# The Synthesis, Thermal and Photochemical Properties of Cyclophanedienes and Dihydropyrenes with Different Internal Substituents

by

Khurshid Ayub

B.Sc. University of the Punjab, Lahore, Pakistan, 1999
M.Sc. University of the Punjab, Lahore, Pakistan, 2002

A Dissertation Submitted in Partial Fulfillment of the
Requirements for the Degree of

**DOCTOR OF PHILOSOPY**

in the Department of Chemistry

# The Synthesis, Thermal and Photochemical Properties of Cyclophanedienes and Dihydropyrenes with Different Internal Substituents

by

Khurshid Ayub

B.Sc. University of the Punjab, Lahore, Pakistan, 1999
M.Sc. University of the Punjab, Lahore, Pakistan, 2002

**Supervisory Committee**

Dr. Reginald H. Mitchell, Supervisor
(Department of Chemistry)

Dr. Frank C. J. M. van Veggel, Departmental Member
(Department of Chemistry)

Dr. Robin G. Hicks, Departmental Member
(Department of Chemistry)

Dr. Ben F. Koop, Outside Member
(Biology department, Centre for Biomedical Research)

**Supervisory Committee**

Dr. Reginald H. Mitchell, Supervisor
(Department of Chemistry)

Dr. Frank C. J. M. van Veggel, Departmental Member
(Department of Chemistry)

Dr. Robin G. Hicks, Departmental Member
(Department of Chemistry)

Dr. Ben F. Koop, Outside Member
(Biology department, Centre for Biomedical Research)

## Abstract

A series of cyclophanedienes (CPDs) with different internal functional groups were synthesized. Dicyano CPD **85**, cyano methyl CPD **127** and phenylethynyl/methyl CPD **138** were synthesized from bis-bromomethyl aromatics via a thiacyclophane-thiomethylcyclophane route. Diformyl cyclophanediene **152** and bis(hydroxymethyl) CPD **159** were obtained by the functional group transformation of CPDs **85** and **152** respectively. Cyclophanedienes with internal olefinic groups were obtained by three different routes: the best was the functional group transformations of the dicyano mercaptomethylcyclophane **99** followed by a Hoffmann elimination. Using the best synthetic route, CPDs with substituted vinyl groups such as alkylvinyl (**162, 163, 178** and **198**), butadienyl (**184**, **185** and **186**), styryl (**202, 203** and **204**), nitro-substituted styryl (**210, 211** and **212**), methoxy-substituted styryl (**218, 219** and **220**) and methyl-

substituted styryl (**226, 227** and **228**) were synthesized. Cyclophanediene **235** with an internal ethynyl (alkynyl) group was also synthesized by a similar synthetic route; however, it gave two major interesting side products; vinyl-ethynyl CPD **237** and vinyl-styryl CPD **240**. The cyclophanedienes except dicyano **85,** cyano-methyl **127** and diformyl **152** were converted to their corresponding dihydropyrenes both thermally and photochemically. Dicyano CPD **85** and cyano-methyl CPD **127** were converted photochemically to the DHPs **86** and **128,** respectively. Diformyl CPD **152** underwent decomposition in any attempt to transform it into the DHP **154** either thermally or photochemically. Diphenylethynyl DHPs **141** and **247** were obtained by the Sonogashira coupling of diethynyl DHP **236**. The Eglinton coupling reaction was used to achieve butadiynyl DHPs **257** and **254**. Naphthoyl DHPs **248** and **250** were synthesized by the Friedel-Crafts acylation reaction of DHPs **179** and **167,** respectively. All compounds were characterized by NMR, IR, and UV spectroscopy and mass spectrometry.

Dicyano CPD **85** was quite stable towards thermal isomerization to the dihydropyrene **86** and showed a calculated half life of ~ 36 years (three orders of magnitude higher than that of benzo CPD **53** i.e., 7.3 days) at room temperature, whereas CPDs **127** (cyano methyl)**, 138** (phenylethynyl/methyl) and **152** (diformyl) showed half lives less than a month at 20 $^{o}$C. Cyclophanedienes with internal ethynyl and substituted vinyl groups were quite stable thermally and showed half lives of several years (1-16 years) at room temperature. CPDs with *cis* substituted internal vinyl groups were thermally more stable than their *trans* counterparts. Electron withdrawing substituent ($NO_2$) at the *para* positions of the internal styryl groups accelerate, whereas electron donating groups (MeO, Me) decelerate the thermal return reaction. Naphthoyl CPDs **249**

and **251** isomerized at rates about 6-12 times faster than their non naphthoylated analogues **178** and **166** respectively.

DHPs with internal ethenyl (**167, 238** and **241**), substituted ethynyl (**139, 141** and **247**) and *trans* substituted vinyl (**199, 207, 215, 223** and **231**) groups failed to open under visible light irradiation. Dicyano DHP **86,** diethynyl DHP **236** and the unsymmetrical isomers of internal olefinic CPDs (**206, 214, 222** and **230**) formed photostationary states (pss). Disubstituted vinyl (**179**) and *cis* substituted vinyl DHPs (**164, 205, 213, 221** and **229**) opened completely; however their opening rates although faster than the parent **43**, were 4-6 times slower than the benzo DHP **47**. Introduction of an electron withdrawing substituent on the internal styryl group decelerated the visible opening reaction whereas electron donating groups accelerated it. 2-Naphthoyl divinyl DHP **250** opened at rates quite comparable to those of benzo DHP **47** whereas 2-naphthoyl diisobutenyl **248** opened about 25 times faster than the benzo DHP.

The [1,5]-sigmatropic rearrangement of the internal nitrile (DHPs **86** and **128**) and formyl (DHP **153**) groups was observed**.** The sigmatropic rearrangement of the nitrile group in **86** was quite favorable in $CDCl_3$ ($E_{act}$ = 23.4 $\pm$ 0.7 kcal/mol) compared to benzene ($E_{act}$ = 28.6 $\pm$ 1.2 kcal/mol). Formyl groups showed a much higher migration aptitude and $E_{act}$ is estimated to be < 20 kcal/mol in any solvent.

In this study, the best switch pair obtained was naphthoyl diisobutyl **248/249** which in comparison with previously the best switch pair **47/53** (benzo) showed much higher stability of the cyclophanediene (two orders of magnitude); moreover, the dihydropyrene opened about 25 times faster as well and is one of the best new photochromes yet.

# Table of Contents

.....

