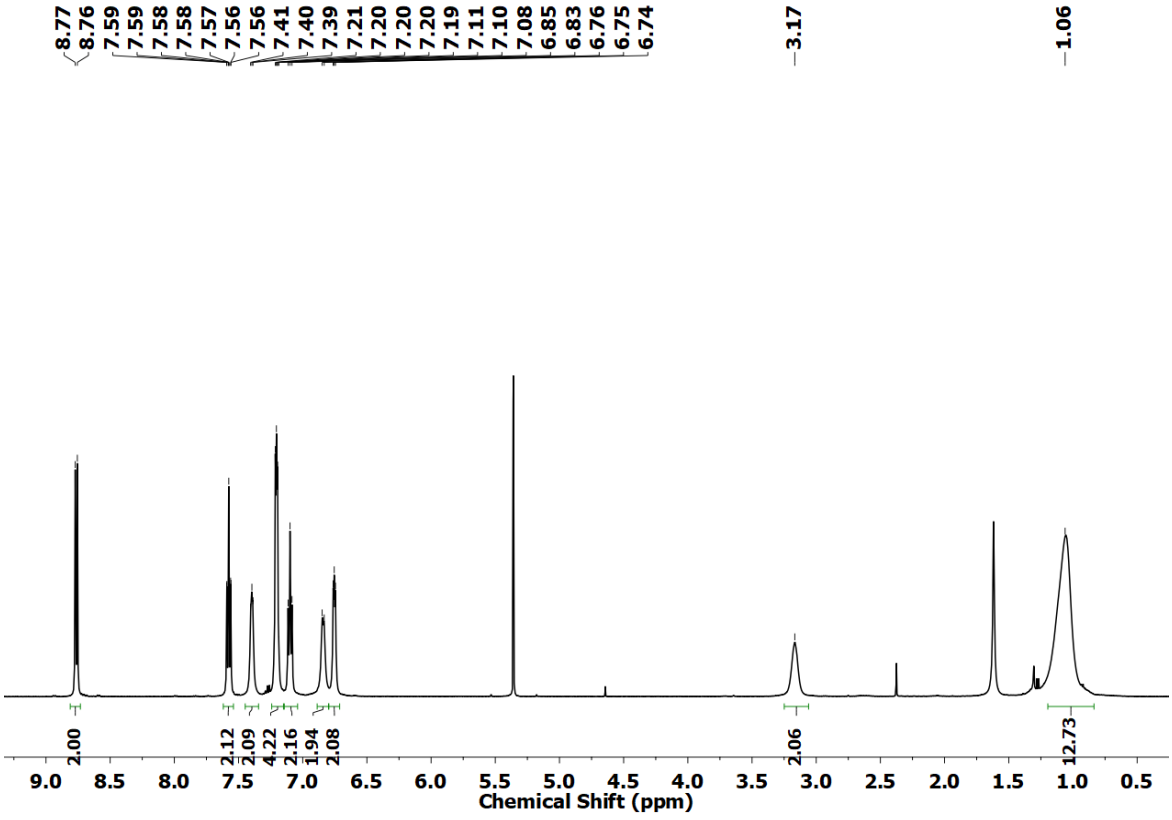


Figure A97 ^{1}H NMR (500 MHz) of 3.16b in CD_2Cl_2 at 298 K

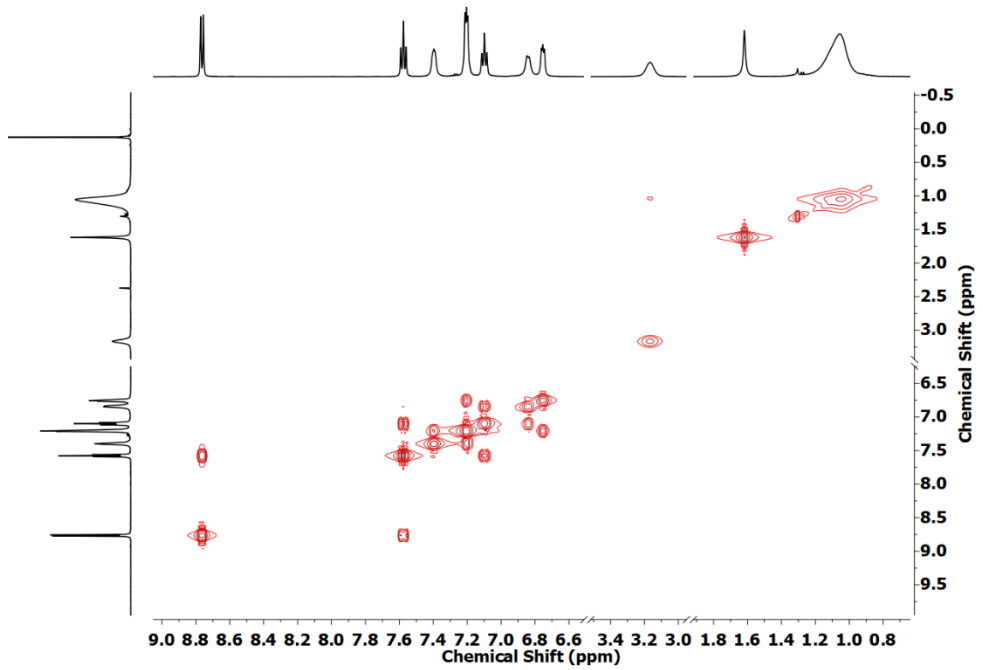


Figure A98 COSY (500 MHz, 500 MHz) of 3.16b in CD_2Cl_2 at 298 K

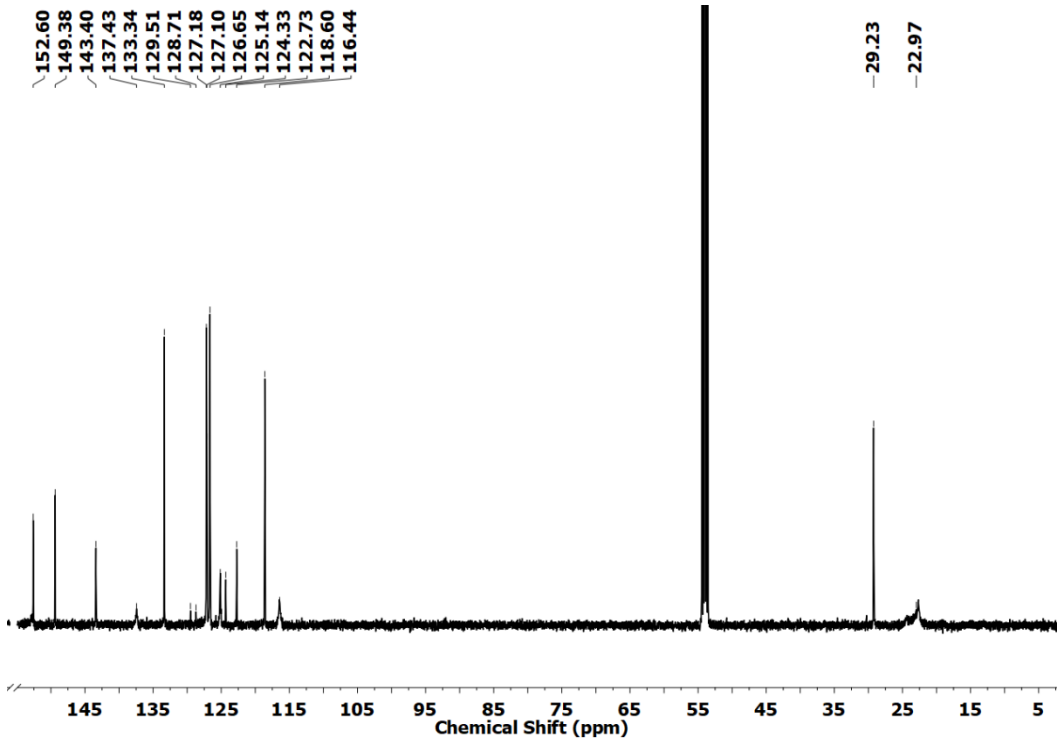


Figure A99 ^{13}C NMR (126 MHz) of 3.16b in CD_2Cl_2 at 298 K

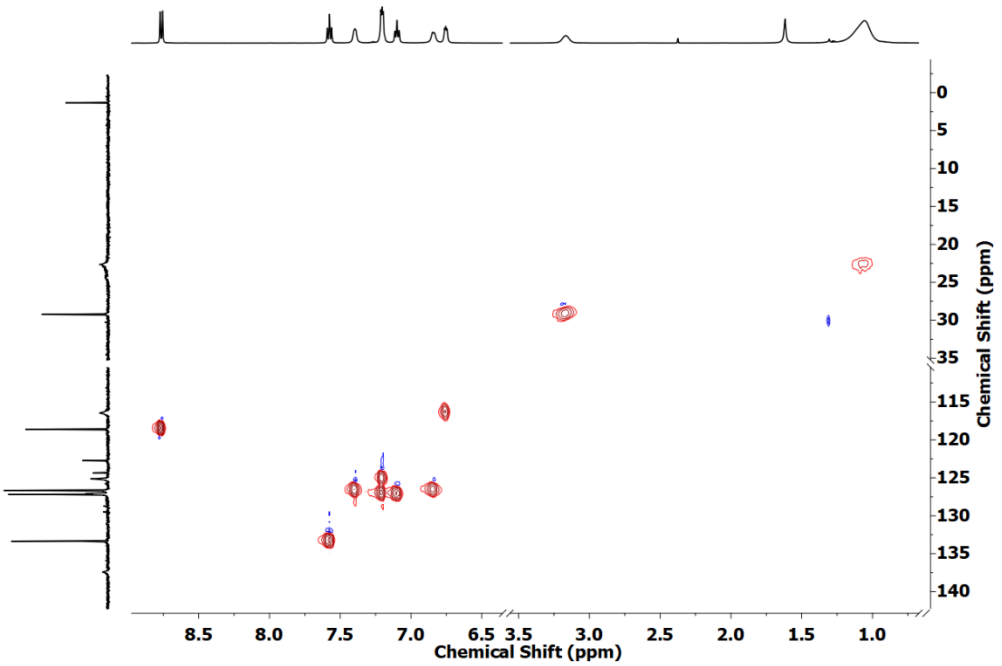


Figure A100 HSQC (500 MHz, 126 MHz) of 3.16b in CD_2Cl_2 at 298 K

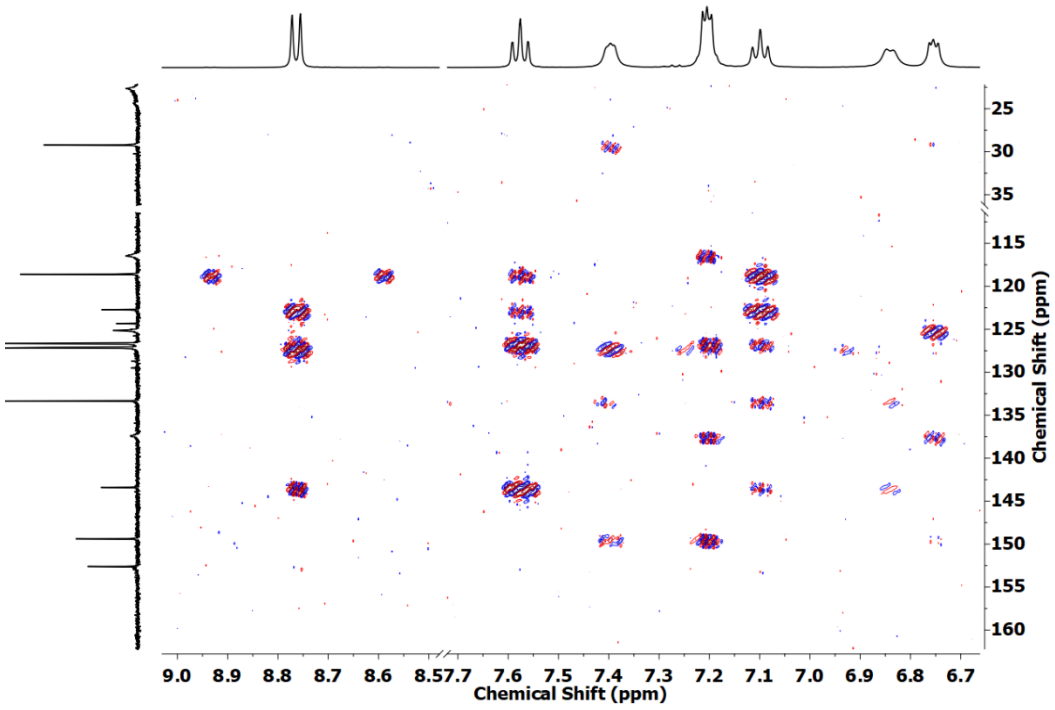


Figure A101 HMBC (500 MHz, 126 MHz) of 3.16b in CD_2Cl_2 at 298 K

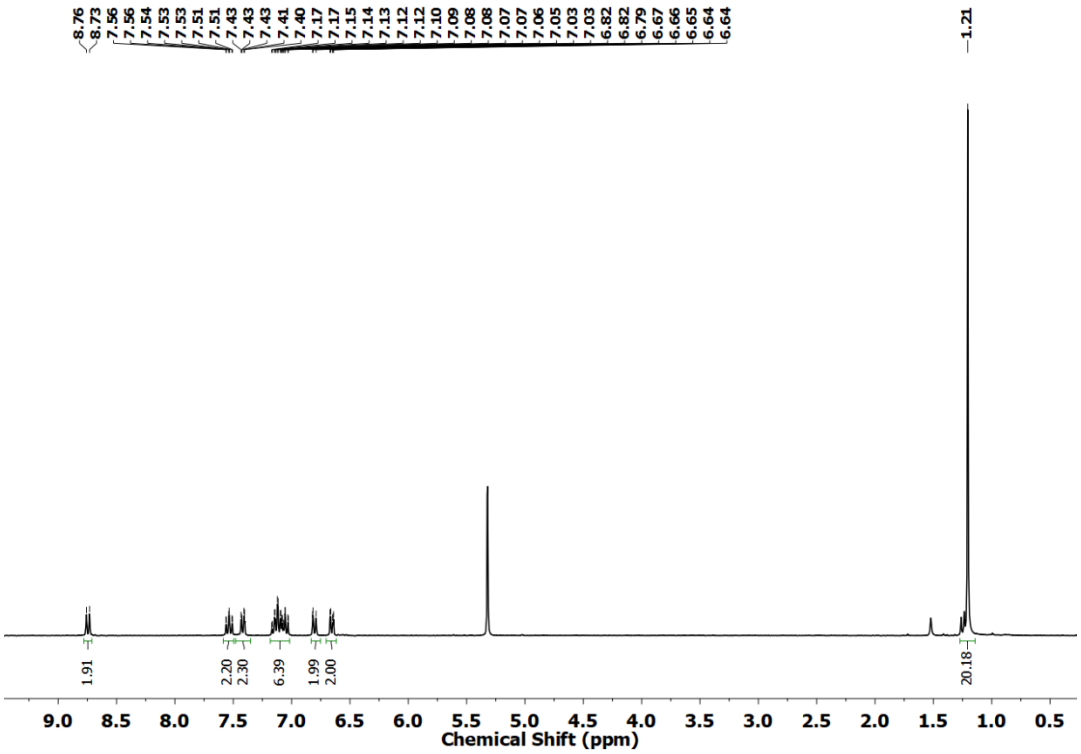


Figure A102 ^{1}H NMR (300 MHz) of 3.16c in CD_2Cl_2 at 298 K

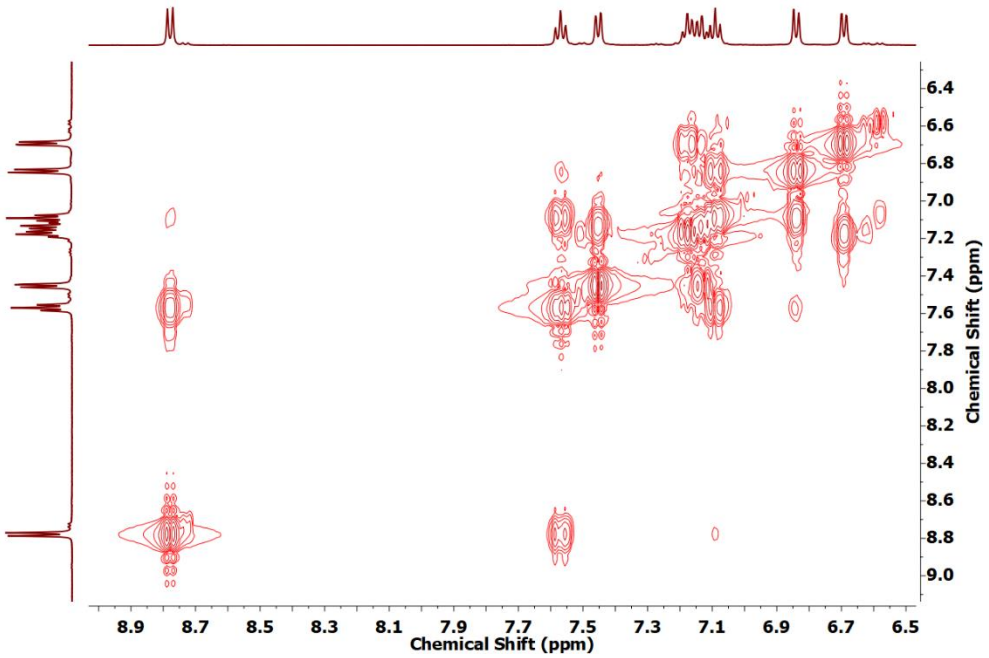


Figure A103 COSY (500 MHz, 500 MHz) of 3.16c in CD_2Cl_2 at 298 K

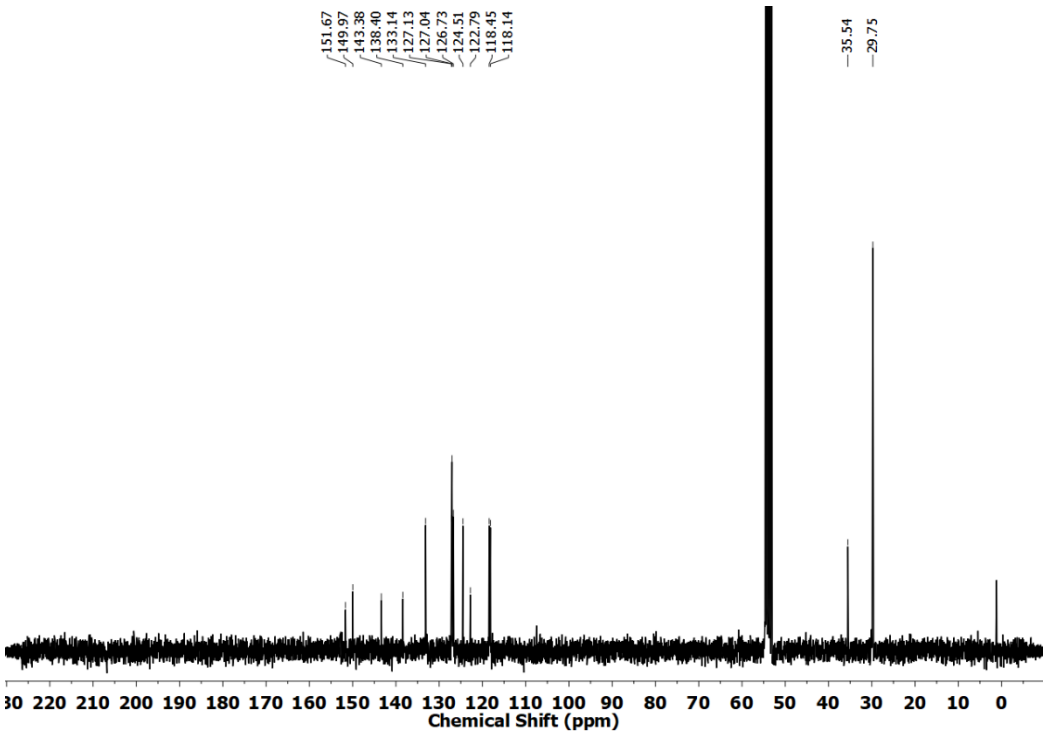


Figure A104 ^{13}C NMR (76 MHz) of 3.16c in CD_2Cl_2 at 298 K

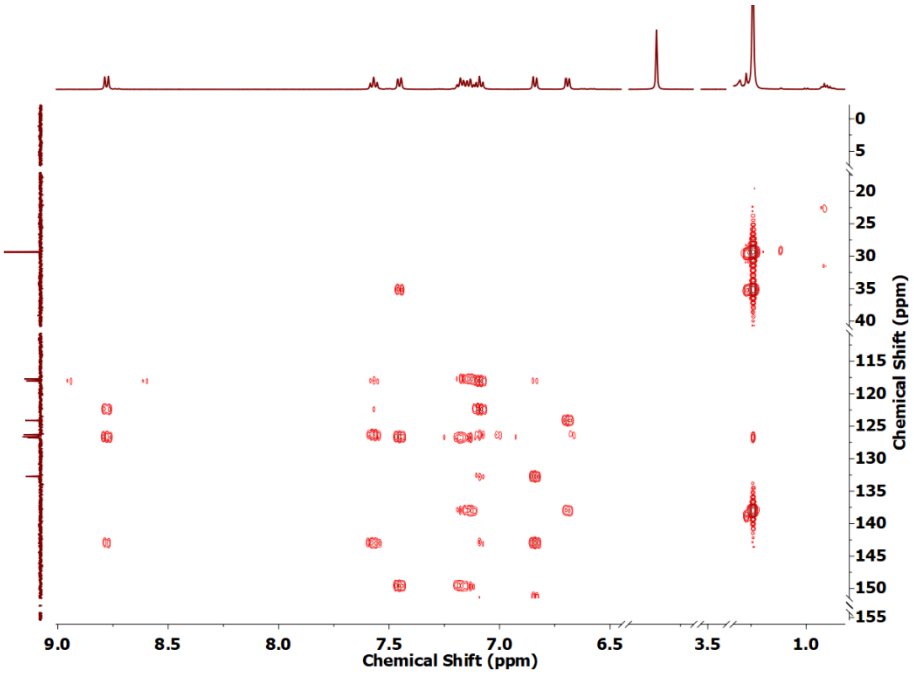


Figure A105 HMBC (500 MHz, 126 MHz) of 3.16c in CD_2Cl_2 at 298 K

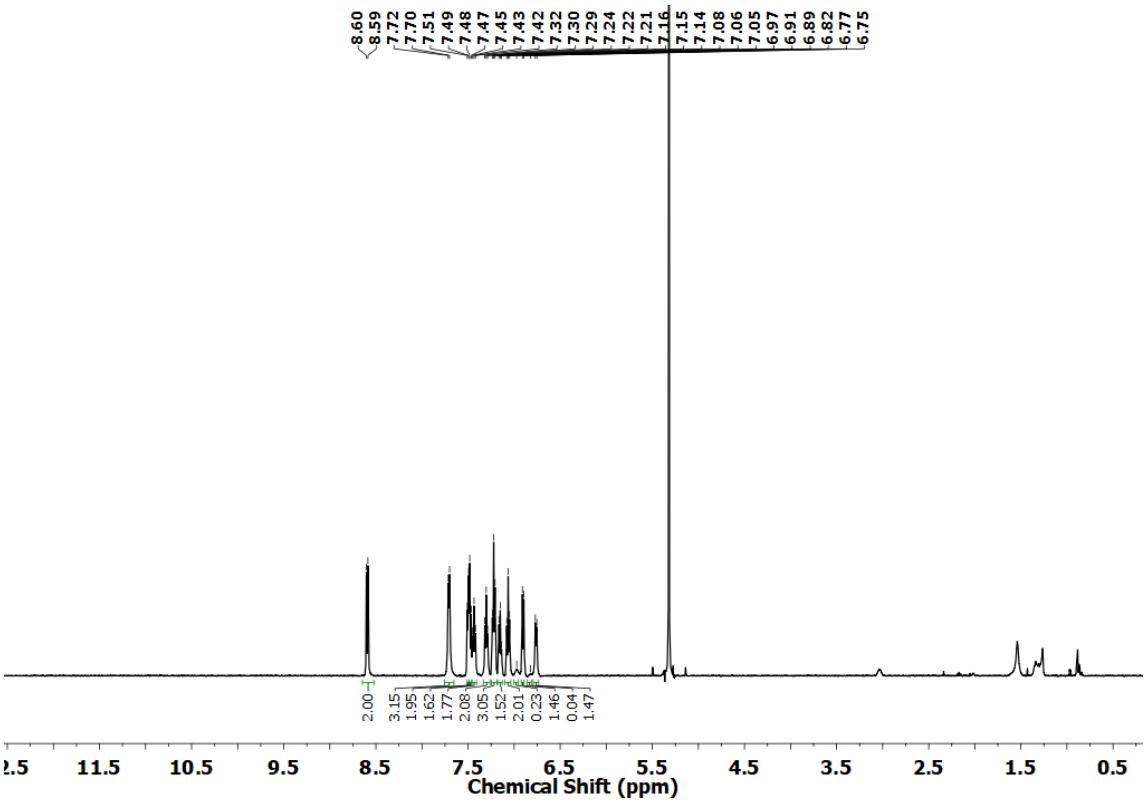


Figure A106 ^{1}H NMR (500 MHz) of 3.16d in CD_2Cl_2 at 298 K

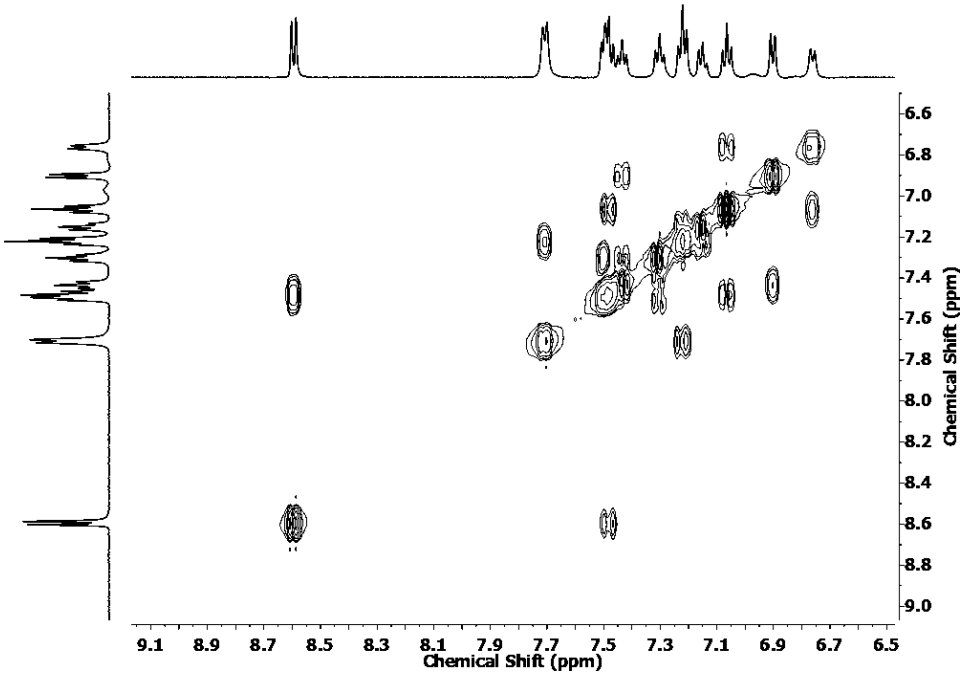


Figure A107 COSY (500 MHz, 500 MHz) of 3.16d in CD_2Cl_2 at 298 K

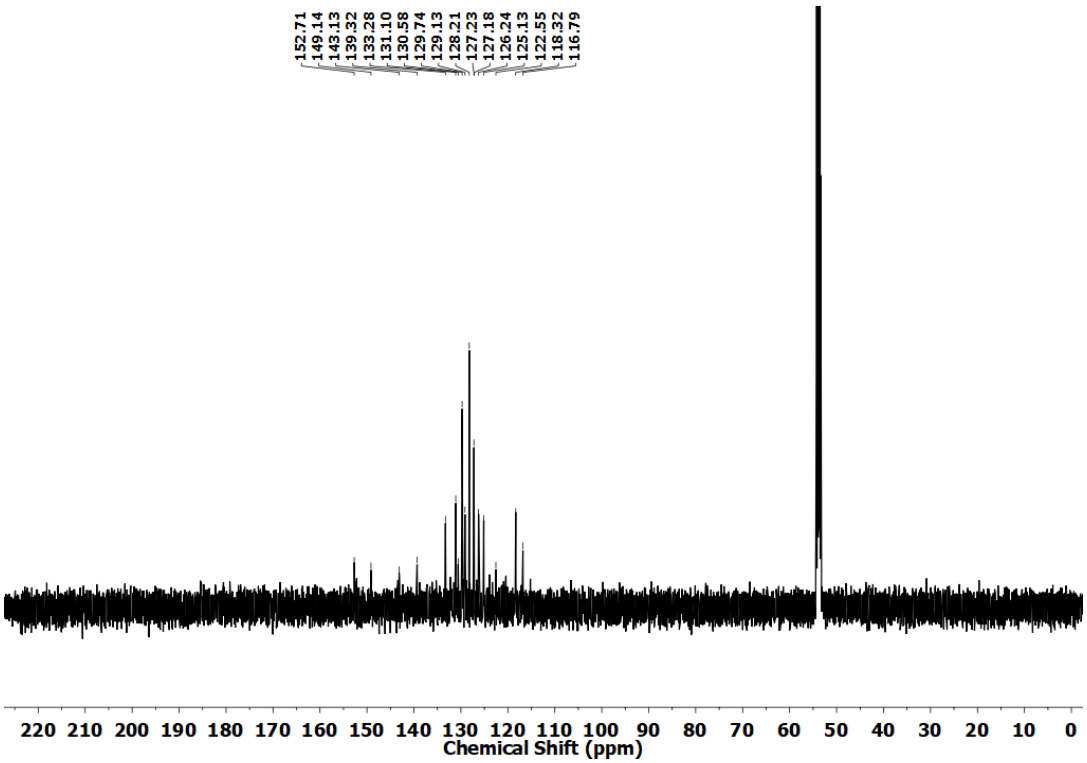


Figure A108 ^{13}C NMR (126 MHz) of 3.16d in CD_2Cl_2 at 298K

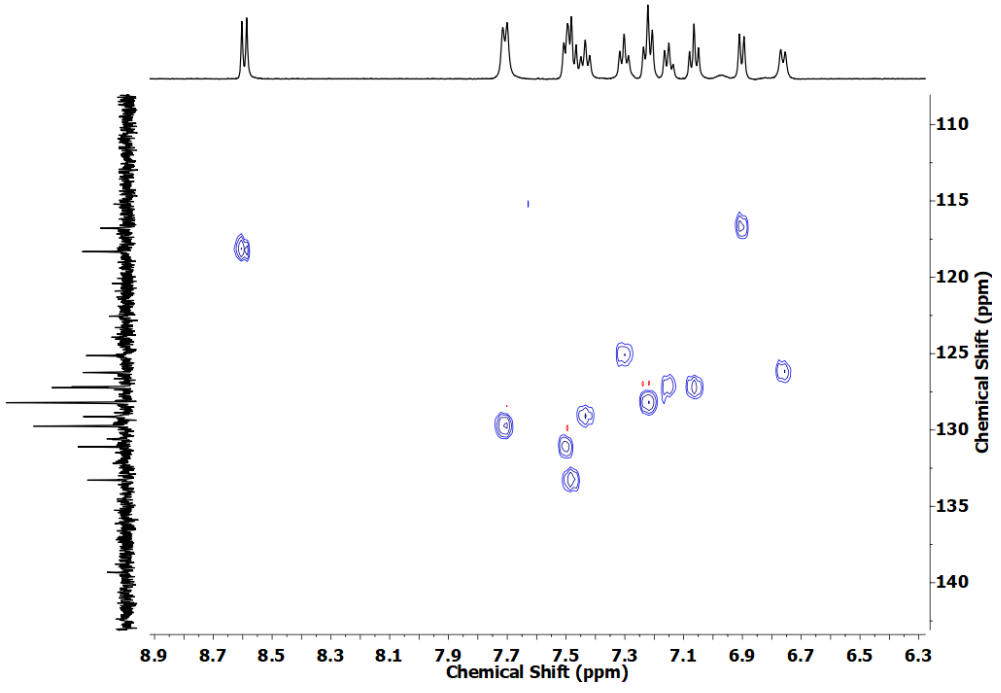


Figure A109 HSQC (500MHz, 126 MHz) of 3.16d in CD_2Cl_2 at 298 K

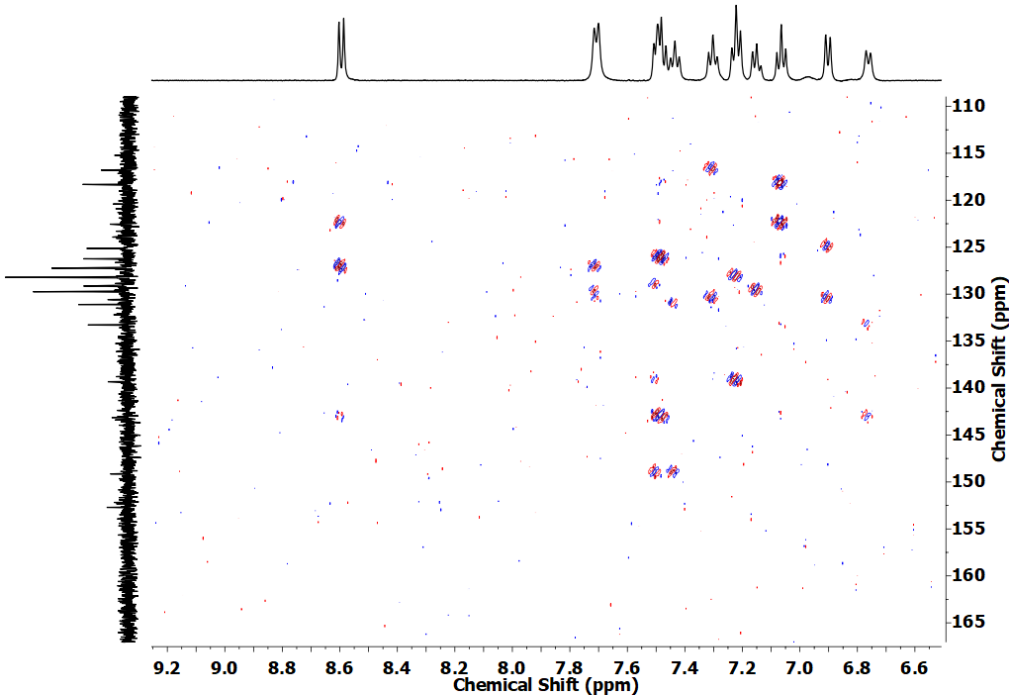


Figure A110 HMBC (500 MHz, 126 MHz) of 3.16d in CD_2Cl_2 at 298 K

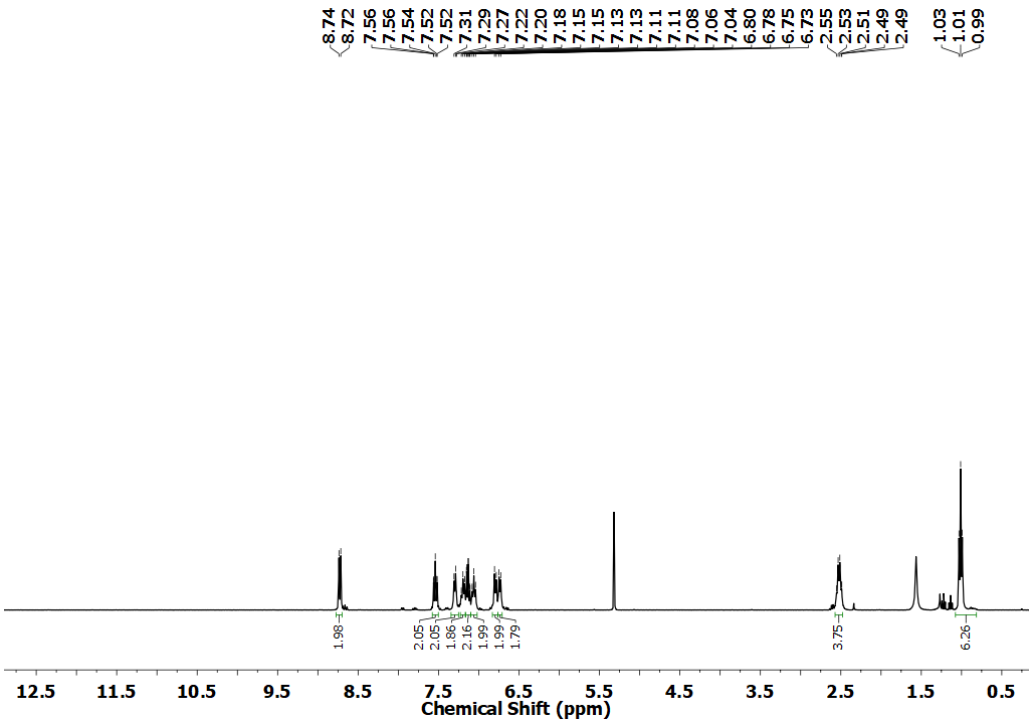


Figure A11 ^{1}H NMR (500 MHz) of 3.16e in CD_2Cl_2 at 298 K

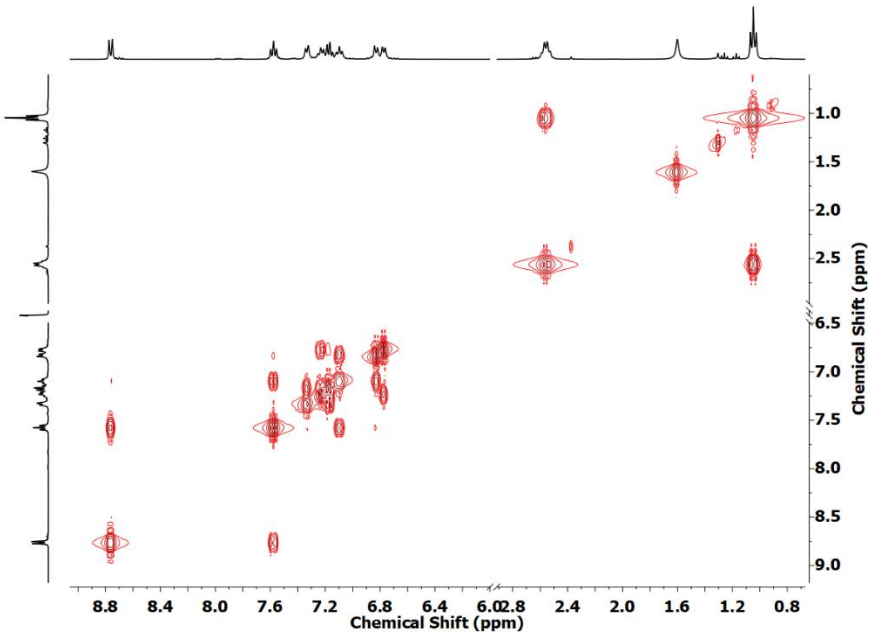


Figure A112 COSY (500 MHz, 500 MHz) of 3.16e in CD_2Cl_2 at 298 K

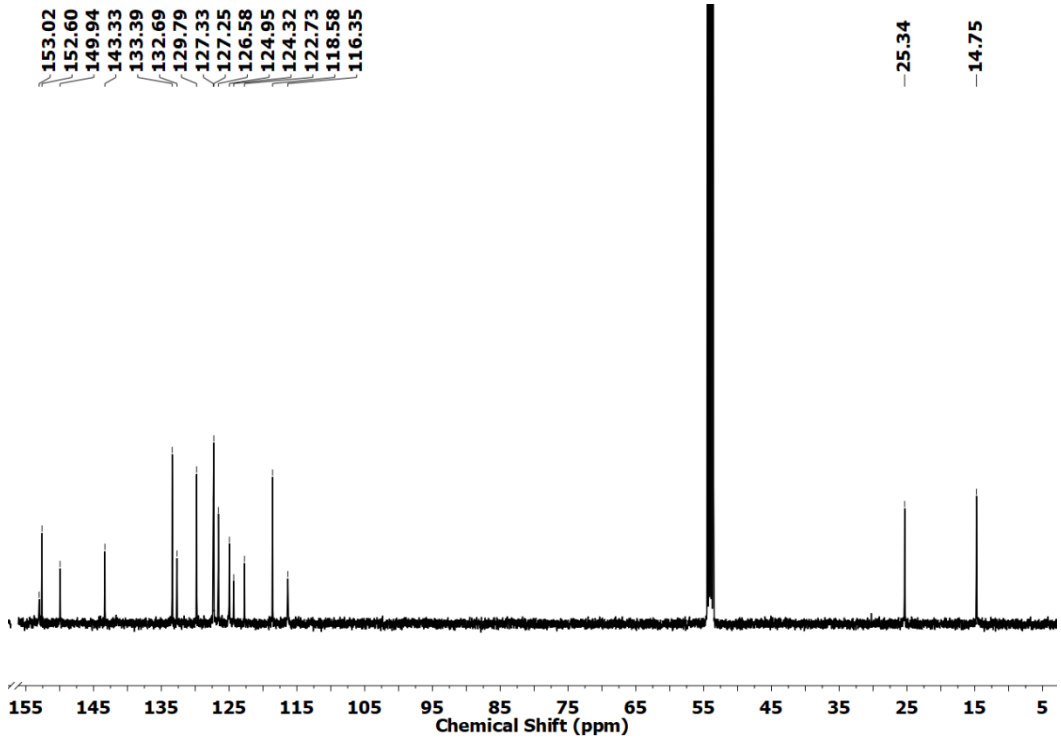


Figure A113 ^{13}C NMR (500 MHz) of 3.16e in CD_2Cl_2 at 298 K

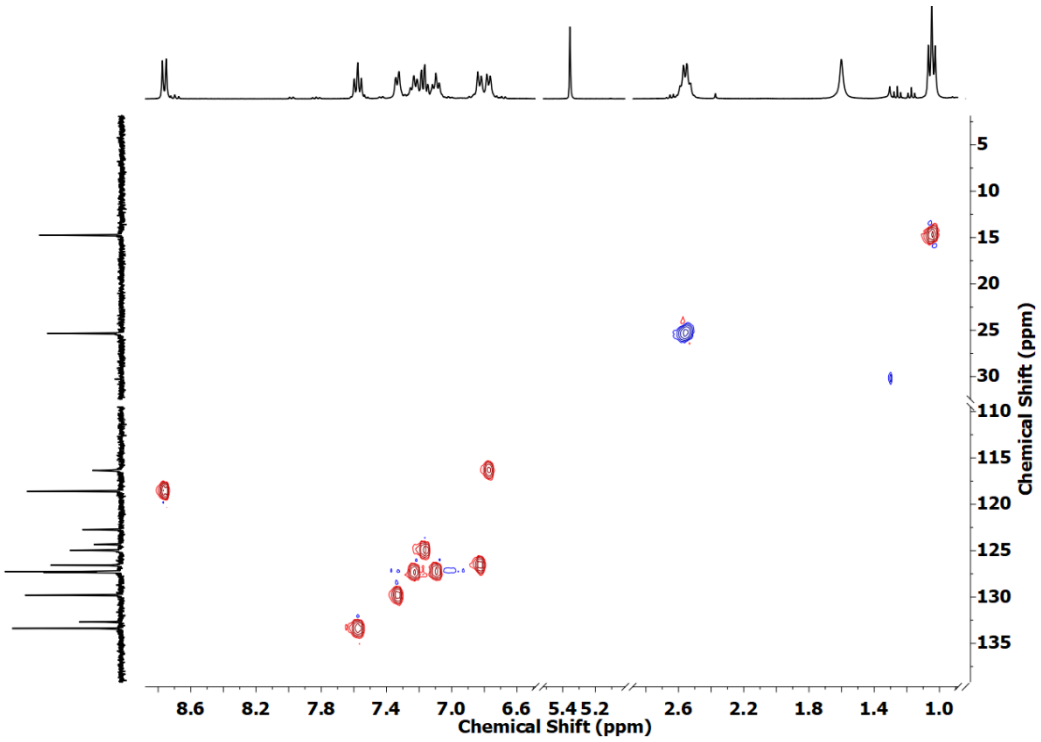


Figure A114 HSQC (500 MHz, 126 MHz) of 3.16e in CD_2Cl_2 at 298 K

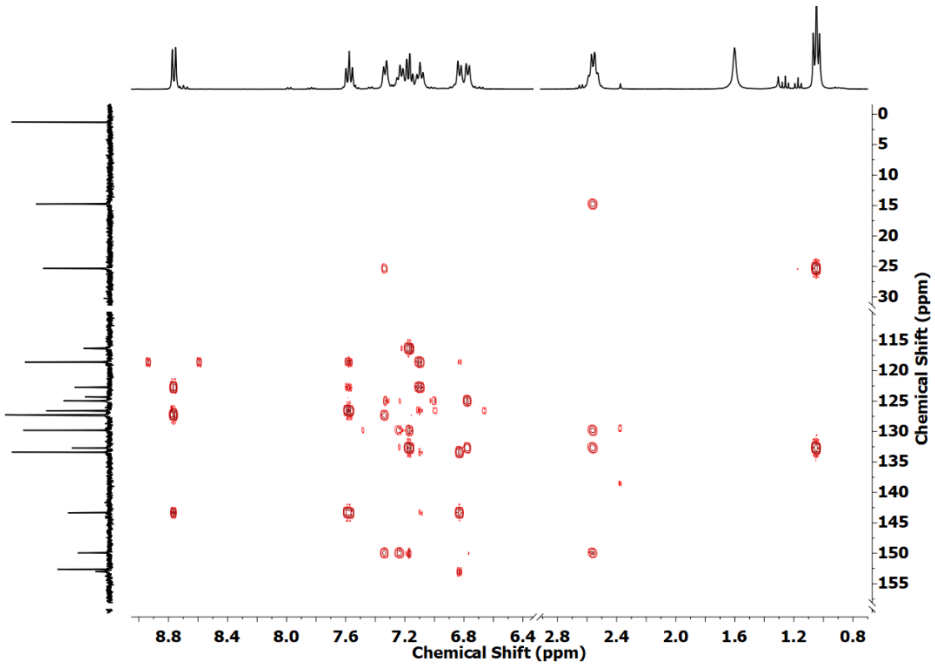


Figure A115 HMBC (500 MHz, 126 MHz) of 3.16e in CD_2Cl_2 at 298 K

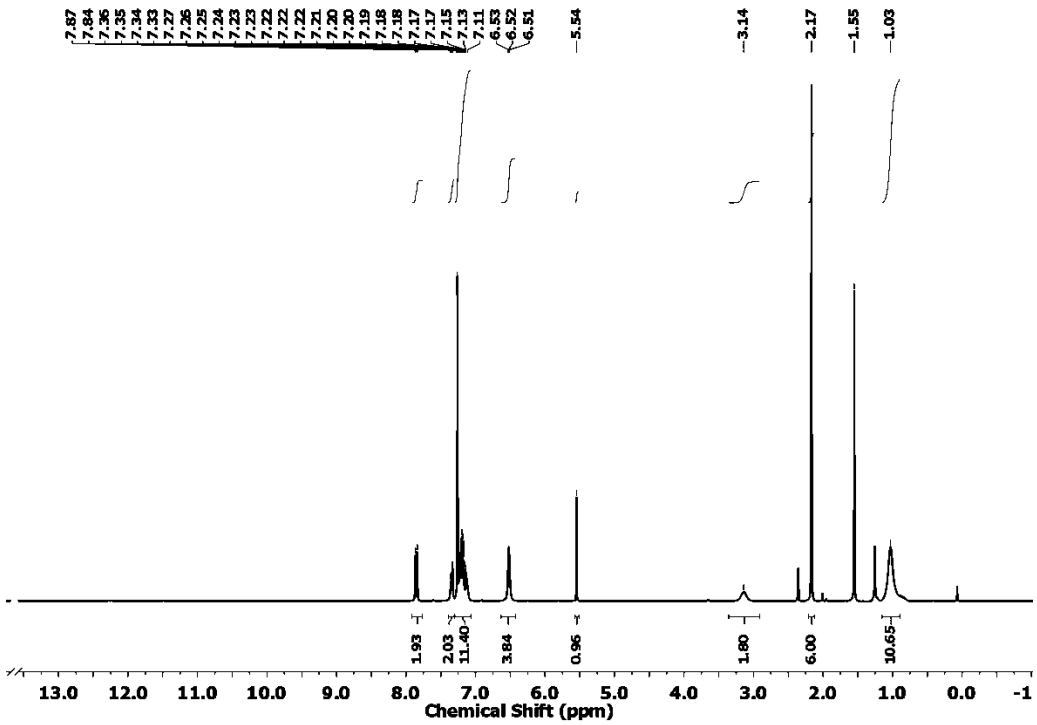


Figure A116 ^{1}H NMR (500 MHz) of 4.5b in CD_2Cl_2

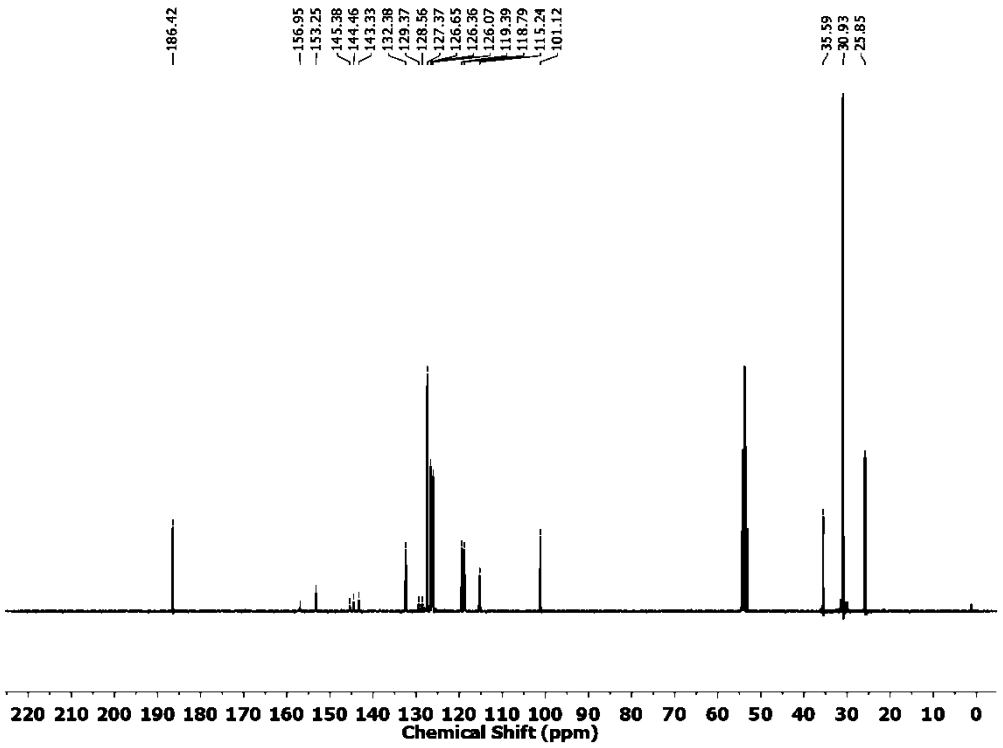


Figure A117 ^{13}C NMR (126 MHz) of 4.5b in CD_2Cl_2 at 298 K

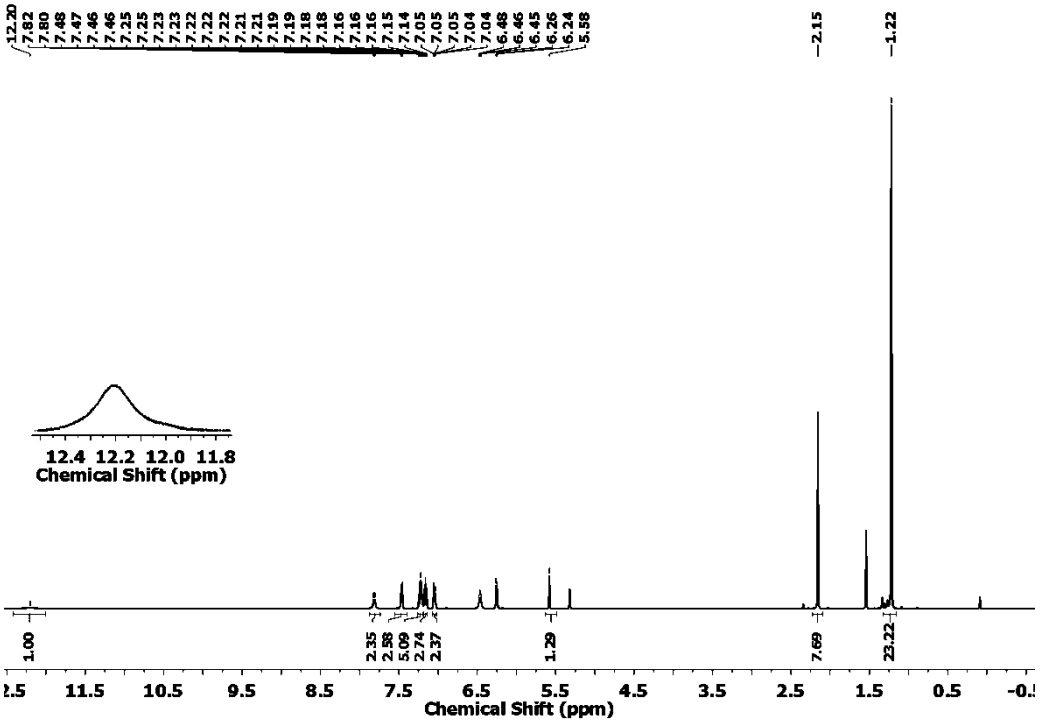


Figure A118 ^{1}H NMR (500 MHz) of 4.5c in CD_2Cl_2 at 298 K

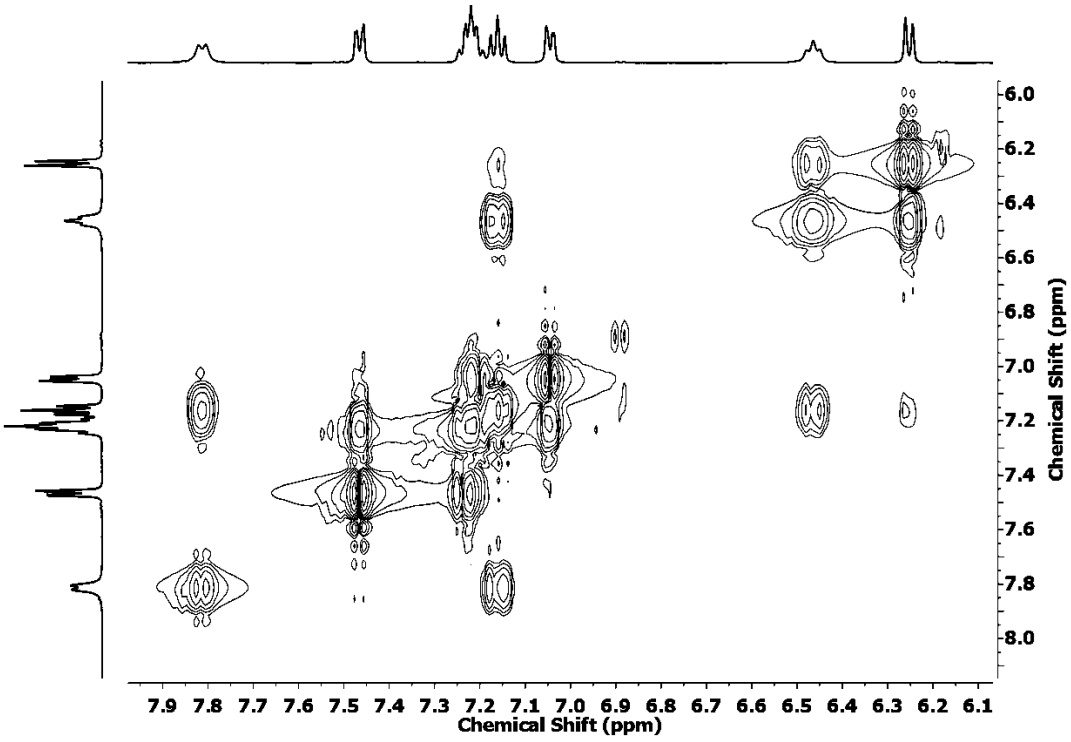


Figure A119 COSY (500 MHz, 500 MHz) of 4.5c in CD_2Cl_2 at 298 K

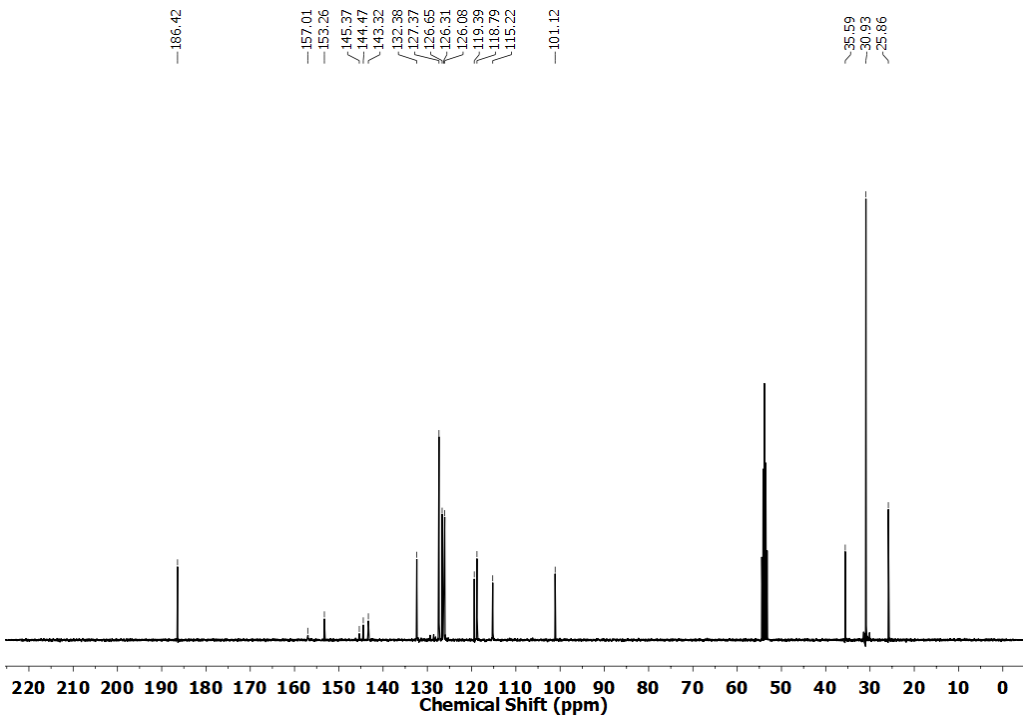


Figure A120 UDEFT (91 MHz) of 4.5c in CD_2Cl_2 at 298 K

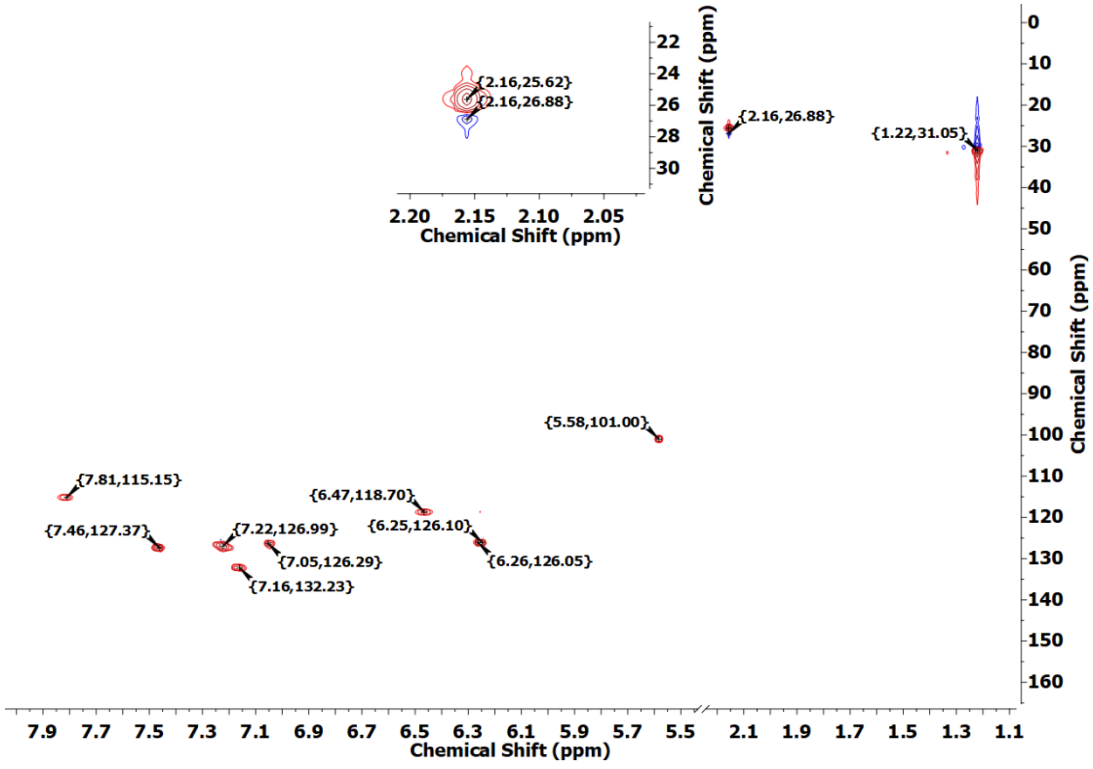


Figure A121 HSQC (500 MHz, 126 MHz) of 4.5c in CD_2Cl_2 at 298 K

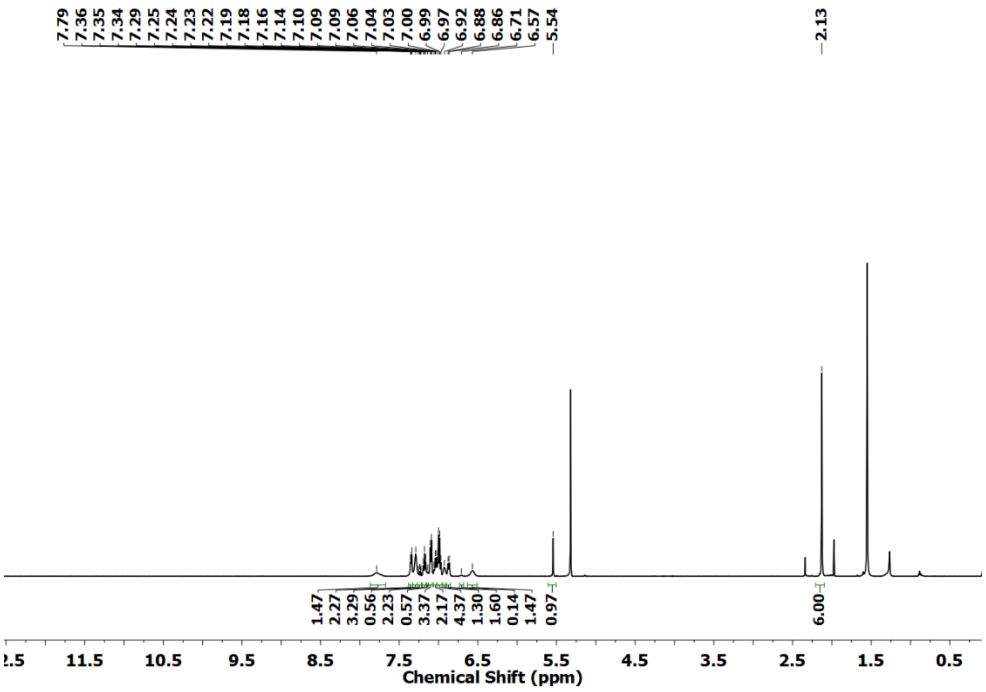


Figure A122 ^{1}H NMR (500 MHz) of 4.5d in CD_2Cl_2 at 298 K

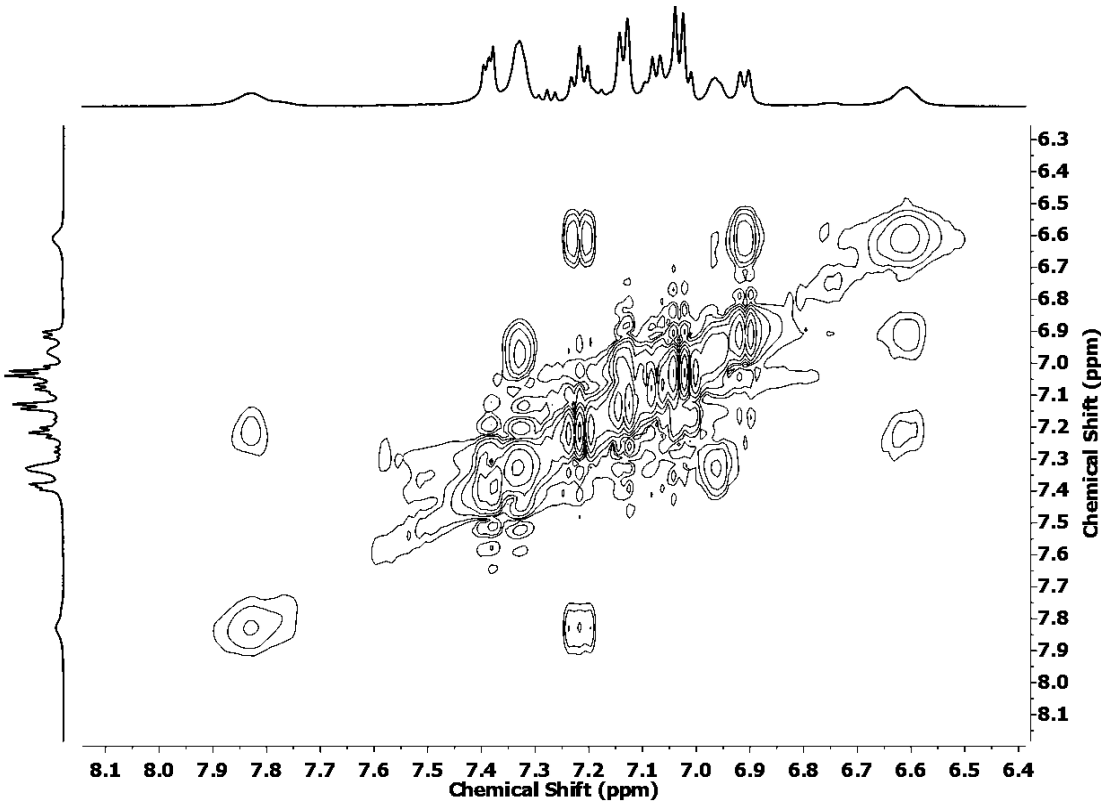


Figure A123 COSY (500 MHz, 500 MHz) of 4.5d in CD_2Cl_2 at 298 K

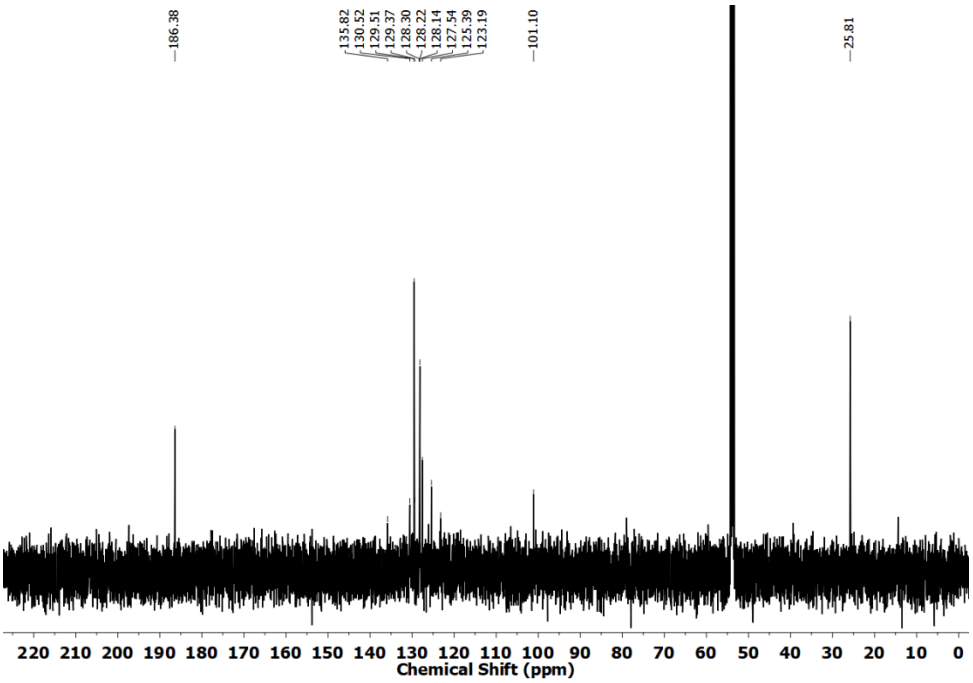


Figure A124 ^{13}C NMR (126 MHz) of 4.5d in CD_2Cl_2 at 298 K

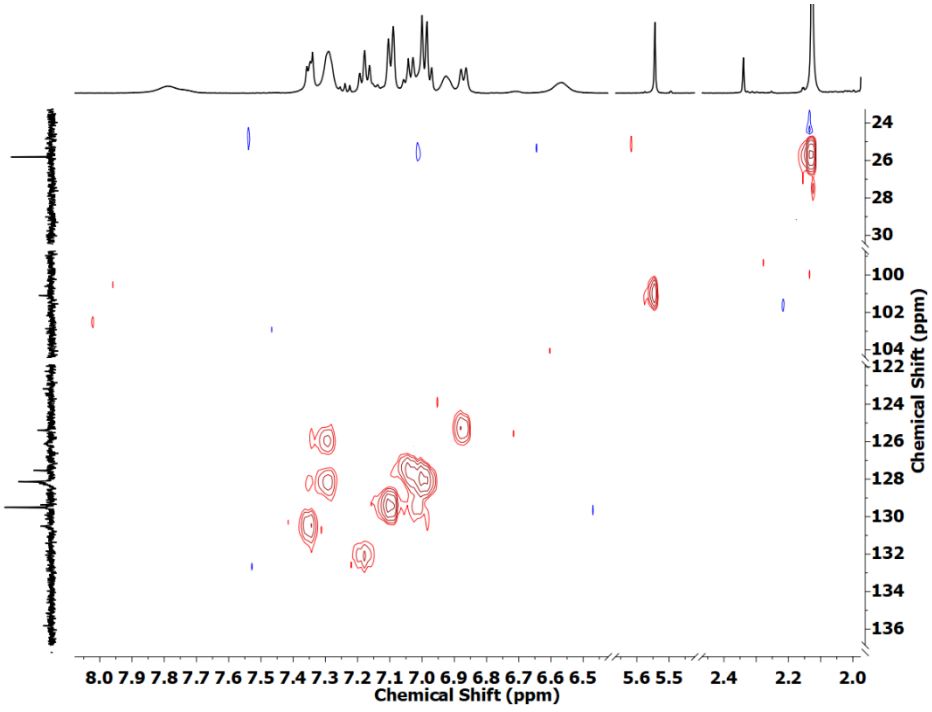


Figure A125 HSQC (500 MHz, 126 MHz) of 4.5d in CD_2Cl_2 at 298 K

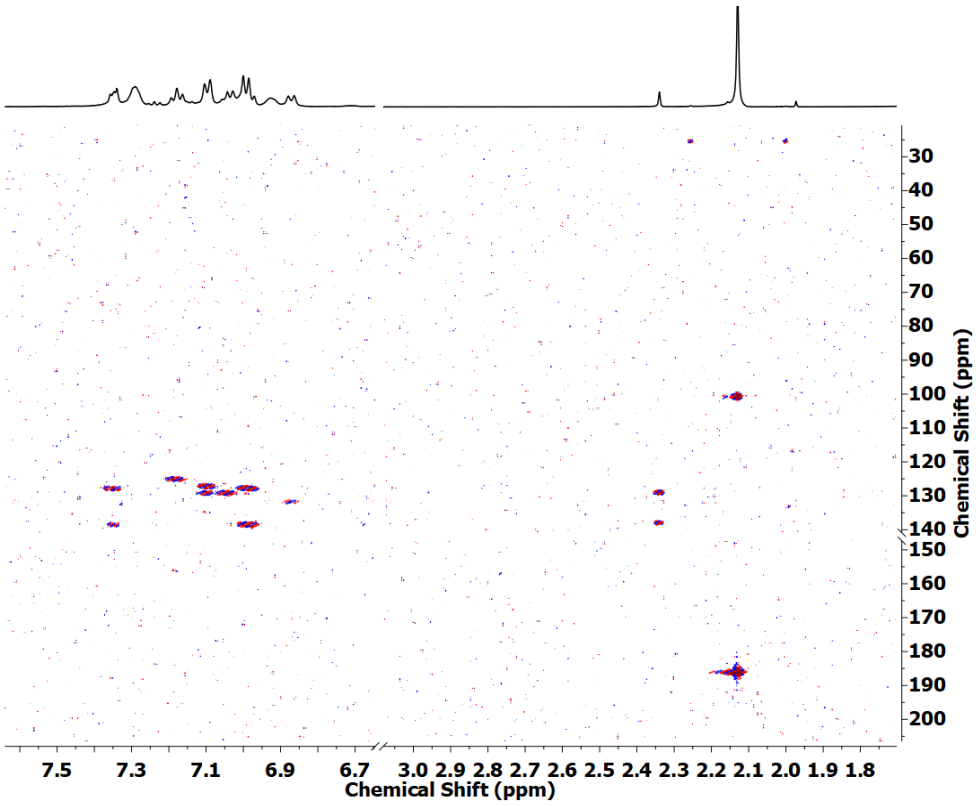


Figure A126 HMBC (500 MHz, 126 MHz) of 4.5d in CD_2Cl_2 at 298 K

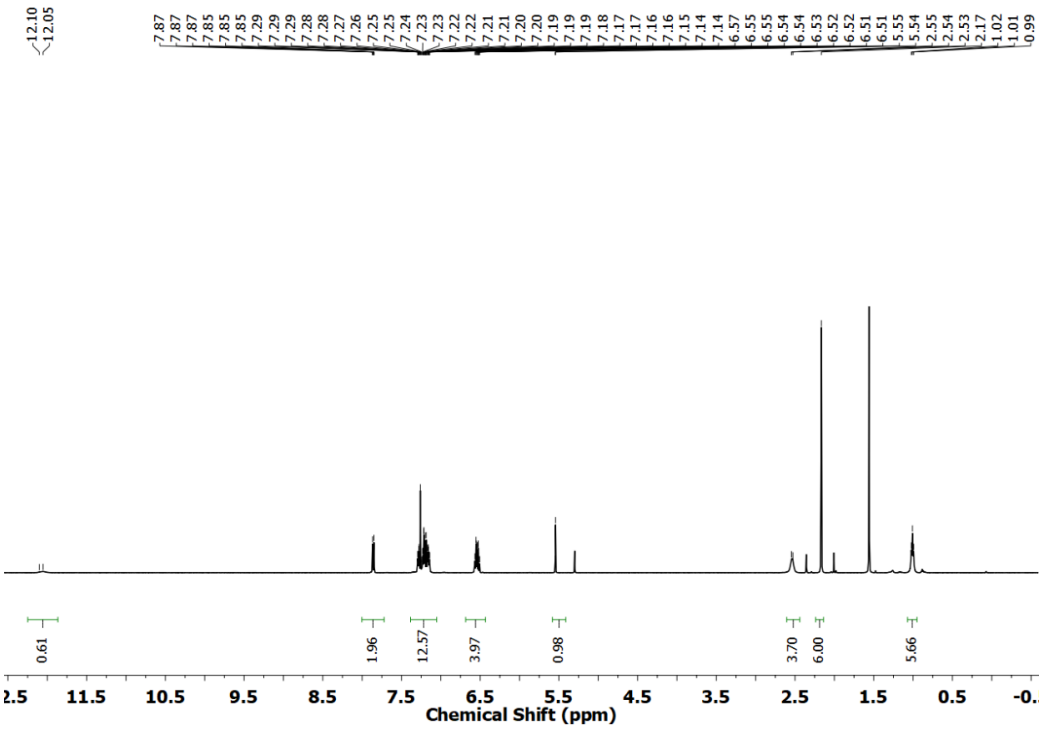


Figure A127 ^{1}H NMR (500 MHz) of 4.5e in $CDCl_3$ at 298 K

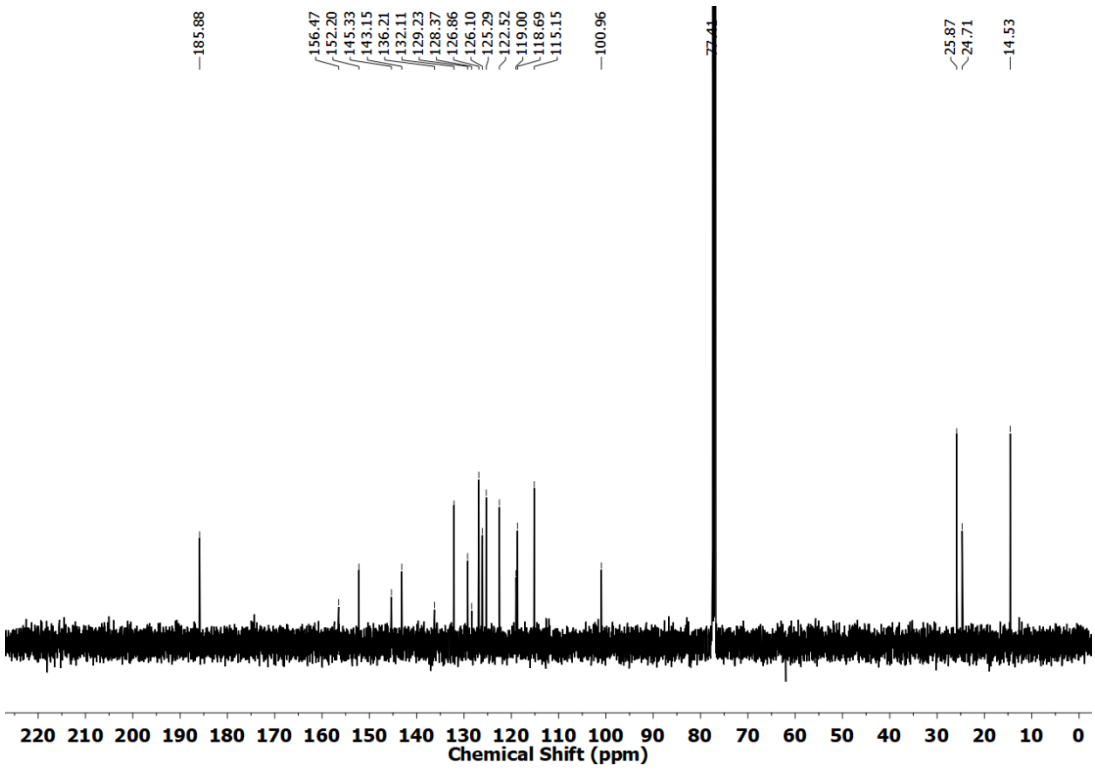


Figure A128 ^{13}C NMR (126 MHz) of 4.5e in $CDCl_3$ at 298 K

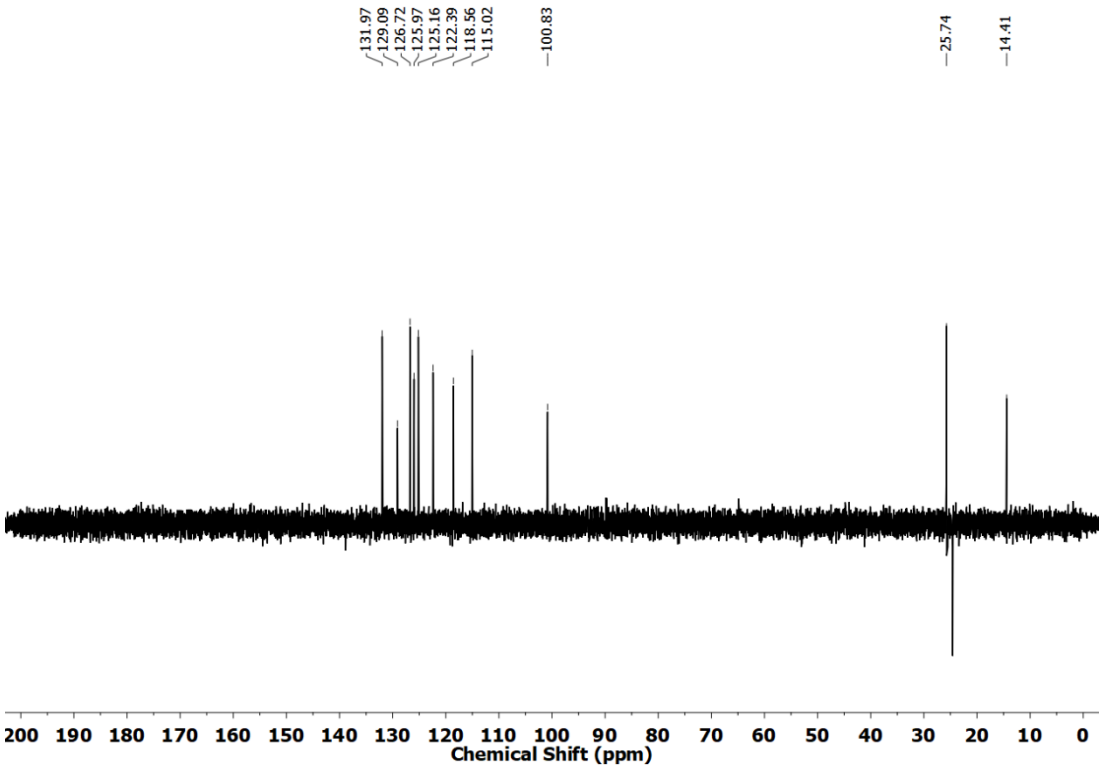


Figure A129 DEPT135 (126 MHz) of 4.5e in $CDCl_3$ at 298 K

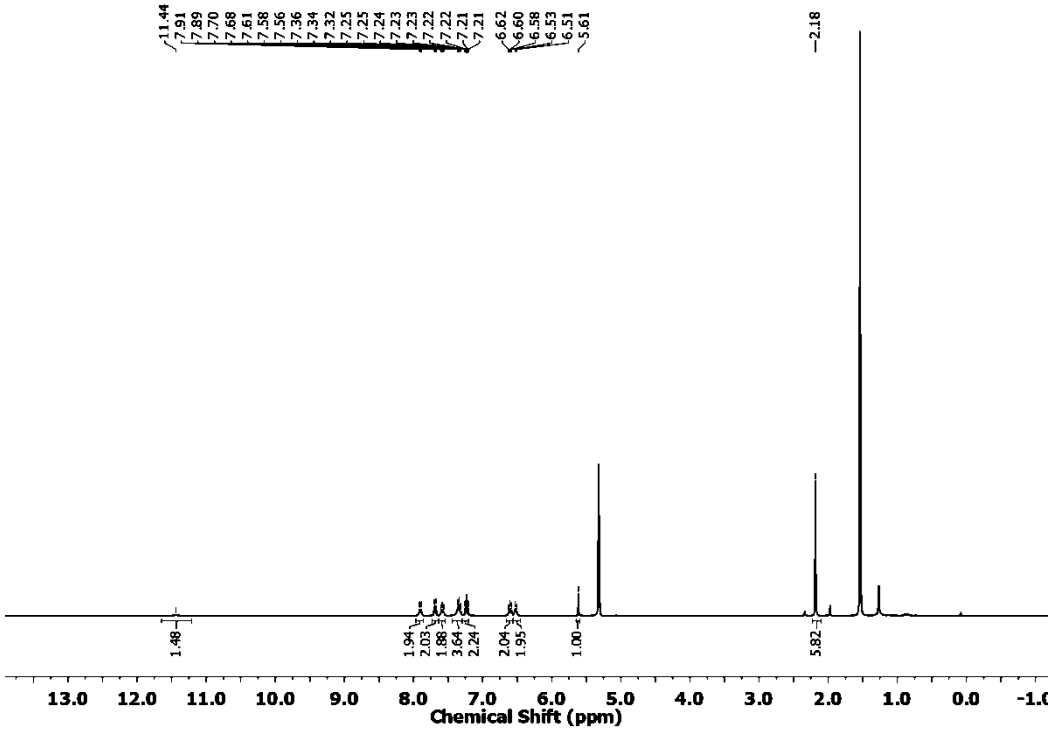


Figure A130 ^{1}H NMR (360 MHz) of 4.5f in CD_2Cl_2 at 298 K

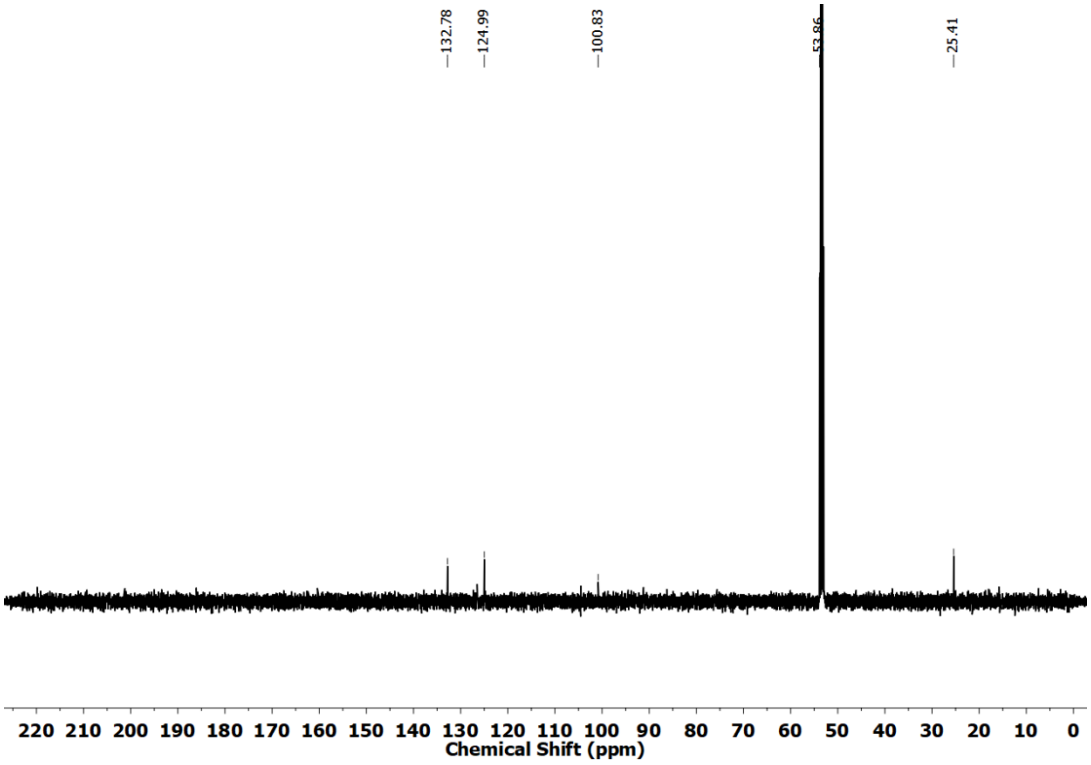


Figure A131 UDEFT (126 MHz) of 4.5f in CD_2Cl_2 at 298 K

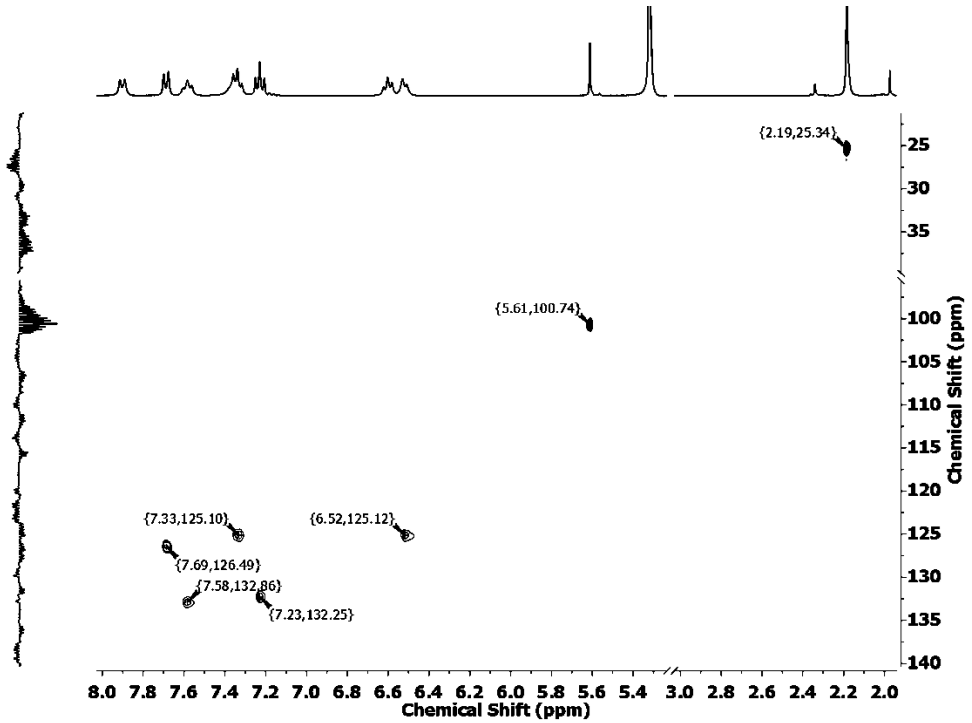


Figure A132 HSQC (500 MHz, 126 MHz) of 4.5f in CD_2Cl_2 at 298 K

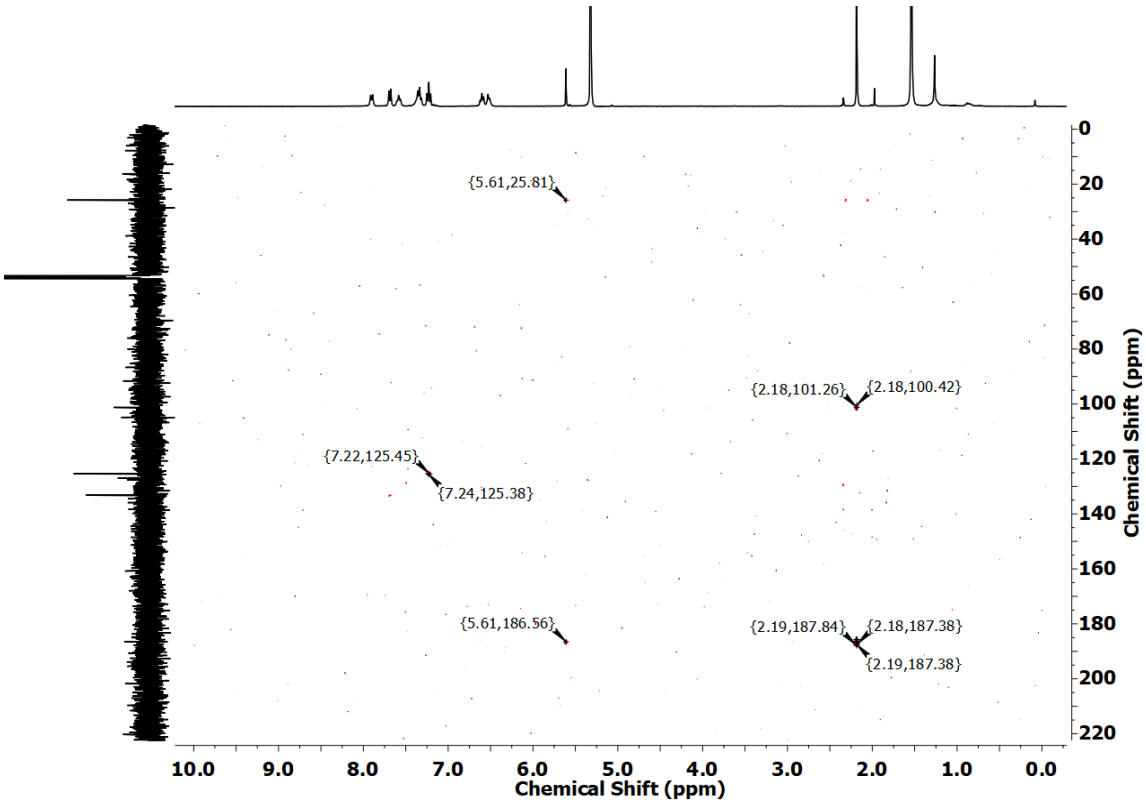


Figure A133 HMBC (500 MHz, 126 MHz) of 4.5f in CD_2Cl_2 at 298 K

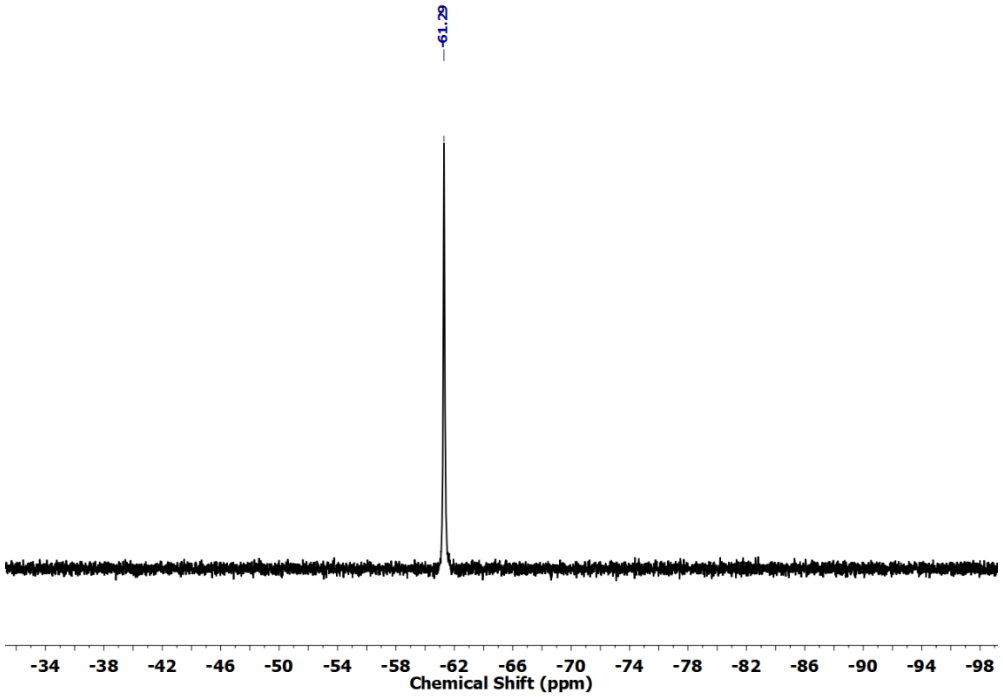


Figure A134 ^{19}F NMR (283 MHz) of 4.5f in CD_2Cl_2 at 298 K

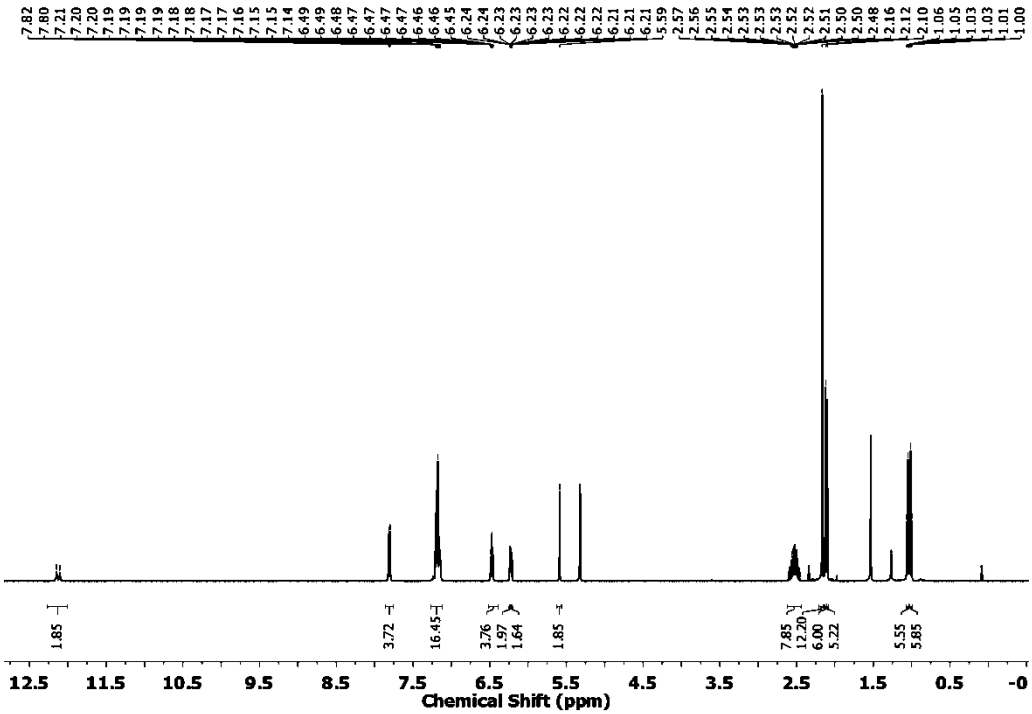


Figure A153 ^{1}H NMR (500 MHz) of 4.5g in CD_2Cl_2 at 298 K

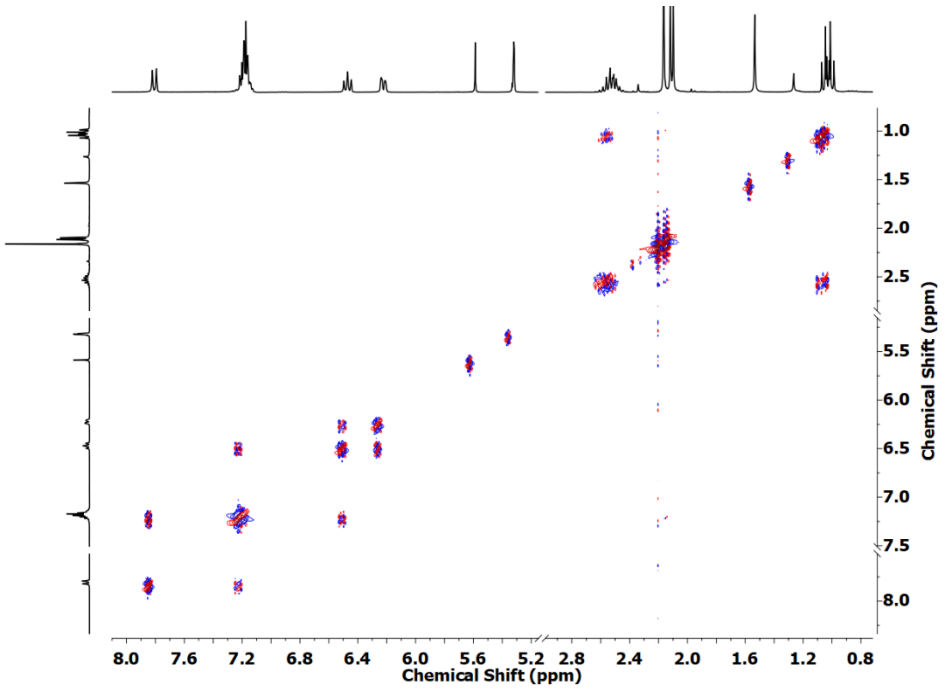


Figure A154 COSY (500 MHz, 500 MHz) of 4.5g in CD_2Cl_2 at 298 K

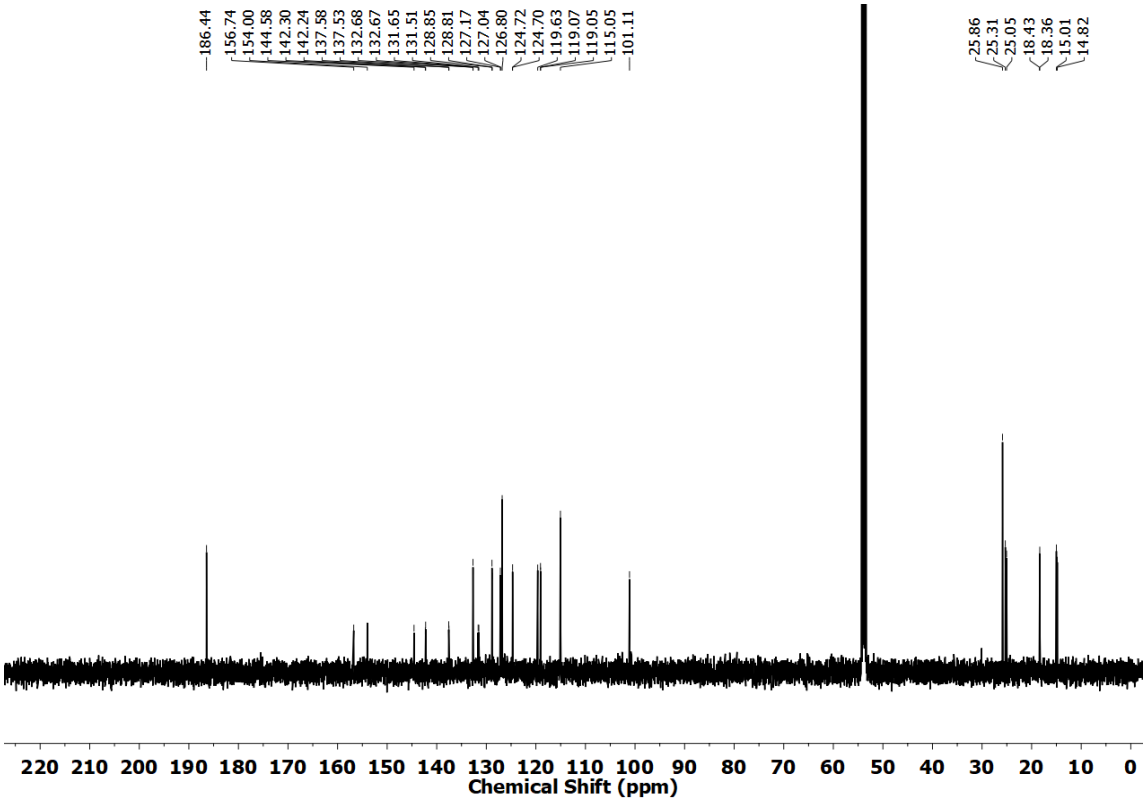


Figure A155 13C NMR (126 MHz) of 4.5g in CD_2Cl_2 at 298 K

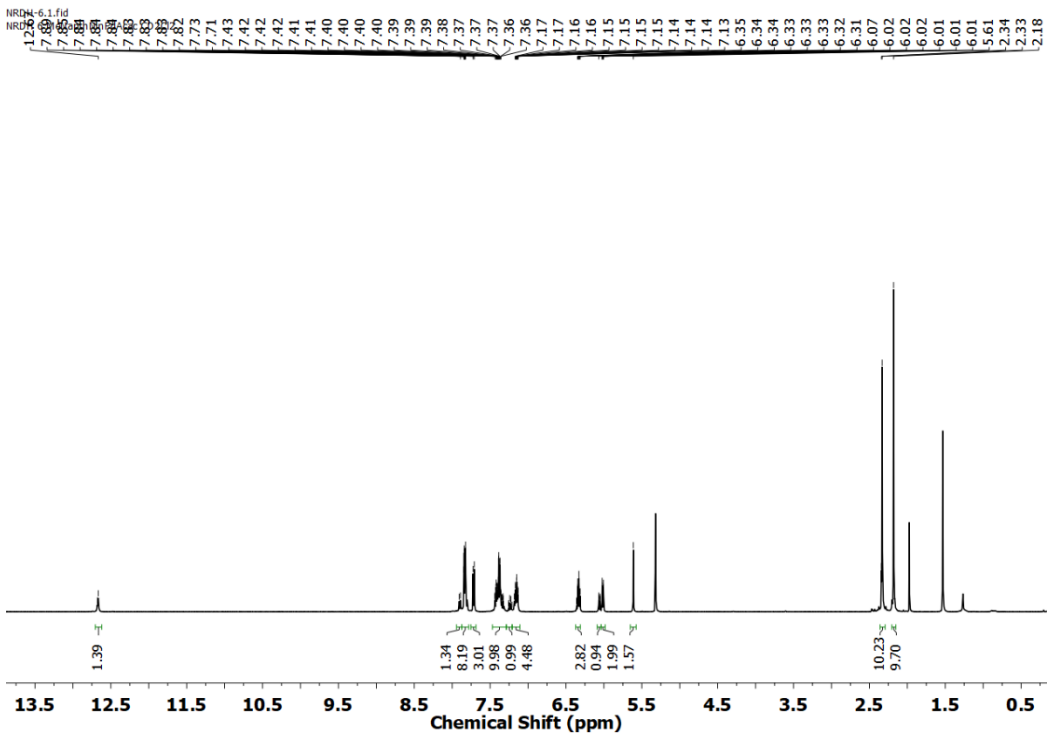


Figure A156 ^{1}H NMR (500 MHz) of 4.5h in CD_2Cl_2 at 298 K

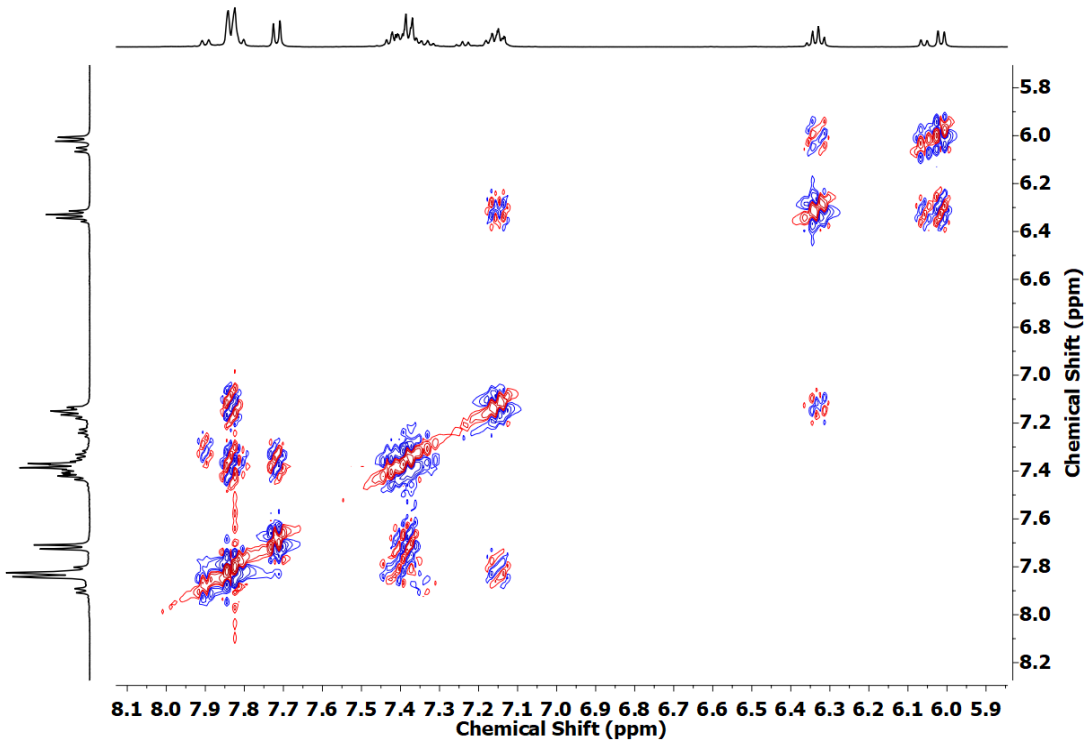


Figure A157 COSY (500 MHz, 500 MHz) of 4.5h in CD_2Cl_2 at 298 K

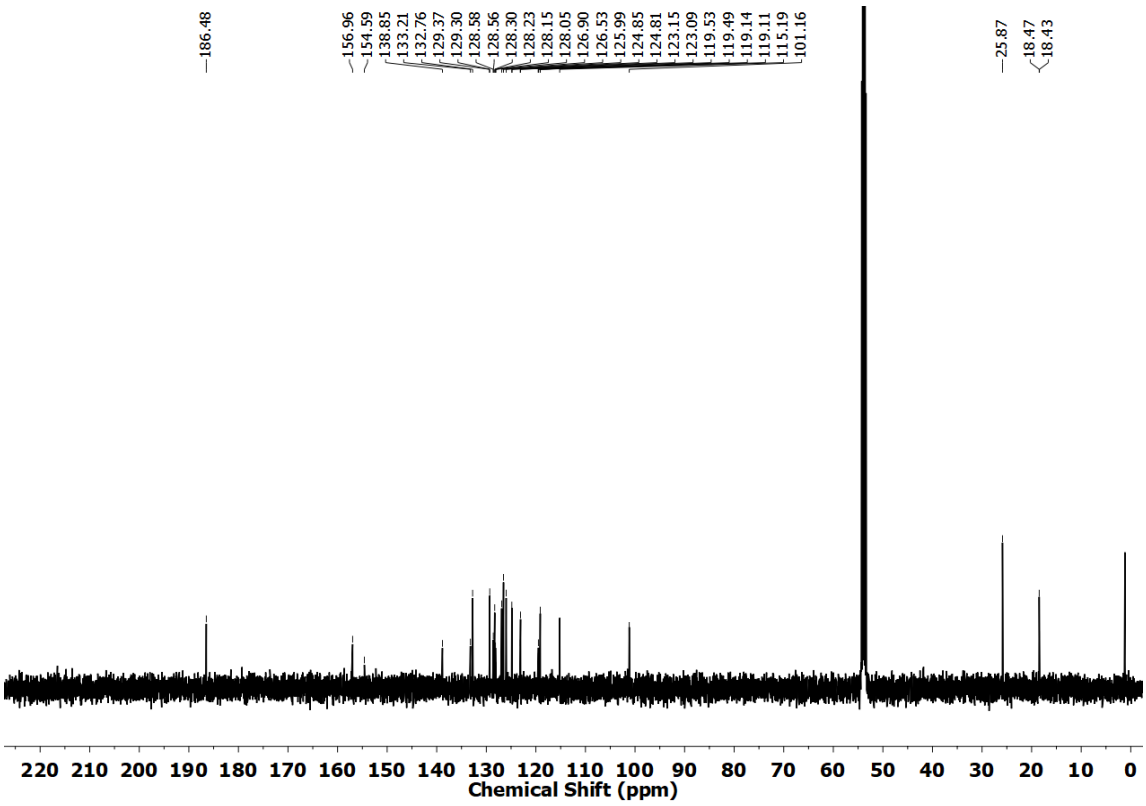


Figure A158 ^{13}C NMR (126 MHz) of 4.5h in CD_2Cl_2 at 298 K

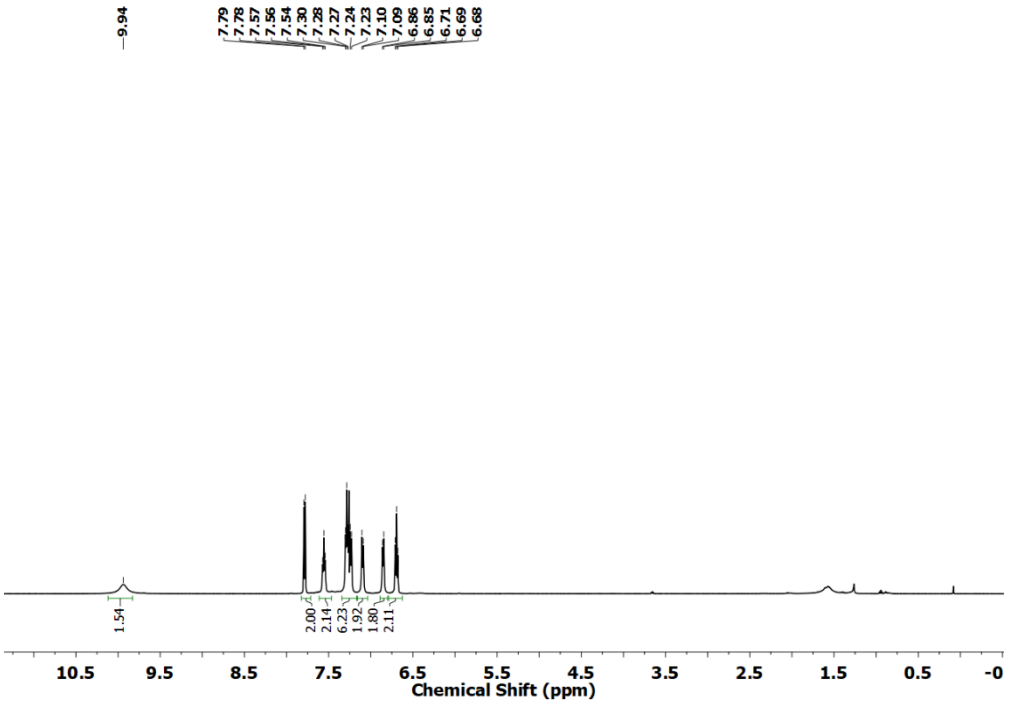


Figure A159 ^{1}H NMR (500 MHz) of 4.6 in $CDCl_3$ at 298 K

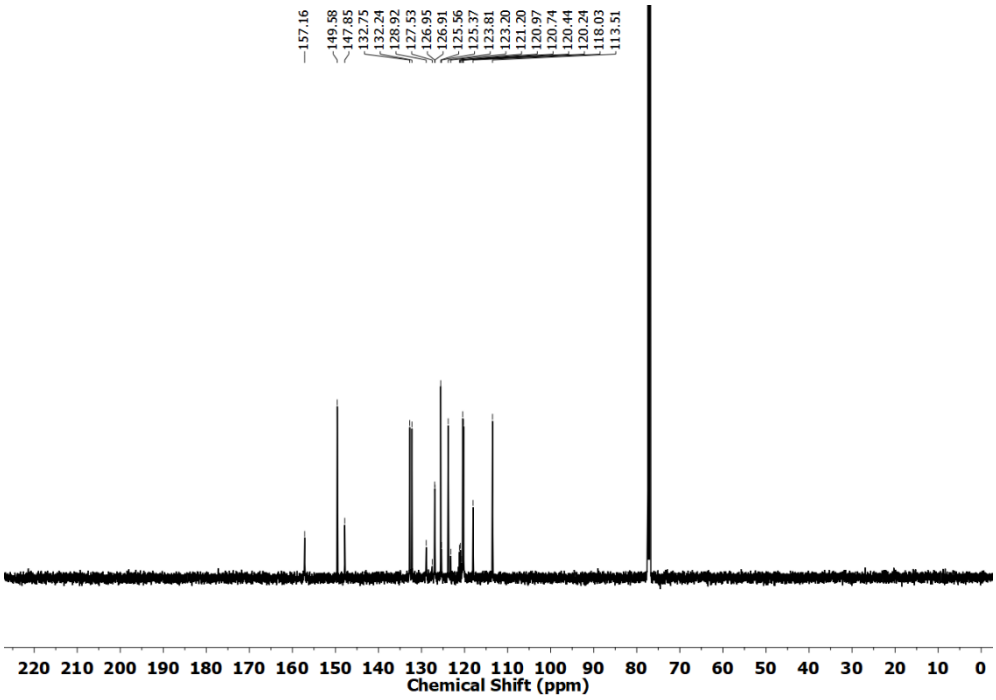


Figure A 160 13C NMR (126 MHz) of 4.6 in $CDCl_3$ at 298 K

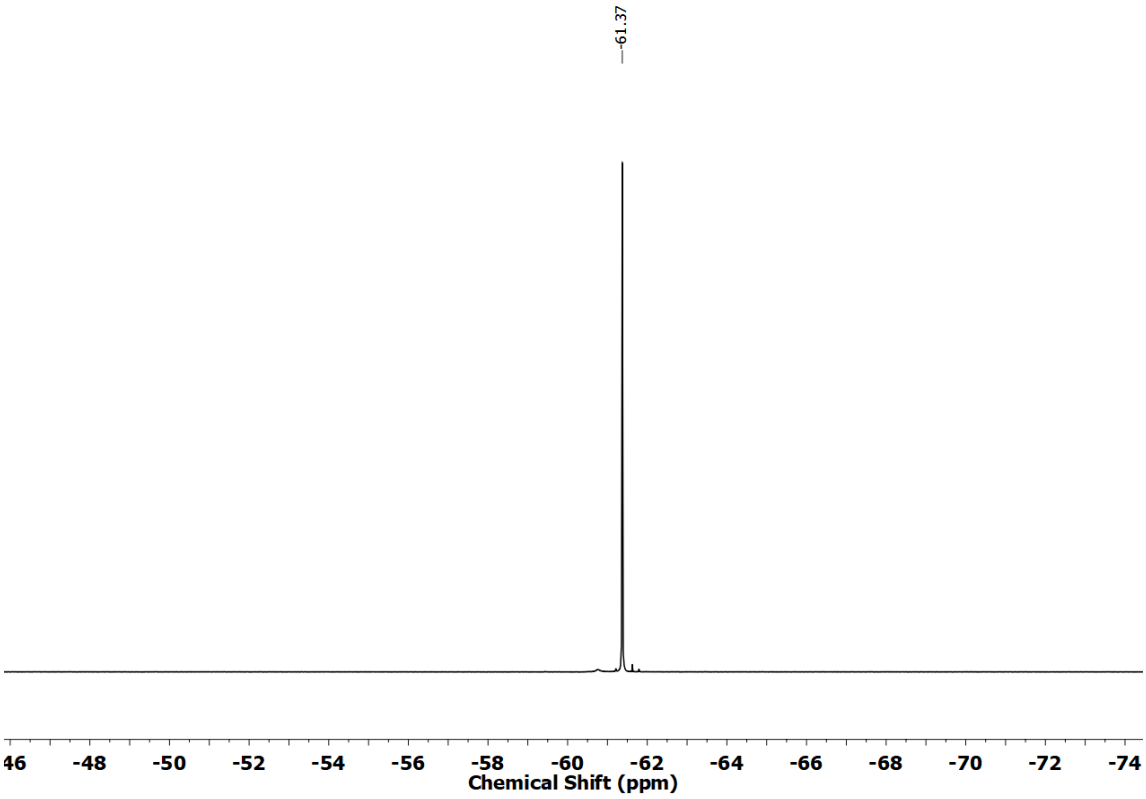


Figure A161 ^{19}F NMR (471 MHz) of 4.6 in CDCl3 at 298 K

Appendix B: Lineshape analysis

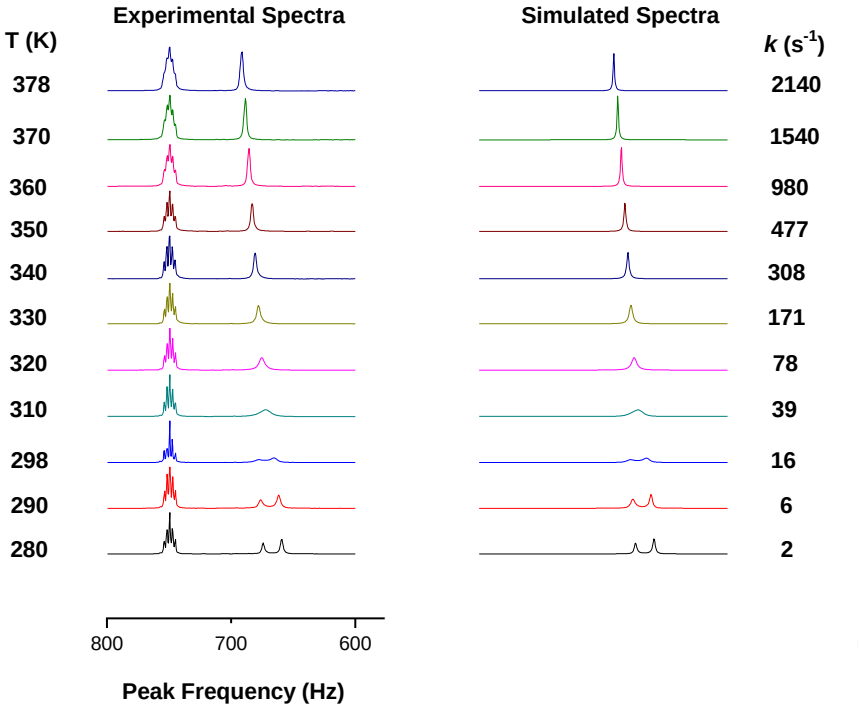


Figure B1 Lineshape analysis of **2.2a**

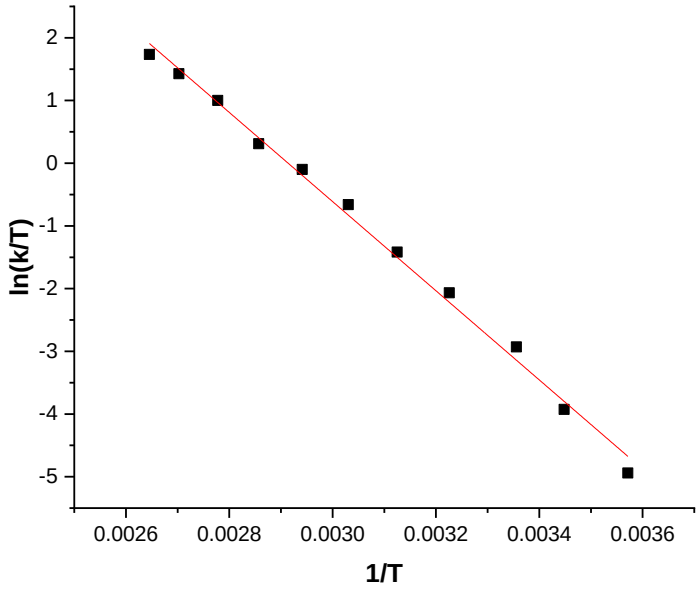


Figure B2 Eyring plot for the determination of activation parameters for **2.2a** (Trendline Equation: -7109.9x + 20.7, R^2 = 0.9950) $\Delta H^{\ddagger}$ =14.1 kcal/mol $\Delta S^{\ddagger}$ = -6.0 cal/K $\Delta G^{\ddagger}$ = 15.9 kcal/mol

Table B1 Rate constant data of **2.2a**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	ln(k_{app}/T)
280	0.00357	4	2	-4.94164
290	0.00345	11.44	5.72	-3.92591
298	0.00336	31.8	15.9	-2.93077
310	0.00323	78.5	39.25	-2.06662
320	0.00313	155	77.5	-1.41804
330	0.00303	341	170.5	-0.66036
340	0.00294	615	307.5	-0.10047
350	0.00286	954	477	0.30958
360	0.00278	1960	980	1.00145
370	0.0027	3080	1540	1.42603
378	0.00265	4280	2140	1.73367

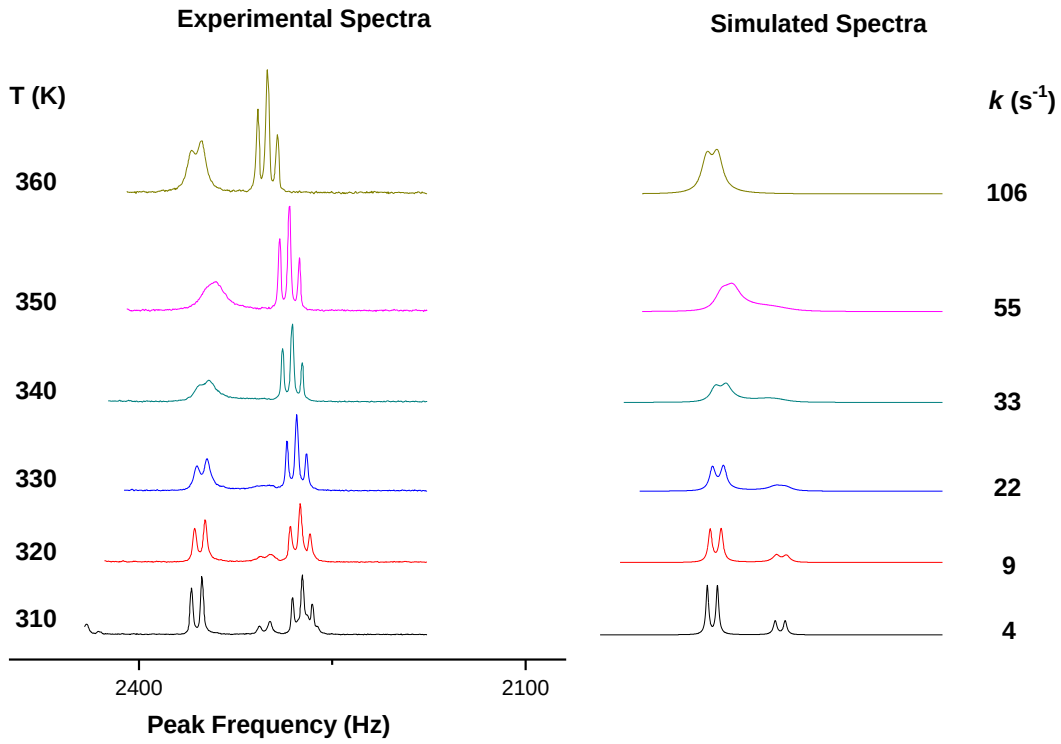


Figure B3 Lineshape analysis of **2.2b**

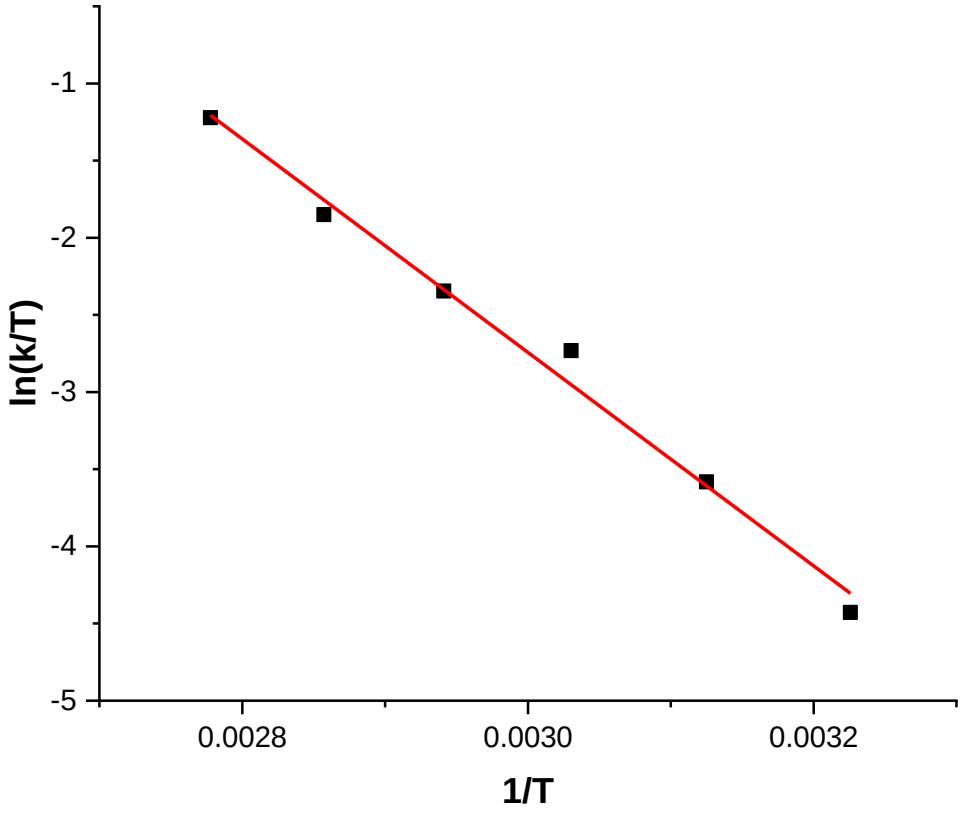


Figure B4 Eyring plot for the determination of activation parameters for **2.2b** (Trendline Equation: -6926.7x + 18.0, R^2 = 0.9890) $\Delta H^{\ddagger}$ =13.7 kcal/mol $\Delta S^{\ddagger}$ = -11.4 cal/K $\Delta G_{298}^{\ddagger}$ = 17.1 kcal/mol; $\Delta G_{350}^{\ddagger}$ = 17.7 kcal/mol

Table B2 Rate constant data from lineshape analysis of **2.2b**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	ln(k_{app}/T)
310	0.003226	7.4	3.7	-4.428239478
320	0.003125	17.8	8.9	-3.582269719
330	0.00303	43	21.5	-2.731039719
340	0.002941	65.1	32.55	-2.346168249
350	0.002857	110	55	-1.850599969
360	0.002778	212	106	-1.222664937

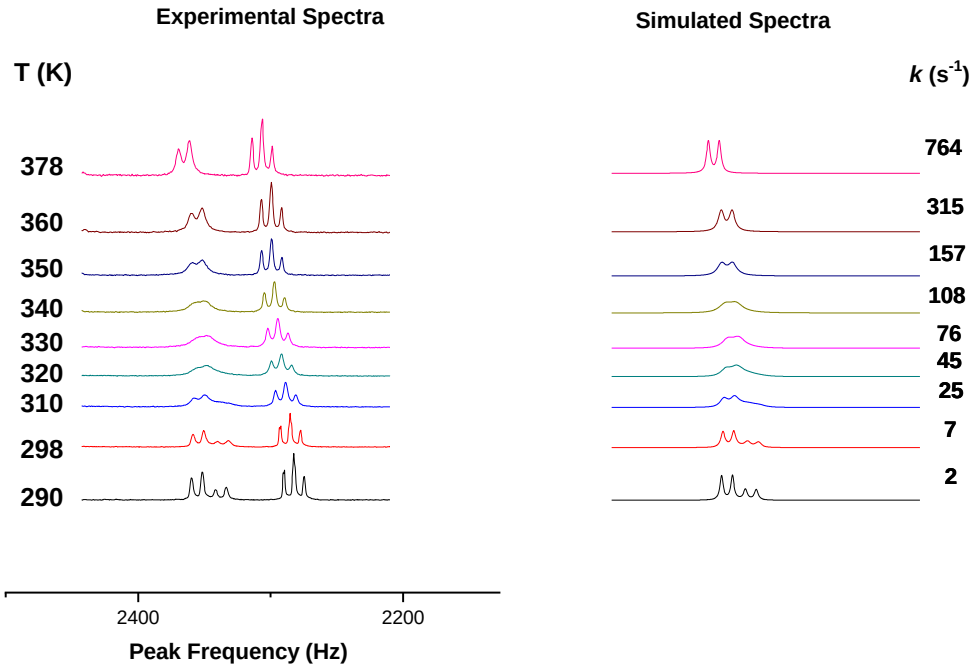


Figure B5 Lineshape analysis of **2.2e**

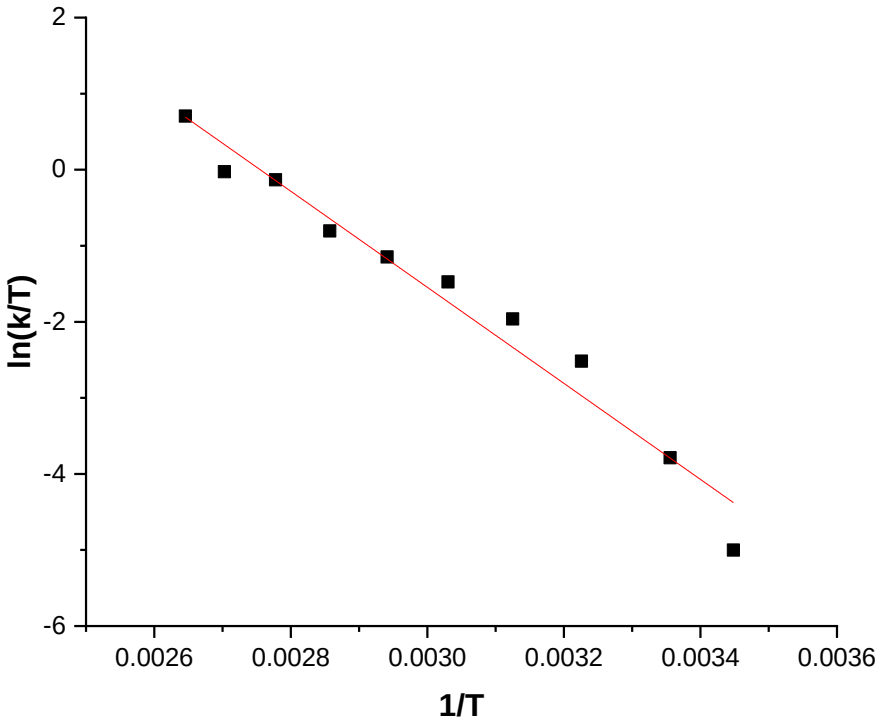


Figure B6 Eyring plot for the determination of activation parameters for **2.2e** (Trendline equation: -6314.1x +17,4, R^2 = 0.9658) $\Delta H^{\ddagger}$ = 12.5 kcal/mol, $\Delta S^{\ddagger}$ = -12.6 cal/K, $\Delta G_{298}^{\ddagger}$ = 16.3 kcal/mol; $\Delta G^{\ddagger}$ = 16.6 kcal/mol

Table B3 Rate constant data from lineshape analysis of **2.2e**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	$ln(k_{app}/T)$
290	0.003448	3.9	1.95	-5.00205
298	0.003356	13.5	6.75	-3.78755
310	0.003226	50	25	-2.5177
320	0.003125	90	45	-1.96166
330	0.00303	151	75.5	-1.47496
340	0.002941	216	108	-1.14681
350	0.002857	313	156.5	-0.80488
360	0.002778	630	315	-0.13353
370	0.002703	720	360	-0.0274
378	0.002646	1528.8	764.4	0.704197

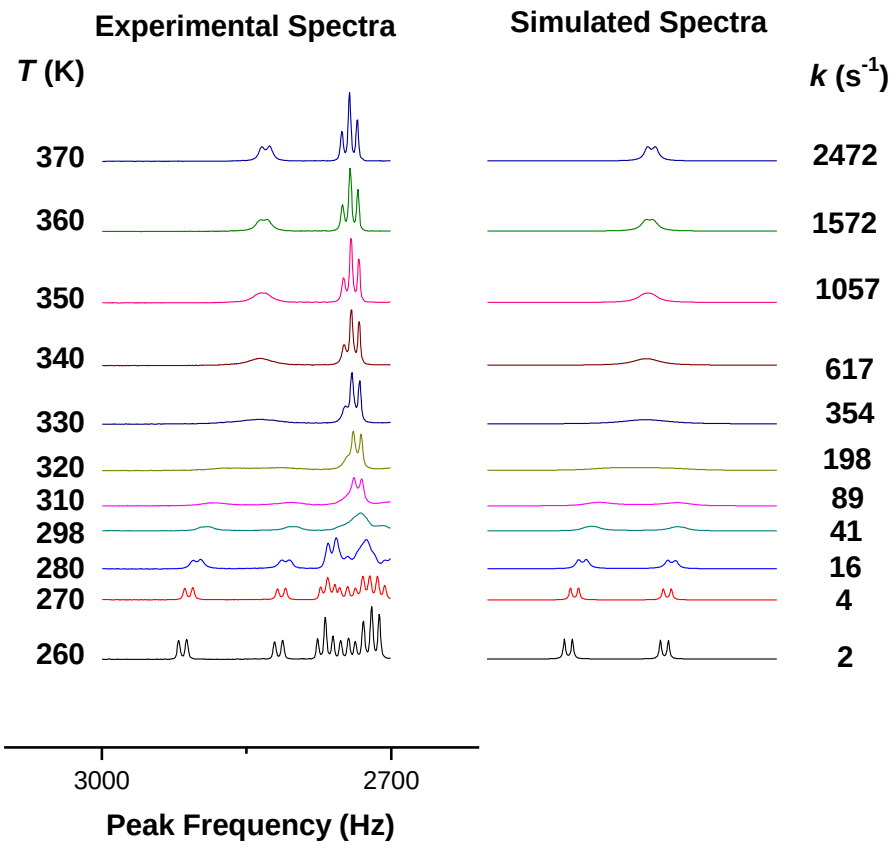


Figure B7 Lineshape analysis of **2.2f**

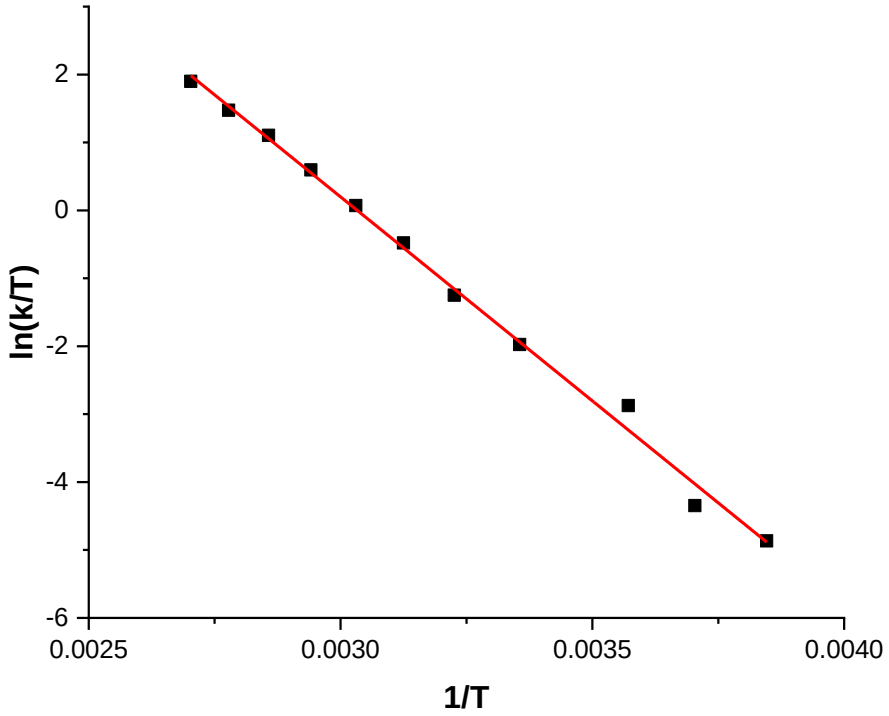


Figure B8 Eyring plot for the determination of activation parameters for **2.2f** (Trendline Equation: -6006.2x + 18.2, R^2 = 0.9951) $\Delta H^{\ddagger}$ = 11.9 kcal/mol, $\Delta S^{\ddagger}$ = -11.0 cal/K, $\Delta G_{298}^{\ddagger}$ = 15.2 kcal/mol; $\Delta G_{320}^{\ddagger}$ = 15.5 kcal/mol;

Table B4 Rate constant data from lineshape analysis of **2.2f**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	ln(k_{app}/T)
260	0.003846	4	2	-4.86753
270	0.003704	7	3.5	-4.34566
280	0.003571	31.6	15.8	-2.87478
298	0.003356	82.6	41.3	-1.97623
310	0.003226	177.6	88.8	-1.25019
320	0.003125	396	198	-0.48005
330	0.00303	708.6	354.3	0.071051
340	0.002941	1233.6	616.8	0.595599
350	0.002857	2114	1057	1.105257
360	0.002778	3143.6	1571.8	1.473873
370	0.002703	4943	2471.5	1.899078

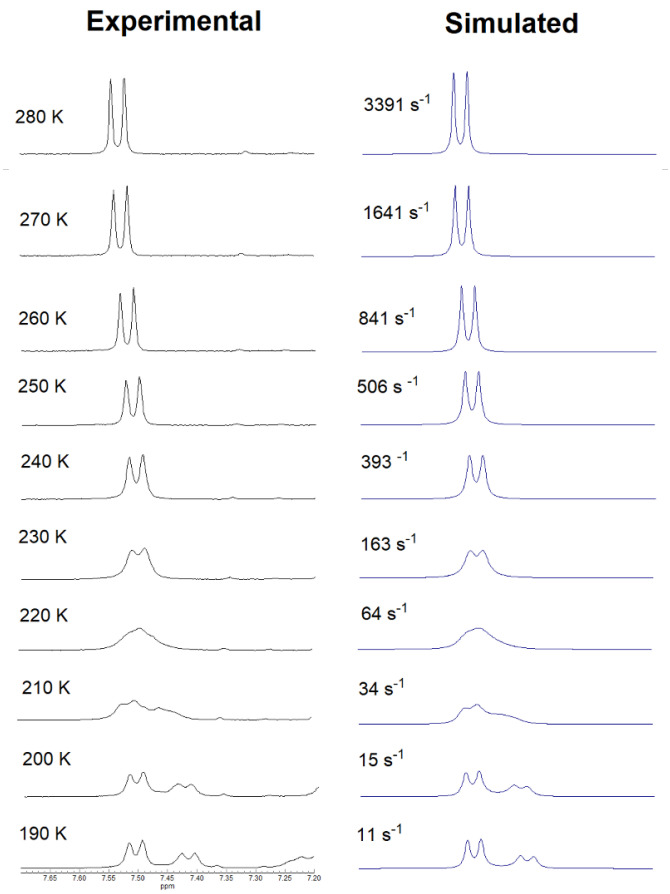


Figure B9 Lineshape analysis of **2.2g**

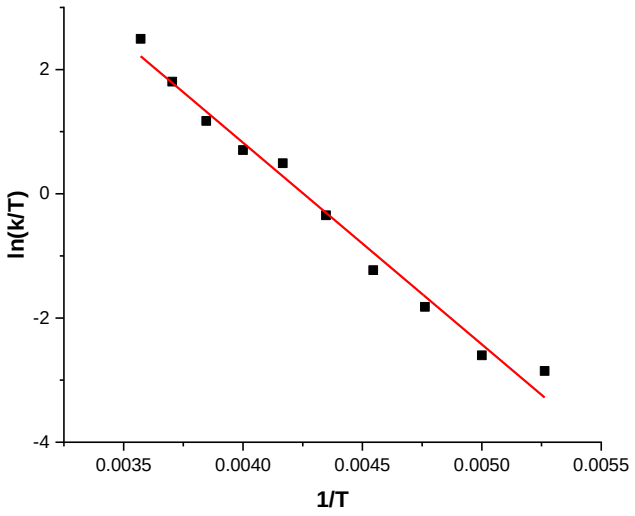


Figure B10 Eyring plot for the determination of activation parameters for **2.2g** (Trendline Equation: -3248.2x + 13.8, R^2 = 0.9845) $\Delta H^{\ddagger}$ = 6.5 kcal/mol, $\Delta S^{\ddagger}$ = -19.8 cal/K, $\Delta G_{298}^{\ddagger}$ = 12.3 kcal/mol; $\Delta G_{220}^{\ddagger}$ = 10.8 kcal/mol

Table B5 Rate constant data from lineshape analysis of **2.2g**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	$ln(k_{app}/T)$
190	0.005263	21.9	10.95	-2.853684616
200	0.005	29.7	14.85	-2.600317501
210	0.004762	68	34	-1.820747006
220	0.004545	128.7	64.35	-1.229290612
230	0.004348	325	162.5	-0.347401307
240	0.004167	785	392.5	0.491897614
250	0.004	1011	505.5	0.704087121
260	0.003846	1681.1	840.55	1.173374808
270	0.003704	3281.1	1640.55	1.804364871
280	0.003571	6781.1	3390.55	2.493957826

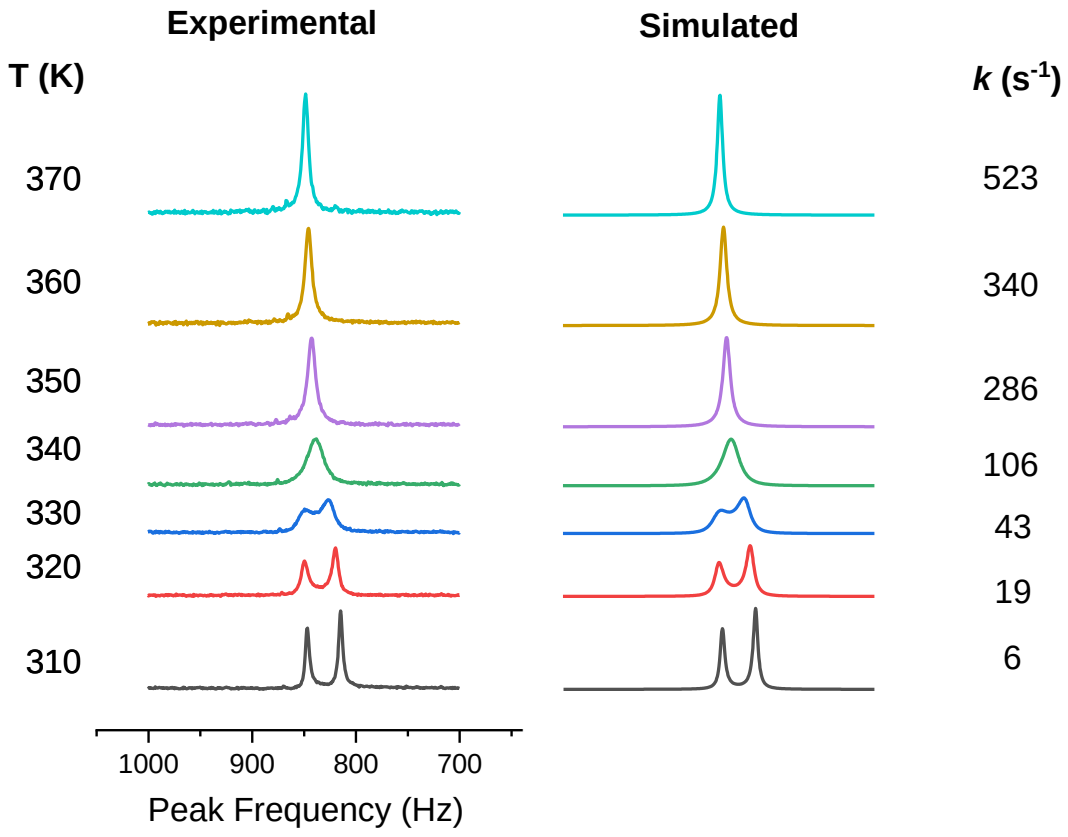


Figure B11 Lineshape analysis of **3.15a**

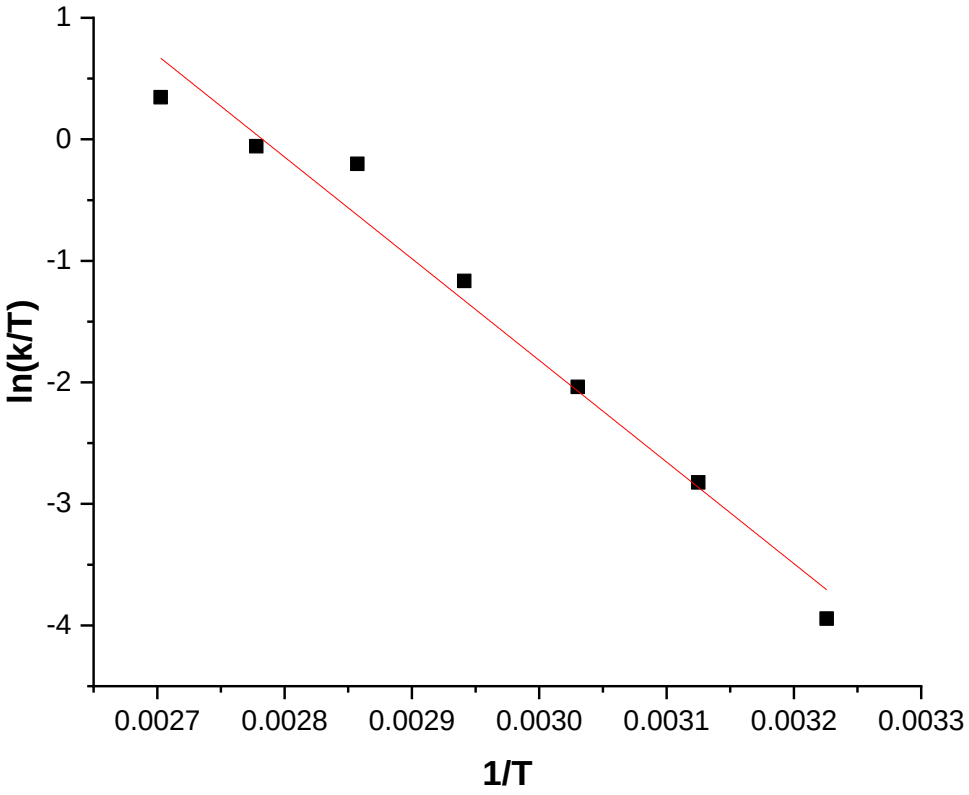


Figure B12 Eyring plot for the determination of activation parameters for **3.15a** (Trendline Equation: -8363.9x + 23.3, R^2 = 0.9753) $\Delta H^{\ddagger}$ = 16.6 kcal/mol, $\Delta S^{\ddagger}$ = -0.97 cal/K, $\Delta G_{298}^{\ddagger}$ = 16.9 kcal/mol;

Table B6 Rate constant data from lineshape analysis of **3.15a**

Temperature (K)	**1/T (K^{-1})**	**k (s^{-1})**	**k_{app} (s^{-1})**	**ln(k_{app}/T)**
310	0.003226	12	6	-3.94481
320	0.003125	38	19	-2.82388
330	0.00303	86	43	-2.03789
340	0.002941	212	106	-1.16551
350	0.002857	572	286	-0.20194
360	0.002778	680	340	-0.05716
370	0.002703	1046	523	0.346078

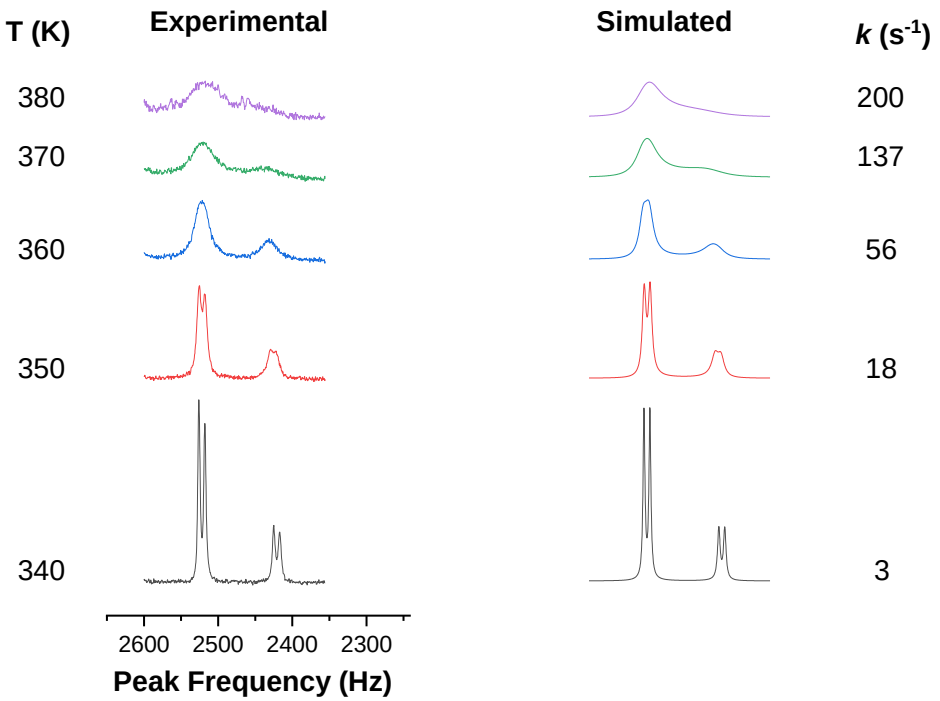


Figure B13 Lineshape analysis of **3.15b**

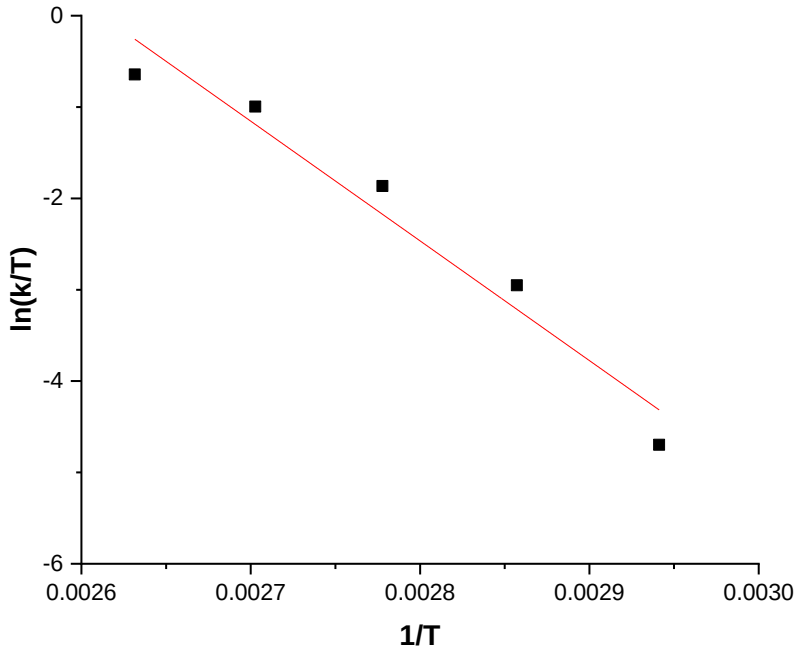


Figure B14 Eyring plot for the determination of activation parameters for **3.15b** (Trendline Equation: -13104.6x + 34.2, R^2 = 0.9539) $\Delta H^{\ddagger}$ = 26.0 kcal/mol, $\Delta S^{\ddagger}$ = 20.8 cal/K, $\Delta G_{298}^{\ddagger}$ = 19.8 kcal/mol; $\Delta G_{390}^{\ddagger}$ = 17.9 kcal/mol

Table B7 Rate constant data from lineshape analysis of **3.15b**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	ln(k_{app}/T)
340	0.002941	6.2	3.1	-2.95103
350	0.002857	36.6	18.3	-1.86433
360	0.002778	111.6	55.8	-0.99498
370	0.002703	273.6	136.8	-0.64285
380	0.002632	399.6	199.8	-2.95103

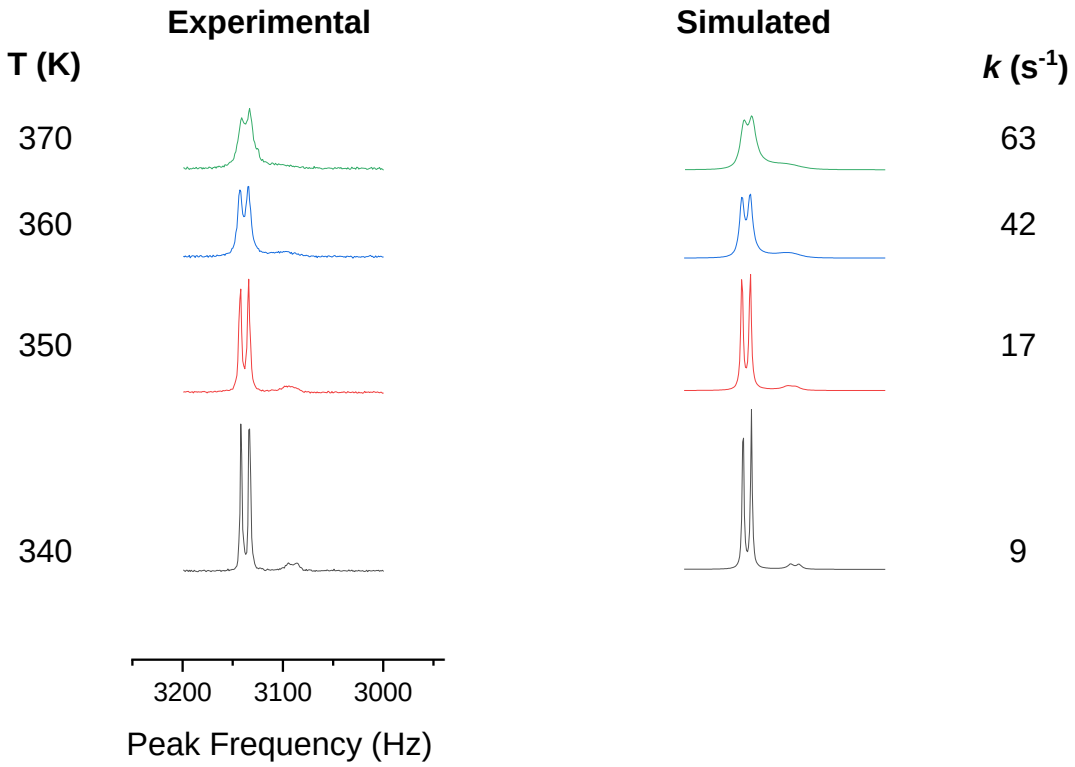


Figure B15 Lineshape analysis of **3.15d**

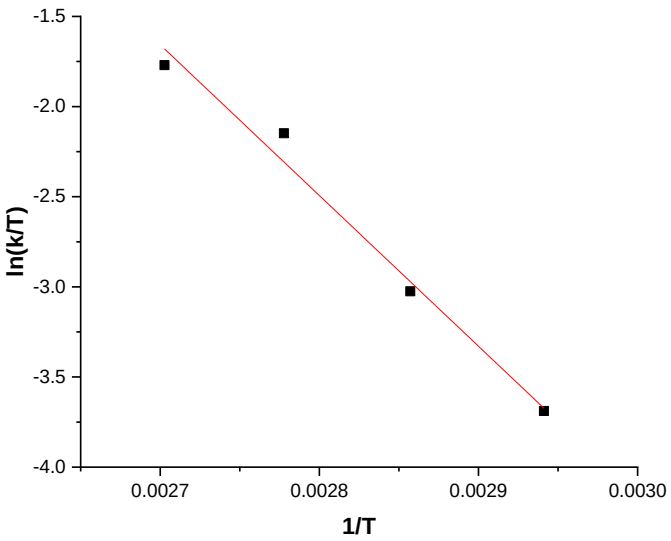


Figure B16 Eyring plot for the determination of activation parameters for **3.15d** (Trendline Equation: -8358.7x + 20.9, R^2 = 0.9837) $\Delta H^{\ddagger}$ = 23.5 kcal/mol, $\Delta S^{\ddagger}$ = 13.5 cal/K, $\Delta G_{298}^{\ddagger}$ = 19.5 kcal/mol; $\Delta G_{380}^{\ddagger}$ = 18.4 kcal/mol