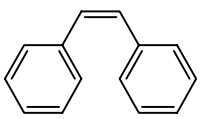
# List of Tables

# List of Appendix Tables

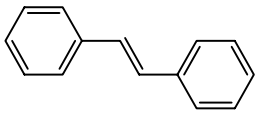
# List of Figures

## List of Schemes

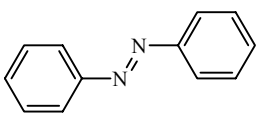
## List of Numbered Compounds



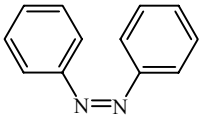
**1**



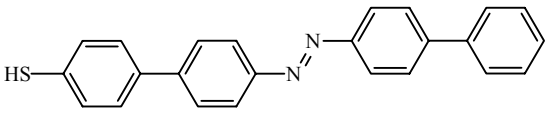
**2**



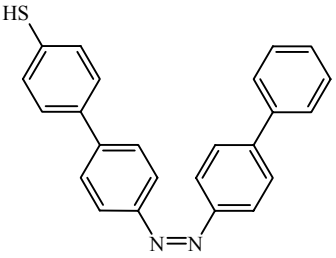
**3**



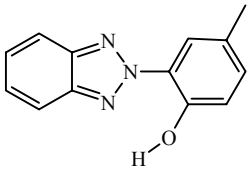
**4**



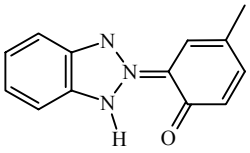
**5**



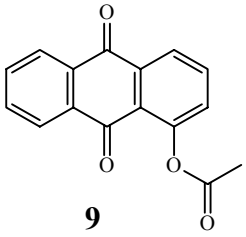
**6**



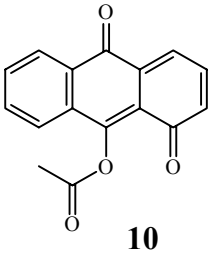
**7**



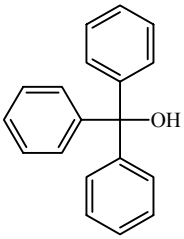
**8**



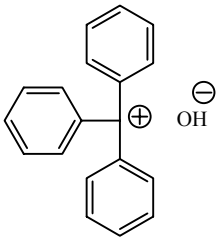
**9**



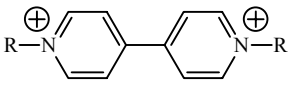
**10**



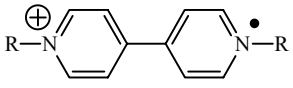
**11**



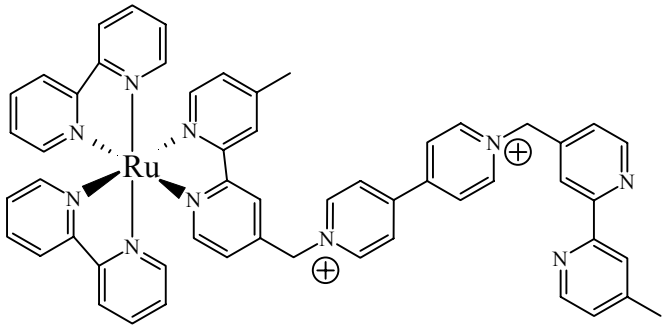
**12**



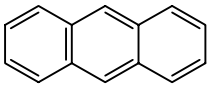
**13**



**14**

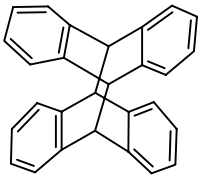


**15**



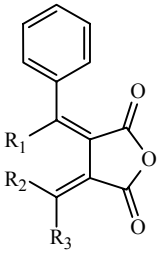
**16**

**18**

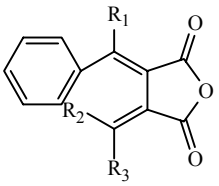


**17**

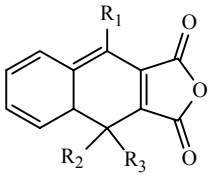
**19**



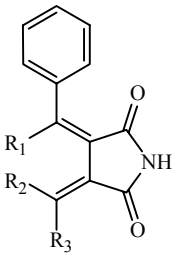

**20**



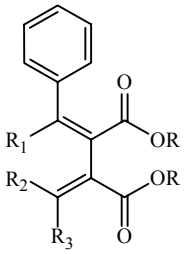

**21**



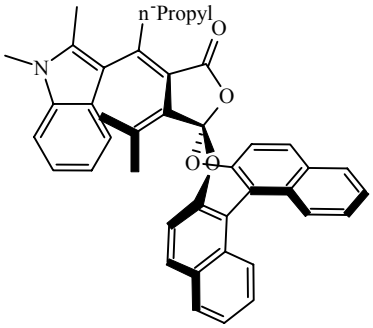

**22**



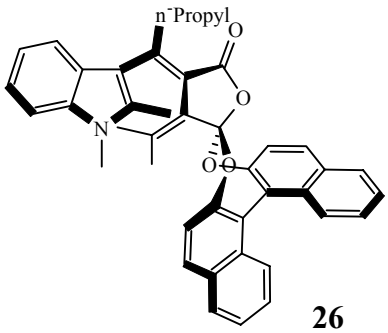

**23**



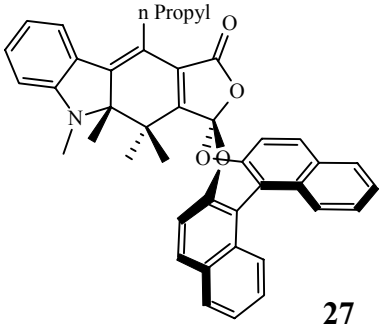

**24**



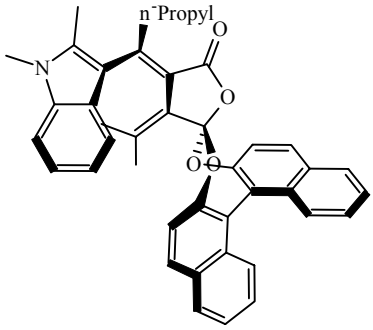

**25**



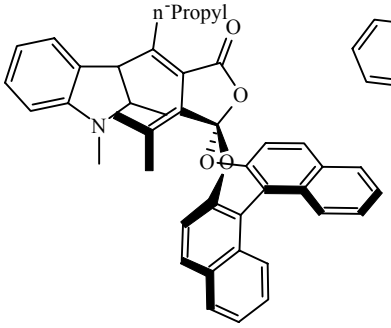

**26**



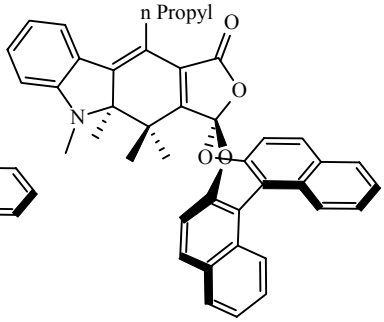

**27**



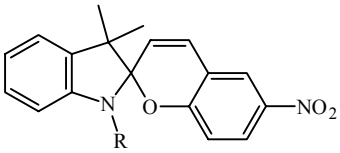

**28**



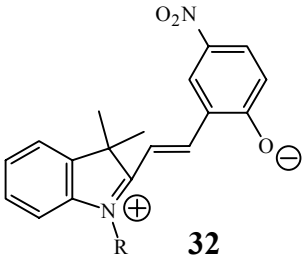

**29**



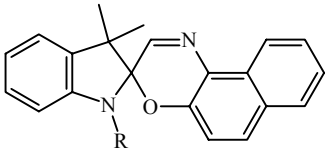

**30**



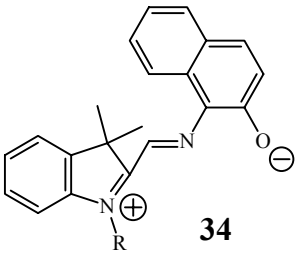

**31**



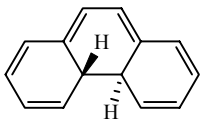

**32**



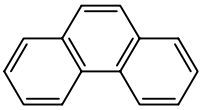

**33**



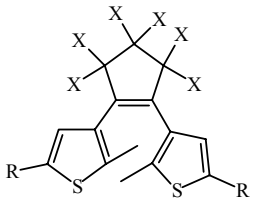

**34**



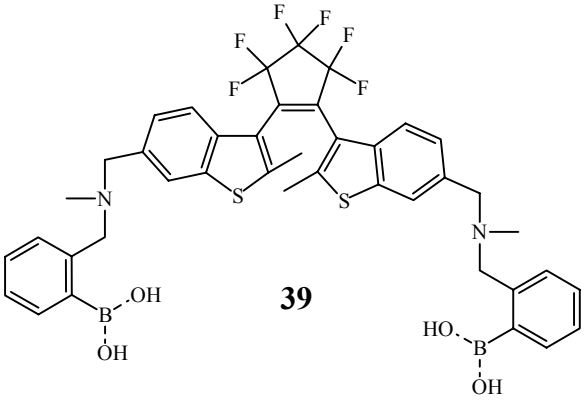

**35**



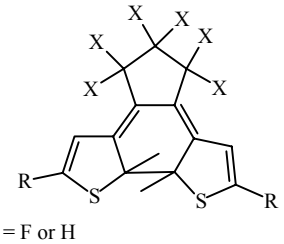
**36**




**37** X = F or H

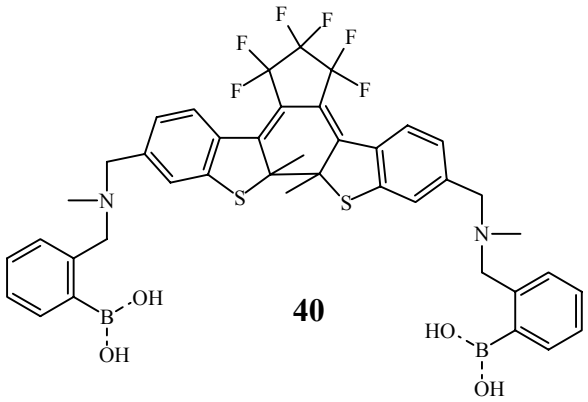



**39**

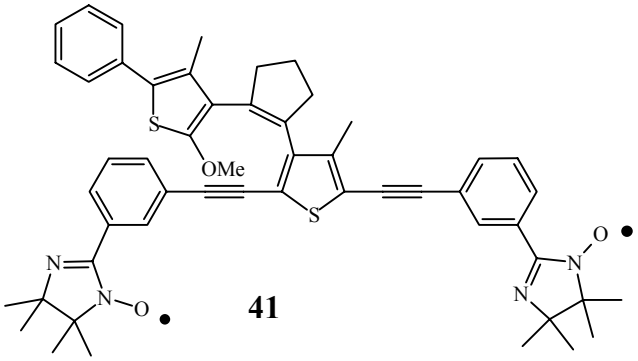



X = F or H

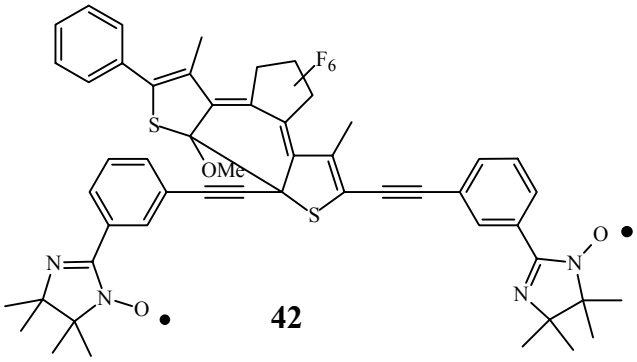
**38**



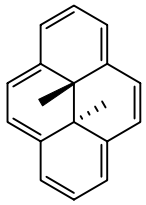
**40**



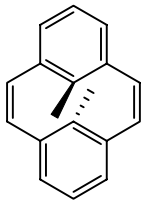
**41**



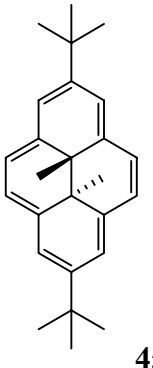
**42**



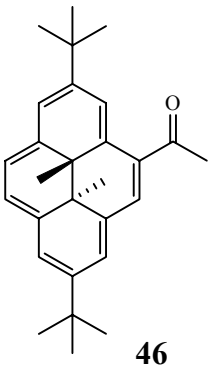
**43**



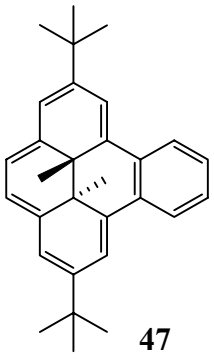
**44**



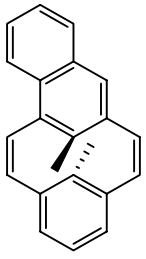
**45**



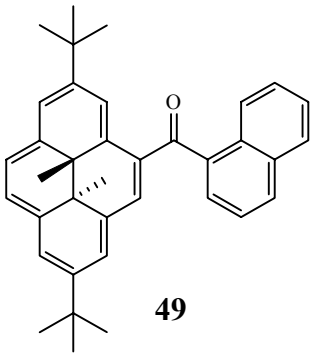
**46**



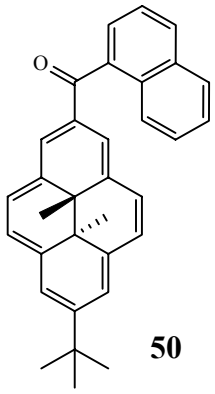
**47**



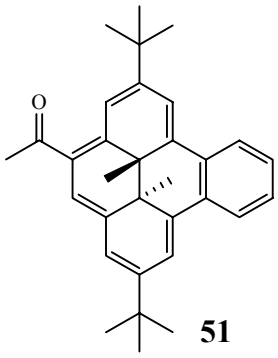
**48**



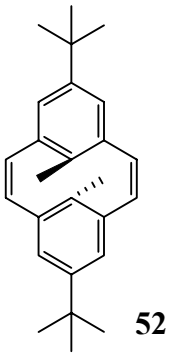

**49**



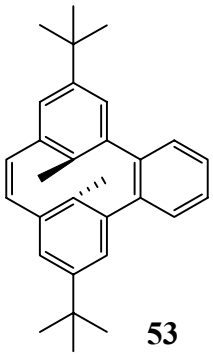

**50**



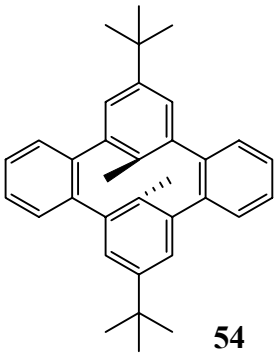

**51**



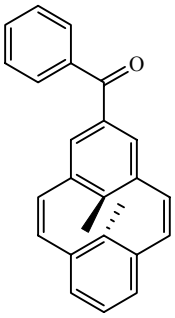
**52**



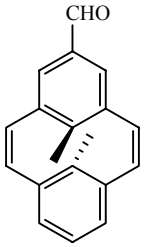
**53**



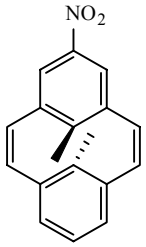
**54**



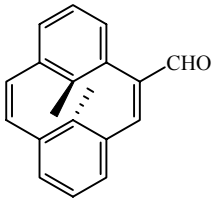

**55**



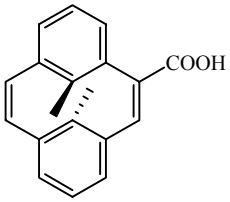

**56**



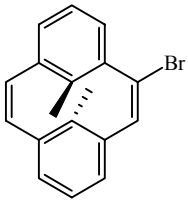

**57**



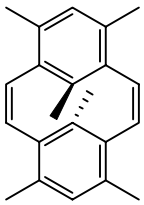

**58**



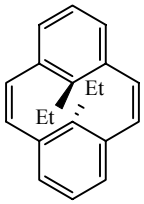

**59**



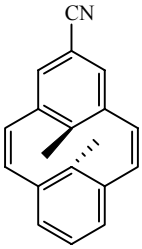

**60**



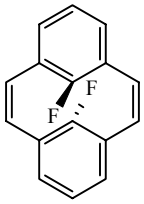
**61**



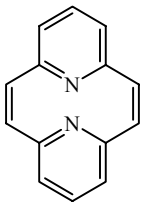

**62**



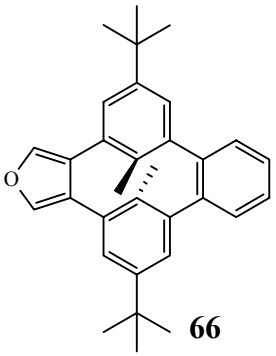

**63**



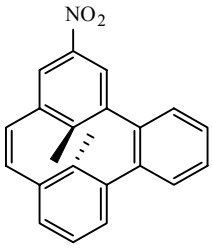

**64**



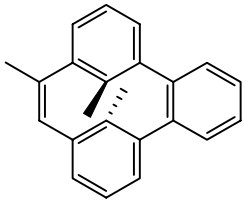

**65**



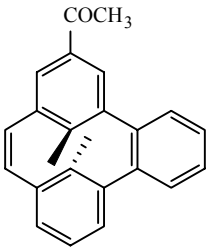

**66**



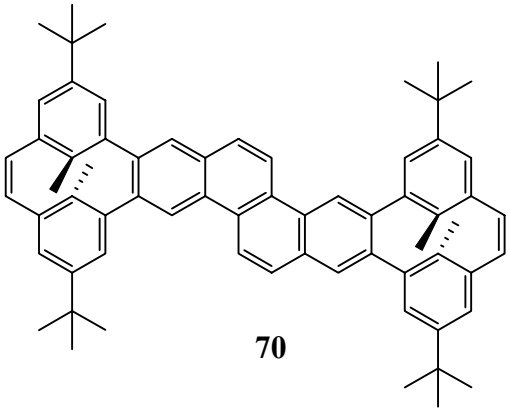

**67**



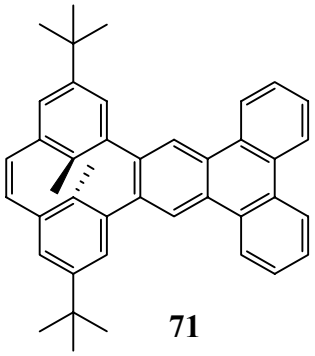
**68**



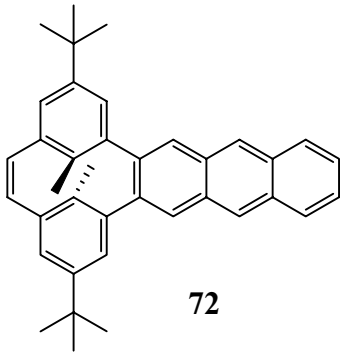

**69**



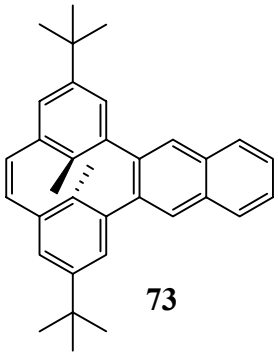
**70**



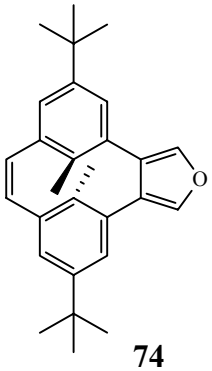
**71**



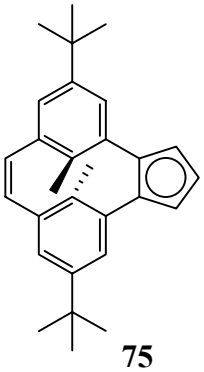
**72**



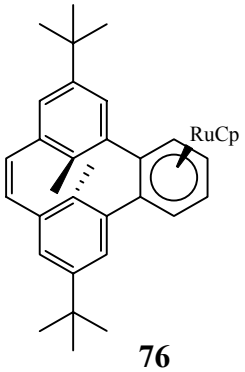
**73**



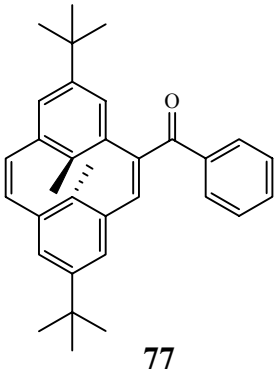

**74**



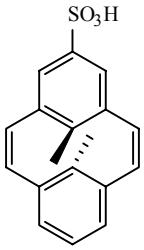
**75**



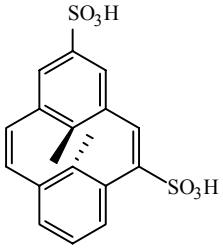

**76**



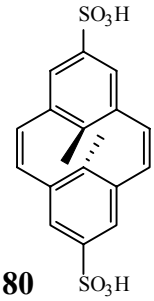

**77**



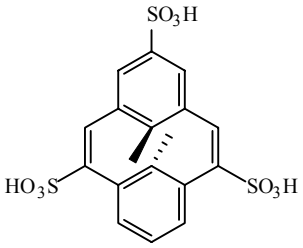

**78**



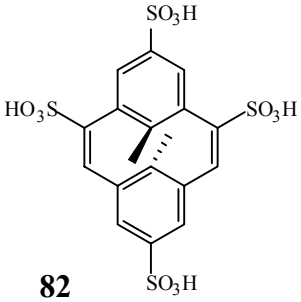

**79**



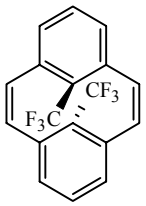

**80**



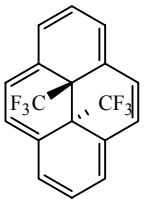

**81**



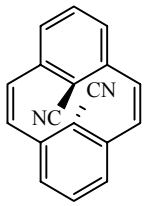

**82**



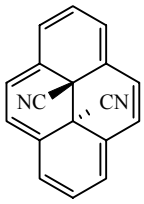

**83**



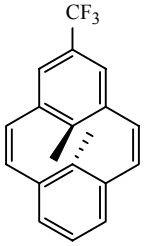

**84**



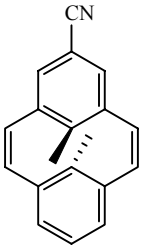

**85**



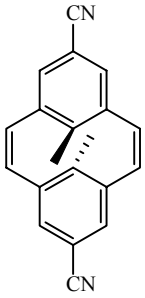

**86**



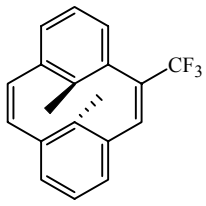

**87**



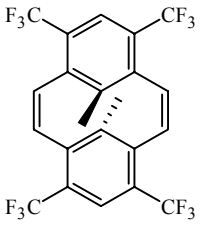

**88**



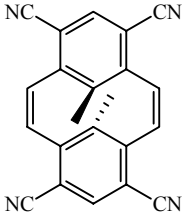

**89**



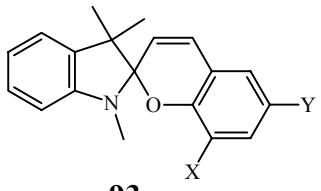

**90**



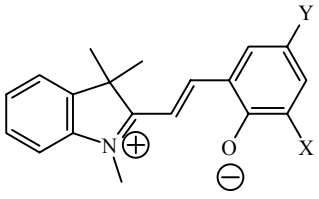

**91**



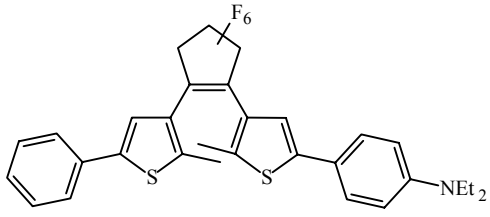

**92**



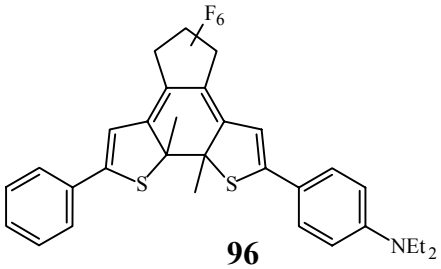

**93**



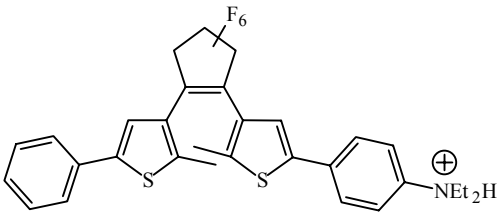

**94**



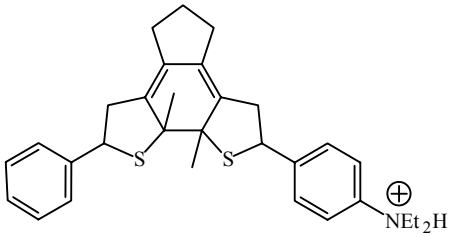

**95**



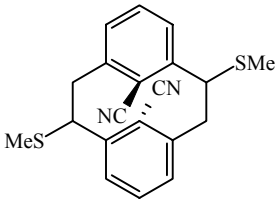

**96**



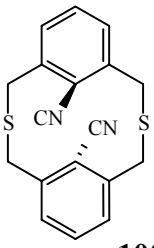

**97**



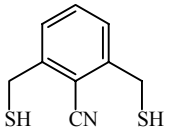

**98**



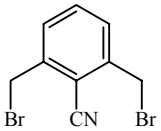

**99**



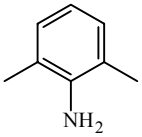

**100**



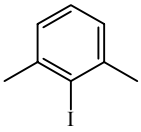

**101**



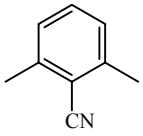

**102**



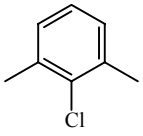

**103**



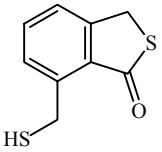

**104**



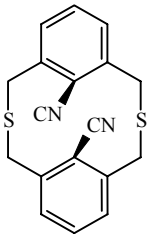

**105**



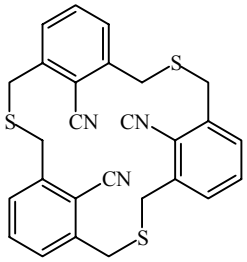

**106**



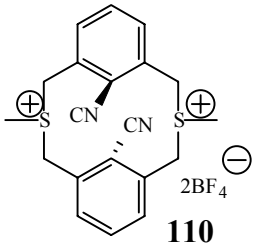

**107**



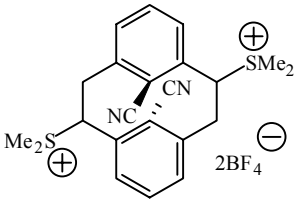

**108**



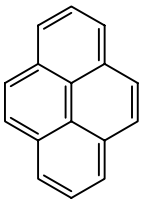

**109**



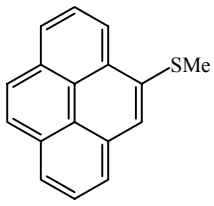

**110**



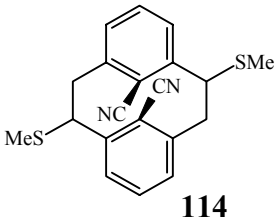

**111**



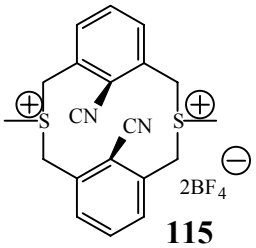
**112**



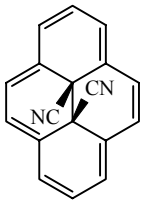

**113**



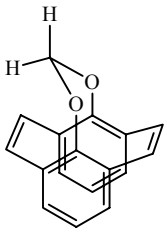

**114**



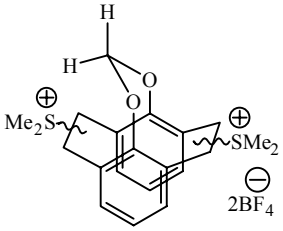

**115**



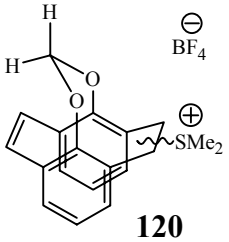

**117**



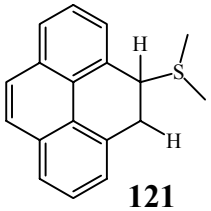

**118**



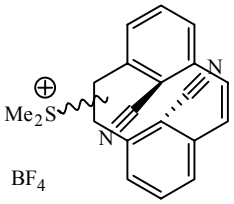

**119**



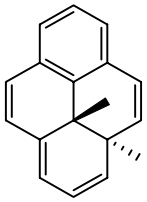

**120**



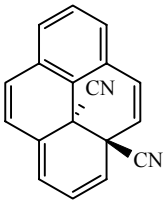

**121**



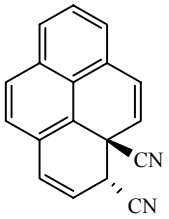

**122**



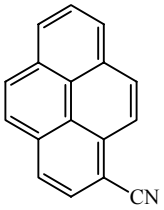
**123**



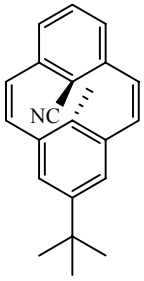

**124**



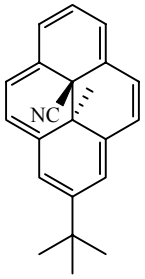

**125**



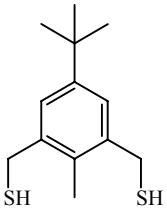

**126**



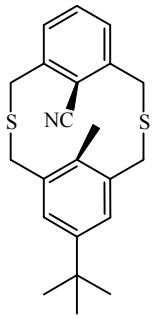

**127**



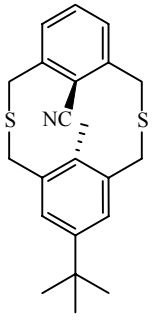

**128**



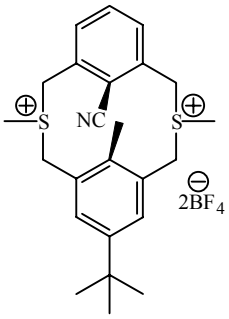

**129**



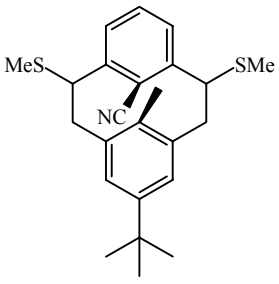

**130**



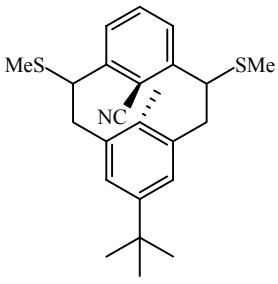

**131**



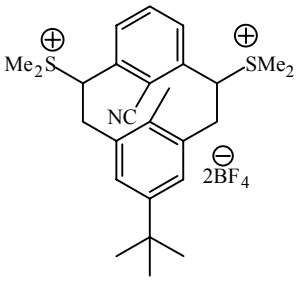

**132**



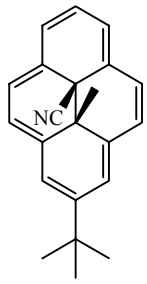

**133**



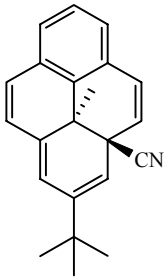

**134**



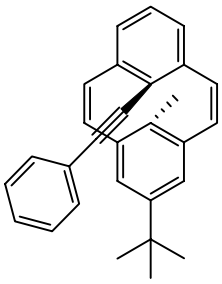

**135**



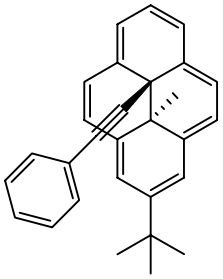

**136**



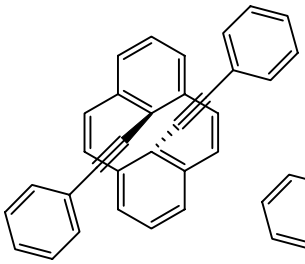

**137**



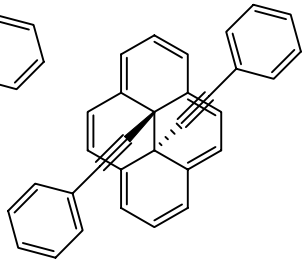
**138**



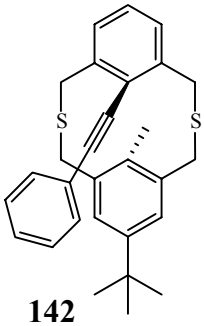
**139**



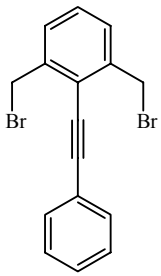
**140**



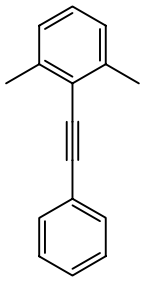
**141**



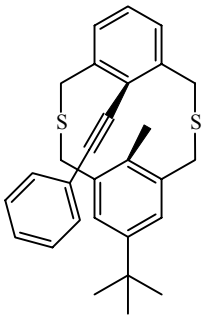

**142**



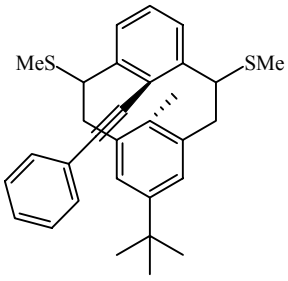

**143**



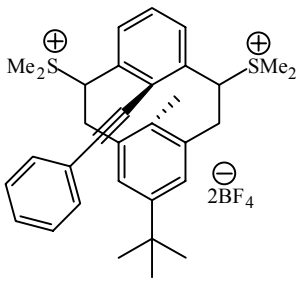
**144**



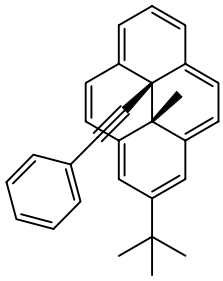

**145**



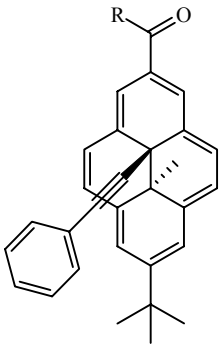

**146**



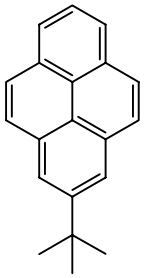

**147**



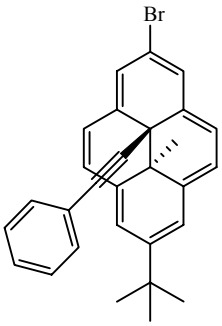
**148**



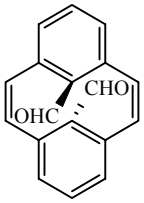

**149**



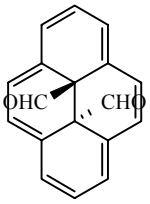
**150**



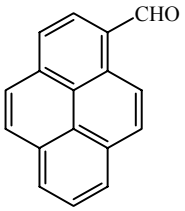

**151**



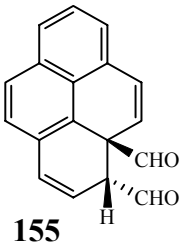

**152**



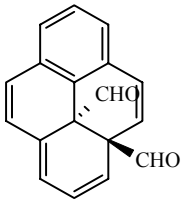

**153**



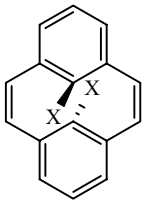

**154**



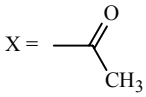

**155**

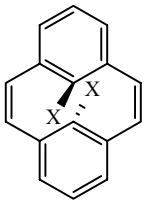



**156**



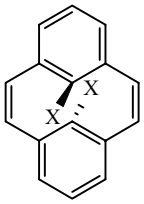

**157**



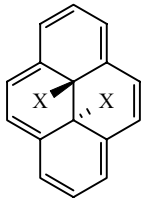

X = $CH_2NH_2$

**158**



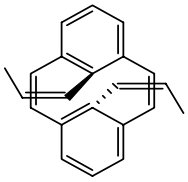

X = $CH_2OH$

**159**

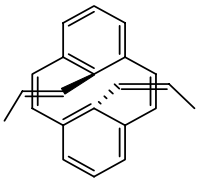



X = $CH_2OH$

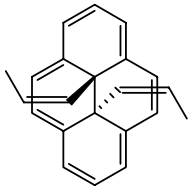
**160**



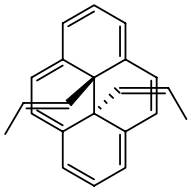
**162**



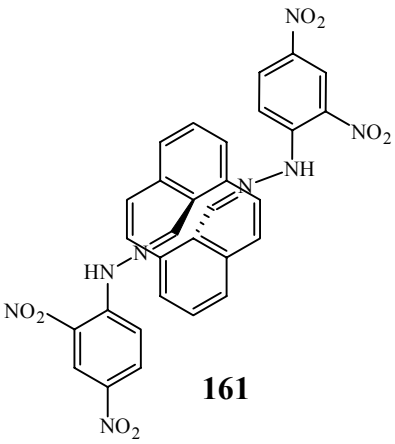
**163**



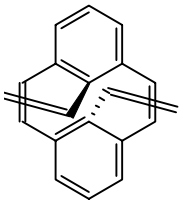
**164**



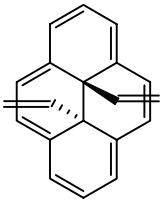
**165**



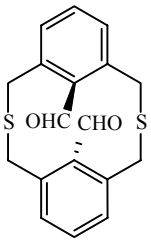

**161**



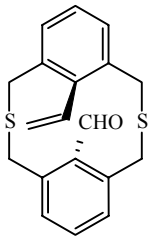
**166**



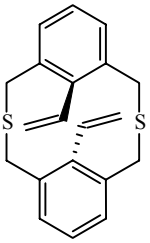
**167**



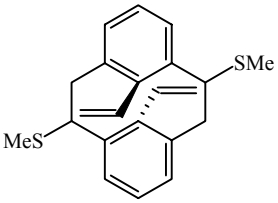

**168**



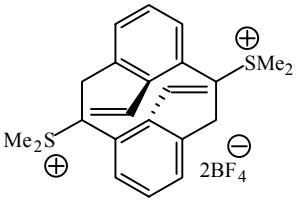

**169**




**170**

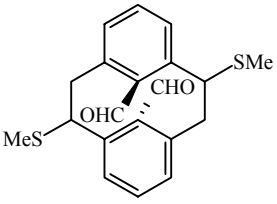



**171**

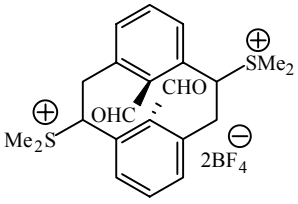



**172**

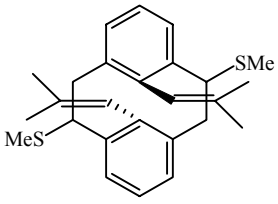

**173**



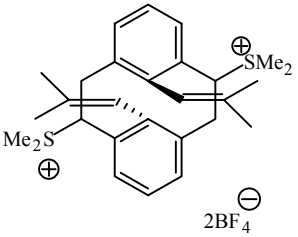

**174**



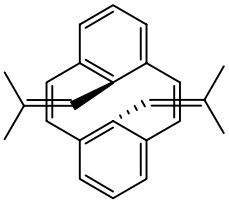

**175**



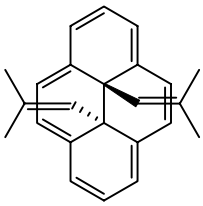

**176**



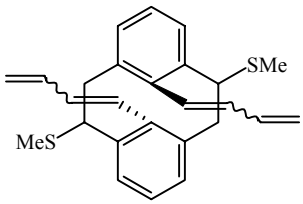

**177**



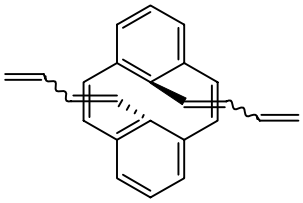
**178**



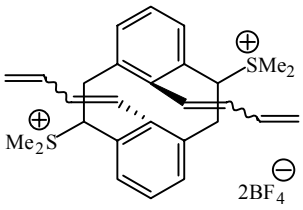
**179**



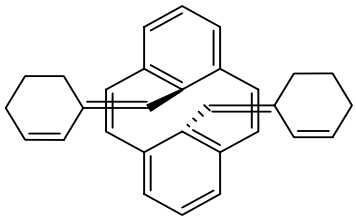

**180**



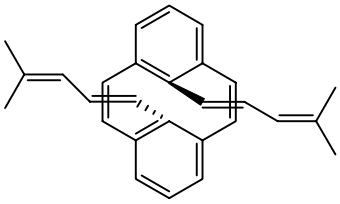
**181**



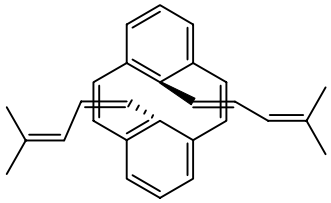

**182**



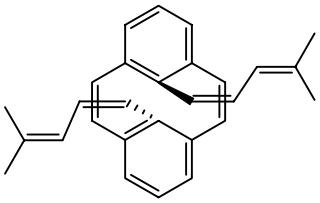
**183**



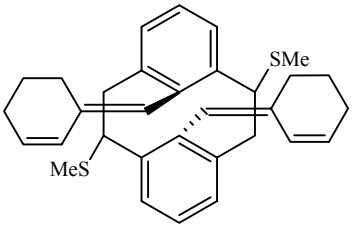
**184**



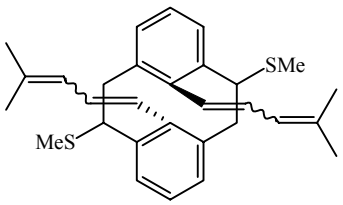
**185**



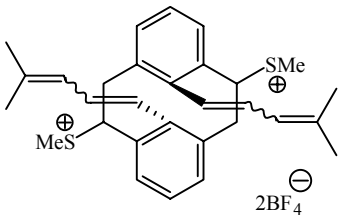
**186**



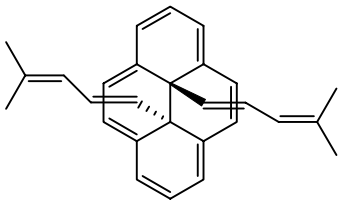

**187**



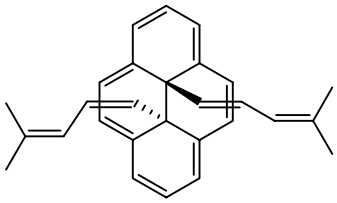

**188**



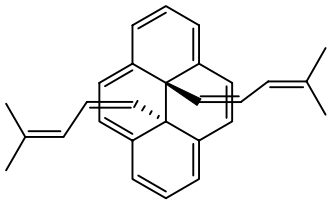

**189**



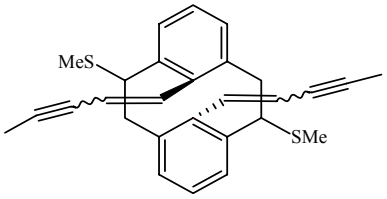
**190**



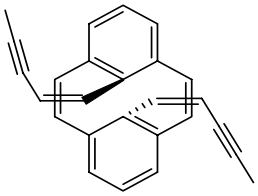
**191**



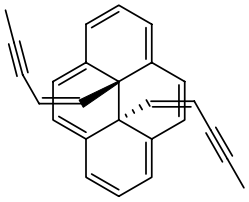
**192**



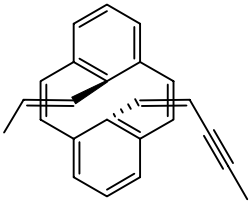

**193**



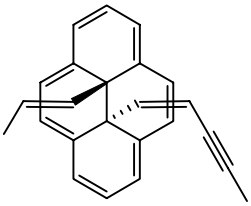
**194**



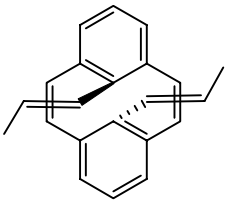
**195**



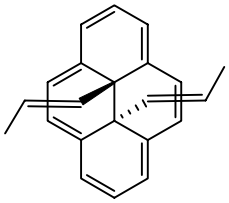
**196**



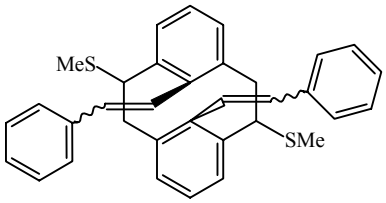
**197**



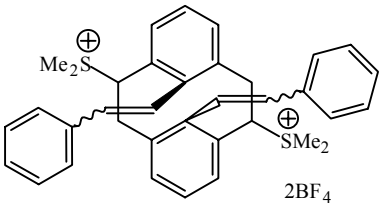
**198**



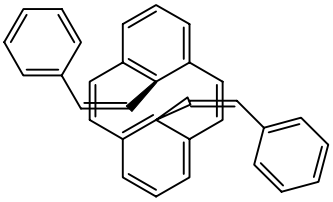
**199**



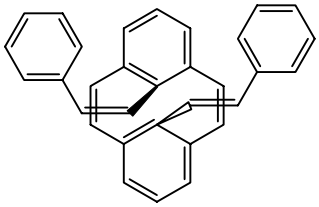

**200**



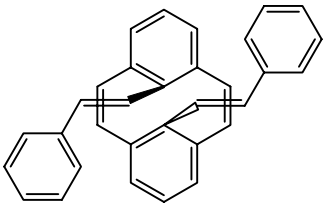

**201**



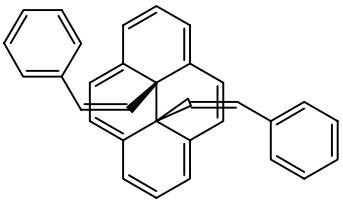
**202**



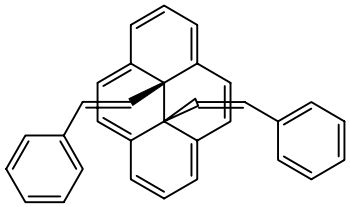
**203**



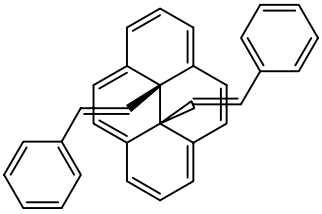
**204**



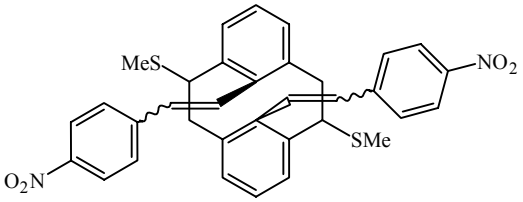
**205**



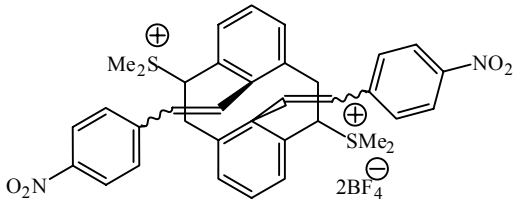
**206**



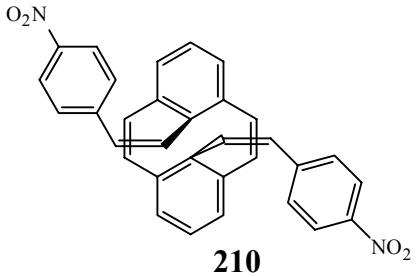
**207**



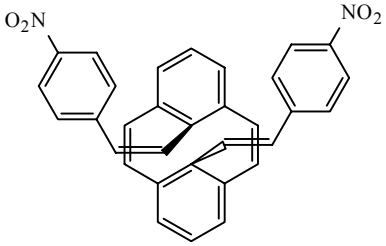

**208**



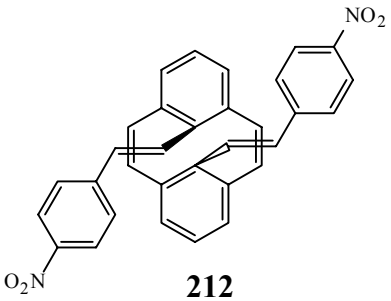

**209**



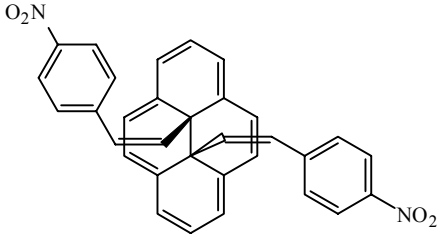

**210**



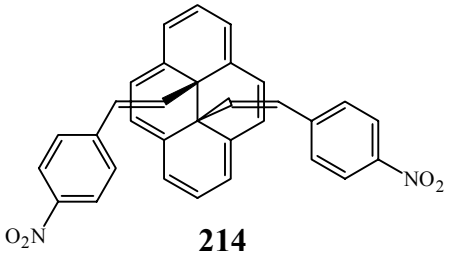

**211**



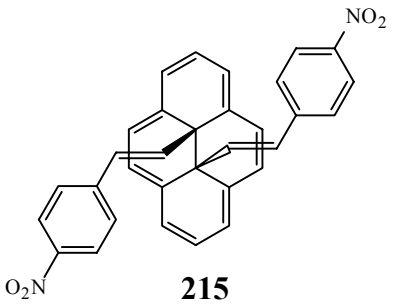

**212**



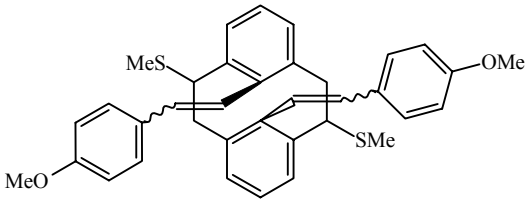

**213**



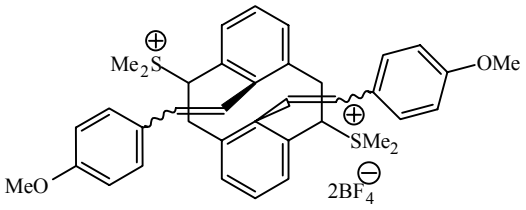

**214**



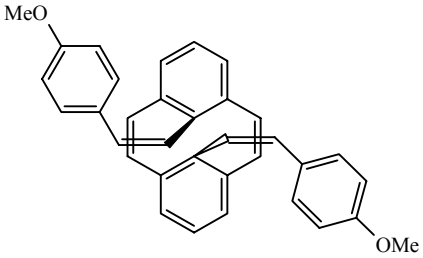

**215**



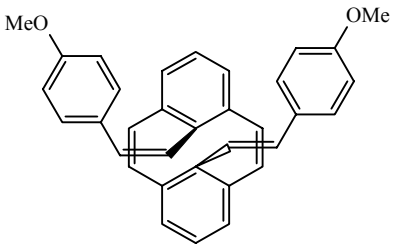

**216**



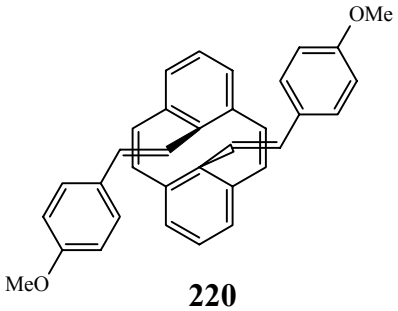

**217**



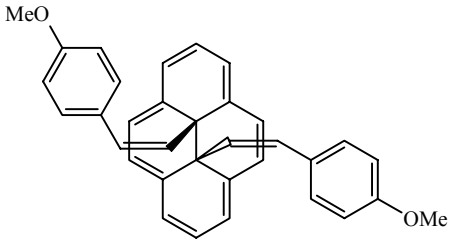

**218**



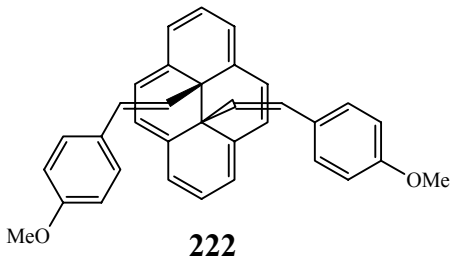

**219**



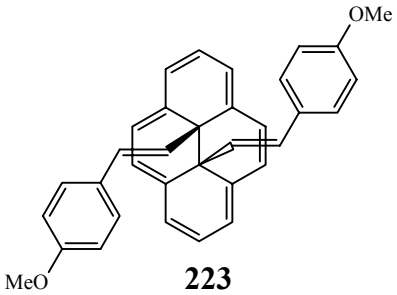

**220**



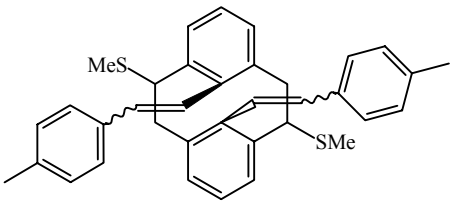

**221**



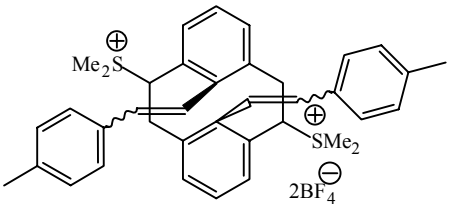

**222**



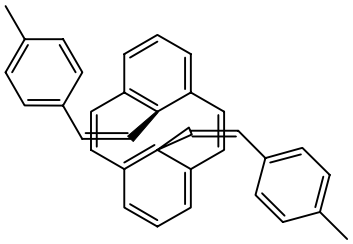

**223**



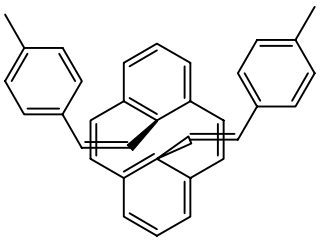

**224**



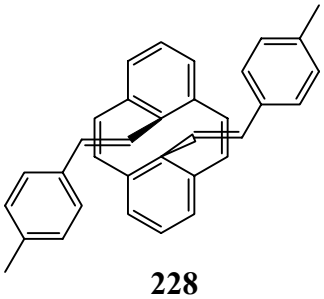

**225**



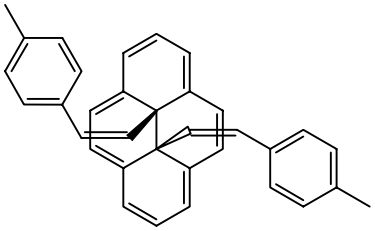
**226**



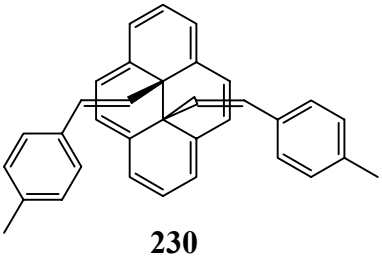
**227**



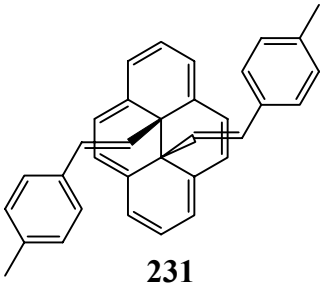
**228**



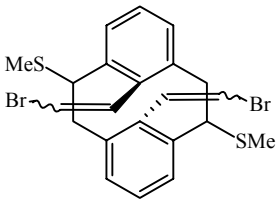
**229**



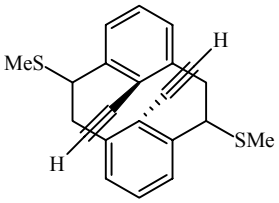
**230**



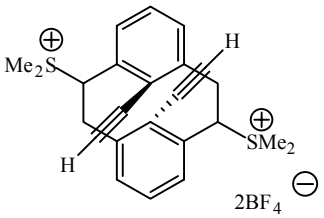
**231**



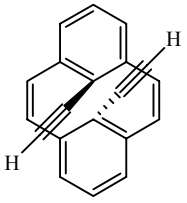

**232**



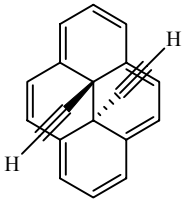

**233**



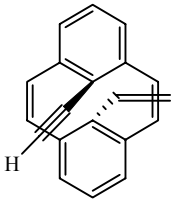

**234**



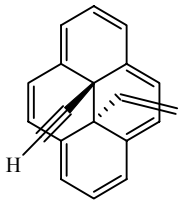

**235**



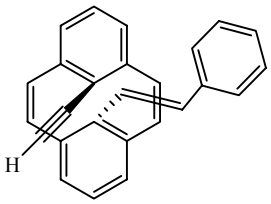

**236**



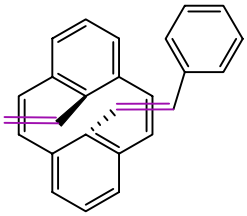

**237**



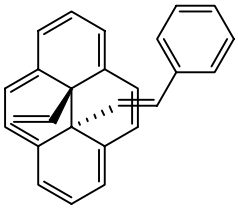

**238**



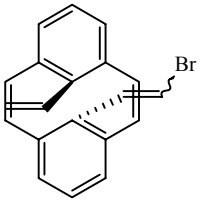

**239**



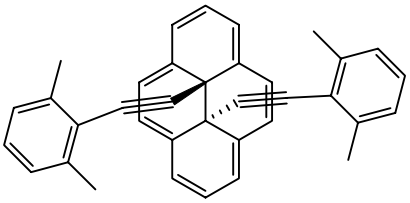
**240**



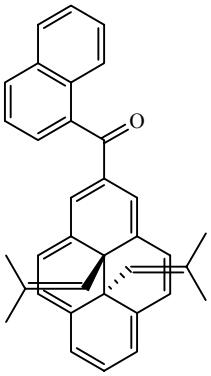
**241**



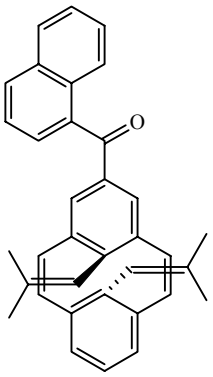

**246**



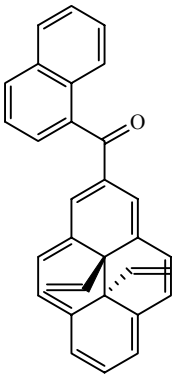
**247**



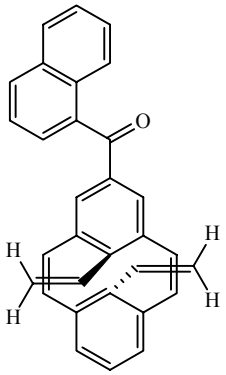

**248**



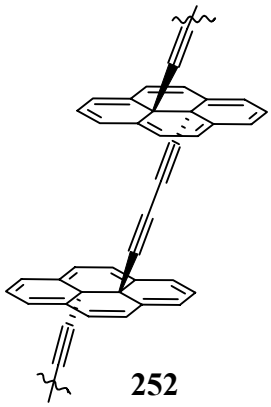

**249**



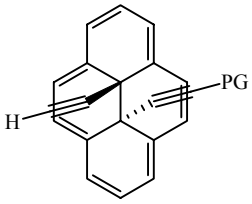

**250**



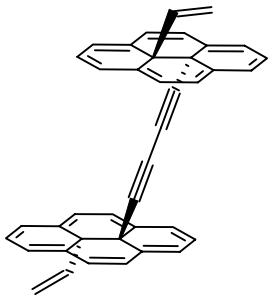

**251**



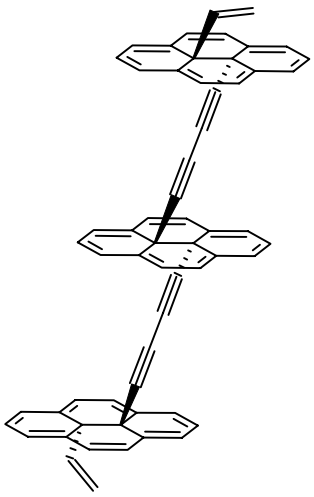
**252**



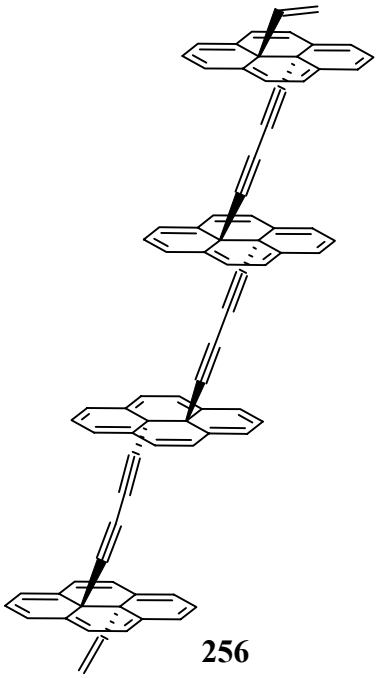

**253**



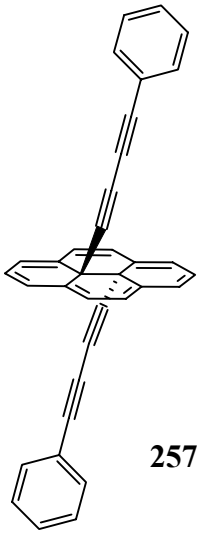
**254**



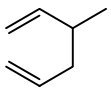
**255**



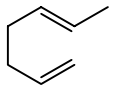
**256**



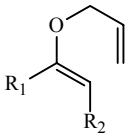
**257**



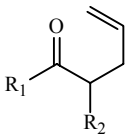
**258**



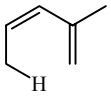
**259**



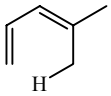

**260**



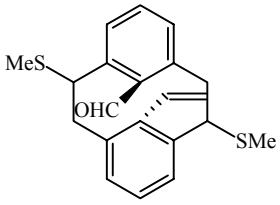

**261**



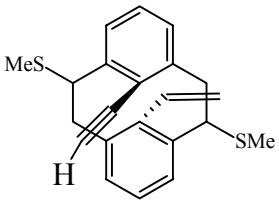

**262**



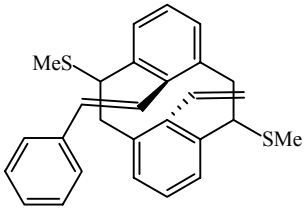

**263**



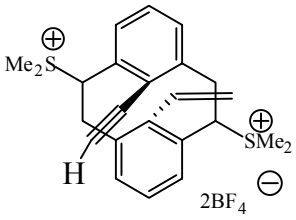

**264**



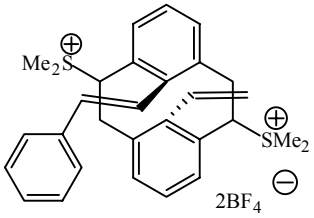

**265**



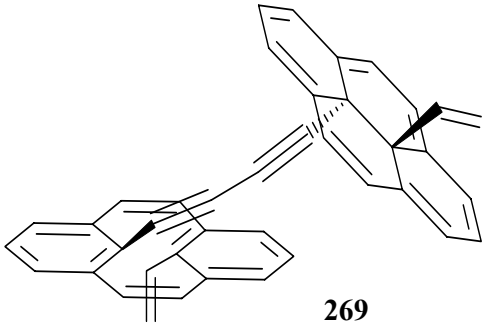

**266**



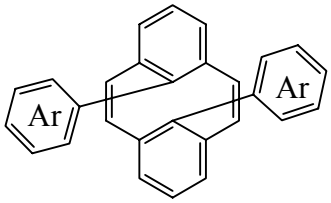

**267**



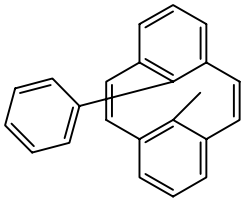

**268**



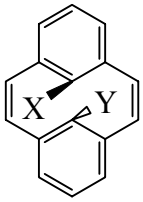
**269**



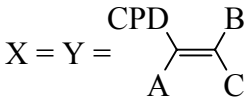

**270**



**271**




**272**



## List of Symbols, Abbreviations and Nomenclature

| Symbol | Definition |
|---|---|
| $^{13}$C NMR | Carbon-13 nuclear magnetic resonance |
| $^{1}$H NMR | Proton nuclear magnetic resonance |
| a | Antarafacial |
| Å | Angstrom |
| AIBN | Azo-bis(isobutyronitrile) |
| BDHP | Benzo[e]dimethyldihydropyrene |
| bp | Boiling point |
| bs | Broad singlet |
| c | Closed |
| CI | Conical intersection |
| COSY | Correlated spectroscopy |
| CPD | Cyclophanediene |
| *d* | Deuterium |
| d | Doublet |
| DCM | Dichloromethane |
| dd | Doublet of doublets |
| *de* | Diastereomeric excess |
| dec | Decomposition |
| DEPT | Distortionless enhancement of polarisation transfer (NMR) |
| DFT | Density functional theory (calculations) |

| | |
|---|---|
| DHP | Dihydropyrene |
| DMF | Dimethyformamide |
| EI | Electron impact |
| Et | Ethyl |
| EtOAc | Ethyl acetate |
| EtOH | Ethanol |
| E | Entgegen (*trans* orientation of high priority groups on alkene, Cahn-Ingold-Prelog Nomenclature) |
| ev | Electron volts |
| $E_{act}$ | Energy of activation |
| FG | Functional group |
| g | Grams |
| GS | Ground state |
| HMBC | Heteronuclear multiple bond correlation |
| HRMS | High resolution mass spectrometry |
| h | Hours |
| HSQC | Heteronuclear single quantum coherence |
| Hz | Hertz |
| IR | Infrared |
| *J* | Coupling constant |
| K | Kelvin |
| kcal | Kilo calorie |
| L | Litre |

| | |
|---|---|
| L.A. | Lewis acid |
| LDA | Lithium diisopropylamide |
| M | Molecular ion |
| MeLi | Methyl lithium |
| Me | Methyl |
| MeI | Methyl iodide |
| MeO | Methoxy |
| MeOH | Methanol |
| MeS | Thiomethyl |
| mg | Milligram |
| min | Minute |
| MHz | Mega hertz |
| mL | Milli litre |
| mp | Melting point |
| MS | Mass spectrometry |
| MV | Methylviologen |
| *m/z* | Mass per unit charge |
| NBS | N-bromo succinimide |
| *n*-BuLi | *normal* butyl lithium |
| nm | Nanometer |
| NMR | Nuclear magnetic resonance |
| NMP | *N*-methylpyrrolidone |
| NOESY | Nuclear Overhauser enhancement spectroscopy |

| | |
|---|---|
| o | Open |
| P | Photochemically reversible |
| **P** | Positive helicity |
| Ph | Phenyl |
| ppm | Parts per million |
| Pr | Propyl |
| pss | Photostationary state |
| q | Quartet (NMR) |
| R | Rectus (clockwise orientation of high priority groups, Cahn-Ingold-Prelog Nomenclature) |
| R | alkyl |
| $R_f$ | Ratio of distance travelled by compound to that of solvent on TLC |
| r.t. | Room temperature |
| s | Singlet (NMR) or seconds |
| S | Sinister (counter clockwise orientation of high priority groups) |
| s | Suprafacial (pericyclic reactions) |
| sh | Shoulder |
| S/N | Signal to noise ratio |
| t | Triplet (NMR) |
| T | Thermally reversible photochrome |
| TEA | Triethyl amine |
| THF | Tetrahydrofuran |
| TIN | Tinuvin P |

| | |
|---|---|
| TIPS | Triisopropylsilyl |
| TLC | Thin layer chromatography |
| $TS^{‡}$ | Transition state |
| UV | Ultraviolet |
| vis | Visible |
| W | Watt |
| ε | Extinction coefficient |
| $\lambda_{max}$ | Maximum wavelength absorption |
| Δ | Heat |
| δ | Chemical shift in ppm from standard |
| π | Pi electron |
| σ | Sigma electron |
| Φ | Quantum yield |
| $\Delta H^{‡}$ | Enthalpy of activation |
| $\Delta E^{‡}$ | Energy of activation |

## Acknowledgement

I would like to express my sincerest gratitude to Dr Reginald H Mitchell for his excellent guidance, suggestions and constant encouragement as well as giving me extraordinary experience throughout the work. I gratefully acknowledge useful discussions with the members of the supervisory committee and with the departmental faculty members during the course of the research. I would like to thank Dr Brendan Twamley (University of Idaho) for X-ray structure determinations. I would also like to thank Dr Richard V. Williams for DFT calculations. My special thanks go to Christine Greenwood for training me on how to operate NMR spectrometers as I benefitted extensively from this facility. I would like to thank David McGillivray for mass spectrometric analysis

I would like to thank my family members who provided a consistent moral support. I also wish to thanks all current and former group members with whom I had a chance to work in the lab; Wei Fan, Rui Zhang, Stephen G Robinson, Pengrong Zhang, Yanhong Yang, Olga Sarycheva, Tracy Lohr, Sarah Bennet, Leah Paile, Derek Mendal and Kate Waldie.

Financial support from the University of Victoria and from NSERC Canada is gratefully acknowledged

Words fail me to express my greatest thanks to almighty Allah (God) Who is the source of strength and Whose bounties are countless.

**To**

**All prophets of Allah and in particular to Nooh (Noah), Eesa (Jesus), Moosa (Moses), Ibraheem (Abraham) and above all, Muhammad (peace be upon them all) who were sent as a guidance to mankind.**

# Chapter 1: Introduction

## 1.1 Introduction

The active components of future computers and other electronic devices will probably be molecule based because of the massive size reduction using molecules[1] as building blocks compared to conventional silicon based methods. For a molecule based device to be functional there are two important requirements.

1. The molecule must be designed and tuned to give the desired properties.
2. They must be integrated together to form a macro device.

A tremendous amount of research over the past three decades,[2] has made it possible to screen molecules suitable for molecular devices and successful examples of rectification[3a], wiring[3b], storage[3c]and switching processes[3d] have been reported. It is however, now recognized that it is difficult to obtain communication between molecules in macro devices.

## 1.2 Molecular switches

Molecular switches are at the core of molecule based devices. A "Molecular Switch" is a broad concept which can be defined as;

"Molecules capable of inducing chemical and physical changes in response to external stimuli such as electrical current, light and heat."[1]

A brief list of external stimuli and the processes associated with them would include:[4]

1. Light: Photochromism, Light induced energy transfer, Phototropism, Heliochromism.
2. Electrical current: Electrochromism

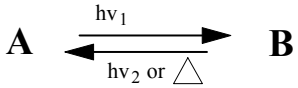
3. Heat: Thermochromism
4. Chemical: Halosolvatochromism, Solvatochromism, Acidochromism, Ionochromism
5. Mechanical: Piezochromism, Tribochromism.

Among the above mentioned phenomena, only photochromism will be described here.

## 1.3 Photochromism

"Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiations between two forms A and B having different absorption spectra"[4]

**Figure 1.1 Photochromism**




**P type and T type photochromes**

Photochromic chromophores can be divided into two categories based on the stability of the photogenerated species. If the photogenerated species (B) reverts back thermally to the initial state (A) in the dark then it is called T type (thermally reversible). If no such thermal reversion is observed in dark then it is called P type (photochemically reversible). Unfortunately most photochromic chromophores belong to the T type and are thus less generally applicable in photoswitchable molecular systems.

Photochromism can be positive or negative. If $\lambda_{max}$ of B > $\lambda_{max}$ of A, then it is called positive photochromism. Most of the photochromic chromophores belong to this division. If $\lambda_{max}$ B < $\lambda_{max}$ of A, then it is called negative photochromism.[4]

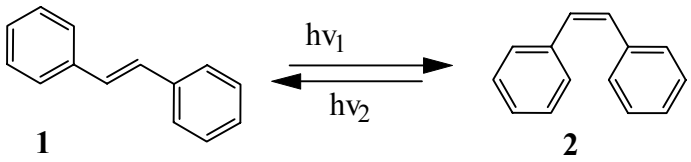
According to the type of the reaction taking place through light, photochromic compounds can be divided into six categories[4].

1. *Cis-trans* (*E/Z*) isomerization
2. Intramolecular hydrogen transfer
3. Intramolecular group transfer
4. Dissociation processes
5. Electron transfers (redox)
6. Pericyclic reactions

### 1.3.1 *Cis-trans* (*E/Z*) isomerization

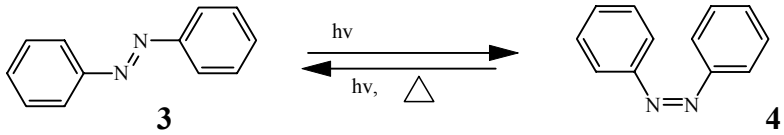
Both *cis* and *trans*-stilbenes interconvert reversibly upon excitation of the double bond (Scheme 1.1). This is one of the best understood photochemical systems but has not yet found applications in memory devices.

**Scheme 1.1 *Cis-trans* isomerization of stilbenes**




A particularly well-studied example in this category is azobenzene **3** (Scheme 1.2). *trans*-Azobenzene **3** isomerizes into *cis*-azobenzene **4** by irradiation with UV light. The *cis* or Z-form **4** is thermally unstable and reverts to the *trans* or E form **3**, which renders it unsuitable for memory devices. However, because of the appreciable change in distance between the two ends upon isomerization, this system has gained some unusual applications, some of which are given below.

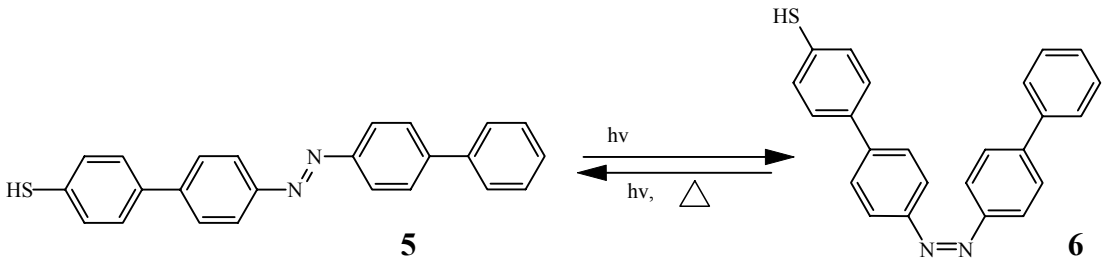
**Scheme 1.2 *Cis-trans* isomerization of azobenzene**




**3** **4**

Rampie[5] and coworkers have shown that the change in the structure upon isomerization can be applied to gain mechanical work by use of the biphenyl example shown in Scheme 1.3 below.

**Scheme 1.3 An azobenzene type photoswitch**




**5** **6**

The thiol group was used to anchor to a gold surface. The difference of the distance between two ends in *trans* **5** and *cis* **6** is about 7.0 Å which is almost double that of azobenzene itself (3.5 Å)

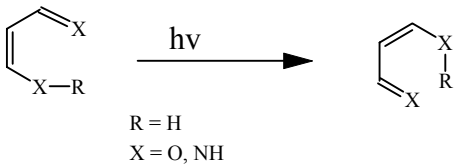
Azobenzene based polymers upon photoisomerization influence polymer swelling properties,[6a] wettability,[6b] membrane properties,[6c] viscosity and solubility.[7] Azobenzene based photoswitches also have applications in liquid crystals[8] because of their interesting nonlinear properties.

Other systems which also show *cis-trans* isomerization are overcrowded alkenes,[1] azines, thioindigoids[4] etc.

### 1.3.2 Intramolecular hydrogen transfer

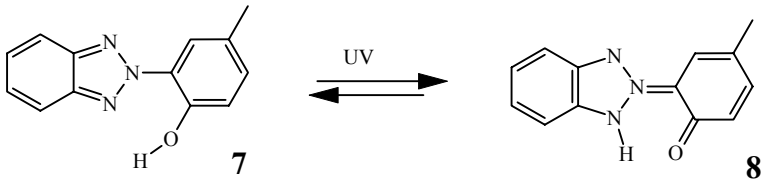
Intramolecular hydrogen transfer takes place from the electronically excited state of a molecule of the type shown in Scheme 1.4. This is also called phototautomerization.

**Scheme 1.4 Phototautomerization**




Generally the species generated in this process is thermally highly unstable and soon reverts back and dissipates energy in the form of heat. These kinds of molecules are generally used as UV stabilizers for polymers. A commercial UV stabilizer for polymers is 2-(2'-hydroxy-5'-methylphenyl)benzotriazole[4b] **7** (trade name Tinuvin P (TIN)), which is a benzotriazole based hydrogen transfer system. The process taking place on absorption of UV light is shown in Scheme 1.5. The phenolic hydrogen is transferred to the triazole part on irradiation and generates an ortho-quinoid species **8** which is unstable and reverts back to **7**.

**Scheme 1.5 Photochemistry of Tinuvin P**



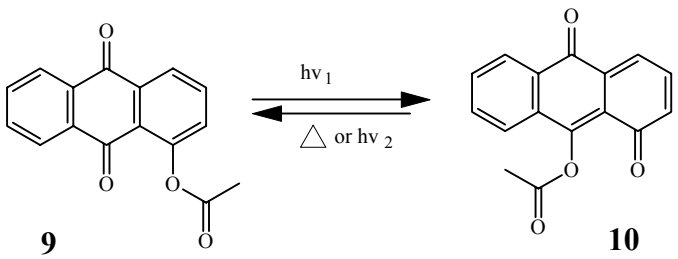

**7** **8**

Other families of compounds showing this kind of behavior are anils,[9] benzylpyridines, aci-nitro compounds, salicylates, oxazoles, and perimidinespiro hexadieneones.[1]

### 1.3.3 Intramolecular group transfer

This is similar to hydrogen transfer except that in this case the migrating group is other than hydrogen. A well known example (Scheme 1.6) is the migration of an acetoxy group in polycyclic quinines (periaryloxyquinones).[10]

**Scheme 1.6 Acyl migration in a polycyclic quinone**




**9** **10**

### 1.3.4 Dissociation processes

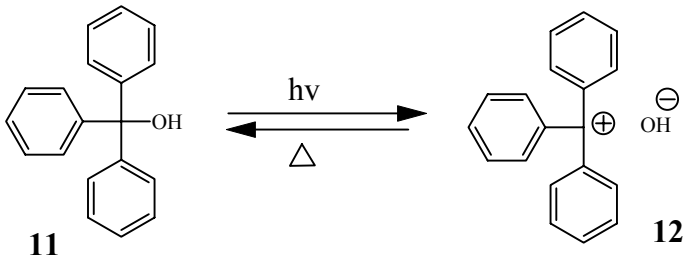
Light can cause homolytic or heterolytic cleavage of a bond to form more or less separated radicals or ion pairs. This dissociation, accompanied by a color change forms the basis of photochromism. Triarylimidazole dimers, tetrachloronaphthalenes, nitroso dimers and triaryl methanes are among the classes of compounds which can show bond dissociation photochromism.

These classes of compounds have gained little interest as photochromic compounds but they have a variety of other industrial applications. For example,

1. Triarylimidazole dimers are used in microlithography and silver free imaging processes.
2. Light mediated C-C cleavage of benzil and benzoin derivatives is used in radical polymer initiation.[11]

3. Malachite green derivatives are UV actinometers and are used in flash blind protection.[12]
4. Triphenyl leucohydroxides provide $HO^-$ ions on photoirradiation and thus cause pH to change.[13] The dissociation process is shown in Scheme 1.7.

**Scheme 1.7 Dissociation of triphenylcarbinol to release $HO^-$**



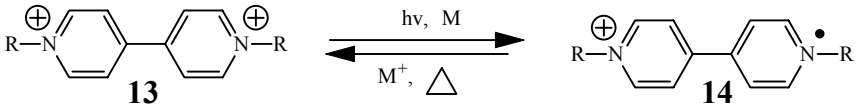

**11** **12**

This release of an $HO^-$ group from **11** causes the pH of the medium to change from 5.6 to 10.0 which slowly reduces because of the thermal back reaction.

### 1.3.5 Oxido-reduction (electron transfer) processes

Viologens undergo electron transfer in the presence of metals upon irradiation with light, shown in Scheme 1.8.

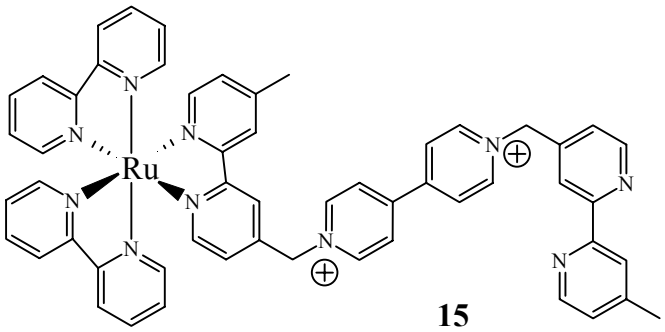
**Scheme 1.8 Electron transfer in viologens**




**13** **14**

The R group is methyl or other alkyl derivative. Methyl viologens are interesting in their behavior. e.g. Hammarstrom[14] has shown that the $MV^{+2}$ part of **15** oxidizes the excited ruthenium complex, while in the $MV^{+1}$ or the $MV^{o}$ state it reduces the complex. So the direction of electron flow can be controlled by an externally applied bias.

**Figure 1.2 Viologens-ruthenium complex dyad 15**



**15**

Another example of a photo redox system is the early photochromic ophthalmic spectacles[15] by Corning. The chemistry involves a redox pair of Ag and Cu. Silver, present as $Ag^{+1}$, accepts an electron from halide and forms metallic silver in the presence of light. At the same time $Cu^{+1}$ present in the mixture reduces halogen back to halide.[15] While in dark, $Cu^{+2}$ oxidizes the Ag into $Ag^{+1}$ and this causes bleaching.

$$X^{\ominus} \xrightarrow{hv} X + e^{\ominus}$$

$$Ag^{+} + e^{\ominus} \longrightarrow Ag$$

$$X + Cu^{+1} \longrightarrow Cu^{+2} + X^{\ominus}$$

### 1.3.6 Pericyclic reactions

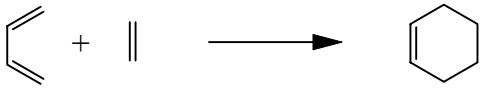
The two common pericyclic reactions in photochromism are cycloaddition reactions and electrocyclic reactions.

#### 1.3.6.1 Cycloaddition reactions

Cycloaddition reactions are defined as: "Reaction in which two or more unsaturated molecules or parts of the same molecule combine with the formation of a cyclic adduct in which there is a net reduction of the bond multiplicity."[16]

Cycloaddition reactions are generally symbolized as [i + j + …] where i and j are the number of electron in the interacting units that take part in the formation of the ring. According to this notation the Diels-Alder reaction is described as [4 + 2]. Very often symbols "s" and "a" are added as subscripts to these numbers which specifies the stereochemistry of addition of each unit. "s" and "a" stand for suprafacial and antarafacial selectivity respectively. So the Diels-Alder reaction would be [4s + 2s].

**Scheme 1.9 The Diels Alder reaction**

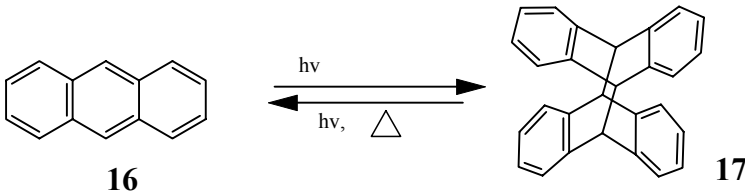


According to selectivity rules, a photochemical [2+2] reaction occurs readily while a thermal [2+2] requires quite drastic conditions. On the other hand, the thermal [4+2] cycloadditions is quite feasible while the photochemical is difficult.[19]

**[4 + 4] cycloadditions**

A well known example of a [4+4] cycloaddition reaction is the dimerization of anthracene (Scheme 1.10).[17]

**Scheme 1.10 The Photo-dimerization of anthracene**



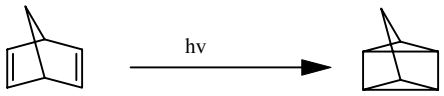

**16** **17**

**[2 + 2] Cycloadditions**

An example of a [2+2] cycloaddition reaction is the norboradiene rearrangement shown in Scheme 1.11. This system has achieved considerable generality including

examples with a variety of functional groups which affect both the UV-vis spectrum and the thermal stability of the photogenerated species[18].

**Scheme 1.11 The norbornadiene rearrangement**




**18** **19**

### 1.3.6.2 Electrocyclic reactions

"An electrocyclic reaction is characterized by the opening or closing of a ring, within a single molecule leading to the conversion to 2σ electrons to 2π electrons or the reverse."[19]

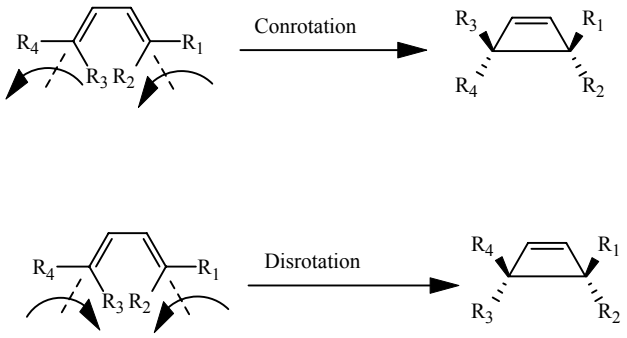
There are two different modes of cyclization, namely conrotatory and disrotatory cyclization. Taking butadiene as an example (Figure 1.3) if both ends move in the same direction, it is called conrotatory cyclization (Conrotation), while movement in opposite directions is termed as disrotatory cyclization (Disrotation).

**The general rules for photochemical and thermal electrocyclization**

**Table 1.1 Allowed modes for photochemical and thermal electrocycliations**

| Entry | Number of π electrons | Photochemical | Thermal |
|---|---|---|---|
| 1 | 4n π | Disrotatory | Conrotatory |
| 2 | 4n + 2 π | Conrotatory | Disrotatory |

**Figure 1.3 Conrotatory and disrotatory mode of cyclization**

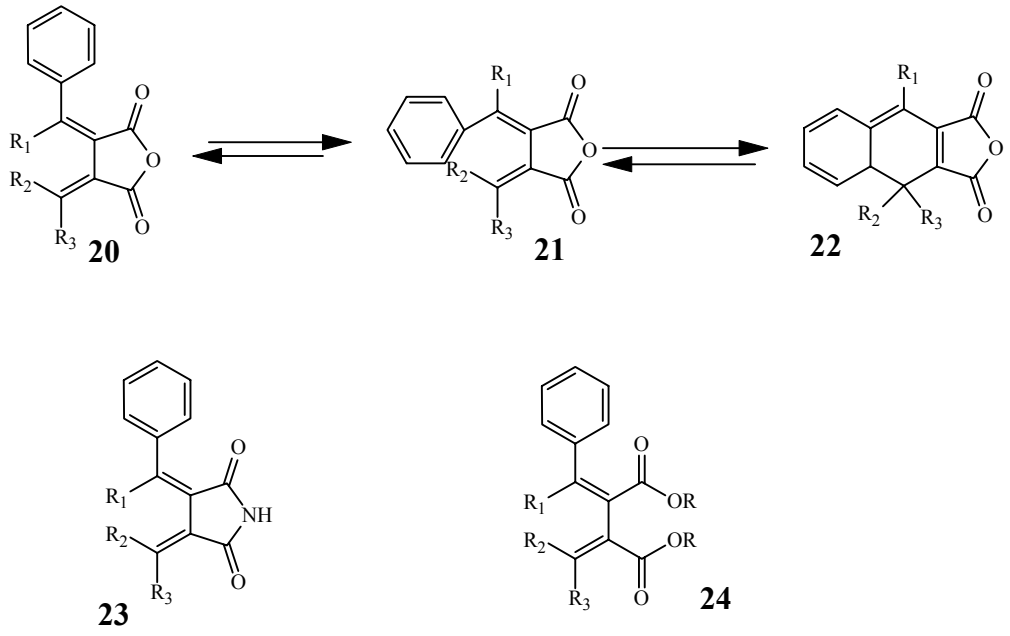



In this section only 6π 6-carbon electrocyclic reactions will be described. Most popular photoswitches for memory devices i.e dithienylethenes and fulgides belong to this class. These two systems generally show thermal irreversibility and are P type photochromes. Other families are spiropyrans, spirooxazines and chromenes. Dihydropyrenes, negative type photochromes, also fall under this category.

**Fulgides /Fulgimides/ Fulgenates**

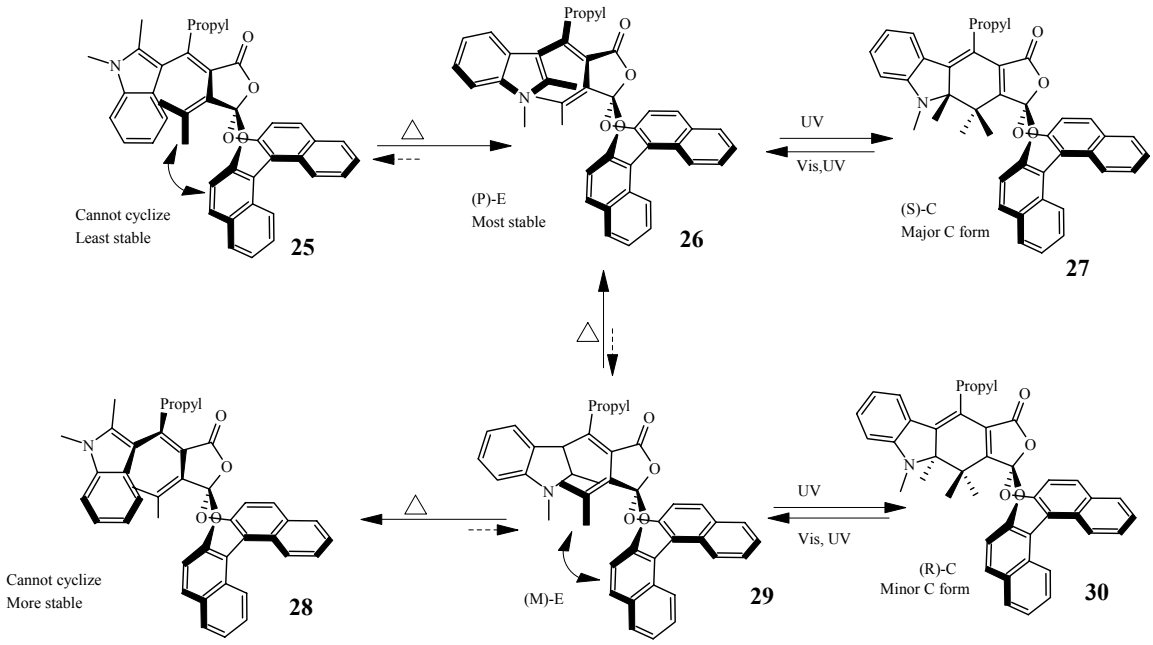
Fulgides, the common name for bismethylenesuccinic anhydrides possessing at least one aromatic ring on the methylene carbon atoms such as molecule **20**, were first synthesized by Stobbe in the early 20$^{th}$ century.[20] Upon irradiation with UV light, the colorless form **21** isomerizes into the colored form **22** and to another colorless form **20**. Switching between E-**21** and Z-**20** and between E-**21** and C-**22** continues until the photostationary state is formed. Fulgimides **23** are the imides instead of anhydrides while diesters are called fulgenates **24** (Scheme 1.12).

**Scheme 1.12 Photoisomerization of fulgides**




Molecule **25** shown in Scheme 1.13 was reported by Yokoyama et al.[21] as a highly diastereoselective photochromic system. Because of the steric repulsion between one of the binaphthol naphthalene rings and an isopropylidene methyl group pointing away from the molecule, the hexatriene moiety is forced to adopt positive (**P**) helicity **26**. This results in high diastereoselectivity in the closed form (90% de) with the S diastereomer predominant. This has application in chiral nematic crystals (liquid crystals). The specific rotation values of hexatriene and its photo stationary state (closed) at the sodium D line are -572$^{o}$ and -186$^{o}$, respectively. These quite distinct values, along with the fact the sodium D line does not cause a photochromic reaction, provide a tool for non-destructive readout.

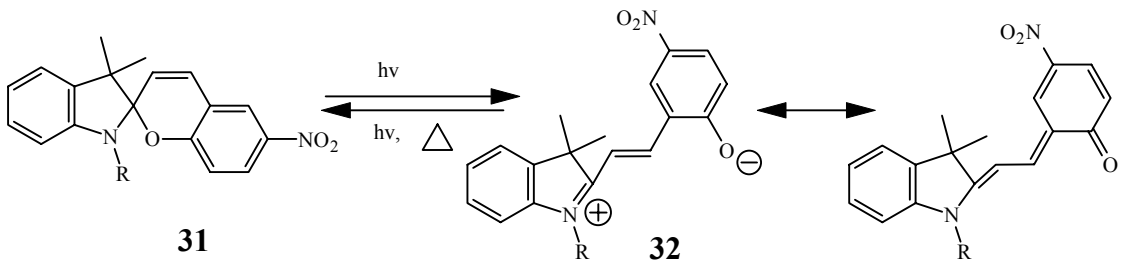
**Scheme 1.13 Highly diastereoselective cyclization of ketal fulgide 25**




## Spirooxazine and spiropyrans

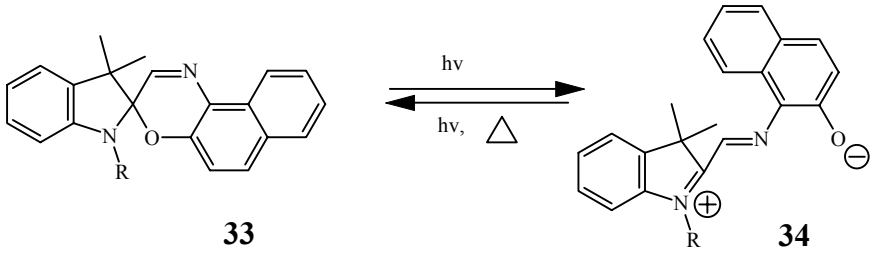
The photochromism of spiropyrans was first observed by Fischer and Hirschberg[22] in 1952, even though thermochromism of these compounds has been known since 1921. In solution, spiropyran **31** (Scheme 1.14) shows absorption in the UV region (200-400 nm). Irradiation with light in this region causes the spiropyran to open into a colored species called a merocyanine **32**.

**Scheme 1.14 Photochromism of spiropyran 31**



Spirooxazines **33** are structurally similar to spiropyrans except that one of the methine carbons in the spiropyrans is replaced by a nitrogen in the spirooxazine. Both spiropyrans and spirooxazines are T type positive photochromes.

**Scheme 1.15 Photochromism of spirooxazine 33**



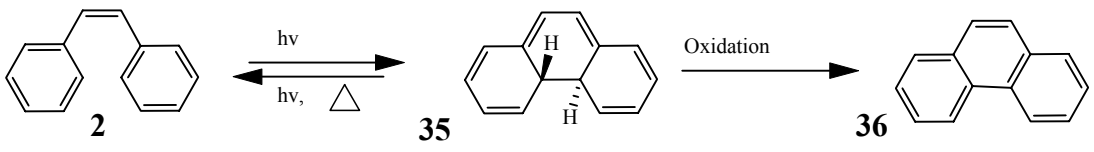

**33** **34**

Spiropyrans and spirooxazines have some interesting applications e.g. in self developing photography, actinometry, displays, filters, and lenses of variable optical density including eye protection glasses and more recently in three dimensional optical memories based on two photon conversion.[23]

**Dithienylethenes**

Dithienylethenes belong to the diarylethene class of photoswitches, the parent example of which is the interconversion between *cis*-stilbene **2** and dihydrophenanthrene **35** (Scheme 1.16). The dihydrophenanthrene is quite reactive towards oxidation and irreversibly forms phenanthrene **36**.