Table B8 Rate constant data from lineshape analysis of **3.15d**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	ln(k_{app}/T)
340	0.002941	17	8.5	-3.68888
350	0.002857	34	17	-3.02472
360	0.002778	84	42	-2.14843
370	0.002703	126	63	-1.77037

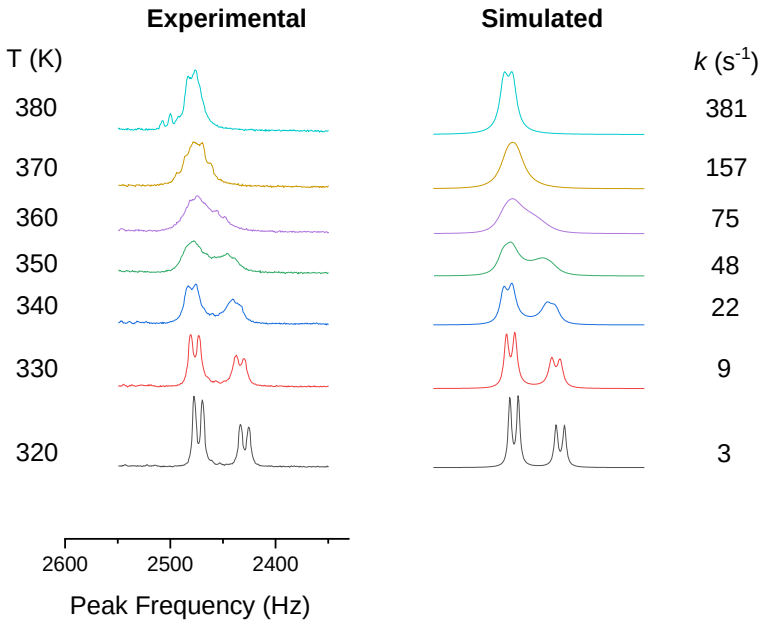


Figure B17 Lineshape analysis of **3.15e**

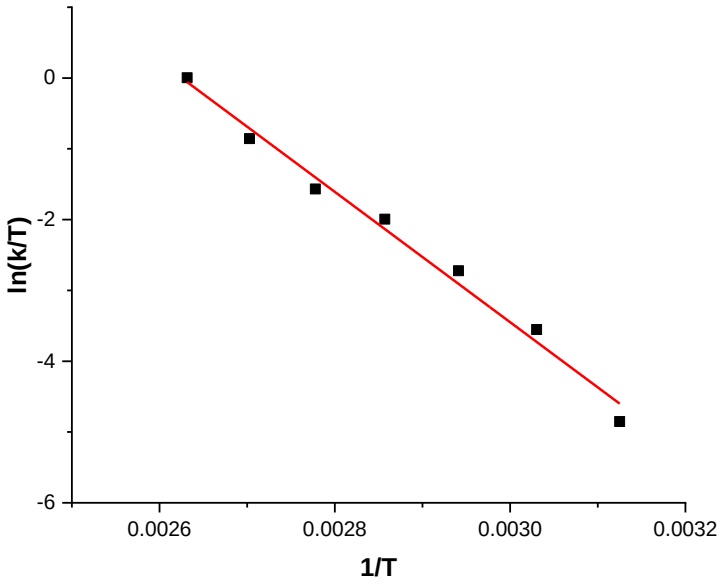


Figure B18 Eyring plot for the determination of activation parameters for **3.15e** (Trendline Equation: -9204.2x + 24.2, R^2 = 0.9876) $\Delta H^{\ddagger}$ = 18.3 kcal/mol, $\Delta S^{\ddagger}$ = 0.8 cal/K, $\Delta G_{298}^{\ddagger}$ = 18.1 kcal/mol; $\Delta G_{370}^{\ddagger}$ = 18.0 kcal/mol

Table B9 Rate constant data from lineshape analysis of **3.15e**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	ln(k_{app}/T)
320	0.003125	5	2.5	-4.85203
330	0.00303	18.9	9.45	-3.55308
340	0.002941	44.7	22.35	-2.72212
350	0.002857	95.4	47.7	-1.993
360	0.002778	150	75	-1.56862
370	0.002703	314	157	-0.85726
380	0.002632	761.97	380.985	0.002589

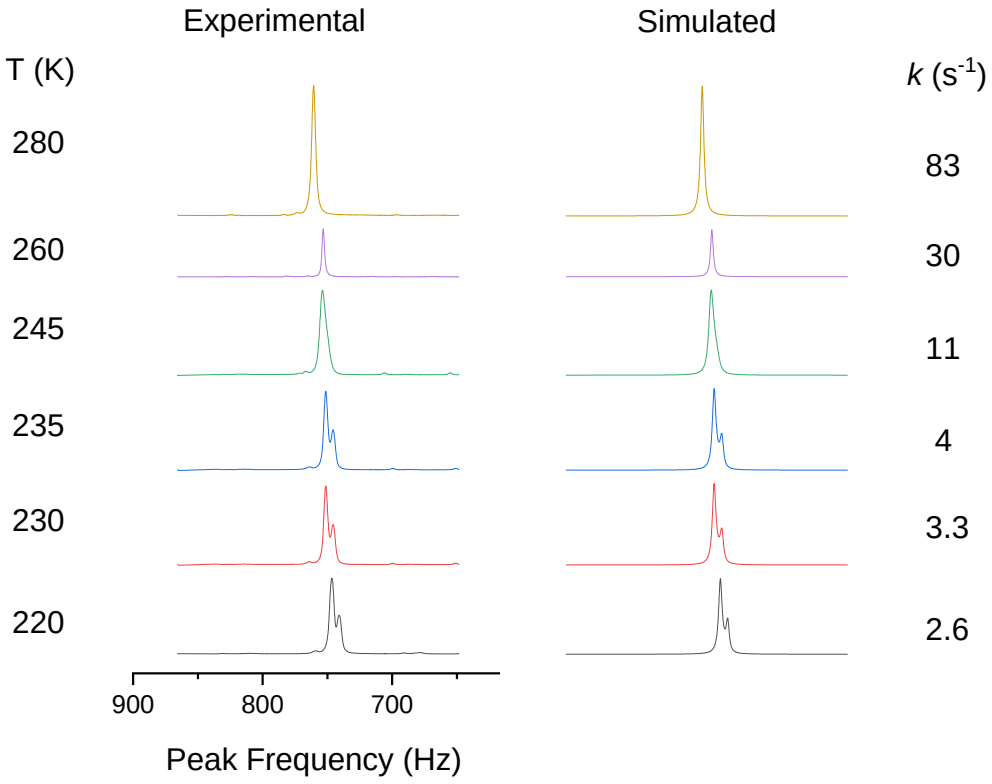


Figure B19 Lineshape analysis of **3.16a**

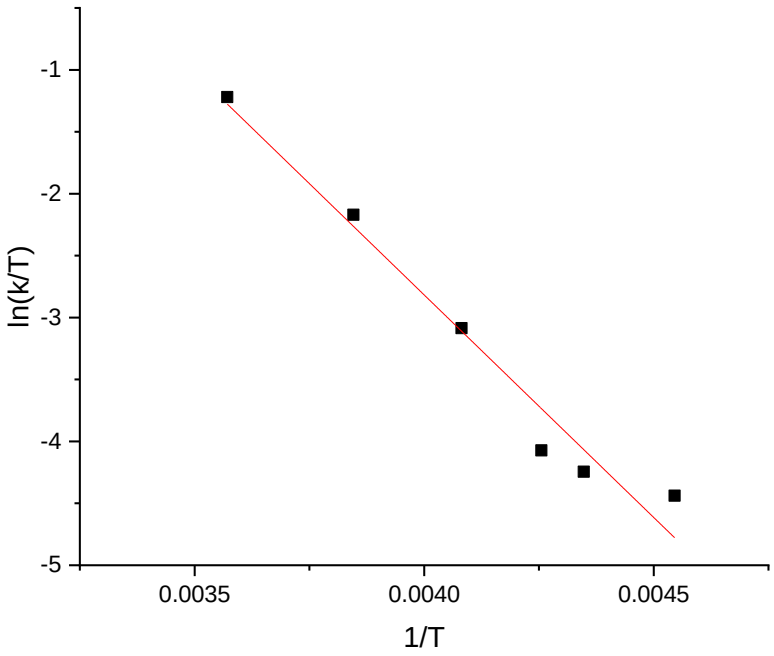


Figure B20 Eyring plot for the determination of activation parameters for **3.16a** (Trendline Equation: -3594.1x + 11.6, R^2 = 0.9673) $\Delta H^{\ddagger}$ = 7.1 kcal/mol, $\Delta S^{\ddagger}$ = -24.2 cal/K, $\Delta G_{298}^{\ddagger}$ = 14.4 kcal/mol; $\Delta G_{245}^{\ddagger}$ = 13.1 kcal/mol

Table B10 Rate constant data from lineshape analysis of **3.16a**

Temperature (K)	**1/T (K^{-1})**	**k (s^{-1})**	**k_{app} (s^{-1})**	**ln(k_{app}/T)**
280	0.003571	165.4	82.7	-1.219570001
260	0.003846	59.4	29.7	-2.169534585
245	0.004082	22.4	11.2	-3.085344432
235	0.004255	8	4	-4.073291153
230	0.004348	6.6	3.3	-4.24415684
220	0.004545	5.2	2.6	-4.438116101

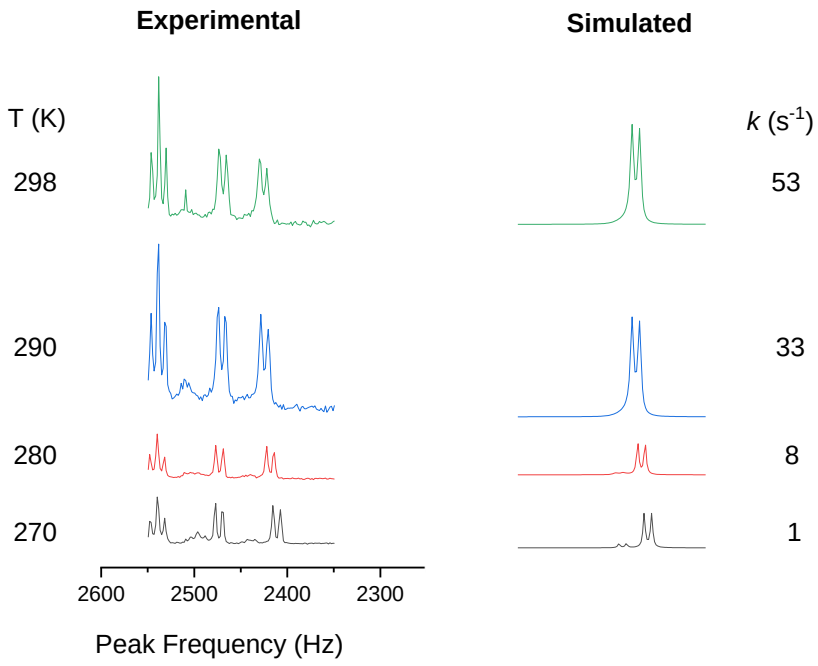


Figure B21 Lineshape analysis of **3.16d**

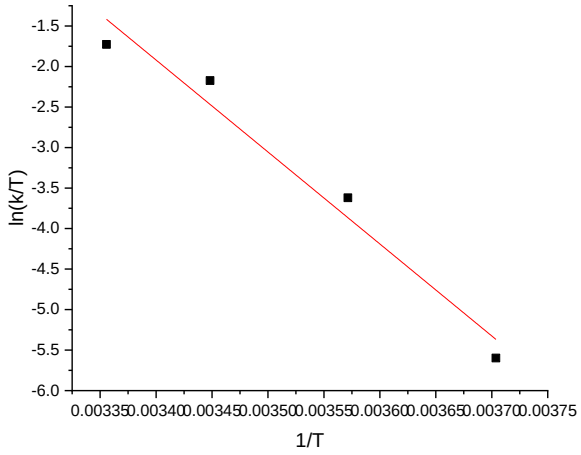


Figure B22 Eyring plot for the determination of activation parameters for **3.16d** (Trendline Equation: -11351.9x + 36.7, R^2 = 0.9675) $\Delta H^{\ddagger}$ = 22.6 kcal/mol, $\Delta S^{\ddagger}$ = 25.7 cal/K, $\Delta G_{298}^{\ddagger}$ = 14.9 kcal/mol; $\Delta G_{315}^{\ddagger}$ = 14.5 kcal/mol

Table B11 Rate constant data from lineshape analysis of **3.16d**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	$ln(k_{app}/T)$
298	0.003356	106	53	-1.726801573
290	0.003448	66	33	-2.173373362
280	0.003571	15	7.5	-3.619886583
270	0.003704	2	1	-5.598421959

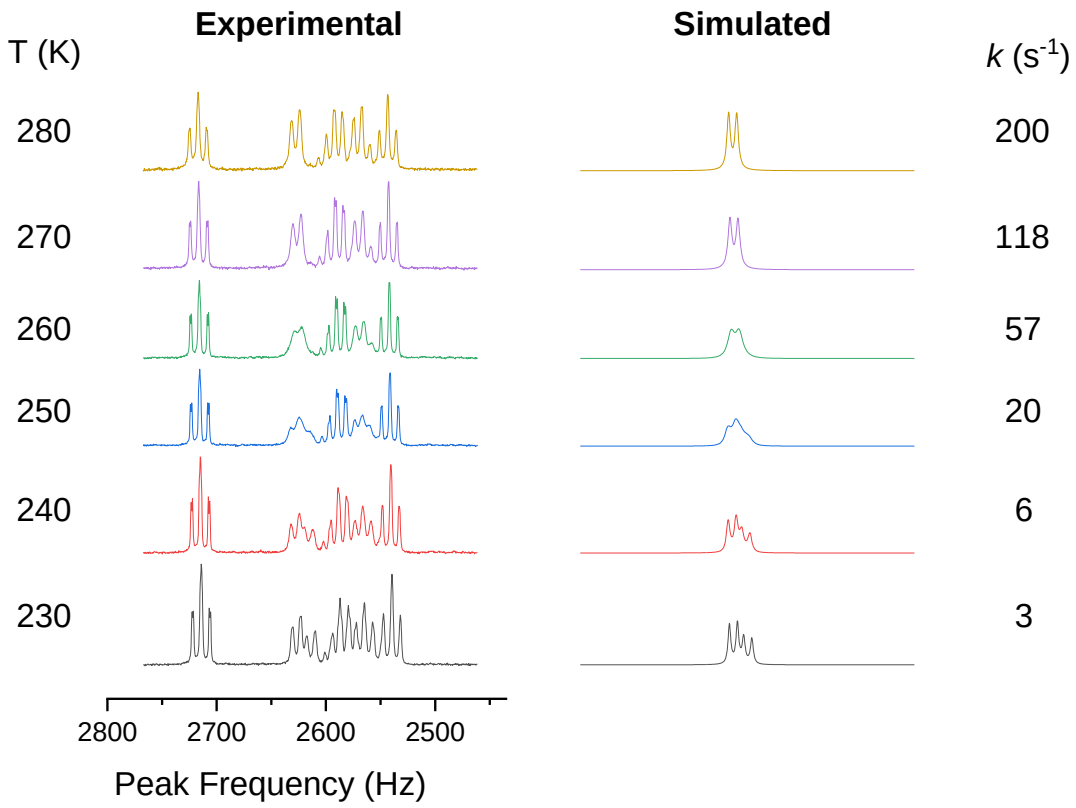


Figure B23 Lineshape analysis of **3.16e**

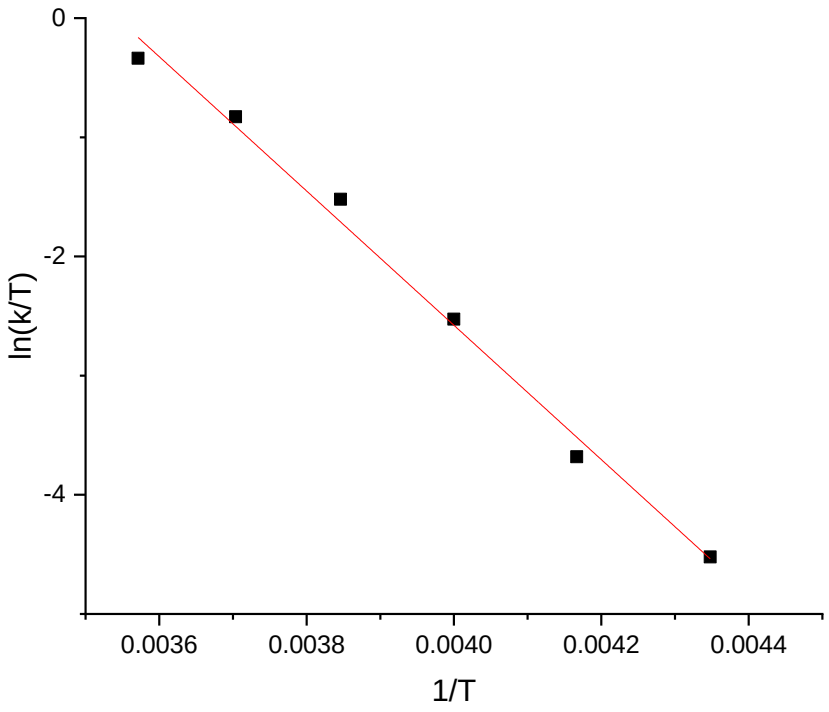


Figure B24 Eyring plot for the determination of activation parameters for **3.16e** (Trendline Equation: -5635.3x + 20.0, R^2 = 0.9924) $\Delta H^{\ddagger}$ = 11.2 kcal/mol, $\Delta S^{\ddagger}$ = -7.5 cal/K, $\Delta G_{298}^{\ddagger}$ = 13.5 kcal/mol; $\Delta G_{255}^{\ddagger}$ = 13.1 kcal/mol

Table B12 Rate constant data from lineshape analysis of **3.16e**

Temperature (K)	**1/T (K^{-1})**	**k (s^{-1})**	**k_{app} (s^{-1})**	**ln(k_{app}/T)**
280	0.003571	400	200	-0.336472237
270	0.003704	235.8	117.9	-0.828585151
260	0.003846	113.7	56.85	-1.520265411
250	0.004	40	20	-2.525728644
240	0.004167	12.1	6.05	-3.680580651
230	0.004348	5	2.5	-4.521788577

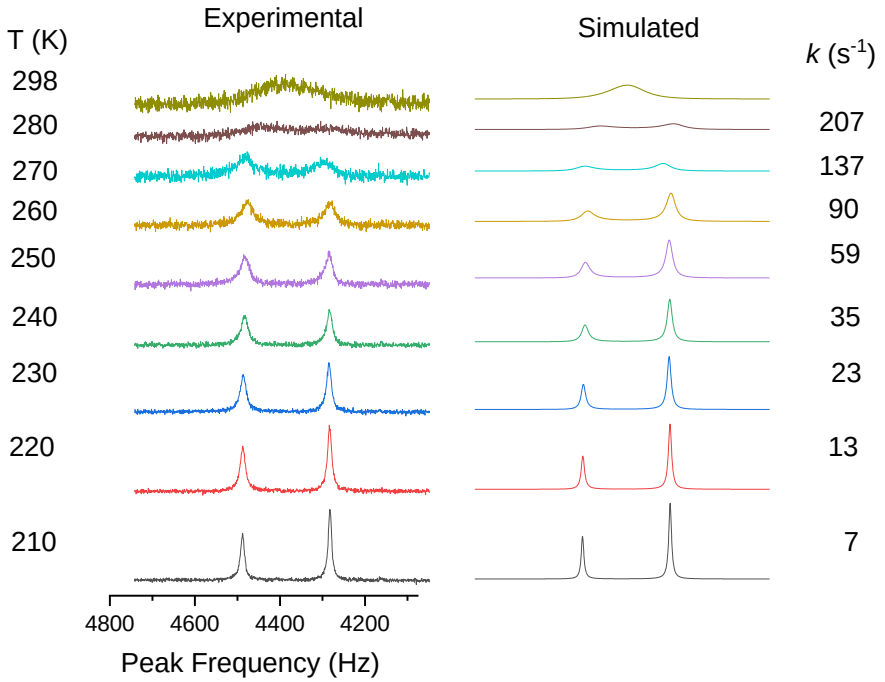


Figure B25 Lineshape analysis of **4.5b**

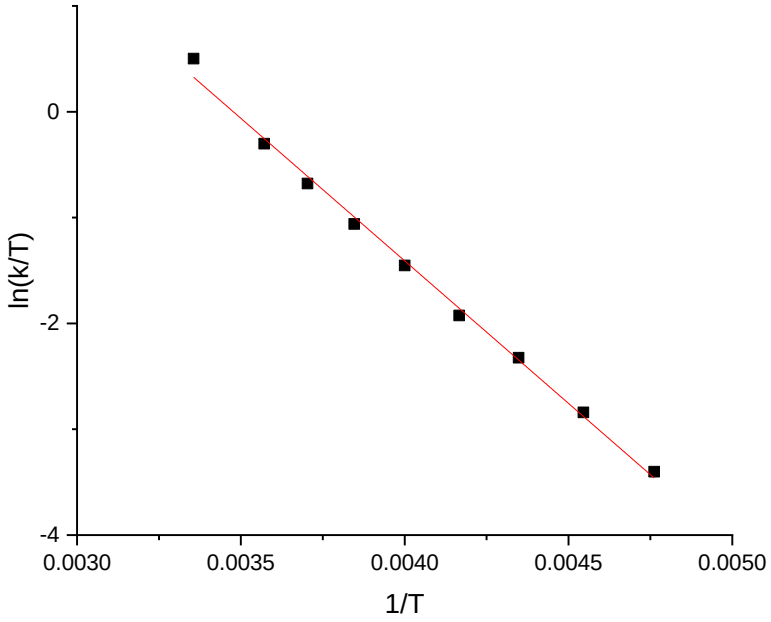


Figure B26 Eyring plot for the determination of activation parameters for **4.5b** (Trendline Equation: -2689.4 + 9.3, R^2 = 0.9953) $\Delta H^{\ddagger}$ = 5.3 kcal/mol, $\Delta S^{\ddagger}$ = -28.6 cal/K, $\Delta G_{298}^{\ddagger}$ = 13.9 kcal/mol

Table B13 Rate constant data from lineshape analysis for **4.5b**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	$ln(k_{app}/T)$
298	0.003356	984	492	0.501385
280	0.003571	414	207	-0.30207
270	0.003704	274	137	-0.67844
260	0.003846	180	90	-1.06087
250	0.004	117	58.5	-1.45243
240	0.004167	70	35	-1.92529
230	0.004348	45	22.5	-2.32456
220	0.004545	25.7	12.85	-2.84028
210	0.004762	14	7	-3.4012

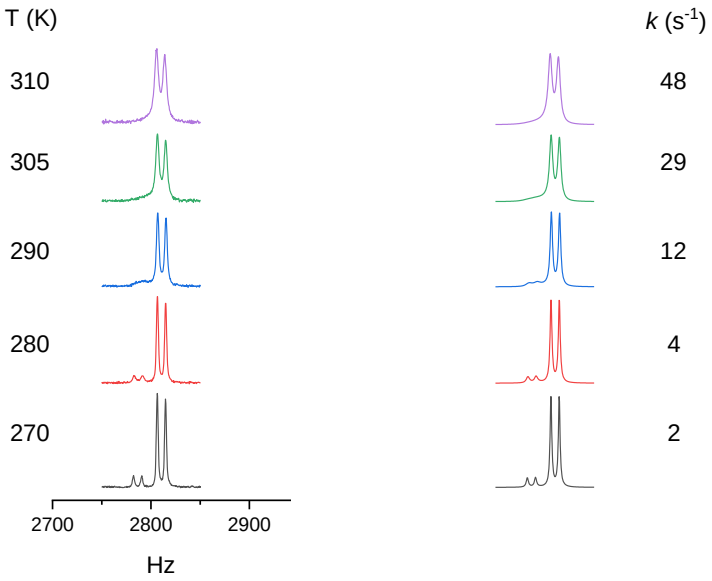


Figure B27 Lineshape analysis of **4.5d**

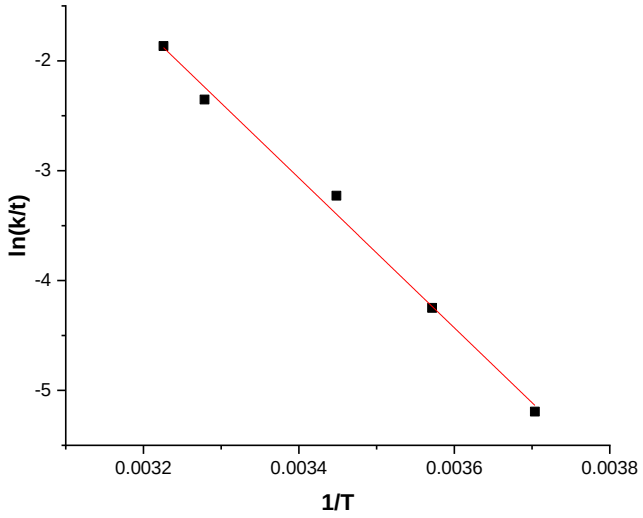


Figure B28 Eyring plot for the determination of activation parameters for **4.5d** (Trendline Equation: -6815.6x + 20.1, R^2 = 0.9940) $\Delta H^{\ddagger}$ =13.5 kcal/mol $\Delta S^{\ddagger}$ = -7.26 cal/K cal/K $\Delta G^{\ddagger}$ = 15.8 kcal/mol

Table B14 Rate constant data from lineshape analysis of **4.5d**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	ln(k_{app}/T)
270	0.003704	3	1.5	-5.19296
280	0.003571	8	4	-4.2485
290	0.003448	23	11.5	-3.22753
305	0.003279	58	29	-2.35302
310	0.003226	96	48	-1.86537

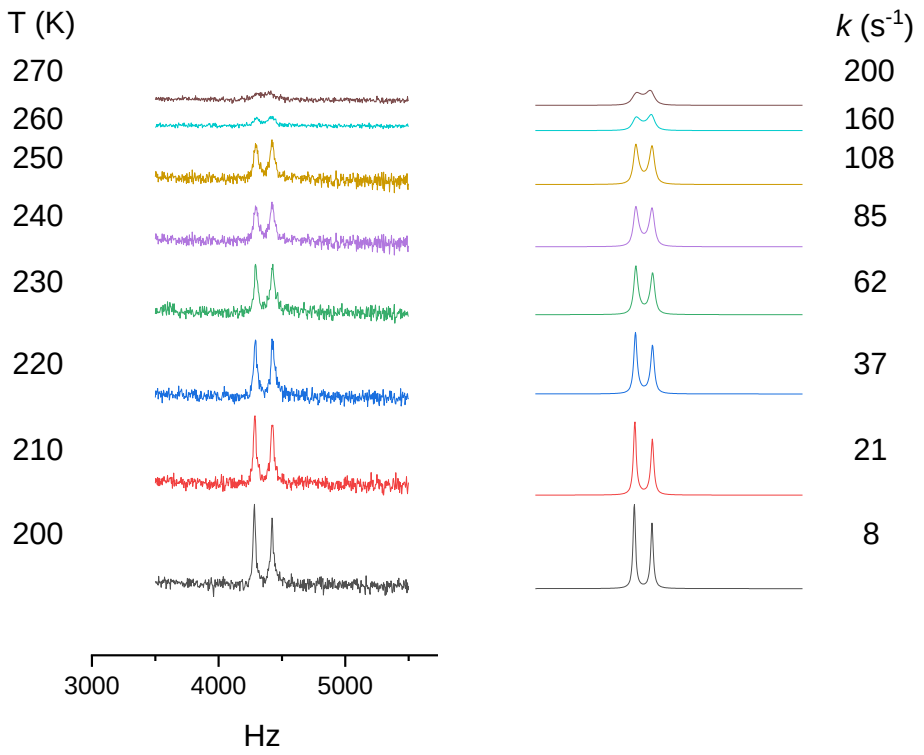


Figure B29 Lineshape analysis of **4.5e**

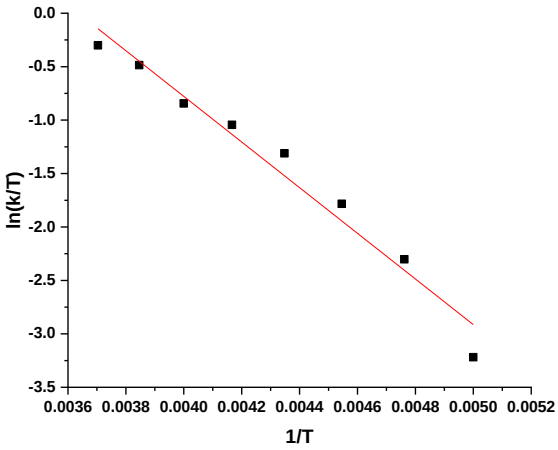


Figure B30 Eyring plot for the determination of activation parameters for **4.5e** (Trendline Equation: -2135.9x + 7.8, R^2 = 0.9688) $\Delta H^{\ddagger}$ = 4.2 kcal/mol $\Delta S^{\ddagger}$ = -31.8 cal/K $\Delta G^{\ddagger}$ = 13.7 kcal/mol

Table B15 Rate constant data from lineshape analysis of **4.5e**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	ln(k_{app}/T)
200	0.005	16	8	-3.218875825
210	0.004761905	42	21	-2.302585093
220	0.004545455	74	37	-1.782709634
230	0.004347826	124	62	-1.310944924
240	0.004166667	169	84.5	-1.043887389
250	0.004	215	107.5	-0.84397007
260	0.003846154	320	160	-0.485507816
270	0.003703704	400	200	-0.300104592

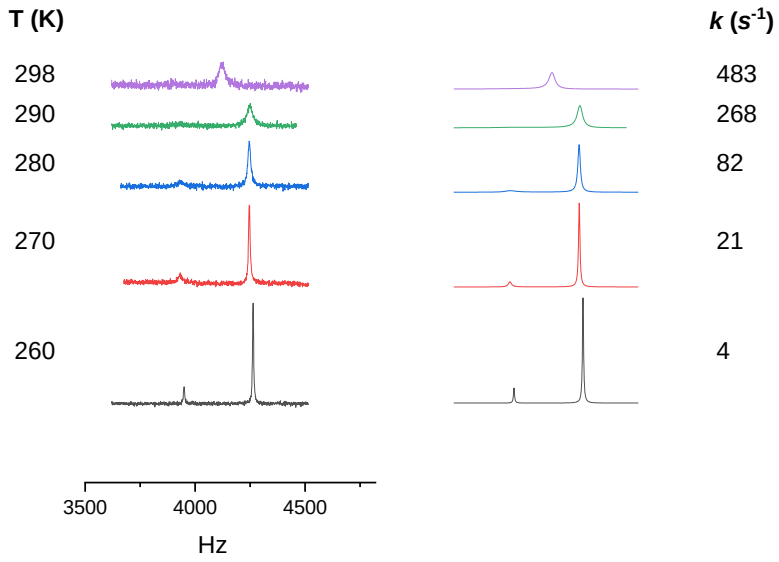


Figure B31 Lineshape analysis of **4.5f**

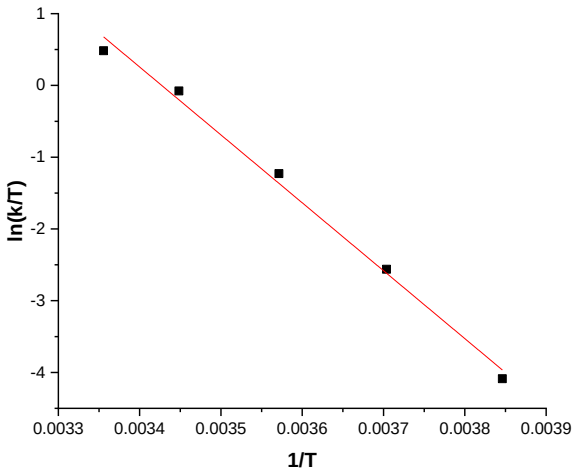


Figure B32 Eyring plot for the determination of activation parameters for **4.5f** (Trendline Equation: -9462.8x + 32.4, R^2 = 0.9936) $\Delta H^{\ddagger}$ = 18.8 kcal/mol $\Delta S^{\ddagger}$ = 17.8 cal/K $\Delta G^{\ddagger}$ = 13.5 kcal/mol

Table B16 Rate constant data from lineshape analysis of **4.5f**

Temperature (K)	1/T (K^{-1})	k (s^{-1})	k_{app} (s^{-1})	$ln(k_{app}/T)$
298	966.7	483.35	0.483648	0.003356
290	536.7	268.35	-0.07759	0.003448
280	163.7	81.85	-1.2299	0.003571
270	41.7	20.85	-2.56107	0.003704
260	8.72	4.36	-4.08821	0.003846

Appendix C: Infrared Spectroscopy

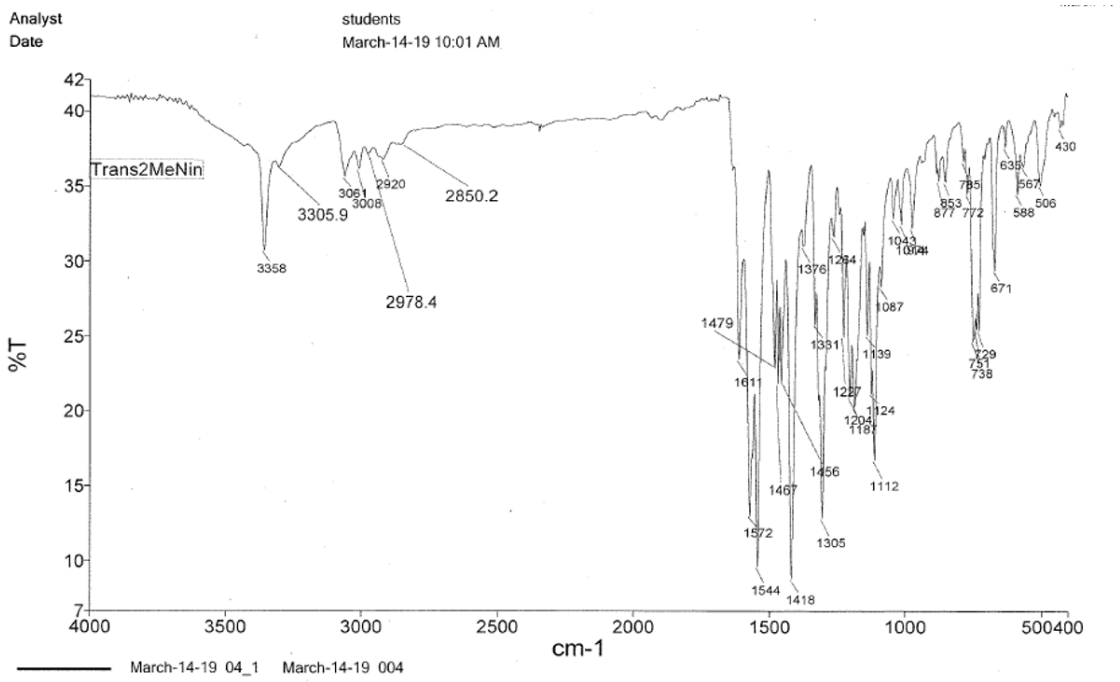


Figure C1 FT-IR spectrum of **2.1a**; KBr pellet, air background

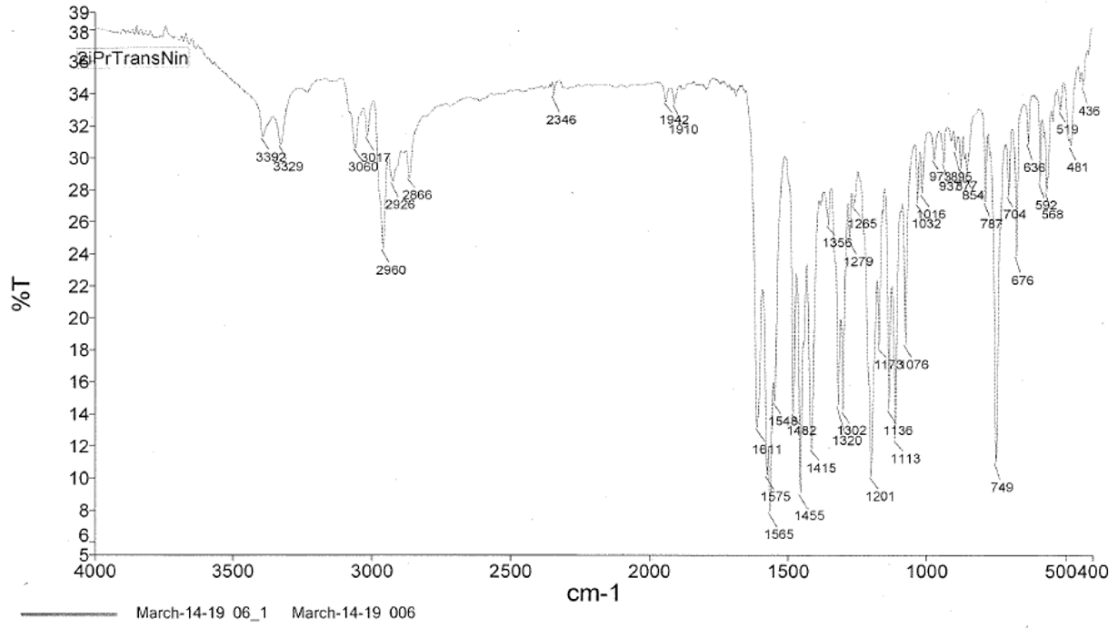


Figure C2 FT-IR spectrum of **2.1b**; KBr pellet, air background

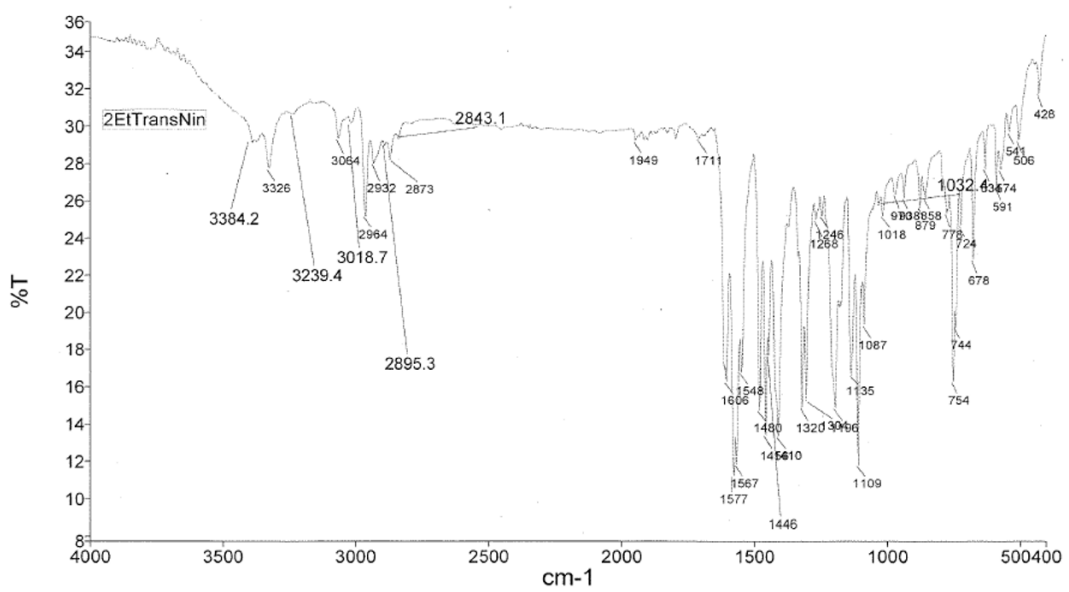


Figure C3 FT-IR spectrum of **2.1e**; KBr pellet, air background

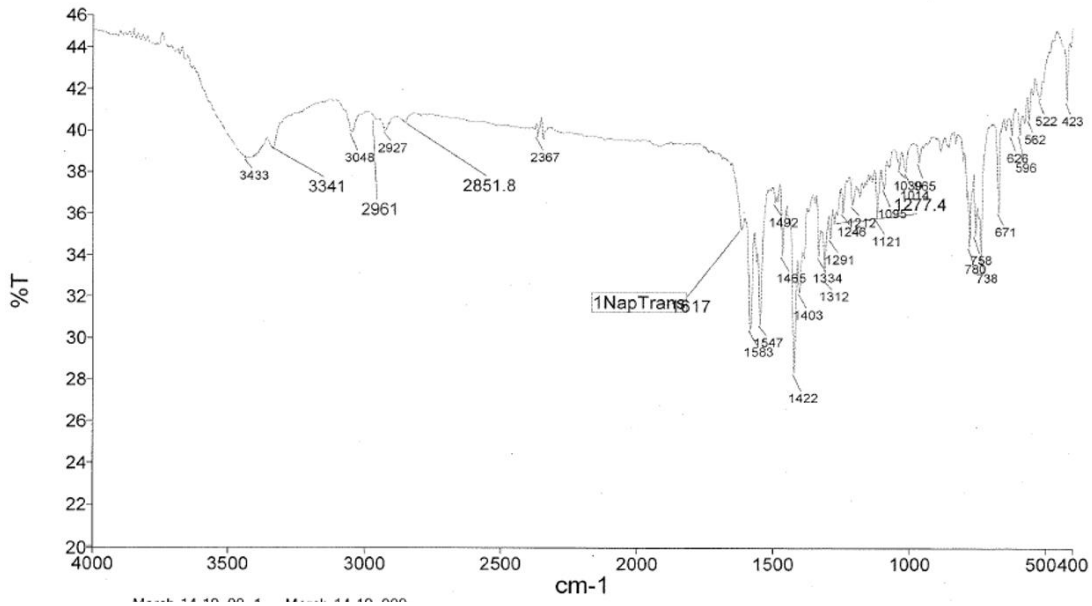


Figure C4 FT-IR spectrum of **2.1f**; KBr pellet, air background

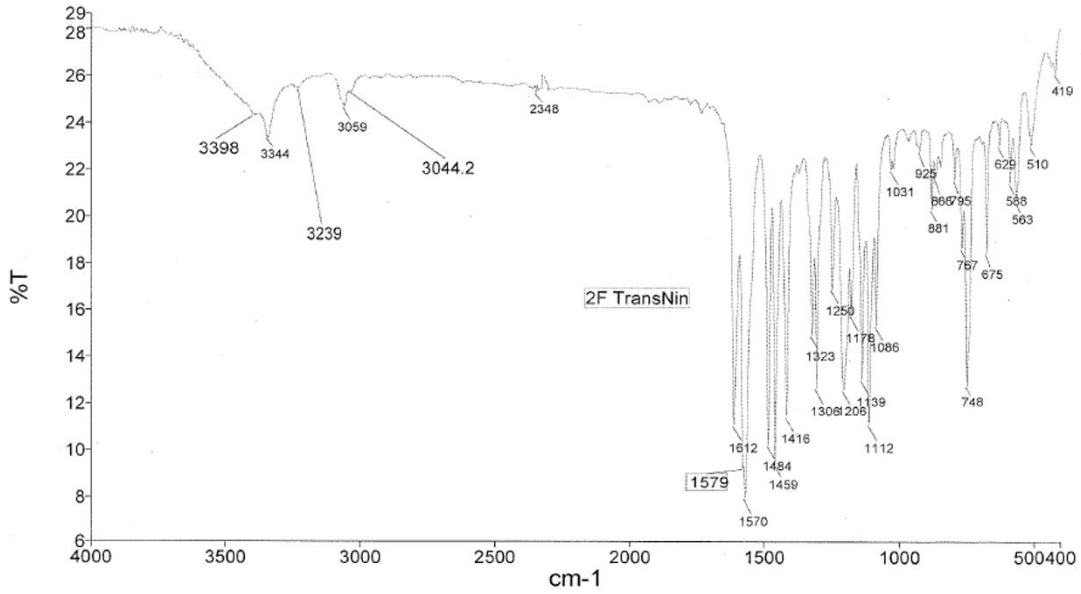


Figure C5 FT-IR spectrum of **2.1g**; KBr pellet, air background

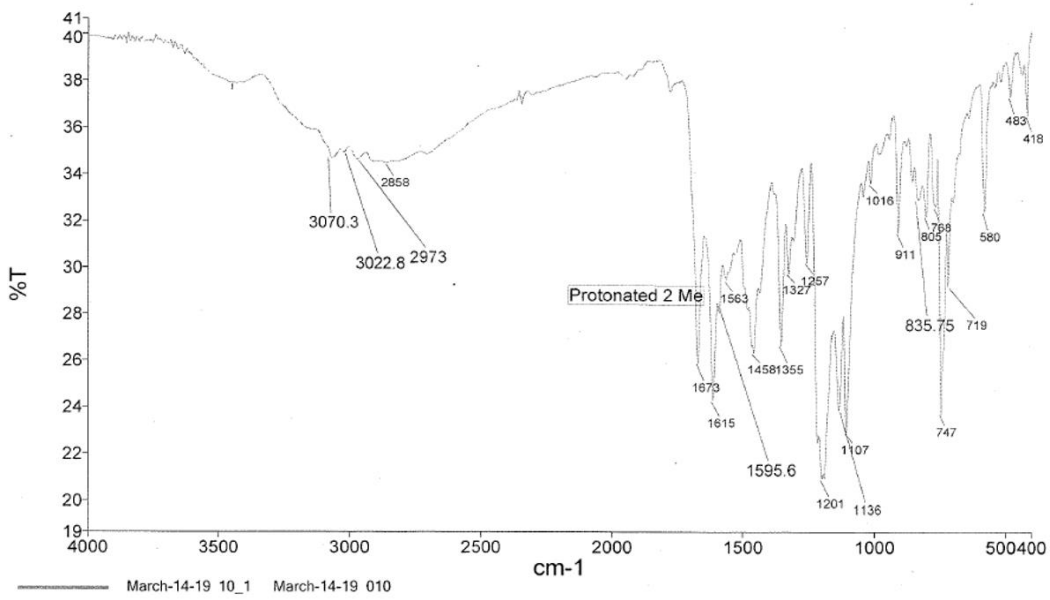


Figure C6 FT-IR spectrum of **2.2a**; KBr pellet, air background

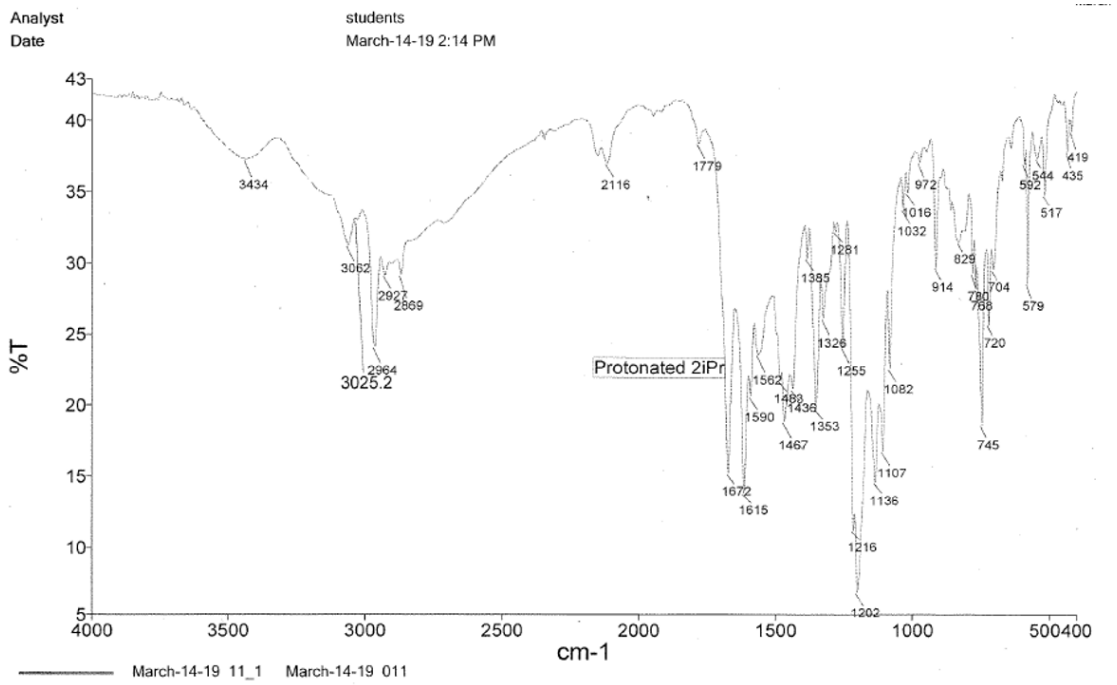


Figure C7 FT-IR spectrum of **2.2b**; KBr pellet, air background

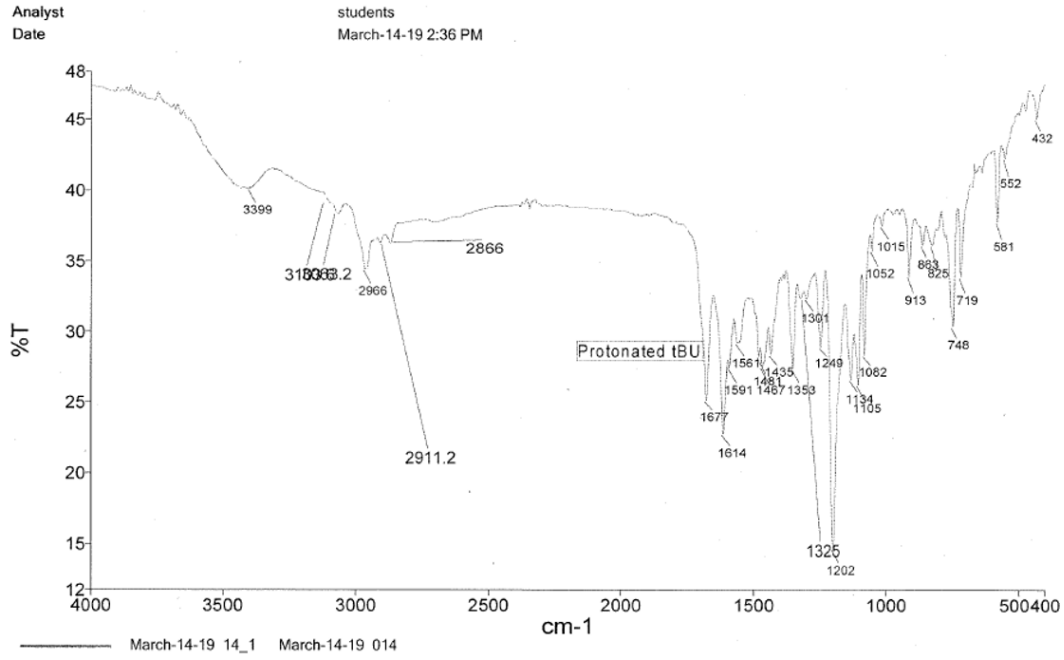


Figure C8 FT-IR spectrum of **2.2c**; KBr pellet, air background

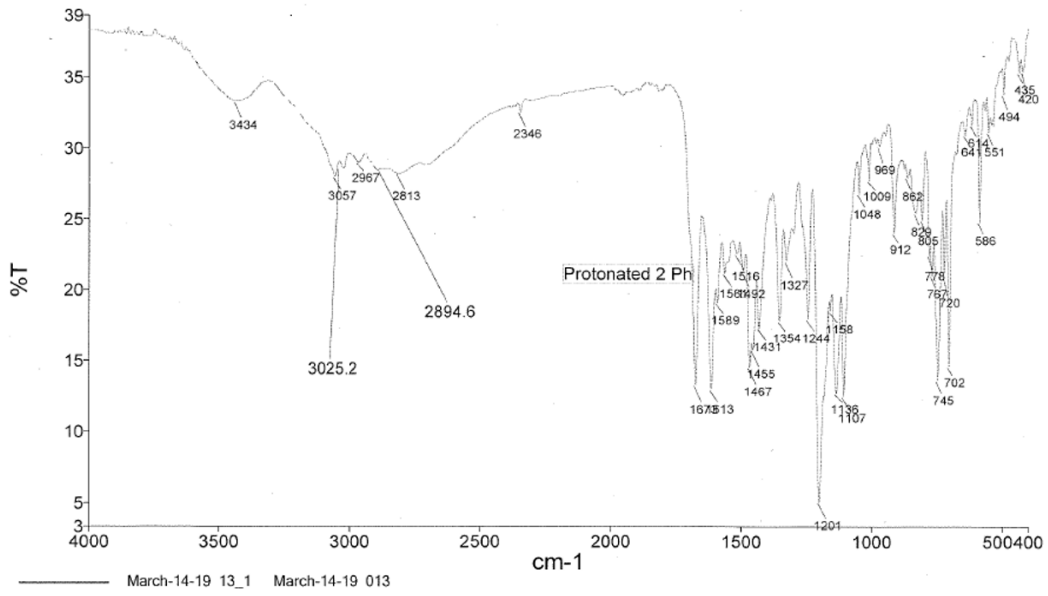


Figure C9 FT-IR spectrum of **2.2d**; KBr pellet, air background

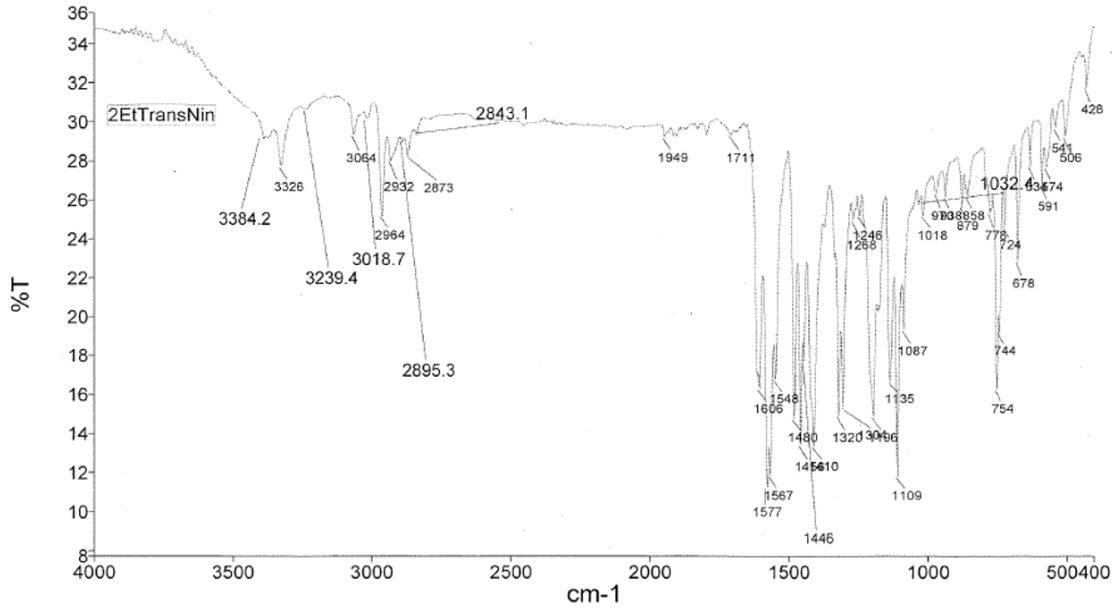


Figure C10 FT-IR spectrum of **2.2e**; KBr pellet, air background

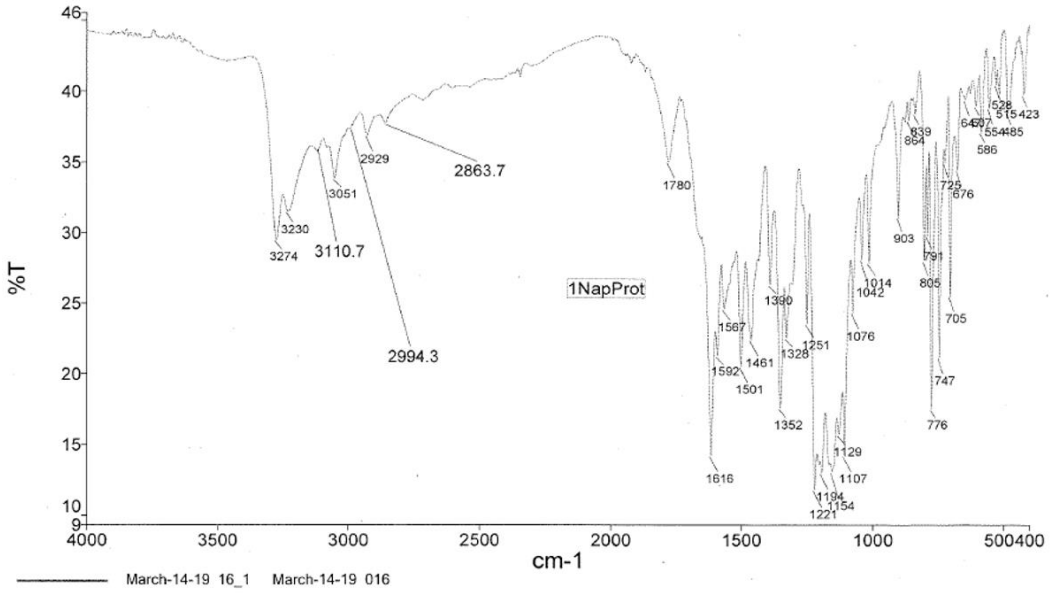


Figure C11 FT-IR spectrum of **2.2f**; KBr pellet, air background

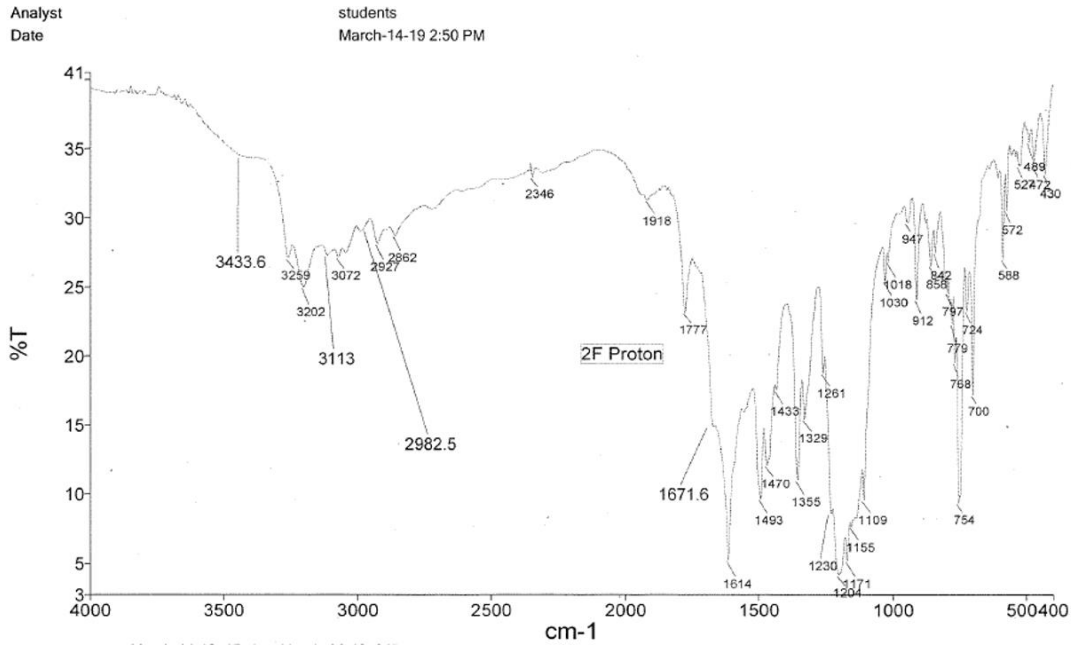


Figure C12 FT-IR spectrum of **2.2g**; KBr pellet, air background

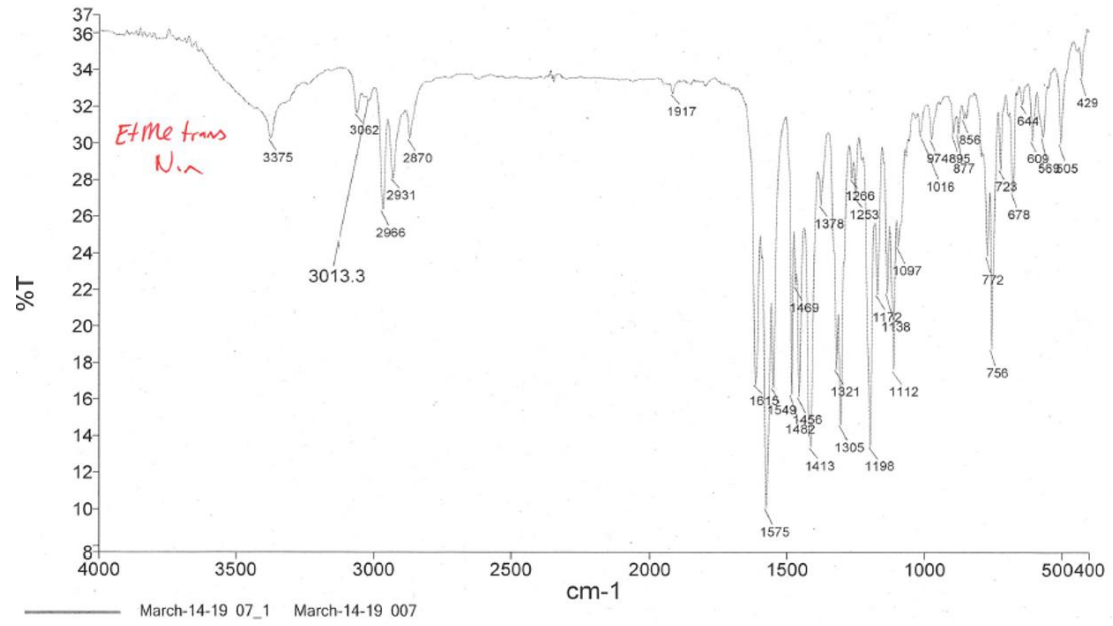


Figure C13 FT-IR spectrum of **2.7a**; KBr pellet, air background

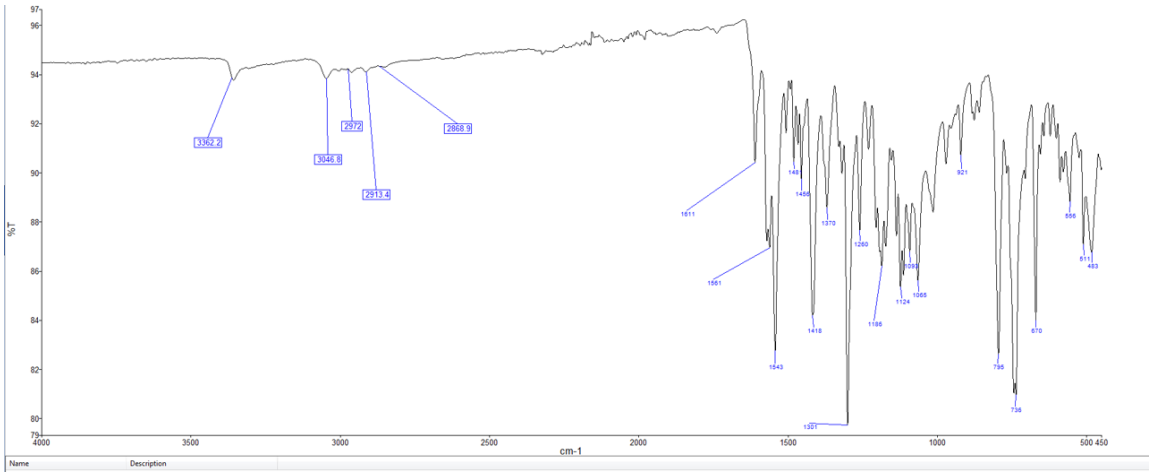


Figure C14 FT-IR spectrum of **2.7b**; ATR, air background

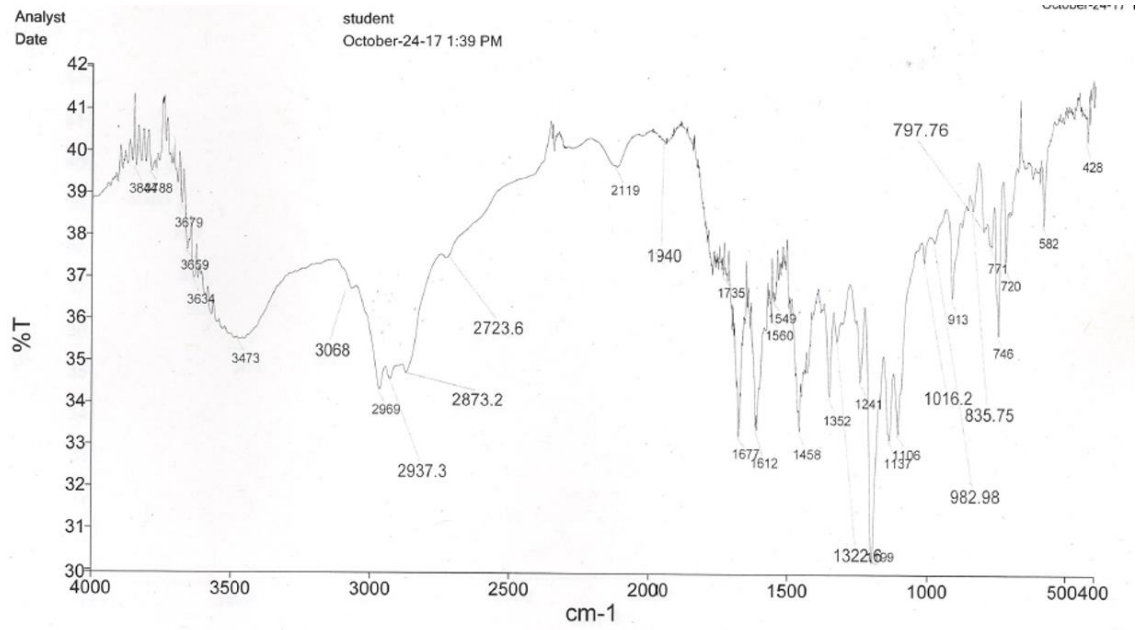


Figure C15 FT-IR spectrum of **2.8a**; KBr, air background

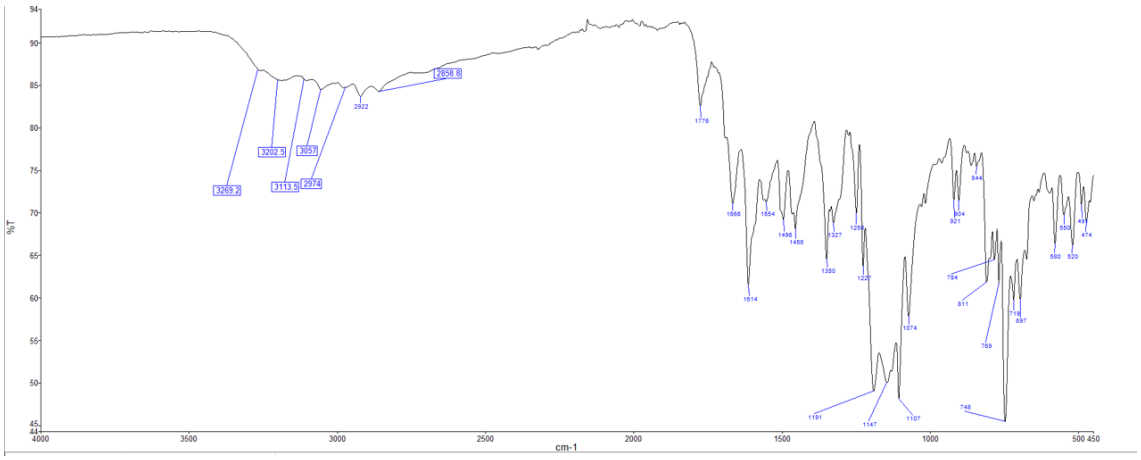


Figure C16 FT-IR spectrum of **2.8b**; ATR, air background

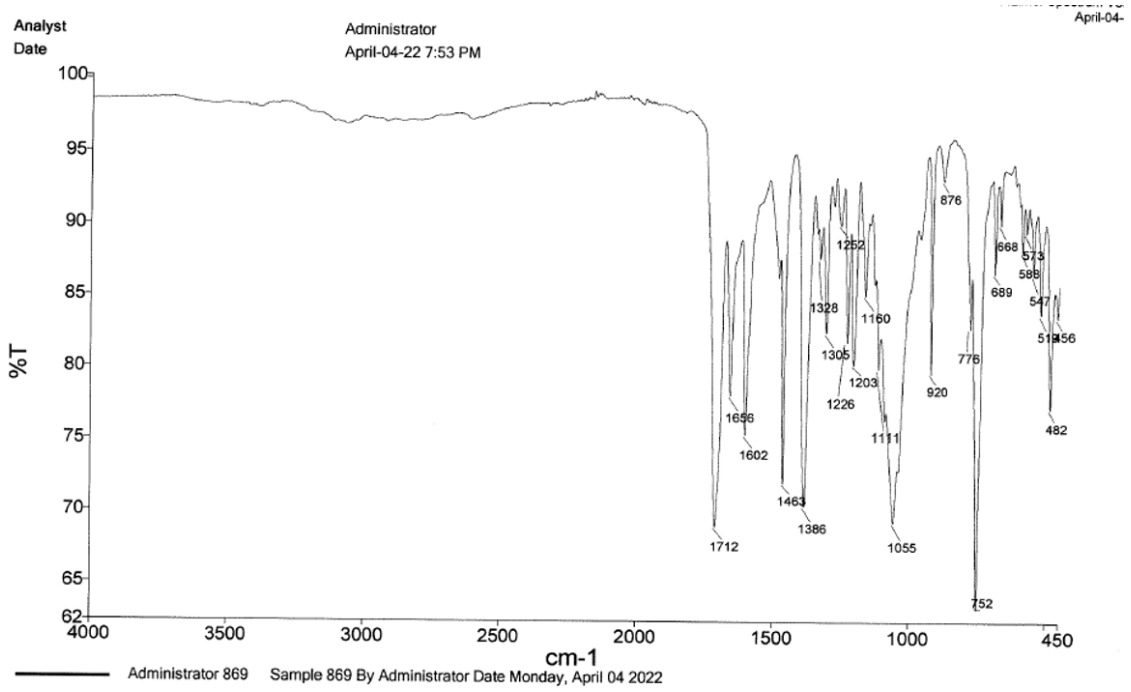


Figure C17 FT-IR spectrum of **3.15a-BF4**; air background

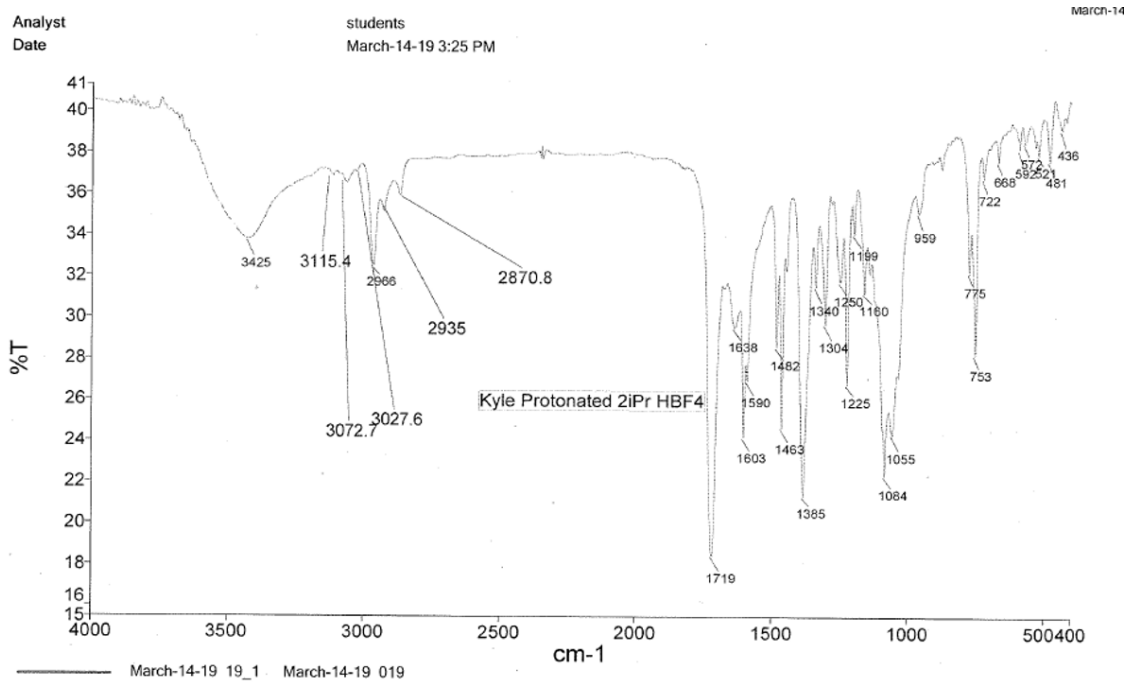


Figure C18 FT-IR spectrum of **3.15b-BF4**; KBr pellet, air background

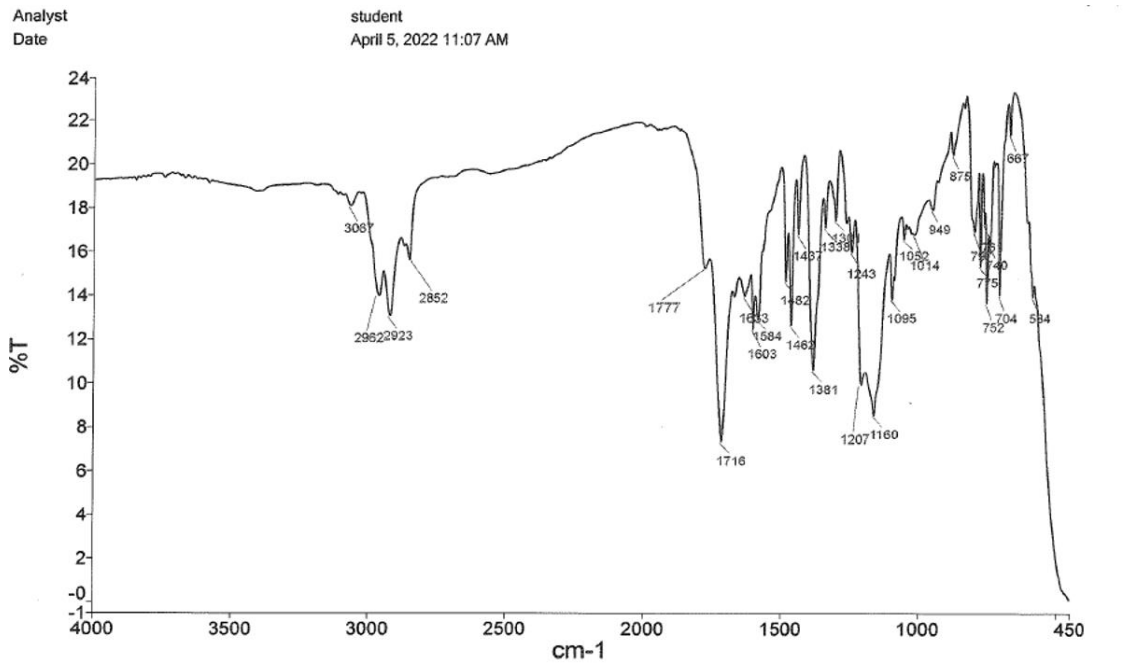


Figure 19 FT-IR spectrum of **3.15c-TFA**; NaCl plate, air background

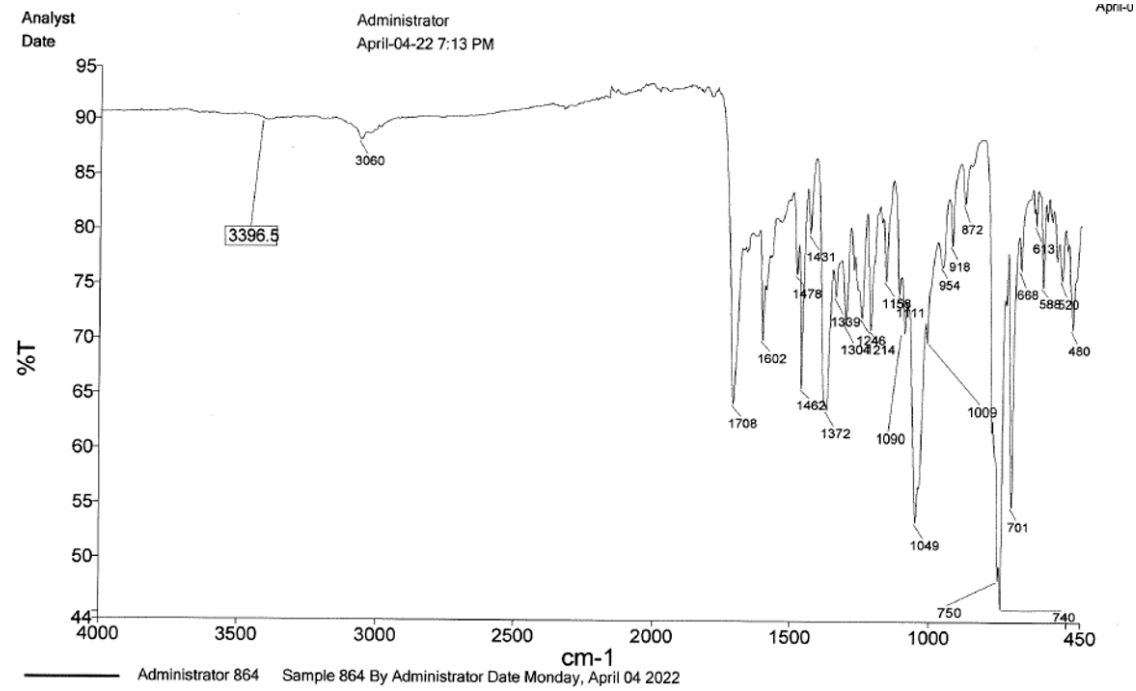


Figure C20 FT-IR spectrum of **3.15d**; ATR, air background

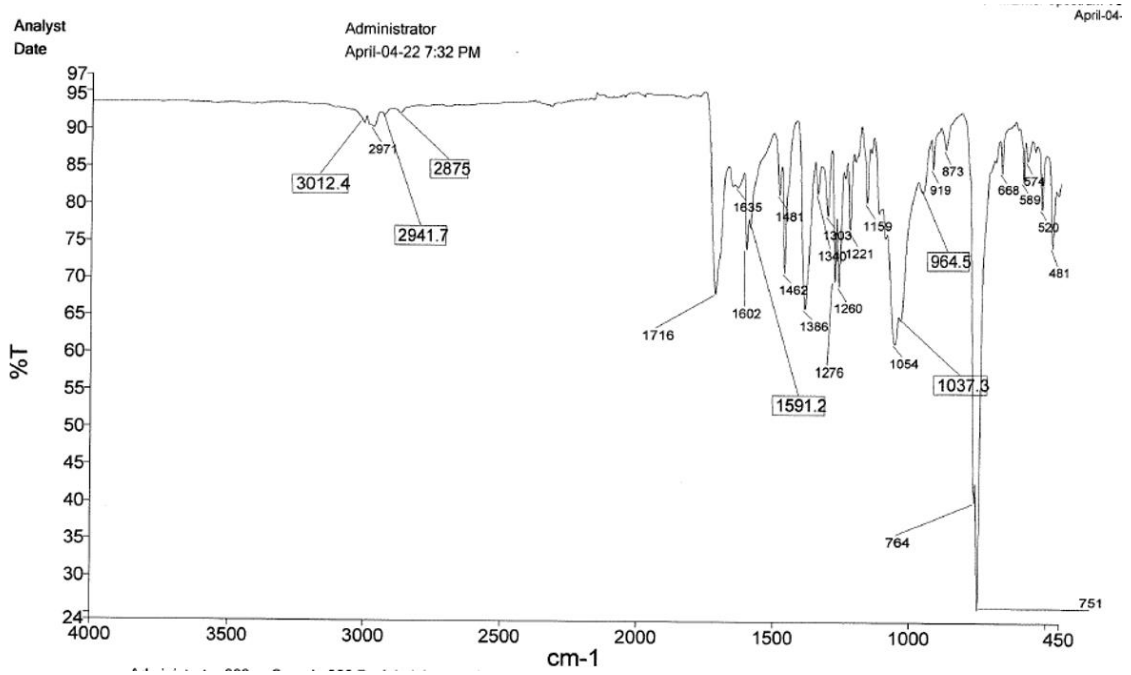


Figure C21 FT-IR spectrum of **3.15e**; ATR, air background

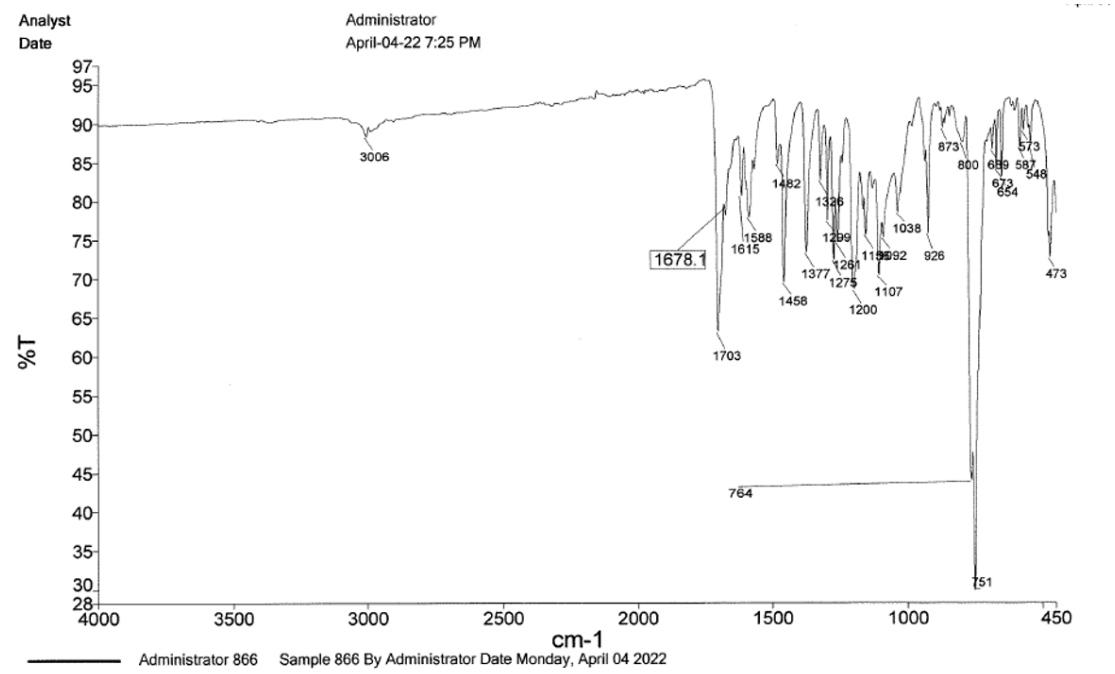


Figure C22 FT-IR spectrum of **3.16a**; air background

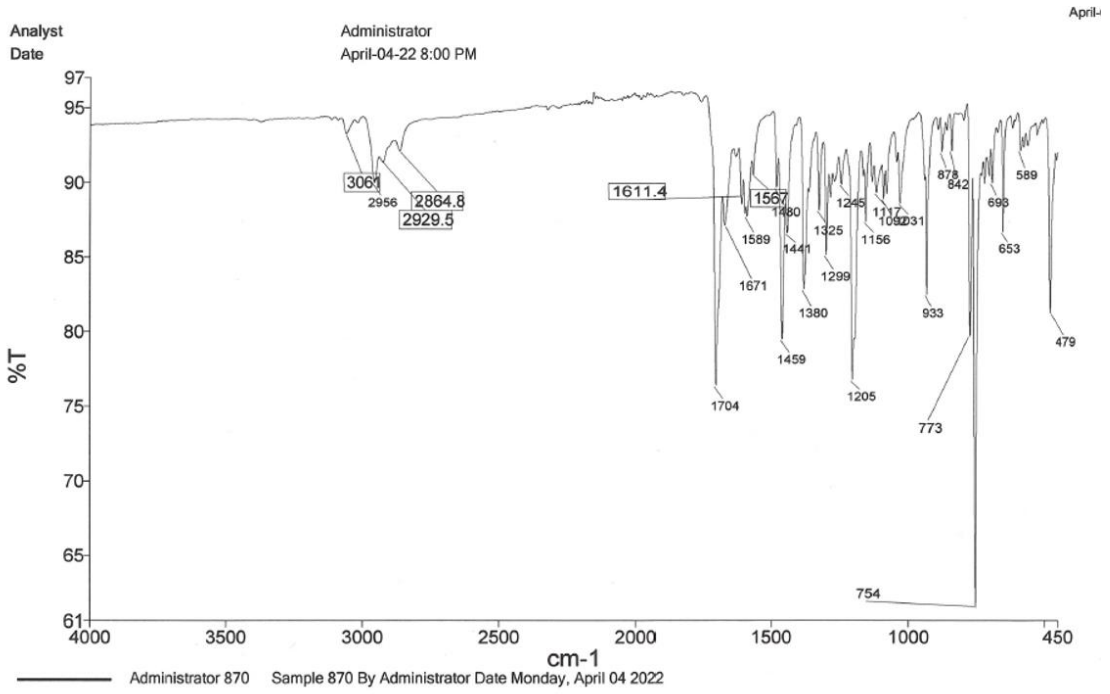


Figure C23 FT-IR spectrum of **3.16b**; ATR, air background

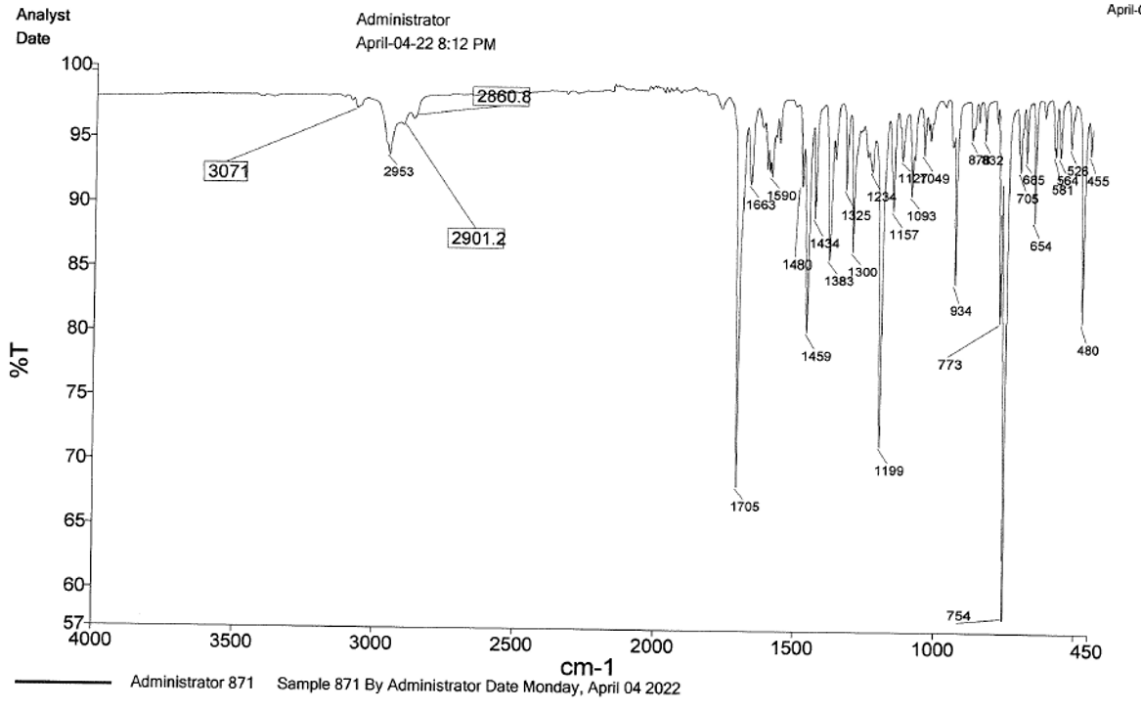


Figure C24 FT-IR spectrum of **3.16c**; ATR, air background

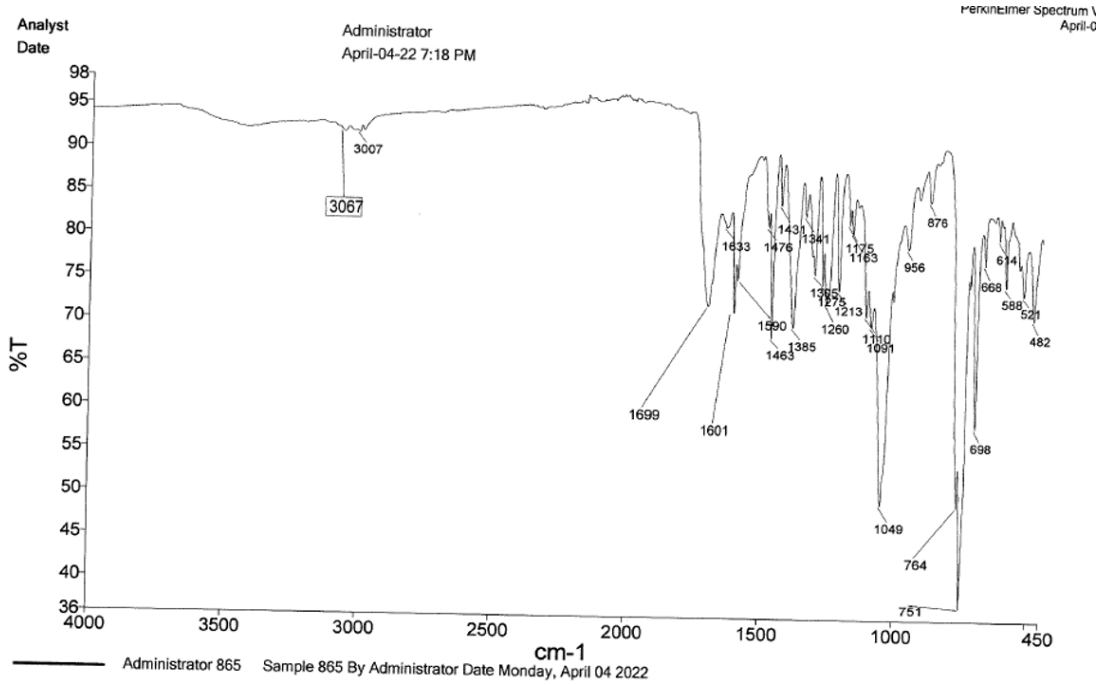


Figure C25 FT-IR spectrum of **3.16d**; air background

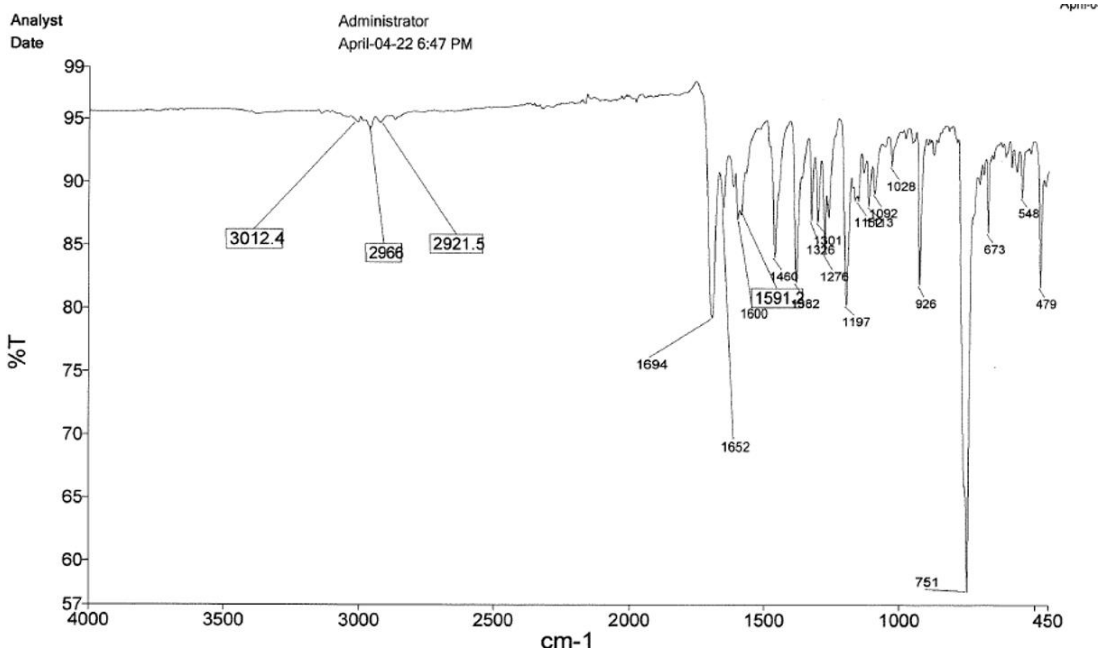


Figure C26 FT-IR spectrum of **3.16e**; ATR, air background

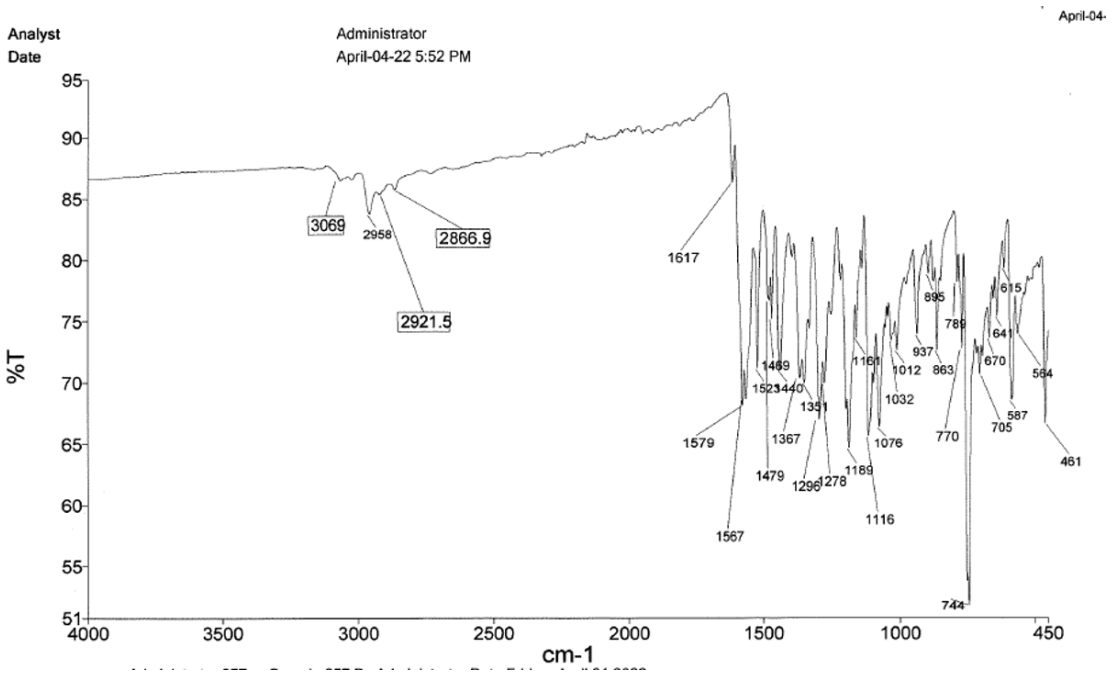


Figure C27 FT-IR spectrum of **4.5b**; ATR, air background

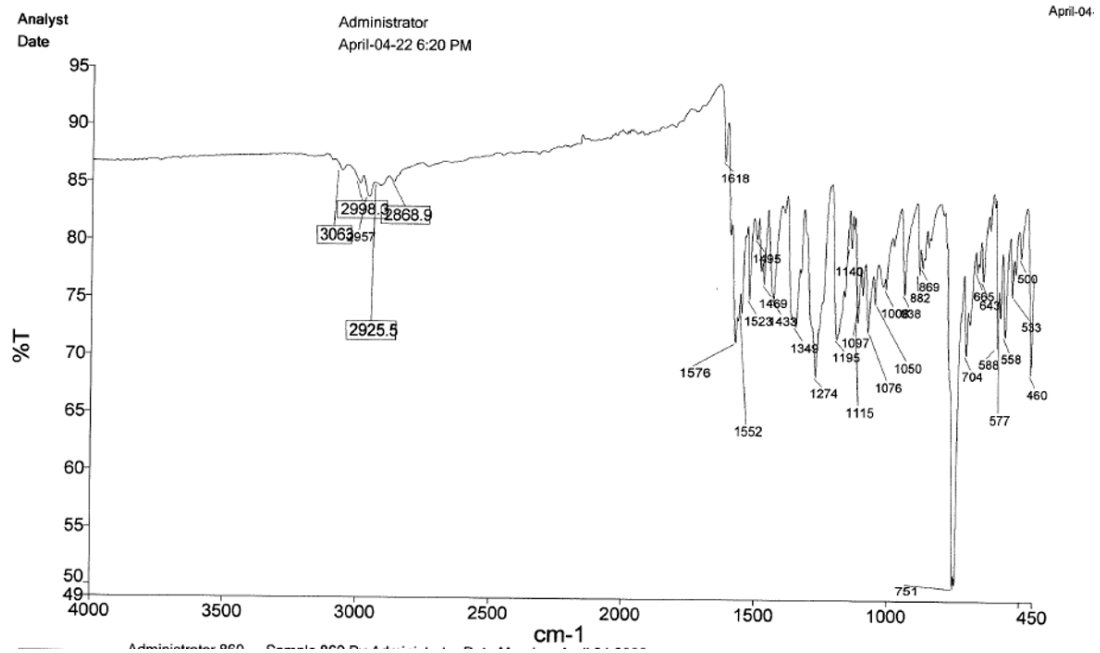


Figure C28 FT-IR spectrum of **4.5c**; ATR, air background

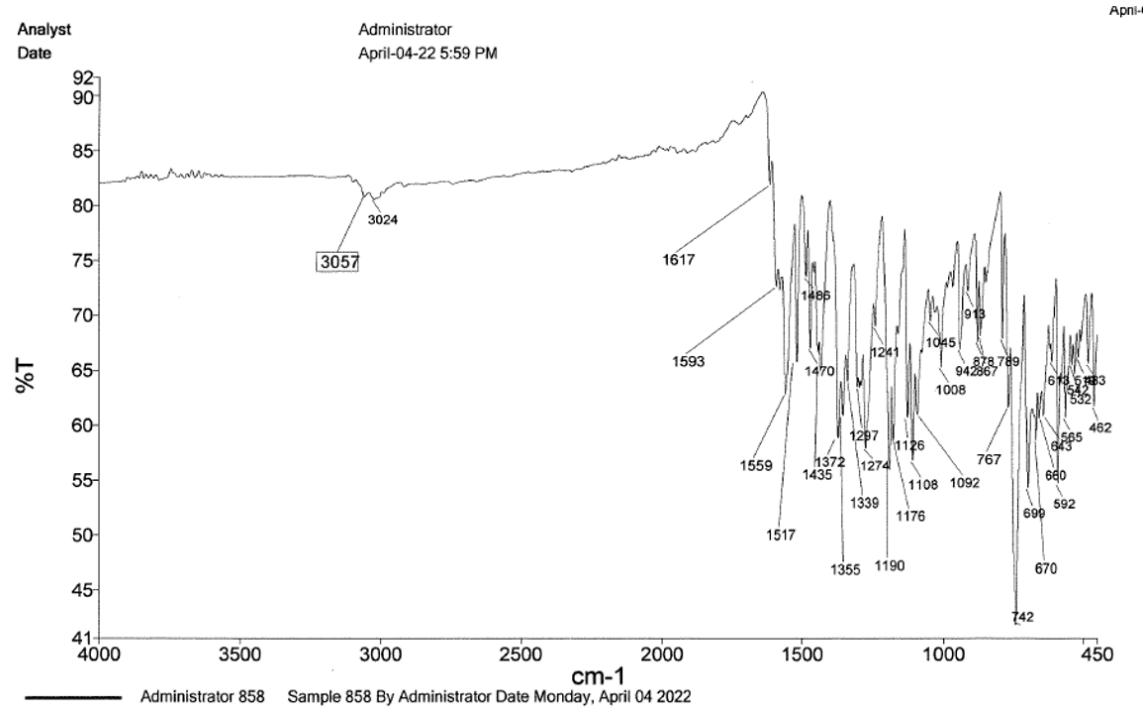


Figure C29 FT-IR spectrum of **4.5d**; ATR, air background

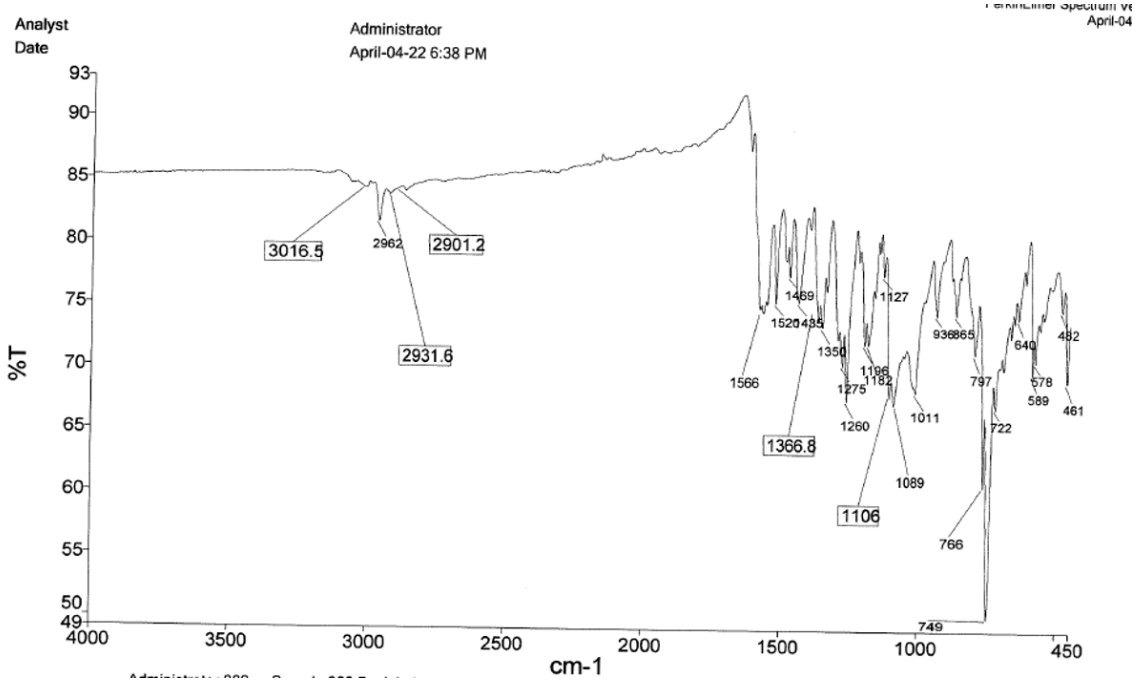


Figure C30 FT-IR spectrum of **4.5e**; ATR, air background

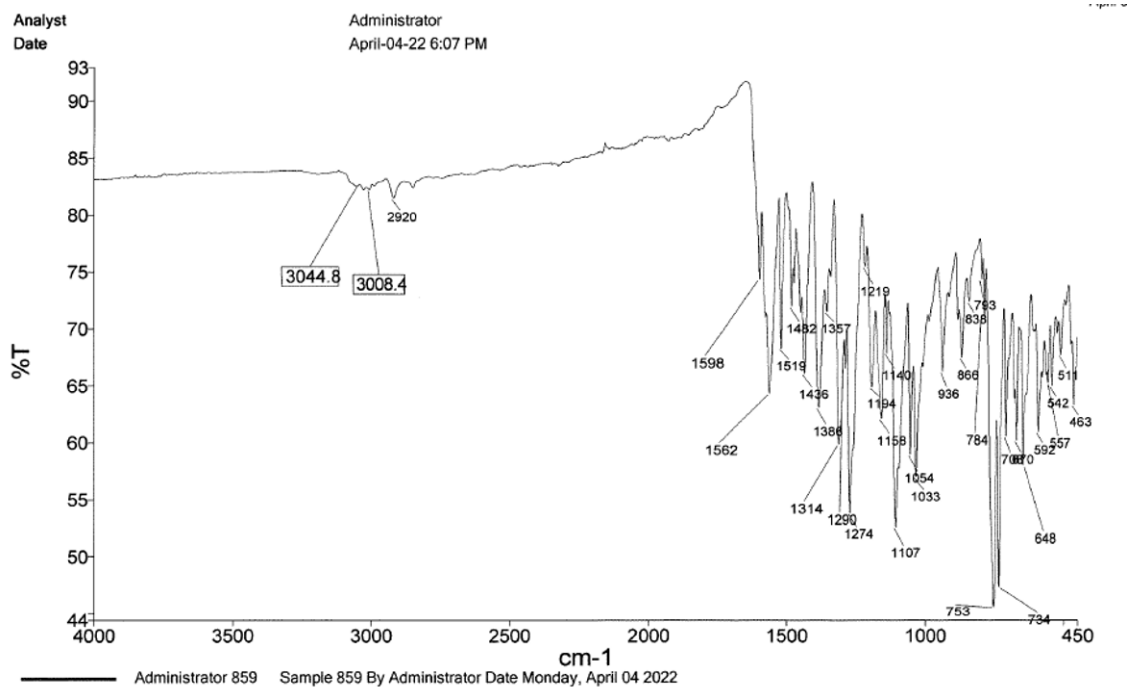


Figure C31 FT-IR spectrum of **4.5f**; ATR, air background

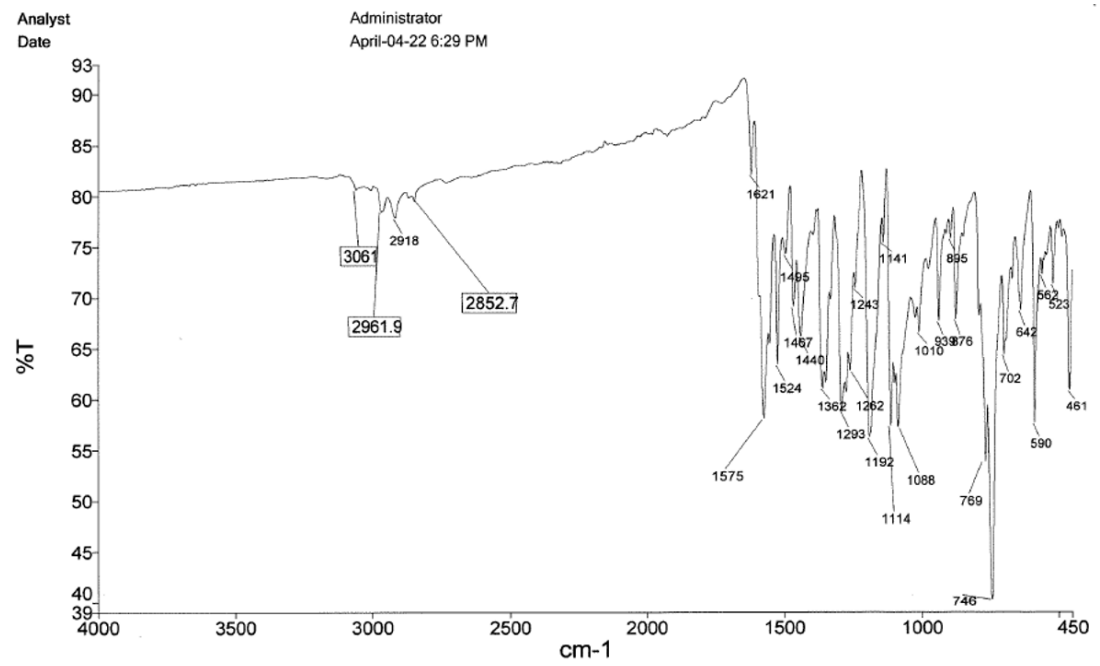


Figure C32 FT-IR spectrum of **4.5g**; ATR, air background

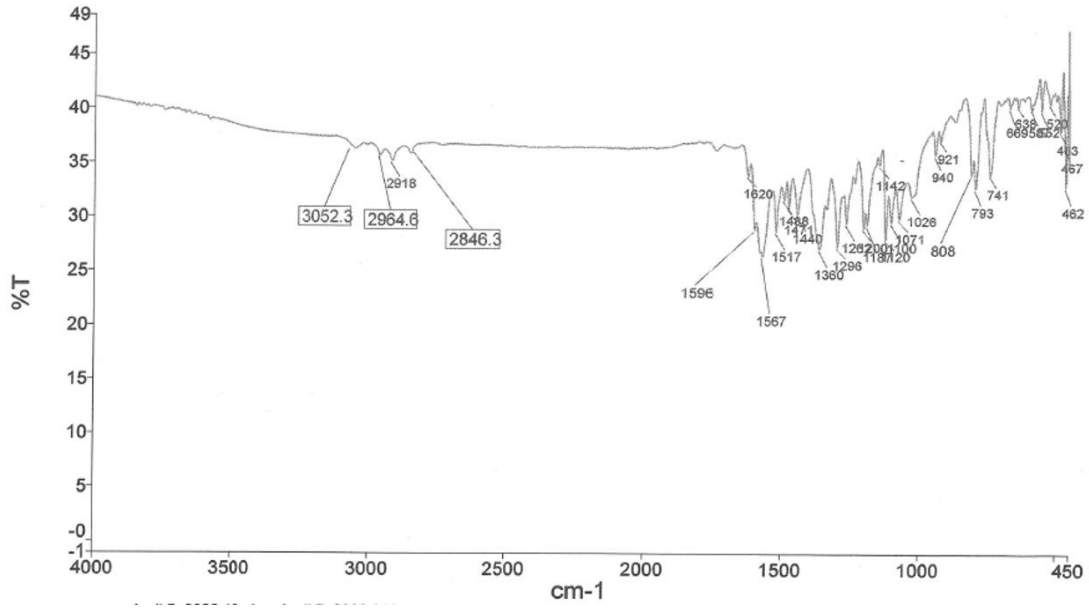


Figure C33 FT-IR spectrum of **4.5h**; NaCl plate, air background

Appendix D: Mass Spectrometry Data

High-resolution mass spectra

In order of appearance in this dissertation

High resolution mass spectra of **2.1a**, **2.1b**, **2.1e**, **2.1g**, **2.2a – 2.2e**, **2.7a**, **2.8a**, **3.15b**, **3.16c**, and **3.16d** were collected at the Mass Spectrometry Center at the University of British Columbia; High resolution mass spectra of **2.1f**, **2.2f**, **2.2g**, **2.7b**, **2.8b**, **3.15a**, **3.15c**, **3.15d**, **3.15e**, **3.16a**, **3.16b**, **3.16e**, **4.5b**, **4.5c**, **4.5d**, **4.5e**, **4.5f**, **4.5g**, and **4.5h**, were collected at the Mass Spectrometry Facility at the University of Victoria