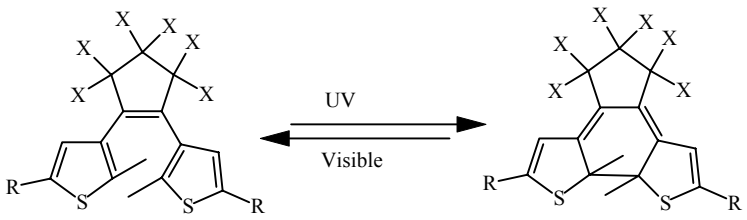
**Scheme 1.16 Phenanthrene from *cis*-stilbene**




**2** **35** **36**

This problematic oxidation reaction can be avoided by replacing the hydrogens with methyl groups. In the parent example, the thermal back reaction is rapid but when the phenyl ring is replaced with a heteroaryl ring such as thiophene, the thermal back reaction is quenched (P type photochromes).

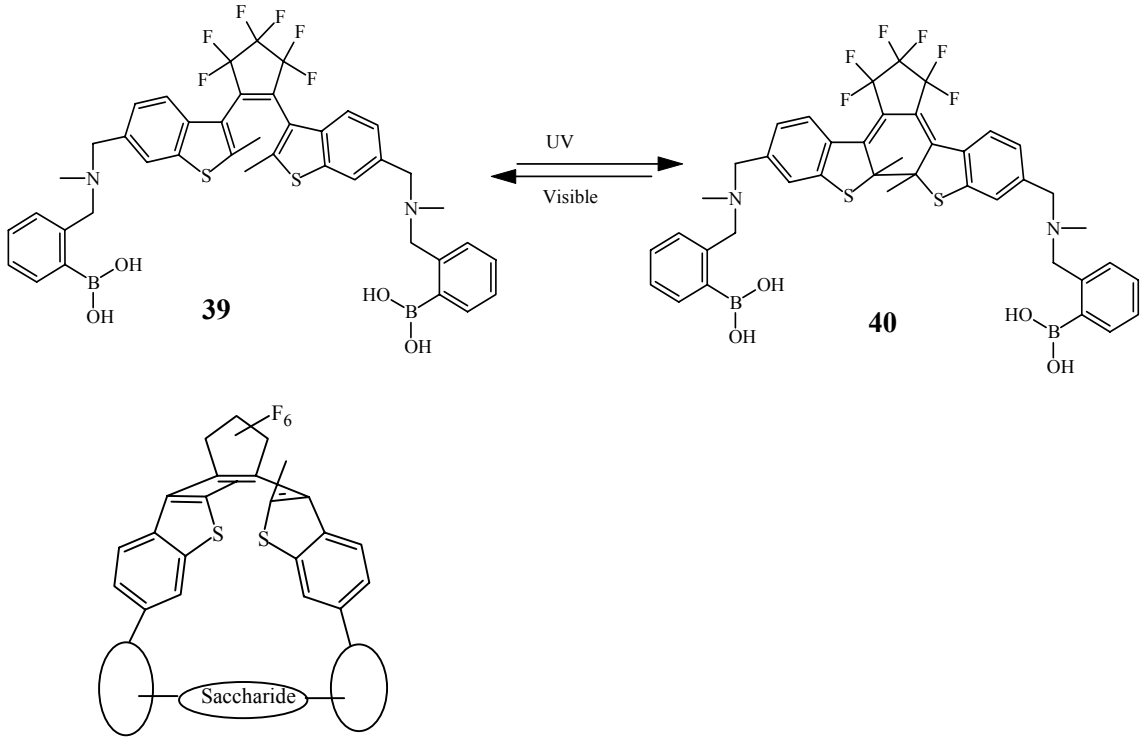
**Scheme 1.17 Irie's dithienylethene photoswitch**




**37** X = F or H **38**

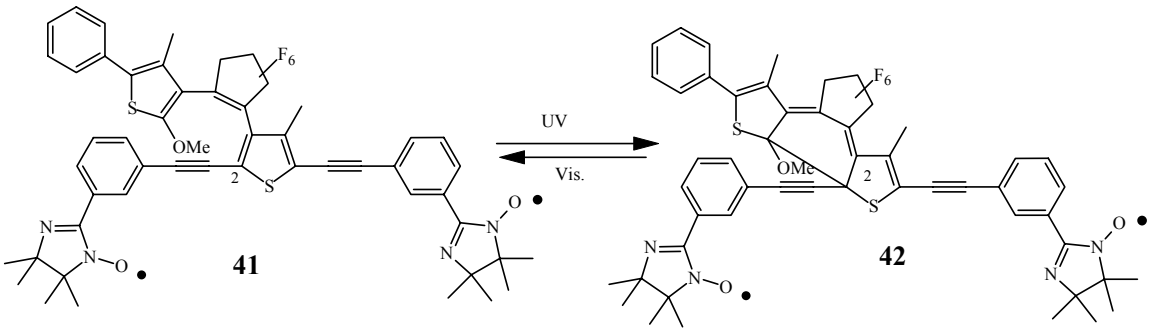
Dithienylethene photoswitches (Scheme 1.17) are characterized by a number of practical advantages including thermal stability of isomers, fatigue resistance (stable up to 10000 cycles) and fast response time which make them suitable for applications in molecular devices.[24] This photoisomerization has application not only in molecular devices but also in biology where a molecule or an ion binds selectively to one isomer. One example is the reversible binding of saccharides to molecule **39** which contains two boronic acids functional groups (Scheme 1.18). Open isomer **39** binds to saccharide and forms the complex[25] which can be monitored easily by the growth of a CD spectrum. Upon irradiation with UV light, ε drops to 40% while the photostationary state contains 60% of the closed isomer, this indicates that the closed form **40** hardly binds to the saccharide at all. The ε value returned upon irradiation with visible light.

**Scheme 1.18 Photo-controlled release of saccharide from dithienylethene 39**




2,5-Bis(arylethynyl)thiophene has been applied for the switching of magnetism when the aryl group contains imino nitroxide radicals (Scheme 1.19). In the open form **41**, the system is fully conjugated and the two radicals interact with each another ("ON" state). Upon UV closing, the conjugation is broken (carbon 2 changes from $sp^2$ to $sp^3$) and the switch represents the "OFF" state.[26]

**Scheme 1.19 Photoswitching magnetism**

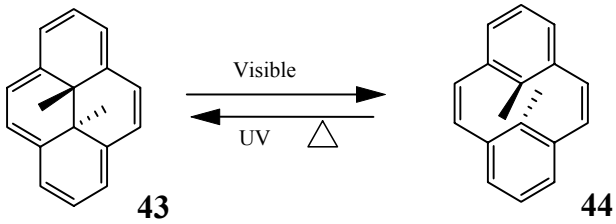



Other applications of dithienylethene photoswitches involve photoelectrochromism,[27] gated reactivity,[28, 24] liquid crystalline switches and many others.[24]

## 1.4 Dihydropyrene photoswitches

Dihydropyrene photoswitches are of negative T type[29] in which the colored form **43** (closed/DHP) is more stable and isomerizes upon irradiation with visible light into the colorless form, cyclophanediene **44** (Scheme 1.20)**,** which returns back either thermally or photochemically with UV light. Quite analogous to many other photoswitches, the bond forming termini of the 6π electrocyclic system should not contain hydrogen atoms so as to avoid oxidation. 10b,10c-Dimethyldihydropyrene[30] **43** and 2,7-di-*tert*-butyl-10b,10c-dimethyldihydropyrene **45** are the molecules in this series which have been studied in some detail.

**Scheme 1.20 Photoswitching of dihydropyrene 43**




**43** **44**

Quite a number of factors were involved for this photoswitch to stay dormant both from a research and a commercial point of view.

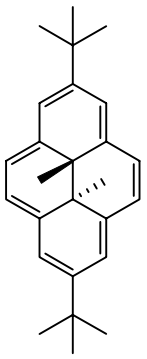
1. Tedious synthesis
2. Poor quantum efficiency for opening
3. Decomposition/side reactions
4. Thermal back reaction.

A brief outline is mentioned towards the success of solving each problem.

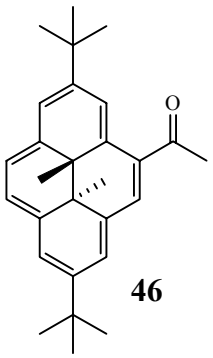
### 1.4.1 Tedious syntheses

The very first synthesis reported by Boekelheide[31] involved 14 steps with a 3% overall yield starting from *p*-cresol. This small yield limited the study of dimethyldihydropyrene derivatives. In the 70s, Mitchell[32] reported an improved synthesis of dimethyldihydropyrene with 36% yield starting from 2,6-dichlorotoluene. This was a major breakthrough in the chemistry of dimethyldihydropyrene because it allowed the study of these molecules in greater detail. Further improvement came when *t*-butylderivative[33] **45** was reported in 35-45% yield in just six steps starting from *t*-butyltoluene. This synthesis could provide gram quantities of dihydropyrene **45** in a span of two weeks or less.

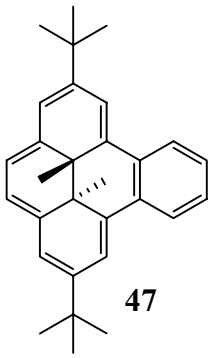
### 1.4.2 Quantum yield



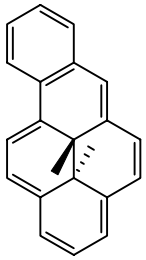
**45**




**46**

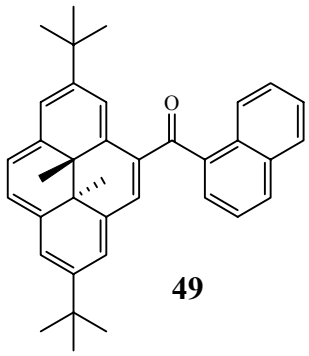


**47**

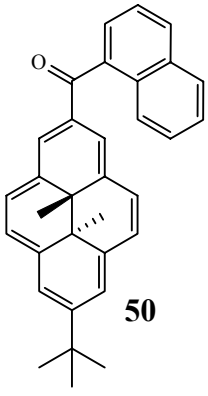


**48**

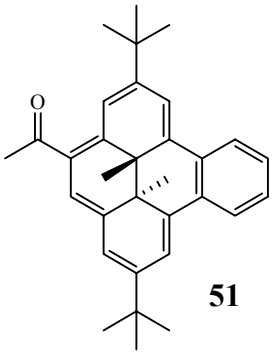
Dimethyldihydropyrene **43** has a low quantum yield for ring opening (0.006) which rendered it inapplicable for practical devices. *t*-Butylated dimethyldihydropyrene **45** has an even poorer quantum yield[34] (0.0015), about 4 times less than the parent. Quite a large number of compounds have been scanned for their photophysical properties but the quantum yield for ring opening is generally low. However, introduction of a carbonyl functional group at the 2 and 4 positions or [e]-annelation with a benzene ring (BDHP **47**) enhances the photoopening rates. Dihydropyrenes **46, 47** and **51** have ring opening quantum yields of 0.0038, 0.042 and 0.095 respectively.[34] Robinson[35] has reported that the naphthoyl group at the 2-position, dihydropyrene **50**, has even higher ring opening rates but the quantum yield was not reported.




**49**




**50**



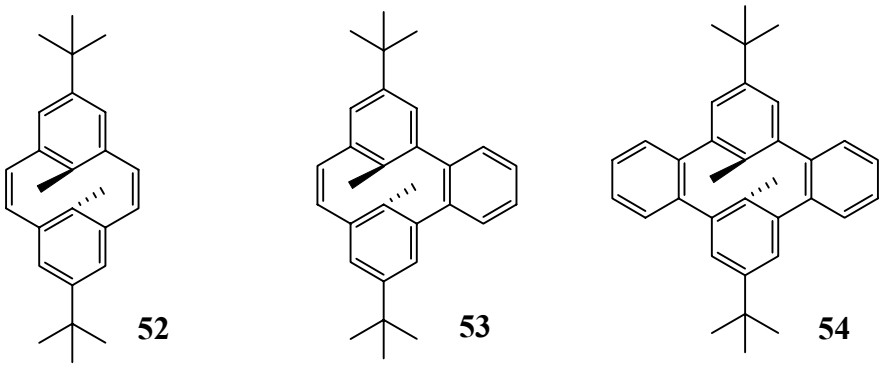

**51**

### 1.4.3 Decompositions/side reactions

Even though the improved synthesis of dimethyldihydropyrene has opened up a new gate and allowed the synthesis of many derivatives of dihydropyrene, a basic question is still there: how robust is dihydropyrene to different reaction conditions. The answer is not that simple. Dihydropyrenes have been shown to be quite sensitive to mineral and lewis acids.[36] Thanks to the patience of Mitchell and other researchers working in this field, a wide variety of reaction can now be carried out with moderate to good yields.

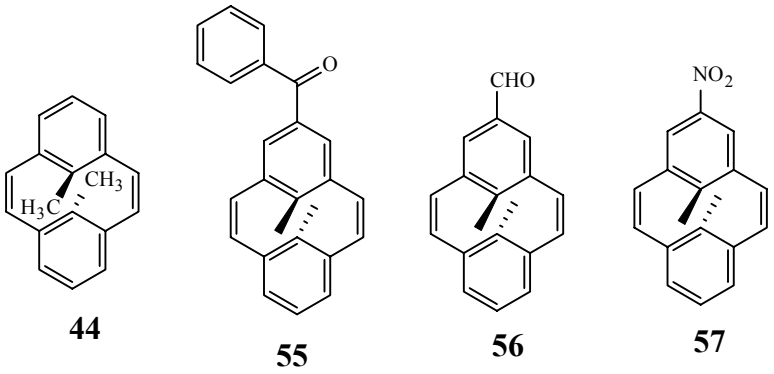
### 1.4.4 Thermal return

The problem of the thermal instability of the open form, cyclophanediene **43**, is the major cause for these switches not gaining proper attention. This problem still has not yet been solved. For switches and memory purposes, both isomers should be stable enough to store information for a long time. *t*-Butylated cyclophanediene **52**, obtained from photoopening of **45**, has a half life of about 42 hours at room temperature[37] (20 $^{o}$C). [e]-Annelation of one benzene ring **53**[34] increases the half life to 7.3 days at 20 $^{o}$C, but still this number is much smaller than required for practical purposes. Annelating a benzene ring on each side reversed the direction of photochromism, making the open form **54** more stable than the closed form[38] (a positive photochrome).

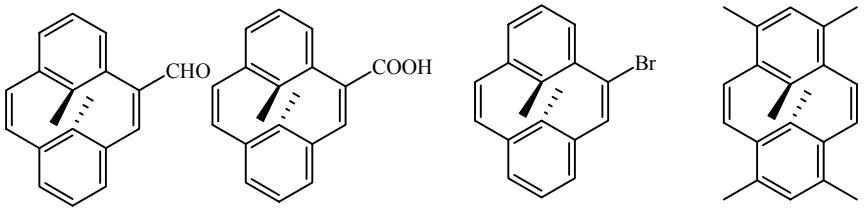


**52** **53** **54**

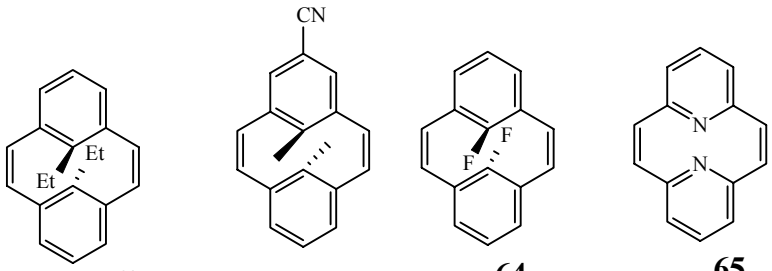
## 1.5 The nature of the transition state



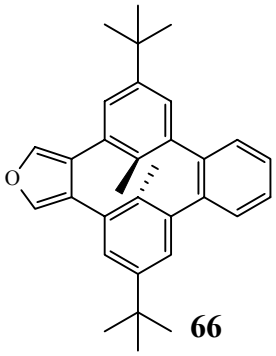

**44** **55** **56** **57**



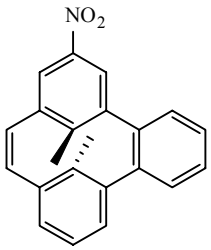

**58** **59** **60** **61**



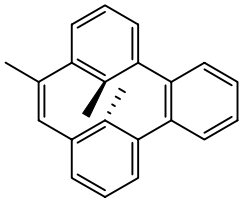

**62** **63** **64** **65**



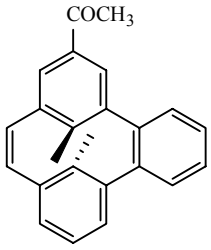

**66**



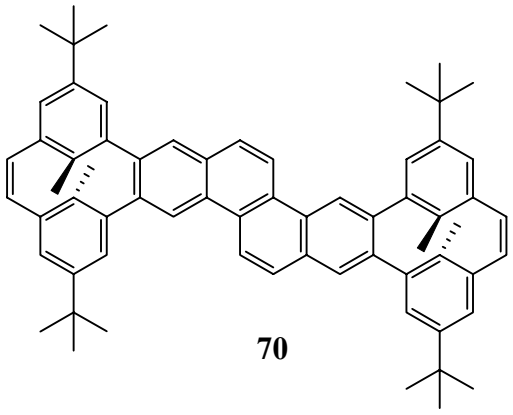

**67**



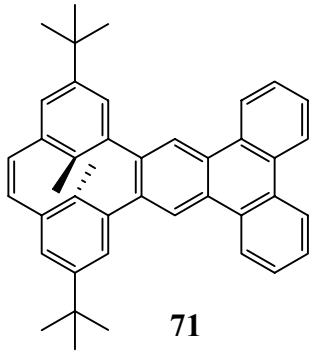
**68**



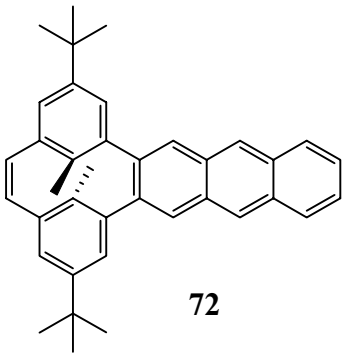

**69**



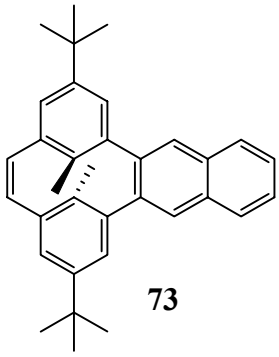
**70**



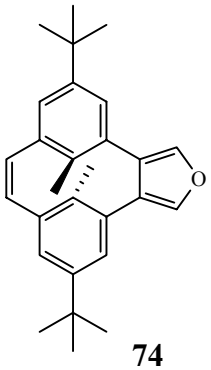
**71**



**72**



**73**




**74**

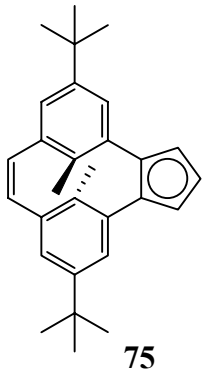
The following table is a partial representation of the thermal closing data which was available at the start of this thesis.

**Table 1.2 Half lives of some cyclophanedienes at 20 $^{o}$C[39,41]**

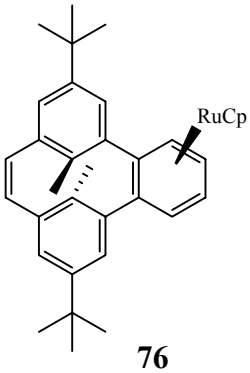
| Entry No. | Compound | $\tau_{1/2}$* | Entry No. | Compound | $\tau_{1/2}$* |
|---|---|---|---|---|---|
| 1 | **74** | 90 days | 17 | **72** | 5 h |
| 2 | **53** | 7.3 days | 18 | **61** | 5 h |
| 3 | **71** | 4.5 days | 19 | **57** | 3h |
| 4 | **60** | 83 h | 20 | **55** | 90 min |
| 5 | **59** | 78 h | 21 | **68** | 51 min (32 $^{o}$C) |
| 6 | **70** | 58 h | 22 | **56** | 42 min |
| 7 | **76** | 55 h | 23 | **67** | 12 min (32 $^{o}$C) |
| 8 | **52** | 54 h | 24 | **81** | 6 min (22 $^{o}$C) |
| 9 | **58** | 49 h | 25 | **82** | 198 s (22 $^{o}$C) |
| 10 | **77** | 45 h | 26 | **79** | 79 s (22 $^{o}$C) |
| 11 | **44** | 42 h | 27 | **78** | 25 s (22 $^{o}$C) |
| 12 | **75** | 39 h | 28 | **80** | 25 s (22 $^{o}$C) |
| 13 | **69** | 27 h (32 $^{o}$C) | 29 | **54**[§] | - |
| 14 | **73** | 25 h | 30 | **66**[§] | - |
| 15 | **62** | 2 h (30 $^{o}$C) | 31 | **65**[#] | - |
| 16 | **63** | 2 h (30 $^{o}$C) | 32 | **64**[#] | - |

[#]non photochromic / non thermochromic, § CPD form is more stable than the DHP form

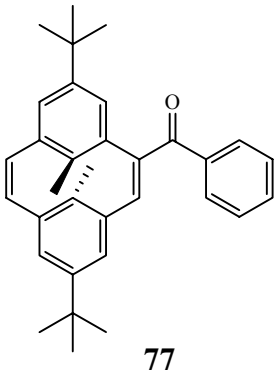
* Errors in half lives, where available, were less than 5%.



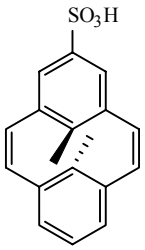
**75**



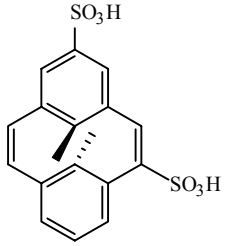

**76**



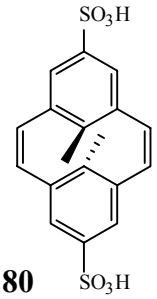

**77**



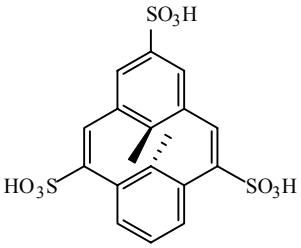

**78**



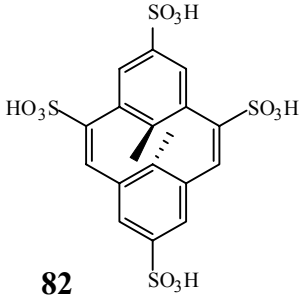

**79**




**80**




**81**

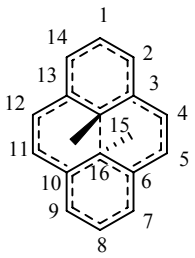



**82**

Difluorocyclophanedienes **64** and pyridine CPD **65** failed to close thermally but, they are not photochromic as well. Ideally, we would like compounds which show greater thermal stability (i.e., slow/no thermal return of the CPD into the DHP) but are photochromic. We asked Dr. Williams (University of Idaho) to model the transition state for the thermal back reaction.

The thermal back reaction (conrotation, 6π e) is forbidden by Woodward-Hoffmann rules.[40] For a forbidden reaction, the transition state may involve radical or ionic components so Williams[41] used unrestricted DFT (UB3LYP) calculations involving electron correlations[42] and found that the transition state has radical character[43, 44] and shows equal contribution from singlet and triplet states (spin contamination $< S^2 > = 1$).

**Figure 1.4 Numbering system for description in section 1.5**




The positions of the highest spin density were carbons 15 and 16 followed by carbons 1 and 8 (Figure 1.4). Based on spin density calculations, a radical destabilizing substituent such as $CF_3$ at these positions would make the $TS^{‡}$ higher in energy and would slow down the thermal return.

### 1.5.1 Radicals

A species that possesses one or more unpaired ("odd" or "single") electrons is called a free radical. It can be neutral, or positively or negatively charged.[45]

The stability of carbon based radicals is important in understanding the reactions involving radicals as reactants, intermediates or products. Substituents are known to have a remarkable effect on the stability of radicals. Substituted methyl radicals have been studied both theoretically[46] and experimentally[47] to unravel the effect of the substituent on the stability of radicals. The stability of radicals is determined by the bond dissociation energy difference between substituted methanes and methane in the gas phase. If the bond dissociation energy is lowered because of the substituent then the substituent is stabilizing, and vice versa. The difference in the bond dissociation energies is a measure of the strength of the substituent.[47] Radicals are electron deficient, so an electron rich substituent is expected to stabilize the radicals but several studies carried out

on radicals so far reveal that most substituents stabilize radicals either by hyperconjugation or by lone pair participation or by the delocalization of the radical on the π system of the substituent even with electron withdrawing substituents. When the electron withdrawing power of the substituent overcomes the delocalization stability, then the substituent becomes destabilizing and this is true only with either positively charged or highly fluorinated substituents. Examples of radical destabilizing substituents[48] are $H_3P^+ < HSO_2 < CF_3 < H_2S^+ < H_3N^+$. The following table gives a brief summary of the most common functional groups as a substituent in the order of decreasing stability from top to bottom

**Table 1.3 Radical stabilizing functional groups and their bond stabilization energies for FG─$CH_2$˙˙˙H**

| Sr. No. | Functional group | Δ(BDS) in kcal/mol |
|---|---|---|
| 1 | $NH_2$ | 22 |
| 2 | $CH{=}CH_2$ etc. | 19 |
| 3 | Ph | 17 |
| 4 | PhS, RS, MeO, CN | 12 |
| 5 | MeCO, HO | 11 |
| 6 | MeOCO | 10 |
| 7 | PhSe | 8 |
| 8 | Me, $NO_2$ | 7 |
| 9 | $PhSO_2$, $Me_3Si$ | 6 |
| 10 | Cl | 4 |

| | | |
|---|---|---|
| 11 | F | 3 |
| 12 | H | 0 |

### 1.5.2 The effect of the internal substituent on the thermal closing

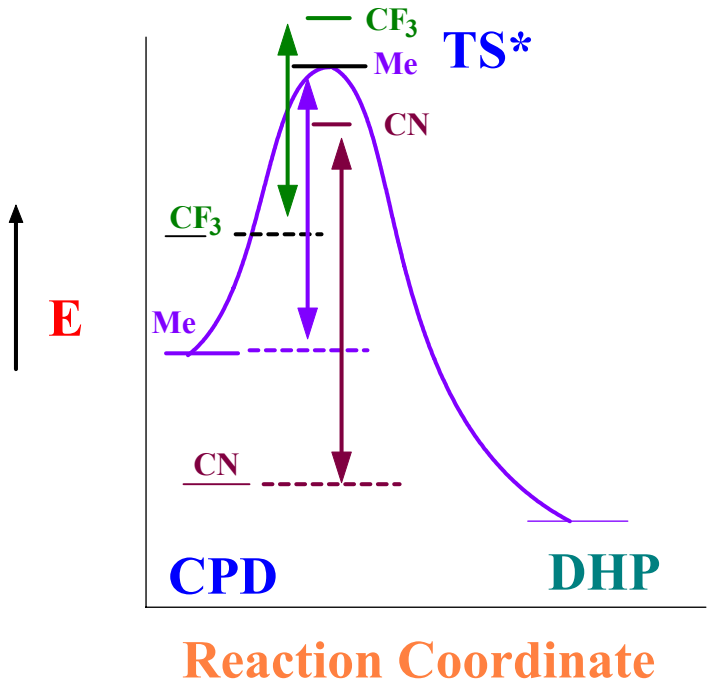
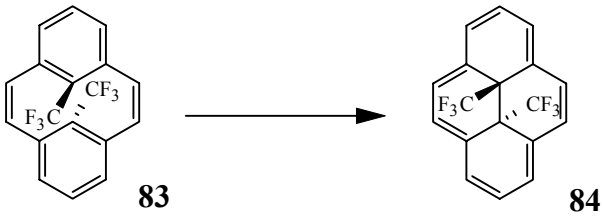



**Figure 1.5 Substituents' effect on the energies of cyclophanedienes and the TS‡**

Williams studied computationally two internal substituents i.e., $CF_3$ and CN. $CF_3$ is a radical destabilizing group and is expected to increase the energy of the TS‡ and thus $E_{act}$. In reality the $E_{act}$ is calculated to decrease, which is counter-intuitive. The explanation is that it destabilizes the TS‡ but at the same time it also destabilizes the CPD (Figure 1.5) and the destabilization for CPD is more than that for the TS‡, so the activation barrier for the conversion of **83** in to **84** (Scheme 1.21) is lower compared to the conversion of **44** into **43.**

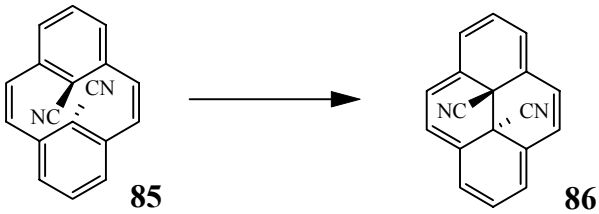
**Scheme 1.21 A dihydropyrene based photoswitch with $CF_3$ internal groups**




**83** **84**

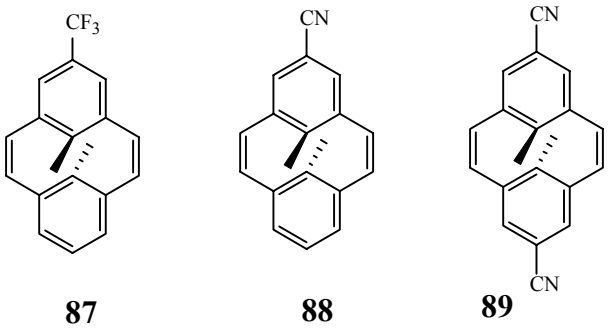
The radical stabilizing group, nitrile was also investigated by Williams at the internal position and it stabilizes the CPD more than the TS‡ which would increase the activation barrier for the thermal back reaction.

**Scheme 1.22 A photoswitch with a high calculated activation barrier**




**85** **86**

### 1.5.3 The effect of substituents at the 1 and 8 positions on the thermal closing

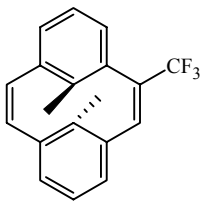



**87** **88** **89**

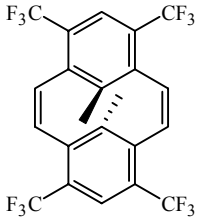
The next highest spin density is calculated to be at positions 1 and 8 (Figure 1.4). A radical stabilizing substituent at these positions should lower the energy of activation, e.g. compounds **88** and **89** shown above lower the calculated activation barrier from the CPD to the TS‡ by 1 and 2 kcal/mol respectively, an additive effect. In **87**, the $CF_3$ group

at the 1 or 8 positions surprisingly has no effect on $E_{act}$. This implies that direct radical stabilization is not the only principle factor in determining the activation barrier.

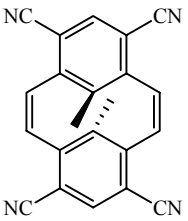
### 1.5.4 The effect of substituents at other positions




**90**




**91**




**92**

Williams's calculations suggested that.

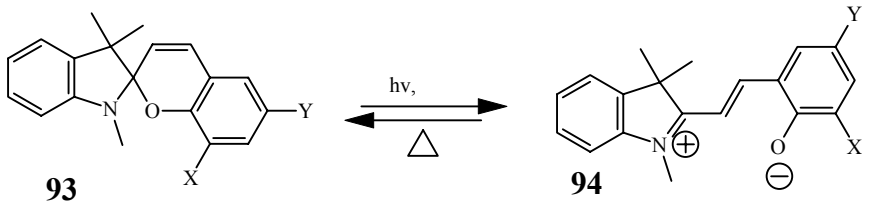
1. Nitrile groups at the 2,7,9,14 positions, **92** would have almost no effect on $E_{act.}$
2. A $CF_3$ group at the 4 position in **90** would have no effect.
3. $CF_3$ groups at positions 2,7,9,14 in **91** should increase the activation barrier by 2 kcal/mol.

Though these calculations gave no obvious trend in activation barrier with regards to both, the nature and the position of the substituents, these calculations were useful enough to identify the positions of the greatest effect, i.e 15 and 16 (Figure 1.4).

### 1.5.5 Substituent effects in other photochromic systems

Substituents have been shown to have great influence on the thermal stability of a variety of other photoswitches as well. An early example dates back to 1959 when Berman[49] showed that substituents X and Y (Scheme 1.23) in the spiropyran-merocyanine photoswitch can affect the rate of thermal closing by more than three orders of magnitude.

**Scheme 1.23 The effect of substituents on the thermal return of merocyanine to spiropyran**



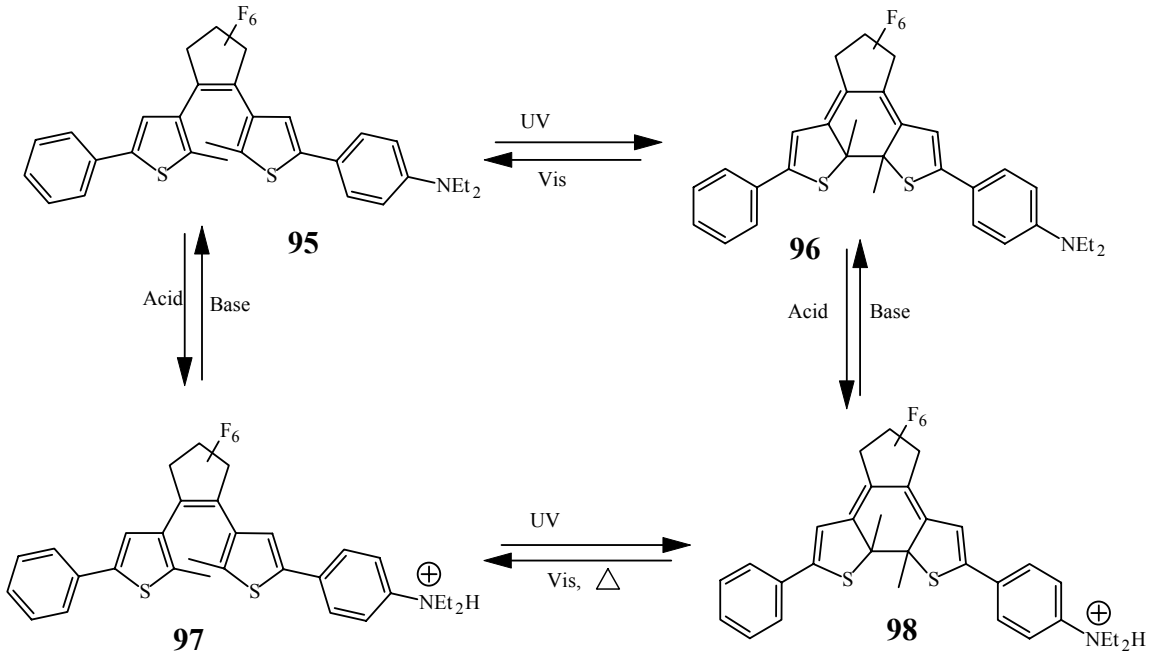

**93** **94**

$X = F, Y = NO_2$ rate = $6.33 \times 10^{-6} s^{-1}$

$X = NO_2, Y = OMe$ rate = $1.32 \times 10^{-2} s^{-1}$

Substituent change can also convert a P type chromophore into a T type chromophore as shown in Scheme 1.24. Dithienylethenes are P type chromophores provided they have an electron donating group on the phenyl ring such as the $NEt_2$ in molecule **95**. Upon acidification, the $NEt_2$ is transformed into an $^{+}NEt_2H$, an electron withdrawing group, and this change of functional group makes the photoswitch **97** a T type. This switching between the P and T types can be controlled by acid or base.[50]

**Scheme 1.24 Switching between a P and T type photochrome**




Substituents not only affect the thermal back reaction but also affect other physical properties such as shifting of the UV-vis spectrum to longer or shorter wavelength, improving the quantum yield for photophysical processes etc.[51,52]

## 1.6 Thesis Research Objectives

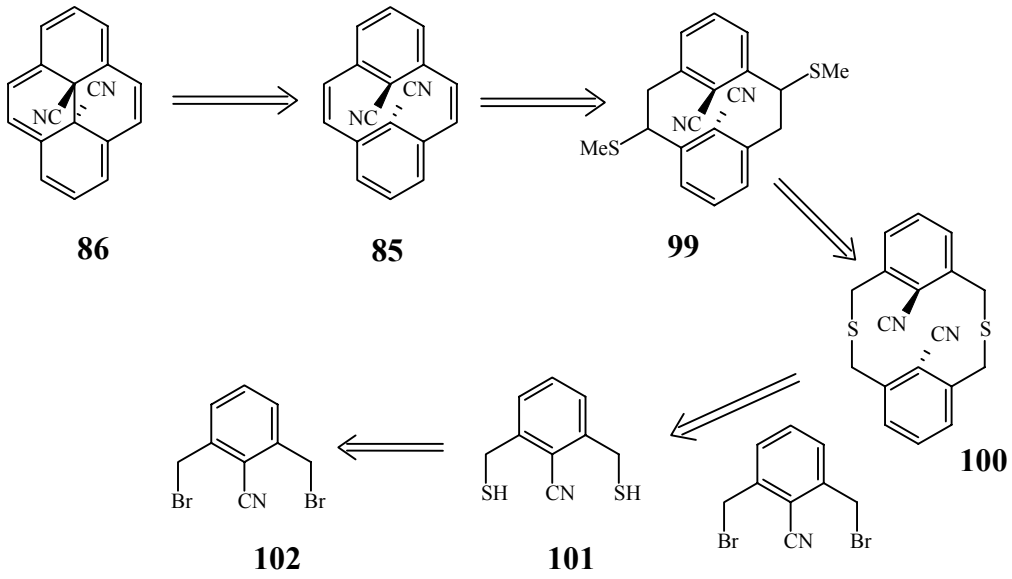
Given the calculations discussed above, the first objective was to synthesize and study the dinitrile switch pair **85/86**, and then, depending on the results obtained, to investigate the effect of other internal substituents such as ethynyl, vinyl and formyl, on the thermal and photochemical properties. The next objective was to synthesize naphthoyl (carbonyl) derivatives to improve photoopening properties once thermal stability has been attained.

# Chapter 2: Syntheses

## 2.1 Synthesis of the CPD/DHP pair 85, 86 with internal nitrile groups

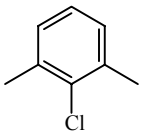
Calculations suggested that internal nitrile groups should slow down the thermal return of the cyclophanediene **85** into the dihydropyrene **86**, thus we decided to synthesize these two species. The reterosynthetic analysis of **86** is shown in Scheme 2.1 and it involves thiacyclophane **100** as an intermediate. Thiacyclophanes are key intermediates[31,32,33] in the synthesis of dihydropyrenes and can be synthesized either by coupling dibromide with dithiol or by reacting dibromide with sodium sulfide. Generally, Wittig rearrangement followed by Hoffmann elimination converts the thiacyclophanes into the cyclophanedienes. However, a nitrile group is sensitive to the BuLi used in the Wittig rearrangement,[53] so in this case the Stevens rearrangement[54] is preferred which uses a two step process to convert **100** into **99**.

**Scheme 2.1 Reterosynthetic analysis of dicyano DHP 86**



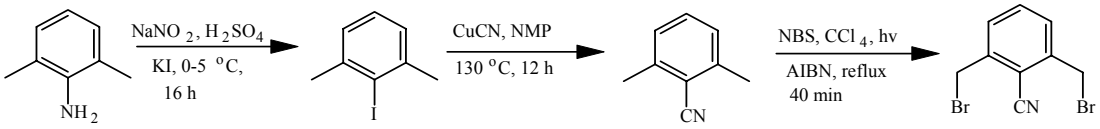
### 2.1.1 Synthesis of 2,6-bis-bromomethylbenzonitrile 102

Dibromide **102** was synthesized according to the literature procedure[55] with slight improvements. Diazotization of **103** using $H_2SO_4/NaNO_2$ followed by treatment with KI gave **104** in 67% yield (Scheme 2.2). When HCl was used, a 3:1 mixture of 2,6-dimethyliodobenzene **104** and 2,6-dimethylchlorobenzene **106** was obtained. This was surprising because chloride generally does not incorporate under these conditions unless cuprous salts are used.[56] 2,6-Dimethyl-chlorobenzene formation was confirmed from a control experiment, when KCl was used instead of KI, the chloro product was obtained although in relatively small quantities.




**106**

**Scheme 2.2 Synthesis of 2,6-bis-bromomethylbenzonitrile 102**

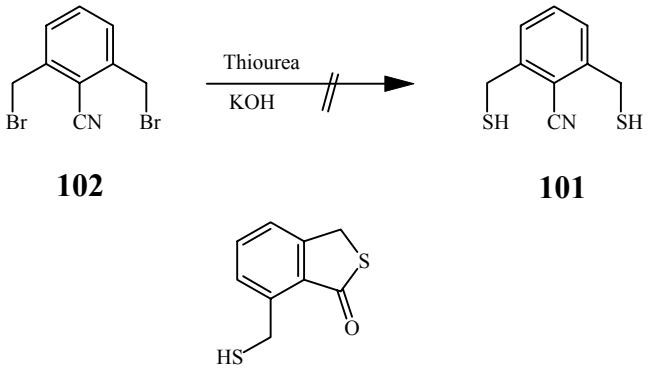



**103** **104** **105** **102**

Reaction of 2,6-dimethyliodobenzene with CuCN in NMP at 120 °C overnight gave almost quantitatively 2,6-dimethylbenzonitrile **105**. The reaction could be carried out in greater than 97% yield even on the large scale (200 g). Then, free radical benzylic bromination of **105** using NBS gave 56% of dibromide **102** (Scheme 2.2). The reaction gave four or five products with very close $R_f$ values on TLC. The desired product crystallized out cleanly from the product mixture using cyclohexane:dichloromethane (4:

1) as recrystallizing solvent mixture. Attempts were made to purify the side products using column chromatography, but these were unsuccessful.

**Scheme 2.3 Attempted formation of thiol 101**




**102** **101**

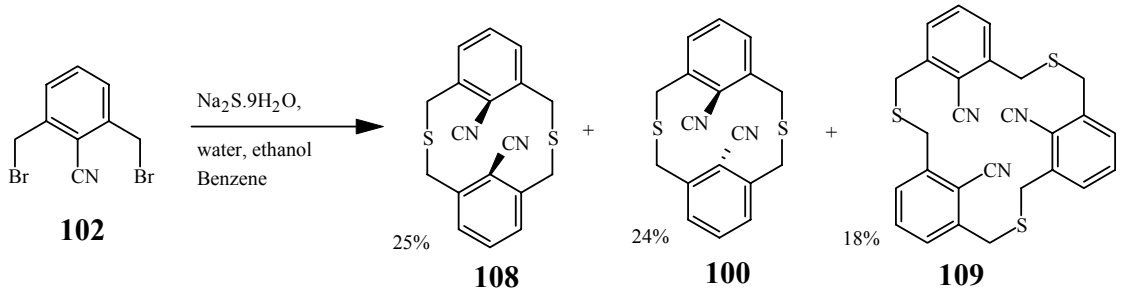
**107**

The functional group interconversion of bromide **102** to thiol **101** (Scheme 2.3) using thiourea and then KOH was unsuccessful. The pale yellow product mixture changed to orange red in a few minutes after the work up. Probably, the thiol formed reacted with the nitrile group to give a product, tentatively assigned as **107**. Change of the reaction conditions including temperature, KOH concentration, acid concentration during the acidification step and protection of the product from air also did not help to isolate the desired product.

### 2.1.2 Synthesis of dicyanothiacyclophanes 100 and 108

Although the synthesis of most dithiacyclophanes involved bis-thiol-bis-bromide coupling, many have been made by coupling dibromide with $Na_2S.9H_2O$, even the parent.[32]

**Scheme 2.4 Synthesis of nitrile thiacyclophanes 100, 108 and 109**




Bodwell[57] has reported that use of the reagent $Na_2S.9H_2O/Al_2O_3$ avoids high dilution conditions which are usually required. Addition of dibromide in small portions to $Na_2S.9H_2O/Al_2O_3$ gives moderate yields of thiacyclophanes (13-65%). The reaction is quite sensitive to the size of the internal groups. When hydrogens are the internal substituents, the yield is > 60% but it drops dramatically to 13% for the methyl analogue. Since a nitrile group is linear and sterically less demanding, it was anticipated to give a moderate yield. Bodwell's method, when tried on the small scale (sub millimolar quantities), gave 25-30% yield of the dicyanothiacyclophanes as a mixture of *syn*-**108** and *anti*-**100** isomers, however a gram scale reaction gave a very poor yield.

Under high dilution conditions, reaction of dibromide **102** and $Na_2S.9H_2O$ by slow addition from two dropping funnels in ethanol-benzene-water gave a 1:1 mixture of the *syn*- and *anti*-isomers **108** and **100** in 50% yield (Scheme 2.4). The major side product was the trimer **109**. Because of low atom efficiency, a 30 g scale reaction gave less than 8 g of the thiacyclophanes. Vogtle[58] first made this thiacyclophane in the seventies but little experimental data was reported, and so he may have obtained one or both isomers. We were able to purify each isomer and the trimeric species. Purification was a tedious job because these compounds were not soluble in most useful solvents

except dichloromethane, in which they were partially soluble. The low bp of dichloromethane ruled out recrystallization or selective dissolution. Separation was achieved by column chromatography but it required a long column and much solvent.

The assignment of structure for the *syn*- and *anti*-isomers was quite apparent from their $^{1}$H NMR spectra. Aromatic protons in the *syn*-isomer were shielded[32] to δ 7.15-7.07 vs. 7.66-7.60 in the *anti*-isomer because both benzene rings of **108** are parallel and experience each other's ring current. The aliphatic bridge protons of **108** showed a more widely spaced AB quartet at δ 4.55-3.81 while a closely spaced AB quartet at δ 3.94-3.88 was observed for **100**. The trimer **109** showed a singlet in the aliphatic region because of freely tumbling bridge protons while the aromatic protons were at δ 7.46-7.39. X-ray crystallographic analysis confirmed the *syn* and *anti* orientation in **108** and **100** respectively.

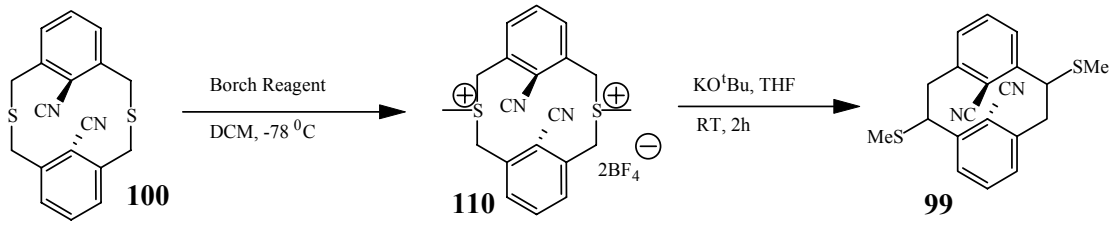
### 2.1.3 The Stevens rearrangement of the thiacyclophanes

The Wittig rearrangement is generally preferred for the conversion of thiacyclophanes to thiomethylcyclophanes. A nitrile group is sensitive to BuLi and thus LDA was used as the base to affect the Wittig rearrangement but it failed to give the desired product. The Stevens rearrangement involves the formation of a sulfonium salt intermediate which upon treatment with relatively mild base usually rearranges to the thiomethylcyclophanes as shown in Scheme 2.5. The Stevens rearrangement was carried out separately on the *syn*- and *anti*-thiacyclophanes.

### 2.1.3.1 The Stevens rearrangement of the *anti*-thiacyclophane 100 into the thiomethylcyclophane 99

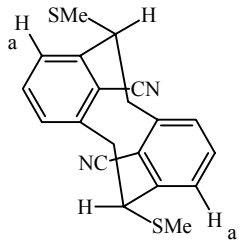
Methylation of **100** with dimethoxycarbonium fluoroborate[59] gave almost quantitatively the bis-sulfonium salt **110** (Scheme 2.5)**.** The $^1$H NMR spectrum showed all peaks deshielded relative to the thiacyclophane starting material. The methyl protons appeared at δ 3.45. The bridge aliphatic protons were four doublets between δ 5.2 and 4.2 while the aromatic protons were at δ 7.97 (d) and δ 8.14 (t). The sulfonium salt **110**, when reacted with potassium *tert*-butoxide in THF gave a mixture of the thiomethyl-*anti*-cyclophanes **99**.

**Scheme 2.5 The Stevens rearrangement of *anti*-thiacyclophane 100 into the thiomethylcyclophane 99**




The major isomer could be obtained in 48% yield by careful chromatography over silica using 60:40 dichloromethane:hexanes as eluant. This isomer, based on its $^1$H NMR spectrum, was assigned to contain both thiomethyl groups equatorially orientated.[32] The thiomethyl protons appeared as singlet at δ 2.17 while the bridge protons appeared as three doublets of doublets between δ 2.8 and 4.3. Complete assignment of the structure was made through HMBC, HSQC, COSY and NOESY experiments and is given in the experimental section. The IR spectrum confirmed the presence of the nitrile group by a

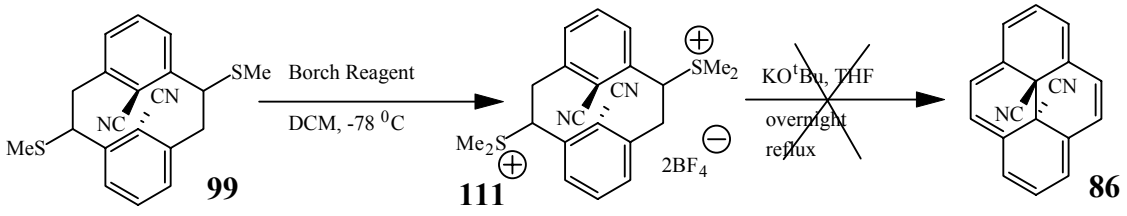
band at 2215 $cm^{-1}$. Cyclophane **99** had the expected HRMS at *m/z* 350.0902 (calculated 350.0911)




### 2.1.4 Formation of the sulfonium salt 111 and the subsequent Hoffmann elimination

In the subsequent steps, the single isomer of **99** was employed; however the reactions could be carried out on the mixture of isomers. The pure isomer, on treatment with dimethoxycarbonium fluoroborate gave the bis-sulfonium salt **111** in quantitative yield (Scheme 2.6). The $^{1}H$ NMR chemical shifts of **111** were similar to those of **99** but were deshielded because of the positive charge. The aliphatic protons alpha to the positive sulfur atoms were most deshielded and appeared at δ 4.92 while the other aliphatic protons appeared at δ 4.0 and 3.2.