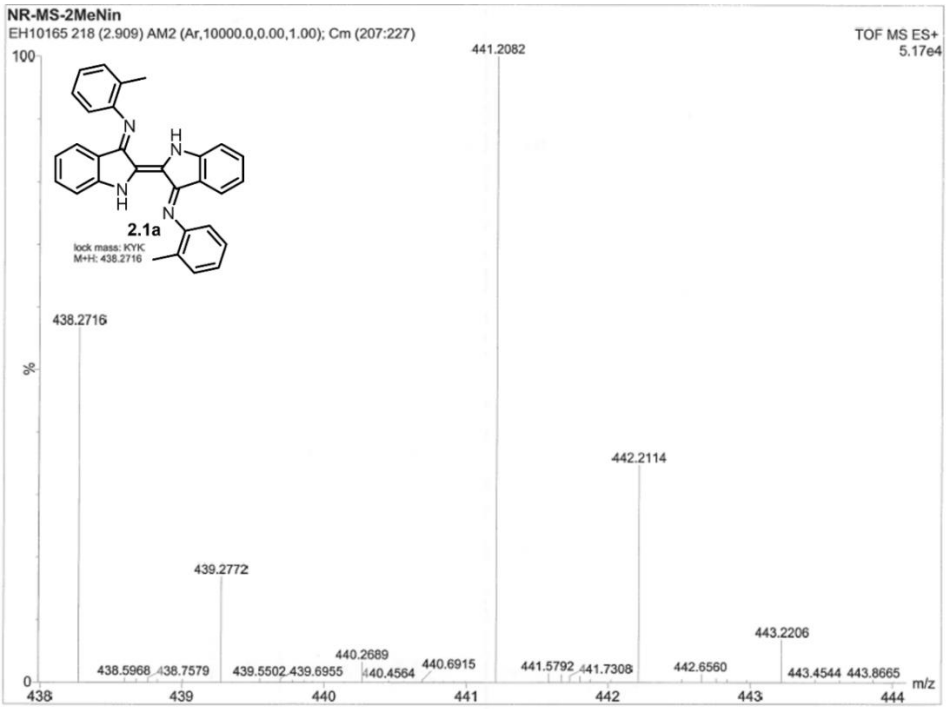


Figure D1 High-resolution mass spectrum of **2.1a**

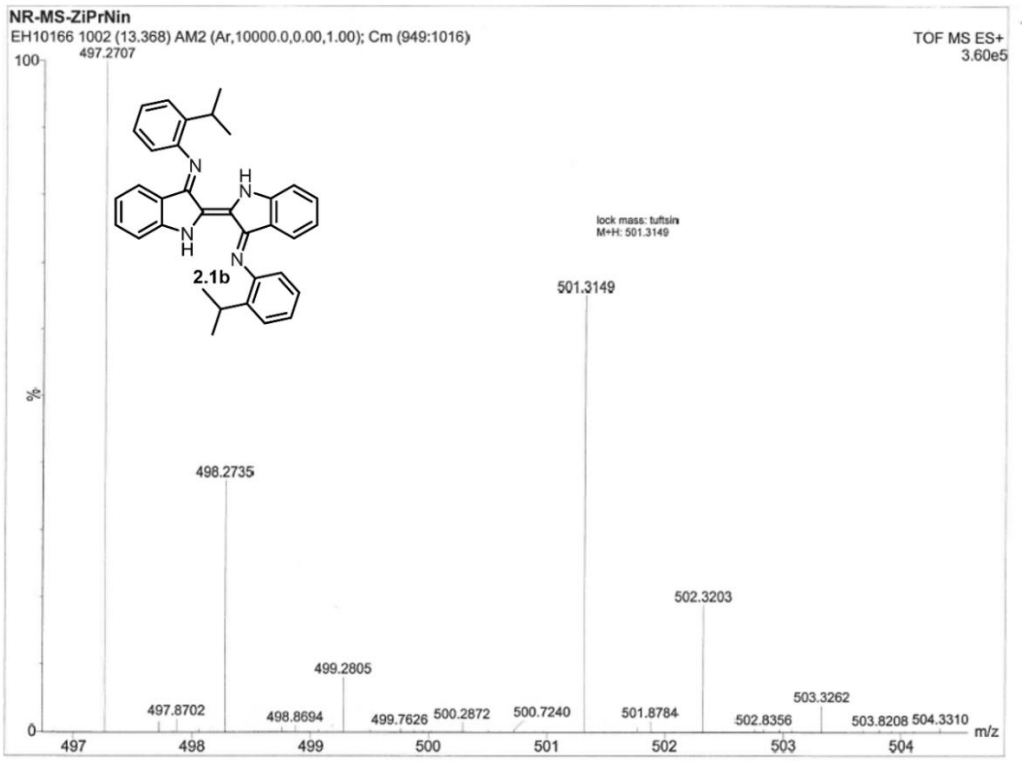


Figure D2 High-resolution mass spectrum of **2.1b**

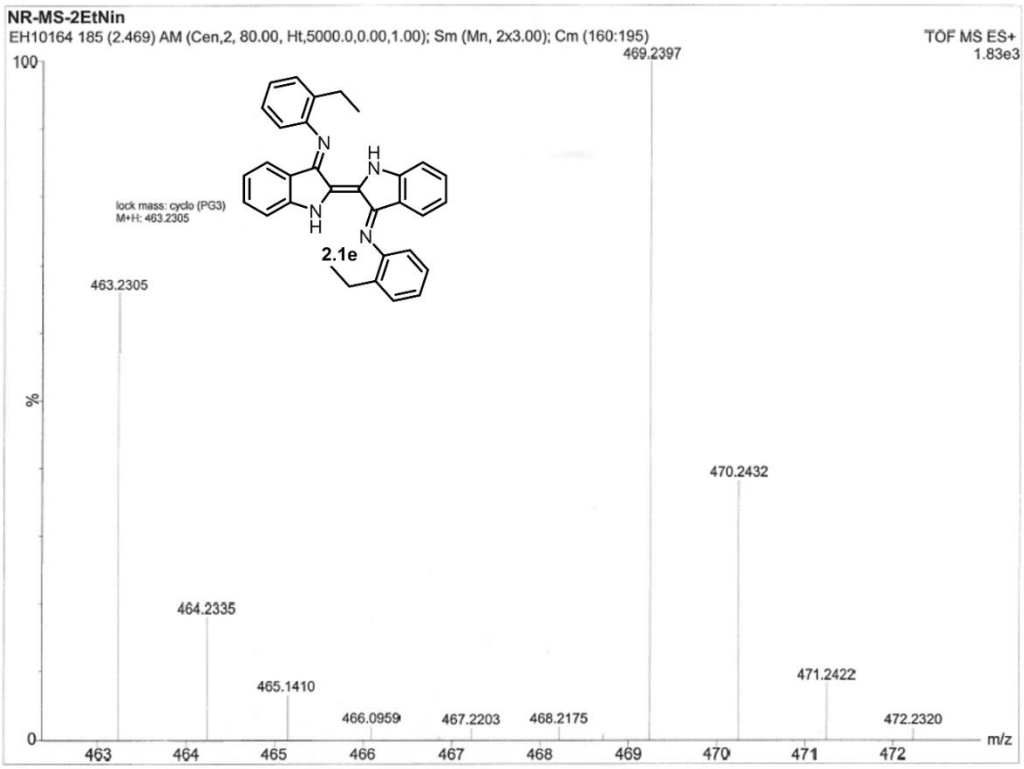


Figure D3 High-resolution mass spectrum of **2.1e**

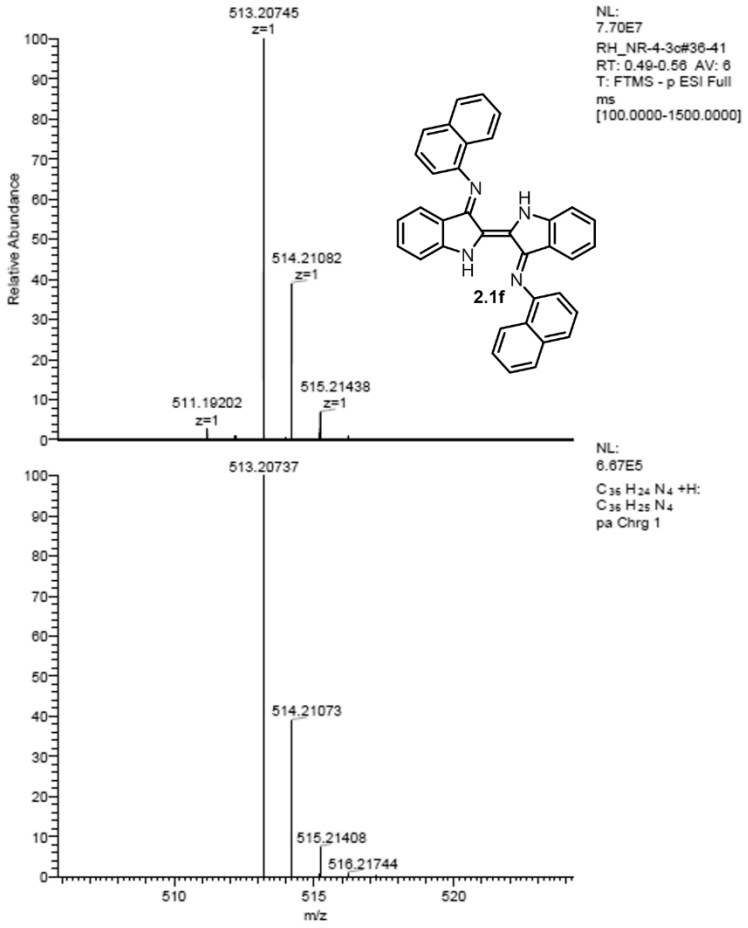


Figure D4 High-resolution mass spectrum of **2.1f**

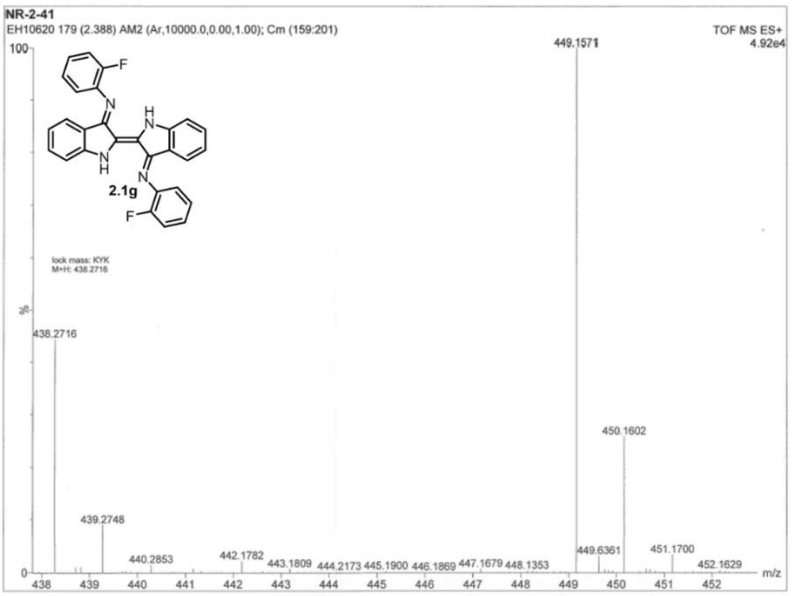


Figure D5 High-resolution mass spectrum of **2.1g**

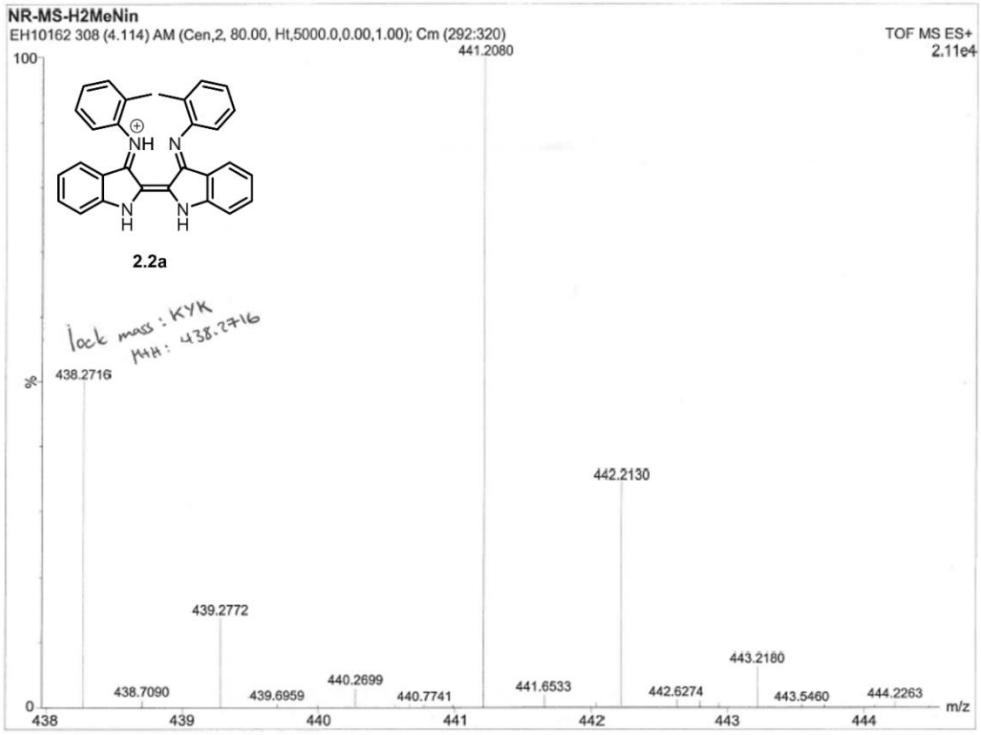


Figure D6 High-resolution mass spectrum of **2.2a**

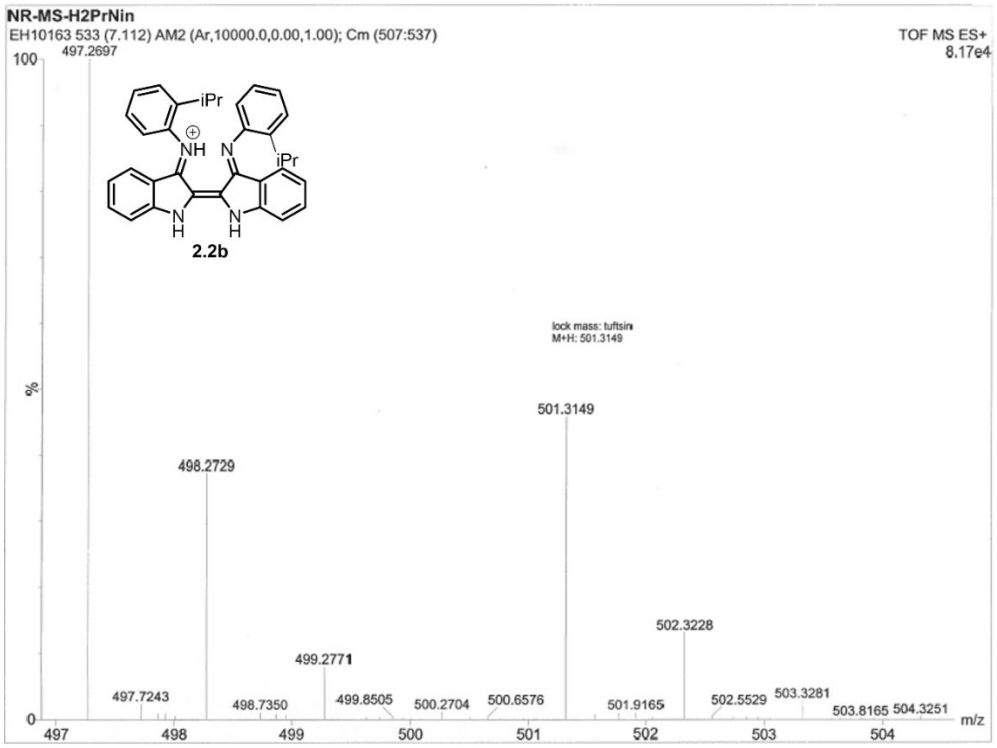


Figure D7 High-resolution mass spectrum of **2.2b**

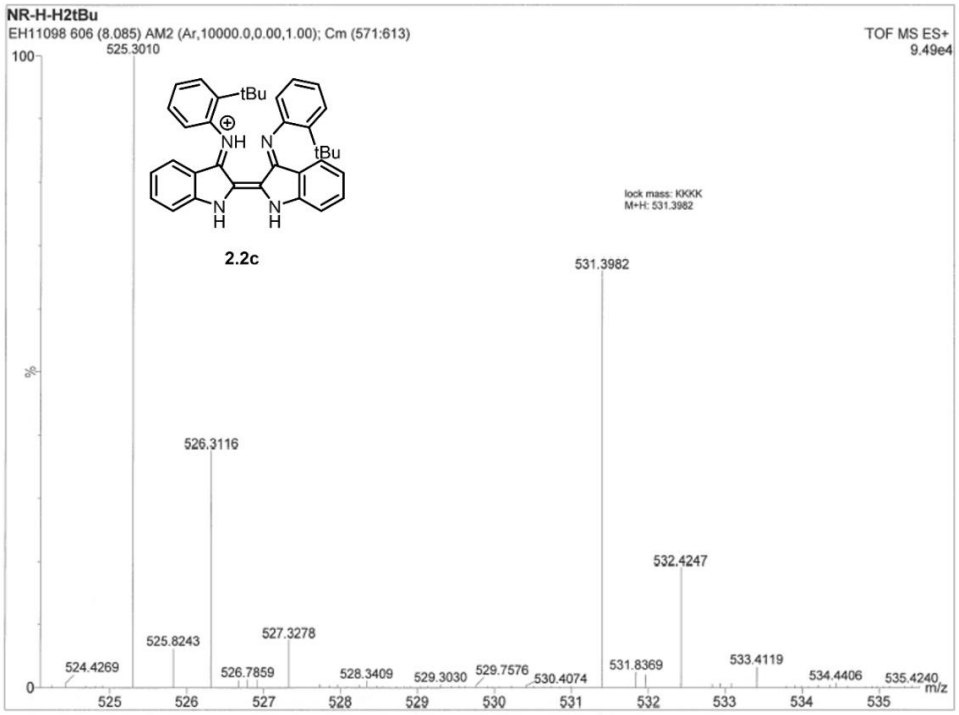


Figure D8 High-resolution mass spectrum of **2.2c**

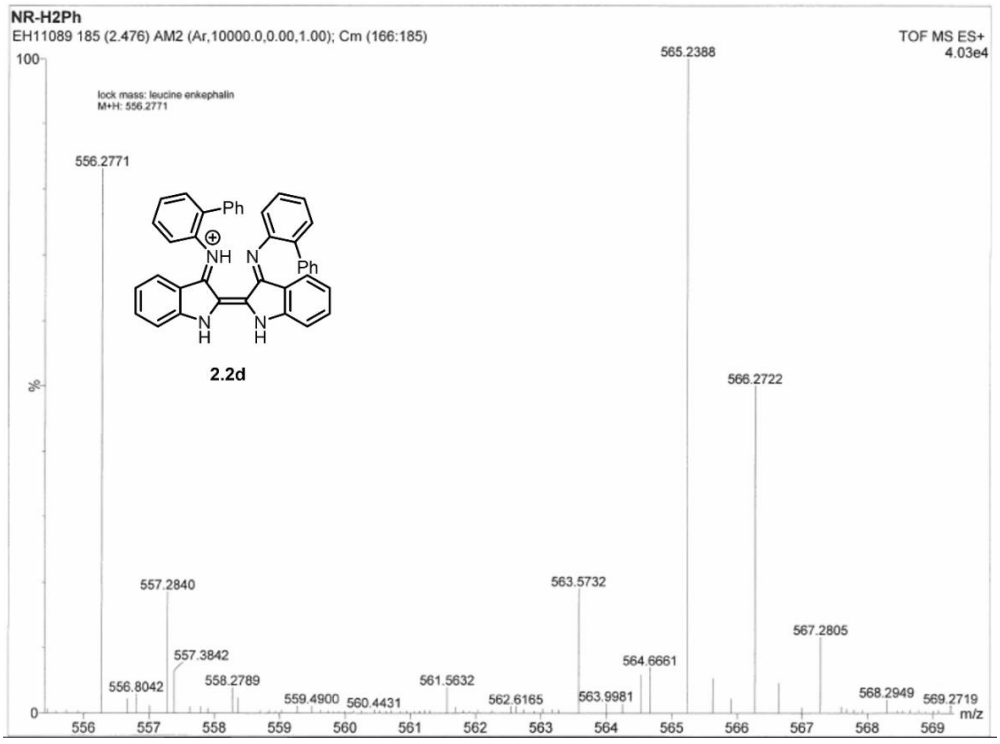


Figure D9 High-resolution mass spectrum of **2.2d**

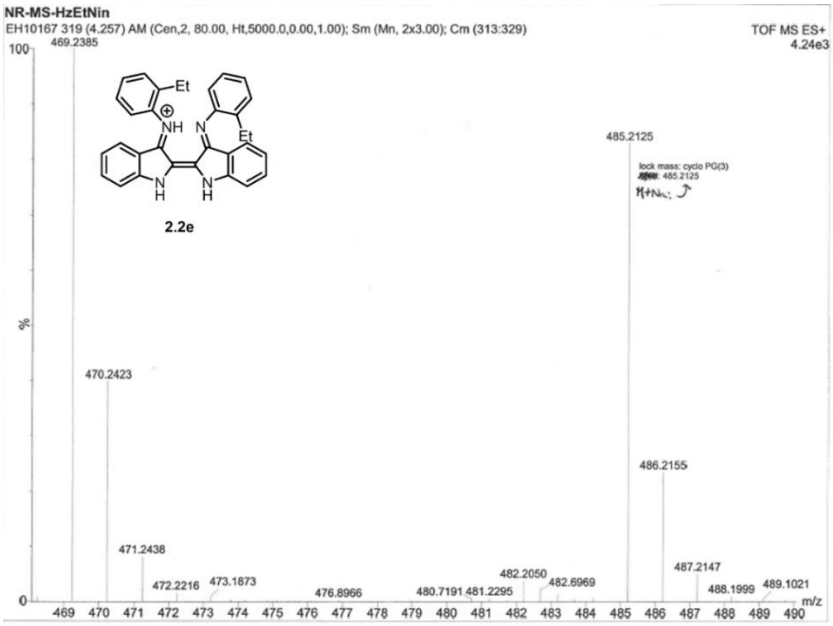


Figure D10 High-resolution mass spectrum of **2.2e**

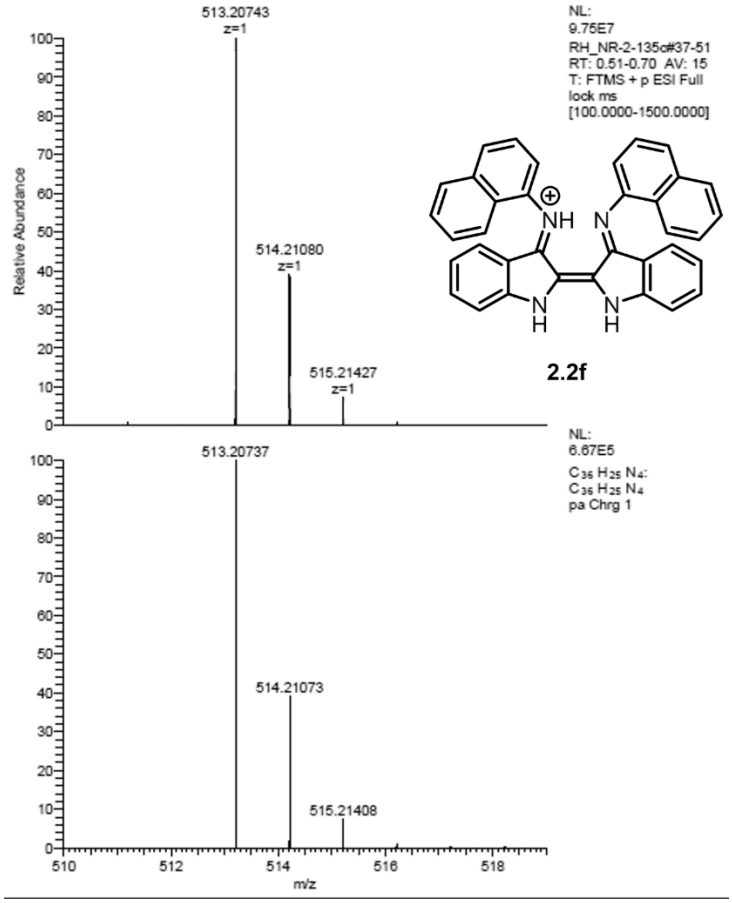


Figure D11 High-resolution mass spectrum of **2.2f**

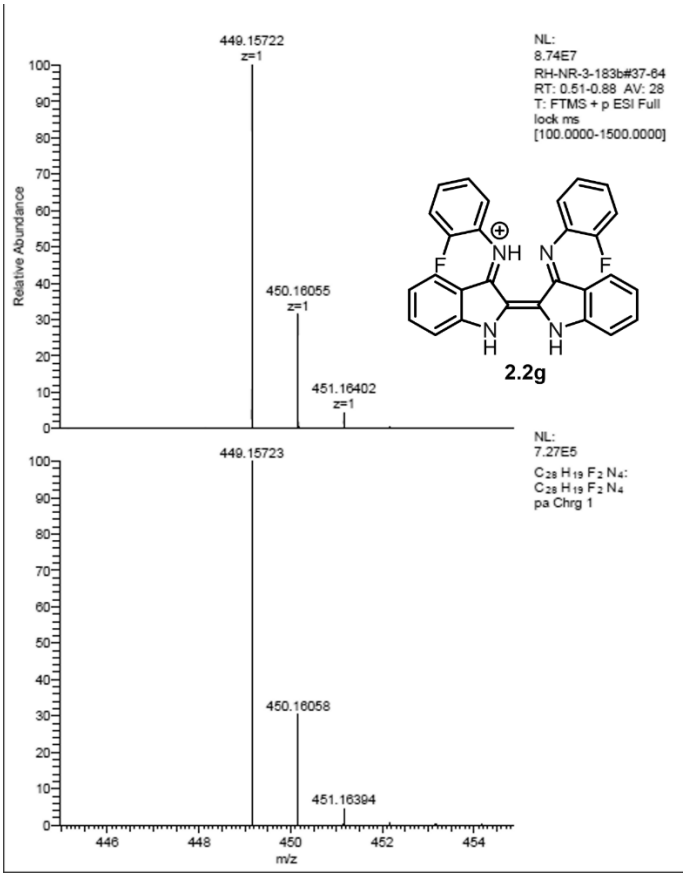


Figure D12 High-resolution mass spectrum of **2.2g**

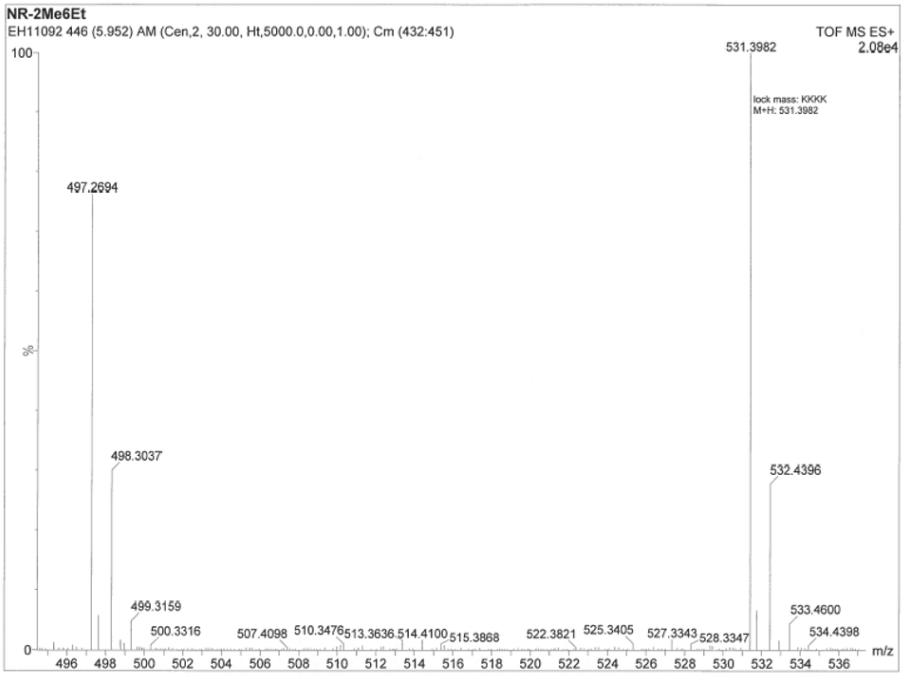


Figure D13 High-resolution mass spectrum of **2.7a**

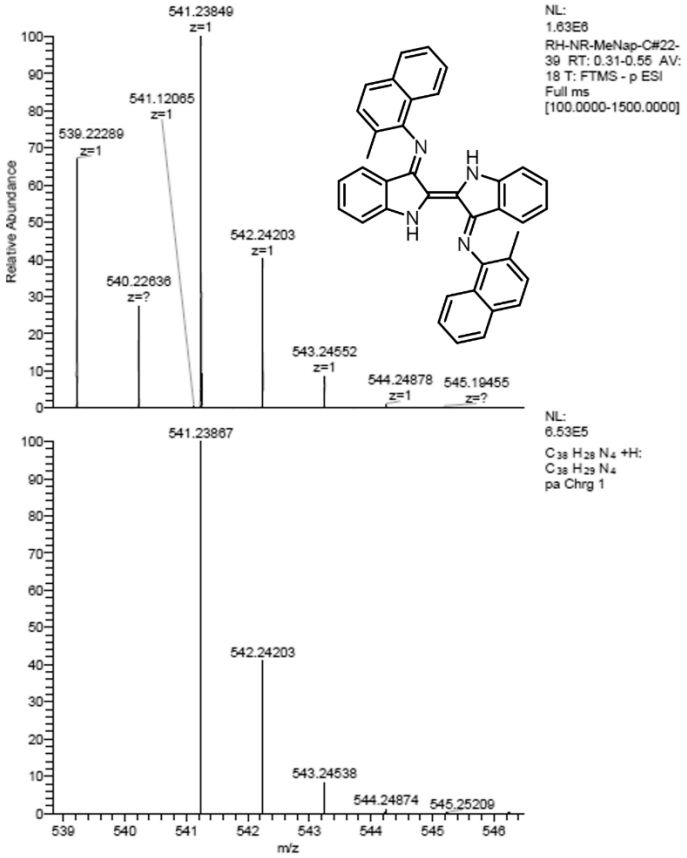


Figure D14 High-resolution mass spectrum of **2.7b**

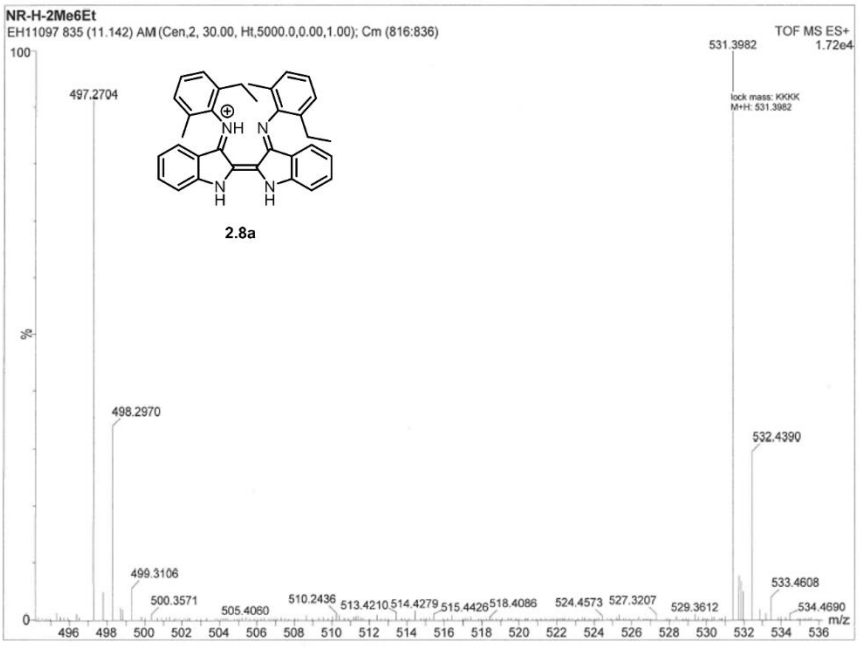


Figure D15 High-resolution mass spectrum of **2.8a**

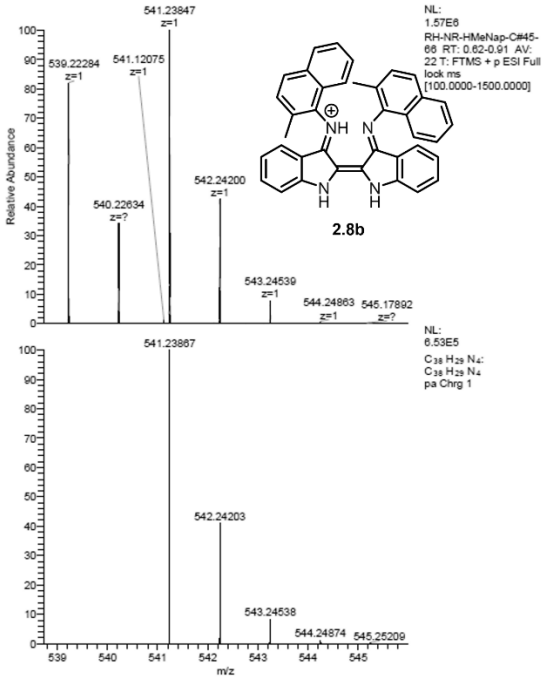


Figure D16 High-resolution mass spectrum of **2.8b**

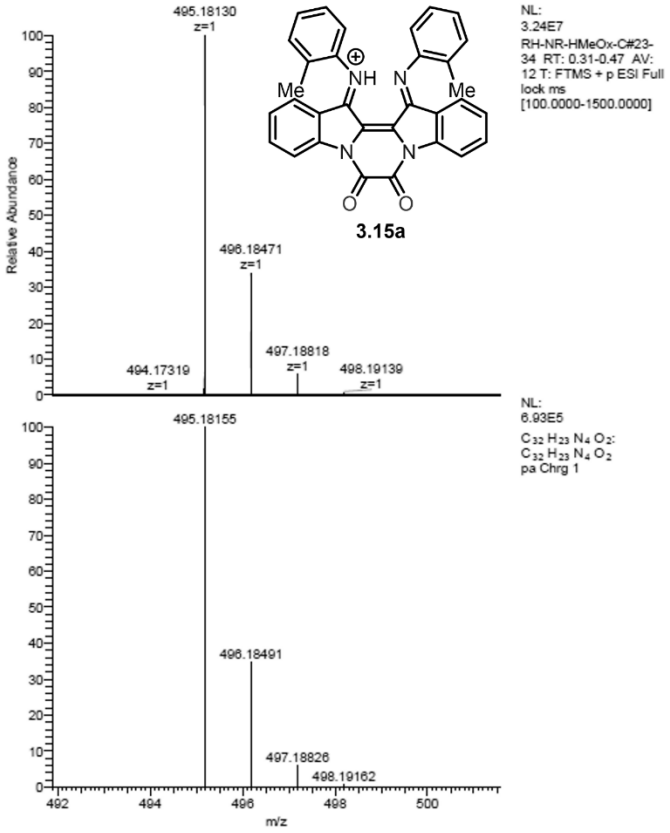


Figure D17 High-resolution mass spectrum of **3.15a**

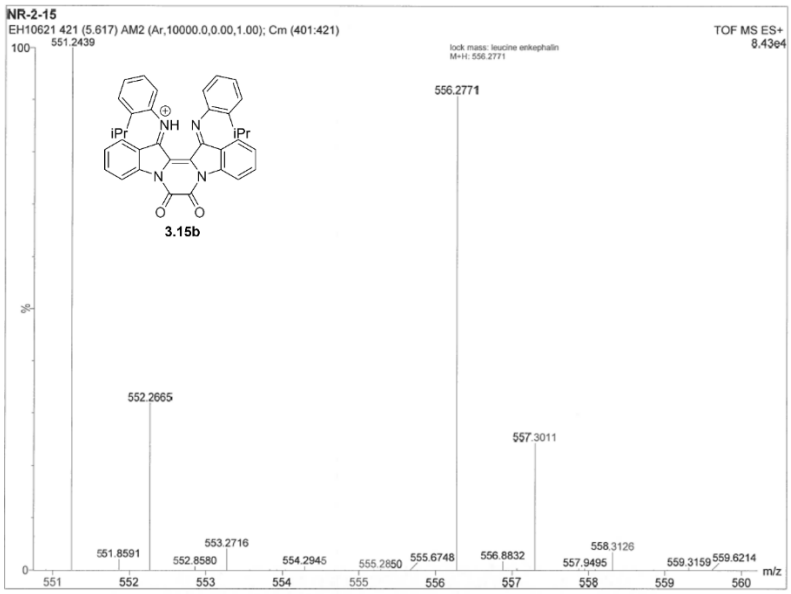


Figure D18 High-resolution mass spectrum of **3.15b**

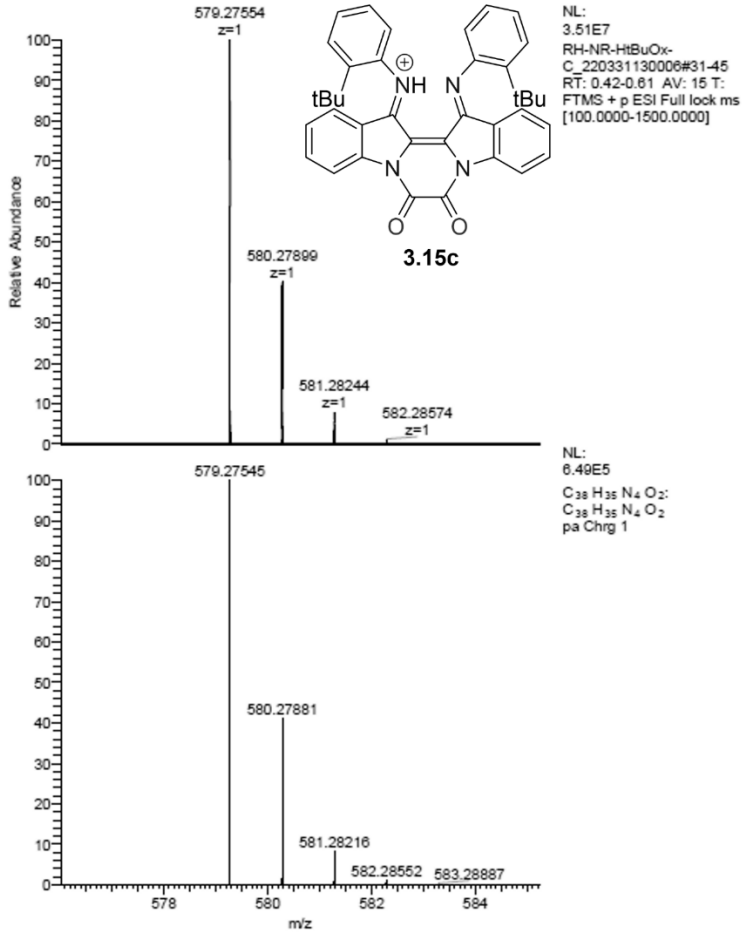


Figure D19 High-resolution mass spectrum of **3.15c**

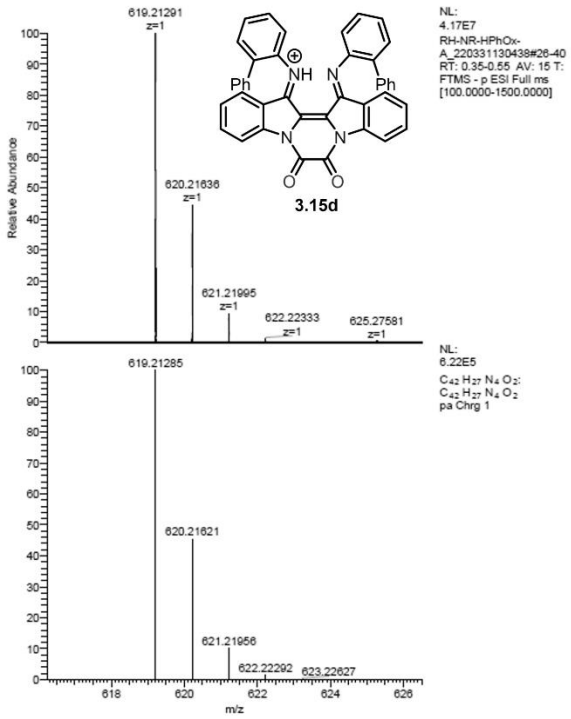


Figure D20 High-resolution mass spectrum of **3.15d**

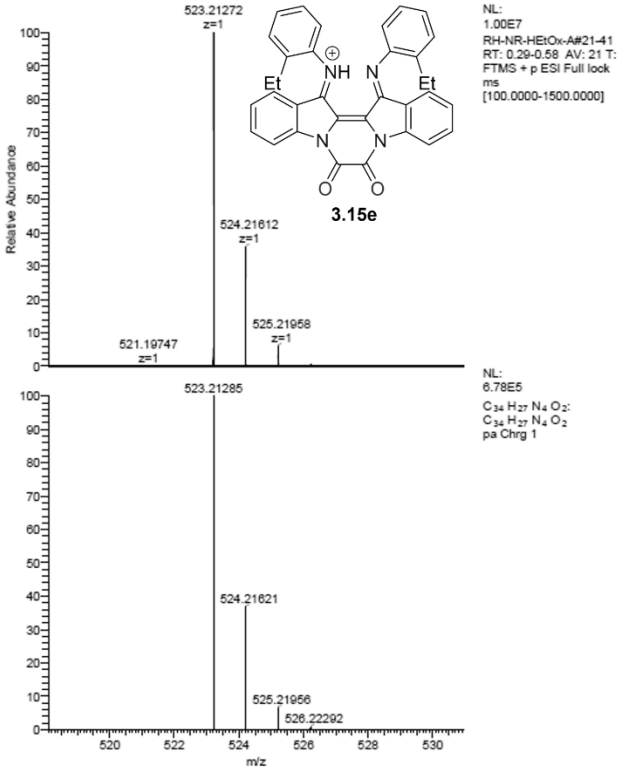


Figure D21 High-resolution mass spectrum of **3.15e**

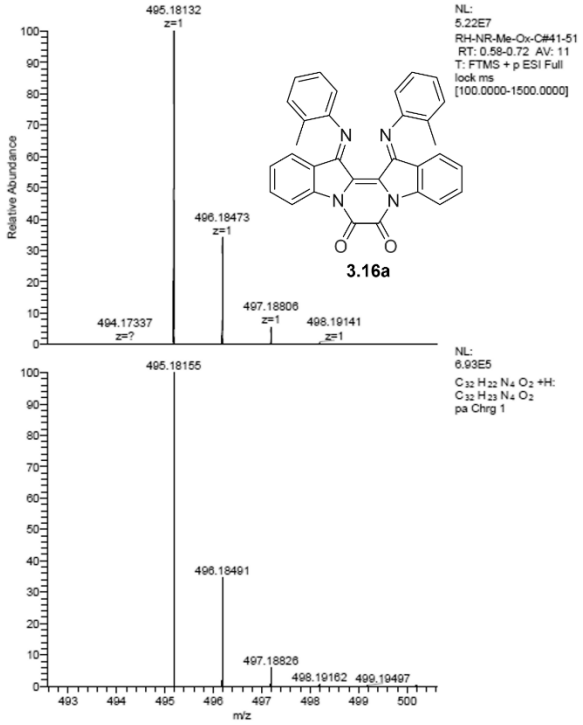


Figure D22 High-resolution mass spectrum of **3.16a**

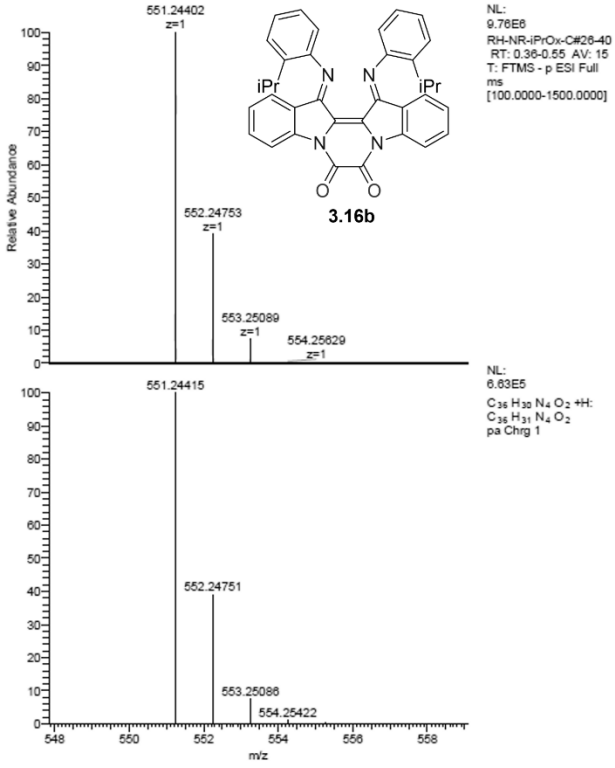


Figure D23 High-resolution mass spectrum of **3.16b**

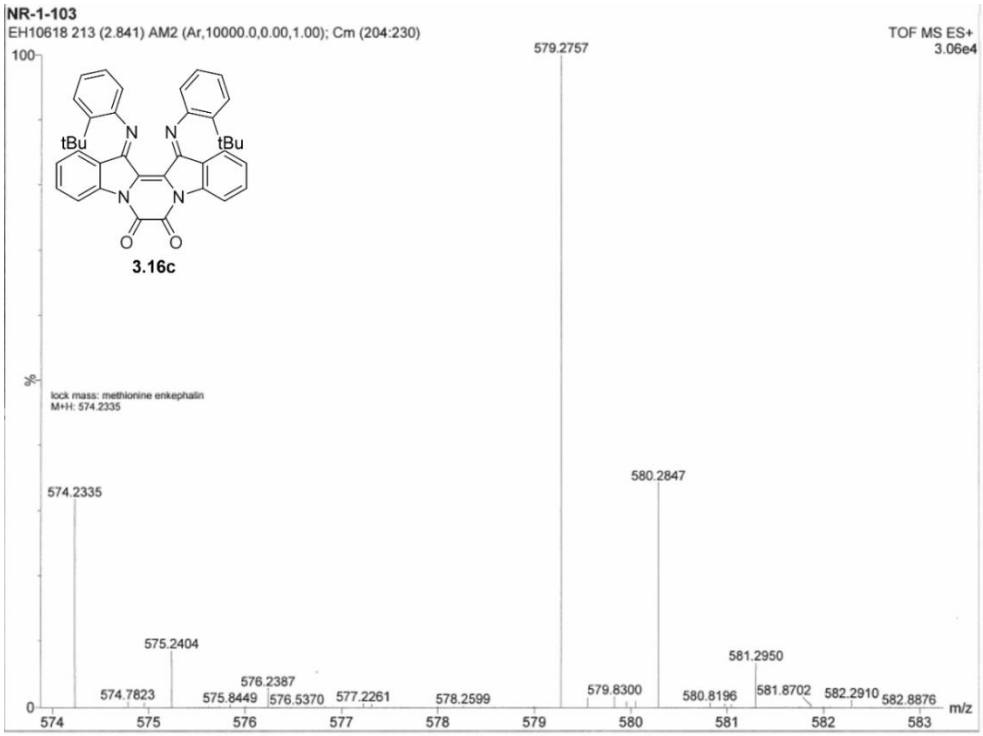


Figure D24 High-resolution mass spectrum of **3.16c**

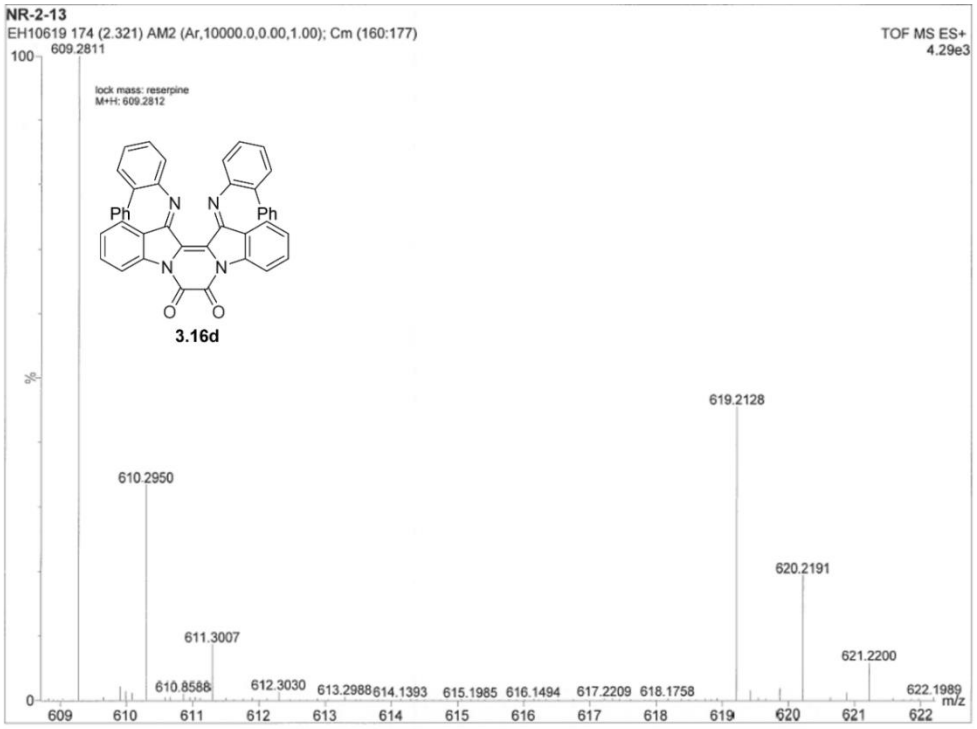


Figure D25 High-resolution mass spectrum of **3.16d**

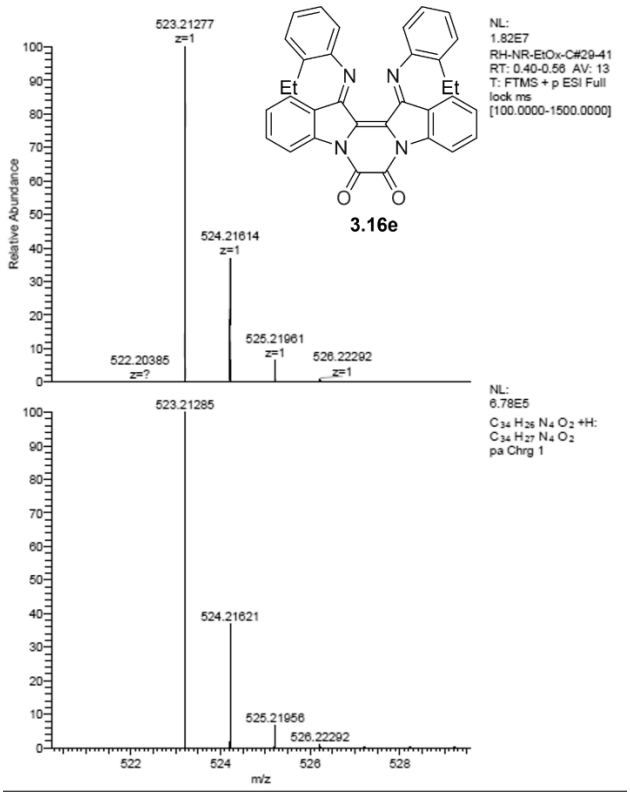


Figure D26 High-resolution mass spectrum of **3.16e**

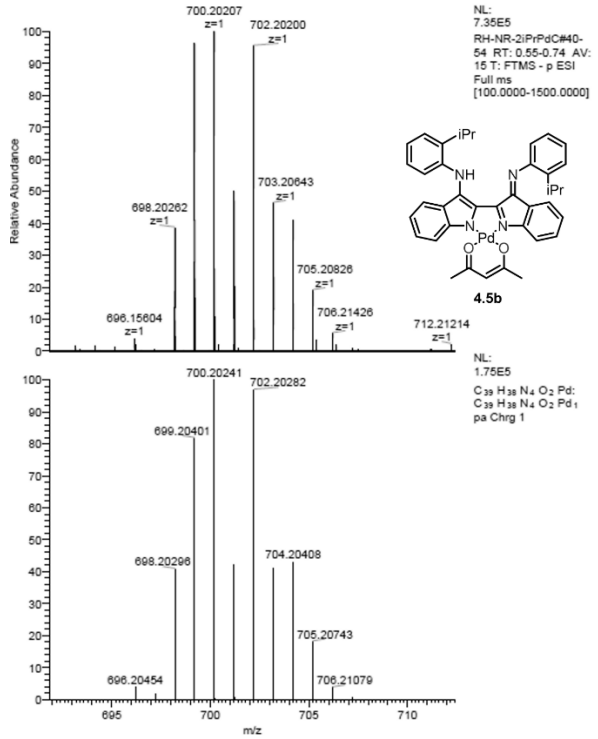


Figure D27 High-resolution mass spectrum of **4.5b**

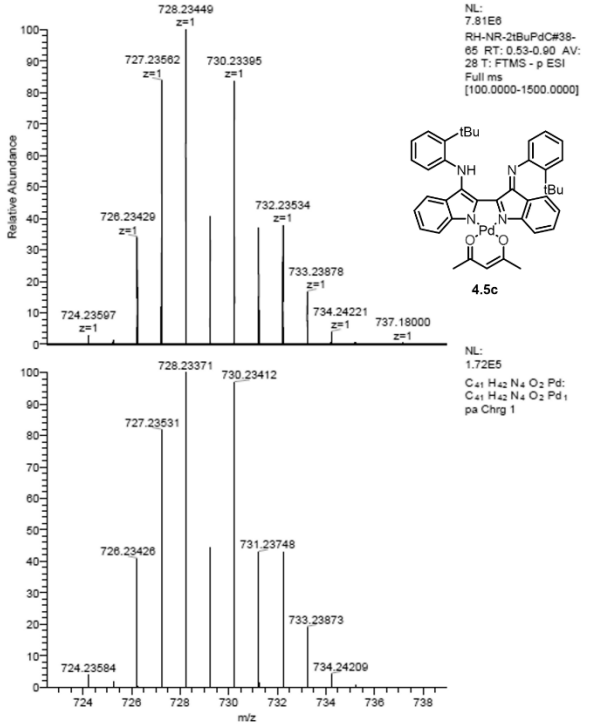


Figure D28 High-resolution mass spectrum of **4.5c**

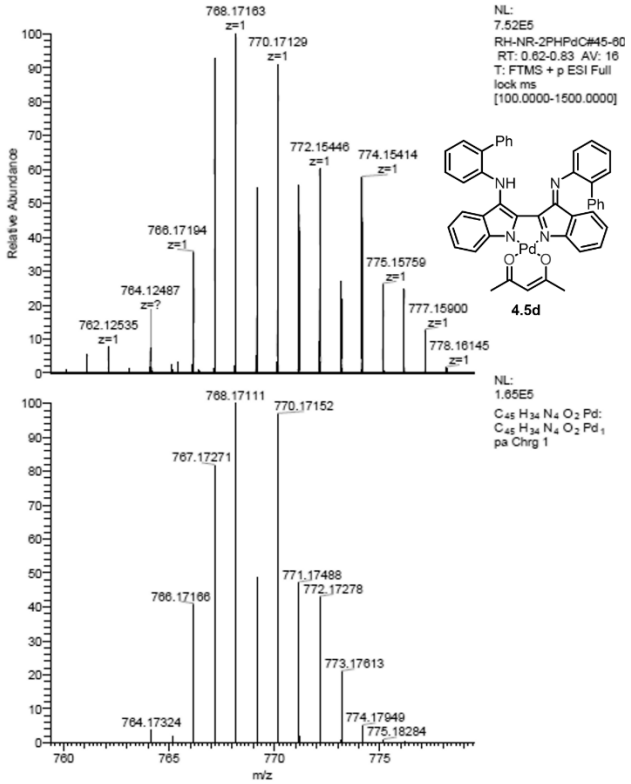


Figure D29 High-resolution mass spectrum of **4.5d**

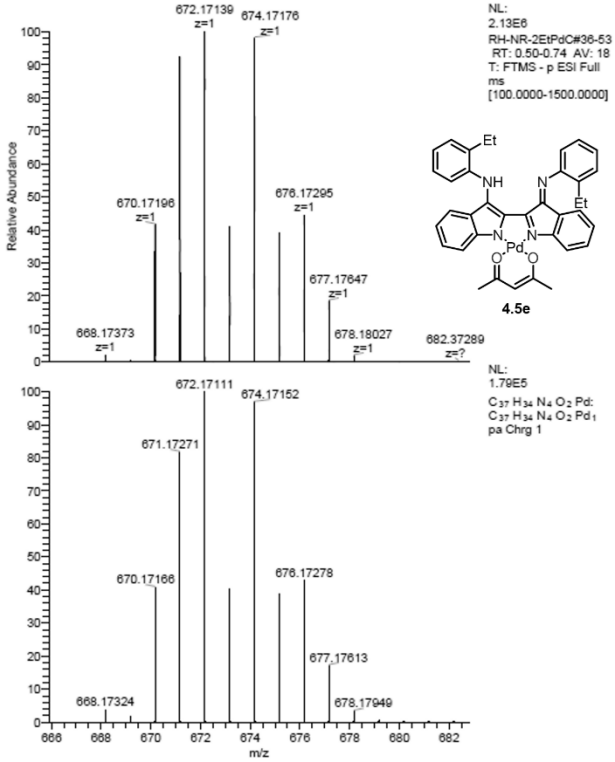


Figure D30 High-resolution mass spectrum of **4.5e**

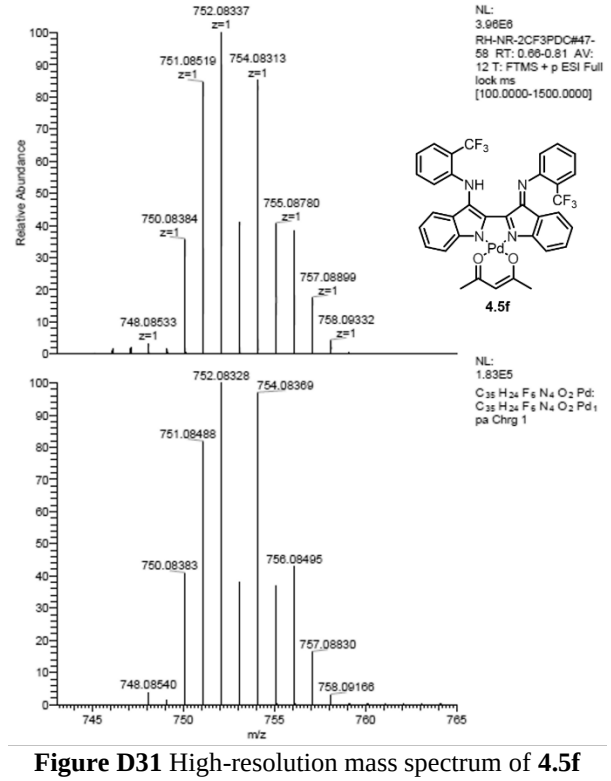


Figure D31 High-resolution mass spectrum of **4.5f**

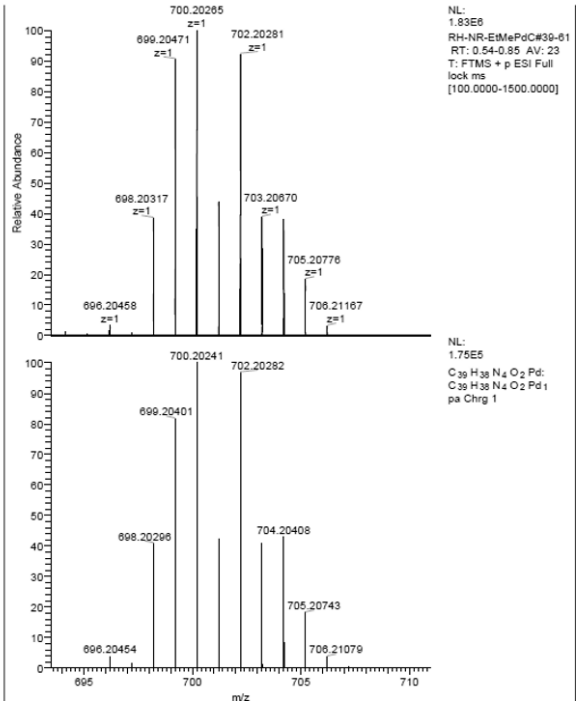


Figure D32 High-resolution mass spectrum of **4.5g**

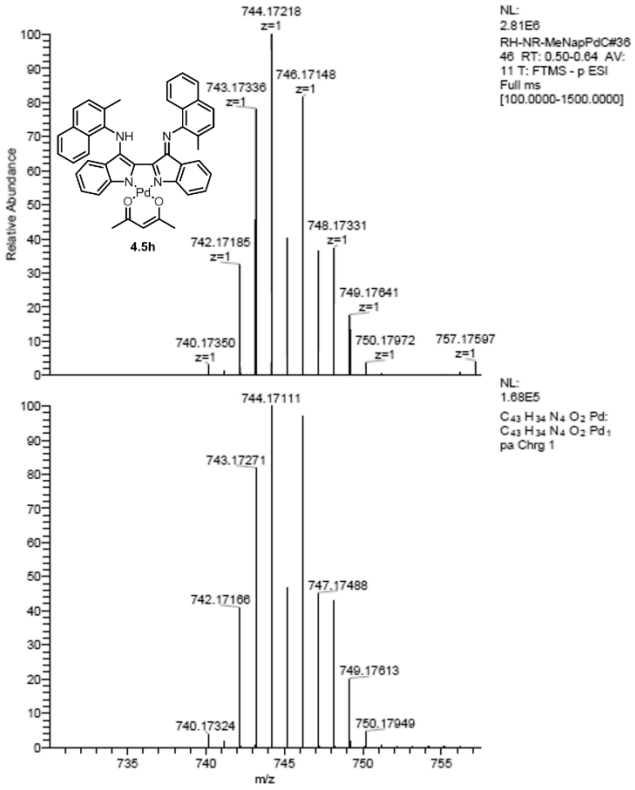


Figure D33 High-resolution mass spectrum of **4.5h**

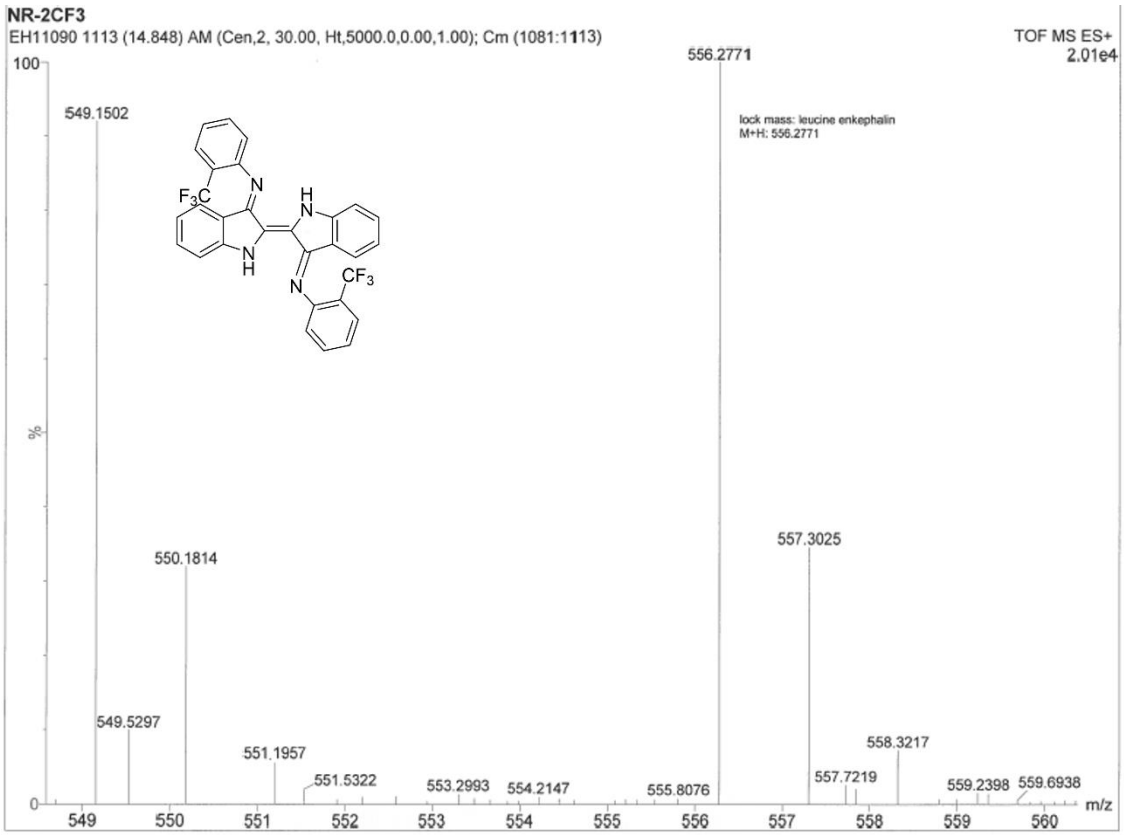


Figure D33 High-resolution mass spectrum of **4.6**

Appendix E : UV-Visible Spectra

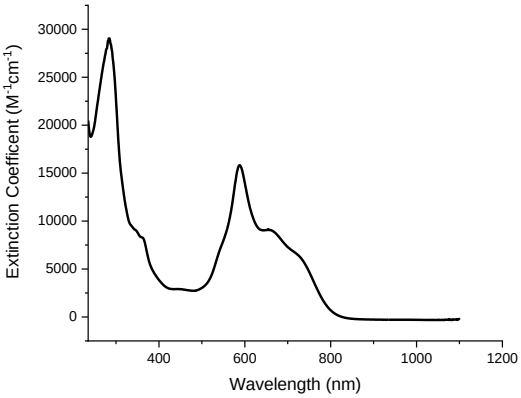


Figure E1 UV-visible spectrum of **2.1a** in CH_2Cl_2, $8.2x10^{-5}$ M, 298 K

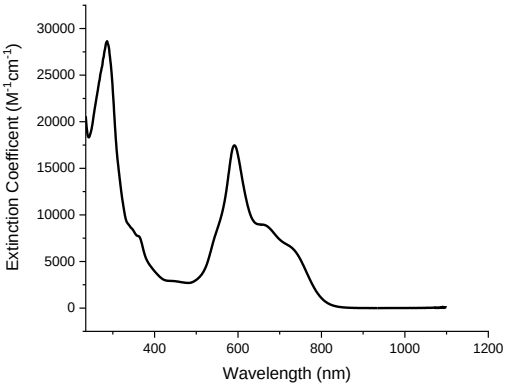


Figure E2 UV-visible spectrum of **2.1b** in CH_2Cl_2, $8.3x10^{-5}$ M, 298 K

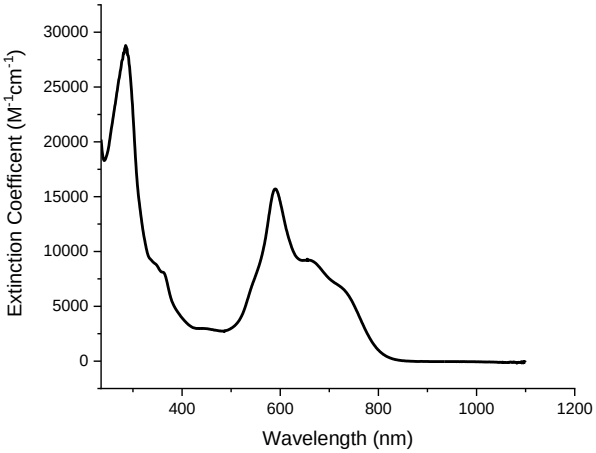


Figure E3 UV-visible spectrum of **2.1e** in CH_2Cl_2, $8.7x10^{-5}$ M, 298 K

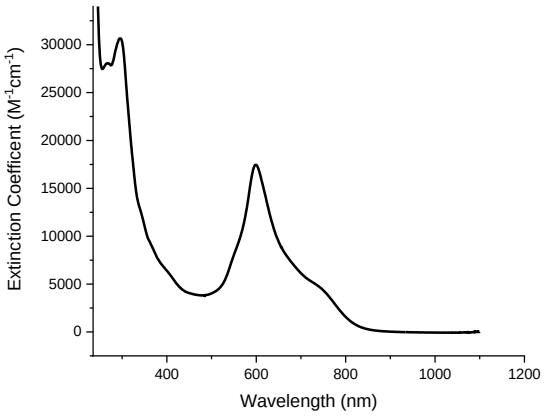


Figure E4 UV-visible spectrum of **2.1f** in CH_2Cl_2, $5.5x10^{-5}$ M, 298 K

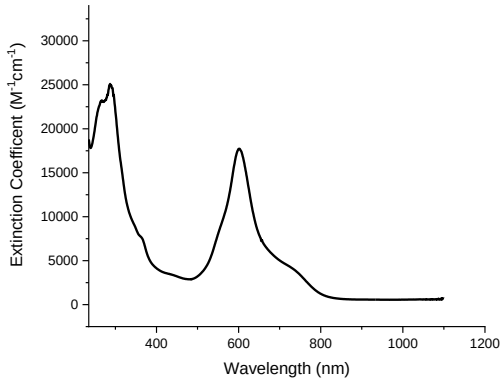


Figure E5 UV-visible spectrum of **2.1g** in CH_2Cl_2, $10.3x10^{-5}$ M, 298 K

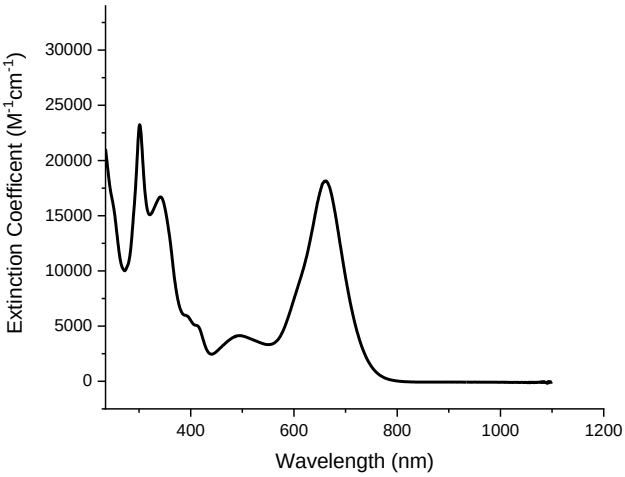


Figure E3 UV-visible spectrum of **2.2a** in CH_2Cl_2, $7.0x10^{-5}$ M, 298 K

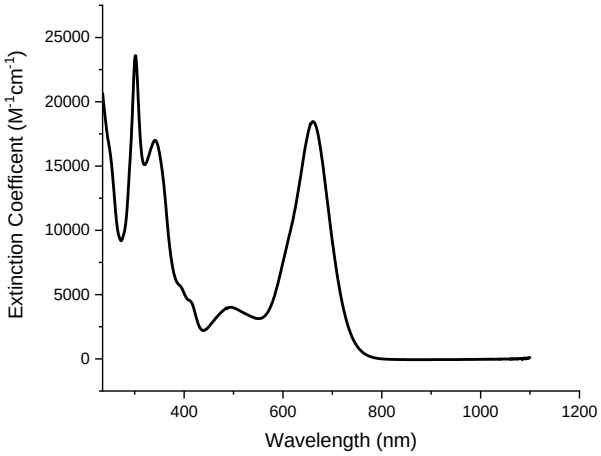


Figure E6 UV-visible spectrum of **2.2b** in CH_2Cl_2, $4.78x10^{-5}$ M, 298 K

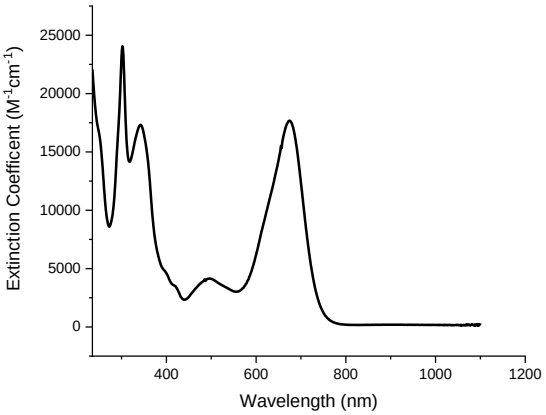


Figure E7 UV-visible spectrum of **2.2c** in CH_2Cl_2, $3.26x10^{-5}$ M, 298 K

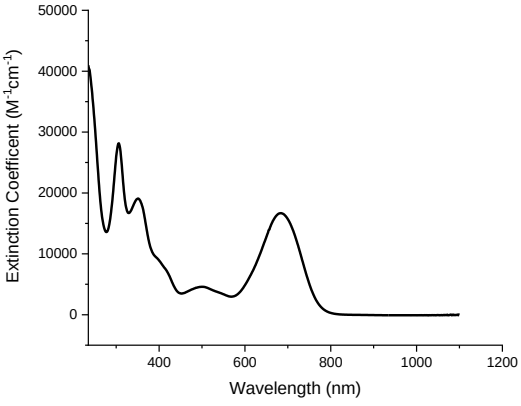


Figure E8 UV-visible spectrum of **2.2d** in CH_2Cl_2, $6.34x10^{-5}$ M, 298 K

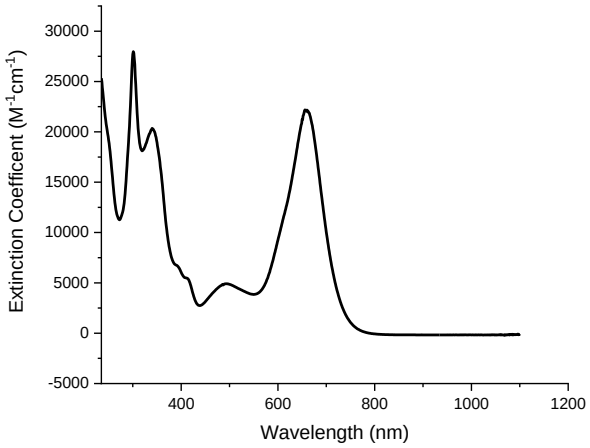


Figure E9 UV-visible spectrum of **2.2e** in CH_2Cl_2, $9.27x10^{-5}$ M, 298 K

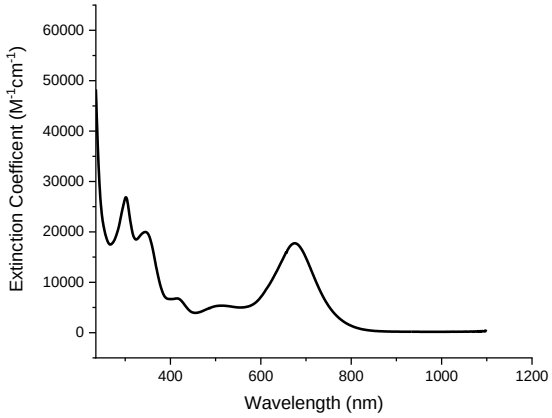


Figure E10 UV-visible spectrum of **2.2f** in CH_2Cl_2, $3.83x10^{-5}$ M, 298 K

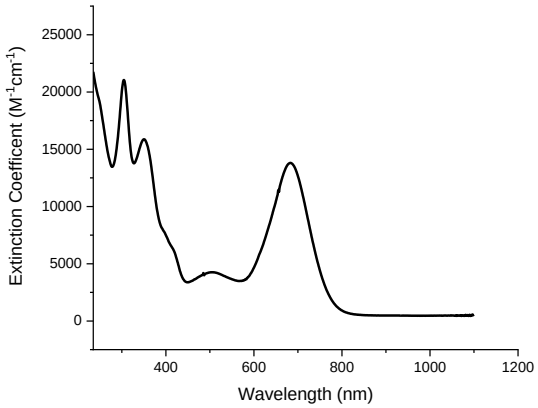


Figure E11 UV-visible spectrum of **2.2g** in CH_2Cl_2, $4.27x10^{-5}$ M, 298 K

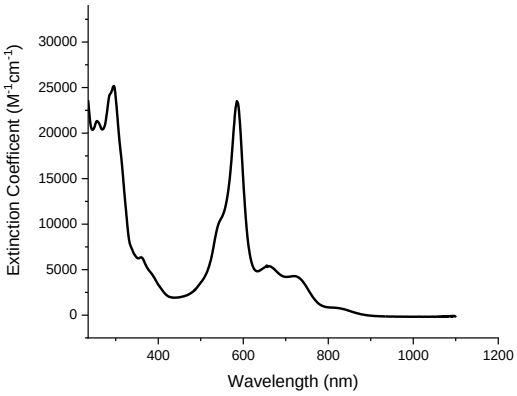


Figure E12 UV-visible spectrum of **2.7a** in CH_2Cl_2, $7.9x10^{-5}$ M 298 K

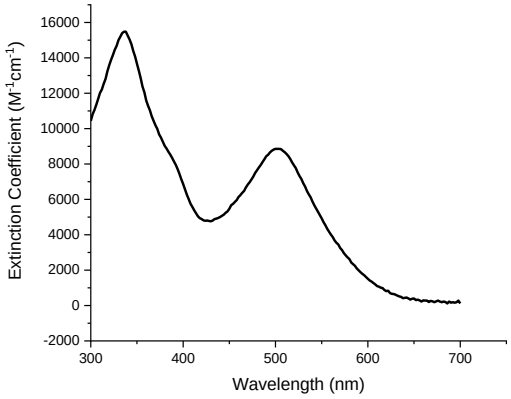


Figure E14 UV-visible spectrum of **3.15a** in CH_2Cl_2, $7.53x10^{-5}$ M, 298 K

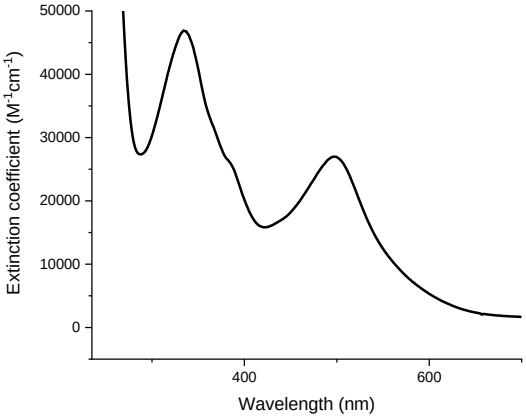


Figure E15 UV-visible spectrum of **3.15b** in CH_2Cl_2, $3.85x10^{-5}$ M, 298 K

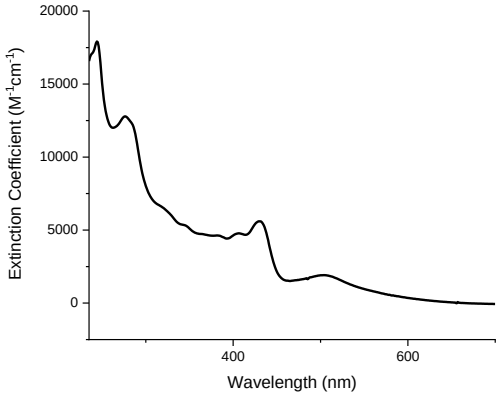


Figure E16 UV-visible spectrum of **3.15c** in CH_2Cl_2, $3.18x10^{-5}$ M, 298 K

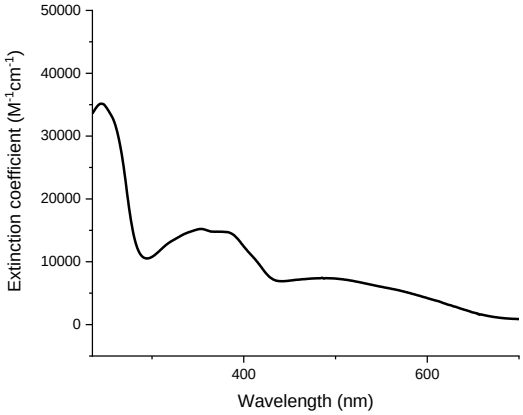


Figure E17 UV-visible spectrum of **3.15d** in CH_2Cl_2, $3.67x10^{-5}$ M, 298 K

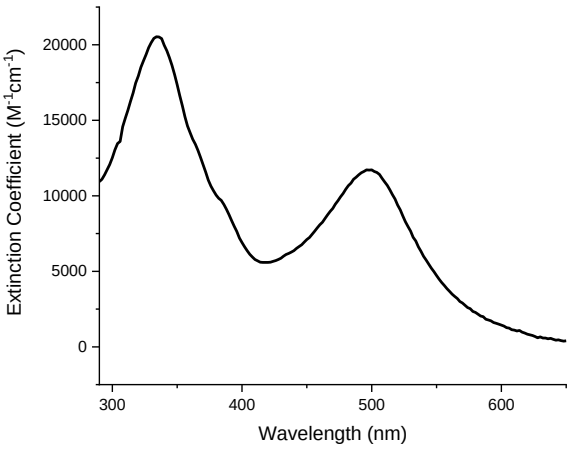


Figure E18 UV-visible spectrum of **3.15e** in CH_2Cl_2, $8.19x10^{-5}$ M, 298 K

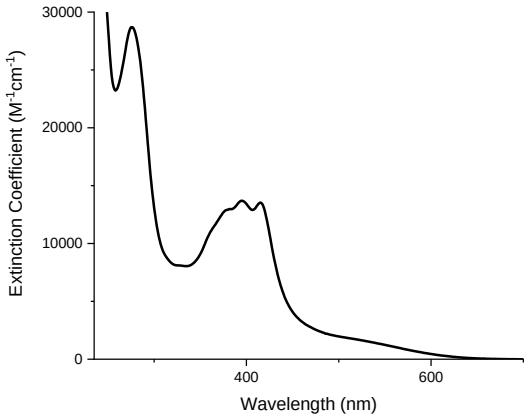


Figure E19 UV-visible spectrum of **3.16a** in CH_2Cl_2, M, 298 K

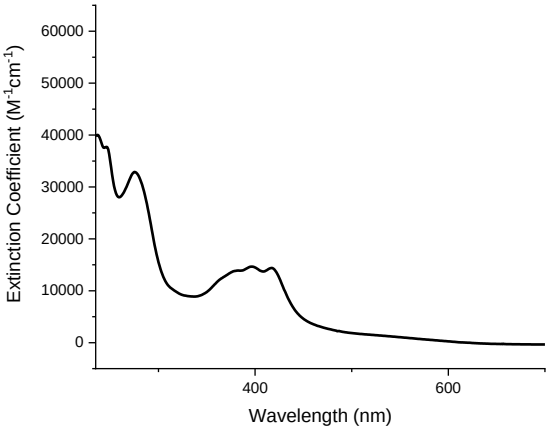


Figure E20 UV-visible spectrum of **3.16b** in CH_2Cl_2, $3.50x10^{-5}$ M, 298 K

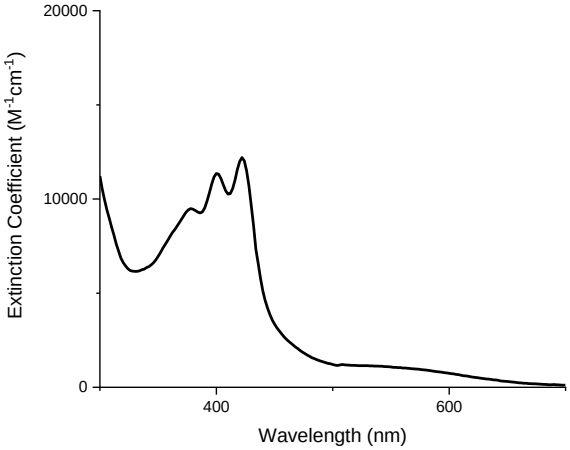


Figure E21 UV-visible spectrum of **3.16c** in CH_2Cl_2, $15.2x10^{-5}$ M, 298 K

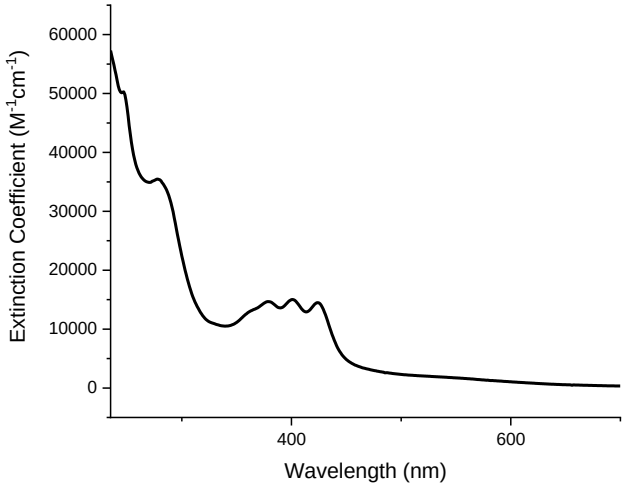


Figure E22 UV-visible spectrum of **3.16d** in CH_2Cl_2, $4.23x10^{-5}$ M, 298 K

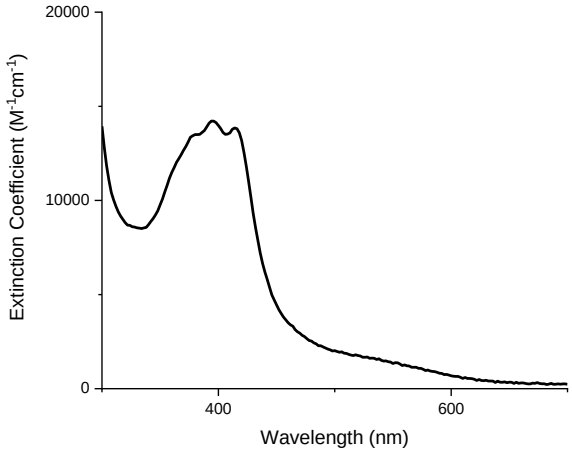


Figure E23 UV-visible spectrum of **3.16e** in CH_2Cl_2, $13.0x10^{-5}$ M, 298 K

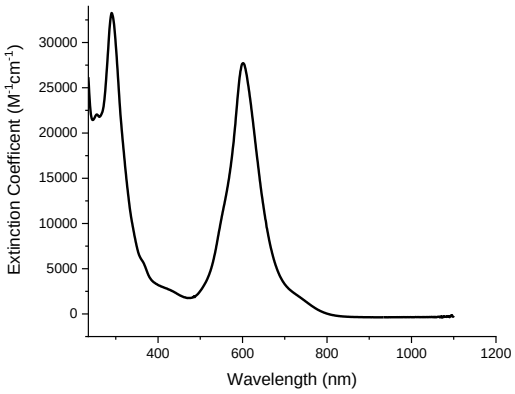


Figure E29 UV-visible spectrum of **4.6** in CH_2Cl_2, M, 298 K

Appendix F: Crystallography

Table F1 Table of crystallographic parameters for **2.1a** and **2.1b**

Crystal	**2.1a**	**2.1b**
Identification code	rh160	rh145
Empirical formula	$C_{30}H_{24}N_4$	$C_{37}H_{38}N_4O$
Formula weight	440.53	554.71
Temperature/K	90	90
Crystal system	triclinic	monoclinic
Space group	P-1	C2/c
a/Å	8.3392(2)	24.959(7)
b/Å	10.5210(2)	7.248(2)
c/Å	12.7083(3)	17.087(5)
α/°	90.2200(10)	90
β/°	95.4060(10)	101.009(5)
γ/°	90.2220(10)	90
Volume/Å^3	1110.01(4)	3034.4(15)
Z	2	4
ρ_{calc}g/cm^3	1.318	1.214
μ/mm^{-1}	0.613	0.074
F(000)	464.0	1184.0
Crystal size/mm^3	0.48 × 0.21 × 0.19	0.4 × 0.2 × 0.16
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.986 to 133.28	3.324 to 52.142
Index ranges	$-9 \leq h \leq 9$, $-11 \leq k \leq 12$, $-15 \leq l \leq 15$	$-30 \leq h \leq 30$, $-8 \leq k \leq 8$, $-21 \leq l \leq 20$
Reflections collected	12650	19366
Independent reflections	3892 [R_{int} = 0.0414, R_{sigma} = 0.0409]	2980 [R_{int} = 0.0400, R_{sigma} = 0.0245]
Data/restraints/parameters	3892/0/465	2980/0/194
Goodness-of-fit on F^2	1.025	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.1111	R_1 = 0.0505, wR_2 = 0.1321
Final R indexes [all data]	R_1 = 0.0502, wR_2 = 0.1162	R_1 = 0.0599, wR_2 = 0.1417
Largest diff. peak/hole / e Å^{-3}	0.24/-0.17	0.81/-0.39

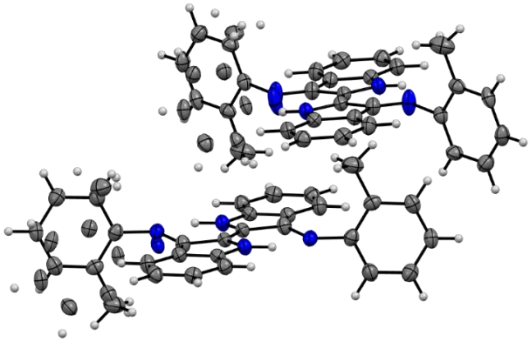


Figure F1 X-ray structure of **2.1a**. Thermal ellipsoids are shown at the 50% probability level

Table F2 Table of bond lengths **2.1a**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C1[1]	1.396(3)	C1A	C1A[2]	1.394(3)
C1	C2	1.450(2)	C1A	C2A	1.452(2)
C1	N1	1.3638(19)	C1A	N1A	1.365(2)
C2	C3	1.459(2)	C2A	C3A	1.455(2)
C2	N2	1.275(12)	C2A	N2A	1.328(9)
C2	N2B	1.376(18)	C2A	N2C	1.327(9)
C3	C4	1.403(2)	C3A	C4A	1.399(2)
C3	C8	1.410(2)	C3A	C8A	1.409(2)
C4	C5	1.367(2)	C4A	C5A	1.377(2)
C5	C6	1.403(2)	C5A	C6A	1.395(2)
C6	C7	1.379(2)	C6A	C7A	1.380(2)
C7	C8	1.389(2)	C7A	C8A	1.390(2)
C8	N1	1.387(2)	C8A	N1A	1.3836(19)
C9	C10	1.368(8)	C9A	C10A	1.384(14)
C9	C14	1.399(5)	C9A	C14A	1.391(6)
C9	N2	1.423(15)	C9A	N2A	1.430(10)
C10	C11	1.399(8)	C10A	C11A	1.382(14)
C11	C12	1.375(6)	C11A	C12A	1.377(6)
C12	C13	1.375(7)	C12A	C13A	1.370(7)
C13	C14	1.397(6)	C13A	C14A	1.388(8)
C14	C15	1.488(10)	C14A	C15A	1.488(10)
C9B	C10B	1.403(14)	C9C	C10C	1.375(13)
C9B	C14B	1.400(7)	C9C	C14C	1.400(6)
C9B	N2B	1.498(19)	C9C	N2C	1.418(10)
C10B	C11B	1.422(13)	C10C	C11C	1.413(13)
C11B	C12B	1.381(8)	C11C	C12C	1.377(6)
C12B	C13B	1.377(9)	C12C	C13C	1.368(8)
C13B	C14B	1.392(9)	C13C	C14C	1.385(7)
C14B	C15B	1.518(8)	C14C	C15C	1.480(11)

Table F3 Bond angles for **2.1a**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1[1]	C1	C2	126.19(17)	C1A[2]	C1A	C2A	126.31(17)
N1	C1	C1[1]	124.21(17)	N1A	C1A	C1A[2]	124.26(16)
N1	C1	C2	109.60(13)	N1A	C1A	C2A	109.43(13)
C1	C2	C3	105.44(12)	C1A	C2A	C3A	105.47(13)
N2	C2	C1	124.3(6)	N2A	C2A	C1A	120.8(4)
N2	C2	C3	130.2(6)	N2A	C2A	C3A	132.3(4)
N2B	C2	C1	117.2(8)	N2C	C2A	C1A	121.0(4)
N2B	C2	C3	137.0(8)	N2C	C2A	C3A	132.1(4)
C4	C3	C2	134.44(14)	C4A	C3A	C2A	134.34(14)
C4	C3	C8	119.62(14)	C4A	C3A	C8A	119.68(14)
C8	C3	C2	105.91(13)	C8A	C3A	C2A	105.95(13)
C5	C4	C3	119.24(14)	C5A	C4A	C3A	118.97(14)
C4	C5	C6	120.56(15)	C4A	C5A	C6A	120.78(14)
C7	C6	C5	121.46(14)	C7A	C6A	C5A	121.30(15)
C6	C7	C8	118.19(14)	C6A	C7A	C8A	118.27(14)
C7	C8	C3	120.93(14)	C7A	C8A	C3A	120.99(14)
N1	C8	C3	110.60(13)	N1A	C8A	C3A	110.66(13)
N1	C8	C7	128.47(13)	N1A	C8A	C7A	128.34(13)
C10	C9	C14	121.3(5)	C10A	C9A	C14A	121.2(6)
C10	C9	N2	123.6(7)	C10A	C9A	N2A	118.4(6)
C14	C9	N2	115.2(8)	C14A	C9A	N2A	120.4(5)
C9	C10	C11	120.5(4)	C11A	C10A	C9A	119.8(8)
C12	C11	C10	119.1(3)	C12A	C11A	C10A	119.4(5)
C13	C12	C11	120.1(4)	C13A	C12A	C11A	120.6(5)
C12	C13	C14	121.9(5)	C12A	C13A	C14A	121.3(6)
C9	C14	C15	121.9(7)	C9A	C14A	C15A	121.9(9)
C13	C14	C9	117.1(4)	C13A	C14A	C9A	117.7(4)
C13	C14	C15	121.0(7)	C13A	C14A	C15A	120.4(9)
C1	N1	C8	108.45(12)	C1A	N1A	C8A	108.48(12)
C2	N2	C9	124.3(11)	C2A	N2A	C9A	122.1(7)
C10B	C9B	N2B	122.3(11)	C10C	C9C	C14C	120.8(6)
C14B	C9B	C10B	122.2(6)	C10C	C9C	N2C	116.9(6)
C14B	C9B	N2B	115.2(11)	C14C	C9C	N2C	122.1(6)
C9B	C10B	C11B	117.4(9)	C9C	C10C	C11C	120.0(7)
C12B	C11B	C10B	120.3(6)	C12C	C11C	C10C	119.1(5)
C13B	C12B	C11B	120.8(6)	C13C	C12C	C11C	120.0(5)
C12B	C13B	C14B	121.1(7)	C12C	C13C	C14C	122.5(6)
C9B	C14B	C15B	120.4(8)	C9C	C14C	C15C	119.3(9)
C13B	C14B	C9B	118.2(5)	C13C	C14C	C9C	117.7(4)
C13B	C14B	C15B	121.4(8)	C13C	C14C	C15C	123.0(9)
C2	N2B	C9B	113.4(12)	C2A	N2C	C9C	120.2(7)

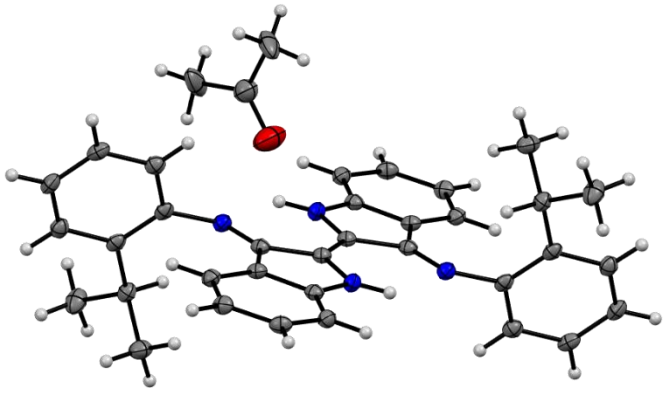


Figure F2 X-ray structure of **2.1b**. Thermal ellipsoids are shown at the 50% probability level

Table F4 Bond lengths for **2.1b.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.380(2)	C9	C10	1.403(3)
N1	C8	1.386(2)	C9	C14	1.403(2)
N2	C2	1.299(2)	C10	C11	1.402(2)
N2	C9	1.424(2)	C10	C15	1.523(2)
C1	C1[1]	1.368(3)	C11	C12	1.388(3)
C1	C2	1.466(2)	C12	C13	1.392(3)
C2	C3	1.479(2)	C13	C14	1.390(3)
C3	C4	1.401(2)	C15	C16	1.531(3)
C3	C8	1.415(2)	C15	C17	1.534(3)
C4	C5	1.392(3)	O1	C18	1.221(4)
C5	C6	1.402(3)	C18	C19	1.485(3)
C6	C7	1.390(3)	C18	C19[2]	1.485(3)
C7	C8	1.396(2)			

Table F5 Bond angles for **2.1b.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C8	109.54(14)	C7	C8	C3	121.65(16)
C2	N2	C9	119.22(15)	C10	C9	N2	119.90(15)
N1	C1	C2	108.83(15)	C14	C9	N2	119.16(16)
$C1^1$	C1	N1	124.2(2)	C14	C9	C10	120.77(16)
$C1^1$	C1	C2	126.9(2)	C9	C10	C15	119.99(15)
N2	C2	C1	120.89(15)	C11	C10	C9	117.70(16)
N2	C2	C3	134.10(16)	C11	C10	C15	122.24(16)
C1	C2	C3	105.00(14)	C12	C11	C10	121.66(17)
C4	C3	C2	133.93(17)	C11	C12	C13	119.98(17)
C4	C3	C8	119.58(16)	C14	C13	C12	119.68(17)
C8	C3	C2	106.45(15)	C13	C14	C9	120.15(17)
C5	C4	C3	118.97(17)	C10	C15	C16	113.33(15)
C4	C5	C6	120.49(17)	C10	C15	C17	110.18(15)
C7	C6	C5	121.71(16)	C16	C15	C17	110.82(16)
C6	C7	C8	117.57(17)	O1	C18	C19	118.04(15)
N1	C8	C3	110.18(15)	O1	C18	$C19^2$	118.03(15)
N1	C8	C7	128.17(16)	C19	C18	$C19^2$	123.9(3)

Table F6 Table of crystallographic parameters for **2.1e** and **2.2a**

Crystal	**2.1e**	**2.2a**
Identification code	rh194	rh161
Empirical formula	$C_{32}H_{28}N_4$	$C_{65}H_{52}Cl_2F_6N_8O_4$
Formula weight	468.58	1194.04
Temperature/K	90	90
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P-1
a/Å	11.1380(4)	12.2519(5)
b/Å	7.4832(2)	14.7062(6)
c/Å	16.0558(5)	17.7741(7)
α/°	90	72.108(2)
β/°	109.979(2)	80.791(2)
γ/°	90	68.745(2)
Volume/Å^3	1257.68(7)	2836.0(2)
Z	2	2
ρ_{calc}g/cm^3	1.237	1.398
μ/mm^{-1}	0.074	1.689
F(000)	496.0	1236.0
Crystal size/mm^3	0.36 × 0.26 × 0.11	0.16 × 0.09 × 0.07
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2Θ range for data collection/°	3.904 to 60.21	5.232 to 133.968
Index ranges	-15 ≤ h ≤ 15, -10 ≤ k ≤ 10, -22 ≤ l ≤ 22	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21
Reflections collected	15677	41057
Independent reflections	3698 [R_{int} = 0.0346, R_{sigma} = 0.0304]	9960 [R_{int} = 0.0516, R_{sigma} = 0.0503]
Data/restraints/parameters	3698/0/168	9960/2/794
Goodness-of-fit on F^2	1.009	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1142	R_1 = 0.0674, wR_2 = 0.1789
Final R indexes [all data]	R_1 = 0.0550, wR_2 = 0.1220	R_1 = 0.0926, wR_2 = 0.1984
Largest diff. peak/hole / e Å^{-3}	0.41/-0.26	1.61/-0.76

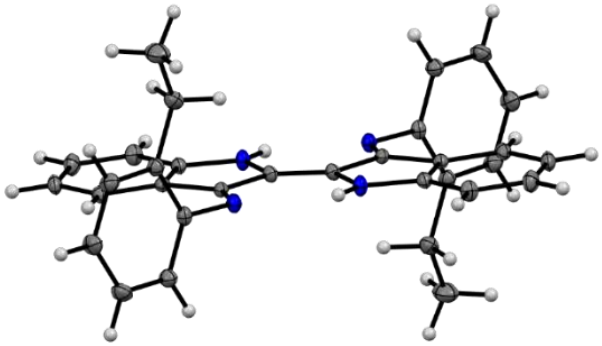


Figure F3 X-ray structure of **2.1e**. Thermal ellipsoids are shown at the 50% Probability level

Table F7 Bond lengths for **2.1e**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.3822(13)	C6	C7	1.3860(15)
N1	C8	1.3813(13)	C7	C8	1.3915(14)
N2	C2	1.2938(13)	C9	C10	1.3932(15)
N2	C9	1.4208(13)	C9	C14	1.4053(15)
C1	C1[1]	1.3631(19)	C10	C11	1.3870(16)
C1	C2	1.4641(14)	C11	C12	1.3858(16)
C2	C3	1.4719(14)	C12	C13	1.3900(16)
C3	C4	1.3991(14)	C13	C14	1.3923(15)
C3	C8	1.4081(14)	C14	C15	1.5131(15)
C4	C5	1.3876(15)	C15	C16	1.5236(17)
C5	C6	1.4000(16)			

Table F8 Bond angles for **2.1e**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	N1	C1	109.54(9)	N1	C8	C3	110.25(9)
C2	N2	C9	119.17(9)	N1	C8	C7	127.94(10)
N1	C1	C2	108.47(8)	C7	C8	C3	121.81(9)
C1[1]	C1	N1	124.59(12)	C10	C9	N2	118.82(10)
C1[1]	C1	C2	126.93(12)	C10	C9	C14	120.83(10)
N2	C2	C1	121.20(9)	C14	C9	N2	120.20(9)
N2	C2	C3	133.68(9)	C11	C10	C9	120.11(10)
C1	C2	C3	105.11(8)	C12	C11	C10	119.82(10)
C4	C3	C2	133.62(10)	C11	C12	C13	119.91(10)
C4	C3	C8	119.76(9)	C12	C13	C14	121.54(10)
C8	C3	C2	106.62(9)	C9	C14	C15	119.93(9)
C5	C4	C3	118.55(10)	C13	C14	C9	117.79(10)

C4	C5	C6	120.81(10)	C13	C14	C15	122.27(10)
C7	C6	C5	121.58(10)	C14	C15	C16	115.48(10)
C6	C7	C8	117.47(10)				

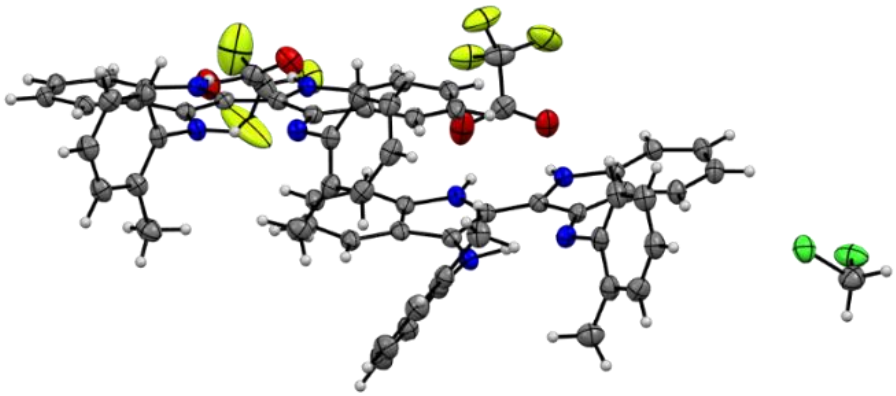


Figure F4 X-ray structure of **2.2a.** Thermal ellipsoids are shown at the 50% probability level

Table F9 Bond lengths for **2.2a.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.475(5)	C4A	C5A	1.378(5)
C1	C17	1.387(5)	C5A	C6A	1.404(5)
C1	N1	1.374(4)	C6A	C7A	1.390(5)
C2	C3	1.447(5)	C7A	C8A	1.381(5)
C2	N2	1.311(5)	C8A	N1A	1.380(5)
C3	C4	1.404(5)	C9A	C10A	1.388(5)
C3	C8	1.411(5)	C9A	C14A	1.392(5)
C4	C5	1.372(5)	C9A	N2A	1.434(5)
C5	C6	1.402(6)	C10A	C11A	1.386(5)
C6	C7	1.377(5)	C11A	C12A	1.380(6)
C7	C8	1.384(5)	C12A	C13A	1.389(6)
C8	N1	1.383(5)	C13A	C14A	1.394(5)
C9	C10	1.395(5)	C14A	C15A	1.503(5)
C9	C14	1.394(5)	C16A	C30A	1.487(6)
C9	N2	1.423(4)	C17A	C18A	1.464(5)
C10	C11	1.390(5)	C17A	N3A	1.367(4)
C11	C12	1.389(6)	C18A	C19A	1.449(5)
C12	C13	1.380(6)	C18A	N4A	1.316(4)
C13	C14	1.398(5)	C19A	C20A	1.405(5)
C14	C15	1.506(5)	C19A	C24A	1.406(5)
C16	C30	1.490(6)	C20A	C21A	1.378(5)
C17	C18	1.471(5)	C21A	C22A	1.399(6)
C17	N3	1.371(4)	C22A	C23A	1.377(5)
C18	C19	1.464(5)	C23A	C24A	1.395(5)
C18	N4	1.311(4)	C24A	N3A	1.372(5)
C19	C20	1.388(5)	C25A	C26A	1.387(5)
C19	C24	1.406(5)	C25A	C30A	1.399(5)

C20	C21	1.385(5)	C25A	N4A	1.427(4)
C21	C22	1.392(5)	C26A	C27A	1.391(5)
C22	C23	1.375(5)	C27A	C28A	1.384(6)
C23	C24	1.386(5)	C28A	C29A	1.372(6)
C24	N3	1.381(4)	C29A	C30A	1.406(5)
C25	C26	1.393(5)	C31	C32	1.550(5)
C25	C30	1.394(5)	C31	O1	1.224(5)
C25	N4	1.429(5)	C31	O2	1.227(5)
C26	C27	1.392(5)	C32	F1	1.331(6)
C27	C28	1.369(6)	C32	F2	1.327(5)
C28	C29	1.373(6)	C32	F3	1.338(5)
C29	C30	1.412(5)	C31A	C32A	1.533(6)
C1A	C2A	1.471(5)	C31A	O1A	1.234(5)
C1A	C17A	1.388(5)	C31A	O2A	1.229(5)
C1A	N1A	1.380(4)	C32A	F1A	1.248(6)
C2A	C3A	1.453(5)	C32A	F2A	1.386(7)
C2A	N2A	1.298(4)	C32A	F3A	1.306(5)
C3A	C4A	1.406(5)	C33	Cl1	1.779(5)
C3A	C8A	1.406(5)	C33	Cl2	1.745(5)

Table F10 Bond angles for **2.2a**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	C1	C2	130.8(3)	C4A	C5A	C6A	120.8(3)
N1	C1	C2	107.2(3)	C7A	C6A	C5A	121.6(3)
N1	C1	C17	121.8(3)	C8A	C7A	C6A	117.2(3)
C3	C2	C1	106.3(3)	C7A	C8A	C3A	122.3(3)
N2	C2	C1	122.3(3)	N1A	C8A	C3A	109.9(3)
N2	C2	C3	131.4(3)	N1A	C8A	C7A	127.8(3)
C4	C3	C2	135.0(3)	C10A	C9A	C14A	121.4(3)
C4	C3	C8	118.6(3)	C10A	C9A	N2A	118.2(3)
C8	C3	C2	106.2(3)	C14A	C9A	N2A	120.4(3)
C5	C4	C3	119.1(4)	C11A	C10A	C9A	119.7(3)
C4	C5	C6	120.9(4)	C12A	C11A	C10A	119.9(4)
C7	C6	C5	121.6(4)	C11A	C12A	C13A	120.1(4)
C6	C7	C8	117.3(4)	C12A	C13A	C14A	121.1(4)
C7	C8	C3	122.5(3)	C9A	C14A	C13A	117.9(4)
N1	C8	C3	110.3(3)	C9A	C14A	C15A	121.5(3)
N1	C8	C7	127.2(3)	C13A	C14A	C15A	120.6(3)
C10	C9	N2	120.2(3)	C1A	C17A	C18A	130.6(3)
C14	C9	C10	121.5(3)	N3A	C17A	C1A	122.0(3)
C14	C9	N2	118.1(3)	N3A	C17A	C18A	107.4(3)
C11	C10	C9	119.6(4)	C19A	C18A	C17A	106.0(3)
C12	C11	C10	119.7(4)	N4A	C18A	C17A	123.3(3)
C13	C12	C11	120.1(4)	N4A	C18A	C19A	130.7(3)
C12	C13	C14	121.7(4)	C20A	C19A	C18A	134.6(3)
C9	C14	C13	117.5(4)	C20A	C19A	C24A	118.9(3)
C9	C14	C15	122.3(3)	C24A	C19A	C18A	106.4(3)
C13	C14	C15	120.2(3)	C21A	C20A	C19A	118.7(4)
C1	C17	C18	131.6(3)	C20A	C21A	C22A	121.4(4)
N3	C17	C1	121.3(3)	C23A	C22A	C21A	121.3(4)
N3	C17	C18	106.9(3)	C22A	C23A	C24A	117.4(4)

C19	C18	C17	106.4(3)	C23A	C24A	C19A	122.3(3)
N4	C18	C17	122.7(3)	N3A	C24A	C19A	109.8(3)
N4	C18	C19	130.9(3)	N3A	C24A	C23A	127.9(3)
C20	C19	C18	134.7(3)	C26A	C25A	C30A	121.6(3)
C20	C19	C24	119.4(3)	C26A	C25A	N4A	120.3(3)
C24	C19	C18	105.8(3)	C30A	C25A	N4A	118.0(3)
C21	C20	C19	118.6(3)	C25A	C26A	C27A	119.7(4)
C20	C21	C22	121.0(4)	C28A	C27A	C26A	119.6(4)
C23	C22	C21	121.4(3)	C29A	C28A	C27A	120.6(4)
C22	C23	C24	117.5(3)	C28A	C29A	C30A	121.3(4)
C23	C24	C19	122.1(3)	C25A	C30A	C16A	121.8(3)
N3	C24	C19	110.2(3)	C25A	C30A	C29A	117.2(4)
N3	C24	C23	127.7(3)	C29A	C30A	C16A	121.0(4)
C26	C25	C30	121.5(4)	C8A	N1A	C1A	110.4(3)
C26	C25	N4	120.3(3)	C2A	N2A	C9A	121.8(3)
C30	C25	N4	117.6(3)	C17A	N3A	C24A	110.5(3)
C27	C26	C25	119.5(4)	C18A	N4A	C25A	124.2(3)
C28	C27	C26	119.8(4)	O1	C31	C32	115.2(4)

Table F11 Bond angles for **2.2a** continued

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C27	C28	C29	121.0(4)	O1	C31	O2	128.9(4)
C28	C29	C30	121.1(4)	O2	C31	C32	115.9(4)
C25	C30	C16	120.6(4)	F1	C32	C31	113.1(4)
C25	C30	C29	117.1(4)	F1	C32	F3	106.7(4)
C29	C30	C16	122.2(4)	F2	C32	C31	112.4(4)
C1	N1	C8	109.8(3)	F2	C32	F1	106.8(4)
C2	N2	C9	125.9(3)	F2	C32	F3	107.7(4)
C17	N3	C24	110.6(3)	F3	C32	C31	109.9(3)
C18	N4	C25	124.2(3)	O1A	C31A	C32A	114.7(4)
C17A	C1A	C2A	131.2(3)	O2A	C31A	C32A	115.6(4)
N1A	C1A	C2A	106.9(3)	O2A	C31A	O1A	129.7(4)
N1A	C1A	C17A	121.8(3)	F1A	C32A	C31A	114.8(4)
C3A	C2A	C1A	106.3(3)	F1A	C32A	F2A	101.3(5)
N2A	C2A	C1A	123.5(3)	F1A	C32A	F3A	111.9(5)
N2A	C2A	C3A	130.2(3)	F2A	C32A	C31A	107.6(4)
C4A	C3A	C2A	133.8(3)	F3A	C32A	C31A	116.0(4)
C4A	C3A	C8A	119.6(3)	F3A	C32A	F2A	103.3(4)
C8A	C3A	C2A	106.5(3)	Cl2	C33	Cl1	111.8(3)
C5A	C4A	C3A	118.4(3)				

Table F12 Table of crystallographic parameters for **2.2b** and **2.2c**

Crystal	**2.2b**	**2.2c**
Identification code	rh147	rh234_0m
Empirical formula	$C_{34}H_{33}ClN_4$	$C_{39.67}H_{38.47}F_{5.5}N_4O_{3.98}$
Formula weight	533.09	738.55
Temperature/K	90	90
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	8.3718(9)	10.9961(5)
b/Å	13.4606(14)	14.7925(6)
c/Å	13.7482(14)	22.0809(9)
α/°	101.754(8)	90
β/°	107.060(8)	90.7040(10)
γ/°	106.540(7)	90
Volume/Å^3	1348.3(3)	3591.4(3)
Z	2	4
ρ_{calc}g/cm^3	1.313	1.366
μ/mm^{-1}	1.485	0.108
F(000)	564.0	1540.0
Crystal size/mm^3	0.19 × 0.08 × 0.03	0.35 × 0.31 × 0.16
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.082 to 114.126	3.314 to 61.134
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 14, -14 ≤ l ≤ 13	-15 ≤ h ≤ 15, -21 ≤ k ≤ 21, -31 ≤ l ≤ 31
Reflections collected	8163	50863
Independent reflections	3527 [R_{int} = 0.0532, R_{sigma} = 0.0650]	10993 [R_{int} = 0.0364, R_{sigma} = 0.0346]
Data/restraints/parameters	3527/0/368	10993/63/636
Goodness-of-fit on F^2	1.026	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0435, wR_2 = 0.1073	R_1 = 0.0622, wR_2 = 0.1658
Final R indexes [all data]	R_1 = 0.0684, wR_2 = 0.1280	R_1 = 0.0895, wR_2 = 0.1859
Largest diff. peak/hole / e Å^{-3}	0.33/-0.26	1.17/-0.45

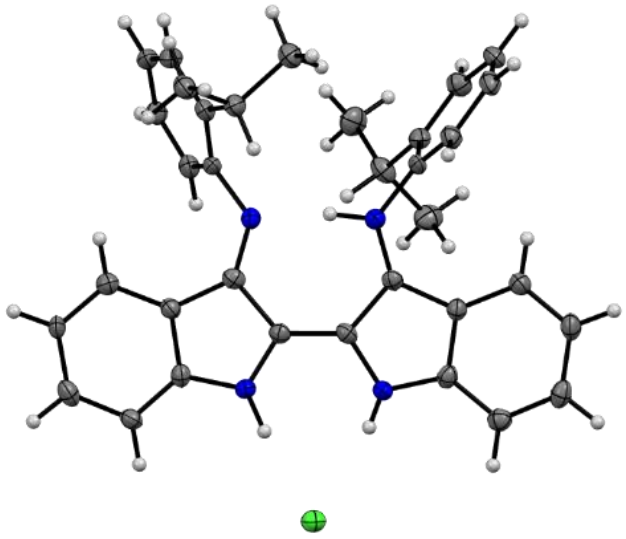


Figure F5 X-ray structure of **2.2b**; Thermal ellipsoids are shown at the 50% probability level

Table F13 Bond lengths for **2.2b.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.387(4)	C13	C14	1.391(4)
N1	C8	1.366(4)	C14	C15	1.521(5)
N2	C2	1.312(4)	C15	C16	1.520(5)
N2	C9	1.437(4)	C15	C34	1.528(5)
N3	C17	1.361(4)	C17	C18	1.474(4)
N3	C24	1.377(4)	C18	C19	1.461(4)
N4	C18	1.301(4)	C19	C20	1.397(4)
N4	C25	1.417(4)	C19	C24	1.396(4)
C1	C2	1.453(4)	C20	C21	1.382(4)
C1	C17	1.389(4)	C21	C22	1.388(5)
C2	C3	1.453(4)	C22	C23	1.399(5)
C3	C4	1.407(4)	C23	C24	1.378(4)
C3	C8	1.400(4)	C25	C26	1.398(4)
C4	C5	1.369(5)	C25	C30	1.401(5)
C5	C6	1.404(5)	C26	C27	1.392(4)
C6	C7	1.379(5)	C27	C28	1.379(5)
C7	C8	1.394(5)	C28	C29	1.383(5)
C9	C10	1.386(4)	C29	C30	1.393(4)
C9	C14	1.398(5)	C30	C31	1.515(5)
C10	C11	1.390(4)	C31	C32	1.531(4)
C11	C12	1.373(5)	C31	C33	1.538(5)
C12	C13	1.381(5)			

Table F14 Bond angles for **2.2b.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	N1	C1	110.1(3)	C16	C15	C14	113.6(3)
C2	N2	C9	125.0(3)	C16	C15	C34	111.7(3)
C17	N3	C24	111.0(3)	N3	C17	C1	122.3(3)
C18	N4	C25	122.7(3)	N3	C17	C18	107.2(3)
N1	C1	C2	107.1(3)	C1	C17	C18	130.4(3)
N1	C1	C17	121.8(3)	N4	C18	C17	123.1(3)
C17	C1	C2	130.9(3)	N4	C18	C19	131.5(3)
N2	C2	C1	123.7(3)	C19	C18	C17	105.3(3)
N2	C2	C3	130.1(3)	C20	C19	C18	133.4(3)
C1	C2	C3	106.2(3)	C24	C19	C18	106.9(3)
C4	C3	C2	133.5(3)	C24	C19	C20	119.5(3)
C8	C3	C2	106.4(3)	C21	C20	C19	118.4(3)
C8	C3	C4	120.0(3)	C20	C21	C22	120.9(3)
C5	C4	C3	118.1(3)	C21	C22	C23	121.7(3)
C4	C5	C6	121.3(3)	C24	C23	C22	116.5(3)
C7	C6	C5	121.5(3)	N3	C24	C19	109.5(3)
C6	C7	C8	117.4(3)	N3	C24	C23	127.7(3)
N1	C8	C3	110.2(3)	C23	C24	C19	122.8(3)

Table F15 Bond angles for **2.2b** continued

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C8	C7	128.2(3)	C26	C25	N4	118.3(3)
C7	C8	C3	121.6(3)	C26	C25	C30	120.8(3)
C10	C9	N2	119.5(3)	C30	C25	N4	120.4(3)
C10	C9	C14	122.2(3)	C27	C26	C25	120.2(3)
C14	C9	N2	118.2(3)	C28	C27	C26	119.1(3)
C9	C10	C11	118.8(3)	C27	C28	C29	120.6(3)
C12	C11	C10	120.5(3)	C28	C29	C30	121.6(3)
C11	C12	C13	119.9(3)	C25	C30	C31	121.8(3)
C12	C13	C14	121.9(3)	C29	C30	C25	117.5(3)
C9	C14	C15	121.3(3)	C29	C30	C31	120.6(3)
C13	C14	C9	116.9(3)	C30	C31	C32	109.9(3)
C13	C14	C15	121.8(3)	C30	C31	C33	112.0(3)
C14	C15	C34	109.0(3)	C32	C31	C33	109.9(3)

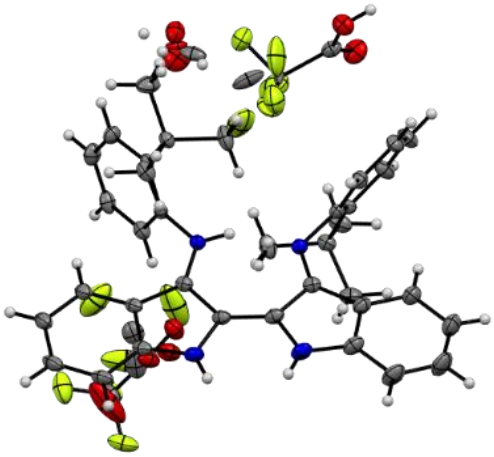


Figure F6 X-ray structure of **2.2c**; Thermal ellipsoids are shown at the 50% probability level

Table F16 Bond lengths **for 2.2c**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.374(2)	C13	C14	1.405(2)
N1	C8	1.381(2)	C13’	C14’	1.399(2)
N1’	C1’	1.378(2)	C14	C15	1.537(2)
N1’	C8’	1.382(3)	C14’	C15’	1.539(2)
N2	C2	1.3056(19)	C15	C16	1.533(2)
N2	C9	1.432(2)	C15	C17	1.531(2)
N2’	C2’	1.314(2)	C15	C18	1.539(2)
N2’	C9’	1.434(2)	C15’	C16’	1.536(2)
C1	C1’	1.382(2)	C15’	C17’	1.536(3)
C1	C2	1.480(2)	C15’	C18’	1.537(2)
C1’	C2’	1.469(2)	F1	C20	1.298(5)
C2	C3	1.460(2)	F2	C20	1.304(5)
C2’	C3’	1.450(2)	F3	C20	1.314(5)
C3	C4	1.399(2)	O1	C19	1.257(9)
C3	C8	1.407(2)	O2	C19	1.234(12)
C3’	C4’	1.402(3)	C19	C20	1.546(11)
C3’	C8’	1.405(2)	F1’	C20’	1.337(5)
C4	C5	1.389(2)	F2’	C20’	1.333(5)
C4’	C5’	1.385(3)	F3’	C20’	1.334(5)
C5	C6	1.402(3)	O1’	C19’	1.256(8)
C5’	C6’	1.403(3)	O2’	C19’	1.241(9)
C6	C7	1.379(3)	C20’	C19’	1.535(8)
C6’	C7’	1.371(3)	O3’	C21’	1.193(4)
C7	C8	1.394(2)	O4’	C21’	1.305(4)
C7’	C8’	1.394(3)	F5’	C22’	1.385(6)
C9	C10	1.399(2)	C22’	C21’	1.572(5)
C9	C14	1.411(2)	C22’	F6’	1.407(4)
C9’	C10’	1.397(2)	C22’	F4’	1.130(6)
C9’	C14’	1.407(2)	O4	C21	1.311(14)
C10	C11	1.381(2)	F4	C22	1.311(8)
C10’	C11’	1.383(2)	O3	C21	1.123(14)
C11	C12	1.385(3)	F6	C22	1.198(10)
C11’	C12’	1.385(3)	C22	F5	1.251(12)
C12	C13	1.391(2)	C22	C21	1.64(2)
C12’	C13’	1.386(3)			

Table F17 Bond angles for **2.2c**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C8	110.41(14)	C13	C14	C15	120.87(14)
C1’	N1’	C8’	109.94(14)	C9’	C14’	C15’	124.09(14)
C2	N2	C9	121.77(14)	C13’	C14’	C9’	115.54(15)
C2’	N2’	C9’	122.24(14)	C13’	C14’	C15’	120.25(15)
N1	C1	C1’	121.76(15)	C14	C15	C18	109.52(12)
N1	C1	C2	107.13(14)	C16	C15	C14	111.44(14)
C1’	C1	C2	131.11(14)	C16	C15	C18	106.77(15)
N1’	C1’	C1	120.85(15)	C17	C15	C14	111.83(13)
N1’	C1’	C2’	107.17(15)	C17	C15	C16	107.00(15)
C1	C1’	C2’	131.82(15)	C17	C15	C18	110.13(14)
N2	C2	C1	122.67(15)	C16’	C15’	C14’	111.42(13)
N2	C2	C3	131.28(15)	C16’	C15’	C18’	108.05(14)
C3	C2	C1	105.90(13)	C17’	C15’	C14’	112.22(14)
N2’	C2’	C1’	123.85(15)	C17’	C15’	C16’	106.82(15)
N2’	C2’	C3’	129.83(15)	C17’	C15’	C18’	109.86(15)
C3’	C2’	C1’	106.30(13)	C18’	C15’	C14’	108.40(14)
C4	C3	C2	134.28(15)	O1	C19	C20	115.9(8)
C4	C3	C8	119.36(15)	O2	C19	O1	126.0(9)
C8	C3	C2	106.32(15)	O2	C19	C20	117.7(6)
C4’	C3’	C2’	133.86(16)	F1	C20	F2	107.6(4)
C4’	C3’	C8’	119.66(16)	F1	C20	F3	107.2(4)
C8’	C3’	C2’	106.37(15)	F1	C20	C19	113.6(5)
C5	C4	C3	118.49(16)	F2	C20	F3	104.7(4)
C5’	C4’	C3’	118.32(18)	F2	C20	C19	109.8(5)
C4	C5	C6	121.01(18)	F3	C20	C19	113.3(5)
C4’	C5’	C6’	120.6(2)	F1’	C20’	C19’	109.8(4)
C7	C6	C5	121.52(16)	F2’	C20’	F1’	106.9(3)
C7’	C6’	C5’	122.25(18)	F2’	C20’	F3’	106.8(3)
C6	C7	C8	117.32(17)	F2’	C20’	C19’	111.7(4)
C6’	C7’	C8’	117.07(18)	F3’	C20’	F1’	107.5(3)
N1	C8	C3	110.22(14)	F3’	C20’	C19’	113.8(4)
N1	C8	C7	127.48(16)	O1’	C19’	C20’	118.1(7)
C7	C8	C3	122.30(17)	O2’	C19’	O1’	128.2(7)
N1’	C8’	C3’	110.15(15)	O2’	C19’	C20’	113.8(6)
N1’	C8’	C7’	127.70(17)	F5’	C22’	C21’	105.8(4)
C7’	C8’	C3’	122.10(18)	F5’	C22’	F6’	100.0(4)
C10	C9	N2	116.09(14)	F6’	C22’	C21’	104.4(3)
C10	C9	C14	121.83(14)	F4’	C22’	F5’	114.8(4)
C14	C9	N2	121.97(14)	F4’	C22’	C21’	118.4(4)
C10’	C9’	N2’	115.34(14)	F4’	C22’	F6’	111.4(4)
C10’	C9’	C14’	121.69(15)	O3’	C21’	O4’	128.6(4)
C14’	C9’	N2’	122.92(14)	O3’	C21’	C22’	124.0(4)
C11	C10	C9	120.41(16)	O4’	C21’	C22’	107.4(3)
C11’	C10’	C9’	120.70(16)	F4	C22	C21	109.3(8)
C10	C11	C12	119.34(16)	F6	C22	F4	104.5(6)
C10’	C11’	C12’	119.01(16)	F6	C22	F5	104.4(10)
C11	C12	C13	120.04(16)	F6	C22	C21	118.1(7)
C11’	C12’	C13’	119.81(16)	F5	C22	F4	110.0(6)
C12	C13	C14	122.69(16)	F5	C22	C21	110.2(7)
C12’	C13’	C14’	123.25(17)	O4	C21	C22	107.1(9)
C9	C14	C15	123.43(14)	O3	C21	O4	132.5(19)
C13	C14	C9	115.66(14)	O3	C21	C22	120.3(14)

Table F18 Table of crystallographic parameters for **2.2d** and **2.2e**

Crystal	**2.2d**	**2.2e**
Identification code	rh151	**2.2e**
Empirical formula	$C_{42}H_{29}F_3N_4O_2$	rh198
Formula weight	678.69	$C_{34}H_{29}F_3N_4O_2$
Temperature/K	90	582.61
Crystal system	monoclinic	90
Space group	$P2_1/c$	Monoclinic
a/Å	11.9990(6)	$P2_1/c$
b/Å	14.7606(7)	15.646(2)
c/Å	18.6694(9)	9.7895(13)
α/°	90	19.471(3)
β/°	105.5510(10)	90
γ/°	90	108.343(4)
Volume/Å^3	3185.5(3)	90
Z	4	2830.7(6)
ρ_{calc}g/cm^3	1.415	4
μ/mm^{-1}	0.100	1.367
F(000)	1408.0	0.100
Crystal size/mm^3	0.34 × 0.29 × 0.09	1216.0
Radiation	MoKα (λ = 0.71073)	0.6 × 0.45 × 0.29
2Θ range for data collection/°	3.524 to 60.158	MoKα (λ = 0.71073)
Index ranges	-16 ≤ h ≤ 16, -20 ≤ k ≤ 20, -26 ≤ l ≤ 26	4.398 to 60.118
Reflections collected	39749	-21 ≤ h ≤ 20, -13 ≤ k ≤ 13, -22 ≤ l ≤ 27
Independent reflections	9352 [R_{int} = 0.0478, R_{sigma} = 0.0419]	34143
Data/restraints/parameters	9352/0/472	8281 [R_{int} = 0.0283, R_{sigma} = 0.0268]
Goodness-of-fit on F^2	1.024	8281/94/483
Final R indexes [I>=2σ (I)]	R_1 = 0.0467, wR_2 = 0.1102	1.039
Final R indexes [all data]	R_1 = 0.0711, wR_2 = 0.1229	R_1 = 0.0588, wR_2 = 0.1726
Largest diff. peak/hole / e Å^{-3}	0.73/-0.33	R_1 = 0.0802, wR_2 = 0.1926

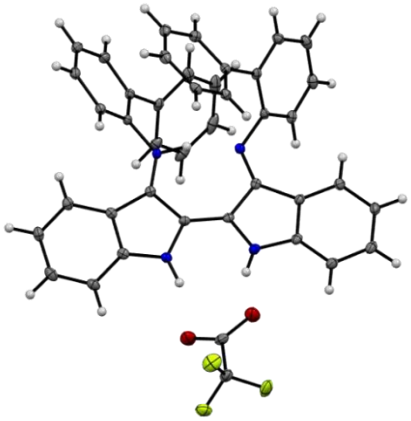


Figure F7 X-ray structure of **2.2d**; Thermal ellipsoids are shown at the 50% probability level.

Table F19 Bond lengths for **2.2d**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.4575(18)	C20	C21	1.3891(19)
C1	C17	1.3915(18)	C21	C22	1.392(2)
C1	N1	1.3871(17)	C22	C23	1.393(2)
C2	C3	1.4486(18)	C23	C24	1.3870(19)
C2	N2	1.3293(17)	C24	N3	1.3928(18)
C3	C4	1.4098(19)	C25	C26	1.3953(18)
C3	C8	1.4120(19)	C25	C30	1.4078(19)
C4	C5	1.379(2)	C25	N4	1.4197(17)
C5	C6	1.405(2)	C26	C27	1.387(2)
C6	C7	1.381(2)	C27	C28	1.389(2)
C7	C8	1.3991(19)	C28	C29	1.386(2)
C8	N1	1.3708(17)	C29	C30	1.3983(19)
C9	C10	1.3940(19)	C30	C31	1.4833(18)
C9	C14	1.4076(19)	C31	C32	1.4017(19)
C9	N2	1.4190(16)	C31	C36	1.3979(19)
C10	C11	1.3865(19)	C32	C33	1.3889(19)
C11	C12	1.389(2)	C33	C34	1.390(2)
C12	C13	1.389(2)	C34	C35	1.388(2)
C13	C14	1.3996(19)	C35	C36	1.3874(19)
C14	C15	1.4887(19)	C37	C38	1.380(3)
C15	C16	1.397(2)	C38	C39	1.388(3)
C15	C40	1.396(2)	C39	C40	1.392(2)
C16	C37	1.394(2)	C41	C42	1.551(2)
C17	C18	1.4925(19)	C41	O1	1.2387(19)
C17	N3	1.3625(17)	C41	O2	1.2352(19)
C18	C19	1.4709(18)	C42	F1	1.3327(17)
C18	N4	1.2946(17)	C42	F2	1.3395(18)
C19	C20	1.3966(19)	C42	F3	1.3422(18)
C19	C24	1.4048(19)			

Table F20 Bond angles for **2.2d**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	C1	C2	132.22(12)	C21	C22	C23	121.33(13)
N1	C1	C2	107.49(11)	C24	C23	C22	116.76(13)
N1	C1	C17	120.28(12)	C23	C24	C19	123.13(13)
C3	C2	C1	106.25(11)	C23	C24	N3	126.73(13)
N2	C2	C1	122.99(12)	N3	C24	C19	110.14(12)
N2	C2	C3	130.70(12)	C26	C25	C30	120.48(12)
C4	C3	C2	134.70(13)	C26	C25	N4	122.07(12)
C4	C3	C8	118.72(12)	C30	C25	N4	117.06(12)
C8	C3	C2	106.39(11)	C27	C26	C25	119.98(13)
C5	C4	C3	118.92(13)	C26	C27	C28	120.21(13)
C4	C5	C6	121.18(13)	C29	C28	C27	119.81(13)
C7	C6	C5	121.56(13)	C28	C29	C30	121.31(13)
C6	C7	C8	117.13(13)	C25	C30	C31	122.16(12)
C7	C8	C3	122.49(13)	C29	C30	C25	118.14(12)
N1	C8	C3	110.09(12)	C29	C30	C31	119.69(12)
N1	C8	C7	127.38(13)	C32	C31	C30	122.32(12)
C10	C9	C14	120.42(12)	C36	C31	C30	119.06(12)
C10	C9	N2	120.94(12)	C36	C31	C32	118.62(12)
C14	C9	N2	118.14(12)	C33	C32	C31	120.39(13)
C11	C10	C9	120.23(13)	C32	C33	C34	120.22(13)
C10	C11	C12	120.09(13)	C35	C34	C33	119.93(13)
C13	C12	C11	119.83(13)	C36	C35	C34	119.94(13)
C12	C13	C14	121.20(13)	C35	C36	C31	120.86(13)
C9	C14	C15	121.75(12)	C38	C37	C16	120.59(15)
C13	C14	C9	118.20(12)	C37	C38	C39	119.72(15)
C13	C14	C15	120.05(12)	C38	C39	C40	120.16(16)
C16	C15	C14	120.22(13)	C39	C40	C15	120.49(15)
C40	C15	C14	120.88(13)	C8	N1	C1	109.73(11)
C40	C15	C16	118.89(14)	C2	N2	C9	127.74(11)
C37	C16	C15	120.11(15)	C17	N3	C24	110.75(12)
C1	C17	C18	131.57(12)	C18	N4	C25	124.20(11)
N3	C17	C1	121.19(12)	O1	C41	C42	114.79(14)
N3	C17	C18	107.24(11)	O2	C41	C42	116.02(13)
C19	C18	C17	105.55(11)	O2	C41	O1	129.17(15)
N4	C18	C17	121.17(12)	F1	C42	C41	113.00(12)
N4	C18	C19	133.15(12)	F1	C42	F2	106.85(12)
C20	C19	C18	134.90(13)	F1	C42	F3	107.40(13)
C20	C19	C24	118.79(12)	F2	C42	C41	112.60(13)
C24	C19	C18	106.31(12)	F2	C42	F3	106.67(12)
C21	C20	C19	118.77(13)	F3	C42	C41	109.98(12)
C20	C21	C22	121.20(13)				

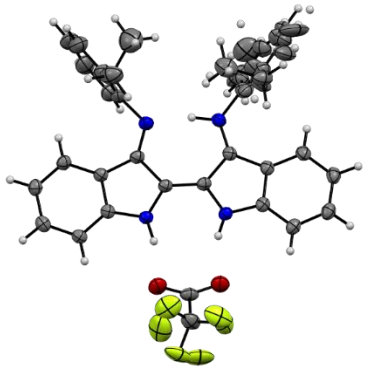


Figure F8 X-ray structure of **2.2c**; Thermal ellipsoids are shown at the 50% probability level

Table F21 Bond lengths for **2.2e**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.3660(19)	C4A	C5A	1.380(2)
N1	C8	1.3889(19)	C5A	C6A	1.404(3)
N2	C2	1.296(2)	C6A	C7A	1.383(2)
N2	C9	1.427(2)	C7A	C8A	1.395(2)
C1	C2	1.493(2)	C9A	C10A	1.388(4)
C1	C1A	1.383(2)	C9A	C14A	1.411(3)
C2	C3	1.460(2)	C10A	C11A	1.391(3)
C3	C4	1.401(2)	C11A	C12A	1.374(4)
C3	C8	1.403(2)	C12A	C13A	1.377(4)
C4	C5	1.383(2)	C13A	C14A	1.399(3)
C5	C6	1.401(2)	C14A	C15A	1.507(3)
C6	C7	1.389(2)	C15A	C16A	1.513(5)
C7	C8	1.388(2)	F1	C18	1.324(5)
C9	C10	1.393(3)	F2	C18	1.393(4)
C9	C14	1.403(3)	F3	C18	1.285(3)
C10	C11	1.390(3)	O1	C17	1.234(2)
C11	C12	1.362(4)	O2	C17	1.242(2)
C12	C13	1.375(4)	C17	C18	1.539(2)
C13	C14	1.410(3)	C18	F3A	1.256(5)
C14	C15	1.509(3)	C18	F1A	1.264(9)
C15	C16	1.511(4)	C18	F2A	1.437(6)
N1A	C1A	1.3853(18)	C16B	C15B	1.47(2)
N1A	C8A	1.376(2)	C15B	C14B	1.5079
N2A	C2A	1.318(2)	C14B	C9B	1.4020
N2A	C9A	1.433(2)	C14B	C13B	1.4020
N2A	C9B	1.447(7)	C9B	C10B	1.3956
C1A	C2A	1.465(2)	C10B	C11B	1.3967
C2A	C3A	1.447(2)	C11B	C12B	1.3966
C3A	C4A	1.411(2)	C12B	C13B	1.3956
C3A	C8A	1.408(2)			

Table F22 Bond angles for **2.2e**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C8	110.63(12)	C7A	C6A	C5A	122.23(15)
C2	N2	C9	121.92(14)	C6A	C7A	C8A	116.75(15)
N1	C1	C2	106.94(12)	N1A	C8A	C3A	110.28(13)
N1	C1	C1A	122.64(13)	N1A	C8A	C7A	127.55(15)
C1A	C1	C2	130.41(13)	C7A	C8A	C3A	122.17(14)
N2	C2	C1	122.86(14)	C10A	C9A	N2A	117.66(19)
N2	C2	C3	131.37(14)	C10A	C9A	C14A	121.5(2)
C3	C2	C1	105.76(12)	C14A	C9A	N2A	120.70(19)
C4	C3	C2	133.68(14)	C9A	C10A	C11A	119.6(2)
C4	C3	C8	119.75(14)	C12A	C11A	C10A	120.0(2)
C8	C3	C2	106.50(13)	C11A	C12A	C13A	120.1(2)
C5	C4	C3	118.28(14)	C12A	C13A	C14A	122.3(2)
C4	C5	C6	121.03(15)	C9A	C14A	C15A	123.1(2)
C7	C6	C5	121.63(15)	C13A	C14A	C9A	116.4(2)
C8	C7	C6	116.92(14)	C13A	C14A	C15A	120.5(2)
N1	C8	C3	110.15(13)	C14A	C15A	C16A	113.5(2)
C7	C8	N1	127.46(14)	O1	C17	O2	129.37(16)
C7	C8	C3	122.38(14)	O1	C17	C18	115.22(16)
C10	C9	N2	117.73(18)	O2	C17	C18	115.40(16)
C10	C9	C14	121.16(17)	F1	C18	F2	102.7(4)
C14	C9	N2	121.03(18)	F1	C18	C17	113.5(4)
C11	C10	C9	119.9(2)	F2	C18	C17	109.0(2)
C12	C11	C10	119.8(2)	F3	C18	F1	110.2(4)
C11	C12	C13	120.8(2)	F3	C18	F2	104.5(3)
C12	C13	C14	121.6(2)	F3	C18	C17	115.7(2)
C9	C14	C13	116.7(2)	F3A	C18	C17	116.5(3)
C9	C14	C15	123.36(19)	F3A	C18	F1A	114.1(8)
C13	C14	C15	119.9(2)	F3A	C18	F2A	100.2(5)
C14	C15	C16	111.5(2)	F1A	C18	C17	115.6(8)
C8A	N1A	C1A	109.86(13)	F1A	C18	F2A	102.4(7)
C2A	N2A	C9A	127.23(16)	F2A	C18	C17	105.1(3)
C2A	N2A	C9B	114.1(4)	C16B	C15B	C14B	118.0(11)
C1	C1A	N1A	121.75(13)	C9B	C14B	C15B	120.9
C1	C1A	C2A	131.23(13)	C13B	C14B	C15B	121.0
N1A	C1A	C2A	107.02(13)	C13B	C14B	C9B	118.1
N2A	C2A	C1A	123.78(14)	C14B	C9B	N2A	115.4(6)
N2A	C2A	C3A	129.64(15)	C10B	C9B	N2A	123.4(6)
C3A	C2A	C1A	106.58(13)	C10B	C9B	C14B	121.1
C4A	C3A	C2A	134.09(15)	C9B	C10B	C11B	120.1
C8A	C3A	C2A	106.22(13)	C12B	C11B	C10B	119.4
C8A	C3A	C4A	119.68(14)	C13B	C12B	C11B	120.1
C5A	C4A	C3A	118.19(16)	C12B	C13B	C14B	121.1
C4A	C5A	C6A	120.91(16)				

Table F23 Table of crystallographic parameters for **2.2f** and **2.2g**

Crystal	**2.2f**	**2.2g**
Identification code	rh211	$C_{124}H_{78}F_{26}N_{16}O_{12}$
Empirical formula	$C_{38.5}H_{26}ClF_3N_4O_2$	2478.02
Formula weight	668.07	90
Temperature/K	90	triclinic
Crystal system	triclinic	P-1
Space group	P-1	14.387(4)
a/Å	10.9774(8)	14.646(5)
b/Å	11.7952(8)	15.315(5)
c/Å	12.5724(9)	69.147(7)
α/°	95.928(4)	70.869(7)
β/°	94.914(4)	68.094(7)
γ/°	95.504(4)	2726.5(15)
Volume/Å^3	1604.2(2)	1
Z	2	1.509
ρ_{calc}g/cm^3	1.383	0.129
μ/mm^{-1}	0.179	1264.0
F(000)	688.0	0.27 × 0.21 × 0.14
Crystal size/mm^3	? × ? × ?	MoKα (λ = 0.71073)
Radiation	MoKα (λ = 0.71073)	2.92 to 60.54
2Θ range for data collection/°	3.272 to 50.762	-20 ≤ h ≤ 20, -20 ≤ k ≤ 20, -21 ≤ l ≤ 21
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -15 ≤ l ≤ 14	66411
Reflections collected	21573	16110 [R_{int} = 0.0425, R_{sigma} = 0.0347]
Independent reflections	5762 [R_{int} = 0.0520, R_{sigma} = 0.0612]	16110/0/877
Data/restraints/parameters	rh211	1.028
Goodness-of-fit on F^2	$C_{38.5}H_{26}ClF_3N_4O_2$	R_1 = 0.0508, wR_2 = 0.1275
Final R indexes [I>=2σ (I)]	668.07	R_1 = 0.0653, wR_2 = 0.1383
Final R indexes [all data]	90	0.65/-0.74
Largest diff. peak/hole / e Å^{-3}	triclinic	mo_rh203_0m

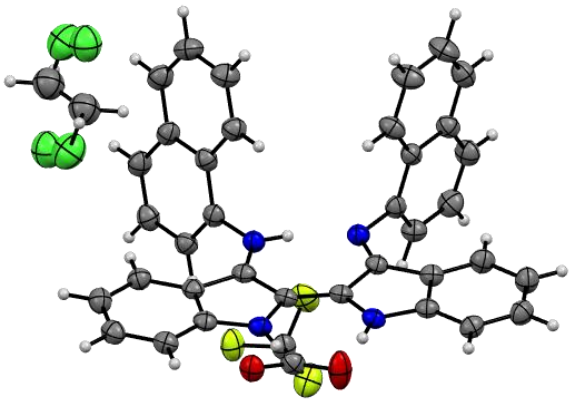


Figure F9 X-ray structure of **2.2f**; Thermal ellipsoids are shown at the 50% probability level

Table F24 Bond lengths for **2.2f**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C38	1.333(3)	C26	C21	1.423(4)
F3	C38	1.350(3)	C26	C25	1.423(4)
F2	C38	1.336(3)	C16	C15	1.398(4)
O1	C37	1.241(3)	C37	C38	1.548(4)
N2	C9	1.369(3)	C27	C28	1.371(4)
N2	C16	1.390(3)	C31	C32	1.410(4)
N1	C1	1.389(3)	C31	C30	1.418(4)
N1	C8	1.385(3)	C18	C19	1.416(4)
O2	C37	1.236(3)	C21	C20	1.420(4)
N4	C10	1.303(3)	C21	C22	1.423(4)
N4	C27	1.438(3)	C4	C5	1.382(4)
N3	C2	1.317(3)	C35	C34	1.365(4)
N3	C17	1.442(3)	C25	C24	1.363(4)
C1	C9	1.382(4)	C15	C14	1.385(4)
C1	C2	1.471(4)	C19	C20	1.370(4)
C3	C2	1.451(4)	C28	C29	1.408(4)
C3	C8	1.409(4)	C6	C5	1.405(4)
C3	C4	1.407(4)	C6	C7	1.383(4)
C9	C10	1.492(4)	C12	C13	1.387(4)
C17	C26	1.417(4)	C14	C13	1.398(4)
C17	C18	1.368(4)	C32	C33	1.365(4)
C8	C7	1.394(4)	C22	C23	1.368(4)
C36	C27	1.417(4)	C30	C29	1.363(4)
C36	C31	1.432(4)	C24	C23	1.404(4)
C36	C35	1.424(4)	C34	C33	1.405(4)
C10	C11	1.470(4)	Cl1	C39	1.751(6)
C11	C16	1.404(4)	Cl2	C39	1.789(7)
C11	C12	1.400(4)			

Table F25 Bond angles for **2.2f**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	N2	C16	110.9(2)	O2	C37	C38	115.2(2)
C8	N1	C1	110.0(2)	C36	C27	N4	118.8(2)
C10	N4	C27	119.0(2)	C28	C27	N4	120.2(3)
C2	N3	C17	125.2(2)	C28	C27	C36	120.9(2)
N1	C1	C2	106.7(2)	C32	C31	C36	117.9(3)
C9	C1	N1	122.0(2)	C32	C31	C30	122.9(3)
C9	C1	C2	131.3(2)	C30	C31	C36	119.1(3)
C8	C3	C2	106.2(2)	C17	C18	C19	120.1(3)
C4	C3	C2	134.4(2)	C20	C21	C26	119.4(3)
C4	C3	C8	119.4(2)	C20	C21	C22	122.0(3)
N2	C9	C1	122.4(2)	C22	C21	C26	118.6(3)
N2	C9	C10	106.6(2)	C5	C4	C3	118.2(2)
C1	C9	C10	130.9(2)	C34	C35	C36	120.8(3)
N3	C2	C1	123.6(2)	C24	C25	C26	120.6(3)

Table F26 Bond angles for **2.2f** continued

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N3	C2	C3	129.4(2)	C14	C15	C16	116.8(2)
C3	C2	C1	106.9(2)	C20	C19	C18	119.7(3)
C26	C17	N3	117.5(2)	C27	C28	C29	120.2(3)
C18	C17	N3	120.4(2)	C7	C6	C5	121.5(3)
C18	C17	C26	122.0(3)	C4	C5	C6	121.3(3)
N1	C8	C3	110.3(2)	C19	C20	C21	121.2(3)
N1	C8	C7	127.3(2)	C13	C12	C11	118.5(3)
C7	C8	C3	122.4(2)	C6	C7	C8	117.1(2)
C27	C36	C31	118.4(2)	C15	C14	C13	121.8(3)
C27	C36	C35	122.9(2)	C33	C32	C31	122.1(3)
C35	C36	C31	118.8(2)	C12	C13	C14	121.0(3)
N4	C10	C9	122.8(2)	F1	C38	F3	106.9(2)
N4	C10	C11	131.1(2)	F1	C38	F2	106.9(2)
C11	C10	C9	106.1(2)	F1	C38	C37	113.6(2)
C16	C11	C10	106.1(2)	F3	C38	C37	110.6(2)
C12	C11	C10	134.3(2)	F2	C38	F3	106.2(2)
C12	C11	C16	119.6(2)	F2	C38	C37	112.2(2)
C17	C26	C21	117.7(2)	C23	C22	C21	120.9(3)
C17	C26	C25	123.4(3)	C29	C30	C31	120.5(3)
C25	C26	C21	118.8(3)	C30	C29	C28	120.8(3)
N2	C16	C11	110.3(2)	C25	C24	C23	120.8(3)
N2	C16	C15	127.4(2)	C22	C23	C24	120.2(3)
C15	C16	C11	122.3(3)	C35	C34	C33	120.6(3)
O1	C37	C38	115.7(2)	C32	C33	C34	119.7(3)
O2	C37	O1	129.1(3)	Cl1	C39	Cl2	111.6(4)

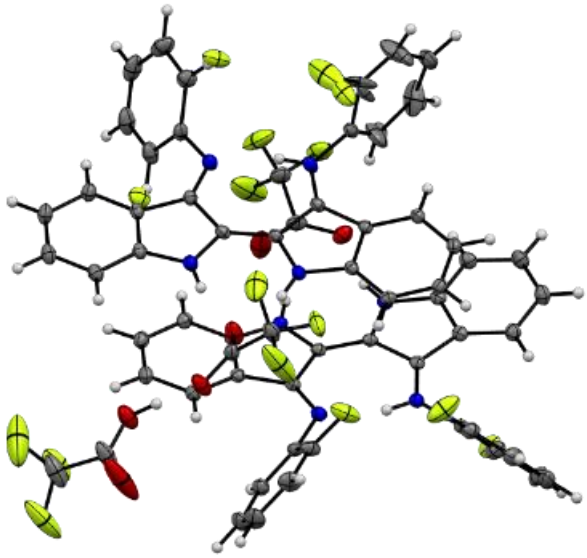


Figure F10 X-ray structure of **2.2g**; Thermal ellipsoids are shown at the 50% probability level

Table F27 Bond lengths for **2.2g**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F(5)	C(30)	1.3283(18)	C(23A)	C(28A)	1.389(2)
O(1A)	C(29A)	1.231(2)	C(23A)	C(24A)	1.386(2)
O(1)	C(29)	1.2403(18)	C(17)	C(22)	1.425(9)
O(2)	C(29)	1.2387(17)	C(17)	C(18')	1.358(6)
F(8)	C(32)	1.314(2)	C(17)	C(22')	1.272(19)
O(3)	C(31)	1.281(2)	C(17)	C(18)	1.445(11)
N(2A)	C(9A)	1.3707(17)	C(15A)	C(14A)	1.386(2)
N(2A)	C(16A)	1.3805(17)	C(12A)	C(13A)	1.382(2)
F(4)	C(30)	1.338(2)	C(23)	C(24)	1.389(2)
N(1)	C(8)	1.3782(17)	C(23)	C(28)	1.393(2)
N(1)	C(1)	1.3808(17)	C(15)	C(14)	1.382(2)
N(2)	C(9)	1.3734(17)	C(29)	C(30)	1.538(2)
N(2)	C(16)	1.3786(17)	C(4A)	C(5A)	1.385(2)
N(3A)	C(2A)	1.3118(17)	C(28A)	C(27A)	1.392(2)
N(3A)	C(17A)	1.4065(17)	C(7A)	C(6A)	1.383(2)
N(1A)	C(1A)	1.3788(16)	C(29A)	C(30A)	1.549(2)
N(1A)	C(8A)	1.3801(17)	C(13A)	C(14A)	1.404(2)
N(4A)	C(10A)	1.3085(17)	C(22A)	C(21A)	1.387(2)
N(4A)	C(23A)	1.4213(17)	C(22A)	F(1A')	1.227(5)
N(4)	C(10)	1.3062(17)	C(12)	C(13)	1.387(2)
N(4)	C(23)	1.4091(18)	C(14)	C(13)	1.403(2)
N(3)	C(2)	1.3138(17)	C(24A)	C(25A)	1.380(2)
N(3)	C(17)	1.4264(17)	C(24A)	F(2A)	1.3544(18)
O(2A)	C(29A)	1.231(2)	C(5A)	C(6A)	1.402(2)
F(6)	C(32)	1.322(3)	F(7)	C(32)	1.319(3)
F(3)	C(30)	1.3075(19)	C(18A)	C(19A)	1.379(2)
C(8)	C(3)	1.4092(18)	C(18A)	F(1A)	1.313(2)
C(8)	C(7)	1.3893(18)	C(24)	C(25)	1.377(2)
C(1)	C(9)	1.3833(18)	C(24)	F(2)	1.316(2)
C(1)	C(2)	1.4704(18)	C(27A)	C(26A)	1.385(2)
C(3)	C(2)	1.4462(18)	C(28)	C(27)	1.386(2)
C(3)	C(4)	1.4011(18)	C(28)	F(2')	1.188(4)
C(10A)	C(11A)	1.4537(18)	C(21A)	C(20A)	1.382(3)
C(10A)	C(9A)	1.4820(18)	C(26A)	C(25A)	1.384(2)
C(9)	C(10)	1.4730(18)	C(20)	C(21)	1.408(7)
C(1A)	C(9A)	1.3841(18)	C(20)	C(19')	1.419(6)
C(1A)	C(2A)	1.4673(18)	C(20)	C(21')	1.301(18)
C(11A)	C(16A)	1.4059(18)	C(20)	C(19)	1.305(16)
C(11A)	C(12A)	1.4054(19)	O(4)	C(31)	1.188(2)
C(2A)	C(3A)	1.4517(18)	C(20A)	C(19A)	1.375(3)
C(3A)	C(8A)	1.4009(19)	C(22)	C(21)	1.392(12)
C(3A)	C(4A)	1.4015(19)	C(27)	C(26)	1.382(3)
C(8A)	C(7A)	1.3959(18)	C(25)	C(26)	1.383(3)
C(10)	C(11)	1.4581(18)	C(18')	C(19')	1.427(8)
C(16A)	C(15A)	1.3927(19)	C(18')	F(1')	1.331(7)
C(16)	C(11)	1.4064(19)	C(31)	C(32)	1.536(3)

Table F28 Bond lengths for **2.2g** continued

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C(16)	C(15)	1.3927(19)	C(22')	C(21')	1.39(3)
C(11)	C(12)	1.3982(19)	C(19)	C(18)	1.276(18)
C(4)	C(5)	1.3800(19)	C(18)	F(1)	1.409(13)
C(7)	C(6)	1.3870(19)	F(4A)	C(30A)	1.314(2)
C(17A)	C(22A)	1.390(2)	C(30A)	F(5A)	1.330(2)
C(17A)	C(18A)	1.391(2)	C(30A)	F(3A)	1.3276(19)
C(6)	C(5)	1.402(2			

Table F29 Bond angles for **2.2g**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(9A)	N(2A)	C(16A)	110.20(11)	C(14)	C(15)	C(16)	117.14(14)
C(8)	N(1)	C(1)	109.90(11)	O(1)	C(29)	C(30)	115.92(13)
C(9)	N(2)	C(16)	110.45(11)	O(2)	C(29)	O(1)	129.40(15)
C(2A)	N(3A)	C(17A)	123.72(11)	O(2)	C(29)	C(30)	114.65(13)
C(1A)	N(1A)	C(8A)	109.88(11)	C(5A)	C(4A)	C(3A)	118.41(13)
C(10A)	N(4A)	C(23A)	123.46(12)	C(23A)	C(28A)	C(27A)	119.82(14)
C(10)	N(4)	C(23)	123.97(12)	C(6A)	C(7A)	C(8A)	117.11(13)
C(2)	N(3)	C(17)	122.55(12)	O(1A)	C(29A)	C(30A)	116.81(13)
N(1)	C(8)	C(3)	110.09(11)	O(2A)	C(29A)	O(1A)	128.86(14)
N(1)	C(8)	C(7)	127.66(12)	O(2A)	C(29A)	C(30A)	114.33(14)
C(7)	C(8)	C(3)	122.24(12)	C(12A)	C(13A)	C(14A)	121.04(13)
N(1)	C(1)	C(9)	121.15(12)	C(15A)	C(14A)	C(13A)	121.59(13)
N(1)	C(1)	C(2)	107.25(11)	C(21A)	C(22A)	C(17A)	120.71(15)
C(9)	C(1)	C(2)	131.57(12)	F(1A')	C(22A)	C(17A)	122.4(2)
C(8)	C(3)	C(2)	106.53(11)	F(1A')	C(22A)	C(21A)	116.8(3)
C(4)	C(3)	C(8)	119.76(12)	C(13)	C(12)	C(11)	118.17(14)
C(4)	C(3)	C(2)	133.70(12)	C(15)	C(14)	C(13)	121.10(13)
N(4A)	C(10A)	C(11A)	131.54(12)	C(25A)	C(24A)	C(23A)	122.81(14)
N(4A)	C(10A)	C(9A)	122.26(12)	F(2A)	C(24A)	C(23A)	118.15(13)
C(11A)	C(10A)	C(9A)	106.15(11)	F(2A)	C(24A)	C(25A)	119.04(14)
N(2)	C(9)	C(1)	121.79(12)	C(12)	C(13)	C(14)	121.58(14)
N(2)	C(9)	C(10)	107.27(11)	C(4A)	C(5A)	C(6A)	121.26(14)
C(1)	C(9)	C(10)	130.94(12)	F(5)	C(30)	F(4)	105.61(13)
N(1A)	C(1A)	C(9A)	121.47(12)	F(5)	C(30)	C(29)	112.01(14)
N(1A)	C(1A)	C(2A)	107.15(11)	F(4)	C(30)	C(29)	110.52(13)
C(9A)	C(1A)	C(2A)	131.36(12)	F(3)	C(30)	F(5)	106.94(15)
C(16A)	C(11A)	C(10A)	106.06(11)	F(3)	C(30)	F(4)	107.96(17)
C(12A)	C(11A)	C(10A)	134.77(12)	F(3)	C(30)	C(29)	113.40(13)
C(12A)	C(11A)	C(16A)	119.11(12)	C(7A)	C(6A)	C(5A)	121.29(13)
N(2A)	C(9A)	C(10A)	107.04(11)	C(19A)	C(18A)	C(17A)	122.08(15)
N(2A)	C(9A)	C(1A)	121.47(12)	F(1A)	C(18A)	C(17A)	120.98(14)
C(1A)	C(9A)	C(10A)	131.40(12)	F(1A)	C(18A)	C(19A)	116.84(15)
N(3A)	C(2A)	C(1A)	123.14(12)	C(25)	C(24)	C(23)	122.23(16)
N(3A)	C(2A)	C(3A)	130.62(12)	F(2)	C(24)	C(23)	118.25(14)

Table F30 Bond angles for **2.2g** continued

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(3A)	C(2A)	C(1A)	106.18(11)	F(2)	C(24)	C(25)	119.52(16)
C(8A)	C(3A)	C(2A)	106.44(12)	C(26A)	C(27A)	C(28A)	120.61(15)
C(8A)	C(3A)	C(4A)	119.40(12)	C(27)	C(28)	C(23)	120.28(16)
C(4A)	C(3A)	C(2A)	133.78(12)	F(2')	C(28)	C(23)	121.3(2)
N(1A)	C(8A)	C(3A)	110.21(11)	F(2')	C(28)	C(27)	117.8(2)
N(1A)	C(8A)	C(7A)	127.23(13)	C(20A)	C(21A)	C(22A)	120.00(16)
C(7A)	C(8A)	C(3A)	122.47(13)	C(25A)	C(26A)	C(27A)	120.20(14)
N(4)	C(10)	C(9)	122.03(12)	C(24A)	C(25A)	C(26A)	118.34(15)
N(4)	C(10)	C(11)	132.07(12)	C(21)	C(20)	C(19')	123.0(5)
C(11)	C(10)	C(9)	105.83(11)	C(21')	C(20)	C(19)	111.0(10)
N(2A)	C(16A)	C(11A)	110.53(11)	C(19A)	C(20A)	C(21A)	120.34(15)
N(2A)	C(16A)	C(15A)	126.78(12)	C(21)	C(22)	C(17)	121.9(8)
C(15A)	C(16A)	C(11A)	122.69(12)	C(26)	C(27)	C(28)	120.37(17)
N(3)	C(2)	C(1)	124.27(12)	C(20A)	C(19A)	C(18A)	119.15(16)
N(3)	C(2)	C(3)	129.50(12)	C(24)	C(25)	C(26)	118.91(17)
C(3)	C(2)	C(1)	106.21(11)	C(17)	C(18')	C(19')	122.8(5)
N(2)	C(16)	C(11)	109.93(11)	F(1')	C(18')	C(17)	120.4(3)
N(2)	C(16)	C(15)	127.46(13)	F(1')	C(18')	C(19')	116.9(5)
C(15)	C(16)	C(11)	122.61(13)	C(27)	C(26)	C(25)	120.18(15)
C(16)	C(11)	C(10)	106.50(11)	C(22)	C(21)	C(20)	117.1(8)
C(12)	C(11)	C(10)	134.06(13)	O(3)	C(31)	C(32)	111.71(16)
C(12)	C(11)	C(16)	119.38(12)	O(4)	C(31)	O(3)	128.85(17)
C(5)	C(4)	C(3)	118.28(12)	O(4)	C(31)	C(32)	119.44(17)
C(6)	C(7)	C(8)	116.82(12)	C(20)	C(19')	C(18')	116.0(5)
C(22A)	C(17A)	N(3A)	119.45(12)	F(8)	C(32)	F(6)	107.31(19)
C(22A)	C(17A)	C(18A)	117.69(13)	F(8)	C(32)	F(7)	105.6(2)
C(18A)	C(17A)	N(3A)	122.76(13)	F(8)	C(32)	C(31)	113.26(16)
C(7)	C(6)	C(5)	121.85(12)	F(6)	C(32)	C(31)	111.89(19)
C(28A)	C(23A)	N(4A)	122.91(13)	F(7)	C(32)	F(6)	108.5(2)
C(24A)	C(23A)	N(4A)	118.80(12)	F(7)	C(32)	C(31)	110.0(2)
C(24A)	C(23A)	C(28A)	118.14(13)	C(17)	C(22')	C(21')	117.7(14)
N(3)	C(17)	C(18)	122.1(5)	C(20)	C(21')	C(22')	128.2(15)
C(22)	C(17)	N(3)	123.5(4)	C(18)	C(19)	C(20)	125.3(14)
C(18')	C(17)	N(3)	117.6(2)	C(19)	C(18)	C(17)	121.3(11)
C(18')	C(17)	C(22)	118.8(4)	C(19)	C(18)	F(1)	125.4(11)
C(22')	C(17)	N(3)	122.4(8)	F(1)	C(18)	C(17)	113.2(8)
C(22')	C(17)	C(18)	114.7(9)	F(4A)	C(30A)	C(29A)	110.47(14)
C(14A)	C(15A)	C(16A)	116.87(13)	F(4A)	C(30A)	F(5A)	110.24(17)
C(13A)	C(12A)	C(11A)	118.64(13)	F(4A)	C(30A)	F(3A)	106.45(16)
C(24)	C(23)	N(4)	118.80(13)	F(5A)	C(30A)	C(29A)	111.19(14)
C(24)	C(23)	C(28)	117.99(14)	F(3A)	C(30A)	C(29A)	113.91(14)
C(28)	C(23)	N(4)	122.71(14)	F(3A)	C(30A)	F(5A)	104.34(14)
C(4)	C(5)	C(6)	121.05(13)				

Appendix G: Computational Chemistry I: XYZ Coordinates

XYZ coordinates of neutral *trans*-Nindigos 1.54 and 2.1a – 2.1g

Table G1 XYZ coordinates of the GS and TS geometries of **1.54** (Ar = Ph)
B3LYP/6-311G(d,p) (gas phase)

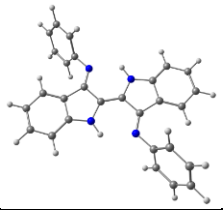
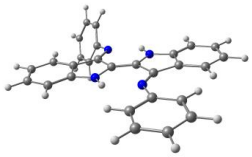
1.54				**TS**			
							
N	-0.259067	1.836254	0.019033	**N**	0.018977	-1.703051	-0.043608
N	-2.426061	-0.951181	-0.100254	**N**	2.414786	0.892064	-0.093702
N	0.259066	-1.836253	-0.019037	**N**	-0.142550	1.984851	-0.053925
N	2.426061	0.951183	0.100256	**N**	-2.531326	-0.594619	0.007897
C	-0.488003	0.475588	-0.010708	**C**	0.355494	-0.368114	-0.052008
C	-1.941257	0.248468	-0.055870	**C**	1.823621	-0.261502	-0.069266
C	-2.533756	1.597481	-0.073028	**C**	2.303343	-1.654589	-0.092757
C	-3.843212	2.071150	-0.175622	**C**	3.570213	-2.235287	-0.181046
C	-4.065264	3.444082	-0.211234	**C**	3.677372	-3.621527	-0.231206
C	-2.991069	4.340591	-0.146209	**C**	2.531538	-4.426532	-0.195168
C	-1.675802	3.895562	-0.057642	**C**	1.256929	-3.873910	-0.122413
C	-1.457431	2.520335	-0.029637	**C**	1.153999	-2.485474	-0.079928
C	0.488002	-0.475587	0.010706	**C**	-0.537675	0.669225	-0.037910
C	1.457431	-2.520334	0.029633	**C**	-1.240307	2.807029	-0.035901
C	1.675802	-3.895561	0.057636	**C**	-1.243742	4.200421	-0.043669
C	2.991068	-4.340589	0.146203	**C**	-2.468465	4.851164	-0.022133
C	4.065264	-3.444081	0.211229	**C**	-3.662352	4.122835	0.006296
C	3.843212	-2.071149	0.175620	**C**	-3.648116	2.733049	0.013823
C	2.533756	-1.597480	0.073026	**C**	-2.436026	2.030399	-0.006780
C	-3.807915	-1.186353	-0.020847	**C**	3.808240	1.008354	0.022361
C	-4.459262	-1.830320	-1.079672	**C**	4.535807	1.622894	-1.004141
C	-4.535130	-0.869987	1.135654	**C**	4.479562	0.605132	1.185964
C	-5.819103	-2.111459	-0.999078	**C**	5.911624	1.789513	-0.886103
C	-5.890283	-1.169345	1.214737	**C**	5.852154	0.790232	1.302870
C	-6.542204	-1.782984	0.146018	**C**	6.577677	1.374597	0.265529
C	1.941257	-0.248466	0.055870	**C**	-2.014418	0.603763	-0.007677
C	3.807915	1.186353	0.020851	**C**	-3.822171	-1.093098	0.038932
C	4.535130	0.869991	-1.135652	**C**	-3.898979	-2.505182	0.049198
C	4.459263	1.830314	1.079678	**C**	-5.041847	-0.391880	0.061560
C	5.890283	1.169347	-1.214733	**C**	-5.111372	-3.173832	0.079543
C	5.819105	2.111452	0.999086	**C**	-6.257961	-1.063942	0.091963
C	6.542205	1.782980	-0.146012	**C**	-6.306522	-2.455043	0.101097
H	-4.673583	1.381435	-0.224018	**H**	4.456502	-1.617849	-0.207563
H	-5.076674	3.823084	-0.288311	**H**	4.654960	-4.082556	-0.297202
H	-3.185693	5.406701	-0.170638	**H**	2.637401	-5.504780	-0.230178
H	-0.847763	4.592936	-0.020571	**H**	0.373132	-4.500166	-0.108046
H	0.847763	-4.592935	0.020563	**H**	-0.311016	4.750927	-0.065435
H	3.185693	-5.406700	0.170630	**H**	-2.498660	5.934495	-0.027313
H	5.076674	-3.823083	0.288307	**H**	-4.611356	4.644069	0.022614
H	4.673583	-1.381433	0.224018	**H**	-4.598185	2.229726	0.035400
H	0.686862	2.198045	0.052722	**H**	-0.959988	-1.962891	-0.039448
H	-6.439892	-0.921387	2.115799	**H**	6.357697	0.476244	2.209142
H	-7.599200	-2.011982	0.209489	**H**	7.647960	1.514514	0.358485
H	-0.686863	-2.198044	-0.052727	**H**	0.844139	2.224326	-0.083831
H	6.439893	0.921392	-2.115796	**H**	-5.126979	-4.257611	0.086557
H	6.314754	2.594842	1.833323	**H**	-7.177880	-0.490388	0.108691
H	7.599202	2.011977	-0.209480	**H**	-7.258685	-2.971178	0.124781
H	-6.314752	-2.594853	-1.833313	**H**	6.465040	2.251115	-1.696017
H	-3.887372	-2.088935	-1.962689	**H**	4.008481	1.948961	-1.892569
H	3.887373	2.088927	1.962696	**H**	-5.048068	0.679949	0.055740
H	-4.024989	-0.392551	1.963694	**H**	3.912361	0.151402	1.989828
H	4.024988	0.392559	-1.963694	**H**	-2.971789	-3.065214	0.033573

Table G2 XYZ coordinates of the GS and TS geometries of **2.1a** B3LYP/6-311G(d,p) (gas phase)

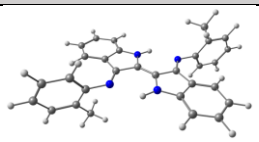
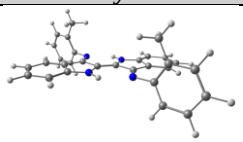
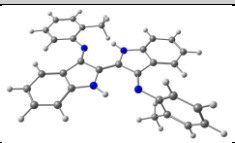
Anti				***Syn***				**TS**			
											
N	0.272377	1.835525	-0.042829	**N**	-0.275189	-1.835596	-0.248999	**N**	-0.046044	-1.609197	-0.105741
N	2.425375	-0.958618	0.182426	**N**	-2.428840	0.967100	-0.233948	**N**	2.404045	0.933750	-0.199339
N	-0.272377	-1.835526	0.042830	**N**	0.275189	1.835595	-0.248998	**N**	-0.123902	2.072279	-0.131671
N	-2.425375	0.958616	-0.182429	**N**	2.428840	-0.967101	-0.233946	**N**	-2.600341	-0.432043	-0.027143
C	0.489191	0.472532	0.017259	**C**	-0.490875	-0.471107	-0.253923	**C**	0.309607	-0.281678	-0.130588
C	1.938767	0.236739	0.112414	**C**	-1.942686	-0.230492	-0.238585	**C**	1.779445	-0.199712	-0.171572
C	2.542413	1.578598	0.100897	**C**	-2.548797	-1.571239	-0.227358	**C**	2.237334	-1.598611	-0.169926
C	3.859577	2.034623	0.175762	**C**	-3.869591	-2.022859	-0.223795	**C**	3.499827	-2.193475	-0.212675
C	4.100272	3.405000	0.142271	**C**	-4.112261	-3.393285	-0.217830	**C**	3.589604	-3.582294	-0.202702
C	3.037441	4.311035	0.038204	**C**	-3.048001	-4.303601	-0.218483	**C**	2.432768	-4.370697	-0.153847
C	1.715071	3.881616	-0.031772	**C**	-1.722445	-3.878422	-0.227884	**C**	1.162994	-3.801795	-0.117140
C	1.477531	2.510075	0.002468	**C**	-1.482966	-2.506804	-0.233968	**C**	1.077570	-2.412028	-0.127657
C	3.823133	-1.149631	0.223865	**C**	0.490874	0.471107	-0.253922	**C**	-0.563537	0.771662	-0.107920
C	4.446748	-1.404415	1.447808	**C**	1.482965	2.506803	-0.233965	**C**	-1.190100	2.931578	-0.101313
C	5.819630	-1.620155	1.508166	**C**	1.722445	3.878421	-0.227880	**C**	-1.132566	4.323938	-0.114088
C	6.576110	-1.602054	0.340005	**C**	3.048001	4.303600	-0.218477	**C**	-2.325448	5.028600	-0.076347
C	5.947618	-1.373115	-0.881918	**C**	4.112260	3.393284	-0.217822	**C**	-3.546813	4.349690	-0.026899
C	4.574076	-1.143224	-0.967353	**C**	3.869591	2.022858	-0.223788	**C**	-3.592189	2.960688	-0.014894
C	3.903538	-0.877670	-2.288998	**C**	2.548796	1.571238	-0.227354	**C**	-2.413746	2.199254	-0.052032
C	-0.489191	-0.472534	-0.017260	**C**	-3.825227	1.160497	-0.165909	**C**	3.814392	0.966860	-0.184226
C	-1.938767	-0.236740	-0.112415	**C**	-4.486119	1.115044	1.076724	**C**	4.510105	1.180707	-1.376830
C	-2.542413	-1.578599	-0.100893	**C**	-4.536768	1.456034	-1.331313	**C**	4.513039	0.846977	1.032718
C	-3.859577	-2.034624	-0.175753	**C**	-5.861540	1.348211	1.100734	**C**	5.899787	1.241759	-1.381512
C	-4.100273	-3.405000	-0.142259	**C**	-5.909736	1.674241	-1.282828	**C**	5.905933	0.922569	1.003453
C	-3.037441	-4.311036	-0.038193	**C**	-6.577913	1.617753	-0.063174	**C**	6.603321	1.109295	-0.187908
C	-1.715072	-3.881617	0.031779	**C**	1.942686	0.230491	-0.238583	**C**	-2.042537	0.751775	-0.055010
C	-1.477531	-2.510076	-0.002464	**C**	3.825227	-1.160497	-0.165910	**C**	-3.913204	-0.870025	0.021663
C	-3.823134	1.149627	-0.223870	**C**	4.486120	-1.115046	1.076723	**C**	-4.095166	-2.284948	0.036417
C	-4.446752	1.404384	-1.447818	**C**	4.536768	-1.456029	-1.331315	**C**	-5.070995	-0.072390	0.057500
C	-5.819634	1.620121	-1.508176	**C**	5.861541	-1.348211	1.100732	**C**	-5.382810	-2.812669	0.084203
C	-6.576112	1.602043	-0.340013	**C**	5.909736	-1.674236	-1.282832	**C**	-6.345018	-0.618113	0.105028
C	-5.947617	1.373130	0.881914	**C**	6.577914	-1.617751	-0.063178	**C**	-6.510895	-1.998504	0.118705
C	-4.574074	1.143243	0.967349	**C**	3.720523	-0.805559	2.335706	**H**	4.392871	-1.585969	-0.253263
C	-3.903531	0.877714	2.288998	**C**	-3.720521	0.805557	2.335706	**H**	4.561853	-4.057949	-0.234229
H	4.678831	1.334292	0.258531	**H**	-4.690087	-1.319106	-0.226418	**H**	2.525828	-5.450694	-0.146414
H	5.116684	3.774050	0.198148	**H**	-5.131403	-3.758996	-0.213940	**H**	0.272192	-4.416819	-0.083461
H	3.246524	5.374413	0.013091	**H**	-3.258611	-5.366963	-0.213480	**H**	-0.175830	4.830651	-0.152436
H	0.898266	4.588902	-0.108452	**H**	-0.904822	-4.588901	-0.231915	**H**	-2.309573	6.112174	-0.085233
H	3.840760	-1.417582	2.345922	**H**	0.904822	4.588900	-0.231913	**H**	-4.473757	4.908720	0.002514
H	6.293849	-1.804164	2.465304	**H**	3.258611	5.366961	-0.213474	**H**	-4.567653	2.511345	0.023686
H	7.645236	-1.774558	0.376527	**H**	5.131402	3.758995	-0.213930	**H**	-1.022600	-1.863615	-0.070603
H	6.534092	-1.368844	-1.794885	**H**	4.690086	1.319104	-0.226410	**H**	6.452202	0.830001	1.936472
H	3.586584	0.166801	-2.371985	**H**	0.666618	-2.209014	-0.258018	**H**	7.685650	1.160936	-0.180862
H	3.006105	-1.491154	-2.403486	**H**	-6.452837	1.890077	-2.195687	**H**	0.870639	2.278020	-0.176163
H	4.580536	-1.090336	-3.117863	**H**	-7.646320	1.791803	-0.014856	**H**	-5.502197	-3.890672	0.094576
H	-0.667267	2.205177	-0.126291	**H**	-0.666619	2.209013	-0.258017	**H**	-7.206898	0.038812	0.131273
H	-4.678832	-1.334292	-0.258521	**H**	6.378994	-1.313892	2.053908	**H**	-7.501027	-2.436857	0.155619
H	-5.116685	-3.774050	-0.198132	**H**	6.452836	-1.890068	-2.195691	**H**	6.428603	1.395033	-2.315180
H	-3.246525	-5.374413	-0.013077	**H**	7.646320	-1.791800	-0.014861	**H**	3.944751	1.284161	-2.295342
H	-0.898267	-4.588904	0.108459	**H**	-6.378992	1.313891	2.053911	**H**	-4.971528	0.992428	0.048037
H	-3.840766	1.417533	-2.345934	**H**	3.998715	-1.498499	-2.270826	**C**	-2.923897	-3.226646	0.001500
H	-6.293856	1.804109	-2.465317	**H**	-3.998716	1.498506	-2.270824	**H**	-2.328394	-3.087064	-0.906316
H	-7.645238	1.774545	-0.376536	**H**	3.401822	0.241381	2.360815	**H**	-2.268487	-3.077818	0.865558
H	-6.534088	1.368877	1.794882	**H**	2.814997	-1.414103	2.403341	**H**	-3.263659	-4.263283	0.018466
H	-3.586576	-0.166756	2.372001	**H**	4.333620	-0.991556	3.218932	**C**	3.766390	0.627224	2.321552
H	-3.006099	1.491201	2.403471	**H**	-3.401821	-0.241383	2.360815	**H**	2.937751	1.333260	2.419730
H	-4.580527	1.090393	3.117860	**H**	-2.814995	1.414100	2.403341	**H**	3.334002	-0.377441	2.365125
H	0.667268	-2.205178	0.126288	**H**	-4.333617	0.991554	3.218933	**H**	4.429789	0.745171	3.179797

Table G3 XYZ coordinates of the GS and TS geometries of **2.1b** B3LYP/6-311G(d,p) (gas phase)

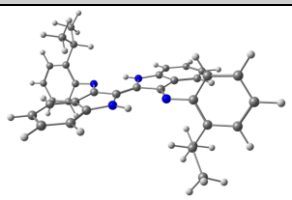
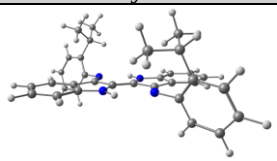
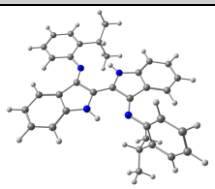
Anti				***Syn***				**TS**			
											
N	0.028113	-1.816425	-0.381579	**N**	0.013505	1.861578	-0.473205	**N**	-2.716663	0.141467	-0.082602
N	2.502354	0.545050	0.505645	**N**	2.452017	-0.693163	-0.564192	**N**	0.172103	2.141218	-0.386457
N	-0.028112	1.816423	0.381572	**N**	-0.139560	-1.846820	-0.561796	**N**	2.446469	0.593945	-0.497985
N	-2.502355	-0.545055	-0.505642	**N**	-2.571791	0.710139	-0.401610	**N**	-0.385314	-1.489195	-0.162181
C	0.418932	-0.534502	-0.046021	**C**	0.375467	0.529120	-0.522489	**C**	-3.608847	-2.556501	0.051547
C	1.871690	-0.537549	0.186247	**C**	1.844135	0.447702	-0.549147	**C**	-4.568999	-1.381201	0.060750
C	2.293786	-1.925019	-0.070310	**C**	2.302705	1.846684	-0.501792	**C**	-5.939542	-1.609716	0.162233
C	3.535073	-2.563917	-0.073147	**C**	3.565521	2.440125	-0.451689	**C**	-6.864929	-0.571359	0.212632
C	3.598736	-3.912429	-0.410597	**C**	3.656248	3.826353	-0.371699	**C**	-6.409784	0.739599	0.154915
C	2.435314	-4.618624	-0.740853	**C**	2.498978	4.614657	-0.342765	**C**	-5.050578	0.991546	0.053426
C	1.186919	-4.003337	-0.752538	**C**	1.228715	4.047258	-0.382061	**C**	-4.090595	-0.034020	0.008406
C	1.127781	-2.652410	-0.420333	**C**	1.142062	2.659712	-0.455820	**C**	-0.715032	3.182884	-0.360630
C	3.880939	0.516438	0.794981	**C**	-0.499502	-0.513636	-0.526289	**C**	-0.396555	4.537045	-0.445341
C	4.793746	1.113319	-0.096328	**C**	-1.268319	-2.643665	-0.527782	**C**	-1.430532	5.457626	-0.391567
C	6.147757	1.099864	0.245061	**C**	-1.357326	-4.033199	-0.515763	**C**	-2.752348	5.024574	-0.253005
C	6.596929	0.533667	1.435341	**C**	-2.626826	-4.599435	-0.444719	**C**	-3.057427	3.671037	-0.171124
C	5.680890	-0.030238	2.319562	**C**	-3.781327	-3.808861	-0.383244	**C**	-2.048982	2.694692	-0.226285
C	4.328897	-0.037423	1.999887	**C**	-3.688755	-2.420547	-0.401342	**C**	-1.951430	1.199668	-0.176353
C	4.288229	1.682877	-1.409287	**C**	-2.427449	-1.828056	-0.481655	**C**	-0.494217	0.945544	-0.280384
C	5.108979	2.871703	-1.920589	**C**	3.857075	-0.758570	-0.648105	**C**	4.167650	1.162093	1.709707
C	4.202021	0.576984	-2.477338	**C**	4.603949	-1.183020	0.468094	**C**	4.720721	0.719064	0.367380
C	-0.418932	0.534499	0.046017	**C**	4.496697	-0.473116	-1.859853	**C**	6.087878	0.551487	0.137108
C	-1.871690	0.537545	-0.186250	**C**	5.991016	-1.272137	0.333276	**C**	6.574230	0.102898	-1.088155
C	-2.293785	1.925016	0.070301	**C**	5.877737	-0.577697	-1.969688	**C**	5.684504	-0.181667	-2.120876
C	-3.535072	2.563915	0.073135	**C**	6.630688	-0.971282	-0.866483	**C**	4.318840	-0.031040	-1.915186
C	-3.598734	3.912428	0.410579	**C**	-1.967628	-0.430117	-0.480423	**C**	3.830394	0.402187	-0.677050
C	-2.435312	4.618624	0.740833	**C**	-3.979577	0.777586	-0.440221	**C**	0.585074	-2.470428	-0.168481
C	-1.186918	4.003337	0.752522	**C**	-4.729635	1.112664	0.705362	**C**	0.438345	-3.850076	-0.046513
C	-1.127780	2.652408	0.420322	**C**	-4.626016	0.572418	-1.666373	**C**	1.593507	-4.626125	-0.054618
C	-3.880941	-0.516443	-0.794976	**C**	-6.118569	1.197698	0.568764	**C**	2.863554	-4.049133	-0.180109
C	-4.793747	-1.113318	0.096339	**C**	-6.006983	0.671899	-1.772668	**C**	3.004920	-2.671106	-0.312974
C	-6.147758	-1.099864	-0.245048	**C**	-6.762730	0.980650	-0.645460	**C**	1.860685	-1.870651	-0.315233
C	-6.596931	-0.533675	-1.435331	**C**	3.891321	-1.461603	1.779035	**C**	1.642566	-0.416297	-0.395066
C	-5.680893	0.030224	-2.319558	**C**	-4.107856	1.348523	2.073126	**C**	0.184100	-0.243372	-0.280270
C	-4.328899	0.037410	-1.999885	**C**	4.568584	-2.541384	2.629882	**H**	1.184742	2.156002	-0.482484
C	-4.288229	-1.682865	1.409302	**C**	3.715931	-0.160571	2.583822	**H**	-2.813496	-2.299285	-0.652320
C	-5.108979	-2.871687	1.920614	**C**	-3.481448	0.074828	2.666217	**H**	-6.301570	-2.628602	0.201861
C	-4.202020	-0.576963	2.477344	**C**	-3.112537	2.520189	2.089263	**H**	-7.923612	-0.788086	0.292581
H	-0.937494	-2.015971	-0.614408	**H**	4.458485	1.832108	-0.477165	**H**	-7.107601	1.568479	0.187795
H	4.432329	-2.019544	0.184447	**H**	4.629251	4.299896	-0.333451	**H**	-4.722001	2.006805	0.008960
H	4.554877	-4.420563	-0.416126	**H**	2.591704	5.693084	-0.284137	**H**	0.635876	4.848482	-0.548699
H	2.506127	-5.669423	-0.997513	**H**	0.337190	4.661485	-0.348679	**H**	-1.211759	6.517116	-0.455146
H	0.292059	-4.553315	-1.017281	**H**	-0.468166	-4.650677	-0.553779	**H**	-3.555651	5.749295	-0.207219
H	6.868428	1.542406	-0.431869	**H**	-2.720955	-5.679293	-0.433303	**H**	-4.097414	3.425443	-0.060187
H	7.653975	0.542251	1.673918	**H**	-4.753290	-4.282293	-0.323119	**H**	-1.380599	-1.575828	-0.025858
H	6.015893	-0.463063	3.255172	**H**	-4.579205	-1.809862	-0.357262	**H**	3.226459	1.680490	1.500090
H	3.601162	-0.471824	2.675179	**H**	-0.962962	2.131210	-0.466853	**H**	6.789625	0.777482	0.930814
H	3.267522	2.031657	-1.221672	**H**	3.893896	-0.168144	-2.707164	**H**	7.641266	-0.013549	-1.237275
H	5.210475	3.645382	-1.155556	**H**	6.362031	-0.352758	-2.912970	**H**	6.050688	-0.519318	-3.083601
H	4.621755	3.315724	-2.792572	**H**	7.708663	-1.053673	-0.940753	**H**	3.610829	-0.248135	-2.706305
H	6.113027	2.568772	-2.231049	**H**	0.836307	-2.117059	-0.590522	**H**	-0.540465	-4.301657	0.052391
H	5.197552	0.177813	-2.693907	**H**	-6.707238	1.441793	1.447071	**H**	1.505263	-5.702326	0.040517
H	3.782079	0.969522	-3.408093	**H**	-6.487412	0.508024	-2.730368	**H**	3.742691	-4.681275	-0.177835
H	3.575285	-0.251820	-2.144009	**H**	-7.841394	1.060314	-0.710591	**H**	3.985178	-2.228282	-0.415026
H	0.937495	2.015970	0.614399	**H**	6.586074	-1.584873	1.182718	**C**	-4.212679	-3.871097	-0.458147
H	-4.432328	2.019541	-0.184457	**H**	2.889622	-1.816948	1.516260	**H**	-3.422763	-4.618526	-0.570361
H	-4.554875	4.420562	0.416106	**H**	-4.020728	0.331904	-2.532476	**H**	-4.948138	-4.282392	0.238267
H	-2.506125	5.669424	0.997489	**H**	-4.939291	1.628108	2.729414	**H**	-4.695600	-3.741238	-1.429319
H	-0.292057	4.553316	1.017262	**H**	3.941640	-2.787370	3.490872	**C**	5.084691	2.131944	2.462720
H	-6.868429	-1.542400	0.431886	**H**	4.734496	-3.456393	2.055961	**H**	5.363992	2.983881	1.837931
H	-7.653978	-0.542260	-1.673907	**H**	5.534184	-2.205863	3.018843	**H**	4.576650	2.513049	3.352407
H	-6.015897	0.463041	-3.255170	**H**	4.691353	0.250716	2.860751	**H**	6.003495	1.643598	2.799733
H	-3.601166	0.471805	-2.675182	**H**	3.185736	0.598194	2.006002	**C**	-3.015480	-2.755827	1.460488
H	-3.267521	-2.031647	1.221689	**H**	3.151109	-0.346668	3.502007	**H**	-2.272415	-3.558281	1.472387
H	-5.210475	-3.645372	1.155586	**H**	-4.190714	-0.755910	2.650619	**H**	-2.545470	-1.843455	1.830512
H	-4.621754	-3.315701	2.792600	**H**	-2.594009	-0.229953	2.110860	**H**	-3.812841	-3.026832	2.157498
H	-6.113027	-2.568754	2.231071	**H**	-3.182914	0.249700	3.703962	**C**	3.828795	-0.060476	2.582373
H	-5.197551	-0.177790	2.693910	**H**	-2.220404	2.282192	1.510194	**H**	3.132642	-0.731333	2.076393
H	-3.782078	-0.969493	3.408102	**H**	-3.564874	3.422866	1.670991	**H**	4.735478	-0.628954	2.810667
H	-3.575284	0.251838	2.144007	**H**	-2.803447	2.737008	3.115836	**H**	3.375388	0.252411	3.527491

Table G4 XYZ coordinates of the GS and TS geometries of **2.1c** B3LYP/6-311G(d,p) (gas phase)

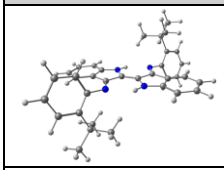
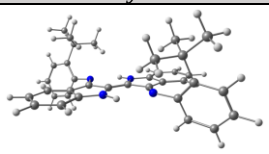
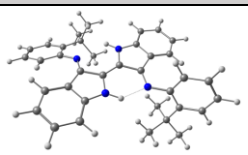
Anti				***Syn***				**TS**			
											
N	-0.048507	1.797281	-0.462368	**N**	0.018853	-1.856340	-0.571259	**N**	-2.760776	0.175467	-0.291040
N	2.527246	-0.417046	0.511472	**N**	-2.547741	0.570733	-0.525131	**N**	0.179824	2.101320	-0.354052
N	0.048504	-1.797291	0.462364	**N**	-0.018857	1.856330	-0.571249	**N**	2.439049	0.585062	-0.401704
N	-2.527247	0.417038	-0.511475	**N**	2.547742	-0.570739	-0.525132	**N**	-0.379849	-1.521144	-0.740968
C	4.045741	-0.573431	-2.274647	**C**	-5.432618	1.617242	2.786414	**C**	-3.823380	-2.441981	0.570729
C	5.952613	-2.116975	-1.889830	**C**	-3.584060	-0.000781	2.424411	**C**	-4.657195	-1.154948	0.464961
C	3.704411	-2.762069	-1.056749	**C**	-3.314185	2.427823	1.777100	**C**	-6.008914	-1.196870	0.810687
C	-3.704405	2.762091	1.056719	**C**	3.584067	0.000782	2.424407	**C**	-6.857046	-0.097540	0.710305
C	-5.952599	2.117000	1.889825	**C**	5.432627	-1.617240	2.786408	**C**	-6.347987	1.102855	0.240566
C	-4.045720	0.573464	2.274641	**C**	3.314193	-2.427822	1.777097	**C**	-5.007576	1.179975	-0.100680
C	0.396473	0.548628	-0.072107	**C**	-0.410479	-0.543075	-0.570788	**C**	-4.121336	0.095751	0.003507
C	1.846434	0.626096	0.163772	**C**	-1.881460	-0.536385	-0.577327	**C**	-0.684976	3.160830	-0.428159
C	2.207478	2.019180	-0.144236	**C**	-2.267873	-1.956483	-0.583227	**C**	-0.333901	4.509085	-0.432425
C	3.420580	2.709650	-0.170910	**C**	-3.498957	-2.613385	-0.539187	**C**	-1.339803	5.446096	-0.608687
C	3.428457	4.042534	-0.569736	**C**	-3.519742	-4.004248	-0.510359	**C**	-2.660810	5.032589	-0.801897
C	2.237913	4.682184	-0.937965	**C**	-2.324303	-4.734232	-0.524861	**C**	-2.999077	3.684277	-0.776745
C	1.017174	4.013832	-0.927666	**C**	-1.084287	-4.103053	-0.556063	**C**	-2.027107	2.697249	-0.541287
C	1.014688	2.678524	-0.533804	**C**	-1.067900	-2.711104	-0.578338	**C**	-1.966312	1.198955	-0.461257
C	3.888806	-0.298508	0.860631	**C**	0.410476	0.543065	-0.570785	**C**	-0.505181	0.914603	-0.470148
C	4.182449	0.339491	2.074159	**C**	1.067895	2.711095	-0.578322	**C**	4.226283	0.806715	1.998850
C	5.486913	0.459226	2.529667	**C**	1.084280	4.103044	-0.556037	**C**	4.721115	0.559761	0.561757
C	6.521438	-0.065243	1.764273	**C**	2.324296	4.734224	-0.524832	**C**	6.087204	0.425131	0.284150
C	6.231432	-0.710425	0.565315	**C**	3.519736	4.004241	-0.510336	**C**	6.578226	0.189603	-0.996977
C	4.926974	-0.858564	0.077937	**C**	3.498952	2.613378	-0.539173	**C**	5.693172	0.084780	-2.063303
C	4.659018	-1.566384	-1.263010	**C**	2.267868	1.956476	-0.583216	**C**	4.332216	0.204248	-1.824972
C	-0.396475	-0.548638	0.072103	**C**	-3.952371	0.567835	-0.654256	**C**	3.834092	0.426815	-0.533410
C	-1.846437	-0.626104	-0.163774	**C**	-4.815220	0.912964	0.413632	**C**	0.605381	-2.485808	-0.791203
C	-2.207481	-2.019187	0.144237	**C**	-4.475602	0.280880	-1.922993	**C**	0.475591	-3.869389	-0.894679
C	-3.420585	-2.709656	0.170915	**C**	-6.187828	0.917991	0.136129	**C**	1.640481	-4.629837	-0.892928
C	-3.428461	-4.042540	0.569743	**C**	-5.841437	0.304546	-2.162747	**C**	2.905047	-4.035851	-0.786889
C	-2.237917	-4.682192	0.937969	**C**	-6.705654	0.619836	-1.121181	**C**	3.030500	-2.654157	-0.689738
C	-1.017177	-4.013840	0.927666	**C**	1.881458	0.536377	-0.577323	**C**	1.876148	-1.867669	-0.698434
C	-1.014691	-2.678533	0.533802	**C**	3.952371	-0.567834	-0.654260	**C**	1.640398	-0.423821	-0.559488
C	-3.888809	0.298503	-0.860629	**C**	4.815224	-0.912962	0.413626	**C**	0.173513	-0.269904	-0.569747
C	-4.182459	-0.339511	-2.074148	**C**	4.475599	-0.280870	-1.922996	**H**	1.197752	2.102133	-0.399728
C	-5.486926	-0.459248	-2.529648	**C**	6.187832	-0.917977	0.136122	**H**	-6.430123	-2.122549	1.172527
C	-6.521446	0.065233	-1.764256	**C**	5.841434	-0.304528	-2.162752	**H**	-7.899615	-0.190114	0.990985
C	-6.231432	0.710430	-0.565308	**C**	6.705654	-0.619816	-1.121187	**H**	-6.981452	1.976526	0.138825
C	-4.926972	0.858572	-0.077938	**C**	4.292352	-1.234330	1.825848	**H**	-4.628304	2.109046	-0.462157
C	-4.659008	1.566406	1.263000	**C**	-4.292345	1.234332	1.825853	**H**	0.702987	4.802381	-0.321916
H	3.919401	-1.062295	-3.245229	**H**	-5.008903	1.853666	3.765262	**H**	-1.095431	6.501779	-0.622478
H	4.700396	0.290846	-2.412238	**H**	-6.144218	0.799380	2.924814	**H**	-3.434959	5.766596	-0.987408
H	3.071105	-0.212463	-1.953810	**H**	-5.979480	2.497933	2.440202	**H**	-4.024090	3.446429	-0.999322
H	5.706731	-2.623694	-2.825977	**H**	-3.274480	0.210337	3.452292	**H**	-1.373857	-1.665733	-0.698929
H	6.444451	-2.843842	-1.238465	**H**	-2.696711	-0.277487	1.859462	**H**	6.800053	0.505767	1.091903
H	6.665598	-1.322266	-2.123314	**H**	-4.258056	-0.860941	2.442432	**H**	7.646316	0.097660	-1.155379
H	3.554609	-3.285928	-2.005361	**H**	-2.981501	2.677101	2.788972	**H**	6.054552	-0.088663	-3.070339
H	2.733614	-2.434648	-0.691651	**H**	-3.804250	3.308146	1.352491	**H**	3.620351	0.125259	-2.638085
H	4.126620	-3.470427	-0.338853	**H**	-2.436736	2.195939	1.177685	**H**	-0.497602	-4.336463	-0.970578
H	-3.554596	3.285960	2.005325	**H**	3.274480	-0.210339	3.452284	**H**	1.564524	-5.708321	-0.971725
H	-4.126620	3.470441	0.338820	**H**	2.696724	0.277494	1.859454	**H**	3.791437	-4.657785	-0.782686
H	-2.733609	2.434668	0.691617	**H**	4.258068	0.860939	2.442436	**H**	4.005814	-2.196226	-0.610388
H	-6.665581	1.322292	2.123321	**H**	5.008914	-1.853658	3.765259	**C**	-4.625034	-3.635568	1.127940
H	-6.444442	2.843861	1.238458	**H**	6.144229	-0.799379	2.924802	**H**	-3.967811	-4.507937	1.171341
H	-5.706711	2.623727	2.825967	**H**	5.979485	-2.497935	2.440199	**H**	-4.987944	-3.446985	2.140957
H	-3.919370	1.062338	3.245217	**H**	2.981496	-2.677088	2.788968	**H**	-5.475859	-3.896992	0.494583
H	-3.071086	0.212494	1.953797	**H**	3.804263	-3.308150	1.352505	**C**	5.394509	0.944399	2.991806
H	-4.700372	-0.290812	2.412247	**H**	2.436752	-2.195944	1.177669	**H**	6.052765	1.778219	2.734888
H	4.338030	2.216482	0.116873	**H**	-4.420775	-2.049535	-0.532402	**H**	4.992573	1.134868	3.989673
H	4.361708	4.591123	-0.593584	**H**	-4.467319	-4.527309	-0.479053	**H**	5.995013	0.032900	3.047334
H	2.265443	5.722343	-1.241848	**H**	-2.362737	-5.817385	-0.506479	**C**	-2.635755	-2.244117	1.542106
H	0.101012	4.511485	-1.221260	**H**	-0.163077	-4.672768	-0.554479	**H**	-1.987309	-3.125644	1.536192
H	3.357314	0.739242	2.651655	**H**	0.163070	4.672759	-0.554449	**H**	-2.040589	-1.369133	1.303144
H	5.689268	0.957165	3.470873	**H**	2.362729	5.817377	-0.506443	**H**	-3.019543	-2.119037	2.557895
H	7.549747	0.016778	2.096178	**H**	4.467313	4.527303	-0.479027	**C**	3.357672	-0.378213	2.475243
H	7.056437	-1.110452	-0.006043	**H**	4.420771	2.049529	-0.532392	**H**	2.447824	-0.480667	1.888259
H	-1.014977	1.940336	-0.729059	**H**	1.006571	-2.077176	-0.604278	**H**	3.914144	-1.316454	2.407736
H	-4.338035	-2.216488	-0.116866	**H**	-6.222547	0.078407	-3.151881	**H**	3.067629	-0.229389	3.519596
H	-4.361713	-4.591129	0.593594	**H**	-7.777172	0.643237	-1.281208	**C**	-3.392890	-2.851145	-0.857610
H	-2.265447	-5.722350	1.241853	**H**	-1.006576	2.077165	-0.604261	**H**	-2.960127	-2.024802	-1.419730
H	-0.101016	-4.511494	1.221258	**H**	6.884382	-1.162515	0.924884	**H**	-2.686477	-3.685668	-0.827607
H	-3.357329	-0.739272	-2.651643	**H**	6.222541	-0.078383	-3.151885	**H**	-4.269424	-3.180476	-1.421108
H	-5.689287	-0.957199	-3.470846	**H**	7.777173	-0.643208	-1.281216	**C**	3.410438	2.115779	2.066632
H	-7.549757	-0.016790	-2.096155	**H**	-6.884376	1.162535	0.924891	**H**	2.515717	2.057915	1.451045
H	-7.056434	1.110466	0.006050	**H**	3.779849	-0.038486	-2.717559	**H**	3.103020	2.308775	3.098624
H	1.014975	-1.940348	0.729050	**H**	-3.779854	0.038495	-2.717558	**H**	4.014069	2.961800	1.726961

Table G5 XYZ coordinates of the GS and TS geometries of **2.1d** B3LYP/6-311G(d,p) (gas phase)

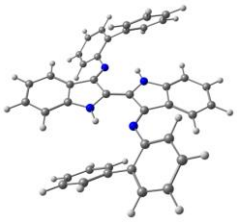
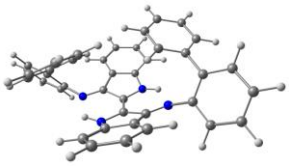
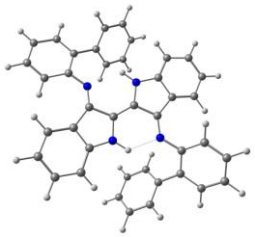
Anti				***Syn***				**TS**			
											
N	-0.885889	-1.576322	-0.412624	**N**	-2.559933	-0.184770	-1.264537	**N**	-2.477110	0.942996	-0.334559
N	2.463975	-0.702286	0.216744	**N**	0.332511	1.826671	-1.513525	**N**	0.964970	1.619958	-0.383087
N	0.885891	1.576318	0.412623	**N**	2.559940	0.184749	-1.264464	**N**	2.419305	-0.660656	-0.433639
N	-2.463972	0.702284	-0.216750	**N**	-0.332488	-1.826698	-1.513553	**N**	-1.003453	-1.505186	-0.497262
C	4.005501	3.588296	-1.455676	**C**	-6.527881	-0.169633	0.099142	**C**	-4.757750	0.350476	0.043763
C	4.842894	3.420046	-0.355560	**C**	-5.535818	-0.853329	0.795950	**C**	-6.116833	0.673023	0.038314
C	3.457618	2.469326	-2.080224	**C**	-6.195293	0.539571	-1.053104	**C**	-6.562544	1.969556	-0.193512
C	5.119529	2.141758	0.123065	**C**	-4.205797	-0.836942	0.368503	**C**	-5.624458	2.977387	-0.390191
C	3.733264	1.193693	-1.601149	**C**	-4.878043	0.571810	-1.497008	**C**	-4.271363	2.674063	-0.409936
C	4.562570	1.009950	-0.486413	**C**	-3.874824	-0.101580	-0.791442	**C**	-3.792639	1.361285	-0.244234
C	-4.005515	-3.588292	1.455677	**C**	-1.742977	0.815008	-1.278297	**C**	0.563369	2.919775	-0.533047
C	-4.842908	-3.420040	0.355562	**C**	6.527883	0.169656	0.099230	**C**	1.387119	4.043384	-0.576020
C	-3.457626	-2.469324	2.080222	**C**	5.535813	0.853359	0.796023	**C**	0.797363	5.270672	-0.836975
C	-5.119538	-2.141752	-0.123065	**C**	6.195301	-0.539570	-1.053005	**C**	-0.579565	5.363437	-1.070774
C	-3.733266	-1.193690	1.601146	**C**	4.205793	0.836958	0.368573	**C**	-1.393474	4.238980	-0.996777
C	-4.562573	-1.009945	0.486410	**C**	4.878052	-0.571824	-1.496910	**C**	-0.853108	2.983596	-0.677137
C	0.104543	-0.667437	-0.112633	**C**	3.874827	0.101571	-0.791358	**C**	-1.353823	1.588253	-0.503926
C	1.395063	-1.372185	-0.089253	**C**	-1.839695	2.230096	-0.884132	**C**	-0.117440	0.777503	-0.434128
C	1.074678	-2.755849	-0.484075	**C**	-2.879546	3.022669	-0.391111	**C**	4.748266	-0.468164	0.086112
C	1.837585	-3.893507	-0.765520	**C**	-2.614452	4.344741	-0.049482	**C**	6.067481	-0.886889	-0.102587
C	1.197226	-5.064675	-1.154092	**C**	-1.326680	4.875924	-0.203192	**C**	6.377334	-1.952655	-0.941148
C	-0.200265	-5.113514	-1.258975	**C**	-0.277032	4.108338	-0.695814	**C**	5.353702	-2.603629	-1.628294
C	-0.985304	-3.994413	-1.009277	**C**	-0.544129	2.784212	-1.029527	**C**	4.033990	-2.215397	-1.446192
C	-0.335614	-2.816703	-0.644263	**C**	-0.315655	0.605641	-1.573910	**C**	3.702011	-1.168781	-0.568397
C	-0.104540	0.667433	0.112629	**C**	0.544138	-2.784241	-1.029532	**C**	-0.497146	-2.786480	-0.443419
C	0.335616	2.816697	0.644268	**C**	0.277031	-4.108370	-0.695838	**C**	-1.191562	-3.994666	-0.431708
C	0.985305	3.994405	1.009288	**C**	1.326662	-4.875956	-0.203180	**C**	-0.454254	-5.164692	-0.302048
C	0.200265	5.113505	1.258989	**C**	2.614426	-4.344770	-0.049417	**C**	0.942738	-5.140144	-0.181953
C	-1.197226	5.064667	1.154103	**C**	2.879530	-3.022697	-0.391029	**C**	1.632885	-3.935203	-0.224639
C	-1.837584	3.893500	0.765525	**C**	1.839698	-2.230123	-0.884088	**C**	0.919511	-2.741764	-0.380132
C	-1.074676	2.755843	0.484079	**C**	1.742991	-0.815033	-1.278251	**C**	1.300485	-1.322336	-0.428724
C	3.744207	-1.193878	0.415326	**C**	0.315677	-0.605667	-1.573903	**C**	0.022965	-0.587907	-0.445254
C	4.823450	-0.334218	0.082836	**H**	-4.611046	1.103339	-2.402660	**H**	1.907385	1.235758	-0.360357
C	4.020567	-2.403270	1.076250	**H**	4.611061	-1.103369	-2.402555	**H**	-6.832755	-0.108224	0.264375
C	6.129326	-0.746659	0.356539	**H**	6.961878	-1.065877	-1.610116	**H**	-7.622769	2.192094	-0.186752
C	5.326431	-2.784890	1.350367	**H**	-7.552385	-0.193625	0.450565	**H**	-5.942988	4.004328	-0.528374
C	6.389968	-1.965749	0.974255	**H**	-5.785548	-1.401970	1.697108	**H**	-3.568946	3.471773	-0.535530
C	-1.395060	1.372180	0.089253	**H**	-6.961866	1.065874	-1.610225	**H**	2.454015	3.940561	-0.420637
C	-3.744202	1.193879	-0.415331	**H**	1.343311	1.825407	-1.395541	**H**	1.412556	6.161834	-0.883767
C	-4.020558	2.403271	-1.076258	**H**	7.552386	0.193661	0.450655	**H**	-1.020474	6.319913	-1.322691
C	-4.823448	0.334223	-0.082841	**H**	5.785538	1.402018	1.697171	**H**	-2.432199	4.366330	-1.248698
C	-5.326421	2.784895	-1.350375	**H**	-1.343292	-1.825438	-1.395606	**H**	-1.969508	-1.212992	-0.424919
C	-6.129322	0.746668	-0.356545	**H**	-3.871457	2.612531	-0.266189	**H**	6.858580	-0.364585	0.423178
C	-6.389961	1.965758	-0.974262	**H**	-3.409074	4.968493	0.340796	**H**	7.407714	-2.261452	-1.070160
H	3.779861	4.582409	-1.823180	**H**	-1.140960	5.907650	0.072938	**H**	5.584445	-3.410529	-2.314510
H	5.274755	4.283965	0.136904	**H**	0.722237	4.513244	-0.791218	**H**	3.245542	-2.692368	-2.012900
H	2.807461	2.591110	-2.938596	**H**	-0.722233	-4.513277	-0.791282	**H**	-2.269593	-4.010505	-0.502049
H	5.749325	2.014791	0.996025	**H**	1.140933	-5.907685	0.072937	**H**	-0.973528	-6.116287	-0.286414
H	3.300423	0.329569	-2.087375	**H**	3.409034	-4.968523	0.340889	**H**	1.488423	-6.067970	-0.062330
H	-3.779879	-4.582405	1.823183	**H**	3.871436	-2.612559	-0.266067	**H**	2.709462	-3.924263	-0.133519
H	-5.274774	-4.283958	-0.136900	**C**	-3.155584	-1.597447	1.093285	**C**	4.451956	0.733060	0.903342
H	-2.807468	-2.591108	2.938593	**C**	-1.972198	-0.981324	1.524177	**C**	3.474385	0.724338	1.907406
H	-5.749334	-2.014783	-0.996025	**C**	-3.317536	-2.967041	1.332106	**C**	5.132850	1.930630	0.647641
H	-3.300421	-0.329567	2.087369	**C**	-0.975507	-1.716842	2.154750	**C**	3.177162	1.879855	2.621024
H	2.915122	-3.866145	-0.688653	**H**	-1.835023	0.079836	1.360853	**H**	2.944308	-0.193950	2.122319
H	1.782686	-5.949135	-1.372721	**C**	-2.319011	-3.704118	1.965156	**C**	4.835440	3.088520	1.361842
H	-0.679768	-6.041714	-1.548326	**H**	-4.223058	-3.457979	0.994113	**H**	5.879270	1.955645	-0.137865
H	-2.064254	-4.024065	-1.097254	**C**	-1.141648	-3.083234	2.371276	**C**	3.851503	3.068294	2.347323
H	2.064254	4.024057	1.097267	**H**	-0.064511	-1.226266	2.476350	**H**	2.412348	1.854628	3.388383
H	0.679768	6.041704	1.548345	**H**	-2.456986	-4.766915	2.128569	**H**	5.366155	4.007848	1.141423
H	-1.782686	5.949126	1.372735	**H**	-0.354709	-3.658621	2.843459	**H**	3.610307	3.970671	2.896670
H	-2.915120	3.866138	0.688657	**C**	3.155578	1.597473	1.093342	**C**	-4.394593	-1.029045	0.456295
H	-1.856315	-1.286082	-0.463071	**C**	1.972185	0.981361	1.524228	**C**	-5.013010	-2.137380	-0.135642
H	5.514033	-3.719803	1.866088	**C**	3.317539	2.967067	1.332159	**C**	-3.545298	-1.245490	1.551579
H	7.411322	-2.266344	1.174637	**C**	0.975495	1.716889	2.154792	**C**	-4.817124	-3.420285	0.371070
H	1.856316	1.286077	0.463076	**H**	1.835003	-0.079798	1.360910	**H**	-5.660411	-1.986399	-0.991650
H	-5.514020	3.719808	-1.866097	**C**	2.319016	3.704153	1.965200	**C**	-3.346917	-2.525725	2.054822
H	-6.949705	0.096628	-0.074565	**H**	4.223067	3.457997	0.994169	**H**	-3.057052	-0.397620	2.014097
H	-7.411314	2.266356	-1.174644	**C**	1.141645	3.083281	2.371314	**C**	-3.992011	-3.616786	1.474849
H	6.949706	-0.096616	0.074561	**H**	0.064493	1.226321	2.476387	**H**	-5.311570	-4.264263	-0.096401
H	3.194906	-3.017851	1.409201	**H**	2.456998	4.766951	2.128610	**H**	-2.691698	-2.672646	2.905207
H	-3.194895	3.017849	-1.409208	**H**	0.354708	3.658675	2.843491	**H**	-3.838626	-4.613116	1.872180

Table G6 XYZ coordinates of the GS and TS geometries of **2.1e** B3LYP/6-311G(d,p) (gas phase)

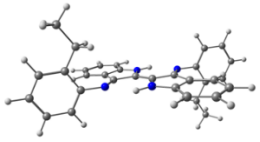
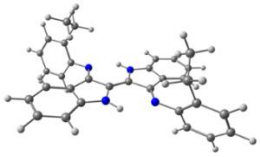
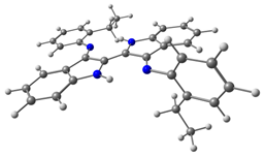
Anti				***Syn***				**TS**			
											
N	-0.203531	1.833431	0.207613	**N**	-0.193624	-1.845941	-0.382129	**N**	-2.670354	-0.089326	-0.030727
N	-2.439906	-0.822000	-0.456379	**N**	-2.464771	0.860760	-0.358166	**N**	0.004099	2.191177	-0.292876
N	0.203528	-1.833424	-0.207624	**N**	0.193627	1.845943	-0.382101	**N**	2.423084	0.845278	-0.433354
N	2.439904	0.822006	0.456370	**N**	2.464774	-0.860756	-0.358159	**N**	-0.221917	-1.481529	-0.176660
C	-5.022254	-1.394357	3.015882	**C**	-3.654176	0.335264	2.825064	**C**	-3.211668	-2.831889	0.047059
C	5.022283	1.394326	-3.015874	**C**	3.654154	-0.335299	2.825084	**C**	-4.321597	-1.807974	0.116298
C	-0.467454	0.494199	-0.005862	**C**	-0.469788	-0.492506	-0.390670	**C**	-5.650552	-2.208656	0.220281
C	-1.912996	0.336512	-0.232609	**C**	-1.930575	-0.316359	-0.379212	**C**	-6.695430	-1.289871	0.285873
C	-2.464111	1.696755	-0.126191	**C**	-2.476957	-1.683424	-0.347717	**C**	-6.405750	0.067877	0.246177
C	-3.754524	2.216538	-0.240802	**C**	-3.773889	-2.194963	-0.276503	**C**	-5.088691	0.489975	0.142443
C	-3.945356	3.585459	-0.076961	**C**	-3.952709	-3.573802	-0.219841	**C**	-4.013372	-0.411990	0.074631
C	-2.859616	4.426985	0.195410	**C**	-2.848605	-4.435252	-0.234694	**C**	-0.982389	3.139338	-0.236019
C	-1.562913	3.933453	0.310118	**C**	-1.545397	-3.950389	-0.296415	**C**	-0.805533	4.520912	-0.282808
C	-1.375280	2.563592	0.146314	**C**	-1.369990	-2.569945	-0.346731	**C**	-1.929803	5.327691	-0.207044
C	-3.835631	-0.935957	-0.637676	**C**	0.469790	0.492509	-0.390659	**C**	-3.201151	4.758551	-0.086181
C	-4.359232	-0.966049	-1.931314	**C**	1.369992	2.569948	-0.346686	**C**	-3.365532	3.379217	-0.041293
C	-5.729140	-1.102808	-2.133404	**C**	1.545398	3.950390	-0.296349	**C**	-2.260647	2.516481	-0.116423
C	-6.578802	-1.226144	-1.039563	**C**	2.848606	4.435253	-0.234613	**C**	-2.014957	1.041508	-0.104492
C	-6.050941	-1.218453	0.250964	**C**	3.952710	3.573802	-0.219765	**C**	-0.542689	0.933790	-0.219183
C	-4.682495	-1.074176	0.481103	**C**	3.773890	2.194964	-0.276448	**C**	3.857400	0.630433	2.022326
C	-4.077800	-1.041336	1.868507	**C**	2.476959	1.683426	-0.347677	**C**	4.583573	0.674100	0.694815
C	0.467452	-0.494191	0.005849	**C**	-3.864109	1.016518	-0.407661	**C**	5.973418	0.620586	0.585989
C	1.912994	-0.336505	0.232598	**C**	-4.555760	1.453680	0.736794	**C**	6.611432	0.644035	-0.653621
C	2.464108	-1.696748	0.126181	**C**	-4.552322	0.812293	-1.609391	**C**	5.855661	0.738073	-1.817074
C	3.754521	-2.216531	0.240792	**C**	-5.935474	1.645353	0.643414	**C**	4.468011	0.801242	-1.735440
C	3.945353	-3.585452	0.076952	**C**	-5.925430	1.014993	-1.678587	**C**	3.830432	0.754543	-0.494507
C	2.859613	-4.426979	-0.195418	**C**	-6.624469	1.428036	-0.546461	**C**	0.830403	-2.374855	-0.215928
C	1.562910	-3.933446	-0.310126	**C**	1.930577	0.316362	-0.379194	**C**	0.802210	-3.765822	-0.161340
C	1.375277	-2.563585	-0.146324	**C**	3.864112	-1.016513	-0.407647	**C**	2.019018	-4.438875	-0.223182
C	3.835628	0.935960	0.637678	**C**	4.555756	-1.453687	0.736808	**C**	3.233653	-3.750673	-0.338132
C	4.359217	0.966058	1.931321	**C**	4.552333	-0.812271	-1.609369	**C**	3.257392	-2.360032	-0.392798
C	5.729124	1.102813	2.133422	**C**	5.935472	-1.645356	0.643435	**C**	2.049914	-1.661939	-0.328215
C	6.578796	1.226140	1.039587	**C**	5.925442	-1.014968	-1.678558	**C**	1.707693	-0.230285	-0.353761
C	6.050946	1.218441	-0.250944	**C**	6.624474	-1.428023	-0.546433	**C**	0.239018	-0.188884	-0.251042
C	4.682501	1.074167	-0.481094	**C**	3.825498	-1.647163	2.042081	**H**	1.009863	2.310047	-0.381856
C	4.077818	1.041319	-1.868504	**C**	-3.825510	1.647138	2.042075	**H**	-2.523851	-2.644123	0.880197
H	-5.844264	-0.678469	3.099235	**H**	-3.121902	0.507685	3.764454	**H**	-2.641588	-2.653699	-0.872109
H	-4.481763	-1.384806	3.965079	**H**	-3.089974	-0.397646	2.245244	**H**	-5.884605	-3.264436	0.251416
H	-5.455269	-2.390099	2.887166	**H**	-4.626808	-0.105333	3.059480	**H**	-7.719294	-1.635266	0.366631
H	5.844291	0.678435	-3.099214	**H**	3.121873	-0.507732	3.764468	**H**	-7.201208	0.802633	0.295489
H	5.455300	2.390068	-2.887162	**H**	3.089953	0.397616	2.245268	**H**	-4.889035	1.539935	0.113281
H	4.481800	1.384770	-3.965075	**H**	4.626782	0.105300	3.059512	**H**	0.188683	4.941100	-0.375392
H	-4.591215	1.566186	-0.453925	**H**	-4.625538	-1.529877	-0.267398	**H**	-1.821018	6.405408	-0.241035
H	-4.940480	4.003691	-0.162028	**H**	-4.953157	-3.984382	-0.165435	**H**	-4.074131	5.396432	-0.025912
H	-3.029853	5.490355	0.319505	**H**	-3.009661	-5.506451	-0.193749	**H**	-4.373487	3.019121	0.054523
H	-0.728137	4.591290	0.519193	**H**	-0.695636	-4.622117	-0.298639	**H**	-1.212126	-1.656718	-0.089080
H	-3.678857	-0.870432	-2.769182	**H**	0.695637	4.622118	-0.298570	**H**	3.107622	1.429121	2.024685
H	-6.126682	-1.114044	-3.141718	**H**	3.009661	5.506452	-0.193652	**H**	3.279347	-0.299747	2.075075
H	-7.646894	-1.336730	-1.185398	**H**	4.953158	3.984382	-0.165348	**H**	6.574194	0.556937	1.484558
H	-6.722573	-1.324906	1.093561	**H**	4.625539	1.529879	-0.267346	**H**	7.692885	0.597683	-0.705220
H	-3.657890	-0.043838	2.044259	**H**	0.764076	-2.176418	-0.376830	**H**	6.340301	0.763969	-2.786267
H	-3.215151	-1.716528	1.878017	**H**	-6.446646	0.852300	-2.614978	**H**	3.859676	0.876027	-2.628962
H	0.739549	2.148983	0.401166	**H**	-7.694942	1.589694	-0.592516	**H**	-0.134031	-4.303248	-0.073908
H	4.591212	-1.566179	0.453914	**H**	-0.764074	2.176420	-0.376804	**H**	2.023940	-5.522128	-0.182356
H	4.940477	-4.003684	0.162020	**H**	6.475685	-1.973859	1.525673	**H**	4.162042	-4.305909	-0.386350
H	3.029850	-5.490348	-0.319512	**H**	6.446664	-0.852262	-2.614944	**H**	4.194910	-1.830140	-0.484577
H	0.728133	-4.591283	-0.519201	**H**	7.694948	-1.589679	-0.592483	**C**	-3.629983	-4.301446	0.083706
H	3.678835	0.870449	2.769182	**H**	-6.475693	1.973846	1.525652	**H**	-2.747079	-4.942511	0.023198
H	6.126657	1.114055	3.141738	**H**	3.994066	-0.492934	-2.481544	**H**	-4.155221	-4.550537	1.009059
H	7.646887	1.336723	1.185430	**H**	-3.994050	0.492966	-2.481567	**H**	-4.281007	-4.557606	-0.755790
H	6.722585	1.324885	-1.093536	**H**	2.838650	-2.072974	1.839707	**C**	4.735693	0.743491	3.266872
H	3.657906	0.043821	-2.044251	**H**	4.372701	-2.368709	2.655838	**H**	5.322001	1.666429	3.261702
H	3.215171	1.716513	-1.878026	**H**	-2.838659	2.072948	1.839712	**H**	4.115761	0.746136	4.166252
H	-0.739552	-2.148976	-0.401176	**H**	-4.372714	2.368679	2.655836	**H**	5.430993	-0.096033	3.350152

Table G7 XYZ coordinates of the GS and TS geometries of **2.1f** B3LYP/6-311G(d,p) (gas phase)

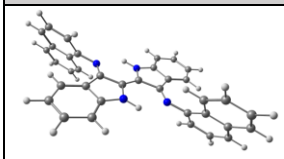
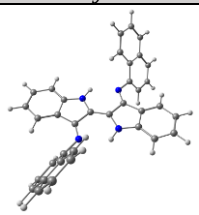
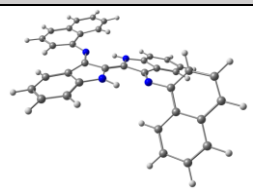
Anti				***Syn***				**TS**			
											
N	0.310479	1.789357	-0.376596	**N**	-0.061759	-1.463919	-0.781388	**N**	2.676802	0.499730	0.061130
N	-2.571357	-0.111594	0.362408	**N**	2.535146	0.920109	-0.533421	**N**	-0.487054	1.970018	0.471260
N	-0.310479	-1.789353	0.376575	**N**	0.030814	2.204455	-0.230012	**N**	-2.456705	0.028610	0.450340
N	2.571358	0.111603	-0.362412	**N**	-2.556407	-0.185712	-0.465567	**N**	0.671755	-1.467332	-0.216043
C	-6.842296	-2.156094	-1.446720	**C**	6.123652	-0.372905	2.880386	**C**	1.736129	1.406311	0.094217
C	-6.648382	0.313373	1.345975	**C**	6.759056	0.888250	-0.574376	**C**	1.581427	2.885537	0.087887
C	-7.228452	-1.313838	-0.433371	**C**	6.791443	0.034302	1.752496	**C**	2.398553	3.992894	-0.180928
C	-5.476335	-2.281392	-1.785473	**C**	4.711230	-0.359324	2.912768	**C**	1.887066	5.283472	-0.108975
C	-5.693286	1.025549	2.030382	**C**	6.045278	1.306620	-1.669552	**C**	0.546590	5.505586	0.223307
C	-6.272656	-0.556711	0.291516	**C**	6.085668	0.468526	0.600856	**C**	-0.311479	4.439191	0.451063
C	-4.524250	-1.558641	-1.107681	**C**	3.995520	0.053349	1.815729	**C**	0.207111	3.149669	0.359292
C	-4.331385	0.917893	1.688101	**C**	4.635183	1.315141	-1.649635	**C**	0.352620	0.907230	0.238845
C	-4.892330	-0.684152	-0.056211	**C**	4.655796	0.470722	0.633086	**C**	-0.122110	-2.580017	-0.412835
C	-3.921096	0.090240	0.657191	**C**	3.941642	0.887791	-0.536074	**C**	0.259690	-3.857700	-0.814272
C	6.842288	2.156060	1.446785	**C**	-6.069485	-2.822870	2.063945	**C**	-0.740939	-4.811141	-0.967872
C	6.648389	-0.313355	-1.345956	**C**	-6.747184	-0.508999	-0.785942	**C**	-2.087551	-4.501625	-0.733094
C	7.228450	1.313823	0.433422	**C**	-6.749749	-2.113249	1.105272	**C**	-2.461529	-3.225567	-0.326293
C	5.476325	2.281354	1.785531	**C**	-4.667006	-2.697056	2.180196	**C**	-1.475703	-2.250197	-0.154156
C	5.693296	-1.025519	-2.030381	**C**	-6.049713	0.316509	-1.634360	**C**	-1.507375	-0.816637	0.184810
C	6.272658	0.556711	-0.291485	**C**	-6.065761	-1.245218	0.215930	**C**	-0.107798	-0.375243	0.099423
C	4.524244	1.558618	1.107719	**C**	-3.973337	-1.860820	1.338925	**C**	4.053484	0.557900	0.028761
C	4.331393	-0.917867	-1.688107	**C**	-4.653639	0.458948	-1.514690	**C**	4.729338	-0.724531	0.099420
C	4.892329	0.684148	0.056235	**C**	-4.647534	-1.118619	0.338692	**C**	4.849619	1.694755	-0.061024
C	3.921099	-0.090229	-0.657188	**C**	-3.949870	-0.230863	-0.542727	**C**	4.046508	-1.928171	0.396903
C	-0.317989	0.599654	-0.070996	**C**	0.382926	-0.167605	-0.614685	**C**	6.144802	-0.789558	-0.091283
C	-1.757525	0.856819	0.077667	**C**	1.853209	-0.171720	-0.667037	**C**	6.245156	1.621281	-0.202989
C	-1.916843	2.292797	-0.210094	**C**	2.221710	-1.578285	-0.884894	**C**	4.702403	-3.137208	0.425457
C	-3.023518	3.138546	-0.315286	**C**	3.444294	-2.234329	-1.036689	**C**	6.789997	-2.053152	-0.078192
C	-2.828524	4.468528	-0.671656	**C**	3.448583	-3.609377	-1.247939	**C**	6.883846	0.407270	-0.257657
C	-1.539591	4.957894	-0.920857	**C**	2.245296	-4.323878	-1.305945	**C**	6.086034	-3.206881	0.159893
C	-0.421151	4.135383	-0.835943	**C**	1.013149	-3.692916	-1.159657	**C**	-3.777051	-0.354167	0.685933
C	-0.622394	2.801823	-0.488393	**C**	1.013166	-2.316538	-0.950924	**C**	-4.815505	0.307253	-0.047014
C	0.317988	-0.599649	0.070978	**C**	-0.422043	0.913829	-0.412294	**C**	-4.113230	-1.256207	1.681229
C	0.622393	-2.801820	0.488364	**C**	-1.035728	3.051992	-0.003831	**C**	-4.528249	1.245742	-1.067978
C	0.421151	-4.135382	0.835907	**C**	-1.018699	4.416680	0.274194	**C**	-6.179078	-0.003411	0.247450
C	1.539591	-4.957894	0.920812	**C**	-2.237114	5.044715	0.510157	**C**	-5.460652	-1.546353	1.969496
C	2.828523	-4.468528	0.671609	**C**	-3.444889	4.335542	0.476607	**C**	-5.541722	1.859330	-1.764276
C	3.023517	-3.138544	0.315247	**C**	-3.458076	2.975047	0.188984	**C**	-7.199234	0.645362	-0.494617
C	1.916842	-2.292793	0.210064	**C**	-2.250268	2.321159	-0.065220	**C**	-6.475742	-0.942388	1.267418
C	1.757524	-0.856813	-0.077685	**C**	-1.890745	0.919228	-0.339439	**C**	-6.890895	1.555228	-1.475698
H	-7.584957	-2.728337	-1.990676	**H**	6.677731	-0.702630	3.751649	**H**	-1.488733	1.818517	0.555713
H	-7.696828	0.399000	1.608115	**H**	7.843033	0.878667	-0.589458	**H**	1.646682	-1.341561	-0.449984
H	-8.276084	-1.214520	-0.170533	**H**	7.875759	0.031516	1.724449	**H**	3.420807	3.880056	-0.498570
H	-5.181453	-2.950052	-2.585896	**H**	4.191841	-0.675012	3.809994	**H**	2.535234	6.123754	-0.324184
H	-5.981513	1.678637	2.846175	**H**	6.561997	1.631310	-2.565402	**H**	0.167450	6.519058	0.282994
H	-3.476018	-1.642504	-1.364093	**H**	2.914295	0.069792	1.845154	**H**	-1.360065	4.594267	0.674459
H	-3.586664	1.475394	2.242907	**H**	4.075653	1.640041	-2.518279	**H**	1.299173	-4.091945	-1.009756
H	7.584947	2.728292	1.990757	**H**	-6.606761	-3.482722	2.735373	**H**	-0.471801	-5.813437	-1.280698
H	7.696837	-0.398980	-1.608092	**H**	-7.822162	-0.615969	-0.876831	**H**	-2.844043	-5.264489	-0.868775
H	8.276083	1.214508	0.170589	**H**	-7.826420	-2.206761	1.013031	**H**	-3.501074	-2.992283	-0.146596
H	5.181439	2.949999	2.585965	**H**	-4.138890	-3.262606	2.939133	**H**	4.393945	2.663448	-0.015164
H	5.981528	-1.678594	-2.846183	**H**	-6.570993	0.866797	-2.409312	**H**	3.003728	-1.879160	0.668733
H	3.476010	1.642477	1.364126	**H**	-2.899796	-1.752425	1.424592	**H**	6.813062	2.540693	-0.287926
H	3.586675	-1.475358	-2.242926	**H**	-4.113257	1.103495	-2.197153	**H**	4.155580	-4.039434	0.674813
H	-4.018547	2.764869	-0.120926	**H**	4.373129	-1.684317	-0.988728	**H**	7.861016	-2.086799	-0.245826
H	-3.679749	5.132650	-0.754781	**H**	4.389419	-4.132202	-1.365317	**H**	7.956586	0.348591	-0.402627
H	-1.408696	5.999397	-1.191165	**H**	2.271067	-5.395210	-1.469209	**H**	6.592732	-4.164755	0.172692
H	0.572550	4.513895	-1.042415	**H**	0.086283	-4.251368	-1.207768	**H**	-3.322321	-1.727480	2.251806
H	-0.572550	-4.513894	1.042379	**H**	-0.085869	4.965760	0.314822	**H**	-3.491727	1.464695	-1.289914
H	1.408696	-5.999399	1.191114	**H**	-2.249073	6.106110	0.729810	**H**	-5.690142	-2.252908	2.758967
H	3.679748	-5.132651	0.754726	**H**	-4.375964	4.852056	0.673674	**H**	-5.308047	2.577848	-2.541372
H	4.018545	-2.764866	0.120885	**H**	-4.391368	2.431310	0.160660	**H**	-8.233689	0.407566	-0.271350
H	1.307732	1.811964	-0.556241	**H**	-1.053624	-1.670519	-0.789290	**H**	-7.512816	-1.167265	1.489146
H	-1.307732	-1.811960	0.556221	**H**	1.023652	2.407685	-0.226752	**H**	-7.682309	2.042715	-2.033295

Table G8 XYZ coordinates of the GS and TS geometries of **2.1g** B3LYP/6-311G(d,p) (gas phase)

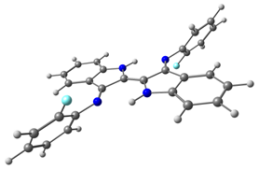
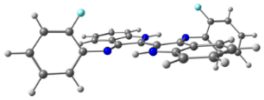
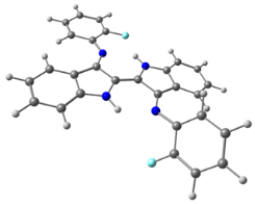
Anti				***Syn***				**TS**			
											
F	3.877721	-2.326197	1.652752	**F**	3.970397	-0.035504	1.892263	**N**	-2.456296	0.615077	0.050521
F	-3.877723	2.326186	-1.652761	**F**	-3.692980	-2.397122	1.644550	**N**	0.217573	-1.684976	0.009045
N	0.050326	1.851711	0.073618	**N**	0.116342	-1.736838	-0.203123	**N**	2.599452	-0.287338	0.054883
N	2.501605	-0.684170	-0.017293	**N**	2.456817	0.905820	-0.275512	**N**	-0.060875	2.002295	0.063529
N	-0.050326	-1.851709	-0.073616	**N**	-0.157018	1.960113	-0.128418	**C**	-6.626988	0.909558	0.507600
N	-2.501604	0.684171	0.017295	**N**	-2.485131	-0.690896	-0.088309	**C**	-5.965546	1.606714	-0.501548
C	0.431965	0.528199	0.024513	**C**	0.435212	-0.396152	-0.204537	**C**	-5.901293	0.089499	1.370069
C	1.900601	0.464096	0.030113	**C**	1.900294	-0.265414	-0.241946	**C**	-4.595869	1.468706	-0.632072
C	2.338820	1.866569	0.128458	**C**	2.401615	-1.645624	-0.272830	**C**	-4.526946	-0.049147	1.216476
C	3.585675	2.482452	0.262503	**C**	3.678631	-2.202149	-0.362779	**C**	-3.839772	0.626690	0.195534
C	3.649695	3.866198	0.382302	**C**	3.812598	-3.585550	-0.402675	**C**	-1.748153	-0.472620	0.021621
C	2.479640	4.637116	0.368814	**C**	2.682197	-4.411403	-0.349480	**C**	6.515972	-1.818161	0.014169
C	1.224168	4.050190	0.254969	**C**	1.397426	-3.883424	-0.271326	**C**	6.355775	-0.435277	0.035348
C	1.164149	2.662695	0.147048	**C**	1.268412	-2.497402	-0.241404	**C**	5.387846	-2.637219	0.006353
C	-0.431965	-0.528197	-0.024512	**C**	-0.476223	0.618253	-0.147030	**C**	5.088022	0.132730	0.049471
C	-1.164149	-2.662693	-0.147046	**C**	-1.302736	2.716622	0.008324	**C**	4.139394	-2.053796	0.020831
C	-1.224169	-4.050188	-0.254967	**C**	-1.423482	4.099364	0.127025	**C**	3.919369	-0.654446	0.043443
C	-2.479640	-4.637113	-0.368811	**C**	-2.698563	4.625748	0.302422	**C**	-2.058241	-1.909105	-0.068808
C	-3.649696	-3.866195	-0.382299	**C**	-3.828949	3.800138	0.364614	**C**	-3.241020	-2.639565	-0.212149
C	-3.585675	-2.482449	-0.262501	**C**	-3.704859	2.421316	0.235407	**C**	-3.173119	-4.023498	-0.328272
C	-2.338820	-1.866566	-0.128456	**C**	-2.437781	1.865390	0.042162	**C**	-1.935984	-4.682312	-0.302966
C	3.879723	-0.817424	-0.167132	**C**	3.839945	1.082257	-0.192204	**C**	-0.742361	-3.980321	-0.179465
C	4.566460	-1.708485	0.668695	**C**	4.514349	1.817793	-1.176439	**C**	-0.815994	-2.593216	-0.074107
C	4.614562	-0.214360	-1.199867	**C**	4.593123	0.654313	0.910021	**C**	-0.277467	-0.403121	0.037254
C	5.919008	-1.963091	0.532885	**C**	5.878497	2.068379	-1.081006	**C**	0.939419	2.942154	0.059166
C	5.971515	-0.470248	-1.358652	**C**	5.947432	0.908183	1.029072	**C**	0.795393	4.328200	0.050895
C	6.630450	-1.337699	-0.489074	**C**	6.600069	1.615941	0.021728	**C**	1.945649	5.103656	0.058172
C	-1.900600	-0.464093	-0.030111	**C**	-1.938155	0.484897	-0.074831	**C**	3.212425	4.507982	0.075512
C	-3.879722	0.817424	0.167132	**C**	-3.860108	-0.892542	-0.171026	**C**	3.346649	3.125237	0.081188
C	-4.614560	0.214365	1.199871	**C**	-4.674331	-0.328990	-1.165934	**C**	2.213504	2.301969	0.069297
C	-4.566461	1.708479	-0.668700	**C**	-4.459614	-1.815685	0.696754	**C**	1.951557	0.844121	0.064691
C	-5.971514	0.470251	1.358653	**C**	-6.022997	-0.652587	-1.257776	**C**	0.480805	0.739762	0.060881
C	-5.919010	1.963082	-0.532892	**C**	-5.802761	-2.137661	0.627704	**H**	-3.957783	-0.671877	1.895239
C	-6.630451	1.337696	0.489070	**C**	-6.594194	-1.550197	-0.357333	**H**	4.999524	1.202328	0.064298
H	4.491287	1.893034	0.272458	**H**	4.554256	-1.570072	-0.406630	**H**	5.462013	-3.717024	-0.010861
H	4.611603	4.352804	0.484599	**H**	4.798142	-4.028873	-0.470352	**H**	-7.698548	1.016072	0.621921
H	2.551703	5.715145	0.455747	**H**	2.808627	-5.487683	-0.373802	**H**	-6.492692	2.258950	-1.186434
H	0.320897	4.647866	0.260635	**H**	0.525960	-4.525788	-0.239921	**H**	-6.405547	-0.439148	2.170149
H	-0.320898	-4.647864	-0.260632	**H**	-0.550360	4.739673	0.095745	**H**	1.217326	-1.855350	-0.003225
H	-2.551704	-5.715143	-0.455743	**H**	-2.817243	5.698747	0.399868	**H**	7.504549	-2.259720	0.003307
H	-4.611603	-4.352800	-0.484595	**H**	-4.807080	4.240055	0.513717	**H**	7.225818	0.210429	0.040814
H	-4.491286	-1.893031	-0.272455	**H**	-4.579944	1.789374	0.285348	**H**	-1.067659	2.129303	0.013756
H	-0.931384	2.104726	0.050500	**H**	-0.849532	-2.034875	-0.122445	**H**	-4.198338	-2.138856	-0.233918
H	6.513752	0.004120	-2.167832	**H**	6.468915	0.549181	1.907559	**H**	-4.084325	-4.598210	-0.438193
H	7.688454	-1.535886	-0.607419	**H**	7.661042	1.815985	0.105306	**H**	-1.906798	-5.762490	-0.388689
H	0.931384	-2.104724	-0.050499	**H**	0.811375	2.258052	-0.142399	**H**	0.215664	-4.485438	-0.176973
H	-6.513750	-0.004113	2.167837	**H**	-6.627463	-0.207433	-2.038998	**H**	-0.189867	4.778121	0.039452
H	-6.393718	2.648152	-1.224046	**H**	-6.207887	-2.844534	1.340837	**H**	1.860668	6.184060	0.051827
H	-7.688455	1.535880	0.607413	**H**	-7.645532	-1.801125	-0.423429	**H**	4.099223	5.129319	0.084258
H	6.393715	-2.648167	1.224034	**H**	6.377046	2.624002	-1.866061	**H**	4.343081	2.718446	0.097192
H	4.095528	0.446526	-1.882880	**H**	3.938894	2.173301	-2.022471	**F**	-3.956380	2.157617	-1.602424
H	-4.095525	-0.446516	1.882887	**H**	-4.223313	0.355359	-1.873713	**F**	3.058221	-2.875992	0.011172

Table G9 XYZ coordinates of the GS geometries of **1.54** and **2.1a** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

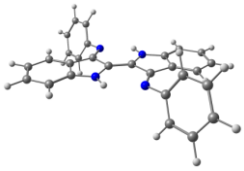
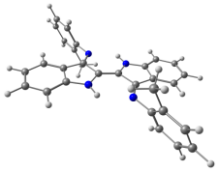
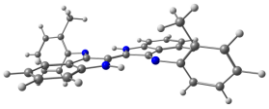
1.54				***Anti***				***Syn***			
											
N	-0.255120	1.838885	0.012246	**N**	0.152229	-1.847648	0.111390	**N**	0.160372	1.850345	-0.128908
N	-2.435468	-0.937649	-0.097397	**N**	2.486465	0.796362	-0.086583	**N**	2.483003	-0.810955	-0.115838
N	0.255121	-1.838885	-0.012239	**N**	-0.152230	1.847649	-0.111381	**N**	-0.160368	-1.850335	-0.128938
N	2.435469	0.937648	0.097398	**N**	-2.486463	-0.796364	0.086583	**N**	-2.483007	0.810959	-0.115839
C	-0.486411	0.478655	-0.012134	**C**	0.458781	-0.504151	0.024276	**C**	0.460847	0.502710	-0.133830
C	-1.943370	0.258662	-0.055108	**C**	1.925669	-0.366783	-0.013530	**C**	1.927394	0.356590	-0.133195
C	-2.530505	1.609768	-0.073271	**C**	2.438477	-1.744316	0.085370	**C**	2.446225	1.735167	-0.112330
C	-3.838928	2.091037	-0.170161	**C**	3.722585	-2.289953	0.158050	**C**	3.732120	2.278234	-0.053987
C	-4.053229	3.465800	-0.204477	**C**	3.864661	-3.668180	0.292670	**C**	3.879981	3.661681	-0.007903
C	-2.972570	4.357407	-0.143419	**C**	2.736149	-4.498173	0.353460	**C**	2.755393	4.499044	-0.020206
C	-1.658973	3.905011	-0.060250	**C**	1.445765	-3.979463	0.293072	**C**	1.463126	3.983582	-0.067680
C	-1.449965	2.527454	-0.033623	**C**	1.309296	-2.598516	0.164990	**C**	1.320665	2.597890	-0.107430
C	0.486413	-0.478656	0.012139	**C**	3.876222	0.945042	-0.229755	**C**	-0.460846	-0.502701	-0.133837
C	1.449965	-2.527455	0.033630	**C**	4.521741	0.548400	-1.408210	**C**	-1.320660	-2.597883	-0.107464
C	1.658972	-3.905012	0.060259	**C**	5.884915	0.768831	-1.574777	**C**	-1.463118	-3.983576	-0.067731
C	2.972569	-4.357409	0.143428	**C**	6.617079	1.387411	-0.562974	**C**	-2.755383	-4.499041	-0.020258
C	4.053228	-3.465803	0.204484	**C**	5.971572	1.792269	0.604474	**C**	-3.879973	-3.661681	-0.007940
C	3.838928	-2.091039	0.170166	**C**	4.602541	1.590836	0.791065	**C**	-3.732115	-2.278233	-0.054009
C	2.530505	-1.609769	0.073276	**C**	3.907634	2.020176	2.054418	**C**	-2.446221	-1.735163	-0.112350
C	-3.817058	-1.175888	-0.020326	**C**	-0.458781	0.504152	-0.024270	**C**	3.876462	-0.971489	-0.205158
C	-4.463201	-1.819217	-1.084258	**C**	-1.925669	0.366783	0.013533	**C**	4.572890	-1.520337	0.890276
C	-4.547261	-0.868776	1.137671	**C**	-2.438478	1.744315	-0.085364	**C**	4.555091	-0.681777	-1.395782
C	-5.822194	-2.110053	-1.006225	**C**	-3.722586	2.289951	-0.158044	**C**	5.946395	-1.735920	0.761268
C	-5.901268	-1.178564	1.213894	**C**	-3.864663	3.668178	-0.292662	**C**	5.922435	-0.913812	-1.503058
C	-6.548697	-1.792013	0.140989	**C**	-2.736151	4.498172	-0.353450	**C**	6.625044	-1.437456	-0.419372
C	1.943371	-0.258663	0.055112	**C**	-1.445767	3.979463	-0.293062	**C**	-1.927394	-0.356584	-0.133206
C	3.817059	1.175887	0.020321	**C**	-1.309296	2.598516	-0.164982	**C**	-3.876466	0.971489	-0.205158
C	4.547258	0.868779	-1.137679	**C**	-3.876222	-0.945044	0.229751	**C**	-4.572897	1.520325	0.890280
C	4.463205	1.819216	1.084251	**C**	-4.521744	-0.548406	1.408206	**C**	-4.555093	0.681786	-1.395786
C	5.901263	1.178570	-1.213907	**C**	-5.884918	-0.768835	1.574767	**C**	-5.946403	1.735905	0.761272
C	5.822197	2.110054	1.006213	**C**	-6.617080	-1.387411	0.562959	**C**	-5.922438	0.913817	-1.503061
C	6.548696	1.792018	-0.141004	**C**	-5.971570	-1.792265	-0.604488	**C**	-6.625050	1.437449	-0.419370
H	-4.675940	1.408981	-0.216230	**C**	-4.602538	-1.590833	-0.791074	**C**	-3.842539	1.834358	2.167486
H	-5.063131	3.850605	-0.277016	**C**	-3.907628	-2.020168	-2.054427	**C**	3.842530	-1.834378	2.167478
H	-3.161723	5.424709	-0.166296	**H**	4.595288	-1.654243	0.109172	**H**	4.601872	1.636692	-0.047202
H	-0.824667	4.595118	-0.025354	**H**	4.854907	-4.103527	0.348683	**H**	4.871682	4.095120	0.035648
H	0.824665	-4.595119	0.025365	**H**	2.868834	-5.569498	0.454029	**H**	2.892649	5.574023	0.011478
H	3.161720	-5.424711	0.166307	**H**	0.575431	-4.621999	0.349689	**H**	0.595713	4.632556	-0.067505
H	5.063130	-3.850609	0.277024	**H**	3.940410	0.070902	-2.188554	**H**	-0.595703	-4.632549	-0.067566
H	4.675941	-1.408985	0.216235	**H**	6.371800	0.458082	-2.492391	**H**	-2.892637	-5.574021	0.011415
H	0.683733	2.218218	0.043545	**H**	7.680014	1.561961	-0.683986	**H**	-4.871673	-4.095123	0.035609
H	-6.453464	-0.937284	2.115485	**H**	6.538795	2.278253	1.391704	**H**	-4.601869	-1.636694	-0.047214
H	-7.604633	-2.027936	0.202355	**H**	3.562114	1.156253	2.631524	**H**	-0.797334	2.180676	-0.119991
H	-0.683733	-2.218217	-0.043537	**H**	3.020851	2.620652	1.830517	**H**	6.435425	-0.685911	-2.430724
H	6.453456	0.937292	-2.115501	**H**	4.575824	2.606029	2.688193	**H**	7.690836	-1.620406	-0.493902
H	6.313621	2.592705	1.843693	**H**	-0.806143	-2.170099	0.174059	**H**	0.797338	-2.180665	-0.120029
H	7.604631	2.027943	-0.202374	**H**	-4.595288	1.654240	-0.109168	**H**	-6.490467	2.147674	1.605155
H	-6.313615	-2.592704	-1.843705	**H**	-4.854909	4.103524	-0.348675	**H**	-6.435426	0.685922	-2.430729
H	-3.890754	-2.071550	-1.969404	**H**	-2.868837	5.569498	-0.454017	**H**	-7.690842	1.620395	-0.493899
H	3.890761	2.071547	1.969400	**H**	-0.575434	4.621999	-0.349677	**H**	6.490457	-2.147698	1.605147
H	-4.043235	-0.391234	1.969674	**H**	-3.940415	-0.070910	2.188553	**H**	-3.996366	0.277315	-2.231938
H	4.043229	0.391238	-1.969681	**H**	-6.371806	-0.458089	2.492381	**H**	3.996366	-0.277296	-2.231932
				H	-7.680015	-1.561960	0.683968	**H**	-3.476752	0.922777	2.651168
				H	-6.538791	-2.278246	-1.391722	**H**	-2.965218	2.459262	1.975265
				H	-3.562109	-1.156243	-2.631530	**H**	-4.494288	2.354048	2.872123
				H	-3.020843	-2.620643	-1.830525	**H**	3.476745	-0.922801	2.651167
				H	-4.575815	-2.606022	-2.688204	**H**	2.965208	-2.459279	1.975252
				H	0.806143	2.170101	-0.174048	**H**	4.494277	-2.354075	2.872112

Table G10 XYZ coordinates of the GS geometries of **2.1b** B3LYP 6-311G(d,p) (SMD = CH_2Cl_2)

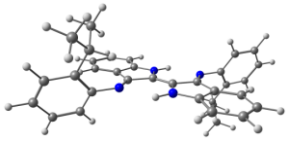
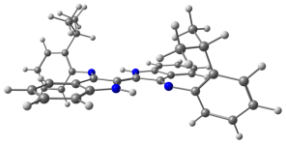
Anti				***Syn***			
							
N	-0.018962	-1.818704	-0.377735	**N**	-0.022733	1.866344	-0.451215
N	2.524178	0.481649	0.470634	**N**	2.470301	-0.634041	-0.537662
N	0.018961	1.818708	0.377741	**N**	-0.102954	-1.846996	-0.532776
N	-2.524177	-0.481645	-0.470637	**N**	-2.589486	0.656809	-0.380550
C	0.405703	-0.545515	-0.051552	**C**	0.365430	0.541541	-0.495526
C	1.863218	-0.585356	0.160602	**C**	1.837774	0.493061	-0.522629
C	2.247269	-1.982774	-0.102214	**C**	2.265447	1.901894	-0.475909
C	3.472496	-2.653259	-0.131572	**C**	3.514239	2.525580	-0.418824
C	3.495668	-4.003197	-0.471113	**C**	3.572245	3.914226	-0.338363
C	2.307212	-4.680822	-0.778454	**C**	2.395425	4.676290	-0.315565
C	1.074637	-4.033653	-0.766468	**C**	1.138708	4.078874	-0.359644
C	1.058050	-2.680955	-0.432469	**C**	1.086722	2.688514	-0.432924
C	3.898427	0.440396	0.767834	**C**	-0.488492	-0.521209	-0.499317
C	4.813931	1.097390	-0.080746	**C**	-1.213353	-2.667276	-0.506455
C	6.164904	1.085789	0.276209	**C**	-1.268413	-4.059571	-0.495505
C	6.609233	0.465863	1.442855	**C**	-2.525100	-4.655514	-0.432160
C	5.691178	-0.157148	2.286031	**C**	-3.699234	-3.890974	-0.376532
C	4.342639	-0.169340	1.948857	**C**	-3.638642	-2.500233	-0.393302
C	4.315350	1.727508	-1.369040	**C**	-2.390448	-1.877532	-0.467137
C	5.141416	2.932849	-1.828536	**C**	3.872197	-0.692296	-0.643529
C	4.229451	0.668882	-2.483300	**C**	4.633114	-1.176713	0.440808
C	-0.405704	0.545519	0.051555	**C**	4.497535	-0.356985	-1.851796
C	-1.863219	0.585360	-0.160601	**C**	6.017801	-1.273635	0.279480
C	-2.247270	1.982777	0.102220	**C**	5.876024	-0.472928	-1.989287
C	-3.472498	2.653261	0.131580	**C**	6.642280	-0.925602	-0.917008
C	-3.495671	4.003197	0.471125	**C**	-1.960599	-0.469582	-0.460763
C	-2.307216	4.680823	0.778468	**C**	-3.995032	0.716883	-0.440603
C	-1.074640	4.033655	0.766479	**C**	-4.759826	1.099503	0.682280
C	-1.058052	2.680958	0.432477	**C**	-4.627218	0.473576	-1.669019
C	-3.898426	-0.440393	-0.767838	**C**	-6.146623	1.194400	0.521695
C	-4.813929	-1.097392	0.080738	**C**	-6.006075	0.584980	-1.799790
C	-6.164901	-1.085794	-0.276218	**C**	-6.775564	0.942397	-0.695122
C	-6.609232	-0.465865	-1.442861	**C**	3.938702	-1.507814	1.749935
C	-5.691177	0.157151	-2.286035	**C**	-4.158751	1.378595	2.052040
C	-4.342638	0.169346	-1.948859	**C**	4.625858	-2.617929	2.551355
C	-4.315348	-1.727514	1.369031	**C**	3.776898	-0.238555	2.605798
C	-5.141410	-2.932858	1.828522	**C**	-3.524628	0.130565	2.688125
C	-4.229451	-0.668891	2.483294	**C**	-3.176714	2.561124	2.050965
H	-0.988050	-2.013723	-0.599534	**H**	4.423375	1.941602	-0.437813
H	4.390403	-2.134454	0.105720	**H**	4.533957	4.410618	-0.294865
H	4.438747	-4.535335	-0.496382	**H**	2.462762	5.756795	-0.257236
H	2.346656	-5.733154	-1.036288	**H**	0.230889	4.669153	-0.330432
H	0.159356	-4.557319	-1.014580	**H**	-0.362797	-4.653129	-0.527626
H	6.887371	1.571639	-0.368611	**H**	-2.594354	-5.737429	-0.421675
H	7.663602	0.478001	1.694397	**H**	-4.660535	-4.386989	-0.321270
H	6.021619	-0.632550	3.202784	**H**	-4.545328	-1.913524	-0.351851
H	3.615920	-0.647872	2.595289	**H**	-0.999877	2.133234	-0.439523
H	3.294882	2.071540	-1.171671	**H**	3.887102	-0.007696	-2.676670
H	5.239833	3.678039	-1.034276	**H**	6.347764	-0.210268	-2.929570
H	4.656026	3.411751	-2.683559	**H**	7.718282	-1.016436	-1.012465
H	6.146431	2.640835	-2.146409	**H**	0.873230	-2.116345	-0.558080
H	5.225121	0.280211	-2.719768	**H**	-6.745142	1.475156	1.382372
H	3.807300	1.101885	-3.395409	**H**	-6.473955	0.392346	-2.758748
H	3.601890	-0.173768	-2.185448	**H**	-7.852517	1.031759	-0.779502
H	0.988048	2.013727	0.599542	**H**	6.623655	-1.629429	1.104179
H	-4.390405	2.134456	-0.105713	**H**	2.932639	-1.851894	1.489095
H	-4.438751	4.535335	0.496396	**H**	-4.014188	0.197734	-2.519463
H	-2.346660	5.733154	1.036304	**H**	-5.002333	1.664935	2.688375
H	-0.159360	4.557321	1.014592	**H**	4.008874	-2.891213	3.411967
H	-6.887368	-1.571648	0.368600	**H**	4.777559	-3.515256	1.945044
H	-7.663600	-0.478005	-1.694405	**H**	5.599029	-2.300056	2.936500
H	-6.021619	0.632556	-3.202787	**H**	4.756404	0.157078	2.892841
H	-3.615920	0.647882	-2.595289	**H**	3.244699	0.544756	2.062016
H	-3.294879	-2.071543	1.171661	**H**	3.217228	-0.458608	3.520120
H	-5.239824	-3.678046	1.034261	**H**	-4.225111	-0.708749	2.693306
H	-4.656021	-3.411760	2.683545	**H**	-2.626003	-0.180697	2.153568
H	-6.146427	-2.640847	2.146395	**H**	-3.241112	0.341197	3.723951
H	-5.225122	-0.280223	2.719763	**H**	-2.270849	2.322953	1.492524
H	-3.807299	-1.101896	3.395402	**H**	-3.631767	3.449799	1.604579
H	-3.601892	0.173762	2.185445	**H**	-2.887584	2.807883	3.077140

Table G11 XYZ coordinates of the GS geometries **2.1c** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

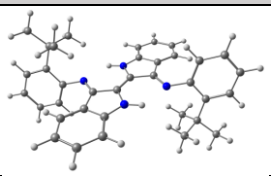
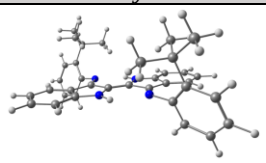
Anti				***Syn***			
							
N	0.075142	-1.798168	-0.459970	**N**	-0.047809	1.856508	-0.546872
N	-2.542335	0.378520	0.485272	**N**	2.562634	-0.522849	-0.498062
N	-0.075145	1.798149	0.459976	**N**	0.047808	-1.856516	-0.546870
N	2.542334	-0.378537	-0.485265	**N**	-2.562632	0.522843	-0.498062
C	-4.068259	0.596094	-2.281432	**C**	5.501938	-1.625519	2.750142
C	-5.980540	2.122710	-1.867438	**C**	3.626581	-0.030421	2.440477
C	-3.732937	2.766262	-1.033482	**C**	3.382841	-2.449636	1.755029
C	3.732961	-2.766242	1.033522	**C**	-3.626572	0.030445	2.440477
C	5.980561	-2.122659	1.867464	**C**	-5.501935	1.625538	2.750135
C	4.068268	-0.596052	2.281438	**C**	-3.382842	2.449656	1.755011
C	-0.388785	-0.554832	-0.075925	**C**	0.401967	0.550627	-0.543208
C	-1.841581	-0.654390	0.148052	**C**	1.875196	0.570851	-0.553082
C	-2.178602	-2.054330	-0.158201	**C**	2.235681	1.998358	-0.564440
C	-3.380364	-2.765768	-0.195661	**C**	3.453841	2.681179	-0.522973
C	-3.362246	-4.100563	-0.590184	**C**	3.446816	4.072957	-0.497759
C	-2.156338	-4.722334	-0.944760	**C**	2.235671	4.779734	-0.513180
C	-0.946977	-4.032958	-0.925588	**C**	1.008302	4.123258	-0.540790
C	-0.972160	-2.695664	-0.535583	**C**	1.021632	2.730180	-0.558921
C	-3.899937	0.254499	0.841014	**C**	-0.401967	-0.550635	-0.543207
C	-4.188713	-0.402934	2.047074	**C**	-1.021634	-2.730187	-0.558921
C	-5.490000	-0.513860	2.516458	**C**	-1.008306	-4.123265	-0.540789
C	-6.527524	0.038395	1.772927	**C**	-2.235676	-4.779740	-0.513181
C	-6.243130	0.700542	0.580527	**C**	-3.446820	-4.072961	-0.497760
C	-4.941881	0.840754	0.079647	**C**	-3.453843	-2.681184	-0.522974
C	-4.682764	1.569616	-1.252618	**C**	-2.235682	-1.998364	-0.564439
C	0.388782	0.554814	0.075932	**C**	3.963467	-0.513748	-0.648692
C	1.841578	0.654373	-0.148048	**C**	4.843230	-0.892068	0.396279
C	2.178597	2.054315	0.158193	**C**	4.468871	-0.201480	-1.920448
C	3.380357	2.765756	0.195640	**C**	6.211410	-0.905452	0.093651
C	3.362238	4.100554	0.590154	**C**	5.830691	-0.235067	-2.185604
C	2.156330	4.722324	0.944734	**C**	6.710632	-0.584771	-1.166925
C	0.946971	4.032945	0.925574	**C**	-1.875196	-0.570857	-0.553082
C	0.972155	2.695648	0.535578	**C**	-3.963467	0.513744	-0.648693
C	3.899934	-0.254510	-0.841014	**C**	-4.843228	0.892072	0.396276
C	4.188700	0.402906	-2.047084	**C**	-4.468872	0.201465	-1.920446
C	5.489985	0.513837	-2.516474	**C**	-6.211408	0.905455	0.093649
C	6.527516	-0.038395	-1.772937	**C**	-5.830691	0.235051	-2.185601
C	6.243132	-0.700525	-0.580525	**C**	-6.710632	0.584763	-1.166925
C	4.941886	-0.840742	-0.079640	**C**	-4.344408	1.243605	1.810782
C	4.682779	-1.569585	1.252637	**C**	4.344411	-1.243589	1.810789
H	-3.943282	1.104394	-3.242496	**H**	5.092708	-1.874726	3.732472
H	-4.722679	-0.265970	-2.437600	**H**	6.209717	-0.803435	2.885505
H	-3.092049	0.230439	-1.968574	**H**	6.052099	-2.498380	2.388913
H	-5.738255	2.638350	-2.800150	**H**	3.332892	-0.267316	3.467725
H	-6.472059	2.843066	-1.208154	**H**	2.727614	0.245164	1.892482
H	-6.693844	1.328878	-2.104323	**H**	4.289327	0.838899	2.470436
H	-3.588352	3.301321	-1.977047	**H**	3.063635	-2.715675	2.767368
H	-2.758167	2.443034	-0.673229	**H**	3.880781	-3.319610	1.316877
H	-4.156093	3.466907	-0.307674	**H**	2.494981	-2.227609	1.166165
H	3.588379	-3.301285	1.977097	**H**	-3.332882	0.267347	3.467724
H	4.156123	-3.466897	0.307728	**H**	-2.727604	-0.245139	1.892482
H	2.758189	-2.443028	0.673263	**H**	-4.289314	-0.838878	2.470443
H	6.693860	-1.328817	2.104331	**H**	-5.092704	1.874751	3.732463
H	6.472083	-2.843024	1.208192	**H**	-6.209711	0.803452	2.885504
H	5.738283	-2.638282	2.800186	**H**	-6.052098	2.498396	2.388902
H	3.943299	-1.104337	3.242511	**H**	-3.063635	2.715703	2.767347
H	3.092053	-0.230412	1.968577	**H**	-3.880788	3.319625	1.316855
H	4.722680	0.266021	2.437589	**H**	-2.494984	2.227628	1.166146
H	-4.311201	-2.289685	0.078045	**H**	4.389028	2.139659	-0.513349
H	-4.286349	-4.664694	-0.621853	**H**	4.384000	4.615201	-0.468352
H	-2.163610	-5.763892	-1.245510	**H**	2.252504	5.863696	-0.498074
H	-0.018335	-4.513050	-1.209402	**H**	0.074164	4.671613	-0.539868
H	-3.363616	-0.823044	2.610573	**H**	-0.074169	-4.671621	-0.539867
H	-5.687311	-1.026414	3.451287	**H**	-2.252509	-5.863702	-0.498075
H	-7.553155	-0.035999	2.115889	**H**	-4.384005	-4.615205	-0.468354
H	-7.070155	1.120410	0.026059	**H**	-4.389030	-2.139663	-0.513349
H	1.043160	-1.947673	-0.717569	**H**	-1.035294	2.078871	-0.577162
H	4.311193	2.289674	-0.078070	**H**	6.196158	0.010095	-3.176486
H	4.286340	4.664688	0.621812	**H**	7.779148	-0.616293	-1.346828
H	2.163602	5.763885	1.245476	**H**	1.035292	-2.078880	-0.577160
H	0.018329	4.513036	1.209391	**H**	-6.919390	1.175001	0.864226
H	3.363596	0.822998	-2.610588	**H**	-6.196160	-0.010120	-3.176480
H	5.687288	1.026376	-3.451313	**H**	-7.779147	0.616284	-1.346827
H	7.553145	0.036004	-2.115903	**H**	6.919392	-1.174992	0.864230
H	7.070162	-1.120375	-0.026052	**H**	-3.764027	-0.065223	-2.699452
H	-1.043161	1.947653	0.717580	**H**	3.764026	0.065201	-2.699455

Table G12 XYZ coordinates of the GS geometries of **2.1d** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

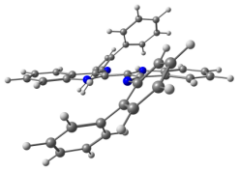
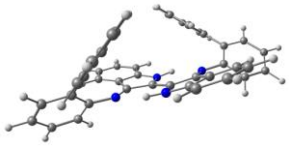
Anti				***Syn***			
							
N	0.803850	1.591946	-0.514164	**N**	2.568694	-0.272661	-0.865285
N	-2.481926	0.626589	0.303702	**N**	-0.634535	-1.745293	-0.914126
N	-0.803846	-1.591952	0.514164	**N**	-2.568700	0.272667	-0.865254
N	2.481929	-0.626593	-0.303698	**N**	0.634527	1.745302	-0.914119
C	-4.045845	-3.573926	-1.647375	**C**	6.704814	-0.980141	-0.825909
C	-4.910281	-3.469176	-0.559085	**C**	6.134000	-0.036813	0.023190
C	-3.463014	-2.422550	-2.175992	**C**	5.887918	-1.715415	-1.684989
C	-5.178876	-2.223400	0.003812	**C**	4.752782	0.186296	0.045135
C	-3.729860	-1.178926	-1.612359	**C**	4.512940	-1.519530	-1.675243
C	-4.586032	-1.060454	-0.507884	**C**	3.924482	-0.585286	-0.807394
C	4.045826	3.573931	1.647359	**C**	1.596110	-1.127374	-0.842674
C	4.910256	3.469183	0.559065	**C**	-6.704821	0.980140	-0.825841
C	3.463008	2.422553	2.175986	**C**	-6.133998	0.036807	0.023247
C	5.178858	2.223407	-0.003828	**C**	-5.887933	1.715422	-1.684922
C	3.729861	1.178928	1.612357	**C**	-4.752780	-0.186300	0.045180
C	4.586028	1.060458	0.507878	**C**	-4.512954	1.519539	-1.675188
C	-0.134140	0.659389	-0.126836	**C**	-3.924487	0.585289	-0.807350
C	-1.448216	1.319686	-0.060698	**C**	1.479849	-2.578705	-0.614653
C	-1.199774	2.699740	-0.516044	**C**	2.398207	-3.592630	-0.324867
C	-2.018812	3.802929	-0.777794	**C**	1.933326	-4.883394	-0.092573
C	-1.445511	4.981294	-1.245049	**C**	0.561355	-5.169576	-0.150182
C	-0.060187	5.070174	-1.448500	**C**	-0.375559	-4.179948	-0.429935
C	0.778228	3.985661	-1.213906	**C**	0.095325	-2.887611	-0.654311
C	0.195365	2.802201	-0.762921	**C**	0.207426	-0.651669	-0.958778
C	0.134144	-0.659395	0.126838	**C**	-0.095333	2.887618	-0.654289
C	-0.195360	-2.802207	0.762925	**C**	0.375553	4.179954	-0.429908
C	-0.778224	-3.985666	1.213910	**C**	-0.561359	5.169579	-0.150140
C	0.060192	-5.070177	1.448509	**C**	-1.933330	4.883397	-0.092521
C	1.445517	-4.981297	1.245062	**C**	-2.398212	3.592633	-0.324819
C	2.018817	-3.802931	0.777804	**C**	-1.479856	2.578712	-0.614620
C	1.199778	-2.699745	0.516051	**C**	-1.596117	1.127381	-0.842648
C	-3.771844	1.095932	0.515675	**C**	-0.207434	0.651678	-0.958771
C	-4.846374	0.247012	0.142988	**H**	3.878549	-2.067544	-2.361046
C	-4.050550	2.276971	1.225057	**H**	-3.878569	2.067559	-2.360991
C	-6.154457	0.640685	0.442783	**H**	-6.321445	2.438854	-2.366223
C	-5.357757	2.639919	1.521639	**H**	7.777323	-1.135071	-0.822411
C	-6.418591	1.828926	1.117650	**H**	6.765100	0.536632	0.692631
C	1.448220	-1.319691	0.060702	**H**	6.321424	-2.438842	-2.366298
C	3.771849	-1.095934	-0.515671	**H**	-1.636899	-1.619453	-0.815873
C	4.050557	-2.276974	-1.225049	**H**	-7.777330	1.135068	-0.822334
C	4.846375	-0.247009	-0.142989	**H**	-6.765093	-0.536643	0.692689
C	5.357765	-2.639917	-1.521634	**H**	1.636891	1.619462	-0.815875
C	6.154459	-0.640676	-0.442786	**H**	3.456749	-3.381244	-0.274308
C	6.418596	-1.828919	-1.117650	**H**	2.637239	-5.674670	0.134951
H	-3.829206	-4.543445	-2.081109	**H**	0.220716	-6.182606	0.031871
H	-5.368762	-4.358070	-0.140470	**H**	-1.436448	-4.395783	-0.458784
H	-2.795502	-2.493066	-3.027295	**H**	1.436441	4.395790	-0.458766
H	-5.833253	-2.151308	0.865016	**H**	-0.220719	6.182609	0.031916
H	-3.275880	-0.291415	-2.032814	**H**	-2.637242	5.674670	0.135015
H	3.829180	4.543450	2.081089	**H**	-3.456754	3.381246	-0.274252
H	5.368725	4.358079	0.140441	**C**	4.174404	1.231914	0.924625
H	2.795500	2.493067	3.027292	**C**	3.056713	0.977613	1.733436
H	5.833230	2.151316	-0.865036	**C**	4.735506	2.516531	0.949203
H	3.275890	0.291415	2.032819	**C**	2.511939	1.978958	2.531183
H	-3.086856	3.746849	-0.623414	**H**	2.620178	-0.012282	1.745065
H	-2.073876	5.839681	-1.449348	**C**	4.189836	3.519516	1.747330
H	0.367353	6.001510	-1.802366	**H**	5.591106	2.734744	0.320447
H	1.846294	4.047162	-1.383367	**C**	3.072697	3.255754	2.537868
H	-1.846290	-4.047168	1.383369	**H**	1.646914	1.761949	3.147556
H	-0.367347	-6.001513	1.802376	**H**	4.632349	4.509329	1.743666
H	2.073883	-5.839682	1.449364	**H**	2.642004	4.037435	3.152988
H	3.086862	-3.746851	0.623428	**C**	-4.174395	-1.231921	0.924660
H	1.781415	1.342986	-0.617974	**C**	-3.056698	-0.977624	1.733464
H	-5.547884	3.553384	2.073897	**C**	-4.735494	-2.516539	0.949235
H	-7.441059	2.113179	1.336887	**C**	-2.511917	-1.978973	2.531202
H	-1.781411	-1.342993	0.617973	**H**	-2.620164	0.012272	1.745096
H	5.547894	-3.553384	-2.073890	**C**	-4.189817	-3.519528	1.747352
H	6.974643	-0.001815	-0.135427	**H**	-5.591098	-2.734750	0.320484
H	7.441066	-2.113167	-1.336889	**C**	-3.072673	-3.255769	2.537884
H	-6.974643	0.001828	0.135419	**H**	-1.646888	-1.761966	3.147570
H	-3.227019	2.887460	1.572239	**H**	-4.632329	-4.509342	1.743685
H	3.227028	-2.887468	-1.572228	**H**	-2.641975	-4.037454	3.152997

Table G13 XYZ coordinates of the GS geometries of **2.1e** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

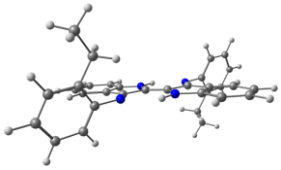
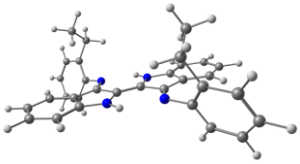
Anti				***Syn***			
							
N	-0.049967	1.826046	0.338013	**N**	-0.155652	-1.851108	-0.364180
N	-2.516432	-0.597141	-0.387883	**N**	-2.485354	0.803843	-0.342309
N	0.049967	-1.826045	-0.338006	**N**	0.155656	1.851117	-0.364154
N	2.516431	0.597144	0.387888	**N**	2.485355	-0.803835	-0.342298
C	-5.121221	-2.453941	2.552568	**C**	-3.690225	0.470191	2.848160
C	5.121213	2.453925	-2.552582	**C**	3.690210	-0.470233	2.848185
C	-0.427209	0.528558	0.051790	**C**	-0.459273	-0.503863	-0.372366
C	-1.890977	0.501351	-0.119360	**C**	-1.925838	-0.361269	-0.362705
C	-2.326722	1.888667	0.113681	**C**	-2.441479	-1.740219	-0.329172
C	-3.577327	2.510283	0.140839	**C**	-3.726062	-2.283592	-0.251675
C	-3.648897	3.869571	0.433569	**C**	-3.871608	-3.666834	-0.191844
C	-2.483569	4.603617	0.696368	**C**	-2.745980	-4.502701	-0.208889
C	-1.225865	4.006432	0.682288	**C**	-1.454735	-3.986311	-0.274506
C	-1.160268	2.644902	0.393242	**C**	-1.314472	-2.600907	-0.327576
C	-3.904026	-0.611411	-0.624763	**C**	0.459276	0.503873	-0.372356
C	-4.414787	-0.135576	-1.837136	**C**	1.314475	2.600915	-0.327532
C	-5.778367	-0.209842	-2.105007	**C**	1.454739	3.986319	-0.274444
C	-6.638760	-0.762259	-1.160017	**C**	2.745983	4.502708	-0.208812
C	-6.126410	-1.246566	0.044084	**C**	3.871610	3.666840	-0.191772
C	-4.761988	-1.188330	0.335271	**C**	3.726065	2.283599	-0.251622
C	-4.170987	-1.686780	1.636360	**C**	2.441483	1.740226	-0.329133
C	0.427209	-0.528556	-0.051785	**C**	-3.882133	0.954461	-0.412327
C	1.890976	-0.501349	0.119365	**C**	-4.579018	1.471973	0.697389
C	2.326722	-1.888664	-0.113675	**C**	-4.564800	0.683979	-1.605998
C	3.577328	-2.510280	-0.140834	**C**	-5.956251	1.674783	0.579778
C	3.648899	-3.869568	-0.433562	**C**	-5.934924	0.901778	-1.700751
C	2.483570	-4.603615	-0.696360	**C**	-6.638408	1.394156	-0.602266
C	1.225866	-4.006430	-0.682280	**C**	1.925841	0.361277	-0.362685
C	1.160269	-2.644901	-0.393236	**C**	3.882135	-0.954454	-0.412309
C	3.904028	0.611413	0.624763	**C**	4.579011	-1.471986	0.697404
C	4.414792	0.135584	1.837137	**C**	4.564810	-0.683957	-1.605972
C	5.778373	0.209849	2.105001	**C**	5.956244	-1.674800	0.579797
C	6.638763	0.762259	1.160006	**C**	5.934934	-0.901761	-1.700720
C	6.126410	1.246561	-0.044096	**C**	6.638409	-1.394158	-0.602238
C	4.761986	1.188327	-0.335277	**C**	3.859429	-1.737414	1.996085
C	4.170980	1.686771	-1.636367	**C**	-3.859445	1.737385	1.996079
H	-5.954681	-1.830495	2.887932	**H**	-3.161067	0.695504	3.778761
H	-4.586983	-2.796621	3.442447	**H**	-3.121294	-0.292523	2.311574
H	-5.538511	-3.333585	2.053756	**H**	-4.663476	0.042219	3.105126
H	5.954670	1.830474	-2.887947	**H**	3.161047	-0.695558	3.778780
H	5.538507	3.333570	-2.053776	**H**	3.121284	0.292492	2.311608
H	4.586973	2.796601	-3.442461	**H**	4.663462	-0.042268	3.105162
H	-4.477161	1.947394	-0.063640	**H**	-4.595920	-1.642352	-0.239729
H	-4.611882	4.364853	0.456865	**H**	-4.862094	-4.101206	-0.132895
H	-2.560914	5.661855	0.919182	**H**	-2.881425	-5.577519	-0.165842
H	-0.328316	4.575101	0.893313	**H**	-0.586659	-4.634381	-0.276684
H	-3.730353	0.289634	-2.562263	**H**	0.586662	4.634389	-0.276619
H	-6.163245	0.163010	-3.047583	**H**	2.881429	5.577525	-0.165750
H	-7.702774	-0.824117	-1.357956	**H**	4.862096	4.101211	-0.132811
H	-6.806545	-1.677075	0.768711	**H**	4.595923	1.642358	-0.239678
H	-3.757998	-0.829463	2.181409	**H**	0.802738	-2.179415	-0.355575
H	-3.302803	-2.311225	1.396902	**H**	-6.450123	0.688317	-2.630651
H	0.916704	2.071127	0.515915	**H**	-7.706450	1.567131	-0.668195
H	4.477162	-1.947391	0.063645	**H**	-0.802734	2.179424	-0.355550
H	4.611884	-4.364850	-0.456858	**H**	6.499089	-2.063276	1.435768
H	2.560916	-5.661853	-0.919174	**H**	6.450138	-0.688288	-2.630614
H	0.328318	-4.575100	-0.893305	**H**	7.706451	-1.567136	-0.668164
H	3.730360	-0.289621	2.562268	**H**	-6.499103	2.063244	1.435751
H	6.163254	-0.162999	3.047579	**H**	4.006036	-0.305106	-2.454086
H	7.702778	0.824117	1.357940	**H**	-4.006020	0.305142	-2.454114
H	6.806542	1.677065	-0.768727	**H**	2.871484	-2.155223	1.780965
H	3.757987	0.829453	-2.181409	**H**	4.415671	-2.486248	2.566919
H	3.302800	2.311220	-1.396908	**H**	-2.871501	2.155202	1.780971
H	-0.916704	-2.071126	-0.515908	**H**	-4.415693	2.486207	2.566922

Table G14 XYZ coordinates of the GS geometries of **2.1f** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

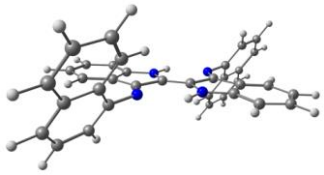
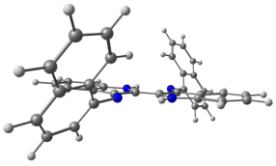
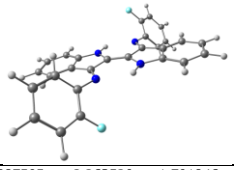
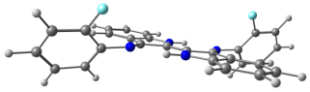
Anti				***Syn***			
							
N	-0.304091	-1.790416	-0.385009	**N**	-0.294500	-1.832659	-0.424528
N	2.574840	0.109119	0.365789	**N**	2.594877	0.194550	-0.418143
N	0.304092	1.790413	0.385019	**N**	0.294500	1.832665	-0.424527
N	-2.574837	-0.109124	-0.365788	**N**	-2.594878	-0.194543	-0.418141
C	6.845981	2.141238	-1.467077	**C**	6.496442	1.895295	2.341552
C	6.654438	-0.291049	1.360568	**C**	6.784181	0.027185	-0.879579
C	7.232846	1.313403	-0.440757	**C**	7.050528	1.276504	1.246843
C	5.479272	2.259362	-1.809539	**C**	5.092338	1.932484	2.503083
C	5.699218	-0.997942	2.052092	**C**	5.959622	-0.549686	-1.816419
C	6.276244	0.563626	0.293047	**C**	6.231848	0.665260	0.260983
C	4.526688	1.543560	-1.122929	**C**	4.269946	1.346089	1.569773
C	4.336771	-0.900423	1.705603	**C**	4.559866	-0.532249	-1.654959
C	4.894955	0.682545	-0.058878	**C**	4.811886	0.701977	0.429349
C	3.924424	-0.086610	0.663810	**C**	3.978571	0.070305	-0.551848
C	-6.845991	-2.141225	1.467071	**C**	-6.496439	-1.895323	2.341539
C	-6.654432	0.291053	-1.360581	**C**	-6.784183	-0.027182	-0.879573
C	-7.232849	-1.313392	0.440747	**C**	-7.050526	-1.276523	1.246837
C	-5.479283	-2.259352	1.809538	**C**	-5.092334	-1.932511	2.503069
C	-5.699207	0.997942	-2.052103	**C**	-5.959626	0.549700	-1.816408
C	-6.276244	-0.563620	-0.293056	**C**	-6.231848	-0.665266	0.260982
C	-4.526695	-1.543556	1.122928	**C**	-4.269945	-1.346106	1.569765
C	-4.336762	0.900420	-1.705609	**C**	-4.559869	0.532264	-1.654949
C	-4.894956	-0.682542	0.058874	**C**	-4.811886	-0.701983	0.429348
C	-3.924421	0.086607	-0.663813	**C**	-3.978573	-0.070299	-0.551843
C	0.318984	-0.599888	-0.073043	**C**	0.325706	-0.600767	-0.436375
C	1.760470	-0.857523	0.078951	**C**	1.782181	-0.815118	-0.433962
C	1.922145	-2.292889	-0.209347	**C**	1.950561	-2.277849	-0.394113
C	3.029392	-3.140688	-0.306555	**C**	3.061803	-3.121443	-0.305942
C	2.834135	-4.471451	-0.662456	**C**	2.864226	-4.496710	-0.232969
C	1.544532	-4.959970	-0.918932	**C**	1.568457	-5.033532	-0.248694
C	0.426109	-4.135850	-0.841126	**C**	0.444237	-4.217014	-0.322242
C	0.628944	-2.801751	-0.492981	**C**	0.648220	-2.839890	-0.385980
C	-0.318982	0.599884	0.073051	**C**	-0.325707	0.600773	-0.436374
C	-0.628945	2.801747	0.492990	**C**	-0.648220	2.839896	-0.385975
C	-0.426111	4.135846	0.841136	**C**	-0.444236	4.217020	-0.322236
C	-1.544535	4.959964	0.918940	**C**	-1.568455	5.033538	-0.248684
C	-2.834137	4.471445	0.662461	**C**	-2.864224	4.496718	-0.232957
C	-3.029392	3.140682	0.306559	**C**	-3.061802	3.121451	-0.305932
C	-1.922144	2.292884	0.209353	**C**	-1.950561	2.277856	-0.394107
C	-1.760468	0.857519	-0.078946	**C**	-1.782183	0.815125	-0.433958
H	7.588123	2.707862	-2.018015	**H**	7.134599	2.358123	3.085790
H	7.703190	-0.369174	1.624322	**H**	7.861315	0.010573	-1.002071
H	8.280050	1.219365	-0.173810	**H**	8.127108	1.245226	1.117902
H	5.184285	2.917324	-2.619017	**H**	4.664912	2.425248	3.368919
H	5.987465	-1.640980	2.876108	**H**	6.381912	-1.026097	-2.694071
H	3.479044	1.626869	-1.383511	**H**	3.194267	1.367442	1.691349
H	3.595273	-1.456788	2.266095	**H**	3.923149	-0.982700	-2.406748
H	-7.588136	-2.707845	2.018008	**H**	-7.134595	-2.358160	3.085773
H	-7.703182	0.369181	-1.624338	**H**	-7.861318	-0.010571	-1.002065
H	-8.280053	-1.219352	0.173796	**H**	-8.127107	-1.245245	1.117897
H	-5.184300	-2.917313	2.619019	**H**	-4.664908	-2.425284	3.368899
H	-5.987449	1.640979	-2.876121	**H**	-6.381917	1.026118	-2.694055
H	-3.479052	-1.626867	1.383514	**H**	-3.194265	-1.367458	1.691340
H	-3.595260	1.456781	-2.266100	**H**	-3.923154	0.982723	-2.406734
H	4.025355	-2.771251	-0.107978	**H**	4.062900	-2.714718	-0.295919
H	3.684959	-5.137451	-0.738857	**H**	3.718539	-5.159324	-0.166801
H	1.414029	-6.001921	-1.188486	**H**	1.436871	-6.108432	-0.197940
H	-0.568389	-4.510494	-1.051114	**H**	-0.556768	-4.631076	-0.320953
H	0.568386	4.510490	1.051125	**H**	0.556770	4.631081	-0.320949
H	-1.414033	6.001916	1.188494	**H**	-1.436868	6.108438	-0.197929
H	-3.684962	5.137444	0.738861	**H**	-3.718537	5.159332	-0.166786
H	-4.025355	2.771244	0.107980	**H**	-4.062899	2.714727	-0.295907
H	-1.299576	-1.835955	-0.568968	**H**	-1.304025	-1.919116	-0.411921
H	1.299576	1.835952	0.568980	**H**	1.304025	1.919121	-0.411919

Table G15 XYZ coordinates of the GS geometries of **2.1g** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

Anti				***Syn***			
							
F	-3.887505	-2.263520	-1.701946	**F**	4.007568	-0.041417	1.897761
F	3.887496	2.263523	1.701947	**F**	-3.742934	-2.290895	1.736147
N	-0.059280	1.852671	-0.084223	**N**	0.126526	-1.747647	-0.187332
N	-2.506122	-0.686938	0.021462	**N**	2.463414	0.898188	-0.249433
N	0.059283	-1.852676	0.084219	**N**	-0.161539	1.951746	-0.093536
N	2.506119	0.686937	-0.021463	**N**	-2.486921	-0.701530	-0.073168
C	-0.433762	0.527662	-0.026543	**C**	0.440674	-0.405266	-0.178422
C	-1.904780	0.461000	-0.025847	**C**	1.907114	-0.273309	-0.222788
C	-2.347682	1.861512	-0.121641	**C**	2.410708	-1.652519	-0.269365
C	-3.598421	2.475203	-0.240404	**C**	3.689050	-2.208487	-0.369223
C	-3.665135	3.859343	-0.361680	**C**	3.822212	-3.592096	-0.422879
C	-2.494872	4.632800	-0.364539	**C**	2.690625	-4.419533	-0.374853
C	-1.236554	4.048092	-0.263648	**C**	1.405702	-3.892504	-0.286871
C	-1.175410	2.660202	-0.152770	**C**	1.278076	-2.505668	-0.241794
C	0.433762	-0.527667	0.026540	**C**	-0.473063	0.609163	-0.117052
C	1.175413	-2.660205	0.152767	**C**	-1.311785	2.705576	0.018229
C	1.236559	-4.048096	0.263645	**C**	-1.435633	4.089615	0.124131
C	2.494878	-4.632802	0.364537	**C**	-2.716049	4.613977	0.270203
C	3.665140	-3.859344	0.361678	**C**	-3.846953	3.785423	0.315569
C	3.598424	-2.475203	0.240402	**C**	-3.718026	2.405165	0.200199
C	2.347684	-1.861515	0.121638	**C**	-2.444392	1.851631	0.038083
C	-3.884954	-0.822557	0.174193	**C**	3.846273	1.084254	-0.182619
C	-4.577886	-1.682547	-0.687078	**C**	4.503333	1.829452	-1.172816
C	-4.615590	-0.252640	1.228918	**C**	4.618088	0.660097	0.907014
C	-5.928413	-1.946937	-0.557840	**C**	5.867000	2.091139	-1.090256
C	-5.972334	-0.516715	1.383924	**C**	5.970625	0.923745	1.016438
C	-6.635209	-1.356804	0.489427	**C**	6.605504	1.641365	0.003683
C	1.904780	-0.461003	0.025845	**C**	-1.938569	0.473064	-0.061087
C	3.884952	0.822558	-0.174191	**C**	-3.863516	-0.898731	-0.172563
C	4.615591	0.252642	-1.228915	**C**	-4.651926	-0.384190	-1.213834
C	4.577880	1.682551	0.687080	**C**	-4.490404	-1.764372	0.732188
C	5.972335	0.516719	-1.383918	**C**	-6.001063	-0.706649	-1.315653
C	5.928407	1.946943	0.557845	**C**	-5.832478	-2.086384	0.655723
C	6.635206	1.356811	-0.489420	**C**	-6.597894	-1.551098	-0.379737
H	-4.505246	1.887411	-0.238038	**H**	4.567082	-1.579339	-0.412722
H	-4.629141	4.344790	-0.452365	**H**	4.807777	-4.034719	-0.499406
H	-2.569816	5.710673	-0.453390	**H**	2.817321	-5.495600	-0.411394
H	-0.332490	4.644574	-0.280055	**H**	0.532388	-4.532806	-0.259843
H	0.332496	-4.644579	0.280051	**H**	-0.561562	4.729197	0.103739
H	2.569823	-5.710675	0.453387	**H**	-2.839450	5.687571	0.356649
H	4.629146	-4.344790	0.452363	**H**	-4.829203	4.224680	0.439815
H	4.505248	-1.887411	0.238037	**H**	-4.594559	1.774058	0.236229
H	0.916078	2.128606	-0.075753	**H**	-0.833165	-2.067775	-0.123918
H	-6.512079	-0.067326	2.209151	**H**	6.506893	0.565665	1.886912
H	-7.692690	-1.560079	0.605760	**H**	7.665753	1.850318	0.076407
H	-0.916076	-2.128612	0.075749	**H**	0.798559	2.274958	-0.105998
H	6.512082	0.067331	-2.209143	**H**	-6.586734	-0.299536	-2.131452
H	6.407463	2.608018	1.269799	**H**	-6.259624	-2.748570	1.399002
H	7.692687	1.560087	-0.605751	**H**	-7.649413	-1.799736	-0.454492
H	-6.407472	-2.608011	-1.269793	**H**	6.352099	2.653721	-1.879103
H	-4.096749	0.388995	1.930449	**H**	3.917864	2.184812	-2.012597
H	4.096753	-0.388995	-1.930446	**H**	-4.183487	0.261442	-1.946610

XYZ coordinates of protonated *cis*-Nindigos 1.65 and 2.2a – 2.2g

Table G16 XYZ coordinates of the GS and TS geometries of **1.65** (Ar = Ph) B3LYP/6-311G(d,p) (gas phase)

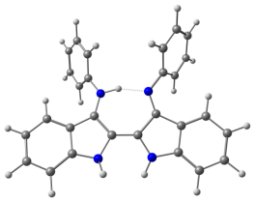
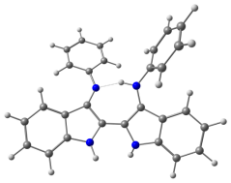
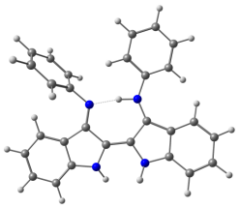
1.65				TS				TS'			
											
C	0.709565	-1.708168	-0.152330	**N**	-1.449490	0.680558	-0.419550	**N**	1.835264	-2.730360	0.164800
C	1.674564	-0.622746	-0.155477	**N**	-1.582879	-2.776809	-0.029683	**N**	1.425258	0.804665	-0.092942
C	2.985678	-1.230709	-0.161219	**N**	1.269841	0.642335	0.021846	**N**	-0.872570	-3.010522	-0.075813
C	4.290002	-0.712167	-0.252848	**N**	1.113671	-2.873585	-0.676755	**N**	-1.260121	0.485672	0.023004
H	4.466459	0.352966	-0.241939	**C**	-1.227380	2.819668	-1.344873	**C**	1.044547	-1.580120	0.064086
C	5.348202	-1.595007	-0.366291	**C**	-1.671335	4.088598	-1.676476	**C**	1.945162	-0.421890	-0.025154
H	6.358450	-1.214011	-0.439796	**C**	-2.964865	4.480209	-1.335700	**C**	3.298539	-0.968047	0.006030
C	5.130525	-2.984116	-0.388105	**C**	-3.805692	3.584845	-0.674805	**C**	4.610830	-0.462228	-0.100140
H	5.979180	-3.651813	-0.472733	**C**	-3.366064	2.312198	-0.342408	**H**	4.815741	0.568392	-0.313965
C	3.852991	-3.520520	-0.304749	**C**	-2.058959	1.902199	-0.662617	**C**	5.696093	-1.307340	0.039630
H	3.690337	-4.590780	-0.326939	**C**	-2.901819	-2.522603	0.357617	**H**	6.695594	-0.901392	-0.044930
C	2.790014	-2.630123	-0.192037	**C**	-3.864413	-3.459032	0.693249	**C**	5.522787	-2.678089	0.279762
C	2.156224	1.776070	0.141384	**C**	-5.100098	-2.983444	1.125774	**H**	6.389423	-3.317441	0.393197
C	2.982423	1.774672	1.267781	**C**	-5.334853	-1.612114	1.234652	**C**	4.252488	-3.225733	0.347399
H	3.026204	0.900895	1.905524	**C**	-4.356328	-0.686900	0.883797	**H**	4.102166	-4.287301	0.499331
C	3.727612	2.907900	1.569443	**C**	-3.119160	-1.128275	0.400458	**C**	3.168179	-2.369773	0.190812
H	4.366079	2.910392	2.444235	**C**	-1.858107	-0.487284	-0.035512	**C**	1.872148	2.144783	-0.133534
C	3.640420	4.042788	0.763550	**C**	-0.883798	-1.615125	-0.168821	**C**	0.839294	3.101293	-0.077393
H	4.220894	4.924293	1.005344	**C**	2.338608	2.825240	0.099340	**C**	1.124788	4.455841	-0.103254
C	2.795522	4.046235	-0.344166	**C**	3.197730	3.727655	0.718458	**H**	0.311081	5.168779	-0.056760
H	2.718810	4.928569	-0.967170	**C**	3.894745	3.358007	1.866109	**C**	2.444685	4.895697	-0.186799
C	2.048428	2.916156	-0.657229	**C**	3.722639	2.082777	2.403759	**H**	2.670645	5.954175	-0.209108
C	-0.665395	-1.723153	-0.033840	**C**	2.859950	1.178146	1.797628	**C**	3.469031	3.956653	-0.240188
C	-1.674745	-0.628918	-0.119610	**C**	2.176746	1.547898	0.636512	**H**	4.500541	4.280256	-0.303616
C	-2.979359	-1.278859	0.068925	**C**	2.486691	-2.660353	-0.719850	**C**	3.191470	2.594588	-0.214474
C	-4.299606	-0.822225	0.016715	**C**	3.493922	-3.566742	-1.038737	**C**	-0.322009	-1.746785	-0.028375
H	-4.519978	0.221949	-0.146914	**C**	4.801154	-3.101400	-1.023319	**C**	-1.456095	-0.784736	-0.011148
C	-5.331776	-1.738564	0.189120	**C**	5.104734	-1.764949	-0.704214	**C**	-2.674718	-1.597294	-0.087393
H	-6.358604	-1.398453	0.154310	**C**	4.103520	-0.864772	-0.390939	**C**	-4.033593	-1.279406	-0.168918
C	-5.060414	-3.092227	0.412480	**C**	2.770111	-1.312936	-0.399721	**H**	-4.368652	-0.254245	-0.119002
H	-5.880813	-3.784728	0.554707	**C**	1.501947	-0.641401	-0.246473	**C**	-4.950458	-2.314894	-0.318006
C	-3.751977	-3.573332	0.442460	**C**	0.474740	-1.635476	-0.434633	**H**	-6.006778	-2.088261	-0.381375
H	-3.544320	-4.625722	0.590653	**H**	-0.240914	2.489868	-1.642169	**C**	-4.524861	-3.645508	-0.386238
C	-2.734976	-2.651256	0.257167	**H**	1.809925	3.100813	-0.803702	**H**	-5.258273	-4.434218	-0.500413
C	-2.189237	1.691294	-0.316218	**H**	-1.125602	-3.660929	0.139351	**C**	-3.173217	-3.981840	-0.311155
C	-2.954231	1.973145	0.823535	**H**	0.287939	0.923080	-0.138292	**H**	-2.847898	-5.013096	-0.368203
H	-2.919591	1.301061	1.672062	**H**	0.701043	-3.516798	-1.339821	**C**	-2.270703	-2.941414	-0.163613
C	-3.725463	3.127454	0.867441	**H**	-1.017110	4.769027	-2.207226	**C**	-2.332368	1.402895	0.138658
H	-4.304090	3.350308	1.755654	**H**	-3.319527	5.471494	-1.589227	**C**	-3.035241	1.518887	1.341843
C	-3.752408	3.998974	-0.221310	**H**	-4.814342	3.882511	-0.415912	**C**	-4.043476	2.469265	1.459761
H	-4.361104	4.893751	-0.184485	**H**	-4.041776	1.647720	0.159055	**H**	-4.584262	2.560772	2.393906
C	-2.980665	3.724856	-1.348915	**H**	-3.659261	-4.520830	0.634698	**C**	-4.357625	3.300153	0.385396
H	-2.992950	4.402936	-2.193370	**H**	-5.876630	-3.686629	1.399464	**H**	-5.146376	4.035848	0.480623
C	-2.181067	2.588700	-1.390572	**H**	-6.286940	-1.258956	1.608878	**C**	-3.646855	3.188067	-0.807603
H	1.074571	-3.722223	-0.616311	**H**	-4.565708	0.355496	1.048390	**H**	-3.885438	3.832149	-1.645201
H	0.319834	0.833438	-0.341514	**H**	3.327340	4.717447	0.298669	**C**	-2.623458	2.252806	-0.931422
H	-0.919519	-3.726025	0.528635	**H**	4.564599	4.061789	2.344122	**H**	0.373955	0.785784	-0.052953
N	1.431199	-2.917118	-0.119332	**H**	4.250894	1.796868	3.304938	**H**	1.512620	-3.513093	0.716673
N	1.339572	0.659827	-0.171778	**H**	2.707309	0.193130	2.220808	**H**	-0.355509	-3.801010	-0.431629
N	-1.355890	-2.887978	0.175839	**H**	3.266873	-4.596157	-1.286176	**H**	-2.063319	2.160261	-1.853927
N	-1.321761	0.585626	-0.369508	**H**	5.607459	-3.784394	-1.261294	**H**	4.011398	1.909686	-0.253945
H	1.393149	2.905540	-1.519697	**H**	6.137118	-1.440197	-0.705380	**H**	-0.189879	2.782235	-0.005836
H	-1.569932	2.368252	-2.257333	**H**	4.343128	0.160351	-0.149694	**H**	-2.783794	0.870545	2.172379

Table G17 XYZ coordinates of the GS, TS, and TS' geometries of **2.2a** B3LYP/6-311G(d,p) (gas phase)

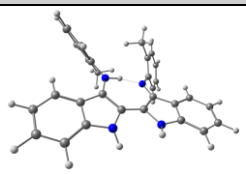
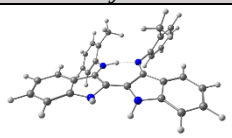
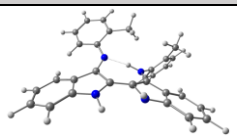
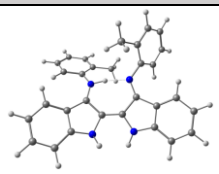
Anti				***Syn***				**TS**				**TS'**			
															
N	1.312856	0.442152	-0.125754	**C**	-0.781270	-1.825127	0.021878	**N**	1.542845	0.668038	-0.283933	**N**	1.285354	0.381670	0.333063
N	1.385847	-3.066415	0.185242	**C**	-1.751660	-0.737963	0.005381	**N**	1.782858	-2.803600	-0.368576	**N**	1.094464	-2.954753	-0.729097
N	-1.347710	0.456147	0.035000	**C**	-3.052883	-1.341165	0.189065	**N**	-1.197513	0.418547	0.276608	**N**	-1.466806	0.645815	-0.068812
N	-1.400325	-3.110791	-0.177661	**C**	-4.346474	-0.814936	0.355401	**N**	-0.930908	-3.000454	-0.758761	**N**	-1.603606	-2.919523	-0.207324
C	2.107001	2.644936	0.487928	**H**	-4.528900	0.245995	0.274239	**C**	1.432488	2.921625	-1.065276	**C**	2.087018	2.174536	1.726160
C	2.944060	3.725768	0.207431	**C**	-5.385344	-1.684439	0.634428	**C**	2.015825	4.177128	-1.227227	**C**	2.969425	3.239123	1.910524
C	3.821591	3.708524	-0.873063	**H**	-6.386899	-1.297047	0.768329	**C**	3.298402	4.456657	-0.771820	**C**	3.937220	3.556425	0.961306
C	3.883490	2.589151	-1.701174	**C**	-5.158842	-3.067360	0.745376	**C**	4.041564	3.452033	-0.155722	**C**	4.042167	2.800415	-0.205289
C	3.082511	1.488948	-1.430945	**H**	-5.992568	-3.725199	0.958416	**C**	3.488641	2.195982	0.012598	**C**	3.196173	1.718950	-0.401315
C	2.205898	1.508052	-0.338231	**C**	-3.890722	-3.611047	0.589087	**C**	2.178979	1.897638	-0.411233	**C**	2.231510	1.392041	0.562344
C	2.756802	-2.808820	0.325912	**H**	-3.721078	-4.676561	0.680044	**C**	3.087083	-2.564062	0.074129	**C**	2.490294	-2.845123	-0.676301
C	3.775941	-3.711073	0.583857	**C**	-2.847382	-2.733899	0.313231	**C**	4.076184	-3.511691	0.271740	**C**	3.435256	-3.817641	-0.959508
C	5.064706	-3.195008	0.714861	**C**	-2.281030	1.629567	-0.421883	**C**	5.275580	-3.082260	0.834578	**C**	4.773028	-3.486474	-0.746970
C	5.315000	-1.823938	0.596403	**C**	-3.212432	1.542334	-1.459181	**C**	5.440676	-1.749680	1.211612	**C**	5.139294	-2.229833	-0.255833
C	4.282836	-0.930205	0.331171	**H**	-3.291487	0.626357	-2.031333	**C**	4.437528	-0.810430	0.989198	**C**	4.179400	-1.256932	0.005914
C	2.984467	-1.428089	0.186534	**C**	-4.015982	2.633244	-1.758506	**C**	3.244497	-1.191178	0.360564	**C**	2.834059	-1.558306	-0.223179
C	1.675037	-0.788548	0.004274	**H**	-4.735685	2.568403	-2.564842	**C**	1.966504	-0.529078	-0.013931	**C**	1.575125	-0.815409	-0.040478
C	0.678216	-1.897625	0.048274	**C**	-3.877239	3.812009	-1.027475	**C**	1.029953	-1.668770	-0.296230	**C**	0.490416	-1.784573	-0.343646
C	1.149699	2.681106	1.649592	**H**	-4.500968	4.667860	-1.254112	**C**	0.053864	2.699747	-1.624195	**C**	1.033483	1.844871	2.748611
C	-1.125846	2.774466	-1.631709	**C**	-2.929029	3.896294	-0.012849	**C**	-3.274716	1.362931	-1.602214	**C**	0.043710	2.575940	-1.622984
C	-2.090244	2.707285	-0.477378	**H**	-2.822321	4.818348	0.546539	**C**	-3.168561	1.828444	-0.173850	**C**	-1.402061	2.759299	-1.250647
C	-2.903509	3.794287	-0.148115	**C**	-2.104469	2.816171	0.309033	**C**	-4.076888	2.769035	0.323488	**C**	-2.052870	3.913445	-1.688744
C	-3.788611	3.742963	0.923911	**C**	-1.065146	2.923727	1.393150	**C**	-4.014510	3.224212	1.635697	**C**	-3.391140	4.162506	-1.413989
C	-3.875034	2.591461	1.704933	**H**	-1.087294	2.059329	2.061212	**C**	-3.024943	2.749497	2.493392	**C**	-4.114926	3.228477	-0.682962
C	-3.079639	1.495662	1.401364	**H**	-1.226311	3.820166	1.991572	**C**	-2.111536	1.812518	2.028064	**C**	-3.495139	2.073837	-0.230225
C	-2.209429	1.550161	0.310164	**H**	-0.056293	2.986639	0.972082	**C**	-2.192241	1.350103	0.714578	**C**	-2.147255	1.818026	-0.496137
C	-2.756825	-2.830811	-0.313509	**C**	2.898114	0.749201	2.378007	**C**	-2.302236	-2.897489	-0.551009	**C**	-2.914648	-2.670877	0.155370
C	-3.801532	-3.720852	-0.538458	**H**	1.869468	0.454881	2.599452	**C**	-3.281591	-3.866136	-0.748692	**C**	-3.916205	-3.615483	0.357886
C	-5.078868	-3.189910	-0.660482	**H**	3.323467	1.195787	3.276825	**C**	-4.581873	-3.546303	-0.382282	**C**	-5.137389	-3.167069	0.832447
C	-5.313931	-1.807185	-0.564686	**H**	3.460421	-0.165223	2.166034	**C**	-4.904323	-2.297004	0.177608	**C**	-5.333348	-1.810378	1.138655
C	-4.273580	-0.924303	-0.337664	**C**	0.583574	-1.840881	-0.156499	**C**	-3.934936	-1.325978	0.350799	**C**	-4.337026	-0.878265	0.921992
C	-2.970817	-1.437718	-0.208992	**C**	1.584114	-0.733936	-0.157175	**C**	-2.616184	-1.615403	-0.043433	**C**	-3.103080	-1.280943	0.365674
C	-1.670345	-0.821540	-0.076188	**C**	2.884890	-1.377096	-0.356040	**C**	-1.391773	-0.849860	-0.050874	**C**	-1.827965	-0.639231	0.093247
C	-0.692315	-1.897199	-0.098449	**C**	4.180565	-0.876211	-0.506868	**C**	-0.340269	-1.743096	-0.465326	**C**	-0.874662	-1.721538	-0.134712
H	0.958510	-3.919567	0.513140	**H**	4.375738	0.184407	-0.438887	**H**	1.356435	-3.717139	-0.303950	**H**	0.612761	-3.688042	-1.226191
H	-0.315310	0.648890	-0.039822	**C**	5.214966	-1.773899	-0.750974	**H**	-0.233453	0.751942	0.121877	**H**	-0.436620	0.745985	-0.026418
H	-1.004896	-3.883537	-0.695942	**H**	6.225723	-1.406130	-0.870454	**H**	-0.597116	-3.520318	-1.560144	**H**	-1.173061	-3.775385	0.117692
H	2.900104	4.599046	0.848096	**C**	4.964558	-3.147018	-0.843781	**H**	1.449429	4.950643	-1.732570	**H**	2.886405	3.836308	2.811257
H	4.448961	4.568413	-1.072556	**H**	5.786715	-3.826366	-1.032268	**H**	3.719450	5.445332	-0.907520	**H**	4.597271	4.399382	1.124467
H	4.548601	2.574985	-2.555766	**C**	3.676915	-3.664935	-0.700106	**H**	5.048785	3.647329	0.190575	**H**	4.772737	3.058248	-0.962101
H	3.108962	0.616844	-2.072943	**H**	3.489020	-4.728604	-0.776641	**H**	4.081928	1.435649	0.474867	**H**	3.248103	1.141661	-1.316025
H	3.583223	-4.771747	0.686295	**C**	2.656066	-2.760327	-0.459372	**H**	3.913506	-4.551901	0.017796	**H**	3.150054	-4.799678	-1.315892
H	5.886053	-3.871834	0.915319	**C**	2.165701	1.558723	0.076257	**H**	6.071271	-3.795772	1.008110	**H**	5.539216	-4.222659	-0.956223
H	6.325773	-1.453981	0.709267	**C**	2.185360	2.506470	-0.951313	**H**	6.355106	-1.438864	1.699957	**H**	6.184117	-2.008539	-0.080606
H	4.485232	0.126411	0.238750	**H**	1.538518	2.364846	-1.808833	**H**	4.589719	0.181599	1.377773	**H**	4.475745	-0.287480	0.377048
H	1.249567	1.798200	2.284935	**C**	3.044562	3.595738	-0.879038	**H**	-0.714536	2.898790	-0.872035	**H**	1.229864	0.880847	3.226277
H	1.325764	3.563227	2.265302	**H**	3.073026	4.314503	-1.688533	**H**	-0.127710	3.384404	-2.453356	**H**	0.998200	2.606685	3.527367
H	0.109353	2.721553	1.311453	**C**	3.854903	3.760703	0.241214	**H**	-0.077448	1.681500	-1.985416	**H**	0.044271	1.776456	2.288996
H	-1.188394	1.883217	-2.260396	**H**	4.519073	4.613016	0.313234	**H**	-3.997084	0.546682	-1.695805	**H**	0.280522	1.546758	-1.898869
H	-1.332111	3.645307	-2.253603	**C**	3.795240	2.837763	1.281413	**H**	-3.615465	2.177680	-2.242498	**H**	0.290099	3.211168	-2.473426
H	-0.089912	2.856435	-1.286702	**H**	4.407740	2.985493	2.163803	**H**	-2.323199	1.001226	-1.989473	**H**	0.708467	2.859784	-0.804470
H	-2.839835	4.693964	-0.749004	**C**	2.958539	1.720800	1.228396	**H**	-4.840749	3.155517	-0.341740	**H**	-1.486403	4.628386	-2.273795
H	-4.405637	4.602625	1.154453	**H**	-1.094018	-3.799815	0.655098	**H**	-4.732318	3.955689	1.986185	**H**	-3.861594	5.070134	-1.770560
H	-4.547448	2.552137	2.552687	**H**	-0.386415	0.720693	-0.087840	**H**	-2.965655	3.103563	3.514813	**H**	-5.160255	3.394852	-0.455090
H	-3.116747	0.600973	2.010424	**H**	0.852508	-3.871395	-0.597602	**H**	-1.336486	1.422374	2.676487	**H**	-4.074244	1.379993	0.340360
H	-3.626402	-4.786544	-0.615999	**N**	-1.498372	-3.028659	0.141595	**H**	-3.035695	-4.840272	-1.152419	**H**	-3.735776	-4.665755	0.165606
H	-5.913676	-3.858072	-0.833393	**N**	-1.421735	0.533991	-0.142777	**H**	-5.364068	-4.283642	-0.515833	**H**	-5.938675	-3.875455	1.002399
H	-6.323169	-1.430864	-0.669387	**N**	1.286655	-3.014680	-0.288451	**H**	-5.924899	-2.095665	0.476171	**H**	-6.271125	-1.491708	1.574616
H	-4.461612	0.136598	-0.267792	**N**	1.236289	0.497147	-0.024236	**H**	-4.187844	-0.368860	0.782405	**H**	-4.505111	0.126693	1.265498

Table G18 XYZ coordinates of the GS, TS, and TS' geometries of **2.2b** B3LYP/6-311G(d,p) (gas phase)

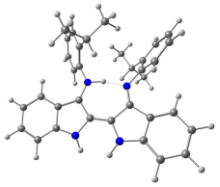
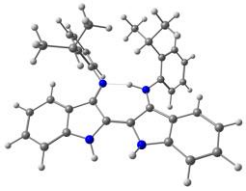
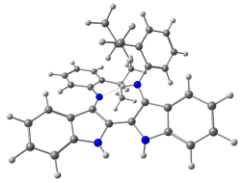
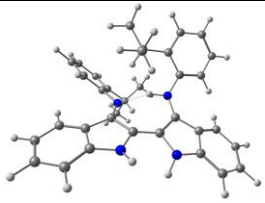
Anti				***Syn***				**TS**				**TS'**			
															
N	1.284736	3.539215	-0.121829	**N**	-1.555681	3.338563	0.266167	**N**	-1.229673	-0.100639	0.046761	**N**	-1.265811	0.002699	0.336862
N	1.306367	-0.030068	-0.106792	**N**	-1.553318	-0.162310	-0.447935	**N**	-1.096726	3.320309	-0.995356	**N**	-0.895074	3.312136	-0.743216
N	-1.524551	3.417580	0.044040	**N**	1.218509	3.335448	-0.272310	**N**	1.498458	-0.259411	-0.532853	**N**	1.497038	-0.414386	-0.066650
N	-1.325792	-0.093354	-0.078280	**N**	1.097864	-0.180648	-0.446707	**N**	1.617229	3.214176	-0.515534	**N**	1.782201	3.147383	-0.165597
C	0.600499	2.307738	-0.131461	**C**	-0.864411	2.151483	-0.033024	**C**	-1.824220	-1.910820	1.557501	**C**	-2.042992	-1.911986	1.577855
C	1.604992	1.253333	-0.112250	**C**	-1.853566	1.084200	-0.134442	**C**	-2.690266	-2.964387	1.860033	**C**	-2.936155	-2.980853	1.678815
C	2.894556	1.904769	-0.073288	**C**	-3.134733	1.674814	0.182862	**C**	-3.803015	-3.245220	1.071855	**C**	-3.954545	-3.173973	0.752592
C	4.212562	1.428232	0.032397	**C**	-4.427847	1.145715	0.340432	**C**	-4.069567	-2.480807	-0.060347	**C**	-4.101400	-2.288085	-0.315855
H	4.415777	0.370441	0.107058	**H**	-4.630306	0.105191	0.135811	**C**	-3.222202	-1.431378	-0.389717	**C**	-3.247771	-1.204078	-0.427934
C	5.248696	2.345548	0.032285	**C**	-5.439564	1.985845	0.770207	**C**	-2.130844	-1.136799	0.425951	**C**	-2.230530	-0.995968	0.520450
H	6.271177	2.000217	0.112264	**H**	-6.440882	1.596360	0.899720	**C**	-2.463563	3.177076	-0.785189	**C**	-2.295437	3.281528	-0.700938
C	4.991067	3.723018	-0.074940	**C**	-5.185306	3.341627	1.039564	**C**	-3.465355	4.125341	-0.968251	**C**	-3.181239	4.305496	-0.993526
H	5.822220	4.417593	-0.083761	**H**	-5.997925	3.977484	1.369123	**C**	-4.753453	3.779703	-0.584130	**C**	-4.536535	4.055148	-0.781408
C	3.695513	4.218496	-0.153534	**C**	-3.916315	3.887030	0.893403	**C**	-5.039862	2.524520	-0.018834	**C**	-4.975780	2.826588	-0.279467
H	3.504184	5.282742	-0.209413	**H**	-3.726078	4.931615	1.105584	**C**	-4.048949	1.572368	0.136097	**C**	-4.074532	1.801087	-0.009578
C	2.655246	3.295996	-0.133261	**C**	-2.900504	3.039369	0.465448	**C**	-2.741723	1.884140	-0.280810	**C**	-2.713887	2.018952	-0.242152
C	2.190581	-1.144412	-0.195362	**C**	-2.454405	-1.206231	-0.800136	**C**	-1.493952	1.152791	-0.292978	**C**	-1.498543	1.208848	-0.044176
C	2.131276	-2.141928	0.787953	**C**	-3.392084	-0.979254	-1.813159	**C**	-0.469537	2.082522	-0.703440	**C**	-0.360315	2.115884	-0.341071
C	2.958723	-3.256894	0.612592	**C**	-4.249086	-1.996084	-2.202882	**C**	-0.616583	-1.575205	2.419230	**C**	-0.909376	-1.753069	2.574310
H	2.947436	-4.042089	1.358507	**H**	-4.972217	-1.822619	-2.989889	**C**	0.187242	-2.385467	-2.011219	**C**	-0.045365	-2.174374	-1.765534
C	3.790935	-3.383475	-0.492786	**C**	-4.157784	-3.244316	-1.586439	**C**	1.506693	-2.542065	-1.275920	**C**	1.402828	-2.450788	-1.400481
H	4.414954	-4.262328	-0.599350	**H**	-4.821654	-4.046526	-1.884478	**C**	2.153600	-3.777668	-1.344759	**C**	2.054749	-3.568695	-1.919349
C	3.815365	-2.387186	-1.468401	**C**	-3.205847	-3.465638	-0.599302	**C**	3.435059	-3.973838	-0.848816	**C**	3.389680	-3.849820	-1.648012
H	4.446882	-2.488267	-2.342139	**H**	-3.141849	-4.442733	-0.136463	**C**	4.128813	-2.899855	-0.292960	**C**	4.107304	-2.994822	-0.825085
C	3.009010	-1.268739	-1.321194	**C**	-2.325317	-2.460464	-0.184165	**C**	3.511539	-1.668355	-0.196738	**C**	3.487231	-1.874544	-0.289695
C	-0.775007	2.269888	-0.040597	**C**	0.491056	2.168018	-0.266708	**C**	2.187536	-1.460875	-0.637109	**C**	2.153810	-1.576151	-0.569168
C	-1.735822	1.126511	-0.020915	**C**	1.464351	1.051198	-0.447978	**C**	2.892545	3.008254	0.023610	**C**	3.073860	2.837482	0.217931
C	-3.070950	1.731619	0.050861	**C**	2.773324	1.688102	-0.606331	**C**	3.828415	3.981668	0.327911	**C**	4.113291	3.733767	0.449220
C	-4.365340	1.206211	0.006470	**C**	4.050170	1.183466	-0.864334	**C**	4.983185	3.577940	0.994452	**C**	5.301109	3.226285	0.947966
H	-4.529095	0.140491	-0.056766	**H**	4.218228	0.119615	-0.945008	**C**	5.155945	2.244665	1.367415	**C**	5.426552	1.860280	1.251324
C	-5.443644	2.083191	0.055355	**C**	5.099840	2.083373	-1.020440	**C**	4.211381	1.278228	1.033124	**C**	4.393803	0.976575	1.005451
H	-6.452391	1.692398	0.024123	**H**	6.096964	1.713290	-1.220370	**C**	3.074444	1.636163	0.296859	**C**	3.194202	1.439297	0.421034
C	-5.241002	3.464068	0.151650	**C**	4.881603	3.461535	-0.922631	**C**	1.855682	0.941387	-0.192856	**C**	1.897490	0.857549	0.120405
H	-6.096549	4.126332	0.200186	**H**	5.714949	4.142239	-1.045916	**C**	0.896734	2.053950	-0.496884	**C**	0.998037	1.981983	-0.112879
C	-3.958021	4.009804	0.173485	**C**	3.611975	3.983655	-0.671925	**H**	-0.775240	3.856663	-1.790734	**H**	-0.366911	4.019278	-1.230904
H	-3.804950	5.080621	0.224007	**H**	3.449381	5.051951	-0.602255	**H**	1.153800	4.109774	-0.450369	**H**	0.467886	-0.479811	-0.043173
C	-2.893224	3.125400	0.109528	**C**	2.575597	3.077376	-0.520247	**H**	-2.491514	-3.581893	2.725517	**H**	1.385352	4.017842	0.164017
C	-2.112724	-1.240175	0.122229	**C**	2.017001	-1.258457	-0.520949	**H**	-4.452922	-4.070570	1.335484	**H**	-2.824204	-3.684736	2.494583
C	-1.961976	-2.326627	-0.762433	**C**	2.795865	-1.634834	0.588272	**H**	-4.916714	-2.711471	-0.694098	**H**	-4.623062	-4.020216	0.852824
C	-2.674034	-3.494630	-0.477740	**C**	3.598412	-2.771610	0.445638	**H**	-3.389621	-0.849722	-1.287358	**H**	-4.870065	-2.450415	-1.061460
H	-2.596513	-4.336072	-1.155339	**H**	4.201970	-3.093693	1.285716	**H**	-3.243362	5.105548	-1.371201	**H**	-3.328251	-0.533781	-1.273621
C	-3.467725	-3.610284	0.657734	**C**	3.645689	-3.499747	-0.737533	**H**	-5.552594	4.500717	-0.705850	**H**	-2.838043	5.266865	-1.355145
H	-3.994809	-4.535352	0.856344	**H**	4.285051	-4.370813	-0.810598	**H**	-6.050680	2.301857	0.297315	**H**	-5.258033	4.833216	-0.997745
C	-3.572477	-2.539976	1.546382	**C**	2.863332	-3.110310	-1.822162	**H**	-4.279659	0.611545	0.569785	**H**	-6.031652	2.668848	-0.101652
H	-4.166709	-2.630636	2.447286	**H**	2.888440	-3.670402	-2.748713	**H**	1.647060	-4.606278	-1.821804	**H**	-4.428152	0.855118	0.372390
C	-2.903373	-1.357502	1.275963	**C**	2.037504	-2.000840	-1.706185	**H**	3.899505	-4.950078	-0.917304	**H**	1.502282	-4.242041	-2.559154
H	0.269878	-0.228927	-0.104847	**H**	-0.518704	-0.364831	-0.476695	**H**	5.144589	-3.023949	0.061208	**H**	3.855417	-4.731568	-2.070038
H	0.914786	4.326441	-0.635923	**H**	-1.115198	4.038536	0.847271	**H**	4.069712	-0.845713	0.200136	**H**	5.143505	-3.196205	-0.584021
H	-1.139758	4.304831	0.328794	**H**	0.796590	4.233784	-0.453555	**H**	3.656178	5.021737	0.079797	**H**	4.054605	-1.246301	0.362753
H	-2.957843	-0.525492	1.967161	**H**	1.409308	-1.687677	-2.531433	**H**	5.735232	4.312658	1.253302	**H**	3.985850	4.792518	0.261011
C	-1.104471	-2.222550	-2.010667	**C**	2.745568	-0.896188	1.917172	**H**	6.028886	1.955394	1.938027	**H**	6.130272	3.895671	1.140787
C	-1.988566	-2.117869	-3.265775	**C**	4.142541	-0.495461	2.415738	**H**	4.351981	0.279948	1.413603	**H**	6.337382	1.496895	1.708954
H	-2.672710	-1.268528	-3.197664	**H**	4.672977	0.106966	1.675930	**C**	-0.924054	-0.360393	3.314739	**H**	4.504174	-0.036686	1.348745
H	-1.372008	-1.991115	-4.159183	**H**	4.059908	0.091401	3.333733	**H**	-1.237906	0.504949	2.727111	**C**	-1.431625	-1.617129	4.013404
H	-2.589213	-3.021760	-3.396520	**H**	4.755220	-1.371462	2.641019	**H**	-1.727914	-0.599351	4.015629	**H**	-2.131334	-0.782982	4.102555
C	-0.098996	-3.377772	-2.125635	**C**	2.000969	-1.731901	2.972613	**H**	-0.041645	-0.077577	3.894155	**H**	-1.947195	-2.523916	4.339384
H	0.534699	-3.445347	-1.239681	**H**	0.985534	-1.964430	2.646565	**C**	-0.106365	-2.754615	3.252468	**H**	-0.601532	-1.442520	4.702254
H	-0.602918	-4.338231	-2.257770	**H**	2.517586	-2.676708	3.159691	**H**	-0.815727	-3.036942	4.034306	**C**	0.095234	-2.910565	2.446733
H	0.549596	-3.225226	-2.991284	**H**	1.940067	-1.188730	3.919068	**H**	0.087696	-3.631660	2.630940	**H**	-0.367767	-3.866535	2.704670
H	-0.534293	-1.293173	-1.941597	**H**	2.177215	0.024717	1.776374	**H**	0.826861	-2.478742	3.748016	**H**	0.485829	-2.993418	1.429909
H	2.994803	-0.493220	-2.077143	**H**	-3.432368	-0.009462	-2.293621	**C**	0.461691	-2.280507	-3.524529	**H**	0.940169	-2.756447	3.122703
C	1.242323	-2.020405	2.013847	**C**	-1.304518	-2.733899	0.906916	**H**	-0.473521	-2.119178	-4.067045	**C**	-0.153117	-1.010034	-2.768805
H	0.607175	-1.140975	1.885117	**H**	-0.692949	-1.837889	1.032837	**H**	1.135442	-1.449660	-3.745940	**H**	-1.202204	-0.769549	-2.959380
C	2.093007	-1.786782	3.274119	**C**	-0.360069	-3.884368	0.524508	**H**	0.920060	-3.196454	-3.905604	**H**	0.344276	-0.105507	-2.413108
H	2.722374	-0.899748	3.168160	**H**	0.142319	-3.688353	-0.423930	**C**	-0.808712	-3.514584	-1.708627	**H**	0.308029	-1.287407	-3.719840
H	1.451153	-1.649560	4.147765	**H**	0.408599	-4.011886	1.289532	**H**	-0.460426	-4.475353	-2.093952	**C**	-0.809276	-3.395240	-2.289090
H	2.747253	-2.640367	3.468827	**H**	-0.901418	-4.829325	0.435677	**H**	-0.985488	-3.620727	-0.637141	**H**	-0.455774	-3.710829	-3.273749
C	0.314005	-3.233543	2.176692	**C**	-2.000013	-2.998516	2.252929	**H**	-1.766698	-3.302591	-2.186209	**H**	-0.730726	-4.241873	-1.604088
H	-0.299500	-3.388303	1.288001	**H**	-1.258620	-3.145083	3.042224	**H**	-0.266536	-1.444306	-1.716586	**H**	-1.866558	-3.142173	-2.385329
H	0.880455	-4.148929	2.364175	**H**	-2.643082	-2.162361	2.537957	**H**	0.200297	-1.292339	1.747339	**H**	-0.561019	-1.888129	-0.852849
H	-0.356904	-3.080503	3.024815	**H**	-2.619231	-3.897660	2.206225	**H**	-0.243846	-0.364552	-0.104382	**H**	-0.385566	-0.827512	2.328209

Table G19 XYZ coordinates of the GS, TS, and TS' geometries of **2.2c** B3LYP/6-311G(d,p) (gas phase)

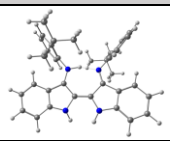
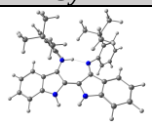
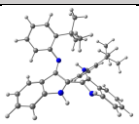
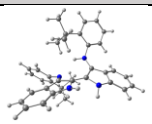
Anti				***Syn***				**TS**				**TS'**			
															
N	1.357349	3.390890	-0.342150	**N**	1.389143	3.348092	-0.051912	**N**	-1.928329	-0.462505	-0.092722	**N**	-1.388580	-0.086250	0.346407
N	1.332344	-0.182586	-0.153863	**N**	1.225637	-0.186702	-0.515004	**N**	-2.026399	2.887954	-0.893344	**N**	-0.947204	2.554315	-1.901363
N	-1.397352	3.350379	0.216849	**N**	-1.378295	3.293957	0.467991	**N**	1.075175	-0.042625	0.344523	**N**	1.746447	-0.451789	0.002401
N	-1.354192	-0.163359	0.017135	**N**	-1.475257	-0.095879	-0.516604	**N**	0.597894	2.953222	-1.575000	**N**	1.437803	3.058648	-0.621319
C	0.650252	2.176036	-0.221948	**C**	0.636651	2.163480	-0.171498	**C**	-2.430956	-2.765426	-0.695191	**C**	-2.591825	-1.129906	2.222402
C	1.623963	1.096543	-0.281681	**C**	1.564406	1.083764	-0.456138	**C**	-3.373532	-3.795791	-0.717005	**C**	-3.545322	-2.086434	2.591262
C	2.919417	1.712812	-0.451786	**C**	2.875248	1.678054	-0.574904	**C**	-4.609450	-3.710669	-0.085984	**C**	-4.225385	-2.878571	1.669305
C	4.226314	1.199693	-0.535260	**C**	4.145275	1.158021	-0.881726	**C**	-4.946875	-2.553394	0.602620	**C**	-3.978188	-2.727373	0.309278
H	4.413045	0.139857	-0.454645	**H**	4.286669	0.101830	-1.052689	**C**	-4.048908	-1.503546	0.626750	**C**	-3.070537	-1.765309	-0.102242
C	5.270836	2.085389	-0.731212	**C**	5.212290	2.034531	-0.971302	**C**	-2.794281	-1.557664	-0.010307	**C**	-2.379290	-0.961884	0.823235
H	6.284382	1.712491	-0.800076	**H**	6.197838	1.656492	-1.209730	**C**	-3.213988	2.871701	-0.150331	**C**	-2.318059	2.357802	-2.118726
C	5.033391	3.466049	-0.846346	**C**	5.033417	3.412337	-0.758988	**C**	-4.111877	3.913963	-0.001609	**C**	-3.162359	3.104362	-2.924678
H	5.870158	4.134910	-1.007176	**H**	5.887338	4.074414	-0.835559	**C**	-5.136728	3.750539	0.928913	**C**	-4.513567	2.758545	-2.924369
C	3.753630	3.997367	-0.746126	**C**	3.789101	3.947940	-0.450113	**C**	-5.211529	2.592553	1.702620	**C**	-4.986205	1.710719	-2.130878
H	3.581526	5.064067	-0.815355	**H**	3.660808	5.009958	-0.282963	**C**	-4.310313	1.546849	1.516352	**C**	-4.118806	0.961128	-1.338382
C	2.706802	3.107284	-0.533917	**C**	2.718504	3.065788	-0.357969	**C**	-3.324389	1.641466	0.526665	**C**	-2.755764	1.274060	-1.337068
C	2.270779	-1.258482	-0.320778	**C**	2.153764	-1.263504	-0.716523	**C**	-2.180414	0.801091	0.067783	**C**	-1.572903	0.762188	-0.604050
C	2.771387	-1.997646	0.767885	**C**	2.921065	-1.820092	0.321856	**C**	-1.273933	1.783808	-0.619154	**C**	-0.440392	1.639662	-1.029294
C	3.674382	-3.019258	0.440125	**C**	3.830307	-2.816786	-0.075959	**C**	-1.063639	-3.004549	-1.350290	**C**	-1.855675	-0.302890	3.299937
H	4.098085	-3.621891	1.228894	**H**	4.468143	-3.266658	0.672356	**C**	3.756143	-1.690545	-0.295789	**C**	1.117505	-2.755115	-1.900052
C	4.054377	-3.297252	-0.869253	**C**	3.948829	-3.260535	-1.384886	**C**	3.173269	-1.255663	1.070695	**C**	2.480096	-2.497418	-1.213882
H	4.756174	-4.099786	-1.061240	**H**	4.667584	-4.034627	-1.624641	**C**	3.918300	-1.633465	2.204041	**C**	3.539066	-3.374830	-1.478329
C	3.530977	-2.557207	-1.922534	**C**	3.138942	-2.720185	-2.379817	**C**	3.541250	-1.337228	3.504567	**C**	4.804538	-3.252233	-0.915148
H	3.809968	-2.769921	-2.946806	**H**	3.208174	-3.064314	-3.403936	**C**	2.368355	-0.627672	3.742025	**C**	5.049366	-2.215114	-0.031810
C	2.633822	-1.538013	-1.639008	**C**	2.246764	-1.718608	-2.036182	**C**	1.607886	-0.230373	2.656038	**C**	4.026703	-1.326560	0.266005
C	-0.699815	2.182563	0.043715	**C**	-0.718076	2.160591	0.065029	**C**	1.995656	-0.533775	1.344966	**C**	2.757577	-1.428107	-0.307767
C	-1.688757	1.067455	0.168390	**C**	-1.758912	1.116660	-0.182569	**C**	1.946238	3.050505	-1.249116	**C**	2.604407	3.066640	0.118175
C	-2.981459	1.712759	0.429584	**C**	-3.043259	1.767530	0.113581	**C**	2.869587	4.005891	-1.663133	**C**	3.390098	4.173271	0.439004
C	-4.280386	1.221308	0.579849	**C**	-4.363342	1.307862	0.138645	**C**	4.143316	3.947259	-1.113818	**C**	4.440448	3.980454	1.319181
H	-4.478683	0.160590	0.545342	**H**	-4.610814	0.310907	-0.192827	**C**	4.492411	2.968995	-0.166180	**C**	4.670651	2.720435	1.902939
C	-5.314688	2.129370	0.787398	**C**	-5.359798	2.166260	0.593197	**C**	3.584515	1.999366	0.219785	**C**	3.901115	1.625823	1.563415
H	-6.327278	1.767143	0.908496	**H**	-6.387323	1.827051	0.613460	**C**	2.301342	2.014635	-0.353281	**C**	2.870723	1.762592	0.603333
C	-5.061303	3.502878	0.848189	**C**	-5.052643	3.462675	1.017314	**C**	1.155519	1.139698	-0.247493	**C**	1.816658	0.903705	0.100270
H	-5.881411	4.189161	1.019700	**H**	-5.846543	4.113514	1.362384	**C**	0.073383	1.791532	-0.935270	**C**	0.843324	1.786218	-0.511312
C	-3.772874	4.013463	0.682568	**C**	-3.741128	3.937791	1.007256	**H**	-1.570530	3.754225	-1.147242	**H**	-0.370042	3.164738	-2.461254
H	-3.584120	5.079332	0.711768	**H**	-3.504544	4.939319	1.344361	**H**	0.182902	-0.526188	0.234636	**H**	0.802716	-0.770699	-0.177936
C	-2.755724	3.099400	0.466522	**C**	-2.759644	3.071965	0.554242	**H**	0.309232	3.152684	-2.524648	**H**	0.843205	3.877107	-0.577256
C	-2.258116	-1.222513	0.293082	**C**	-2.512205	-0.947837	-0.989558	**H**	-3.142135	-4.708871	-1.241886	**H**	-3.765646	-2.233579	3.638122
C	-2.716227	-2.105563	-0.709358	**C**	-3.084576	-0.574934	-2.214037	**H**	-5.295444	-4.547874	-0.130879	**H**	-4.937555	-3.616454	2.019233
C	-3.536617	-3.154841	-0.275429	**C**	-4.080811	-1.339015	-2.800120	**H**	-5.898484	-2.463941	1.111593	**H**	-4.480278	-3.351117	-0.420736
H	-3.925578	-3.853050	-1.001161	**H**	-4.506169	-1.041032	-3.750448	**H**	-4.332523	-0.615754	1.147671	**H**	-2.848008	-1.648837	-1.155826
C	-3.876785	-3.345473	1.060425	**C**	-4.521518	-2.483524	-2.146566	**H**	-4.002866	4.833141	-0.563895	**H**	-2.794518	3.931330	-3.520297
H	-4.506971	-4.181260	1.338538	**H**	-5.306123	-3.093923	-2.576495	**H**	-5.854867	4.546995	1.078269	**H**	-5.204993	3.319033	-3.541834
C	-3.403589	-2.467918	2.028653	**C**	-3.945265	-2.855661	-0.935929	**H**	-5.968893	2.507382	2.471026	**H**	-6.042455	1.472459	-2.133656
H	-3.651765	-2.605259	3.073861	**H**	-4.311007	-3.750929	-0.456373	**H**	-4.355024	0.710421	2.196537	**H**	-4.504374	0.149819	-0.739585
C	-2.599593	-1.408102	1.638886	**C**	-2.919921	-2.124338	-0.322281	**H**	4.834247	-2.188833	2.057454	**H**	3.377823	-4.193081	-2.162511
H	2.204375	-0.942085	-2.434664	**H**	-2.725870	0.324780	-2.699345	**H**	4.162716	-1.662401	4.330008	**H**	5.578683	-3.967585	-1.164817
H	0.311851	-0.398892	-0.084385	**H**	1.617395	-1.255211	-2.786228	**H**	2.054985	-0.385455	4.749589	**H**	6.017893	-2.094531	0.437994
H	0.940033	4.159894	-0.848565	**H**	0.196773	-0.380852	-0.511594	**H**	0.694160	0.333423	2.802095	**H**	4.229141	-0.547450	0.970424
H	-0.949695	4.224373	0.446665	**H**	0.989550	4.222761	-0.364308	**H**	2.596632	4.782928	-2.366070	**H**	3.169775	5.151373	0.028633
C	2.395253	-1.715834	2.235506	**H**	-0.913959	4.057330	0.935776	**H**	4.878605	4.687012	-1.406133	**H**	5.070032	4.818617	1.592669
C	3.032776	-2.743165	3.189028	**C**	2.889631	-1.467644	1.827246	**H**	5.484437	2.977243	0.266524	**H**	5.447290	2.613470	2.649599
H	4.124051	-2.710536	3.160138	**C**	2.675962	-2.772942	2.630691	**H**	3.854386	1.253636	0.951068	**H**	4.047934	0.705282	2.105715
H	2.727314	-2.514464	4.211752	**H**	3.472078	-3.499535	2.469384	**C**	-0.043714	-3.160314	-0.201297	**C**	-2.376995	-0.610710	4.719124
H	2.707925	-3.762340	2.967209	**H**	2.651305	-2.545060	3.698785	**H**	-0.250101	-4.078656	0.353240	**H**	-3.439401	-0.377879	4.828241
C	0.866248	-1.798729	2.431697	**H**	1.730249	-3.245881	2.360160	**H**	0.969608	-3.226835	-0.593261	**H**	-2.218767	-1.654051	5.002357
H	0.340967	-0.979250	1.946641	**C**	1.784302	-0.491895	2.272742	**H**	-0.090597	-2.349179	0.522671	**H**	-1.831594	0.005195	5.437715
H	0.466220	-2.737694	2.042718	**H**	1.958797	0.524851	1.922939	**C**	-0.688978	-1.886139	-2.351010	**C**	-2.058347	1.212386	3.063477
H	0.629854	-1.748612	3.497457	**H**	0.791194	-0.811037	1.956142	**H**	-0.536031	-0.921808	-1.878355	**H**	-1.600959	1.545139	2.132167
C	2.905553	-0.319803	2.654734	**H**	1.783339	-0.454483	3.364195	**H**	0.221051	-2.162795	-2.887547	**H**	-3.121450	1.466939	3.036493
H	3.985238	-0.239650	2.508936	**C**	4.248444	-0.846643	2.221047	**H**	-1.485585	-1.770992	-3.090644	**H**	-1.600393	1.777545	3.879972
H	2.427881	0.483992	2.096577	**H**	5.080346	-1.519720	2.006947	**C**	-1.014673	-4.317457	-2.159658	**C**	-0.346680	-0.645384	3.278946
H	2.696361	-0.154337	3.714609	**H**	4.423624	0.088609	1.684940	**H**	-1.186182	-5.199427	-1.540273	**H**	-0.188620	-1.708237	3.480115
H	-2.210237	-0.714528	2.374027	**H**	4.260460	-0.630204	3.292321	**H**	-1.736570	-4.318223	-2.979651	**H**	0.109046	-0.404221	2.320560
C	-2.411624	-1.905224	-2.205364	**C**	-2.297423	-2.605105	1.000126	**H**	-0.018920	-4.420842	-2.595841	**H**	0.171220	-0.076627	4.056893
C	-2.967854	-3.059443	-3.058637	**C**	-3.053333	-3.812478	1.584836	**C**	3.847807	-3.235666	-0.311265	**C**	0.070206	-3.148384	-0.831921
H	-4.055454	-3.132801	-2.993522	**H**	-3.018124	-4.681154	0.924309	**H**	2.874601	-3.698413	-0.144159	**H**	-0.105917	-2.391143	-0.067186
H	-2.716226	-2.881209	-4.105967	**H**	-2.584543	-4.102250	2.527408	**H**	4.225327	-3.571876	-1.279883	**H**	-0.891955	-3.358252	-1.304477
H	-2.536254	-4.021664	-2.772780	**H**	-4.099311	-3.575699	1.793922	**H**	4.526110	-3.610680	0.456156	**H**	0.391369	-4.053954	-0.311781
C	-0.890340	-1.840088	-2.459657	**C**	-2.322446	-1.495128	2.072763	**C**	2.959388	-1.246812	-1.532521	**C**	0.670199	-1.533883	-2.743171
H	-0.451880	-0.928225	-2.061242	**H**	-1.677565	-0.656928	1.817897	**H**	1.929653	-1.589808	-1.515276	**H**	-0.279460	-1.753913	-3.238525
H	-0.377252	-2.694832	-2.012812	**H**	-3.336919	-1.115890	2.217868	**H**	2.963898	-0.164207	-1.655305	**H**	0.535361	-0.617283	-2.170578
H	-0.698247	-1.855495	-3.535491	**H**	-1.975534	-1.898360	3.027300	**H**	3.435317	-1.671811	-2.419210	**H**	1.409708	-1.322317	-3.519712
C	-3.078557	-0.600818	-2.694794	**C**	-0.847336	-3.054789	0.729910	**C**	5.186098	-1.121914	-0.456405	**C**	1.174540	-3.938541	-2.893049
H	-4.158918	-0.635368	-2.536246	**H**	-0.227147	-2.240930	0.361442	**H**	5.849347	-1.424076	0.354668	**H**	1.893370	-3.769136	-3.697960
H	-2.689255	0.278071	-2.181034	**H**	-0.394679	-3.428103	1.651622	**H**	5.617376	-1.491038	-1.390087	**H**	1.416555	-4.882492	-2.400618
H	-2.898337	-0.467992	-3.764867	**H**	-0.821678	-3.856964	-0.010586	**H**	5.178077	-0.032153	-0.503456	**H**	0.190480	-4.057740	-3.352217

Table G20 XYZ coordinates of the GS, TS, and TS' geometries of **2.2d** B3LYP/6-311G(d,p) (gas phase)

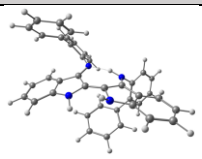
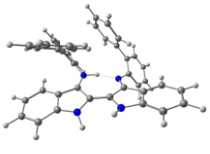
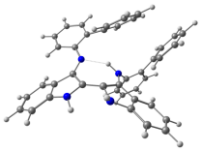
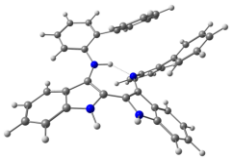
Anti				*Syn*				TS				TS'			
															
N	-1.607261	-2.633159	-0.956585	**N**	-1.243621	-3.159260	-0.872072	**N**	-1.906749	-0.918034	-0.364847	**N**	-2.041195	-0.732927	-0.093234
N	-1.586427	0.957824	-0.871860	**N**	-0.785512	0.387252	-0.937471	**N**	-3.190711	2.199799	-1.166487	**N**	-2.978287	2.528569	-1.123323
N	0.841208	-2.532707	0.416795	**N**	1.402794	-3.374964	0.049634	**N**	0.569849	0.387272	0.358848	**N**	0.482843	0.222944	0.526597
N	1.063097	0.891333	-0.327344	**N**	1.874198	0.036387	-0.689234	**N**	-0.657715	3.190312	-1.539480	**N**	-0.310971	3.329480	-0.889544
C	-0.917315	-1.415272	-0.771425	**C**	-0.402371	-2.032149	-0.788447	**C**	-1.129840	-3.172554	-0.297225	**C**	-1.406939	-3.058164	-0.107041
C	-1.853368	-0.339217	-0.995229	**C**	-1.218343	-0.858592	-1.039144	**C**	-1.350717	-4.515280	0.034470	**C**	-1.722387	-4.390908	0.178988
C	-3.123186	-0.950295	-1.295484	**C**	-2.544484	-1.331418	-1.345546	**C**	-2.604550	-4.978449	0.404426	**C**	-3.013098	-4.788761	0.497666
C	-4.392014	-0.421211	-1.587615	**C**	-3.725205	-0.680548	-1.739441	**C**	-3.693075	-4.103358	0.402244	**C**	-4.036859	-3.846023	0.475858
H	-4.568543	0.644423	-1.557127	**H**	-3.766403	0.396807	-1.807017	**C**	-3.494429	-2.764578	0.127135	**C**	-3.746063	-2.510770	0.244546
C	-5.410270	-1.297614	-1.915167	**C**	-4.831923	-1.449928	-2.047231	**C**	-2.209649	-2.252396	-0.152087	**C**	-2.430586	-2.085385	0.030858
H	-6.396181	-0.914997	-2.145198	**H**	-5.750954	-0.970135	-2.357737	**C**	-4.347623	1.707753	-0.542014	**C**	-4.222602	2.074396	-0.708338
C	-5.181499	-2.685702	-1.956992	**C**	-4.780478	-2.852365	-1.959188	**C**	-5.570188	2.346278	-0.424752	**C**	-5.427649	2.765064	-0.779783
H	-5.998216	-3.347498	-2.218525	**H**	-5.664761	-3.429894	-2.199856	**C**	-6.535418	1.740348	0.377897	**C**	-6.532060	2.199293	-0.161814
C	-3.937994	-3.230229	-1.665555	**C**	-3.624269	-3.517352	-1.571649	**C**	-6.255718	0.552377	1.055894	**C**	-6.419494	0.991582	0.544464
H	-3.773657	-4.300139	-1.692429	**H**	-3.592661	-4.597669	-1.506950	**C**	-5.029261	-0.088566	0.902500	**C**	-5.224099	0.297206	0.583871
C	-2.917239	-2.348152	-1.323331	**C**	-2.511303	-2.740464	-1.268457	**C**	-4.063635	0.462231	0.052182	**C**	-4.099682	0.798782	-0.104838
C	-2.571920	1.886305	-0.403383	**C**	-1.595225	1.549158	-0.792064	**C**	-2.660658	0.134445	-0.306963	**C**	-2.695895	0.423404	-0.218264
C	-3.120452	1.679677	0.875424	**C**	-2.550448	1.647333	0.238770	**C**	-2.123125	1.401083	-0.880509	**C**	-2.000704	1.632058	-0.665223
C	-4.129037	2.543169	1.303913	**C**	-3.286521	2.835025	0.316890	**C**	2.605638	-0.144007	1.727857	**C**	2.813241	-0.494029	1.224391
H	-4.564020	2.396637	2.285137	**H**	-4.013606	2.939567	1.112732	**C**	3.129232	-0.204933	3.033596	**C**	3.566657	-0.912300	2.340328
C	-4.553222	3.598120	0.498197	**C**	-3.080805	3.883414	-0.573550	**C**	2.372192	0.089860	4.158205	**C**	3.010832	-1.179254	3.581596
H	-5.332341	4.262817	0.850687	**H**	-3.664680	4.790848	-0.479214	**C**	1.041909	0.474229	4.020347	**C**	1.638068	-1.044921	3.761000
C	-3.968717	3.810834	-0.748172	**C**	-2.118068	3.771092	-1.572845	**C**	0.499721	0.561553	2.746614	**C**	0.865440	-0.600526	2.700232
H	-4.291178	4.637920	-1.368222	**H**	-1.947831	4.584317	-2.267155	**C**	1.262919	0.260701	1.616781	**C**	1.432900	-0.282082	1.459497
C	-2.974791	2.949074	-1.204478	**C**	-1.373223	2.603485	-1.676019	**C**	0.520520	3.706896	-1.015454	**C**	0.865462	3.692097	-0.219918
C	0.296520	-1.401984	-0.119549	**C**	0.901337	-2.166200	-0.366096	**C**	1.113825	4.940755	-1.268039	**C**	1.554390	4.892478	-0.276763
C	1.247763	-0.284974	0.156686	**C**	2.032768	-1.196931	-0.348491	**C**	2.262649	5.257002	-0.556436	**C**	2.682357	5.017786	0.534996
C	2.286458	-0.862277	1.014942	**C**	3.186541	-1.947247	0.165373	**C**	2.812226	4.371500	0.388203	**C**	3.099193	3.976920	1.369625
C	3.363728	-0.312732	1.710475	**C**	4.491413	-1.581094	0.507230	**C**	2.239199	3.134823	0.618726	**C**	2.412381	2.767011	1.397918
H	3.598064	0.738253	1.626773	**H**	4.852723	-0.580003	0.323219	**C**	1.089262	2.779590	-0.110444	**C**	1.284135	2.619592	0.589226
C	4.128026	-1.145447	2.522867	**C**	5.322805	-2.533857	1.087220	**C**	0.310603	1.564133	-0.204567	**C**	0.400640	1.480256	0.286580
H	4.966034	-0.735212	3.071342	**H**	6.336703	-2.266134	1.354894	**C**	-0.829530	1.873608	-1.030130	**C**	-0.697430	2.051231	-0.542160
C	3.831143	-2.506770	2.633301	**C**	4.867301	-3.835116	1.322960	**H**	-3.054971	3.186576	-1.338630	**H**	-2.798150	3.520446	-1.045154
H	4.446011	-3.137362	3.263588	**H**	5.535512	-4.561595	1.768631	**H**	-0.029965	-0.386056	0.054261	**H**	-0.718196	3.867471	-1.637095
C	2.752713	-3.073307	1.951307	**C**	3.566106	-4.218120	0.998984	**H**	-0.897203	3.381357	-2.503812	**H**	-0.941091	-5.132667	0.074481
H	2.519790	-4.126537	2.045924	**H**	3.212713	-5.223293	1.192605	**H**	-0.533514	-5.216679	-0.071594	**H**	-3.226806	-5.830246	0.702293
C	1.994646	-2.228886	1.159101	**C**	2.746864	-3.257298	0.428422	**H**	-2.746268	-6.026595	0.637959	**H**	-5.064650	-4.145136	0.638700
C	2.006601	1.931955	-0.210488	**C**	2.932045	0.933620	-0.912167	**H**	-4.691118	-4.469738	0.608239	**H**	-4.556239	-1.813142	0.195113
C	3.315358	1.824089	-0.733960	**C**	3.960875	0.601832	-1.806134	**H**	-4.346453	-2.112195	0.084694	**H**	-5.489261	3.725033	-1.277024
C	4.167565	2.923007	-0.580930	**C**	4.911907	1.546688	-2.160381	**H**	-5.759925	3.293185	-0.914942	**H**	-7.483697	2.715304	-0.191651
H	5.165883	2.862114	-0.997050	**H**	5.693658	1.285203	-2.862910	**H**	-7.501655	2.214014	0.498282	**H**	-7.274527	0.606402	1.084426
C	3.753757	4.088311	0.055806	**C**	4.849197	2.832292	-1.622351	**H**	-6.998209	0.125218	1.717505	**H**	-5.158125	-0.577149	1.209270
H	4.438645	4.921253	0.154568	**H**	5.593012	3.571906	-1.891430	**H**	-4.827412	-0.977613	1.479785	**H**	4.637392	-1.008207	2.227784
C	2.449348	4.191741	0.533527	**C**	3.829079	3.164201	-0.738224	**H**	4.172952	-0.461183	3.156803	**H**	3.646934	-1.491771	4.400369
H	2.110928	5.101617	1.013364	**H**	3.790058	4.155331	-0.302777	**H**	2.826367	0.032721	5.139864	**H**	1.175555	-1.265072	4.715151
C	1.574324	3.124921	0.379432	**C**	2.852320	2.233081	-0.370931	**H**	0.439036	0.711515	4.887802	**H**	-0.202851	-0.466281	2.818759
H	-0.576960	1.180740	-0.755362	**H**	0.251588	0.488038	-0.844047	**H**	-0.531147	0.864826	2.607338	**H**	1.229365	5.705590	-0.913991
H	-1.130533	-3.420288	-1.375830	**H**	-0.875468	-4.022612	-1.248703	**H**	0.682165	5.637090	-1.976079	**H**	3.240950	5.945572	0.520003
H	0.278045	-3.351401	0.595222	**H**	0.806282	-4.122235	0.371476	**H**	2.738347	6.216088	-0.721569	**H**	3.970248	4.111204	1.997530
H	-2.528659	3.076275	-2.183145	**H**	-0.626432	2.487919	-2.451944	**H**	3.696435	4.663330	0.939693	**H**	2.747889	1.960745	2.032426
C	-2.601131	0.575042	1.730240	**H**	3.980095	-0.387610	-2.246118	**H**	2.668129	2.458731	1.342891	**C**	-0.086433	-2.784395	-0.719973
C	-3.361006	-0.573241	1.966798	**C**	-2.811406	0.550212	1.203285	**C**	0.165607	-2.820468	-0.919071	**C**	1.081318	-3.349586	-0.194317
C	-1.302324	0.646148	2.246039	**C**	-4.128344	0.145317	1.452059	**C**	1.359162	-3.377848	-0.441696	**C**	-0.021751	-2.120669	-1.953713
C	-2.823702	-1.639271	2.685780	**C**	-1.770815	-0.116496	1.861685	**C**	0.200380	-2.080628	-2.112708	**C**	2.272849	-3.284896	-0.904338
H	-4.364123	-0.640717	1.563401	**C**	-4.397996	-0.907363	2.320722	**C**	2.542923	-3.236149	-1.154949	**H**	1.048910	-3.845756	0.768140
C	-0.765259	-0.416511	2.965719	**H**	-4.944118	0.640256	0.939185	**H**	1.354524	-3.935343	0.487425	**C**	1.176159	-2.046947	-2.653702
H	-0.711398	1.538451	2.080035	**C**	-2.040433	-1.166484	2.731738	**C**	1.388036	-1.932416	-2.816820	**H**	-0.925376	-1.711590	-2.390583
C	-1.523584	-1.566703	3.179404	**H**	-0.751335	0.203672	1.702499	**H**	-0.716823	-1.665792	-2.508027	**C**	2.322733	-2.641530	-2.137856
H	-3.422899	-2.525228	2.858756	**C**	-3.354415	-1.571049	2.959733	**C**	2.559508	-2.522094	-2.348810	**H**	3.168406	-3.731118	-0.491412
H	0.240220	-0.345115	3.363017	**H**	-5.423205	-1.211530	2.493856	**H**	3.453252	-3.683248	-0.780447	**H**	1.210578	-1.544788	-3.612916
H	-1.108605	-2.393343	3.744133	**H**	-1.223367	-1.662858	3.242790	**H**	1.393674	-1.379818	-3.748991	**H**	3.255156	-2.586346	-2.683006
H	0.553837	3.193732	0.737147	**H**	-3.563719	-2.390472	3.636758	**H**	3.480430	-2.423280	-2.906869	**C**	3.536093	-0.355935	-0.072767
C	3.790364	0.609496	-1.440963	**C**	1.788848	2.600343	0.591775	**C**	3.525249	-0.451428	0.601071	**C**	4.665555	-1.166707	-0.295444
C	5.022739	0.037566	-1.103885	**C**	1.011774	3.746452	0.386125	**C**	4.503049	-1.443993	0.776564	**C**	3.179920	0.521913	-1.104656
C	3.028814	0.012606	-2.453756	**C**	1.568649	1.835214	1.745281	**C**	3.536832	0.270593	-0.598214	**C**	5.409327	-1.085854	-1.464500
C	5.472650	-1.112512	-1.744663	**C**	0.029923	4.110838	1.301498	**C**	5.475415	-1.677529	-0.187616	**H**	4.951697	-1.901369	0.444484
H	5.621993	0.485169	-0.320134	**H**	1.168140	4.341427	-0.505664	**H**	4.494357	-2.048333	1.675025	**C**	3.917047	0.599592	-2.282253
C	3.479581	-1.134569	-3.096279	**C**	0.598785	2.211083	2.668367	**C**	4.512152	0.039893	-1.562460	**H**	2.333570	1.173798	-1.004299
H	2.086373	0.459511	-2.745668	**H**	2.187633	0.966201	1.934884	**H**	2.809200	1.043079	-0.781142	**C**	5.040448	-0.196575	-2.470646
C	4.699854	-1.706053	-2.738524	**C**	-0.180180	3.344173	2.443656	**C**	5.492029	-0.926571	-1.360143	**H**	6.271615	-1.729215	-1.593798
H	6.426232	-1.544711	-1.466113	**H**	-0.576093	4.988813	1.117773	**H**	6.220603	-2.446601	-0.022177	**H**	3.611726	1.298567	-3.052261
H	2.886400	-1.574762	-3.889386	**H**	0.451072	1.622746	3.565964	**H**	4.508399	0.627282	-2.473073	**H**	5.617372	-0.129414	-3.385009
H	5.051023	-2.599424	-3.240718	**H**	-0.943237	3.628397	3.157746	**H**	6.257159	-1.096421	-2.108099	**H**	-1.005612	-0.603972	-0.074207

Table G21 XYZ coordinates of the GS, TS, and TS' geometries of **2.2e** B3LYP/6-311G(d,p) (gas phase)

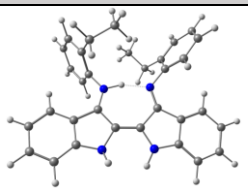
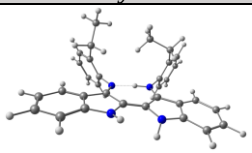
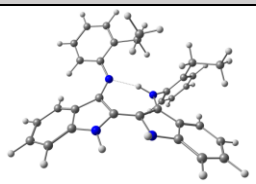
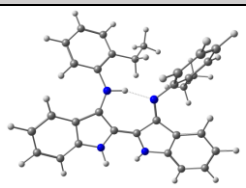
Anti				***Syn***				**TS**				**TS'**			
															