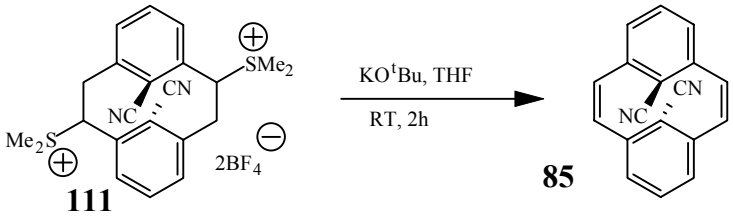
**Scheme 2.6 The attempted Hoffmann elimination to synthesize DHP 86**




Sulfonium salt **111,** on reaction with *t*-BuOK in refluxing THF failed to give the dihydropyrene **86** (Scheme 2.6). TLC analysis of the reaction showed a mixture of

fluorescent compounds which were thought to be pyrenes based on the chemical shifts in the $^1$H NMR spectrum. KH in refluxing THF also yielded a mixture of pyrenes; different from the one obtained using *t*-BuOK. NaH failed to give any products under similar conditions. Surprisingly, carrying out the reaction at room temperature gave the dicyano CPD **85** in > 90% as pale yellow crystals (Scheme 2.7) along with ~ 6% yield of **99**, obtained by demethylation. The course of the reaction was monitored using TLC. A pale yellow spot appeared immediately after the addition of *t*-BuOK to the suspension of sulfonium salt **111** in THF. This pale yellow product increased with time and stabilized after 20 minutes, so the reaction was quenched after a total of 30 min.

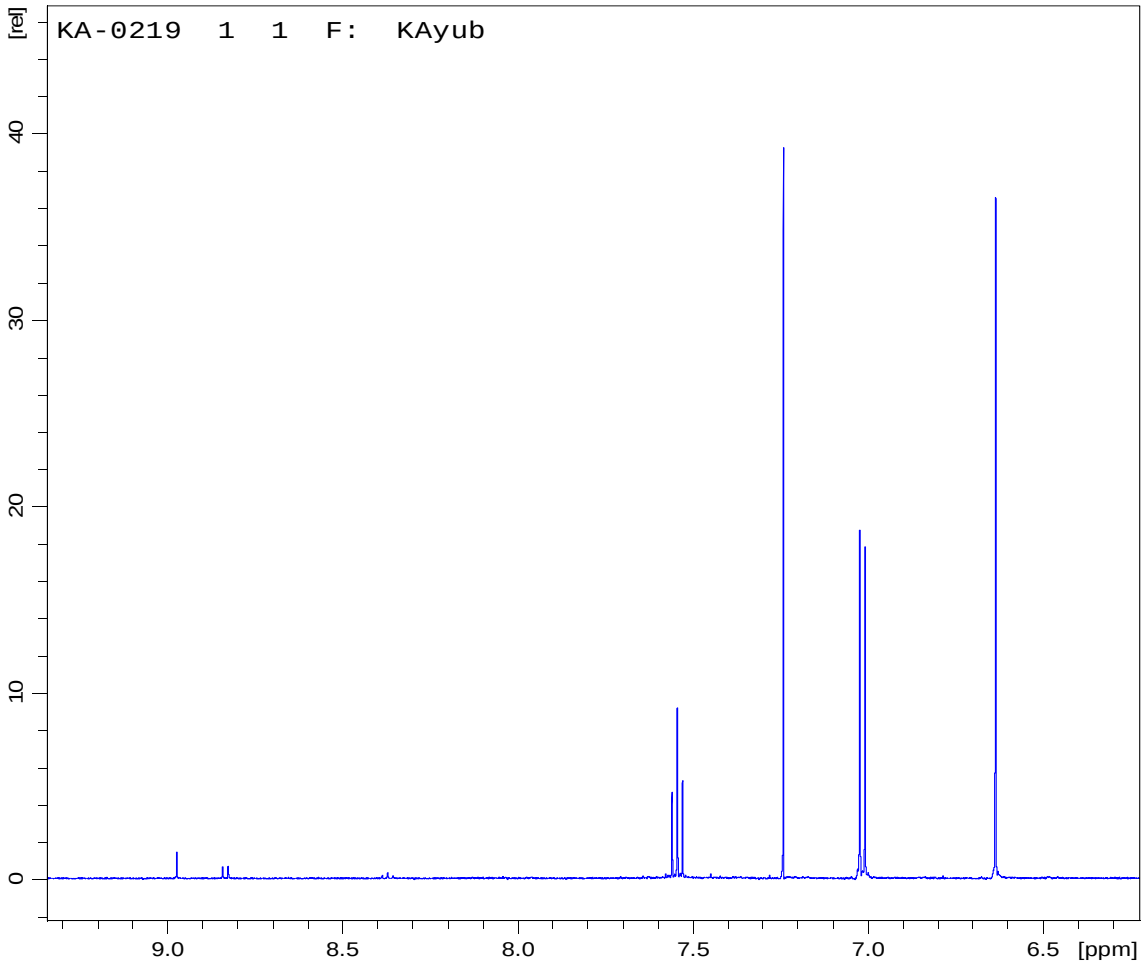
**Scheme 2.7 The Hoffmann elimination at room temperature**



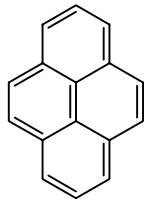

**111** **85**

The cyclophanediene **85** had poor solubility in most solvents except for dichloromethane and chloroform where it was soluble enough to obtain NMR spectra or to perform column chromatography. The $^1$H NMR spectrum of **85** (Figure 2.1), as expected because of symmetry, showed only three peaks, a singlet at δ 6.63 corresponding to the bridge alkene protons, a doublet at δ 7.01 and a triplet at δ 7.54. The nitrile group was confirmed by the IR band at 2215 cm$^{-1}$. Mass spectrometry gave the correct molecular ion peak at *m/z* 254.

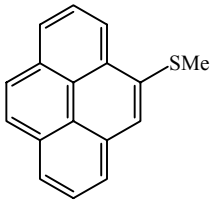
**Figure 2.1** **$^1$H NMR spectrum of dicyano CPD 85 in $CDCl_3$ at 500 MHz**




The mixture of isomers **99** when subjected to the S-methylation-Hoffmann elimination sequence also gave predominantly the cyclophanediene **85**. Pyrene **112** and the thiomethylpyrene **113** were also obtained in variable quantities and sometimes the only products of the reaction; however a small scale reaction at low temperature minimized the formation of the side products.



**112**

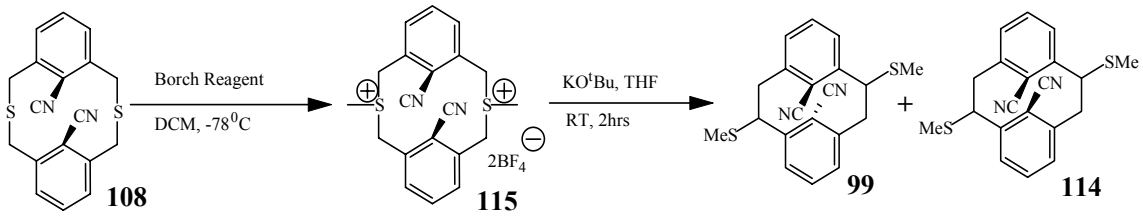



**113**

### 2.1.5 The Stevens rearrangement of the *syn*-thiacyclophane 108 to the thiomethylcyclophanes

Stevens' rearrangement of *syn*-**108** gave predominantly the *anti*-cyclophane **99** as a mixture of isomers. A small amount of the *syn*-isomers **114** was also obtained, which eventually gave the *cis*-DHP (Scheme 2.8) when this mixture was used directly in the subsequent steps. The fact that the *syn*-thiacyclophane yields a mixture of the *syn*- and *anti*-thiomethylcyclophanes is probably because of the high degree of steric strain in the *syn*- isomer which is relieved upon isomerization. The sulfonium salt **115,** formed by the methylation of **108,** showed methyl protons at δ 3.4 in the $^1$H NMR spectrum. Aliphatic bridge protons appeared as two doublets at δ 4.10 and δ 4.22 while aromatic protons were at δ 7.1- 7.5.

**Scheme 2.8 Stevens rearrangement of *syn*-thiacyclophane 108 into the thiomethyl cyclophanes**

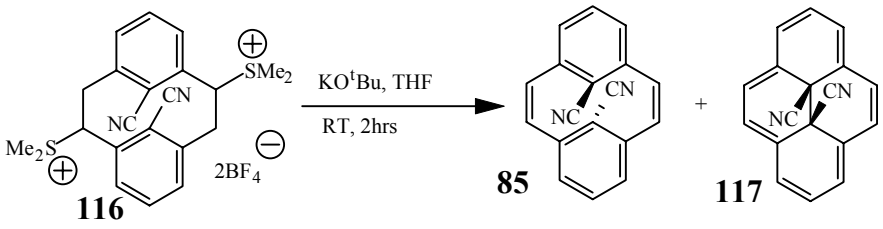



Attempts were made to obtain more of the *syn*-cyclophane (**114**) but were not successful. Low temperature or change of base e.g., LDA or NaH instead of *t*-BuOK gave more or less the same results.

### 2.1.6 Synthesis of the *cis*-DHP 117

The mixture of *syn*- and *anti*-isomers was methylated to yield the bis(dimethylsulfonium) fluoroborate salt **116** which on reaction with *t*-BuOK in THF at 20 $^{o}$C gave 90% of the *anti*-cyclophanediene **85** and 5% of the green *cis*-dihydropyrene **117**, mp 192 $^{o}$C (Scheme 2.9). The dihydropyrene showed three peaks in the $^{1}$H NMR spectrum, a singlet at δ 8.97, a doublet at δ 8.66 and a triplet at δ 8.10. The *cis* relationship of the internal nitrile groups was established by the X-ray structure determination.

**Scheme 2.9 The Hoffmann elimination at room temperature**




The *anti*-cyclophanediene **85** could not be cyclized thermally into the *trans*-dihydropyrene **86** in useful yields because of the subsequent migrations of the nitrile groups (Scheme 2.10). However irradiation with UV light converted **85** into the green *trans*-dihydropyrene **86** quantitatively (Scheme 2.10). Presence of the *trans*-dihydropyrene was quite apparent from its $^{1}$H NMR spectrum which showed a singlet at δ 8.97, a doublet at δ 8.83 and a triplet at δ 8.37 (Figure 2.2). The aromatic protons are strongly deshielded by the aromatic ring current from those of CPD **85**. The IR stretch at 2227 cm$^{-1}$ confirmed the presence of a nitrile group. The structure was confirmed by X-ray analysis.

**Scheme 2.10 Attempted thermal closing of dicyano CPD 85**

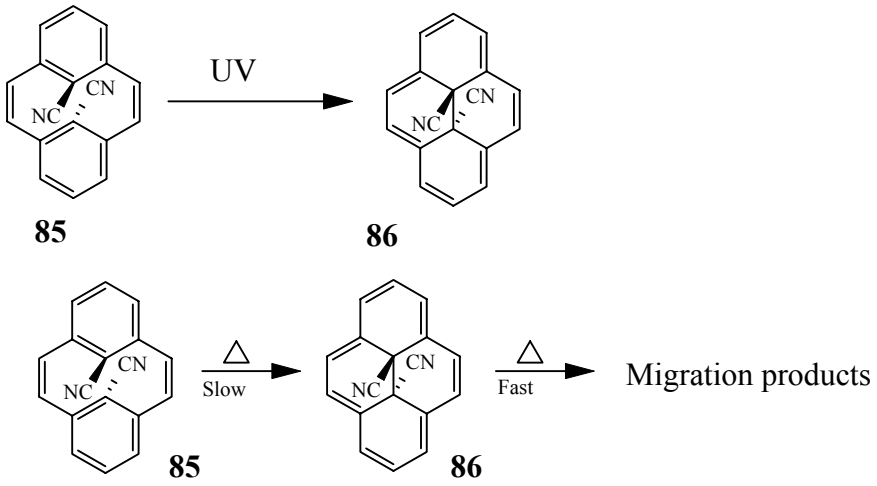
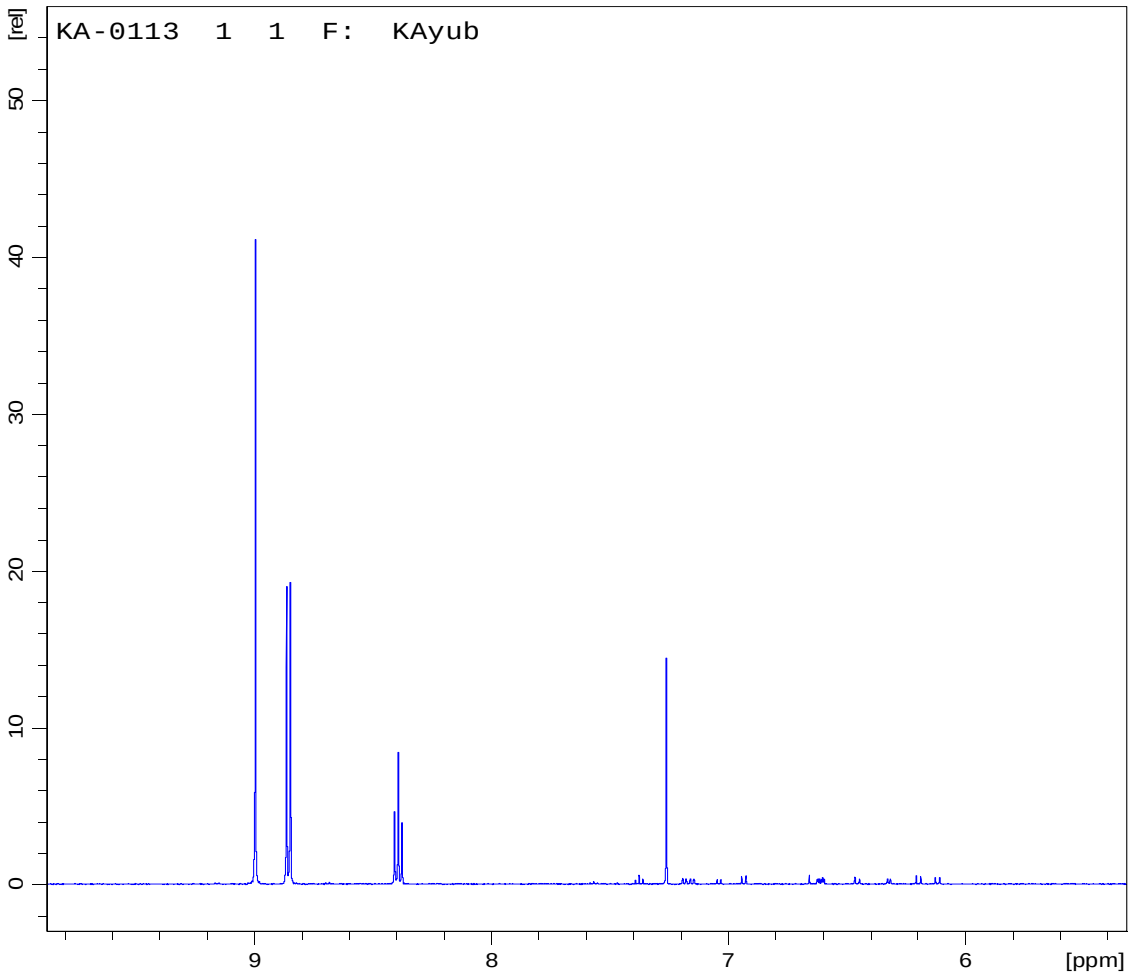


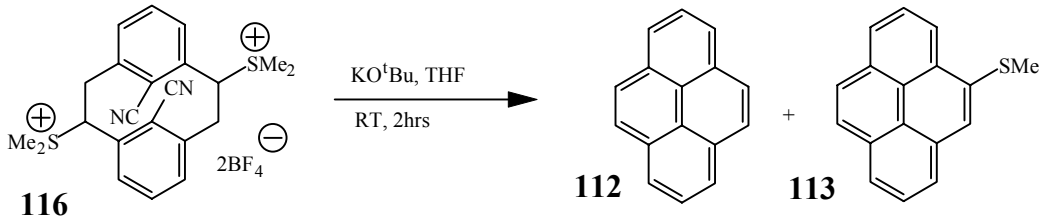
**Figure 2.2** **$^1$H NMR spectrum of dicyano DHP 86 in $CDCl_3$ at 500 MHz**




### 2.1.7 Pyrene and thiomethylpyrene formation

A nuisance in the Hoffmann elimination to prepare cyclophanediene **85** was the formation of pyrenes **112** and **113** in variable quantities (Scheme 2.11). Sometimes these pyrenes were the only products.

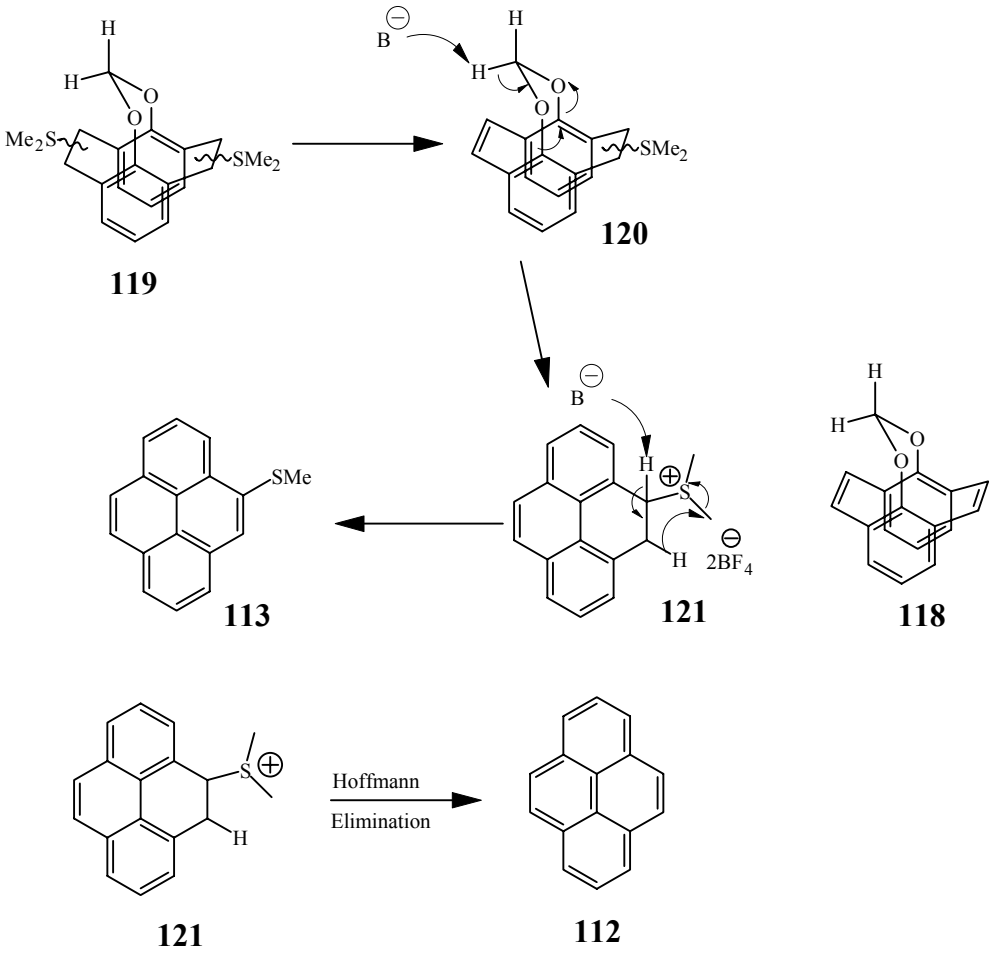
**Scheme 2.11 Formation of pyrene 112 and thiomethylpyrene 113**




**116** **112** **113**

Lai and Eu[60] have reported that pyrene **112** and 4-methylthiopyrene **113** are the only products in an attempted synthesis of the cyclophanediene **118**. The postulated mechanism is shown in Scheme 2.12 which involves an initial Hoffmann elimination in **119** to generate **120**.

**Scheme 2.12 Mechanism for the formation of the pyrenes**



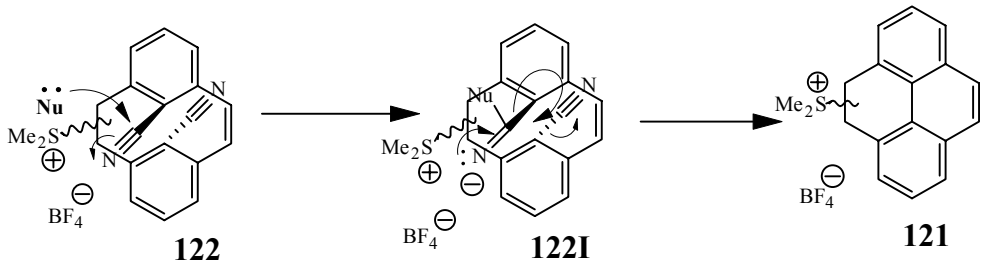

A proton abstraction from the central methylenedioxy bridge drives the extrusion of the internal substituents and forms a closed ring species **121** which upon Hoffmann elimination gives pyrene. Alternatively, abstraction of the most acidic proton in **121**, next to the positive sulfur atom, followed by a 1,4-hydride transfer and concomitant elimination of a methane molecule generates the 4-methylthiopyrene **113**.

In our case, the problem arose when;

1. The reaction was carried out on a large scale, one gram or more of the sulfonium salt **116**.

2. Crude thiomethylcyclophane **99** was employed directly in the formation of the sulfonium salt without purification on the column. This effect was more pronounced when NaH was used to affect the Stevens rearrangement (Scheme 2.5 & 2.8).
3. Neutral (non acidic) work up was used.

**Scheme 2.13 Mechanism for the elimination of the internal nitrile groups during the Hoffmann elimination.**

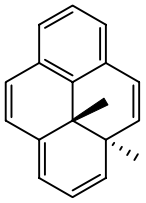



Thiomethylpyrene **113** was the major product in the first two cases while in the third case, only pyrene **112** was formed.

A mechanism involving abstraction of a proton from the internal substituent is excluded when nitriles are the internal substituents. A plausible mechanism could be the attack of a nucleophile on the nitrile in **122** to form the intermediate **122I**. Then, the electronically driven elimination of the internal substituents would form **121** as shown in Scheme 2.13. Monoene **121** would eventually lead to the pyrenes via Lai's mechanism[60] (Scheme 2.12).

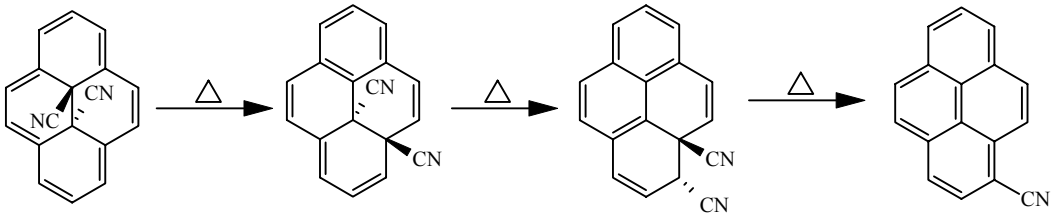
### 2.1.8 Migration of the nitrile groups over the π system and finally an elimination of HCN

When the *anti*-DHP **86** was left at room temperature for a week, partial decomposition was observed (TLC showed a new colorless spot). EI MS indicated that this new product was isomeric with **86**. Heating the NMR sample of **86** at 70 $^{o}$C for 30 minutes gave a clean spectrum of this isomeric colorless product.



**123**

**Scheme 2.14 Migration and elimination of nitrile group**




**86** **124** **125** **126**

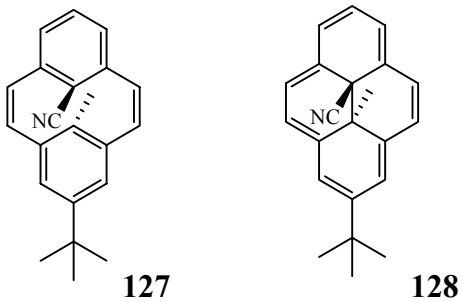
Boekelheide[61] reported that the internal methyl-substituted DHP **43** rearranged on heating at 200 $^{o}$C to **123.** With other internal groups such as Et, Pr and H, lower isomerization temperatures have been observed.[62] The spectrum of our isomerization product was consistent with structure **124,** analogous to **123**. The presence of the nitrile groups was confirmed by the IR band at 2227 cm$^{-1}$ and by the $^{13}$C NMR peaks at δ 116.65 and 116.15. The relative orientation of the two nitrile groups is based on the Woodward-Hoffmann rules.

When this 1st migration product **124** was heated at 70 °C for 4 days, formation of another isomeric colorless product **125** was observed (Scheme 2.14). This product, in contrast to its isomeric **124**, was quite sensitive to chromatography using silica as adsorbent and decomposed to 1-cyanopyrene **126**. The 2nd migration product **125,** which contains a naphthalene skeleton, has its $^1$H NMR peaks somewhat downfield compared to the 1st migration product **124.** The aliphatic CH bearing the CN group appeared at δ 3.92 as doublet of doublets. In its IR spectrum, the nitrile band was at 2224 cm$^{-1}$. Once again the *anti* relationship of the nitriles was based on the Woodward-Hoffmann rules. Each proton and carbon in isomeric products **124** and **125** were assigned using NOESY, COSY, HMBC and HSQC techniques.

The 2nd migration product when heated at 110 °C for 8 hrs or passed through a silica column gave 1-cyanopyrene **126,** which is commercially available and showed identical physical properties (mp, $^1$H NMR data) to literature values.[63]

## 2.2 Synthesis of 2-(*t*-butyl)-10b-methyl-10c-cyano-*trans*-10b,10c-dihydropyrene 128

Introduction of the internal nitrile groups has enhanced the thermal stability of the cyclophanediene **85** but the migration of the nitriles in the DHP **86** prohibits its use as a photoswitch. A requirement for a photoswitch is the stability of both isomers. It was, however, of interest to synthesize the switch pair **127/128** to see how does a combination of a nitrile and a methyl as the internal substituents affect the properties of the photoswitch.

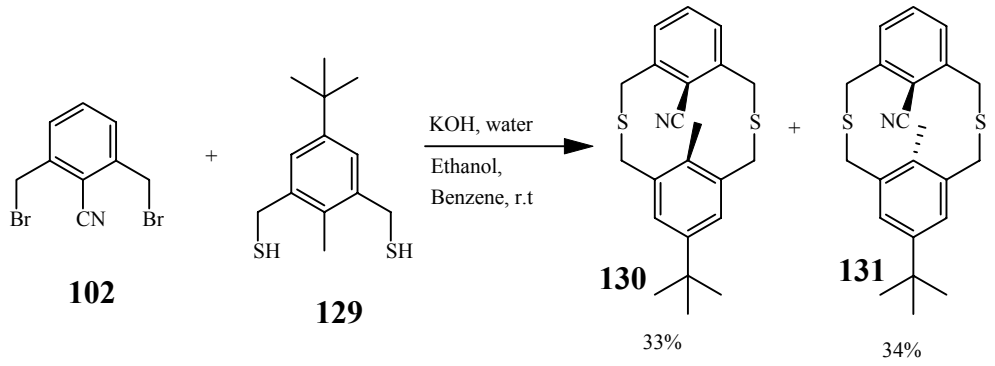



**127** **128**

### 2.2.1 Synthesis of the cyano-methylthiacyclophanes 130 and 131

Under high dilution conditions, coupling of dibromide **102** and dithiol[33,64] **129** gave a 1:1 mixture of the *syn*-**130** and *anti*-**131** thiacyclophanes in 67% yield (Scheme 2.15).

**Scheme 2.15 Synthesis of thiacyclophanes 130 and 131**




**102** **129** **130** **131**

33% 34%

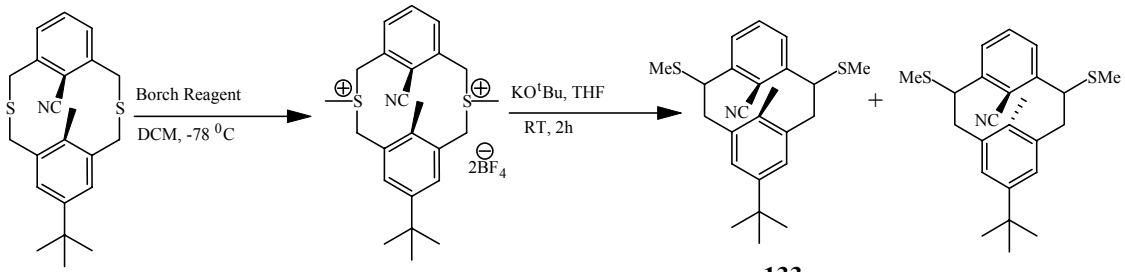
The *ant*- and *syn* isomers were separated by column chromatography on silica using 35:65 and 45:55 dichloromethane:hexanes respectively. Both isomers were readily identified by their $^{1}$H NMR spectra. The aromatic protons in **130** were shielded and appeared at δ 6.9-7.1 whereas in the *anti*-isomer they appeared at δ 7.5. The internal methyl protons in **130** appeared at δ 2.56 whereas in **131** they were shielded by the opposite aromatic ring and appeared at δ 1.43. The IR stretches at 2217 cm$^{-1}$ and 2214 cm$^{-1}$ in **131** and **130,** respectively, confirmed the presence of the internal nitrile groups.

Satisfactory elemental analyses were obtained for both isomers. Finally, both isomers were confirmed by X-ray structures. The Stevens rearrangement was then carried out separately on each of the *syn*- and *anti*-thiacyclophanes.

### 2.2.2 The Stevens rearrangement of the *syn*-thiacyclophane 130

Treatment of *syn*-dithiacyclophane **130** with dimethoxycarbonium fluoroborate afforded the bis-sulfonium salt **132** quantitatively which underwent the Stevens rearrangement in the presence of *t*-BuOK to give a mixture of the *syn*- and *anti*-thiomethylcyclophanes, **133** and **134,** respectively (Scheme 2.16). In the $^1$H NMR spectrum, the protons of the internal methyl group of **134** appeared at δ 0.5-0.8 compared to δ 2.0-2.2 in **133**. In addition, the aromatic protons in the *syn*- isomer were shielded to δ 6.3-7.2 when compared to the *anti*-isomers, δ 7.0-8.0.

**Scheme 2.16 Stevens rearrangement of the *syn*-thiacyclophane 130**




**130** **132** **133** **134**

An *anti*-isomer of **134** could be purified by careful chromatography over silica using 30:70 dichloromethane:hexanes. This isomer, based on its $^1$H-NMR spectrum was assigned to contain two equatorial thiomethyl groups. The internal methyl protons showed an upfield signal at δ 0.54 (singlet) while the aromatic protons were at δ 7.2-8.0.

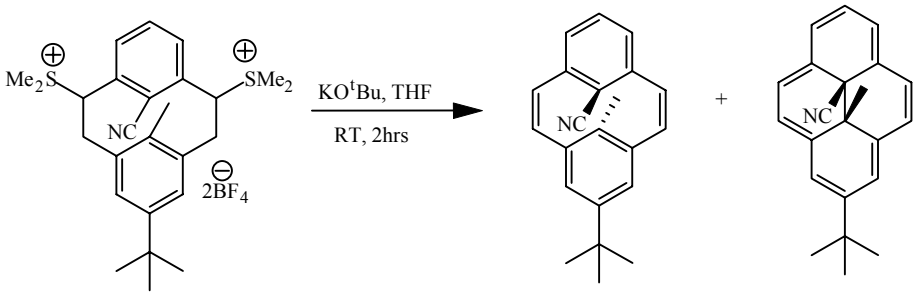
The IR spectrum confirmed the presence of the nitrile by a stretch at 2216 $cm^{-1}$. Finally, X-ray analysis established the structure.

### 2.2.3 The Hoffmann elimination of the thiomethylcyclophanes 133 and 134

The mixture of thiomethylcyclophanes was methylated to give the air sensitive sulfonium salt **135** which on Hoffmann elimination with *t*-BuOK in THF at room temperature gave 60% of the *cis*-dihydropyrene **136** and 28% of the *anti*-cyclophanediene **127** (Scheme 2.17). Both products were separated by column chromatography on silica gel.

Cyano-methyl CPD **127**, as expected because of its symmetry, showed a total of seven peaks in the $^{1}H$ NMR spectrum. The bridge alkene protons showed an AB pattern at δ 6.6-6.3 with a coupling constant of 11.3 Hz. The aromatic protons appeared as a triplet δ 7.28, a doublet at δ 6.85 and a singlet at δ 6.79. The peak corresponding to the protons of the internal methyl was a singlet at δ 1.57, a characteristic of *anti*-cyclophanedienes. A peak at δ 115.92 in the $^{13}C$ NMR spectrum indicated the presence of the nitrile which was confirmed by a band at 2215 $cm^{-1}$ in the IR spectrum.

**Scheme 2.17 The Hoffmann elimination to generate cyano-methyl CPD 127 and *cis*-DHP 136**




**135** **127** **136**

The mass spectrum showed the correct molecular ion peak at *m/z* 299. A satisfactory elemental analysis could not be obtained probably because of higher percentages of carbon. Extended combustion using $V_2O_5$ also failed to give the correct analysis.

The *cis*-DHP **136** was obtained as dark green crystals, mp 108-109 $^oC$. A peak at δ -1.60 in the $^1H$ NMR spectrum corresponding to the internal methyl protons indicated the *cis* relationship of the internal substituents. *Cis*-dihydropyrenes are generally saucer shaped which results in different chemical shifts for the external and internal protons when compared with their *trans* counterparts. Moreover, the internal methyl group is farther away from the center of the ring than in the *trans*-DHP and appears relatively downfield at ~ δ -2.0 (*trans*-DHP ~ δ -4.0). The dihydropyrene protons were between δ 7.8 and 9.0. The *cis*-DHP had the expected HRMS at *m/z* 299.1670 (calculated 299.1674). All peaks in the $^1H$ and $^{13}C$ NMR spectrum of the cyano-methyl CPD **127** and *cis*-DHP **136** could be assigned.

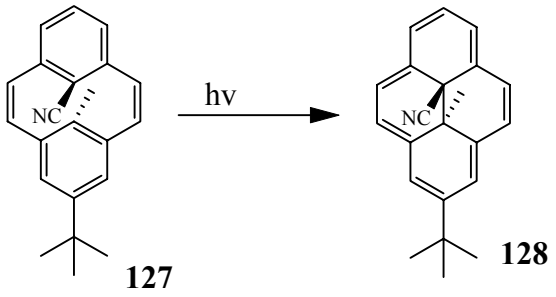
### 2.2.4 The Stevens rearrangement of the *anti*-thiacyclophane 131

The Stevens rearrangement-Hoffmann elimination sequence starting from thiacyclophane **131** gave the *anti*-CPD **127** exclusively. Lai and Zhou[65] have reported that in the non *t*-butylated analogue, the *anti*-thiacyclophane gives *cis*-DHP through the Stevens rearrangement-Hoffmann elimination sequence. However we did not see any such isomerization.

### 2.2.5 Photochemical isomerization of cyano-methyl CPD 127 into the *trans*-DHP 128

Cyano-methyl DHP **128** was obtained photochemically from the CPD **127** (Scheme 2.18); an attempted thermal closure gave the migration product **137** (Scheme 2.19). Facile migration of the internal nitrile of **128** at room temperature did not permit obtaining clean NMR spectra of **128**. The *trans*-dihydropyrene nucleus was readily identified by a peak at -4 ppm in the $^{1}$H NMR spectrum corresponding to the internal methyl protons. The DHP protons appeared at δ 8.6 -7.7.

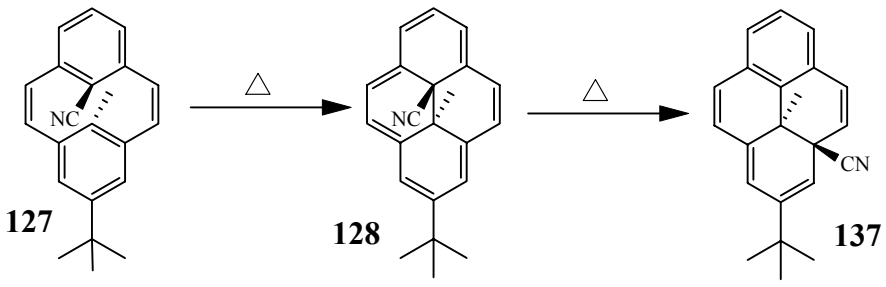
**Scheme 2.18 Generation of 128 by photochemical isomerization**




### 2.2.6 Migration of the internal nitrile in cyano-methyl DHP 128

Cyclophanediene **127,** when heated at 70 $^{o}$C for three hours gave the migration product **137**.

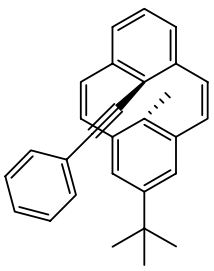
**Scheme 2.19 Migration of the internal nitrile group in 128**



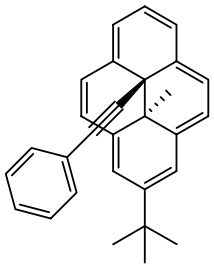
The cyclophanediene **127** closes thermally to the dihydropyrene **128** which rapidly decomposes to **137** by a [1,5]-sigmatropic shift of the nitrile. Complete assignment of all protons and carbons was made in the DHP **128** and in the migration product **137**.

## 2.3 Synthesis of phenylethynyl/methyl DHP 139

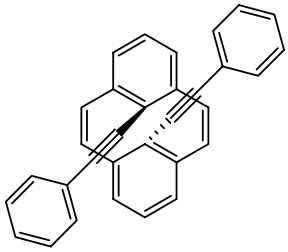
The cyano-methyl switch pair **127/128** showed much higher migration and thermal closing rates when compared with the dinitrile switch pair **85/86.** Both switch pairs were more stable to the thermal return than the methyl parent, **52/45**. Nitrile groups at the internal positions reduce the thermal closing rates of the CPDs to the DHPs but they have much higher migration aptitude compared to the methyl groups. Replacement of the nitrile group in **127/128** by a phenylethynyl substituent was anticipated to slow down the migration of the internal group in phenylethynyl/methyl DHP **139**. The choice of the phenylethynyl group was based on its structural similarity with the nitrile; both groups are rod-like in nature. The switch pair **138/139** was preferred over the pair **140/141** because of the ease of the synthesis of the former.



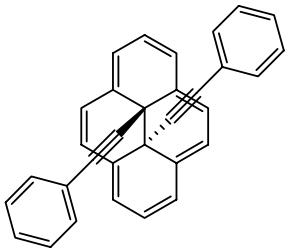
**138**



**139**



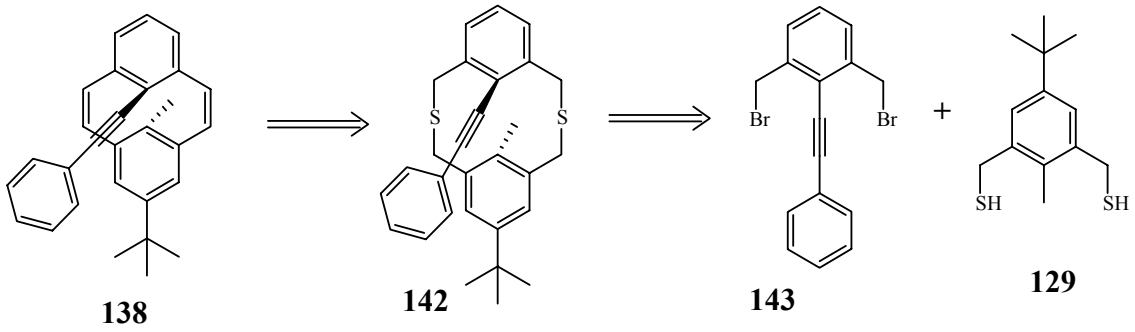
**140**



**141**

Our approach towards the synthesis of **138** was based on the synthesis of the thiacyclophane intermediate **142.** The thiacyclophane in turn can be made from dibromide **143** by coupling with **129** (Scheme 2.20).

**Scheme 2.20 Reterosynthetic analysis of phenylethynyl/methyl CPD 138**

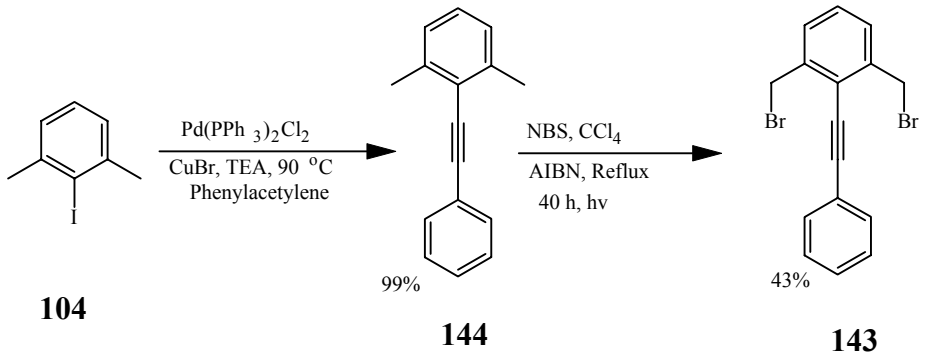



**138** **142** **143** **129**

### 2.3.1 Synthesis of the bis(bromomethyl) diphenylacetylene 143

Dibromide **143** was prepared as shown in Scheme 2.21. Sonogashira coupling of the iodide **104** with phenylacetylene using $Pd(PPh_3)_2Cl_2$ as a catalyst in refluxing TEA gave the diphenylethynyl derivative **144** in quantitative yields. Alkyne **144** was brominated at the benzylic positions with NBS in refluxing $CCl_4$ under photochemical conditions to give **143** in ~ 43% yield. The reaction was sluggish and required relatively large quantities of the AIBN catalyst. Fortunately, the desired product could be selectively crystallized from a mixture of five or six compound with very close $R_f$ values on TLC. The mp and the NMR data of **143** were identical to the literature values.[66]

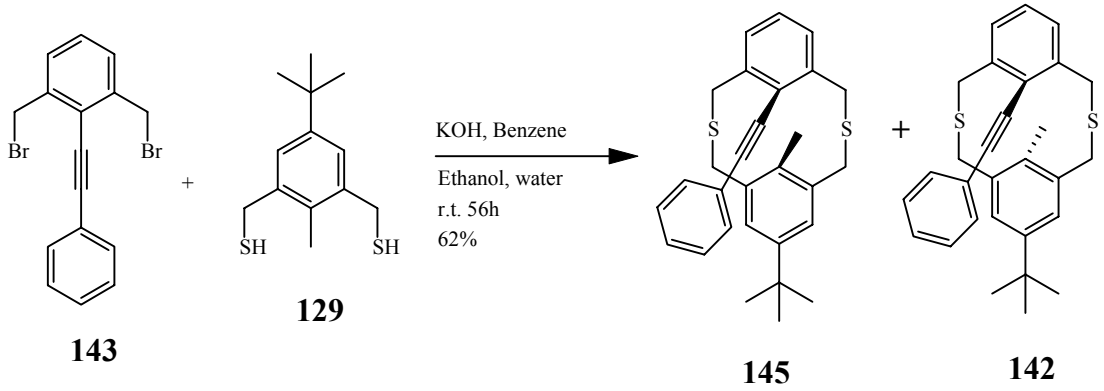
**Scheme 2.21 Synthesis of the dibromide 143**



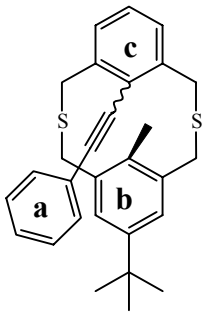

### 2.3.2 Thiacyclophane formation by coupling dibromide 143 and dithiol 129

Slow addition (one drop per seven seconds) of dibromide **143** and dithiol **129** in ethanol-benzene-water containing KOH under high dilution conditions gave a 3:1 mixture of the *syn*- and *anti*-dithiacyclophanes in 62% yield (Scheme 2.22). The slow drop rate was required probably due to the sterically demanding phenylethynyl group. The *syn*- isomer could be crystallized selectively from cyclohexane while the purification of the *anti*-isomer required multiple columns using column chromatography on silica gel.

**Scheme 2.22 Coupling reaction to yield dithiacyclophanes 142 and 145**



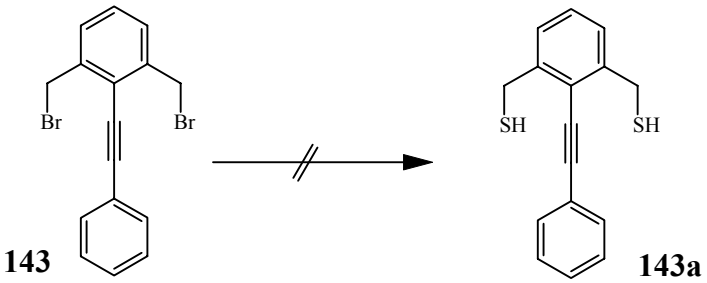
. The protons of the internal methyl group of *anti*-**142** showed an upfield shift due to the ring current of ring "**c**" and appear at δ 1.42 in the $^{1}$H NMR spectrum whereas the corresponding protons in **145** were normal and appeared at δ 2.54.




In addition, the aromatic protons of **142** showed the normal *anti*-thiacyclophane pattern and appeared at δ 7.40-7.27 where as the aromatic protons of **145** were shifted upfield to δ 7.00. Moreover, in the *anti*-isomer **142**, protons from the phenylethynyl aromatic ring (ring **a)** experience the shielding effect of ring **b** and appear at δ 7.43-7.31 when compared with the *syn*-isomer, δ 7.62-7.44 and this close spatial orientation was further supported by an NOE interaction of the *meta* protons of ring **a** with the aromatic protons of ring **b**.

The *sp*-carbons of the phenylethynyl group in both isomers were confirmed by $^{13}$C NMR spectroscopy by peaks at δ 100-87. All protons and carbons in **145** could be assigned but in **142,** complete assignment in the $^{1}$H NMR spectrum was not possible because of overlapping peaks. The correct structures were indicated by HRMS at *m/z* 442.1782 and 442.1779 for **145** and **142** (calculated 442.1788). The structure of the *syn*-isomer was also confirmed by X-ray analysis.

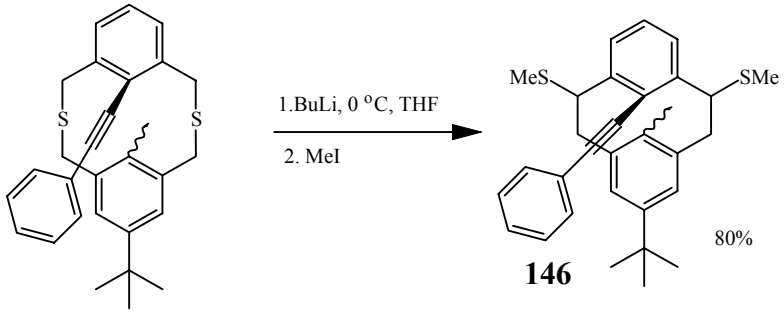
**Scheme 2.23 An attempted synthesis of 2,6-bis-(thiomethyl)diphenylacetylene**




An attempted reaction to convert dibromide **143** to dithiol **143a** (Scheme 2.23) using thiourea and then KOH was unsuccessful. Quite analogous to the reaction of **102,** an orange red product was obtained.

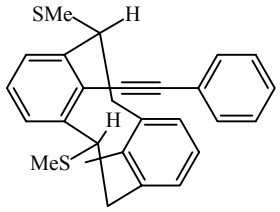
### 2.3.3 The Wittig rearrangement on the phenylethynylthiacyclophanes

**Scheme 2.24 Wittig rearrangement to prepare thiomethylcyclophanes 146**




Wittig rearrangement of the thiacyclophanes (mixture of isomers) using BuLi in THF followed by MeI gave a mixture of *syn*- and *anti*-thiomethylcyclophanes **146** in 80% yield (Scheme 2.24). The Wittig rearrangement was accomplished successfully on the smaller scale (less than a millimole); however a large scale reaction gave an insoluble gum like material.

The product mixture consisted mostly of *anti*-isomers. This inference is based on the comparison of the peaks at δ 2.5 for the internal methyl groups in the *syn*-isomers with those of the *anti*-isomers at δ 0.6 in the $^{1}$H NMR spectrum. The major isomer of **146** was purified by column chromatography using hexane:dichloromethane 7:1 and was fully characterized. X-ray structure determination confirmed the geometry shown in **146a**.

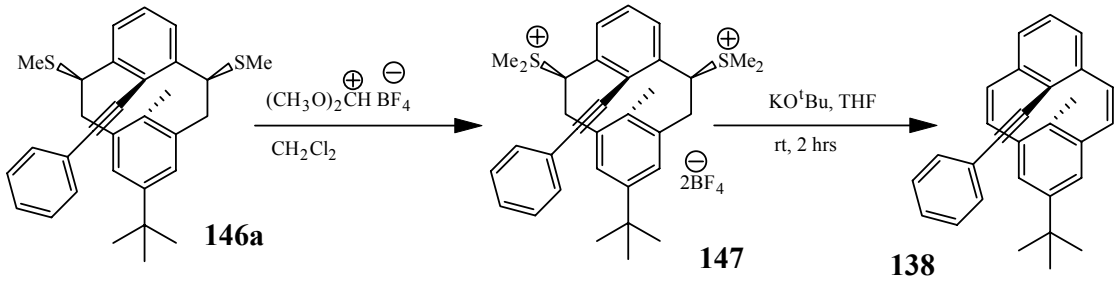



**146a**

### 2.3.4 Synthesis of CPD 138 by Hoffmann elimination and its isomerization to the DHP 139

Isomer **146a** when reacted with dimethoxycarbonium fluoroborate afforded the sulfonium salt **147** which on Hoffmann elimination gave the *anti*-cyclophanediene **138** (Scheme 2.25). These two steps were carried out in greater than 90% yield. To avoid thermal return, cyclophanediene **138** was chromatographed in a jacketed column with ice water flowing through it. In its $^{1}$H NMR spectrum, the phenylethynyl protons were at δ 7.25. Protons from the CPD nucleus showed seven peaks at δ 7.12-6.32. The internal methyl protons appeared at δ 1.65, characteristic of *anti*-CPDs. The ethynyl carbons were confirmed by the $^{13}$C NMR peaks at δ 89.98 and 95.13.

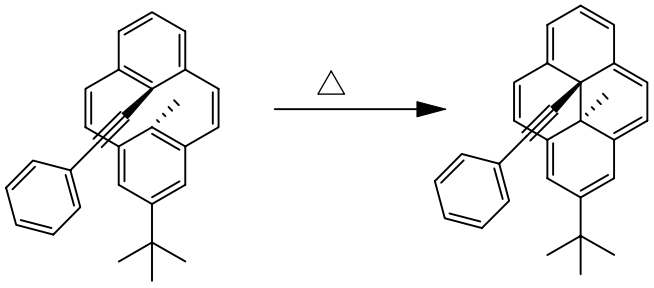
**Scheme 2.25 Synthesis of the phenylethynyl/methylcyclophanediene 138**




**146a** **147** **138**

Diene **138** was isomerized thermally into the green *trans*-DHP **139,** mp 112-113 $^oC$ (Scheme 2.26)**.** The transformation could be monitored by the growth of the peak at δ -4 in the $^1H$ NMR spectrum, corresponding to the internal methyl protons. The DHP protons were at δ 8.72-8.07. A decrease in the diatropic ring current of the DHP with distance was shown by the chemical shifts of the phenylethynyl protons. The *ortho* protons are close to the DHP ring and are shielded to δ 6.04 when compared with the *meta* (δ 6.72) or *para* (δ 6.83) protons. The ethynyl spacer was confirmed by the $^{13}C$ NMR spectrum in which the carbons appeared significantly shielded at δ 84.61 and 75.41 as compared to those of CPD **138** (δ 95.13 and 89.98). Besides spectral data, the structure of the *trans*-DHP **139** was also confirmed by a crystal structure.

**Scheme 2.26 Thermal closure of phenylethynyl/methyl CPD 138 to the DHP 139**

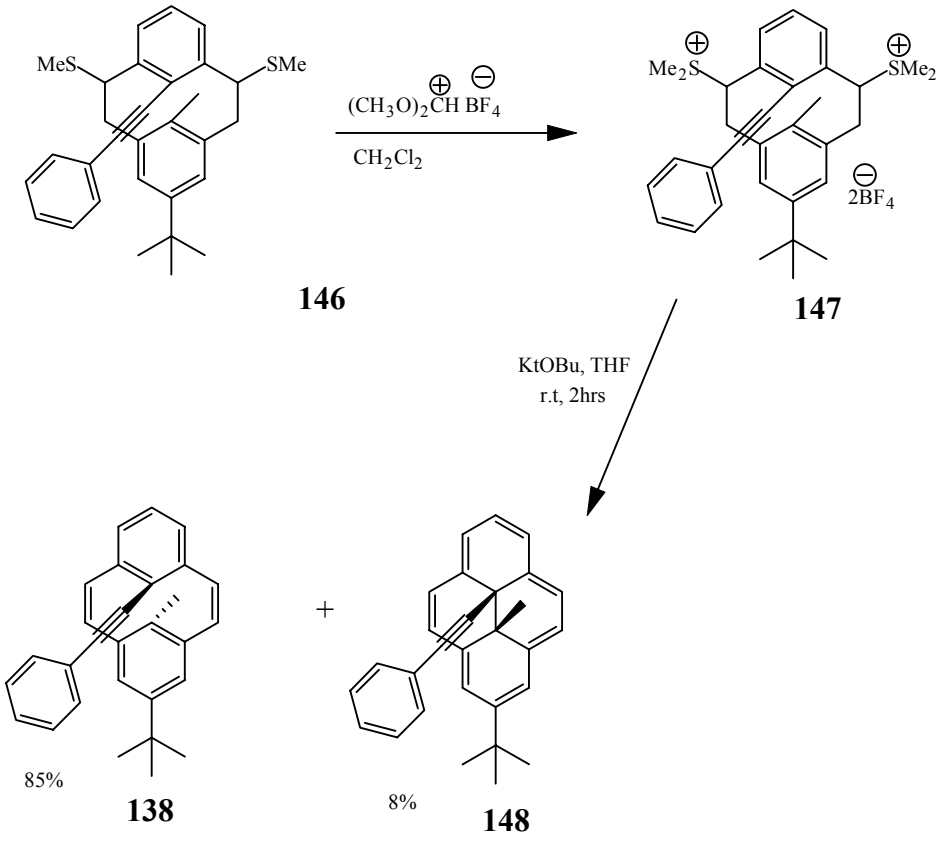



**138** **139**

### 2.3.5 Synthesis of the *cis*-DHP 148

Methylation of **146** (mixture of *syn*- and *anti*-isomers) with Borch[59] reagent gave the sulfonium salt mixture **147** (Scheme 2.27) which underwent Hoffmann elimination to afford **138** as the major product (85% yield) along with an 8% yield of the green *cis*-DHP **148,** mp 159-160 $^{o}$C.

**Scheme 2.27 Hoffmann elimination of mixed isomers of 147**

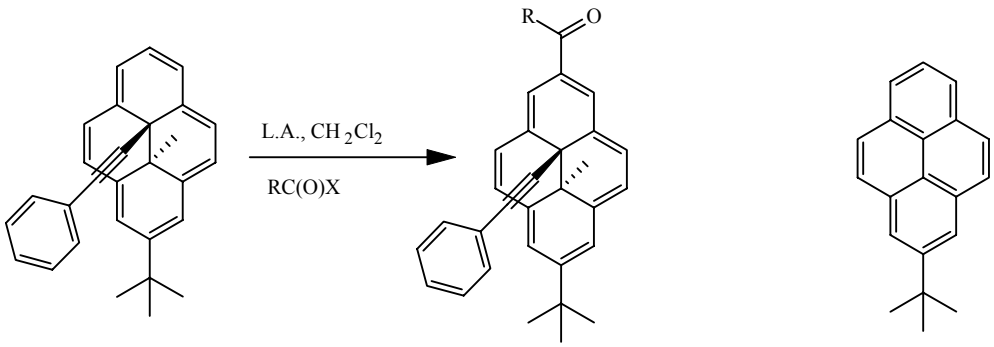



The *cis* orientation of the internal groups in the DHP **148** was easily established by a peak at δ -1.55 in the $^{1}$H NMR spectrum. The *ortho* protons of the phenylethynyl ring were shielded to δ 6.67 when compared with the *meta* and *para* protons, δ 6.97-7.00. The structure of the *cis*-DHP **148** was confirmed by an X-ray structure determination.

### 2.3.6 Attempted syntheses of acyl DHP 149 by Friedel-Crafts acylation

Phenylethynyl/methyl DHP **139** was quite stable and did not decompose to any migration product(s) when heated at 70 $^{o}$C. Moreover, the cyclophanediene **138** isomerized to the DHP **139** at slower rates when compared with the benzo CPD **53** (for details see Chapter 3). But an attempted photobleaching of **139** did not produce **138** at all. Carbonyl functionality at the 2- and 4- positions of DHP is known to enhance the visible opening rates.[67] We became interested in installing an acyl group at the C-2 position of DHP **139**.

**Scheme 2.28 Attempted Friedel-Craft acylation to yield 149**



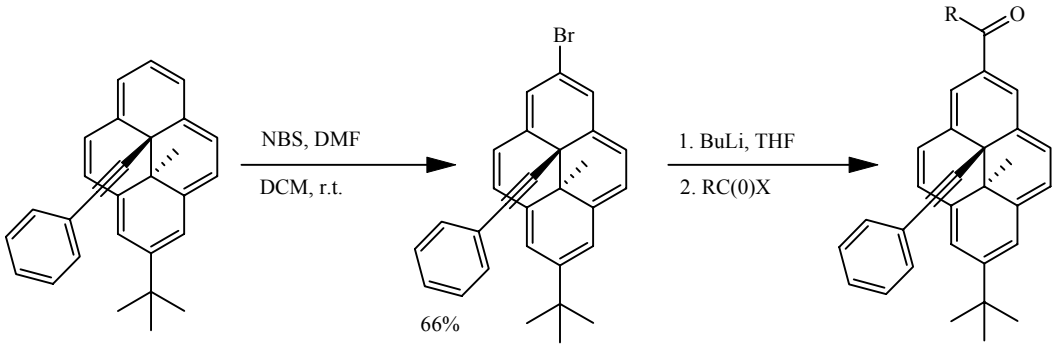

**139** **149** **150**

Different combinations of Lewis acids (L.A.) ($BF_3.Et_2O$, $AlCl_3$) and acylating agents (acetic anhydride, benzoyl chloride, naphthoyl chloride) were tried to prepare **149** but were unsuccessful. The green color of the dihydropyrene faded to pale yellow in a few minutes after the addition of Lewis acid which indicated its decomposition. The major isolated product was *t*-butylpyrene **150** which is formed probably by the migration and subsequent eliminations of the internal groups.

### 2.3.7 An anionic approach to the synthesis of the acyl DHP

An alternative approach to synthesize **149** is shown in Scheme 2.29 which avoids the use of Lewis acids. Phenylethynyl/methyl DHP **139** was brominated to **151** using NBS in dry DMF and dry DCM in variable yields. Robinson[35] has reported that carrying out the bromination reaction at room temperature gives high yields and the results are quite reproducible. We failed to gain reproducible results under similar conditions and the yield varied between 0-66%. A 1:1 ratio of M and M+2 peaks in the mass spectrum of **151** confirmed the presence of a bromine atom. Bromide **151** was lithiated with *n*-BuLi in THF to generate an anion of the DHP which on treatment with benzoyl bromide afforded a product probably the desired one.

**Scheme 2.29 Attempted synthesis of 149 involving a bromide intermediate 151**




**139** **151** **149**

This product could not be purified by column chromatography from a co-eluting side product. Selective recrystallization also failed. No further attempts were made to prepare **149**; rather attention was diverted towards the synthesis of other photoswitches.

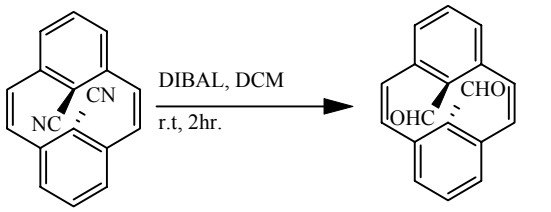
## 2.4 Chemistry at the internal substituents

The switch pairs **85/86** (dicyano)**, 127/128** (cyano-methyl) and **138/139** (phenylethynyl), though synthesized successfully, required lengthy and time consuming syntheses. Each of them required the synthesis of a new thiacyclophane. If FG transformations could be performed on a preformed cyclophanediene or dihydropyrene nucleus then it would generate a new switch pair in a single step. For this purpose, switch pair **85/86** was chosen. Dicyano CPD **85** was preferred over the DHP **86** for its use in a chemical reaction because it is thermally stable. Moreover, the CPDs formed from the reaction would allow performing kinetic analysis even if the corresponding DHPs are not photochromic.

### 2.4.1 DIBAL-H reduction of the dinitrile 85

DIBAL-H reduction of **85** in DCM (Scheme 2.30) at room temperature gave **152** in 56% yield. The desired product could be purified either by crystallization from methanol or by column chromatography using EtOAc:DCM 1:9 as eluant.

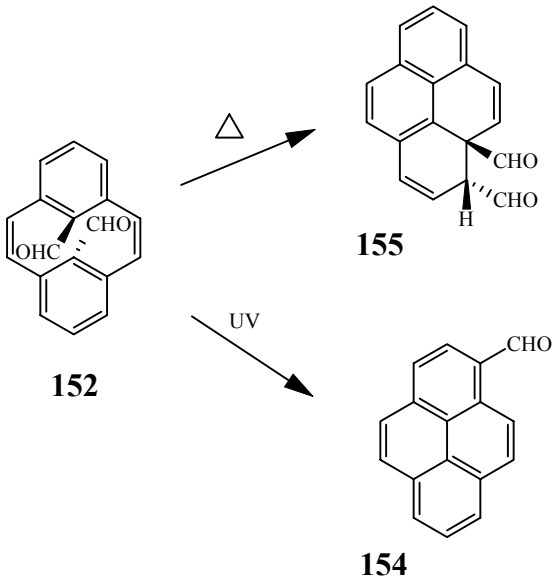
**Scheme 2.30 Reduction of the dinitrile 85 to the dialdehyde 152**




**85** 55% **152**

The aldehyde group was identified by the $^{1}H$ NMR and $^{13}C$ NMR peaks at δ 9.35 and 185.77 respectively. The IR bands at 2768 and 1712 $cm^{-1}$ confirmed the aldehyde group. The side products were minimized at lower temperature.

**Scheme 2.31 Thermal rearrangement of the internal formyl groups**




**152** **155** **154**

When diformyl CPD **152** was irradiated with UV light (254 nm), it gave 1-formylpyrene, **154** (Scheme 2.31) instead of the DHP **153** while the attempted thermal isomerization gave the migration product **155**.


**153** **156**

### 2.4.1.1 The [1,5]-sigmatropic rearrangement of the formyl groups

An NMR sample of **152** in $CDCl_3$, when heated at 70 $^oC$ for one hour gave the migration product **154**. No traces of the first migration product **156** analogous to **123** or **124** (Scheme 2.14, page # 48) could be found by $^1H$ NMR spectroscopy. This could be either due to the simultaneous migration of both formyl groups in **153** or because of the

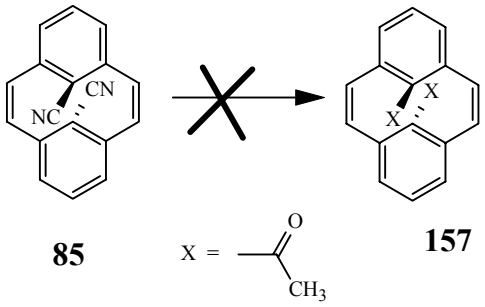
high instability of **156.** Dehydroformylation of **155** was observed on attempted column chromatography giving **154**.

The structure **155** was assigned to the migration product based on its NMR spectroscopic analysis. In the $^{1}H$ NMR spectrum, the signals of the two formyl protons were found at δ 9.71 and 9.34. In the $^{13}C$ NMR spectrum, both formyl carbons were also quite distinct and appeared at δ 198.74 and 190.97. The relative position of the formyl groups was assigned based on the HMBC and HSQC techniques. The IR stretches at 2721 and 1719 $cm^{-1}$ confirmed the presence of the aldehyde groups. The mass spectrum showed molecular ion peak at *m/z* 260. The base peak at *m/z* 202 in the mass spectrum indicated decomposition to pyrene **112**.

### 2.4.2 The attempted synthesis of the acyl substituted CPD 157

MeLi treatment of **85** was expected to give the methyl ketone **157 (**Scheme 2.32), however it failed to furnish the desired product. Pyrene **112** was the only isolated product. The reaction was monitored by TLC and it was revealed that the pyrene formation started at -20 $^{o}C$ and was complete before the reaction mixture reached room temperature.

**Scheme 2.32 Attempted synthesis of the acetyl CPD 157**

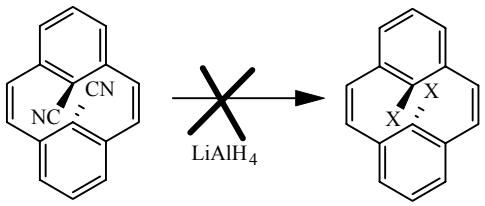



**85** **157**

### 2.4.3 Reduction of the nitrile 85 into the primary amine 158

Complete reduction of the nitrile **85** using $LiAlH_4$ to the primary amine **158** failed (Scheme 2.33). Once again pyrene **112** was the major product. Our interest in investigating the chemistry of the internal nitriles was limited by this pyrene formation. Thus we did not endeavor to hydrolyze the nitrile **85** to the corresponding amide or carboxylic acid derivatives because of its sensitivity to many nucleophiles.

**Scheme 2.33 Attempted reduction of nitrile 85 to primary amine 158**



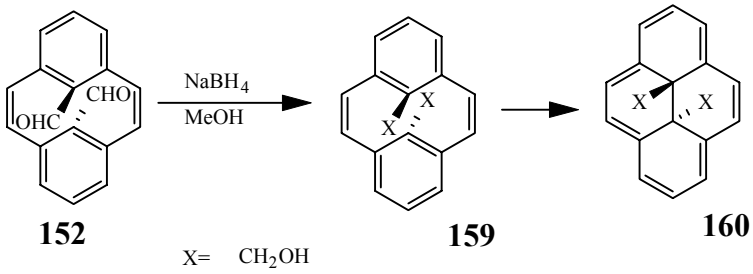

**85** X = $CH_2NH_2$ **158**

### 2.4.4 Reduction the internal formyl groups using $NaBH_4$

Attention was directed towards the chemistry of diformyl CPD **152**. The CPD has relatively short half life (11 days at rt) so a reaction involving mild conditions such as reduction with $NaBH_4$ would be an ultimate starting point.

Reduction of the aldehyde **152** with $NaBH_4$ in methanol at room temperature (Scheme 2.34) delivered the primary alcohol **159** in quantitative yields. Hydroxymethyl CPD **159** was thermally unstable and isomerized to the dihydropyrene **160** in less than an hour which subsequently decomposed to pyrene **112** in a few hours at room temperature. Thus characterization was carried out on the non chromatographed sample.

**Scheme 2.34 Reduction of the diformyl CPD 152 to the primary alcohol 159**




In the $^{1}H$ NMR spectrum, replacement of the aldehyde peak at δ 9.35 by the hydroxymethylene peak at δ 3.80 indicated the formation of the desired product. The peak corresponding to the OH protons was not located. Probably it was broad and unresolved to the base line. The methylene carbons bearing the OH groups were at δ 62.73 in the $^{13}C$ NMR spectrum. The IR spectrum supported the presence of the OH group by a stretch at 3390 $cm^{-1}$. Mass spectrometry did not show a molecular ion peak, rather a peak at *m/z* 202 which indicated decomposition to the pyrene **112**.

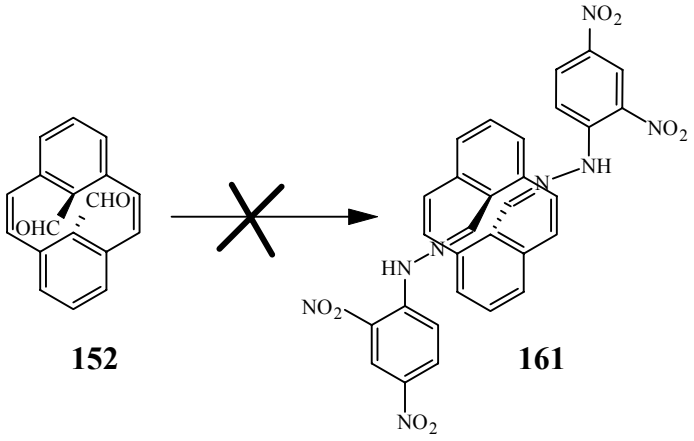
Hydroxymethyl CPD **159** transformed at room temperature to the dihydropyrene **160** in an hour. The methylene and hydroxyl protons in **160** were at δ -1.77 (doublet) and -2.1 (triplet) respectively in the $^{1}H$ NMR spectrum.

### 2.4.5 The 2,4-dinitrophenyl hydrazone of the cyclophanediene 152

2,4-Dinitrophenylhydrazone formation is a textbook reaction to test for the presence of an aldehyde or a ketone functional group.[68] We were quite surprised to know that the **152** when reacted with 2,4-dinitrophenylhydrazine failed to produce the hydrazone **161** (Scheme 2.35). This abnormality in reactivity could be attributed either to the insolubility of the formyl CPD **152** in the methanol-glycerol solvent mixture or to steric constraints associated with the approach of the hydrazine to the hindered carbonyl

functionality. The latter was excluded by a reaction of **152** with hydrazine hydrochloride which also failed to give any products.

**Scheme 2.35 Attempted synthesis of a bis hydrazone**

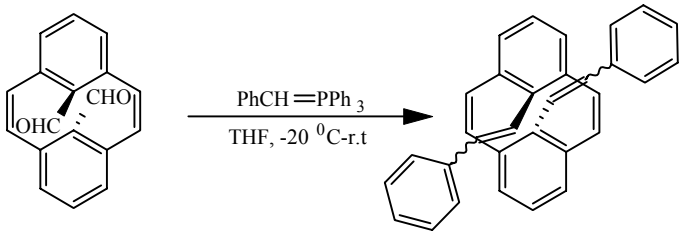



**152** **161**

### 2.4.6 Wittig reaction of the diformyl CPD 152

Wittig reaction of **152** with benzyltriphenylphosphonium bromide using BuLi in THF at room temperature resulted in the formation of pyrenes. However, when the reaction was carried out at lower temperature, it gave a mixture of four or five pale green to colorless products with very close $R_f$ values on TLC.

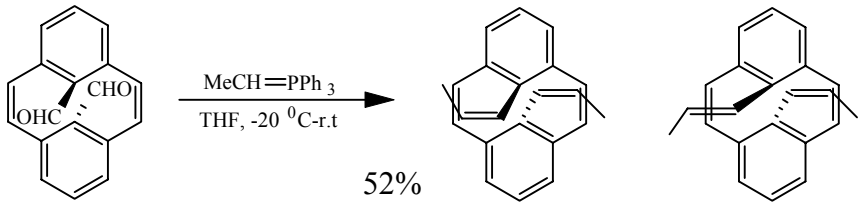
**Scheme 2.36 Wittig reaction of 152 to produce styryl CPDs**




$^1$H NMR analysis was complicated by the jumbled peaks at δ 7.5-5.0. Overlap of the styryl protons with the CPD protons with an added effect of the number of isomers at

the double bond would lead to the complicated spectrum. Thus it was predicted that the replacement of the styryl group by an alkyl substituted alkene would simplify the $^1$H NMR spectrum, and hence the analysis.

**Scheme 2.37 Synthesis of the CPDs with internal propenyl substituents**




**152** **162** **163**

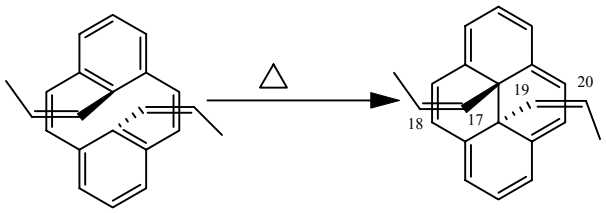
Dialdehyde **152,** when subjected to the ylide derived from ethyltriphenylphosphonium bromide gave a 6:1 mixture of **162** and **163** in 52% yield (Scheme 2.37). The major isomer **162,** as expected, gave a total of six peaks in the $^1$H NMR spectrum. The *cis* orientation of the double bond was established by a coupling constant of 12 Hz between the olefinic protons, which was also supported by the IR band at 711 cm$^{-1}$. The olefinic protons were found as doublets of quartets at δ 6.12 and 5.23 while the methyl protons appeared as a doublet of doublets at δ 1.55. The product was confirmed by mass spectrometry which gave the correct molecular weight of *m/z* 284.

All protons and carbon in the major isomer (**162)** could easily be accounted for but in the minor isomer **163**, the *cis*-propenyl protons and carbons were obscure. This could be due to overlap with peaks of the major isomer. The *trans*-propenyl internal group in **163** was identified by a coupling constant of 15.4 Hz for the alkene protons at δ 5.94 and by the IR stretch at 962 cm$^{-1}$.

### 2.4.6.1 A photoswitch with low thermal and migration rates

The mixture of propenyl CPDs **162** and **163** when heated at 100 $^{o}$C for 12 hours furnished the dihydropyrenes **164** and **165** without any *cis-trans* isomerization of the internal olefinic groups. In the $^{1}$H NMR spectrum of **164,** the DHP protons appeared at δ 8.65-8.05. The internal propenyl protons were shielded to different extents depending on their distance from the diatropic ring.

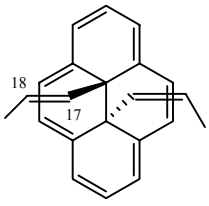
**Scheme 2.38 Thermal isomerization of 162 to 164**




**162** **164**

The protons H-17/19 were the most shielded protons followed by H-18/20 (Scheme 2.38) and appeared at δ 0.09 and δ 3.21 respectively as doublets of quartets. A coupling constant of 12.4 Hz indicated the *cis* geometry of the double bond. The methyl protons were at δ 0.33.

The internal *trans*-propenyl protons in **165**, H-17 and H-18, appeared at δ 0.15 and 2.36 respectively in the $^{1}$H NMR spectrum and indicated a significant shielding of H-18 when compared with the *cis* analogue H-20 at δ 3.14.




**165**

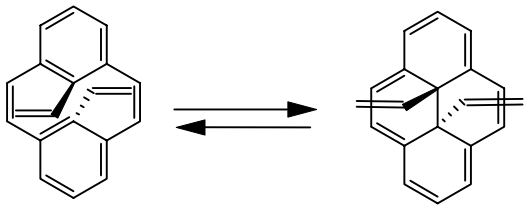
Internal alkene substituted CPD and DHP pairs, **162/164** and **163/165** showed high stability towards:

1. The thermal closure of the cyclophanedienes to the dihydropyrenes
2. The migration of the internal substituents in the DHP.
3. The thermal *cis-trans* isomerization of the internal olefin.

## 2.5 Improved syntheses of the dihydropyrenes with internal olefin groups

The thermal stability of switch pairs **162/164** and **163/165** fascinated us and it drove our attention towards the synthesis of a series of dihydropyrene photoswitches with different internal olefin substituents. The synthetic strategy for the internal olefin substituted cyclophanedienes had some limitations such as the involvement of small scale and heat sensitive FG transformations (Schemes 2.30 and 2.37), and thus required revision.

**Scheme 2.39 A photoswitch with internal vinyl substituents**

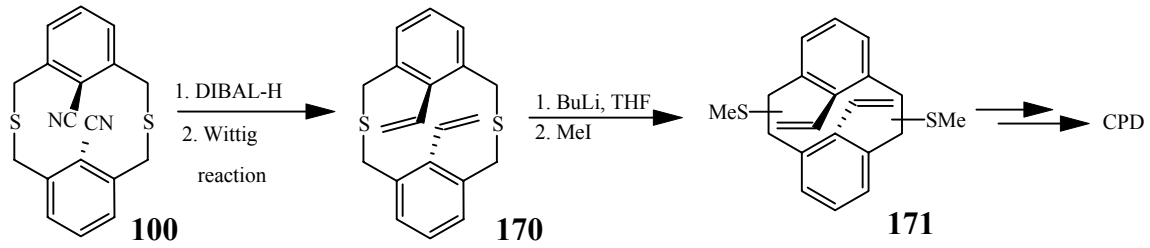


**166** **167**

FG transformations either in the dicyanothiacyclophane **100** or in the Stevens product **99** and their subsequent conversion to cyclophanedienes was anticipated to improve the yield. In order to eliminate complications arising from the *cis-trans* isomers, the vinyl substituted switch pair **166/167** (Scheme 2.39) was chosen as the synthetic

target. Scheme 2.40 represents a brief outline of the proposed synthetic route with FG transformations in the thiacyclophane **100**.

**Scheme 2.40 Modified synthesis of CPDs with internal olefin substituents**

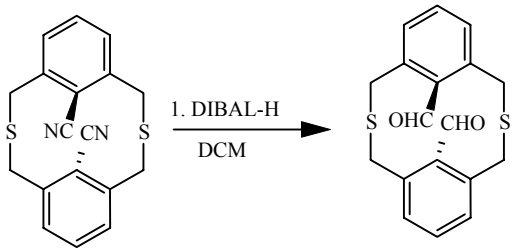



**100** **170** **171**

## 2.5.1 DIBAL-H reduction-Wittig reaction sequence to synthesize the thiacyclophane 170

DIBAL-H reduction of **100** at room temperature in DCM gave ~ 90% yield of the diformylthiacyclophane **168** (Scheme 2.41). The formyl protons appeared at δ 9.93 in the $^{1}$H NMR spectrum. The chemical shift of the carbonyl carbon at δ 191.49 in the $^{13}$C NMR spectrum and the IR stretches at 2773 cm$^{-1}$ and 1683 cm$^{-1}$ confirmed the aldehyde functional group. The bridge protons in **168** were at δ 4.32-3.79 and were relatively widely spaced when compared with the nitrile analogue **100** (δ 3.94-3.88).

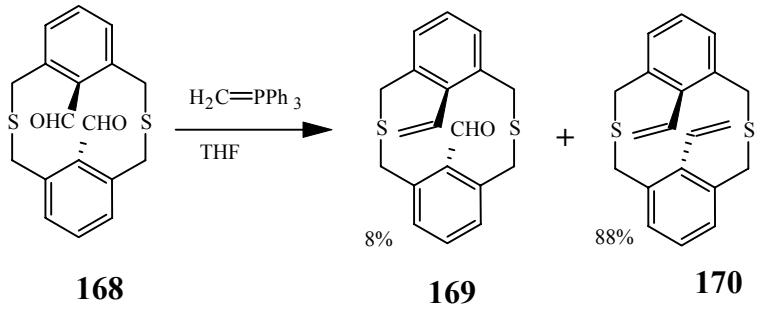
**Scheme 2.41 Synthesis of the diformyl-*anti*-thiacyclophane 168**




**100** **168**

Thiacyclophane **168**, when treated with the ylide derived from methyltriphenyl phosphonium bromide in THF gave 88% of the divinylthiacyclophane **170** along with 8% of the monovinyl thiacyclophane **169** (Scheme 2.42). Both products were isolated by column chromatography and their assignment was made on the basis of NMR spectroscopy. The replacement of the formyl proton peak at δ 9.93 in the $^1$H NMR spectrum by the vinyl proton peaks at δ 5.93-4.68 indicated the formation of the desired product **170**. The $^1$H NMR spectrum showed a total of seven peaks as expected because of symmetry. Satisfactory elemental analysis was obtained for **170.**

**Scheme 2.42 Wittig reaction of 168 to synthesize 169 and 170**




**168** **169** **170**

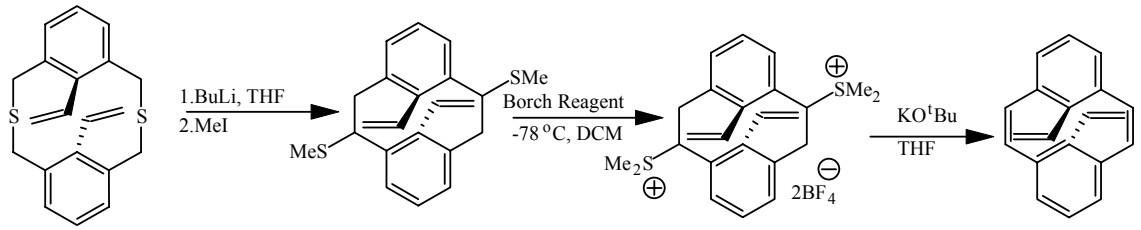
The minor product, **169** indicated the presence of the formyl and vinyl groups by peaks at δ 9.82 and δ 6.00-4.78 respectively in the $^1$H NMR spectrum. IR bands at 2780 and 1679 cm$^{-1}$ confirmed the presence of the aldehyde functional group.

### 2.5.2 Synthesis of the divinylcyclophanediene 166

Wittig rearrangement of the divinylthiacyclophane **170** followed by treatment with MeI gave greater than 90% yield of the thiomethylcyclophanes **171** as a mixture of isomers (Scheme 2.43). The success of the reaction was shown by the appearance of the methyl groups as singlets at δ 2.1 in the $^1$H NMR spectrum. The vinyl protons were centered at δ 4.9-4.2. The di-equatorial isomer of **171** was purified using column

chromatography and fully characterized. Mass spectrometry gave the correct molecular mass at *m/z* 352.

**Scheme 2.43 Wittig rearrangement of the thiacyclophane 170 and subsequent Hoffmann elimination**




**170** **171** **172** **166**

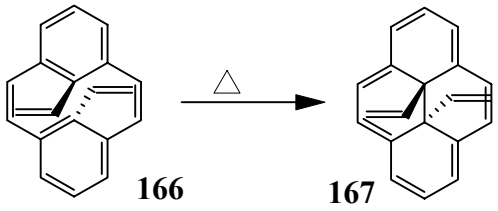
Mixed isomers of **171**, when treated with dimethoxycarbonium tetrafluoroborate gave the sulfonium salts **172** which on Hoffmann elimination furnished the cyclophanediene **166** in quantitative yield. The desired product could easily be identified by its $^1$H NMR spectrum. Protons from the internal vinyl substituent appeared at δ 6.32-4.84 as three doublets of doublets. The molecular ion peak at *m/z* 256 confirmed the formula.

### 2.5.3 Thermal isomerization of the cyclophanediene 166 into the dihydropyrene 167

A solution of cyclophanediene **166** in toluene when heated at 100 $^o$C for 8 hours yielded the dihydropyrene **167**. The vinylic -C<u>H</u>=$CH_2$ was highly shielded and appeared at δ 0.5 as doublet of doublets in the $^1$H NMR spectrum. The -CH=<u>$CH_2$</u> protons were at δ 2.06 and 2.67 (doublets of doublets). The mass spectrum confirmed the molecular

formula by a peak at *m/z* 256. A satisfactory elemental analysis was obtained for **167**. Finally an X-ray structure determination confirmed the structure.

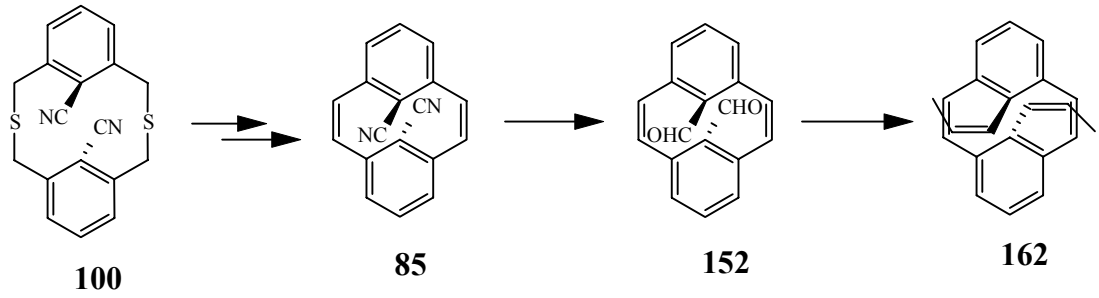
**Scheme 2.39 Thermal return of the divinyl CPD 166 to the dihydropyrene 167**




### 2.5.4 A comparison of the synthetic routes to the olefin substituted CPDs

Starting from the *anti*-thiacyclophane **100,** the sequence of reactions described in Scheme 2.40 gave an overall yield of 72% for divinyl CPD **166**. On the other hand the cyclophanediene route shown in Scheme 2.44 gave ~ 23% of the CPD **162**.

**Scheme 2.44 Synthesis of propenyl DHP 162 via CPD 152**



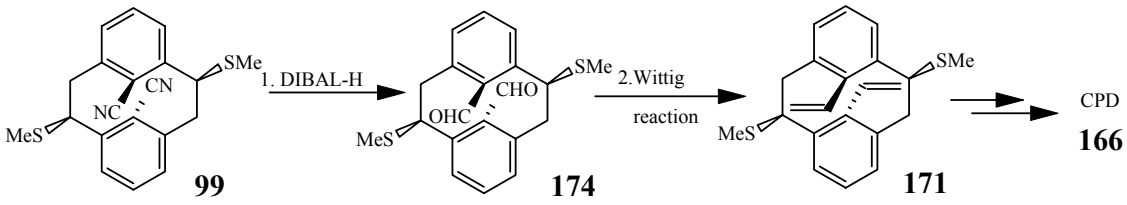

However the revised scheme (Scheme 2.40) had some limitation as well. For example, the *syn*-dicyanothiacyclophane **108**, when subjected to the DIBAL-H reduction failed to give any yields of the diformyl-*syn*-thiacyclophane **173**. Moreover, successful reduction of **100** using DIBAL-H was limited to a small scale reaction (sub millimolar scale).


**173**

### 2.5.5 Another improvement in the synthesis of divinyl CPD 166

It was expected that the FG transformations in the dicyanothiomethylcyclophanes **99** would eliminate or at least reduce the above mentioned problems because **99** is generally obtained as a mixture of *anti*-isomers. Reduction of **99** (mixed isomers) with DIBAL-H furnished the diformyl MeS-cyclophanes **174** quantitatively. Appearance of singlets at δ 9.1-8.8 in the $^{1}$H NMR spectrum corresponding to the aldehyde protons indicated the success of the reaction. The reaction could be carried out on a two gram scale.

**Scheme 2.45 Improved synthesis of divinyl CPD 166 starting from thiomethylcyclophane 99**




**99** **174** **171** **166**

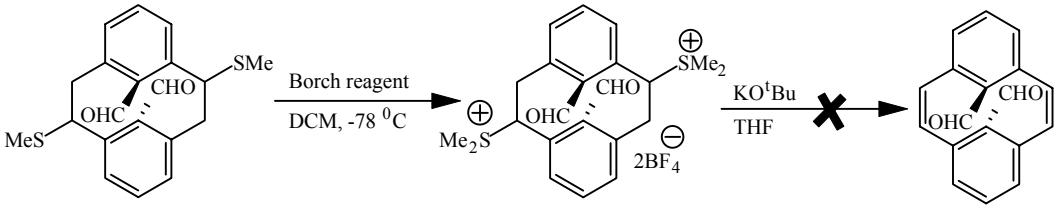
When a single isomer of **99** was employed, it gave **174** as a pure isomer (Scheme 2.45). This isomer of **174** was fully characterized and complete assignment of all the protons and carbon was made. The internal formyl protons appeared at δ 8.95. The aldehyde group was further confirmed by the $^{13}$C NMR peak at δ 188.74 and by the IR

stretches at 2786 and 1682 $cm^{-1}$. The mass spectrum confirmed the molecular formula with *m/z* 356.

Wittig reaction of **174** with methyltriphenylphosphonium bromide using BuLi as the base generated the olefin substituted thiomethylcyclophane **171** in greater than 90% yield. With this improved methodology, cyclophanediene **166** could be made in gram quantities in > 70% yield starting from the dicyanothiacyclophanes **108** and **100** (*syn*-and *anti*). The above mentioned scheme (Scheme 2.45) served as a standard protocol for the syntheses of a variety of olefin substituted cyclophanedienes.

It was however of interest to see if the diformylcyclophanes **174** could be converted to the cyclophanediene **152**. Sulfonium salt **175** was successfully prepared but the subsequent Hoffmann elimination gave a mixture of pyrenes instead of **152** (Scheme 2.46)**.**

**Scheme 2.46 Attempted synthesis of diformyl CPD 152 by the Hoffmann elimination**



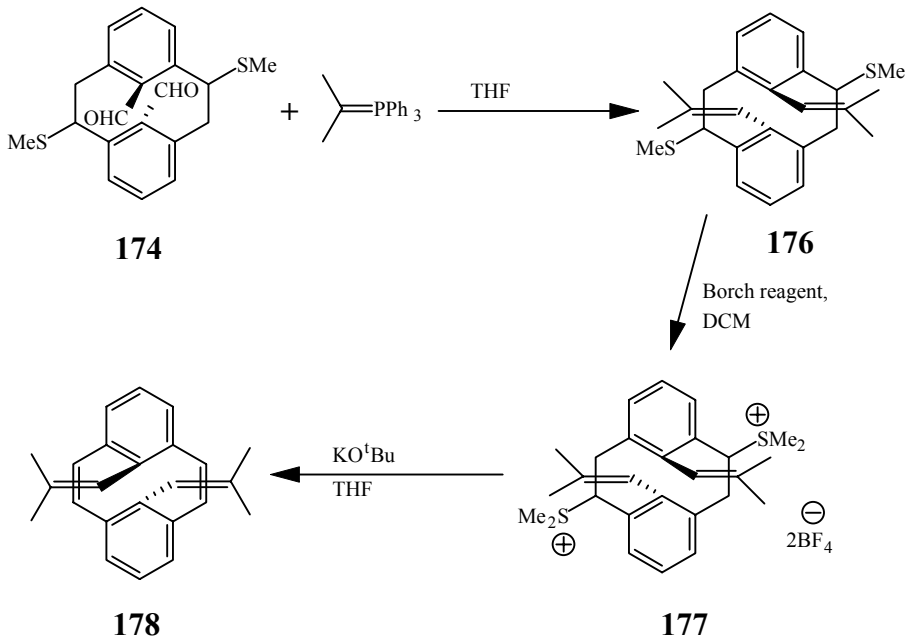

**174** **175** **152**

### 2.5.6 Synthesis of the diisobutenyl CPD 178

A comparison of the thermal return rates of divinyl (**166)** and dipropenyl (**162**) cyclophanedienes (Chapter 3 for details) revealed that the methyl substituent on the internal olefin had a substantial decelerating effect. Thus, the CPD **178** with two methyls

on the internal olefin substituent was predicted to show even higher thermal stability. Diisobutenyl CPD **178** was successfully synthesized in two steps (Scheme 2.47) starting from the diformylcyclophane **174** in an overall yield of ~ 70%. Isopropyltriphenyl phosphonium bromide,[69] when reacted with BuOK, generated the ylide that on reaction with **174** gave a 71% yield of **176**. The isobutenyl functional group was confirmed by the methyl protons peaks at δ 0.8-1.6 in the $^1$H NMR spectrum. No attempts were made to purify isomers of **176.** Methylation of **176** with Borch reagent delivered **177** quantitatively and subsequent Hoffmann elimination gave the cyclophanediene **178** in 96% yield.

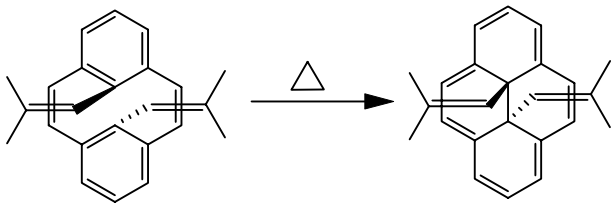
**Scheme 2.47 Synthesis of the diisobutenyl CPD 178**




The olefinic CH proton of the internal isobutenyl substituent in **178** appeared as septet at δ 5.70 in the $^1$H NMR spectrum, and the signal of methyl protons were at δ 1.57. Mass spectrometry showed the correct molecular ion peak at *m/z* 312. Successive losses of 55 mass units in the mass spectrum further confirmed the presence of the internal

butenyl groups. X-ray structure determination was also obtained for the cyclophanediene **178**, which confirmed its structure.

**Scheme 2.48 The thermal closure of diisobutenyl CPD 178 to the DHP 179**



**178** **179**

Diisobutenyl DHP **179** was obtained by the thermal closure of **178** at 110 $^{o}$C for 12 hours (Scheme 2.48). The internal vinyl protons were observed at δ -0.16 in the $^{1}$H NMR spectrum, and the methyl protons were observed as two doublets at δ 0.17 and 0.14. Partial decomposition of the dihydropyrene **179** was seen in deuterated chloroform, probably because of the acid present in it. An X-ray structure was obtained for **179.**

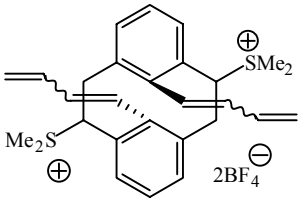
### 2.6 .6 Syntheses of the olefinic CPDs with extended conjugation

The high thermal stability of **178,** as expected, has shown that a slight change in the internal substituent can lead to dramatic effects on the thermal closure reaction. Thus, we became interested in modifying the internal olefin by extending the conjugation by a double or a triple bond and by a phenyl ring (substituted and non-substituted), and study their influence on the photoswitch.

### 2.6.1 Butadienyl as the internal substituents

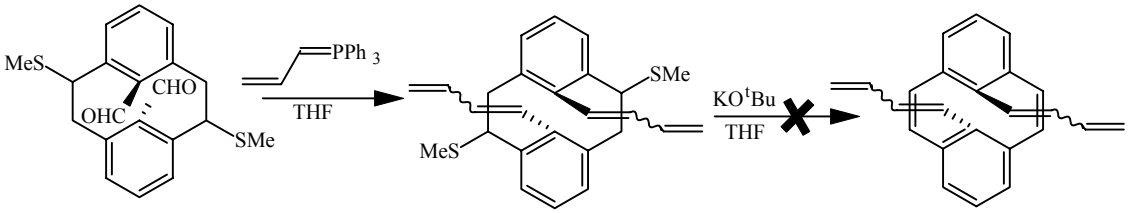
Our standard protocol for the synthesis of internal olefin substituted cyclophanedienes starting from **174** through **180** failed to yield **181** at all (Scheme 2.49).

The $^{1}H$ and $^{13}C$ NMR spectra of the crude mixture indicated the presence of aliphatic protons and carbons respectively and this could not be accounted for. On the other hand, a peak at *m/z* 308 in the mass spectrum was quite consistent with the given formula of **181**. It could be possible that the desired product might have isomerized by the Diels-Alder type reaction of the diene moiety in the cyclophanediene. The product mixture could not be resolved into its components by column chromatography. The $^{1}H$ NMR analysis of the thiomethylcyclophane **180** and the sulfonium salt **182** did not indicate any such complexity.



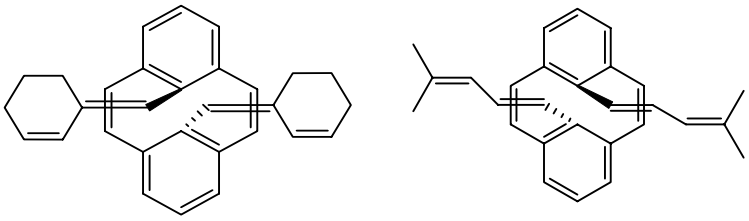

**182**

**Scheme 2.49 Attempted synthesis of butadienyl CPDs 181**




**174** **180** **181**

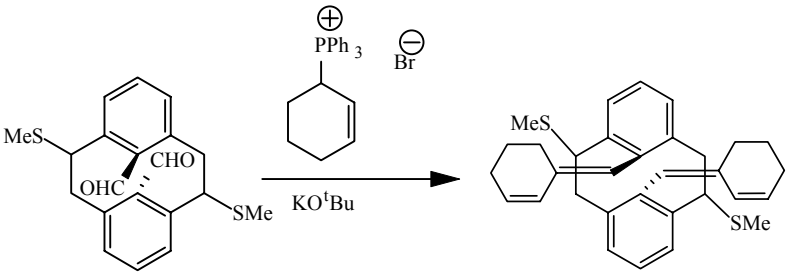
Introduction of steric bulk at the butadiene functionality (**184**) or its conformational lock in the s-*trans* conformer (**183**) was expected to eliminate or at least diminish the unwanted side reaction.



**183** **184**

Synthesis of **183** could not be accomplished however, because the Wittig reaction shown in Scheme 2.50 failed to furnish the thiomethylcyclophane **187**. Cyclohexenyl triphenylphosphonium bromide when treated with *t*-BuOK formed globules, probably clusters of ions, which then failed to react with the formylcyclophane **174**. No precedent example of the Wittig reaction from this salt is found in the literature probably because of similar reasons.

**Scheme 2.50 Attempted synthesis of thiomethylcyclophane 187**

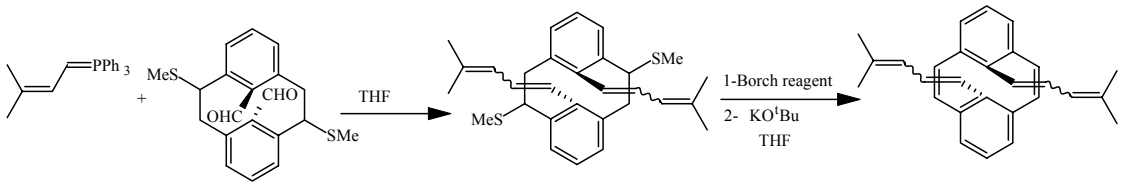



**174** **187**

Wittig reaction of **174** with the ylide derived from 3-methyl-2-butenyltriphenyl phosphonium bromide gave 54% of the cyclophane **188** in an unoptimized reaction (Scheme 2.51). The $^{1}$H NMR spectrum revealed the presence of the desired product by the alkene protons at δ 6.2-4.0 and by the methyl protons at δ 2.0-1.5. Butadiene **188**, on treatment with Borch reagent gave the sulfonium salt which on Hoffmann elimination yielded the desired cyclophanediene as a mixture of three isomers. Attempted column

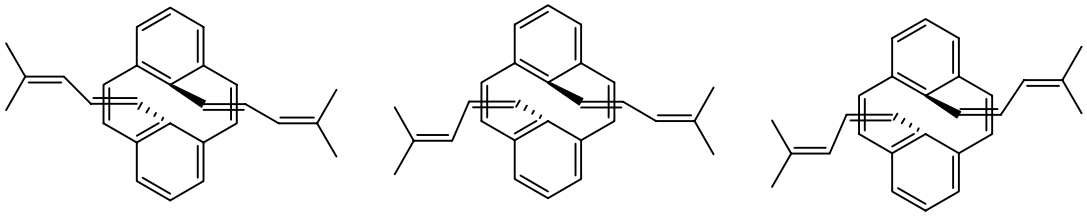
chromatography failed to separate the isomers however fractions rich in one or the other isomer were obtained.

**Scheme 2.51 Synthesis of CPDs containing methyl substituted butadienyl internal groups**




**174** **188** **184-186**

Virtually all protons and carbons in all the isomers could be assigned by NMR spectroscopy. Because of symmetry in the isomers **184** and **186**, a total of eight peaks appeared in their $^1$H NMR spectra while the unsymmetrical isomer **185** was found to contain 16 peaks. The all *trans*-isomer **184** was characterized by a coupling constant of 15.4 Hz for the alkene protons at δ 6.80 and 6.09. The methyl protons were observed at δ 1.72 and 1.78 as poorly resolved doublets.

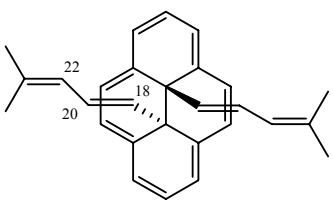


**184** **185** **186**

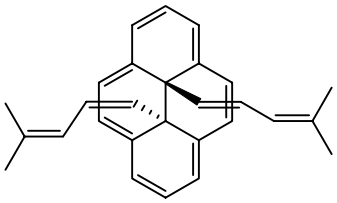
A coupling constant of 12.4 Hz of alkene protons at δ 5.76 indicated the *cis* orientation of double bond in **186**. The methyl protons were observed at δ 1.74 and 1.71.

### 2.6.1.1 Dihydropyrenes 190-192 by the thermal closure of the CPDs 184-186

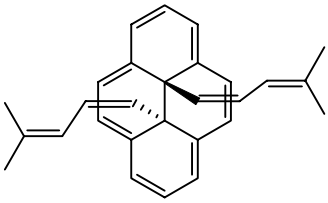
Dihydropyrenes **190-192** were obtained by heating the cyclophanedienes **184-186** respectively in refluxing toluene for 8 hrs. The isomers were purified by column chromatography. In its $^{1}$H NMR spectrum, the *trans*-isomer **190** showed peaks at δ 0.22, 2.95 and 4.04 for the protons 18, 20 and 22, respectively, (shown below) whereas the corresponding protons in the *cis*-isomer **192** appeared at δ -0.02, 3.90 and 4.53. The *trans* orientation of the double bond in **190** was confirmed by the coupling constant of 15 Hz.




**190**



**191**



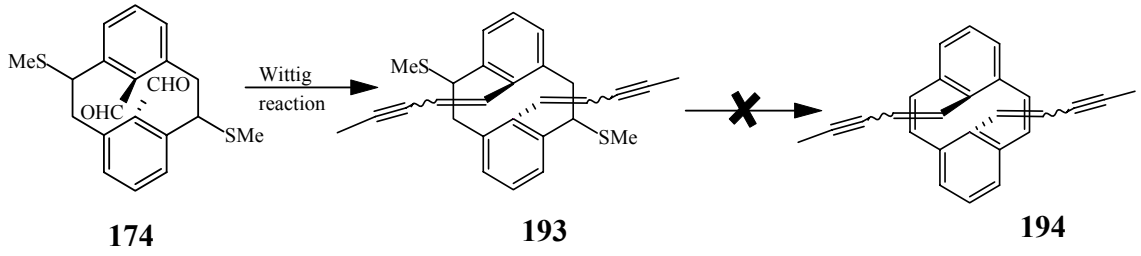
**192**

In the unsymmetrical isomer **191**, chemical shifts of the protons from the *cis* and *trans* internal substituent were comparable to those of **192** and **190**, respectively.