N	-1.588091	3.204170	-0.104560	**N**	1.251181	3.100687	0.035427	**N**	1.670709	0.645196	-0.161016	**N**	0.594838	-3.142620	-0.742380
N	-1.359546	-0.306249	0.083569	**N**	1.256184	-0.350145	-0.660409	**N**	1.958687	-2.801647	-0.458086	**N**	1.046224	0.092757	0.538094
C	-0.827525	2.065845	-0.016493	**C**	0.565182	1.939332	-0.211578	**N**	-1.070144	0.292252	0.476473	**C**	0.073254	-1.938031	-0.323511
C	-1.775271	0.910775	0.008490	**C**	1.587756	0.867772	-0.409933	**N**	-0.759331	-3.001748	-0.904039	**C**	1.211242	-1.129934	0.183997
C	-3.115016	1.498687	-0.130548	**C**	2.887989	1.533630	-0.273405	**C**	1.610775	2.918226	-0.894045	**C**	2.379625	-2.018426	0.140247
C	-4.393411	0.950445	-0.269666	**C**	4.206406	1.096242	-0.422468	**C**	2.230810	4.156810	-1.045158	**C**	3.698311	-1.887108	0.580507
H	-4.549131	-0.116164	-0.209069	**H**	4.424338	0.066907	-0.666703	**C**	3.524231	4.394796	-0.593203	**H**	4.027567	-0.986922	1.079615
C	-5.467710	1.807114	-0.487234	**C**	5.237108	2.014451	-0.246264	**C**	4.239367	3.363626	0.009460	**C**	4.581895	-2.939166	0.359239
H	-6.463578	1.397344	-0.595017	**H**	6.264332	1.692505	-0.357577	**C**	3.649662	2.122015	0.169109	**H**	5.606666	-2.857343	0.697420
C	-5.278628	3.190480	-0.564365	**C**	4.962478	3.346808	0.077079	**C**	2.331601	1.866734	-0.254311	**C**	4.162322	-4.100138	-0.298166
H	-6.131570	3.837469	-0.728037	**H**	5.781753	4.040768	0.219006	**C**	3.245172	-2.577315	0.045817	**H**	4.870998	-4.900994	-0.469529
C	-4.010398	3.757002	-0.438745	**C**	3.652121	3.807691	0.209258	**C**	4.243952	-3.520135	0.214540	**C**	2.844233	-4.257655	-0.727574
H	-3.864602	4.827702	-0.509544	**H**	3.443150	4.845086	0.438856	**C**	5.407262	-3.114809	0.865805	**H**	2.519548	-5.167070	-1.217681
C	-2.949655	2.891541	-0.228691	**C**	2.636680	2.885572	0.018787	**C**	5.526956	-1.814972	1.357518	**C**	1.970897	-3.210391	-0.482541
C	-2.216759	-1.411991	0.262572	**C**	2.191203	-1.407294	-0.746015	**C**	4.516400	-0.877599	1.160335	**C**	2.110368	0.909759	0.989756
C	-3.059023	-1.458904	1.383562	**C**	2.238637	-2.096787	-1.964872	**C**	3.366942	-1.228674	0.441433	**C**	2.018064	1.385197	2.301258
H	-3.080688	-0.615799	2.063361	**H**	1.596680	-1.767694	-2.772901	**C**	2.093164	-0.560175	0.070039	**H**	1.179170	1.070458	2.909994
C	-3.829256	-2.583659	1.631415	**C**	3.119417	-3.152671	-2.140850	**C**	1.181780	-1.690741	-0.308260	**C**	2.998191	2.223510	2.816233
H	-4.465830	-2.620080	2.506862	**H**	3.170101	-3.662075	-3.095083	**C**	0.241222	2.729187	-1.498778	**H**	2.932332	2.566617	3.841248
C	-3.776161	-3.663962	0.750009	**C**	3.928310	-3.553790	-1.079635	**C**	-3.100868	1.698328	-1.170755	**C**	4.050758	2.625172	2.000678
H	-4.384547	-4.542061	0.928155	**H**	4.617298	-4.380556	-1.200811	**C**	-3.032849	1.785482	0.339138	**H**	4.816120	3.288770	2.383819
C	-2.933588	-3.615619	-0.353920	**C**	3.836558	-2.903210	0.145274	**C**	-3.952792	2.578843	1.035037	**C**	4.110786	2.191366	0.678738
H	-2.898385	-4.458681	-1.034664	**H**	4.453205	-3.243084	0.968254	**C**	-3.928251	2.687111	2.420229	**H**	4.920685	2.540156	0.052277
C	-2.120714	-2.508195	-0.613213	**C**	2.972966	-1.822327	0.351973	**C**	-2.968685	1.998349	3.158865	**C**	3.155140	1.329085	0.135718
C	-1.194699	-2.510835	-1.809034	**C**	2.891830	-1.167252	1.715133	**C**	-2.039594	1.207703	2.495917	**C**	3.217131	0.889371	-1.313854
H	-0.741326	-1.525333	-1.929484	**H**	2.046963	-0.478118	1.744553	**C**	-2.075230	1.103787	1.105300	**H**	2.205659	0.918092	-1.729522
H	-1.789019	-2.682834	-2.712329	**H**	3.783760	-0.548788	1.868496	**C**	-2.126524	-2.947363	-0.655057	**H**	3.517409	-0.161767	-1.360613
C	-0.095549	-3.580595	-1.715628	**C**	2.756556	-2.160025	2.877075	**C**	-3.095559	-3.906326	-0.933434	**C**	4.155478	1.696416	-2.212295
H	0.532196	-3.428763	-0.836530	**H**	1.890088	-2.809271	2.737182	**C**	-4.391588	-3.650238	-0.505993	**H**	3.930110	2.764961	-2.181273
H	0.548859	-3.546889	-2.596340	**H**	2.632449	-1.622745	3.819826	**C**	-4.720124	-2.473760	0.190756	**H**	4.057610	1.362476	-3.246987
H	-0.524027	-4.582779	-1.650276	**H**	3.637629	-2.795799	2.977559	**C**	-3.762210	-1.508754	0.444872	**H**	5.201657	1.566443	-1.926989
H	-1.204532	4.086397	-0.408631	**H**	0.824243	3.910862	0.457329	**C**	-2.449293	-1.731250	-0.007642	**H**	0.122879	-3.758936	-1.385532
N	1.208722	3.362699	0.152588	**N**	-1.559315	3.087332	-0.082477	**C**	-1.240427	-0.943029	0.031232	**N**	-2.128741	-2.820250	-0.537989
N	1.302883	-0.204356	-0.083202	**N**	-1.407818	-0.463517	-0.502447	**C**	-0.184697	-1.768664	-0.495996	**N**	-1.648944	0.647767	0.140294
C	0.544324	2.121244	0.088861	**C**	-0.810231	1.906496	-0.265205	**H**	1.546526	-3.723901	-0.480489	**C**	-1.288105	-1.737821	-0.241589
C	1.561286	1.085409	0.017518	**C**	-1.750508	0.801026	-0.347165	**H**	-0.132202	0.681093	0.307525	**C**	-2.143238	-0.599613	0.112283
C	2.841231	1.750393	0.081352	**C**	-3.073073	1.367526	-0.221670	**H**	-0.435865	-3.429567	-1.762113	**C**	-3.487158	-1.147077	0.254165
C	4.167532	1.283586	0.097037	**C**	-4.364113	0.810324	-0.246419	**H**	1.684126	4.953183	-1.536226	**C**	-4.700218	-0.727854	0.844736
H	4.386738	0.231576	-0.007152	**H**	-4.507330	-0.257065	-0.322022	**H**	3.971847	5.373207	-0.718031	**H**	-4.790460	0.210198	1.361615
C	5.188098	2.204339	0.255270	**C**	-5.451168	1.663488	-0.178364	**H**	5.253088	3.525528	0.354086	**C**	-5.789373	-1.578067	0.871569
H	6.216468	1.867815	0.272396	**H**	-6.453892	1.256951	-0.197194	**H**	4.225188	1.339997	0.618764	**H**	-6.708052	-1.245054	1.336443
C	4.907478	3.574675	0.393942	**C**	-5.271481	3.054569	-0.087078	**H**	4.114936	-4.540678	-0.124280	**C**	-5.712950	-2.873393	0.336720
H	5.727063	4.272450	0.515456	**H**	-6.141514	3.697909	-0.036786	**H**	6.208601	-3.826375	1.020395	**H**	-6.584413	-3.515842	0.359518
C	3.605453	4.059215	0.374086	**C**	-4.005766	3.626481	-0.053820	**H**	6.409539	-1.531013	1.915803	**C**	-4.519533	-3.353808	-0.175697
H	3.398588	5.117103	0.476055	**H**	-3.875994	4.698594	0.023952	**H**	4.620229	0.084129	1.634732	**H**	-4.429081	-4.368739	-0.542198
C	2.581009	3.133322	0.211965	**C**	-2.914181	2.767539	-0.115115	**H**	-4.700615	3.126385	0.473700	**C**	-3.425087	-2.495228	-0.181434
C	2.273765	-1.229908	-0.314841	**C**	-2.305496	-1.576938	-0.408049	**H**	-4.655373	3.312479	2.923774	**C**	-2.209829	1.941967	-0.041102
C	2.598931	-2.119547	0.716086	**C**	-2.666297	-2.232239	-1.582409	**H**	-2.942872	2.077346	4.238369	**C**	-1.370324	2.950468	-0.589039
C	3.517404	-3.131945	0.419749	**H**	-2.278726	-1.875207	-2.528774	**H**	-1.283689	0.659458	3.044860	**C**	-1.920478	4.216839	-0.785618
H	3.792243	-3.831258	1.201432	**C**	-3.532396	-3.319170	-1.528408	**H**	-2.844753	-4.827737	-1.443811	**H**	-1.299392	4.993190	-1.208964
C	4.085033	-3.252983	-0.844025	**H**	-3.820352	-3.827532	-2.439930	**H**	-5.164940	-4.383753	-0.699023	**C**	-3.240730	4.516080	-0.469870
H	4.794113	-4.047440	-1.042140	**C**	-4.025517	-3.741425	-0.297223	**H**	-5.736284	-2.323595	0.531574	**H**	-3.625422	5.514660	-0.635168
C	3.745248	-2.353435	-1.853152	**H**	-4.702589	-4.585202	-0.244163	**H**	-4.019170	-0.607525	0.980274	**C**	-4.053892	3.521060	0.053807
H	4.181695	-2.444109	-2.839922	**C**	-3.645433	-3.085318	0.870742	**C**	0.247083	1.817217	-2.735224	**H**	-5.086633	3.724225	0.307583
C	2.834534	-1.339597	-1.586865	**H**	-4.025851	-3.427513	1.826481	**H**	0.532644	0.798440	-2.468220	**C**	-3.536255	2.252487	0.265118
H	0.812737	4.109425	0.707334	**C**	-2.776020	-1.992412	0.846493	**H**	-0.741213	1.790147	-3.198854	**H**	-1.805311	-3.757641	-0.338492
H	0.286928	-0.459484	-0.009388	**C**	-2.331475	-1.328459	2.127846	**H**	0.957381	2.183108	-3.480000	**H**	-0.608819	0.638724	0.192996
H	2.548630	-0.632121	-2.355789	**H**	-3.016687	-1.620721	2.926450	**C**	-4.463343	1.248077	-1.716859	**H**	-4.180235	1.508917	0.678905
C	1.974221	-2.021714	2.086655	**H**	-2.411425	-0.241361	2.042574	**H**	-5.264610	1.924285	-1.413191	**C**	0.066879	2.687164	-0.976410
H	1.764202	-0.976074	2.325760	**C**	-0.895773	-1.711204	2.518741	**H**	-4.443175	1.230523	-2.808691	**H**	0.131399	1.703990	-1.451819
H	2.699054	-2.371516	2.825869	**H**	-0.605836	-1.228770	3.454831	**H**	-4.717899	0.245912	-1.368746	**H**	0.670336	2.620179	-0.067427
C	0.683447	-2.847715	2.209765	**H**	-0.182908	-1.410980	1.748448	**H**	-0.458785	2.351204	-0.757184	**C**	0.709894	3.717555	-1.905275
H	0.274057	-2.773148	3.219485	**H**	-0.806230	-2.791448	2.650912	**H**	-0.137011	3.713656	-1.783457	**H**	1.706350	3.379662	-2.191665
H	-0.083201	-2.505279	1.513172	**H**	-1.249658	3.944328	-0.520565	**H**	-2.327588	1.024744	-1.538600	**H**	0.126756	3.857980	-2.818369
H	0.875301	-3.902118	1.998712	**H**	-0.382239	-0.631046	-0.647598	**H**	-2.863571	2.686029	-1.580379	**H**	0.827141	4.688334	-1.420082

Table G22 XYZ coordinates of the GS, TS, and TS' geometries of **2.2f** B3LYP/6-311G(d,p) (gas phase)

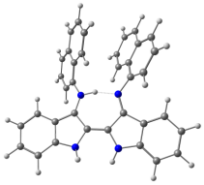
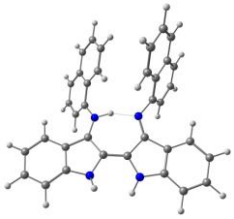
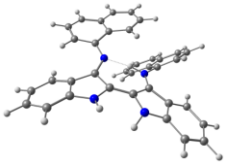
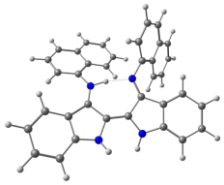
Anti				***Syn***				**TS**				**TS'**			
															
N	3.492725	2.075623	-0.213503	**N**	0.104834	3.927795	-0.022268	**N**	-2.168953	3.296141	-0.580883	**N**	-0.381420	-3.521918	-0.642802
N	-0.000871	1.365359	0.046084	**H**	0.841241	4.599923	-0.176436	**N**	0.606933	1.088870	-0.161599	**N**	0.690316	-0.464291	0.710266
N	3.974655	-0.652762	0.215786	**N**	2.666541	2.948417	0.598271	**N**	-3.840141	1.073900	-0.483268	**C**	-0.639213	-2.234725	-0.225603
N	0.521219	-1.254744	-0.140310	**H**	2.514673	3.731840	1.219103	**N**	-1.099924	-1.082808	-0.473733	**C**	0.640220	-1.675163	0.270039
C	2.430769	1.158412	-0.110815	**N**	-1.076119	0.618772	-0.009858	**C**	-1.636100	1.994530	-0.461139	**C**	1.621697	-2.757876	0.154917
C	1.197279	1.920439	-0.088380	**N**	1.435553	-0.333356	-0.140624	**C**	-0.213588	2.128205	-0.252846	**C**	2.962648	-2.881113	0.527111
C	1.560616	3.309754	-0.246397	**H**	0.406342	-0.185793	-0.043820	**C**	0.069647	3.540938	-0.139972	**H**	3.484476	-2.063735	1.001120
C	0.814937	4.492737	-0.392637	**C**	1.600921	2.072597	0.314334	**C**	1.223984	4.283983	0.169460	**C**	3.618575	-4.080880	0.269713
H	-0.262087	4.482625	-0.313367	**C**	3.579218	0.855852	0.392680	**H**	2.173067	3.795867	0.328873	**H**	4.656853	-4.193472	0.553343
C	1.488005	5.673062	-0.650919	**C**	0.342423	2.580013	0.057188	**C**	1.119208	5.658234	0.282387	**C**	2.955317	-5.140141	-0.357341
H	0.930466	6.592911	-0.770396	**C**	2.158282	0.742289	0.157209	**H**	1.996598	6.243402	0.525427	**H**	3.490543	-6.060032	-0.558175
C	2.889838	5.696235	-0.758844	**C**	1.864761	-1.543445	-0.728156	**C**	-0.111810	6.308590	0.085326	**C**	1.611494	-5.043987	-0.720189
H	3.390451	6.636573	-0.954613	**C**	3.837106	2.207694	0.714745	**H**	-0.161819	7.387026	0.173000	**H**	1.095969	-5.874110	-1.186908
C	3.648193	4.541701	-0.619884	**C**	-2.803621	-0.949348	0.670942	**C**	-1.265158	5.598950	-0.217731	**C**	0.965897	-3.850455	-0.441778
H	4.727193	4.564272	-0.707857	**C**	-0.960701	1.895087	-0.154806	**H**	-2.212601	6.102055	-0.365472	**H**	-0.979006	-4.020981	-1.283739
C	2.968236	3.355044	-0.365193	**C**	-1.931871	2.962322	-0.423768	**C**	-1.158901	4.215445	-0.321186	**N**	-2.978839	-2.636211	-0.451716
C	2.690660	-0.188555	0.060170	**C**	1.185374	-2.739805	-0.346980	**C**	-2.479770	0.897525	-0.424958	**N**	-1.754719	0.665760	0.118790
C	1.800858	-1.377234	0.013926	**C**	-1.239029	4.183463	-0.333039	**C**	-2.253094	-0.557772	-0.167086	**C**	-1.931819	-1.747552	-0.169593
C	2.677063	-2.536150	0.220356	**C**	-2.237823	-0.104383	-0.331352	**C**	-3.576694	-1.064123	0.267829	**C**	-2.525399	-0.435223	0.084883
C	2.438432	-3.904266	0.385269	**C**	-3.866647	-1.826971	0.298509	**C**	-4.029397	-2.183151	0.978425	**C**	-3.962643	-0.653859	0.153116
H	1.442398	-4.309449	0.283733	**C**	2.823631	-1.555160	-1.721330	**H**	-3.341628	-2.927227	1.348918	**C**	-5.078144	0.074817	0.620823
C	3.508979	-4.738990	0.684419	**H**	3.290251	-0.628922	-2.030953	**C**	-5.385314	-2.317957	1.259226	**H**	-4.978746	1.051697	1.058715
H	3.338929	-5.799947	0.814129	**C**	1.522045	-3.950805	-1.029048	**H**	-5.729492	-3.182502	1.811877	**C**	-6.332512	-0.505777	0.624444
C	4.805042	-4.227026	0.814107	**C**	4.621249	-0.085270	0.472085	**C**	-6.304503	-1.351468	0.843477	**H**	-7.176637	0.061561	0.994104
H	5.624079	-4.898984	1.038773	**H**	4.447854	-1.125113	0.236971	**H**	-7.358589	-1.486902	1.050914	**C**	-6.523294	-1.825375	0.185785
C	5.064234	-2.866085	0.663470	**C**	-2.361873	-0.931238	2.015457	**C**	-5.876076	-0.190459	0.204549	**H**	-7.518184	-2.253018	0.188730
H	6.065723	-2.469697	0.775950	**H**	-1.578210	-0.241187	2.302227	**H**	-6.573980	0.593085	-0.063925	**C**	-5.445375	-2.599634	-0.210180
C	3.986160	-2.044216	0.374115	**C**	0.195183	-2.773919	0.662077	**C**	-4.517011	-0.056933	-0.031140	**H**	-5.570461	-3.634270	-0.504362
H	4.322767	1.819335	-0.730645	**H**	-0.041456	-1.877841	1.216933	**H**	-3.086037	3.492201	-0.204853	**C**	-4.185228	-2.010439	-0.196927
H	4.722977	-0.062617	0.547119	**C**	-1.863497	5.408833	-0.498862	**H**	-4.297144	1.890960	-0.852839	**H**	-2.879259	-3.609817	-0.196758
C	-1.221182	1.974475	0.410881	**H**	-1.315400	6.340082	-0.428069	**C**	2.025352	1.096785	-0.099868	**H**	-0.758905	0.408695	0.283288
C	-2.412121	1.499108	-0.214344	**C**	3.169921	-2.760312	-2.357719	**C**	2.653987	0.263592	0.868628	**C**	-1.955279	2.048211	-0.080440
C	-1.273927	2.891827	1.441978	**H**	3.924825	-2.751201	-3.133826	**C**	2.763198	1.785200	-1.037500	**C**	-0.803060	2.819867	-0.487639
C	-2.405374	0.563032	-1.275881	**C**	-2.720376	-0.128461	-1.626482	**C**	1.929402	-0.498666	1.816726	**C**	-3.162265	2.695155	0.100670
C	-3.665628	1.976337	0.281464	**H**	-2.255723	0.497312	-2.378892	**C**	4.081003	0.172842	0.849118	**C**	0.424336	2.254370	-0.901797
C	-2.512150	3.389743	1.883658	**C**	6.110871	1.696549	1.174949	**C**	4.169715	1.712359	-1.025537	**C**	-0.923872	4.247269	-0.531951
H	-0.360477	3.201789	1.933187	**H**	7.105236	2.005866	1.472818	**H**	2.257095	2.368495	-1.796318	**C**	-3.275680	4.090455	-0.004943
C	-3.583900	0.073208	-1.782979	**C**	5.875102	0.344888	0.864931	**C**	2.584751	-1.333404	2.688132	**H**	-4.042536	2.139747	0.342402
H	-1.463989	0.223076	-1.686722	**H**	6.688342	-0.365830	0.933987	**H**	0.850452	-0.422923	1.851786	**C**	1.498265	3.040986	-1.248833
C	-4.862187	1.457196	-0.274796	**C**	2.531435	-3.931625	-2.022684	**C**	4.723533	-0.689915	1.772624	**H**	0.526737	1.184494	-0.981099
C	-3.683245	2.936627	1.321257	**H**	2.784870	-4.856548	-2.527374	**C**	4.813797	0.924041	-0.102024	**C**	0.205757	5.031447	-0.875626
H	-2.535669	4.109155	2.692553	**C**	-3.309999	2.971511	-0.655074	**H**	4.735503	2.265686	-1.764625	**C**	-2.172683	4.859437	-0.274520
C	-4.823427	0.516582	-1.273133	**H**	-3.866497	2.048271	-0.719493	**C**	3.993767	-1.433062	2.665788	**H**	-4.241623	4.550993	0.159465
H	-3.562844	-0.658331	-2.581122	**C**	5.098917	2.643859	1.107602	**H**	2.019210	-1.917730	3.403774	**C**	1.399711	4.445146	-1.211507
H	-5.810881	1.815981	0.107298	**H**	5.284161	3.682387	1.351813	**H**	5.805253	-0.755966	1.755875	**H**	2.421397	2.571234	-1.562602
H	-4.639021	3.300338	1.680023	**C**	-3.235661	5.395322	-0.748026	**H**	5.895285	0.853410	-0.101509	**H**	0.098918	6.109903	-0.884528
H	-5.743895	0.118269	-1.681767	**H**	-3.755982	6.335160	-0.885321	**H**	4.495090	-2.094774	3.361348	**H**	-2.246236	5.939628	-0.314334
C	-0.366975	-2.290158	-0.430727	**C**	-4.426825	-2.675644	1.286582	**C**	-0.711165	-2.409083	-0.565811	**H**	2.255303	5.054621	-1.474759
C	-1.649579	-2.269791	0.206107	**H**	-5.234414	-3.340863	1.003414	**C**	0.674368	-2.657070	-0.906957	**C**	1.844608	0.206462	1.133824
C	-0.110041	-3.192812	-1.453423	**C**	-3.951566	4.195525	-0.814349	**C**	-1.545822	-3.515442	-0.399774	**C**	2.994881	0.375941	0.294047
C	-1.957214	-1.387757	1.266478	**H**	-5.017856	4.219683	-0.998074	**C**	1.526342	-1.677760	-1.455835	**C**	1.780148	0.840789	2.362573
C	-2.655799	-3.171246	-0.258784	**C**	0.827924	-5.139955	-0.691120	**C**	1.196415	-3.981447	-0.752315	**C**	3.074638	-0.111695	-1.033454
C	-1.101884	-4.088454	-1.883398	**H**	1.084716	-6.056229	-1.209963	**C**	-1.040065	-4.817866	-0.347854	**C**	4.089093	1.144429	0.804489
H	0.846451	-3.164338	-1.960029	**C**	-4.330983	-1.829420	-1.041102	**H**	-2.607833	-3.376858	-0.322149	**C**	2.877109	1.561185	2.863225
C	-3.222831	-1.348276	1.801389	**H**	-5.133171	-2.504441	-1.315222	**C**	2.852271	-1.943556	-1.709073	**H**	0.874845	0.741806	2.948361
H	-1.186660	-0.736026	1.656151	**C**	-3.770614	-0.996930	-1.980008	**H**	1.120717	-0.717450	-1.727469	**C**	4.186560	0.120375	-1.807750
C	-3.946654	-3.114096	0.324820	**H**	-4.122243	-1.012569	-3.004183	**C**	2.576186	-4.217828	-0.982160	**H**	2.248863	-0.667503	-1.454229
C	-2.349645	-4.079101	-1.301020	**C**	-0.469997	-3.940370	0.953465	**C**	0.316494	-5.043138	-0.447490	**C**	5.225852	1.353893	-0.018062
H	-0.883308	-4.770916	-2.695402	**H**	-1.240054	-3.939723	1.714893	**H**	-1.722479	-5.645614	-0.200123	**C**	4.012436	1.705348	2.102980
C	-4.228994	-2.213162	1.321764	**C**	-0.153583	-5.133939	0.269355	**C**	3.396476	-3.212880	-1.429678	**H**	2.815405	2.009058	3.847091
H	-3.449941	-0.649118	2.596617	**H**	-0.682889	-6.047403	0.511332	**H**	3.479758	-1.168783	-2.131774	**C**	5.279103	0.851829	-1.294248
H	-4.709451	-3.796142	-0.032714	**C**	-2.923781	-1.771355	2.947423	**H**	2.962955	-5.217974	-0.824919	**H**	4.223654	-0.258223	-2.822029
H	-3.119980	-4.758931	-1.645955	**H**	-2.575238	-1.752801	3.973069	**H**	0.717206	-6.044823	-0.343345	**H**	6.050874	1.934013	0.379107
H	-5.222199	-2.170582	1.751481	**C**	-3.963771	-2.653992	2.579571	**H**	4.447494	-3.402185	-1.608776	**H**	4.857863	2.270268	2.477625
H	0.005605	0.317553	-0.037260	**H**	-4.401918	-3.306195	3.325230	**H**	0.137944	0.167362	-0.249892	**H**	6.151253	1.022970	-1.913127

Table G23 XYZ coordinates of the GS, TS, and TS' geometries of **2.2g** B3LYP/6-311G(d,p) (gas phase)

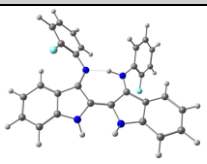
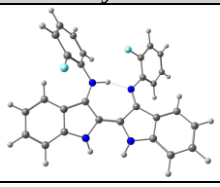
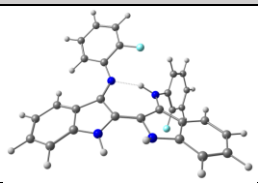
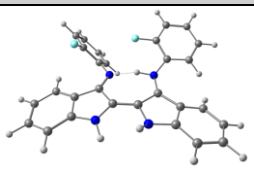
Anti				***Syn***				**TS**				**TS'**			
															
N	-1.372037	-2.964891	-0.295075	**N**	-1.245128	-3.037261	-0.397860	**N**	-1.084869	-2.886291	-0.874217	**N**	-1.784209	-2.871260	-0.356031
N	-1.343789	0.602110	-0.059254	**N**	-1.244393	0.530795	-0.135467	**N**	-1.194797	0.595189	-0.022779	**N**	-1.509919	0.657237	0.154228
N	1.379382	-2.915282	0.251724	**N**	1.504094	-2.979772	0.127383	**N**	1.580409	-2.880750	-0.153753	**N**	0.948059	-3.077891	-0.267751
N	1.323462	0.589127	-0.080817	**N**	1.440075	0.509125	-0.316977	**N**	1.572269	0.596213	-0.373891	**N**	1.193262	0.378794	0.277519
C	-0.674075	-1.749465	-0.171346	**C**	-0.552014	-1.816992	-0.291665	**C**	-0.429663	-1.671375	-0.565042	**C**	-1.015485	-1.711047	-0.149241
C	-1.656175	-0.679239	-0.193768	**C**	-1.541820	-0.753424	-0.274298	**C**	-1.445029	-0.671207	-0.343177	**C**	-1.938067	-0.613019	0.124603
C	-2.942411	-1.296153	-0.391787	**C**	-2.829969	-1.380635	-0.430812	**C**	-2.719361	-1.315661	-0.529639	**C**	-3.255061	-1.219115	0.233966
C	-4.240887	-0.784646	-0.563494	**C**	-4.137370	-0.878316	-0.553937	**C**	-4.046114	-0.851485	-0.490822	**C**	-4.515116	-0.820678	0.727855
H	-4.436332	0.275650	-0.500939	**H**	-4.338568	0.179778	-0.475081	**H**	-4.273146	0.164690	-0.203062	**H**	-4.654009	0.114486	1.240435
C	-5.268885	-1.667113	-0.837419	**C**	-5.167576	-1.766954	-0.799325	**C**	-5.060621	-1.721015	-0.844312	**C**	-5.589527	-1.686203	0.649174
H	-6.274762	-1.293329	-0.976923	**H**	-6.180414	-1.399787	-0.901005	**H**	-6.088734	-1.383847	-0.823350	**H**	-6.551343	-1.375614	1.035663
C	-5.025719	-3.048799	-0.935617	**C**	-4.917729	-3.145747	-0.916017	**C**	-4.775333	-3.043059	-1.231901	**C**	-5.444559	-2.971803	0.102861
H	-5.851578	-3.717121	-1.146631	**H**	-5.745220	-3.819125	-1.103236	**H**	-5.591355	-3.702539	-1.501063	**H**	-6.305956	-3.624689	0.035833
C	-3.753338	-3.578838	-0.767234	**C**	-3.636140	-3.666725	-0.794809	**C**	-3.474331	-3.525089	-1.274497	**C**	-4.201117	-3.438266	-0.292313
H	-3.573745	-4.643793	-0.843612	**H**	-3.450986	-4.729700	-0.884578	**H**	-3.262440	-4.544516	-1.571530	**H**	-4.065176	-4.453955	-0.642141
C	-2.720999	-2.688490	-0.493247	**C**	-2.602172	-2.770113	-0.549370	**C**	-2.454815	-2.650090	-0.912723	**C**	-3.119322	-2.571213	-0.177075
C	-2.223950	1.686578	0.160757	**C**	-2.138776	1.588771	0.148004	**C**	-2.101790	1.501041	0.576893	**C**	-2.132113	1.911636	-0.019858
C	-3.140562	1.675965	1.214507	**C**	-2.996588	1.534971	1.248473	**C**	-2.788643	1.149731	1.742332	**C**	-1.307261	2.942653	-0.510507
C	-3.961796	2.758220	1.473530	**C**	-3.833847	2.587875	1.568292	**C**	-3.657030	2.024780	2.367815	**C**	-1.758911	4.225018	-0.741681
H	-4.659670	2.701480	2.298838	**H**	-4.482990	2.499258	2.429697	**H**	-4.168228	1.704469	3.266339	**H**	-1.059829	4.957854	-1.122717
C	-3.851742	3.895128	0.676468	**C**	-3.801411	3.737780	0.782952	**C**	-3.834370	3.297629	1.830423	**C**	-3.093928	4.528686	-0.496587
H	-4.488083	4.748223	0.874374	**H**	-4.450610	4.568667	1.028117	**H**	-4.509368	3.991548	2.315036	**H**	-3.462307	5.530984	-0.672052
C	-2.924696	3.938176	-0.364097	**C**	-2.934643	3.822851	-0.305719	**C**	-3.144230	3.676927	0.680426	**C**	-3.943953	3.531300	-0.030196
H	-2.838129	4.824152	-0.979576	**H**	-2.907519	4.719728	-0.910765	**H**	-3.282648	4.666969	0.265539	**H**	-4.986963	3.749355	0.159645
C	-2.111993	2.840227	-0.618930	**C**	-2.103052	2.755015	-0.618403	**C**	-2.281068	2.784202	0.055559	**C**	-3.471226	2.246156	0.204918
C	0.684389	-1.748702	0.063589	**C**	0.809599	-1.813716	-0.076158	**C**	0.916953	-1.693268	-0.254952	**C**	0.359532	-1.847985	-0.115846
C	1.684576	-0.639511	0.083797	**C**	1.806547	-0.706061	-0.079832	**C**	1.916135	-0.601207	-0.018813	**C**	1.458907	-0.865813	0.084992
C	2.971943	-1.276534	0.365682	**C**	3.093012	-1.334697	0.247895	**C**	3.133730	-1.303124	0.448622	**C**	2.698922	-1.647610	0.089034
C	4.257343	-0.778221	0.594041	**C**	4.368437	-0.832919	0.527847	**C**	4.353226	-0.929791	1.027179	**C**	4.040311	-1.323098	0.304054
H	4.467404	0.278820	0.526623	**H**	4.579441	0.223495	0.455233	**H**	4.580446	0.092027	1.274800	**H**	4.349071	-0.302569	0.472853
C	5.270235	-1.669921	0.929270	**C**	5.368345	-1.718482	0.913293	**C**	5.286277	-1.902123	1.373140	**C**	4.982016	-2.347258	0.315070
H	6.270826	-1.299192	1.109391	**H**	6.359053	-1.342367	1.132983	**H**	6.223404	-1.599876	1.822145	**H**	6.024989	-2.111444	0.481681
C	5.013458	-3.040764	1.031261	**C**	5.111185	-3.089529	1.019160	**C**	5.022929	-3.256906	1.166543	**C**	4.599687	-3.675921	0.109260
H	5.820106	-3.716699	1.286730	**H**	5.908263	-3.760935	1.313573	**H**	5.764293	-3.997848	1.438153	**H**	5.352071	-4.454818	0.115293
C	3.736501	-3.558661	0.814139	**C**	3.844208	-3.610107	0.761162	**C**	3.800742	-3.668508	0.640912	**C**	3.264711	-4.021878	-0.102555
H	3.538921	-4.619656	0.902071	**H**	3.641993	-4.669366	0.859528	**H**	3.570117	-4.718227	0.507712	**H**	2.969500	-5.052281	-0.256523
C	2.737244	-2.657447	0.488384	**C**	2.855242	-2.714454	0.387942	**C**	2.882589	-2.685952	0.312617	**C**	2.339569	-2.992233	-0.103423
C	2.199903	1.672439	-0.217289	**C**	2.298118	1.590162	-0.515087	**C**	2.263368	1.781176	-0.542869	**C**	2.169353	1.376716	0.402523
C	3.228131	1.698770	-1.168664	**C**	3.433335	1.561414	-1.340010	**C**	1.567094	2.770893	-1.277084	**C**	3.125454	1.615825	-0.590505
C	4.020615	2.815182	-1.362189	**C**	4.164373	2.718075	-1.570939	**C**	2.093696	4.009530	-1.575991	**C**	4.017555	2.669008	-0.511402
H	4.796014	2.781736	-2.116719	**H**	5.029623	2.683370	-2.220628	**H**	1.502753	4.708146	-2.153566	**H**	4.731104	2.812523	-1.312598
C	3.793686	3.950012	-0.587666	**C**	3.782246	3.923656	-0.979964	**C**	3.376372	4.317758	-1.132302	**C**	3.966945	3.516884	0.592363
H	4.413540	4.826142	-0.728820	**H**	4.359778	4.822534	-1.153750	**H**	3.803185	5.287680	-1.353628	**H**	4.665628	4.340472	0.666036
C	2.764728	3.960089	0.354330	**C**	2.644981	3.981224	-0.177876	**C**	4.103898	3.375815	-0.406013	**C**	3.013083	3.312026	1.589245
H	2.583692	4.844210	0.951982	**H**	2.315581	4.902084	0.285424	**H**	5.101883	3.611855	-0.059630	**H**	2.968807	3.975397	2.443481
C	1.961485	2.840608	0.520780	**C**	1.915247	2.826050	0.024251	**C**	3.559789	2.133428	-0.121122	**C**	2.106604	2.266501	1.481420
H	-0.311613	0.802134	-0.081077	**H**	-0.223407	0.752651	-0.197508	**H**	-0.223180	0.889024	-0.197433	**H**	-0.460944	0.715945	0.130839
H	-0.948178	-3.732733	-0.797987	**H**	-0.831725	-3.798644	-0.919095	**H**	-0.677458	-3.498668	-1.569034	**H**	-1.499659	-3.545264	-1.052862
H	0.929381	-3.770095	0.542934	**H**	1.048539	-3.822176	0.446282	**H**	1.087899	-3.754905	-0.038800	**H**	0.444135	-3.937485	-0.108999
H	1.151478	2.839229	1.240003	**H**	-1.427192	2.804293	-1.462890	**H**	4.145261	1.430973	0.437074	**H**	1.346250	2.106090	2.235550
H	-1.392276	2.855914	-1.428254	**F**	-3.004875	0.422554	2.007897	**H**	-1.746559	3.060827	-0.842487	**H**	-4.160634	1.510424	0.561855
F	-3.221081	0.577429	1.989594	**H**	3.710380	0.632349	-1.820865	**F**	-2.600457	-0.081082	2.257939	**F**	-0.020047	2.659154	-0.792346
F	3.435727	0.603032	-1.926837	**F**	0.792969	2.868541	0.773073	**F**	0.327836	2.483683	-1.729934	**F**	3.162593	0.796493	-1.661867

Table G24 XYZ coordinates of the GS geometries of **2.2a** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

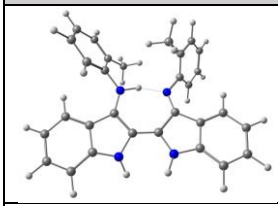
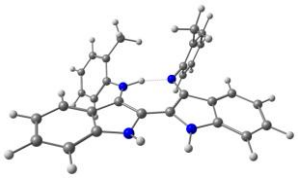
Anti				***Syn***			
							
N	1.314598	0.438565	-0.140973	**C**	-0.806628	-1.830230	0.037681
N	1.375883	-3.061599	0.198135	**C**	-1.757308	-0.724785	0.019382
N	-1.355090	0.470624	0.015299	**C**	-3.071583	-1.308045	0.157270
N	-1.430317	-3.091820	-0.171707	**C**	-4.363327	-0.767665	0.294264
C	2.163662	2.616598	0.494189	**H**	-4.530709	0.297442	0.235562
C	3.013963	3.688441	0.214716	**C**	-5.423583	-1.627782	0.517187
C	3.870449	3.673873	-0.883941	**H**	-6.424026	-1.228330	0.626204
C	3.893928	2.566650	-1.730578	**C**	-5.219623	-3.018320	0.605449
C	3.076124	1.476333	-1.462780	**H**	-6.069866	-3.667835	0.777504
C	2.222402	1.492671	-0.352841	**C**	-3.956283	-3.577319	0.482295
C	2.740907	-2.812261	0.327881	**H**	-3.797767	-4.645590	0.560523
C	3.759090	-3.720946	0.576983	**C**	-2.888844	-2.708306	0.258922
C	5.049293	-3.209291	0.708528	**C**	-2.247955	1.655277	-0.387355
C	5.303827	-1.836624	0.603364	**C**	-3.126411	1.601351	-1.471505
C	4.272328	-0.936925	0.349489	**H**	-3.185541	0.697465	-2.064736
C	2.973756	-1.430808	0.199980	**C**	-3.907187	2.706557	-1.785090
C	1.664567	-0.791467	0.008686	**H**	-4.588023	2.663841	-2.626712
C	0.666408	-1.903486	0.050238	**C**	-3.798081	3.867661	-1.021310
C	1.221196	2.651793	1.666069	**H**	-4.403139	4.734559	-1.259607
C	-1.124700	2.811938	-1.610341	**C**	-2.903376	3.918964	0.044579
C	-2.095144	2.729007	-0.464432	**H**	-2.818203	4.825699	0.633019
C	-2.905755	3.814430	-0.121401	**C**	-2.106108	2.822621	0.382266
C	-3.792801	3.750676	0.949635	**C**	-1.131492	2.888208	1.526609
C	-3.881159	2.587597	1.713732	**H**	-1.234955	2.025051	2.189351
C	-3.086732	1.493971	1.395733	**H**	-1.288534	3.794530	2.112433
C	-2.214611	1.559884	0.306468	**H**	-0.098333	2.899393	1.165352
C	-2.773596	-2.815576	-0.308427	**C**	2.566255	1.093538	2.491800
C	-3.824981	-3.705622	-0.524706	**H**	1.491825	1.011366	2.679584
C	-5.097652	-3.170436	-0.657993	**H**	3.030608	1.581720	3.349672
C	-5.326240	-1.782776	-0.586227	**H**	2.960046	0.074036	2.429303
C	-4.281781	-0.901556	-0.370558	**C**	0.565317	-1.863285	-0.115957
C	-2.981322	-1.417851	-0.224860	**C**	1.573392	-0.758138	-0.128964
C	-1.677982	-0.810734	-0.088369	**C**	2.874142	-1.410598	-0.307144
C	-0.708552	-1.895779	-0.095975	**C**	4.179209	-0.925929	-0.415923
H	0.965898	-3.965830	0.386796	**H**	4.386538	0.132902	-0.364038
H	-0.327313	0.668978	-0.061642	**C**	5.213355	-1.840648	-0.599798
H	-1.031954	-3.943464	-0.543974	**H**	6.232409	-1.485200	-0.686365
H	2.994702	4.552060	0.870646	**C**	4.950156	-3.213215	-0.676679
H	4.510069	4.525849	-1.082324	**H**	5.771039	-3.905388	-0.822249
H	4.544982	2.550989	-2.596759	**C**	3.652683	-3.715344	-0.570079
H	3.077725	0.611209	-2.114719	**H**	3.449435	-4.777290	-0.629012
H	3.556538	-4.780454	0.672099	**C**	2.633424	-2.794260	-0.382522
H	5.869406	-3.890548	0.901817	**C**	2.209548	1.516155	0.023054
H	6.315940	-1.469425	0.718503	**C**	2.446028	2.233396	-1.150557
H	4.479391	0.120121	0.271145	**H**	1.924829	1.948104	-2.056770
H	1.320359	1.761530	2.292266	**C**	3.350876	3.290824	-1.146618
H	1.410214	3.530162	2.284727	**H**	3.541228	3.838726	-2.062089
H	0.180019	2.696734	1.332020	**C**	4.002206	3.640322	0.033888
H	-1.183921	1.928868	-2.251684	**H**	4.705104	4.465080	0.046081
H	-1.322884	3.695917	-2.217531	**C**	3.739248	2.933556	1.205762
H	-0.093437	2.880098	-1.249782	**H**	4.239285	3.212358	2.127079
H	-2.836925	4.722177	-0.710417	**C**	2.841833	1.863703	1.229371
H	-4.408610	4.608869	1.191858	**H**	-1.167935	-3.868827	0.502871
H	-4.556299	2.535301	2.559400	**H**	-0.378784	0.729595	-0.012082
H	-3.128530	0.589932	1.990146	**H**	0.848793	-3.937528	-0.396645
H	-3.647716	-4.771904	-0.589545	**N**	-1.550774	-3.010385	0.130068
H	-5.935697	-3.836965	-0.824783	**N**	-1.410439	0.549391	-0.089449
H	-6.333230	-1.402173	-0.702374	**N**	1.265453	-3.029618	-0.244669
H	-4.467596	0.161235	-0.324744	**N**	1.247958	0.475546	0.010351

Table G25 XYZ coordinates of the GS geometries of **2.2b** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

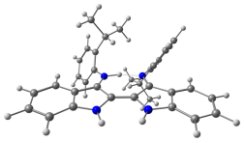
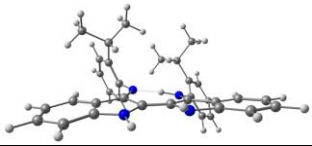
Anti				***Syn***			
							
N	1.352961	3.496776	-0.042204	**N**	-1.542210	3.334327	0.318892
N	1.324778	-0.056146	-0.082568	**N**	-1.530383	-0.161034	-0.392982
N	-1.503107	3.405472	0.083943	**N**	1.250703	3.333848	-0.234734
N	-1.301643	-0.103872	0.066871	**N**	1.122223	-0.174513	-0.408626
C	0.639604	2.299489	-0.032254	**C**	-0.841848	2.161554	0.021882
C	1.632787	1.227738	-0.071623	**C**	-1.827146	1.092249	-0.089810
C	2.930416	1.858511	-0.065127	**C**	-3.112985	1.682444	0.200007
C	4.247737	1.368832	-0.013886	**C**	-4.412018	1.158721	0.328415
H	4.446379	0.307507	0.001941	**H**	-4.614103	0.116487	0.131168
C	5.292585	2.275725	0.017743	**C**	-5.433390	2.005642	0.720753
H	6.313355	1.917192	0.058404	**H**	-6.439609	1.619771	0.825322
C	5.045260	3.661893	-0.004785	**C**	-5.181872	3.365381	0.986065
H	5.883611	4.348580	0.012733	**H**	-6.002496	4.005836	1.287468
C	3.755972	4.172892	-0.040068	**C**	-3.909019	3.905895	0.874319
H	3.567768	5.239248	-0.042227	**H**	-3.715368	4.949856	1.086909
C	2.704064	3.256973	-0.057740	**C**	-2.881097	3.050519	0.480246
C	2.196563	-1.163698	-0.275294	**C**	-2.433541	-1.182594	-0.796937
C	2.213728	-2.195250	0.675207	**C**	-3.310822	-0.933391	-1.857901
C	3.026618	-3.302360	0.403276	**C**	-4.169276	-1.930160	-2.297240
H	3.067823	-4.111536	1.122887	**H**	-4.847404	-1.735103	-3.119325
C	3.780890	-3.386768	-0.761626	**C**	-4.140869	-3.182695	-1.682727
H	4.397964	-4.259089	-0.942637	**H**	-4.805995	-3.969242	-2.019611
C	3.736956	-2.354070	-1.698915	**C**	-3.250705	-3.427036	-0.643325
H	4.311009	-2.417123	-2.615493	**H**	-3.233592	-4.405178	-0.177417
C	2.939123	-1.244955	-1.456986	**C**	-2.373975	-2.440163	-0.176811
C	-0.742437	2.269311	0.036915	**C**	0.518041	2.179472	-0.215467
C	-1.699857	1.119655	0.082353	**C**	1.484123	1.057565	-0.424626
C	-3.039322	1.719481	0.108447	**C**	2.792774	1.691245	-0.604515
C	-4.331370	1.188898	0.065557	**C**	4.066681	1.188015	-0.875108
H	-4.495327	0.121611	0.046619	**H**	4.235360	0.125767	-0.973673
C	-5.412622	2.065308	0.049145	**C**	5.119209	2.088595	-1.019049
H	-6.420246	1.670282	0.016670	**H**	6.115267	1.718787	-1.227380
C	-5.213095	3.451096	0.078114	**C**	4.903712	3.466407	-0.896643
H	-6.070864	4.113266	0.072352	**H**	5.738379	4.147828	-1.011377
C	-3.932441	4.000764	0.105098	**C**	3.636694	3.987502	-0.632283
H	-3.774664	5.071998	0.110281	**H**	3.469839	5.053625	-0.543089
C	-2.863891	3.115108	0.109676	**C**	2.598089	3.079710	-0.490049
C	-2.120323	-1.231635	0.258174	**C**	2.028528	-1.256726	-0.524857
C	-2.069143	-2.276086	-0.687003	**C**	2.809897	-1.678795	0.566662
C	-2.807429	-3.430707	-0.415889	**C**	3.591084	-2.826124	0.389729
H	-2.799531	-4.242680	-1.132470	**H**	4.195192	-3.179169	1.217317
C	-3.541091	-3.570818	0.759542	**C**	3.614482	-3.525065	-0.812981
H	-4.091576	-4.485489	0.946278	**H**	4.235858	-4.407238	-0.913518
C	-3.555205	-2.540007	1.698021	**C**	2.831161	-3.090969	-1.880851
H	-4.107378	-2.646858	2.624294	**H**	2.836157	-3.628068	-2.822038
C	-2.849545	-1.371523	1.445941	**C**	2.028874	-1.967056	-1.730243
H	0.292243	-0.257324	-0.010308	**H**	-0.500870	-0.373750	-0.411041
H	0.953357	4.420938	-0.084004	**H**	-1.112015	4.126268	0.776695
H	-1.150042	4.350609	0.110756	**H**	0.855917	4.264000	-0.248955
H	-2.837289	-0.565494	2.169592	**H**	1.398473	-1.620454	-2.540627
C	-1.287717	-2.105908	-1.977184	**C**	2.785464	-0.964604	1.909226
C	-2.184240	-1.487402	-3.064225	**C**	4.196114	-0.644160	2.423353
H	-2.608459	-0.535618	-2.734351	**H**	4.767618	-0.074312	1.686925
H	-1.610691	-1.307039	-3.978223	**H**	4.134590	-0.049566	3.339215
H	-3.012394	-2.159566	-3.308496	**H**	4.754987	-1.554138	2.657529
C	-0.635174	-3.400828	-2.472403	**C**	1.993460	-1.782084	2.942920
H	-0.023571	-3.864038	-1.694115	**H**	0.968683	-1.954733	2.607084
H	-1.378901	-4.131199	-2.802466	**H**	2.462216	-2.755586	3.113040
H	0.013081	-3.184290	-3.325709	**H**	1.954683	-1.252545	3.899526
H	-0.486868	-1.390396	-1.776749	**H**	2.265664	-0.014802	1.780195
H	2.877499	-0.437759	-2.176412	**H**	-3.306492	0.040309	-2.332094
C	1.415814	-2.121244	1.965938	**C**	-1.424973	-2.734946	0.971419
H	0.816293	-1.209309	1.941887	**H**	-0.818645	-1.844913	1.147457
C	2.352446	-2.019718	3.180563	**C**	-0.468562	-3.887195	0.629930
H	3.018933	-1.157239	3.093740	**H**	0.102983	-3.672808	-0.275795
H	1.770391	-1.911031	4.100151	**H**	0.239753	-4.044937	1.446870
H	2.970299	-2.917021	3.276678	**H**	-1.015271	-4.821585	0.475269
C	0.449245	-3.306884	2.104732	**C**	-2.200186	-3.018093	2.267653
H	-0.232570	-3.365231	1.253971	**H**	-1.505182	-3.173611	3.097613
H	0.991589	-4.254118	2.173902	**H**	-2.857540	-2.182822	2.524209
H	-0.151581	-3.198266	3.011639	**H**	-2.815989	-3.916746	2.171335

Table G26 XYZ coordinates of the GS geometries of **2.2c** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

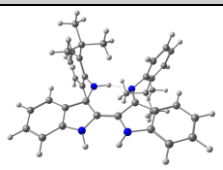
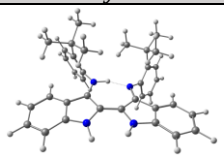
Anti				***Syn***			
							
N	1.375139	3.409582	-0.239589	**N**	-1.373612	3.363017	-0.066537
N	1.337407	-0.152664	-0.125861	**N**	-1.234570	-0.158204	0.413363
N	-1.438478	3.358764	0.218704	**N**	1.436794	3.297409	-0.505056
N	-1.336235	-0.155316	0.080026	**N**	1.448880	-0.111361	0.404441
C	0.653689	2.215942	-0.142055	**C**	-0.624903	2.187894	0.045590
C	1.626308	1.131661	-0.232811	**C**	-1.560371	1.116693	0.355174
C	2.920898	1.744756	-0.403973	**C**	-2.860130	1.725610	0.501217
C	4.227772	1.235458	-0.514149	**C**	-4.132292	1.225361	0.830249
H	4.416088	0.173305	-0.479287	**H**	-4.285388	0.173565	1.018098
C	5.274486	2.126285	-0.673471	**C**	-5.189466	2.114797	0.919236
H	6.287277	1.753836	-0.761263	**H**	-6.176602	1.750764	1.174710
C	5.039208	3.513696	-0.727102	**C**	-4.997185	3.489113	0.683871
H	5.877738	4.187220	-0.860416	**H**	-5.842986	4.162180	0.762434
C	3.762480	4.043126	-0.605713	**C**	-3.752502	4.006938	0.351871
H	3.585583	5.110994	-0.634240	**H**	-3.608618	5.064528	0.169390
C	2.710642	3.144584	-0.430448	**C**	-2.690479	3.109878	0.257981
C	2.259942	-1.224312	-0.366781	**C**	-2.140321	-1.224175	0.728091
C	2.766648	-2.031561	0.670875	**C**	-2.960418	-1.852148	-0.225362
C	3.641877	-3.053577	0.273555	**C**	-3.808116	-2.857154	0.277718
H	4.067942	-3.705857	1.021123	**H**	-4.474667	-3.365483	-0.406185
C	3.994176	-3.268329	-1.056015	**C**	-3.829173	-3.235759	1.612475
H	4.675612	-4.074110	-1.303189	**H**	-4.504846	-4.018724	1.936583
C	3.471110	-2.458668	-2.057880	**C**	-2.978676	-2.616428	2.525253
H	3.730386	-2.618256	-3.097498	**H**	-2.973811	-2.905378	3.569216
C	2.599546	-1.438609	-1.703769	**C**	-2.140003	-1.610837	2.073675
C	-0.709980	2.210575	0.077961	**C**	0.740193	2.174363	-0.150064
C	-1.681806	1.075992	0.199957	**C**	1.753900	1.109777	0.126772
C	-2.992850	1.700145	0.418094	**C**	3.059391	1.755464	-0.064069
C	-4.285894	1.189364	0.552534	**C**	4.374357	1.285968	-0.007163
H	-4.469360	0.125543	0.538787	**H**	4.592325	0.277045	0.309583
C	-5.341621	2.083812	0.710921	**C**	5.406749	2.149139	-0.363755
H	-6.350440	1.705576	0.818583	**H**	6.431726	1.803139	-0.318356
C	-5.113420	3.464433	0.736257	**C**	5.135650	3.459098	-0.776687
H	-5.949855	4.140773	0.866863	**H**	5.956190	4.112953	-1.047439
C	-3.831046	3.993501	0.589468	**C**	3.830001	3.942615	-0.852633
H	-3.654134	5.061748	0.595288	**H**	3.618170	4.951733	-1.183228
C	-2.791170	3.091150	0.423613	**C**	2.811249	3.072590	-0.491703
C	-2.236165	-1.218185	0.347241	**C**	2.431090	-0.990546	0.934105
C	-2.708496	-2.089549	-0.660283	**C**	2.872802	-0.687749	2.230272
C	-3.526327	-3.144014	-0.230476	**C**	3.792483	-1.496031	2.881642
H	-3.924762	-3.832890	-0.960712	**H**	4.118239	-1.247234	3.884827
C	-3.853784	-3.350903	1.106908	**C**	4.285138	-2.619029	2.226744
H	-4.484412	-4.188612	1.380983	**H**	5.009735	-3.264605	2.709162
C	-3.365933	-2.486016	2.080210	**C**	3.839379	-2.921955	0.942936
H	-3.603776	-2.633421	3.127133	**H**	4.241770	-3.801467	0.462357
C	-2.561755	-1.423656	1.694446	**C**	2.899816	-2.139809	0.257248
H	2.170651	-0.790108	-2.457496	**H**	2.474579	0.194517	2.717084
H	0.319809	-0.374358	-0.031816	**H**	-1.475893	-1.093277	2.755514
H	0.967719	4.304892	-0.464678	**H**	-0.207697	-0.364019	0.385717
H	-1.055135	4.290986	0.279003	**H**	-0.969554	4.281452	0.054112
C	2.431693	-1.815019	2.159724	**H**	1.020510	4.141486	-0.873373
C	3.074258	-2.895971	3.047342	**C**	-3.042553	-1.575883	-1.744235
H	4.165216	-2.884518	2.987203	**C**	-2.754207	-2.898695	-2.491473
H	2.799524	-2.704478	4.087157	**H**	-3.467068	-3.683342	-2.233643
H	2.722581	-3.898225	2.788952	**H**	-2.817820	-2.730823	-3.570083
C	0.907859	-1.879376	2.395248	**H**	-1.750483	-3.263477	-2.261561
H	0.385133	-1.028307	1.965736	**C**	-2.067588	-0.524246	-2.301027
H	0.481772	-2.792918	1.973219	**H**	-2.301540	0.481041	-1.952527
H	0.704487	-1.877433	3.469713	**H**	-1.027202	-0.745856	-2.064807
C	2.976620	-0.449274	2.629622	**H**	-2.165472	-0.517983	-3.389718
H	4.055771	-0.384414	2.468804	**C**	-4.471806	-1.099648	-2.086458
H	2.504364	0.385484	2.113986	**H**	-5.227604	-1.836349	-1.807959
H	2.786275	-0.328728	3.700036	**H**	-4.704296	-0.162992	-1.574146
H	-2.163515	-0.737968	2.432205	**H**	-4.552628	-0.926567	-3.163451
C	-2.410453	-1.883597	-2.157834	**C**	2.441188	-2.527209	-1.159584
C	-2.979114	-3.028587	-3.014716	**C**	3.173120	-3.776712	-1.679960
H	-4.067525	-3.095234	-2.944710	**H**	2.982801	-4.654250	-1.057199
H	-2.727760	-2.843390	-4.061782	**H**	2.812320	-4.001690	-2.686471
H	-2.553962	-3.996323	-2.735637	**H**	4.253573	-3.622212	-1.740569
C	-0.890546	-1.830900	-2.416281	**C**	2.723294	-1.386097	-2.159458
H	-0.436881	-0.937726	-1.994658	**H**	2.151500	-0.487614	-1.935900
H	-0.389101	-2.705073	-1.993660	**H**	3.784840	-1.125569	-2.163117
H	-0.702626	-1.820945	-3.493680	**H**	2.451607	-1.709553	-3.168446
C	-3.065460	-0.572883	-2.643759	**C**	0.934430	-2.850261	-1.141624
H	-4.145628	-0.592881	-2.477003	**H**	0.339720	-1.989698	-0.847292
H	-2.659754	0.302617	-2.138168	**H**	0.608867	-3.154503	-2.139884
H	-2.890482	-0.448330	-3.716593	**H**	0.719009	-3.667336	-0.448096

Table G27 XYZ coordinates of the GS geometries of **2.2d** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

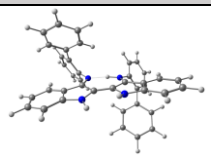
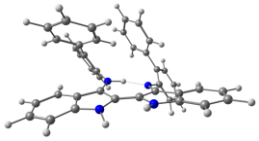
Anti				***Syn***			
							
N	-1.344734	-2.791928	-0.676396	**N**	-1.170463	-3.230717	-0.755354
N	-1.261571	0.765550	-0.479056	**N**	-0.776771	0.308802	-0.919246
N	1.213718	-2.806384	0.587820	**N**	1.511483	-3.373831	0.143277
N	1.248513	0.703008	0.366736	**N**	1.867520	0.040091	-0.622355
C	-0.657272	-1.617313	-0.361146	**C**	-0.352091	-2.098420	-0.684923
C	-1.547540	-0.509634	-0.683111	**C**	-1.188693	-0.948119	-0.986651
C	-2.751777	-1.085294	-1.223384	**C**	-2.497111	-1.458170	-1.305806
C	-3.934067	-0.534872	-1.748702	**C**	-3.687837	-0.852881	-1.743337
H	-4.091408	0.533435	-1.764443	**H**	-3.757194	0.218968	-1.858043
C	-4.896087	-1.391350	-2.252728	**C**	-4.772362	-1.660028	-2.035367
H	-5.813750	-0.987561	-2.661383	**H**	-5.698217	-1.213372	-2.375215
C	-4.697751	-2.785794	-2.240390	**C**	-4.689575	-3.058469	-1.892244
H	-5.470423	-3.432487	-2.639543	**H**	-5.557408	-3.665095	-2.123366
C	-3.538456	-3.354660	-1.732855	**C**	-3.524976	-3.681401	-1.466042
H	-3.386189	-4.426579	-1.729384	**H**	-3.462166	-4.757410	-1.363058
C	-2.570625	-2.489156	-1.224237	**C**	-2.432147	-2.865978	-1.175862
C	-2.191025	1.844134	-0.506989	**C**	-1.581591	1.478952	-0.889676
C	-3.278500	1.880751	0.386607	**C**	-2.593475	1.660561	0.074133
C	-4.160412	2.963436	0.287061	**C**	-3.307787	2.864630	0.036646
H	-5.002943	3.011843	0.966427	**H**	-4.081306	3.030363	0.776630
C	-3.956017	3.983966	-0.636662	**C**	-3.021894	3.856639	-0.895586
H	-4.650495	4.814493	-0.682084	**H**	-3.587649	4.780683	-0.887616
C	-2.852997	3.946130	-1.487003	**C**	-1.998900	3.667595	-1.821760
H	-2.682689	4.741623	-2.202263	**H**	-1.760631	4.438455	-2.544463
C	-1.971488	2.872627	-1.421611	**C**	-1.279731	2.479132	-1.813809
C	0.584817	-1.643520	0.243258	**C**	0.964249	-2.194001	-0.275762
C	1.528890	-0.533486	0.583458	**C**	2.067315	-1.188003	-0.288151
C	2.710570	-1.181662	1.158122	**C**	3.257987	-1.904258	0.186309
C	3.900629	-0.694879	1.703781	**C**	4.565035	-1.505568	0.478617
H	4.107805	0.364461	1.734876	**H**	4.894759	-0.494200	0.290540
C	4.822733	-1.605874	2.211070	**C**	5.443732	-2.440757	1.017800
H	5.752189	-1.246058	2.634027	**H**	6.461287	-2.148661	1.245183
C	4.564012	-2.981217	2.176997	**C**	5.029422	-3.755199	1.265314
H	5.298958	-3.671633	2.573693	**H**	5.733644	-4.466645	1.680046
C	3.376957	-3.486437	1.647121	**C**	3.725939	-4.169577	0.995183
H	3.171270	-4.549376	1.628181	**H**	3.398829	-5.181516	1.199048
C	2.466895	-2.566783	1.147696	**C**	2.860090	-3.226083	0.461261
C	2.179653	1.747168	0.550198	**C**	2.882043	0.973094	-0.887666
C	3.313973	1.873158	-0.280585	**C**	3.874938	0.682462	-1.834626
C	4.181014	2.946020	-0.043061	**C**	4.772800	1.662930	-2.232913
H	5.051700	3.058784	-0.678205	**H**	5.529549	1.428937	-2.972359
C	3.937225	3.871020	0.967518	**C**	4.689862	2.945536	-1.690240
H	4.626083	4.692418	1.124646	**H**	5.389478	3.714194	-1.996078
C	2.796676	3.748082	1.758612	**C**	3.703926	3.237439	-0.753356
H	2.591090	4.468874	2.541086	**H**	3.646236	4.228768	-0.319409
C	1.913598	2.696912	1.540098	**C**	2.784717	2.268117	-0.336892
H	-0.277822	0.957348	-0.163952	**H**	0.258326	0.428367	-0.809529
H	-0.893162	-3.681119	-0.836067	**H**	-0.803638	-4.155976	-0.934147
H	0.790306	-3.723234	0.569355	**H**	0.977119	-4.196732	0.385525
H	-1.120724	2.808741	-2.089284	**H**	-0.485393	2.304765	-2.529616
C	-3.510241	0.816473	1.395339	**H**	3.909383	-0.306554	-2.274756
C	-4.772133	0.219598	1.506692	**C**	-2.920652	0.642954	1.104213
C	-2.483673	0.384357	2.245771	**C**	-4.256247	0.290485	1.337900
C	-4.998506	-0.794615	2.433102	**C**	-1.920013	0.009832	1.852406
H	-5.571029	0.535374	0.846809	**C**	-4.581183	-0.680719	2.280770
C	-2.711022	-0.627761	3.172787	**H**	-5.041592	0.760893	0.758715
H	-1.506196	0.846150	2.184262	**C**	-2.244758	-0.958722	2.796324
C	-3.967622	-1.225093	3.265822	**H**	-0.886752	0.285974	1.700005
H	-5.978575	-1.252939	2.498436	**C**	-3.576281	-1.313355	3.009691
H	-1.906839	-0.947296	3.825760	**H**	-5.619510	-0.948850	2.438585
H	-4.142197	-2.017449	3.984535	**H**	-1.456013	-1.434493	3.368145
H	1.024408	2.582935	2.148428	**H**	-3.828388	-2.073436	3.740147
C	3.604256	0.903344	-1.366699	**C**	1.753836	2.596960	0.675771
C	4.881336	0.339316	-1.480001	**C**	0.926373	3.714385	0.506231
C	2.621468	0.530895	-2.294397	**C**	1.604451	1.816277	1.830502
C	5.165399	-0.582398	-2.484355	**C**	-0.034373	4.036724	1.460623
H	5.647948	0.608266	-0.763292	**H**	1.022902	4.317205	-0.388539
C	2.905950	-0.388748	-3.298544	**C**	0.655643	2.150198	2.792087
H	1.631536	0.965487	-2.229394	**H**	2.252175	0.961926	1.985581
C	4.177893	-0.953012	-3.394532	**C**	-0.171499	3.257028	2.606806
H	6.157025	-1.015267	-2.550663	**H**	-0.681702	4.890953	1.303179
H	2.134817	-0.661409	-4.010109	**H**	0.558043	1.543315	3.684759
H	4.397431	-1.672520	-4.174904	**H**	-0.921659	3.505428	3.348325

Table G28 XYZ coordinates of the GS geometries of **2.2e** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

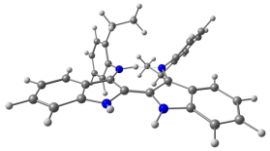
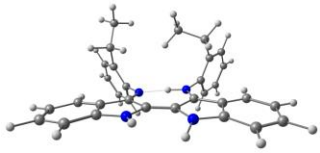
Anti				***Syn***			
							
N	-1.586880	3.200568	-0.096723	**N**	1.254291	3.115668	0.094866
N	-1.358020	-0.304386	0.091074	**N**	1.255227	-0.334490	-0.586690
C	-0.821910	2.071431	-0.012307	**C**	0.560660	1.963592	-0.147884
C	-1.766939	0.912461	0.002222	**C**	1.580149	0.888316	-0.358693
C	-3.108422	1.497391	-0.139038	**C**	2.882547	1.554496	-0.251001
C	-4.386572	0.951533	-0.285509	**C**	4.199262	1.114400	-0.403798
H	-4.544459	-0.116158	-0.253564	**H**	4.418307	0.083326	-0.639218
C	-5.463372	1.813044	-0.476379	**C**	5.231910	2.035258	-0.247756
H	-6.459918	1.404781	-0.589120	**H**	6.258624	1.711382	-0.363095
C	-5.274290	3.199280	-0.521431	**C**	4.957938	3.373416	0.058151
H	-6.128767	3.849866	-0.665150	**H**	5.778278	4.070811	0.179888
C	-4.005892	3.763437	-0.392495	**C**	3.649669	3.835032	0.202949
H	-3.853191	4.834242	-0.442105	**H**	3.436885	4.872671	0.427588
C	-2.941894	2.892529	-0.208966	**C**	2.631053	2.908509	0.036903
C	-2.225740	-1.403700	0.259131	**C**	2.198628	-1.378986	-0.726512
C	-3.051663	-1.463868	1.390938	**C**	2.288857	-1.980595	-1.987807
H	-3.056632	-0.630612	2.083268	**H**	1.671984	-1.596992	-2.791886
C	-3.834845	-2.584138	1.626495	**C**	3.171944	-3.029711	-2.204006
H	-4.463290	-2.626342	2.508339	**H**	3.251282	-3.474695	-3.188890
C	-3.808511	-3.648328	0.723991	**C**	3.945325	-3.505346	-1.146437
H	-4.425466	-4.522962	0.893645	**H**	4.636323	-4.325980	-1.300005
C	-2.979715	-3.587516	-0.391070	**C**	3.818442	-2.932948	0.115140
H	-2.958810	-4.417957	-1.088666	**H**	4.413015	-3.322585	0.932854
C	-2.158599	-2.482645	-0.639952	**C**	2.948898	-1.864528	0.362698
C	-1.238102	-2.476560	-1.839568	**C**	2.839709	-1.267674	1.749833
H	-0.790322	-1.488478	-1.958043	**H**	1.972508	-0.608901	1.795535
H	-1.832209	-2.659685	-2.740996	**H**	3.713460	-0.630637	1.930125
C	-0.131702	-3.537056	-1.742570	**C**	2.729809	-2.304287	2.873693
H	0.496776	-3.372655	-0.865595	**H**	1.885053	-2.976784	2.705566
H	0.509288	-3.505311	-2.627190	**H**	2.578454	-1.802688	3.833191
H	-0.555523	-4.541888	-1.669148	**H**	3.633150	-2.912174	2.959333
H	-1.223698	4.127658	-0.269625	**H**	0.840718	3.992505	0.379347
N	1.233090	3.341949	0.141708	**N**	-1.586310	3.082591	-0.038806
N	1.309507	-0.220252	-0.059126	**N**	-1.395550	-0.452841	-0.457284
C	0.554823	2.119123	0.083173	**C**	-0.818133	1.925556	-0.203200
C	1.566543	1.073629	0.023093	**C**	-1.750361	0.810821	-0.316923
C	2.849808	1.732924	0.081141	**C**	-3.078353	1.368072	-0.232011
C	4.177013	1.267613	0.106275	**C**	-4.366901	0.807981	-0.295603
H	4.398937	0.214350	0.022390	**H**	-4.506590	-0.258105	-0.396052
C	5.199469	2.189621	0.247121	**C**	-5.459557	1.655093	-0.233946
H	6.227551	1.850926	0.270166	**H**	-6.460377	1.244920	-0.282414
C	4.920528	3.564777	0.361965	**C**	-5.286979	3.047018	-0.111485
H	5.741702	4.263526	0.471423	**H**	-6.161474	3.685773	-0.068399
C	3.620645	4.050129	0.337738	**C**	-4.026644	3.624233	-0.043339
H	3.408511	5.108174	0.428004	**H**	-3.897742	4.695050	0.052114
C	2.592000	3.120555	0.192383	**C**	-2.926701	2.769408	-0.098007
C	2.280815	-1.242012	-0.293683	**C**	-2.282395	-1.574626	-0.409318
C	2.606231	-2.137676	0.732839	**C**	-2.603370	-2.213523	-1.604478
C	3.527414	-3.147784	0.435613	**H**	-2.196661	-1.831018	-2.532878
H	3.799633	-3.849830	1.216208	**C**	-3.450778	-3.317302	-1.592908
C	4.100600	-3.261094	-0.827356	**H**	-3.706418	-3.812766	-2.521807
H	4.812655	-4.053351	-1.027104	**C**	-3.966942	-3.773292	-0.382370
C	3.761471	-2.356208	-1.832623	**H**	-4.630690	-4.629887	-0.362603
H	4.200986	-2.439995	-2.819265	**C**	-3.627501	-3.133058	0.807385
C	2.847040	-1.345286	-1.563890	**H**	-4.024655	-3.497795	1.748308
H	0.820385	4.177512	0.533230	**C**	-2.776487	-2.024594	0.824743
H	0.297209	-0.480779	0.013864	**C**	-2.377884	-1.376418	2.128635
H	2.562290	-0.633504	-2.329223	**H**	-3.081666	-1.694257	2.901208
C	1.978793	-2.044979	2.101841	**H**	-2.467081	-0.289787	2.053992
H	1.785998	-0.998190	2.349434	**C**	-0.948613	-1.744618	2.553730
H	2.692842	-2.422197	2.838404	**H**	-0.692108	-1.264690	3.501980
C	0.671008	-2.843364	2.206204	**H**	-0.219650	-1.426303	1.806483
H	0.248220	-2.757694	3.210899	**H**	-0.849325	-2.825475	2.681389
H	-0.073703	-2.479500	1.496945	**H**	-1.245911	4.008937	-0.256495
H	0.842921	-3.902681	1.998087	**H**	-0.364489	-0.618534	-0.568030

Table G29 XYZ coordinates of the GS geometries of **2.2f** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

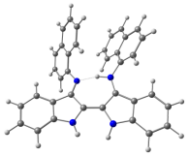
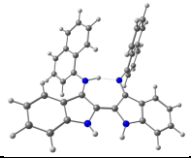
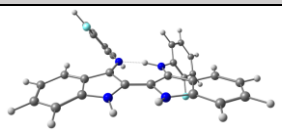
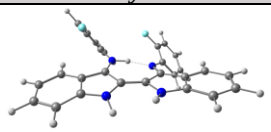
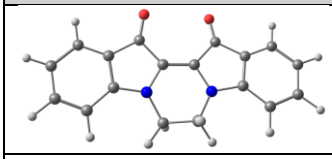
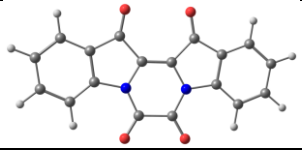
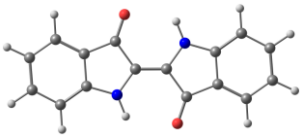
Anti				***Syn***			
							
N	-3.296467	2.379975	-0.154459	**N**	-0.398214	3.893873	0.016456
N	-1.265058	-0.557382	-0.010580	**H**	0.209565	4.700511	0.040681
N	-0.941244	3.893890	0.235532	**N**	2.305519	3.228391	0.561818
N	0.919714	0.948746	-0.227720	**H**	2.085991	4.106471	1.011239
C	-2.034054	1.779016	-0.094796	**N**	-1.127377	0.463496	-0.127335
C	-2.245643	0.340700	-0.083177	**N**	1.463930	-0.166568	-0.157064
C	-3.668223	0.132388	-0.208083	**H**	0.419621	-0.139333	-0.093301
C	-4.465166	-1.016466	-0.368100	**C**	1.347372	2.252035	0.277507
H	-4.026417	-2.001214	-0.340757	**C**	3.452293	1.269304	0.356759
C	-5.821320	-0.861196	-0.590366	**C**	0.026231	2.598097	0.049114
H	-6.441671	-1.737013	-0.735091	**C**	2.055919	0.991181	0.124926
C	-6.402569	0.420172	-0.636416	**C**	2.045486	-1.324765	-0.717675
H	-7.468273	0.510531	-0.810481	**C**	3.549364	2.649168	0.662127
C	-5.640083	1.570734	-0.483095	**C**	-2.719074	-1.246197	0.551381
H	-6.088912	2.554305	-0.537910	**C**	-1.178069	1.747633	-0.188009
C	-4.268908	1.411814	-0.279924	**C**	-2.291047	2.683071	-0.389047
C	-0.892935	2.544026	0.039661	**C**	1.577311	-2.593296	-0.258673
C	0.546862	2.167272	-0.040137	**C**	-1.765193	3.980390	-0.247029
C	1.291177	3.412802	0.173977	**C**	-2.204874	-0.378394	-0.459047
C	2.652529	3.717661	0.292433	**C**	-3.710938	-2.206978	0.182758
H	3.407586	2.954435	0.161414	**C**	2.958609	-1.236830	-1.747371
C	3.020386	5.032541	0.563307	**H**	3.268009	-0.264575	-2.108401
H	4.068830	5.287603	0.648785	**C**	2.079891	-3.770170	-0.898443
C	2.049494	6.030581	0.722972	**C**	4.602709	0.462388	0.429710
H	2.358250	7.048667	0.928847	**H**	4.555211	-0.594721	0.212715
C	0.689351	5.742613	0.631445	**C**	-2.292652	-1.174226	1.900709
H	-0.061913	6.509352	0.769013	**H**	-1.554089	-0.433614	2.180378
C	0.337383	4.432175	0.353316	**C**	0.641226	-2.730461	0.795349
H	-3.441148	3.315223	-0.509020	**H**	0.278266	-1.849680	1.306297
H	-1.773251	4.411346	0.452440	**C**	-2.552355	5.118087	-0.344221
C	-1.343743	-1.912383	0.365039	**H**	-2.127303	6.108032	-0.235232
C	-0.461353	-2.831787	-0.272894	**C**	3.467281	-2.404674	-2.347424
C	-2.153234	-2.321295	1.404977	**H**	4.185719	-2.313475	-3.153141
C	0.377226	-2.468018	-1.350290	**C**	-2.657970	-0.466825	-1.759979
C	-0.414807	-4.175427	0.217211	**H**	-2.237854	0.186933	-2.514593
C	-2.131500	-3.654332	1.849447	**C**	5.877376	2.423167	1.084227
H	-2.794686	-1.603391	1.894786	**H**	6.832591	2.853450	1.361360
C	1.261646	-3.375245	-1.887755	**C**	5.802197	1.046549	0.792805
H	0.337072	-1.468259	-1.757766	**H**	6.697185	0.440213	0.853858
C	0.508272	-5.087436	-0.362223	**C**	3.036765	-3.644330	-1.937266
C	-1.272843	-4.563412	1.277023	**H**	3.414923	-4.543466	-2.410185
H	-2.781497	-3.950075	2.664304	**C**	-3.660461	2.515112	-0.607012
C	1.341048	-4.692952	-1.381296	**H**	-4.091253	1.530137	-0.709336
H	1.907557	-3.074588	-2.704578	**C**	4.759029	3.240528	1.027975
H	0.540514	-6.099623	0.025124	**H**	4.814641	4.296427	1.261736
H	-1.233224	-5.585479	1.636006	**C**	-3.914547	4.929808	-0.576632
H	2.046639	-5.393650	-1.812315	**H**	-4.559743	5.796426	-0.658632
C	2.224910	0.533082	-0.505415	**C**	-4.223050	-3.074105	1.182631
C	2.759205	-0.563007	0.239941	**H**	-4.974528	-3.803170	0.900537
C	2.916221	1.038085	-1.592461	**C**	-4.464283	3.648235	-0.698759
C	2.103100	-1.094197	1.370894	**H**	-5.527361	3.536217	-0.871305
C	4.007672	-1.127939	-0.167795	**C**	1.600817	-5.036252	-0.473052
C	4.148819	0.476577	-1.978248	**H**	1.981702	-5.925316	-0.963126
H	2.481816	1.837867	-2.180618	**C**	-4.153921	-2.271187	-1.163556
C	2.622466	-2.174796	2.043675	**H**	-4.903006	-3.007122	-1.432522
H	1.182701	-0.641440	1.711524	**C**	-3.636868	-1.419287	-2.109779
C	4.517085	-2.244536	0.545000	**H**	-3.972131	-1.476524	-3.138626
C	4.687939	-0.579645	-1.284232	**C**	0.191324	-3.972305	1.175822
H	4.666330	0.878858	-2.840600	**H**	-0.536549	-4.058257	1.973716
C	3.833879	-2.766212	1.618510	**C**	0.672088	-5.135994	0.534543
H	2.093410	-2.582115	2.897320	**H**	0.308313	-6.108378	0.845407
H	5.457582	-2.680325	0.226788	**C**	-2.808121	-2.032165	2.843252
H	5.634740	-1.013159	-1.586839	**H**	-2.470049	-1.973467	3.871303
H	4.227824	-3.622333	2.153965	**C**	-3.780787	-2.992340	2.480995
H	-0.300231	-0.143890	-0.106514	**H**	-4.179351	-3.661890	3.234356

Table G30 XYZ coordinates of the GS geometries of **2.2g** B3LYP/6-311G(d,p) (SMD = CH_2Cl_2)

Anti				***Syn***			
							
N	-1.391577	-2.978072	-0.214605	**N**	-1.281103	-3.054957	-0.276589
N	-1.336960	0.581244	-0.051281	**N**	-1.246785	0.505038	-0.103788
N	1.410640	-2.933105	0.236927	**N**	1.516035	-2.994672	0.166616
N	1.314164	0.570512	-0.036900	**N**	1.410941	0.494062	-0.239726
C	-0.676283	-1.782685	-0.114847	**C**	-0.573153	-1.853685	-0.192558
C	-1.653032	-0.702442	-0.162617	**C**	-1.556797	-0.780604	-0.217931
C	-2.942401	-1.312634	-0.356292	**C**	-2.845408	-1.399720	-0.389476
C	-4.238124	-0.801495	-0.556164	**C**	-4.147258	-0.897089	-0.569120
H	-4.430995	0.261490	-0.540788	**H**	-4.347035	0.164557	-0.547516
C	-5.270336	-1.688608	-0.800166	**C**	-5.176780	-1.790387	-0.802138
H	-6.273434	-1.313714	-0.959506	**H**	-6.184455	-1.421643	-0.946343
C	-5.034497	-3.076670	-0.845242	**C**	-4.932363	-3.176594	-0.855204
H	-5.863843	-3.747487	-1.036423	**H**	-5.759677	-3.852524	-1.036964
C	-3.767009	-3.607419	-0.656205	**C**	-3.658678	-3.699114	-0.685564
H	-3.585234	-4.673958	-0.699127	**H**	-3.470268	-4.764268	-0.734630
C	-2.727706	-2.711029	-0.411477	**C**	-2.622261	-2.796519	-0.451993
C	-2.205082	1.680231	0.119069	**C**	-2.112216	1.597802	0.102600
C	-3.151343	1.719529	1.144236	**C**	-3.051686	1.614267	1.134826
C	-3.961204	2.820567	1.351483	**C**	-3.857585	2.711616	1.374066
H	-4.684815	2.797939	2.156717	**H**	-4.575446	2.670787	2.183700
C	-3.808359	3.933678	0.527685	**C**	-3.706528	3.845127	0.578328
H	-4.435213	4.802700	0.684252	**H**	-4.329714	4.711656	0.761235
C	-2.849644	3.930709	-0.485210	**C**	-2.752792	3.865736	-0.439107
H	-2.726573	4.798267	-1.121222	**H**	-2.629301	4.749667	-1.052093
C	-2.050463	2.811501	-0.686695	**C**	-1.957737	2.750367	-0.672781
C	0.693615	-1.781117	0.079938	**C**	0.798961	-1.845918	-0.013218
C	1.681831	-0.657711	0.102199	**C**	1.785403	-0.723766	-0.038898
C	2.984314	-1.282704	0.340066	**C**	3.090818	-1.341097	0.222424
C	4.270663	-0.775836	0.543981	**C**	4.374014	-0.829944	0.439323
H	4.469459	0.285416	0.508453	**H**	4.572073	0.229552	0.372416
C	5.303967	-1.667377	0.814953	**C**	5.402121	-1.713199	0.752626
H	6.306328	-1.290517	0.974613	**H**	6.401113	-1.331139	0.921159
C	5.063646	-3.045146	0.880449	**C**	5.161490	-3.089333	0.850075
H	5.885574	-3.719905	1.088094	**H**	5.979878	-3.757935	1.089139
C	3.786096	-3.570680	0.691201	**C**	3.886975	-3.618733	0.655820
H	3.595058	-4.634648	0.753469	**H**	3.692876	-4.679906	0.749257
C	2.765550	-2.669612	0.427201	**C**	2.870230	-2.725133	0.351991
C	2.177511	1.666527	-0.149694	**C**	2.261564	1.579873	-0.453071
C	3.168030	1.752803	-1.134185	**C**	3.311145	1.583595	-1.383085
C	3.947359	2.881906	-1.302767	**C**	4.033465	2.745554	-1.624223
H	4.697175	2.891021	-2.084219	**H**	4.835864	2.733776	-2.351641
C	3.742759	3.975523	-0.464188	**C**	3.726011	3.922988	-0.941231
H	4.351097	4.863222	-0.584761	**H**	4.293917	4.826418	-1.125678
C	2.750950	3.927097	0.515815	**C**	2.673963	3.946498	-0.027210
H	2.584055	4.778650	1.163763	**H**	2.403120	4.845100	0.512787
C	1.962776	2.792036	0.657742	**C**	1.955691	2.786644	0.187674
H	-0.304129	0.781428	-0.064709	**H**	-0.218700	0.711678	-0.158307
H	-0.977638	-3.847399	-0.521006	**H**	-0.864244	-3.916862	-0.600577
H	1.009255	-3.847252	0.392767	**H**	1.110424	-3.899205	0.363966
H	1.178822	2.746048	1.404046	**H**	-1.215818	2.748307	-1.462016
H	-1.304027	2.790593	-1.471649	**F**	-3.171214	0.521787	1.923313
F	-3.274488	0.644768	1.956332	**H**	3.532238	0.674082	-1.926819
F	3.358232	0.693056	-1.956708	**F**	0.915200	2.800016	1.055094

XYZ coordinates of indigo, 3.3a, 3.6, protonated (3.13, 3.15a - 3.15e) and neutral (3.14, 3.16a – 3.16e) N,N'-oxalyl bridged *cis*-Nindigos

Table G31 XYZ coordinates of **3.3a** and **3.6**, B3LYP/Def2TZVPP/SMD(ACN)

3.3a				3.6				Indigo*			
											
C	-2.480702	3.573025	-0.003430	**C**	-2.462038	3.609998	-0.021553	**O**	-2.328693	1.216553	0.000000
C	-1.100799	3.827087	0.069874	**C**	-1.082149	3.824354	-0.019868	**O**	2.328693	-1.216553	0.000000
C	-0.618660	5.129049	0.107209	**C**	-0.559712	5.109634	-0.019130	**N**	1.160318	1.448650	0.000000
C	-1.529764	6.177066	0.059829	**C**	-1.446446	6.178898	-0.020112	**N**	-1.160318	-1.448650	0.000000
C	-2.901284	5.911655	-0.027377	**C**	-2.823117	5.950542	-0.021794	**C**	0.821947	2.790912	0.000000
C	-3.401150	4.612912	-0.063549	**C**	-3.360634	4.662993	-0.022551	**C**	1.650647	3.905593	0.000000
C	-1.495303	1.521797	0.003839	**C**	-1.496028	1.512846	-0.020563	**C**	1.044364	5.156618	0.000000
C	-0.394652	2.536415	0.085706	**C**	-0.387044	2.527990	-0.019136	**C**	-0.347350	5.307451	0.000000
H	0.445572	5.315626	0.165524	**H**	0.510368	5.264664	-0.017825	**C**	-1.168744	4.189569	0.000000
H	-1.183142	7.200708	0.085506	**H**	-1.072075	7.192895	-0.019576	**C**	-0.581192	2.930406	0.000000
H	-3.597231	6.739237	-0.069629	**H**	-3.499958	6.794190	-0.022542	**C**	-1.160318	1.584096	0.000000
H	-4.463294	4.428702	-0.135261	**H**	-4.424478	4.501960	-0.023849	**C**	0.021293	0.676226	0.000000
C	-1.494324	0.159486	-0.050289	**C**	-1.496148	0.167101	-0.020678	**C**	-0.021293	-0.676226	0. 000000
C	-0.392466	-0.853306	-0.138286	**C**	-0.387343	-0.848240	-0.019427	**C**	-0.821947	-2.790912	0.000000
C	-1.096374	-2.145146	-0.118529	**C**	-1.082679	-2.144480	-0.020375	**C**	-1.650647	-3.905593	0.000000
C	-2.476266	-1.893372	-0.037544	**C**	-2.462530	-1.929879	-0.022018	**C**	-1.044364	-5.156618	0.000000
C	-0.612292	-3.446308	-0.158554	**C**	-0.560470	-3.429854	-0.019856	**C**	0.347350	-5.307451	0.000000
C	-3.394640	-2.934783	0.027693	**C**	-3.361314	-2.982714	-0.023188	**C**	1.168744	-4.189569	0.000000
C	-1.521379	-4.495833	-0.106107	**C**	-1.447395	-4.498959	-0.021013	**C**	0.581192	-2.930406	0.000000
H	0.451907	-3.631120	-0.222794	**H**	0.509582	-3.585074	-0.018582	**C**	1.160318	-1.584096	0.000000
C	-2.892831	-4.232695	-0.011266	**C**	-2.824025	-4.270359	-0.022650	**H**	2.083289	1.044706	0.000000
H	-4.456672	-2.752333	0.105319	**H**	-4.425129	-2.821492	-0.024455	**H**	2.727280	3.807057	0.000000
H	-1.173210	-5.518900	-0.133719	**H**	-1.073203	-5.513023	-0.020648	**H**	1.669762	6.039378	0.000000
H	-3.587159	-5.061430	0.034855	**H**	-3.501016	-5.113886	-0.023536	**H**	-0.777289	6.2988 00	0.000000
C	-3.949570	1.537256	-0.320177	**N**	-2.709046	2.209081	-0.021968	**H**	-2.083289	-1.044706	0.000000
C	-3.946721	0.139960	0.287384	**N**	-2.709289	-0.528918	-0.022199	**H**	-2.727280	-3.807057	0.000000
H	-4.778782	2.107953	0.090465	**O**	0.805992	2.319507	-0.017707	**H**	-1.669762	-6.039378	0.000000
H	-4.072778	1.474172	-1.404404	**O**	0.805729	-0.639969	-0.017986	**H**	0.777289	-6.298800	0.000000
H	-4.063996	0.202846	1.372281	**C**	-3.943860	1.605242	-0.023508	**H**	-2.246308	4.280601	0.000000
H	-4.777258	-0.432112	-0.118638	**C**	-3.943996	0.075140	-0.023637	**H**	2.246308	-4.280601	0.000000
N	-2.701716	2.205149	-0.002206	**O**	-4.990922	2.214499	-0.024722				
N	-2.699551	-0.525864	-0.037530	**O**	-4.991166	-0.533931	-0.024946				
O	0.806693	2.341269	0.167722								
O	0.808079	-0.656169	-0.226988								

*Optimized using B3LYP/Def2TZVPP Gas Phase

Table G32 XYZ coordinates of **3.13** and **3.14**, B3LYP/Def2TZVPP/SMD(ACN)

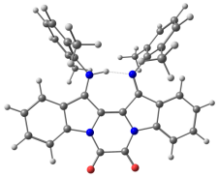
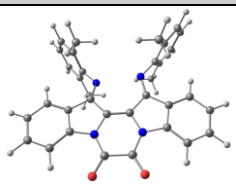
3.13				**3.14**			
							
O	1.466483	4.869920	0.060568	**O**	-1.364829	4.829856	-0.126659
O	-1.277291	4.930551	-0.090095	**O**	1.364827	4.829856	0.126657
N	1.420119	2.588586	0.068091	**N**	-1.359042	2.547392	-0.098624
N	1.309912	-0.938489	0.003525	**N**	-1.437375	-0.985817	0.142668
N	-1.321684	2.649462	-0.066359	**N**	1.359041	2.547393	0.098621
N	-1.360426	-0.898315	0.007867	**N**	1.437375	-0.985816	-0.142674
C	0.706362	1.398760	0.034612	**C**	-0.675321	1.319491	-0.032060
C	1.678417	0.283184	0.053048	**C**	-1.699945	0.244780	-0.028515
C	2.995935	0.917658	0.130060	**C**	-2.991137	0.939494	-0.185603
C	4.277372	0.382285	0.204409	**C**	-4.290544	0.455166	-0.288238
H	4.434141	-0.684391	0.202974	**H**	-4.490267	-0.603903	-0.276035
C	5.355535	1.255827	0.279266	**C**	-5.333728	1.366357	-0.410510
H	6.359824	0.860748	0.337620	**H**	-6.349981	1.007006	-0.493459
C	5.154552	2.634495	0.277249	**C**	-5.080204	2.735941	-0.426483
H	6.006967	3.297521	0.332762	**H**	-5.903590	3.430889	-0.520629
C	3.876944	3.189516	0.206718	**C**	-3.784543	3.239157	-0.325662
H	3.729050	4.255203	0.209512	**H**	-3.592766	4.297305	-0.340258
C	2.814651	2.308054	0.136098	**C**	-2.755784	2.318167	-0.208429
C	2.209496	-2.028205	-0.034526	**C**	-2.415818	-1.987835	0.180558
C	2.386238	-2.776430	1.136948	**C**	-2.718943	-2.689283	-0.997725
C	3.233459	-3.880697	1.086625	**C**	-3.638879	-3.732478	-0.928182
H	3.391876	-4.460107	1.987122	**H**	-3.883951	-4.273638	-1.833651
C	3.863797	-4.243262	-0.097033	**C**	-4.237292	-4.083366	0.276308
H	4.515518	-5.106534	-0.121090	**H**	-4.948675	-4.897804	0.313202
C	3.645096	-3.505390	-1.253450	**C**	-3.908636	-3.389915	1.435041
H	4.121394	-3.796159	-2.180954	**H**	-4.365054	-3.662916	2.378400
C	2.814665	-2.386634	-1.247276	**C**	-2.995308	-2.338703	1.410599
C	-0.646325	1.422254	-0.022847	**C**	0.675321	1.319491	0.032056
C	-1.650367	0.368003	-0.040708	**C**	1.699945	0.244781	0.028511
C	-2.936967	1.022124	-0.116557	**C**	2.991136	0.939495	0.185604
C	-4.237640	0.521136	-0.188199	**C**	4.290543	0.455168	0.288243
H	-4.427235	-0.539804	-0.183603	**H**	4.490266	-0.603902	0.276040
C	-5.285939	1.423827	-0.265567	**C**	5.333726	1.366359	0.410518
H	-6.301614	1.059491	-0.322000	**H**	6.349979	1.007008	0.493470
C	-5.043508	2.798775	-0.268426	**C**	5.080202	2.735942	0.426490
H	-5.878116	3.484022	-0.325328	**H**	5.903587	3.430891	0.520639
C	-3.753347	3.320369	-0.202022	**C**	3.784541	3.239158	0.325665
H	-3.576571	4.381684	-0.209294	**H**	3.592763	4.297306	0.340260
C	-2.713135	2.412451	-0.129276	**C**	2.755782	2.318168	0.208429
C	-2.291108	-1.985178	0.039480	**C**	2.415819	-1.987834	-0.180561
C	-2.484080	-2.706266	-1.141926	**C**	2.718941	-2.689282	0.997723
C	-3.375297	-3.776111	-1.104326	**C**	3.638878	-3.732476	0.928184
H	-3.551081	-4.345500	-2.007380	**H**	3.883948	-4.273635	1.833654
C	-4.030150	-4.112316	0.073552	**C**	4.237295	-4.083364	-0.276304
H	-4.718886	-4.946659	0.086829	**H**	4.948678	-4.897801	-0.313196
C	-3.796665	-3.391756	1.237495	**C**	3.908642	-3.389913	-1.435039
H	-4.296532	-3.666948	2.156734	**H**	4.365063	-3.662915	-2.378395
C	-2.915490	-2.311924	1.246447	**C**	2.995313	-2.338702	-1.410600
C	0.836317	3.839862	0.032249	**C**	-0.757175	3.779915	-0.064566
C	-0.693012	3.872613	-0.048407	**C**	0.757173	3.779916	0.064562
C	-2.656648	-1.530248	2.501699	**C**	2.645042	-1.576508	-2.655873
C	-1.762052	-2.325699	-2.401628	**C**	2.073799	-2.297042	2.295617
C	2.577793	-1.588085	-2.497093	**C**	-2.645033	-1.576508	2.655871
C	1.692209	-2.374716	2.406050	**C**	-2.073805	-2.297043	-2.295620
H	-0.679657	-2.352110	-2.260379	**H**	0.985708	-2.276776	2.204002
H	-2.018063	-3.007323	-3.210217	**H**	2.342497	-2.995131	3.087072
H	-2.018230	-1.311279	-2.713964	**H**	2.381370	-1.296253	2.608333
H	-1.587619	-1.410975	2.683743	**H**	1.563701	-1.540139	-2.806179
H	-3.088358	-0.528847	2.441517	**H**	2.990210	-0.541385	-2.600604
H	-3.097898	-2.034180	3.359264	**H**	3.100548	-2.037221	-3.531215
H	2.993962	-2.101925	-3.361811	**H**	-3.100537	-2.037221	3.531215
H	1.512177	-1.427968	-2.671117	**H**	-1.563691	-1.540139	2.806174
H	3.044400	-0.602449	-2.436434	**H**	-2.990202	-0.541386	2.600603
H	2.042921	-1.403669	2.762707	**H**	-2.381378	-1.296255	-2.608335
H	0.614329	-2.285285	2.254332	**H**	-0.985714	-2.276776	-2.204009
H	1.869745	-3.108286	3.190529	**H**	-2.342505	-2.995133	-3.087074
H	-0.328086	-1.120404	0.005840				

Table G33 XYZ coordinates of the GS, TS, and TS' geometries of **3.15a** B3LYP/Def2SVP (gas phase)

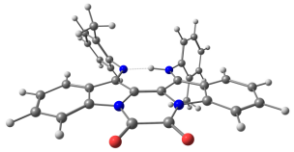
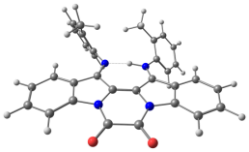
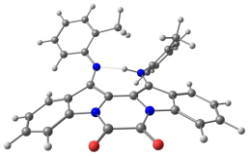
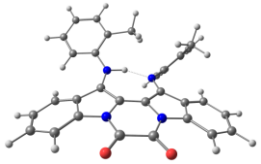
Anti				***Syn***				**TS**				**TS'**			
															
O	1.518083	-4.715270	0.117344	**O**	-1.080112	-4.889851	-0.132353	**C**	1.157001	-1.017827	-0.053045	**C**	1.088233	-1.074061	-0.013636
O	-1.240050	-4.800570	-0.139054	**O**	1.675934	-4.765902	0.119927	**C**	1.863705	0.278062	0.182031	**C**	1.859625	0.158059	0.227173
N	1.447326	-2.425020	0.112818	**N**	-1.175944	-2.601152	-0.174302	**C**	3.251814	-0.127351	0.523692	**C**	3.227451	-0.284379	0.489384
N	1.297104	1.115539	0.059841	**N**	-1.284964	0.939153	-0.174701	**C**	4.336684	0.489952	1.167903	**C**	4.360369	0.288954	1.107217
N	-1.299552	-2.511253	-0.117316	**N**	1.569965	-2.479170	0.035754	**H**	4.252737	1.476166	1.614123	**H**	4.321875	1.262700	1.583708
N	-1.368921	1.056334	-0.050124	**N**	1.368225	1.078344	-0.153529	**C**	5.536345	-0.206046	1.331793	**C**	5.534509	-0.447634	1.217768
C	0.727316	-1.240897	0.055178	**C**	-0.542804	-1.365402	-0.153656	**H**	6.372129	0.283038	1.835119	**H**	6.403138	0.001361	1.702090
C	1.690743	-0.111648	0.107471	**C**	-1.588009	-0.313711	-0.202037	**C**	5.670270	-1.519959	0.873840	**C**	5.605026	-1.764108	0.737949
C	3.012283	-0.734798	0.246264	**C**	-2.862288	-1.032324	-0.298972	**H**	6.621077	-2.043709	0.990978	**H**	6.542447	-2.318949	0.814589
C	4.293358	-0.193760	0.414618	**C**	-4.182627	-0.586255	-0.438522	**C**	4.582775	-2.198739	0.311960	**C**	4.477613	-2.403867	0.218635
H	4.447129	0.884235	0.427823	**H**	-4.412812	0.478095	-0.463051	**H**	4.651167	-3.239833	0.008467	**H**	4.496047	-3.445566	-0.090003
C	5.370404	-1.069694	0.564773	**C**	-5.197252	-1.539446	-0.545062	**C**	3.389124	-1.496140	0.188332	**C**	3.299553	-1.663494	0.147211
H	6.376487	-0.668245	0.697621	**H**	-6.233141	-1.214213	-0.655315	**C**	1.670523	2.686172	-0.321608	**C**	1.793775	2.653611	-0.227524
C	5.174282	-2.457307	0.542976	**C**	-4.900111	-2.909060	-0.508941	**C**	0.767053	3.563142	-1.004850	**C**	0.922872	3.553133	-0.909625
H	6.032580	-3.123097	0.655145	**H**	-5.710832	-3.636430	-0.587870	**C**	1.166527	4.881546	-1.252398	**C**	1.408055	4.831098	-1.218107
C	3.899892	-3.020424	0.386511	**C**	-3.584975	-3.377209	-0.379150	**H**	0.477239	5.544825	-1.779787	**H**	0.744231	5.519031	-1.746166
H	3.742445	-4.096015	0.379926	**H**	-3.350533	-4.438567	-0.360195	**C**	2.414933	5.362930	-0.862516	**C**	2.698866	5.240247	-0.892949
C	2.837102	-2.135696	0.247029	**C**	-2.585056	-2.416458	-0.281860	**H**	2.690128	6.400037	-1.065464	**H**	3.036892	6.246638	-1.147214
C	2.175567	2.219670	0.001955	**C**	-2.227855	1.985601	-0.099929	**C**	3.315286	4.501065	-0.228925	**C**	3.554353	4.342246	-0.252940
C	2.996828	2.446429	-1.127853	**C**	-3.010573	2.180133	1.062984	**H**	4.306335	4.851894	0.065091	**H**	4.576054	4.629727	0.001540
C	3.797976	3.596861	-1.119868	**C**	-3.867816	3.289203	1.083741	**C**	2.946522	3.188825	0.026865	**C**	3.102816	3.069109	0.070828
H	4.432190	3.797309	-1.987018	**H**	-4.474525	3.463498	1.975818	**C**	-0.172587	-1.366923	-0.126849	**C**	-0.251493	-1.372602	-0.071114
C	3.798730	4.488972	-0.045809	**C**	-3.957208	4.173413	0.006681	**C**	-1.392405	-0.633591	0.148396	**C**	-1.456192	-0.549961	0.178983
H	4.441659	5.371017	-0.072067	**H**	-4.641020	5.023099	0.056085	**C**	-2.470244	-1.601105	0.186947	**C**	-2.583785	-1.491100	0.198126
C	2.959886	4.261725	1.048750	**C**	-3.155427	3.979768	-1.121632	**C**	-3.838174	-1.499247	0.501811	**C**	-3.943589	-1.333280	0.495843
H	2.942099	4.960091	1.887798	**H**	-3.207582	4.672387	-1.964008	**H**	-4.277966	-0.546428	0.790248	**H**	-4.347015	-0.359718	0.768945
C	2.133168	3.140890	1.060825	**C**	-2.276344	2.899808	-1.164616	**H**	-4.617406	-2.650131	0.448061	**C**	-4.772291	-2.455670	0.441942
C	-0.637967	-1.274291	-0.049758	**C**	0.823460	-1.295233	-0.065043	**H**	-5.679523	-2.594214	0.692171	**H**	-5.833753	-2.352723	0.673859
C	-1.650784	-0.224707	-0.109830	**C**	1.761278	-0.173279	-0.045213	**C**	-4.053036	-3.885362	0.081746	**C**	-4.257052	-3.7106 00	0.090098
C	-2.930531	-0.892212	-0.243561	**C**	3.084390	-0.746838	0.131318	**H**	-4.689751	-4.771679	0.038258	**H**	-4.925752	-4.572660	0.043053
C	-4.243198	-0.407860	-0.388566	**C**	4.356360	-0.176639	0.322145	**C**	-2.694455	-4.017581	-0.220864	**C**	-2.897507	-3.895049	-0.195350
H	-4.447508	0.661309	-0.401957	**H**	4.494528	0.902556	0.315440	**H**	-2.251892	-4.972645	-0.492808	**H**	-2.491063	-4.869055	-0.455036
C	-5.276604	-1.331142	-0.516829	**C**	5.441485	-1.023721	0.524513	**C**	-1.917494	-2.863288	-0.148460	**C**	-2.082671	-2.770500	-0.120216
H	-6.303186	-0.979507	-0.631666	**H**	6.435164	-0.599116	0.676526	**N**	2.116323	-2.011608	-0.177199	**N**	2.010246	-2.125220	-0.163596
C	-5.013677	-2.712226	-0.499360	**C**	5.274116	-2.419314	0.529762	**N**	1.235621	1.382163	-0.108147	**N**	1.298131	1.356620	0.060319
H	-5.844031	-3.414906	-0.597647	**H**	6.144307	-3.062235	0.678848	**N**	-0.529869	-2.715721	-0.334717	**N**	-0.670344	-2.682162	-0.286452
C	-3.716354	-3.219515	-0.363985	**C**	4.019416	-3.013208	0.358397	**H**	3.664264	2.539931	0.500916	**H**	3.786628	2.397922	0.560455
H	-3.509723	-4.286987	-0.357493	**H**	3.881889	-4.091456	0.378109	**C**	0.370921	-3.742503	-0.594264	**C**	0.180626	-3.758166	-0.549733
C	-2.687775	-2.289831	-0.242058	**C**	2.937115	-2.157434	0.172233	**C**	1.851599	-3.349220	-0.512351	**C**	1.678933	-3.445165	-0.481777
C	-2.325243	2.120249	-0.016908	**C**	2.163340	2.241951	-0.319424	**O**	0.045504	-4.878574	-0.821329	**O**	-0.209215	-4.872067	-0.778746
C	-2.452857	2.932938	-1.147767	**C**	3.153431	2.279640	-1.312561	**O**	2.715430	-4.166156	-0.684262	**O**	2.496406	-4.308950	-0.661430
C	-3.367411	3.985888	-1.141598	**C**	3.895730	3.440867	-1.505972	**C**	-0.577709	3.125857	-1.511838	**H**	0.242877	1.282208	0.052493
H	-3.477119	4.617860	-2.024846	**H**	4.661824	3.474271	-2.282937	**H**	-0.883335	3.746893	-2.364896	**C**	-0.470667	3.206740	-1.349851
C	-4.136613	4.221888	0.000573	**C**	3.640932	4.563604	-0.710881	**H**	-0.575366	2.078024	-1.836117	**H**	-0.777009	3.859652	-2.177563
H	-4.854248	5.044727	0.016319	**H**	4.220379	5.477921	-0.853890	**H**	-1.354657	3.244090	-0.740362	**H**	-0.563074	2.167549	-1.692747
C	-3.982331	3.416275	1.131248	**C**	2.638026	4.523084	0.259033	**N**	-1.423546	0.671579	0.326510	**H**	-1.197465	3.351445	-0.536802
H	-4.574918	3.621691	2.025852	**H**	2.442386	5.406568	0.871007	**C**	-2.582558	1.465610	0.588106	**N**	-1.365198	0.723343	0.349394
C	-3.071898	2.350389	1.155739	**C**	1.867982	3.371386	0.473162	**C**	-2.653776	2.114747	1.826925	**C**	-2.485354	1.555384	0.555720
C	0.873936	-3.703058	0.061276	**C**	-0.511567	-3.831894	-0.103057	**C**	-3.575622	1.641473	-0.397868	**C**	-2.525310	2.283592	1.757245
C	-0.659404	-3.749542	-0.076461	**C**	1.020453	-3.761972	0.029286	**C**	-3.742422	2.931967	2.124060	**C**	-3.471224	1.751597	-0.441404
H	-1.843522	2.724924	-2.029397	**H**	3.322724	1.403122	-1.940201	**H**	-1.854638	1.961558	2.554811	**C**	-3.576682	3.157976	2.018308
H	1.463144	2.949366	1.901326	**H**	-1.632684	2.736412	-2.031218	**C**	-4.660140	2.468833	-0.067271	**H**	-1.727912	2.133230	2.487462
H	-0.325172	1.280171	-0.005100	**H**	0.303526	1.198794	-0.162220	**C**	-4.751929	3.102612	1.172425	**C**	-4.502598	2.659286	-0.157601
C	3.003633	1.517037	-2.313550	**C**	-2.911755	1.261393	2.252359	**H**	-3.802529	3.430638	3.093184	**C**	-4.572967	3.345236	1.055379
C	-2.906575	1.492164	2.382103	**C**	0.767610	3.349039	1.500461	**H**	-5.444004	2.625990	-0.812194	**H**	-3.613035	3.698619	2.966153
H	1.999138	1.124244	-2.532224	**H**	-1.869987	0.968546	2.454717	**H**	-5.609835	3.741296	1.392387	**H**	-5.266943	2.833766	-0.919168
H	3.367086	2.037181	-3.210354	**H**	-3.308551	1.749142	3.153037	**C**	-3.507224	0.992137	-1.754479	**H**	-5.395437	4.038634	1.241843
H	3.662882	0.648392	-2.149720	**H**	-3.485766	0.332100	2.102508	**H**	-2.476977	0.767296	-2.060621	**C**	-3.431574	1.059146	-1.778682
H	-3.341202	1.983218	3.262963	**H**	0.870728	4.188075	2.201385	**H**	-4.066830	0.042268	-1.771639	**H**	-2.411328	0.783520	-2.079842
H	-3.410992	0.518077	2.266129	**H**	-0.223373	3.440898	1.023695	**H**	-3.953349	1.646072	-2.516884	**H**	-4.025922	0.130539	-1.771383
H	-1.846471	1.285869	2.594572	**H**	0.765083	2.415365	2.083311	**H**	-0.494986	1.141937	0.200800	**H**	-3.852192	1.707535	-2.560331

Table G34 XYZ coordinates of the GS, TS, and TS' geometries of **3.15b** B3LYP/Def2SVP (gas phase)

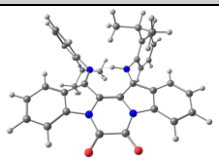
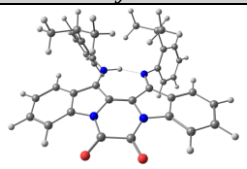
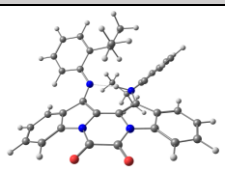
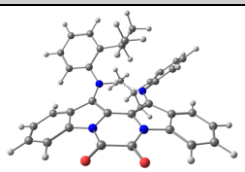
Anti				***Syn***				**TS**				**TS'**			
															
O	-1.496856	5.023368	-0.053606	**O**	-1.563738	4.959512	0.311666	**C**	-1.821694	0.296736	-0.052241	**C**	-1.839401	0.023106	-0.035037
O	1.269699	5.089714	0.079413	**O**	1.182982	5.037795	-0.045725	**C**	-1.516229	-1.150018	0.181479	**C**	-1.329668	-1.338305	0.201804
N	-1.441475	2.732648	-0.054829	**N**	-1.529833	2.679497	0.084106	**C**	-2.820588	-1.727680	0.597828	**C**	-2.499888	-2.139201	0.548744
N	-1.324231	-0.809265	-0.046041	**N**	-1.457941	-0.849954	-0.313340	**C**	-3.217590	-2.884134	1.289647	**C**	-2.702952	-3.366290	1.217630
N	1.310653	2.799961	0.091876	**N**	1.207171	2.756214	-0.238666	**H**	-2.495387	-3.574120	1.715793	**H**	-1.882231	-3.914985	1.667851
N	1.361163	-0.769665	0.111409	**N**	1.238964	-0.802606	-0.384268	**C**	-4.572780	-3.120826	1.530323	**C**	-3.995258	-3.839274	1.414943
C	-0.728823	1.543588	-0.011344	**C**	-0.829809	1.494314	-0.088895	**H**	-4.869401	-4.022503	2.068905	**H**	-4.144429	-4.785124	1.938211
C	-1.700315	0.421689	-0.092214	**C**	-1.813071	0.383502	-0.165385	**C**	-5.544657	-2.210875	1.104691	**C**	-5.104989	-3.102760	0.973017
C	-3.023070	1.055660	-0.171095	**C**	-3.129028	1.019179	0.001768	**H**	-6.601602	-2.419557	1.281915	**H**	-6.111362	-3.501331	1.117468
C	-4.318983	0.525387	-0.207581	**C**	-4.424044	0.492287	0.097928	**C**	-5.180468	-1.001703	0.500947	**C**	-4.951663	-1.835006	0.408057
H	-4.482422	-0.550239	-0.229634	**H**	-4.605663	-0.573603	-0.023150	**H**	-5.918471	-0.253972	0.223845	**H**	-5.803353	-1.220501	0.129462
C	-5.398912	1.410957	-0.219488	**C**	-5.482760	1.368013	0.346699	**C**	-3.823314	-0.773555	0.300857	**C**	-3.651224	-1.359362	0.250903
H	-6.416637	1.018018	-0.248645	**H**	-6.498174	0.975407	0.423247	**C**	0.099999	-2.888377	-0.480055	**C**	0.604169	-2.857519	-0.420077
C	-5.190553	2.796457	-0.200062	**C**	-5.258094	2.743687	0.491018	**C**	1.271917	-3.005803	-1.304131	**C**	1.772394	-2.750448	-1.235495
H	-6.050239	3.469670	-0.216864	**H**	-6.102860	3.410471	0.676154	**C**	1.697306	-4.287575	-1.666580	**C**	2.391820	-3.937804	-1.640645
C	-3.902494	3.348618	-0.154069	**C**	-3.970582	3.291511	0.410931	**H**	2.576702	-4.394108	-2.299578	**H**	3.280370	-3.876194	-2.267100
H	-3.737024	4.422654	-0.128395	**H**	-3.788809	4.355876	0.535727	**C**	1.035616	-5.443180	-1.248074	**C**	1.912114	-5.197462	-1.281380
C	-2.838578	2.454723	-0.135248	**C**	-2.926212	2.405621	0.172054	**H**	1.409866	-6.424293	-1.547980	**H**	2.431571	-6.097021	-1.617230
C	-2.218622	-1.880750	-0.283075	**C**	-2.412778	-1.840663	-0.652105	**C**	-0.100354	-5.332399	-0.446131	**C**	0.769165	-5.289930	-0.490671
C	-2.543991	-2.805842	0.732761	**C**	-2.664828	-2.960654	0.172121	**H**	-0.632579	-6.222349	-0.105056	**H**	0.372768	-6.261375	-0.190000
C	-3.386697	-3.871136	0.377424	**C**	-3.611609	-3.890122	-0.286540	**C**	-0.554480	-4.073677	-0.077909	**C**	0.130040	-4.129576	-0.067450
H	-3.666883	-4.589617	1.151771	**H**	-3.837187	-4.752349	0.345886	**C**	-1.039852	1.420354	-0.195425	**C**	-1.264250	1.267864	-0.148957
C	-3.874277	-4.038953	-0.919132	**C**	-4.266125	-3.752097	-1.510982	**C**	0.378081	1.653351	-0.001127	**C**	0.130484	1.732216	0.030986
H	-4.518850	-4.888391	-1.153516	**H**	-4.989514	-4.504841	-1.830516	**C**	0.581150	3.089213	-0.027630	**C**	0.068726	3.203384	-0.004521
C	-3.531590	-3.117176	-1.911649	**C**	-3.985568	-2.650786	-2.323983	**C**	1.704480	3.906290	0.199935	**C**	1.021213	4.204126	0.231254
H	-3.898588	-3.236341	-2.933102	**H**	-4.477941	-2.531998	-3.291271	**H**	2.672856	3.474742	0.443410	**H**	2.052787	3.951931	0.467709
C	-2.710449	-2.040199	-1.590822	**C**	-3.069272	-1.698779	-1.890043	**C**	1.549987	5.285841	0.113670	**C**	0.621904	5.539800	0.160897
C	0.638184	1.566594	0.065300	**C**	0.531120	1.525010	-0.239468	**H**	2.408398	5.936163	0.289866	**H**	1.352589	6.329520	0.344245
C	1.646171	0.511143	0.122645	**C**	1.523794	0.475615	-0.429157	**C**	0.302254	5.852774	-0.201923	**C**	-0.702408	5.877132	-0.148625
C	2.936138	1.171876	0.163769	**C**	2.798919	1.137764	-0.615436	**H**	0.211306	6.938736	-0.274558	**H**	-0.990050	6.928602	-0.212890
C	4.254479	0.681359	0.180057	**C**	4.085144	0.653243	-0.911342	**C**	-0.833155	5.066378	-0.417934	**C**	-1.676995	4.895503	-0.368298
H	4.454440	-0.387980	0.187932	**H**	4.266645	-0.412790	-1.033844	**H**	-1.802747	5.500108	-0.649458	**H**	-2.709578	5.150332	-0.591424
C	5.300217	1.599622	0.185559	**C**	5.121402	1.572931	-1.043203	**C**	-0.673919	3.686276	-0.312070	**C**	-1.266372	3.569500	-0.274958
H	6.331309	1.242709	0.197335	**H**	6.128420	1.222065	-1.274332	**N**	-3.201581	0.434287	-0.114419	**N**	-3.243402	-0.066819	-0.113151
C	5.044016	2.981831	0.179890	**C**	4.886592	2.949265	-0.878271	**N**	-0.349040	-1.601528	-0.183804	**N**	-0.055752	-1.653944	-0.045709
H	5.883445	3.680535	0.190151	**H**	5.719493	3.648483	-0.979709	**N**	-1.647854	2.674202	-0.410703	**N**	-2.058610	2.388664	-0.366851
C	3.742298	3.495447	0.157337	**C**	3.613450	3.457454	-0.594609	**H**	-1.434857	-4.010927	0.538627	**H**	-0.744512	-4.230278	0.550903
H	3.541415	4.563900	0.145392	**H**	3.427623	4.522324	-0.477085	**C**	-3.010051	2.870982	-0.605447	**C**	-3.440497	2.362000	-0.572487
C	2.702246	2.570747	0.144249	**C**	2.580420	2.532304	-0.477106	**C**	-3.879892	1.618364	-0.444577	**C**	-4.101875	0.989793	-0.424055
C	2.312191	-1.824323	0.306348	**C**	2.192119	-1.868758	-0.478203	**O**	-3.507067	3.942098	-0.838188	**O**	-4.095174	3.341696	-0.811260
C	2.805259	-2.004313	1.605788	**C**	2.976324	-2.267917	0.622666	**O**	-5.074467	1.680524	-0.557684	**O**	-5.292714	0.864779	-0.541816
C	3.719812	-3.019728	1.872205	**C**	3.852972	-3.345665	0.392511	**C**	2.017237	-1.790826	-1.829005	**H**	0.536534	-0.789224	-0.104041
H	4.100916	-3.160241	2.885429	**H**	4.474110	-3.691289	1.222777	**H**	2.169040	-1.127765	-0.974530	**C**	2.309952	-1.415013	-1.716296
C	4.132399	-3.856259	0.831697	**C**	3.946307	-3.993914	-0.836421	**C**	1.193488	-1.034463	-2.885957	**H**	2.298704	-0.741423	-0.857082
H	4.846994	-4.659391	1.023086	**H**	4.641012	-4.827425	-0.958555	**H**	0.206931	-0.738355	-2.502629	**C**	1.411189	-0.809806	-2.810051
C	3.627882	-3.669823	-0.455619	**C**	3.139071	-3.587567	-1.902857	**H**	1.727336	-0.127336	-3.210621	**H**	0.362063	-0.715726	-2.490757
H	3.958861	-4.328937	-1.261704	**H**	3.192101	-4.092762	-2.868975	**H**	1.034861	-1.665275	-3.774650	**H**	1.772489	0.192155	-3.088580
C	2.704838	-2.655017	-0.759929	**C**	2.258458	-2.527536	-1.715336	**C**	3.423542	-2.085996	-2.359315	**H**	1.425910	-1.439093	-3.713396
C	-0.858070	4.006562	-0.021072	**C**	-0.937326	3.948956	0.140318	**H**	3.404004	-2.667990	-3.293712	**C**	3.769846	-1.447085	-2.177082
C	0.679099	4.042399	0.055662	**C**	0.589686	3.991786	-0.052750	**H**	3.935787	-1.136975	-2.576038	**H**	3.899519	-2.006142	-3.116576
H	-2.426773	-1.312912	-2.353991	**H**	1.614289	-2.185728	-2.527829	**H**	4.032239	-2.632168	-1.623182	**H**	4.115279	-0.418712	-2.356040
C	-2.120513	-2.652739	2.186347	**H**	-2.838434	-0.831093	-2.511362	**N**	1.235459	0.670855	0.183837	**H**	4.426397	-1.891360	-1.414234
H	-2.439903	-3.583781	2.681330	**C**	-1.979281	-3.211658	1.506687	**C**	2.656891	0.764597	0.273966	**N**	1.079948	0.880431	0.209848
C	-2.874198	-1.500178	2.871125	**H**	-2.542848	-4.034284	1.975503	**C**	3.316414	0.155960	1.357486	**C**	2.445941	1.199692	0.270339
H	-3.963363	-1.622110	2.773905	**C**	-2.047457	-2.028498	2.482689	**C**	3.364590	1.370544	-0.775285	**C**	3.246466	0.576176	1.256450
H	-2.630438	-1.461960	3.944428	**H**	-3.078934	-1.658832	2.589690	**C**	4.719750	0.201335	1.356372	**C**	3.037845	1.988417	-0.737371
H	-2.604652	-0.525897	2.433850	**H**	-1.695919	-2.338691	3.478745	**C**	4.754854	1.404482	-0.744843	**C**	4.626564	0.820067	1.225101
C	-0.604836	-2.536652	2.402967	**H**	-1.418619	-1.187505	2.160180	**H**	2.816616	1.797948	-1.616533	**C**	4.412495	2.192620	-0.755454
H	-0.046807	-3.272454	1.804598	**C**	-0.546060	-3.725797	1.297125	**C**	5.433411	0.817222	0.328954	**H**	2.409262	2.409112	-1.523642
H	-0.235040	-1.533613	2.150050	**H**	-0.541445	-4.645512	0.693872	**H**	5.265865	-0.257399	2.182501	**C**	5.210826	1.615429	0.239364
H	-0.363031	-2.711861	3.462654	**H**	0.080275	-2.990892	0.774596	**H**	5.307482	1.873568	-1.561132	**H**	5.262208	0.368164	1.989437
H	2.461377	-1.341046	2.401469	**H**	-0.064765	-3.947216	2.262524	**H**	6.524746	0.833532	0.360761	**H**	4.863515	2.793083	-1.548153
C	2.243093	-2.480577	-2.200155	**C**	2.991912	-1.669896	2.032406	**C**	2.553584	-0.559537	2.460591	**H**	6.290736	1.776615	0.238296
H	2.653664	-3.348661	-2.739758	**H**	3.076984	-2.552156	2.688870	**H**	1.493802	-0.272366	2.371059	**C**	2.639107	-0.316184	2.325520
C	2.852458	-1.226213	-2.848470	**C**	1.749659	-0.907681	2.508762	**C**	3.016683	-0.140382	3.862380	**H**	1.558878	-0.375979	2.124507
H	3.948851	-1.218669	-2.755713	**H**	1.701090	0.114796	2.106762	**C**	2.641615	-2.083854	2.270323	**C**	2.806845	0.294241	3.725806
H	2.602534	-1.190665	-3.920117	**H**	0.815795	-1.426238	2.259370	**H**	4.052075	-0.457451	4.061236	**C**	3.207016	-1.742123	2.255709
H	2.468902	-0.301326	-2.390669	**H**	1.790333	-0.810277	3.603933	**H**	2.965234	0.951077	3.994127	**H**	3.869944	0.375126	4.002312
C	0.718876	-2.527772	-2.383379	**C**	4.258020	-0.825370	2.269692	**H**	2.379948	-0.608613	4.628404	**H**	2.369401	1.303092	3.777227
H	0.261541	-3.355946	-1.821695	**H**	5.171480	-1.370425	1.990064	**H**	2.277290	-2.395353	1.280290	**H**	2.312312	-0.333659	4.483272
H	0.235797	-1.594120	-2.064473	**H**	4.230024	0.107803	1.688338	**H**	3.682829	-2.430243	2.365838	**H**	3.068734	-2.185872	1.257949
H	0.473312	-2.667156	-3.447213	**H**	4.337336	-0.554560	3.333675	**H**	2.041668	-2.604915	3.032552	**H**	4.284387	-1.758703	2.483497
H	0.323653	-0.996622	0.048377	**H**	0.202855	-1.031765	-0.315350	**H**	0.808577	-0.282583	0.090380	**H**	2.704886	-2.392659	2.988765

Table G35 XYZ coordinates of the GS, TS, and TS' geometries of **3.15c** B3LYP/Def2SVP (gas phase)

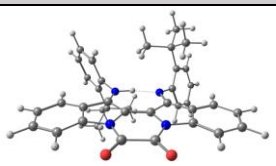
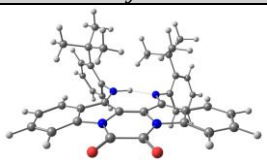
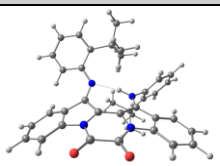
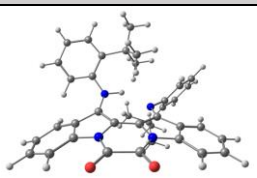
Anti				***Syn***				**TS**				**TS'**			
															
O	-1.165540	5.333786	-0.140221	**O**	1.309846	5.184343	0.241960	**C**	-1.244425	1.324165	-0.133834	**C**	-1.262659	1.315154	-0.071086
O	1.591160	5.219542	0.109343	**O**	-1.438341	5.152612	0.591059	**C**	-1.922226	0.054665	0.281190	**C**	-1.907770	0.054291	0.328580
N	-1.246284	3.045086	-0.146144	**N**	1.273412	2.924693	-0.127669	**C**	-3.181399	0.525037	0.921067	**C**	-3.198966	0.439141	0.883094
N	-1.363408	-0.523833	-0.149754	**N**	1.214927	-0.612918	-0.545498	**C**	-4.069607	-0.013202	1.865559	**C**	-4.099132	-0.157277	1.794721
N	1.495761	2.930181	0.110780	**N**	-1.464271	2.896597	0.189926	**H**	-3.884699	-0.975092	2.338641	**H**	-3.868803	-1.098200	2.287338
N	1.321359	-0.609757	0.097604	**N**	-1.487656	-0.595986	-0.462644	**C**	-5.176823	0.731795	2.279255	**C**	-5.252939	0.523083	2.164066
C	-0.597611	1.799648	-0.088852	**C**	0.565392	1.715357	-0.223230	**H**	-5.863239	0.306637	3.013552	**H**	-5.942289	0.063737	2.874312
C	-1.621500	0.762771	-0.183716	**C**	1.529441	0.658276	-0.497405	**C**	-5.404582	2.014683	1.772335	**C**	-5.525716	1.802934	1.653545
C	-2.896251	1.446498	-0.281147	**C**	2.823436	1.299411	-0.629902	**H**	-6.286995	2.575472	2.086926	**H**	-6.450602	2.310523	1.935637
C	-4.221441	0.979291	-0.347347	**C**	4.100814	0.807373	-0.952461	**C**	-4.485906	2.620020	0.905990	**C**	-4.604545	2.472856	0.845334
H	-4.439321	-0.086532	-0.360940	**H**	4.258704	-0.248283	-1.162052	**H**	-4.614161	3.640712	0.555622	**H**	-4.765929	3.493468	0.508839
C	-5.249701	1.915759	-0.395097	**C**	5.161402	1.707711	-1.002215	**C**	-3.372000	1.872673	0.539698	**C**	-3.431290	1.793944	0.521173
H	-6.285781	1.577169	-0.445861	**H**	6.161186	1.349432	-1.252662	**C**	-2.120662	-2.278103	-0.422640	**C**	-2.059479	-2.359144	-0.385738
C	-4.969271	3.293323	-0.383335	**C**	4.960302	3.072383	-0.732334	**C**	-1.596510	-3.190333	-1.410854	**C**	-1.498533	-3.186962	-1.413174
H	-5.795081	4.006732	-0.428274	**H**	5.811365	3.755753	-0.772368	**C**	-2.387794	-4.301450	-1.734328	**C**	-2.288619	-4.264041	-1.841963
C	-3.660546	3.783863	-0.311217	**C**	3.697579	3.588795	-0.419262	**H**	-2.037325	-4.996000	-2.492720	**H**	-1.911400	-4.903310	-2.635144
H	-3.441248	4.848594	-0.293625	**H**	3.537156	4.645307	-0.218689	**C**	-3.610619	-4.579879	-1.124141	**C**	-3.537917	-4.572791	-1.305220
C	-2.638340	2.840870	-0.255187	**C**	2.640819	2.684059	-0.381727	**H**	-4.172420	-5.469731	-1.416074	**H**	-4.096482	-5.430507	-1.684792
C	-2.312454	-1.559199	-0.441217	**C**	2.154423	-1.673835	-0.772628	**C**	-4.093903	-3.723291	-0.137470	**C**	-4.042074	-3.790256	-0.273428
C	-2.776138	-2.460015	0.544004	**C**	2.199161	-2.145106	-2.094758	**H**	-5.038654	-3.923805	0.371236	**H**	-5.001322	-4.017518	0.194834
C	-3.675645	-3.442110	0.090214	**C**	3.100525	-3.135138	-2.466045	**C**	-3.355643	-2.597419	0.189920	**C**	-3.300220	-2.702719	0.170642
H	-4.073675	-4.165746	0.797878	**H**	3.133640	-3.492618	-3.496786	**C**	0.047719	1.652909	-0.472816	**C**	0.020673	1.708471	-0.365417
C	-4.091171	-3.531337	-1.239239	**C**	3.965064	-3.648901	-1.496870	**C**	1.303200	0.959566	-0.282088	**C**	1.324391	1.018439	-0.202656
H	-4.791016	-4.316938	-1.531559	**H**	4.694467	-4.417674	-1.760024	**C**	2.360662	1.930920	-0.487204	**C**	2.351218	2.044596	-0.463633
C	-3.613911	-2.626471	-2.187573	**C**	3.892797	-3.190061	-0.184431	**C**	3.761203	1.878265	-0.342618	**C**	3.748791	2.041241	-0.360411
H	-3.925079	-2.689335	-3.231915	**H**	4.575101	-3.623076	0.546858	**H**	4.259090	0.970927	-0.011360	**H**	4.287051	1.143248	-0.067429
C	-2.719477	-1.642335	-1.780446	**C**	2.980164	-2.203372	0.243495	**C**	4.501165	3.021136	-0.625631	**C**	4.444326	3.218927	-0.643346
C	0.765217	1.753066	0.040190	**C**	-0.795716	1.709592	-0.073073	**H**	5.586745	2.999363	-0.516811	**H**	5.532939	3.230683	-0.566137
C	1.713413	0.615606	0.163811	**C**	-1.807380	0.634525	-0.230884	**C**	3.869530	4.202757	-1.052853	**C**	3.763254	4.379297	-1.031529
C	3.041772	1.227577	0.300918	**C**	-3.106792	1.290896	-0.018108	**H**	4.476246	5.082565	-1.278103	**H**	4.327831	5.285267	-1.261596
C	4.325505	0.675314	0.394349	**C**	-4.415977	0.793578	0.036845	**C**	2.481271	4.289348	-1.189233	**C**	2.365491	4.412381	-1.123654
H	4.468628	-0.402968	0.427626	**H**	-4.626565	-0.254462	-0.165205	**H**	1.986000	5.203442	-1.506928	**H**	1.829838	5.313888	-1.408582
C	5.419195	1.542092	0.448916	**C**	-5.451290	1.676233	0.351087	**C**	1.745175	3.145793	-0.886211	**C**	1.688265	3.236147	-0.820559
H	6.427794	1.131865	0.522880	**H**	-6.477082	1.306450	0.396712	**N**	-2.208092	2.323724	-0.141664	**N**	-2.273455	2.302512	-0.083645
C	5.235886	2.930946	0.416172	**C**	-5.190260	3.030364	0.599711	**N**	-1.459382	-1.069906	-0.185907	**N**	-1.405260	-1.145624	0.006302
H	6.105593	3.589362	0.467599	**H**	-6.017254	3.703745	0.834540	**N**	0.349427	2.976229	-0.863751	**N**	0.280070	3.018083	-0.750075
C	3.960738	3.504853	0.313429	**C**	-3.888294	3.547624	0.561879	**H**	-3.749666	-1.941361	0.946050	**H**	-3.700719	-2.120272	0.980302
H	3.815087	4.581426	0.277091	**H**	-3.678149	4.594134	0.767099	**C**	-0.592258	3.978316	-1.066316	**C**	-0.693187	4.002452	-0.948549
C	2.883189	2.629188	0.252307	**C**	-2.867620	2.654449	0.256748	**C**	-2.023339	3.618794	-0.650496	**C**	-2.115357	3.610479	-0.543774
C	2.176331	-1.693978	0.412503	**C**	-2.482355	-1.517638	-0.880916	**O**	-0.324594	5.080392	-1.469355	**O**	-0.446620	5.106798	-1.354195
C	2.577030	-1.790363	1.758045	**C**	-3.084777	-1.239079	-2.123274	**O**	-2.907985	4.429195	-0.714573	**O**	-3.015118	4.407574	-0.597573
C	3.330898	-2.870035	2.203974	**C**	-4.050449	-2.082933	-2.658585	**C**	-0.211600	-3.071940	-2.071825	**H**	-0.393395	-1.093084	-0.191141
H	3.624086	-2.936973	3.253567	**H**	-4.499604	-1.857030	-3.627733	**C**	0.022704	-1.689538	-2.722158	**C**	-0.089417	-3.026906	-2.014866
C	3.695684	-3.860740	1.292408	**C**	-4.432946	-3.212923	-1.935663	**C**	-0.003772	-4.096718	-3.206817	**C**	0.114630	-1.633968	-2.656808
H	4.286371	-4.719926	1.616392	**H**	-5.197632	-3.887281	-2.326340	**C**	0.816689	-3.422557	-0.974199	**C**	0.184296	-4.036177	-3.148707
C	3.305336	-3.755816	-0.043793	**C**	-3.829824	-3.490634	-0.707793	**H**	-0.089016	-0.855593	-2.026849	**C**	0.915630	-3.354848	-0.889273
H	3.619133	-4.540970	-0.728214	**H**	-4.152739	-4.381111	-0.172876	**H**	1.030587	-1.652236	-3.163610	**H**	0.027473	-0.786187	-1.970144
C	2.535074	-2.687017	-0.533768	**C**	-2.831203	-2.677923	-0.144018	**H**	-0.699762	-1.535790	-3.538510	**H**	1.116353	-1.577760	-3.107050
C	-0.594982	4.276299	-0.088589	**C**	0.688897	4.158165	0.153858	**H**	-0.741704	-3.975121	-4.013774	**H**	-0.621855	-1.482217	-3.460345
C	0.936561	4.213877	0.051549	**C**	-0.838683	4.141657	0.342964	**H**	0.993707	-3.941298	-3.643792	**H**	-0.509099	-3.912819	-3.993845
H	-2.317290	-0.925718	-2.498834	**H**	-2.771902	-0.345015	-2.666194	**H**	-0.039109	-5.136414	-2.852169	**H**	1.202851	-3.869387	-3.528298
C	-2.386951	-2.368792	2.033918	**C**	-2.168047	-3.061589	1.192210	**H**	0.669366	-4.464163	-0.651703	**H**	0.136138	-5.078013	-2.802378
C	-2.982992	-3.534647	2.843438	**C**	-2.895777	-4.233514	1.876061	**H**	1.845377	-3.325713	-1.346094	**H**	0.758250	-4.390431	-0.553324
H	-2.625082	-4.510712	2.482681	**H**	-2.867334	-5.152562	1.273142	**H**	0.709544	-2.804943	-0.076160	**H**	1.950204	-3.263857	-1.244437
H	-2.676918	-3.437224	3.895107	**H**	-2.400910	-4.458152	2.832372	**N**	1.394513	-0.310674	0.062104	**H**	0.809050	-2.714054	-0.008147
H	-4.082605	-3.536897	2.823017	**H**	-3.947332	-3.992033	2.093333	**C**	2.631395	-1.014408	0.248793	**N**	1.381893	-0.210019	0.170525
C	-2.940060	-1.055662	2.630658	**C**	-2.171078	-1.883421	2.189617	**C**	3.041641	-1.466979	1.521696	**C**	2.618260	-0.888474	0.247428
H	-2.514771	-0.163278	2.152120	**H**	-1.524254	-1.058956	1.867623	**C**	3.392495	-1.238995	-0.905136	**C**	3.065799	-1.499160	1.447725
H	-4.034808	-1.007116	2.527616	**H**	-3.188523	-1.487336	2.332144	**C**	4.268331	-2.156541	1.553158	**C**	3.346068	-1.025954	-0.949142
H	-2.699389	-0.999612	3.703603	**H**	-1.803163	-2.223666	3.169627	**C**	4.603505	-1.918689	-0.832455	**C**	4.259261	-2.235793	1.360795
H	2.266378	-1.008534	2.453817	**C**	-0.722618	-3.514889	0.902156	**H**	3.016625	-0.871260	-1.861006	**C**	4.515973	-1.774441	-0.997112
C	2.197957	-2.577098	-2.034185	**H**	-0.125154	-2.723643	0.433978	**C**	5.037998	-2.380139	0.410767	**H**	2.959620	-0.551113	-1.852026
C	2.632098	-3.835663	-2.806626	**H**	-0.220715	-3.804270	1.837831	**H**	4.644612	-2.532110	2.501910	**C**	4.973636	-2.386105	0.170614
H	2.128575	-4.740406	-2.433322	**H**	-0.712127	-4.383036	0.226605	**H**	5.193742	-2.091979	-1.734158	**H**	4.653941	-2.714624	2.254273
H	2.365786	-3.719829	-3.867431	**H**	1.522727	-1.702936	-2.828841	**H**	5.982732	-2.920889	0.497446	**H**	5.060074	-1.882477	-1.937627
H	3.718651	-3.998499	-2.760362	**C**	3.002528	-1.835957	1.748015	**C**	2.231972	-1.226287	2.814047	**H**	5.889547	-2.980350	0.161731
C	2.955656	-1.371844	-2.634033	**C**	2.840285	-3.137521	2.569352	**C**	2.043260	0.287921	3.058903	**C**	2.338394	-1.325844	2.796541
H	2.665871	-0.422520	-2.162528	**H**	1.884476	-3.630602	2.341819	**C**	0.859229	-1.929895	2.729581	**C**	2.253187	0.173730	3.157297
H	4.042813	-1.492199	-2.511807	**H**	3.644994	-3.860070	2.379319	**C**	2.958715	-1.797869	4.045439	**C**	0.920603	-1.932729	2.730951
H	2.743278	-1.286902	-3.711416	**H**	2.857638	-2.902404	3.644224	**H**	1.567795	0.449299	4.038480	**C**	3.087266	-2.031106	3.941301
C	0.681248	-2.401030	-2.256991	**C**	1.898797	-0.872400	2.223470	**H**	3.012829	0.808869	3.066427	**H**	1.808605	0.295483	4.157357
H	0.336292	-1.406828	-1.953553	**H**	0.892274	-1.206172	1.938463	**H**	1.403816	0.766299	2.306645	**H**	3.254468	0.630842	3.175315
H	0.445618	-2.511606	-3.326473	**H**	1.928390	-0.826856	3.321835	**H**	0.207856	-1.510735	1.952277	**H**	1.632286	0.738028	2.449670
H	0.100183	-3.155412	-1.705045	**H**	2.050535	0.154417	1.865730	**H**	0.978615	-3.005533	2.531364	**H**	0.292931	-1.423574	1.991739
C	-0.854312	-2.423496	2.209135	**C**	4.365972	-1.192346	2.086171	**H**	0.325983	-1.819826	3.686485	**H**	0.961598	-3.002387	2.475876
H	-0.604803	-2.542954	3.274216	**H**	4.417313	-0.966840	3.162566	**H**	3.100593	-2.886359	3.974335	**H**	0.429012	-1.837819	3.711864
H	-0.413011	-3.271954	1.664690	**H**	5.206633	-1.858477	1.844313	**H**	3.941011	-1.327321	4.199934	**H**	3.163227	-3.116711	3.779382
H	-0.358316	-1.507144	1.871494	**H**	4.510897	-0.250219	1.536957	**H**	2.355473	-1.603374	4.944038	**H**	4.101474	-1.628481	4.081660
H	-0.335073	-0.767935	-0.046103	**H**	0.175739	-0.824433	-0.488617	**H**	0.505028	-0.836422	0.057957	**H**	2.538736	-1.876855	4.882139

Table G36 XYZ coordinates of the GS, TS, and TS' geometries of **3.15d** B3LYP/Def2SVP (gas phase)

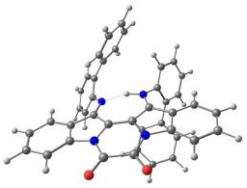
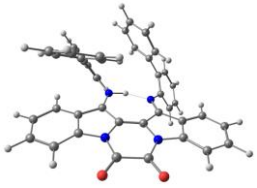
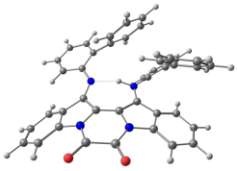
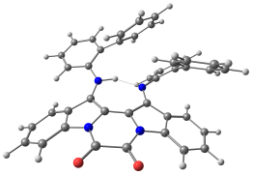
Anti				***Syn***				**TS**				**TS'**			
															
O	-0.789699	-5.296508	0.872910	**O**	1.148012	5.108285	-0.339754	**C**	0.782595	0.545372	0.648582	**C**	0.770083	0.555239	0.615364
O	1.917896	-4.807169	1.185344	**O**	-1.521912	5.182657	0.392429	**C**	2.106242	-0.070179	0.342432	**C**	2.078001	-0.039206	0.310782
N	-1.154811	-3.060760	0.529495	**N**	0.985355	2.845682	-0.651204	**C**	3.048430	1.082732	0.399080	**C**	3.030577	1.070407	0.398366
N	-1.657373	0.401031	-0.042524	**N**	0.764486	-0.702304	-0.921579	**C**	4.318888	1.351416	-0.138167	**C**	4.314389	1.323016	-0.132937
N	1.532236	-2.568729	0.893759	**N**	-1.679874	2.923086	0.047228	**H**	4.826460	0.635733	-0.778671	**H**	4.806762	0.611233	-0.788369
N	0.918716	0.917209	0.436185	**N**	-1.883880	-0.565558	-0.544281	**C**	4.922473	2.588876	0.094171	**C**	4.932685	2.544066	0.113027
C	-0.685129	-1.755522	0.462935	**C**	0.232482	1.659615	-0.624828	**H**	5.908149	2.789548	-0.329319	**H**	5.921913	2.735925	-0.305797
C	-1.815778	-0.876891	0.090395	**C**	1.129287	0.561339	-0.960482	**C**	4.277241	3.569953	0.854358	**C**	4.294383	3.533364	0.877709
C	-2.984957	-1.764526	-0.006974	**C**	2.412931	1.153972	-1.269650	**H**	4.775025	4.521628	1.050925	**H**	4.809030	4.474260	1.083414
C	-4.348058	-1.515593	-0.217756	**C**	3.615889	0.608877	-1.747420	**C**	2.975206	3.371364	1.326315	**C**	2.985766	3.361488	1.332086
H	-4.708743	-0.509261	-0.423693	**H**	3.709733	-0.460290	-1.930932	**H**	2.433602	4.146205	1.862530	**H**	2.450052	4.144448	1.862535
C	-5.241048	-2.586625	-0.161303	**C**	4.683448	1.468704	-1.984830	**C**	2.376219	2.147758	1.043961	**C**	2.361198	2.150963	1.035546
H	-6.305510	-2.408573	-0.323774	**H**	5.626462	1.068813	-2.361100	**C**	3.302750	-2.198456	0.137960	**C**	3.328562	-2.223912	0.077857
C	-4.785974	-3.887670	0.094775	**C**	4.563692	2.846942	-1.736239	**C**	3.077781	-3.611547	0.057214	**C**	3.087780	-3.629119	0.024993
H	-5.501255	-4.712285	0.123572	**H**	5.420896	3.498850	-1.918191	**C**	4.163845	-4.446961	-0.256116	**C**	4.179762	-4.473738	-0.240445
C	-3.431670	-4.159434	0.326473	**C**	3.373070	3.416300	-1.270582	**H**	3.987436	-5.521036	-0.330879	**H**	3.995232	-5.547873	-0.290964
H	-3.074310	-5.162657	0.544077	**H**	3.272742	4.483840	-1.091060	**C**	5.461984	-3.958314	-0.371619	**C**	5.483270	-3.996005	-0.336239
C	-2.556098	-3.079548	0.279003	**C**	2.304508	2.550361	-1.057465	**H**	6.284744	-4.638511	-0.601308	**H**	6.307898	-4.684408	-0.530443
C	-2.558158	1.274941	-0.653376	**C**	1.613787	-1.842095	-0.909442	**C**	5.707995	-2.605700	-0.109971	**C**	5.725631	-2.640864	-0.097220
C	-2.722729	2.581343	-0.119513	**C**	2.656188	-1.968911	0.040142	**H**	6.728641	-2.218025	-0.103499	**H**	6.745757	-2.253150	-0.072163
C	-3.539741	3.479992	-0.827137	**C**	3.420457	-3.145893	-0.006407	**C**	4.645470	-1.751072	0.141432	**C**	4.660392	-1.773113	0.107390
H	-3.712113	4.472689	-0.407992	**H**	4.219910	-3.275076	0.725520	**C**	-0.511860	0.175211	0.370859	**C**	-0.526465	0.205681	0.327090
C	-4.145801	3.127724	-2.031340	**C**	3.159438	-4.157441	-0.931801	**C**	-1.068419	-0.914741	-0.409666	**C**	-1.089360	-0.929484	-0.435055
H	-4.773030	3.851069	-2.556074	**H**	3.771801	-5.061523	-0.932342	**C**	-2.435340	-0.551741	-0.720747	**C**	-2.479131	-0.553754	-0.726375
C	-3.943940	1.849995	-2.568888	**C**	2.108695	-4.020524	-1.842348	**C**	-3.406351	-1.115606	-1.565949	**C**	-3.463082	-1.120241	-1.543456
H	-4.391526	1.575810	-3.526290	**H**	1.893021	-4.810307	-2.564376	**H**	-3.187905	-2.005888	-2.151718	**H**	-3.257187	-2.017585	-2.123175
C	-3.161016	0.931177	-1.881951	**C**	1.332604	-2.863837	-1.823545	**C**	-4.650158	-0.499182	-1.651569	**C**	-4.713443	-0.502376	-1.610524
C	0.648593	-1.501493	0.659776	**C**	-1.096961	1.708071	-0.290213	**H**	-5.415476	-0.918053	-2.306864	**H**	-5.490961	-0.929267	-2.246261
C	1.435214	-0.278593	0.610079	**C**	-2.150855	0.668030	-0.262461	**C**	-4.936637	0.649434	-0.894638	**C**	-4.984058	0.649389	-0.861836
C	2.820041	-0.666031	0.790477	**C**	-3.373856	1.362223	0.167006	**H**	-5.927489	1.103320	-0.965837	**H**	-5.974958	1.105316	-0.914225
C	4.013231	0.074814	0.848829	**C**	-4.662749	0.905023	0.472274	**C**	-3.983686	1.241580	-0.059018	**C**	-4.007770	1.246735	-0.052027
H	4.008880	1.155458	0.720236	**H**	-4.929541	-0.142998	0.346745	**H**	-4.194695	2.139989	0.515594	**H**	-4.206075	2.151025	0.517498
C	5.204578	-0.608713	1.072852	**C**	-5.604746	1.823379	0.939024	**C**	-2.731386	0.636168	-0.006562	**C**	-2.760411	0.635297	-0.022296
H	6.143638	-0.054958	1.121816	**H**	-6.613349	1.483748	1.180958	**N**	1.010323	1.795493	1.211358	**N**	1.003704	1.823728	1.180994
C	5.213173	-2.005225	1.235403	**C**	-5.272441	3.176538	1.092611	**N**	2.189857	-1.366564	0.227863	**N**	2.214916	-1.353942	0.125927
H	6.162750	-2.517387	1.405377	**H**	-6.028733	3.879291	1.448468	**N**	-1.566312	1.066094	0.659218	**N**	-1.567881	1.078085	0.621980
C	4.038236	-2.763808	1.192253	**C**	-3.986714	3.654700	0.808276	**H**	4.859696	-0.718061	0.370969	**H**	4.876620	-0.737685	0.318283
H	4.039921	-3.842701	1.326487	**H**	-3.718472	4.699798	0.940111	**C**	-1.431652	2.243235	1.385947	**C**	-1.431735	2.263541	1.347887
C	2.850967	-2.071371	0.971179	**C**	-3.055855	2.725226	0.356415	**C**	0.012747	2.648932	1.705245	**C**	0.010389	2.684256	1.653730
C	1.677921	2.067477	0.061840	**C**	-2.826694	-1.572380	-0.785527	**O**	-2.355899	2.950888	1.693117	**O**	-2.360709	2.958572	1.663994
C	2.304928	2.087168	-1.203383	**C**	-2.593419	-2.866729	-0.256652	**O**	0.253603	3.677185	2.279148	**O**	0.245363	3.725412	2.209248
C	3.090067	3.205177	-1.518227	**C**	-3.448987	-3.907779	-0.649056	**C**	1.827400	-4.286224	0.480428	**H**	1.284082	-1.824089	-0.040328
H	3.584368	3.243168	-2.491081	**H**	-3.292492	-4.901492	-0.224630	**C**	1.320096	-5.387544	-0.231664	**C**	1.830593	-4.290603	0.454968
C	3.220807	4.270127	-0.622553	**C**	-4.499659	-3.688871	-1.539779	**C**	1.266631	-3.979751	1.734915	**C**	1.313587	-5.391866	-0.248382
H	3.831597	5.133311	-0.895267	**H**	-5.151246	-4.516443	-1.827184	**C**	0.283192	-6.159347	0.291692	**C**	1.281640	-3.973223	1.711391
C	2.562903	4.240607	0.610285	**C**	-4.717486	-2.407975	-2.061850	**H**	1.745402	-5.641251	-1.203621	**C**	0.274955	-6.152919	0.286364
H	2.656088	5.076059	1.306803	**H**	-5.527181	-2.232509	-2.773131	**C**	0.247355	-4.769480	2.267105	**H**	1.732771	-5.653839	-1.220439
C	1.787173	3.133028	0.956055	**C**	-3.888626	-1.356306	-1.686239	**H**	1.674250	-3.150802	2.316425	**C**	0.256690	-4.749402	2.252759
C	-0.354744	-4.178594	0.800977	**C**	0.486169	4.103566	-0.322678	**C**	-0.251301	-5.857953	1.546561	**H**	1.703779	-3.150841	2.293914
C	1.148270	-3.903998	0.986227	**C**	-0.998746	4.146808	0.079679	**H**	-0.102224	-7.005209	-0.279971	**C**	-0.252641	-5.837985	1.540931
H	1.279088	3.077227	1.918593	**H**	-4.026624	-0.364957	-2.121136	**H**	-0.157056	-4.539193	3.254880	**H**	-0.119357	-6.999606	-0.277598
H	-2.972320	-0.055921	-2.306879	**H**	0.509863	-2.731799	-2.528810	**H**	-1.052998	-6.469842	1.964783	**H**	-0.141213	-4.509968	3.240840
H	-0.136991	0.933338	0.338534	**C**	-1.501907	-3.115035	0.714418	**N**	-0.388980	-2.005544	-0.699010	**H**	-1.058570	-6.439686	1.965515
C	-2.068938	3.005556	1.140474	**C**	-0.615895	-4.190972	0.530977	**C**	-0.863570	-3.179873	-1.353327	**N**	-0.372217	-1.972373	-0.675552
C	-1.514198	4.296260	1.239943	**C**	-1.357764	-2.311186	1.860386	**C**	-0.124780	-3.600888	-2.465742	**C**	-0.841567	-3.132664	-1.315111
C	-2.005820	2.163504	2.267257	**C**	0.395262	-4.446917	1.457931	**C**	-1.975636	-3.919982	-0.884186	**C**	-0.080919	-3.565141	-2.415915
C	-0.918539	4.730133	2.423657	**H**	-0.712087	-4.819341	-0.356339	**C**	-0.481841	-4.753063	-3.160163	**C**	-1.960755	-3.891895	-0.875023
H	-1.532974	4.957931	0.371935	**C**	-0.358417	-2.580710	2.796354	**H**	0.730790	-3.002371	-2.784589	**C**	-0.438331	-4.699004	-3.137333
C	-1.399502	2.594603	3.448451	**H**	-2.061897	-1.495595	2.037152	**C**	-2.302026	-5.083757	-1.605411	**H**	0.787276	-2.970955	-2.706918
H	-2.472609	1.178797	2.232939	**C**	0.526626	-3.643537	2.593309	**C**	-1.579439	-5.497750	-2.722834	**C**	-2.266863	-5.056213	-1.602604
C	-0.855144	3.879727	3.532263	**H**	1.085001	-5.276165	1.290693	**H**	0.094710	-5.067504	-4.032061	**C**	-1.537778	-5.454230	-2.721847
H	-0.494057	5.735027	2.478469	**H**	-0.271273	-1.961942	3.692057	**H**	-3.134768	-5.693959	-1.252933	**H**	0.148214	-5.000779	-4.007389
H	-1.373686	1.932094	4.316581	**H**	1.314356	-3.846317	3.321802	**H**	-1.868695	-6.411471	-3.246015	**H**	-3.096413	-5.676701	-1.259887
H	-0.393007	4.220656	4.461359	**C**	2.970843	-0.914211	1.038328	**C**	-2.823661	-3.526447	0.272274	**H**	-1.818765	-6.362925	-3.258043
C	2.149635	0.948811	-2.146971	**C**	4.300362	-0.493611	1.210592	**C**	-4.219008	-3.684571	0.183188	**C**	-2.821054	-3.521138	0.278996
C	3.275124	0.254317	-2.616422	**C**	1.967036	-0.287264	1.796849	**C**	-2.298592	-2.965975	1.449241	**C**	-4.213390	-3.704922	0.187717
C	0.872274	0.525850	-2.555376	**C**	4.614958	0.542449	2.092333	**C**	-5.058815	-3.285388	1.223902	**C**	-2.309742	-2.959947	1.461842
C	3.127640	-0.851012	-3.458094	**H**	5.093321	-0.961604	0.623830	**H**	-4.659102	-4.094883	-0.727537	**C**	-5.062346	-3.328983	1.229821
H	4.271680	0.570081	-2.300238	**C**	2.281001	0.747210	2.678268	**C**	-3.135786	-2.566413	2.490060	**H**	-4.644410	-4.117051	-0.726513
C	0.725922	-0.577699	-3.396029	**H**	0.936425	-0.625346	1.704929	**H**	-1.223965	-2.857999	1.560628	**C**	-3.155405	-2.582625	2.503695
H	-0.010534	1.075881	-2.223916	**C**	3.605381	1.173346	2.822735	**C**	-4.521380	-2.718410	2.381142	**H**	-1.237214	-2.829894	1.571192
C	1.853358	-1.274135	-3.844492	**H**	5.653352	0.861854	2.203606	**H**	-6.139135	-3.411033	1.124815	**C**	-4.538144	-2.759597	2.391687
H	4.012369	-1.385795	-3.810392	**H**	1.488702	1.216324	3.266642	**H**	-2.702316	-2.140406	3.397987	**H**	-6.139975	-3.474331	1.127803
H	-0.272089	-0.887709	-3.715480	**H**	3.849826	1.986559	3.509431	**H**	-5.176419	-2.401289	3.195318	**H**	-2.731945	-2.154930	3.415748
H	1.739011	-2.138279	-4.502586	**H**	-0.277950	-0.852237	-0.765736	**H**	0.599883	-2.008775	-0.350237	**H**	-5.200357	-2.460206	3.206802

Table G37 XYZ coordinates of the GS, TS, and TS' geometries of **3.15e** B3LYP/Def2SVP (gas phase)

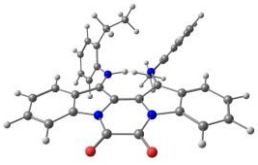
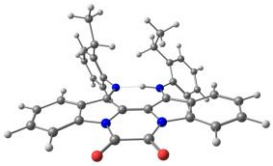
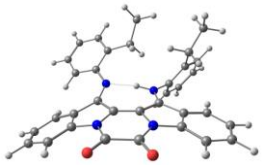
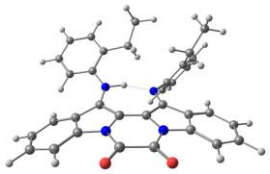
Anti				***Syn***				**TS**				**TS'**			
															
O	3.062104	4.333887	-0.080972	**O**	-0.731787	-5.079118	-0.034353	**C**	1.534655	-0.876405	-0.041706	**C**	1.481141	-0.947538	0.007089
O	4.837562	2.212097	0.034161	**O**	2.007384	-4.772695	0.250280	**C**	1.972995	0.524493	0.245881	**C**	1.994272	0.406964	0.290377
N	1.303586	2.864647	-0.052370	**N**	-0.960622	-2.808624	-0.238139	**C**	3.435372	0.396871	0.489041	**C**	3.441361	0.246939	0.443153
N	-1.387574	0.559142	0.044408	**N**	-1.278151	0.708879	-0.495592	**C**	4.413406	1.181725	1.122885	**C**	4.479397	1.000954	1.034736
N	3.072488	0.752605	0.029159	**N**	1.768102	-2.506746	0.015155	**H**	4.162738	2.094752	1.653646	**H**	4.284633	1.906884	1.597404
N	0.305390	-1.496516	-0.004600	**N**	1.363514	1.014496	-0.406770	**C**	5.738706	0.743467	1.167888	**C**	5.785487	0.524767	1.009688
C	0.814973	1.566127	-0.019493	**C**	-0.399777	-1.540183	-0.298254	**H**	6.487845	1.362551	1.664478	**H**	6.576848	1.114398	1.475262
C	-0.668125	1.632022	0.001074	**C**	-1.502685	-0.556996	-0.435706	**C**	6.108469	-0.479260	0.601023	**C**	6.089505	-0.710236	0.418907
C	-0.995389	3.063794	-0.078283	**C**	-2.734680	-1.351203	-0.468881	**H**	7.152250	-0.798605	0.625315	**H**	7.124380	-1.057493	0.389074
C	-2.210751	3.752508	-0.191091	**C**	-4.079795	-0.987964	-0.610391	**C**	5.146731	-1.332131	0.047753	**C**	5.079952	-1.537457	-0.076525
H	-3.159394	3.219437	-0.180965	**H**	-4.368920	0.057612	-0.705813	**H**	5.405507	-2.314012	-0.338846	**H**	5.287463	-2.528849	-0.469623
C	-2.182394	5.142556	-0.315140	**C**	-5.040457	-2.001582	-0.625457	**C**	3.828658	-0.888726	0.044136	**C**	3.772396	-1.060706	-0.010675
H	-3.120218	5.693568	-0.404438	**H**	-6.095062	-1.743095	-0.734891	**C**	1.265297	2.867816	-0.067884	**C**	1.391553	2.859874	0.037750
C	-0.965637	5.838052	-0.319032	**C**	-4.665272	-3.346459	-0.501344	**C**	0.173076	3.590073	-0.656963	**C**	0.330427	3.613026	-0.553464
H	-0.967944	6.926586	-0.406091	**H**	-5.434649	-4.121394	-0.513722	**C**	0.300385	4.973394	-0.820166	**C**	0.555156	4.973307	-0.796793
C	0.262568	5.171025	-0.221703	**C**	-3.323722	-3.731470	-0.363903	**H**	-0.519313	5.531241	-1.271502	**H**	-0.238550	5.560232	-1.256543
H	1.209917	5.703592	-0.239205	**H**	-3.029929	-4.774145	-0.272438	**C**	1.447011	5.666455	-0.432031	**C**	1.756898	5.605015	-0.480134
C	0.217978	3.785535	-0.111820	**C**	-2.378889	-2.712488	-0.352897	**H**	1.501961	6.748803	-0.566686	**H**	1.884386	6.670389	-0.681650
C	-2.780383	0.529594	0.224395	**C**	-2.315394	1.674462	-0.513819	**C**	2.523405	4.964636	0.114340	**C**	2.787202	4.861358	0.092402
C	-3.556456	-0.269638	-0.651241	**C**	-2.983700	2.004864	0.688041	**H**	3.436472	5.485274	0.409069	**H**	3.738788	5.328781	0.351578
C	-4.931194	-0.351112	-0.402770	**C**	-3.956286	3.011010	0.622067	**C**	2.427873	3.591219	0.283765	**C**	2.598182	3.508119	0.344489
H	-5.561744	-0.938872	-1.069899	**H**	-4.488850	3.297838	1.529418	**C**	0.306041	-1.497508	-0.056182	**C**	0.235907	-1.527046	0.020248
C	-5.518117	0.292466	0.691080	**C**	-4.262155	3.660947	-0.577101	**C**	-1.019225	-1.052683	0.326135	**C**	-1.097963	-0.992969	0.373442
H	-6.591837	0.195155	0.863863	**H**	-5.031158	4.435872	-0.591923	**C**	-1.860424	-2.230466	0.392507	**C**	-1.991741	-2.157044	0.431767
C	-4.732547	1.046808	1.566516	**C**	-3.575965	3.330641	-1.746902	**C**	-3.192958	-2.432576	0.797790	**C**	-3.332110	-2.300516	0.812556
H	-5.180879	1.532759	2.435387	**H**	-3.801316	3.840972	-2.685452	**H**	-3.802299	-1.604238	1.154714	**H**	-3.914082	-1.442396	1.144604
C	-3.366392	1.171762	1.328471	**C**	-2.588019	2.346254	-1.711519	**C**	-3.713660	-3.720819	0.738303	**C**	-3.905837	-3.572103	0.757460
C	1.689363	0.509160	0.009142	**C**	0.955699	-1.380328	-0.184809	**H**	-4.743382	-3.901480	1.051087	**H**	-4.947903	-3.706018	1.052819
C	1.494145	-0.937201	0.020216	**C**	1.822901	-0.202232	-0.209005	**C**	-2.929180	-4.794015	0.277993	**C**	-3.159738	-4.676806	0.324134
C	2.815113	-1.534261	0.084028	**C**	3.170683	-0.680299	0.048707	**H**	-3.366097	-5.793985	0.232952	**H**	-3.632050	-5.660431	0.279911
C	3.254797	-2.866435	0.185504	**C**	4.397373	-0.020617	0.247533	**C**	-1.599308	-4.622813	-0.118058	**C**	-1.814265	-4.557643	-0.049491
H	2.545675	-3.691719	0.196531	**H**	4.469970	1.062575	0.176955	**H**	-0.986868	-5.451311	-0.465111	**H**	-1.229709	-5.413495	-0.376761
C	4.622777	-3.107033	0.272321	**C**	5.523213	-0.783961	0.540787	**C**	-1.080057	-3.332089	-0.039917	**C**	-1.253324	-3.287146	0.025878
H	4.985750	-4.132917	0.353454	**H**	6.482680	-0.289212	0.700259	**N**	2.667794	-1.638120	-0.285916	**N**	2.588459	-1.768210	-0.271722
C	5.542974	-2.044518	0.251995	**C**	5.440825	-2.184390	0.627521	**N**	1.116092	1.489899	0.063801	**N**	1.186378	1.468651	0.237787
H	6.611595	-2.261775	0.313000	**H**	6.342079	-2.761112	0.846498	**N**	0.226517	-2.883329	-0.310985	**N**	0.090861	-2.889077	-0.230363
C	5.131940	-0.710136	0.161949	**C**	4.231926	-2.865392	0.450452	**H**	3.274529	3.068678	0.695008	**H**	3.406499	2.959348	0.792194
H	5.840087	0.114817	0.157489	**H**	4.159385	-3.947019	0.532876	**C**	1.299025	-3.681865	-0.690007	**C**	1.125304	-3.743738	-0.615242
C	3.761453	-0.477668	0.086613	**C**	3.107647	-2.092226	0.174095	**C**	2.664129	-2.983030	-0.690013	**C**	2.519860	-3.112387	-0.650012
C	0.014055	-2.884455	-0.147831	**C**	2.110869	2.205606	-0.611900	**O**	1.203427	-4.851558	-0.956639	**O**	0.965234	-4.907496	-0.871511
C	-0.740486	-3.540045	0.842511	**C**	3.114141	2.233360	-1.591501	**O**	3.663620	-3.585842	-0.974444	**O**	3.483604	-3.766883	-0.949309
C	-1.031622	-4.897178	0.628443	**C**	3.821577	3.409007	-1.826138	**C**	-1.080903	2.896789	-1.135627	**H**	0.170607	1.174576	0.251503
H	-1.601408	-5.437694	1.388257	**H**	4.597826	3.433461	-2.593301	**H**	-0.805276	1.899237	-1.506425	**C**	-0.995378	2.996973	-0.928174
C	-0.607324	-5.567141	-0.518043	**C**	3.516309	4.556809	-1.087229	**H**	-1.738570	2.729168	-0.266334	**H**	-0.819995	1.998442	-1.358222
H	-0.850937	-6.623141	-0.651629	**H**	4.065423	5.483795	-1.264319	**C**	-1.887643	3.625737	-2.210063	**H**	-1.565714	2.821482	-0.002942
C	0.125647	-4.887626	-1.498405	**C**	2.496754	4.525201	-0.134139	**H**	-1.266511	3.876662	-3.083625	**C**	-1.875628	3.795547	-1.886417
H	0.448302	-5.401872	-2.405698	**H**	2.255677	5.429781	0.429057	**H**	-2.712637	2.986635	-2.555869	**H**	-1.355302	4.025280	-2.828977
C	0.434779	-3.543920	-1.313405	**C**	1.760874	3.359659	0.120512	**H**	-2.339048	4.556027	-1.834929	**H**	-2.775709	3.213467	-2.128716
C	2.664200	3.200851	-0.046465	**C**	-0.226827	-3.989622	-0.072330	**N**	-1.318952	0.209291	0.553091	**H**	-2.217229	4.742419	-1.443079
C	3.650380	2.021124	0.011099	**C**	1.295745	-3.818576	0.080219	**C**	-2.603379	0.722636	0.920462	**N**	-1.282824	0.266569	0.557210
H	0.997351	-2.991919	-2.068738	**H**	3.322681	1.335288	-2.175513	**C**	-2.736700	1.260051	2.204387	**C**	-2.555277	0.812021	0.848923
H	-2.735250	1.743981	2.011005	**H**	-2.030847	2.078022	-2.611186	**C**	-3.665469	0.740238	-0.011815	**C**	-2.724263	1.408555	2.106635
H	-0.505642	-0.800580	0.019901	**H**	0.295220	1.075813	-0.456495	**C**	-3.954394	1.807334	2.607767	**C**	-3.584783	0.853257	-0.125307
C	-2.887938	-0.989218	-1.803595	**C**	-2.634752	1.288028	1.977436	**H**	-1.882270	1.234880	2.883596	**C**	-3.937899	2.004870	2.446271
H	-2.129659	-1.675269	-1.385543	**C**	0.671261	3.344241	1.167475	**C**	-4.875764	1.296471	0.425860	**H**	-1.895577	1.381991	2.816883
H	-2.314464	-0.254924	-2.395014	**H**	-1.541549	1.147367	2.011576	**C**	-5.025957	1.817932	1.713777	**C**	-4.782764	1.481035	0.241134
C	-3.808212	-1.782526	-2.725855	**H**	-3.053085	0.265542	1.941741	**H**	-4.062800	2.219525	3.612639	**C**	-4.970844	2.039286	1.508662
H	-4.342411	-2.577429	-2.182725	**H**	0.410286	4.385180	1.409155	**H**	-5.722722	1.333857	-0.259182	**H**	-4.069938	2.446746	3.435878
H	-4.558663	-1.137220	-3.207863	**H**	-0.246210	2.901937	0.747937	**H**	-5.985754	2.243075	2.014520	**H**	-5.594440	1.540471	-0.484130
H	-3.222806	-2.263692	-3.523002	**C**	-3.094006	1.969996	3.263658	**C**	-3.494343	0.195937	-1.415346	**H**	-5.923026	2.512892	1.755884
C	-1.237914	-2.841970	2.087923	**H**	-2.705646	2.998251	3.335113	**H**	-2.506862	0.506700	-1.791879	**C**	-3.379081	0.268739	-1.509056
H	-0.938328	-3.438817	2.965406	**H**	-4.190903	2.019259	3.336852	**H**	-3.446921	-0.905420	-1.368454	**H**	-2.378719	0.563282	-1.868049
H	-0.740347	-1.867053	2.200044	**H**	-2.734856	1.411021	4.140388	**C**	-4.572332	0.593999	-2.421044	**H**	-3.339776	-0.830880	-1.433697
C	-2.761021	-2.650872	2.102127	**C**	1.060739	2.606250	2.455621	**H**	-4.314381	0.214132	-3.420328	**C**	-4.423975	0.643207	-2.557618
H	-3.079725	-2.142207	3.024188	**H**	1.950165	3.060954	2.917463	**H**	-5.555462	0.175549	-2.157789	**H**	-4.148681	0.218438	-3.534064
H	-3.099106	-2.044295	1.250321	**H**	0.240468	2.646051	3.188355	**H**	-4.680588	1.687208	-2.493685	**H**	-5.420508	0.252665	-2.301665
H	-3.283933	-3.618106	2.052876	**H**	1.289527	1.545785	2.266012	**H**	-0.521295	0.872797	0.403126	**H**	-4.512279	1.734006	-2.679481