### 2.6.2 Extending the conjugation with a triple bond

Pentenynyl CPD **194** represents an example of elongation of the internal olefin by a triple bond. The terminal methyl groups were chosen to avoid unfavorable Glaser coupling.[70] The Glaser coupling is the homocoupling of terminal alkynes to form diynes in the presence of a catalyst and an oxidant. Wittig reaction of **174** delivered the thiomethylcyclophanes **193** in moderate yield but subsequent Hoffmann elimination failed to yield the cyclophanediene **194** (Scheme 2.52). Pyrene **112** was obtained as the product of the reaction.

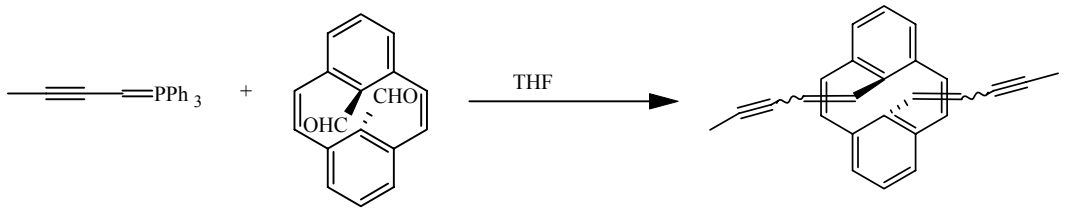
**Scheme 2.52 Attempted synthesis of pentenynyl CPD by the Wittig reaction-Hoffmann elimination sequence**



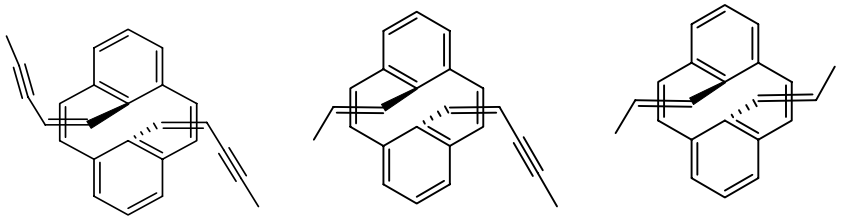

**174** **193** **194**

However the Wittig reaction of diformyl **152** (Scheme 2.53) gave the desired product **194** along with two unexpected side products **196** and **198**. Attempts to purify these three products using column chromatography were unsuccessful.

**Scheme 2.53 Synthesis of 194 by Wittig reaction of 152**



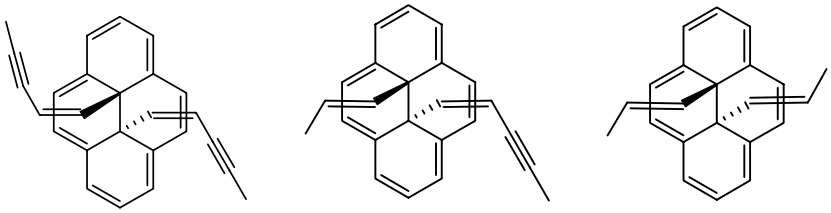

**152** **194**



**194** **196** **198**

The $^{1}$H NMR spectrum of the cyclophanedienes mixture (**194**, **196** and **198**) was quite complex and it failed to locate the propenyl substituent because of its resemblance with the pentenynyl substituent in terms of number of peaks and associated chemical shifts. However, the $^{13}$C NMR spectrum pointed out the absence of the sp carbon atoms

and this was supported by the mass spectrum peaks at *m/z* 308 and 284 corresponding to **196** and **198**, respectively. The cyclophanediene mixture was heated in toluene overnight to give a mixture of dihydropyrenes.



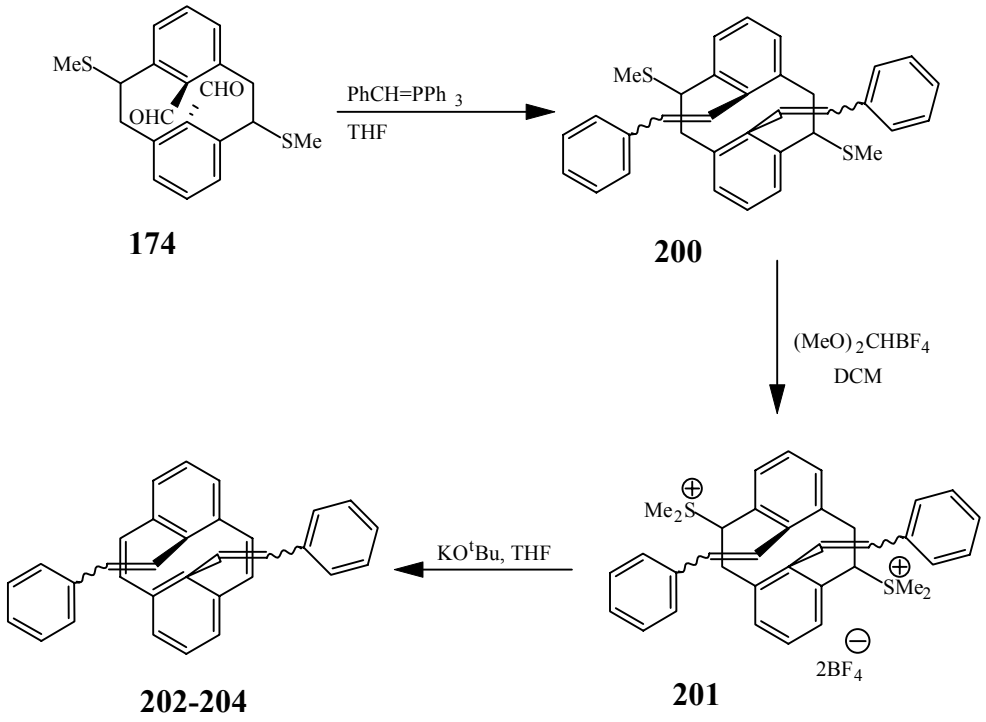
**195** **197** **199**

Dihydropyrenes **195, 197** and **199**, quite contrary to the CPDs, could be separated by column chromatography and showed fairly distinct $^{1}$H NMR chemical shifts for the methyl protons from the propenyl and the pentenynyl groups. The signal of the methyl protons in **199** and **195** were found at δ 0.1 and 1.94 respectively. The upfield chemical shift of the methyl protons in **199** along with a coupling constant of 6.0 Hz with the neighboring alkene proton indicated the presence of the propenyl substituent, which was further corroborated by the absence of the resonances for the sp carbons in the $^{13}$C NMR spectrum. A coupling constant of 15.5 Hz indicated the *trans* geometry of the propenyl substituent in **197** and **199**. We are not clear how the *trans* propenyl group was incorporated.

### 2.6.3 Distyryl CPDs 202-204, an example of extended conjugation by phenyl rings

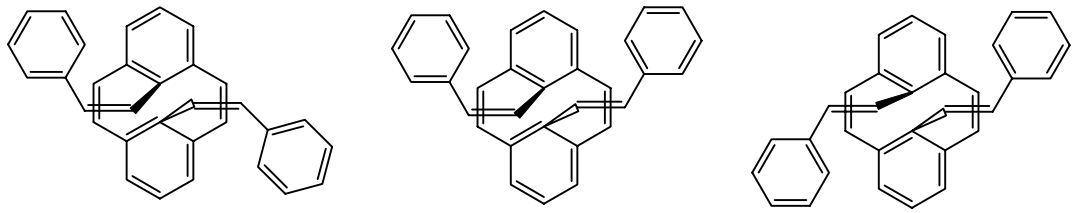
Mixed isomers **174** on treatment with an ylide derived from benzyltriphenylphosphonium bromide gave 20% of the thiomethylcyclophanes **200** in an unoptimized reaction (Scheme 2.54). The styryl protons of **200** appeared at δ 5.0-7.5 in the $^{1}$H NMR spectrum. The *cis*-styryl group because of its close proximity in space shielded the thiomethyl protons to δ 1.4 when compared with the *anti* analogue at δ 2.3.

**Scheme 2.54 Synthesis of CPDs with internal styryl groups 202-204**




**174** **200** **201** **202-204**

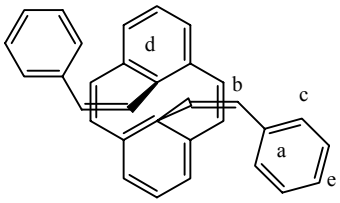
The thiomethylcyclophane **200** on treatment with Borch reagent gave the sulfonium salt **201** which on subsequent elimination provided a mixture of the cyclophanedienes, **202-204** in 80% overall yield. The isomers were separated by column chromatography.



**202** **203** **204**

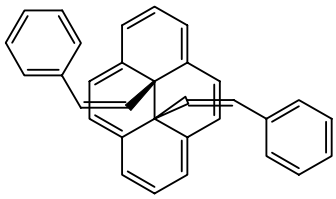
All *cis*-isomer **202** eluted first from the column and showed the CPD bridge alkene protons (proton b) at δ 5.84 in the $^{1}$H NMR spectrum, slightly upfield compared to

δ 6.5 for most of the *anti*-CPDs. PC Model[71] has shown a close spatial relationship of the phenyl ring "a" to the bridge alkene protons "b" which results in mutual shielding and is shown by the chemical shift of protons "c" at δ 6.78, slightly upfield compared to protons "e" at δ 7.05. The structure was further supported by the molecular ion peak at *m/z* 408 in the mass spectrum and was finally confirmed by X-ray structure determination.

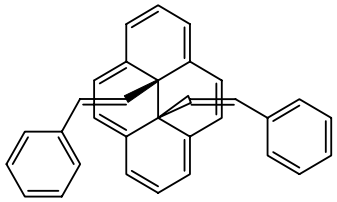



**202**

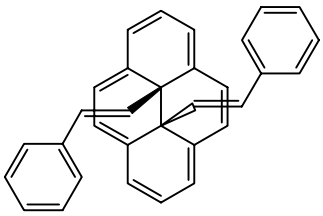
The styryl aromatic protons in the all *trans*-isomer **204** appeared at δ 7.22-7.20 and the bridge alkene CPD protons were a singlet at δ 6.48.



**205**



**206**



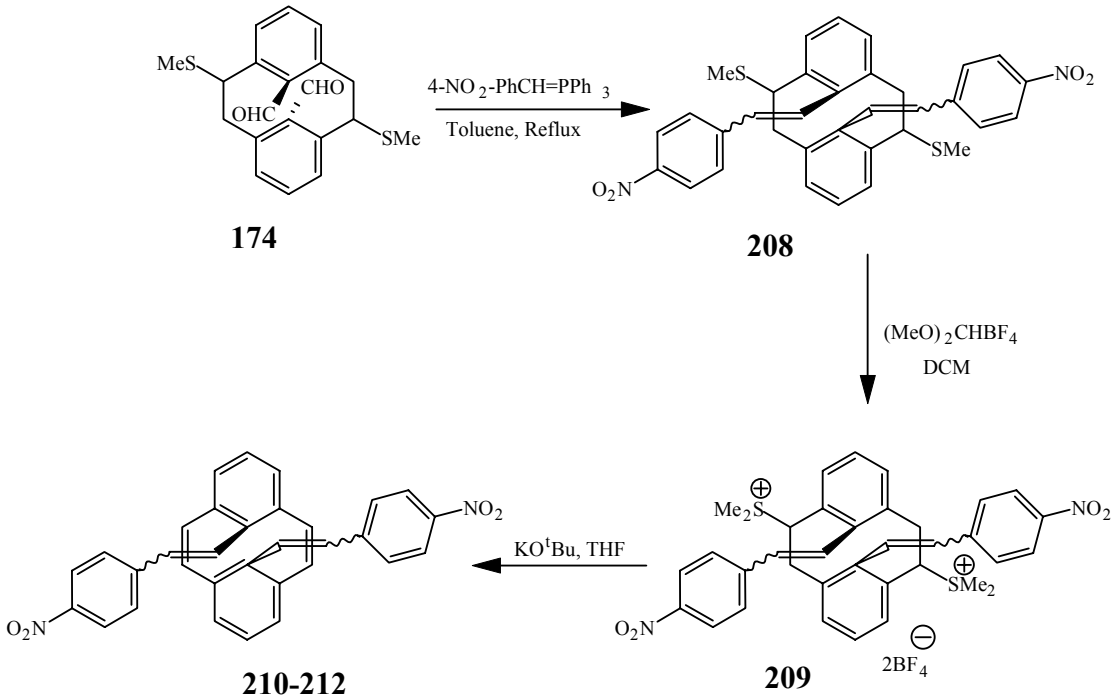
**207**

The cyclophanediene **202** when heated at 100 $^{o}$C for 12 hrs yielded the orange dihydropyrene **205**, mp 152-154 $^{o}$C. The *cis* geometry of the styryl group was confirmed by a coupling constant of 12.6 Hz between olefin protons at δ 4.21 and 0.28 in the $^{1}$H NMR spectrum. Phenyl protons of the styryl ring appeared at δ 7.15 (*p*), 7.03 (*m*) and 6.02 (*o*). Styryl DHPs **206** and **207** were also obtained by the thermal closure of their corresponding CPDs and no *cis*-*trans* isomerization of the styryl double bond was observed.

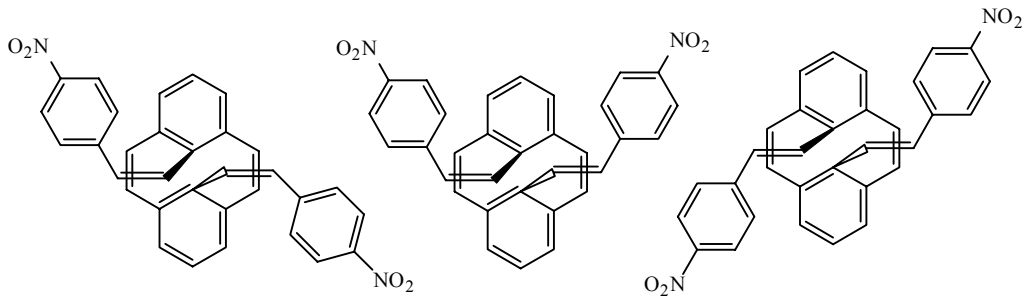
### 2.6.4 Synthesis of nitro-styryl CPDs 210-212, an exploration of the electronic effects on the thermal back reaction

Wittig reaction of **174** with 4-nitrobenzyl triphenylphosphonium bromide failed to give the desired product **208** when *t*-BuOK was used as the base in THF at room temperature. On addition of base to 4-nitrobenzyl triphenylphosphonium bromide, the solution instantly turned dark purple red which indicated the generation of the anion (ylide). However this anion failed to react with **174** probably because of the stability of the anion by delocalization onto the nitro group. Other bases such as $K_2CO_3$ in refluxing methanol or NaH in refluxing THF also failed to afford the desired product. Finally, a successful Wittig reaction was carried out in refluxing toluene with *t*-BuOK as base (Scheme 2.55).

**Scheme 2.55 Synthesis of nitro-styryl CPDs 210-212**



The high temperature Wittig reaction was expected to generate exclusively *trans* double bonds.[72] However the $^1$H NMR analysis of **208** indicated almost 1:1 ratio of *cis* and *trans* double bonds. Protons *ortho* to the nitro group were located as doublets at δ 7.8-8.2 in the $^1$H NMR spectrum. The mass spectrum of **208** gave the correct molecular mass of *m/z* 594.

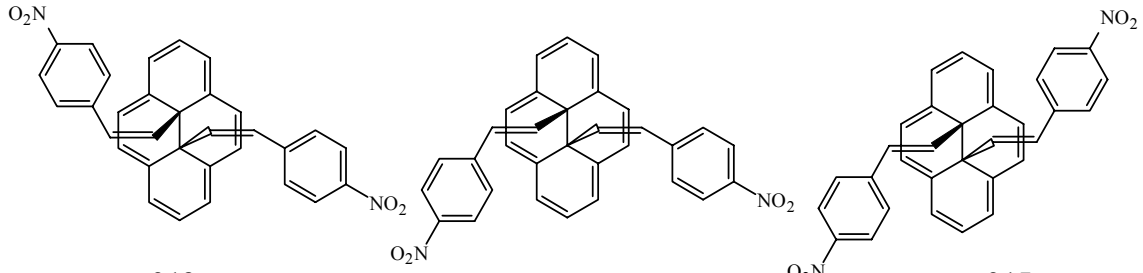



**210** **211** **212**

S-methylation of **208** quantitatively afforded the sulfonium salt **209** which on subsequent Hoffmann elimination gave a 1:2:1 mixture of the cyclophanedienes **210, 211** and **212** respectively. Column chromatography failed to separate the isomers efficiently. Since nitro-styryl CPDs **210** and **212** were almost insoluble in most common organic solvents except DCM so partial separation by column chromatography followed by washing with toluene or chloroform afforded the cyclophanedienes in reasonable purity.

The CPD alkene bridge protons were shielded to δ 5.84 in the $^1$H NMR spectrum of **210**, characteristic of *cis*-styryl CPDs. Doublets at δ 7.94 and 6.91 indicated a *para*-disubstituted phenyl ring which was further supported by a peak at 855 cm$^{-1}$ in the IR spectrum. The expected molecular mass at *m/z* 498 in the mass spectrum along with two successive losses of 148 mass units confirmed the nitro-styryl internal groups in **210**. Protons from the nitro-styryl ring in the *trans*-isomer **212** appeared as doublets at δ 8.17

and 7.35 in the $^{1}$H NMR spectrum. Almost every proton and carbon in the isomers could be assigned.



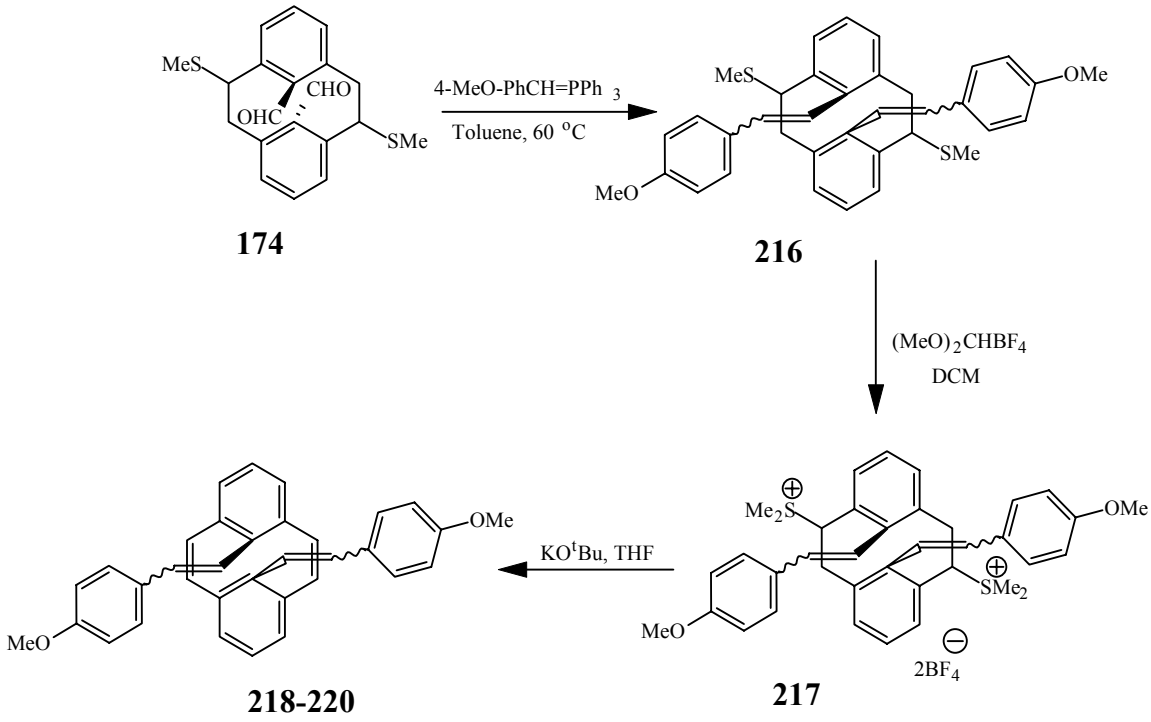

**213** **214** **215**

The dihydropyrenes **213-215** were obtained by the thermal closure of their corresponding cyclophanedienes. The all *trans*-isomer, **215** was insoluble in commonly available organic solvents which resulted in its failure to yield a useful $^{13}$C NMR spectrum. For example, a high temperature $^{13}$C NMR spectrum with scans as high as 40000 failed to show quaternary carbons at all. The other isomers **213** and **214** could be characterized completely even though the *cis*-isomer **213** had poor solubility in most organic solvents.

### 2.6.5 *para*-Methoxy-styryl CPDs 218-220, an example of an electron rich internal olefin

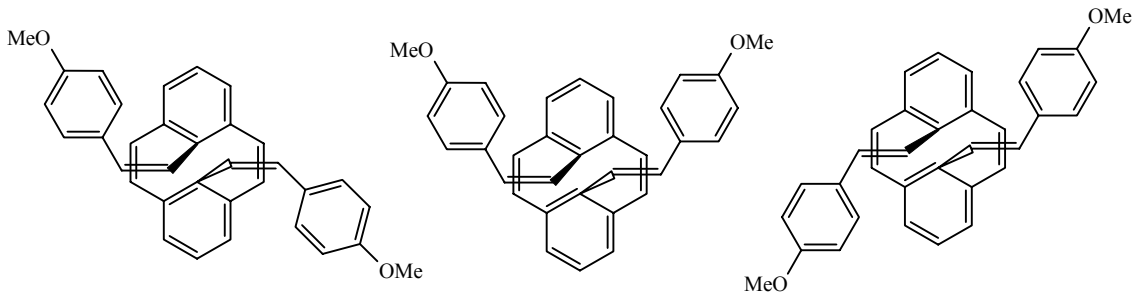
The nitro-substituted styryl cyclophanedienes **210-212** showed higher thermal closing rates when compared with the non-substituted styryl CPDs **202-204**. Based on these results, it was projected that an electron donating substituent such as methoxy at the *para*-positions of the styryl rings would decelerate the thermal return. Cyclophanedienes with *para*-methoxy-styryl internal substituents were synthesized as shown in Scheme 2.56.

**Scheme 2.56 Synthesis of *p*-methoxy-styryl CPDs 218-220**




**174** **216** **217** **218-220**

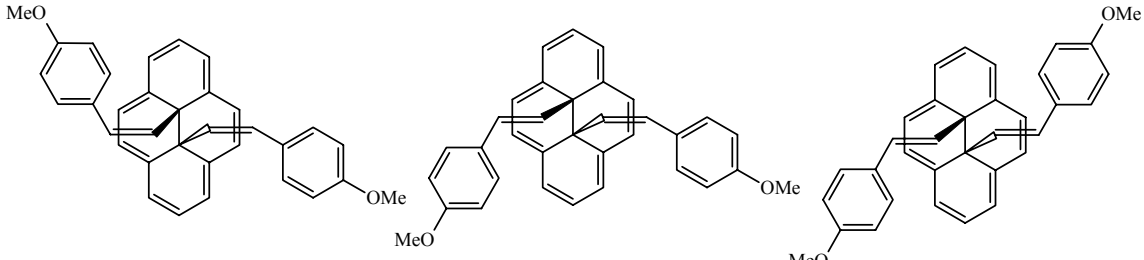
The diformyl MeS-cyclophanes **174** on Wittig reaction in toluene at 60 °C gave 50% yield of the *p*-methoxy-styrylcyclophanes **216**. Appearance of singlets at δ 3.9-3.6 in the $^1$H NMR spectrum indicated the formation of the desired product. S-Methylation of **216** and the subsequent elimination on the sulfonium salt generated the *p*-methoxy-styryl CPDs **218-220**.




**218** **219** **220**

The isomeric cyclophanedienes could be purified by column chromatography and showed distinct peaks for methoxy groups in the $^{1}H$ and $^{13}C$ NMR spectra. The protons of the methoxy groups in **218** appeared at δ 3.74 and, the methyl carbons at δ 55.34 in the $^{1}H$ and $^{13}C$ NMR spectra, respectively, slightly shielded when compared with the *trans*-isomer **220** (δ 3.81 and 55.49). In the unsymmetrical isomer **219**, the protons of the methoxy substituents were found at δ 3.82 and 3.75 in the $^{1}H$ NMR spectrum and the corresponding carbons at δ 55.47 and 55.33 in the $^{13}C$ NMR spectrum. The presence of the methoxy groups was further confirmed by the C-O stretches at 1252 and 1032 $cm^{-1}$ in the IR spectrum.

Cyclophanedienes **218-220** were thermally isomerized to the dihydropyrenes **221-223** at rates slower than those of non substituted styryl CPDs **202-204**, as expected, with no observable *cis-trans* isomerization of the styryl double bond.



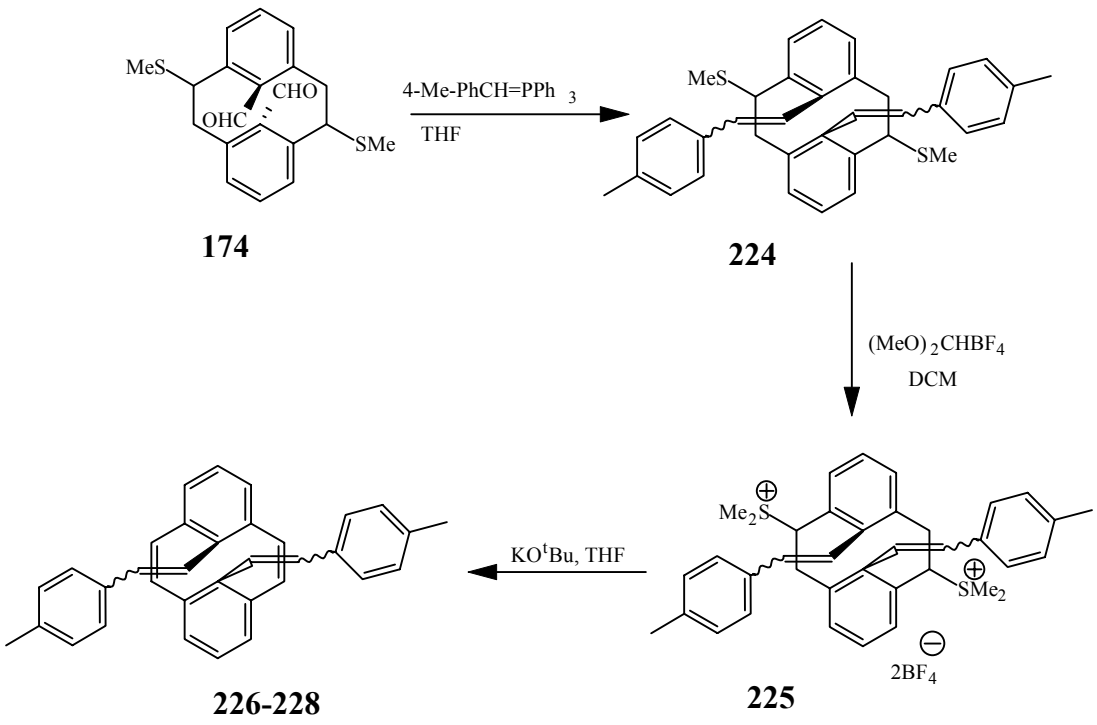

**221** **222** **223**

The methoxy protons were also quite distinct in different isomers **221-223** besides the general differences in the DHP protons. The methoxy protons and carbons in the all *cis*-isomer **221** appeared at δ 3.83 and 55.74, respectively, compared to δ 3.51 and 55.49 for the all *trans* isomer **223.**

### 2.6.6 Synthesis of *para*-methyl-styryl CPDs 226-228

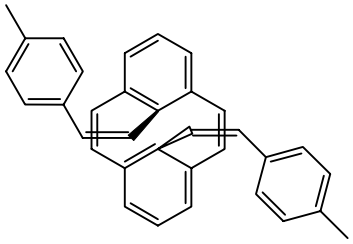
A comparison of the nitro- and methoxy-substituted cyclophanedienes revealed that an electron withdrawing substituent on the phenyl ring of internal styryl group has accelerated the thermal closure whereas an electron donating group has slowed it down. We were interested in studying the behavior of the more electronically neutral methyl substituent at the *para*-position of styryl group.

**Scheme 2.57 Synthesis of *p*-methyl-styryl CPDs 226-228**

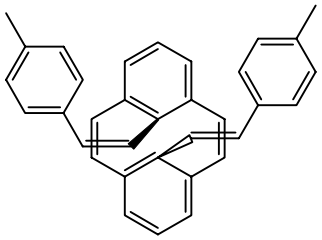



Wittig reaction of **174** in THF at room temperature afforded the thiomethylcyclophanes **224** in >57% yield (Scheme 2.57). The desired product **224** was identified by the $^1$H NMR peaks at δ 2.4-2.0 corresponding to the benzylic protons. Methylation of **224** with Borch reagent gave **225** and the subsequent Hoffmann

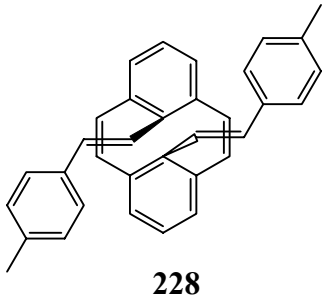
elimination gave a 5:2:1 mixture of cyclophanedienes **226**:**227**:**228** in 38% combined yield. The isomeric CPDs were purified by column chromatography over silica gel.



**226**



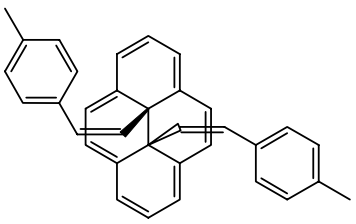
**227**



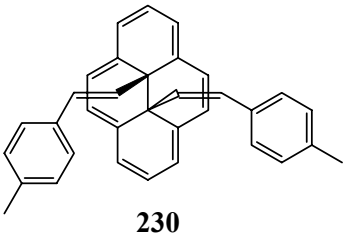
**228**

The all *cis*-isomer **226**, eluted first from the column, was the major product of the reaction and was easily identified by its $^{1}H$ NMR spectrum. The protons of the methyl group in **226** appeared at δ 2.25 and, the corresponding carbon at 21.36 in the $^{1}H$ and $^{13}C$ NMR spectra respectively, slightly shielded when compared with the *trans*-isomer **228** (δ 2.34 and 21.49). In the unsymmetrical isomer **227**, protons of the methyl substituents were found at δ 2.32 and 2.24 in the $^{1}H$ NMR spectrum and, the corresponding carbons at δ 21.48 and 21.38 in the $^{13}C$ NMR spectrum.

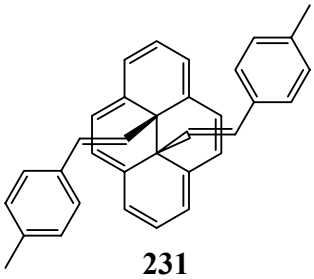
Cyclophanedienes **226-228** were thermally isomerized to the dihydropyrenes **229-231** at rates quite comparable to those of methoxy CPDs **218-220.**



**229**



**230**



**231**

The methyl protons were also quite distinct in different isomers besides the general differences in the DHP protons. The methyl protons and carbons in the all *cis*-

isomer **229** appeared at δ 2.34 and 21.47 respectively compared to 1.99 and 21.04 for the all *trans*-isomer **231.**

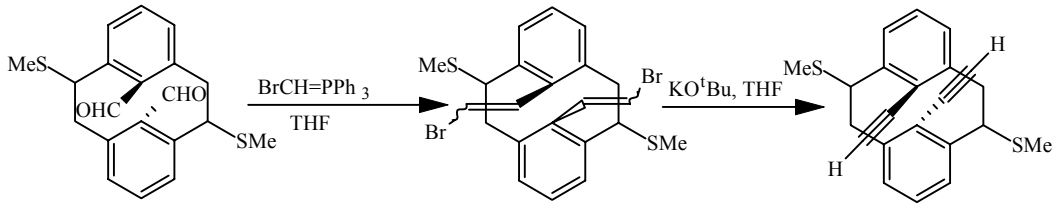
## 2.7 Alkynes as the internal substituents.

### 2.7.1 Synthesis of diethynyl CPD 235

Internal olefin substituted cyclophanedienes have shown slow rates for the unwanted thermal return. Moreover, dihydropyrenes are stable and show no tendency towards migration which makes them excellent candidates as photoswitches. We became interested in introducing alkyne substituents at both internal positions. A cyclophanediene with one internal alkyne substituent, **138** has already been described but it was postulated that a cyclophanediene with two internal alkyne substituents, for example **235** or **140** would behave quite differently and this was based on the comparison of the behavior of pairs **127/128** and **85/86.**

The thiomethylcyclophane **233,** required for the synthesis of the CPD **235** could be generated from the diformyl MeS-cyclophane **174** in one pot (Scheme 2.58). Wittig reaction of **174** with the ylide afforded **232** which eliminated HBr in-situ to give the desired products **233.**

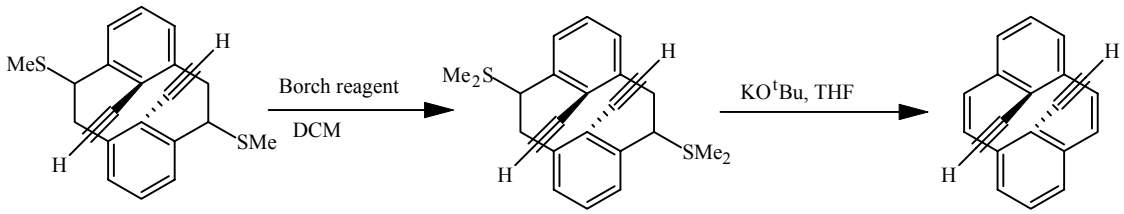
**Scheme 2.58 Synthesis of diethynyl-thiomethylcyclophane 233**




**174** **232** **233**

The ethynyl group in **233** was identified by peaks at δ 2.3 and δ 86.94 in the $^{1}H$ and $^{13}C$ NMR spectra, respectively. Thiomethylcyclophanes **233** when treated with dimethoxycarbonium tetrafluoroborate gave 63% of the sulfonium salt mixture **234** which on Hoffmann elimination using *t*-BuOK as base in THF afforded the desired product **235** in variable yields, the origin of what will be discussed in the next section. (Scheme 2.59).

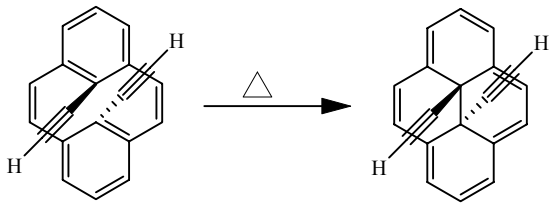
**Scheme 2.59 Synthesis of the diethynyl CPD 235**




**233** **234** **235**

Diethynyl CPD **235** was purified by column chromatography and could easily be identified by its $^{1}H$ NMR spectrum. The ethynyl protons appeared at δ 2.84. The ethynyl group was further supported by the $^{13}C$ NMR peaks at δ 83.39 and 81.84 and finally confirmed by the IR stretches at 3293 and 2578 $cm^{-1}$. An X-ray analysis established the structure **235**.

**Scheme 2.60 Thermal isomerization of diethynyl CPD 235 into DHP 236**

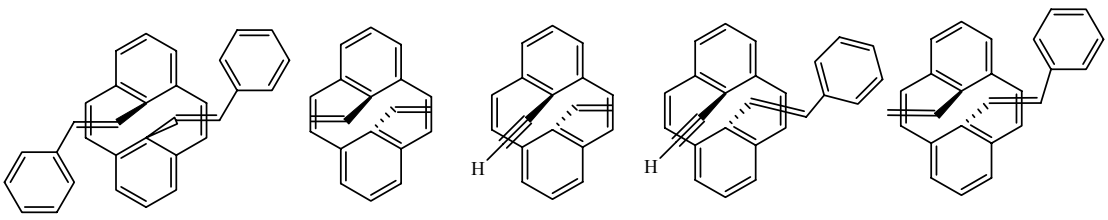



**235** **236**

The dihydropyrene **236** was obtained by thermal isomerization of **235** (Scheme 2.60) and showed its internal ethynyl protons shielded to δ -0.09 in the $^{1}$H NMR spectrum. The ethynyl carbons also appeared highly shielded at δ 65.00 and 75.36 in the $^{13}$C NMR spectrum. The alkyne C-H stretch at 3264 cm$^{-1}$ confirmed the ethynyl group. Mass spectrometry gave the correct molecular mass of *m/z* 252 and the structure was finally established by X-ray analysis.

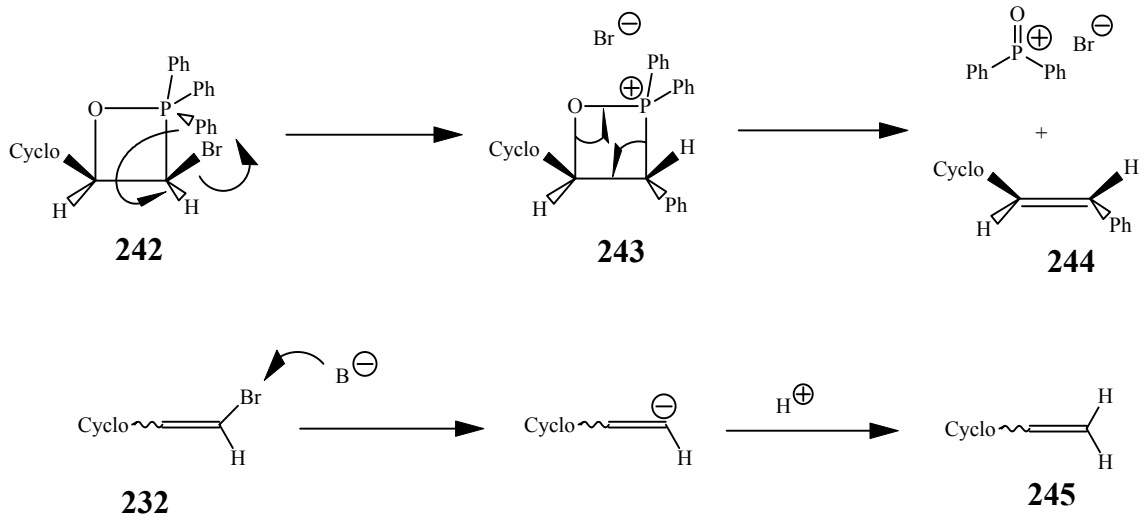
### 2.7.1.1 Unexpected products from Wittig reaction

It has already been stated that the CPD **235** was obtained in variable yields. The side products of the reaction involved one or more of the following cyclophanedienes. Divinyl CPD **166** was the most common side product. CPDs **166** and **204** (*trans*-distyryl) were identified by comparison of spectral data. The cyclophanedienes **237** and **240** were purified and fully characterized while structure was tentatively assigned to **239**. A large excess of base and high temperature were key factors in the formation of the side products.




**204** **166** **237** **239** **240**

**Scheme 2.61 Mechanism of vinyl and styryl incorporation during the Wittig reaction**



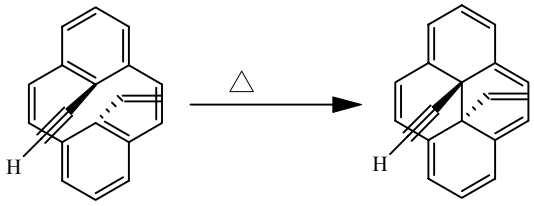

A plausible mechanism for the formation of the vinyl and styryl cyclophanedienes is shown in Scheme 2.61. The Wittig reaction of the aldehyde **174** and the ylide generates betaine **242**. A phenyl group attached to the phosphorous atom undergoes a 1,2 migration and expels the bromine atom in an $S_N2$ fashion and generates **243** which upon elimination generates the *trans*-styryl olefin **244**. The phenyl group attacks the bromide *anti* to the cyclophane (cyclo) probably because of steric reasons which results in the *trans* double bond in the resulting olefin.

The vinyl group is generated probably through the bromide abstraction-protonation sequence shown in Scheme 2.61. Although a mixture of t-BuOK/ DMSO[73] has been shown to abstract a vinylic bromide, we are not certain how *t*-BuOK itself abstracts the bromide.

A $^1$H NMR signal at δ 2.80 indicated the presence of an ethynyl group in **237** which was supported by the $^{13}$C chemical shifts at δ 82.28 and 81.96. The ethynyl group

was confirmed by the IR stretch at 3303 $cm^{-1}$. Protons from the vinyl group were observed as three doublets of doublets at δ 6.32, 5.45 and 4.80 in the $^{1}H$ NMR spectrum. The CPD alkene bridge protons were found as an AB quartets at δ 6.55-6.33 with a coupling constant of 11.4 Hz. Mass spectrometry confirmed the formula by the molecular ion peak at *m/z* 254.

**Scheme 2.62 Thermal isomerization of the CPD 237 to DHP 238**



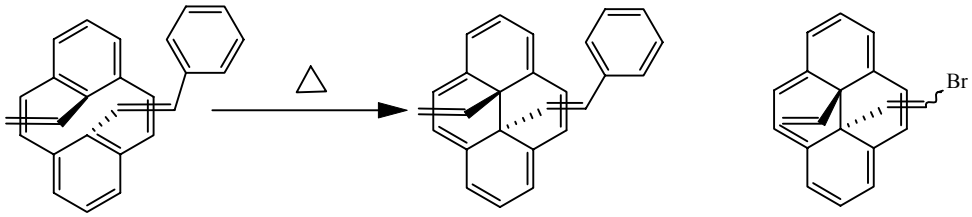

**237** **238**

The internal ethynyl and vinyl group were quite distinct in the dihydropyrene **238** and could easily be accounted for. The proton of ethynyl group expressed itself as a singlet in the $^{1}H$ NMR spectrum at δ -0.14. In the $^{13}C$ NMR spectrum, signals at δ 63.44 and 77.23 further supported the presence of the ethynyl group, which was finally corroborated by a band at 3267 $cm^{-1}$ in the IR spectrum. A molecular ion at *m/z* 254 in the mass spectrum confirmed the molecular formula.

Vinyl-styryl CPD **240** was initially considered to be **246** and this conclusion was based on the analysis of the 300 MHz $^{1}H$ NMR spectrum. Phenyl protons at δ 7.24 were masked by the residual $CDCl_3$ peak. However, phenyl protons became more obvious in the 500 MHz NMR spectrum. An AB quartet at δ 6.43 with 15.4 Hz coupling constant indicated the *trans* orientation of the double bond. Mass spectrometry confirmed the

molecular formula by a peak at *m/z* 332. The loss of the styryl and ethenyl groups was suggested by peaks at $[M-103]^+$ and $[M-130]^+$ in the mass spectrum.

**Scheme 2.63 Thermal isomerization of the CPD 240 to the DHP 241**



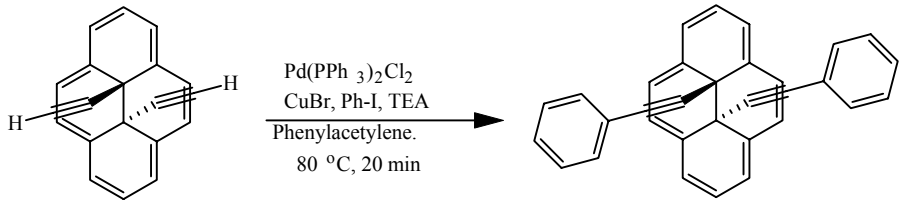

**240** **241** **246**

The vinyl and styryl groups were more obvious in the dihydropyrene **241** (Scheme 2.63). The olefin protons at δ 0.84 and 3.21 showed a coupling constant of 16 Hz, confirming the *trans*-styryl group.

### 2.7.2 Diphenylethynyl DHP

The high stability of switch pair **235/236** refreshed our interest in the bis(phenylethynyl) DHP **141.** We realized that **141** might be synthesized in one step from **236** by Sonogashira coupling with phenyl iodide.

**Scheme 2.64 Sonogashira coupling to synthesize 141**




**236** **141**

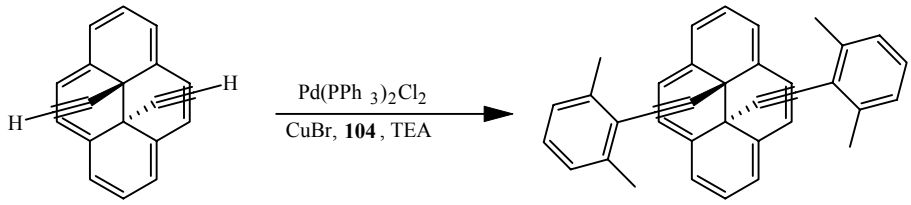
The Sonogashira coupling of **236** with iodobenzene in refluxing TEA using $Pd(PPh_3)_2Cl_2$ as a catalyst failed to furnish the desired product **141**. Variation of the

reaction conditions including temperature, catalyst loading or concentration gave either the starting material or the pyrene **112**. It was noticed that a diluted reaction at higher temperature gave pyrene instantly. Moreover, high catalyst loading was detrimental as well.

In the Sonogashira coupling[74], acetylene reacts with the $Pd^{+2}$ catalyst and forms an acetylide complex which undergoes reductive elimination of the bis-acetylene to generate an active Pd(0) catalyst. We thought that this Pd(0) generation step is the main source of pyrene formation under high catalyst loading conditions. If Pd(0) could be generated by some other acetylene such as phenylacetylene, then the Sonogashira coupling of **236** with phenyl iodide would yield the desired product **141**.

Thus, Pd(0) was generated by reacting the $Pd^{+2}$ catalyst with phenylacetylene at 80 $^{o}$C in TEA in the presence of iodobenzene. This Pd(0), on reaction with **236** afforded the desired product in ~ 70% yield in less than 20 minutes (Scheme 2.64). A 15% yield of the pyrene **112** was also obtained. Phenylethynyl DHP **141** was purified by column chromatography. The phenylethynyl group was identified in the $^{1}$H NMR spectrum by peaks at δ 6.06, 6.78 and 6.89 corresponding to *ortho, meta* and *para* protons respectively. The ethynyl carbon resonances were found at δ 81.55 and 76.96 in the $^{13}$C NMR spectrum. DHP **247,** a dimethyl derivative of **141** was also prepared by the Sonogashira coupling of **236** with 2,6-dimethyliodobenzene **104** in 25% yield (Scheme 2.65).

**Scheme 2.65 Sonogashira coupling to synthesize 247**




**236** **247**

## 2.8 Synthesis of naphthoyl dihydropyrenes

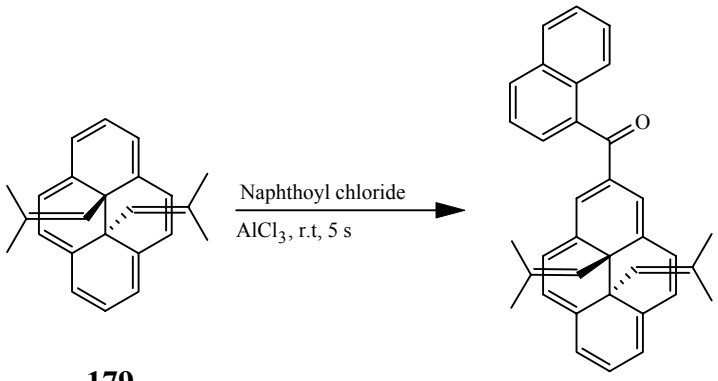
Slow thermal return along with the stability of both isomers render the pair **178/179** as an excellent cyclophanediene/dihydropyrene based photoswitch. However the photoopening of the isobutenyl DHP **179** is relatively slow when compared with the benzo-DHP. It has already been stated that introduction of carbonyl functional groups can accelerate the photoopening reaction of dihydropyrenes. Robinson[35] has reported that a naphthoyl substituent at the two position of DHP can accelerate the photoopening reaction up to two orders of magnitude; however it speeds up the thermal return as well.

### 2.8.1 2-Naphthoyl diisobutenyl DHP 248

Addition of $AlCl_3$ to the mixture of DHP **179** and naphthoyl chloride afforded the naphthoylated DHP **248** instantly. The desired product could only be isolated in useful yields if the reaction was quenched within 10 seconds of the addition of $AlCl_3$ (Scheme 2.66). Longer reaction times gave a mixture of at least five or six pyrenes as revealed by fluorescent spots on TLC. The formation of pyrenes could also be visualized by change in color from purple to orange and finally to pale yellow. Column chromatography using alumina failed to separate **248** from a co-eluting pyrene, while use of silica resulted in the

decomposition of the DHP. Recrystallization from methanol yielded nice purple crystals of **248**, mp 179-180 $^{o}$C.

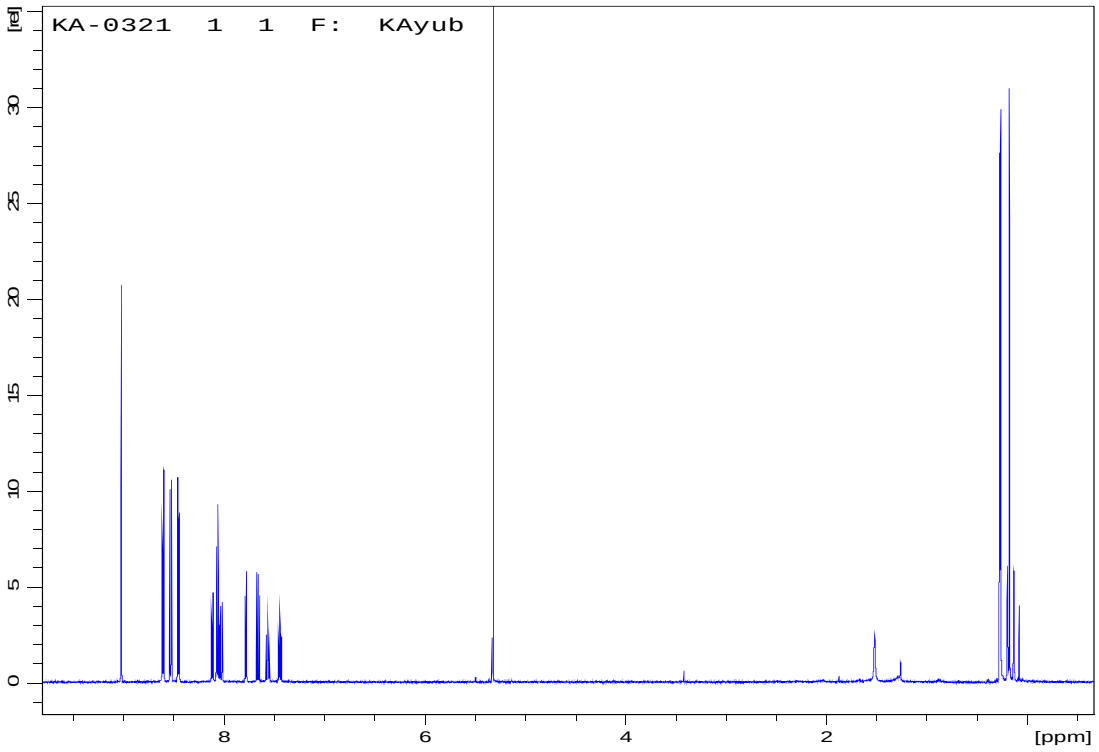
**Scheme 2.66 Friedel-Crafts naphthoylation of diisobutenyl DHP 179**



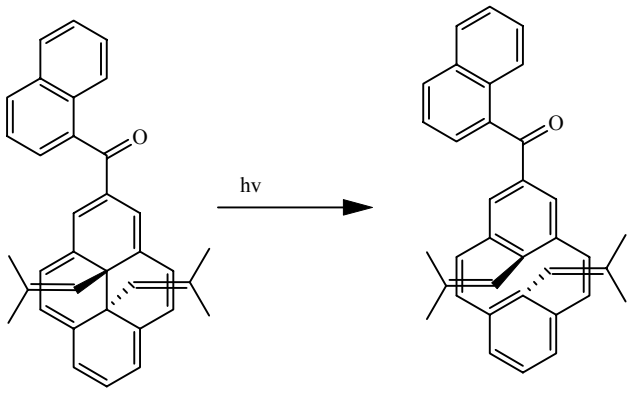

**179** **248**

In the $^{1}$H NMR spectrum (Figure 2.3), appearance of five peaks from the DHP protons indicated the naphthoyl group at the two position, an assignment that was further supported by a downfield singlet at δ 9.06 corresponding to H-1,3, the protons *ortho* to the naphthoyl substituent. The position of the naphthoyl group was confirmed by HMBC and HSQC experiments. The naphthoyl protons appeared at δ 8.08-7.46 and were completely assigned. The $^{13}$C NMR signal at δ 198.30 indicated the carbonyl functional group which was confirmed by the IR stretch at 1637 cm$^{-1}$, a highly conjugated ketone.