Table G38 XYZ coordinates of the GS, TS, and TS' geometries of **3.15a** B3LYP/Def2SVP (SMD = 1,1,2-trichloroethane)

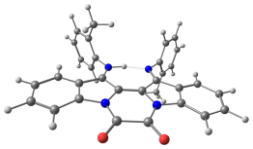
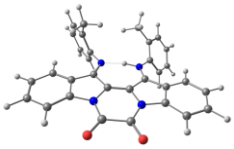
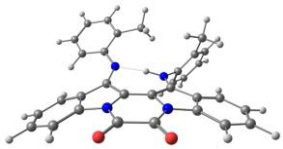
Anti				***Syn***				**TS**			
											
O	1.462589	-4.746133	0.068193	**O**	-1.015164	-4.900837	-0.063680	**C**	1.151996	-1.016470	-0.044464
O	-1.287478	-4.801935	-0.055091	**O**	1.728716	-4.744399	0.074328	**C**	1.856310	0.280531	0.185424
N	1.423377	-2.456406	0.073000	**N**	-1.147538	-2.615543	-0.125214	**C**	3.238126	-0.123143	0.554806
N	1.309940	1.085456	0.082330	**N**	-1.306656	0.922843	-0.158211	**C**	4.306189	0.504363	1.214469
N	-1.329623	-2.512749	-0.066595	**N**	1.599814	-2.458574	0.016559	**H**	4.210599	1.498045	1.642158
N	-1.358588	1.052782	-0.087128	**N**	1.348903	1.094984	-0.125470	**C**	5.502462	-0.189491	1.413339
C	0.710978	-1.264294	0.039194	**C**	-0.527586	-1.370726	-0.117665	**H**	6.327076	0.307432	1.927767
C	1.683757	-0.143769	0.089587	**C**	-1.584896	-0.331804	-0.174441	**C**	5.645813	-1.509149	0.975627
C	3.006719	-0.779642	0.148010	**C**	-2.853030	-1.067820	-0.244972	**H**	6.593218	-2.032432	1.121287
C	4.299030	-0.246289	0.209252	**C**	-4.179961	-0.634837	-0.341230	**C**	4.571317	-2.194322	0.396499
H	4.461193	0.830019	0.220387	**H**	-4.422307	0.426128	-0.373812	**H**	4.650291	-3.238939	0.109102
C	5.379985	-1.130372	0.255872	**C**	-5.189453	-1.598928	-0.396553	**C**	3.380308	-1.494683	0.236410
H	6.396607	-0.735797	0.303443	**H**	-6.231763	-1.283799	-0.472582	**C**	1.680000	2.678876	-0.358508
C	5.172495	-2.515764	0.242471	**C**	-4.877687	-2.964321	-0.354212	**C**	0.777521	3.549617	-1.049731
H	6.031957	-3.188895	0.278797	**H**	-5.682824	-3.701295	-0.396192	**C**	1.185641	4.860966	-1.326020
C	3.885586	-3.069134	0.183227	**C**	-3.554190	-3.417299	-0.260557	**H**	0.493749	5.518520	-1.857721
H	3.726176	-4.144106	0.173915	**H**	-3.313926	-4.476667	-0.230346	**C**	2.441981	5.339012	-0.957392
C	2.819901	-2.178417	0.136960	**C**	-2.559885	-2.447360	-0.209719	**H**	2.723991	6.370065	-1.182832
C	2.224583	2.166336	0.104685	**C**	-2.285378	1.943834	-0.165102	**C**	3.340012	4.481586	-0.314779
C	2.791955	2.618697	-1.105547	**C**	-2.957790	2.287142	1.028711	**H**	4.337491	4.827471	-0.035242
C	3.656213	3.719814	-1.044014	**C**	-3.872098	3.348246	0.973415	**C**	2.962331	3.176703	-0.029826
H	4.107397	4.083174	-1.971077	**H**	-4.401612	3.628819	1.887719	**C**	-0.172451	-1.365985	-0.131842
C	3.949168	4.354719	0.166474	**C**	-4.117655	4.045982	-0.212162	**C**	-1.397025	-0.633720	0.134115
H	4.628610	5.209959	0.181920	**H**	-4.839861	4.865498	-0.222037	**C**	-2.475969	-1.603668	0.149626
C	3.365199	3.898422	1.350718	**C**	-3.428602	3.700696	-1.377658	**C**	-3.847909	-1.501707	0.436835
H	3.582174	4.391477	2.301157	**H**	-3.606169	4.244303	-2.308462	**H**	-4.294949	-0.552104	0.723183
C	2.493571	2.808187	1.319562	**C**	-2.501312	2.658350	-1.351028	**C**	-4.629154	-2.651210	0.357697
C	-0.651596	-1.284221	-0.035145	**C**	0.834776	-1.284544	-0.055391	**H**	-5.696303	-2.593053	0.579088
C	-1.653357	-0.221419	-0.092505	**C**	1.757521	-0.149040	-0.049229	**C**	-4.060399	-3.883168	-0.005715
C	-2.946940	-0.875901	-0.153567	**C**	3.094002	-0.706915	0.079209	**H**	-4.696473	-4.768942	-0.068409
C	-4.257586	-0.375276	-0.223849	**C**	4.360883	-0.118442	0.230627	**C**	-2.695708	-4.013285	-0.283462
H	-4.451002	0.695483	-0.242055	**H**	4.483670	0.962438	0.232647	**H**	-2.254573	-4.968668	-0.554771
C	-5.310002	-1.286665	-0.269963	**C**	5.466361	-0.950715	0.385927	**C**	-1.918623	-2.862023	-0.187828
H	-6.336961	-0.921454	-0.324214	**H**	6.458095	-0.511218	0.506328	**N**	2.115583	-2.012459	-0.151124
C	-5.064170	-2.669053	-0.247677	**C**	5.320332	-2.347309	0.384513	**N**	1.237081	1.379883	-0.126110
H	-5.906899	-3.363130	-0.283754	**H**	6.204128	-2.979160	0.497147	**N**	-0.526534	-2.713254	-0.351493
C	-3.766588	-3.190719	-0.180564	**C**	4.068389	-2.957723	0.252226	**H**	3.680409	2.531622	0.450783
H	-3.579244	-4.261115	-0.164522	**H**	3.952824	-4.038144	0.268197	**C**	0.377206	-3.725036	-0.609302
C	-2.721042	-2.274967	-0.134971	**C**	2.967570	-2.118318	0.111439	**C**	1.852546	-3.336738	-0.491208
C	-2.310394	2.122678	-0.104752	**C**	2.133664	2.267693	-0.283573	**O**	0.064513	-4.865645	-0.862633
C	-2.617408	2.732187	-1.323115	**C**	3.055830	2.356202	-1.334417	**O**	2.714683	-4.167508	-0.648409
C	-3.541108	3.778430	-1.352035	**C**	3.789079	3.527166	-1.511550	**C**	-0.576909	3.114485	-1.527779
H	-3.790922	4.258073	-2.300762	**H**	4.506283	3.600614	-2.331727	**H**	-0.904890	3.742932	-2.367557
C	-4.137973	4.203954	-0.162452	**C**	3.591501	4.604238	-0.641224	**H**	-0.584502	2.067753	-1.857028
H	-4.861628	5.022263	-0.176304	**H**	4.163561	5.525559	-0.772076	**H**	-1.331570	3.228397	-0.733994
C	-3.809224	3.591663	1.050166	**C**	2.655970	4.510546	0.391734	**N**	-1.430684	0.664788	0.325016
H	-4.275114	3.935602	1.976851	**H**	2.504206	5.356768	1.066041	**C**	-2.582082	1.457474	0.623106
C	-2.885882	2.538699	1.109954	**C**	1.898629	3.347977	0.591728	**C**	-2.638121	2.054410	1.888529
C	0.834228	-3.715906	0.041335	**C**	-0.466569	-3.825192	-0.060981	**C**	-3.578356	1.680743	-0.348221
C	-0.700529	-3.746021	-0.030914	**C**	1.064392	-3.736671	0.016790	**C**	-3.719087	2.865865	2.226444
H	-2.138461	2.375442	-2.237014	**H**	3.183207	1.509373	-2.010703	**H**	-1.832809	1.865089	2.600879
H	2.023102	2.438035	2.232797	**H**	-1.945224	2.377563	-2.247825	**C**	-4.655244	2.501682	0.023560
H	-0.316248	1.275273	-0.029705	**H**	0.284074	1.210666	-0.117188	**C**	-4.733933	3.083353	1.289153
C	2.484298	1.920486	-2.401703	**C**	-2.706117	1.533665	2.306137	**H**	-3.768576	3.324523	3.216166
C	-2.533919	1.860444	2.404881	**C**	0.877870	3.254775	1.692356	**H**	-5.442654	2.692404	-0.709916
H	1.397413	1.807459	-2.547820	**H**	-1.628360	1.412346	2.498307	**H**	-5.586214	3.718267	1.541865
H	2.893067	2.477502	-3.256275	**H**	-3.153678	2.056467	3.162886	**C**	-3.521257	1.086988	-1.728673
H	2.916519	0.905615	-2.422609	**H**	-3.141540	0.520838	2.268102	**H**	-2.496450	0.840375	-2.035153
H	-2.984328	2.386107	3.257842	**H**	0.975731	4.100149	2.387050	**H**	-4.117239	0.160638	-1.786791
H	-2.896789	0.818779	2.419526	**H**	-0.146993	3.277046	1.284966	**H**	-3.939564	1.789454	-2.464064
H	-1.442935	1.823854	2.555966	**H**	0.981045	2.320323	2.265828	**H**	-0.504435	1.141487	0.212661

Table G39 XYZ coordinates of the GS, TS, and TS' geometries of **3.15b** B3LYP/Def2SVP (SMD = 1,1,2-trichloroethane)

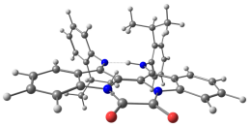
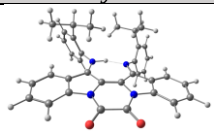
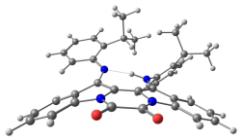
Anti				***Syn***				**TS**			
											
O	-1.495806	5.020926	-0.063374	**O**	-1.542333	4.972704	0.307930	**C**	-1.918773	-1.151352	-0.028809
O	1.252216	5.091906	0.064236	**O**	1.185651	5.043858	-0.045298	**C**	-2.547296	0.185562	-0.256641
N	-1.443856	2.731363	-0.068982	**N**	-1.520599	2.693025	0.090181	**C**	-3.981134	-0.145783	-0.499325
N	-1.322623	-0.810987	-0.073749	**N**	-1.457561	-0.840022	-0.279605	**C**	-5.046967	0.494161	-1.152122
N	1.306068	2.802909	0.078659	**N**	1.212749	2.763739	-0.248005	**H**	-4.915539	1.444544	-1.662322
N	1.368543	-0.764469	0.096150	**N**	1.239521	-0.790854	-0.400640	**C**	-6.295627	-0.129289	-1.216915
C	-0.727208	1.541363	-0.029375	**C**	-0.821746	1.503293	-0.082105	**H**	-7.117523	0.377321	-1.726229
C	-1.696092	0.418788	-0.105401	**C**	-1.806500	0.394667	-0.149383	**C**	-6.497637	-1.389983	-0.647541
C	-3.021412	1.051383	-0.171463	**C**	-3.122285	1.036473	0.004830	**H**	-7.485860	-1.853319	-0.683396
C	-4.314509	0.516725	-0.197807	**C**	-4.418523	0.513277	0.087530	**C**	-5.433841	-2.096312	-0.075121
H	-4.476488	-0.559139	-0.210851	**H**	-4.602473	-0.552914	-0.026468	**H**	-5.560240	-3.104027	0.311089
C	-5.398508	1.397978	-0.206681	**C**	-5.479411	1.392094	0.317554	**C**	-4.190622	-1.473144	-0.058064
H	-6.414879	1.000391	-0.227580	**H**	-6.496489	1.001137	0.382995	**C**	-2.210563	2.598696	0.056740
C	-5.194634	2.783845	-0.192376	**C**	-5.253027	2.767329	0.459722	**C**	-1.215896	3.551107	0.450186
H	-6.056200	3.455149	-0.205039	**H**	-6.097651	3.437944	0.632410	**C**	-1.573338	4.907479	0.496446
C	-3.907988	3.338892	-0.155361	**C**	-3.963091	3.310122	0.393288	**H**	-0.814633	5.638426	0.779284
H	-3.750509	4.413867	-0.133576	**H**	-3.784628	4.374903	0.516207	**C**	-2.865957	5.351742	0.234417
C	-2.839385	2.449990	-0.140210	**C**	-2.916441	2.422392	0.169907	**H**	-3.099459	6.418073	0.277742
C	-2.216559	-1.883298	-0.300713	**C**	-2.401646	-1.840968	-0.611993	**C**	-3.863785	4.413545	-0.045999
C	-2.564309	-2.787015	0.727395	**C**	-2.664737	-2.945340	0.230444	**H**	-4.898065	4.726315	-0.204741
C	-3.407110	-3.855411	0.379268	**C**	-3.590443	-3.895421	-0.231196	**C**	-3.533532	3.069847	-0.127115
H	-3.702254	-4.556044	1.164754	**H**	-3.820122	-4.746805	0.414973	**C**	-0.635509	-1.622382	-0.143387
C	-3.875220	-4.046212	-0.921762	**C**	-4.218228	-3.789952	-1.473087	**C**	0.579228	-1.014628	-0.654350
H	-4.521909	-4.896402	-1.150155	**H**	-4.927153	-4.556687	-1.793441	**C**	1.507798	-2.096155	-0.925310
C	-3.509155	-3.146182	-1.925979	**C**	-3.929442	-2.702167	-2.301289	**C**	2.768671	-2.138786	-1.543715
H	-3.861332	-3.281126	-2.951198	**H**	-4.402669	-2.604940	-3.281019	**H**	3.229317	-1.237111	-1.942210
C	-2.685694	-2.067703	-1.613179	**C**	-3.030531	-1.732652	-1.867357	**C**	3.417708	-3.365758	-1.641587
C	0.636223	1.568349	0.047972	**C**	0.534627	1.534116	-0.243223	**H**	4.397205	-3.420213	-2.119762
C	1.646907	0.514673	0.109887	**C**	1.525177	0.483136	-0.445681	**C**	2.828910	-4.532814	-1.125755
C	2.935931	1.179616	0.158856	**C**	2.801469	1.144382	-0.636179	**H**	3.364305	-5.481713	-1.203088
C	4.252771	0.690448	0.177662	**C**	4.085350	0.655989	-0.926770	**C**	1.567474	-4.519263	-0.521648
H	4.455819	-0.378225	0.183060	**H**	4.265831	-0.410007	-1.049835	**H**	1.107121	-5.424219	-0.134018
C	5.298893	1.609747	0.186997	**C**	5.126503	1.572539	-1.053116	**C**	0.915683	-3.291213	-0.447365
H	6.329889	1.252322	0.200812	**H**	6.133421	1.217167	-1.278616	**N**	-2.934541	-2.058607	0.252506
C	5.041636	2.990304	0.181703	**C**	4.895670	2.947878	-0.888110	**N**	-1.835884	1.258088	-0.062991
H	5.879385	3.691201	0.194677	**H**	5.730199	3.645973	-0.984946	**N**	-0.378298	-2.998072	0.028836
C	3.738516	3.500859	0.154617	**C**	3.622399	3.458291	-0.606837	**H**	-4.327822	2.366626	-0.319338
H	3.541839	4.569515	0.141306	**H**	3.445676	4.523993	-0.487353	**C**	-1.303297	-3.911558	0.495393
C	2.699287	2.576359	0.138042	**C**	2.586346	2.537481	-0.492751	**C**	-2.732493	-3.382927	0.632640
C	2.314519	-1.817373	0.316491	**C**	2.181604	-1.863873	-0.515136	**O**	-1.054292	-5.073012	0.723081
C	2.792646	-1.975842	1.623999	**C**	2.955180	-2.295222	0.580030	**O**	-3.624370	-4.116786	0.984849
C	3.699417	-2.990997	1.917758	**C**	3.818326	-3.380684	0.333271	**C**	0.159990	3.184538	0.977024
H	4.069990	-3.113684	2.937561	**H**	4.431005	-3.749388	1.160096	**N**	0.718919	0.283803	-0.795695
C	4.119946	-3.847311	0.896576	**C**	3.908772	-4.003360	-0.909221	**C**	1.837826	1.010585	-1.312718
H	4.829541	-4.650050	1.109529	**H**	4.593680	-4.843308	-1.046004	**C**	1.584466	1.779319	-2.456377
C	3.630887	-3.680993	-0.399699	**C**	3.113478	-3.562164	-1.971430	**C**	3.093515	1.025887	-0.667393
H	3.968071	-4.353317	-1.192422	**H**	3.165546	-4.046710	-2.948540	**C**	2.586621	2.577931	-3.000760
C	2.715699	-2.667365	-0.731489	**C**	2.245485	-2.494616	-1.766335	**H**	0.592594	1.738436	-2.910782
C	-0.861859	3.993938	-0.034385	**C**	-0.924846	3.948980	0.139701	**C**	4.078661	1.845315	-1.242108
C	0.671027	4.032422	0.040631	**C**	0.597306	3.988188	-0.055744	**C**	3.839862	2.609732	-2.385087
H	-2.385930	-1.355073	-2.383505	**H**	1.608361	-2.124866	-2.572184	**H**	2.387498	3.170787	-3.895805
C	-2.154115	-2.618568	2.183674	**H**	-2.793090	-0.874910	-2.499886	**H**	5.062933	1.892703	-0.774990
H	-2.489649	-3.539814	2.686251	**C**	-2.007217	-3.168937	1.584516	**H**	4.637586	3.234014	-2.793942
C	-2.898385	-1.449717	2.849126	**H**	-2.589914	-3.973067	2.061841	**C**	3.389704	0.254475	0.614459
H	-3.988934	-1.556756	2.741859	**C**	-2.074574	-1.961645	2.528887	**H**	-0.130603	0.836074	-0.531415
H	-2.665344	-1.410458	3.925729	**H**	-3.105506	-1.584707	2.621478	**H**	0.351707	2.129810	0.761757
H	-2.610307	-0.481396	2.411153	**H**	-1.730527	-2.252237	3.534331	**H**	2.721987	-0.613565	0.657176
C	-0.639739	-2.516067	2.410483	**H**	-1.439047	-1.131843	2.191992	**C**	1.286510	4.014027	0.347795
H	-0.089016	-3.283325	1.845454	**C**	-0.577093	-3.704278	1.413662	**H**	2.264210	3.634115	0.675099
H	-0.248973	-1.531077	2.122381	**H**	-0.574551	-4.639745	0.833292	**H**	1.257556	3.971584	-0.750123
H	-0.411339	-2.656258	3.479160	**H**	0.068180	-2.988896	0.887128	**H**	1.228210	5.071135	0.650576
H	2.443858	-1.294254	2.401580	**H**	-0.117451	-3.908791	2.393825	**C**	4.823072	-0.287728	0.669721
C	2.277083	-2.514657	-2.181512	**C**	2.977225	-1.718821	1.997582	**H**	4.925762	-0.975483	1.523398
H	2.680402	-3.400562	-2.696800	**H**	3.042703	-2.611549	2.641657	**H**	5.090324	-0.840375	-0.243669
C	2.918099	-1.284135	-2.843004	**C**	1.754113	-0.930931	2.479053	**H**	5.561089	0.517468	0.810672
H	4.014356	-1.300733	-2.743544	**H**	1.744476	0.104006	2.107889	**C**	0.156052	3.331060	2.510559
H	2.675592	-1.262400	-3.917699	**H**	0.807599	-1.409832	2.200453	**H**	1.140006	3.068937	2.928795
H	2.552798	-0.343623	-2.402989	**H**	1.782489	-0.870024	3.578124	**H**	-0.068863	4.367870	2.806485
C	0.755944	-2.535172	-2.387280	**C**	4.260444	-0.905856	2.244035	**H**	-0.599480	2.676208	2.972490
H	0.278797	-3.353404	-1.827080	**H**	5.162625	-1.470056	1.963621	**C**	3.079969	1.102260	1.855822
H	0.283082	-1.591749	-2.082293	**H**	4.253938	0.031794	1.669255	**H**	2.018722	1.376542	1.891190
H	0.526208	-2.679368	-3.454828	**H**	4.341058	-0.644944	3.311414	**H**	3.312472	0.534575	2.770956
H	0.333913	-0.998544	0.022092	**H**	0.205534	-1.022293	-0.311422	**H**	3.677499	2.027457	1.868040

Table G40 XYZ coordinates of the GS, TS, and TS' geometries of **3.15c** B3LYP/Def2SVP (SMD = 1,1,2-trichloroethane)

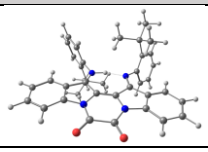
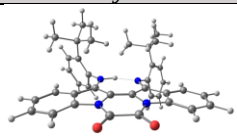
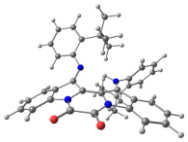
Anti				***Syn***				**TS**			
											
O	-1.181451	5.304808	-0.190706	**O**	1.271974	5.200352	0.295088	**O**	4.874013	2.774694	-1.658881
O	1.545252	5.208821	0.165176	**O**	-1.464881	5.152228	0.577394	**O**	3.161813	3.330391	-3.738695
N	-1.258080	3.016618	-0.188534	**N**	1.268909	2.939630	-0.066707	**N**	3.180858	1.661040	-0.591580
N	-1.360908	-0.550172	-0.153118	**N**	1.242735	-0.593369	-0.500262	**N**	0.543838	-0.090027	1.055703
N	1.474381	2.919917	0.149721	**N**	-1.473971	2.895749	0.185364	**N**	1.487921	2.185747	-2.674352
N	1.325152	-0.620378	0.105763	**N**	-1.458412	-0.605952	-0.414599	**N**	-0.723090	-0.290014	-1.646899
C	-0.604190	1.775668	-0.105923	**C**	0.572382	1.724560	-0.165419	**C**	1.883879	1.101089	-0.598722
C	-1.622034	0.731812	-0.207802	**C**	1.548298	0.675679	-0.438713	**C**	1.647996	0.538770	0.715804
C	-2.898311	1.409622	-0.338003	**C**	2.837884	1.329757	-0.562020	**C**	2.808326	0.856734	1.528656
C	-4.217310	0.933442	-0.421913	**C**	4.120542	0.845741	-0.867040	**C**	3.108138	0.670782	2.890810
H	-4.430856	-0.133112	-0.420703	**H**	4.289455	-0.208829	-1.072788	**H**	2.395860	0.207156	3.568055
C	-5.251199	1.862790	-0.503377	**C**	5.176946	1.753224	-0.904386	**C**	4.341823	1.106083	3.365292
H	-6.283752	1.515636	-0.568776	**H**	6.182245	1.400021	-1.140327	**H**	4.589454	0.971648	4.419708
C	-4.979364	3.240689	-0.504545	**C**	4.963063	3.115320	-0.639164	**C**	5.271216	1.712831	2.504160
H	-5.807360	3.949743	-0.574369	**H**	5.808813	3.805981	-0.669432	**H**	6.236774	2.036483	2.899147
C	-3.674304	3.738579	-0.412785	**C**	3.692532	3.621618	-0.339436	**C**	4.991390	1.926096	1.150983
H	-3.466908	4.805275	-0.404477	**H**	3.528786	4.677380	-0.140167	**H**	5.703584	2.408375	0.487115
C	-2.647851	2.803913	-0.324595	**C**	2.641825	2.710886	-0.312218	**C**	3.747854	1.504245	0.687583
C	-2.299714	-1.599176	-0.427240	**C**	2.165475	-1.651535	-0.795017	**C**	0.300702	-0.681511	2.339995
C	-2.791068	-2.455705	0.583982	**C**	2.167105	-2.060628	-2.138670	**C**	1.095723	-1.786807	2.665459
C	-3.679016	-3.457232	0.149681	**C**	3.037083	-3.051069	-2.577666	**C**	0.934724	-2.438089	3.883776
H	-4.098944	-4.148705	0.877110	**H**	3.036362	-3.360298	-3.624799	**H**	1.556686	-3.300008	4.133470
C	-4.056113	-3.605143	-1.186343	**C**	3.912865	-3.629635	-1.655626	**C**	-0.039899	-1.973584	4.767720
H	-4.748967	-4.403126	-1.462813	**H**	4.616775	-4.402403	-1.972577	**H**	-0.190818	-2.467523	5.730341
C	-3.550241	-2.743780	-2.160000	**C**	3.885808	-3.229484	-0.322496	**C**	-0.832562	-0.875525	4.429071
H	-3.832369	-2.851791	-3.209262	**H**	4.575448	-3.710523	0.371613	**H**	-1.580189	-0.546121	5.147380
C	-2.666841	-1.740984	-1.772451	**C**	3.008179	-2.240808	0.171501	**C**	-0.696410	-0.186771	3.209117
C	0.751604	1.736413	0.057532	**C**	-0.788347	1.708588	-0.045972	**C**	1.048095	1.339837	-1.660795
C	1.703897	0.605317	0.190695	**C**	-1.786890	0.626108	-0.222492	**C**	-0.333667	0.888384	-2.030902
C	3.025816	1.225786	0.359657	**C**	-3.097189	1.280155	-0.078307	**C**	-0.768389	1.894708	-3.038346
C	4.309013	0.679482	0.476579	**C**	-4.403557	0.776094	-0.087278	**C**	-2.013612	2.360215	-3.485503
H	4.460124	-0.397864	0.499498	**H**	-4.598464	-0.275267	-0.287892	**H**	-2.944154	2.003660	-3.050152
C	5.397473	1.550916	0.563396	**C**	-5.459009	1.655473	0.165002	**C**	-2.068560	3.365875	-4.454587
H	6.406247	1.144273	0.656069	**H**	-6.483997	1.280128	0.159770	**H**	-3.040934	3.722208	-4.799585
C	5.207633	2.938608	0.535473	**C**	-5.216665	3.011638	0.419648	**C**	-0.895983	3.923374	-4.972103
H	6.072127	3.602170	0.608542	**H**	-6.056981	3.682986	0.609671	**H**	-0.953134	4.693034	-5.744893
C	3.931815	3.505210	0.408786	**C**	-3.916702	3.534161	0.444529	**C**	0.358884	3.551038	-4.474170
H	3.785672	4.581499	0.376477	**H**	-3.726941	4.583319	0.654392	**H**	1.272238	4.027029	-4.819761
C	2.858904	2.625943	0.318818	**C**	-2.876182	2.646221	0.195605	**C**	0.386364	2.575161	-3.484207
C	2.180016	-1.708373	0.401515	**C**	-2.422332	-1.546602	-0.859363	**C**	-1.657115	-1.157766	-2.225442
C	2.530077	-1.866237	1.754818	**C**	-2.910152	-1.339716	-2.163655	**C**	-2.637346	-0.715579	-3.143851
C	3.288205	-2.954292	2.175030	**C**	-3.831252	-2.212968	-2.732485	**C**	-3.478767	-1.579695	-3.828835
H	3.544536	-3.066390	3.230918	**H**	-4.194352	-2.039888	-3.748035	**H**	-4.219715	-1.179411	-4.523994
C	3.705982	-3.892460	1.231002	**C**	-4.281022	-3.301206	-1.984802	**C**	-3.354143	-2.950222	-3.615827
H	4.301448	-4.756655	1.534124	**H**	-5.011123	-3.997941	-2.402881	**H**	-3.993033	-3.660525	-4.145735
C	3.360594	-3.729190	-0.112106	**C**	-3.791208	-3.507307	-0.693466	**C**	-2.409534	-3.416222	-2.701540
H	3.712105	-4.475432	-0.821867	**H**	-4.164233	-4.366162	-0.138944	**H**	-2.348021	-4.490539	-2.549851
C	2.588697	-2.649720	-0.577273	**C**	-2.845101	-2.660433	-0.089648	**C**	-1.558475	-2.574399	-1.969681
C	-0.614509	4.239984	-0.115701	**C**	0.667886	4.158209	0.196610	**C**	3.738118	2.358778	-1.644636
C	0.907011	4.187568	0.079688	**C**	-0.859766	4.132881	0.348786	**C**	2.789086	2.664908	-2.802663
H	-2.245864	-1.052679	-2.507189	**H**	-2.545974	-0.476436	-2.724333	**H**	-2.747942	0.338543	-3.330855
C	-2.447880	-2.296232	2.079761	**C**	-2.319228	-2.952735	1.328475	**C**	-0.650182	-3.217033	-0.905340
C	-3.031307	-3.448750	2.915955	**C**	-3.076564	-4.116451	1.991122	**C**	-0.641381	-4.757505	-0.982021
H	-2.640855	-4.427059	2.595707	**H**	-2.963221	-5.059247	1.435701	**H**	-0.277205	-5.121479	-1.955031
H	-2.749437	-3.305148	3.969830	**H**	-2.669893	-4.280565	3.000562	**H**	0.039020	-5.142223	-0.207134
H	-4.130039	-3.482203	2.872934	**H**	-4.151640	-3.902177	2.095052	**H**	-1.629934	-5.199526	-0.791514
C	-3.058735	-0.980305	2.607648	**C**	-2.474601	-1.726334	2.251918	**C**	-1.264422	-2.852087	0.462794
H	-2.646915	-0.094041	2.107564	**H**	-1.826445	-0.892473	1.957402	**H**	-1.405620	-1.773750	0.594485
H	-4.151213	-0.970324	2.471495	**H**	-3.515537	-1.366875	2.264431	**H**	-2.263221	-3.307119	0.550961
H	-2.850378	-0.877586	3.684734	**H**	-2.201861	-2.002882	3.282620	**H**	-0.646075	-3.230765	1.287849
H	2.180594	-1.122987	2.473511	**C**	-0.834927	-3.356895	1.233556	**C**	0.827344	-2.792338	-1.047647
C	2.294238	-2.479521	-2.081500	**H**	-0.224257	-2.574758	0.767986	**H**	0.976320	-1.712643	-0.990856
C	2.750052	-3.706590	-2.890043	**H**	-0.430040	-3.544752	2.239808	**H**	1.430723	-3.274315	-0.262705
H	2.238054	-4.625444	-2.564221	**H**	-0.714757	-4.275130	0.638150	**H**	1.219451	-3.128380	-2.020974
H	2.508798	-3.548401	-3.952067	**H**	1.479855	-1.571393	-2.831640	**H**	1.840521	-2.126518	1.945149
H	3.835387	-3.872981	-2.822545	**C**	3.077355	-1.943333	1.688971	**C**	-1.591063	1.026723	2.878600
C	3.066525	-1.252800	-2.612875	**C**	2.839984	-3.269948	2.447244	**C**	-2.522378	1.373219	4.053624
H	2.761137	-0.321573	-2.116534	**H**	1.852266	-3.690337	2.207603	**H**	-3.209749	0.548931	4.295637
H	4.150675	-1.375820	-2.464317	**H**	3.597895	-4.029006	2.207994	**H**	-1.959832	1.634498	4.962960
H	2.883368	-1.129611	-3.692704	**H**	2.881202	-3.089603	3.532867	**H**	-3.136087	2.244545	3.780237
C	0.785274	-2.295589	-2.342204	**C**	2.054548	-0.927123	2.225791	**C**	-2.487523	0.709677	1.663113
H	0.418848	-1.326756	-1.986280	**H**	1.019927	-1.185457	1.965427	**H**	-3.113372	-0.174858	1.855423
H	0.587811	-2.339165	-3.424851	**H**	2.123456	-0.916141	3.324044	**H**	-3.155331	1.561935	1.460166
H	0.194510	-3.089212	-1.859878	**H**	2.263182	0.095853	1.886677	**H**	-1.914449	0.524956	0.745749
C	-0.921405	-2.294796	2.306434	**C**	4.484911	-1.408798	2.032244	**C**	-0.733702	2.279200	2.592802
H	-0.707254	-2.363616	3.384215	**H**	4.559857	-1.227784	3.116351	**H**	-1.388825	3.159637	2.500963
H	-0.439978	-3.152502	1.812765	**H**	5.277049	-2.120311	1.756821	**H**	-0.025654	2.470602	3.414198
H	-0.440691	-1.377606	1.948332	**H**	4.686329	-0.457680	1.516575	**H**	-0.163976	2.203817	1.658468
H	-0.332502	-0.790941	-0.042188	**H**	0.205394	-0.814240	-0.438092	**H**	-0.123363	-0.265779	0.287743

Table G41 XYZ coordinates of the GS, TS, and TS' geometries of **3.15d** B3LYP/Def2SVP (SMD = 1,1,2-trichloroethane)

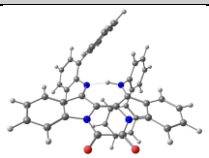
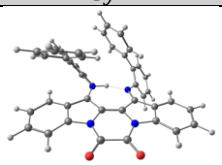
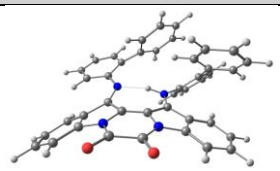
Anti				***Syn***				**TS**			
											
O	-2.378315	4.845312	-0.806639	**O**	0.730279	5.217397	-0.307371	**C**	-1.857589	-1.140596	0.090516
O	0.319886	5.188202	-1.216929	**O**	-1.930520	5.095633	0.378549	**C**	-2.497144	0.194766	-0.092313
N	-2.049716	2.606008	-0.457120	**N**	0.754433	2.947290	-0.600428	**C**	-3.940507	-0.134976	-0.269650
N	-1.471161	-0.845927	0.090013	**N**	0.799339	-0.602705	-0.878686	**C**	-5.034298	0.517531	-0.861556
N	0.650032	2.947401	-0.884618	**N**	-1.912610	2.825082	0.078560	**H**	-4.925289	1.486891	-1.339685
N	1.135238	-0.547429	-0.375358	**N**	-1.847504	-0.671474	-0.498031	**C**	-6.280915	-0.111127	-0.894052
C	-1.203488	1.504779	-0.397562	**C**	0.094630	1.707264	-0.571319	**H**	-7.124744	0.403189	-1.357806
C	-2.010118	0.322472	-0.021599	**C**	1.071508	0.680368	-0.915810	**C**	-6.455303	-1.386330	-0.346693
C	-3.393121	0.813766	0.092087	**C**	2.304903	1.371330	-1.234167	**H**	-7.442370	-1.853438	-0.355566
C	-4.612340	0.163785	0.321765	**C**	3.540308	0.922003	-1.725741	**C**	-5.368571	-2.099335	0.170936
H	-4.650314	-0.905089	0.523401	**H**	3.715559	-0.134146	-1.922286	**H**	-5.476867	-3.115325	0.540585
C	-5.789248	0.914073	0.288784	**C**	4.538678	1.862270	-1.966352	**C**	-4.127431	-1.471060	0.153842
H	-6.746316	0.420019	0.466804	**H**	5.506453	1.534820	-2.349978	**C**	-2.164137	2.609990	0.102051
C	-5.754198	2.291990	0.036573	**C**	4.317014	3.224868	-1.710339	**C**	-1.140970	3.602666	0.241788
H	-6.685406	2.862587	0.025481	**H**	5.120578	3.941692	-1.893378	**C**	-1.490841	4.955506	0.082519
C	-4.549060	2.960543	-0.212809	**C**	3.088681	3.698793	-1.234302	**H**	-0.705602	5.708487	0.167380
H	-4.520156	4.025711	-0.426001	**H**	2.913386	4.755754	-1.052074	**C**	-2.811768	5.362952	-0.080949
C	-3.386279	2.197640	-0.188008	**C**	2.091070	2.754382	-1.016071	**H**	-3.048509	6.423976	-0.187004
C	-2.059202	-1.976695	0.660367	**C**	1.703256	-1.695257	-0.956761	**C**	-3.830621	4.405862	-0.026772
C	-1.839324	-3.246937	0.063065	**C**	2.803265	-1.814118	-0.074838	**H**	-4.880115	4.705976	-0.059828
C	-2.331284	-4.380205	0.734171	**C**	3.616760	-2.950373	-0.219330	**C**	-3.504420	3.060687	0.065412
H	-2.202143	-5.360734	0.272346	**H**	4.464113	-3.073081	0.457737	**C**	-0.583984	-1.607772	-0.112446
C	-2.988591	-4.279274	1.959173	**C**	3.345014	-3.933396	-1.171576	**C**	0.605691	-0.986115	-0.667140
H	-3.356293	-5.180603	2.454375	**H**	3.995128	-4.807835	-1.246223	**C**	1.504495	-2.060835	-1.041285
C	-3.170414	-3.024518	2.553173	**C**	2.234107	-3.809066	-2.010308	**C**	2.711157	-2.090236	-1.759095
H	-3.663704	-2.936852	3.523645	**H**	2.006407	-4.579882	-2.749294	**H**	3.147188	-1.179272	-2.162665
C	-2.712427	-1.882885	1.905923	**C**	1.410450	-2.691758	-1.895501	**C**	3.333542	-3.318692	-1.961782
C	0.137986	1.666282	-0.617789	**C**	-1.234544	1.654650	-0.246257	**H**	4.270359	-3.361123	-2.519939
C	1.262515	0.740812	-0.575731	**C**	-2.206370	0.537907	-0.222443	**C**	2.776391	-4.499471	-1.445833
C	2.460224	1.530533	-0.792217	**C**	-3.483040	1.140295	0.191248	**H**	3.292865	-5.449073	-1.602816
C	3.820885	1.188729	-0.859010	**C**	-4.735905	0.586965	0.482475	**C**	1.565975	-4.499413	-0.743538
H	4.151339	0.161613	-0.718494	**H**	-4.921175	-0.478863	0.360882	**H**	1.125601	-5.415503	-0.359160
C	4.744532	2.200123	-1.111420	**C**	-5.752093	1.431949	0.932755	**C**	0.936276	-3.270633	-0.572166
H	5.807388	1.958104	-1.165472	**H**	-6.734445	1.015707	1.163845	**N**	-2.858069	-2.057373	0.400501
C	4.323811	3.527392	-1.295086	**C**	-5.526301	2.806701	1.084555	**N**	-1.776804	1.271628	0.040057
H	5.068078	4.303170	-1.487971	**H**	-6.337716	3.451474	1.429310	**N**	-0.322543	-2.988846	-0.001739
C	2.973014	3.890283	-1.241364	**C**	-4.277421	3.379540	0.812520	**H**	-4.309193	2.343304	0.132977
H	2.648783	4.916863	-1.390308	**H**	-4.095905	4.442717	0.944591	**C**	-1.219636	-3.915616	0.491663
C	2.056781	2.874233	-0.989145	**C**	-3.271769	2.523729	0.375365	**C**	-2.636746	-3.391339	0.730061
C	2.216157	-1.443406	-0.114247	**C**	-2.701864	-1.749048	-0.757343	**O**	-0.960687	-5.084405	0.665674
C	2.874991	-1.386053	1.131763	**C**	-2.376212	-3.024387	-0.230401	**O**	-3.508714	-4.135941	1.109416
C	3.968177	-2.244087	1.325282	**C**	-3.138316	-4.128405	-0.643922	**C**	0.228197	3.336707	0.747053
H	4.496620	-2.215504	2.280518	**H**	-2.907345	-5.110562	-0.226101	**C**	1.343267	4.002761	0.207018
C	4.366872	-3.140991	0.331098	**C**	-4.188971	-3.988542	-1.551101	**C**	0.397181	2.587564	1.926623
H	5.215294	-3.804937	0.511610	**H**	-4.766725	-4.864520	-1.854112	**C**	2.589276	3.927483	0.829231
C	3.677627	-3.199728	-0.883516	**C**	-4.499142	-2.725585	-2.069217	**H**	1.228637	4.586710	-0.707299
H	3.980532	-3.905872	-1.659380	**H**	-5.310380	-2.608481	-2.791288	**C**	1.639500	2.535277	2.560272
C	2.597842	-2.344828	-1.108704	**C**	-3.761663	-1.613490	-1.675221	**H**	-0.463100	2.084598	2.372356
C	-1.629810	3.899804	-0.746258	**C**	0.154610	4.154401	-0.288530	**C**	2.739638	3.201149	2.013526
C	-0.124877	4.089406	-0.979654	**C**	-1.329659	4.087405	0.094001	**H**	3.445214	4.442448	0.389034
H	2.055640	-2.355755	-2.054039	**H**	-3.971765	-0.632779	-2.104952	**H**	1.749405	1.971790	3.489254
H	-2.822572	-0.903923	2.374627	**H**	0.538998	-2.568588	-2.541481	**H**	3.712294	3.149182	2.507818
H	0.132385	-0.882573	-0.259159	**C**	-1.280546	-3.195338	0.753829	**N**	0.761485	0.315971	-0.741632
C	-1.119851	-3.400375	-1.224602	**C**	-0.310329	-4.196664	0.571093	**C**	1.907414	1.032541	-1.194522
C	-0.218898	-4.469093	-1.399669	**C**	-1.211077	-2.389272	1.905199	**C**	1.684953	1.947598	-2.230121
C	-1.321739	-2.515589	-2.301573	**C**	0.708544	-4.379777	1.507772	**C**	3.185699	0.876642	-0.607684
C	0.457207	-4.646067	-2.606740	**H**	-0.346395	-4.821534	-0.323056	**C**	2.731929	2.716845	-2.729933
H	-0.032476	-5.155871	-0.571756	**C**	-0.202237	-2.586382	2.849838	**H**	0.678380	2.037973	-2.642950
C	-0.637913	-2.688981	-3.506691	**H**	-1.973007	-1.626081	2.075509	**C**	4.217954	1.677257	-1.131600
H	-2.046846	-1.706636	-2.209752	**C**	0.764470	-3.577005	2.650763	**C**	4.005335	2.578667	-2.173156
C	0.253849	-3.754267	-3.664846	**H**	1.465289	-5.149141	1.340564	**H**	2.550792	3.424238	-3.541653
H	1.158412	-5.476734	-2.716341	**H**	-0.168381	-1.961395	3.745259	**H**	5.210621	1.603687	-0.685055
H	-0.815691	-1.995600	-4.332369	**H**	1.562215	-3.719183	3.383413	**H**	4.836271	3.184628	-2.540834
H	0.784992	-3.891199	-4.609789	**C**	3.121613	-0.802613	0.965996	**C**	3.500583	-0.091990	0.477015
C	2.443531	-0.430013	2.184707	**C**	4.443419	-0.348001	1.115973	**C**	4.713603	-0.804843	0.429383
C	3.361647	0.480036	2.733271	**C**	2.128569	-0.263497	1.802171	**C**	2.621431	-0.357824	1.541136
C	1.110021	-0.401683	2.631122	**C**	4.758998	0.635003	2.056265	**C**	5.030892	-1.754155	1.402305
C	2.953221	1.407367	3.695519	**H**	5.226591	-0.747299	0.468748	**H**	5.405580	-0.639367	-0.398210
H	4.396996	0.473394	2.385703	**C**	2.444407	0.716885	2.743463	**C**	2.937518	-1.305662	2.514606
C	0.703826	0.524238	3.593034	**H**	1.104981	-0.625205	1.725398	**H**	1.686440	0.188835	1.618760
H	0.389704	-1.117470	2.230994	**C**	3.759471	1.176742	2.868801	**C**	4.141604	-2.013203	2.448143
C	1.623144	1.435298	4.124545	**H**	5.789972	0.985032	2.147280	**H**	5.973958	-2.301644	1.334610
H	3.676806	2.115605	4.106366	**H**	1.658821	1.118997	3.388045	**H**	2.237126	-1.489659	3.333037
H	-0.334242	0.529330	3.934696	**H**	4.004381	1.950245	3.600512	**H**	4.384843	-2.760418	3.207162
H	1.303541	2.162583	4.874677	**H**	-0.231009	-0.828312	-0.719585	**H**	-0.060779	0.876645	-0.410420

Table G42 XYZ coordinates of the GS, TS, and TS' geometries of **3.15e** B3LYP/Def2SVP (SMD = 1,1,2-trichloroethane)

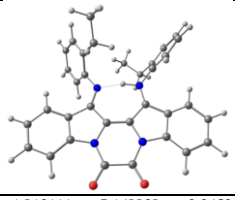
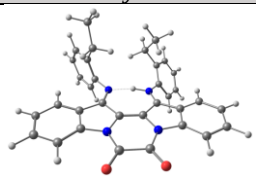
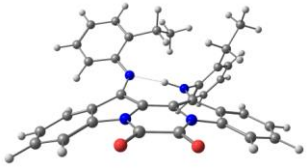
Anti				***Syn***				**TS**			
											
O	1.210111	5.142202	0.046043	**O**	0.798035	5.081036	-0.012774	**C**	-1.874756	-1.123488	-0.155966
O	-1.539733	5.073958	0.022535	**O**	-1.921742	4.799670	0.295995	**C**	-2.497640	0.225375	-0.314409
N	1.274504	2.852496	0.011138	**N**	1.014102	2.810191	-0.216266	**C**	-3.949571	-0.070058	-0.447560
N	1.320634	-0.690786	-0.085468	**N**	1.301722	-0.711305	-0.435674	**C**	-5.050810	0.615397	-0.982474
N	-1.479039	2.784976	0.020156	**N**	-1.714594	2.532551	0.047800	**H**	-4.940098	1.572683	-1.483967
N	-1.347018	-0.775580	0.040806	**N**	-1.351609	-0.989842	-0.388595	**C**	-6.315796	0.022035	-0.957476
C	0.618905	1.626253	-0.001121	**C**	0.440980	1.544676	-0.267061	**H**	-7.166742	0.563893	-1.374461
C	1.645443	0.555909	-0.055972	**C**	1.533142	0.551648	-0.403209	**C**	-6.496407	-1.255803	-0.420911
C	2.939641	1.255963	-0.026351	**C**	2.773783	1.335776	-0.445256	**H**	-7.494386	-1.698131	-0.389289
C	4.260042	0.793409	0.026909	**C**	4.115629	0.958157	-0.567191	**C**	-5.403535	-2.006737	0.028295
H	4.482665	-0.271635	0.008032	**H**	4.396768	-0.089825	-0.657750	**H**	-5.520709	-3.026319	0.384431
C	5.293286	1.729713	0.104495	**C**	5.088424	1.961023	-0.570973	**C**	-4.149984	-1.408983	-0.036468
H	6.328313	1.385542	0.147045	**H**	6.141576	1.689529	-0.664253	**C**	-2.082408	2.596844	0.176932
C	5.015897	3.102880	0.122900	**C**	4.726412	3.309660	-0.457120	**C**	-1.062839	3.411020	0.764885
H	5.839198	3.818783	0.175105	**H**	5.503464	4.077347	-0.462348	**C**	-1.388270	4.720141	1.150848
C	3.701927	3.587200	0.083201	**C**	3.387443	3.707502	-0.336041	**H**	-0.612696	5.331272	1.618353
H	3.484808	4.651466	0.111076	**H**	3.108284	4.754085	-0.247948	**C**	-2.659049	5.257415	0.969509
C	2.683149	2.642980	0.016631	**C**	2.430268	2.699837	-0.332418	**H**	-2.871087	6.283682	1.278085
C	2.218787	-1.755106	-0.277929	**C**	2.329663	-1.683237	-0.496159	**C**	-3.659146	4.465381	0.396525
C	2.227710	-2.809843	0.666483	**C**	2.914073	-2.139151	0.707067	**H**	-4.666581	4.860005	0.248275
C	3.053342	-3.908579	0.399871	**C**	3.881955	-3.147360	0.608866	**C**	-3.370888	3.162932	0.018163
H	3.095416	-4.732003	1.113776	**H**	4.354215	-3.524411	1.517172	**C**	-0.593244	-1.591969	-0.295531
C	3.820429	-3.982807	-0.767619	**C**	4.260904	-3.682102	-0.626778	**C**	0.610909	-0.987501	-0.832923
H	4.443489	-4.861082	-0.951206	**H**	5.021599	-4.465124	-0.667820	**C**	1.563514	-2.061854	-1.043306
C	3.783812	-2.941299	-1.697927	**C**	3.661988	-3.222484	-1.801275	**C**	2.843856	-2.104486	-1.622731
H	4.369828	-2.997168	-2.617991	**H**	3.946987	-3.639669	-2.769825	**H**	3.303510	-1.210973	-2.039988
C	2.987819	-1.824492	-1.450050	**C**	2.685587	-2.226561	-1.735534	**C**	3.514583	-3.323329	-1.660842
C	-0.748405	1.585672	0.016559	**C**	-0.912237	1.398152	-0.151449	**H**	4.508958	-3.376608	-2.107516
C	-1.707248	0.483619	0.031531	**C**	-1.792593	0.230870	-0.195346	**C**	2.927792	-4.483714	-1.128581
C	-3.029976	1.083684	0.007106	**C**	-3.140274	0.724370	0.039187	**H**	3.478889	-5.426189	-1.161666
C	-4.321450	0.534671	-0.058300	**C**	-4.375578	0.075651	0.206472	**C**	1.649695	-4.470913	-0.561124
H	-4.476261	-0.542094	-0.065680	**H**	-4.462073	-1.005149	0.119762	**H**	1.191823	-5.370297	-0.158107
C	-5.408726	1.403095	-0.115122	**C**	-5.498941	0.847891	0.490018	**C**	0.978900	-3.250920	-0.540972
H	-6.420283	0.996806	-0.168287	**H**	-6.466249	0.360700	0.624484	**N**	-2.884689	-2.022997	0.164003
C	-5.218205	2.794267	-0.101212	**C**	-5.402545	2.244554	0.598929	**N**	-1.754864	1.274038	-0.119790
H	-6.087441	3.454705	-0.139208	**H**	-6.300312	2.829229	0.811629	**N**	-0.325838	-2.962198	-0.094361
C	-3.941646	3.364997	-0.045533	**C**	-4.182218	2.912888	0.452516	**H**	-4.166086	2.573456	-0.406862
H	-3.794879	4.441764	-0.046483	**H**	-4.103909	3.991976	0.554014	**C**	-1.247827	-3.876482	0.376189
C	-2.860451	2.490454	0.000789	**C**	-3.062323	2.132144	0.183113	**C**	-2.677268	-3.351695	0.525184
C	-2.199413	-1.909517	0.185943	**C**	-2.123104	-2.155129	-0.646683	**O**	-0.994865	-5.035750	0.611222
C	-2.255603	-2.866925	-0.843002	**C**	-3.068691	-2.137785	-1.681268	**O**	-3.562547	-4.088107	0.888430
C	-3.083910	-3.981441	-0.634119	**C**	-3.803759	-3.285275	-1.966885	**C**	0.349503	2.955555	1.040353
H	-3.158234	-4.734002	-1.423285	**H**	-4.537178	-3.273602	-2.775872	**N**	0.731178	0.300174	-1.067550
C	-3.809776	-4.143546	0.545825	**C**	-3.583879	-4.448936	-1.222462	**C**	1.866043	0.958170	-1.640752
H	-4.445380	-5.022353	0.676014	**H**	-4.155029	-5.354305	-1.440034	**C**	1.703259	1.506078	-2.916578
C	-3.721158	-3.185851	1.562776	**C**	-2.622668	-4.461094	-0.209619	**C**	3.066490	1.096348	-0.912929
H	-4.276097	-3.312554	2.494679	**H**	-2.446722	-5.376266	0.361027	**C**	2.758266	2.190540	-3.518506
C	-2.913058	-2.066666	1.382856	**C**	-1.861640	-3.324235	0.097501	**H**	0.747075	1.382718	-3.428937
C	0.628589	4.084135	0.030217	**C**	0.291825	3.985370	-0.046748	**C**	4.109909	1.785795	-1.548346
C	-0.905608	4.045007	0.023231	**C**	-1.226537	3.827463	0.117766	**C**	3.966079	2.322551	-2.829944
H	-2.823462	-1.308103	2.162315	**H**	-3.212810	-1.224531	-2.260806	**H**	2.636138	2.614817	-4.517231
H	2.934649	-1.006166	-2.170663	**H**	2.196160	-1.856710	-2.638764	**H**	5.055868	1.921196	-1.023041
H	-0.292323	-0.934292	-0.015708	**H**	-0.286133	-1.076142	-0.410309	**H**	4.802086	2.855899	-3.288211
C	1.370543	-2.705736	1.909239	**C**	2.493162	-1.519754	2.023130	**C**	3.208479	0.547853	0.490709
H	0.317694	-2.603269	1.593155	**C**	-0.839805	-3.353450	1.208619	**H**	-0.099985	0.872242	-0.797374
H	1.607805	-1.756908	2.420674	**H**	1.395983	-1.412025	2.018451	**H**	0.551159	3.111047	2.113937
C	1.479615	-3.860116	2.898490	**H**	2.879940	-0.484892	2.060308	**H**	0.449829	1.879422	0.869394
H	1.183749	-4.818229	2.442580	**H**	-0.617106	-4.404672	1.444672	**H**	2.248889	0.674100	1.014160
H	2.504813	-3.972436	3.285838	**H**	0.105994	-2.915326	0.855027	**H**	3.364654	-0.543035	0.433405
H	0.815754	-3.683515	3.758827	**C**	2.922957	-2.267197	3.280303	**C**	1.389264	3.737626	0.228321
C	-1.451014	-2.740776	-2.115207	**H**	2.549545	-3.304052	3.280595	**H**	2.407888	3.412908	0.481951
H	-2.112895	-2.949611	-2.971627	**H**	4.018526	-2.304126	3.386262	**H**	1.246470	3.594951	-0.853141
H	-1.096930	-1.706562	-2.238791	**H**	2.523540	-1.765450	4.175265	**H**	1.321374	4.816796	0.435555
C	-0.257501	-3.703526	-2.153588	**C**	-1.290663	-2.630807	2.483371	**C**	4.328118	1.156749	1.329853
H	0.315057	-3.577772	-3.085829	**H**	-2.214519	-3.077627	2.883640	**H**	4.297156	0.745303	2.350416
H	0.427729	-3.528287	-1.311525	**H**	-0.514453	-2.701411	3.261390	**H**	5.323547	0.931665	0.917187
H	-0.592982	-4.751265	-2.100239	**H**	-1.488231	-1.562799	2.301098	**H**	4.232055	2.251622	1.404265

Table G43 XYZ coordinates of GS geometries of **3.15a** B3LYP/Def2TZVPP/SMD(CH_2Cl_2)

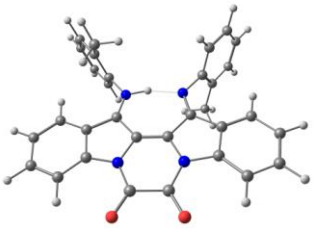
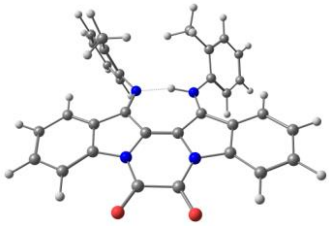
Anti				***Syn***			
							
O	-1.454003	4.733782	0.071727	**O**	-1.037457	-4.877922	-0.075536
O	1.291509	4.787874	-0.060594	**O**	1.703396	-4.733892	0.076394
N	-1.413675	2.451913	0.070143	**N**	-1.155814	-2.599564	-0.130608
N	-1.311971	-1.076483	0.069382	**N**	-1.307514	0.924936	-0.133269
N	1.328295	2.506273	-0.068376	**N**	1.580079	-2.455577	0.027255
N	1.361614	-1.044691	-0.081419	**N**	1.353901	1.085751	-0.112901
C	-0.703411	1.261110	0.035440	**C**	-0.531862	-1.359692	-0.113977
C	-1.678353	0.147314	0.084196	**C**	-1.584845	-0.321788	-0.169856
C	-2.995187	0.785633	0.145148	**C**	-2.850092	-1.052485	-0.252309
C	-4.280732	0.256317	0.205832	**C**	-4.167218	-0.615753	-0.352063
H	-4.443073	-0.809135	0.217843	**H**	-4.403343	0.435632	-0.382919
C	-5.356095	1.135073	0.250666	**C**	-5.176347	-1.568707	-0.412949
H	-6.362642	0.744395	0.297162	**H**	-6.206317	-1.250883	-0.491047
C	-5.149710	2.512642	0.236524	**C**	-4.873660	-2.928089	-0.373083
H	-6.000215	3.179477	0.271190	**H**	-5.674043	-3.653706	-0.419279
C	-3.869121	3.062259	0.178669	**C**	-3.559460	-3.385077	-0.276701
H	-3.716897	4.127351	0.169287	**H**	-3.332538	-4.436395	-0.248927
C	-2.809843	2.175866	0.134246	**C**	-2.566503	-2.425347	-0.220499
C	-2.231338	-2.152489	0.098733	**C**	-2.288200	1.943740	-0.142764
C	-2.785002	-2.621757	-1.100520	**C**	-2.942759	2.300018	1.045703
C	-3.645193	-3.715486	-1.028954	**C**	-3.849984	3.356570	0.989246
H	-4.085894	-4.088756	-1.944587	**H**	-4.365354	3.644333	1.896754
C	-3.946049	-4.328124	0.182533	**C**	-4.103983	4.039129	-0.194783
H	-4.619048	-5.174478	0.206348	**H**	-4.816407	4.852844	-0.206370
C	-3.374218	-3.855059	1.357183	**C**	-3.431694	3.680199	-1.356823
H	-3.596286	-4.327467	2.304469	**H**	-3.614866	4.208590	-2.282603
C	-2.507757	-2.770393	1.314783	**C**	-2.513211	2.639575	-1.327922
C	0.649693	1.280468	-0.036969	**C**	0.820611	-1.280360	-0.043856
C	1.650976	0.224094	-0.090099	**C**	1.748370	-0.156326	-0.036355
C	2.939791	0.875833	-0.149463	**C**	3.076777	-0.717920	0.090540
C	4.242356	0.375516	-0.215763	**C**	4.337025	-0.135017	0.245277
H	4.432975	-0.684857	-0.232533	**H**	4.460549	0.934953	0.247061
C	5.291611	1.278741	-0.259861	**C**	5.434514	-0.964332	0.403363
H	6.307583	0.914567	-0.310368	**H**	6.416877	-0.531148	0.525448
C	5.050406	2.653834	-0.239899	**C**	5.286575	-2.352841	0.401953
H	5.886098	3.339237	-0.274135	**H**	6.159753	-2.980219	0.516121
C	3.760298	3.175461	-0.177484	**C**	4.040013	-2.957511	0.267815
H	3.583598	4.236774	-0.164239	**H**	3.928977	-4.027535	0.285887
C	2.718805	2.267258	-0.133682	**C**	2.948033	-2.120662	0.123581
C	2.311105	-2.117247	-0.100395	**C**	2.151147	2.247439	-0.291161
C	2.614891	-2.713425	-1.316290	**C**	3.047149	2.312633	-1.354159
C	3.524938	-3.761637	-1.351811	**C**	3.783851	3.467926	-1.558708
H	3.772031	-4.229283	-2.294689	**H**	4.478618	3.524143	-2.385060
C	4.110441	-4.200644	-0.170411	**C**	3.614574	4.550892	-0.701895
H	4.820374	-5.016512	-0.188826	**H**	4.186843	5.456006	-0.853524
C	3.784112	-3.599222	1.039597	**C**	2.703027	4.478640	0.344216
H	4.239851	-3.950436	1.956005	**H**	2.572527	5.325694	1.004590
C	2.874380	-2.544928	1.104770	**C**	1.942948	3.332180	0.569913
C	-0.826318	3.704151	0.040714	**C**	-0.483658	-3.805792	-0.066474
C	0.703563	3.733209	-0.034162	**C**	1.042609	-3.724395	0.019666
H	2.147385	-2.348049	-2.220175	**H**	3.152587	1.463305	-2.014165
H	-2.050017	-2.389370	2.217578	**H**	-1.973699	2.350260	-2.219623
H	0.333019	-1.271975	-0.031371	**H**	0.304122	1.215428	-0.096152
C	-2.471329	-1.951007	-2.405934	**C**	-2.683236	1.564151	2.327914
C	2.527867	-1.881617	2.404931	**C**	0.946605	3.263254	1.689955
H	-1.393826	-1.900277	-2.576871	**H**	-1.614766	1.492865	2.537937
H	-2.924674	-2.491651	-3.234651	**H**	-3.163500	2.070902	3.162885
H	-2.847172	-0.925665	-2.425543	**H**	-3.071737	0.544150	2.286995
H	3.011030	-2.391819	3.235510	**H**	1.034343	4.136949	2.332331
H	2.852210	-0.838788	2.413107	**H**	-0.075338	3.233046	1.306091
H	1.450238	-1.886071	2.578713	**H**	1.091938	2.370961	2.300524

Table G44 XYZ coordinates of GS geometries of **3.15b** B3LYP/Def2TZVPP/SMD(CH_2Cl_2)

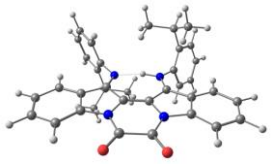
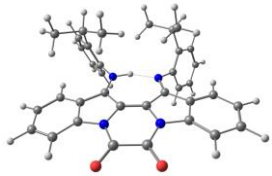
Anti				***Syn***			
							
O	-1.498242	4.999154	-0.079988	**O**	-1.502335	4.956119	0.333332
O	1.243826	5.073911	0.078970	**O**	1.227740	5.012557	0.019070
N	-1.440552	2.717566	-0.076067	**N**	-1.489387	2.687227	0.087056
N	-1.324500	-0.811104	-0.074770	**N**	-1.450831	-0.830725	-0.297011
N	1.296884	2.792606	0.083845	**N**	1.236693	2.743369	-0.216722
N	1.373779	-0.760246	0.087855	**N**	1.252705	-0.795458	-0.389846
C	-0.724020	1.530068	-0.034184	**C**	-0.796737	1.496476	-0.084706
C	-1.693142	0.412136	-0.111005	**C**	-1.787790	0.399836	-0.170527
C	-3.013347	1.045444	-0.183842	**C**	-3.096154	1.050477	-0.036244
C	-4.298907	0.513290	-0.216011	**C**	-4.389002	0.536591	0.018510
H	-4.459592	-0.551898	-0.228446	**H**	-4.574849	-0.516941	-0.107486
C	-5.378314	1.387807	-0.231099	**C**	-5.443935	1.413774	0.235161
H	-6.383945	0.992776	-0.256566	**H**	-6.453965	1.031642	0.277985
C	-5.177492	2.766091	-0.216079	**C**	-5.214192	2.778727	0.392921
H	-6.030817	3.430016	-0.232700	**H**	-6.049529	3.445878	0.554701
C	-3.898132	3.318967	-0.173156	**C**	-3.926982	3.312114	0.354582
H	-3.749188	4.384217	-0.150908	**H**	-3.752934	4.365053	0.490288
C	-2.834900	2.435782	-0.153393	**C**	-2.887406	2.425527	0.142514
C	-2.223555	-1.880879	-0.293859	**C**	-2.405140	-1.818325	-0.644043
C	-2.585113	-2.764149	0.735369	**C**	-2.728786	-2.891461	0.202267
C	-3.424887	-3.826712	0.392363	**C**	-3.651586	-3.823642	-0.279871
H	-3.729176	-4.509831	1.175076	**H**	-3.928513	-4.647527	0.365535
C	-3.876635	-4.030471	-0.904492	**C**	-4.216555	-3.731064	-1.544148
H	-4.519262	-4.871350	-1.127576	**H**	-4.922388	-4.479596	-1.877599
C	-3.493573	-3.151297	-1.910316	**C**	-3.864676	-2.674576	-2.375644
H	-3.829355	-3.296310	-2.928147	**H**	-4.285884	-2.587306	-3.367973
C	-2.672421	-2.079571	-1.601834	**C**	-2.968032	-1.722852	-1.921765
C	0.629616	1.559094	0.047043	**C**	0.551636	1.520235	-0.229006
C	1.642436	0.514130	0.108736	**C**	1.538068	0.471695	-0.430235
C	2.924678	1.179917	0.165996	**C**	2.813874	1.125763	-0.608378
C	4.234645	0.694890	0.188454	**C**	4.088669	0.634273	-0.895750
H	4.437707	-0.362778	0.189818	**H**	4.262214	-0.421120	-1.025297
C	5.274820	1.608994	0.206442	**C**	5.131449	1.538899	-1.008413
H	6.295605	1.255378	0.223149	**H**	6.126797	1.181581	-1.229825
C	5.018436	2.981512	0.205541	**C**	4.911192	2.906307	-0.832201
H	5.847032	3.676057	0.225089	**H**	5.742533	3.592529	-0.917303
C	3.721652	3.488307	0.174191	**C**	3.646561	3.420134	-0.553466
H	3.532679	4.547409	0.164323	**H**	3.484244	4.476271	-0.426383
C	2.689292	2.568415	0.149563	**C**	2.609726	2.510937	-0.454104
C	2.323259	-1.811137	0.308406	**C**	2.188882	-1.875028	-0.498698
C	2.781117	-1.973269	1.612975	**C**	2.935729	-2.320590	0.596977
C	3.682825	-2.980920	1.912250	**C**	3.785068	-3.408746	0.354973
H	4.036574	-3.106433	2.926058	**H**	4.374551	-3.787384	1.180171
C	4.117913	-3.824893	0.897330	**C**	3.887616	-4.017090	-0.884857
H	4.820869	-4.618165	1.112809	**H**	4.557706	-4.855667	-1.017720
C	3.647394	-3.653978	-0.397092	**C**	3.119195	-3.558009	-1.949680
H	3.993469	-4.314470	-1.181245	**H**	3.181336	-4.027840	-2.921255
C	2.737653	-2.647293	-0.733594	**C**	2.265310	-2.488270	-1.748369
C	-0.863038	3.974080	-0.041637	**C**	-0.888993	3.931625	0.160254
C	0.663910	4.014516	0.046273	**C**	0.631193	3.962569	-0.014336
H	-2.360406	-1.386140	-2.370144	**H**	1.653261	-2.106026	-2.553774
C	-2.181871	-2.597094	2.189097	**H**	-2.685467	-0.891237	-2.552774
H	-2.536045	-3.500007	2.689818	**C**	-2.144572	-3.110704	1.585751
C	-2.895603	-1.409792	2.848786	**H**	-2.774813	-3.872752	2.047997
H	-3.977252	-1.484883	2.732752	**C**	-2.195692	-1.886167	2.504125
H	-2.670844	-1.384274	3.916709	**H**	-3.198120	-1.456723	2.532792
H	-2.575341	-0.460352	2.419490	**H**	-1.927544	-2.179211	3.520394
C	-0.668896	-2.525118	2.418770	**H**	-1.501835	-1.108914	2.193132
H	-0.140946	-3.302507	1.866451	**C**	-0.732520	-3.702321	1.490790
H	-0.263012	-1.560262	2.124057	**H**	-0.742809	-4.641210	0.936014
H	-0.452037	-2.660006	3.479731	**H**	-0.047079	-3.026101	0.984761
H	2.422587	-1.303764	2.381916	**H**	-0.332779	-3.899489	2.486927
C	2.314672	-2.502185	-2.184245	**C**	2.945454	-1.764078	2.017759
H	2.736166	-3.371913	-2.690611	**H**	2.997528	-2.654601	2.648433
C	2.932846	-1.260802	-2.840788	**C**	1.727661	-0.969465	2.491910
H	4.017125	-1.251665	-2.727025	**H**	1.738331	0.058581	2.132831
H	2.704804	-1.253851	-3.907967	**H**	0.788433	-1.429486	2.197096
H	2.540294	-0.338457	-2.413353	**H**	1.745200	-0.923640	3.581585
C	0.799025	-2.550326	-2.404219	**C**	4.228452	-0.961107	2.282164
H	0.339426	-3.373215	-1.856905	**H**	5.120172	-1.524282	2.007810
H	0.312017	-1.625748	-2.101447	**H**	4.228613	-0.028759	1.718861
H	0.588419	-2.692944	-3.465127	**H**	4.296587	-0.712790	3.342631
H	0.354452	-1.002222	0.012586	**H**	0.231613	-1.028025	-0.303424

Table G45 XYZ coordinates of GS geometries of **3.15c** B3LYP/Def2TZVPP/SMD(CH_2Cl_2)

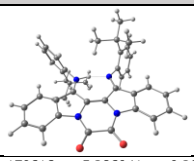
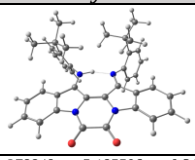
Anti				***Syn***			
							
O	1.170616	5.286041	0.209745	**O**	1.278849	5.185506	0.314555
O	-1.549052	5.184906	-0.171148	**O**	-1.457599	5.142134	0.563485
N	1.248297	3.005611	0.193553	**N**	1.270787	2.933683	-0.053025
N	1.368129	-0.546319	0.143899	**N**	1.253710	-0.584435	-0.486394
N	-1.470104	2.904344	-0.157989	**N**	-1.461448	2.890479	0.190337
N	-1.325895	-0.622179	-0.106984	**N**	-1.454369	-0.599285	-0.401166
C	0.598078	1.765373	0.104560	**C**	0.574507	1.721126	-0.154304
C	1.618399	0.730811	0.206442	**C**	1.550947	0.679750	-0.428120
C	2.887003	1.409848	0.345319	**C**	2.835072	1.332396	-0.550938
C	4.199145	0.938005	0.430861	**C**	4.110007	0.849790	-0.854187
H	4.412813	-0.117526	0.427668	**H**	4.277111	-0.194322	-1.058577
C	5.226499	1.862489	0.517628	**C**	5.162518	1.749893	-0.888690
H	6.248900	1.519437	0.584003	**H**	6.157347	1.398674	-1.121963
C	4.954960	3.232237	0.521647	**C**	4.952370	3.103853	-0.621450
H	5.773458	3.935088	0.594891	**H**	5.790684	3.786354	-0.649018
C	3.656140	3.726002	0.427776	**C**	3.689005	3.608677	-0.321692
H	3.455896	4.783080	0.421675	**H**	3.534803	4.654479	-0.120826
C	2.637063	2.795743	0.335029	**C**	2.642972	2.705017	-0.298115
C	2.311416	-1.592249	0.418518	**C**	2.175432	-1.641512	-0.792326
C	2.809705	-2.439352	-0.585301	**C**	2.179318	-2.023967	-2.135039
C	3.695950	-3.430432	-0.147640	**C**	3.034592	-3.011916	-2.583799
H	4.120453	-4.112200	-0.865944	**H**	3.036521	-3.299829	-3.625721
C	4.061785	-3.577602	1.183956	**C**	3.892552	-3.614180	-1.671215
H	4.750478	-4.364094	1.461565	**H**	4.581699	-4.382776	-1.993948
C	3.545125	-2.726311	2.149730	**C**	3.863229	-3.237929	-0.339576
H	3.815601	-2.833595	3.190868	**H**	4.537055	-3.732881	0.343327
C	2.664751	-1.733132	1.757943	**C**	2.999964	-2.250706	0.163172
C	-0.747382	1.723573	-0.064041	**C**	-0.776819	1.704431	-0.037419
C	-1.699394	0.596876	-0.198655	**C**	-1.776533	0.628184	-0.216660
C	-3.015579	1.217796	-0.376433	**C**	-3.081313	1.285824	-0.083177
C	-4.290633	0.673898	-0.500633	**C**	-4.380643	0.785589	-0.099984
H	-4.440343	-0.392712	-0.523467	**H**	-4.573582	-0.254856	-0.301769
C	-5.373878	1.538563	-0.595787	**C**	-5.431931	1.659222	0.146424
H	-6.371407	1.134362	-0.693865	**H**	-6.446759	1.287773	0.134727
C	-5.187224	2.918689	-0.568301	**C**	-5.192148	3.007115	0.404207
H	-6.042982	3.574820	-0.647570	**H**	-6.024583	3.671807	0.589445
C	-3.919368	3.483185	-0.433826	**C**	-3.898812	3.526021	0.437031
H	-3.781489	4.549640	-0.402577	**H**	-3.717689	4.565046	0.649180
C	-2.852444	2.609688	-0.336227	**C**	-2.863246	2.643138	0.192558
C	-2.187946	-1.707006	-0.393809	**C**	-2.418979	-1.535602	-0.854492
C	-2.525255	-1.876097	-1.739780	**C**	-2.875537	-1.332333	-2.161454
C	-3.285237	-2.955850	-2.152683	**C**	-3.782240	-2.199240	-2.744589
H	-3.531359	-3.075894	-3.198973	**H**	-4.120199	-2.028545	-3.757660
C	-3.717701	-3.874121	-1.206939	**C**	-4.248803	-3.277838	-2.007554
H	-4.313472	-4.727351	-1.501955	**H**	-4.965856	-3.966196	-2.434053
C	-3.381239	-3.700864	0.129615	**C**	-3.787644	-3.481035	-0.713145
H	-3.739200	-4.430378	0.837677	**H**	-4.171656	-4.328185	-0.168582
C	-2.606012	-2.630040	0.586513	**C**	-2.856165	-2.640442	-0.095314
C	0.606095	4.221269	0.123801	**C**	0.673288	4.145449	0.209538
C	-0.908655	4.166156	-0.082061	**C**	-0.850674	4.121855	0.348219
H	2.237747	-1.054915	2.483037	**H**	-2.501049	-0.479761	-2.711438
C	2.469352	-2.292229	-2.077791	**C**	-2.360863	-2.936397	1.327542
C	3.077139	-3.431312	-2.909202	**C**	-3.129450	-4.097875	1.973468
H	2.709182	-4.407546	-2.591175	**H**	-3.003789	-5.031435	1.425310
H	2.793584	-3.291588	-3.952233	**H**	-2.743736	-4.255114	2.980960
H	4.166075	-3.440004	-2.863762	**H**	-4.196289	-3.885118	2.054348
C	3.047779	-0.969647	-2.615446	**C**	-2.530682	-1.716740	2.251507
H	2.610892	-0.098347	-2.134193	**H**	-1.889153	-0.887754	1.968564
H	4.128211	-0.931318	-2.472932	**H**	-3.563855	-1.367219	2.252640
H	2.845142	-0.891497	-3.684944	**H**	-2.270540	-1.997970	3.273069
H	-2.167303	-1.150516	-2.456738	**C**	-0.879107	-3.342521	1.263210
C	-2.308736	-2.460043	2.085224	**H**	-0.263786	-2.563104	0.824992
C	-2.785906	-3.670703	2.900148	**H**	-0.504187	-3.539968	2.268036
H	-2.296942	-4.592364	2.581566	**H**	-0.751856	-4.247200	0.667366
H	-2.538380	-3.507535	3.949150	**H**	1.509062	-1.519548	-2.817371
H	-3.864637	-3.812892	2.836378	**C**	3.073042	-1.975583	1.679289
C	-3.049731	-1.219385	2.618706	**C**	2.818524	-3.304336	2.421317
H	-2.720589	-0.303972	2.132321	**H**	1.831135	-3.699503	2.184436
H	-4.125768	-1.315253	2.468495	**H**	3.556033	-4.064076	2.169535
H	-2.865821	-1.111515	3.689329	**H**	2.868708	-3.134705	3.497688
C	-0.799084	-2.307534	2.342756	**C**	2.070780	-0.954063	2.233164
H	-0.418336	-1.356943	1.984929	**H**	1.040266	-1.198236	1.986357
H	-0.607083	-2.351997	3.415797	**H**	2.155538	-0.953868	3.320147
H	-0.233663	-3.108618	1.866166	**H**	2.284701	0.058311	1.898856
C	0.947256	-2.326433	-2.307499	**C**	4.485630	-1.466325	2.026571
H	0.743655	-2.401659	-3.376318	**H**	4.559429	-1.302631	3.102929
H	0.492000	-3.187236	-1.817583	**H**	5.258404	-2.179269	1.742781
H	0.450496	-1.428399	-1.953984	**H**	4.694819	-0.520602	1.526406
H	0.355294	-0.795491	0.031872	**H**	0.231529	-0.812741	-0.416645

Table G46 XYZ Coordinates of GS geometries of **3.15d** B3LYP/Def2TZVPP/SMD(CH_2Cl_2)

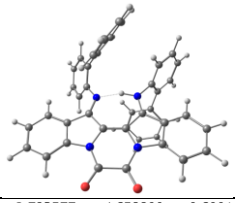
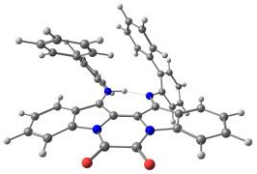
Anti				***Syn***			
							
O	-2.793577	4.658800	-0.600163	**O**	0.948121	5.184505	-0.262125
O	-0.144731	5.254902	-1.023941	**O**	-1.711286	5.144353	0.429759
N	-2.259323	2.457654	-0.322119	**N**	0.888336	2.927337	-0.587833
N	-1.375324	-0.927101	0.124207	**N**	0.813671	-0.604474	-0.905962
N	0.384473	3.051179	-0.759142	**N**	-1.770224	2.888136	0.091128
N	1.194812	-0.381659	-0.348149	**N**	-1.835661	-0.585495	-0.536247
C	-1.315333	1.440764	-0.289214	**C**	0.186003	1.713553	-0.574338
C	-2.010954	0.184222	0.051224	**C**	1.127288	0.662604	-0.924473
C	-3.427489	0.542144	0.175317	**C**	2.381215	1.310590	-1.226969
C	-4.570042	-0.224748	0.386812	**C**	3.595041	0.822878	-1.713195
H	-4.503402	-1.286209	0.561415	**H**	3.733825	-0.227239	-1.911701
C	-5.807264	0.405762	0.371367	**C**	4.622750	1.722356	-1.941082
H	-6.703565	-0.175545	0.535245	**H**	5.570590	1.366013	-2.317842
C	-5.904386	1.778574	0.153330	**C**	4.450426	3.082592	-1.678177
H	-6.876438	2.251912	0.153880	**H**	5.271513	3.764578	-1.851035
C	-4.775363	2.562657	-0.076174	**C**	3.244068	3.594656	-1.206178
H	-4.855383	3.619508	-0.260791	**H**	3.114172	4.646452	-1.020155
C	-3.551655	1.918730	-0.067011	**C**	2.218183	2.690899	-0.999709
C	-1.879096	-2.126162	0.635096	**C**	1.677555	-1.728623	-1.000798
C	-1.614983	-3.326521	-0.054939	**C**	2.744155	-1.917594	-0.105865
C	-1.998420	-4.526542	0.549963	**C**	3.507474	-3.077378	-0.265942
H	-1.831033	-5.453279	0.018665	**H**	4.326296	-3.254548	0.417223
C	-2.595734	-4.549859	1.801395	**C**	3.216069	-4.014620	-1.246658
H	-2.878960	-5.494484	2.244984	**H**	3.822389	-4.905898	-1.332196
C	-2.824351	-3.358045	2.484628	**C**	2.135834	-3.819228	-2.099591
H	-3.270511	-3.368231	3.469631	**H**	1.893875	-4.550242	-2.858174
C	-2.471197	-2.153867	1.902793	**C**	1.363739	-2.676437	-1.969916
C	-0.006215	1.726194	-0.513354	**C**	-1.133891	1.702241	-0.250863
C	1.196280	0.910054	-0.516202	**C**	-2.143959	0.625713	-0.243841
C	2.308772	1.805544	-0.739347	**C**	-3.393950	1.266237	0.175884
C	3.685011	1.587829	-0.834217	**C**	-4.657012	0.751343	0.454839
H	4.103076	0.601366	-0.721537	**H**	-4.874134	-0.294949	0.313943
C	4.507782	2.675487	-1.076394	**C**	-5.640066	1.615769	0.917836
H	5.575849	2.530274	-1.151354	**H**	-6.626067	1.232179	1.138687
C	3.972029	3.956377	-1.223512	**C**	-5.370319	2.971658	1.094303
H	4.634704	4.790053	-1.410686	**H**	-6.151950	3.629869	1.447718
C	2.602701	4.196532	-1.138144	**C**	-4.109465	3.505232	0.834268
H	2.197600	5.186307	-1.255990	**H**	-3.900626	4.549490	0.987001
C	1.788797	3.105302	-0.895008	**C**	-3.138551	2.629777	0.383004
C	2.362378	-1.198672	-0.226011	**C**	-2.746724	-1.613603	-0.807585
C	3.043692	-1.257979	0.996091	**C**	-2.522417	-2.891972	-0.262999
C	4.207401	-2.028380	1.043716	**C**	-3.335381	-3.943246	-0.692011
H	4.754202	-2.088445	1.974579	**H**	-3.183890	-4.924526	-0.263545
C	4.655030	-2.726233	-0.070491	**C**	-4.335909	-3.747555	-1.633080
H	5.555733	-3.321038	-0.003037	**H**	-4.951030	-4.579671	-1.947087
C	3.945142	-2.670188	-1.264409	**C**	-4.544183	-2.479534	-2.169086
H	4.285336	-3.217874	-2.132182	**H**	-5.313159	-2.318969	-2.912369
C	2.793545	-1.899920	-1.342756	**C**	-3.755634	-1.419488	-1.757893
C	-1.961778	3.785103	-0.572336	**C**	0.334709	4.143430	-0.258117
C	-0.486400	4.115362	-0.811736	**C**	-1.146249	4.122191	0.125809
H	2.233648	-1.825012	-2.263136	**H**	-3.888146	-0.438700	-2.191791
H	-2.616837	-1.223740	2.433600	**H**	0.520817	-2.498246	-2.623444
H	0.243732	-0.810887	-0.214160	**C**	-1.479558	-3.127163	0.757740
C	-0.959917	-3.333033	-1.379607	**C**	-0.574106	-4.182256	0.610338
C	0.046785	-4.265054	-1.656850	**C**	-1.401470	-2.330549	1.904921
C	-1.327638	-2.430575	-2.384330	**C**	0.389755	-4.428742	1.579197
C	0.670821	-4.289531	-2.896232	**H**	-0.616800	-4.799012	-0.276668
H	0.356426	-4.959092	-0.887562	**C**	-0.448892	-2.589633	2.881368
C	-0.700896	-2.454392	-3.623543	**H**	-2.110321	-1.526422	2.046260
H	-2.127649	-1.727105	-2.206440	**C**	0.453190	-3.635479	2.719429
C	0.301819	-3.382439	-3.883968	**H**	1.094292	-5.237532	1.440696
H	1.455927	-5.009147	-3.085826	**H**	-0.408589	-1.971982	3.768580
H	-1.005196	-1.754560	-4.390507	**H**	1.203965	-3.826562	3.474122
H	0.789739	-3.400059	-4.849264	**C**	3.076530	-0.960489	0.974591
C	2.576595	-0.510197	2.186900	**C**	4.402410	-0.559780	1.163562
C	3.437505	0.377169	2.836436	**C**	2.093392	-0.433113	1.816120
C	1.278009	-0.672370	2.678755	**C**	4.733114	0.358573	2.151478
C	3.005747	1.097578	3.943763	**H**	5.174691	-0.950389	0.515541
H	4.442539	0.513767	2.460615	**C**	2.424109	0.481919	2.805809
C	0.848660	0.045167	3.787116	**H**	1.068640	-0.751355	1.707803
H	0.607708	-1.377374	2.207953	**C**	3.744257	0.887822	2.972819
C	1.709325	0.936724	4.419978	**H**	5.763108	0.665755	2.273739
H	3.681675	1.787403	4.431202	**H**	1.649719	0.873115	3.452438
H	-0.156131	-0.098267	4.161909	**H**	4.000246	1.605890	3.740197
H	1.373561	1.497417	5.281999	**H**	-0.212156	-0.799821	-0.756307

Table G47 XYZ coordinates of GS geometries of **3.15e** B3LYP/Def2TZVPP/SMD(CH_2Cl_2)

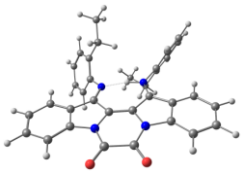
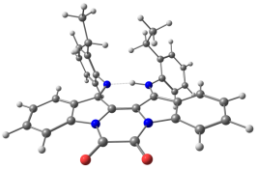
Anti				***Syn***			
							
O	-1.483626	5.059153	0.083352	**O**	0.804786	5.080951	-0.013993
O	-3.840448	3.651076	-0.010203	**O**	-1.915724	4.803170	0.289530
N	-0.308523	3.102385	0.052808	**N**	1.019029	2.809568	-0.213090
N	1.473473	0.058250	-0.063972	**N**	1.303560	-0.712199	-0.432923
N	-2.663166	1.696086	-0.022104	**N**	-1.710048	2.535045	0.049052
N	-0.806348	-1.329322	-0.000536	**N**	-1.351462	-0.988138	-0.385455
C	-0.276817	1.715127	0.016098	**C**	0.444715	1.544506	-0.263298
C	1.140998	1.293969	-0.015981	**C**	1.535907	0.550428	-0.400102
C	1.918460	2.535698	0.046453	**C**	2.777324	1.333744	-0.442376
C	3.287268	2.776900	0.122216	**C**	4.118770	0.954897	-0.563946
H	3.995632	1.965228	0.103200	**H**	4.398761	-0.093354	-0.654550
C	3.726531	4.090667	0.221542	**C**	5.092796	1.956770	-0.567063
H	4.786186	4.295229	0.279987	**H**	6.145724	1.684160	-0.660011
C	2.816754	5.145661	0.240489	**C**	4.732048	3.305824	-0.452910
H	3.179067	6.162022	0.309786	**H**	5.509860	4.072800	-0.457633
C	1.441836	4.925742	0.179192	**C**	3.393302	3.704826	-0.332082
H	0.742655	5.742837	0.207420	**H**	3.115064	4.751643	-0.243767
C	1.020156	3.611891	0.089333	**C**	2.435024	2.698039	-0.329047
C	2.787464	-0.408850	-0.244624	**C**	2.329166	-1.686130	-0.496506
C	3.323752	-1.300680	0.701268	**C**	2.912799	-2.147843	0.705071
C	4.587493	-1.825402	0.442591	**C**	3.877694	-3.158686	0.603073
H	5.035701	-2.502048	1.155150	**H**	4.349160	-3.540068	1.510001
C	5.284262	-1.510783	-0.720010	**C**	4.254675	-3.690687	-0.634516
H	6.258124	-1.947285	-0.895994	**H**	5.013010	-4.475923	-0.678345
C	4.726220	-0.647083	-1.654268	**C**	3.656771	-3.225194	-1.807353
H	5.254548	-0.408473	-2.567286	**H**	3.940218	-3.639881	-2.777497
C	3.479826	-0.090780	-1.412672	**C**	2.683393	-2.226410	-1.737871
C	-1.438996	1.012279	-0.008952	**C**	-0.908657	1.399586	-0.148519
C	-1.734463	-0.413744	-0.019261	**C**	-1.790295	0.233330	-0.192996
C	-3.175680	-0.539118	-0.073394	**C**	-3.137784	0.728576	0.039439
C	-4.023397	-1.644997	-0.171299	**C**	-4.373772	0.081052	0.205389
H	-3.631744	-2.648278	-0.188446	**H**	-4.460885	-0.999718	0.118868
C	-5.388882	-1.426254	-0.246781	**C**	-5.496925	0.854408	0.487459
H	-6.060731	-2.269144	-0.322511	**H**	-6.464892	0.368126	0.620759
C	-5.906532	-0.129788	-0.220805	**C**	-5.399162	2.251019	0.596604
H	-6.976634	0.016240	-0.272106	**H**	-6.296536	2.836679	0.808426
C	-5.081666	0.988626	-0.137626	**C**	-4.177857	2.918068	0.451467
H	-5.485249	1.985862	-0.131592	**H**	-4.098650	3.997068	0.553318
C	-3.719048	0.760622	-0.072157	**C**	-3.058365	2.136218	0.183126
C	-0.974759	-2.736745	0.139569	**C**	-2.125273	-2.151427	-0.646768
C	-0.455127	-3.589110	-0.838927	**C**	-3.064967	-2.132286	-1.686727
C	-0.606453	-4.961920	-0.628483	**C**	-3.801925	-3.278037	-1.975236
H	-0.229117	-5.646275	-1.377107	**H**	-4.530918	-3.264817	-2.788251
C	-1.225697	-5.461367	0.507379	**C**	-3.589833	-4.441673	-1.228348
H	-1.325770	-6.530150	0.639667	**H**	-4.162592	-5.345550	-1.448129
C	-1.712576	-4.590085	1.478589	**C**	-2.634475	-4.455535	-0.209834
H	-2.183489	-4.971896	2.373694	**H**	-2.464705	-5.370460	0.363153
C	-1.585124	-3.224618	1.294173	**C**	-1.871999	-3.320361	0.100446
C	-1.470232	3.852832	0.051600	**C**	0.297745	3.985454	-0.046374
C	-2.782406	3.067621	0.002157	**C**	-1.221098	3.829486	0.115816
H	-1.949804	-2.527929	2.035988	**H**	-3.203455	-1.219208	-2.267934
H	3.024104	0.576240	-2.131282	**H**	2.194894	-1.851858	-2.639690
H	0.181030	-0.954690	-0.035738	**H**	-0.286451	-1.076547	-0.406508
C	2.529975	-1.641715	1.939440	**C**	2.494133	-1.531732	2.023430
H	1.557183	-2.029951	1.625028	**C**	-0.857386	-3.350515	1.218117
H	2.309243	-0.716671	2.479323	**H**	1.396805	-1.424998	2.021151
C	3.175638	-2.640050	2.890668	**H**	2.879842	-0.496566	2.061792
H	3.364789	-3.596890	2.401723	**H**	-0.636882	-4.401897	1.455645
H	4.122867	-2.269823	3.285216	**H**	0.090549	-2.912068	0.870745
H	2.513575	-2.825310	3.736959	**C**	2.927390	-2.281199	3.278392
C	0.244350	-3.086491	-2.076262	**H**	2.553598	-3.317962	3.278136
H	-0.237026	-3.530715	-2.950356	**H**	4.023302	-2.318554	3.381065
H	0.120247	-2.008219	-2.169838	**H**	2.530235	-1.780545	4.175012
C	1.735964	-3.435327	-2.093705	**C**	-1.316392	-2.627272	2.489829
H	2.206345	-3.050688	-2.999137	**H**	-2.243480	-3.073183	2.883705
H	2.252421	-3.004173	-1.237058	**H**	-0.545341	-2.698529	3.272951
H	1.885831	-4.515044	-2.068556	**H**	-1.511207	-1.559139	2.305499

Table G48 XYZ coordinates of GS geometries of **3.16a** B3LYP/Def2TZVPP/SMD(CH_2Cl_2)

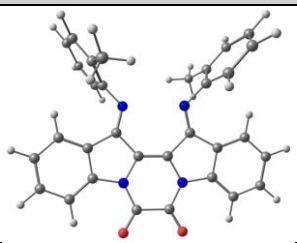
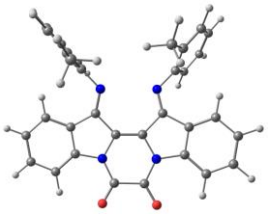
Anti				***Syn***			
							
O	1.367872	-4.763118	-0.086377	**O**	-1.390544	4.736214	0.163756
O	-1.367866	-4.763119	0.086380	**O**	1.338109	4.752870	-0.096221
N	1.361099	-2.480318	-0.056738	**N**	-1.377443	2.455302	0.069791
N	1.430772	1.056174	0.153082	**N**	-1.444416	-1.070111	-0.285927
N	-1.361096	-2.480319	0.056732	**N**	1.340258	2.469940	-0.125635
N	-1.430772	1.056173	-0.153087	**N**	1.424794	-1.065211	0.033727
C	0.676577	-1.251281	-0.013284	**C**	-0.690680	1.230819	-0.030199
C	1.702474	-0.177614	0.022285	**C**	-1.714313	0.155582	-0.087101
C	2.998528	-0.875748	-0.091634	**C**	-3.008610	0.844112	0.091768
C	4.300383	-0.395307	-0.184620	**C**	-4.305293	0.355550	0.211754
H	4.503458	0.662841	-0.168823	**H**	-4.506236	-0.701990	0.163224
C	5.342235	-1.308483	-0.299635	**C**	-5.344861	1.259518	0.397776
H	6.359824	-0.950932	-0.373451	**H**	-6.358240	0.895228	0.493424
C	5.086207	-2.677562	-0.317411	**C**	-5.092188	2.628008	0.458791
H	5.908958	-3.374432	-0.402281	**H**	-5.913309	3.317925	0.598353
C	3.788436	-3.177261	-0.234063	**C**	-3.799321	3.135453	0.350732
H	3.592637	-4.234512	-0.256831	**H**	-3.605047	4.191679	0.408368
C	2.760574	-2.253485	-0.127304	**C**	-2.773381	2.220405	0.173707
C	2.395631	2.058000	0.287190	**C**	-2.417866	-2.057889	-0.464782
C	2.635313	2.928241	-0.790504	**C**	-3.102984	-2.158648	-1.678248
C	3.547520	3.964391	-0.606278	**C**	-4.012424	-3.186316	-1.885798
H	3.746352	4.632882	-1.434963	**H**	-4.537644	-3.254100	-2.829456
C	4.197243	4.159824	0.608465	**C**	-4.244785	-4.120537	-0.882682
H	4.896540	4.976998	0.723993	**H**	-4.953465	-4.923322	-1.035851
C	3.930872	3.305962	1.672901	**C**	-3.549332	-4.024248	0.318503
H	4.420051	3.451422	2.627138	**H**	-3.722317	-4.755147	1.098852
C	3.033016	2.259445	1.514115	**C**	-2.622922	-3.010135	0.548857
C	-0.676575	-1.251282	0.013277	**C**	0.660939	1.238415	-0.091466
C	-1.702474	-0.177615	-0.022291	**C**	1.687694	0.167285	-0.126962
C	-2.998526	-0.875751	0.091631	**C**	2.978377	0.870450	-0.267741
C	-4.300382	-0.395312	0.184619	**C**	4.283807	0.398180	-0.355765
H	-4.503460	0.662836	0.168823	**H**	4.490811	-0.659084	-0.374264
C	-5.342233	-1.308490	0.299635	**C**	5.323752	1.318304	-0.424977
H	-6.359822	-0.950940	0.373453	**H**	6.343454	0.966493	-0.497283
C	-5.086203	-2.677569	0.317411	**C**	5.063020	2.686255	-0.403666
H	-5.908953	-3.374440	0.402283	**H**	5.883887	3.388217	-0.460118
C	-3.788431	-3.177265	0.234061	**C**	3.763165	3.178480	-0.308389
H	-3.592631	-4.234516	0.256829	**H**	3.564405	4.235221	-0.286208
C	-2.760571	-2.253488	0.127300	**C**	2.737671	2.248630	-0.241110
C	-2.395631	2.057999	-0.287191	**C**	2.386053	-2.077865	-0.029714
C	-2.635323	2.928228	0.790510	**C**	2.849675	-2.663302	1.161364
C	-3.547531	3.964378	0.606288	**C**	3.752742	-3.719275	1.064911
H	-3.746370	4.632859	1.434978	**H**	4.123247	-4.169521	1.977651
C	-4.197244	4.159823	-0.608458	**C**	4.182439	-4.203985	-0.166288
H	-4.896543	4.976997	-0.723982	**H**	4.881162	-5.028586	-0.210384
C	-3.930863	3.305973	-1.672901	**C**	3.697511	-3.629287	-1.335801
H	-4.420035	3.451443	-2.627140	**H**	4.014499	-4.001795	-2.301052
C	-3.033006	2.259456	-1.514120	**C**	2.801327	-2.571489	-1.268799
C	0.758652	-3.713980	-0.041866	**C**	-0.779433	3.691241	0.071838
C	-0.758648	-3.713981	0.041859	**C**	0.734487	3.700199	-0.059420
H	-2.816485	1.588076	-2.334241	**H**	2.414245	-2.116205	-2.170453
H	2.816502	1.588056	2.334231	**H**	-2.913953	-1.424725	-2.450121
C	-1.936037	2.715178	2.101179	**C**	2.394998	-2.133144	2.489660
H	-2.260775	1.788802	2.581659	**H**	2.777939	-1.125747	2.670615
H	-0.856718	2.633351	1.958553	**H**	1.305911	-2.067350	2.533192
H	-2.136764	3.537552	2.786369	**H**	2.737575	-2.773219	3.301524
C	1.936015	2.715206	-2.101169	**C**	-1.871447	-2.906648	1.843567
H	2.260750	1.788836	-2.581662	**H**	-0.796546	-2.846741	1.664146
H	0.856697	2.633376	-1.958534	**H**	-2.148329	-2.005958	2.396889
H	2.136735	3.537588	-2.786352	**H**	-2.071821	-3.768103	2.479051

Table G49 XYZ coordinates of GS geometries of **3.16b** B3LYP/Def2TZVPP/SMD(CH_2Cl_2)

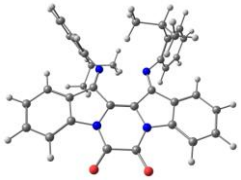
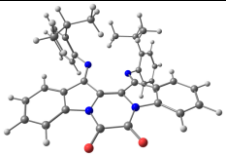
Anti				***Syn***			
							
O	1.366474	5.009873	0.092362	**O**	-1.287396	4.930586	0.462269
O	-1.366472	5.009874	-0.092356	**O**	1.369355	4.926033	-0.226126
N	1.358673	2.726784	0.086247	**N**	-1.346805	2.662275	0.210995
N	1.432183	-0.817643	0.075325	**N**	-1.569624	-0.795107	-0.543080
N	-1.358673	2.726785	-0.086238	**N**	1.323873	2.645892	-0.332693
N	-1.432188	-0.817641	-0.075310	**N**	1.395623	-0.858381	-0.037354
C	0.676124	1.495852	0.042483	**C**	-0.705163	1.433314	-0.037183
C	1.701858	0.422934	0.116267	**C**	-1.764582	0.396708	-0.135841
C	2.997761	1.126950	0.181846	**C**	-3.014085	1.091152	0.238548
C	4.305320	0.652515	0.198710	**C**	-4.303412	0.616822	0.456632
H	4.511133	-0.404873	0.202380	**H**	-4.539610	-0.426405	0.325862
C	5.349168	1.570137	0.210532	**C**	-5.288443	1.514953	0.849575
H	6.370656	1.216426	0.225119	**H**	-6.294957	1.160751	1.023591
C	5.090085	2.938768	0.205387	**C**	-4.991264	2.866004	1.016308
H	5.914014	3.639294	0.219372	**H**	-5.771854	3.552285	1.315233
C	3.788147	3.432984	0.174649	**C**	-3.703507	3.357779	0.816492
H	3.590730	4.489943	0.158436	**H**	-3.471684	4.398280	0.959742
C	2.758747	2.504452	0.157462	**C**	-2.730686	2.446507	0.436132
C	2.375607	-1.829206	0.268260	**C**	-2.640382	-1.618301	-0.930342
C	2.737045	-2.700521	-0.777759	**C**	-2.931604	-2.831978	-0.279443
C	3.625330	-3.733987	-0.478069	**C**	-3.989326	-3.594492	-0.778317
H	3.923470	-4.399915	-1.278584	**H**	-4.233996	-4.520645	-0.272998
C	4.127833	-3.938395	0.801594	**C**	-4.724881	-3.212767	-1.893458
H	4.807849	-4.757409	0.993794	**H**	-5.532496	-3.837238	-2.251247
C	3.736961	-3.088004	1.829363	**C**	-4.400997	-2.030748	-2.548998
H	4.105314	-3.235380	2.836117	**H**	-4.948730	-1.720200	-3.428993
C	2.869002	-2.041686	1.561649	**C**	-3.369903	-1.242081	-2.066323
C	-0.676125	1.495853	-0.042470	**C**	0.630711	1.426412	-0.238447
C	-1.701861	0.422936	-0.116259	**C**	1.627328	0.342051	-0.384544
C	-2.997763	1.126953	-0.181845	**C**	2.881667	1.017498	-0.772066
C	-4.305322	0.652520	-0.198711	**C**	4.140748	0.523946	-1.094489
H	-4.511136	-0.404869	-0.202383	**H**	4.318709	-0.536519	-1.163405
C	-5.349169	1.570142	-0.210536	**C**	5.171573	1.426607	-1.330868
H	-6.370658	1.216432	-0.225125	**H**	6.154859	1.058116	-1.588157
C	-5.090084	2.938773	-0.205389	**C**	4.949243	2.798331	-1.237475
H	-5.914013	3.639300	-0.219376	**H**	5.763215	3.486031	-1.422353
C	-3.788146	3.432988	-0.174648	**C**	3.696556	3.312236	-0.908456
H	-3.590729	4.489947	-0.158433	**H**	3.527040	4.371691	-0.831459
C	-2.758748	2.504455	-0.157459	**C**	2.678058	2.400289	-0.683993
C	-2.375608	-1.829205	-0.268257	**C**	2.342054	-1.884694	-0.166160
C	-2.869004	-2.041673	-1.561648	**C**	3.052265	-2.374757	0.946671
C	-3.736957	-3.087991	-1.829373	**C**	3.919512	-3.447203	0.730559
H	-4.105310	-3.235358	-2.836129	**H**	4.483772	-3.825642	1.574058
C	-4.127826	-3.938396	-0.801615	**C**	4.078273	-4.041294	-0.515499
H	-4.807838	-4.757411	-0.993823	**H**	4.757595	-4.874315	-0.636924
C	-3.625323	-3.734000	0.478051	**C**	3.347463	-3.561808	-1.595751
H	-3.923461	-4.399938	1.278558	**H**	3.445636	-4.016152	-2.572857
C	-2.737043	-2.700534	0.777752	**C**	2.484888	-2.491372	-1.418244
C	0.757362	3.960347	0.049791	**C**	-0.720794	3.884794	0.218462
C	-0.757361	3.960348	-0.049782	**C**	0.758615	3.880685	-0.134538
H	2.554199	-1.373264	2.351421	**H**	1.903282	-2.108526	-2.245958
C	2.231419	-2.551269	-2.200732	**H**	-3.109200	-0.318094	-2.564655
H	2.657751	-3.391661	-2.753156	**C**	-2.160150	-3.345565	0.920004
C	2.737124	-1.271274	-2.878573	**H**	-2.648468	-4.279100	1.208262
H	3.823070	-1.190613	-2.812442	**C**	-2.230606	-2.411789	2.133803
H	2.463155	-1.275212	-3.935558	**H**	-3.264937	-2.174378	2.387927
H	2.303438	-0.379428	-2.428522	**H**	-1.773284	-2.891307	3.001115
C	0.705671	-2.665272	-2.301657	**H**	-1.700506	-1.478678	1.954521
H	0.350833	-3.596215	-1.856927	**C**	-0.711583	-3.678619	0.546062
H	0.214162	-1.843586	-1.786667	**H**	-0.678265	-4.384469	-0.285520
H	0.398507	-2.652823	-3.349488	**H**	-0.171191	-2.781945	0.256038
H	-2.554203	-1.373240	-2.351413	**H**	-0.193633	-4.130691	1.393170
C	-2.231420	-2.551292	2.200728	**C**	2.948889	-1.791077	2.345949
H	-2.657752	-3.391689	2.753144	**H**	3.551928	-2.447822	2.976797
C	-2.737128	-1.271303	2.878577	**C**	1.524842	-1.813326	2.911423
H	-3.823074	-1.190646	2.812448	**H**	0.853985	-1.179366	2.334591
H	-2.463157	-1.275246	3.935561	**H**	1.117714	-2.823839	2.907705
H	-2.303445	-0.379453	2.428530	**H**	1.530745	-1.454093	3.942513
C	-0.705672	-2.665295	2.301654	**C**	3.563454	-0.389781	2.457514
H	-0.350832	-3.596234	1.856917	**H**	4.573165	-0.364332	2.046422
H	-0.214162	-1.843604	1.786672	**H**	2.967968	0.355977	1.934061
H	-0.398510	-2.652855	3.349486	**H**	3.617419	-0.091689	3.506498

Table G50 XYZ coordinates of GS geometries of **3.16c** B3LYP/Def2TZVPP/SMD(CH_2Cl_2)

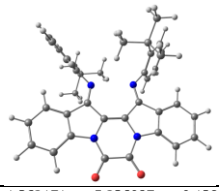
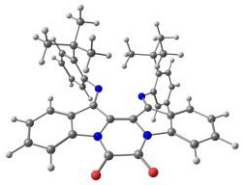
Anti				***Syn***			
							
O	1.362171	5.236087	0.139649	**O**	1.283375	5.149780	0.128095
O	-1.362175	5.236086	-0.139652	**O**	-1.400836	5.093458	0.687344
N	1.354693	2.953060	0.131572	**N**	1.250554	2.890500	-0.199868
N	1.433443	-0.592227	0.125040	**N**	1.327040	-0.630821	-0.341084
N	-1.354695	2.953059	-0.131573	**N**	-1.434602	2.850847	0.261379
N	-1.433443	-0.592228	-0.125040	**N**	-1.598027	-0.588030	-0.609259
C	0.674762	1.721441	0.063729	**C**	0.562679	1.664443	-0.240853
C	1.697715	0.650022	0.177716	**C**	1.566093	0.606216	-0.496213
C	2.989617	1.354885	0.290812	**C**	2.832018	1.321686	-0.751499
C	4.296416	0.881186	0.348156	**C**	4.103830	0.867168	-1.083606
H	4.502173	-0.176159	0.360392	**H**	4.289855	-0.178933	-1.262244
C	5.339016	1.799066	0.390381	**C**	5.137264	1.791873	-1.187282
H	6.359682	1.445757	0.437384	**H**	6.130513	1.454572	-1.449082
C	5.079746	3.167721	0.374936	**C**	4.904330	3.145392	-0.956723
H	5.902525	3.868642	0.414004	**H**	5.720232	3.850424	-1.040302
C	3.779371	3.661189	0.300988	**C**	3.638391	3.619322	-0.618374
H	3.582161	4.717970	0.274791	**H**	3.460823	4.664582	-0.437123
C	2.751301	2.732065	0.253198	**C**	2.618006	2.686526	-0.525125
C	2.358755	-1.599256	0.411469	**C**	2.283316	-1.620761	-0.614654
C	2.756959	-2.558848	-0.548157	**C**	2.355966	-2.033195	-1.954741
C	3.612803	-3.570122	-0.104491	**C**	3.228328	-3.026113	-2.356952
H	3.956718	-4.313091	-0.806611	**H**	3.269602	-3.321568	-3.396999
C	4.043074	-3.672100	1.213743	**C**	4.047951	-3.629982	-1.409872
H	4.698366	-4.482411	1.504123	**H**	4.746786	-4.404097	-1.697155
C	3.616516	-2.737960	2.147556	**C**	3.955535	-3.238255	-0.084237
H	3.927451	-2.805149	3.181808	**H**	4.602051	-3.721257	0.634133
C	2.783125	-1.710228	1.742614	**C**	3.073511	-2.246396	0.368757
C	-0.674764	1.721440	-0.063730	**C**	-0.777282	1.646773	-0.057983
C	-1.697716	0.650020	-0.177716	**C**	-1.822162	0.603727	-0.218862
C	-2.989619	1.354882	-0.290812	**C**	-3.090748	1.272933	0.135828
C	-4.296417	0.881183	-0.348155	**C**	-4.385203	0.782268	0.275506
H	-4.502173	-0.176162	-0.360390	**H**	-4.610919	-0.251880	0.075159
C	-5.339018	1.799062	-0.390379	**C**	-5.390193	1.652059	0.681347
H	-6.359684	1.445753	-0.437381	**H**	-6.400611	1.284350	0.793857
C	-5.079748	3.167717	-0.374935	**C**	-5.107551	2.991379	0.940716
H	-5.902527	3.868638	-0.414003	**H**	-5.902925	3.655969	1.249586
C	-3.779373	3.661187	-0.300989	**C**	-3.815928	3.498412	0.820745
H	-3.582164	4.717967	-0.274793	**H**	-3.595985	4.529136	1.034906
C	-2.751303	2.732063	-0.253198	**C**	-2.823806	2.615342	0.423374
C	-2.358754	-1.599258	-0.411468	**C**	-2.637186	-1.442378	-1.009611
C	-2.783122	-1.710231	-1.742614	**C**	-3.302606	-1.103294	-2.195435
C	-3.616511	-2.737965	-2.147556	**C**	-4.302564	-1.906787	-2.714736
H	-3.927445	-2.805155	-3.181809	**H**	-4.801475	-1.623769	-3.632246
C	-4.043069	-3.672105	-1.213743	**C**	-4.655148	-3.067731	-2.041088
H	-4.698360	-4.482416	-1.504123	**H**	-5.439245	-3.709147	-2.420744
C	-3.612800	-3.570124	0.104492	**C**	-3.983174	-3.414848	-0.874624
H	-3.956716	-4.313093	0.806612	**H**	-4.273911	-4.326849	-0.377729
C	-2.756958	-2.558849	0.548158	**C**	-2.954937	-2.640614	-0.329957
C	0.754859	4.186539	0.075644	**C**	0.673435	4.100457	0.095030
C	-0.754862	4.186539	-0.075647	**C**	-0.818199	4.071687	0.386261
H	2.433028	-0.975413	2.454606	**H**	-3.014350	-0.191891	-2.701623
C	2.301900	-2.491290	-2.013291	**C**	-2.226690	-3.080105	0.947607
C	2.855580	-3.657617	-2.842552	**C**	-2.758215	-4.415378	1.485086
H	2.528460	-4.623910	-2.456654	**H**	-2.637947	-5.223861	0.763030
H	2.487685	-3.568433	-3.865448	**H**	-2.193544	-4.684373	2.378611
H	3.945850	-3.654111	-2.882143	**H**	-3.811275	-4.357280	1.764733
C	2.802317	-1.188549	-2.665542	**C**	-2.408480	-2.035601	2.064909
H	2.380385	-0.305207	-2.194294	**H**	-1.968851	-1.076736	1.807012
H	3.889910	-1.118893	-2.609294	**H**	-3.466180	-1.880271	2.284000
H	2.517588	-1.170825	-3.719492	**H**	-1.923990	-2.387200	2.977925
H	-2.433024	-0.975417	-2.454606	**C**	-0.729677	-3.260992	0.641968
C	-2.301900	-2.491289	2.013291	**H**	-0.278469	-2.339034	0.289340
C	-2.855578	-3.657617	2.842554	**H**	-0.205829	-3.579541	1.544409
H	-2.528456	-4.623909	2.456657	**H**	-0.583905	-4.029412	-0.119615
H	-2.487684	-3.568432	3.865450	**H**	1.708544	-1.545646	-2.670878
H	-3.945848	-3.654113	2.882144	**C**	3.101325	-1.925695	1.877744
C	-2.802318	-1.188549	2.665542	**C**	2.866154	-3.227970	2.669757
H	-2.380387	-0.305207	2.194294	**H**	1.886459	-3.647861	2.439469
H	-3.889911	-1.118895	2.609293	**H**	3.616618	-3.986657	2.454005
H	-2.517590	-1.170824	3.719492	**H**	2.903211	-3.019491	3.740427
C	-0.765391	-2.554579	2.088049	**C**	2.052733	-0.915185	2.363641
H	-0.303859	-1.737214	1.543827	**H**	1.041719	-1.198140	2.080132
H	-0.443921	-2.506387	3.130507	**H**	2.098490	-0.873485	3.453449
H	-0.397410	-3.490927	1.664958	**H**	2.245969	0.088730	1.993366
C	0.765391	-2.554582	-2.088049	**C**	4.489535	-1.361182	2.235880
H	0.443922	-2.506392	-3.130506	**H**	4.535955	-1.133877	3.302983
H	0.397412	-3.490931	-1.664956	**H**	5.286229	-2.069321	2.008658
H	0.303858	-1.737217	-1.543828	**H**	4.687374	-0.440775	1.684482

Table G51 XYZ coordinates of GS geometries of **3.16d** B3LYP/Def2TZVPP/SMD(CH_2Cl_2)

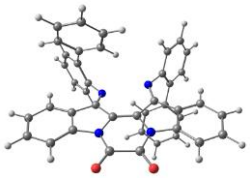
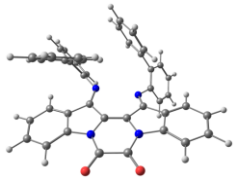
Anti				***Syn***			
							
O	1.329196	4.973299	-0.338153	**O**	1.757584	4.886644	-0.357622
O	-1.329190	4.973301	0.338151	**O**	-0.842881	5.237228	0.443034
N	1.308780	2.690878	-0.382382	**N**	1.347798	2.665187	-0.684983
N	1.260469	-0.833763	-0.682544	**N**	0.849644	-0.825505	-0.855078
N	-1.308776	2.690880	0.382381	**N**	-1.252314	3.025526	0.054946
N	-1.260469	-0.833761	0.682545	**N**	-1.988438	-0.342255	-0.751944
C	0.640442	1.465191	-0.215898	**C**	0.476824	1.560434	-0.673068
C	1.593241	0.387864	-0.577706	**C**	1.287597	0.359840	-0.985546
C	2.868878	1.074939	-0.850741	**C**	2.626382	0.873343	-1.323374
C	4.120934	0.590419	-1.213291	**C**	3.765983	0.232710	-1.793610
H	4.301034	-0.468095	-1.302703	**H**	3.766511	-0.829660	-1.977962
C	5.144507	1.499165	-1.455513	**C**	4.909581	0.988488	-2.021063
H	6.124770	1.137595	-1.733242	**H**	5.805590	0.506335	-2.386399
C	4.918368	2.868798	-1.341728	**C**	4.912660	2.359827	-1.774679
H	5.726615	3.561808	-1.531829	**H**	5.814394	2.931389	-1.947680
C	3.668744	3.374298	-0.988927	**C**	3.775495	3.021551	-1.315754
H	3.494571	4.432506	-0.906585	**H**	3.777689	4.082046	-1.136020
C	2.659989	2.455565	-0.748533	**C**	2.639875	2.255136	-1.107921
C	2.156303	-1.867846	-0.951123	**C**	1.621591	-1.981335	-0.903010
C	3.043768	-2.350377	0.035032	**C**	2.619259	-2.261556	0.059170
C	3.879601	-3.418548	-0.300310	**C**	3.284409	-3.486819	-0.022160
H	4.557970	-3.799182	0.451665	**H**	4.038687	-3.713773	0.719573
C	3.849619	-4.006375	-1.557650	**C**	2.990064	-4.418260	-1.008674
H	4.506760	-4.835031	-1.783636	**H**	3.521262	-5.359846	-1.039528
C	2.956260	-3.533636	-2.513058	**C**	1.993778	-4.138575	-1.938309
H	2.914572	-3.985870	-3.495052	**H**	1.742859	-4.859176	-2.705367
C	2.106938	-2.481543	-2.206094	**C**	1.304866	-2.938158	-1.872994
C	-0.640440	1.465192	0.215898	**C**	-0.821775	1.745264	-0.339963
C	-1.593240	0.387866	0.577706	**C**	-2.010637	0.860028	-0.339026
C	-2.868876	1.074942	0.850740	**C**	-3.108187	1.687183	0.197882
C	-4.120933	0.590424	1.213289	**C**	-4.419720	1.372576	0.536283
H	-4.301033	-0.468090	1.302702	**H**	-4.805542	0.376484	0.391184
C	-5.144504	1.499171	1.455511	**C**	-5.229350	2.369011	1.068615
H	-6.124768	1.137603	1.733239	**H**	-6.251355	2.140609	1.337196
C	-4.918365	2.868804	1.341725	**C**	-4.736302	3.658949	1.255078
H	-5.726611	3.561815	1.531826	**H**	-5.382370	4.424001	1.663720
C	-3.668740	3.374303	0.988925	**C**	-3.421290	3.989665	0.935711
H	-3.494565	4.432510	0.906583	**H**	-3.038470	4.982436	1.093509
C	-2.659985	2.455568	0.748532	**C**	-2.623961	2.981886	0.416069
C	-2.156304	-1.867843	0.951124	**C**	-3.105983	-1.141071	-0.974702
C	-3.043770	-2.350374	-0.035030	**C**	-3.198547	-2.405649	-0.359163
C	-3.879604	-3.418544	0.300312	**C**	-4.243312	-3.253495	-0.732824
H	-4.557973	-3.799178	-0.451662	**H**	-4.325475	-4.217388	-0.248033
C	-3.849622	-4.006370	1.557653	**C**	-5.175122	-2.882524	-1.692920
H	-4.506765	-4.835025	1.783640	**H**	-5.974288	-3.559325	-1.962965
C	-2.956264	-3.533630	2.513061	**C**	-5.069361	-1.636389	-2.303879
H	-2.914577	-3.985863	3.495056	**H**	-5.781872	-1.336335	-3.060935
C	-2.106940	-2.481538	2.206097	**C**	-4.045552	-0.774043	-1.947578
C	0.734593	3.924395	-0.197602	**C**	0.991616	3.944726	-0.338911
C	-0.734587	3.924396	0.197601	**C**	-0.453215	4.141356	0.094484
H	-1.407666	-2.105020	2.939863	**H**	-3.943473	0.186608	-2.433506
H	1.407663	-2.105025	-2.939861	**H**	0.514492	-2.713899	-2.575974
C	-3.126810	-1.739161	-1.382592	**C**	-2.221328	-2.833661	0.667006
C	-4.373931	-1.438422	-1.938902	**C**	-1.563051	-4.060662	0.546147
C	-1.978123	-1.455394	-2.129986	**C**	-1.946753	-2.035575	1.781422
C	-4.472693	-0.868213	-3.202566	**C**	-0.648402	-4.474373	1.506841
H	-5.271938	-1.636720	-1.369390	**H**	-1.752029	-4.680730	-0.319837
C	-2.077385	-0.887097	-3.392516	**C**	-1.043743	-2.455266	2.749025
H	-1.004574	-1.669864	-1.714427	**H**	-2.456093	-1.089248	1.898274
C	-3.324281	-0.588366	-3.934319	**C**	-0.386634	-3.673717	2.612712
H	-5.447463	-0.635404	-3.610840	**H**	-0.131676	-5.416979	1.384241
H	-1.177550	-0.676402	-3.955832	**H**	-0.847087	-1.827225	3.607835
H	-3.399279	-0.140676	-4.916457	**H**	0.329698	-3.991786	3.358285
C	3.126807	-1.739163	1.382593	**C**	2.973454	-1.301810	1.131102
C	4.373928	-1.438421	1.938902	**C**	4.314075	-1.000175	1.388421
C	1.978120	-1.455395	2.129986	**C**	1.991477	-0.673544	1.903412
C	4.472689	-0.868211	3.202567	**C**	4.663017	-0.087760	2.376749
H	5.271936	-1.636719	1.369391	**H**	5.087099	-1.465180	0.791863
C	2.077381	-0.887098	3.392515	**C**	2.338776	0.236506	2.892017
H	1.004571	-1.669868	1.714427	**H**	0.952032	-0.903375	1.727275
C	3.324276	-0.588364	3.934318	**C**	3.676409	0.538891	3.129686
H	5.447458	-0.635400	3.610840	**H**	5.706340	0.140689	2.550709
H	1.177546	-0.676403	3.955831	**H**	1.562508	0.709344	3.479630
H	3.399274	-0.140673	4.916456	**H**	3.946345	1.254618	3.894809

Table G52 XYZ coordinates of GS geometries of **3.16e** B3LYP/Def2TZVPP/SMD(CH_2Cl_2)

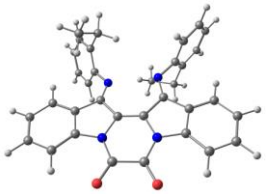
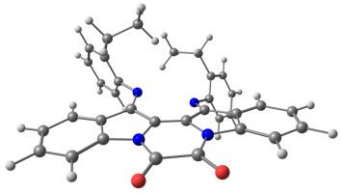
Anti				***Syn***			
							
O	-1.467161	4.878334	-0.137085	**O**	1.305811	4.894000	-0.134056
O	1.273188	4.921747	-0.062974	**O**	-1.395174	4.866634	0.341465
N	-1.437981	-0.934985	0.246340	**N**	1.385746	-0.916200	-0.133242
N	-1.425407	2.598710	-0.023161	**N**	1.296967	2.614456	-0.255241
N	1.408399	-0.900081	-0.139019	**N**	-1.518161	-0.893243	-0.481571
N	1.298996	2.639231	-0.020009	**N**	-1.399344	2.592687	0.139765
C	-0.894570	-2.753363	-2.413482	**C**	1.602733	-1.653860	3.010084
C	-2.329183	-2.279475	-2.156474	**C**	2.924307	-1.372887	2.287898
C	2.527270	-1.793195	2.937587	**C**	-0.566385	-4.002901	0.925155
C	1.850016	-2.770873	1.971150	**C**	-1.797544	-3.169114	1.295368
C	-0.841004	3.839867	-0.077776	**C**	0.702377	3.841242	-0.094439
C	0.678188	3.863547	-0.051314	**C**	-0.797310	3.826735	0.153679
C	-2.840705	-2.327340	1.627530	**C**	2.531848	-2.701358	-1.274004
C	-3.739650	-3.375073	1.773810	**C**	3.442970	-3.748769	-1.280979
C	-4.191708	-4.062737	0.653722	**C**	4.185703	-4.028752	-0.140194
C	-3.730265	-3.694391	-0.605823	**C**	4.005828	-3.252178	0.999767
C	-2.829500	-2.646537	-0.783666	**C**	3.106225	-2.188973	1.033745
C	-2.394839	-1.950007	0.358608	**C**	2.369162	-1.913400	-0.133268
C	-2.823137	2.351630	-0.028745	**C**	2.680420	2.394349	-0.487190
C	-3.868221	3.259955	-0.089124	**C**	3.698204	3.323100	-0.634373
C	-5.161669	2.742014	-0.088084	**C**	4.980032	2.829229	-0.868691
C	-5.397286	1.370615	-0.029339	**C**	5.230519	1.461559	-0.952279
C	-4.337778	0.472617	0.035282	**C**	4.199230	0.542176	-0.795786
C	-3.039300	0.971176	0.036160	**C**	2.913996	1.016646	-0.558609
C	-1.730129	0.292764	0.105737	**C**	1.637885	0.313575	-0.324611
C	-0.721679	1.380518	0.022811	**C**	0.616311	1.383730	-0.220202
C	2.557779	-2.875501	0.648076	**C**	-2.694238	-2.941951	0.106453
C	3.451494	-3.910934	0.383291	**C**	-3.689558	-3.864573	-0.213762
C	4.119541	-4.008047	-0.832406	**C**	-4.492241	-3.719128	-1.338972
C	3.893274	-3.050870	-1.816454	**C**	-4.301123	-2.625831	-2.177715
C	3.021003	-2.000617	-1.573461	**C**	-3.331715	-1.682931	-1.872482
C	2.363792	-1.896830	-0.342669	**C**	-2.536272	-1.824687	-0.729876
C	2.703227	2.433443	0.008097	**C**	-2.782956	2.351733	0.343466
C	3.720118	3.373433	0.071623	**C**	-3.785081	3.254538	0.662782
C	5.026345	2.893626	0.135134	**C**	-5.065372	2.741054	0.856310
C	5.300922	1.527872	0.142768	**C**	-5.327786	1.377846	0.740911
C	4.269885	0.598633	0.069575	**C**	-4.313481	0.487348	0.408973
C	2.959742	1.058682	-0.008652	**C**	-3.030481	0.982391	0.199491
C	1.670642	0.340464	-0.058579	**C**	-1.759245	0.307662	-0.137003
C	0.631542	1.399925	-0.004456	**C**	-0.727311	1.374057	-0.071108
H	-0.567489	-2.467363	-3.415006	**H**	1.514514	-1.031853	3.902679
H	-0.825508	-3.839522	-2.332333	**H**	1.543304	-2.698581	3.318128
H	-0.205766	-2.315447	-1.693003	**H**	0.750484	-1.444172	2.364599
H	1.807506	-3.760004	2.429678	**H**	-2.363163	-3.683952	2.074281
H	0.822267	-2.446278	1.797816	**H**	-1.474743	-2.215260	1.711684
H	-2.376862	-1.196965	-2.291564	**H**	2.980956	-0.309001	2.050144
H	-2.997670	-2.717049	-2.899384	**H**	3.756489	-1.583650	2.960848
H	3.552374	-2.102463	3.149544	**H**	-0.864715	-4.979174	0.538931
H	1.984754	-1.746800	3.883612	**H**	0.073289	-4.162539	1.793694
H	2.562301	-0.786111	2.521159	**H**	0.024770	-3.503044	0.159482
H	-4.083939	-3.650573	2.762053	**H**	3.566238	-4.344979	-2.175547
H	-4.892634	-4.880047	0.757876	**H**	4.894869	-4.845589	-0.134351
H	-4.078740	-4.228592	-1.481462	**H**	4.581808	-3.468667	1.891333
H	-3.689031	4.319291	-0.136839	**H**	3.506839	4.379772	-0.573146
H	-5.997582	3.426710	-0.135220	**H**	5.794641	3.530256	-0.989953
H	-6.412514	0.999090	-0.032299	**H**	6.235555	1.110026	-1.139688
H	-4.525066	-0.587441	0.082824	**H**	4.396123	-0.515494	-0.860783
H	3.614880	-4.661510	1.147171	**H**	-3.831248	-4.717662	0.438842
H	4.799288	-4.829610	-1.014553	**H**	-5.253578	-4.454487	-1.562086
H	4.392743	-3.121756	-2.773791	**H**	-4.908976	-2.502177	-3.064372
H	3.509755	4.428123	0.079100	**H**	-3.581161	4.305663	0.764375
H	5.841016	3.603163	0.186443	**H**	-5.867977	3.420750	1.108292
H	6.324631	1.185744	0.204006	**H**	-6.329662	1.007341	0.907571
H	4.487075	-0.456676	0.074669	**H**	-4.523151	-0.565732	0.319127
H	2.832645	-1.253785	-2.332858	**H**	-3.178990	-0.824289	-2.512378
H	-2.479650	-1.784819	2.491032	**H**	1.938027	-2.478542	-2.150195

Table G53 XYZ coordinates of the GS and TS geometries of **3.16a** B3LYP/Def2SVP (gas phase)

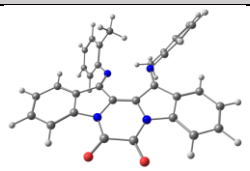
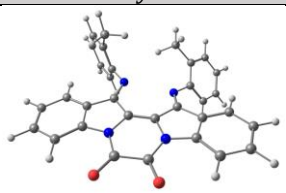
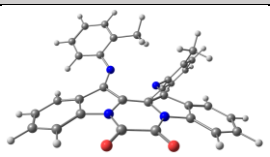
Anti				***Syn***				**TS**			
											
O	-1.368240	-4.838236	0.173717	**O**	1.736480	-4.678076	0.147637	**C**	1.170995	-0.986060	-0.034241
O	1.368208	-4.838244	-0.173712	**O**	-0.997060	-4.845703	-0.179717	**C**	1.895682	0.312745	0.137811
N	-1.362832	-2.547340	0.122014	**N**	1.595192	-2.392360	0.066827	**C**	3.280615	-0.104072	0.529069
N	-1.423243	0.996197	-0.149770	**N**	1.432235	1.144688	-0.230080	**C**	4.379830	0.537813	1.113455
N	1.362815	-2.547347	-0.122009	**N**	-1.125852	-2.557943	-0.175994	**H**	4.311639	1.555379	1.485304
N	1.423246	0.996189	0.149780	**N**	-1.415354	0.984511	-0.002269	**C**	5.577955	-0.157288	1.302466
C	-0.681158	-1.314710	0.040540	**C**	0.841702	-1.205136	-0.032745	**H**	6.425780	0.353773	1.763215
C	-1.705889	-0.236904	0.026255	**C**	1.798613	-0.065858	-0.053402	**C**	5.693668	-1.495878	0.917906
C	-3.000384	-0.933139	0.228347	**C**	3.133287	-0.680858	0.157175	**H**	6.640462	-2.022928	1.055173
C	-4.300624	-0.452978	0.414884	**C**	4.401917	-0.123247	0.347171	**C**	4.597852	-2.187973	0.392618
H	-4.504801	0.616203	0.399867	**H**	4.543549	0.955660	0.320899	**H**	4.650400	-3.240532	0.128973
C	-5.332878	-1.372093	0.618992	**C**	5.485257	-0.977065	0.569298	**C**	3.404456	-1.483867	0.241762
H	-6.353299	-1.012553	0.766555	**H**	6.481341	-0.555546	0.719135	**C**	1.689782	2.715018	-0.411645
C	-5.071610	-2.748756	0.630871	**C**	5.306370	-2.366479	0.596034	**C**	0.753969	3.530988	-1.122027
H	-5.893367	-3.452265	0.783225	**H**	6.167243	-3.018258	0.761790	**C**	1.060217	4.878407	-1.348662
C	-3.776139	-3.249768	0.460201	**C**	4.043831	-2.944901	0.423817	**H**	0.340964	5.492271	-1.897258
H	-3.558898	-4.314123	0.480501	**H**	3.889533	-4.019875	0.456396	**C**	2.248262	5.450838	-0.896206
C	-2.755339	-2.318623	0.270511	**C**	2.971270	-2.078097	0.216401	**H**	2.455057	6.507317	-1.083015
C	-2.330029	2.029975	-0.340265	**C**	2.268944	2.235516	-0.421841	**C**	3.171604	4.659170	-0.208207
C	-2.218163	3.176683	0.485726	**C**	3.214551	2.271879	-1.464900	**H**	4.111418	5.086744	0.148810
C	-3.068131	4.259036	0.233118	**C**	3.973780	3.418264	-1.690803	**C**	2.894140	3.316766	0.021975
H	-2.996655	5.141820	0.874389	**H**	4.696622	3.436723	-2.510048	**C**	-0.148178	-1.331701	-0.074346
C	-3.985290	4.242810	-0.821679	**C**	3.804151	4.539148	-0.872790	**C**	-1.406642	-0.592940	0.205245
H	-4.626193	5.108562	-1.002696	**H**	4.398580	5.439857	-1.041603	**C**	-2.478755	-1.614881	0.136360
C	-4.063406	3.120827	-1.652037	**C**	2.852799	4.510179	0.151275	**C**	-3.852161	-1.547488	0.395510
H	-4.761192	3.103429	-2.492751	**H**	2.706865	5.393295	0.779285	**H**	-4.316512	-0.607319	0.688172
C	-3.243880	2.019846	-1.411997	**C**	2.059688	3.381882	0.385409	**C**	-4.617420	-2.710372	0.278067
C	0.681148	-1.314714	-0.040533	**C**	-0.516516	-1.286019	-0.119893	**H**	-5.690520	-2.671473	0.476102
C	1.705884	-0.236913	-0.026250	**C**	-1.601579	-0.268742	-0.155118	**C**	-4.021054	-3.922716	-0.093214
C	3.000375	-0.933157	-0.228349	**C**	-2.854613	-1.044795	-0.314658	**H**	-4.637090	-4.819822	-0.189081
C	4.300616	-0.453003	-0.414892	**C**	-4.189757	-0.643636	-0.428083	**C**	-2.646459	-4.017678	-0.336249
H	4.504799	0.616177	-0.399877	**H**	-4.454628	0.411923	-0.438511	**H**	-2.169531	-4.954483	-0.610699
C	5.332865	-1.372123	-0.619005	**C**	-5.176627	-1.628194	-0.532243	**C**	-1.894706	-2.850188	-0.201626
H	6.353287	-1.012589	-0.766574	**H**	-6.223863	-1.333194	-0.624059	**N**	2.140093	-2.002972	-0.129577
C	5.071587	-2.748785	-0.630883	**C**	-4.834826	-2.986561	-0.521229	**N**	1.322037	1.395671	-0.239836
H	5.893340	-3.452299	-0.783241	**H**	-5.620983	-3.740632	-0.603828	**N**	-0.493478	-2.682120	-0.319126
C	3.776115	-3.249790	-0.460206	**C**	-3.504630	-3.408143	-0.406659	**H**	3.627709	2.721451	0.544493
H	3.558868	-4.314145	-0.480505	**H**	-3.228537	-4.458898	-0.395500	**C**	0.406074	-3.701771	-0.580943
C	2.755323	-2.318638	-0.270511	**C**	-2.531633	-2.414891	-0.305612	**C**	1.881035	-3.331371	-0.436196
C	2.330042	2.029959	0.340270	**C**	-2.452122	1.920236	-0.013645	**O**	0.080242	-4.835927	-0.853290
C	2.218186	3.176667	-0.485722	**C**	-3.063495	2.294102	1.206126	**O**	2.740808	-4.175448	-0.552678
C	3.068167	4.259010	-0.233120	**C**	-4.058150	3.277863	1.170703	**C**	-0.545776	2.979874	-1.630513
H	2.996697	5.141793	-0.874393	**H**	-4.540620	3.568075	2.108280	**H**	-0.843590	3.478503	-2.565134
C	3.985329	4.242776	0.821673	**C**	-4.444348	3.890190	-0.025199	**H**	-0.479770	1.898942	-1.787323
H	4.626243	5.108522	1.002686	**H**	-5.223823	4.655148	-0.021758	**H**	-1.348740	3.147460	-0.895309
C	4.063436	3.120795	1.652034	**C**	-3.817336	3.524519	-1.218834	**N**	-1.446260	0.648677	0.508280
H	4.761225	3.103392	2.492746	**H**	-4.100556	4.002259	-2.159871	**C**	-2.606454	1.386835	0.716967
C	3.243896	2.019822	1.412000	**C**	-2.818886	2.550071	-1.213613	**C**	-2.758946	2.011537	1.971400
C	-0.760014	-3.795612	0.086151	**C**	1.067285	-3.674922	0.047757	**C**	-3.556178	1.636202	-0.309859
C	0.759988	-3.795616	-0.086146	**C**	-0.450897	-3.767505	-0.117283	**C**	-3.861223	2.815381	2.244055
H	3.287939	1.142284	2.060182	**H**	-2.311202	2.259115	-2.135087	**H**	-1.989789	1.836148	2.725629
H	-3.287929	1.142308	-2.060178	**H**	3.331971	1.393755	-2.103065	**C**	-4.639181	2.476631	-0.012639
C	1.216474	3.189287	-1.606941	**C**	-2.652341	1.617474	2.485832	**C**	-4.811551	3.053119	1.246046
H	1.531313	2.527978	-2.432594	**H**	-2.949772	0.554749	2.493158	**H**	-3.970382	3.269993	3.231595
H	0.244742	2.806836	-1.261234	**H**	-1.557176	1.637279	2.607777	**H**	-5.368892	2.679685	-0.801817
H	1.086511	4.201497	-2.015571	**H**	-3.112979	2.101648	3.358628	**H**	-5.672323	3.696380	1.441389
C	-1.216454	3.189295	1.606948	**C**	1.008761	3.347440	1.460219	**C**	-3.437996	1.033713	-1.685976
H	-1.531299	2.527980	2.432596	**H**	0.078009	2.915684	1.063122	**H**	-2.397777	0.807068	-1.951590
H	-0.244724	2.806845	1.261241	**H**	1.315430	2.703922	2.302936	**H**	-4.002007	0.088824	-1.762385
H	-1.086493	4.201502	2.015586	**H**	0.809388	4.352993	1.857171	**H**	-3.842392	1.720061	-2.444669

Table G54 XYZ coordinates of the GS and TS geometries of **3.16b** B3LYP/Def2SVP (gas phase)

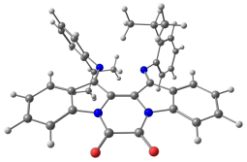
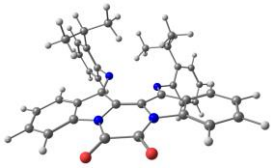
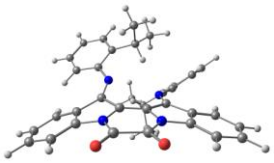
Anti				***Syn***				**TS**			
											
O	-1.377852	5.044405	0.002959	**O**	-1.339802	4.936923	0.464698	**C**	-1.759540	-0.465407	-0.165271
O	1.377851	5.044405	-0.002968	**O**	1.338665	4.946381	-0.208208	**C**	-0.884052	-1.669864	-0.001626
N	-1.366643	2.753178	-0.017854	**N**	-1.387223	2.662147	0.193686	**C**	-1.825588	-2.721026	0.499280
N	-1.442076	-0.805292	-0.126631	**N**	-1.572599	-0.824029	-0.515611	**C**	-1.673908	-3.941859	1.168487
N	1.366642	2.753178	0.017847	**N**	1.300647	2.658249	-0.322188	**H**	-0.701325	-4.276783	1.518108
N	1.442077	-0.805291	0.126627	**N**	1.383130	-0.864780	-0.054012	**C**	-2.798261	-4.716938	1.468252
C	-0.682325	1.518318	-0.016699	**C**	-0.736358	1.432750	-0.043911	**H**	-2.670473	-5.665217	1.994289
C	-1.710535	0.442536	-0.083885	**C**	-1.787017	0.382596	-0.145180	**C**	-4.078143	-4.284111	1.108924
C	-3.013945	1.147801	-0.061637	**C**	-3.053419	1.076339	0.199059	**H**	-4.946407	-4.908719	1.330391
C	-4.329321	0.673191	-0.018238	**C**	-4.352611	0.598391	0.401532	**C**	-4.272043	-3.037503	0.504753
H	-4.536097	-0.394801	-0.033862	**H**	-4.584463	-0.456631	0.269207	**H**	-5.261307	-2.658950	0.262786
C	-5.373530	1.599417	0.044266	**C**	-5.348981	1.503243	0.776115	**C**	-3.140372	-2.264976	0.248856
H	-6.405838	1.245369	0.077813	**H**	-6.367685	1.145299	0.938195	**C**	1.334857	-2.561752	-0.625608
C	-5.108506	2.974954	0.060218	**C**	-5.055053	2.863549	0.939349	**C**	2.489557	-2.080764	-1.323729
H	-5.938821	3.683633	0.102528	**H**	-5.850143	3.556655	1.223705	**C**	3.573779	-2.945298	-1.508229
C	-3.799552	3.469709	0.031197	**C**	-3.759380	3.359881	0.756259	**H**	4.459841	-2.580813	-2.029283
H	-3.582066	4.533734	0.055375	**H**	-3.515713	4.409795	0.893356	**C**	3.551846	-4.265035	-1.053391
C	-2.768593	2.532215	-0.021688	**C**	-2.774101	2.441385	0.395986	**H**	4.418829	-4.911707	-1.208764
C	-2.408128	-1.789149	-0.353357	**C**	-2.626959	-1.666332	-0.892881	**C**	2.411389	-4.753128	-0.413223
C	-2.731318	-2.746649	0.638513	**C**	-2.892268	-2.884364	-0.220813	**H**	2.366718	-5.789945	-0.071785
C	-3.665795	-3.736593	0.302985	**C**	-3.952634	-3.670445	-0.694494	**C**	1.323402	-3.911412	-0.207151
H	-3.935440	-4.470969	1.067081	**H**	-4.176422	-4.603298	-0.169705	**C**	-1.526718	0.878665	-0.220909
C	-4.248838	-3.819655	-0.963317	**C**	-4.714987	-3.310930	-1.807730	**C**	-0.321393	1.711790	0.025986
H	-4.965659	-4.613003	-1.185990	**H**	-5.527002	-3.957191	-2.148221	**C**	-0.812385	3.113116	0.018514
C	-3.894744	-2.887462	-1.941383	**C**	-4.416284	-2.127461	-2.486865	**C**	-0.192401	4.332760	0.316715
H	-4.326427	-2.942285	-2.943629	**H**	-4.986771	-1.834367	-3.371428	**H**	0.861601	4.369399	0.584432
C	-2.982963	-1.880576	-1.636006	**C**	-3.384256	-1.313905	-2.028798	**C**	-0.947850	5.506245	0.270997
C	0.682325	1.518318	0.016693	**C**	0.610948	1.431988	-0.236411	**H**	-0.472118	6.461896	0.500729
C	1.710535	0.442536	0.083882	**C**	1.612032	0.347375	-0.384354	**C**	-2.305979	5.468703	-0.071931
C	3.013944	1.147802	0.061636	**C**	2.872428	1.031057	-0.759609	**H**	-2.878069	6.398301	-0.116472
C	4.329320	0.673192	0.018239	**C**	4.144055	0.543734	-1.076467	**C**	-2.954502	4.260956	-0.348254
H	4.536097	-0.394800	0.033865	**H**	4.326066	-0.526568	-1.151126	**H**	-4.011204	4.213918	-0.596457
C	5.373529	1.599418	-0.044265	**C**	5.175415	1.460619	-1.299030	**C**	-2.189825	3.095904	-0.278856
H	6.405838	1.245369	-0.077811	**H**	6.173044	1.097146	-1.553546	**N**	-3.093918	-0.919237	-0.191068
C	5.108505	2.974955	-0.060221	**C**	4.942224	2.838140	-1.197232	**N**	0.315346	-1.643345	-0.454376
H	5.938820	3.683634	-0.102531	**H**	5.762553	3.538013	-1.372327	**N**	-2.619254	1.753830	-0.417600
C	3.799552	3.469709	-0.031203	**C**	3.678275	3.346224	-0.873831	**H**	0.440815	-4.314678	0.268017
H	3.582065	4.533735	-0.055382	**H**	3.486229	4.412172	-0.786196	**C**	-3.928657	1.359572	-0.641008
C	2.768592	2.532216	0.021683	**C**	2.658302	2.420105	-0.663598	**C**	-4.202563	-0.133805	-0.471304
C	2.408128	-1.789147	0.353359	**C**	2.344191	-1.874651	-0.190076	**O**	-4.832078	2.127487	-0.886741
C	2.982962	-1.880570	1.636009	**C**	3.084068	-2.345507	0.921858	**O**	-5.332467	-0.563620	-0.535721
C	3.894741	-2.887455	1.941390	**C**	3.986146	-3.395656	0.696033	**C**	2.494095	-0.688054	-1.922362
H	4.326423	-2.942275	2.943637	**H**	4.574465	-3.760809	1.542506	**H**	1.880919	-0.073885	-1.257605
C	4.248836	-3.819652	0.963329	**C**	4.153011	-3.986670	-0.557869	**C**	1.783709	-0.707555	-3.286995
H	4.965656	-4.613000	1.186005	**H**	4.863486	-4.805957	-0.687323	**H**	0.755649	-1.086442	-3.187865
C	3.665796	-3.736593	-0.302975	**C**	3.393544	-3.528056	-1.636329	**H**	1.734254	0.309650	-3.709140
H	3.935441	-4.470973	-1.067068	**H**	3.496786	-3.985341	-2.623268	**H**	2.318501	-1.349448	-4.006941
C	2.731319	-2.746651	-0.638507	**C**	2.493263	-2.481420	-1.450078	**C**	3.884109	-0.057771	-2.030620
C	-0.763774	4.001806	-0.002531	**C**	-0.763798	3.901451	0.219749	**H**	4.522834	-0.574690	-2.765861
C	0.763773	4.001806	0.002522	**C**	0.728276	3.905047	-0.123643	**H**	3.794971	0.988670	-2.356490
H	-2.692369	-1.145831	-2.389472	**H**	1.881997	-2.113512	-2.276347	**H**	4.404038	-0.055620	-1.060805
C	-2.123401	-2.729425	2.032652	**H**	-3.141347	-0.383967	-2.546778	**N**	0.825255	1.194417	0.260668
H	-2.565321	-3.591728	2.560396	**C**	-2.077596	-3.368097	0.967035	**C**	2.054335	1.817535	0.382971
C	-2.507308	-1.476354	2.836585	**H**	-2.546704	-4.314596	1.285674	**C**	2.974369	1.263926	1.315009
H	-3.596839	-1.315989	2.835351	**C**	-2.132943	-2.415384	2.170973	**C**	2.481390	2.834819	-0.495674
H	-2.179300	-1.579801	3.883518	**H**	-3.172641	-2.174441	2.443625	**C**	4.254542	1.822050	1.394342
H	-2.030073	-0.573020	2.430557	**H**	-1.649388	-2.877181	3.046446	**C**	3.770650	3.353035	-0.412024
C	-0.601427	-2.936049	2.000943	**H**	-1.604828	-1.474915	1.962531	**H**	1.798350	3.186353	-1.270302
H	-0.339442	-3.873559	1.486936	**C**	-0.633099	-3.680068	0.549218	**C**	4.656727	2.861214	0.550634
H	-0.104865	-2.114503	1.469282	**H**	-0.611863	-4.399809	-0.283344	**H**	4.966325	1.421128	2.118185
H	-0.198018	-2.985889	3.025352	**H**	-0.119293	-2.765110	0.229915	**H**	4.087654	4.133990	-1.107406
H	2.692368	-1.145821	2.389471	**H**	-0.070095	-4.116031	1.389224	**H**	5.667656	3.267636	0.628096
C	2.123405	-2.729430	-2.032648	**C**	2.971255	-1.753069	2.321283	**C**	2.530806	0.101703	2.183434
H	2.565329	-3.591733	-2.560389	**H**	3.592200	-2.401347	2.962389	**H**	1.792893	-0.449093	1.579642
C	2.507309	-1.476359	-2.836581	**C**	1.544410	-1.798271	2.886021	**C**	1.799005	0.605041	3.438756
H	3.596840	-1.315991	-2.835347	**H**	0.852574	-1.200864	2.275956	**C**	3.663247	-0.863854	2.541847
H	2.179302	-1.579808	-3.883514	**H**	1.160669	-2.828237	2.909083	**H**	2.476400	1.193585	4.079586
H	2.030071	-0.573027	-2.430554	**H**	1.529290	-1.403618	3.914706	**H**	0.946617	1.247211	3.169374
C	0.601431	-2.936060	-2.000942	**C**	3.569576	-0.339927	2.425269	**H**	1.414383	-0.239268	4.034016
H	0.339450	-3.873570	-1.486934	**H**	4.580470	-0.297516	1.992355	**H**	4.192547	-1.211106	1.640968
H	0.104865	-2.114516	-1.469283	**H**	2.952426	0.405552	1.904952	**H**	4.402035	-0.407935	3.221300
H	0.198025	-2.985903	-3.025352	**H**	3.635468	-0.032825	3.481498	**H**	3.255625	-1.749556	3.054039

Table G55 XYZ coordinates of the GS and TS geometries of **3.16c** B3LYP/Def2SVP (gas phase)

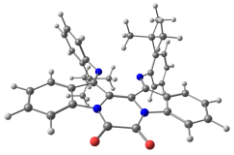
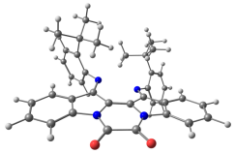
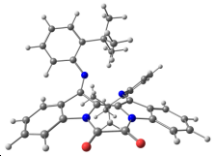
Anti				***Syn***				**TS**			
											
O	1.375408	5.264580	0.080949	**O**	1.286917	5.158985	0.087752	**C**	-0.831663	1.497243	-0.079194
O	-1.375422	5.264576	-0.080956	**O**	-1.413059	5.109897	0.650834	**C**	-1.796497	0.396899	0.245651
N	1.363765	2.973291	0.090574	**N**	1.246620	2.890597	-0.232501	**C**	-2.870971	1.099998	1.014378
N	1.437812	-0.586726	0.147562	**N**	1.304593	-0.647810	-0.409562	**C**	-3.827708	0.698127	1.953367
N	-1.363774	2.973288	-0.090578	**N**	-1.450174	2.858627	0.225561	**H**	-3.859408	-0.326198	2.319895
N	-1.437813	-0.586729	-0.147560	**N**	-1.621382	-0.598906	-0.627514	**C**	-4.712122	1.640471	2.487776
C	0.681020	1.738205	0.048620	**C**	0.553466	1.663464	-0.283223	**H**	-5.455173	1.323624	3.222371
C	1.705302	0.662529	0.155892	**C**	1.555990	0.596669	-0.529636	**C**	-4.645677	2.981067	2.094829
C	3.006781	1.368175	0.217460	**C**	2.838514	1.307591	-0.745255	**H**	-5.357016	3.702497	2.503040
C	4.322820	0.893896	0.240591	**C**	4.124010	0.847549	-1.049898	**C**	-3.649712	3.428473	1.219267
H	4.528314	-0.174351	0.261273	**H**	4.310506	-0.209808	-1.225547	**H**	-3.546269	4.474834	0.944563
C	5.368536	1.820313	0.239158	**C**	5.165320	1.776976	-1.129795	**C**	-2.753274	2.479420	0.732047
H	6.401309	1.466552	0.258708	**H**	6.174075	1.435073	-1.369842	**C**	-2.613370	-1.737326	-0.641918
C	5.104251	3.196042	0.217404	**C**	4.927169	3.138894	-0.905589	**C**	-2.301248	-2.647113	-1.710018
H	5.935412	3.904956	0.223946	**H**	5.754936	3.848769	-0.971209	**C**	-3.268418	-3.605233	-2.045908
C	3.795511	3.690560	0.178846	**C**	3.648488	3.619148	-0.598033	**H**	-3.068068	-4.301542	-2.856813
H	3.579302	4.754683	0.148402	**H**	3.452265	4.672867	-0.420078	**C**	-4.490326	-3.718330	-1.381057
C	2.763395	2.752764	0.171404	**C**	2.619759	2.681305	-0.526521	**H**	-5.203150	-4.489809	-1.681911
C	2.376012	-1.578854	0.441159	**C**	2.278292	-1.628110	-0.641932	**C**	-4.784413	-2.846801	-0.335592
C	2.743996	-2.579646	-0.499128	**C**	2.404227	-2.063489	-1.977862	**H**	-5.731640	-2.915375	0.204216
C	3.637743	-3.565621	-0.051886	**C**	3.328429	-3.036108	-2.337149	**C**	-3.855242	-1.875526	0.016499
H	3.961510	-4.340743	-0.744334	**H**	3.413257	-3.350290	-3.380077	**C**	0.485848	1.557605	-0.416360
C	4.131546	-3.606983	1.254212	**C**	4.141559	-3.599203	-1.350657	**C**	1.605813	0.599084	-0.249518
H	4.817168	-4.403931	1.550469	**H**	4.883009	-4.359418	-1.605729	**C**	2.823300	1.356224	-0.643483
C	3.733247	-2.635327	2.172244	**C**	3.990270	-3.191082	-0.027690	**C**	4.187902	1.039853	-0.626377
H	4.094252	-2.657490	3.203199	**H**	4.632946	-3.648451	0.725957	**H**	4.526577	0.053651	-0.318878
C	2.864004	-1.630082	1.762570	**C**	3.056358	-2.220112	0.383191	**C**	5.115862	2.011033	-1.009136
C	-0.681026	1.738204	-0.048623	**C**	-0.796331	1.649828	-0.097017	**H**	6.180513	1.768568	-1.000648
C	-1.705305	0.662525	-0.155894	**C**	-1.843046	0.600660	-0.239791	**C**	4.694880	3.285888	-1.407914
C	-3.006786	1.368168	-0.217463	**C**	-3.112118	1.270897	0.138475	**H**	5.434491	4.028712	-1.715538
C	-4.322824	0.893885	-0.240595	**C**	-4.410202	0.778880	0.314871	**C**	3.341034	3.635803	-1.411643
H	-4.528315	-0.174362	-0.261276	**H**	-4.639786	-0.267662	0.125749	**H**	2.998402	4.625767	-1.699871
C	-5.368542	1.820300	-0.239164	**C**	-5.409161	1.658800	0.738586	**C**	2.428450	2.659441	-1.012451
H	-6.401314	1.466536	-0.258714	**H**	-6.426784	1.289276	0.880212	**N**	-1.560263	2.703927	0.001246
C	-5.104260	3.196030	-0.217411	**C**	-5.119207	3.008640	0.977084	**N**	-1.699859	-0.723302	-0.376143
H	-5.935423	3.904942	-0.223955	**H**	-5.916132	3.682874	1.299185	**N**	1.028439	2.788328	-0.847174
C	-3.795521	3.690550	-0.178853	**C**	-3.824914	3.517683	0.822163	**H**	-4.104613	-1.196624	0.817197
H	-3.579315	4.754675	-0.148409	**H**	-3.584357	4.558857	1.017903	**C**	0.313721	3.966969	-0.992636
C	-2.763404	2.752757	-0.171409	**C**	-2.836924	2.623411	0.411236	**C**	-1.114201	3.938378	-0.446171
C	-2.376010	-1.578860	-0.441155	**C**	-2.667681	-1.454766	-0.993836	**O**	0.780487	4.988734	-1.444017
C	-2.864006	-1.630089	-1.762565	**C**	-3.415970	-1.099185	-2.134620	**O**	-1.773599	4.951759	-0.387047
C	-3.733246	-2.635338	-2.172237	**C**	-4.449290	-1.903880	-2.602015	**C**	-0.953296	-2.640417	-2.453622
H	-4.094254	-2.657501	-3.203191	**H**	-5.013240	-1.607500	-3.489592	**C**	-0.645946	-1.262904	-3.083238
C	-4.131539	-3.606995	-1.254204	**C**	-4.754179	-3.082527	-1.921450	**C**	-0.914117	-3.671388	-3.597537
H	-4.817158	-4.403946	-1.550459	**H**	-5.567868	-3.726821	-2.261838	**C**	0.138250	-3.027047	-1.438616
C	-3.637733	-3.565633	0.051893	**C**	-3.999565	-3.448715	-0.804342	**H**	-0.548666	-0.486041	-2.318687
H	-3.961494	-4.340756	0.744341	**H**	-4.252543	-4.380275	-0.301067	**H**	0.296884	-1.319281	-3.651406
C	-2.743988	-2.579654	0.499133	**C**	-2.933331	-2.676248	-0.316550	**H**	-1.443593	-0.967730	-3.784113
C	0.762271	4.221934	0.046867	**C**	0.670744	4.118055	0.056355	**H**	-1.678407	-3.472455	-4.365082
C	-0.762283	4.221932	-0.046872	**C**	-0.830271	4.093321	0.348969	**H**	0.069356	-3.619237	-4.088479
H	2.532492	-0.862537	2.464532	**H**	-3.163273	-0.168861	-2.647039	**H**	-1.042429	-4.703082	-3.236791
C	2.212079	-2.576284	-1.944144	**C**	-2.094399	-3.141831	0.886708	**H**	-0.070615	-4.016022	-1.000789
C	2.748311	-3.768320	-2.754947	**C**	-2.592404	-4.483510	1.449858	**H**	1.119697	-3.079311	-1.932901
H	2.457160	-4.731933	-2.309873	**H**	-2.544406	-5.288466	0.700931	**H**	0.194761	-2.290294	-0.631986
H	2.326448	-3.733322	-3.770924	**H**	-1.951070	-4.780800	2.293532	**N**	1.433538	-0.545465	0.300110
H	3.845136	-3.747835	-2.850988	**H**	-3.625964	-4.419819	1.824994	**C**	2.424022	-1.501525	0.512213
C	2.658954	-1.287897	-2.669527	**C**	-2.159765	-2.109182	2.032942	**C**	2.547759	-2.124334	1.786686
H	2.232603	-0.386829	-2.212310	**H**	-1.706580	-1.151778	1.750979	**C**	3.209739	-1.946142	-0.569170
H	3.756213	-1.191236	-2.659987	**H**	-3.201744	-1.922983	2.338447	**C**	3.525893	-3.122805	1.912238
H	2.329044	-1.313450	-3.720672	**H**	-1.611443	-2.487625	2.910564	**C**	4.149019	-2.959891	-0.414405
H	-2.532498	-0.862544	-2.464528	**C**	-0.634611	-3.326853	0.424485	**H**	3.047806	-1.489653	-1.546837
C	-2.212067	-2.576291	1.944148	**H**	-0.218771	-2.389697	0.038142	**C**	4.319533	-3.542256	0.841830
C	-2.748287	-3.768334	2.754948	**H**	-0.009775	-3.663457	1.266909	**H**	3.672001	-3.607874	2.875682
H	-2.457124	-4.731942	2.309873	**H**	-0.572380	-4.089881	-0.366814	**H**	4.739402	-3.293963	-1.270875
H	-2.326425	-3.733333	3.770925	**H**	1.754576	-1.604211	-2.725088	**H**	5.056942	-4.334188	0.990896
H	-3.845111	-3.747862	2.850989	**C**	3.015858	-1.867771	1.889711	**C**	1.640830	-1.739870	2.971908
C	-2.658953	-1.287910	2.669533	**C**	2.845195	-3.170096	2.705445	**C**	1.756442	-0.232587	3.287722
H	-2.232625	-0.386836	2.212307	**H**	1.893017	-3.662391	2.456212	**C**	0.176247	-2.094900	2.626297
H	-3.756213	-1.191268	2.660010	**H**	3.653744	-3.892085	2.525365	**C**	2.020252	-2.505058	4.251814
H	-2.329026	-1.313454	3.720674	**H**	2.840109	-2.941191	3.782771	**H**	1.178906	0.005504	4.195589
C	-0.671702	-2.667195	1.928984	**C**	1.875103	-0.925591	2.319785	**H**	2.805149	0.052740	3.467933
H	-0.223975	-1.836344	1.373263	**H**	0.894715	-1.267406	1.965485	**H**	1.365357	0.386132	2.471466
H	-0.281059	-2.651874	2.959455	**H**	1.849413	-0.888011	3.420223	**H**	-0.161286	-1.563380	1.729323
H	-0.341666	-3.605533	1.456660	**H**	2.028358	0.101874	1.966693	**H**	0.072420	-3.176503	2.447953
C	0.671715	-2.667202	-1.928983	**C**	4.352817	-1.195182	2.272080	**H**	-0.484370	-1.822480	3.465979
H	0.281072	-2.651879	-2.959454	**H**	4.359722	-0.938051	3.343921	**H**	1.918826	-3.593942	4.128909
H	0.341686	-3.605546	-1.456664	**H**	5.212750	-1.853523	2.077166	**H**	3.050644	-2.287113	4.573544
H	0.223981	-1.836358	-1.373258	**H**	4.501056	-0.267740	1.697503	**H**	1.346438	-2.202728	5.067873

Table G56 XYZ coordinates of the GS and TS geometries of **3.16d** B3LYP/Def2SVP (gas phase)

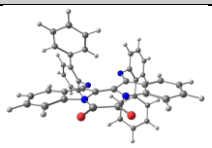
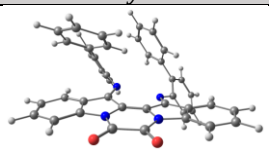
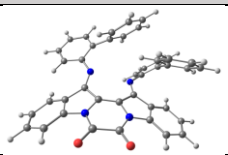
Anti				***Syn***				**TS**			
											
O	-1.348953	-4.931613	-0.298404	**O**	1.555279	4.938652	-0.437200	**C**	0.770561	0.484248	0.649648
O	1.348989	-4.931599	0.298421	**O**	-1.065223	5.227415	0.381173	**C**	2.114726	-0.115488	0.386003
N	-1.315962	-2.641881	-0.379669	**N**	1.203664	2.694418	-0.734377	**C**	3.025593	1.079610	0.402354
N	-1.220953	0.883904	-0.767265	**N**	0.782240	-0.822892	-0.874158	**C**	4.290347	1.370322	-0.126873
N	1.315979	-2.641868	0.379672	**N**	-1.416254	2.994131	0.010047	**H**	4.807499	0.662471	-0.768843
N	1.220939	0.883921	0.767244	**N**	-2.018966	-0.437958	-0.684775	**C**	4.876052	2.617513	0.109748
C	-0.641776	-1.415138	-0.225898	**C**	0.361518	1.564414	-0.708942	**H**	5.859842	2.835139	-0.311086
C	-1.582104	-0.331747	-0.607901	**C**	1.200023	0.375762	-1.006498	**C**	4.212661	3.584035	0.872052
C	-2.874014	-1.010600	-0.850042	**C**	2.535291	0.918267	-1.335699	**H**	4.692771	4.544610	1.071695
C	-4.132316	-0.523740	-1.217097	**C**	3.702485	0.298040	-1.786180	**C**	2.917077	3.357480	1.346868
H	-4.305390	0.545559	-1.320719	**H**	3.728054	-0.778415	-1.951408	**H**	2.358475	4.114195	1.891207
C	-5.164719	-1.437356	-1.444529	**C**	4.833396	1.085620	-2.013171	**C**	2.334052	2.124240	1.058836
H	-6.154649	-1.072464	-1.725744	**H**	5.755803	0.618663	-2.364443	**C**	3.358851	-2.219264	0.215899
C	-4.942786	-2.814202	-1.312261	**C**	4.796782	2.467819	-1.785074	**C**	3.108633	-3.626722	0.184512
H	-5.764008	-3.512111	-1.491045	**H**	5.694629	3.065725	-1.957883	**C**	4.158107	-4.497287	-0.154701
C	-3.687884	-3.324038	-0.958124	**C**	3.632559	3.109868	-1.346311	**H**	3.950276	-5.568353	-0.191653
H	-3.501116	-4.390005	-0.859921	**H**	3.590751	4.182134	-1.175496	**C**	5.456368	-4.039515	-0.367566
C	-2.669268	-2.400139	-0.733518	**C**	2.509336	2.310869	-1.139840	**H**	6.252594	-4.744028	-0.618709
C	-2.100613	1.939439	-0.982117	**C**	1.566690	-1.963641	-0.846787	**C**	5.735274	-2.681147	-0.194248
C	-3.023899	2.349276	0.019214	**C**	2.588843	-2.156758	0.126685	**H**	6.758277	-2.308255	-0.284865
C	-3.851816	3.448277	-0.258316	**C**	3.273030	-3.381384	0.130237	**C**	4.702660	-1.796151	0.092749
H	-4.551239	3.778638	0.512941	**H**	4.041921	-3.542445	0.889423	**C**	-0.501346	0.137717	0.301144
C	-3.784720	4.135234	-1.471432	**C**	2.983488	-4.393457	-0.786405	**C**	-1.065488	-0.950999	-0.535922
H	-4.440829	4.989141	-1.652955	**H**	3.535715	-5.335155	-0.753590	**C**	-2.463002	-0.543690	-0.804640
C	-2.856023	3.737316	-2.437244	**C**	1.970010	-4.197393	-1.729268	**C**	-3.442576	-1.070326	-1.650065
H	-2.782137	4.273262	-3.386408	**H**	1.722477	-4.984662	-2.445424	**H**	-3.230514	-1.942524	-2.266217
C	-2.009234	2.659897	-2.185941	**C**	1.255035	-3.003152	-1.742586	**C**	-4.696492	-0.457249	-1.689752
C	0.641782	-1.415131	0.225897	**C**	-0.948661	1.718002	-0.365765	**H**	-5.472818	-0.858484	-2.344332
C	1.582098	-0.331731	0.607902	**C**	-2.102047	0.784678	-0.326653	**C**	-4.970867	0.657164	-0.886435
C	2.874011	-1.010572	0.850059	**C**	-3.232350	1.591030	0.192742	**H**	-5.963447	1.112519	-0.917278
C	4.132303	-0.523700	1.217131	**C**	-4.541005	1.245431	0.543732	**C**	-3.998284	1.212877	-0.047273
H	4.305366	0.545600	1.320755	**H**	-4.897461	0.224129	0.417733	**H**	-4.194622	2.084911	0.570540
C	5.164713	-1.437307	1.444575	**C**	-5.382216	2.236754	1.055825	**C**	-2.744063	0.604509	-0.042271
H	6.154635	-1.072406	1.725803	**H**	-6.407059	1.983504	1.334811	**N**	0.981351	1.747868	1.240518
C	4.942795	-2.814154	1.312303	**C**	-4.924353	3.552436	1.209153	**N**	2.256935	-1.392797	0.367527
H	5.764022	-3.512055	1.491096	**H**	-5.599679	4.315251	1.603443	**N**	-1.563044	1.012009	0.628288
C	3.687902	-3.324002	0.958150	**C**	-3.614549	3.916721	0.876081	**H**	4.943661	-0.754518	0.250497
H	3.501145	-4.389971	0.859944	**H**	-3.244477	4.930621	1.002162	**C**	-1.448076	2.145949	1.414678
C	2.669280	-2.400112	0.733533	**C**	-2.783961	2.913516	0.377961	**C**	-0.016288	2.577826	1.731899
C	2.100591	1.939464	0.982091	**C**	-3.061895	-1.330520	-0.866305	**O**	-2.389208	2.821849	1.765835
C	3.023884	2.349290	-0.019239	**C**	-2.979420	-2.617193	-0.272226	**O**	0.201069	3.620683	2.306699
C	3.851793	3.448300	0.258283	**C**	-3.953064	-3.571891	-0.597258	**C**	1.843156	-4.252794	0.639962
H	4.551222	3.778652	-0.512973	**H**	-3.894786	-4.554933	-0.123990	**C**	1.242670	-5.289247	-0.091074
C	3.784681	4.135276	1.471387	**C**	-4.987251	-3.287542	-1.491131	**C**	1.347222	-3.959573	1.923187
H	4.440783	4.989189	1.652903	**H**	-5.732195	-4.050235	-1.727875	**C**	0.180218	-6.019328	0.445447
C	2.855977	3.737368	2.437196	**C**	-5.058850	-2.021004	-2.080166	**H**	1.605816	-5.519424	-1.093865
H	2.782079	4.273328	3.386351	**H**	-5.855790	-1.787657	-2.790504	**C**	0.304722	-4.707235	2.468165
C	2.009196	2.659940	2.185902	**C**	-4.108439	-1.051500	-1.769995	**H**	1.811901	-3.160890	2.503446
C	-0.744179	-3.890086	-0.183206	**C**	0.814154	3.982567	-0.402273	**C**	-0.284882	-5.739098	1.731129
C	0.744206	-3.890079	0.183216	**C**	-0.643781	4.145824	0.038797	**H**	-0.285600	-6.807469	-0.148693
H	1.273837	2.341245	2.926896	**H**	-4.142415	-0.070169	-2.247309	**H**	-0.060285	-4.477246	3.471936
H	-1.273880	2.341195	-2.926937	**H**	0.441117	-2.838678	-2.450225	**H**	-1.113729	-6.310656	2.154197
C	3.135719	1.638124	-1.319446	**C**	-1.886497	-2.942188	0.677157	**N**	-0.399627	-1.989190	-0.868454
C	4.399839	1.308817	-1.837864	**C**	-1.074406	-4.068336	0.469782	**C**	-0.888716	-3.122018	-1.500537
C	1.993657	1.279119	-2.060079	**C**	-1.649613	-2.143165	1.808815	**C**	-0.168637	-3.573264	-2.624551
C	4.523534	0.637714	-3.056479	**C**	-0.043690	-4.380162	1.358284	**C**	-1.978823	-3.901157	-1.012032
H	5.295699	1.561122	-1.266065	**H**	-1.234298	-4.684847	-0.417065	**C**	-0.530294	-4.733660	-3.300581
C	2.119382	0.608400	-3.276323	**C**	-0.633019	-2.465655	2.707799	**H**	0.685702	-2.976123	-2.947452
H	1.001545	1.507869	-1.668783	**H**	-2.282937	-1.272638	1.991780	**C**	-2.299977	-5.082024	-1.702447
C	3.383079	0.282523	-3.780224	**C**	0.180371	-3.580029	2.479874	**C**	-1.603037	-5.500033	-2.835345
H	5.515961	0.382758	-3.436171	**H**	0.600894	-5.238559	1.159682	**H**	0.037240	-5.050155	-4.179002
H	1.219992	0.336871	-3.835191	**H**	-0.466491	-1.839830	3.587690	**H**	-3.111437	-5.701175	-1.314267
H	3.477609	-0.248000	-4.730739	**H**	0.993303	-3.815755	3.170163	**H**	-1.884395	-6.426987	-3.339727
C	-3.135718	1.638131	1.319434	**C**	2.948816	-1.100828	1.108062	**C**	-2.783821	-3.522963	0.178044
C	-4.399832	1.308832	1.837873	**C**	4.296800	-0.765049	1.318817	**C**	-4.182019	-3.670264	0.152011
C	-1.993647	1.279141	2.060061	**C**	1.966697	-0.390770	1.821903	**C**	-2.198345	-2.995472	1.341835
C	-4.523512	0.637753	3.056503	**C**	4.653578	0.260218	2.197279	**C**	-4.969132	-3.290802	1.240811
H	-5.295698	1.561126	1.266080	**H**	5.072211	-1.291296	0.758087	**H**	-4.663627	-4.054311	-0.749596
C	-2.119357	0.608446	3.276320	**C**	2.322039	0.634028	2.698157	**C**	-2.982597	-2.614939	2.429443
H	-1.001540	1.507886	1.668750	**H**	0.918558	-0.647123	1.678181	**H**	-1.118937	-2.885919	1.392660
C	-3.383047	0.282577	3.780242	**C**	3.667080	0.969940	2.885452	**C**	-4.373347	-2.754358	2.384022
H	-5.515934	0.382804	3.436212	**H**	5.707480	0.514818	2.332773	**H**	-6.054881	-3.401988	1.188271
H	-1.219960	0.336929	3.835182	**H**	1.542320	1.173854	3.241686	**H**	-2.501673	-2.207738	3.322435
H	-3.477566	-0.247927	4.730768	**H**	3.943403	1.780131	3.564268	**H**	-4.987209	-2.446146	3.233558

Table G57 XYZ coordinates of the GS and TS geometries of **3.16e** B3LYP/Def2SVP (gas phase)

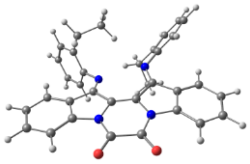
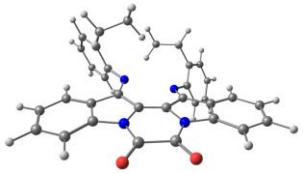
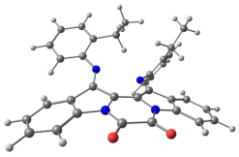
Anti				***Syn***				**TS**			
											
O	1.071710	5.011736	0.243943	**O**	1.268820	4.910503	-0.134997	**C**	-1.492704	-0.898701	0.042601
O	-1.671233	4.876212	-0.030370	**O**	-1.448837	4.864590	0.335814	**C**	-2.034963	0.482893	-0.187674
N	1.432944	-0.797929	-0.292270	**N**	1.382468	-0.927515	-0.178557	**C**	-3.485049	0.243828	-0.487519
N	1.184204	2.726791	0.113554	**N**	1.274032	2.622209	-0.248029	**C**	-4.506683	0.981916	-1.099661
N	-1.409188	-0.949033	0.227434	**N**	-1.516853	-0.935422	-0.418097	**H**	-4.309483	1.933299	-1.583343
N	-1.545290	2.588409	-0.035646	**N**	-1.435925	2.582855	0.124502	**C**	-5.801031	0.459130	-1.176140
C	0.953796	-2.735110	2.247471	**C**	1.588354	-1.552674	2.942124	**H**	-6.586090	1.044435	-1.659199
C	2.379691	-2.197373	2.064051	**C**	2.934056	-1.305766	2.247400	**C**	-6.091637	-0.803052	-0.652076
C	-1.450283	-2.504638	-2.706453	**C**	-0.424980	-3.931351	0.880843	**H**	-7.110974	-1.192566	-0.699463
C	-0.998687	-3.204434	-1.417782	**C**	-1.714984	-3.232162	1.329113	**C**	-5.081634	-1.599928	-0.104024
C	0.516018	3.941411	0.143730	**C**	0.669332	3.860172	-0.094027	**H**	-5.272643	-2.604590	0.262042
C	-1.007300	3.865761	0.016556	**C**	-0.840603	3.835451	0.148514	**C**	-3.791961	-1.071826	-0.071066
C	2.953488	-2.016997	-1.722037	**C**	2.550190	-2.722811	-1.297510	**C**	-1.506699	2.869518	0.162960
C	3.937142	-2.989212	-1.904365	**C**	3.494041	-3.749998	-1.291525	**C**	-0.446035	3.617527	0.769535
C	4.428144	-3.698587	-0.806392	**C**	4.258013	-3.988654	-0.147289	**C**	-0.576292	5.005413	0.882468
C	3.920747	-3.428307	0.467758	**C**	4.066387	-3.191137	0.984651	**H**	0.231601	5.579957	1.336136
C	2.936480	-2.456225	0.683825	**C**	3.137611	-2.144197	1.005879	**C**	-1.712323	5.680096	0.430539
C	2.460963	-1.735128	-0.437146	**C**	2.378755	-1.908220	-0.167227	**H**	-1.778575	6.766307	0.529325
C	2.593653	2.568804	0.167941	**C**	2.660989	2.413753	-0.466203	**C**	-2.756051	4.957158	-0.146632
C	3.577752	3.548106	0.292116	**C**	3.675836	3.359800	-0.601858	**H**	-3.655250	5.465321	-0.502544
C	4.908033	3.112367	0.325818	**C**	4.970059	2.875896	-0.828170	**C**	-2.648204	3.575824	-0.274550
C	5.238952	1.754129	0.237481	**C**	5.236654	1.503418	-0.916534	**C**	-0.244390	-1.450776	0.010569
C	4.240883	0.784028	0.107564	**C**	4.209220	0.566896	-0.771849	**C**	1.098097	-0.944092	-0.383137
C	2.905906	1.199322	0.073807	**C**	2.910382	1.030616	-0.540481	**C**	1.972534	-2.140499	-0.412782
C	1.640584	0.440680	-0.066419	**C**	1.629948	0.315196	-0.329118	**C**	3.305993	-2.310439	-0.801791
C	0.562993	1.462782	0.027440	**C**	0.600979	1.382452	-0.218508	**H**	3.890498	-1.467356	-1.165747
C	-2.047765	-3.199851	-0.335454	**C**	-2.654710	-3.008001	0.169108	**C**	3.873152	-3.583697	-0.712451
C	-2.851298	-4.315846	-0.077141	**C**	-3.650433	-3.942783	-0.141128	**H**	4.912594	-3.732956	-1.011563
C	-3.810282	-4.310933	0.939455	**C**	-4.477238	-3.799527	-1.258170	**C**	3.121480	-4.668178	-0.240214
C	-3.978548	-3.166342	1.724875	**C**	-4.309080	-2.696274	-2.099563	**H**	3.584911	-5.654960	-0.169420
C	-3.211289	-2.031246	1.472564	**C**	-3.340071	-1.739839	-1.804266	**C**	1.782617	-4.522503	0.138917
C	-2.260512	-2.029033	0.433782	**C**	-2.519350	-1.877082	-0.668549	**H**	1.187828	-5.357477	0.498339
C	-2.924855	2.286814	-0.178896	**C**	-2.821884	2.337214	0.306080	**C**	1.226956	-3.247107	0.030455
C	-3.994658	3.164761	-0.349483	**C**	-3.835703	3.247669	0.602248	**N**	-2.595353	-1.745749	0.274440
C	-5.260630	2.597569	-0.534458	**C**	-5.123771	2.730186	0.780069	**N**	-1.304022	1.501888	0.082771
C	-5.445886	1.208751	-0.554763	**C**	-5.383189	1.357623	0.673415	**N**	-0.103934	-2.834975	0.282985
C	-4.365697	0.343120	-0.365455	**C**	-4.358121	0.460007	0.363904	**H**	-3.470218	3.037034	-0.718648
C	-3.094172	0.889087	-0.162914	**C**	-3.065552	0.958267	0.167346	**C**	-1.121916	-3.679191	0.691133
C	-1.763509	0.262573	0.033208	**C**	-1.776827	0.282767	-0.129921	**C**	-2.522268	-3.075625	0.664854
C	-0.797731	1.393473	0.003652	**C**	-0.753566	1.363613	-0.071442	**O**	-0.956396	-4.840252	0.993317
H	0.594487	-2.552342	3.272836	**H**	1.474942	-0.899692	3.821990	**O**	-3.489998	-3.755248	0.922922
H	0.916935	-3.819962	2.061577	**H**	1.506643	-2.597456	3.279452	**C**	0.774588	2.903496	1.296123
H	0.260860	-2.244095	1.551101	**H**	0.751956	-1.355780	2.255513	**H**	0.491768	2.396463	2.237926
H	-0.717732	-4.245654	-1.642890	**H**	-2.225132	-3.839375	2.094807	**H**	0.996395	2.087939	0.600238
H	-0.103903	-2.691159	-1.035568	**H**	-1.461959	-2.271552	1.803097	**C**	2.008385	3.770591	1.529453
H	2.387051	-1.113473	2.271005	**H**	3.019194	-0.236143	1.992665	**H**	1.854098	4.526904	2.315744
H	3.052983	-2.655298	2.806364	**H**	3.756936	-1.513218	2.949728	**H**	2.857305	3.146807	1.841056
H	-2.337832	-2.993556	-3.139463	**H**	-0.648099	-4.909655	0.426691	**H**	2.308821	4.294837	0.608398
H	-0.648448	-2.520236	-3.461918	**H**	0.257658	-4.093609	1.728712	**N**	1.360155	0.279354	-0.640491
H	-1.707219	-1.451471	-2.513931	**H**	0.102115	-3.319509	0.137426	**C**	2.637103	0.765788	-0.934809
H	4.317485	-3.191409	-2.908586	**H**	3.624842	-4.368892	-2.182453	**C**	2.869854	1.278198	-2.221442
H	5.197279	-4.462463	-0.939476	**H**	4.994535	-4.794888	-0.131246	**C**	3.641381	0.865063	0.066251
H	4.299355	-3.985180	1.329580	**H**	4.658397	-3.380025	1.884653	**C**	4.102328	1.839254	-2.552776
H	3.310012	4.598893	0.360487	**H**	3.457383	4.422038	-0.535426	**H**	2.063324	1.218381	-2.954532
H	5.703040	3.855152	0.424450	**H**	5.787651	3.591677	-0.940680	**C**	4.859228	1.455592	-0.292450
H	6.286579	1.448111	0.268447	**H**	6.256814	1.159925	-1.099344	**C**	5.103412	1.929964	-1.584794
H	4.496909	-0.271365	0.035737	**H**	4.414950	-0.499811	-0.839137	**H**	4.272889	2.215971	-3.564111
H	-2.704076	-5.217030	-0.678903	**H**	-3.771736	-4.810410	0.513808	**H**	5.645148	1.548825	0.458212
H	-4.411614	-5.202814	1.129463	**H**	-5.240887	-4.549657	-1.475251	**H**	6.069203	2.379013	-1.826795
H	-4.705958	-3.158254	2.540209	**H**	-4.936161	-2.575871	-2.986268	**C**	3.382426	0.339784	1.464287
H	-3.835617	4.239603	-0.346814	**H**	-3.619246	4.308189	0.695546	**H**	2.385586	0.681523	1.785756
H	-6.119406	3.258230	-0.673796	**H**	-5.940340	3.416966	1.014566	**H**	3.302726	-0.759481	1.424939
H	-6.444398	0.797218	-0.715585	**H**	-6.396982	0.983412	0.829593	**C**	4.417795	0.708763	2.523692
H	-4.511151	-0.735642	-0.375028	**H**	-4.563260	-0.605063	0.277943	**H**	4.108939	0.323084	3.507140
H	-3.326097	-1.136223	2.087056	**H**	-3.203063	-0.869437	-2.449106	**H**	5.406677	0.279108	2.299177
H	2.555214	-1.456477	-2.570064	**H**	1.932461	-2.530910	-2.176659	**H**	4.541235	1.799455	2.616010

Table G58 XYZ coordinates of the GS and TS geometries of **3.16a** B3LYP/Def2TZVPP (gas phase)

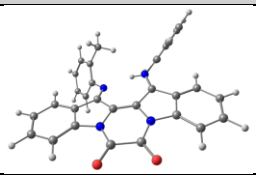
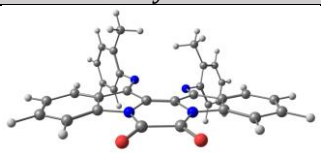
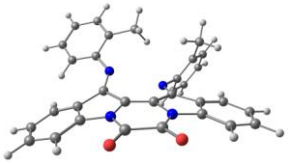
Anti				***Syn***				**TS**			
											
O	-1.365949	-4.802655	0.194156	**O**	-1.390547	4.736221	0.163758	**C**	1.104589	-1.019416	-0.023000
O	1.365885	-4.802671	-0.194145	**O**	1.338106	4.752882	-0.096217	**C**	1.884301	0.239476	0.161400
N	-1.357189	-2.519611	0.133947	**N**	-1.377440	2.455308	0.069811	**C**	3.235596	-0.241538	0.576700
N	-1.418193	0.999474	-0.223431	**N**	-1.444406	-1.070109	-0.285891	**C**	4.333402	0.338251	1.206900
N	1.357151	-2.519628	-0.133943	**N**	1.340260	2.469951	-0.125616	**H**	4.294812	1.339551	1.595600
N	1.418200	0.999456	0.223434	**N**	1.424804	-1.065198	0.033780	**C**	5.487795	-0.407461	1.418100
C	-0.675182	-1.291969	0.040255	**C**	-0.690674	1.230824	-0.030169	**H**	6.331899	0.052131	1.912700
C	-1.696141	-0.217689	0.013068	**C**	-1.714305	0.155585	-0.087077	**C**	5.559381	-1.733761	1.010400
C	-2.983053	-0.905512	0.251279	**C**	-3.008605	0.844115	0.091773	**H**	6.468976	-2.297571	1.164200
C	-4.269939	-0.418685	0.451444	**C**	-4.305289	0.355553	0.211750	**C**	4.457775	-2.365850	0.442400
H	-4.467583	0.640695	0.427010	**H**	-4.506230	-0.701988	0.163219	**H**	4.478764	-3.405050	0.165500
C	-5.297906	-1.325256	0.680087	**C**	-5.344859	1.259519	0.397764	**C**	3.307283	-1.613139	0.271500
H	-6.303795	-0.962728	0.838817	**H**	-6.358239	0.895228	0.493405	**C**	1.843925	2.624476	-0.428100
C	-5.044903	-2.695211	0.701280	**C**	-5.092188	2.628010	0.458780	**C**	0.991234	3.473585	-1.183600
H	-5.859322	-3.385703	0.872352	**H**	-5.913311	3.317925	0.598335	**C**	1.389947	4.781481	-1.437500
C	-3.761748	-3.202751	0.515325	**C**	-3.799321	3.135456	0.350731	**H**	0.736654	5.418488	-2.019500
H	-3.557560	-4.258678	0.542700	**H**	-3.605049	4.191682	0.408369	**C**	2.593752	5.285469	-0.964800
C	-2.745643	-2.284099	0.301856	**C**	-2.773379	2.220409	0.173714	**H**	2.873563	6.309366	-1.172200
C	-2.356549	2.010362	-0.413883	**C**	-2.417851	-2.057884	-0.464779	**C**	3.432544	4.461660	-0.226500
C	-2.315664	3.130145	0.436552	**C**	-3.102959	-2.158617	-1.678253	**H**	4.375948	4.834051	0.149200
C	-3.198083	4.176893	0.186369	**C**	-4.012392	-3.186283	-1.885836	**C**	3.060931	3.153864	0.031200
H	-3.182384	5.037175	0.843677	**H**	-4.537602	-3.254047	-2.829502	**C**	-0.217014	-1.306703	-0.071500
C	-4.079270	4.148784	-0.888393	**C**	-4.244760	-4.120528	-0.882745	**C**	-1.441306	-0.523890	0.214900
H	-4.744425	4.982612	-1.065695	**H**	-4.953436	-4.923312	-1.035939	**C**	-2.551216	-1.495079	0.120900
C	-4.085575	3.051785	-1.742195	**C**	-3.549320	-4.024265	0.318450	**C**	-3.913715	-1.372065	0.374500
H	-4.752324	3.025244	-2.593532	**H**	-3.722311	-4.755182	1.098780	**H**	-4.334505	-0.426261	0.674900
C	-3.231004	1.986653	-1.505062	**C**	-2.622915	-3.010154	0.548836	**C**	-4.724426	-2.491757	0.238100
C	0.675158	-1.291977	-0.040258	**C**	0.660945	1.238423	-0.091435	**H**	-5.784826	-2.409246	0.430900
C	1.696130	-0.217710	-0.013069	**C**	1.687701	0.167295	-0.126934	**C**	-4.183539	-3.716663	-0.146800
C	2.983032	-0.905546	-0.251283	**C**	2.978382	0.870463	-0.267734	**H**	-4.831247	-4.575556	-0.256900
C	4.269922	-0.418733	-0.451459	**C**	4.283813	0.398196	-0.355761	**C**	-2.820840	-3.867476	-0.385700
H	4.467576	0.640646	-0.427032	**H**	4.490820	-0.659067	-0.374257	**H**	-2.394050	-4.813081	-0.670500
C	5.297879	-1.325315	-0.680103	**C**	5.323756	1.318323	-0.424982	**C**	-2.024029	-2.742585	-0.232300
H	6.303770	-0.962798	-0.838840	**H**	6.343457	0.966514	-0.497291	**N**	2.030078	-2.071426	-0.129300
C	5.044862	-2.695267	-0.701286	**C**	5.063020	2.686273	-0.403675	**N**	1.372412	1.337581	-0.243700
H	5.859273	-3.385769	-0.872359	**H**	5.883885	3.388237	-0.460134	**N**	-0.617528	-2.634099	-0.340800
C	3.761703	-3.202794	-0.515324	**C**	3.763164	3.178495	-0.308391	**H**	3.728525	2.537857	0.594600
H	3.557504	-4.258719	-0.542694	**H**	3.564402	4.235235	-0.286211	**C**	0.235962	-3.679707	-0.625300
C	2.745607	-2.284131	-0.301855	**C**	2.737673	2.248642	-0.241104	**C**	1.720365	-3.374922	-0.469200
C	2.356575	2.010326	0.413888	**C**	2.386053	-2.077858	-0.029692	**O**	-0.137850	-4.789104	-0.928700
C	2.315728	3.130100	-0.436560	**C**	2.849633	-2.663366	1.161368	**O**	2.547156	-4.245931	-0.605600
C	3.198164	4.176832	-0.186375	**C**	3.752689	-3.719346	1.064884	**C**	-0.325171	2.990598	-1.710300
H	3.182496	5.037106	-0.843694	**H**	4.123162	-4.169645	1.977610	**H**	-0.700364	3.665302	-2.478700
C	4.079330	4.148719	0.888405	**C**	4.182411	-4.203998	-0.166328	**H**	-0.243581	1.988097	-2.121500
H	4.744499	4.982536	1.065709	**H**	4.881123	-5.028608	-0.210449	**H**	-1.061271	2.943806	-0.909700
C	4.085596	3.051731	1.742221	**C**	3.697523	-3.629231	-1.335825	**N**	-1.427394	0.705909	0.542400
H	4.752328	3.025188	2.593572	**H**	4.014531	-4.001695	-2.301087	**C**	-2.565986	1.480421	0.756800
C	3.231008	1.986613	1.505084	**C**	2.801355	-2.571423	-1.268791	**C**	-2.718780	2.063222	2.021300
C	-0.757356	-3.763319	0.095410	**C**	-0.779433	3.691249	0.071850	**C**	-3.474183	1.800630	-0.273800
C	0.757304	-3.763328	-0.095402	**C**	0.734487	3.700210	-0.059407	**C**	-3.786872	2.899133	2.296000
H	3.221491	1.130334	2.165487	**H**	2.414305	-2.116085	-2.170432	**H**	-1.983783	1.834415	2.780300
H	-3.221518	1.130365	-2.165453	**H**	-2.913922	-1.424676	-2.450107	**C**	-4.521774	2.671441	0.025100
C	1.351681	3.162331	-1.586438	**C**	2.394926	-2.133273	2.489679	**C**	-4.697769	3.209243	1.291800
H	1.654372	2.472795	-2.378417	**H**	2.777897	-1.125901	2.670710	**H**	-3.898768	3.320334	3.285900
H	0.358991	2.846881	-1.265974	**H**	1.305841	-2.067441	2.533175	**H**	-5.217172	2.928548	-0.764500
H	1.290376	4.160835	-2.016096	**H**	2.737451	-2.773409	3.301518	**H**	-5.525962	3.875851	1.488500
C	-1.351594	3.162372	1.586410	**C**	-1.871453	-2.906695	1.843556	**C**	-3.354989	1.235029	-1.661900
H	-1.654282	2.472851	2.378403	**H**	-0.796551	-2.846786	1.664146	**H**	-2.327791	0.985419	-1.914100
H	-0.358916	2.846899	1.265931	**H**	-2.148339	-2.006015	2.396892	**H**	-3.944198	0.321635	-1.770100
H	-1.290261	4.160879	2.016055	**H**	-2.071835	-3.768162	2.479021	**H**	-3.722081	1.950633	-2.396600

Table G59 XYZ coordinates of the GS and TS geometries of **3.16b** B3LYP/Def2TZVPP (gas phase)

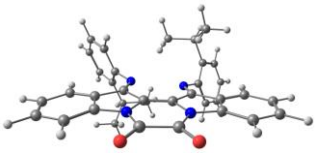
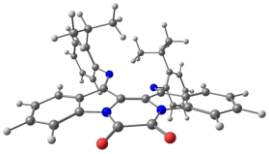
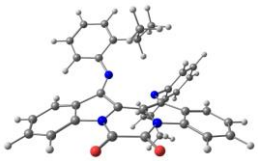
Anti				***Syn***				**TS**			
											
O	-1.377009	5.025487	-0.006978	**O**	-1.322055	4.920832	0.480370	**C**	-1.468697	0.962197	-0.060605
O	1.377015	5.025486	0.006981	**O**	1.354379	4.926437	-0.197090	**C**	-1.930192	-0.434605	0.175795
N	-1.361188	2.741688	-0.020823	**N**	-1.369792	2.654149	0.204388	**C**	-3.294693	-0.262709	0.751895
N	-1.434719	-0.803350	-0.127599	**N**	-1.560153	-0.809956	-0.535919	**C**	-4.151290	-1.073312	1.490895
N	1.361192	2.741687	0.020824	**N**	1.306500	2.646293	-0.317588	**H**	-3.845387	-2.046211	1.833395
N	1.434719	-0.803351	0.127601	**N**	1.383086	-0.858171	-0.030742	**C**	-5.402592	-0.597017	1.866495
C	-0.677497	1.509678	-0.017674	**C**	-0.721884	1.427643	-0.039006	**H**	-6.060089	-1.231319	2.444295
C	-1.704039	0.438182	-0.086613	**C**	-1.772774	0.384758	-0.147416	**C**	-5.807196	0.685482	1.515495
C	-3.002555	1.142529	-0.069366	**C**	-3.032126	1.076194	0.204781	**H**	-6.789597	1.037078	1.798695
C	-4.310145	0.668766	-0.030352	**C**	-4.324044	0.599738	0.402681	**C**	-4.948799	1.546685	0.838395
H	-4.514573	-0.388754	-0.048433	**H**	-4.555383	-0.443195	0.261285	**H**	-5.227503	2.558584	0.602295
C	-5.350469	1.587621	0.028980	**C**	-5.314881	1.496456	0.782360	**C**	-3.695098	1.062889	0.502295
H	-6.371872	1.235150	0.058576	**H**	-6.323368	1.140918	0.940173	**C**	-1.458584	-2.735603	-0.544005
C	-5.089542	2.955802	0.046790	**C**	-5.022500	2.847657	0.955195	**C**	-0.518882	-3.361300	-1.411805
H	-5.912622	3.656016	0.086790	**H**	-5.809168	3.531627	1.242741	**C**	-0.685477	-4.708400	-1.713705
C	-3.788288	3.450138	0.021964	**C**	-3.733957	3.343082	0.775063	**H**	0.021324	-5.193698	-2.369905
H	-3.580393	4.505065	0.047378	**H**	-3.498191	4.382754	0.919244	**C**	-1.733975	-5.454904	-1.191405
C	-2.761715	2.519439	-0.028785	**C**	-2.754973	2.432514	0.408722	**H**	-1.828471	-6.503104	-1.441505
C	-2.405465	-1.784514	-0.354504	**C**	-2.623409	-1.646067	-0.911690	**C**	-2.653277	-4.848007	-0.348005
C	-2.743919	-2.726001	0.634819	**C**	-2.909793	-2.844568	-0.232889	**H**	-3.477175	-5.413510	0.065795
C	-3.673756	-3.708656	0.296488	**C**	-3.968411	-3.618115	-0.709279	**C**	-2.513182	-3.508007	-0.032805
H	-3.955336	-4.428560	1.054799	**H**	-4.209805	-4.532708	-0.182329	**C**	-0.258899	1.521601	-0.284405
C	-4.236840	-3.798931	-0.969886	**C**	-4.707653	-3.263619	-1.829964	**C**	1.126103	1.025706	-0.132705
H	-4.947635	-4.582372	-1.193548	**H**	-5.515541	-3.896648	-2.170160	**C**	1.988499	2.180809	-0.467405
C	-3.864952	-2.883150	-1.945774	**C**	-4.386012	-2.098982	-2.515107	**C**	3.370198	2.350014	-0.450605
H	-4.277783	-2.944084	-2.943660	**H**	-4.935703	-1.811196	-3.401039	**H**	4.023101	1.527816	-0.211105
C	-2.957487	-1.884159	-1.636746	**C**	-3.355002	-1.298602	-2.054391	**C**	3.897494	3.599616	-0.751605
C	0.677499	1.509677	0.017674	**C**	0.615010	1.424798	-0.231138	**H**	4.969293	3.740519	-0.745105
C	1.704040	0.438180	0.086613	**C**	1.610905	0.342223	-0.380910	**C**	3.060590	4.667913	-1.065005
C	3.002557	1.142526	0.069366	**C**	2.863841	1.020884	-0.771990	**H**	3.489687	5.631114	-1.304705
C	4.310147	0.668761	0.030352	**C**	4.122377	0.531739	-1.103430	**C**	1.675990	4.528308	-1.069605
H	4.514573	-0.388759	0.048433	**H**	4.298321	-0.528583	-1.181127	**H**	1.021288	5.351206	-1.296405
C	5.350472	1.587615	-0.028979	**C**	5.149585	1.438912	-1.335654	**C**	1.165095	3.277206	-0.758705
H	6.371874	1.235143	-0.058576	**H**	6.132299	1.074825	-1.600462	**N**	-2.605500	1.786693	-0.038705
C	5.089546	2.955796	-0.046789	**C**	4.925622	2.809395	-1.228871	**N**	-1.244089	-1.388202	-0.324405
H	5.912627	3.656010	-0.086789	**H**	5.738500	3.498933	-1.410798	**N**	-0.189104	2.887101	-0.630305
C	3.788293	3.450133	-0.021963	**C**	3.674606	3.319896	-0.891011	**H**	-3.239683	-3.055709	0.609195
H	3.580399	4.505061	-0.047377	**H**	3.495796	4.377054	-0.801211	**C**	-1.276707	3.722998	-0.779305
C	2.761719	2.519436	0.028785	**C**	2.658915	2.403237	-0.672080	**C**	-2.625605	3.121593	-0.397105
C	2.405463	-1.784517	0.354505	**C**	2.339721	-1.872712	-0.173169	**O**	-1.195511	4.874198	-1.140605
C	2.957484	-1.884165	1.636747	**C**	3.079611	-2.347019	0.925755	**O**	-3.626307	3.799289	-0.396305
C	3.864947	-2.883158	1.945773	**C**	3.965219	-3.399683	0.693778	**C**	0.603315	-2.553896	-2.029505
H	4.277778	-2.944094	2.943658	**H**	4.551826	-3.767229	1.526517	**H**	0.931713	-1.858495	-1.263205
C	4.236834	-3.798937	0.969883	**C**	4.115473	-3.988749	-0.554650	**C**	0.076312	-1.715398	-3.203705
H	4.947628	-4.582380	1.193543	**H**	4.809924	-4.806535	-0.688682	**H**	-0.727590	-1.056900	-2.879405
C	3.673751	-3.708659	-0.296491	**C**	3.355009	-3.526187	-1.620503	**H**	0.876110	-1.099495	-3.619705
H	3.955330	-4.428563	-1.054803	**H**	3.444238	-3.979814	-2.598312	**H**	-0.304186	-2.356999	-4.001205
C	2.743915	-2.726003	-0.634821	**C**	2.472081	-2.476271	-1.426987	**C**	1.802118	-3.394492	-2.466705
C	-0.761308	3.985787	-0.006585	**C**	-0.747020	3.887730	0.231605	**H**	1.558320	-4.055792	-3.300205
C	0.761313	3.985786	0.006585	**C**	0.740537	3.889077	-0.113233	**H**	2.606716	-2.740589	-2.800805
H	-2.653975	-1.165844	-2.385911	**H**	1.862429	-2.108310	-2.240661	**H**	2.188320	-4.001290	-1.647705
C	-2.157787	-2.709948	2.033164	**H**	-3.095680	-0.386555	-2.574319	**N**	1.400207	-0.127393	0.334395
H	-2.611978	-3.557205	2.553223	**C**	-2.124638	-3.330943	0.967894	**C**	2.688108	-0.647189	0.442895
C	-2.532064	-1.450764	2.826391	**H**	-2.615691	-4.252907	1.289609	**C**	3.144910	-1.076787	1.703995
H	-3.608322	-1.276020	2.809020	**C**	-2.165646	-2.364630	2.157894	**C**	3.467809	-0.864986	-0.697405
H	-2.222867	-1.558592	3.867302	**H**	-3.191115	-2.091481	2.410057	**C**	4.397112	-1.680083	1.775995
H	-2.038467	-0.566991	2.426557	**H**	-1.714135	-2.830629	3.034834	**C**	4.703411	-1.483182	-0.599605
C	-0.640585	-2.932722	2.024271	**H**	-1.609965	-1.453741	1.947760	**H**	3.084008	-0.552187	-1.658305
H	-0.384681	-3.863241	1.517055	**C**	-0.685261	-3.683504	0.575078	**C**	5.176613	-1.885780	0.643095
H	-0.132019	-2.122142	1.509837	**H**	-0.672429	-4.410387	-0.237358	**H**	4.771713	-2.006581	2.735795
H	-0.261130	-2.989101	3.046075	**H**	-0.149145	-2.796288	0.251198	**H**	5.291312	-1.653479	-1.491505
H	2.653973	-1.165851	2.385912	**H**	-0.152322	-4.114734	1.423281	**H**	6.141014	-2.366977	0.730795
C	2.157783	-2.709946	-2.033164	**C**	2.984460	-1.764726	2.325473	**C**	2.284209	-0.815390	2.920595
H	2.611971	-3.557203	-2.553225	**H**	3.613401	-2.405697	2.948222	**H**	1.249009	-0.920294	2.584695
C	2.532063	-1.450761	-2.826389	**C**	1.568634	-1.822869	2.908904	**C**	2.460504	0.633011	3.403095
H	3.608319	-1.276004	-2.808995	**H**	0.874211	-1.221759	2.325537	**C**	2.516012	-1.798989	4.066395
H	2.222891	-1.558596	-3.867306	**H**	1.193171	-2.844939	2.921437	**H**	3.484203	0.799814	3.743995
H	2.038447	-0.566992	-2.426569	**H**	1.571300	-1.447927	3.933751	**H**	2.253702	1.346110	2.605895
C	0.640581	-2.932716	-2.024273	**C**	3.566313	-0.348156	2.429836	**H**	1.786603	0.848008	4.234195
H	0.384674	-3.863236	-1.517060	**H**	4.558449	-0.291149	1.982554	**H**	2.422816	-2.832189	3.731095
H	0.132016	-2.122136	-1.509837	**H**	2.932996	0.384049	1.933285	**H**	3.503812	-1.675686	4.513895
H	0.261126	-2.989090	-3.046077	**H**	3.647087	-0.055302	3.477844	**H**	1.782012	-1.630992	4.855395

Table G60 XYZ coordinates of the GS and TS geometries of **3.16c** B3LYP/Def2TZVPP (gas phase)

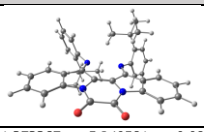
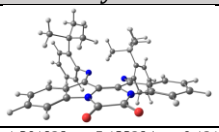
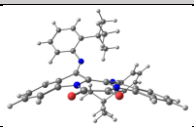
Anti				***Syn***				**TS**			
											
O	1.373367	5.240581	0.099097	**O**	1.301928	5.133294	0.121391	**C**	-0.836090	1.463109	-0.089844
O	-1.373365	5.240582	-0.099097	**O**	-1.399212	5.089047	0.674207	**C**	-1.801410	0.366390	0.218576
N	1.357589	2.956732	0.100481	**N**	1.251138	2.874871	-0.213968	**C**	-2.865473	1.060904	1.000583
N	1.430784	-0.589905	0.147259	**N**	1.303938	-0.647567	-0.379537	**C**	-3.798194	0.650865	1.947395
N	-1.357588	2.956732	-0.100482	**N**	-1.436130	2.847130	0.239568	**H**	-3.826005	-0.368948	2.295726
N	-1.430784	-0.589905	-0.147260	**N**	-1.605577	-0.593427	-0.625184	**C**	-4.665157	1.583325	2.507017
C	0.675939	1.724438	0.052623	**C**	0.556193	1.652426	-0.265975	**H**	-5.386440	1.262685	3.245453
C	1.698303	0.653066	0.164310	**C**	1.553314	0.588976	-0.519855	**C**	-4.605280	2.920517	2.129969
C	2.994085	1.358001	0.238575	**C**	2.828065	1.297994	-0.755353	**H**	-5.300194	3.630798	2.556030
C	4.302230	0.885008	0.270814	**C**	4.100260	0.838678	-1.080086	**C**	-3.630721	3.374759	1.245426
H	4.505611	-0.172665	0.293684	**H**	4.279732	-0.207764	-1.263480	**H**	-3.535947	4.415132	0.987242
C	5.343589	1.804367	0.277939	**C**	5.138042	1.759396	-1.168200	**C**	-2.750829	2.435539	0.733609
H	6.365240	1.452406	0.305074	**H**	6.131734	1.418941	-1.423224	**C**	-2.630974	-1.738167	-0.694858
C	5.083225	3.172679	0.254703	**C**	4.909882	3.112635	-0.931390	**C**	-2.324307	-2.638904	-1.760805
H	5.906764	3.873372	0.267527	**H**	5.730692	3.812987	-1.002973	**C**	-3.292566	-3.583150	-2.100825
C	3.782447	3.666381	0.206849	**C**	3.644307	3.592653	-0.603198	**H**	-3.097385	-4.270918	-2.906266
H	3.575693	4.721367	0.175523	**H**	3.462031	4.636404	-0.417039	**C**	-4.511400	-3.688116	-1.444932
C	2.755152	2.735093	0.192127	**C**	2.619176	2.663305	-0.525192	**H**	-5.221985	-4.445271	-1.748002
C	2.374293	-1.579445	0.439297	**C**	2.272466	-1.630645	-0.629336	**C**	-4.801506	-2.820555	-0.405643
C	2.762697	-2.557956	-0.503126	**C**	2.365487	-2.063860	-1.960132	**H**	-5.743400	-2.880090	0.122617
C	3.653415	-3.536388	-0.056953	**C**	3.269239	-3.037210	-2.337960	**C**	-3.870116	-1.864556	-0.047673
H	3.992534	-4.291583	-0.747744	**H**	3.327802	-3.349330	-3.371806	**C**	0.472929	1.523739	-0.415801
C	4.123209	-3.591307	1.249526	**C**	4.097342	-3.600960	-1.375035	**C**	1.587781	0.568636	-0.241183
H	4.804451	-4.378063	1.543076	**H**	4.820817	-4.358186	-1.643782	**C**	2.804366	1.324451	-0.620362
C	3.700982	-2.643014	2.169400	**C**	3.979209	-3.193702	-0.057097	**C**	4.159685	1.004739	-0.589491
H	4.039871	-2.676689	3.195985	**H**	4.630634	-3.649189	0.674389	**H**	4.488010	0.025086	-0.287681
C	2.835117	-1.645401	1.760125	**C**	3.065671	-2.221299	0.371696	**C**	5.090005	1.969685	-0.953773
C	-0.675937	1.724439	-0.052624	**C**	-0.783996	1.641000	-0.083651	**H**	6.143075	1.726232	-0.935213
C	-1.698302	0.653066	-0.164311	**C**	-1.830158	0.599562	-0.239144	**C**	4.680009	3.241266	-1.346677
C	-2.994084	1.358002	-0.238575	**C**	-3.096616	1.271781	0.123401	**H**	5.417893	3.976177	-1.637848
C	-4.302229	0.885009	-0.270813	**C**	-4.391583	0.785261	0.273912	**C**	3.334571	3.594179	-1.363564
H	-4.505611	-0.172664	-0.293683	**H**	-4.620575	-0.247757	0.071172	**H**	3.007327	4.578763	-1.647972
C	-5.343588	1.804368	-0.277937	**C**	-5.389065	1.659258	0.687387	**C**	2.419734	2.623631	-0.984022
H	-6.365239	1.452407	-0.305071	**H**	-6.399755	1.295419	0.807865	**N**	-1.564182	2.666046	-0.003480
C	-5.083224	3.172680	-0.254702	**C**	-5.100407	2.998096	0.942164	**N**	-1.704427	-0.736518	-0.422179
H	-5.906762	3.873374	-0.267524	**H**	-5.891870	3.664918	1.255679	**N**	1.019567	2.754269	-0.832746
C	-3.782445	3.666382	-0.206848	**C**	-3.809484	3.502334	0.811340	**H**	-4.118957	-1.190263	0.743109
H	-3.575691	4.721368	-0.175523	**H**	-3.576893	4.531798	1.019017	**C**	0.307761	3.928068	-0.981252
C	-2.755151	2.735093	-0.192127	**C**	-2.824106	2.614116	0.408234	**C**	-1.121691	3.896269	-0.448906
C	-2.374293	-1.579445	-0.439297	**C**	-2.652702	-1.447522	-1.000600	**O**	0.777691	4.947661	-1.429586
C	-2.835119	-1.645400	-1.760126	**C**	-3.352477	-1.110635	-2.166117	**O**	-1.787031	4.903967	-0.396380
C	-3.700985	-2.643013	-2.169399	**C**	-4.372570	-1.909816	-2.649270	**C**	-0.984613	-2.633705	-2.509141
H	-4.039875	-2.676687	-3.195984	**H**	-4.897756	-1.629330	-3.552225	**C**	-0.682497	-1.259911	-3.142145
C	-4.123213	-3.591304	-1.249524	**C**	-4.711487	-3.063505	-1.958237	**C**	-0.951060	-3.661001	-3.652406
H	-4.804456	-4.378060	-1.543073	**H**	-5.511859	-3.700549	-2.308767	**C**	0.116965	-3.020590	-1.510608
C	-3.653417	-3.536386	0.056954	**C**	-4.002989	-3.410930	-0.814657	**H**	-0.562556	-0.491201	-2.387902
H	-3.992537	-4.291580	0.747746	**H**	-4.281170	-4.319448	-0.305087	**H**	0.237564	-1.324598	-3.726144
C	-2.762697	-2.557955	0.503126	**C**	-2.951550	-2.642911	-0.309348	**H**	-1.486497	-0.962227	-3.817656
C	0.759238	4.200848	0.055096	**C**	0.681550	4.097076	0.083902	**H**	-1.709526	-3.460217	-4.410360
C	-0.759237	4.200848	-0.055097	**C**	-0.816266	4.075008	0.370973	**H**	0.022871	-3.607007	-4.138715
H	2.486535	-0.899212	2.460663	**H**	-3.074569	-0.203207	-2.684387	**H**	-1.078408	-4.682827	-3.294589
C	2.252420	-2.547424	-1.950508	**C**	-2.168685	-3.089790	0.931952	**H**	-0.077978	-4.007675	-1.088212
C	2.816154	-3.718428	-2.766998	**C**	-2.700727	-4.410860	1.503792	**H**	1.082970	-3.058287	-2.013699
H	2.535739	-4.682460	-2.341920	**H**	-2.632083	-5.224622	0.781604	**H**	0.175359	-2.301651	-0.702395
H	2.408809	-3.673598	-3.777157	**H**	-2.098922	-4.688775	2.369261	**N**	1.410325	-0.568596	0.306931
H	3.903315	-3.678849	-2.847555	**H**	-3.736989	-4.328382	1.834855	**C**	2.410991	-1.513103	0.532376
C	2.681899	-1.248186	-2.659309	**C**	-2.265662	-2.036339	2.052210	**C**	2.561274	-2.093568	1.814324
H	2.231985	-0.369562	-2.206952	**H**	-1.787583	-1.102396	1.774344	**C**	3.170522	-1.982836	-0.544992
H	3.766058	-1.130352	-2.631481	**H**	-3.306731	-1.829461	2.304312	**C**	3.536715	-3.083144	1.946484
H	2.371957	-1.277886	-3.705312	**H**	-1.768895	-2.407207	2.950316	**C**	4.108042	-2.986299	-0.383148
H	-2.486537	-0.899212	-2.460664	**C**	-0.695380	-3.302539	0.541201	**H**	2.992764	-1.554090	-1.520854
C	-2.252420	-2.547422	1.950508	**H**	-0.252748	-2.391457	0.152517	**C**	4.303171	-3.531187	0.877519
C	-2.816154	-3.718427	2.766998	**H**	-0.123657	-3.620943	1.414336	**H**	3.702338	-3.535344	2.911058
H	-2.535738	-4.682458	2.341921	**H**	-0.609222	-4.080693	-0.218146	**H**	4.675936	-3.339223	-1.233390
H	-2.408809	-3.673595	3.777157	**H**	1.708021	-1.607036	-2.686577	**H**	5.035944	-4.311347	1.031814
H	-3.903315	-3.678848	2.847554	**C**	3.061593	-1.877993	1.875513	**C**	1.689137	-1.673536	3.006725
C	-2.681900	-1.248184	2.659308	**C**	2.870182	-3.178306	2.683631	**C**	1.818454	-0.162110	3.277974
H	-2.231989	-0.369560	2.206949	**H**	1.912492	-3.640769	2.445894	**C**	0.216887	-2.029961	2.714024
H	-3.766060	-1.130353	2.631484	**H**	3.651694	-3.909694	2.487753	**C**	2.094695	-2.400827	4.296659
H	-2.371954	-1.277882	3.705311	**H**	2.885425	-2.955315	3.751385	**H**	1.269640	0.097858	4.184802
C	-0.717173	-2.665589	1.958657	**C**	1.961513	-0.908433	2.334796	**H**	2.862815	0.118023	3.423512
H	-0.250928	-1.853750	1.411334	**H**	0.971609	-1.224033	2.015920	**H**	1.415069	0.430544	2.462789
H	-0.349023	-2.650591	2.986226	**H**	1.972309	-0.869169	3.425088	**H**	-0.141348	-1.532243	1.818476
H	-0.401785	-3.604844	1.502611	**H**	2.130267	0.103386	1.975043	**H**	0.105820	-3.106404	2.577767
C	0.717173	-2.665592	-1.958657	**C**	4.419691	-1.247585	2.241034	**H**	-0.409599	-1.728769	3.556250
H	0.349023	-2.650595	-2.986226	**H**	4.447815	-1.007147	3.305465	**H**	1.985454	-3.481882	4.208577
H	0.401784	-3.604846	-1.502610	**H**	5.249445	-1.920063	2.025923	**H**	3.123362	-2.179488	4.584359
H	0.250927	-1.853752	-1.411336	**H**	4.579799	-0.326007	1.680572	**H**	1.445965	-2.071200	5.108350

Table G61 XYZ coordinates of the GS and TS geometries of **3.16d** B3LYP/Def2TZVPP (gas phase)

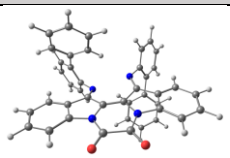
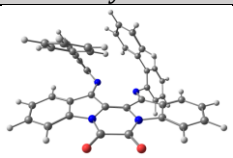
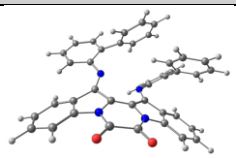
Anti				***Syn***				**TS**			
											
O	1.350237	4.950551	-0.287154	**O**	1.771162	4.834374	-0.445334	**C**	-1.784306	-1.121130	0.081063
O	-1.350240	4.950550	0.287162	**O**	-0.828335	5.210773	0.403392	**C**	-2.452707	0.194280	-0.109374
N	1.314948	2.668071	-0.362131	**N**	1.331752	2.615049	-0.754938	**C**	-3.878035	-0.188700	-0.363602
N	1.233358	-0.845132	-0.743632	**N**	0.787398	-0.869296	-0.862030	**C**	-4.956913	0.412701	-1.006784
N	-1.314950	2.668070	0.362134	**N**	-1.261774	3.004952	0.003073	**H**	-4.845380	1.353419	-1.518165
N	-1.233357	-0.845134	0.743630	**N**	-2.013796	-0.358177	-0.797779	**C**	-6.185546	-0.236836	-1.049629
C	0.640894	1.443298	-0.213572	**C**	0.447257	1.521725	-0.737144	**H**	-7.016642	0.233891	-1.555822
C	1.587237	0.365374	-0.582643	**C**	1.241593	0.305693	-1.023470	**C**	-6.351083	-1.482177	-0.453429
C	2.874565	1.046135	-0.816411	**C**	2.589609	0.797204	-1.359727	**H**	-7.318818	-1.963943	-0.471176
C	4.128604	0.561976	-1.171915	**C**	3.722949	0.135207	-1.812977	**C**	-5.274714	-2.144742	0.127938
H	4.302336	-0.496516	-1.272929	**H**	3.707451	-0.931139	-1.974995	**H**	-5.370401	-3.133321	0.542276
C	5.157119	1.469957	-1.391231	**C**	4.876768	0.873293	-2.043064	**C**	-4.048294	-1.499950	0.116705
H	6.139020	1.108328	-1.662382	**H**	5.769366	0.375562	-2.395210	**C**	-2.189045	2.605028	0.105209
C	4.935547	2.838992	-1.262633	**C**	4.895789	2.247860	-1.815380	**C**	-1.162831	3.558527	0.333989
H	5.749500	3.529948	-1.434169	**H**	5.806438	2.804306	-1.989960	**C**	-1.433427	4.910569	0.110587
C	3.684549	3.346339	-0.920418	**C**	3.765720	2.931768	-1.373780	**H**	-0.636410	5.624406	0.265730
H	3.504449	4.402876	-0.827006	**H**	3.772660	3.994388	-1.205397	**C**	-2.701551	5.356644	-0.224353
C	2.670263	2.427572	-0.704054	**C**	2.619486	2.181797	-1.164323	**H**	-2.883578	6.411287	-0.379396
C	2.124175	-1.887853	-0.986204	**C**	1.552123	-2.026544	-0.825121	**C**	-3.744675	4.440237	-0.291460
C	3.018548	-2.340480	0.008551	**C**	2.539215	-2.239012	0.165570	**H**	-4.757352	4.773853	-0.473935
C	3.849130	-3.419612	-0.298678	**C**	3.191230	-3.472401	0.187417	**C**	-3.486478	3.091964	-0.129464
H	4.525610	-3.781259	0.464024	**H**	3.930913	-3.648638	0.956984	**C**	-0.535600	-1.578419	-0.162465
C	3.810753	-4.044957	-1.537128	**C**	2.901347	-4.472944	-0.729730	**C**	0.653162	-0.976311	-0.805617
H	4.464407	-4.881417	-1.741490	**H**	3.423758	-5.418382	-0.682523	**C**	1.562757	-2.109212	-1.062952
C	2.909253	-3.604078	-2.498790	**C**	1.922007	-4.255263	-1.692342	**C**	2.754945	-2.196156	-1.771252
H	2.858137	-4.089537	-3.463861	**H**	1.676253	-5.029462	-2.406664	**H**	3.176111	-1.324170	-2.244726
C	2.061181	-2.544712	-2.217709	**C**	1.240691	-3.050319	-1.724739	**C**	3.394369	-3.425615	-1.856801
C	-0.640896	1.443298	0.213573	**C**	-0.846133	1.721934	-0.398410	**H**	4.323906	-3.507578	-2.402364
C	-1.587237	0.365372	0.582642	**C**	-2.034080	0.839943	-0.377029	**C**	2.856042	-4.549568	-1.234322
C	-2.874566	1.046132	0.816413	**C**	-3.118354	1.670113	0.186245	**H**	3.376596	-5.495339	-1.297385
C	-4.128605	0.561971	1.171917	**C**	-4.425128	1.362706	0.547371	**C**	1.652422	-4.490056	-0.537210
H	-4.302336	-0.496520	1.272929	**H**	-4.815684	0.367973	0.403907	**H**	1.223886	-5.356661	-0.064920
C	-5.157119	1.469951	1.391235	**C**	-5.219453	2.364546	1.092108	**C**	1.016146	-3.259963	-0.484161
H	-6.139020	1.108322	1.662386	**H**	-6.237580	2.142359	1.379258	**N**	-2.782821	-2.048416	0.433228
C	-4.935549	2.838987	1.262638	**C**	-4.717113	3.652613	1.265919	**N**	-1.807345	1.271979	0.136675
H	-5.749502	3.529942	1.434177	**H**	-5.352937	4.420907	1.683984	**N**	-0.251637	-2.941654	0.060997
C	-3.684552	3.346336	0.920423	**C**	-3.407919	3.978587	0.920785	**H**	-4.307813	2.405399	-0.156681
H	-3.504452	4.402872	0.827013	**H**	-3.010937	4.968472	1.063038	**C**	-1.115556	-3.844563	0.646248
C	-2.670265	2.427569	0.704057	**C**	-2.624948	2.964874	0.390707	**C**	-2.551433	-3.355899	0.815865
C	-2.124173	-1.887857	0.986200	**C**	-3.120869	-1.182540	-0.958436	**O**	-0.809431	-4.978422	0.932641
C	-3.018545	-2.340483	-0.008556	**C**	-3.143422	-2.436242	-0.317338	**O**	-3.421548	-4.105317	1.192683
C	-3.849123	-3.419619	0.298670	**C**	-4.177574	-3.321638	-0.617680	**C**	0.139584	3.240646	0.961929
H	-4.525601	-3.781266	-0.464033	**H**	-4.200767	-4.277288	-0.110919	**C**	1.341004	3.697134	0.421388
C	-3.810743	-4.044969	1.537118	**C**	-5.169671	-2.996535	-1.533225	**C**	0.153645	2.662947	2.235923
H	-4.464394	-4.881432	1.741478	**H**	-5.960147	-3.701525	-1.749810	**C**	2.524420	3.598673	1.142609
C	-2.909244	-3.604089	2.498780	**C**	-5.134963	-1.760314	-2.169430	**H**	1.350371	4.125984	-0.570820
H	-2.858124	-4.089551	3.463850	**H**	-5.895226	-1.497300	-2.892636	**C**	1.330797	2.588083	2.964436
C	-2.061176	-2.544719	2.217702	**C**	-4.120760	-0.860636	-1.884484	**H**	-0.773744	2.310082	2.664703
C	0.743330	3.911814	-0.175676	**C**	0.994249	3.909418	-0.412195	**C**	2.521392	3.058829	2.421224
C	-0.743333	3.911813	0.175681	**C**	-0.449469	4.121828	0.041240	**H**	3.448284	3.942099	0.699139
H	-1.349951	-2.195632	2.953234	**H**	-4.072742	0.092419	-2.393027	**H**	1.322224	2.154324	3.955337
H	1.349956	-2.195624	-2.953240	**H**	0.456602	-2.872046	-2.446705	**H**	3.441583	2.985727	2.983987
C	-3.100536	-1.695431	-1.339268	**C**	-2.095142	-2.803933	0.661168	**N**	0.753877	0.270815	-1.034870
C	-4.344057	-1.370439	-1.886910	**C**	-1.315850	-3.944586	0.467559	**C**	1.883272	0.932703	-1.495658
C	-1.949192	-1.402358	-2.077729	**C**	-1.869654	-2.024866	1.798350	**C**	1.704886	1.781679	-2.595279
C	-4.438422	-0.766956	-3.134461	**C**	-0.325806	-4.291647	1.377717	**C**	3.140043	0.896512	-0.843325
H	-5.242868	-1.573112	-1.320165	**H**	-1.466990	-4.543306	-0.420138	**C**	2.745580	2.547334	-3.089905
C	-2.044676	-0.800298	-3.323484	**C**	-0.895569	-2.382352	2.719064	**H**	0.724208	1.819504	-3.048214
H	-0.977889	-1.629489	-1.664177	**H**	-2.472856	-1.142895	1.966344	**C**	4.163429	1.699481	-1.353443
C	-3.288243	-0.477632	-3.857493	**C**	-0.113769	-3.512795	2.506921	**C**	3.986707	2.510804	-2.463649
H	-5.410563	-0.514506	-3.536222	**H**	0.293412	-5.157971	1.191747	**H**	2.583741	3.183582	-3.949528
H	-1.142839	-0.581039	-3.880030	**H**	-0.737354	-1.773337	3.599005	**H**	5.115775	1.699879	-0.840799
H	-3.359224	-0.003104	-4.826841	**H**	0.663473	-3.775187	3.211297	**H**	4.802820	3.121734	-2.823812
C	3.100535	-1.695433	1.339266	**C**	2.897812	-1.197110	1.155414	**C**	3.410492	0.060683	0.347652
C	4.344055	-1.370431	1.886907	**C**	4.239696	-0.884556	1.386308	**C**	4.610342	-0.650403	0.443467
C	1.949190	-1.402376	2.077732	**C**	1.921509	-0.487582	1.861258	**C**	2.492166	-0.052809	1.393677
C	4.438416	-0.766954	3.134461	**C**	4.597036	0.117817	2.278610	**C**	4.877312	-1.461752	1.537835
H	5.242867	-1.573093	1.320158	**H**	5.007505	-1.409757	0.834749	**H**	5.327272	-0.593159	-0.364201
C	2.044671	-0.800322	3.323489	**C**	2.277316	0.513159	2.753062	**C**	2.756883	-0.862337	2.487198
H	0.977890	-1.629514	1.664181	**H**	0.881212	-0.723939	1.703540	**H**	1.569466	0.500448	1.351550
C	3.288237	-0.477646	3.857497	**C**	3.616694	0.826375	2.961297	**C**	3.947427	-1.577123	2.563136
H	5.410556	-0.514496	3.536221	**H**	5.641804	0.354040	2.429272	**H**	5.806390	-2.014041	1.581868
H	1.142833	-0.581076	3.880039	**H**	1.505919	1.050130	3.289434	**H**	2.031073	-0.930559	3.286698
H	3.359214	-0.003122	4.826848	**H**	3.892095	1.614867	3.648302	**H**	4.147568	-2.216434	3.412198

Table G62 XYZ coordinates of the GS and TS geometries of **3.16e** B3LYP/Def2TZVPP (gas phase)

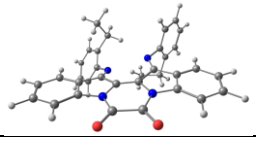
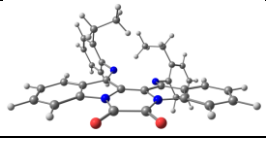
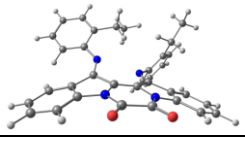
Anti				***Syn***				**TS**			
											
O	-1.231511	4.956220	-0.251797	**O**	1.315044	4.880929	-0.134356	**C**	1.412897	-0.967277	-0.028241
O	1.513162	4.896934	0.026824	**O**	-1.398481	4.854342	0.361699	**C**	2.028302	0.370075	0.230221
N	-1.419005	-0.837433	0.299214	**N**	1.372339	-0.931912	-0.143040	**C**	3.448476	0.042176	0.564649
N	-1.275899	2.676218	-0.123858	**N**	1.296967	2.600511	-0.253629	**C**	4.482216	0.701239	1.225609
N	1.411989	-0.906825	-0.277307	**N**	-1.513225	-0.904444	-0.491935	**H**	4.326391	1.643285	1.718704
N	1.446002	2.614293	0.029298	**N**	-1.402007	2.581920	0.132306	**C**	5.732943	0.103552	1.333988
C	-0.916405	-2.897531	-2.196157	**C**	1.623791	-1.585332	2.988752	**H**	6.525175	0.624951	1.852617
C	-2.324725	-2.317545	-2.020801	**C**	2.947656	-1.325710	2.261489	**C**	5.966082	-1.155112	0.794496
C	1.733619	-2.350205	2.716854	**C**	-0.535428	-3.915218	0.933526	**H**	6.948169	-1.601215	0.867735
C	1.244673	-3.112655	1.479908	**C**	-1.796698	-3.135662	1.322435	**C**	4.936222	-1.875927	0.198736
C	-0.644716	3.904667	-0.151207	**C**	0.705932	3.838218	-0.091985	**H**	5.083894	-2.872933	-0.176747
C	0.875949	3.871541	-0.022484	**C**	-0.798888	3.824643	0.161181	**C**	3.689645	-1.274434	0.133883
C	-2.914092	-2.058034	1.740706	**C**	2.511738	-2.733342	-1.262283	**C**	1.697310	2.761774	-0.198189
C	-3.872625	-3.040819	1.941549	**C**	3.438355	-3.766136	-1.264772	**C**	0.766335	3.563223	-0.911473
C	-4.342682	-3.780272	0.864067	**C**	4.206604	-4.010596	-0.134139	**C**	1.080273	4.897648	-1.162323
C	-3.837969	-3.530521	-0.406746	**C**	4.035330	-3.214612	0.992596	**H**	0.379773	5.496082	-1.729729
C	-2.876961	-2.549928	-0.639077	**C**	3.121864	-2.164649	1.021424	**C**	2.250464	5.479430	-0.703891
C	-2.426264	-1.797245	0.459101	**C**	2.360904	-1.922532	-0.137064	**H**	2.459858	6.520017	-0.911891
C	-2.678638	2.475560	-0.183192	**C**	2.678425	2.376621	-0.485316	**C**	3.144277	4.712804	0.033934
C	-3.685518	3.419190	-0.310990	**C**	3.696742	3.305494	-0.630051	**H**	4.057084	5.148827	0.416724
C	-4.994837	2.945719	-0.349790	**C**	4.975953	2.809055	-0.869377	**C**	2.868284	3.380827	0.274963
C	-5.282550	1.585837	-0.262546	**C**	5.223807	1.441415	-0.960666	**C**	0.143640	-1.439424	-0.034989
C	-4.261390	0.652224	-0.128648	**C**	4.192614	0.522321	-0.805662	**C**	-1.167163	-0.862300	0.346353
C	-2.946815	1.104709	-0.090105	**C**	2.909033	0.998150	-0.561861	**C**	-2.103925	-2.006442	0.359004
C	-1.665011	0.385000	0.057400	**C**	1.629612	0.297249	-0.330258	**C**	-3.437077	-2.109012	0.745226
C	-0.619687	1.433580	-0.039581	**C**	0.613195	1.370510	-0.224789	**H**	-3.970364	-1.251231	1.120641
C	2.228577	-3.081531	0.343417	**C**	-2.703143	-2.928673	0.138143	**C**	-4.071090	-3.340199	0.637881
C	3.085104	-4.148113	0.086852	**C**	-3.711347	-3.844310	-0.154938	**H**	-5.106406	-3.434231	0.934035
C	3.986390	-4.123228	-0.970753	**C**	-4.516528	-3.715907	-1.279691	**C**	-3.386253	-4.451369	0.150433
C	4.039366	-3.009022	-1.800939	**C**	-4.313485	-2.648170	-2.146131	**H**	-3.898772	-5.399823	0.065589
C	3.214305	-1.923461	-1.553982	**C**	-3.330821	-1.711391	-1.868004	**C**	-2.048246	-4.375052	-0.224512
C	2.322748	-1.942920	-0.476650	**C**	-2.534957	-1.834400	-0.724995	**H**	-1.510520	-5.230979	-0.592329
C	2.831165	2.347336	0.178941	**C**	-2.785766	2.340348	0.328573	**C**	-1.426183	-3.141601	-0.097016
C	3.872288	3.244356	0.360703	**C**	-3.786909	3.245683	0.644132	**N**	2.467295	-1.869895	-0.254986
C	5.143605	2.708372	0.548521	**C**	-5.068239	2.732885	0.828434	**N**	1.368648	1.422158	-0.072367
C	5.360794	1.332190	0.560305	**C**	-5.332811	1.370745	0.707242	**N**	-0.073197	-2.804382	-0.335074
C	4.308291	0.447323	0.360458	**C**	-4.319755	0.478126	0.378416	**H**	3.575488	2.812154	0.837431
C	3.033025	0.962282	0.156389	**C**	-3.034489	0.971363	0.178631	**C**	0.895806	-3.692929	-0.750397
C	1.726329	0.303863	-0.054688	**C**	-1.760122	0.295830	-0.151446	**C**	2.324876	-3.174897	-0.688381
C	0.731775	1.402752	-0.017641	**C**	-0.730595	1.363180	-0.080488	**O**	0.664890	-4.831282	-1.087373
H	-0.549364	-2.725492	-3.208972	**H**	1.535029	-0.947725	3.869271	**O**	3.256415	-3.896474	-0.956997
H	-0.917290	-3.972670	-2.013202	**H**	1.559260	-2.624106	3.313322	**C**	-0.549970	3.029076	-1.409610
H	-0.222055	-2.432427	-1.500661	**H**	0.776910	-1.386170	2.333855	**H**	-0.571241	3.104731	-2.501060
H	1.043916	-4.150970	1.748551	**H**	-2.341032	-3.677269	2.098483	**H**	-0.619571	1.978988	-1.149039
H	0.306787	-2.670410	1.142801	**H**	-1.508652	-2.174487	1.748293	**C**	-1.744045	3.792847	-0.826614
H	-2.300173	-1.247453	-2.237795	**H**	3.014056	-0.266114	2.006432	**H**	-1.689161	4.858656	-1.049200
H	-3.003723	-2.765131	-2.748407	**H**	3.780552	-1.527419	2.936597	**H**	-2.680343	3.416629	-1.233767
H	2.665151	-2.773041	3.096004	**H**	-0.798046	-4.894786	0.532137	**H**	-1.784390	3.676132	0.255763
H	0.991306	-2.391244	3.515026	**H**	0.116470	-4.062388	1.794382	**N**	-1.358845	0.369976	0.598687
H	1.913795	-1.301096	2.481877	**H**	0.026679	-3.375510	0.175105	**C**	-2.615897	0.897683	0.917303
H	-4.249282	-3.225549	2.938547	**H**	3.552703	-4.380397	-2.147660	**C**	-2.813752	1.370749	2.215265
H	-5.089975	-4.547814	1.010386	**H**	4.927580	-4.816227	-0.124925	**C**	-3.621316	1.059372	-0.058879
H	-4.199295	-4.107927	-1.248779	**H**	4.629905	-3.406013	1.877335	**C**	-4.016533	1.956664	2.579976
H	-3.457344	4.468319	-0.378586	**H**	3.499001	4.360818	-0.562418	**H**	-2.008947	1.264946	2.929445
H	-5.803307	3.656724	-0.451004	**H**	5.792151	3.508180	-0.989422	**C**	-4.810643	1.667503	0.332977
H	-6.309721	1.251062	-0.296986	**H**	6.227523	1.089489	-1.153118	**C**	-5.022561	2.105110	1.635714
H	-4.485475	-0.399460	-0.056341	**H**	4.384514	-0.536156	-0.874020	**H**	-4.159589	2.303994	3.594265
H	3.028234	-5.023074	0.722488	**H**	-3.861138	-4.679652	0.518130	**H**	-5.594344	1.808744	-0.397151
H	4.628981	-4.972903	-1.156138	**H**	-5.287835	-4.446176	-1.481941	**H**	-5.961405	2.570255	1.902837
H	4.718908	-2.985941	-2.642192	**H**	-4.922046	-2.539738	-3.033766	**C**	-3.394590	0.586280	-1.476640
H	3.695466	4.305562	0.364556	**H**	-3.573494	4.294982	0.747133	**H**	-2.375177	0.843603	-1.766726
H	5.976968	3.381461	0.696030	**H**	-5.871394	3.412798	1.077476	**H**	-3.431503	-0.506037	-1.499730
H	6.357922	0.947562	0.722136	**H**	-6.336502	1.002423	0.866360	**C**	-4.365125	1.127004	-2.521493
H	4.478129	-0.617026	0.361701	**H**	-4.528922	-0.574238	0.279074	**H**	-4.072112	0.784847	-3.513961
H	3.240378	-1.055103	-2.197878	**H**	-3.167999	-0.871134	-2.529016	**H**	-5.385590	0.784544	-2.347435
H	-2.536469	-1.475798	2.570015	**H**	1.894256	-2.538857	-2.128106	**H**	-4.376232	2.217755	-2.533664

Table 63 GXYZ coordinates of the GS and TS geometries of **3.16a** B3LYP/Def2SVP (IEFPCM = CH_2Cl_2)

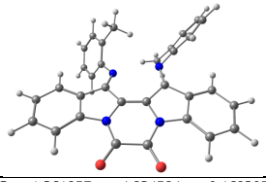
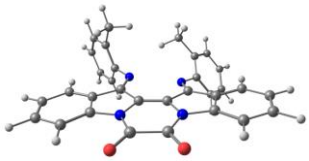
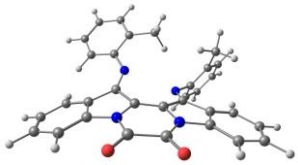
Anti				***Syn***				**TS**			
											
O	-1.361957	-4.834584	0.169305	**O**	1.672259	-4.697747	0.106207	**C**	1.093970	-1.033568	-0.000311
O	1.361957	-4.834584	-0.169304	**O**	-1.055289	-4.831459	-0.166450	**C**	1.893389	0.222010	0.177535
N	-1.362245	-2.543331	0.129176	**N**	1.561699	-2.409488	0.042298	**C**	3.242655	-0.273808	0.592777
N	-1.425714	0.996215	-0.174911	**N**	1.446868	1.131385	-0.235742	**C**	4.355119	0.301627	1.219615
N	1.362245	-2.543331	-0.129177	**N**	-1.161985	-2.542830	-0.177928	**H**	4.327951	1.314732	1.609331
N	1.425714	0.996215	0.174911	**N**	-1.409937	1.007580	-0.087233	**C**	5.508822	-0.460206	1.430840
C	-0.680605	-1.311415	0.042020	**C**	0.822222	-1.213414	-0.059347	**H**	6.368743	-0.002509	1.923550
C	-1.705987	-0.233926	0.024247	**C**	1.794311	-0.086132	-0.068823	**C**	5.563332	-1.797809	1.028729
C	-2.998320	-0.927486	0.243383	**C**	3.119975	-0.716922	0.143202	**H**	6.476128	-2.376988	1.183592
C	-4.295910	-0.444362	0.440103	**C**	4.394219	-0.173445	0.337219	**C**	4.445190	-2.423727	0.466068
H	-4.499748	0.624708	0.424943	**H**	4.548823	0.903560	0.318519	**H**	4.452058	-3.475003	0.193866
C	-5.328490	-1.360788	0.657141	**C**	5.469026	-1.039559	0.555166	**C**	3.296326	-1.654851	0.293574
H	-6.346607	-0.998942	0.813214	**H**	6.469163	-0.629345	0.707747	**C**	1.895514	2.610581	-0.440042
C	-5.069512	-2.738009	0.671580	**C**	5.275384	-2.427251	0.574455	**C**	1.042423	3.472193	-1.198633
H	-5.890577	-3.439633	0.834405	**H**	6.128812	-3.089098	0.737302	**C**	1.463261	4.776280	-1.478898
C	-3.775515	-3.240889	0.490438	**C**	4.005930	-2.990498	0.398097	**H**	0.805333	5.426695	-2.060676
H	-3.564085	-4.305948	0.513512	**H**	3.844765	-4.064128	0.425682	**C**	2.695592	5.261865	-1.034363
C	-2.754890	-2.312936	0.288036	**C**	2.942640	-2.112069	0.194286	**H**	2.995207	6.287545	-1.261945
C	-2.340870	2.023707	-0.370373	**C**	2.305909	2.210426	-0.405584	**C**	3.537345	4.424823	-0.299004
C	-2.240914	3.174251	0.451692	**C**	3.234526	2.255909	-1.463382	**H**	4.506004	4.784433	0.055368
C	-3.099093	4.249393	0.192767	**C**	4.014924	3.392643	-1.669883	**C**	3.140888	3.121114	-0.011549
H	-3.037125	5.135164	0.830932	**H**	4.726318	3.417386	-2.498886	**C**	-0.239797	-1.308716	-0.058137
C	-4.014033	4.220883	-0.864649	**C**	3.882721	4.494000	-0.818360	**C**	-1.461557	-0.511845	0.227931
H	-4.662365	5.080159	-1.050258	**H**	4.494030	5.386190	-0.971516	**C**	-2.587677	-1.466122	0.094638
C	-4.081630	3.093737	-1.689870	**C**	2.948495	4.455365	0.222097	**C**	-3.962315	-1.327381	0.317731
H	-4.779458	3.065282	-2.530214	**H**	2.833384	5.322296	0.878461	**H**	-4.383628	-0.371314	0.622290
C	-3.252824	2.000264	-1.443460	**C**	2.135895	3.336615	0.438492	**C**	-4.789342	-2.440709	0.146937
C	0.680605	-1.311415	-0.042021	**C**	-0.537196	-1.277715	-0.144054	**H**	-5.863658	-2.344676	0.315385
C	1.705986	-0.233926	-0.024247	**C**	-1.613034	-0.248869	-0.182053	**C**	-4.252539	-3.675412	-0.240913
C	2.998319	-0.927486	-0.243385	**C**	-2.877583	-1.013221	-0.290142	**H**	-4.914914	-4.532960	-0.378185
C	4.295909	-0.444362	-0.440106	**C**	-4.210362	-0.597733	-0.378614	**C**	-2.878357	-3.841202	-0.449266
H	4.499747	0.624708	-0.424946	**H**	-4.464907	0.460062	-0.393912	**H**	-2.451676	-4.797771	-0.736031
C	5.328489	-1.360787	-0.657144	**C**	-5.211616	-1.570940	-0.449855	**C**	-2.065662	-2.723218	-0.263689
H	6.346606	-0.998941	-0.813219	**H**	-6.256987	-1.264458	-0.520239	**N**	2.009411	-2.099103	-0.104630
C	5.069511	-2.738009	-0.671583	**C**	-4.885379	-2.933195	-0.432547	**N**	1.401291	1.334101	-0.231398
H	5.890576	-3.439633	-0.834409	**H**	-5.681372	-3.678988	-0.488757	**N**	-0.653178	-2.631573	-0.343833
C	3.775514	-3.240889	-0.490440	**C**	-3.556894	-3.368005	-0.345064	**H**	3.813922	2.493358	0.553051
H	3.564085	-4.305948	-0.513514	**H**	-3.297419	-4.422411	-0.331082	**C**	0.194350	-3.684237	-0.614330
C	2.754890	-2.312935	-0.288037	**C**	-2.570156	-2.386089	-0.275653	**C**	1.681574	-3.397055	-0.442939
C	2.340871	2.023706	0.370374	**C**	-2.437927	1.953852	-0.073733	**O**	-0.180835	-4.799626	-0.919716
C	2.240914	3.174252	-0.451690	**C**	-3.025337	2.326882	1.159107	**O**	2.494560	-4.290697	-0.572826
C	3.099094	4.249393	-0.192764	**C**	-4.007194	3.324740	1.145785	**C**	-0.284958	2.985731	-1.702572
H	3.037125	5.135165	-0.830928	**H**	-4.470347	3.615281	2.092907	**H**	-0.166818	2.093210	-2.335107
C	4.014034	4.220882	0.864651	**C**	-4.406340	3.949055	-0.040484	**H**	-0.926315	2.686153	-0.866198
H	4.662366	5.080158	1.050261	**H**	-5.176792	4.722929	-0.019321	**H**	-0.795784	3.765501	-2.284709
C	4.081631	3.093735	1.689871	**C**	-3.805379	3.581465	-1.247386	**N**	-1.437353	0.714048	0.592779
H	4.779459	3.065279	2.530215	**H**	-4.100917	4.065306	-2.181519	**C**	-2.567296	1.504106	0.802072
C	3.252825	2.000262	1.443461	**C**	-2.817692	2.595228	-1.263938	**C**	-2.732548	2.072615	2.081522
C	-0.758533	-3.783634	0.086278	**C**	1.018016	-3.678306	0.019550	**C**	-3.461841	1.854673	-0.243952
C	0.758533	-3.783634	-0.086278	**C**	-0.499830	-3.752302	-0.121729	**C**	-3.797616	2.925696	2.355559
H	3.291088	1.118470	2.086249	**H**	-2.333606	2.301181	-2.197238	**H**	-2.007676	1.814262	2.855916
H	-3.291087	1.118473	-2.086249	**H**	3.325467	1.392672	-2.125776	**C**	-4.506240	2.742505	0.056705
C	1.243915	3.199598	-1.577259	**C**	-2.607262	1.637371	2.430072	**C**	-4.692866	3.267658	1.336080
H	1.547747	2.524659	-2.395866	**H**	-2.916756	0.578310	2.433790	**H**	-3.920339	3.335552	3.360931
H	0.262779	2.841106	-1.231589	**H**	-1.511054	1.643821	2.542719	**H**	-5.194498	3.022913	-0.745739
H	1.138201	4.211147	-1.994272	**H**	-3.053961	2.121506	3.309817	**H**	-5.523199	3.949406	1.533009
C	-1.243916	3.199596	1.577261	**C**	1.104916	3.294591	1.532878	**C**	-3.336772	1.303270	-1.641088
H	-1.547747	2.524655	2.395868	**H**	0.142780	2.938003	1.134484	**H**	-2.316499	0.972116	-1.870674
H	-0.262779	2.841105	1.231592	**H**	1.391292	2.587557	2.330156	**H**	-3.998624	0.432785	-1.785626
H	-1.138203	4.211144	1.994277	**H**	0.967446	4.284613	1.990193	**H**	-3.626925	2.061565	-2.383246

Table G64 XYZ coordinates of the GS and TS geometries of **3.16b** B3LYP/Def2SVP (PCM = CH_2Cl_2)

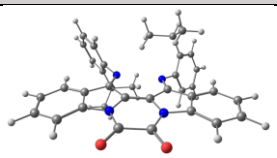
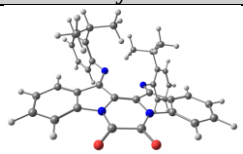
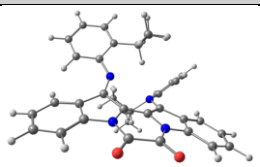
Anti				Syn				TS			
											
O	-1.370606	5.043212	-0.034521	**O**	-1.306136	4.943531	0.448991	**C**	-1.779007	-0.056243	-0.020259
O	1.370603	5.043212	0.034522	**O**	1.360955	4.939721	-0.211028	**C**	-1.262332	-1.456894	0.093173
N	-1.366437	2.751802	-0.028375	**N**	-1.368694	2.667837	0.188704	**C**	-2.439234	-2.230063	0.596241
N	-1.441871	-0.806493	-0.122476	**N**	-1.578355	-0.814682	-0.528903	**C**	-2.607069	-3.474800	1.215549
N	1.366436	2.751802	0.028375	**N**	1.317804	2.651915	-0.332824	**H**	-1.756336	-4.081260	1.512430
N	1.441871	-0.806492	0.122475	**N**	1.383019	-0.871921	-0.070793	**C**	-3.891431	-3.924946	1.537950
C	-0.681957	1.517279	-0.019762	**C**	-0.724260	1.435811	-0.053677	**H**	-4.011807	-4.895089	2.023794
C	-1.710381	0.441503	-0.086256	**C**	-1.781462	0.391244	-0.149480	**C**	-5.013678	-3.140912	1.254636
C	-3.013545	1.146064	-0.071722	**C**	-3.041300	1.088867	0.207029	**H**	-6.012187	-3.511342	1.496327
C	-4.328687	0.670586	-0.029254	**C**	-4.340335	0.614865	0.420208	**C**	-4.875666	-1.862899	0.700914
H	-4.535938	-0.397242	-0.037966	**H**	-4.577397	-0.439459	0.292766	**H**	-5.731876	-1.219938	0.519378
C	-5.374889	1.595607	0.025383	**C**	-5.331903	1.522381	0.802334	**C**	-3.585545	-1.421720	0.415385
H	-6.406697	1.240657	0.058370	**H**	-6.350030	1.167431	0.973105	**C**	0.578718	-2.889697	-0.719964
C	-5.111355	2.971661	0.034838	**C**	-5.032649	2.882018	0.962898	**C**	1.729796	-2.708323	-1.554070
H	-5.942076	3.679839	0.071347	**H**	-5.822950	3.577677	1.253402	**C**	2.477711	-3.832214	-1.920234
C	-3.801816	3.466455	0.006857	**C**	-3.736024	3.373320	0.769265	**H**	3.354923	-3.705775	-2.555322
H	-3.589923	4.531289	0.026427	**H**	-3.492382	4.422869	0.905697	**C**	2.135770	-5.118182	-1.493707
C	-2.769463	2.530592	-0.038226	**C**	-2.756041	2.452672	0.401361	**H**	2.747152	-5.972996	-1.792472
C	-2.405556	-1.793239	-0.347212	**C**	-2.642058	-1.648667	-0.902433	**C**	1.013048	-5.300333	-0.684335
C	-2.733507	-2.743938	0.650146	**C**	-2.916200	-2.865428	-0.231263	**H**	0.729681	-6.298238	-0.342173
C	-3.661318	-3.741308	0.315575	**C**	-3.980859	-3.645421	-0.707349	**C**	0.249621	-4.199495	-0.307047
H	-3.934793	-4.470237	1.083545	**H**	-4.211894	-4.577068	-0.183537	**C**	-1.184795	1.165868	-0.127208
C	-4.234689	-3.836536	-0.954945	**C**	-4.740327	-3.279502	-1.821154	**C**	0.211944	1.635257	0.057736
H	-4.947292	-4.634030	-1.176600	**H**	-5.556413	-3.920012	-2.162851	**C**	0.149923	3.109867	-0.108847
C	-3.878083	-2.908898	-1.937422	**C**	-4.434796	-2.095512	-2.497587	**C**	1.115407	4.115883	0.021265
H	-4.304301	-2.971232	-2.941589	**H**	-5.004297	-1.796233	-3.380715	**H**	2.151754	3.868685	0.239336
C	-2.971949	-1.895785	-1.633249	**C**	-3.397413	-1.288746	-2.037777	**C**	0.730424	5.449640	-0.135479
C	0.681957	1.517279	0.019762	**C**	0.622351	1.428985	-0.249140	**H**	1.477708	6.239756	-0.039515
C	1.710380	0.441503	0.086255	**C**	1.620562	0.340273	-0.394200	**C**	-0.601032	5.780781	-0.419414
C	3.013544	1.146065	0.071722	**C**	2.885868	1.018295	-0.759687	**H**	-0.882254	6.828236	-0.548836
C	4.328686	0.670588	0.029253	**C**	4.156867	0.524370	-1.068855	**C**	-1.587445	4.795015	-0.532739
H	4.535938	-0.397240	0.037966	**H**	4.335454	-0.546510	-1.140518	**H**	-2.625522	5.040904	-0.736137
C	5.374888	1.595609	-0.025383	**C**	5.194612	1.435296	-1.287832	**C**	-1.188958	3.469298	-0.362357
H	6.406697	1.240660	-0.058370	**H**	6.191699	1.066494	-1.535842	**N**	-3.185201	-0.126617	-0.003026
C	5.111353	2.971664	-0.034838	**C**	4.967449	2.814272	-1.190357	**N**	-0.120341	-1.735389	-0.419123
H	5.942074	3.679842	-0.071346	**H**	5.791581	3.510032	-1.362430	**N**	-1.993326	2.301932	-0.357722
C	3.801814	3.466457	-0.006858	**C**	3.703230	3.328008	-0.874658	**H**	-0.618696	-4.362650	0.314152
H	3.589921	4.531291	-0.026427	**H**	3.520358	4.395465	-0.791664	**C**	-3.363598	2.278586	-0.508288
C	2.769462	2.530593	0.038226	**C**	2.677584	2.408009	-0.667560	**C**	-4.034267	0.931243	-0.260802
C	2.405557	-1.793238	0.347212	**C**	2.339157	-1.888754	-0.193024	**O**	-4.037566	3.256300	-0.769163
C	2.971949	-1.895783	1.633249	**C**	3.058975	-2.364989	0.930326	**O**	-5.246040	0.841460	-0.273173
C	3.878083	-2.908896	1.937423	**C**	3.950645	-3.427978	0.719750	**C**	2.088473	-1.324958	-2.065600
H	4.304301	-2.971229	2.941590	**H**	4.523508	-3.797467	1.574872	**H**	1.853074	-0.634034	-1.249262
C	4.234689	-3.836535	0.954947	**C**	4.127110	-4.025155	-0.530582	**C**	1.184844	-0.937616	-3.248668
H	4.947292	-4.634029	1.176603	**H**	4.829259	-4.853454	-0.648053	**H**	0.124122	-0.981159	-2.961868
C	3.661318	-3.741307	-0.315573	**C**	3.390139	-3.558065	-1.621688	**H**	1.408041	0.089259	-3.582058
H	3.934794	-4.470238	-1.083543	**H**	3.503935	-4.016414	-2.606969	**H**	1.340246	-1.614839	-4.105192
C	2.733508	-2.743938	-0.650146	**C**	2.500272	-2.499308	-1.450212	**C**	3.565515	-1.161609	-2.430817
C	-0.762020	3.992489	-0.017721	**C**	-0.739470	3.896872	0.207896	**H**	3.848629	-1.770541	-3.304953
C	0.762018	3.992489	0.017721	**C**	0.749869	3.893240	-0.132407	**H**	3.773074	-0.111927	-2.683646
H	-2.681465	-1.164321	-2.390022	**H**	1.910506	-2.123450	-2.288617	**H**	4.223418	-1.437519	-1.592101
C	-2.141573	-2.710419	2.051069	**H**	-3.150033	-0.358766	-2.553724	**N**	1.163119	0.850423	0.403423
H	-2.581291	-3.572336	2.580551	**C**	-2.110574	-3.354382	0.961048	**C**	2.509388	1.188922	0.493999
C	-2.546702	-1.454315	2.839760	**H**	-2.587361	-4.297547	1.276854	**C**	3.232752	0.787603	1.647439
H	-3.638260	-1.309230	2.828264	**C**	-2.167423	-2.402130	2.165388	**C**	3.187519	1.777790	-0.590396
H	-2.225496	-1.544279	3.890036	**H**	-3.207976	-2.159135	2.432572	**C**	4.607401	1.046422	1.685481
H	-2.078887	-0.548428	2.428201	**H**	-1.689753	-2.867691	3.042111	**C**	4.561489	2.003688	-0.534120
C	-0.617384	-2.903598	2.041106	**H**	-1.636490	-1.462065	1.961776	**H**	2.622510	2.036238	-1.487741
H	-0.340975	-3.841403	1.534090	**C**	-0.665656	-3.678319	0.553270	**C**	5.275382	1.647402	0.612416
H	-0.118926	-2.079628	1.514401	**H**	-0.646050	-4.402548	-0.276091	**H**	5.179296	0.763655	2.570727
H	-0.229409	-2.947533	3.071809	**H**	-0.140413	-2.769328	0.234579	**H**	5.072524	2.453522	-1.388633
H	2.681464	-1.164319	2.390022	**H**	-0.112584	-4.116070	1.399070	**H**	6.351442	1.825927	0.671078
C	2.141574	-2.710420	-2.051069	**C**	2.943684	-1.763047	2.325774	**C**	2.505741	0.055768	2.765302
H	2.581291	-3.572338	-2.580549	**H**	3.538460	-2.424652	2.977366	**H**	1.499656	0.498998	2.838502
C	2.546708	-1.454318	-2.839761	**C**	1.511003	-1.762798	2.877033	**C**	3.172999	0.190836	4.136395
H	3.638267	-1.309238	-2.828267	**H**	0.844467	-1.140050	2.264119	**C**	2.323011	-1.423653	2.379757
H	2.225499	-1.544281	-3.890037	**H**	1.092598	-2.779332	2.894713	**H**	4.146404	-0.324693	4.170806
H	2.078897	-0.548428	-2.428201	**H**	1.501849	-1.370654	3.906701	**H**	3.338207	1.245462	4.407507
C	0.617386	-2.903595	-2.041107	**C**	3.581465	-0.366994	2.427401	**H**	2.537566	-0.265524	4.911348
H	0.340974	-3.841397	-1.534089	**H**	4.600114	-0.359666	2.010708	**H**	1.794012	-1.513379	1.422171
H	0.118928	-2.079622	-1.514405	**H**	2.994954	0.391825	1.890980	**H**	3.302291	-1.921019	2.285318
H	0.229411	-2.947532	-3.071810	**H**	3.639776	-0.053903	3.482273	**H**	1.741190	-1.957940	3.148731

Table G65 XYZ coordinates of the GS and TS geometries of **3.16c** B3LYP/Def2SVP (PCM = CH_2Cl_2)

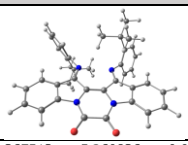
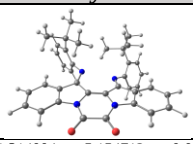
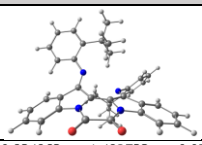
Anti				***Syn***				**TS**			
											
O	1.367513	5.260836	0.099320	**O**	1.314004	5.154712	0.069289	**C**	-0.834963	1.492733	-0.071510
O	-1.367533	5.260831	-0.099329	**O**	-1.369647	5.118903	0.642153	**C**	-1.801456	0.391557	0.247128
N	1.363095	2.969412	0.100619	**N**	1.270171	2.885145	-0.242946	**C**	-2.875477	1.090265	1.018999
N	1.436918	-0.590012	0.149768	**N**	1.310822	-0.653665	-0.418287	**C**	-3.831924	0.680918	1.955376
N	-1.363107	2.969407	-0.100622	**N**	-1.424666	2.866276	0.224957	**H**	-3.866702	-0.345981	2.314110
N	-1.436916	-0.590018	-0.149771	**N**	-1.624566	-0.585294	-0.643180	**C**	-4.715612	1.620403	2.497094
C	0.680360	1.734745	0.052905	**C**	0.570936	1.661625	-0.292337	**H**	-5.458753	1.297988	3.228803
C	1.704434	0.659024	0.162477	**C**	1.570179	0.589616	-0.533910	**C**	-4.647926	2.964314	2.115311
C	3.005357	1.363602	0.231778	**C**	2.857349	1.292812	-0.741530	**H**	-5.357516	3.683424	2.530071
C	4.320854	0.888006	0.259527	**C**	4.142350	0.824366	-1.035514	**C**	-3.651710	3.416791	1.241527
H	4.526795	-0.180088	0.275966	**H**	4.325565	-0.234484	-1.204257	**H**	-3.550593	4.465930	0.978378
C	5.368451	1.812870	0.266367	**C**	5.190140	1.747007	-1.113827	**C**	-2.757816	2.471047	0.745011
H	6.400532	1.457898	0.289277	**H**	6.198320	1.398209	-1.345312	**C**	-2.623213	-1.732207	-0.658559
C	5.105795	3.189116	0.247892	**C**	4.958207	3.111541	-0.898533	**C**	-2.306987	-2.641598	-1.726352
H	5.937266	3.897239	0.260612	**H**	5.789816	3.816664	-0.962811	**C**	-3.278686	-3.590602	-2.076751
C	3.796768	3.684074	0.204443	**C**	3.679376	3.599248	-0.601112	**H**	-3.076212	-4.286651	-2.887436
H	3.586294	4.748997	0.176285	**H**	3.492455	4.655407	-0.430656	**C**	-4.509609	-3.694984	-1.425753
C	2.763406	2.748281	0.188889	**C**	2.644898	2.668244	-0.530411	**H**	-5.225724	-4.459042	-1.737270
C	2.372891	-1.585093	0.440872	**C**	2.279554	-1.641839	-0.641229	**C**	-4.807260	-2.824625	-0.379473
C	2.749305	-2.575999	-0.507088	**C**	2.420557	-2.072767	-1.977613	**H**	-5.760023	-2.887207	0.151006
C	3.636260	-3.569683	-0.061648	**C**	3.335533	-3.058302	-2.327530	**C**	-3.873139	-1.862419	-0.013167
H	3.966377	-4.337832	-0.758982	**H**	3.433006	-3.367638	-3.370814	**C**	0.481415	1.554210	-0.410736
C	4.117132	-3.626233	1.249337	**C**	4.124364	-3.638397	-1.330491	**C**	1.602062	0.595603	-0.249120
H	4.798769	-4.427429	1.543490	**H**	4.858497	-4.408445	-1.577266	**C**	2.818150	1.352185	-0.647627
C	3.712712	-2.662163	2.173723	**C**	3.960487	-3.231711	-0.007932	**C**	4.182149	1.032872	-0.640323
H	4.065740	-2.694250	3.207198	**H**	4.586947	-3.700355	0.752292	**H**	4.522240	0.045178	-0.339914
C	2.848795	-1.650562	1.766443	**C**	3.035279	-2.247632	0.393163	**C**	5.110777	2.003014	-1.025867
C	-0.680367	1.734742	-0.052910	**C**	-0.778152	1.654602	-0.102518	**H**	6.174611	1.757696	-1.025298
C	-1.704438	0.659017	-0.162477	**C**	-1.832647	0.611970	-0.240978	**C**	4.690458	3.280202	-1.418017
C	-3.005363	1.363591	-0.231776	**C**	-3.094148	1.285963	0.152182	**H**	5.429409	4.022476	-1.727782
C	-4.320859	0.887991	-0.259522	**C**	-4.392136	0.797893	0.340247	**C**	3.336369	3.631717	-1.412433
H	-4.526797	-0.180104	-0.275959	**H**	-4.627631	-0.247906	0.155014	**H**	2.998436	4.623963	-1.696633
C	-5.368460	1.812851	-0.266360	**C**	-5.385297	1.680313	0.773503	**C**	2.423645	2.656708	-1.011516
H	-6.400539	1.457875	-0.289268	**H**	-6.402443	1.313873	0.924746	**N**	-1.563644	2.698944	0.013159
C	-5.105808	3.189098	-0.247888	**C**	-5.088850	3.029257	1.010167	**N**	-1.704737	-0.724313	-0.382299
H	-5.937282	3.897218	-0.260607	**H**	-5.880210	3.705905	1.340052	**N**	1.022732	2.786177	-0.840019
C	-3.796782	3.684060	-0.204442	**C**	-3.793438	3.533226	0.843487	**H**	-4.125632	-1.187508	0.790130
H	-3.586312	4.748984	-0.176286	**H**	-3.551962	4.573743	1.039213	**C**	0.306257	3.956607	-0.980741
C	-2.763418	2.748271	-0.188889	**C**	-2.811785	2.636925	0.423005	**C**	-1.120836	3.924461	-0.440678
C	-2.372884	-1.585103	-0.440874	**C**	-2.682026	-1.429544	-1.009020	**O**	0.767310	4.988077	-1.428926
C	-2.848787	-1.650578	-1.766445	**C**	-3.426839	-1.060594	-2.148349	**O**	-1.782041	4.943003	-0.394664
C	-3.712701	-2.662183	-2.173722	**C**	-4.466698	-1.854530	-2.621396	**C**	-0.950124	-2.644948	-2.454033
H	-4.065728	-2.694274	-3.207197	**H**	-5.028428	-1.547322	-3.506703	**C**	-0.625851	-1.270300	-3.081533
C	-4.117119	-3.626251	-1.249333	**C**	-4.780897	-3.035890	-1.948608	**C**	-0.903577	-3.678023	-3.595785
H	-4.798754	-4.427450	-1.543484	**H**	-5.599317	-3.671799	-2.293471	**C**	0.127220	-3.036899	-1.425714
C	-3.636248	-3.569696	0.061652	**C**	-4.031003	-3.413955	-0.831634	**H**	-0.538248	-0.491934	-2.317171
H	-3.966363	-4.337843	0.758989	**H**	-4.293495	-4.345756	-0.333595	**H**	0.326164	-1.332873	-3.633445
C	-2.749295	-2.576008	0.507089	**C**	-2.959915	-2.651460	-0.337069	**H**	-1.410736	-0.974702	-3.796781
C	0.760205	4.210056	0.055416	**C**	0.698421	4.108298	0.041150	**H**	-1.656755	-3.474668	-4.372993
C	-0.760221	4.210053	-0.055425	**C**	-0.798033	4.090998	0.339470	**H**	0.086815	-3.633293	-4.073535
H	2.514592	-0.888540	2.473208	**H**	-3.167540	-0.128821	-2.654994	**H**	-1.045638	-4.707939	-3.235269
C	2.236577	-2.553270	-1.959201	**C**	-2.133901	-3.126197	0.871850	**H**	-0.094883	-4.024088	-0.989494
C	2.778609	-3.737820	-2.777307	**C**	-2.640643	-4.469896	1.422500	**H**	1.113222	-3.096696	-1.909831
H	2.479333	-4.705749	-2.347131	**H**	-2.588268	-5.270563	0.669194	**H**	0.180955	-2.297802	-0.620600
H	2.369731	-3.688256	-3.798029	**H**	-2.007994	-4.772632	2.270790	**N**	1.431474	-0.548130	0.301949
H	3.876511	-3.719857	-2.858491	**H**	-3.677610	-4.405266	1.787371	**C**	2.422646	-1.504018	0.514210
C	2.698366	-1.258104	-2.663174	**C**	-2.210491	-2.099071	2.022465	**C**	2.552519	-2.119666	1.792030
H	2.270050	-0.360001	-2.201839	**H**	-1.760241	-1.137735	1.748773	**C**	3.202188	-1.955164	-0.569127
H	3.795788	-1.167413	-2.636749	**H**	-3.255578	-1.919509	2.320934	**C**	3.528911	-3.120641	1.917621
H	2.383113	-1.271209	-3.719021	**H**	-1.666465	-2.480346	2.901485	**C**	4.140789	-2.970177	-0.414027
H	-2.514586	-0.888557	-2.473212	**C**	-0.668917	-3.312695	0.426964	**H**	3.038033	-1.503382	-1.548546
C	-2.236566	-2.553273	1.959201	**H**	-0.242393	-2.373725	0.056176	**C**	4.316009	-3.547712	0.844467
C	-2.778591	-3.737823	2.777311	**H**	-0.057530	-3.660188	1.274672	**H**	3.679742	-3.601147	2.882704
H	-2.479317	-4.705752	2.347133	**H**	-0.600524	-4.069767	-0.370216	**H**	4.727562	-3.307492	-1.271606
H	-2.369704	-3.688259	3.798030	**H**	1.793387	-1.598547	-2.734939	**H**	5.052802	-4.340224	0.993783
H	-3.876492	-3.719862	2.858505	**C**	2.985552	-1.893521	1.899222	**C**	1.656356	-1.724054	2.982009
C	-2.698361	-1.258107	2.663171	**C**	2.805115	-3.192858	2.717738	**C**	1.784150	-0.215839	3.289001
H	-2.270055	-0.360003	2.201829	**H**	1.852895	-3.683332	2.463977	**C**	0.186778	-2.071211	2.649641
H	-3.795784	-1.167426	2.636752	**H**	3.613948	-3.916874	2.547716	**C**	2.040122	-2.485097	4.263174
H	-2.383102	-1.271205	3.719016	**H**	2.791972	-2.958667	3.793739	**H**	1.211505	0.030537	4.197702
C	-0.695566	-2.637853	1.967025	**C**	1.846904	-0.944957	2.320827	**H**	2.835853	0.061512	3.464690
H	-0.242152	-1.814318	1.404301	**H**	0.866686	-1.285191	1.964233	**H**	1.395805	0.402232	2.470826
H	-0.320852	-2.605284	3.003049	**H**	1.817093	-0.904839	3.421007	**H**	-0.153962	-1.543565	1.751342
H	-0.356748	-3.583598	1.514892	**H**	2.005319	0.080830	1.965602	**H**	0.075234	-3.153946	2.481286
C	0.695578	-2.637860	-1.967027	**C**	4.323861	-1.226682	2.287507	**H**	-0.465542	-1.788502	3.492202
H	0.320865	-2.605297	-3.003051	**H**	4.325112	-0.967933	3.358914	**H**	1.932587	-3.574026	4.146105
H	0.356764	-3.583606	-1.514891	**H**	5.180832	-1.890560	2.098505	**H**	3.073928	-2.271388	4.576457
H	0.242158	-1.814325	-1.404307	**H**	4.479114	-0.300994	1.711838	**H**	1.373019	-2.174261	5.081551

Table G66 XYZ coordinates of the GS and TS geometries of **3.16d** B3LYP/Def2SVP (PCM = CH_2Cl_2)

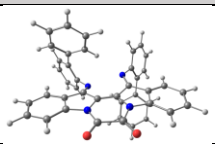
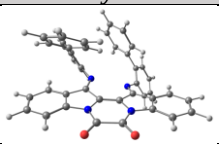
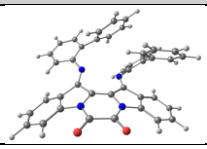
Anti				***Syn***				**TS**			
											
O	-1.340849	4.944632	0.302367	**O**	1.657510	4.904121	-0.423581	**C**	0.774909	0.486149	0.636758
O	1.340840	4.944633	-0.302367	**O**	-0.951889	5.238670	0.363014	**C**	2.117177	-0.105006	0.339825
N	-1.316441	2.654434	0.378785	**N**	1.272173	2.667717	-0.737499	**C**	3.021617	1.093344	0.338556
N	-1.220061	-0.870632	0.767031	**N**	0.791428	-0.842661	-0.915373	**C**	4.270752	1.390481	-0.223219
N	1.316435	2.654435	-0.378782	**N**	-1.343313	3.010612	-0.001384	**H**	4.775392	0.688367	-0.881016
N	1.220058	-0.870631	-0.767026	**N**	-2.019891	-0.402457	-0.720063	**C**	4.857577	2.639302	0.004013
C	-0.641880	1.428006	0.224896	**C**	0.409239	1.552207	-0.725752	**H**	5.829365	2.861866	-0.440771
C	-1.582211	0.344481	0.607575	**C**	1.231799	0.351016	-1.022754	**C**	4.210355	3.600263	0.787200
C	-2.874457	1.022222	0.848732	**C**	2.581222	0.871139	-1.327167	**H**	4.691290	4.561920	0.978331
C	-4.133532	0.533716	1.211998	**C**	3.742967	0.231624	-1.765742	**C**	2.927650	3.365586	1.294145
H	-4.308143	-0.535233	1.314830	**H**	3.753880	-0.844319	-1.934272	**H**	2.383710	4.120763	1.854314
C	-5.168526	1.445765	1.436594	**C**	4.890839	0.999222	-1.977327	**C**	2.343060	2.131191	1.017660
H	-6.158602	1.079277	1.714310	**H**	5.808833	0.516451	-2.317857	**C**	3.373882	-2.199049	0.146755
C	-4.947966	2.823086	1.305609	**C**	4.876006	2.381570	-1.746498	**C**	3.134271	-3.608533	0.112714
H	-5.770108	3.520049	1.482260	**H**	5.785854	2.964203	-1.906756	**C**	4.184478	-4.469901	-0.247930
C	-3.691779	3.333602	0.954609	**C**	3.716828	3.042160	-1.320295	**H**	3.985258	-5.542450	-0.290787
H	-3.510676	4.400281	0.858190	**H**	3.695963	4.114614	-1.149743	**C**	5.476201	-4.000490	-0.479002
C	-2.671194	2.411932	0.732170	**C**	2.577141	2.263168	-1.128543	**H**	6.273348	-4.697176	-0.747818
C	-2.096399	-1.927169	0.993851	**C**	1.558689	-1.996554	-0.874517	**C**	5.746973	-2.640225	-0.303943
C	-3.020131	-2.351640	-0.000973	**C**	2.558205	-2.207195	0.118773	**H**	6.764459	-2.257607	-0.411632
C	-3.841351	-3.453133	0.289761	**C**	3.221779	-3.443368	0.135795	**C**	4.711861	-1.764204	0.003294
H	-4.544692	-3.793722	-0.473378	**H**	3.975486	-3.617106	0.907276	**C**	-0.504014	0.134700	0.320630
C	-3.765919	-4.128916	1.509023	**C**	2.930493	-4.452382	-0.784085	**C**	-1.088918	-0.951378	-0.506599
H	-4.417451	-4.984044	1.700749	**H**	3.464668	-5.403854	-0.739007	**C**	-2.494884	-0.547551	-0.732978
C	-2.837215	-3.715587	2.469236	**C**	1.937890	-4.240123	-1.745993	**C**	-3.494504	-1.070245	-1.557604
H	-2.758621	-4.240764	3.423994	**H**	1.688892	-5.024051	-2.465153	**H**	-3.298302	-1.936949	-2.186241
C	-1.997972	-2.634620	2.205364	**C**	1.246424	-3.031932	-1.775165	**C**	-4.750913	-0.459993	-1.562083
C	0.641874	1.428007	-0.224892	**C**	-0.898957	1.728351	-0.384801	**H**	-5.541995	-0.858672	-2.200005
C	1.582207	0.344482	-0.607571	**C**	-2.071794	0.817481	-0.347051	**C**	-5.008036	0.648199	-0.744272
C	2.874452	1.022224	-0.848730	**C**	-3.183515	1.639631	0.184437	**H**	-6.001663	1.101787	-0.747035
C	4.133526	0.533719	-1.211996	**C**	-4.495764	1.313517	0.540927	**C**	-4.014552	1.199669	0.074008
H	4.308138	-0.535229	-1.314827	**H**	-4.870368	0.298975	0.415708	**H**	-4.200843	2.067793	0.699704
C	5.168519	1.445770	-1.436594	**C**	-5.318819	2.316268	1.061019	**C**	-2.759228	0.594529	0.044223
H	6.158596	1.079282	-1.714311	**H**	-6.345896	2.078379	1.344403	**N**	0.995003	1.746283	1.231314
C	4.947958	2.823091	-1.305610	**C**	-4.838915	3.623812	1.217045	**N**	2.266261	-1.381655	0.318113
H	5.770099	3.520054	-1.482263	**H**	-5.499219	4.396058	1.617730	**N**	-1.560528	1.001502	0.685538
C	3.691771	3.333605	-0.954609	**C**	-3.524186	3.966991	0.878440	**H**	4.948939	-0.720878	0.155695
H	3.510666	4.400284	-0.858191	**H**	-3.141401	4.975103	1.008669	**C**	-1.425144	2.121742	1.477263
C	2.671186	2.411934	-0.732168	**C**	-2.712538	2.952990	0.372241	**C**	0.009452	2.557061	1.758333
C	2.096397	-1.927166	-0.993849	**C**	-3.093890	-1.263528	-0.893771	**O**	-2.358270	2.795579	1.867735
C	3.020135	-2.351635	0.000970	**C**	-3.061944	-2.542719	-0.280199	**O**	0.229905	3.598389	2.344237
C	3.841359	-3.453125	-0.289769	**C**	-4.063862	-3.469408	-0.602234	**C**	1.879996	-4.247096	0.584494
H	4.544705	-3.793712	0.473366	**H**	-4.042649	-4.448859	-0.118308	**C**	1.266305	-5.272531	-0.151672
C	3.765924	-4.128906	-1.509032	**C**	-5.080533	-3.161556	-1.509252	**C**	1.411057	-3.977225	1.883358
H	4.417459	-4.984030	-1.700762	**H**	-5.848725	-3.901673	-1.743217	**C**	0.216529	-6.014287	0.394978
C	2.837214	-3.715579	-2.469240	**C**	-5.104141	-1.900309	-2.114473	**H**	1.610469	-5.486733	-1.164718
H	2.758618	-4.240754	-3.423999	**H**	-5.888087	-1.648001	-2.832609	**C**	0.380495	-4.735644	2.437579
C	1.997968	-2.634615	-2.205363	**C**	-4.122340	-0.959877	-1.809850	**H**	1.886291	-3.188202	2.468696
C	-0.742295	3.894865	0.184673	**C**	0.901116	3.953990	-0.403376	**C**	-0.221977	-5.756961	1.695311
C	0.742287	3.894866	-0.184671	**C**	-0.553206	4.142183	0.025337	**H**	-0.260305	-6.793814	-0.201920
H	1.265130	-2.302669	-2.943153	**H**	-4.120576	0.016589	-2.298247	**H**	0.036086	-4.522065	3.452199
H	-1.265137	-2.302672	2.943157	**H**	0.451941	-2.855958	-2.502109	**H**	-1.039956	-6.338789	2.125866
C	3.142778	-1.653108	1.307593	**C**	-1.988891	-2.889934	0.685831	**N**	-0.430023	-1.985109	-0.867162
C	4.413200	-1.346053	1.826299	**C**	-1.182048	-4.020212	0.477852	**C**	-0.936192	-3.114605	-1.495448
C	2.007507	-1.287050	2.056041	**C**	-1.763171	-2.103383	1.829111	**C**	-0.246301	-3.553636	-2.643124
C	4.548642	-0.690263	3.052675	**C**	-0.165753	-4.348120	1.378137	**C**	-2.011649	-3.899890	-0.985282
H	5.304741	-1.604279	1.250621	**H**	-1.334228	-4.627827	-0.416544	**C**	-0.623658	-4.708697	-3.320580
C	2.144586	-0.632329	3.280544	**C**	-0.760146	-2.441338	2.738778	**H**	0.597244	-2.952517	-2.986906
H	1.010460	-1.496974	1.666613	**H**	-2.389625	-1.227298	2.010036	**C**	-2.350053	-5.074698	-1.678570
C	3.414357	-0.328680	3.784578	**C**	0.047510	-3.560790	2.511717	**C**	-1.682741	-5.481103	-2.833672
H	5.545480	-0.453268	3.432425	**H**	0.474857	-5.209891	1.180429	**H**	-0.078830	-5.015949	-4.216365
H	1.250181	-0.356338	3.845089	**H**	-0.599940	-1.822569	3.624828	**H**	-3.151187	-5.698850	-1.277442
H	3.518402	0.189020	4.741143	**H**	0.848325	-3.810194	3.211514	**H**	-1.976091	-6.404066	-3.338391
C	-3.142771	-1.653110	-1.307594	**C**	2.915734	-1.160354	1.111347	**C**	-2.785945	-3.537341	0.230332
C	-4.413192	-1.346066	-1.826309	**C**	4.265020	-0.841995	1.343135	**C**	-4.184381	-3.690491	0.239104
C	-2.007497	-1.287038	-2.056032	**C**	1.931704	-0.446076	1.818736	**C**	-2.171932	-3.024543	1.386215
C	-4.548630	-0.690274	-3.052685	**C**	4.620941	0.172007	2.235878	**C**	-4.943664	-3.331860	1.355170
H	-5.304734	-1.604303	-1.250639	**H**	5.042674	-1.372856	0.790095	**H**	-4.689097	-4.063781	-0.654156
C	-2.144573	-0.632314	-3.280534	**C**	2.285750	0.567712	2.709150	**C**	-2.927889	-2.664486	2.501299
H	-1.010451	-1.496952	-1.666596	**H**	0.882120	-0.689053	1.662102	**H**	-1.092080	-2.911317	1.411915
C	-3.414344	-0.328677	-3.784578	**C**	3.632321	0.886959	2.917377	**C**	-4.319278	-2.810455	2.491181
H	-5.545467	-0.453288	-3.432442	**H**	5.675774	0.412647	2.388758	**H**	-6.029833	-3.448443	1.330075
H	-1.250166	-0.356312	-3.845070	**H**	1.504077	1.111106	3.245975	**H**	-2.424128	-2.269572	3.387106
H	-3.518386	0.189025	-4.741141	**H**	3.908408	1.687491	3.607743	**H**	-4.911334	-2.520146	3.362309

Table G67 XYZ coordinates of the GS and TS geometries of **3.16e** B3LYP/Def2SVP (PCM = CH_2Cl_2)

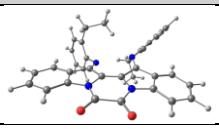
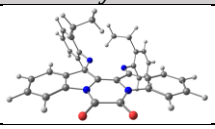
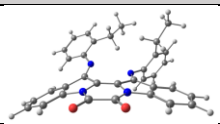
Anti				***Syn***				**TS**			
											
O	1.098639	5.006040	0.242648	**O**	1.315751	4.895286	-0.133140	**C**	1.483905	-0.912343	-0.033347
O	-1.632848	4.887515	-0.023181	**O**	-1.387600	4.875064	0.337608	**C**	2.036558	0.465316	0.197336
N	1.433453	-0.803407	-0.297798	**N**	1.381289	-0.942436	-0.196076	**C**	3.482801	0.217070	0.501628
N	1.204149	2.720821	0.116736	**N**	1.305138	2.607407	-0.256607	**C**	4.505527	0.949117	1.119727
N	-1.411251	-0.937822	0.237697	**N**	-1.528589	-0.919158	-0.444861	**H**	4.314070	1.900359	1.605861
N	-1.525857	2.598427	-0.038357	**N**	-1.403825	2.593348	0.123361	**C**	5.796797	0.418242	1.200231
C	0.940486	-2.769704	2.228635	**C**	1.595912	-1.537675	2.946559	**H**	6.582900	0.998467	1.687137
C	2.365580	-2.228079	2.049846	**C**	2.936970	-1.311883	2.235897	**C**	6.082098	-0.845446	0.676353
C	-1.520412	-2.483481	-2.708621	**C**	-0.506776	-3.907900	0.946173	**H**	7.098514	-1.241453	0.727929
C	-1.049495	-3.188285	-1.429149	**C**	-1.795254	-3.178304	1.348824	**C**	5.068410	-1.635672	0.123725
C	0.541686	3.931230	0.144300	**C**	0.711269	3.842679	-0.097438	**H**	5.258631	-2.641017	-0.239568
C	-0.979251	3.864801	0.018765	**C**	-0.795195	3.832285	0.146886	**C**	3.782719	-1.099884	0.084605
C	2.949653	-2.021783	-1.733920	**C**	2.520069	-2.770663	-1.290654	**C**	1.532202	2.854177	-0.170504
C	3.925046	-3.002053	-1.921912	**C**	3.445658	-3.814899	-1.271729	**C**	0.481568	3.609108	-0.787013
C	4.406475	-3.725907	-0.828249	**C**	4.206452	-4.051357	-0.124138	**C**	0.629839	4.994406	-0.914592
C	3.898636	-3.461151	0.447549	**C**	4.031043	-3.233612	0.996669	**H**	-0.168017	5.575472	-1.377664
C	2.922565	-2.481211	0.668664	**C**	3.121581	-2.168853	1.003950	**C**	1.773469	5.659674	-0.465257
C	2.455560	-1.746860	-0.447594	**C**	2.364473	-1.936517	-0.171664	**H**	1.853816	6.743721	-0.575593
C	2.613720	2.554224	0.175001	**C**	2.691801	2.386486	-0.473508	**C**	2.805435	4.929634	0.125249
C	3.604532	3.525735	0.303017	**C**	3.716375	3.321559	-0.608143	**H**	3.708757	5.429584	0.481876
C	4.932556	3.081950	0.341915	**C**	5.006766	2.825864	-0.834072	**C**	2.680012	3.550413	0.266909
C	5.254215	1.721237	0.255228	**C**	5.259462	1.450640	-0.923631	**C**	0.231646	-1.454739	-0.006343
C	4.248981	0.758616	0.121211	**C**	4.221701	0.524996	-0.780162	**C**	-1.108264	-0.940734	0.388515
C	2.916940	1.182923	0.081320	**C**	2.927565	1.001534	-0.548521	**C**	-1.993449	-2.128685	0.400777
C	1.647888	0.432855	-0.064906	**C**	1.640779	0.298290	-0.342142	**C**	-3.329761	-2.290675	0.783667
C	0.575687	1.460856	0.028999	**C**	0.619978	1.374472	-0.231709	**H**	-3.909817	-1.446859	1.152367
C	-2.081084	-3.180095	-0.329743	**C**	-2.709502	-2.963410	0.166506	**C**	-3.908758	-3.557944	0.681875
C	-2.890895	-4.290767	-0.065143	**C**	-3.714157	-3.889891	-0.142852	**H**	-4.950559	-3.699991	0.975444
C	-3.837652	-4.280340	0.963818	**C**	-4.525886	-3.750976	-1.272189	**C**	-3.165185	-4.645324	0.203353
C	-3.987263	-3.135424	1.753552	**C**	-4.333701	-2.660519	-2.125949	**H**	-3.636619	-5.627253	0.122491
C	-3.212150	-2.006046	1.495892	**C**	-3.353086	-1.713960	-1.833678	**C**	-1.823158	-4.506854	-0.169278
C	-2.272625	-2.010407	0.446824	**C**	-2.546252	-1.848434	-0.687584	**H**	-1.237922	-5.346520	-0.531982
C	-2.908135	2.303376	-0.184198	**C**	-2.792070	2.360294	0.312557	**C**	-1.256353	-3.237987	-0.048929
C	-3.974047	3.184511	-0.358885	**C**	-3.796647	3.277415	0.617671	**N**	2.581122	-1.765831	-0.266459
C	-5.242969	2.622885	-0.545501	**C**	-5.089335	2.771459	0.799761	**N**	1.313505	1.488373	-0.081333
C	-5.433779	1.234628	-0.563349	**C**	-5.361523	1.401609	0.688100	**N**	0.080666	-2.834685	-0.291835
C	-4.356706	0.365225	-0.370639	**C**	-4.344956	0.496651	0.370240	**H**	3.492052	3.008132	0.724864
C	-3.083541	0.906708	-0.166830	**C**	-3.048906	0.984466	0.170180	**C**	1.091662	-3.675247	-0.703521
C	-1.757437	0.274544	0.034485	**C**	-1.770142	0.298970	-0.140934	**C**	2.494545	-3.085841	-0.663713
C	-0.784785	1.399778	0.003265	**C**	-0.734187	1.368402	-0.082242	**O**	0.924624	-4.835962	-1.023921
H	0.576178	-2.584430	3.251910	**H**	1.500043	-0.874922	3.821047	**O**	3.456042	-3.781126	-0.924582
H	0.909148	-3.855856	2.047362	**H**	1.506145	-2.578341	3.294815	**C**	-0.748668	2.905872	-1.307868
H	0.249872	-2.283116	1.526472	**H**	0.754039	-1.336336	2.267982	**H**	-0.470443	2.373446	-2.236717
H	-0.778886	-4.230482	-1.662045	**H**	-2.329847	-3.761929	2.115717	**H**	-0.993201	2.108883	-0.597740
H	-0.146010	-2.679504	-1.060335	**H**	-1.538069	-2.211493	1.808075	**C**	-1.964253	3.790221	-1.570816
H	2.369525	-1.145134	2.260348	**H**	3.028583	-0.246548	1.967473	**H**	-1.787904	4.526077	-2.371320
H	3.037942	-2.688474	2.791011	**H**	3.763546	-1.519215	2.933431	**H**	-2.820912	3.174623	-1.877641
H	-2.415759	-2.970746	-3.127053	**H**	-0.736460	-4.892084	0.507790	**H**	-2.262108	4.341941	-0.664770
H	-0.731604	-2.499315	-3.477734	**H**	0.150261	-4.063809	1.815377	**N**	-1.357985	0.281804	0.664014
H	-1.773251	-1.430470	-2.509128	**H**	0.051296	-3.321092	0.204403	**C**	-2.631541	0.779628	0.958484
H	4.306853	-3.198390	-2.926772	**H**	3.565215	-4.447263	-2.154777	**C**	-2.859549	1.285089	2.249372
H	5.169411	-4.495300	-0.965754	**H**	4.928867	-4.870084	-0.097386	**C**	-3.633866	0.897927	-0.043119
H	4.271010	-4.027658	1.305798	**H**	4.621178	-3.419928	1.898376	**C**	-4.085465	1.859603	2.584472
H	3.348304	4.578958	0.371016	**H**	3.513007	4.386363	-0.542339	**H**	-2.056700	1.207663	2.985184
H	5.731878	3.819313	0.443691	**H**	5.831197	3.533561	-0.945450	**C**	-4.844695	1.501754	0.319439
H	6.299286	1.407804	0.291091	**H**	6.275971	1.097064	-1.106354	**C**	-5.084271	1.970482	1.615357
H	4.499389	-0.298160	0.052270	**H**	4.417855	-0.543288	-0.849025	**H**	-4.252475	2.229475	3.598942
H	-2.760144	-5.190980	-0.672206	**H**	-3.856769	-4.745317	0.523750	**H**	-5.629566	1.608840	-0.430452
H	-4.445278	-5.167065	1.158028	**H**	-5.298117	-4.492894	-1.487297	**H**	-6.044981	2.429285	1.859582
H	-4.707318	-3.121604	2.575278	**H**	-4.951271	-2.541529	-3.019507	**C**	-3.384393	0.376950	-1.444432
H	-3.815005	4.258941	-0.359061	**H**	-3.574719	4.335956	0.715533	**H**	-2.385008	0.708492	-1.768151
H	-6.098425	3.286796	-0.688006	**H**	-5.898238	3.464458	1.041324	**H**	-3.316272	-0.722932	-1.409852
H	-6.433416	0.826820	-0.725244	**H**	-6.377665	1.035815	0.847546	**C**	-4.419581	0.760163	-2.498913
H	-4.507731	-0.712612	-0.380146	**H**	-4.560719	-0.566040	0.282841	**H**	-4.115991	0.374484	-3.483902
H	-3.314516	-1.110931	2.112487	**H**	-3.198129	-0.853610	-2.487980	**H**	-5.411493	0.339121	-2.272193
H	2.560882	-1.449901	-2.578852	**H**	1.907832	-2.579711	-2.174025	**H**	-4.533120	1.852234	-2.587380

Table G68 XYZ coordinates of the GS and TS geometries of **3.16a** B3LYP/Def2SVP (CPCM = CH_2Cl_2)

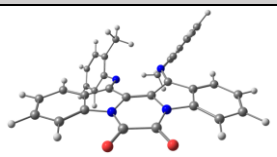
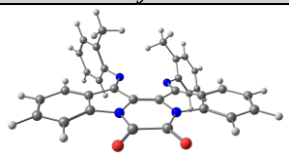
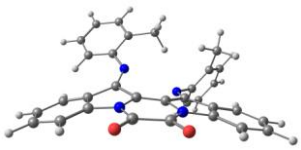
Anti				***Syn***				**TS**			
											
O	-1.361549	-4.833703	0.172481	**O**	1.662291	-4.700880	0.100361	**C**	1.094157	-1.033650	0.000848
O	1.361555	-4.833702	-0.172476	**O**	-1.065270	-4.830090	-0.164226	**C**	1.893271	0.222254	0.177667
N	-1.362116	-2.542623	0.130641	**N**	1.555574	-2.412433	0.040274	**C**	3.242546	-0.272767	0.593441
N	-1.426211	0.996282	-0.178384	**N**	1.447437	1.129019	-0.234383	**C**	4.354604	0.303666	1.220162
N	1.362119	-2.542621	-0.130651	**N**	-1.168866	-2.541294	-0.174118	**H**	4.327337	1.317261	1.608582
N	1.426207	0.996284	0.178374	**N**	-1.410261	1.009570	-0.088710	**C**	5.508262	-0.457844	1.433024
C	-0.680552	-1.310897	0.042358	**C**	0.817823	-1.215221	-0.059173	**H**	6.367829	0.000632	1.925581
C	-1.705949	-0.233481	0.024246	**C**	1.791895	-0.089597	-0.068958	**C**	5.562964	-1.796058	1.032800
C	-2.997894	-0.926635	0.246216	**C**	3.116667	-0.722633	0.140492	**H**	6.475622	-2.375042	1.189176
C	-4.295090	-0.443147	0.444569	**C**	4.391999	-0.181107	0.332691	**C**	4.445148	-2.422769	0.470247
H	-4.498874	0.625923	0.429093	**H**	4.548195	0.895668	0.314908	**H**	4.452287	-3.474501	0.199857
C	-5.327503	-1.359268	0.663917	**C**	5.465918	-1.049044	0.547969	**C**	3.296388	-1.654182	0.295840
H	-6.345331	-0.997249	0.821375	**H**	6.466928	-0.640529	0.699224	**C**	1.894839	2.610177	-0.442976
C	-5.068613	-2.736532	0.679028	**C**	5.270114	-2.436479	0.566463	**C**	1.041045	3.471288	-1.201579
H	-5.889461	-3.437944	0.843755	**H**	6.122769	-3.099748	0.727462	**C**	1.461805	4.775234	-1.483073
C	-3.774915	-3.239687	0.496226	**C**	3.999483	-2.997676	0.391672	**H**	0.803657	5.425264	-2.065018
H	-3.563818	-4.304782	0.519979	**H**	3.837004	-4.071112	0.418673	**C**	2.694722	5.261009	-1.040069
C	-2.754457	-2.312073	0.291497	**C**	2.937169	-2.117507	0.190380	**H**	2.994255	6.286432	-1.268843
C	-2.342577	2.022637	-0.375218	**C**	2.310494	2.205361	-0.403107	**C**	3.537213	4.424281	-0.305078
C	-2.244302	3.174521	0.445182	**C**	3.231246	2.252866	-1.467655	**H**	4.506408	4.783730	0.047946
C	-3.103571	4.248433	0.184382	**C**	4.015639	3.387180	-1.672950	**C**	3.140807	3.120788	-0.016221
H	-3.042989	5.135162	0.821344	**H**	4.721319	3.413332	-2.506763	**C**	-0.239492	-1.308990	-0.057759
C	-4.018188	4.217258	-0.873326	**C**	3.895200	4.483964	-0.813724	**C**	-1.461339	-0.512594	0.228795
H	-4.667595	5.075408	-1.060321	**H**	4.509871	5.374005	-0.965827	**C**	-2.587514	-1.466104	0.091953
C	-4.084325	3.088655	-1.696772	**C**	2.968942	4.443182	0.233839	**C**	-3.962534	-1.327320	0.312780
H	-4.782145	3.057909	-2.537026	**H**	2.863575	5.306230	0.896921	**H**	-4.384438	-0.371713	0.617858
C	-3.254248	1.996476	-1.448511	**C**	2.152844	3.326742	0.449671	**C**	-4.789629	-2.440139	0.138855
C	0.680553	-1.310896	-0.042370	**C**	-0.541827	-1.277404	-0.141332	**H**	-5.864218	-2.343935	0.305306
C	1.705948	-0.233479	-0.024256	**C**	-1.615916	-0.246829	-0.179480	**C**	-4.252459	-3.674451	-0.249788
C	2.997895	-0.926631	-0.246220	**C**	-2.881901	-1.008845	-0.284520	**H**	-4.914824	-4.531576	-0.389577
C	4.295091	-0.443143	-0.444567	**C**	-4.214042	-0.590954	-0.371273	**C**	-2.877896	-3.840279	-0.455886
H	4.498874	0.625928	-0.429091	**H**	-4.466842	0.467271	-0.386783	**H**	-2.451210	-4.796630	-0.743301
C	5.327507	-1.359263	-0.663911	**C**	-5.217207	-1.562360	-0.440489	**C**	-2.065174	-2.722845	-0.267302
H	6.345334	-0.997243	-0.821365	**H**	-6.262160	-1.254171	-0.509485	**N**	2.009837	-2.098892	-0.102797
C	5.068618	-2.736527	-0.679022	**C**	-4.893326	-2.925225	-0.422888	**N**	1.400752	1.333798	-0.232600
H	5.889467	-3.437939	-0.843745	**H**	-5.690723	-3.669608	-0.477563	**N**	-0.652601	-2.631382	-0.345129
C	3.774920	-3.239683	-0.496225	**C**	-3.565463	-3.362342	-0.337011	**H**	3.814457	2.493417	0.548065
H	3.563824	-4.304778	-0.519979	**H**	-3.308122	-4.417259	-0.322832	**C**	0.195310	-3.683642	-0.614357
C	2.754459	-2.312070	-0.291501	**C**	-2.576823	-2.382219	-0.269544	**C**	1.682142	-3.396720	-0.440260
C	2.342572	2.022639	0.375217	**C**	-2.435494	1.958909	-0.078821	**O**	-0.179219	-4.799082	-0.921221
C	2.244306	3.174523	-0.445183	**C**	-3.021992	2.339259	1.152295	**O**	2.495107	-4.290992	-0.568011
C	3.103572	4.248435	-0.184375	**C**	-3.999128	3.341775	1.134539	**C**	-0.286464	2.984628	-1.705670
H	3.042997	5.135163	-0.821337	**H**	-4.461581	3.637958	2.080231	**H**	-0.167930	2.093673	-2.340396
C	4.018177	4.217260	0.873343	**C**	-4.394757	3.963493	-0.054370	**H**	-0.928288	2.682425	-0.870499
H	4.667582	5.075410	1.060346	**H**	-5.161660	4.740959	-0.036524	**H**	-0.797898	3.765054	-2.286373
C	4.084305	3.088657	1.696790	**C**	-3.795476	3.587998	-1.259710	**N**	-1.437078	0.712389	0.597227
H	4.782116	3.057912	2.537052	**H**	-4.088910	4.068965	-2.195983	**C**	-2.567312	1.502220	0.806956
C	3.254231	1.996478	1.448520	**C**	-2.812389	2.596996	-1.271877	**C**	-2.733716	2.067721	2.087714
C	-0.758336	-3.782498	0.087588	**C**	1.009719	-3.679868	0.016862	**C**	-3.460653	1.855759	-0.239142
C	0.758339	-3.782498	-0.087600	**C**	-0.508406	-3.751384	-0.120352	**C**	-3.798208	2.921318	2.362656
H	3.291593	1.113497	2.089729	**H**	-2.330235	2.296326	-2.204150	**H**	-2.010508	1.806358	2.862715
H	-3.291617	1.113495	-2.089719	**H**	3.313560	1.392909	-2.135439	**C**	-4.504654	2.743863	0.062565
C	1.247999	3.202589	-1.571344	**C**	-2.608491	1.652267	2.426115	**C**	-4.692029	3.266498	1.342900
H	1.552774	2.529938	-2.391493	**H**	-2.922964	0.594721	2.433003	**H**	-3.921843	3.328607	3.368946
H	0.266838	2.842718	-1.227010	**H**	-1.512419	1.653578	2.540186	**H**	-5.192183	3.026175	-0.739808
H	1.142430	4.215188	-1.985867	**H**	-3.053923	2.141580	3.303611	**H**	-5.522092	3.948352	1.540534
C	-1.247982	3.202587	1.571331	**C**	1.131529	3.282086	1.553130	**C**	-3.335950	1.307109	-1.637424
H	-1.552746	2.529936	2.391483	**H**	0.164051	2.931505	1.162054	**H**	-2.318387	0.966638	-1.865079
H	-0.266825	2.842717	1.226984	**H**	1.422446	2.569094	2.343382	**H**	-4.006007	0.443666	-1.786131
H	-1.142409	4.215187	1.985852	**H**	1.002206	4.269742	2.017865	**H**	-3.616700	2.070167	-2.378322

Table G69 XYZ coordinates of the GS and TS geometries of **3.16b** B3LYP/Def2SVP (CPCM = CH_2Cl_2)

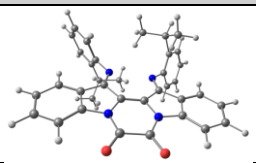
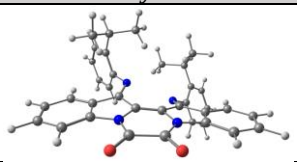
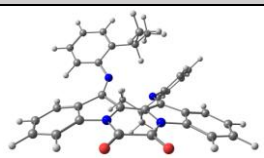
Anti				***Syn***				**TS**			
											
O	1.370602	5.038679	0.031953	**O**	-1.304360	4.943498	0.452069	**C**	-1.712328	0.570693	-0.035892
O	-1.370602	5.038679	-0.031953	**O**	1.362758	4.939895	-0.209063	**C**	-1.701427	-0.919886	0.108017
N	1.366339	2.747368	0.034792	**N**	-1.367120	2.668153	0.189881	**C**	-3.069708	-1.237105	0.621055
N	1.440212	-0.810927	0.121225	**N**	-1.577183	-0.813431	-0.531891	**C**	-3.647520	-2.336696	1.267798
N	-1.366339	2.747368	-0.034793	**N**	1.319334	2.652297	-0.331248	**H**	-3.051913	-3.188554	1.582852
N	-1.440212	-0.810927	-0.121225	**N**	1.384835	-0.870982	-0.065670	**C**	-5.007534	-2.317274	1.593832
C	0.681773	1.513145	0.023068	**C**	-0.722719	1.436361	-0.052715	**H**	-5.448151	-3.177664	2.101035
C	1.709422	0.437045	0.092706	**C**	-1.779941	0.391984	-0.150202	**C**	-5.798432	-1.206009	1.286980
C	3.012741	1.141160	0.088246	**C**	-3.039686	1.089154	0.206977	**H**	-6.862657	-1.210263	1.531991
C	4.328049	0.665356	0.056406	**C**	-4.338639	0.614838	0.420071	**C**	-5.236930	-0.063488	0.705245
H	4.535153	-0.402484	0.066749	**H**	-4.575724	-0.439454	0.292379	**H**	-5.825148	0.827280	0.505368
C	5.374953	1.590142	0.010254	**C**	-5.330259	1.521964	0.803141	**C**	-3.874413	-0.092339	0.416602
H	6.406928	1.235032	-0.014340	**H**	-6.348279	1.166846	0.974122	**C**	-0.461572	-2.910873	-0.666628
C	5.111729	2.966255	-0.001614	**C**	-5.031021	2.881518	0.964665	**C**	0.683617	-3.151538	-1.493914
H	5.942827	3.674266	-0.031697	**H**	-5.821254	3.576867	1.256045	**C**	1.001695	-4.470741	-1.833656
C	3.802051	3.461290	0.016007	**C**	-3.734435	3.373041	0.771079	**H**	1.870288	-4.665166	-2.463382
H	3.590662	4.526168	-0.005403	**H**	-3.491031	4.422492	0.908552	**C**	0.238183	-5.553026	-1.388072
C	2.769110	2.525788	0.053309	**C**	-2.754390	2.452850	0.402272	**H**	0.519956	-6.571303	-1.666369
C	2.402092	-1.800401	0.340593	**C**	-2.642017	-1.646362	-0.905738	**C**	-0.881447	-5.323160	-0.586545
C	2.739597	-2.735939	-0.668104	**C**	-2.919735	-2.861837	-0.233548	**H**	-1.491507	-6.156279	-0.230353
C	3.664735	-3.738099	-0.340064	**C**	-3.985059	-3.640438	-0.710732	**C**	-1.221804	-4.020086	-0.235127
H	3.945905	-4.455101	-1.116440	**H**	-4.219074	-4.570784	-0.185972	**C**	-0.739481	1.517331	-0.161573
C	4.226639	-3.852134	0.934124	**C**	-4.741984	-3.274314	-1.826218	**C**	0.734515	1.489690	0.018300
H	4.937852	-4.652386	1.150171	**H**	-5.558933	-3.913494	-2.168304	**C**	1.174607	2.895238	-0.172847
C	3.860785	-2.939281	1.927108	**C**	-4.433114	-2.091530	-2.503368	**C**	2.424042	3.517104	-0.057292
H	4.278403	-3.016192	2.933871	**H**	-5.000903	-1.791937	-3.387479	**H**	3.316280	2.937686	0.168060
C	2.956736	-1.921992	1.630157	**C**	-3.394795	-1.286246	-2.042791	**C**	2.512861	4.899494	-0.238593
C	-0.681773	1.513145	-0.023068	**C**	0.623969	1.429573	-0.246957	**H**	3.483795	5.391525	-0.154469
C	-1.709422	0.437045	-0.092706	**C**	1.622097	0.340879	-0.391016	**C**	1.371171	5.656759	-0.532294
C	-3.012741	1.141159	-0.088246	**C**	2.886981	1.018393	-0.758415	**H**	1.460747	6.735084	-0.681138
C	-4.328049	0.665355	-0.056406	**C**	4.157564	0.524240	-1.069009	**C**	0.108948	5.061204	-0.630993
H	-4.535153	-0.402485	-0.066748	**H**	4.336186	-0.546658	-1.140315	**H**	-0.785138	5.640478	-0.841644
C	-5.374954	1.590142	-0.010253	**C**	5.194996	1.435003	-1.290328	**C**	0.035661	3.682030	-0.436341
H	-6.406928	1.235032	0.014341	**H**	6.191685	1.066108	-1.539718	**N**	-3.059334	0.981091	-0.025870
C	-5.111729	2.966254	0.001614	**C**	4.967837	2.814095	-1.193748	**N**	-0.723085	-1.580839	-0.392368
H	-5.942828	3.674266	0.031697	**H**	5.791601	3.509751	-1.367880	**N**	-1.116095	2.855789	-0.414635
C	-3.802051	3.461290	-0.016007	**C**	3.704026	3.327989	-0.876543	**H**	-2.095895	-3.863950	0.379742
H	-3.590662	4.526168	0.005402	**H**	3.521299	4.395516	-0.794417	**C**	-2.413076	3.295083	-0.570361
C	-2.769110	2.525788	-0.053309	**C**	2.678680	2.408205	-0.667068	**C**	-3.500206	2.257799	-0.310488
C	-2.402092	-1.800401	-0.340593	**C**	2.339199	-1.889033	-0.191633	**O**	-2.716713	4.439723	-0.846754
C	-2.956736	-1.921993	-1.630157	**C**	3.060115	-2.370029	0.929063	**O**	-4.671265	2.582273	-0.334658
C	-3.860785	-2.939281	-1.927108	**C**	3.948548	-3.434931	0.713848	**C**	1.495606	-1.985368	-2.027703
H	-4.278402	-3.016192	-2.933871	**H**	4.522461	-3.807881	1.566730	**H**	1.511283	-1.239487	-1.226081
C	-4.226638	-3.852135	-0.934124	**C**	4.121001	-4.029444	-0.538415	**C**	0.780406	-1.334344	-3.223999
H	-4.937851	-4.652386	-1.150171	**H**	4.820919	-4.859102	-0.659398	**H**	-0.230684	-1.005061	-2.943677
C	-3.664735	-3.738100	0.340064	**C**	3.383377	-3.557394	-1.627011	**H**	1.343062	-0.453452	-3.574355
H	-3.945905	-4.455102	1.116440	**H**	3.494613	-4.012917	-2.613887	**H**	0.694023	-2.040447	-4.066848
C	-2.739596	-2.735939	0.668104	**C**	2.496785	-2.496564	-1.450922	**C**	2.938976	-2.346112	-2.386015
C	0.761964	3.987622	0.018293	**C**	-0.737718	3.896739	0.210196	**H**	2.995721	-3.031821	-3.247123
C	-0.761964	3.987622	-0.018294	**C**	0.751522	3.893223	-0.130414	**H**	3.494411	-1.436502	-2.655893
H	2.659467	-1.201674	2.394924	**H**	1.907539	-2.116150	-2.287706	**H**	3.462121	-2.816184	-1.538626
C	2.162109	-2.680505	-2.074607	**H**	-3.144997	-0.357068	-2.559036	**N**	1.366737	0.435059	0.376505
H	2.605295	-3.535750	-2.611816	**C**	-2.119306	-3.350465	0.962492	**C**	2.749407	0.302838	0.459727
C	2.578740	-1.414458	-2.841222	**H**	-2.596284	-4.294497	1.275135	**C**	3.304692	-0.296768	1.620140
H	3.670316	-1.271790	-2.814272	**C**	-2.185202	-2.398967	2.166927	**C**	3.577627	0.609304	-0.636996
H	2.270467	-1.490200	-3.896459	**H**	-3.228160	-2.164984	2.432648	**C**	4.686871	-0.513776	1.652121
H	2.107555	-0.512955	-2.423993	**H**	-1.704738	-2.860719	3.044141	**C**	4.948223	0.362450	-0.586075
C	0.637384	-2.870559	-2.084700	**H**	-1.662753	-1.453952	1.964239	**H**	3.125536	1.025645	-1.538934
H	0.354539	-3.817909	-1.599048	**C**	-0.671519	-3.672948	0.563833	**C**	5.509883	-0.191312	0.566923
H	0.134134	-2.055550	-1.548222	**H**	-0.646295	-4.394723	-0.267666	**H**	5.137186	-0.955733	2.542437
H	0.260728	-2.894594	-3.120218	**H**	-0.142976	-2.763230	0.252625	**H**	5.574093	0.599184	-1.449732
H	-2.659467	-1.201674	-2.394924	**H**	-0.125489	-4.114204	1.412397	**H**	6.583954	-0.382645	0.621337
C	-2.162109	-2.680505	2.074608	**C**	2.950621	-1.770759	2.326122	**C**	2.382604	-0.723167	2.752200
H	-2.605295	-3.535750	2.611816	**H**	3.547558	-2.434055	2.973935	**H**	1.577118	0.026186	2.810370
C	-2.578741	-1.414457	2.841222	**C**	1.520366	-1.770298	2.883757	**C**	3.062646	-0.780760	4.122487
H	-3.670317	-1.271790	2.814271	**H**	0.852161	-1.143357	2.277046	**C**	1.725152	-2.070545	2.401202
H	-2.270467	-1.490199	3.896458	**H**	1.100162	-2.786163	2.899636	**H**	3.814428	-1.584886	4.173322
H	-2.107555	-0.512955	2.423992	**H**	1.517009	-1.382216	3.914970	**H**	3.564343	0.168335	4.368553
C	-0.637384	-2.870559	2.084700	**C**	3.589896	-0.375385	2.427517	**H**	2.315955	-0.985565	4.905476
H	-0.354539	-3.817909	1.599049	**H**	4.606938	-0.368454	2.006844	**H**	1.195439	-2.007370	1.441580
H	-0.134134	-2.055550	1.548222	**H**	3.001531	0.384781	1.895053	**H**	2.487881	-2.863154	2.327075
H	-0.260728	-2.894594	3.120219	**H**	3.652734	-0.064398	3.482729	**H**	1.000652	-2.365437	3.177940

Table G70 XYZ coordinates of the GS and TS geometries of **3.16c** B3LYP/Def2SVP (CPCM = CH_2Cl_2)

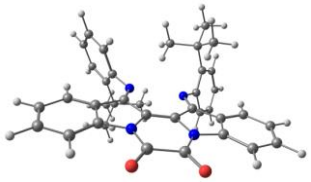
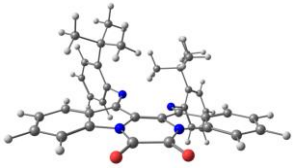
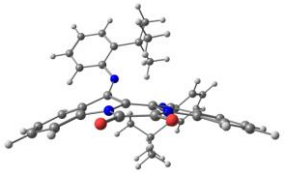
Anti				***Syn***				**TS**			
											