**Figure 2.3 1H NMR spectrum of naphthoyl DHP 248 in $CD_2Cl_2$ at 500 MHz**




**Scheme 2.67 Photoopening of DHP 248**

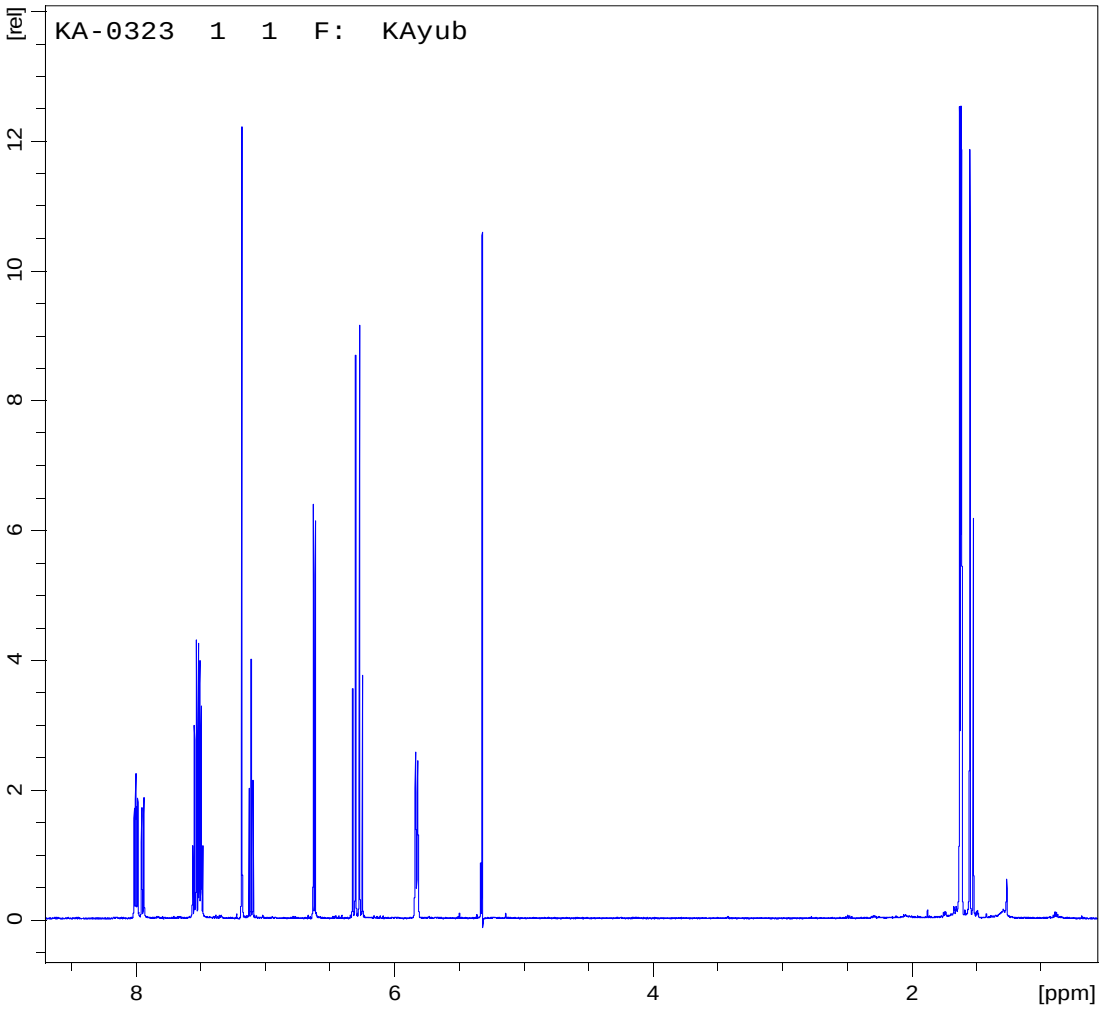



**248** **249**

The naphthoyl dihydropyrene, when irradiated with visible light, opened instantaneously to the cyclophanediene **249** (For details; see chapter 4). The carbonyl carbon was identified by the $^{13}C$ NMR chemical shift at 196.73 ppm, and the presence of

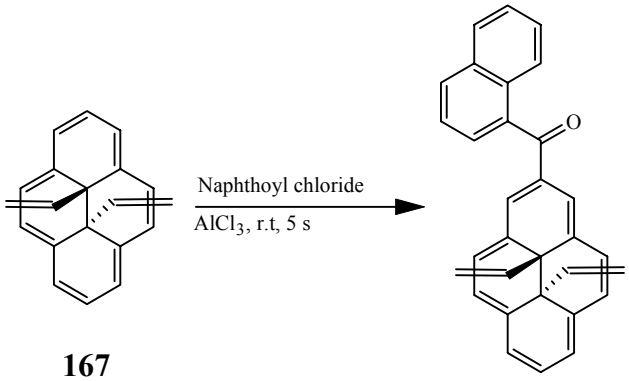
a carbonyl was supported by the IR band at 1653 $cm^{-1}$. The cyclophanediene had the expected HRMS signal at *m/z* 466.2292 (calculated 466.2296)

**Figure 2.4 $^{1}H$ NMR spectrum of naphthoyl CPD 249 in $CD_2Cl_2$ at 500 MHz**



### 2.8.2 Synthesis of 2-naphthoyldivinyl DHP 250 and its photoopening to the CPD 251

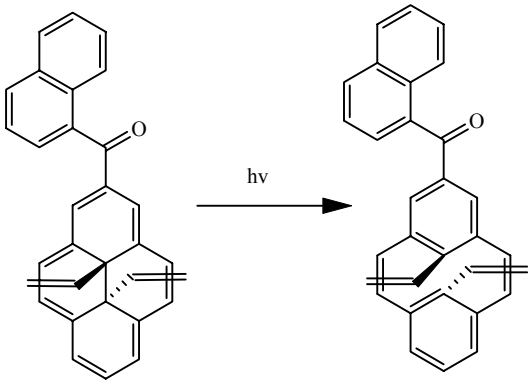
**Scheme 2.68 Synthesis of the naphthoyl DHP 250**




**167** **250**

Friedel-Crafts naphthoylation of **167** gave 67% of the dark maroon **250** (Scheme 2.68). Photoirradiation of the DHP afforded the cyclophanediene **251**. All protons and carbons in DHP **250** could be assigned. However in the CPD, naphthoyl protons were not fully assigned because they overlapped with each other.

**Scheme 2.69 Visible opening of the DHP 250 to the cyclophanediene**




**250** **251**

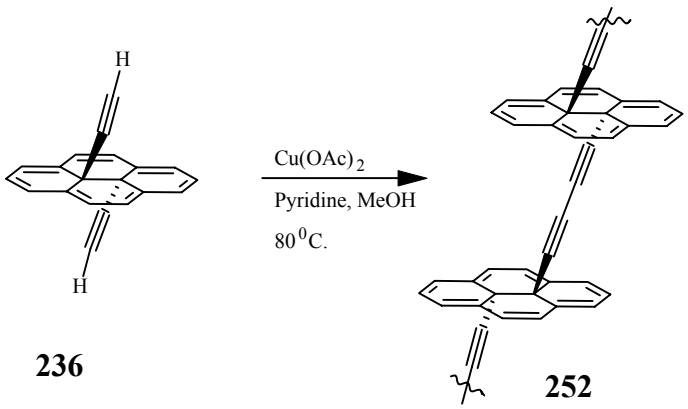
## 2.9 Synthesis of dimer, oligomers and polymers

Practical applications of photoswitches require that they can be used in the solid phase, either crystalline or in a polymeric phase[75]. Literature[1,76] suggests that most of the examples involve a photoswitch pendant on a polymer backbone. We became interested in the synthesis of a polymer in which the monomer unit itself is a photoswitch. An example of a DHP based polymer is shown in Scheme 2.70.

### 2.9.1 Polymerization of the acetylene DHP 236

Eglinton[77] coupling of the diethynyl DHP **236** using $Cu(OAc)_2$ in pyridine/methanol at 80 $^oC$ gave an olive green solid, practically insoluble in all common solvents (Scheme 2.70). Its UV-vis spectrum in dichloromethane showed the characteristic DHP absorption bands at 470 and 385 nm which suggested the formation of the desired product. A $^1H$ NMR spectrum could not be obtained, because of the insolubility of the polymer and also due to the presence of paramagnetic copper species.

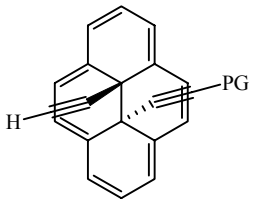
**Scheme 2.70 Attempted synthesis of the DHP based polymer**



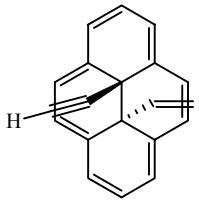

**236** **252**

### 2.9.2 Formation of a dimer by Eglinton coupling

Eglinton coupling of mono protected DHP **253** was expected to give a dimer which would be easy to characterize. We realized that the vinyl-ethynyl DHP **238**, already available to us, can function like a mono-protected DHP **253**.

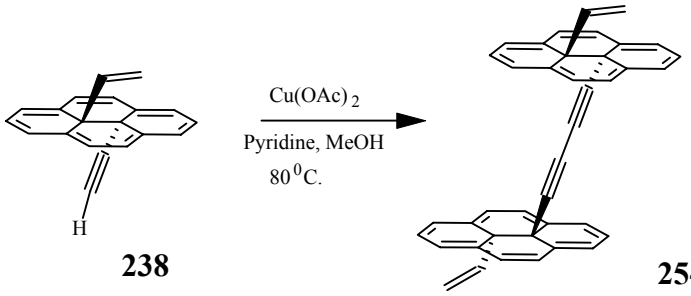



**253**




**238**

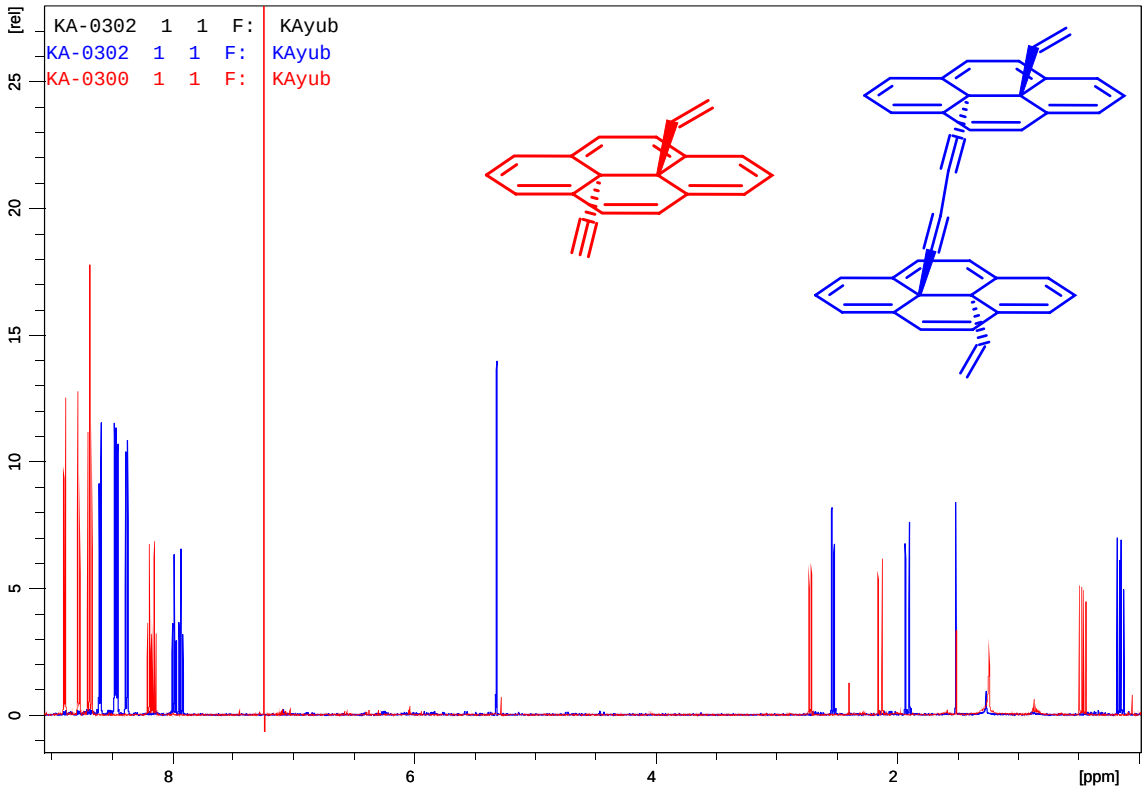
**Scheme 2.71 Synthesis of the dimer 254**




**238** **254**

The self Eglinton coupling of **238** using $Cu(OAc)_2$ in pyridine/methanol at 80 $^oC$ gave >90% yield of the dimer **254** (Scheme 2.71). The product was purified by column chromatography. The disappearance of the ethynyl peak at δ -0.14 in the $^1H$ NMR spectrum (Figure 2.5) suggested formation of the desired product. All protons in the dimer were shielded by 0.2-0.3 ppm when compared with the monomer. In the $^{13}C$ NMR spectrum, the ethyl carbons were found at δ 70.90 and 58.95.

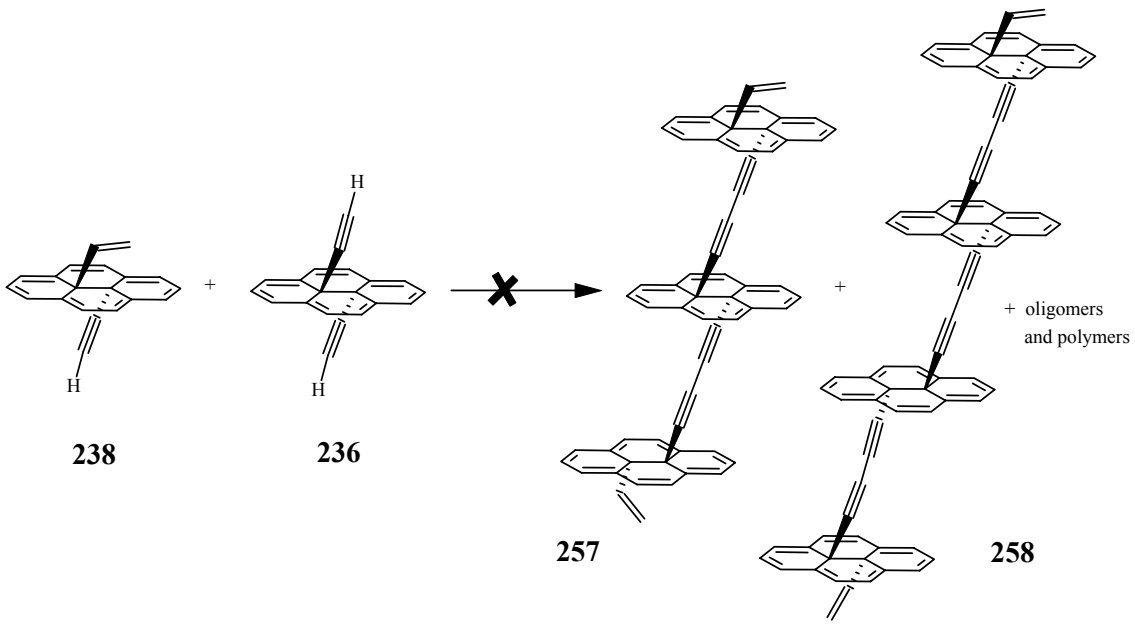
**Figure 2.5** **$^1$H NMR spectra of monomer 238 and dimer 254 in $CDCl_3$ at 500 MHz**




### 2.9.3 Cross coupling between vinyl-ethynyl DHP 238 and diethynyl DHP 236

A cross coupling of the dihydropyrenes **238** and **236** in equimolar quantities failed to afford the oligomers **255** and **256**. Analysis of the product mixture indicated unreacted **238**, the dimer **254** and some long chain oligomers/polymers with no unreacted **236** which indicated the low reactivity of **238**. We are not certain how the vinyl substituent in **238** decelerates the Eglinton coupling even though it is electronically and sterically isolated from the ethynyl group.

**Scheme 2.72 Attempted synthesis of the oligomers**

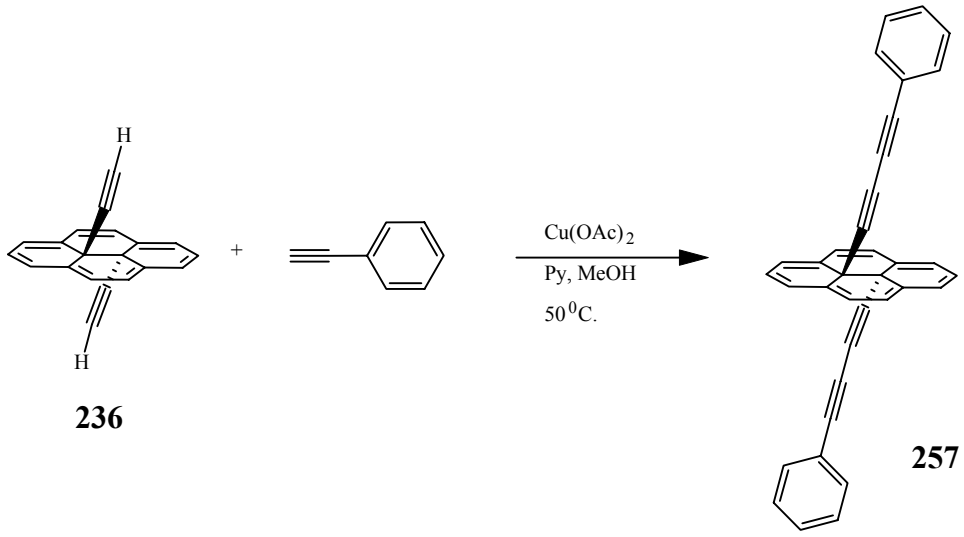



An Eglinton coupling with three to four fold excess of **238** also failed to afford the oligomers in useful yields. TLC indicated two or three spots with $R_f$ values slightly lower than the dimer **254** but these compounds comprised less than 5% of the product mixture. Other modifications such as higher temperature or change of the acetylene to TIPS-acetylene gave pyrene **112**.

### 2.9.4 Bis Phenbutadienyl DHP 257

Eglinton coupling of diethynyl DHP **236** with a large excess of phenylacetylene afforded a ~30% yield of the diyne DHP **257** (Scheme 2.73). The desired product was purified from the starting material and the mono-coupled product by repeated washing with dichloromethane.

**Scheme 2.73 Eglinton coupling of the diethynyl DHP 236 with phenylacetylene**



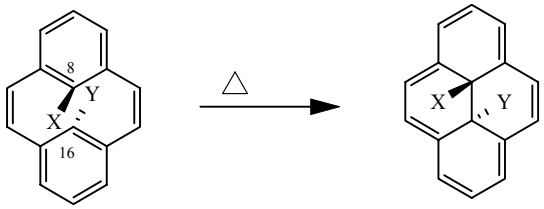

**236** **257**

The phenyl protons were found at δ 6.99 (*o*), 7.09 (*m*) and 7.19 (*p*) in the $^{1}$H NMR spectrum. The alkyne carbons appeared in the $^{13}$C NMR spectrum at δ 62.15, 72.32, 74.93 and 76.44 but their complete assignment was not possible.

# Chapter 3: Thermochemical Reaction

## 3.1 Electrocyclic reaction

Williams[41] has shown by DFT calculations that the transition state for the unfavorable thermal reaction of cyclophanedienes has biradical character with most of the spin density at the 8-, and 16- internal positions. A change in functional group at these positions was calculated to have a marked influence on the magnitude of the activation barrier for the thermal isomerization, thus a series of cyclophanedienes with different internal substituents were prepared as outlined in Chapter 2. A schematic representation of the thermal reaction is given below.




The thermal reaction of the cyclophanedienes was monitored by $^1$H NMR spectroscopy. Diformyl CPD **152** and *cis*-dipropenyl CPD **162** were studied by variable temperature (VT) NMR spectroscopy. For other CPDs except **85**, as a general procedure, an NMR sample was held at the experiment temperature for the desired time interval, immersed in ice-water to quench the thermal reaction, and its $^1$H NMR spectrum was then taken as quickly as possible. Dicyano CPD **85**, practically insoluble in all useful organic solvents, was studied in the solid phase. Six NMR samples containing ~2 mg each were held at the reaction temperature, taken out one by one at desired intervals, dissolved in $CDCl_3$ and then the $^1$H NMR spectrum was obtained. The NMR samples were wrapped in aluminum foil in order to prevent the photochemical reaction.

Corresponding hydrogens in the cyclophanediene and dihydropyrene were chosen for integration purposes, except in the cases of CPDs **85** (dicyano)**, 127** (cyano-methyl) and **152** (diformyl), where the dihydropyrenes decomposed into the migration products. However, integration of the corresponding protons in the CPD and in the migration products gave acceptable results. Moreover, multiple protons in the CPD and DHP/migration products were integrated and averaged in order to reduce the errors arising from integration.

First order rate constants (k) were obtained by plotting ln[CPD/CPD+DHP] against time. These rate constants were used in the Arrhenius equation (3.2) to obtain $E_{act}$ from the slope of ln(k) vs. 1/T plot and ln(A) from the intercept. The slope and intercept in the Eyring plot of ln(k/T) vs. 1/T (equation 3.5), were used to calculate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ respectively.

$$\mathbf{k = Ae^{-Eact/RT}} \qquad \mathbf{3.1}$$

**From (3.1)** $$\mathbf{ln(k) = ln(A) - E_{act}/RT} \qquad \mathbf{3.2}$$

$$\mathbf{k = (k_b.\ T/h)e^{-\Delta H^{\ddagger}/RT}.e^{\Delta S^{\ddagger}/R}} \qquad \mathbf{3.3}$$

**From (3.3)** $$\mathbf{lnk = ln(k_b.T/h) - \Delta H^{\ddagger}/R.T + \Delta S/R} \qquad \mathbf{3.4}$$

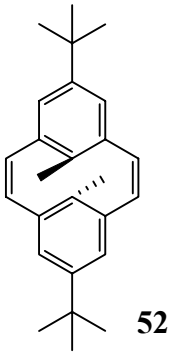
**or**

$$\mathbf{ln(k/T) = ln(k_b/h) - \Delta H^{\ddagger}/RT + \Delta S/R} \qquad \mathbf{3.5}$$

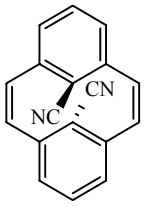
$k_b = 1.381 \times 10^{-23}$ J $K^{-1}$ (Boltzmann constant)

$R = 8.314$ J $K^{-1}$ $mol^{-1}$ (gas constant), $h = 6.626 \times 10^{-34}$ Js (Planks constant)

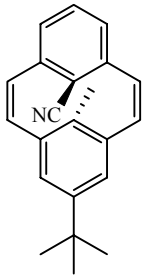
The following cyclophanedienes were studied for their thermal closure to the dihydropyrenes and the results are shown in Tables 3.1 and 3.2.



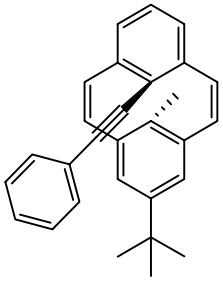
**52**



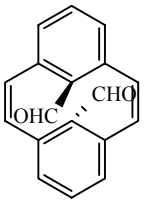

**85**



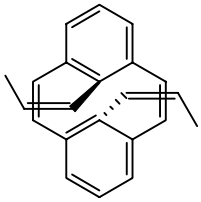

**127**



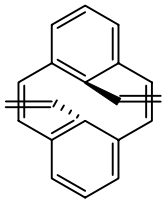
**138**



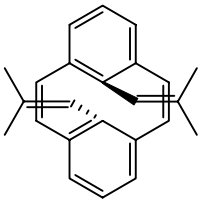

**152**



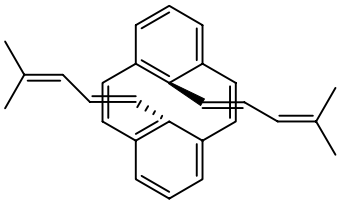
**162**



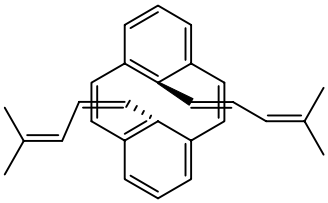
**166**



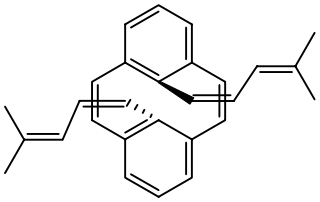
**178**



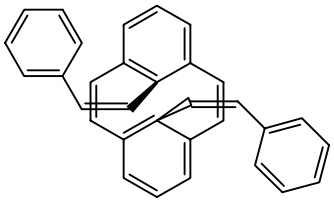
**184**



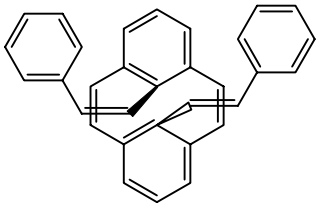
**185**



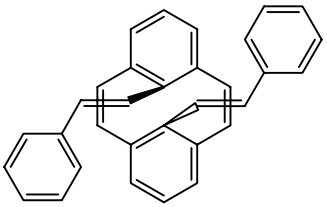
**186**



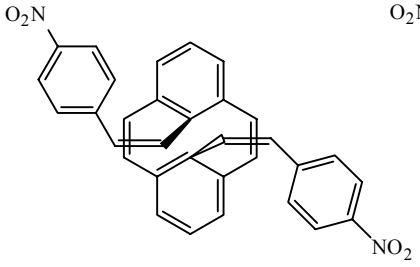
**202**



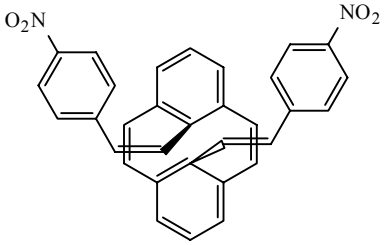
**203**



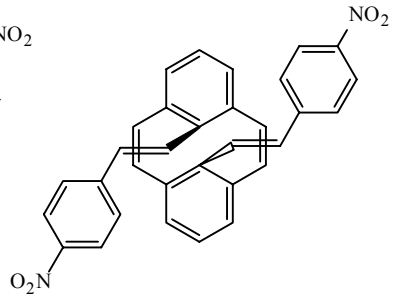
**204**



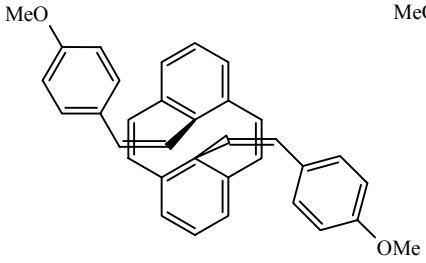

**210**



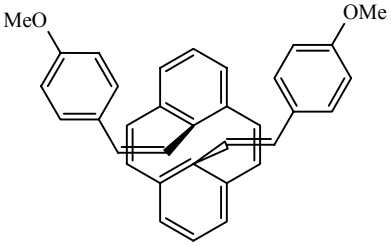

**211**



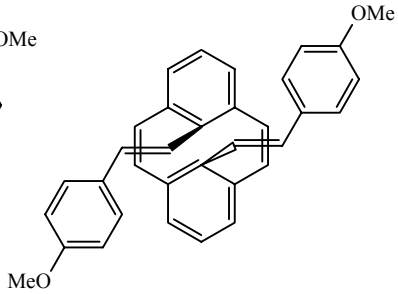

**212**



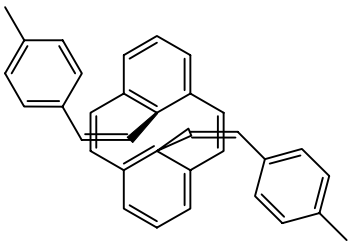

**218**



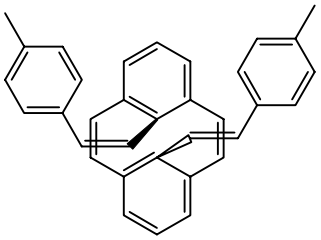

**219**



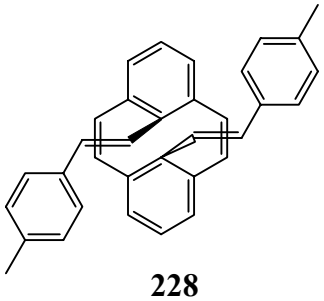

**220**



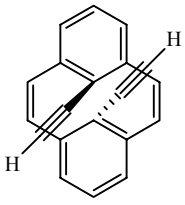
**226**



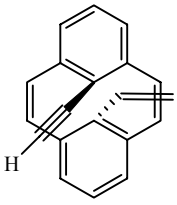
**227**



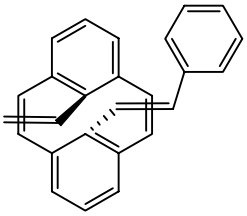
**228**



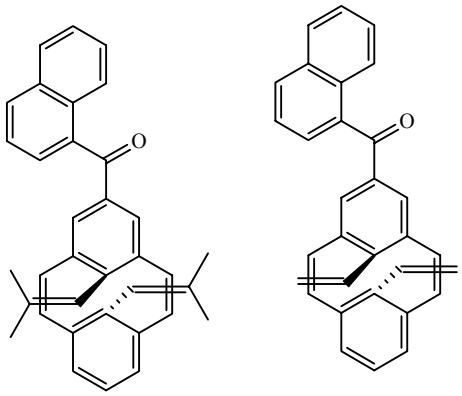

**235**




**237**



**240**



**249** **251**

**Table 3.1 Thermodynamic parameters for the thermal back reaction of cyclophanedienes**

| Compound | $E_{act}$ kcal/mol | $\Delta H^{\ddagger}$ kcal/mol | $\Delta S^{\ddagger}$ cal/mol | lnA |
|---|---|---|---|---|
| **52** | 20 ± 2 | 20 ± 2 | 15 ± 6 | 22.8 ± 3 |
| **85**[§] | 30 ± 1 | 29.1 ± 1 | -1 ± 2.5 | 30.2 ± 1.3 |
| **127**[*] | 24 ± 0.6 | 23.2 ± 0.5 | -7.6 ± 1.4 | 26.9 ± 0.8 |
| **127**[#] | 23.8 ± 0.2 | 23.0 ± 0.2 | -7.8 ± 0.6 | 26.8 ± 0.2 |
| **138**[*] | 24.4 ± 0.3 | 23.7 ± 0.3 | -7.6 ± 1 | 26.7 ± 0.5 |
| **152**[#] | 26.2 ± 0.3 | 25.6 ± 0.3 | 0.6 ± 0.8 | 30.8 ± 0.4 |
| **162**[∞] | 29.9 ± 0.6 | 29.2 ± 0.6 | 1.3 ± 1.6 | 31.3 ± 0.8 |
| **166**[∞] | 25.0 ± 0.9 | 24.4 ± 1 | 4.3 ± 3 | 26.8 ± 1.4 |
| **178**[∞] | 28.2 ± 0.5 | 27.5 ± 0.5 | -5.4 ±1.2 | 28.0 ± 0.6 |
| **184**[∞] | 26.7 ± 0.2 | 26.0 ± 0.2 | -5.8 ± 0.5 | 27.8 ± 0.2 |
| **185**[∞] | 27.6 ± 0.1 | 26.8 ± 0.1 | -4.9 ± 0.1 | 28.4 ± 0.1 |

| | | | | |
|---|---|---|---|---|
| **186**$^{\infty}$ | 26.8 ± 0.6 | 26.1 ± 0.6 | -7.5 ± 1.6 | 26.9 ± 0.8 |
| **202**$^{\infty}$ | 27.2 ± 0.6 | 26.5 ± 0.6 | -5.9 ± 1.5 | 27.7 ± 0.8 |
| **203**$^{\infty}$ | 26.9 ± 0.1 | 26.2 ± 0.1 | -6.3 ± 0.3 | 27.5 ± .1 |
| **204**$^{\infty}$ | 26.3 ± 0.6 | 25.6 ± 0.6 | -6.7 ± 1.5 | 27.3 ± 0.8 |
| **210**$^{\infty}$ | 25.7 ± 0.1 | 25 ± 0.1 | -9.6 ± 0.3 | 25.8 ± 0.1 |
| **211**$^{\infty}$ | 26.4 ± 0.5 | 25.6 ± 0.5 | -7.3 ± 1.2 | 26.9 ± 0.6 |
| **212**$^{\infty}$ | 26.3 ± 0.4 | 25.6 ± 0.4 | -7.4 ± 1 | 27 ± 0.5 |
| **218**$^{\infty}$ | 27.4 ± 0.1 | 26.7 ± 0.1 | -6.4 ± 0.1 | 27.6 ± 0.1 |
| **219**$^{\infty}$ | 26.6 ± 0.2 | 25.9 ± 0.2 | -7.5 ± 0.6 | 26.9 ± 0.3 |
| **220**$^{\infty}$ | 26.4 ± 0.2 | 25.7 ± 0.2 | -7.4 ± 0.4 | 27 ± 0.2 |
| **226**$^{\infty}$ | 26.9 ± 0.3 | 26.1 ± 0.3 | -7.6 ± 0.8 | 26.9 ± 0.4 |
| **227**$^{\infty}$ | 26.2 ± 0.5 | 25.3 ± 0.5 | -8.8 ± 1.4 | 26.2 ± 0.7 |
| **228**$^{\infty}$ | 25.9 ± 0.1 | 25.1 ± 0.1 | -8.8 ± 0.2 | 26.2 ± 0.1 |
| **235**$^{\infty}$ | 28.4 ± 0.8 | 27.7 ± 0.6 | -3.2 ± 1.6 | 29 ± 1.1 |
| **237**$^{\infty}$ | 25.7 ± 0.5 | 25 ± 0.5 | -7.4 ± 1.4 | 27 ± 0.7 |
| **240**$^{\infty}$ | 26.1 ± 0.1 | 25.4 ± 0.1 | -5.8 ± 0.1 | 27.7 ± 0.1 |
| **249**$^{\infty}$ | 27.3 ± 1 | 26.6 ± 1 | -4.1 ± 2.9 | 28.6 ± 1.4 |
| **251**$^{\#}$ | 24.2 ± 0.8 | 23.5 ± 0.8 | -5.2 ± 2.6 | 28 ± 1.3 |

$^{\infty}$ = Toluene, # = CDCl3, * = Benzene, § = Solid phase

**Table 3.2 Half lives of the cyclophanedienes at three different temperatures**

| Compound | $\tau_{1/2}$ (20 °C)* | $\tau_{1/2}$ (50 °C)* | $\tau_{1/2}$ (100 °C) |
|---|---|---|---|
| **85** | ~ 36 years | 107 days | 5 h |
| **178** | 16 years | 65 days | 4.5 h |
| **162** | 10 years | 33 days | 94 min |
| **235** | 8 years | 49 days | 124 min |
| **218** | 6 years | 27.7 days | 130 min |
| **226** | 5 years | 25 days | 132 min |
| **186** | 4.5 years | 23 days | 115 min |
| **202** | 4.3 years | 20 days | 91 min |
| **185** | 4 years | 18 days | 82 min |
| **219** | 3.1 years | 16.4 days | 92 min |
| **203** | 2.8 years | 14 days | 73 min |
| **227** | 2.5 years | 14 days | 87 min |
| **220** | 2 years | 11 days | 64 min |
| **249** | 2 years | 8.5 days | 43 min |
| **210** | 1.9 years | 11.3 days | 77 min |
| **211** | 1.8 years | 9.8 days | 59 min |
| **228** | 1.7 years | 10 days | 63 min |
| **212** | 1.7 years | 9.2 days | 55 min |
| **184** | 1.6 years | 8.5 days | 45 min |
| **204** | 1.2 years | 6.3 days | 40 min |

| | | | |
|---|---|---|---|
| **237** | 200 days | 80 h | 24 min |
| **240** | 197 days | 74 h | 23 min |
| **198** | - | - | ~15 min |
| **166** | 56 days | 24 h | 7.7 min |
| **138** | 30 days | 15.2 h | - |
| **127** (benzene) | 12.3 days | 6.7 h | - |
| **152** | 11 days | 4.2 h | - |
| **127** $CDCl_3$ | 9.5 days | 5.2 h | - |
| **251** | 5.8 days | 3 h | - |

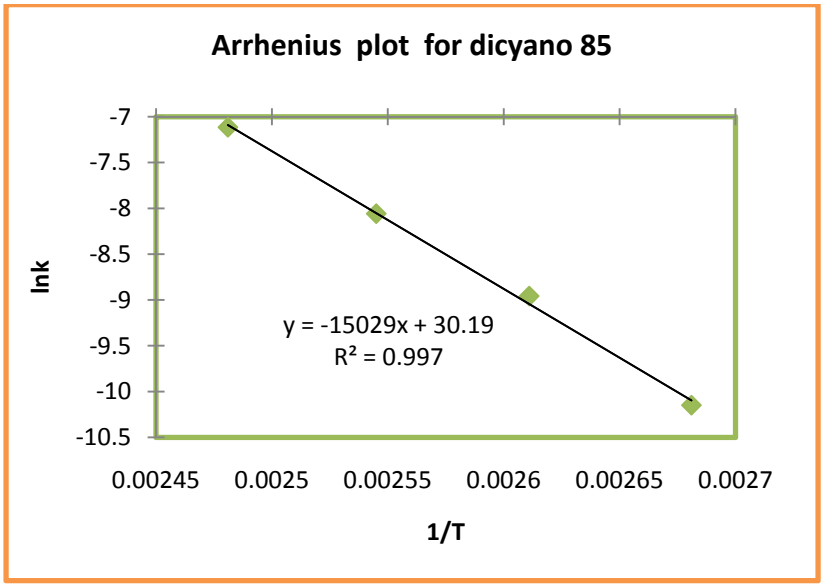
***** Errors estimated are < 5%

The dicyano CPD **85** was calculated by Williams, to have an activation barrier of about 25-27 kcal/mol for the thermal closure. The nitrile group is a radical stabilizing group and was anticipated to lower the activation barrier however conjugation of the aryl rings with the nitriles stabilizes the CPD more than the $TS^{\ddagger}$ and thus increases the activation barrier.

Nitrile **85** when heated at 70 $^{o}$C for 12 hours failed to isomerize to the dihydropyrene **86** which indicated its high activation barrier, quite consistent with Williams' calculations. However, heating **85** at 100 $^{o}$C did not lead to **86** as the only product, rather a mixture of *trans*-DHP **86**, migration and elimination products **124**, **125** and **126** was observed. The mole fraction of the CPD [**85**/**85**+**86**+**124**+**125**+**126**] when plotted against time gave rate constants of 3.90, 12.9, 31.6 and 81.3 x $10^{-5}$ $s^{-1}$ at 100, 110, 120 and 130 $^{o}$C respectively. The Arrhenius plot yielded $E_{act}$ ~ 30 kcal/mol. The Eyring plot gave $\Delta H^{\ddagger}$ ~ 29.3 kcal/mol. The activation barrier was about 3-5 kcal/mol higher than

the calculated value. This high activation barrier should be viewed cautiously since there could be a temperature lag in the solid phase. However we believe that the temperature lag, if any, cannot account for 3-5 kcal/mol. We thought that the entropy change might be unfavorable in the solid phase and thus has resulted in the slow thermal return. However the $\Delta S^{\ddagger}$ value obtained for **85** was -1.0 $\pm$ 2.5 cal $mol^{-1}$ $K^{-1}$, considerably higher and favorable than the methyl analogue **52** (-15 $\pm$ 6) cal $K^{-1}$ $mol^{-1}$). Thus, while the DFT calculations were quite successful in predicting a high activation barrier for the cyano CPD **85**, they did underestimate the value.

**Figure 3.1 Arrhenius plot for the thermal reaction of dicyano CPD 85 in the solid phase**



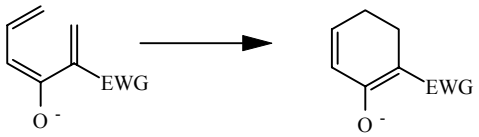

Dicyano CPD **85** has a calculated half life of > 30 years at 20 $^{o}$C which is about three orders of magnitude higher than for the benzo-CPD **53** (7.3 days) which previously was the best switch. The high stability of the cyclophanediene **85** however was flawed by a relatively facile migration of the internal nitrile groups of the dihydropyrene **86** (for details see, Chapter 3 sigmatropic rearrangements).

The cyano-methylcyclophanediene **127** was made with anticipation that the migration and thermal return rates would be an average of those for **52** and **85**. This turned out to be the case for the thermal return; however migration rates were higher than **85**. The thermodynamic data was obtained in benzene and in $CDCl_3$ in order to determine the solvent effect on the thermal closure. The rates were slightly higher in $CDCl_3$ (~ 20%) although other thermodynamic parameters were quite comparable. Cyano-methyl CPD **127** has calculated half lives of 12 and 10 days at 20 $^oC$ in benzene and $CDCl_3$ respectively, slightly higher than that of the benzo-CPD **53** (7.3 days).

It was anticipated that the replacement of the nitrile group in **127** with a phenylethynyl group (CPD **138**) would have little effect on the thermal return because both groups are structurally similar and are rod like in nature. However the thermal return of **138** to **139** is approximately 3 times slower than **127** to **128** and has a calculated half life of ~ 30 days in benzene at 20 $^oC$**.** The energy of activation was ~ 24.3 kcal/mol for **138** and was quite comparable to **127 (**24 kcal/mol). The phenylethynyl group is better at stabilizing radicals than the nitrile and should make the transition state lower in energy and hence $E_{act}$; however this is not the case. The relatively fast thermal return of **127** can be explained by the "captodative effect"[78] of the internal substituents.

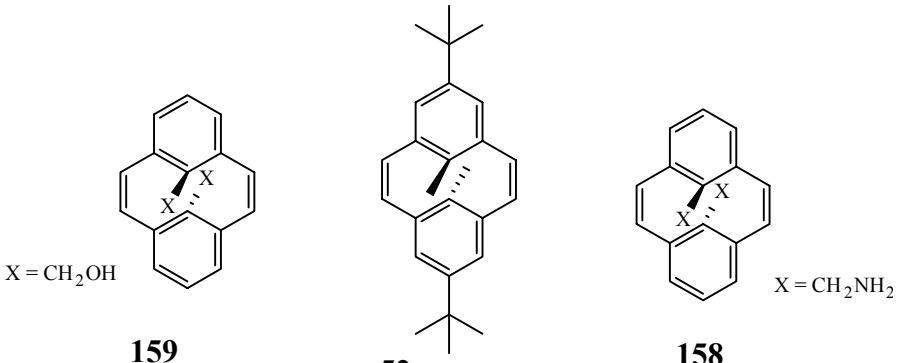
The word "captodative" is generally used to describe the combined effect of electron withdrawing (captor) and electron donating (dative) substituents, both attached to the radical centre or unsaturated compounds. An elegant example of the captodative effect in thermal 6π electrocyclic reactions is reported by Megomedov[79] et al. and is shown in Scheme 3.1. The presence of electron withdrawing groups at C-2 of the 3-oxido hexatrienes enormously lowers $E_{act}$, making the reaction feasible at -78 $^oC$.

**Scheme 3.1 An example of the captodative effect in electrocyclization**




Since nitrile is an electron withdrawing group, and the methyl is a weak electron donor through hyperconjugation, the captodative effect could be a possible explanation. Alternatively, it may be possible that the TS‡ has some anionic character as well, which might not have been pointed out by the DFT calculations. Nitrile, an electron withdrawing group would favor an anionic transition state and would decrease $E_{act}$.

Diformyl CPD **152** is expected to close thermally at rates comparable to those of **85** because both groups, nitrile and aldehyde, stabilize radicals to a comparable extent. Moreover, the captodative effect would also be comparable: however the formylcyclophanediene **152** has a much faster thermal return ($\tau_{1/2}$ = 11 days at 20 $^{o}$C) than **85** ($\tau_{1/2}$ = ~ 36 years at 20 $^{o}$C). A number of factors may be contributing towards the fast thermal reaction of **152**. The formyl groups in **152** may not be in plane with the phenyl rings which would result in decreased conjugation. A low stability of the CPD due to the decreased conjugation would facilitate the thermal isomerization. Alternatively, the formyl group with its more electronegative oxygen atom can better stabilize the anionic transition state, as we proposed earlier, than a nitrile. Dihydropyrenes are electron rich in nature so it may be possible that an electron withdrawing substituent may favour the TS‡ by delocalizing the electron density.

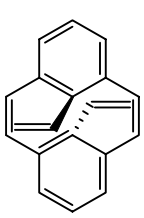



**159** **52** **158**

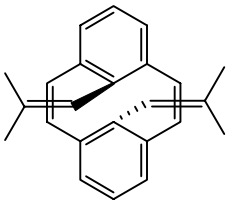
Reduction of the formyl CPD **152** gave **159** which is thermally unstable and isomerizes to the dihydropyrene with a half life less than an hour at 20 $^{o}$C, much shorter than the parent methyl analogue **52** ($\tau_{1/2}$ = 42 hours at 20 $^{o}$C). The high instability of **159** not only demonstrates the importance of conjugation at the internal positions but also supports the notion that the internal electron withdrawing groups accelerate the thermal reaction. However, we failed to obtain **158** which would give us a better understanding of the effect of electron withdrawing groups at the internal positions. It is anticipated that the aminomethyl CPD **158**, once formed, would have a half life higher than that of **159**. We did not explore the captodative effect in detail. However it may be of considerable significance in accelerating the electrocyclic reaction.

Kinetic data of the above mentioned CPDs suggests that a conjugated internal group without any electron withdrawing atoms/substituents would slow down the thermal return. It was realized that alkenes and alkynes might fulfil this criteria.

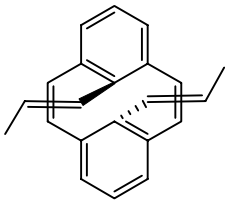
### 3.1.1 Cyclophanedienes with internal olefin substituents



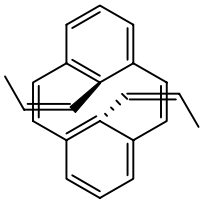
**166**



**178**



**198**

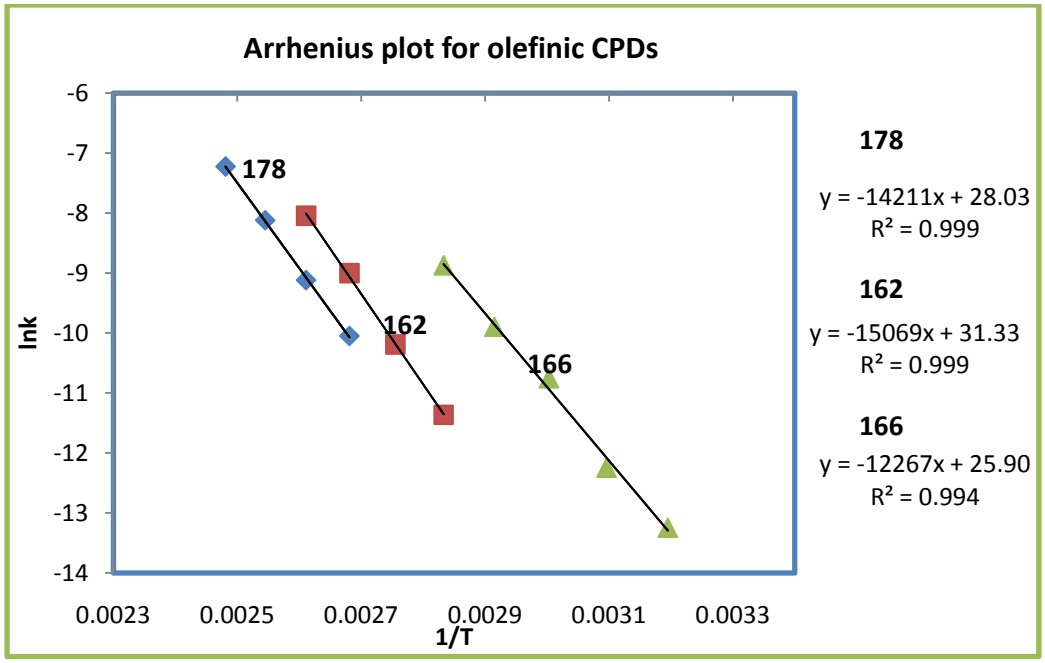


**162**

As it was anticipated, cyclophanedienes with internal olefinic substituents have high stability towards thermal isomerization. The energy of activation is somewhat misleading in this series and this is probably due to variation in the pre-exponential factor A, thus half-lives give more useful comparison. In our series, diisobutenyl CPD **178** shows the best thermal stability and has a calculated half life of ~ 16 years at 20 $^{o}$C whereas CPDs **162** and **166** have half lives ~ 10 years and 56 days respectively. Why the thermal return of **178** to **179** is slow in this series is not immediately obvious. The high stability of the methyl substituted cyclophanedienes, however, cannot be explained only on the basis of radicaloid TS$^{‡}$ because the methyl substituents at the terminal olefin carbon would be expected to stabilize somewhat the radicaloid transition state, thus lowering $E_{act}$.

A comparison of the rate constants of the olefinic CPDs reveals that introduction of the *trans* methyl groups (**198**) decelerates the thermal return by a factor of two to three whereas the *cis* methyl groups have a twelvefold effect (**162**). Introduction of both *cis* and *trans* methyl groups (**178**) have an even more pronounced effect, i.e., the thermal reaction is slowed by a factor of ~ 34. A significant difference in the behaviour of the *cis*- and *trans* methyl groups strongly suggests the involvement of steric factors.