O	1.367672	5.257961	0.096636	**O**	1.316102	5.153801	0.078736	**C**	-0.835967	1.492145	-0.070562
O	-1.367661	5.257963	-0.096639	**O**	-1.370725	5.119634	0.635853	**C**	-1.802912	0.390919	0.246583
N	1.363058	2.966676	0.100590	**N**	1.271296	2.885241	-0.240222	**C**	-2.876733	1.088897	1.019292
N	1.436855	-0.592659	0.153680	**N**	1.311663	-0.653280	-0.420961	**C**	-3.833375	0.678214	1.954938
N	-1.363051	2.966678	-0.100591	**N**	-1.424281	2.866546	0.222411	**H**	-3.869372	-0.349462	2.311245
N	-1.436855	-0.592657	-0.153680	**N**	-1.624022	-0.585302	-0.644672	**C**	-4.716301	1.617283	2.498678
C	0.680290	1.732151	0.053287	**C**	0.571821	1.662056	-0.292375	**H**	-5.459609	1.293742	3.229688
C	1.704058	0.656498	0.165039	**C**	1.571315	0.590267	-0.533839	**C**	-4.647520	2.962012	2.119799
C	3.004941	1.360913	0.235138	**C**	2.858767	1.293320	-0.738764	**H**	-5.356316	3.680836	2.536389
C	4.320328	0.885172	0.265660	**C**	4.143850	0.824895	-1.032381	**C**	-3.651189	3.415495	1.246608
H	4.526338	-0.182876	0.283664	**H**	4.326996	-0.233727	-1.202673	**H**	-3.549410	4.465184	0.985938
C	5.368115	1.809890	0.272995	**C**	5.192054	1.747279	-1.108289	**C**	-2.758228	2.470073	0.747760
H	6.400113	1.454866	0.298090	**H**	6.200337	1.398631	-1.339471	**C**	-2.626204	-1.730812	-0.662296
C	5.105614	3.186158	0.252101	**C**	4.960257	3.111550	-0.890876	**C**	-2.308501	-2.641563	-1.728628
H	5.937120	3.894210	0.265065	**H**	5.792109	3.816536	-0.953167	**C**	-3.281128	-3.588680	-2.081851
C	3.796657	3.681145	0.205968	**C**	3.681250	3.599130	-0.593864	**H**	-3.077529	-4.285707	-2.891423
H	3.586453	4.746046	0.175932	**H**	3.494707	4.655081	-0.421837	**C**	-4.514698	-3.689758	-1.435172
C	2.763149	2.745544	0.190249	**C**	2.646328	2.668427	-0.525743	**H**	-5.231462	-4.452299	-1.748861
C	2.373833	-1.586526	0.445993	**C**	2.279412	-1.642014	-0.644951	**C**	-4.813955	-2.817994	-0.390445
C	2.757820	-2.573529	-0.503098	**C**	2.419679	-2.071391	-1.982066	**H**	-5.768651	-2.877878	0.136828
C	3.644533	-3.566817	-0.055870	**C**	3.332424	-3.058591	-2.333564	**C**	-3.878761	-1.857811	-0.021209
H	3.980376	-4.331944	-0.753790	**H**	3.429642	-3.366111	-3.377402	**C**	0.480274	1.553877	-0.410197
C	4.118780	-3.626178	1.257471	**C**	4.119818	-3.642025	-1.337291	**C**	1.600998	0.595209	-0.249642
H	4.800889	-4.426556	1.552714	**H**	4.852445	-4.413137	-1.585145	**C**	2.816930	1.352043	-0.647967
C	3.707728	-2.665403	2.182490	**C**	3.956974	-3.236654	-0.014077	**C**	4.180872	1.032448	-0.642285
H	4.056090	-2.699258	3.217488	**H**	4.582956	-3.707339	0.745221	**H**	4.521264	0.044346	-0.343646
C	2.843435	-1.654580	1.773768	**C**	3.034007	-2.251015	0.388620	**C**	5.109404	2.002829	-1.027608
C	-0.680285	1.732152	-0.053287	**C**	-0.777529	1.654960	-0.104416	**H**	6.173152	1.757205	-1.028489
C	-1.704055	0.656500	-0.165038	**C**	-1.832026	0.612366	-0.243412	**C**	4.688955	3.280574	-1.417893
C	-3.004937	1.360918	-0.235138	**C**	-3.093783	1.286426	0.148276	**H**	5.427748	4.023079	-1.727424
C	-4.320325	0.885179	-0.265659	**C**	-4.391964	0.798398	0.335371	**C**	3.334856	3.632197	-1.410920
H	-4.526337	-0.182868	-0.283661	**H**	-4.627399	-0.247562	0.151031	**H**	2.996988	4.624811	-1.693851
C	-5.368110	1.809900	-0.272994	**C**	-5.385669	1.681046	0.767013	**C**	2.422277	2.656883	-1.010476
H	-6.400109	1.454877	-0.298089	**H**	-6.402930	1.314700	0.917598	**N**	-1.564331	2.698398	0.015758
C	-5.105607	3.186167	-0.252101	**C**	-5.089432	3.030157	1.003111	**N**	-1.706463	-0.724439	-0.383904
H	-5.937112	3.894221	-0.265066	**H**	-5.881098	3.706987	1.331841	**N**	1.021452	2.786092	-0.838550
C	-3.796648	3.681151	-0.205969	**C**	-3.793819	3.533998	0.837417	**H**	-4.132873	-1.182154	0.781008
H	-3.586443	4.746052	-0.175934	**H**	-3.552845	4.574655	1.032867	**C**	0.304890	3.956155	-0.978171
C	-2.763142	2.745548	-0.190250	**C**	-2.811620	2.637539	0.418525	**C**	-1.121669	3.923723	-0.437533
C	-2.373834	-1.586521	-0.445993	**C**	-2.681651	-1.430338	-1.008672	**O**	0.765350	4.988304	-1.426066
C	-2.843433	-1.654576	-1.773768	**C**	-3.424406	-1.065353	-2.150676	**O**	-1.782665	4.942651	-0.390789
C	-3.707728	-2.665397	-2.182491	**C**	-4.463910	-1.860740	-2.622348	**C**	-0.949331	-2.648178	-2.452022
H	-4.056088	-2.699252	-3.217490	**H**	-5.024403	-1.556510	-3.509455	**C**	-0.620754	-1.274932	-3.080367
C	-4.118786	-3.626169	-1.257472	**C**	-4.779589	-3.039550	-1.945647	**C**	-0.900732	-3.682982	-3.592110
H	-4.800896	-4.426546	-1.552716	**H**	-5.597889	-3.676302	-2.289190	**C**	0.124254	-3.040434	-1.419866
C	-3.644541	-3.566808	0.055869	**C**	-4.031651	-3.413677	-0.825989	**H**	-0.535635	-0.495234	-2.317086
H	-3.980388	-4.331933	0.753790	**H**	-4.295639	-4.343287	-0.324683	**H**	0.333624	-1.339512	-3.627881
C	-2.757826	-2.573522	0.503098	**C**	-2.961113	-2.649588	-0.332449	**H**	-1.402223	-0.979936	-3.799622
C	0.760200	4.206897	0.054457	**C**	0.699666	4.107746	0.045203	**H**	-1.650943	-3.479382	-4.372090
C	-0.760191	4.206898	-0.054459	**C**	-0.797915	4.091033	0.336960	**H**	0.091361	-3.640562	-4.066516
H	2.504272	-0.895014	2.480818	**H**	-3.164165	-0.135332	-2.660079	**H**	-1.046079	-4.712127	-3.230693
C	2.253957	-2.546843	-1.958322	**C**	-2.137807	-3.120025	0.880127	**H**	-0.101142	-4.026828	-0.983245
C	2.803397	-3.727579	-2.777047	**C**	-2.646408	-4.461351	1.434903	**H**	1.111443	-3.102466	-1.901222
H	2.504053	-4.697657	-2.351738	**H**	-2.593122	-5.265014	0.684835	**H**	0.176976	-2.299793	-0.616007
H	2.400428	-3.675510	-3.799981	**H**	-2.015705	-4.760984	2.285722	**N**	1.430798	-0.548892	0.300782
H	3.901685	-3.706792	-2.851590	**H**	-3.684080	-4.394584	1.797231	**C**	2.422519	-1.504263	0.512924
C	2.717446	-1.248492	-2.655338	**C**	-2.216113	-2.088568	2.026765	**C**	2.553915	-2.118714	1.791290
H	2.283481	-0.352557	-2.195134	**H**	-1.764116	-1.128621	1.751109	**C**	3.201174	-1.956112	-0.570834
H	3.814407	-1.155322	-2.620535	**H**	-3.261825	-1.906959	2.321677	**C**	3.530476	-3.119703	1.916754
H	2.410037	-1.259799	-3.713487	**H**	-1.674881	-2.467483	2.908489	**C**	4.140049	-2.970980	-0.415761
H	-2.504267	-0.895011	-2.480819	**C**	-0.671808	-3.309435	0.439458	**H**	3.036246	-1.505144	-1.550487
C	-2.253967	-2.546836	1.958324	**H**	-0.243357	-2.372078	0.066555	**C**	4.316517	-3.547644	0.843045
C	-2.803417	-3.727565	2.777050	**H**	-0.063177	-3.654472	1.290102	**H**	3.682527	-3.599253	2.882128
H	-2.504079	-4.697647	2.351745	**H**	-0.602730	-4.070089	-0.354447	**H**	4.726303	-3.308512	-1.273582
H	-2.400450	-3.675496	3.799985	**H**	1.794650	-1.593785	-2.739107	**H**	5.053666	-4.339826	0.992281
H	-3.901705	-3.706769	2.851591	**C**	2.987153	-1.897176	1.894922	**C**	1.659717	-1.721436	2.982254
C	-2.717447	-1.248479	2.655334	**C**	2.812043	-3.196657	2.714405	**C**	1.789689	-0.213138	3.288001
H	-2.283475	-0.352549	2.195128	**H**	1.860581	-3.689983	2.463149	**C**	0.189169	-2.067034	2.652465
H	-3.814408	-1.155301	2.620529	**H**	3.622746	-3.918422	2.543798	**C**	2.044448	-2.482094	4.263356
H	-2.410041	-1.259785	3.713483	**H**	2.800132	-2.961599	3.790182	**H**	1.217998	0.034523	4.196927
C	-0.713172	-2.634648	1.976230	**C**	1.847526	-0.951158	2.319668	**H**	2.841927	0.062713	3.462926
H	-0.253946	-1.815277	1.411780	**H**	0.866960	-1.294323	1.966877	**H**	1.401789	0.405220	2.469826
H	-0.345002	-2.597085	3.014428	**H**	1.821192	-0.910909	3.419904	**H**	-0.152388	-1.539357	1.754474
H	-0.374551	-3.584405	1.532065	**H**	2.001866	0.074947	1.963842	**H**	0.076017	-3.149945	2.485544
C	0.713161	-2.634644	-1.976225	**C**	4.325197	-1.227460	2.279315	**H**	-0.461536	-1.782992	3.495750
H	0.344989	-2.597081	-3.014422	**H**	4.329096	-0.969541	3.350899	**H**	1.935968	-3.571022	4.147051
H	0.374535	-3.584397	-1.532056	**H**	5.182996	-1.889333	2.086987	**H**	3.078859	-2.269178	4.575119
H	0.253944	-1.815268	-1.411775	**H**	4.476364	-0.300963	1.703907	**H**	1.378647	-2.170118	5.082342

Table G71 XYZ coordinates of the GS and TS geometries of **3.16d** B3LYP/Def2SVP (CPCM = CH_2Cl_2)

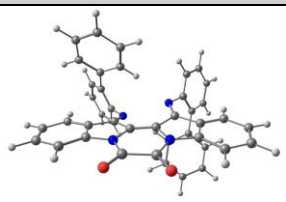
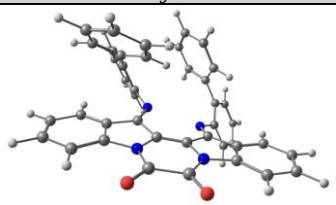
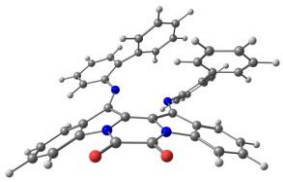
Anti				***Syn***				**TS**			
											
O	1.341826	4.951127	-0.298666	**O**	1.365247348200	4.994547204900	-0.395225730200	**C**	0.771849	0.488408	0.635201
O	-1.341853	4.951120	0.298674	**O**	-1.243239784100	5.162278235900	0.444170452800	**C**	2.117153	-0.114253	0.376178
N	1.317203	2.661111	-0.375877	**N**	1.107673934100	2.743408964200	-0.733100057300	**C**	3.028885	1.078359	0.385004
N	1.220986	-0.863633	-0.765878	**N**	0.833494320800	-0.786839554400	-0.951142292300	**C**	4.292292	1.362579	-0.150946
N	-1.317218	2.661104	0.375883	**N**	-1.508884585300	2.920099856800	0.054816337200	**H**	4.807802	0.651226	-0.790117
N	-1.220985	-0.863640	0.765877	**N**	-2.000185799600	-0.516447228900	-0.702518358500	**C**	4.881313	2.610178	0.077484
C	0.642370	1.434810	-0.223331	**C**	0.312734070200	1.578391836700	-0.722053772300	**H**	5.864318	2.822562	-0.347093
C	1.582913	0.351396	-0.605796	**C**	1.200338076500	0.432373552300	-1.048301443600	**C**	4.222072	3.582636	0.836125
C	2.875432	1.029029	-0.845470	**C**	2.511410210700	1.035414862000	-1.366205768800	**H**	4.704161	4.543453	1.028512
C	4.135043	0.540386	-1.206883	**C**	3.701951514000	0.471264636600	-1.830365239800	**C**	2.926780	3.360338	1.316059
H	4.309788	-0.528439	-1.310716	**H**	3.774387666200	-0.600117475100	-2.012174086100	**H**	2.374900	4.124484	1.855931
C	5.170879	1.452359	-1.428312	**C**	4.798727171700	1.308287472900	-2.049877601100	**C**	2.341286	2.126613	1.038570
H	6.161344	1.085849	-1.704479	**H**	5.738277901800	0.885021533800	-2.410077778700	**C**	3.366737	-2.217030	0.238633
C	4.950398	2.829645	-1.296422	**C**	4.705321137200	2.684628864400	-1.801807758600	**C**	3.120715	-3.625600	0.215949
H	5.773041	3.526532	-1.470895	**H**	5.576213035000	3.322271381600	-1.968824345000	**C**	4.174589	-4.496973	-0.107884
C	3.693648	3.340199	-0.947278	**C**	3.515807056700	3.270051171300	-1.349789892100	**H**	3.970332	-5.568863	-0.143383
H	3.512877	4.406858	-0.850256	**H**	3.434240191900	4.337397577700	-1.165975971700	**C**	5.474275	-4.037079	-0.312418
C	2.672314	2.418698	-0.727596	**C**	2.427573500500	2.422363629500	-1.150059091000	**H**	6.274012	-4.741042	-0.553001
C	2.096648	-1.919447	-0.999631	**C**	1.667184984500	-1.894519010100	-0.935121152400	**C**	5.747786	-2.676054	-0.147679
C	3.018712	-2.353234	-0.007347	**C**	2.693030585200	-2.057476799500	0.040229681100	**H**	6.769502	-2.299747	-0.235317
C	3.838201	-3.454083	-0.306099	**C**	3.426422943700	-3.253724718100	0.033468033900	**C**	4.710148	-1.790814	0.122752
H	4.541028	-3.801563	0.454385	**H**	4.201606083900	-3.391485580700	0.790781172000	**C**	-0.501856	0.143391	0.291982
C	3.762550	-4.120330	-1.530592	**C**	3.178115104900	-4.268954591900	-0.892136281400	**C**	-1.074307	-0.943398	-0.542752
H	4.413039	-4.974818	-1.728511	**H**	3.766468335500	-5.188595873900	-0.865529972700	**C**	-2.473878	-0.535929	-0.798684
C	2.835736	-3.697523	-2.488590	**C**	2.159210201800	-4.104799592800	-1.835781685200	**C**	-3.459328	-1.060096	-1.639392
H	2.757619	-4.214493	-3.447850	**H**	1.943429518600	-4.894813132300	-2.558959323300	**H**	-3.254830	-1.932077	-2.257977
C	1.998383	-2.616892	-2.217083	**C**	1.399712595700	-2.937817808800	-1.841327801000	**C**	-4.712702	-0.444266	-1.673315
C	-0.642379	1.434807	0.223334	**C**	-0.997150492600	1.671830488900	-0.355401514500	**H**	-5.492707	-0.844125	-2.323956
C	-1.582917	0.351388	0.605798	**C**	-2.113876794800	0.692883981200	-0.308783313100	**C**	-4.980687	0.671207	-0.868861
C	-2.875440	1.029014	0.845472	**C**	-3.260764812200	1.440384926700	0.256677543600	**H**	-5.971791	1.129508	-0.894998
C	-4.135049	0.540365	1.206885	**C**	-4.543985533700	1.032279991300	0.633809511300	**C**	-4.000994	1.224144	-0.034891
H	-4.309789	-0.528462	1.310716	**H**	-4.860401203900	-0.000994626100	0.501857187500	**H**	-4.195838	2.097987	0.580140
C	-5.170889	1.452332	1.428315	**C**	-5.414233833100	1.977459943300	1.184015123500	**C**	-2.748134	0.613011	-0.034914
H	-6.161352	1.085816	1.704482	**H**	-6.419450674800	1.675248473100	1.483930045400	**N**	0.986451	1.751630	1.225007
C	-4.950415	2.829619	1.296427	**C**	-5.009324950400	3.309019893000	1.349355281900	**N**	2.259095	-1.392140	0.372225
H	-5.773061	3.526502	1.470901	**H**	-5.705803454400	4.035401875900	1.773832660500	**N**	-1.560964	1.018326	0.628219
C	-3.693667	3.340180	0.947285	**C**	-3.724216488700	3.733958937800	0.990266280100	**H**	4.949426	-0.746878	0.267044
H	-3.512902	4.406840	0.850264	**H**	-3.399309750400	4.761214099800	1.127675004200	**C**	-1.435937	2.143045	1.414720
C	-2.672329	2.418683	0.727600	**C**	-2.864446629000	2.776654041500	0.454012132700	**C**	-0.005427	2.572139	1.723455
C	-2.096641	-1.919459	0.999628	**C**	-3.028563448100	-1.434337079100	-0.865743291800	**O**	-2.373360	2.824796	1.780907
C	-3.018702	-2.353246	0.007341	**C**	-2.916698446300	-2.715245695100	-0.265331761100	**O**	0.208011	3.616925	2.306211
C	-3.838186	-3.454100	0.306087	**C**	-3.872694226400	-3.692089850600	-0.579244746200	**C**	1.851318	-4.252260	0.663459
H	-4.541011	-3.801579	-0.454399	**H**	-3.789764853600	-4.673397860500	-0.105845412200	**C**	1.244721	-5.275461	-0.081656
C	-3.762535	-4.120351	1.530578	**C**	-4.920735145000	-3.431702124500	-1.465153759600	**C**	1.357098	-3.972841	1.950984
H	-4.413021	-4.974842	1.728492	**H**	-5.651954243400	-4.210198774300	-1.692856282800	**C**	0.177379	-6.006225	0.445749
C	-2.835724	-3.697543	2.488578	**C**	-5.023239127600	-2.168152674200	-2.057299190200	**H**	1.608675	-5.496980	-1.086239
H	-2.757606	-4.214516	3.447837	**H**	-5.832684563500	-1.952036277500	-2.758729599600	**C**	0.308337	-4.720005	2.486236
C	-1.998374	-2.616907	2.217077	**C**	-4.088105771200	-1.178766786200	-1.760811133100	**H**	1.826374	-3.185279	2.543226
C	0.742711	3.901243	-0.182786	**C**	0.667123238000	4.000556222300	-0.374726000600	**C**	-0.286399	-5.739773	1.735519
C	-0.742733	3.901240	0.182793	**C**	-0.787016414400	4.095878844700	0.083108609100	**H**	-0.292877	-6.784714	-0.157703
H	-1.267832	-2.276823	2.953470	**H**	-4.148318247700	-0.199128070100	-2.238995481100	**H**	-0.055979	-4.498642	3.492189
H	1.267838	-2.276808	-2.953473	**H**	0.585299407300	-2.801203838800	-2.554688945000	**H**	-1.117755	-6.313519	2.151087
C	-3.142949	-1.664316	-1.304284	**C**	-1.808446811600	-3.013759517700	0.677301788000	**N**	-0.410301	-1.979030	-0.888132
C	-4.414510	-1.367611	-1.826657	**C**	-0.944200709200	-4.094799449100	0.439193395400	**C**	-0.902437	-3.111279	-1.522425
C	-2.008835	-1.297889	-2.054412	**C**	-1.603864481700	-2.229081649100	1.825936864400	**C**	-0.185230	-3.556357	-2.651034
C	-4.551879	-0.721650	-3.058091	**C**	0.107182195100	-4.375502607500	1.314910882100	**C**	-1.989648	-3.894373	-1.034257
H	-5.305420	-1.626090	-1.250188	**H**	-1.080759948000	-4.700222717000	-0.459260198300	**C**	-0.545750	-4.715210	-3.331170
C	-2.147792	-0.653096	-3.284058	**C**	-0.564563375000	-2.520367517900	2.710850145500	**H**	0.666027	-2.956759	-2.978271
H	-1.010881	-1.499503	-1.663036	**H**	-2.273993298000	-1.391367592700	2.030321145400	**C**	-2.311624	-5.072596	-1.729683
C	-3.418602	-0.359801	-3.791668	**C**	0.299599057900	-3.590092999700	2.453635268500	**C**	-1.616524	-5.485055	-2.866090
H	-5.549526	-0.492737	-3.440639	**H**	0.790341685500	-5.198052491600	1.093945166000	**H**	0.020719	-5.027093	-4.211767
H	-1.254060	-0.376747	-3.849384	**H**	-0.420923232300	-1.903316852900	3.600893423800	**H**	-3.122242	-5.694857	-1.345045
H	-3.524256	0.150132	-4.752197	**H**	1.127211021300	-3.802436903700	3.134259416900	**H**	-1.897564	-6.410687	-3.372856
C	3.142961	-1.664311	1.304282	**C**	3.005645131100	-1.002735641000	1.039697141600	**C**	-2.790391	-3.527799	0.162719
C	4.414522	-1.367621	1.826660	**C**	4.338238805400	-0.610842609500	1.255617104700	**C**	-4.188564	-3.682890	0.142901
C	2.008848	-1.297875	2.054407	**C**	1.993661746200	-0.353927594200	1.770444094300	**C**	-2.200953	-3.011055	1.329562
C	4.551894	-0.721665	3.058097	**C**	4.649674981000	0.411378838500	2.155707265100	**C**	-4.971037	-3.322288	1.242302
H	5.305432	-1.626107	1.250194	**H**	5.136250677500	-1.090388868300	0.685011188600	**H**	-4.674364	-4.059815	-0.759239
C	2.147807	-0.653088	3.284056	**C**	2.303032425800	0.668561857300	2.667640724200	**C**	-2.980013	-2.648367	2.427820
H	1.010893	-1.499476	1.663028	**H**	0.957124499600	-0.654275509800	1.627078957700	**H**	-1.121961	-2.897158	1.377495
C	3.418618	-0.359808	3.791672	**C**	3.632432209000	1.061520497100	2.859954084300	**C**	-4.370811	-2.796382	2.389416
H	5.549543	-0.492765	3.440650	**H**	5.691463213400	0.709368240300	2.296615611000	**H**	-6.056239	-3.441114	1.195481
H	1.254076	-0.376732	3.849380	**H**	1.499834308500	1.160665512400	3.221712245800	**H**	-2.494856	-2.250543	3.322608
H	3.524275	0.150120	4.752203	**H**	3.873210038000	1.868504099300	3.556005062000	**H**	-4.981076	-2.504870	3.247484

Table G72 XYZ coordinates of the GS and TS geometries of **3.16e** B3LYP/Def2SVP (CPCM = CH_2Cl_2)

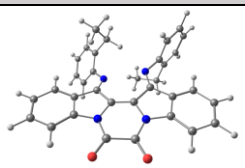
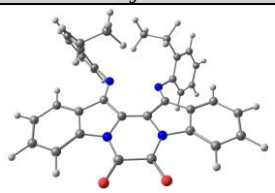
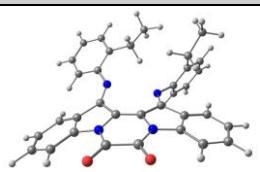
Anti				***Syn***				**TS**			
											
O	-1.108297	5.004625	-0.237050	**O**	1.340700	4.885292	-0.118875	**C**	-1.479877	-0.916455	0.029575
O	1.622677	4.890480	0.025059	**O**	-1.363904	4.876019	0.345668	**C**	-2.037198	0.459298	-0.201855
N	-1.434461	-0.806219	0.293429	**N**	1.379761	-0.951872	-0.205047	**C**	-3.482422	0.206232	-0.505890
N	-1.209917	2.718862	-0.117092	**N**	1.318939	2.598294	-0.254384	**C**	-4.506813	0.934331	-1.125873
N	1.412868	-0.935343	-0.237796	**N**	-1.531042	-0.915900	-0.449204	**H**	-4.317802	1.885442	-1.613268
N	1.520223	2.601281	0.037327	**N**	-1.390063	2.595286	0.124498	**C**	-5.796372	0.399166	-1.206383
C	-0.933556	-2.792464	-2.220437	**C**	1.614076	-1.525147	2.945926	**H**	-6.584005	0.976110	-1.694656
C	-2.357825	-2.246574	-2.048054	**C**	2.950141	-1.312138	2.222131	**C**	-6.077884	-0.864759	-0.680832
C	1.548522	-2.470556	2.717014	**C**	-0.549740	-3.869084	1.010758	**H**	-7.092940	-1.264171	-0.732688
C	1.067749	-3.177997	1.442626	**C**	-1.849577	-3.141864	1.379968	**C**	-5.062070	-1.650976	-0.126214
C	-0.549666	3.930160	-0.141710	**C**	0.731008	3.835221	-0.089088	**H**	-5.249511	-2.656437	0.238234
C	0.971146	3.866229	-0.017660	**C**	-0.775756	3.830930	0.152964	**C**	-3.778162	-1.111016	-0.086941
C	-2.953953	-2.017270	1.732533	**C**	2.501609	-2.794722	-1.291480	**C**	-1.543409	2.849774	0.169500
C	-3.928361	-2.997976	1.923775	**C**	3.419907	-3.845409	-1.269922	**C**	-0.496247	3.608127	0.787858
C	-4.405317	-3.729560	0.833176	**C**	4.185016	-4.078769	-0.124506	**C**	-0.651218	4.992393	0.919407
C	-3.894088	-3.471969	-0.442805	**C**	4.021938	-3.250907	0.990819	**H**	0.143622	5.576125	1.384338
C	-2.918574	-2.492040	-0.667021	**C**	3.120511	-2.179187	0.995062	**C**	-1.798259	5.653297	0.472077
C	-2.455968	-1.749965	0.445979	**C**	2.358024	-1.950635	-0.178163	**H**	-1.883982	6.736575	0.585670
C	-2.619091	2.550167	-0.176159	**C**	2.704248	2.372068	-0.473739	**C**	-2.826686	4.919825	-0.120513
C	-3.611386	3.520166	-0.304234	**C**	3.732881	3.302902	-0.606965	**H**	-3.732460	5.416237	-0.475772
C	-4.938663	3.074333	-0.345508	**C**	5.020493	2.802256	-0.837816	**C**	-2.694641	3.541551	-0.266110
C	-5.258225	1.712930	-0.261245	**C**	5.266714	1.426208	-0.933651	**C**	-0.226150	-1.455483	0.003332
C	-4.251527	0.751850	-0.126921	**C**	4.225036	0.504850	-0.791148	**C**	1.112597	-0.938517	-0.391525
C	-2.920235	1.178336	-0.084297	**C**	2.933722	0.986408	-0.554203	**C**	2.001045	-2.123830	-0.401101
C	-1.650145	0.430170	0.061700	**C**	1.644325	0.288286	-0.348041	**C**	3.338023	-2.282561	-0.783033
C	-0.579283	1.459900	-0.031178	**C**	0.628253	1.368464	-0.233700	**H**	3.916166	-1.437662	-1.152248
C	2.092212	-3.173117	0.336519	**C**	-2.741485	-2.938912	0.178526	**C**	3.920434	-3.548142	-0.679613
C	2.902543	-4.283432	0.071787	**C**	-3.750839	-3.860297	-0.131268	**H**	4.962797	-3.687668	-0.972318
C	3.843177	-4.275330	-0.962928	**C**	-4.545528	-3.730459	-1.273854	**C**	3.179381	-4.637058	-0.200561
C	3.985977	-3.133157	-1.757970	**C**	-4.330874	-2.654723	-2.140828	**H**	3.653353	-5.617658	-0.118613
C	3.210064	-2.004145	-1.500476	**C**	-3.344235	-1.713901	-1.849519	**C**	1.836765	-4.501765	0.171276
C	2.276468	-2.006295	-0.446100	**C**	-2.554550	-1.839455	-0.690662	**H**	1.253793	-5.342887	0.534261
C	2.903201	2.308956	0.181287	**C**	-2.779887	2.368512	0.309165	**C**	1.266643	-3.234508	0.049616
C	3.967782	3.191911	0.354919	**C**	-3.781253	3.289549	0.612913	**N**	-2.574525	-1.772391	0.265477
C	5.238133	2.632544	0.538899	**C**	-5.077226	2.789428	0.788080	**N**	-1.318237	1.485053	0.077690
C	5.431702	1.244620	0.555214	**C**	-5.355842	1.421330	0.670887	**N**	-0.071336	-2.834276	0.291906
C	4.355861	0.373352	0.363843	**C**	-4.342266	0.512225	0.355047	**H**	-3.504089	2.996839	-0.725850
C	3.081357	0.912700	0.162825	**C**	-3.042951	0.994336	0.162400	**C**	-1.079613	-3.675938	0.706866
C	1.756371	0.278121	-0.036638	**C**	-1.766651	0.303486	-0.145582	**C**	-2.483750	-3.090059	0.668255
C	0.781387	1.401383	-0.005205	**C**	-0.725877	1.368028	-0.083932	**O**	-0.909736	-4.835826	1.029543
H	-0.565485	-2.611613	-3.243151	**H**	1.530416	-0.855951	3.816687	**O**	-3.442982	-3.786832	0.934411
H	-0.905801	-3.878197	-2.035577	**H**	1.521144	-2.562867	3.302016	**C**	0.737487	2.909465	1.307080
H	-0.244312	-2.304820	-1.517555	**H**	0.767048	-1.322628	2.274181	**H**	0.463214	2.377559	2.237390
H	0.798061	-4.219416	1.680194	**H**	-2.397668	-3.722168	2.139628	**H**	0.983419	2.111994	0.597859
H	0.162369	-2.669037	1.078243	**H**	-1.606057	-2.170636	1.837971	**C**	1.950507	3.798347	1.566866
H	-2.358353	-1.164639	-2.263394	**H**	3.045247	-0.249320	1.945741	**H**	1.773525	4.533138	2.368106
H	-3.029141	-2.708965	-2.788839	**H**	3.781209	-1.519289	2.914308	**H**	2.810306	3.185927	1.871244
H	2.445280	-2.959171	3.130724	**H**	-0.766357	-4.851338	0.561478	**H**	2.243426	4.352458	0.660552
H	0.764961	-2.482134	3.491560	**H**	0.080826	-4.029574	1.898522	**N**	1.359368	0.284315	-0.669075
H	1.803353	-1.418872	2.512882	**H**	0.029777	-3.277663	0.289252	**C**	2.632131	0.785791	-0.961014
H	-4.313108	-3.188338	2.928652	**H**	3.530463	-4.484936	-2.148967	**C**	2.861735	1.290764	-2.251928
H	-5.167710	-4.499029	0.973164	**H**	4.901695	-4.902427	-0.095345	**C**	3.631582	0.908574	0.043067
H	-4.263359	-4.044083	-1.298662	**H**	4.615802	-3.434664	1.890578	**C**	4.086303	1.869907	-2.584376
H	-3.357032	4.573915	-0.370732	**H**	3.534778	4.368381	-0.536532	**H**	2.061552	1.208900	-2.990240
H	-5.739010	3.810534	-0.447484	**H**	5.847882	3.506617	-0.948210	**C**	4.840977	1.516974	-0.316890
H	-6.302720	1.397880	-0.299379	**H**	6.281136	1.068808	-1.120393	**C**	5.082025	1.985823	-1.612576
H	-4.500513	-0.305395	-0.060155	**H**	4.416176	-0.564052	-0.864699	**H**	4.254687	2.239106	-3.598852
H	2.777479	-5.181214	0.683630	**H**	-3.911835	-4.703625	0.546424	**H**	5.623625	1.627418	0.434804
H	4.451613	-5.161514	-1.156992	**H**	-5.322415	-4.467673	-1.488299	**H**	6.041612	2.448058	-1.854682
H	4.701625	-3.120989	-2.583548	**H**	-4.935605	-2.542459	-3.043982	**C**	3.381070	0.387128	1.444011
H	3.806996	4.266063	0.356262	**H**	-3.554892	4.346734	0.714886	**H**	2.379621	0.714412	1.765679
H	6.092550	3.297972	0.680439	**H**	-5.883667	3.485703	1.028395	**H**	3.317478	-0.712990	1.409442
H	6.432415	0.838625	0.714860	**H**	-6.374515	1.060234	0.824689	**C**	4.412369	0.774734	2.500685
H	4.508973	-0.704184	0.372305	**H**	-4.562904	-0.549142	0.264005	**H**	4.107924	0.387865	3.484928
H	3.307380	-1.111126	-2.120932	**H**	-3.171800	-0.864656	-2.513905	**H**	5.406503	0.357791	2.276184
H	-2.569264	-1.439067	2.575043	**H**	1.886409	-2.605819	-2.173295	**H**	4.521189	1.867264	2.589413

Table G73 XYZ coordinates of the GS and TS geometries of **3.16a** B3LYP/Def2SVP (SMD = CH_2Cl_2)

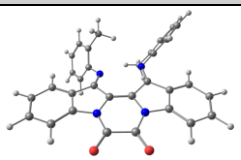
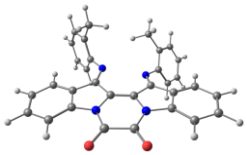
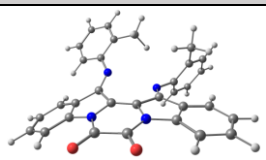
Anti				***Syn***				**TS**			
											
O	1.360593	-4.827220	-0.171844	**O**	1.578530	-4.724193	0.167580	**C**	1.103430	-1.030103	-0.004991
O	-1.360584	-4.827222	0.171843	**O**	-1.145000	-4.830398	-0.137345	**C**	1.891446	0.232622	0.168781
N	1.361745	-2.536646	-0.128897	**N**	1.494230	-2.435977	0.092559	**C**	3.240535	-0.248738	0.599283
N	1.434744	1.005705	0.155838	**N**	1.431072	1.106046	-0.221491	**C**	4.344172	0.342794	1.226853
N	-1.361739	-2.536648	0.128896	**N**	-1.229920	-2.540945	-0.136935	**H**	4.308736	1.362341	1.599455
N	-1.434745	1.005703	-0.155840	**N**	-1.441651	1.001521	0.070906	**C**	5.500594	-0.409240	1.457667
C	0.680921	-1.304326	-0.044304	**C**	0.766767	-1.231485	0.002372	**H**	6.353942	0.060772	1.950971
C	1.709268	-0.228193	-0.030198	**C**	1.753811	-0.116967	-0.040008	**C**	5.566630	-1.751823	1.074183
C	3.001430	-0.925172	-0.236316	**C**	3.075413	-0.764089	0.143016	**H**	6.481628	-2.323707	1.244884
C	4.301653	-0.444975	-0.424011	**C**	4.361165	-0.234700	0.296435	**C**	4.457882	-2.391898	0.508834
H	4.509008	0.623500	-0.414647	**H**	4.530617	0.839831	0.264182	**H**	4.476957	-3.446653	0.250000
C	5.334786	-1.363831	-0.627293	**C**	5.430489	-1.112440	0.494348	**C**	3.305504	-1.633118	0.315738
H	6.355131	-1.003865	-0.775157	**H**	6.439808	-0.713528	0.615418	**C**	1.868698	2.617453	-0.471648
C	5.073429	-2.740485	-0.638617	**C**	5.219372	-2.497031	0.534566	**C**	1.005857	3.464027	-1.237314
H	5.894543	-3.445014	-0.790457	**H**	6.068066	-3.168952	0.682433	**C**	1.412703	4.771390	-1.525870
C	3.776803	-3.240188	-0.468409	**C**	3.938595	-3.045584	0.398377	**H**	0.747955	5.409727	-2.113621
H	3.567037	-4.305754	-0.490574	**H**	3.767638	-4.117344	0.442867	**C**	2.638586	5.274311	-1.083189
C	2.755338	-2.310098	-0.278373	**C**	2.881012	-2.156113	0.212274	**H**	2.926624	6.302014	-1.317973
C	2.357082	2.027220	0.355427	**C**	2.328130	2.147387	-0.445182	**C**	3.489544	4.451626	-0.341828
C	2.295550	3.163338	-0.490457	**C**	3.164396	2.157681	-1.577645	**H**	4.454212	4.824495	0.010752
C	3.164418	4.230134	-0.230970	**C**	3.990519	3.251227	-1.835791	**C**	3.108229	3.145262	-0.046450
H	3.132724	5.103420	-0.888617	**H**	4.630339	3.248514	-2.721980	**C**	-0.228207	-1.314198	-0.071261
C	4.051987	4.208434	0.850151	**C**	3.996928	4.342998	-0.962085	**C**	-1.455653	-0.525628	0.213527
H	4.709527	5.061159	1.035405	**H**	4.644900	5.201252	-1.155375	**C**	-2.575402	-1.485415	0.067993
C	4.080136	3.096933	1.698476	**C**	3.155803	4.338074	0.155779	**C**	-3.953050	-1.354093	0.275933
H	4.756249	3.073863	2.556998	**H**	3.150833	5.196031	0.834026	**H**	-4.384245	-0.402576	0.580495
C	3.241053	2.010855	1.451645	**C**	2.300903	3.263150	0.428025	**C**	-4.772878	-2.470936	0.092366
C	-0.680918	-1.304327	0.044303	**C**	-0.593664	-1.284190	-0.074848	**H**	-5.849651	-2.380331	0.249980
C	-1.709266	-0.228196	0.030198	**C**	-1.657625	-0.244083	-0.109867	**C**	-4.225874	-3.701611	-0.293382
C	-3.001427	-0.925177	0.236317	**C**	-2.926048	-0.991035	-0.280634	**H**	-4.882350	-4.562464	-0.440565
C	-4.301650	-0.444982	0.424013	**C**	-4.254223	-0.563235	-0.379804	**C**	-2.848668	-3.859899	-0.487776
H	-4.509008	0.623493	0.414650	**H**	-4.500970	0.496501	-0.385873	**H**	-2.417130	-4.814853	-0.773748
C	-5.334782	-1.363840	0.627296	**C**	-5.263772	-1.525446	-0.476853	**C**	-2.042869	-2.738918	-0.290219
H	-6.355128	-1.003875	0.775161	**H**	-6.305166	-1.207267	-0.558690	**N**	2.026483	-2.089278	-0.092312
C	-5.073423	-2.740493	0.638619	**C**	-4.951096	-2.890837	-0.471734	**N**	1.390403	1.336246	-0.253724
H	-5.894536	-3.445024	0.790460	**H**	-5.752951	-3.628790	-0.550327	**N**	-0.630913	-2.639059	-0.357721
C	-3.776796	-3.240193	0.468410	**C**	-3.628547	-3.338825	-0.365108	**H**	3.787965	2.528773	0.523562
H	-3.567029	-4.305759	0.490574	**H**	-3.382555	-4.396783	-0.354071	**C**	0.227050	-3.685398	-0.620687
C	-2.755333	-2.310102	0.278374	**C**	-2.632924	-2.367820	-0.269732	**C**	1.709385	-3.390648	-0.426611
C	-2.357086	2.027215	-0.355428	**C**	-2.428631	1.985844	-0.001297	**O**	-0.137563	-4.801518	-0.934901
C	-2.295557	3.163334	0.490456	**C**	-2.909176	2.570075	1.195440	**O**	2.528377	-4.280880	-0.538617
C	-3.164429	4.230126	0.230970	**C**	-3.844853	3.607360	1.094084	**C**	-0.320142	2.966980	-1.735076
H	-3.132737	5.103413	0.888617	**H**	-4.228760	4.057092	2.014242	**H**	-0.785269	3.699111	-2.410778
C	-4.051998	4.208424	-0.850151	**C**	-4.291836	4.076345	-0.145563	**H**	-0.218072	2.008723	-2.263960
H	-4.709541	5.061147	-1.035404	**H**	-5.019051	4.890382	-0.193052	**H**	-1.003516	2.787112	-0.895205
C	-4.080144	3.096923	-1.698476	**C**	-3.793568	3.503362	-1.319508	**N**	-1.437271	0.697641	0.588188
H	-4.756258	3.073851	-2.556997	**H**	-4.126077	3.865583	-2.295718	**C**	-2.565257	1.482760	0.825971
C	-3.241058	2.010847	-1.451645	**C**	-2.864886	2.464237	-1.249422	**C**	-2.714468	2.018896	2.122124
C	0.757442	-3.776538	-0.087062	**C**	0.935652	-3.698107	0.076810	**C**	-3.473479	1.859222	-0.198694
C	-0.757435	-3.776539	0.087061	**C**	-0.580382	-3.756936	-0.077970	**C**	-3.774942	2.865576	2.431325
H	-3.250518	1.140315	-2.110835	**H**	-2.463278	2.009544	-2.157535	**H**	-1.980011	1.740727	2.880986
H	3.250515	1.140322	2.110834	**H**	3.149976	1.300211	-2.253739	**C**	-4.513895	2.739852	0.138024
C	-1.321973	3.186998	1.635525	**C**	-2.435599	2.049765	2.524677	**C**	-4.683210	3.233649	1.432096
H	-1.570660	2.424378	2.393313	**H**	-2.822045	1.034565	2.720808	**H**	-3.884167	3.249981	3.448581
H	-0.303824	2.953307	1.286231	**H**	-1.336178	1.975408	2.551389	**H**	-5.213135	3.038521	-0.648546
H	-1.312656	4.168725	2.130666	**H**	-2.765566	2.700083	3.347767	**H**	-5.510866	3.910509	1.657055
C	1.321968	3.186998	-1.635528	**C**	1.374335	3.259994	1.612029	**C**	-3.372421	1.343279	-1.610714
H	1.570666	2.424387	-2.393320	**H**	0.338763	3.065633	1.290999	**H**	-2.380909	0.936554	-1.843182
H	0.303822	2.953292	-1.286237	**H**	1.632907	2.461870	2.328453	**H**	-4.104788	0.537667	-1.789855
H	1.312640	4.168728	-2.130662	**H**	1.405618	4.220907	2.145556	**H**	-3.590317	2.145680	-2.332099

Table G74 XYZ coordinates of the GS and TS geometries of **3.16b** B3LYP/Def2SVP (SMD = CH_2Cl_2)

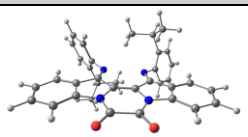
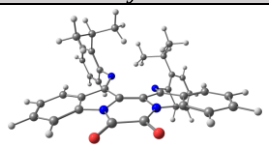
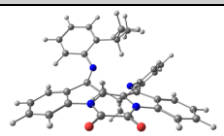
Anti				***Syn***				**TS**			
											
O	1.369564	5.046737	0.048859	**O**	-1.319545	4.945630	0.451008	**C**	-1.658622	0.674025	-0.054655
O	-1.369562	5.046737	-0.048864	**O**	1.340038	4.950989	-0.230888	**C**	-1.745262	-0.812968	0.088581
N	1.365626	2.755727	0.048959	**N**	-1.373818	2.668916	0.202968	**C**	-3.116421	-1.036325	0.639870
N	1.445306	-0.803281	0.094424	**N**	-1.580170	-0.814011	-0.512812	**C**	-3.745763	-2.094819	1.306819
N	-1.365624	2.755728	-0.048961	**N**	1.309283	2.662564	-0.332722	**H**	-3.198661	-2.986806	1.600405
N	-1.445305	-0.803281	-0.094431	**N**	1.396942	-0.859923	-0.054104	**C**	-5.090271	-1.981590	1.675524
C	0.682104	1.521144	0.027327	**C**	-0.725904	1.438474	-0.037462	**H**	-5.573256	-2.809625	2.198543
C	1.712184	0.445681	0.091606	**C**	-1.782227	0.391742	-0.130624	**C**	-5.812850	-0.819140	1.389715
C	3.014057	1.152140	0.104989	**C**	-3.042283	1.087027	0.227894	**H**	-6.867126	-0.750518	1.667604
C	4.330515	0.678969	0.080619	**C**	-4.339700	0.609921	0.443633	**C**	-5.194387	0.282107	0.786270
H	4.541348	-0.388257	0.084647	**H**	-4.575379	-0.445165	0.318982	**H**	-5.729930	1.209259	0.602355
C	5.376528	1.605325	0.049711	**C**	-5.333133	1.515080	0.826405	**C**	-3.846518	0.161206	0.455386
H	6.409341	1.251340	0.031031	**H**	-6.350375	1.157484	0.998991	**C**	-0.666396	-2.880030	-0.725457
C	5.111237	2.980893	0.045129	**C**	-5.036762	2.875504	0.985305	**C**	0.467024	-3.204480	-1.540544
H	5.941344	3.691035	0.026660	**H**	-5.828144	3.569978	1.276883	**C**	0.684339	-4.542895	-1.886572
C	3.800694	3.473511	0.055402	**C**	-3.741689	3.369743	0.789050	**H**	1.545072	-4.801860	-2.504103
H	3.591006	4.539016	0.039263	**H**	-3.503502	4.420793	0.925382	**C**	-0.173229	-5.563033	-1.466563
C	2.768115	2.536649	0.077882	**C**	-2.759390	2.451674	0.419768	**H**	0.030286	-6.598638	-1.750319
C	2.395433	-1.804970	0.304892	**C**	-2.637211	-1.647982	-0.904088	**C**	-1.288548	-5.249153	-0.687490
C	2.711361	-2.744147	-0.708686	**C**	-2.903677	-2.881453	-0.259200	**H**	-1.974817	-6.032546	-0.356981
C	3.619389	-3.764499	-0.388032	**C**	-3.958896	-3.661716	-0.756630	**C**	-1.526615	-3.926572	-0.325375
H	3.882707	-4.484218	-1.168365	**H**	-4.183447	-4.606201	-0.252961	**C**	-0.625665	1.550468	-0.202583
C	4.183492	-3.894605	0.883781	**C**	-4.716293	-3.280332	-1.866824	**C**	0.842877	1.425216	-0.019230
H	4.879618	-4.709947	1.094231	**H**	-5.524541	-3.921818	-2.225987	**C**	1.378912	2.790285	-0.252849
C	3.837540	-2.979550	1.881976	**C**	-4.418112	-2.080127	-2.517774	**C**	2.670749	3.324628	-0.171821
H	4.255410	-3.069638	2.887907	**H**	-4.985179	-1.768736	-3.398702	**H**	3.524303	2.690954	0.057788
C	2.952355	-1.943620	1.592324	**C**	-3.390729	-1.272979	-2.036359	**C**	2.854333	4.692218	-0.391340
C	-0.682102	1.521144	-0.027331	**C**	0.620812	1.436839	-0.238184	**H**	3.859282	5.115708	-0.333570
C	-1.712183	0.445681	-0.091609	**C**	1.624832	0.352824	-0.384010	**C**	1.764689	5.520889	-0.688919
C	-3.014055	1.152141	-0.104988	**C**	2.883972	1.036178	-0.759610	**H**	1.927525	6.586469	-0.867136
C	-4.330514	0.678970	-0.080617	**C**	4.156875	0.547932	-1.070044	**C**	0.462261	5.013944	-0.756150
H	-4.541347	-0.388256	-0.084646	**H**	4.343445	-0.521923	-1.137321	**H**	-0.390218	5.651784	-0.971775
C	-5.376526	1.605327	-0.049709	**C**	5.189118	1.463123	-1.297469	**C**	0.293950	3.648874	-0.524887
H	-6.409339	1.251341	-0.031028	**H**	6.187642	1.098012	-1.546607	**N**	-2.973402	1.174725	-0.016206
C	-5.111235	2.980895	-0.045126	**C**	4.954429	2.841192	-1.207061	**N**	-0.825825	-1.535312	-0.439871
H	-5.941341	3.691037	-0.026656	**H**	5.773906	3.541329	-1.385594	**N**	-0.912029	2.906630	-0.472019
C	-3.800691	3.473512	-0.055400	**C**	3.688372	3.349332	-0.889873	**H**	-2.401116	-3.702981	0.268914
H	-3.591003	4.539017	-0.039261	**H**	3.502843	4.416983	-0.812765	**C**	-2.179827	3.431594	-0.608100
C	-2.768113	2.536649	-0.077882	**C**	2.667987	2.425249	-0.673515	**C**	-3.329579	2.478932	-0.295701
C	-2.395434	-1.804968	-0.304894	**C**	2.349710	-1.879183	-0.184034	**O**	-2.409115	4.588044	-0.903864
C	-2.952357	-1.943623	-1.592326	**C**	3.068975	-2.366679	0.935553	**O**	-4.473922	2.886893	-0.281721
C	-3.837546	-2.979551	-1.881972	**C**	3.954004	-3.434107	0.717036	**C**	1.369513	-2.102841	-2.068962
H	-4.255417	-3.069642	-2.887902	**H**	4.526983	-3.810967	1.569090	**H**	1.431897	-1.351436	-1.274291
C	-4.183500	-3.894600	-0.883773	**C**	4.122023	-4.027130	-0.536697	**C**	0.715712	-1.417600	-3.281039
H	-4.879629	-4.709941	-1.094219	**H**	4.818517	-4.859790	-0.660138	**H**	-0.275204	-1.016050	-3.021594
C	-3.619396	-3.764490	0.388039	**C**	3.383047	-3.551473	-1.623001	**H**	1.340237	-0.580699	-3.635624
H	-3.882715	-4.484206	1.168375	**H**	3.489001	-4.007552	-2.610584	**H**	0.590697	-2.125451	-4.117953
C	-2.711364	-2.744140	0.708688	**C**	2.501773	-2.486586	-1.444330	**C**	2.786952	-2.568173	-2.408715
C	0.761148	3.996089	0.027149	**C**	-0.749751	3.900486	0.211341	**H**	2.803275	-3.269300	-3.259292
C	-0.761145	3.996090	-0.027153	**C**	0.735326	3.902003	-0.139223	**H**	3.406428	-1.703975	-2.690578
H	2.670230	-1.222788	2.362494	**H**	1.910479	-2.104459	-2.279087	**H**	3.271534	-3.059242	-1.550061
C	2.125863	-2.679237	-2.112174	**H**	-3.148311	-0.332008	-2.534778	**N**	1.393753	0.342041	0.386058
H	2.554983	-3.539351	-2.652585	**C**	-2.101815	-3.388187	0.928980	**C**	2.759541	0.108690	0.513860
C	2.550122	-1.417763	-2.880549	**H**	-2.566731	-4.345906	1.216170	**C**	3.237934	-0.466963	1.720670
H	3.644366	-1.290303	-2.871345	**C**	-2.185300	-2.466494	2.154624	**C**	3.636433	0.293101	-0.572386
H	2.226718	-1.486422	-3.932361	**H**	-3.232433	-2.258855	2.427759	**C**	4.596945	-0.792590	1.801311
H	2.098256	-0.509275	-2.456181	**H**	-1.697979	-2.939923	3.022392	**C**	4.981069	-0.060446	-0.470787
C	0.599246	-2.850468	-2.112646	**H**	-1.681573	-1.506109	1.976150	**H**	3.242495	0.701622	-1.504444
H	0.304062	-3.790186	-1.619167	**C**	-0.647847	-3.679912	0.530989	**C**	5.468241	-0.597215	0.723430
H	0.109461	-2.025877	-1.578733	**H**	-0.605095	-4.377089	-0.321017	**H**	4.989284	-1.219810	2.725834
H	0.215553	-2.875595	-3.146017	**H**	-0.129672	-2.755525	0.246900	**H**	5.645087	0.081469	-1.327154
H	-2.670231	-1.222795	-2.362499	**H**	-0.100079	-4.138078	1.369705	**H**	6.521652	-0.872031	0.816994
C	-2.125864	-2.679228	2.112175	**C**	2.954805	-1.777145	2.336800	**C**	2.262206	-0.746070	2.854978
H	-2.554985	-3.539338	2.652589	**H**	3.561148	-2.436899	2.979111	**H**	1.516974	0.065265	2.845419
C	-2.550117	-1.417750	2.880548	**C**	1.524787	-1.802636	2.894498	**C**	2.908761	-0.764123	4.242253
H	-3.644360	-1.290286	2.871345	**H**	0.845602	-1.177483	2.297672	**C**	1.507078	-2.059107	2.582461
H	-2.226712	-1.486409	3.932360	**H**	1.120208	-2.825374	2.902240	**H**	3.593106	-1.619084	4.366644
H	-2.098248	-0.509265	2.456178	**H**	1.515991	-1.425638	3.930374	**H**	3.478959	0.157885	4.439363
C	-0.599247	-2.850464	2.112645	**C**	3.572057	-0.373683	2.448176	**H**	2.132324	-0.855123	5.018584
H	-0.304068	-3.790184	1.619167	**H**	4.593797	-0.349108	2.038509	**H**	0.993905	-2.024457	1.611677
H	-0.109460	-2.025875	1.578729	**H**	2.977292	0.381396	1.915035	**H**	2.204313	-2.913333	2.573848
H	-0.215552	-2.875590	3.146015	**H**	3.622849	-0.066253	3.505708	**H**	0.751121	-2.243796	3.363835

Table G75 XYZ coordinates of the GS and TS geometries of **3.16c** B3LYP/Def2SVP (SMD = CH_2Cl_2)

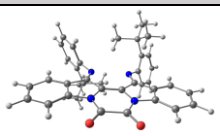
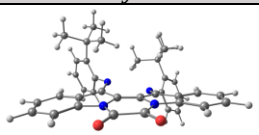
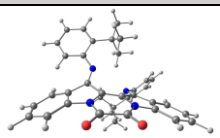
Anti				***Syn***				**TS**			
											
O	1.364398	5.257935	0.126722	**O**	1.256941	5.175665	0.104057	**C**	-0.833329	1.483818	-0.085462
O	-1.364401	5.257935	-0.126721	**O**	-1.426833	5.109642	0.672126	**C**	-1.804786	0.381565	0.212183
N	1.360939	2.967054	0.126590	**N**	1.239400	2.906087	-0.208398	**C**	-2.862944	1.067310	1.016405
N	1.439360	-0.591972	0.126446	**N**	1.327532	-0.631384	-0.359948	**C**	-3.807856	0.638346	1.955690
N	-1.360941	2.967054	-0.126590	**N**	-1.456994	2.857900	0.251710	**H**	-3.846509	-0.399967	2.280745
N	-1.439360	-0.591972	-0.126447	**N**	-1.610232	-0.599612	-0.603849	**C**	-4.676612	1.569665	2.534389
C	0.679788	1.732858	0.062254	**C**	0.555454	1.674303	-0.247286	**H**	-5.411613	1.233362	3.268567
C	1.704201	0.656803	0.173385	**C**	1.565156	0.614408	-0.498011	**C**	-4.606115	2.922463	2.184925
C	3.001893	1.362121	0.278283	**C**	2.836341	1.334588	-0.740585	**H**	-5.305214	3.635564	2.627848
C	4.316722	0.887207	0.331463	**C**	4.120867	0.882436	-1.060301	**C**	-3.621489	3.391258	1.306550
H	4.524774	-0.180650	0.342939	**H**	4.314869	-0.173820	-1.234544	**H**	-3.521386	4.446960	1.069128
C	5.363439	1.812405	0.369617	**C**	5.155587	1.818031	-1.158947	**C**	-2.740441	2.453532	0.772789
H	6.395203	1.457530	0.413312	**H**	6.163247	1.481923	-1.412091	**C**	-2.646615	-1.723036	-0.722280
C	5.099981	3.188422	0.355223	**C**	4.911111	3.179138	-0.936383	**C**	-2.325478	-2.657801	-1.766943
H	5.930292	3.897629	0.391645	**H**	5.732354	3.895264	-1.016424	**C**	-3.292914	-3.619516	-2.095954
C	3.791795	3.682716	0.286284	**C**	3.632778	3.650368	-0.611352	**H**	-3.081944	-4.340051	-2.882952
H	3.584470	4.748548	0.261099	**H**	3.439573	4.704688	-0.434703	**C**	-4.531917	-3.701849	-1.457555
C	2.758914	2.747007	0.241355	**C**	2.610665	2.707163	-0.521924	**H**	-5.244608	-4.476075	-1.752316
C	2.358561	-1.603396	0.410299	**C**	2.288306	-1.616998	-0.627304	**C**	-4.844400	-2.791371	-0.450239
C	2.739514	-2.577857	-0.554270	**C**	2.374201	-2.033505	-1.973967	**H**	-5.807995	-2.828549	0.063457
C	3.597391	-3.599484	-0.114310	**C**	3.264088	-3.024054	-2.371017	**C**	-3.910847	-1.823097	-0.098947
H	3.928417	-4.356625	-0.823518	**H**	3.315952	-3.322626	-3.421042	**C**	0.485205	1.546806	-0.416441
C	4.047670	-3.697772	1.205312	**C**	4.085577	-3.624299	-1.412569	**C**	1.606617	0.588765	-0.248306
H	4.706596	-4.519978	1.494397	**H**	4.800203	-4.400200	-1.696985	**C**	2.823022	1.345917	-0.643922
C	3.641782	-2.748077	2.144064	**C**	3.979355	-3.230372	-0.080206	**C**	4.186473	1.024179	-0.641388
H	3.971514	-2.811841	3.184103	**H**	4.629856	-3.712943	0.650970	**H**	4.527344	0.034999	-0.346549
C	2.805983	-1.710045	1.743800	**C**	3.081279	-2.240921	0.368371	**C**	5.116160	1.994647	-1.023784
C	-0.679789	1.732857	-0.062255	**C**	-0.794628	1.652506	-0.064288	**H**	6.179816	1.747238	-1.026658
C	-1.704202	0.656802	-0.173385	**C**	-1.837111	0.599910	-0.218502	**C**	4.697215	3.274545	-1.408240
C	-3.001894	1.362120	-0.278283	**C**	-3.112402	1.266102	0.139446	**H**	5.436639	4.017686	-1.715835
C	-4.316723	0.887204	-0.331463	**C**	-4.411713	0.769275	0.290890	**C**	3.343671	3.628052	-1.398831
H	-4.524774	-0.180652	-0.342939	**H**	-4.636326	-0.277648	0.098110	**H**	3.009676	4.623170	-1.678684
C	-5.363440	1.812402	-0.369617	**C**	-5.422266	1.644062	0.698921	**C**	2.429324	2.652809	-1.001759
H	-6.395204	1.457527	-0.413312	**H**	-6.441044	1.270482	0.821182	**N**	-1.555347	2.691074	0.029722
C	-5.099983	3.188420	-0.355223	**C**	-5.140608	2.993840	0.948034	**N**	-1.720699	-0.719503	-0.446117
H	-5.930294	3.897625	-0.391644	**H**	-5.944658	3.664867	1.259272	**N**	1.029226	2.782366	-0.830164
C	-3.791797	3.682714	-0.286283	**C**	-3.844470	3.506568	0.817245	**H**	-4.176620	-1.118182	0.674390
H	-3.584473	4.748546	-0.261098	**H**	-3.618157	4.548774	1.023197	**C**	0.314067	3.955930	-0.953379
C	-2.758916	2.747006	-0.241355	**C**	-2.845613	2.618653	0.419462	**C**	-1.107315	3.922563	-0.400479
C	-2.358560	-1.603397	-0.410299	**C**	-2.642935	-1.459976	-1.000132	**O**	0.774813	4.990542	-1.393777
C	-2.805984	-1.710046	-1.743800	**C**	-3.341209	-1.115469	-2.176360	**O**	-1.760587	4.944312	-0.325801
C	-3.641784	-2.748078	-2.144063	**C**	-4.346565	-1.931059	-2.686529	**C**	-0.977592	-2.659644	-2.511913
H	-3.971516	-2.811841	-3.184102	**H**	-4.871775	-1.642503	-3.600513	**C**	-0.707661	-1.298361	-3.190533
C	-4.047670	-3.697773	-1.205312	**C**	-4.672977	-3.110150	-2.015328	**C**	-0.922495	-3.729006	-3.618724
H	-4.706596	-4.519979	-1.494396	**H**	-5.464167	-3.763688	-2.390529	**C**	0.133734	-2.984813	-1.498086
C	-3.597390	-3.599486	0.114310	**C**	-3.970934	-3.462713	-0.859341	**H**	-0.652828	-0.487107	-2.456498
H	-3.928415	-4.356627	0.823519	**H**	-4.242860	-4.392505	-0.362012	**H**	0.246946	-1.340052	-3.740542
C	-2.739512	-2.577859	0.554270	**C**	-2.936460	-2.676833	-0.324156	**H**	-1.502986	-1.059385	-3.915849
C	0.758330	4.207149	0.070410	**C**	0.653688	4.122159	0.077711	**H**	-1.690117	-3.571608	-4.392664
C	-0.758332	4.207148	-0.070410	**C**	-0.842557	4.088141	0.372868	**H**	0.060084	-3.677071	-4.112639
H	2.470094	-0.960288	2.462911	**H**	-3.071351	-0.186973	-2.683943	**H**	-1.034732	-4.749745	-3.222271
C	2.267158	-2.507239	-2.019291	**C**	-2.172597	-3.117461	0.938096	**H**	-0.050042	-3.958331	-1.014891
C	2.798631	-3.686291	-2.851248	**C**	-2.674473	-4.469071	1.472559	**H**	1.107092	-3.042825	-2.007933
H	2.462147	-4.656494	-2.454197	**H**	-2.556151	-5.276297	0.733377	**H**	0.192310	-2.214484	-0.723123
H	2.419650	-3.601000	-3.881564	**H**	-2.085737	-4.746137	2.360846	**N**	1.436071	-0.551720	0.311229
H	3.898572	-3.697961	-2.903612	**H**	-3.732706	-4.431253	1.775461	**C**	2.426157	-1.506893	0.538582
C	2.783371	-1.209145	-2.677052	**C**	-2.351500	-2.081572	2.068611	**C**	2.559379	-2.103015	1.826336
H	2.377803	-0.309341	-2.197763	**H**	-1.934993	-1.101686	1.805876	**C**	3.202601	-1.976957	-0.539456
H	3.882896	-1.154724	-2.631205	**H**	-3.416812	-1.947178	2.316022	**C**	3.533292	-3.105453	1.964210
H	2.487371	-1.180921	-3.738606	**H**	-1.834555	-2.426952	2.978845	**C**	4.138506	-2.992807	-0.371040
H	-2.470096	-0.960288	-2.462911	**C**	-0.676950	-3.268310	0.594407	**H**	3.041085	-1.537477	-1.524738
C	-2.267155	-2.507241	2.019291	**H**	-0.248305	-2.324498	0.237962	**C**	4.315688	-3.551930	0.895450
C	-2.798631	-3.686291	2.851248	**H**	-0.116481	-3.590265	1.486305	**H**	3.685607	-3.571005	2.936578
H	-2.462150	-4.656495	2.454197	**H**	-0.532632	-4.031891	-0.186922	**H**	4.722816	-3.343836	-1.225222
H	-2.419649	-3.601001	3.881565	**H**	1.720151	-1.547166	-2.700591	**H**	5.050576	-4.344679	1.054985
H	-3.898572	-3.697958	2.903613	**C**	3.096161	-1.910633	1.880729	**C**	1.671700	-1.687567	3.016908
C	-2.783364	-1.209145	2.677051	**C**	2.883033	-3.215317	2.681286	**C**	1.803329	-0.175909	3.300994
H	-2.377793	-0.309343	2.197760	**H**	1.900594	-3.657288	2.453574	**C**	0.200216	-2.037735	2.700692
H	-3.882889	-1.154721	2.631204	**H**	3.651419	-3.972007	2.467687	**C**	2.061543	-2.429041	4.307290
H	-2.487363	-1.180921	3.738604	**H**	2.918430	-3.003345	3.761960	**H**	1.238062	0.085178	4.210581
C	-0.725609	-2.548102	2.075093	**C**	2.019310	-0.917019	2.352202	**H**	2.856417	0.104680	3.465344
H	-0.278678	-1.720033	1.513512	**H**	1.009024	-1.218956	2.046940	**H**	1.410109	0.433794	2.478520
H	-0.383428	-2.489124	3.121415	**H**	2.043048	-0.873732	3.452885	**H**	-0.147331	-1.526400	1.795219
H	-0.344405	-3.489409	1.647629	**H**	2.201807	0.101241	1.985370	**H**	0.083049	-3.123053	2.551401
C	0.725612	-2.548096	-2.075094	**C**	4.474513	-1.313745	2.238955	**H**	-0.448234	-1.738292	3.540812
H	0.383432	-2.489117	-3.121417	**H**	4.516742	-1.068659	3.313103	**H**	1.951918	-3.519949	4.210089
H	0.344405	-3.489400	-1.647630	**H**	5.294520	-2.015149	2.022042	**H**	3.097403	-2.212453	4.612641
H	0.278683	-1.720025	-1.513515	**H**	4.661102	-0.388308	1.671433	**H**	1.399537	-2.103696	5.124732

Table G76 XYZ coordinates of the GS and TS geometries of **3.16d** B3LYP/Def2SVP (SMD = CH_2Cl_2)

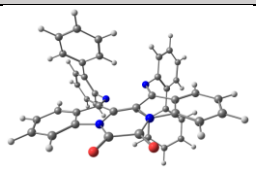
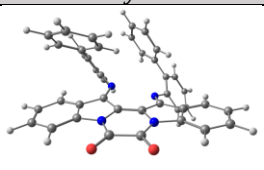
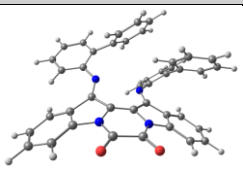
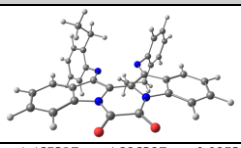
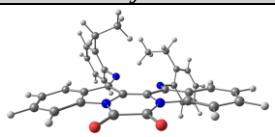
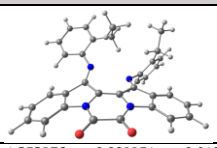
Anti				***Syn***				**TS**			
											
O	1.332254	4.959120	-0.331662	**O**	1.304923	5.028812	-0.461722	**C**	0.781540	0.481270	0.637004
O	-1.332256	4.959120	0.331664	**O**	-1.298245	5.204434	0.392277	**C**	2.119741	-0.115173	0.322411
N	1.313449	2.669053	-0.387818	**N**	1.063695	2.765476	-0.717941	**C**	3.024227	1.082233	0.301203
N	1.245029	-0.865061	-0.722162	**N**	0.819940	-0.770220	-0.783240	**C**	4.257768	1.379901	-0.293812
N	-1.313450	2.669052	0.387819	**N**	-1.558543	2.954190	0.052109	**H**	4.743885	0.680250	-0.968395
N	-1.245029	-0.865062	0.722162	**N**	-2.024454	-0.499667	-0.635649	**C**	4.849721	2.628869	-0.080589
C	0.642688	1.441777	-0.224116	**C**	0.277384	1.597115	-0.658775	**H**	5.808878	2.852952	-0.552091
C	1.589365	0.359017	-0.599003	**C**	1.169100	0.446024	-0.955000	**C**	4.222981	3.588562	0.720578
C	2.873900	1.042787	-0.863468	**C**	2.464707	1.048054	-1.334641	**H**	4.708095	4.550805	0.900016
C	4.132909	0.556137	-1.229594	**C**	3.649619	0.479466	-1.808664	**C**	2.953675	3.353361	1.260201
H	4.312722	-0.512627	-1.326148	**H**	3.726713	-0.594948	-1.968477	**H**	2.426394	4.110520	1.834100
C	5.163105	1.470630	-1.466766	**C**	4.735104	1.317923	-2.075886	**C**	2.361787	2.119422	0.997271
H	6.153198	1.105977	-1.748051	**H**	5.669013	0.890856	-2.447103	**C**	3.383429	-2.209426	0.146792
C	4.937010	2.847748	-1.345013	**C**	4.637182	2.699580	-1.863816	**C**	3.152138	-3.621049	0.165476
H	5.754773	3.547622	-1.532206	**H**	5.499254	3.338799	-2.068496	**C**	4.202905	-4.490666	-0.173247
C	3.681054	3.355565	-0.989358	**C**	3.453927	3.289041	-1.400853	**H**	4.009824	-5.565359	-0.173757
H	3.499696	4.422954	-0.899586	**H**	3.371615	4.361004	-1.244636	**C**	5.488755	-4.023290	-0.438927
C	2.665033	2.431801	-0.753421	**C**	2.375966	2.440796	-1.153930	**H**	6.287136	-4.725613	-0.689922
C	2.131033	-1.910768	-0.968243	**C**	1.657994	-1.877219	-0.819948	**C**	5.751587	-2.655251	-0.325820
C	3.045733	-2.356963	0.024769	**C**	2.723018	-2.060543	0.107075	**H**	6.764336	-2.269965	-0.466586
C	3.880230	-3.442940	-0.287993	**C**	3.455013	-3.257318	0.041891	**C**	4.715547	-1.773354	-0.038337
H	4.579072	-3.799118	0.472409	**H**	4.260674	-3.413409	0.763040	**C**	-0.504731	0.145379	0.331972
C	3.824466	-4.083918	-1.526963	**C**	3.170866	-4.248889	-0.898831	**C**	-1.108025	-0.927686	-0.499387
H	4.484988	-4.928572	-1.735468	**H**	3.759689	-5.168798	-0.917686	**C**	-2.511317	-0.510007	-0.710314
C	2.905391	-3.648342	-2.486690	**C**	2.118209	-4.060407	-1.800043	**C**	-3.525562	-1.022987	-1.523614
H	2.842914	-4.145114	-3.458075	**H**	1.875490	-4.830826	-2.536124	**H**	-3.344452	-1.886500	-2.161141
C	2.055520	-2.580583	-2.202714	**C**	1.358141	-2.894692	-1.745125	**C**	-4.777756	-0.403760	-1.508783
C	-0.642688	1.441777	0.224117	**C**	-1.037229	1.696525	-0.311554	**H**	-5.580308	-0.794321	-2.137863
C	-1.589365	0.359016	0.599003	**C**	-2.154852	0.718440	-0.272289	**C**	-5.015199	0.703650	-0.684000
C	-2.873901	1.042786	0.863468	**C**	-3.316636	1.479998	0.241970	**H**	-6.005535	1.164938	-0.671857
C	-4.132910	0.556135	1.229594	**C**	-4.610252	1.082834	0.595310	**C**	-4.007047	1.245052	0.123042
H	-4.312722	-0.512629	1.326148	**H**	-4.927218	0.047432	0.480630	**H**	-4.182438	2.112137	0.753734
C	-5.163106	1.470628	1.466765	**C**	-5.492606	2.040940	1.101851	**C**	-2.756445	0.630975	0.076054
H	-6.153199	1.105974	1.748051	**H**	-6.506076	1.746416	1.382305	**N**	1.018014	1.736268	1.235750
C	-4.937011	2.847746	1.345014	**C**	-5.089548	3.375181	1.248887	**N**	2.273039	-1.392333	0.313769
H	-5.754775	3.547619	1.532206	**H**	-5.795230	4.112127	1.639469	**N**	-1.548611	1.021567	0.708626
C	-3.681056	3.355564	0.989359	**C**	-3.794665	3.789895	0.914653	**H**	4.949925	-0.723337	0.061174
H	-3.499697	4.422953	0.899587	**H**	-3.473590	4.820224	1.039873	**C**	-1.395150	2.131879	1.511008
C	-2.665034	2.431800	0.753422	**C**	-2.922786	2.820359	0.421104	**C**	0.045528	2.546825	1.786699
C	-2.131033	-1.910768	0.968242	**C**	-3.032105	-1.429232	-0.841909	**O**	-2.317796	2.811563	1.914684
C	-3.045733	-2.356963	-0.024769	**C**	-2.898169	-2.729724	-0.285079	**O**	0.282799	3.576126	2.386369
C	-3.880230	-3.442940	0.287991	**C**	-3.834548	-3.712856	-0.640247	**C**	1.900757	-4.248399	0.661613
H	-4.579071	-3.799118	-0.472411	**H**	-3.739950	-4.707901	-0.198777	**C**	1.282376	-5.291238	-0.047450
C	-3.824465	-4.083919	1.526961	**C**	-4.878856	-3.443105	-1.527080	**C**	1.426801	-3.936770	1.949708
H	-4.484987	-4.928573	1.735466	**H**	-5.593127	-4.227882	-1.786417	**C**	0.228575	-6.013409	0.518832
C	-2.905390	-3.648344	2.486689	**C**	-4.999338	-2.163464	-2.080676	**H**	1.630192	-5.537343	-1.052475
H	-2.842913	-4.145116	3.458074	**H**	-5.804743	-1.940575	-2.785094	**C**	0.391658	-4.674820	2.523172
C	-2.055519	-2.580585	2.202714	**C**	-4.087894	-1.166660	-1.740566	**H**	1.902120	-3.132665	2.514509
C	0.738023	3.909148	-0.196798	**C**	0.615384	4.031033	-0.400418	**C**	-0.211517	-5.716985	1.810767
C	-0.738024	3.909148	0.196799	**C**	-0.837600	4.131483	0.058936	**H**	-0.247777	-6.811836	-0.054172
H	-1.332607	-2.230378	2.942132	**H**	-4.162480	-0.174289	-2.189531	**H**	0.046136	-4.429957	3.530581
H	1.332608	-2.230376	-2.942133	**H**	0.516456	-2.740325	-2.422700	**H**	-1.031362	-6.284399	2.257319
C	-3.153017	-1.689293	-1.349138	**C**	-1.789890	-3.047074	0.650569	**N**	-0.458234	-1.962082	-0.873513
C	-4.417603	-1.392800	-1.889188	**C**	-0.972244	-4.169000	0.429804	**C**	-0.949890	-3.084428	-1.526254
C	-2.009643	-1.342160	-2.094473	**C**	-1.540164	-2.248540	1.781480	**C**	-0.238057	-3.494894	-2.672486
C	-4.538317	-0.766676	-3.132648	**C**	0.072983	-4.476422	1.304103	**C**	-2.022669	-3.892545	-1.046003
H	-5.316118	-1.637514	-1.318392	**H**	-1.142460	-4.789273	-0.452799	**C**	-0.592455	-4.640786	-3.377500
C	-2.131829	-0.717384	-3.336353	**C**	-0.506699	-2.565377	2.664396	**H**	0.603955	-2.878115	-2.992681
H	-1.017817	-1.548305	-1.690371	**H**	-2.175989	-1.383828	1.980361	**C**	-2.337575	-5.058302	-1.767287
C	-3.395658	-0.424637	-3.861294	**C**	0.309774	-3.675644	2.424115	**C**	-1.649851	-5.434333	-2.920762
H	-5.530942	-0.537797	-3.528931	**H**	0.713854	-5.337018	1.099902	**H**	-0.031006	-4.924351	-4.271163
H	-1.230898	-0.456443	-3.898100	**H**	-0.333008	-1.939219	3.542747	**H**	-3.137746	-5.699041	-1.390822
H	-3.488767	0.069618	-4.831605	**H**	1.132120	-3.910103	3.104237	**H**	-1.925706	-6.350744	-3.447457
C	3.153018	-1.689293	1.349137	**C**	3.087678	-1.023005	1.107339	**C**	-2.815090	-3.569123	0.169372
C	4.417604	-1.392800	1.889187	**C**	4.435500	-0.663230	1.287201	**C**	-4.210401	-3.753518	0.164701
C	2.009644	-1.342161	2.094474	**C**	2.113967	-0.361469	1.877621	**C**	-2.219381	-3.073884	1.342264
C	4.538318	-0.766677	3.132648	**C**	4.797390	0.336348	2.193625	**C**	-4.983342	-3.442332	1.285633
H	5.316118	-1.637515	1.318391	**H**	5.205659	-1.152154	0.686800	**H**	-4.701347	-4.117970	-0.739929
C	2.131831	-0.717386	3.336354	**C**	2.474505	0.637207	2.783146	**C**	-2.989548	-2.762354	2.462947
H	1.017818	-1.548306	1.690372	**H**	1.066477	-0.634738	1.760865	**H**	-1.142338	-2.938016	1.379323
C	3.395659	-0.424638	3.861295	**C**	3.817734	0.996034	2.941244	**C**	-4.377018	-2.939046	2.439923
H	5.530943	-0.537798	3.528931	**H**	5.849833	0.608868	2.306415	**H**	-6.066622	-3.583465	1.251181
H	1.230900	-0.456445	3.898101	**H**	1.700194	1.137853	3.370325	**H**	-2.499328	-2.381010	3.362471
H	3.488768	0.069616	4.831606	**H**	4.098551	1.784832	3.643557	**H**	-4.980393	-2.686969	3.315547

Table G77 XYZ coordinates of the GS and TS geometries of **3.16e** B3LYP/Def2SVP (SMD = CH_2Cl_2)

Anti				***Syn***				**TS**			
											
O	-1.465327	4.896397	-0.095330	**O**	1.240524	4.924350	-0.136813	**C**	-1.353276	-0.992251	-0.019755
O	1.276986	4.939330	-0.066803	**O**	-1.460507	4.867577	0.337787	**C**	-1.985952	0.343180	-0.260199
N	-1.442818	-0.943406	0.231378	**N**	1.398844	-0.910397	-0.148241	**C**	-3.384780	0.005598	-0.661599
N	-1.427002	2.608012	0.001509	**N**	1.262876	2.636495	-0.249350	**C**	-4.404143	0.689140	-1.335364
N	1.417560	-0.905823	-0.102440	**N**	-1.520707	-0.930041	-0.415766	**H**	-4.237021	1.671556	-1.768819
N	1.308385	2.648903	-0.027700	**N**	-1.443748	2.585199	0.141219	**C**	-5.644381	0.071346	-1.526909
C	-0.826065	-2.667006	-2.423433	**C**	1.606452	-1.613869	2.982131	**H**	-6.434029	0.608584	-2.056362
C	-2.288888	-2.260148	-2.203078	**C**	2.941223	-1.337720	2.278983	**C**	-5.875334	-1.225121	-1.056801
C	2.522390	-1.795183	2.987033	**C**	-0.440524	-3.984878	0.892351	**H**	-6.854332	-1.689253	-1.196764
C	1.815152	-2.757393	2.023865	**C**	-1.722988	-3.254371	1.309437	**C**	-4.854550	-1.960420	-0.442830
C	-0.840535	3.856205	-0.051709	**C**	0.651451	3.863472	-0.092988	**H**	-5.004723	-2.986010	-0.117499
C	0.684249	3.879867	-0.047665	**C**	-0.852669	3.832491	0.154680	**C**	-3.616815	-1.339179	-0.291625
C	-2.868031	-2.355434	1.587563	**C**	2.571569	-2.685858	-1.295833	**C**	-1.685208	2.737984	0.249338
C	-3.772643	-3.411613	1.706982	**C**	3.506214	-3.722412	-1.301774	**C**	-0.691223	3.536024	0.896623
C	-4.207032	-4.091375	0.565966	**C**	4.258822	-3.989499	-0.155137	**C**	-0.939375	4.896743	1.109998
C	-3.723550	-3.705891	-0.688661	**C**	4.066295	-3.210085	0.990137	**H**	-0.171520	5.498205	1.604044
C	-2.817350	-2.648581	-0.841570	**C**	3.145384	-2.155083	1.023749	**C**	-2.136634	5.495074	0.711779
C	-2.397196	-1.961163	0.323263	**C**	2.395975	-1.892542	-0.150144	**H**	-2.301413	6.561745	0.883280
C	-2.825639	2.363030	0.001249	**C**	2.650094	2.436021	-0.478015	**C**	-3.121931	4.716074	0.098917
C	-3.875145	3.279041	-0.049263	**C**	3.659813	3.385310	-0.626514	**H**	-4.070465	5.163420	-0.208019
C	-5.176398	2.761053	-0.049455	**C**	4.956263	2.908259	-0.857935	**C**	-2.897210	3.360619	-0.126378
C	-5.416646	1.381907	-0.001725	**C**	5.229912	1.536669	-0.938036	**C**	-0.065184	-1.435088	0.034796
C	-4.353533	0.475579	0.053512	**C**	4.207411	0.596251	-0.780875	**C**	1.240567	-0.832289	-0.348769
C	-3.046816	0.974591	0.056376	**C**	2.907064	1.054142	-0.546225	**C**	2.225811	-1.931932	-0.218577
C	-1.732708	0.293841	0.114252	**C**	1.634319	0.332769	-0.317881	**C**	3.592847	-2.002661	-0.510077
C	-0.722379	1.386661	0.037707	**C**	0.597117	1.393989	-0.208511	**H**	4.126883	-1.138900	-0.900527
C	2.527727	-2.899334	0.702330	**C**	-2.645207	-3.022738	0.136009	**C**	4.266686	-3.208726	-0.299291
C	3.410364	-3.957063	0.449721	**C**	-3.624066	-3.967845	-0.200940	**H**	5.333720	-3.275353	-0.521688
C	4.085620	-4.075524	-0.768899	**C**	-4.441905	-3.817054	-1.324287	**C**	3.586459	-4.328656	0.196148
C	3.881551	-3.115894	-1.766202	**C**	-4.283063	-2.694969	-2.143798	**H**	4.130454	-5.261239	0.363775
C	3.022849	-2.041846	-1.535666	**C**	-3.330408	-1.729564	-1.822684	**C**	2.215512	-4.285738	0.475472
C	2.355535	-1.916791	-0.302085	**C**	-2.516408	-1.876061	-0.682290	**H**	1.679802	-5.154508	0.847255
C	2.713713	2.445015	-0.021677	**C**	-2.828702	2.335531	0.327053	**C**	1.554952	-3.078739	0.247990
C	3.735374	3.392901	0.018645	**C**	-3.846747	3.239788	0.627217	**N**	-2.398475	-1.921672	0.143251
C	5.050518	2.914131	0.061952	**C**	-5.133230	2.717759	0.807017	**N**	-1.355600	1.400521	0.100418
C	5.330659	1.541383	0.071813	**C**	-5.387333	1.344219	0.698446	**N**	0.175391	-2.784906	0.381212
C	4.295604	0.603532	0.021435	**C**	-4.357968	0.452142	0.385995	**H**	-3.682480	2.779088	-0.589021
C	2.975594	1.062640	-0.035742	**C**	-3.067752	0.956020	0.187815	**C**	-0.797655	-3.694932	0.736942
C	1.681201	0.342575	-0.055803	**C**	-1.779442	0.286232	-0.115977	**C**	-2.237407	-3.228435	0.557466
C	0.640827	1.406742	-0.000428	**C**	-0.757106	1.368910	-0.056386	**O**	-0.564890	-4.827484	1.111441
H	-0.484144	-2.370534	-3.428705	**H**	1.495323	-0.974565	3.873015	**O**	-3.157573	-4.000247	0.739888
H	-0.701975	-3.758118	-2.330707	**H**	1.541300	-2.664249	3.307346	**C**	0.577537	2.917764	1.422743
H	-0.170340	-2.186067	-1.683806	**H**	0.757341	-1.414606	2.311352	**H**	0.947991	2.185845	0.697240
H	1.727397	-3.748837	2.496141	**H**	-2.253767	-3.848189	2.071269	**H**	1.338842	3.705872	1.533067
H	0.793291	-2.389797	1.835325	**H**	-1.459138	-2.295277	1.780263	**C**	0.363715	2.220882	2.772372
H	-2.383947	-1.169570	-2.339986	**H**	3.005703	-0.263842	2.037667	**H**	-0.339813	1.380337	2.666641
H	-2.924458	-2.725660	-2.973006	**H**	3.771749	-1.545989	2.971647	**H**	1.312339	1.824341	3.165825
H	3.540950	-2.146032	3.220322	**H**	-0.675445	-4.962739	0.441559	**H**	-0.048125	2.916145	3.522295
H	1.967456	-1.707193	3.935420	**H**	0.218090	-4.157914	1.757610	**N**	1.370624	0.369856	-0.767323
H	2.609518	-0.786403	2.553407	**H**	0.121874	-3.396766	0.153860	**C**	2.576298	0.966515	-1.145879
H	-4.136136	-3.701956	2.696131	**H**	3.639625	-4.324581	-2.204148	**C**	2.686211	1.372277	-2.491211
H	-4.914495	-4.919706	0.650138	**H**	4.988482	-4.802680	-0.148424	**C**	3.614480	1.276203	-0.226553
H	-4.058819	-4.236860	-1.584390	**H**	4.650658	-3.419013	1.890938	**C**	3.827551	2.020831	-2.954976
H	-3.685574	4.347801	-0.089273	**H**	3.443758	4.448177	-0.566477	**H**	1.854506	1.152555	-3.164040
H	-6.019534	3.454774	-0.089411	**H**	5.768557	3.628590	-0.980292	**C**	4.740835	1.951959	-0.721971
H	-6.442990	1.009166	-0.006200	**H**	6.250925	1.197068	-1.124114	**C**	4.865330	2.313743	-2.064860
H	-4.543357	-0.595173	0.091805	**H**	4.421930	-0.468815	-0.844344	**H**	3.900923	2.306033	-4.007507
H	3.559207	-4.710961	1.228307	**H**	-3.739581	-4.847966	0.438499	**H**	5.552416	2.195161	-0.032935
H	4.758841	-4.918266	-0.943099	**H**	-5.192657	-4.574469	-1.561912	**H**	5.763682	2.830702	-2.410673
H	4.390365	-3.203881	-2.729581	**H**	-4.904957	-2.566518	-3.033423	**C**	3.537848	0.876457	1.232678
H	3.514042	4.456318	0.023490	**H**	-3.642038	4.302141	0.723731	**H**	2.495664	0.646540	1.491489
H	5.872525	3.633090	0.095209	**H**	-5.951690	3.401384	1.044487	**H**	4.087550	-0.072228	1.370202
H	6.366586	1.198993	0.116693	**H**	-6.399228	0.965136	0.855984	**C**	4.082931	1.909488	2.220432
H	4.516616	-0.461946	0.027850	**H**	-4.561527	-0.613432	0.302670	**H**	3.926084	1.566739	3.255410
H	2.851128	-1.289567	-2.308384	**H**	-3.201128	-0.846227	-2.451683	**H**	5.164061	2.076254	2.095793
H	-2.518553	-1.815960	2.470544	**H**	1.965693	-2.471434	-2.178649	**H**	3.578055	2.881222	2.103574

Appendix H: Computational Chemistry II: Time dependent density functional theory results

Table H1 TD-DFT results of **1.54** and **2.1a – 2.1g** B3LYP/SMD(CH_2Cl_2)

1.54		***Anti*-2.1a**		***Syn*-2.1a**		***Anti*-2.1b**	
6-311G (d,p)		**6-311G (d,p)**		**6-311G (d,p)**		**6-311G (d,p)**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
608	1	603.45	1	602	1	599	1
450	0	456.95	0	449	0.064	455	0
431	0.11	440.65	0.085	448	0.00035	440	0.069
428	0	426.49	0	425	0.00018	425	0
388	0	386.66	0	386	0	385	0
329	0.032	345.83	0	345.3	0.0047	345	0
329	0	345.72	0.013	345.1	0.0058	345	0.010
314	0.041	314.11	0.071	314	0.13	314	0.10
311	0.16	310.97	0.15	311	0.13	311	0.13
310	0	310.63	0	309	0.00018	310.6	0
***Syn*-2.1b**		***Anti*-2.1c**		***Syn*-2.1c**		***Anti*-2.1d**	
6-311G (d,p)		**6-311G (d,p)**		**6-311G (d,p)**		**6-311G (d,p)**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
598	1	602	1	604	1	691	1
452	0.035	463	0	457	0.048	470	0
448	0.013	449	0.058	456	0.00090	437	0.29
424	0.00036	427	0	426	0.00036	434	0
384	0.00018	385	0	386	0.00018	421	0
345	0.0045	346.2	0.018	346	0.012	386	0
344	0.0081	346.0	0	345.9	0.0056	382	0.075
315	0.16	315	0.18	316	0.22	362	0.10
311	0.10	312	0.11	313	0.080	361	0
309	0.0020	311	0	311	0.0029	340	0.099

Table H2 TD-DFT results of **1.54** and **2.1a – 2.1g** B3LYP/SMD(CH_2Cl_2) continued

***Syn*-2.1d**		***Anti*-2.1e**		***Syn*-2.1e**		***Anti*-2.1f**	
6-311G (d,p)		**6-311G (d,p)**		**6-311G (d,p)**		**6-311G (d,p)**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
668	1	590	1	598	1	657	1
454	0.00020	455	0	448	0.055	517	0
443	0.17	443	0.046	446	0.00035	493	0.10
432	0.00059	424	0	424	0.00018	442	0
411	0.0039	381	0	384	0.00018	415	0
380	0.054	344.2	0	344.8	0.0055	373	0.075
378	0.034	344	0.010	344.6	0.0053	360	0
357	0.059	313	0.10	314	0.11	348.1	0.0093
355	0.033	309	0.15	311	0.13	348.0	0
339	0.14	308.7	0	308	0.00053	340	0
***Syn*-2.1f**		***Anti*-2.1g**		***Syn*-2.1g**			
6-311G (d,p)		**6-311G (d,p)**		**6-311G (d,p)**			
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**		
661	1	639	1	632	1		
511	0	463	0	459	0.0025		
498	0.098	434	0	435	0.014		
442	0	433	0.20	431	0.15		
417	0.00045	396	0	392	0.00082		
373	0.078	341	0.017	340	0.0094		
361	0	341	0	336	0.0043		
348.3	0.0012	322	0.19	323	0.16		
348.1	0.0089	320	0	319	0.10		
340	0.010	318	0.13	317	0.14		

Table H3 TD-DFT results of **1.54** and **2.1a – 2.1g** B3LYP/SMD(CH_2Cl_2) continued

1.54		***Anti*-2.1a**		***Syn*-2.1a**		***Anti*-2.1b**	
Def2TZVPP		**Def2TZVPP**		**Def2TZVPP**		**Def2TZVPP**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
611	1	607	1	605	1	603	1
453	0	459	0	451	0.064	458	0
433	0.11	443	0.085	450	0.00035	442	0.069
430	0	428	0	426	0	426	0
393	0	392	0	391	0	391	0
330	0.032	346	0	346	0.0048	346	0
330	0	346	0.012	346	0.0053	346	0.0095
318	0.0044	317	0.021	317	0.061	317	0.049
313	0.17	313	0.16	314	0.16	313	0.15
311	0	312	0	310	0.00018	312	0
***Syn*-2.1b**		***Anti*-2.1c**		***Syn*-2.1c**		***Anti*-2.1d**	
Def2TZVPP		**Def2TZVPP**		**Def2TZVPP**		**Def2TZVPP**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
602	1	607	1	609	1	695	1
453	0.036	465	0	459	0.048	474	0
450	0.012	450	0.059	457	0.00091	440	0.30
425	0.00036	428	0	427	0.00036	436	0
390	0.00018	392	0	392	0.00018	426	0
346	0.0044	347	0.019	347	0.012	387	0
345	0.0082	346	0	346	0.0053	383	0.071
317	0.10	317	0.11	318	0.18	366	0.11
314	0.14	315	0.12	316	0.077	365	0
310	0.0047	313	0	312	0.0027	341	0.11

Table H4 TD-DFT results of **1.54** and **2.1a – 2.1g** B3LYP/SMD(CH_2Cl_2) continued

***Syn*-2.1d**		***Anti*-2.1e**		***Syn*-2.1e**		***Anti*-2.1f**	
Def2TZVPP		**Def2TZVPP**		**Def2TZVPP**		**Def2TZVPP**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
672	1	593	1	602	1	661	1
457	0.00020	457	0	450	0.055	520	0
446	0.17	444	0.046	448	0.00018	495	0.10
433	0.00059	425	0	425	0.00018	443	0
416	0.0034	387	0	390	0	421	0
382	0.054	345	0	346	0.0053	378	0.074
380	0.033	345	0.010	345	0.0050	365	0
361	0.059	315	0.055	317	0.057	349	0.0085
360	0.034	311	0.16	313	0.17	348.8	0
340	0.15	310	0	309	0.00053	341	0
***Syn*-2.1f**		***Anti*-2.1g**		***Syn*-2.1g**			
Def2TZVPP		**Def2TZVPP**		**Def2TZVPP**			
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**		
665	1	643	1	635	1		
514	0	466	0	462	0.0025		
500	0.097	436	0	437	0.012		
443	0	435	0.20	433	0.16		
422	0.00046	401	0	396	0.00083		
378	0.077	342	0.016	341	0.0091		
366	0	342	0	337	0.0038		
349	0.0017	324	0.15	324	0.15		
349	0.0082	321	0	320	0.12		
342	0.011	320	0.12	319	0.11		

Table H5 TD-DFT Results of **1.65** and **2.2a – 2.2g B3LYP/SMD(CH_2Cl_2)**

1.65		***Anti*-2.2a**		***Syn*-2.2a**		***Anti*-2.2b**	
6-311G (d,p)		**6-311G (d,p)**		**6-311G (d,p)**		**6-311G (d,p)**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
627	1	638	1	614	1	648	1
522	0.44	525	0.25	549	0.014	516	0.23
484	0.13	487	0.22	484	0.28	481	0.26
414	0.078	438	0.14	432	0.091	421	0.041
394	0.0081	418	0.21	417	0.13	414	0.23
379	0.0093	409	0.021	409	0.052	406	0.12
367	0.32	366	0.51	363	0.14	371	0.82
347	0.94	349	0.89	345	0.91	346	0.66
341	0.69	338	0.60	336	0.79	334	0.74
313	0.095	321	0.051	316	0.069	322	0.15
***Syn*-2.2b**		***Anti*-2.2c**		***Syn*-2.2c**		***Anti*-2.2d**	
6-311G (d,p)		**6-311G (d,p)**		**6-311G (d,p)**		**6-311G (d,p)**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
623	1	623	1	601	1	630	1
546	0.10	535	0.22	537	0.13	554	0.17
484	0.29	481	0.31	479	0.16	489	0.24
433	0.042	426	0.0059	423	0.014	484	0.023
416	0.15	409	0.056	421	0.025	445	0.025
412	0.14	400	0.11	394	0.051	412	0.028
363	0.26	363	0.15	360	0.072	409	0.030
346	0.95	344	0.91	344	0.66	384	0.15
336	0.79	335	0.97	335	0.76	365	0.16
319	0.091	326	0.55	328	0.53	356	0.55

Table H6 TD-DFT results of **1.65** and **2.2a – 2.2g** B3LYP/SMD(CH_2Cl_2) continued

***Syn*-2.2d**		***Anti*-2.2e**		***Syn*-2.2e**		***Anti*-2.2f**	
6-311G (d,p)		**6-311G (d,p)**		**6-311G (d,p)**		**6-311G (d,p)**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
664	1	616	1	594	1	744	0.80
528	0.29	520	0.22	533	0.17	599	0.82
502	0.16	480	0.22	477	0.19	544	0.49
489	0.21	426	0.0078	423	0.0034	495	0.11
471	0.041	414	0.098	415	0.0043	433	0.0028
430	0.072	399	0.15	384	0.0053	421	0.0072
412	0.072	361	0.31	361	0.043	395	1
396	0.13	344	0.90	342	0.74	391	0.045
370	0.42	335	0.65	336	0.86	362	0.59
367	0.63	325	0.36	322	0.48	356	0.59
***Syn*-2.2f**		***Anti*-2.2g**		***Syn*-2.2g**			
6-311G (d,p)		**6-311G (d,p)**		**6-311G (d,p)**			
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**		
693	1	645	0.82	655	0.89		
652	0.83	509	0.22	512.96	0.28		
525	0.38	491	0.070	487.61	0.090		
494	0.27	413	0.21	419.16	0.28		
428	0.0038	400	0.024	404.47	0.0072		
416	0.032	381	0.033	388.62	0.039		
386	0.091	364	0.40	364.66	0.62		
378	0.84	352	1	354.6	1		
357	0.56	342	0.37	342.41	0.29		
356	0.91	323	0.049	324.88	0.037		

Table H7 TD-DFT results of **1.65** and **2.2a – 2.2g** B3LYP/SMD(CH_2Cl_2) continued

1.65		***Anti*-2.2a**		***Syn*-2.2a**		***Anti*-2.2b**	
Def2TZVPP		**Def2TZVPP**		**Def2TZVPP**		**Def2TZVPP**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
629	1	640	1	615	1	649	0.27
525	0.44	527	0.26	550	0.014	518	0.066
487	0.13	489	0.22	486	0.28	482	0.070
415	0.079	438	0.15	431	0.11	421	0.012
394	0.0079	418	0.20	416	0.12	414	0.065
378	0.0050	409	0.018	408	0.041	406	0.027
370	0.37	369	0.56	366	0.18	374	0.23
349	0.88	350	0.82	347	0.85	347	0.17
343	0.71	340	0.62	338	0.80	335	0.21
314	0.15	321	0.044	317	0.062	323	0.037
***Syn*-2.2b**		***Anti*-2.2c**		***Syn*-2.2c**		***Anti*-2.2d**	
Def2TZVPP		**Def2TZVPP**		**Def2TZVPP**		**Def2TZVPP**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
624	1	624	1	602	1	631	1
547	0.11	536	0.23	538	0.13	554	0.18
485	0.29	482	0.30	480	0.15	490	0.24
432	0.049	425	0.0056	422	0.015	482	0.018
416	0.17	409	0.063	420	0.025	443	0.025
412	0.11	400	0.10	393	0.049	409	0.036
366	0.30	365	0.19	362	0.11	406	0.032
347	0.88	345	0.91	344	0.69	383	0.13
337	0.81	336	0.97	337	0.73	367	0.23
320	0.079	327	0.50	329	0.49	357	0.54

Table H8 TD-DFT results of **1.65** and **2.2a – 2.2g** B3LYP/SMD(CH_2Cl_2) Continued

***Syn*-2.2d**		***Anti*-2.2e**		***Syn*-2.2e**		***Anti*-2.2f**	
Def2TZVPP		**Def2TZVPP**		**Def2TZVPP**		**Def2TZVPP**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
665	1	617	1	595	1	747	0.79
529	0.31	522	0.22	535	0.18	601	0.83
501	0.17	481	0.21	478	0.18	544	0.50
489	0.18	425	0.0075	422	0.0031	496	0.097
471	0.043	414	0.11	414	0.0041	432	0.0028
428	0.076	399	0.14	383	0.0050	421	0.0068
410	0.081	364	0.36	364	0.064	399	1
395	0.11	345	0.87	344	0.79	391	0.039
373	0.70	336	0.66	338	0.81	363	0.57
368	0.40	326	0.32	323	0.47	357	0.57
***Syn*-2.2f**		***Anti*-2.2g**		***Syn*-2.2g**			
Def2TZVPP		**Def2TZVPP**		**Def2TZVPP**			
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**		
694	1	647	0.88	657.27	0.96		
653	0.85	511	0.23	515.52	0.30		
525	0.41	493	0.071	490.65	0.093		
495	0.25	413	0.23	419.24	0.30		
427	0.0039	400	0.023	404.91	0.0069		
415	0.033	381	0.018	388.56	0.029		
387	0.25	366	0.50	367.86	0.73		
381	0.72	355	1	356.77	1		
357	0.54	343	0.40	344.48	0.32		
357	0.65	324	0.045	325.79	0.033		

Table H9 TD-DFT results of **3.3** SMD(ACN)

B3LYP		PBE0		CAM-B3LYP		wB97XD	
6-311++G(d,p)		6-311++G(d,p)		6-311++G(d,p)		6-311++G(d,p)	
Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength
584	0.75	568	0.58	519	0.45	515	0.45
472	0.015	451	0.015	399	0.0099	404	0.012
455	0.020	444	0.017	394	0.042	388	0.046
373	0.0038	366	0.00095	338	0	342	0.00040
362	0.16	349	0.13	307	0.11	301	0.099
326	0.61	313	0.54	283	1	280	1
313	0.12	300	0.092	272	0.0066	268	0.0046
304	0.25	294	0.29	261	0.098	255	0.11
288	1	278	1	254	0.19	242	0.53
285	0.63	273	0.065	245	0.40	238	0.11

Table H10 TD-DFT results of **3.3** SMD(ACN) continued

B3LYP		PBE0		CAM-B3LYP		wB97XD	
Def2TZVPP		Def2TZVPP		Def2TZVPP		Def2TZVPP	
Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength
581	0.69	566	0.56	517	0.44	513	0.44
468	0.013	450	0.014	400	0.010	406	0.012
458	0.020	447	0.017	393	0.039	387	0.044
375	0.0017	369	0.00056	340	0.00013	344	0.00039
361	0.13	349	0.11	307	0.095	300	0.085
324	0.56	311	0.53	282	1	280	1
311	0.097	299	0.081	271	0.0046	267	0.0055
303	0.23	293	0.30	260	0.087	254	0.094
287	1	278	1	245	0.58	240	0.62
284	0.52	272	0.057	231	0.052	224	0.10

Table H11 TD-DFT results of **3.6** SMD(ACN) continued

B3LYP		PBE0		CAM-B3LYP		wB97XD	
6-311++G(d,p)		6-311++G(d,p)		6-311++G(d,p)		6-311++G(d,p)	
Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength
451	0	439	0	394	0	398	0
441	1	425	1	376	1	372	1
415	0.072	396	0.089	341	0.27	339	0
371	0	364	0	336	0	336	0.31
336	0.74	323	0.64	293	0.58	291	0.49
334	0.51	321	0.76	288	0.70	285	0.67
326	0.56	312	0.39	282	0.0013	283	0.0013
322	0	306	0.42	273	0.22	269	0.20
320	0.51	305	0	271	0.39	268	0.37
307	0.0014	300	0.0013	250	0	249	0

Table H12 TD-DFT results of **3.6** SMD(ACN) continued

B3LYP		PBE0		CAM-B3LYP		wB97XD	
Def2TZVPP		Def2TZVPP		Def2TZVPP		Def2TZVPP	
Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength	Wavelength (nm)	Oscillator Strength
453	0	443	0	396	0	401	0
440	1	425	1	376	1	373	1
414	0.068	395	0.084	342	0.24	341	0
374	0	367	0	338	0	337	0.28
333	0.74	322	0.62	292	0.53	290	0.46
333	0.51	320	0.76	288	0.70	285	0.00098
324	0.44	311	0.31	283	0.0010	284	0.66
323.5	0	308	0	273	0.17	269	0.15
317	0.47	304	0.39	270	0.34	267	0.34
308	0.00094	302	0.00087	251	0	251	0

Table H13 TD-DFT results of **3.14** SMD(ACN)

B3LYP		PBE0		CAM-B3LYP		wB97XD	
6-311++G(d,p)		6-311++G(d,p)		6-311++G(d,p)		6-311++G(d,p)	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
611	0.0019	582	0.0014	476	0.00086	466	0.00085
492	0.0015	471	0.0014	392	0.00064	385	0.00064
431	0.0046	415	1	371	0.75	369	0.77
426	1	397	0.0060	321	1	319	1
390	0.0076	369	0.015	298	0.017	294	0.0077
387	0.0053	367	0.0028	292	0.0011	282	0.00064
370	0.0057	357	0.51	285	0.0013	278	0.0092
370	0.36	345	0.0056	284	0.00043	276	0.0028
355	0.85	343	0.70	280	0.00064	275	0.00043
336	0.0027	316	0.0018	275	0.0011	272	0.0075

Table H14 TD-DFT Results of 3.14 SMD(ACN) Continued

B3LYP		PBE0		CAM-B3LYP		wB97XD	
Def2TZVPP		Def2TZVPP		Def2TZVPP		Def2TZVPP	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
610	0.0015	582	0.0011	475	0.00071	465	0.00093
490	0.0015	470	0.0014	391	0.00094	384	0.00070
429	1	418	1	374	0.81	372	0.83
426	0.0045	393	0.0064	321	1	319	1
388	0.0087	368	0.021	299	0.029	295	0.013
385	0.0038	365	0.0021	290	0.0021	283	0.00046
371	0.31	358	0.44	284	0.0014	276	0.014
366	0.0049	343	0.67	283	0.00047	275	0.0026
355	0.79	341	0.0049	281	0.00047	274	0.00023
336	0.0026	317	0.0021	275	0.0038	272	0.014

Table H15 TD-DFT results of **3.13** SMD(ACN)

B3LYP		**PBE0**		**CAM-B3LYP**		**wB97XD**	
6-311++G(d,p)		6-311++G(d,p)		6-311++G(d,p)		6-311++G(d,p)	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
624	0.14	590	0.13	464	0.14	453	0.32
499	0.091	472	1	415	0.69	411	1
485	1	464	0.38	366	0.36	361	0.65
477	0.43	450	0.068	343	0.030	332	0.12
452	0.38	432	0.38	341	0.027	326	0.014
441	0.026	421	0.017	338	0.018	325	0.018
399	0.13	373	0.15	311	0.39	308	0.61
371	0.21	353	0.24	298	0.56	293	0.95
351	0.42	337	0.83	290	1	289	0.0016
348	0.44	329	0.12	288	0.011	285	0.76

Table H16 TD-DFT results of **3.13** SMD(ACN) continued

B3LYP		**PBE0**		**CAM-B3LYP**		**wB97XD**	
Def2TZVPP		**Def2TZVPP**		**Def2TZVPP**		**Def2TZVPP**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
623	0.12	589	0.11	464	0.15	452	0.30
495	0.20	473	1	417	0.69	414	1
485	1	461	0.12	368	0.36	362	0.61
473	0.14	446	0.034	341	0.046	331	0.12
451	0.32	432	0.29	339	0.022	324	0.011
440	0.026	420	0.026	336	0.014	322	0.015
395	0.11	370	0.11	310	0.38	308	0.58
369	0.19	352	0.20	298	0.58	293	0.93
349	0.63	337	0.64	290	1	291	0.00081
348	0.0067	333	0.0059	289	0.023	285	0.81

Table H17 TD-DFT results of **3.16a** SMD(CH_2Cl_2)

***Anti*-3.16a**				***Syn*-3.16a**			
6-311++G(d,p)				**6-311++G(d,p)**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm**	**Oscillator Strength**
599	0.056	571	0.053	591	0.085	564	0.068
479	0.15	460	0.14	486	0.27	467	0.25
429	1	417	1	428	0.69	412	0.86
426	0.019	393	0.037	417	0.39	388	0.033
370	0.38	357	0.54	376	1	359	1
369	0.0060	350	0.0063	370	0.035	353	0.13
367	0.0041	348	0.015	369	0.012	350	0.016
365	0	342	0.73	367	0.0070	348	0.0037
355	0.90	341	0.00035	346	0.58	329	0.25
334	0.0011	315	0.0028	330	0.0075	311	0.0037

Table H18 TD-DFT results of **3.16a** SMD(CH_2Cl_2) continued

***Anti*-3.16a**				***Syn*-3.16a**			
Def2TZVPP				**Def2TZVPP**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
597	0.056	571	0.053	590	0.085	564	0.078
478	0.15	459	0.14	485	0.30	467	0.32
432	1	420	1	428	0.93	414	1
421	0.022	390	0.041	414	0.15	385	0.025
372	0.33	358	0.46	374	1	360	0.94
367	0.0056	349	0.0060	370	0.047	352	0.34
365	0.0033	347	0.026	367	0.015	349	0.017
362	0	342	0.69	365	0.0043	347	0.0044
355	0.85	338	0.00035	345	0.47	327	0.22
334	0.00074	316	0.0018	330	0.0082	312	0.0053

Table H19 TD-DFT results of **3.16b** SMD(CH_2Cl_2)

***Anti*-3.16b**				***Syn*-3.16b**			
6-311++G(d,p)				**6-311++G(d,p)**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
600	0.093	573	0.077	582	0.082	555	0.077
485	0.34	466	0.30	483	0.19	464	0.19
432	0.60	415	0.94	434	1	422	1
421	0.58	393	0.055	416	0.027	385	0.046
375	1	359	1	373	0.39	359	0.57
370	0.046	352	0.15	372	0.062	352	0.016
369	0.011	350	0.025	368	0.017	349	0.041
368	0.0036	348	0.050	368	0.16	347	0.49
349	0.77	332	0.34	354	0.79	337	0.30
334	0.0073	315	0.010	327	0.0054	310	0.025

Table H20 TD-DFT results of **3.16b** SMD(CH_2Cl_2) continued

***Anti*-3.16b**				***Syn*-3.16b**			
Def2TZVPP				**Def2TZVPP**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
600	0.096	573	0.081	581	0.082	555	0.078
484	0.37	466	0.34	482	0.19	464	0.20
431	0.97	417	1	437	1	425	1
420	0.24	390	0.045	412	0.026	382	0.054
374	1	360	0.85	374	0.36	361	0.49
370	0.059	351	0.33	370	0.016	351	0.015
368	0.014	349	0.029	367	0.013	348	0.058
366	0.030	347	0.064	365	0.27	346	0.56
347	0.65	330	0.27	353	0.66	335	0.20
334	0.0081	316	0.010	328	0.0050	310	0.020

Table H21 TD-DFT results of **3.16c** SMD(CH_2Cl_2)

***Anti*-3.16c**				***Syn*-3.16c**			
6-311++G(d,p)				**6-311++G(d,p)**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm**	**Oscillator Strength**	**Wavelength (nm**	**Oscillator Strength**
630	0.13	602	0.13	576	0.11	550	0.11
487	0.38	468	0.39	487	0.31	468	0.31
440	0.11	423	1	433	1	421	0.96
435	0.93	407	0.18	414	0.016	383	0.018
377	0.062	361	0.46	376	0.99	361	1
374	0.26	357	0.0095	375	0.0097	355	0.038
370	0.016	351	0.020	372	0.0018	353	0.24
369	0.0037	344	0.0017	370	0.013	351	0.021
356	1	341	0.93	351	0.58	333	0.27
345	0.0012	327	0.00042	326	0.023	308	0.12

Table H22 TD-DFT results of **3.16c** SMD(CH_2Cl_2) continued

***Anti*-3.16c**				***Syn*-3.16c**			
Def2TZVPP				**Def2TZVPP**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
629	0.14	602	0.14	575	0.11	551	0.11
485	0.39	467	0.38	487	0.33	469	0.36
437	0.99	426	1	435	1	423	1
436	0.13	404	0.19	409	0.011	380	0.024
376	0.26	363	0.42	375	0.84	362	0.86
374	0.052	355	0.0042	374	0.031	354	0.14
369	0.017	350	0.020	371	0.14	353	0.32
365	0.0031	341	0.0017	368	0.014	349	0.024
355	1	341	0.87	349	0.47	331	0.21
346	0.0018	328	0.0013	326	0.025	309	0.11

Table H23 TD-DFT results of **3.16d** SMD(CH_2Cl_2)

***Anti*-3.16d**				***Syn*-3.16d**			
6-311++G(d,p)				**6-311++G(d,p)**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
624	0.12	594	0.13	613	0.34	586	0.31
50	0.17	480	0.18	492	0.63	472	0.58
435	0.23	421	1	446	1	433	1
433	1	403	0.31	437	0.25	406	0.28
402	0.016	380	0.014	406	0.19	384	0.18
389	0.022	368	0.022	397	0.12	376	0.089
378	0.27	364	0.34	378	0.30	363	0.41
377	0.023	351	0.020	377	0.11	353	0.18
357	0.032	338	0.66	358	0.14	341	0.63
355	0.086	337.9	0.040	357	0.62	339	0.17

Table H24 TD-DFT results of **3.16d** SMD(CH_2Cl_2) continued

***Anti*-3.16d**				***Syn*-3.16d**			
Def2TZVPP				**Def2TZVPP**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
623	0.12	595	0.13	612	0.33	587	0.31
502	0.16	480	0.17	491	0.59	472	0.57
436	1	424	1	448	1	436	1
431	0.23	401	0.31	433	0.24	403	0.29
400	0.015	378	0.013	404	0.17	382	0.17
387	0.024	367	0.070	395	0.11	375	0.087
379	0.25	365	0.26	378	0.29	364	0.34
374	0.021	348	0.019	374	0.084	350	0.22
355	0.033	338	0.68	357	0.17	340	0.62
354	0.15	336	0.041	355	0.56	338	0.10

Table H25 TD-DFT results of **3.16e** SMD(CH_2Cl_2)

***Anti*-3.16e**				***Syn*-3.16e**			
6-311++G(d,p)				**6-311++G(d,p)**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
600	0.093	573	0.077	582	0.082	555	0.077
485	0.34	466	0.30	483	0.19	464	0.19
432	0.60	415	0.94	434	1	422	1
421	0.58	393	0.055	416	0.027	385	0.046
375	1	359	1	373	0.39	359	0.57
370	0.046	352	0.15	372	0.062	352	0.016
369	0.011	350	0.025	368	0.017	349	0.041
368	0.0036	348	0.050	368	0.16	347	0.49
349	0.77	332	0.34	354	0.79	337	0.30
334	0.0073	315	0.010	327	0.0054	310	0.025

Table H26 TD-DFT results of **3.16e** SMD(CH_2Cl_2) continued

***Anti*-3.16e**				***Syn*-3.16e**			
Def2TZVPP				**Def2TZVPP**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
600	0.096	573	0.081	581	0.082	555	0.078
484	0.37	466	0.34	482	0.19	464	0.20
431	0.97	417	1	437	1	425	1
420	0.24	390	0.045	412	0.026	382	0.054
374	1	360	0.85	374	0.36	361	0.49
370	0.059	351	0.33	370	0.016	351	0.015
368	0.014	349	0.029	367	0.013	348	0.058
366	0.030	347	0.064	365	0.27	346	0.56
347	0.65	330	0.27	353	0.66	335	0.20
334	0.0081	316	0.010	328	0.0050	310	0.020

Table H27 TD-DFT results of **3.15a** SMD(CH_2Cl_2)

***Anti*-3.15a**				***Syn*-3.15a**			
6-311++G(d,p)				**6-311++G(d,p)**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
610	0.010	574	0.011	614	0.14	580	0.15
490	0.57	475	0.57	516	1	498	0.92
472	0.0099	443	0.0013	472	0.075	446	0.27
461	0.0031	434.4	0.017	465	0.29	443	0.092
453	0.071	434	0.063	450	0.028	427	0.018
422	0.0045	400	0.0041	432	0.31	413	0.28
388	0.0073	363	0.0080	392	0.18	369	0.20
377	0.076	359	0.083	379	0.16	360	0.24
352	0.28	340	0.32	355	0.97	341	0.83
351	0.00024	335	0.00043	354	0.030	337	0.0048
342	1	330	1	345	0.82	332	1
333	0.022	321	0.043	334	0.58	319	0.27
332	0.028	311	0.013	332	0.063	312	0.15
321	0.56	306	0.48	323	0.21	310	0.20
320	0.0073	299	0.0026	314	0.067	298	0.0085
305	0.00094	297	0.00043	309	0.35	295	0.13
301	0.00047	288	0.0019	305	0.024	292	0.20
300	0.0089	284	0.00065	305	0.0080	291	0.028
297	0.0049	281	0.050	300	0.0021	288	0.0088
294	0.074	279	0.00065	293	0.15	279	0.13

Table H28 TD-DFT results of **3.15a** SMD(CH_2Cl_2) continued

***Anti*-3.15a**				***Syn*-3.15a**			
Def2TZVPP				**Def2TZVPP**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
608	0.011	574	0.012	612.62	0.14	580.61	0.15
491	0.59	477	0.60	516.96	1	499.6	0.90
468	0.0056	440	0.00068	468.82	0.090	445.71	0.32
457	0.0015	435	0.079	464.39	0.25	440.46	0.022
454	0.072	431	0.0034	446.82	0.023	423.96	0.022
420	0.0044	397	0.0043	430.73	0.32	411.76	0.27
385	0.0075	360	0.0081	388.88	0.18	366.78	0.18
375	0.080	358	0.090	377.74	0.17	359.3	0.26
354	0.00024	339	0.33	356.99	0.0067	340.68	0.053
351	0.29	338	0.00023	353.65	0.93	339.56	0.70
341	1	329	1	344.67	0.90	332.01	1
332	0.028	321	0.053	332.12	0.45	317.91	0.19
329	0.019	308	0.020	327.99	0.054	310.89	0.30
320	0.55	306	0.48	323.1	0.23	307.56	0.075
317	0.0041	299	0.0011	310.97	0.075	299.58	0.0018
306	0.00049	297	0.0023	307.34	0.22	292.89	0.14
302	0.00049	290	0.0016	306.59	0.0084	292.11	0.053
301	0.0054	285	0.0036	305.61	0.099	290.18	0.017
296	0.0088	281	0.013	301.57	0.0025	289.55	0.13
293	0.036	278	0.0034	292.35	0.077	278.63	0.049

Table H29 TD-DFT results of **3.15b** SMD(CH_2Cl_2)

***Anti*-3.15b**				***Syn*-3.15b**			
6-311++G(d,p)				**6-311++G(d,p)**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
614	0.14	582	0.16	608	0.21	577	0.23
495	0.54	480	0.56	491	0.55	475	0.59
477	0.0098	447	0.016	475	0.063	448	0.072
463	0.12	443	0.13	474	0.010	445	0.0099
453	0.010	428	0.0037	457	0.078	438	0.071
433	0.10	411	0.11	429	0.052	407	0.057
394	0.17	371	0.19	395	0.19	372	0.20
375	0.18	357	0.29	373	0.17	355	0.27
351	0.27	338	0.28	352	0.065	338	0.30
350	0.0079	335	0.0027	351	0.21	336	0.011
343	1	330	1	342	1	329	1
337	0.010	325	0.031	336	0.076	325	0.10
335	0.018	313	0.032	335	0.0081	313	0.0088
326	0.47	311	0.44	327	0.050	309	0.50
316	0.075	296	0.051	323	0.56	305	0.074
308	0.0055	295	0.0067	308	0.0067	298	0.0037
306	0.12	293	0.0048	306	0.024	293	0.011
303	0.022	291	0.074	303	0.15	290	0.13
302	0.019	287	0.083	300	0.024	284	0.080
289	0.14	275	0.11	288	0.12	277	0.072

Table H30 TD-DFT results of **3.15b** SMD(CH_2Cl_2) continued

***Anti*-3.15b**				***Syn*-3.15b**			
Def2TZVPP				**Def2TZVPP**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
613	0.15	582	0.17	607	0.22	577	0.24
496	0.57	481	0.60	492	0.60	477	0.63
473	0.0081	444	0.083	472	0.054	445	0.096
463	0.12	442	0.069	470	0.016	442	0.0088
450	0.0049	425	0.0074	458	0.074	438	0.053
431	0.11	409	0.11	427	0.056	405	0.062
391	0.18	369	0.19	392	0.19	370	0.20
374	0.20	356	0.32	372	0.19	354	0.30
353	0.00029	338	0.0037	355	0.0071	339	0.041
350	0.29	337	0.30	350	0.29	337	0.30
342	1	330	1	341	1	328	1
337	0.017	325	0.040	336	0.094	325	0.12
331	0.018	310	0.34	331	0.0077	311	0.019
325	0.48	310	0.15	324	0.23	308	0.52
313	0.065	298	0.016	322	0.38	302	0.053
308	0.0086	295	0.0026	308	0.021	300	0.0030
306	0.085	293	0.026	307	0.010	294	0.021
303	0.024	292	0.10	302	0.14	291	0.12
302	0.050	286	0.083	300	0.038	283	0.093
288	0.10	274	0.065	286	0.088	276	0.093

Table H31 TD-DFT results of **3.15c** SMD(CH_2Cl_2)

***Anti*-3.15c**				***Syn*-3.15c**			
6-311++G(d,p)				**6-311++G(d,p)**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
631	0.11	596	0.13	610	0.18	579	0.19
497	0.50	481	0.52	492	0.55	477	0.57
479	0.010	449	0.012	473	0.022	444	0.057
464	0.12	443	0.14	470	0.022	442	0.013
453	0.013	428	0.0043	457	0.069	438	0.055
438	0.091	415	0.097	431	0.038	408	0.042
396	0.15	373	0.15	395	0.15	372	0.15
378	0.17	359	0.26	374	0.15	356	0.24
354	0.00026	337.9	0.030	352	0.089	339	0.27
351	0.28	337.6	0.27	351	0.16	336	0.012
342	1	329	1	342	1	329	1
337	0.024	326	0.048	337	0.074	325	0.10
334	0.016	312	0.027	334	0.014	312	0.012
325	0.42	310	0.39	325	0.21	309	0.49
314	0.064	298	0.027	323	0.36	303	0.029
310	0.00078	296	0.0053	308	0.0043	298	0.0032
308	0.099	294	0.020	306	0.031	293	0.0052
305	0.049	293	0.063	303	0.12	291	0.091
304	0.0083	288	0.080	301	0.0070	284	0.12
290	0.055	279	0.065	293	0.070	283	0.043

Table H32 TD-DFT results of **3.15c** SMD(CH_2Cl_2) continued

***Anti*-3.15c**				***Syn*-3.15c**			
Def2TZVPP				**Def2TZVPP**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
628	0.12	596	0.14	609	0.19	579	0.20
498	0.54	482	0.56	493	0.59	478	0.61
475	0.0080	445	0.038	469	0.021	442	0.090
463	0.13	443	0.12	466	0.027	439	0.018
450	0.0061	425	0.0086	457	0.064	437	0.020
436	0.10	413	0.10	428	0.041	406	0.044
394	0.16	371	0.15	392	0.15	370	0.15
376	0.19	358	0.29	373	0.17	355	0.27
357	0	341	0.00027	355	0.0077	339	0.051
349	0.30	337	0.32	351	0.26	338	0.24
341	1	329	1	341	1	329	1
337	0.038	325	0.055	336	0.090	325	0.11
330	0.017	309	0.18	330	0.012	310	0.062
324	0.42	309	0.26	323	0.47	308	0.45
311	0.053	299	0.017	321	0.093	301	0.024
310	0.010	297	0.0089	308	0.012	300	0.0022
308	0.067	294	0.052	307	0.017	294	0.0056
306	0.0061	292	0.050	303	0.10	292	0.11
304	0.076	286	0.075	300	0.048	283	0.14
288	0.020	279	0.080	292	0.072	282	0.031

Table H33 TD-DFT results of **3.15d** SMD(CH_2Cl_2) continued

***Anti*-3.15d**				***Syn*-3.15d**			
6-311++G(d,p)				**6-311++G(d,p)**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
615	0.74	586	0.73	647	0.40	617	0.42
544	0.074	512	0.11	563	0.13	528	0.15
507	0.29	479	0.33	521	0.11	491	0.12
483	0.64	464	0.51	492	0.36	473	0.37
457	0.057	438	0.073	475	0.021	450	0.048
453	0.050	426	0.041	464	0.12	440	0.12
447	0.010	421	0.012	449	0.087	424	0.073
413	0.018	392	0.036	420	0.038	400	0.081
405	1	382	1	411	1	389	1
376	0.069	356	0.13	392	0.095	373	0.12
371	0.31	353	0.41	373	0.069	354	0.11
363	0.12	341	0.14	370	0.016	348	0.15
359	0.075	340	0.18	365	0.14	346	0.053
353	0.34	336	0.34	356	0.13	338	0.0080
352	0.014	335	0.12	355	0.0042	335	0.15
345	0.66	329	0.82	344	0.23	329	0.28
339	0.83	324	0.084	341	0.41	325	0.31
335	0.22	321	0.33	333	0.42	317	0.36
324	0.74	310	0.74	330	0.024	312	0.12
322	0.0027	302	0.014	325	0.079	309	0.019

Table H34 TD-DFT results of **3.15d** SMD(CH_2Cl_2) continued

***Anti*-3.15d**				***Syn*-3.15d**			
Def2TZVPP				**Def2TZVPP**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
614	0.77	585	0.77	646	0.42	617	0.43
540	0.089	509	0.14	558	0.14	524	0.16
505	0.30	477	0.36	518	0.11	488	0.12
483	0.63	464	0.46	493	0.38	474	0.37
457	0.058	438	0.074	473	0.028	450	0.068
449	0.044	422	0.039	462	0.11	438	0.10
443	0.014	417	0.015	446	0.081	421	0.070
411	0.020	390	0.039	418	0.046	399	0.082
402	1	380	1	409	1	387	1
373	0.081	355	0.17	390	0.10	371	0.12
370	0.33	353	0.41	370	0.083	353	0.11
360	0.15	340	0.14	367	0.018	347	0.20
357	0.078	339	0.038	363	0.14	343	0.018
355	0.0090	338	0.22	358	0.0063	342	0.0063
350	0.36	334	0.52	352	0.12	334	0.18
344	0.77	327	0.76	343	0.27	328	0.28
337	0.61	323	0.017	339	0.40	324	0.28
334	0.24	319	0.28	331	0.41	316	0.32
323	0.74	309	0.71	327	0.0033	312	0.13
319	0.0051	301	0.26	324	0.051	308	0.075

Table H35 TD-DFT results of **3.15e** SMD(CH_2Cl_2)

***Anti*-3.15e**				***Syn*-3.15e**			
6-311++G(d,p)				**6-311++G(d,p)**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
623	0.47	595	0.44	632	0.060	596	0.079
491	0.99	474	0.92	532	0.91	514	0.94
471	0.047	445	0.25	484	0.040	455	0.064
464	0.31	442	0.12	473	0.24	452	0.25
452	0.036	429	0.016	457	0.026	433	0.021
432	0.35	413	0.33	441	0.24	421	0.24
402	0.90	380	0.85	397	0.059	372	0.092
372	0.28	355	0.37	386	0.11	367	0.16
353	0.0030	336	0.016	363	1	348	1
347	0.52	334	0.50	354	0.028	339	0.87
342	1	328	1	352	0.71	337	0.096
335	0.52	322	0.21	338	0.48	323	0.25
332	0.0080	314	0.48	338	0.062	316	0.066
328	0.45	311	0.053	327	0.19	315	0.28
317	0.085	300	0.015	317	0.025	299	0.025
315	0.023	298	0.064	314	0.30	297	0.12
309	0.58	297	0.066	308	0.031	296	0.13
306	0.0025	293	0.45	306	0.0033	293	0.033
301	0.076	289	0.053	303	0.016	292	0.031
286	0.32	273	0.29	299	0.074	285	0.044

Table H36 TD-DFT results of **3.15e** SMD(CH_2Cl_2) continued

***Anti*-3.15e**				***Syn*-3.15e**			
Def2TZVPP				**Def2TZVPP**			
B3LYP		**PBE0**		**B3LYP**		**PBE0**	
Wavelength (nm)	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**	**Wavelength (nm)**	**Oscillator Strength**
623	0.46	595	0.48	631	0.066	595	0.085
492	0.96	475	0.97	533	0.96	515	0.97
468	0.073	445	0.36	480	0.036	453	0.29
463	0.26	440	0.032	473	0.25	451	0.021
449	0.021	426	0.023	454	0.023	430	0.023
431	0.35	411	0.36	439	0.26	420	0.25
399	0.85	378	0.89	394	0.065	370	0.093
371	0.29	355	0.40	385	0.12	366	0.18
356	0.0034	339.92	0.0075	361	1	347	0.98
346	0.53	333.56	0.60	357	0.0069	341	0.025
341	1	327.55	1	351	0.83	338	1
334	0.33	321.55	0.18	337	0.39	322	0.19
329	0.098	313.11	0.55	334	0.054	315	0.30
327	0.39	308.44	0.018	327	0.23	312.71	0.086
315	0.038	300.87	0.033	314	0.028	300.5	0.0030
314	0.083	299.74	0.019	312	0.25	295.9	0.17
308	0.45	294.6	0.15	308.1	0.05	294.48	0.054
307	0.054	291.35	0.36	307.5	0.0042	294.3	0.032
302	0.064	290.26	0.11	305	0.018	292.72	0.071

Appendix I: Linear Free Energy Relationships

Table I1 Data Used for Linear Free Energy Relationship Determination of **2.1**

Compound	Substituent	Barrier	A Value	Interference Value	Charton Parameter	Taft Parameter	B Values Exp	B Values Theo
2.1a	**Me**	**10.5**	**1.7**	**40.4**	**0.52**	**0**	**7.4**	**7.1**
2.1b	**iPr**	**11.5**	**2.15**	**52.6**	**0.76**	**-0.47**	**11.1**	**11.1**
2.1c	**tBu**	**16.4**	**4.9**	**76.6**	**1.24**	**-1.54**	**15.5**	**15.6**
2.1d	**Ph**	**10.5**	**-**	**33.1**	**0.57**	**-2.55**	**-**	**-**
2.1e	**Et**	**10.5**	**1.75**	**-**	**0.56**	**-0.07**	**8.7**	**-**
2.1g	**F**	**6**	**0.15**	**19.2**	**0.27**	**0.49**	**-**	**2.8**
1.54	**H**	**9**	**0**	**4**	**-**	**1.24**	**-**	**2.2**

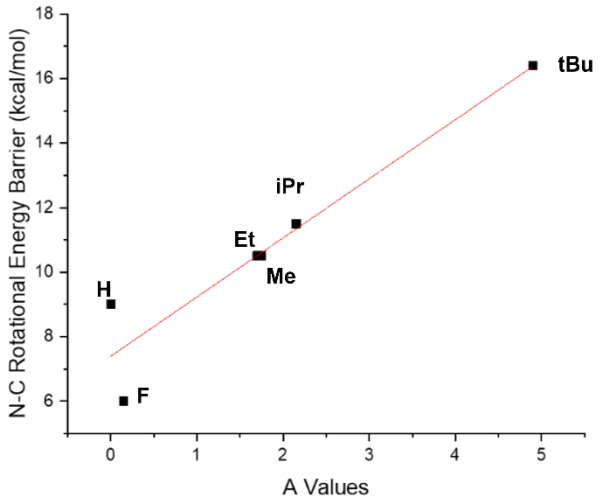


Figure I1 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.1** and A Values
Trendline: y = 1.83316x + 7.39614, R^2 = 0.90713

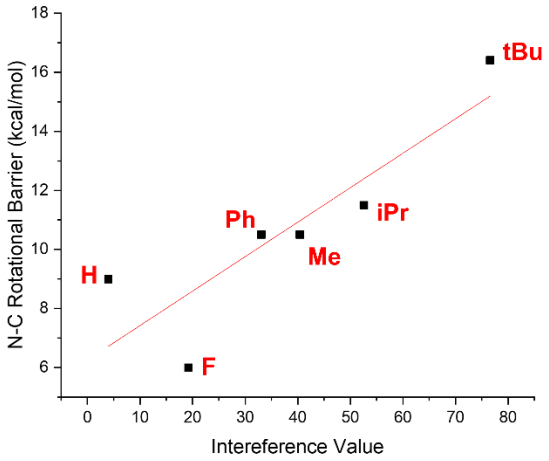


Figure I2 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.1** and Interference Values; Trendline: y = 0.11669x + 6.2567, R^2 = 0.75871

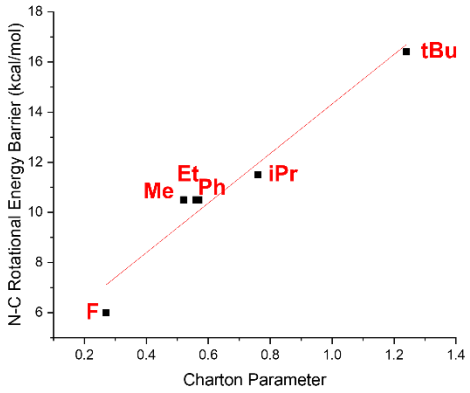


Figure I3 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.1** and Charton Parameter; Trendline: y = 9.87623x + 4.44753, R^2 = 0.94873

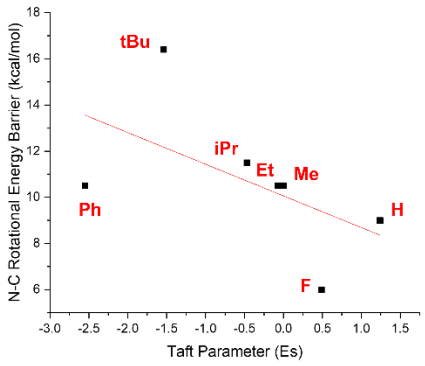


Figure I4 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.1** and Taft Parameter Es; Trendline: y = -1.37136x + 10.06187, R^2 = 0.31271

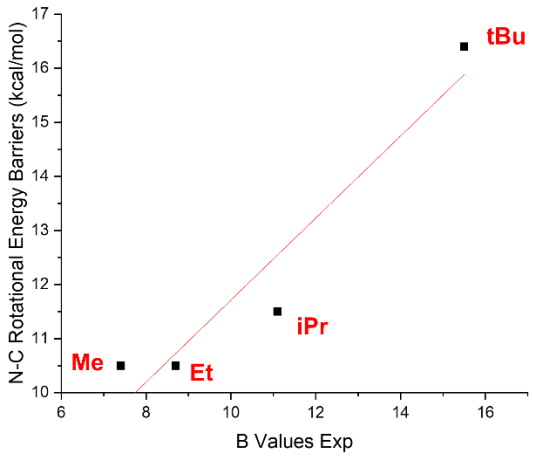


Figure I5 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.1** and B Values Exp; Trendline: y – 0.75858x + 4.12713, R^2 = 0.91676

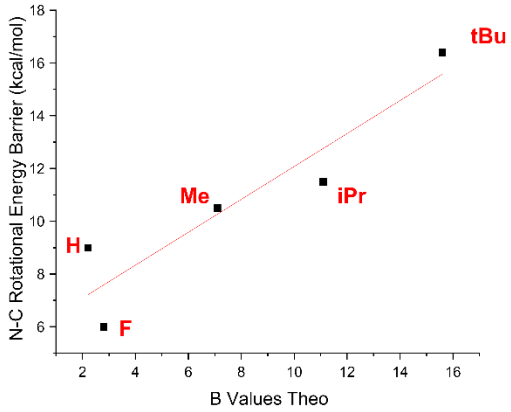


Figure I6 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.1** and B Values Theo

Table I2 Data Used for Linear Free Energy Relationship Determination of **2.2** using Lineshape analysis N-C rotational energy barriers

Compound	Substituent	Barrier	A Value	Interference Value	Charton Parameter	Taft Parameter	B Values Exp	B Values Theo
2.2a	**Me**	**15.9**	**1.7**	**40.4**	**0.52**	**0**	**7.4**	**7.1**
2.2b	**iPr**	**17.1**	**2.15**	**52.6**	**0.76**	**-0.47**	**11.1**	**11.1**
2.2c	**tBu**	**-**	**4.9**	**76.6**	**1.24**	**-1.54**	**15.5**	**15.6**
2.2d	**Ph**	**-**	**-**	**33.1**	**0.57**	**-2.55**	**-**	**-**
2.2e	**Et**	**16.3**	**1.75**	**-**	**0.56**	**-0.07**	**8.7**	**-**
2.2g	**F**	**12.3**	**0.15**	**19.2**	**0.27**	**0.49**	**-**	**2.8**
1.65	**H**	**-**	**0**	**4**	**-**	**1.24**	**-**	**2.2**

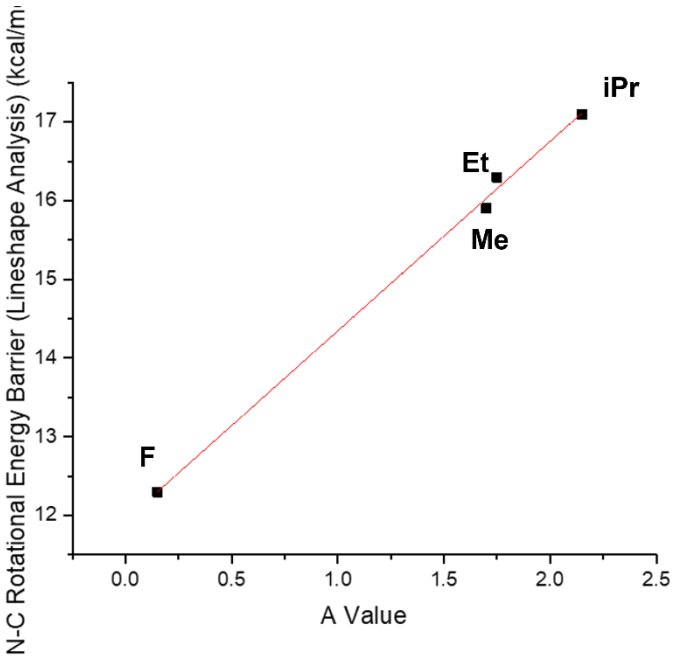


Figure I7 Linear Free Energy Relationship for N-C Rotational Energy Barriers of **2.2** from Lineshape Analysis and A Values; Trendline: 2.4079x + 11.939 R^2 = 0.9971

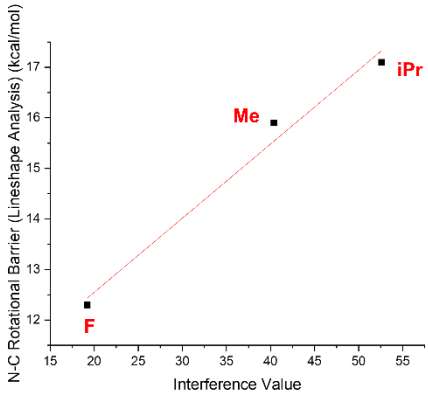


Figure I8 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Lineshape Analysis and Interference Values Trendline: 0.1466x + 9.6165, R^2 = 0.984

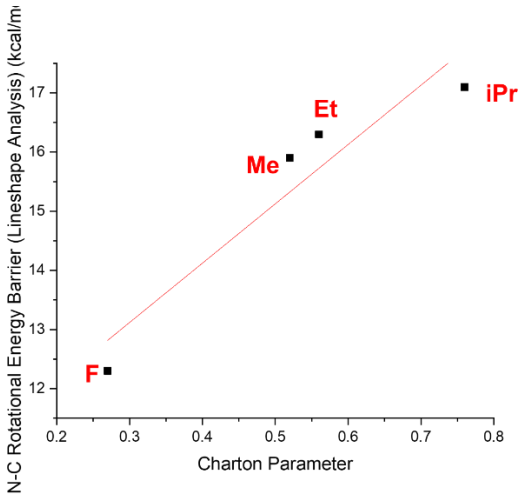


Figure I9 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Lineshape Analysis and Charton Parameter; Trendline: 10.035x + 10.107, R^2 = 0.9021

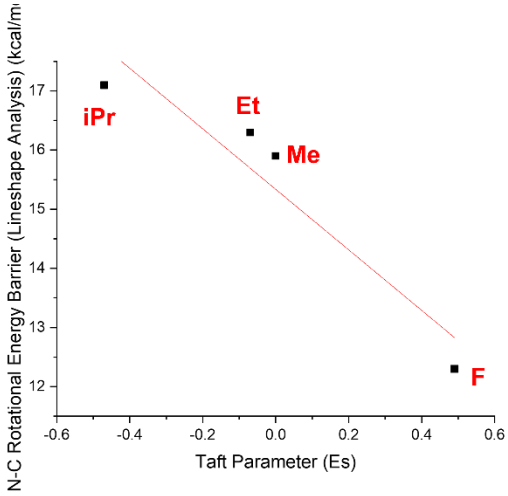


Figure I10 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Lineshape Analysis and Taft parameter Es; Trendline: -5.1174x + 15.336, R^2 = 0.8986

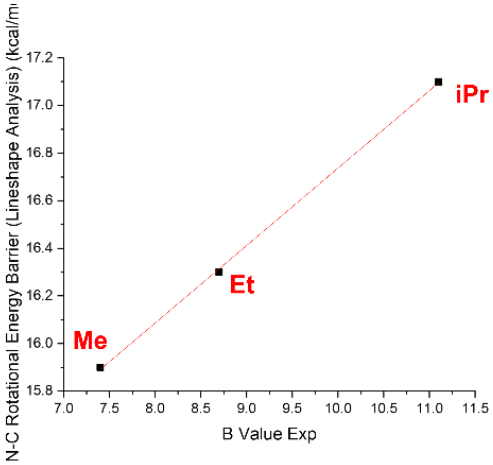


Figure I11 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Lineshape Analysis and B Values Exp; Trendline:0.3254x + 13.483, R^2 = 0.9996

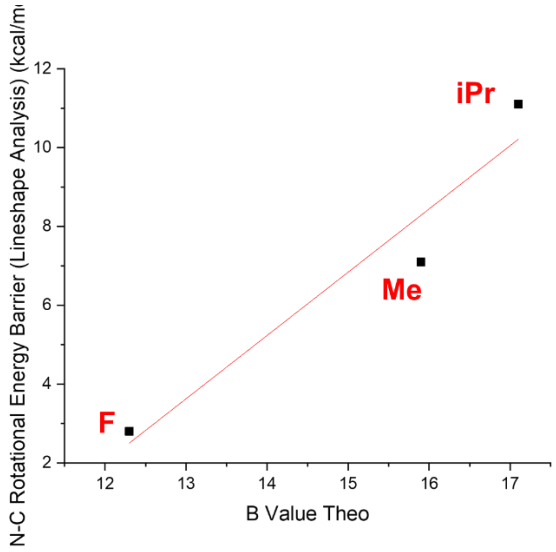


Figure I12 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Lineshape Analysis and B Values Theo; Trendline: 0.5815x + 11.029, R^2 = 0.9338

Table I3 Data Used for Linear Free Energy Relationship Determination of **2.2** using N-C rotational energy barriers determined using Tc;

Compound	Substituent	Barrier	A Value	Interference Value	Charton Parameter	Taft Parameter	B Values Exp	B Values Theo
2.2a	**Me**	**15.9**	**1.7**	**40.4**	**0.52**	**0**	**7.4**	**7.1**
2.2b	**iPr**	**17.3**	**2.15**	**52.6**	**0.76**	**-0.47**	**11.1**	**11.1**
2.2c	**tBu**	**-**	**4.9**	**76.6**	**1.24**	**-1.54**	**15.5**	**15.6**
2.2d	**Ph**	**-**	**-**	**33.1**	**0.57**	**-2.55**	**-**	**-**
2.2e	**Et**	**16.5**	**1.75**	**-**	**0.56**	**-0.07**	**8.7**	**-**
2.2g	**F**	**10.9**	**0.15**	**19.2**	**0.27**	**0.49**	**-**	**2.8**
1.65	**H**	**-**	**0**	**4**	**-**	**1.24**	**-**	**2.2**

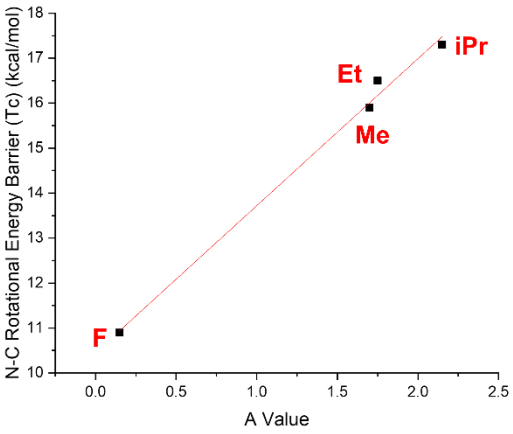


Figure I13 Linear Free Energy Relationship for N-C Rotational Energy Barriers of **2.2** from Coalesence Temperature and A Values; Trendline: 3.2688x + 10.451, R^2 = 0.9939

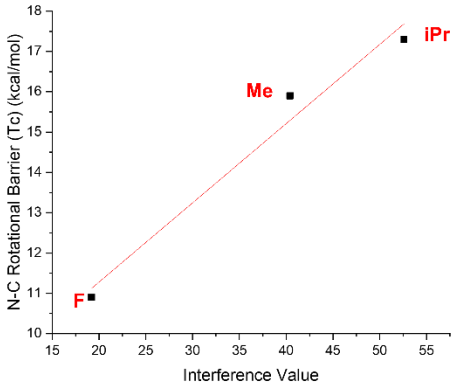


Figure I14 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Coalesence Temperature and Interference Values; Trendline: 0.1965x + 7.3494, R^2 = 0.9747

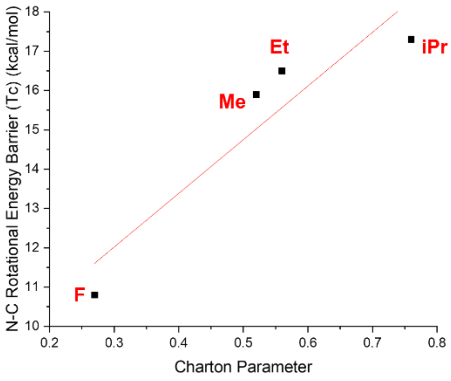


Figure I15 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Coalesence Temperature and Charton Parameter; Trendline: 13.439x + 8.0609, R^2 = 0.8751

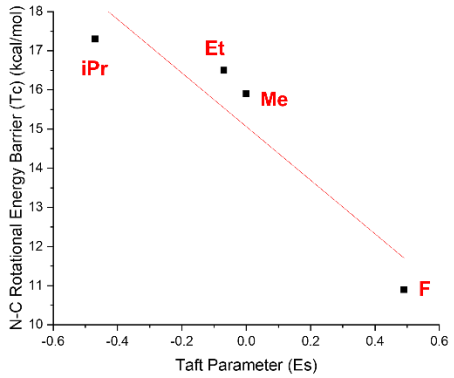


Figure I16 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Coalesence Temperature and Taft parameter Es; Trendline: -6.8508x + 15.064, R^2 = 0.871

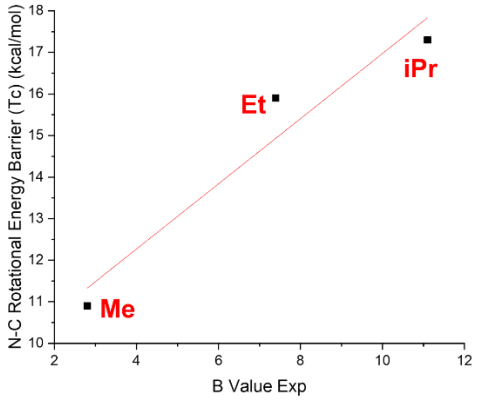


Figure I17 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Coalesence Temperature and B Values Exp: Trendline: 0.3728x + 13.187, R^2 = 0.9923

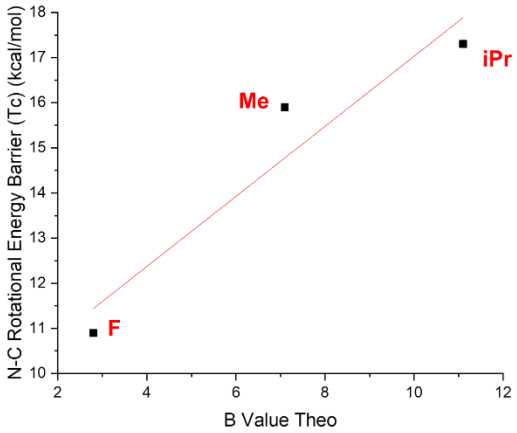


Figure I18 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Coalesence Temperature and B Values Theo:0.776x + 9.2682, R^2 = 0.9165

Table I4 Data Used for Linear Free Energy Relationship Determination of **2.2** using N-C rotational energy barriers determined from TS

Compound	Substituent	Barrier	A Value	Interference Value	Charton Parameter	Taft Parameter	B Values Exp	B Values Theo
2.2a	**Me**	**15.4**	**1.7**	**40.4**	**0.52**	**0**	**7.4**	**7.1**
2.2b	**iPr**	**16.0**	**2.15**	**52.6**	**0.76**	**-0.47**	**11.1**	**11.1**
2.2c	**tBu**	**25.5**	**4.9**	**76.6**	**1.24**	**-1.54**	**15.5**	**15.6**
2.2d	**Ph**	**21.8**	**-**	**33.1**	**0.57**	**-2.55**	**-**	**-**
2.2e	**Et**	**15.3**	**1.75**	**-**	**0.56**	**-0.07**	**8.7**	**-**
2.2g	**F**	**9.3**	**0.15**	**19.2**	**0.27**	**0.49**	**-**	**2.8**
1.65	**H**	**9.7**	**0**	**4**	**-**	**1.24**	**-**	**2.2**

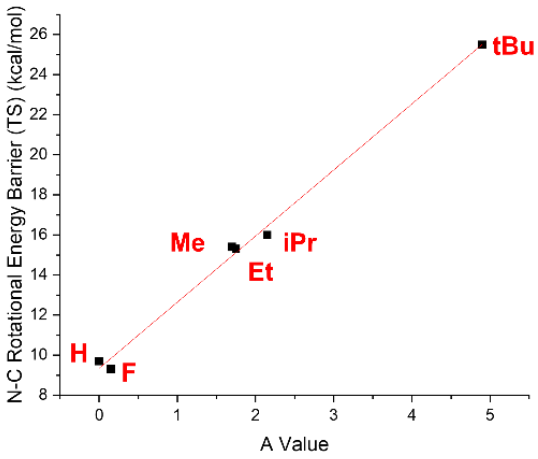


Figure I19 Linear Free Energy Relationship for N-C Rotational Energy Barriers of **2.2** from Density Functional Theory (TS) and A Values; Trendline: 3.2998x + 9.3428, R^2 = 0.9951

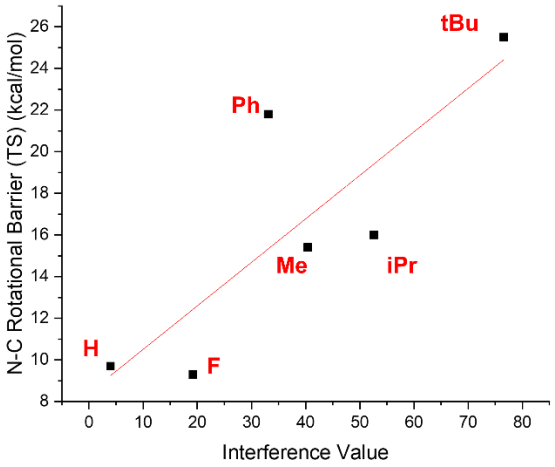


Figure I20 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Density Functional Theory (TS) and Interference Values: Trendline: 0.209x + 8.4133, R^2 = 0.6798

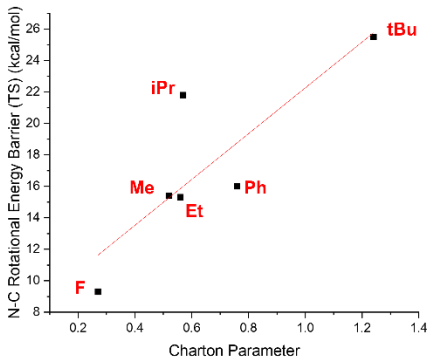


Figure I21 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Density Functional Theory (TS) and Charton Parameter; Trendline: 14.561x + 7.7036, R^2 = 0.7069

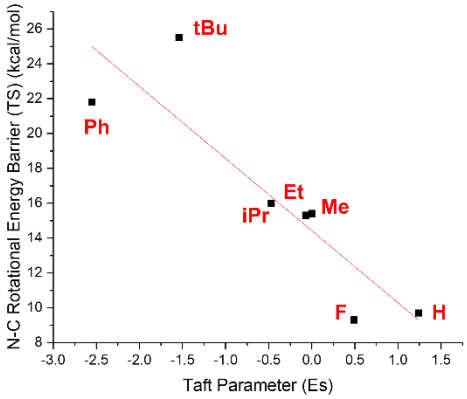


Figure I22 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Density Functional Theory (TS) and Taft parameter Es; Trendline: -4/1392x + 14.428, R^2 = 0.7925

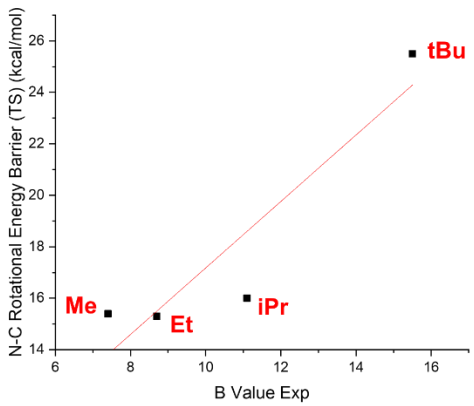


Figure I23 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Density Functional Theory (TS) and B Values Exp: Trendline: 1.2914x + 4.2646, R^2 = 0.855

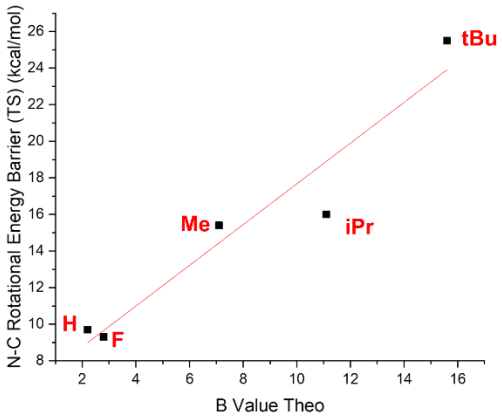


Figure I24 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Density Functional Theory (TS) and B Values Theo: Trendline: 1.1133x + 6.541, R^2 = 0.9274

Table I5 Data Used for Linear Free Energy Relationship Determination of **2.2** using N-C rotational energy barriers determined from TS'

Compound	Substituent	Barrier	A Value	Interference Value	Charton Parameter	Taft Parameter	B Values Exp	B Values Theo
2.2a	**Me**	**16.5**	**1.7**	**40.4**	**0.52**	**0**	**7.4**	**7.1**
2.2b	**iPr**	**17.0**	**2.15**	**52.6**	**0.76**	**-0.47**	**11.1**	**11.1**
2.2c	**tBu**	**144.9**	**4.9**	**76.6**	**1.24**	**-1.54**	**15.5**	**15.6**
2.2d	**Ph**	**27.0**	**-**	**33.1**	**0.57**	**-2.55**	**-**	**-**
2.2e	**Et**	**19.0**	**1.75**	**-**	**0.56**	**-0.07**	**8.7**	**-**
2.2g	**F**	**13.3**	**0.15**	**19.2**	**0.27**	**0.49**	**-**	**2.8**
1.65	**H**	**9.8**	**0**	**4**	**-**	**1.24**	**-**	**2.2**

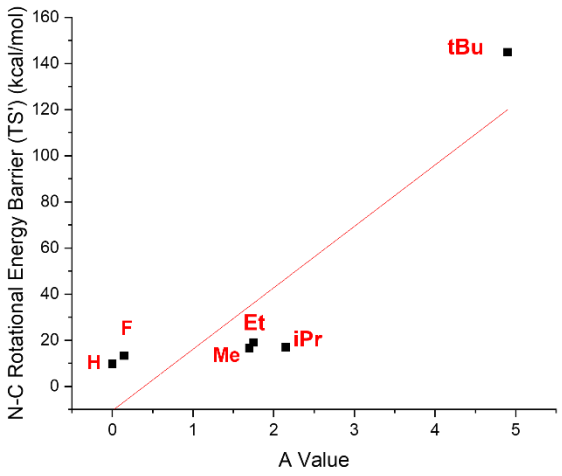


Figure I25 Linear Free Energy Relationship for N-C Rotational Energy Barriers of **2.2** from Density Functional Theory (TS') and A Values: Trendline: 26.648x – 10.55, R^2= 0.7915

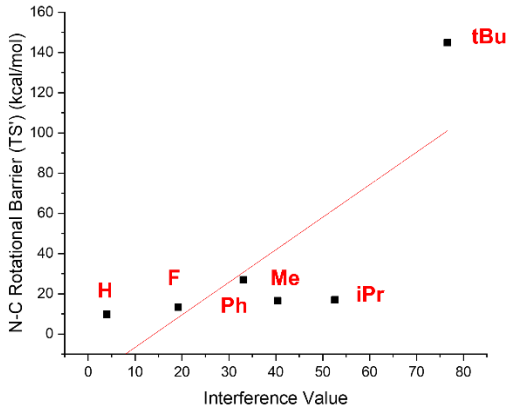


Figure I26 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Density Functional Theory (TS') and Interference Values; 1.6181x – 22.84, R^2 = 0.6125

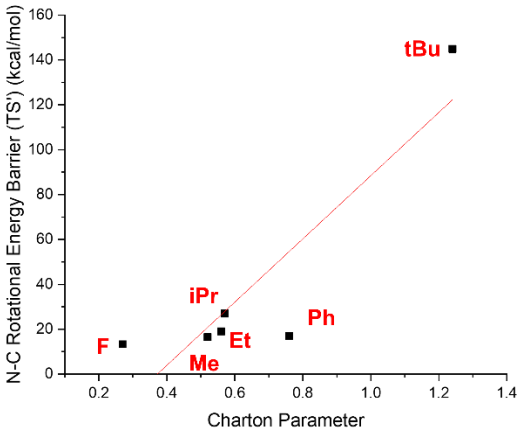


Figure I27 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Density Functional Theory (TS') and Charton Parameter; Trendline: 140.88x – 52.422, R^2 = 0.7933

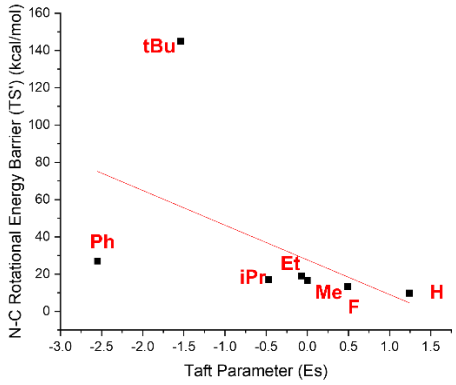


Figure I28 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Density Functional Theory (TS') and Taft parameter Es: Trendline: -18.614x + 27.646, R^2 = 0.2366

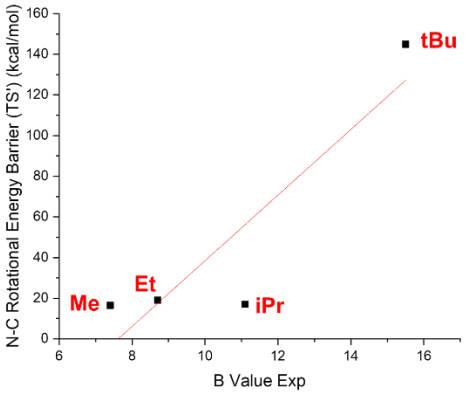


Figure I29 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Density Functional Theory (TS') and B Values Exp: Trendline: 16.142x – 122.96, R^2 = 0.815

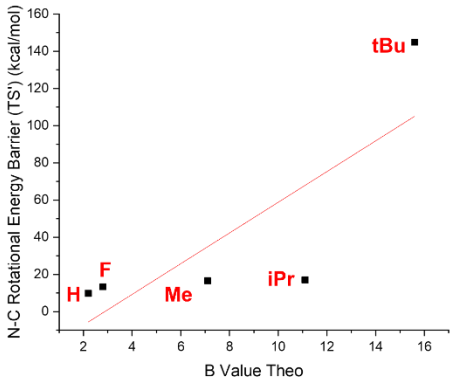


Figure I30 Linear Free Energy Relationship for N-C Rotational Energy Barrier of **2.2** from Density Functional Theory (TS') and B Values Theo: Trendline: 8.2557x – 23.764, $R^2 = 0.6392$