**Figure 3.2 A Combined Arrhenius plot for the internal olefinic cyclophanedienes in toluene**



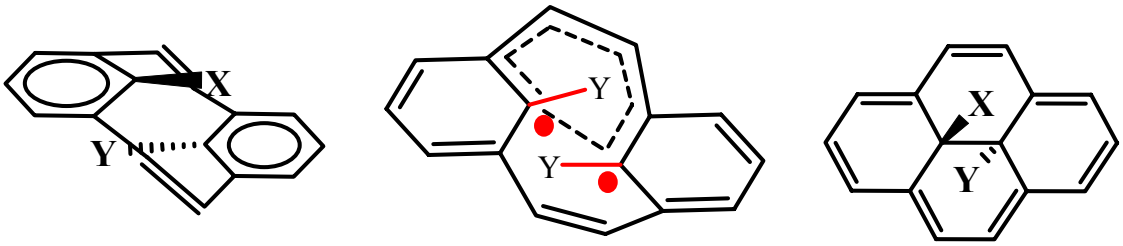

A number of factors may contribute:

1. The TS‡ may be destabilized due the steric effects arising from the additional methyl groups.
2. The CPDs are additionally stabilized by hyperconjugation from the methyl groups.
3. The methyl groups destabilize the anionic TS‡ (as we proposed earlier) by hyper conjugation.

DFT calculations by Williams[41] suggest that the structure of the TS‡ is intermediate between those of cyclophanediene and dihydropyrene for a variety of internal groups (see

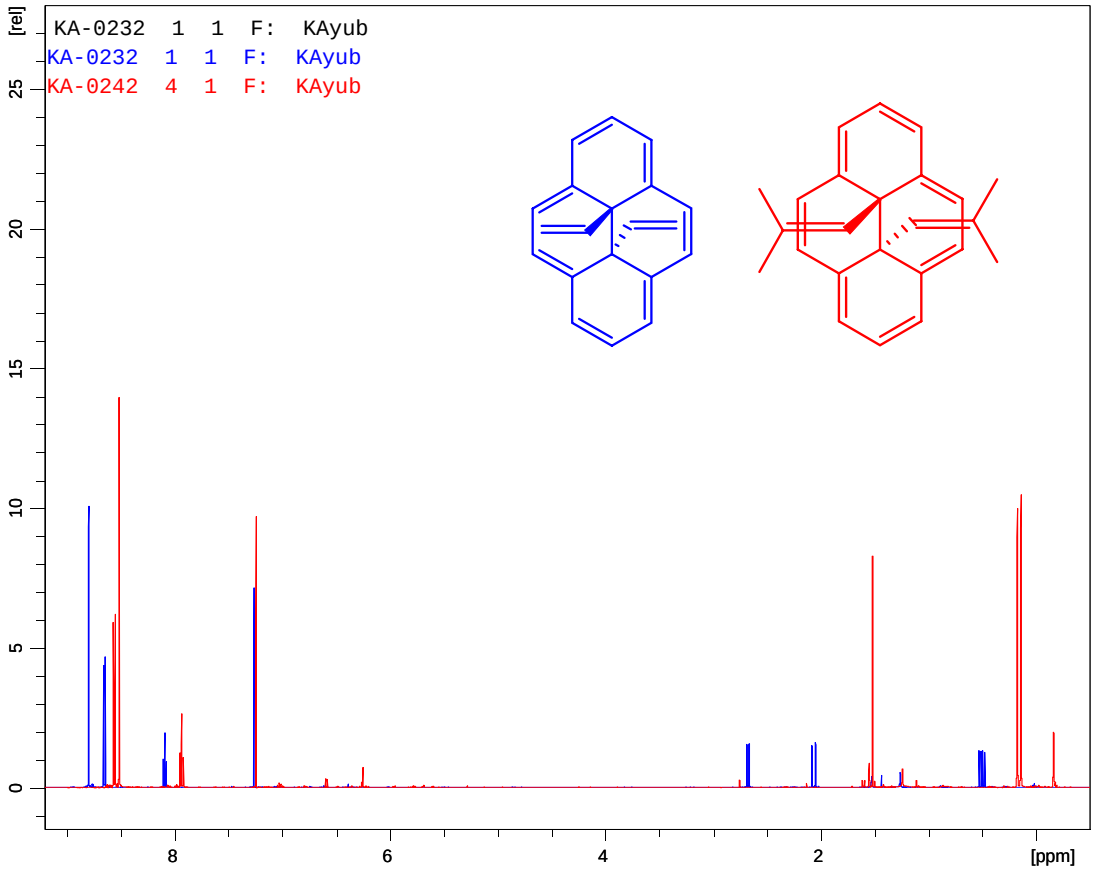
Figure 3.3), thus any unfavorable steric effect in the TS‡ due to the movement of the internal groups is expected to be apparent in the product as well. Divinyl DHP **167** and diisobutenyl DHP **179** were compared in their $^{1}$H NMR spectra and X-ray structures to untangle the steric effect due to the methyl groups.

**Figure 3.3 Structures of CPD (left), TS‡ (middle) and DHP (right)**

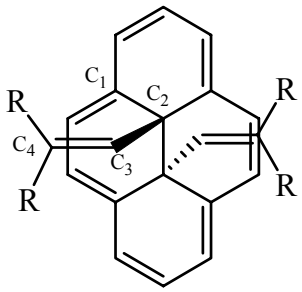



$^{1}$H NMR analysis revealed that the DHP protons in **179** are relatively upfield (Figure 3.4, shown in red) compared to those of **167** (blue). This upfield shift could be either due to the decreased diatropic ring current (decreased planarity) or because of the anisotropic effect of the internal double bond. X-ray structure analysis revealed a difference in the orientation of the internal olefins in **167** and **179** as shown in Figure 3.5 and 3.6. The olefinic double bond in **167** resides at angle < 45 degree to the DHP nucleus whereas in **179**; it is deflected away and is almost perpendicular to the DHP ring

**Figure 3.4 Combined $^{1}$H NMR spectra of 167 and 179 in $CDCl_3$ at 500 MHz**




$^{1}$H NMR analysis revealed that the DHP protons in **179** are relatively upfield (Figure 3.4, shown in red) compared to those of **167** (blue). This upfield shift could be either due to the decreased diatropic ring current (decreased planarity) or because of the anisotropic effect of the internal double bond. X-ray structure analysis revealed a difference in the orientation of the internal olefins in **167** and **179** as shown in Figure 3.5 and 3.6. The olefinic double bond in **167** resides at angle < 45 degree to the DHP nucleus whereas in **179**; it is deflected away and is almost perpendicular to the DHP ring.




The deflection is shown by marked differences in some of the bond angles. The $C_1$-$C_2$-$C_3$ angle is 103.71$^o$ in the case of **167** (R = H) whereas in **179** (R = Me), it is 111.34$^o$. Moreover, $C_2$-$C_3$-$C_4$ angle is 127.01$^o$ in **167** whereas the corresponding angle in **179** is 132.87$^o$.

Although the crystal structure does not have to be the solution structure, there are no strong polar effects at work and so it is probably not so different.

This deflection of the internal olefin in **179** results in the close spatial alignment of the olefinic CH proton to the DHP nucleus and is seen in the $^1$H NMR spectrum where it appears at δ -0.1, shielded by 0.6 ppm compared to the olefinic CH in **167** (δ 0.5). Moreover, the X-ray structure has shown that the 14-annulene **179** is significantly stepped compared to **167** and this is quite consistent with the upfield shift of the DHP protons in the former than the latter due to the reduced diatropicity.

**Figure 3.5 ORTEP diagrams of divinyl DHP 167 (right) and diisobutenyl DHP 179 (left) showing 30% probability ellipsoids.**

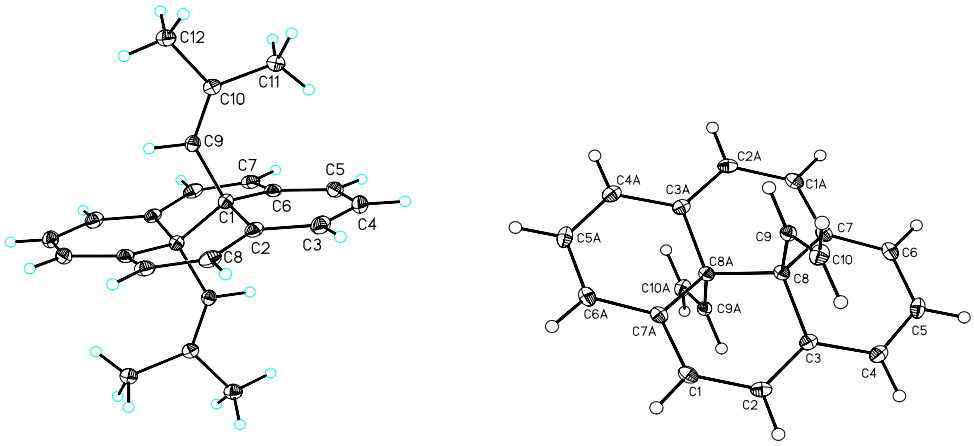
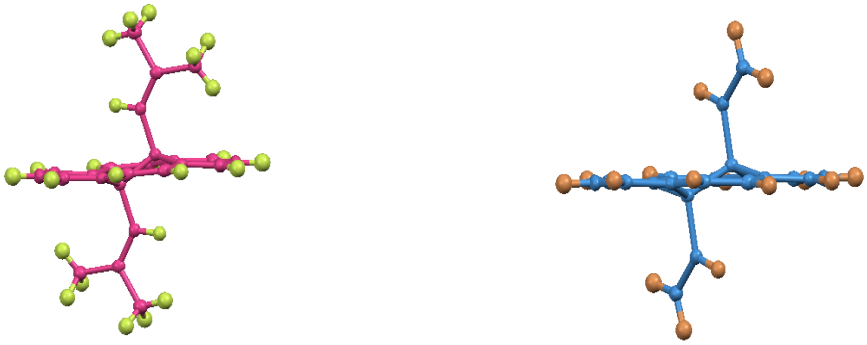



**Figure 3.6 Molecular diagrams of diisobutenyl DHP 178 (left) and divinyl DHP 167 (right) derived from X-ray structures**



The internal olefinic group in **179** aligns away from the DHP nucleus probably because of the repulsion between C-11 methyl and the DHP ring (C-1 to C-6) (Figure 3.5 left). A somewhat similar repulsion is also expected in **164** and is quite apparent from its $^{1}$H NMR spectrum where the chemical shifts of the DHP protons and the internal olefin proton appeared between those of **179** and **167**; however we failed to obtain an X-ray

structure for **164**. This repulsion is probably the principle factor for the slow thermal return of the cyclophanedienes **162** and **178**.

How much CPDs are stabilized or destabilized by the methyl groups present on the olefinic substituents is not clear. $^{1}$H NMR analysis did not yield any fruitful conclusions. Moreover X-ray crystal structures were not obtained for **162** and **166**. X-ray analysis of **178** indicates that the methyl groups cause the internal olefinic group to move away from the plane of the aromatic rings and thus would decrease the activation barrier which is quite contrary to the observations. The X-ray analysis of diisobutenyl CPD **178** will be discussed in detail later in section 3.1.5

The *trans*-methyl groups in **178** and **198** are far away from the DHP nucleus and are considered not to have any steric effects as seen for the *cis* analogue. Thus, these compounds probably would give a better estimate of the electronic effects. A comparison of **166** and **198** or **162** and **178** indicates that the *trans* methyl groups decelerate the thermal reaction by a factor of 2-3. On the other hand *cis*-methyl groups have twelve to 15-fold effects.

### 3.1.2 Extension of conjugation by a double bond in the internal substituents

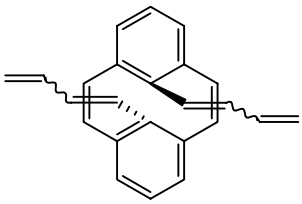
The aforementioned examples reveal that the conjugation in the internal substituent stabilizes the cyclophanedienes. In order to further elaborate the conjugation effects, butadienyl CPDs **184-186** were synthesized and studied for their behaviour in the thermal reaction.

The thermal return experiments in this series were performed on the mixture of isomers as the peaks corresponding to each isomer in the $^{1}$H NMR spectrum could be easily identified both in the cyclophanediene and in the dihydropyrene. The experimental

design was useful not only in saving time but also confirmed that the rate differences in different isomers are not due to experimental errors.

The all *cis*-isomer **186** has the slowest thermal return among the three isomers, probably because of the steric interactions in the $TS^{\ddagger}$, quite similar to those mentioned earlier for **164** or **179.** It is also supported by the fact that the DHP protons in **192** were slightly shielded when compared with the *trans*-isomer **190**. A comparison of the rate constants for **166** and **184** indicates that the additional *trans* double bond (with minimum steric contribution) slows down the thermal reaction by a factor of six. The rate constants gradually decrease along the series **184-186.**

Cyclophanedienes **184-186** contain terminal methyl groups and thus do not give a true estimate of extended conjugation by a double bond. The terminal methyl groups may have accelerating or decelerating effects and so non-methylated butadienyl CPD **181** would give a more accurate estimate. Unfortunately, we failed to prepare it. The thermodynamic data of the cyclophanedienes **184-186** clearly demonstrate that the terminal methyl groups do not have as marked effect as seen in the cases of **162** and **178**.



**181**

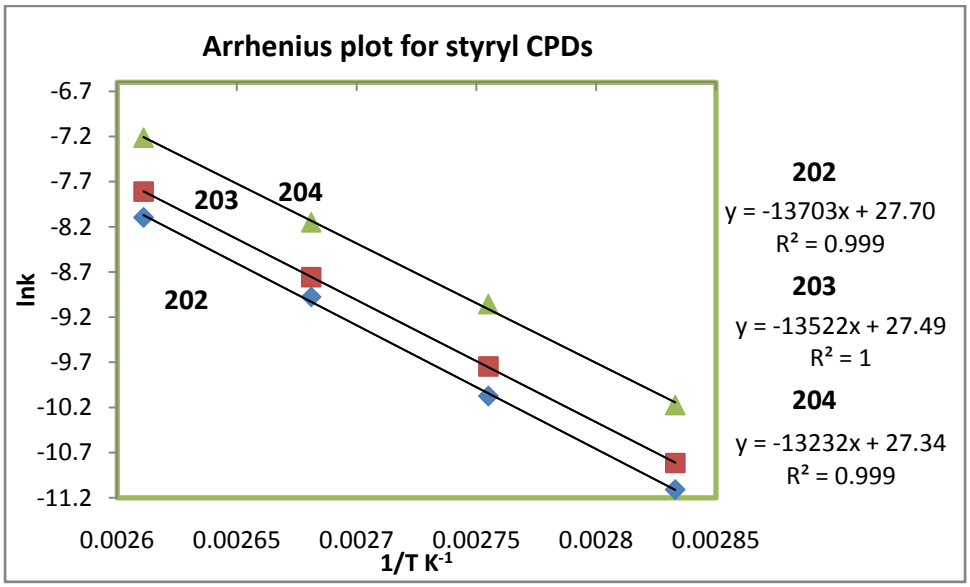
A comparison of the methyl substituted CPDs **162, 198** and **178** with the butadienyl CPDs **184-186** indicate that steric effects play a major role in slowing down the thermal reaction in the former series whereas in the latter series, electronic effect are dominant.

We did not attempt to further extend the conjugation by another double bond due to several reasons such as complications arising from the increasing number of isomers in the hexatriene and its photo and thermal chemistry interfering with the cyclophanediene-dihydropyrene photoswitch properties.

### 3.1.3 Extending the conjugation by a phenyl ring

Quite analogous to the butadiene series, rates of the thermal return decrease upon extending the conjugation by a phenyl ring. The rate constants obtained at 100 $^{o}$C for **202, 203** and **204** are 7.5, 9.4 and 17 x $10^{-3}$ $min^{-1}$ respectively. The relative rate comparison indicates that the butadienyl group in **184-186** has more pronounced decelerating effect than the styryl groups in **202-204**. A possible explanation could be the effect of the terminal methyl groups in the former series absent in the latter.

**Figure 3.7 Arrhenius plot for the styryl CPDs 202-204 in toluene**




The DHP protons in the all *cis*-isomer **205** appeared at δ 8.2-8.3 and are more shielded than the DHP protons in **179** (δ 8.5). The shielding is believed to arise not only

from steric crowding (stepped DHP nucleus) but also from the ring current associated with the phenyl group. This shielding, if arising only from the stepped DHP nucleus, would be expected to make the thermal return of **202** slower than **178**; however this is not the case.

### 3.1.4 An electronic contribution towards thermal isomerization

In order to explore the electronic effects on the thermal return, *para* substituted styryl CPDs were studied. The effect was studied on all the geometrical isomers. The *para* position was chosen in order to have minimal contribution from the steric effects. Nitro and methoxy groups were chosen as representative examples of electron withdrawing and electron donating groups respectively. The electron neutral methyl group was also studied because of its anomalous behavior in the thermal back reactions.

The symmetrical nitro-styryl CPDs **210** and **212** had poor solubility in common organic solvents whereas the unsymmetrical isomer **211** was fairly soluble in toluene or in $CDCl_3$. In order to overcome the solubility problem, a larger number of scans (84 instead of 16 in $^1H$ NMR) were taken so as to increase the S/N ratio. Moreover, kinetic experiments were performed on the mixture of isomers as peaks corresponding to each isomer could easily be identified in the $^1H$ NMR spectrum.

In the cases of **210** and **211**, a relatively fast thermal reaction is observed compared to the non-substituted styryl CPDs **202** and **203** respectively, however the *trans*-nitro-styryl CPD **212** is thermally more stable when compared with the styryl parent CPD **204**. The thermodynamic data for the **212** may be misleading because of the poor solubility of its closed isomer, **215**. We did not observe any precipitate formation, but it may be possible that the dihydropyrene **215** formed suspensions which are invisible

in the colored solution. In this series, the most reliable data is for **211** which shows an accelerated thermal closure over that for **203**.

An electron donating methoxy substituent at the *para* position increases the thermal stability of the cyclophanedienes **218-220** compared to the corresponding non-substituted CPDs **202-204**. *cis*-Styryl CPD **218** has a half life of 130 minutes at 100 $^{o}$C, considerably higher than that of **202**, 90 minutes. A comparison of the relative rates reveals that electron donating substituents at the *para* position of the styryl group decelerate the thermal return whereas electron withdrawing substituents promote the thermal reaction. Surprisingly, introduction of a virtually electron neutral methyl groups enhances the thermal stability of the cyclophanedienes **226-228** and the effect of the methyl is almost comparable to that of the methoxy substituent. The dramatic effect of the methyl groups can be attributed to hyperconjugation.

*p*-Methyl-styryl CPD **226** has a relatively low $E_{act}$ (26.9 $\pm$ 0.3 kcal/mol) relative to *p*-methoxy-styryl **218** (27.4 $\pm$ 0.1 kcal/mol), even though the former is more stable at higher temperatures. The low $E_{act}$ of **226** manifests itself in the relatively short half life at room temperature. Calculated half-lives at 20 $^{o}$C for **226** and **218** are approximately 5 and 6 years respectively. It is already mentioned that the calculations by Williams suggest a radical transition state for the thermal isomerization, but our data, once again, supports anionic character in the TS$^{‡}$.

### 3.1.5 Alkynes as the internal substituents

Diethynyl CPD **235** isomerizes thermally to the DHP **236** at rates slower than those of dipropenyl **162** and divinyl **166**; however it closes faster than diisobutenyl **178**. The ethynyl group is linear and is not expected to exert any steric effects in the TS$^{‡}$. The

high stability of **235** is probably because of a better conjugation in the cyclophanediene. Crystal structures were obtained for three cyclophanedienes; diisobutenyl **178,** distyryl **202** and diethynyl **235,** and their analyses reveal that the degree of bending of the internal carbons from planarity increases with increasing steric bulk.

**Figure 3.8 Molecular diagrams of distyryl 202 (left) and diisobutenyl 178 (right) derived from X-ray structures**

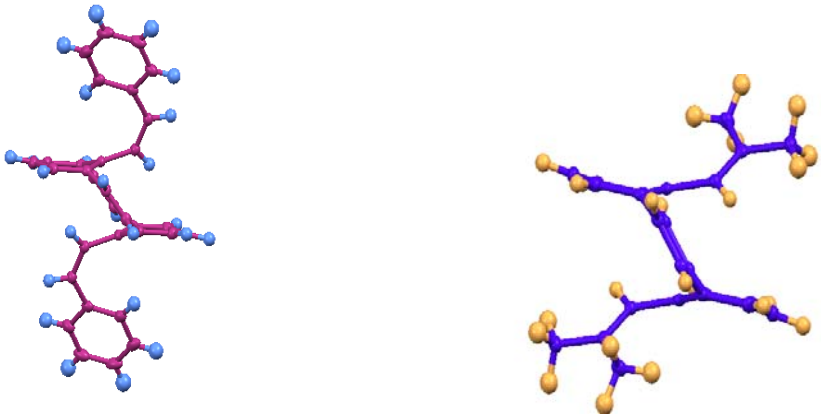
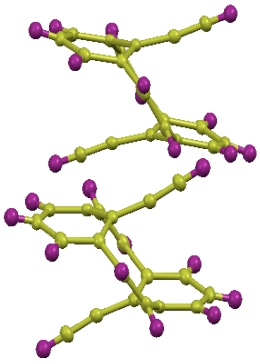
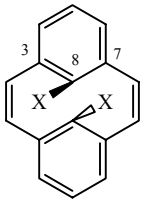


**Figure 3.9 Molecular diagram of diethynyl CPD 235 derived from X-ray structure**

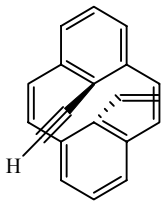


Diethynyl CPD **235** contained the least bending of the phenyl ring and the angle found is 118.40$^{o}$ ($C_3$-$C_8$-$C_7$) whereas the corresponding angles in **202** and **178** are 117.61$^{o}$ and 116.49$^{o}$ respectively. The high planarity of **235** and thus better conjugation are probably the reasons for its slow thermal return. Diisobutenyl CPD **178** is the most sterically unstable of all the three CPDs shown above and it should isomerize easily; but the steric repulsion in the transition state, as mentioned earlier, seems to exert an overwhelming effect.

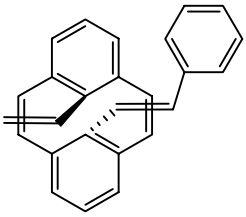



Diethynyl CPD **235**, when compared to the dicyano CPD **85** has a fast thermal return and it is in contradiction to our proposed anionic transition state. However, as we mentioned earlier that the results from the solid phase kinetics of **85** should be taken with caution and it should not be compared with results from solution kinetics to draw some conclusions. However, it may be possible that the nitrile with a smaller nitrogen atom is sterically even less demanding and stabilizes the cyclophanediene **85** more than the ethynyl group stabilizes CPD **235**. We failed to get an X-ray structure of **85** to support this argument.

### 3.1.6 Unsymmetrical CPDs




**237**



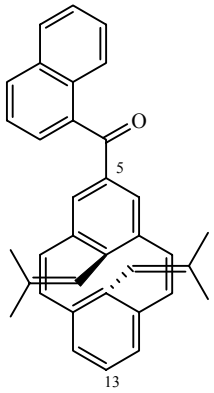
**240**

Thermodynamic data was obtained for the thermal closing reaction of the unsymmetrical CPDs **237** and **240**. CPD **237**, containing a vinyl and an ethynyl group was anticipated to isomerize thermally at an average rate of those for **166** and **235.** The thermal return of **237** to **238** is approximately 3 times slower than **166** to **167**, but more than five times faster than **235** to **236**. The data suggests that both ethynyl groups are required in order to slow down the thermal return. On the other hand, replacing one styryl group in **204** with a vinyl group, **240**, accelerates the thermal return only by a factor of < 2.

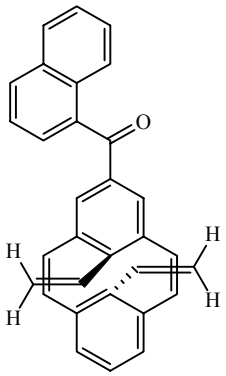
### 3.1.7 5-Naphthoylated CPDs 249 and 251

A naphthoyl group at the 5 position of cyclophanedienes is known to accelerate the thermal return and this is also observed in the cases of **249** and **251**. Rate constants obtained at 100 $^{o}$C are 16.2 and 2.59 x $10^{-3}$ $min^{-1}$ for **249** and its non-naphthoylated analogue **178** respectively, which indicates that the incorporation of a naphthoyl group accelerates the thermal return approximately by a factor of six. This acceleration in the rate is accompanied by a drop in $E_{act}$ by 1 kcal/mol. Introduction of a naphthoyl group at the 5 position in the divinyl CPD **166** has an even more profound effect on the thermal reaction. The thermal reaction of **251** to **250** is approximately 12 times faster than **166** to

**167**, although the drop in $E_{act}$ is still about 1 kcal/mol. The origin of this extra acceleration of the thermal reaction in **251** is not clear. One contributing factor may be solvent. Thermodynamic data for **250** was obtained in $CDCl_3$ whereas **166** was studied in toluene. It is already mentioned that $CDCl_3$ accelerates the thermal return by ~ 20%.




**249**




**251**

Williams' calculations suggest that the 5- and 13- positions of cyclophanedienes (shown above) are the sites of second highest spin density in the TS‡, thus any radical stabilizing group, such as naphthoyl, is expected to accelerate the thermal return and this is consistent with our experimental observations. However, the rest of our data suggest an anionic character in the TS‡ and thus we tried to interpret these results accordingly. The naphthoyl group, besides being a radical stabilizer, is also an electron withdrawing group and it can stabilize the anion as well and it should accelerate the thermal reaction based on the anionic TS‡.

The radical spin density at positions 5 and 13 is strongly negated by the sulfonated CPDs **78-82**. A radical destabilizing $SO_3H$ would be expected to slow down the thermal return but the sulfonated CPDs are highly unstable thermally as evident by their half lives (Table 1.2, pg 23). Most of the 5-substituted CPDs reported in the

literature have faster thermal returns than the corresponding non substituted parent CPDs and contain electron withdrawing groups at this position. A radical stabilizing but electron donating group at these positions can discriminate the anionic vs. radical TS$^{‡}$. A limitation towards this study is the electron rich nature of the dihydropyrene nucleus which prohibits installation of electron donating groups at the 5 and 13 positions.

The thermal return data along with the X-ray structure analysis suggests that the principle factors include

1. A drop in steric bulk at the internal positions of CPD slows down the thermal return.
2. Conjugation at the internal position enhances the half-life of the CPD
3. Steric crowding in the transition state resists the thermal closure.
4. Electron withdrawing groups accelerate while electron donating groups decelerate the thermal return

### 3.1.8 DFT Calculations

We asked Dr Williams (University of Idaho) to perform DFT calculation on some of the thermally stable cyclophanedienes, namely diisobutenyl **178**, dipropenyl **162**, *cis*-distyryl **202**, *trans*-distyryl **204** and divinyl **166**. A comparison of $\Delta G^{‡}$ values is given in Table 3.3. The experimental $\Delta G^{‡}$ values are calculated at 100 $^{o}$C using Equation 3.5.

$$\Delta G^{‡} = \Delta H^{‡} - T\,\Delta S^{‡} \qquad \textbf{Equation 3.5}$$

**Table 3.3 A comparison of theoretical and experimental $\Delta G^{\ddagger}$ values (kcal.mol$^{-1}$)**

| Compound | Theoretical $\Delta G^{\ddagger}$ | Experimental $\Delta G^{\ddagger}$ |
|---|---|---|
| Divinyl **166** | 23.2 | 22.5 |
| *trans*-Distyryl **204** | 24.0 | 28.0 |
| Dipropenyl **162** | 26.6 | 28.6 |
| *cis*-Distyryl **202** | 27.0 | 28.7 |
| Diisobutenyl **178** | 27.5 | 29.4 |

Even though the calculated values are lower (except **166**) than the experimental values, the relative order of theoretical values perfectly agrees with that of the experimental ones. This underestimation of the activation barrier has already been observed in the case of dicyano cyclophanediene **85**.

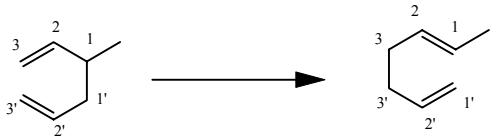
## 3.2 [1,5]-sigmatropic rearrangement

A sigmatropic rearrangement can be defined as: "A molecular rearrangement that involves both the formation of a new σ bond and the concomitant breakage of the existing σ bond with a concurrent relocation of π bonds in the molecule, but the total number of σ and π bonds does not change" Or "a pericyclic reaction wherein the net result is one σ bond changed to another σ bond"

Sigmatropic rearrangements are classified by the substituent that moves and the order of the rearrangement, which is given in brackets [i, j] where i and j denote the number of carbons atoms at each terminus of the sigma bond that moves. Well known

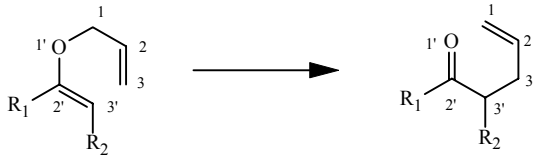
examples of sigmatropic rearrangements are the Cope rearrangement, Claisen rearrangement and [1,5]-hydride shifts. The Cope rearrangement is a [3.3]-sigmatropic rearrangement of 1,5-dienes. The Claisen rearrangement is also a [3.3]-sigmatropic rearrangement of allyl vinyl ethers to give a γ, δ unsaturated carbonyls

**Scheme 3.2 The Cope rearrangement of 258 to 259**



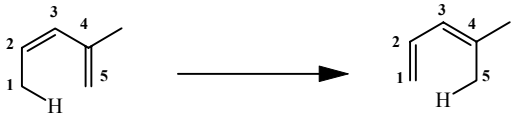
**258** **259**

**Scheme 3.3 The Claisen rearrangement of 260 to 261**



**260** **261**

**Scheme 3.4 A [1,5] hydride shift in conversion of 262 to 263**

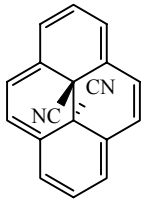


**262** **263**

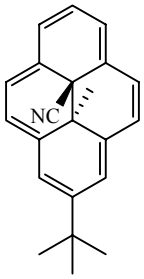
**Table 3.4 The facial migration modes of 4n and 4n +2 π systems**

| π electrons | Photochemically | Thermally | Examples |
|---|---|---|---|
| 4n | Suprafacial | Antarafacial | [1,3]-shift, [1,7]-shift |
| 4n + 2 | Antarafacial | Suprafacial | [1,5]-shift, [3,3]-shift |

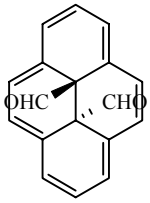
The following three compounds will be discussed. Dicyano DHP **86** was studied quantitatively and the data are reported in Table 3.5. Sigmatropic rearrangements of the internal nitrile and formyl groups in DHPs **128** and **153**, respectively, will be discussed qualitatively.




**86**




**128**




**153**

**Table 3.5 Thermodynamic data for the sigmatropic rearrangement of the internal nitrile group in 86**

| | $E_{act}$ kcal/mol | ln A | $\Delta H^{\ddagger}$ kcal/mol | $\Delta S^{\ddagger}$ cal/mol | $\tau_{(1/2)}$* 20 °C | $\tau_{(1/2)}$* 50 °C |
|---|---|---|---|---|---|---|
| $CDCl_3$ | 23.4 ± 0.7 | 25.9 ± 1 | 22.8 ± 0.7 | -9.22 ± 2.0 | 15 days | 8.3 h |
| Benzene | 28.6 ± 1.2 | 31.9 ± 1.9 | 27.9 ± 1.2 | 2.3 ± 4.0 | 266 days | 66 h |
| Solid phase | 28.6 ± 1.8 | 33.2 ± 2.8 | 27.9 ± 1.8 | 5.41 ± 5.6 | 24 days | 13 h |

* Errors estimated are less than 5%

The sigmatropic rearrangement of the internal groups showed first order kinetics, as expected. Equation 3.2 was used to calculate $E_{act}$ and the pre-exponential factor A whereas the Eyring equation (3.5) gave the enthalpy and entropy of activation.

Rearrangement of the internal methyl groups has a high energy of activation and requires an elevated temperature (~ 200 $^{o}$C). However, the sigmatropic rearrangement of the internal nitriles is quite facile at 50 $^{o}$C in $CDCl_3$ ($E_{act}$ 23.4 kcal/mol). This rearrangement is more favorable in $CDCl_3$ than in benzene or in the solid phase. We believe that this difference arises because of the acid content present in $CDCl_3$ since both mineral and Lewis acid catalysis in sigmatropic rearrangements is a well known phenomenon.[80]

Boekelheide et al.[61,62] concluded that these rearrangement proceed through a 1,5-sigmatropic rearrangement. However, nitriles can also undergo a 1,3-sigmatropic rearrangement with a radical intermediate.[81] We thought that the 1,5-sigmatropic rearrangement may be a sum of two 1,3-sigmatropic rearrangements. However, we did not observe any products arising from a single 1,3-sigmatropic rearrangement. To address this problem further, DFT calculations were performed, which strongly suggested a 1,5-sigmatropic rearrangement. The activation barrier for the arrangement of the nitrile are quite consistent with the experimental values and are about 7 kcal/mol less than that for the rearrangement of the internal methyl group.

The driving force for the rearrangement may be the formation of a benzene ring. Migration of the second nitrile generates a naphthalene derivative from a benzene one and this migration is expected to be more difficult. The second sigmatropic shift probably has $E_{act} > 30$ kcal/mol; however this migration was not studied quantitatively.

Cyano-methyl DHP **128** transformed into the migration product **137** at a much faster rate than the dinitrile DHP **86** and had a half life of a few hours at room temperature. $E_{act}$ is estimated ~ 20-22 kcal/mol in benzene whereas in $CDCl_3$, $E_{act}$ is much lower. The first migration product is quite stable and no further migration was observed even if the sample was heated at > 110 $^{o}$C.

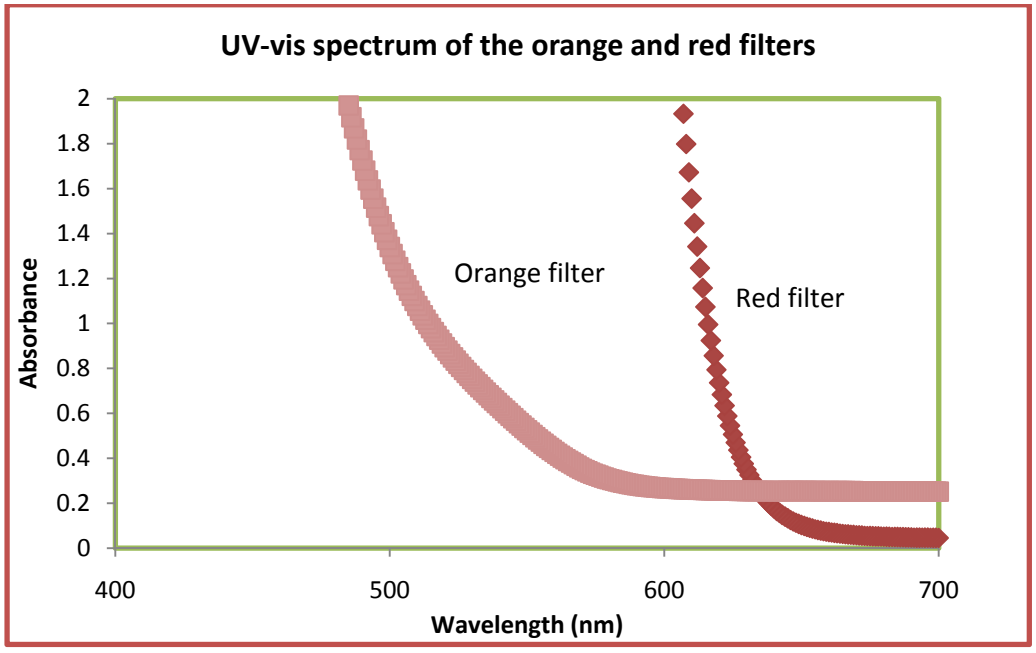
The [1,5]-sigmatropic rearrangement of diformyl DHP **153** was extremely fast. When a sample of cyano-methyl CPD **152** was heated to isomerize it into the DHP **153**, no traces of the DHP and the first migration product **156** could be seen by $^{1}$H NMR spectroscopy, rather it transformed directly into the 2$^{nd}$ migration product **155**. This finding suggests that the energies of activation for both rearrangement processes are much lower than 26 kcal/mol ($E_{act}$ of the thermal isomerization of diformyl CPD **152** into DHP **153)**. DFT calculations suggest that the sigmatropic rearrangement of the internal carbonyls would have $E_{act}$ ~ 17 kcal/mol.

# Chapter 4: Photochemical isomerization

## 4.1 Visible light opening

Visible light opening studies were performed using a 500 W tungsten light with a 490 nm cut off filter (Figure 4.1), and the reaction was monitored by $^{1}$H NMR spectroscopy. A $d_8$-toluene solution (unless otherwise mentioned) of dihydropyrene (1-2 mg) in an NMR tube, cooled by a small cold water bath was irradiated until the sample solution was colorless or photostationary state was reached

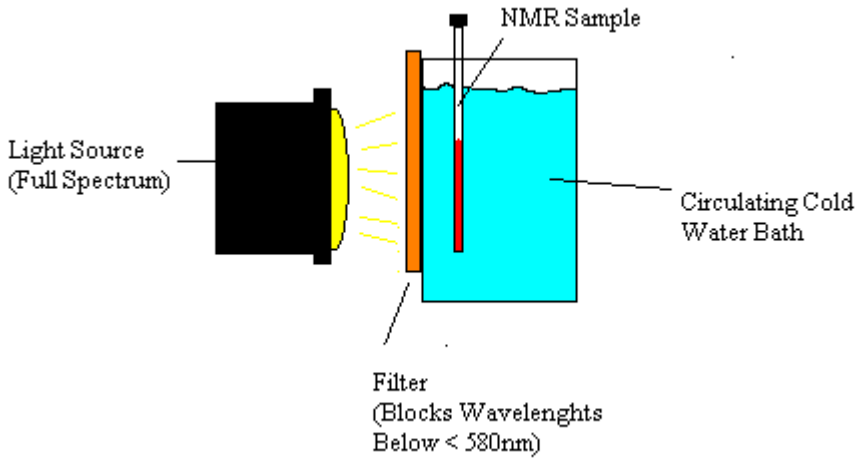
**Figure 4.1 UV-vis spectrum of the orange and red filters**




Benzo DHP **47** was chosen as a standard for the comparison of the visible opening rates. However the compounds studied, except **250,** have either very low or very high opening rates compared to the benzo DHP **47**, thus a direct rate comparison was not possible. For slow opening compounds *p*-methyl-styryl DHP **229**, a DHP with moderately fast opening rate, was calibrated against the benzo DHP **47** and thus used as a

standard. Both, sample and the standard were irradiated side by side and had approximately equal concentration. Rate comparison against the parent dimethyldihydropyrene **43** is reported as well.

**Figure 4.2 Visible light opening experiment setup**




The rate law of a photoopening reaction is typically second order; first order both in photons of light [γ] and in concentration of the dihydropyrene molecule A (4.1). If a large excess of light photons are used then [γ] becomes constant and the reaction rate law becomes a pseudo first order reaction (4.2). Rearrangement of the differential equation (4.3) and subsequent integration yields equation **4.4**. However, a first order kinetic equation did not give the best fit of data for the visible opening experiment. Robinson[35] has reported that a zero order kinetic equation gives the best fit of data when $^{1}$H NMR spectroscopy is used to monitor the reaction. This is due to the fact that NMR samples are concentrated and have little surface area exposed to the light source. Moreover, dihydropyrene molecules are highly colored. Even using a bright light source, only surface molecules are irradiated. As the photochemical reaction proceeds and the outer

molecules open to the cyclophanediene, the inner molecules are exposed to the visible light. At any time, the number of molecules being exposed to the light source is constant and the rate equation becomes independent of the dihydropyrene concentration, i.e, it is a pseudo zero order reaction (**4.5**). After rearrangement of the differential equation (**4.6**) and integration (**4.7**), it can be seen that a plot of [A] vs time yields rate constant (k").

$$\textbf{Rate} = k[A][\gamma] \qquad \textbf{4.1}$$

$$\textbf{Rate} = k'[A] \qquad \textbf{4.2}$$

$$\textbf{Rate} = -d[A]/dt = k'[A] \qquad \textbf{4.3}$$

$$-d[A]/[A] = k'dt$$

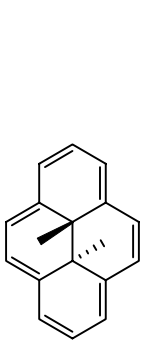
$$\ln[A] = -k't + \ln[A_o] \qquad \textbf{4.4}$$

$$\textbf{Rate} = k'' \qquad \textbf{4.5}$$

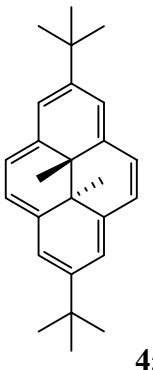
$$\textbf{Rate} = -d[A]/dt = k'' \qquad \textbf{4.6}$$

$$A = -k''t + [A_o] \qquad \textbf{4.7}$$

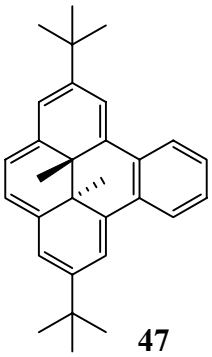
The following dihydropyrenes were studied for visible light isomerization to the cyclophanedienes and the results are shown in Table 4.1.



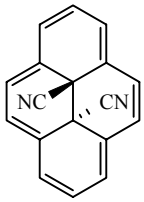
**43**



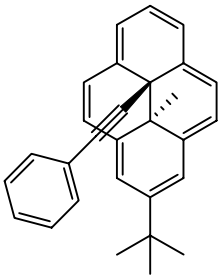
**45**



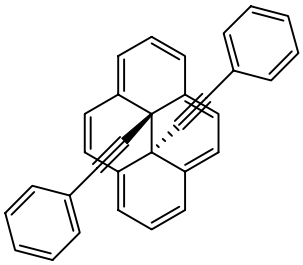
**47**



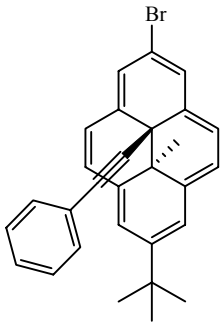

**86**



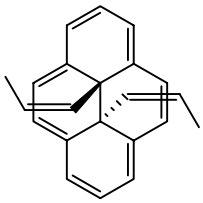
**139**



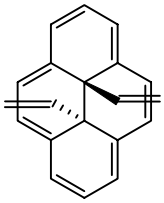
**141**



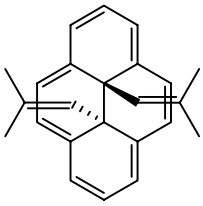

**151**



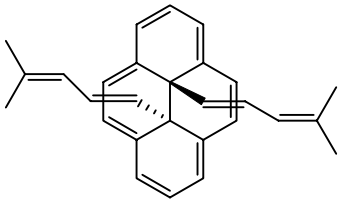
**164**



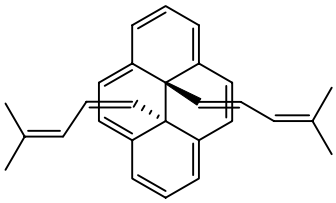
**167**



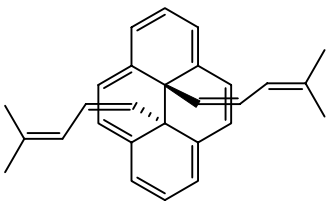
**179**



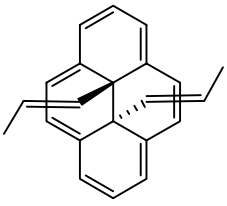
**190**



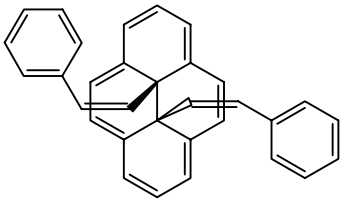
**191**



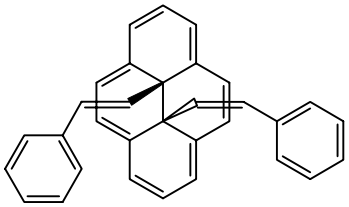
**192**



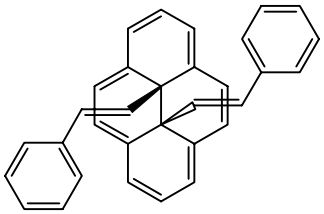
**199**



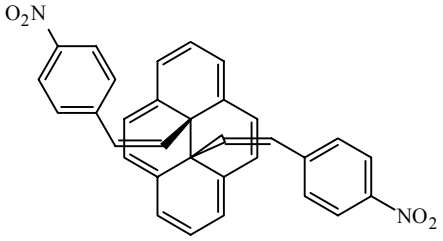
**205**



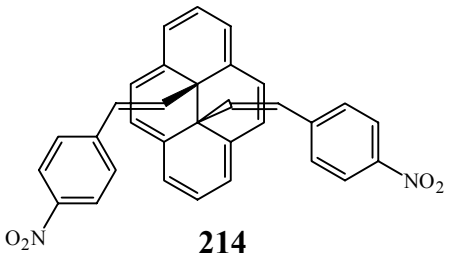
**206**



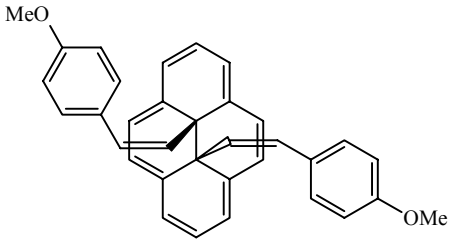
**207**



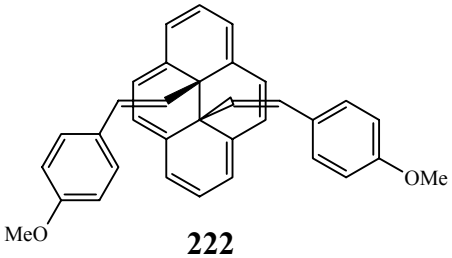

**213**



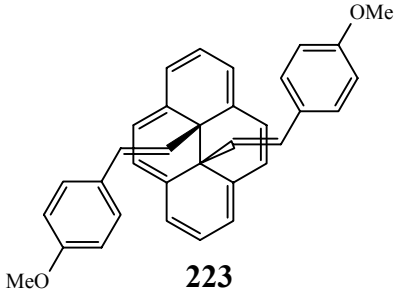

**214**



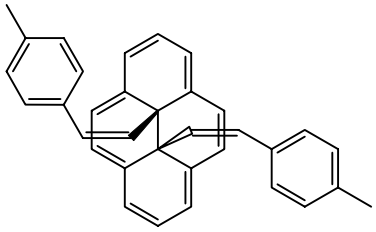

**221**



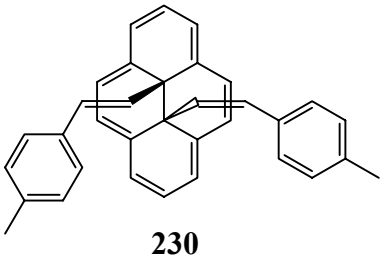

**222**



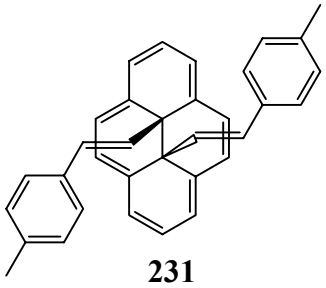

**223**



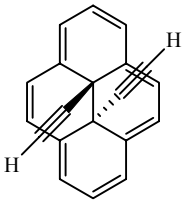
**229**



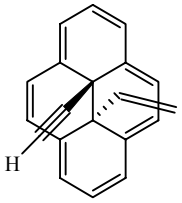
**230**



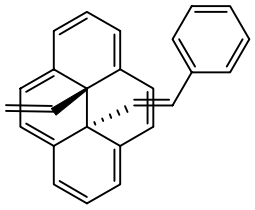
**231**



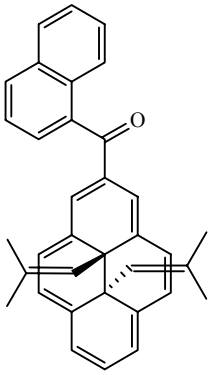

**236**



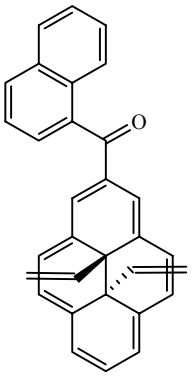

**238**



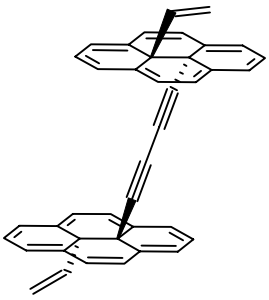
**241**



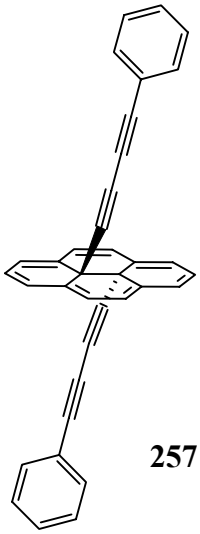

**248**




**250**



**254**



**257**

**Table 4.1 Visible opening of the dihydropyrenes to the cyclophanedienes**

| Compound | Relative rates# vs DHP **43** (1000) | Relative rates vs benzo DHP **47** (1000) |
|---|---|---|
| **139** | Failed to open | Failed to open |
| **141** | Failed to open | Failed to open |
| **151** | Failed to open | Failed to open |
| **190** | Failed to open | Failed to open |
| **199** | Failed to open | Failed to open |
| **207** | Failed to open | Failed to open |
| **223** | Failed to open | Failed to open |
| **231** | Failed to open | Failed to open |
| **238** | Failed to open | Failed to open |
| **241** | Failed to open | Failed to open |
| **257** | Failed to open | Failed to open |
| **167** | Slow opening (dec.) | Slow opening (dec.) |
| **191** | Isomerized to **190** | Isomerized to **190** |
| **192** | Isomerized to **190** | Isomerized to **190** |
| **86*** | ~ 6 | ~ 1 |
| **236*** | 65 | 4 |
| **164** | 180 | 11 |
| **214*** | 200 | 12 |
| **206*** | 740 | 45 |

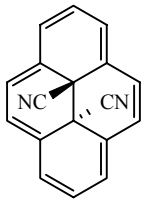
| | | |
|---|---|---|
| **230*** | 980 | 60 |
| **222*** | 1130 | 69 |
| **254** | 200 | 12 |
| **205** | 2500 | 150 |
| **221** | 2900 | 180 |
| **229 (calibrant)** | 2900 | 180 |
| **179** | 3900 | 240 |
| **250** | 18000 | 1100 |
| **248** | ~ 410000 | ~ 25000 |

*photostationary state. # Errors estimates are less than 5%

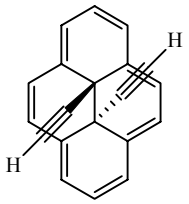
**Discussion of the results**

### 4.1.1 Dicyano DHP 86 and diethynyl DHP 236

The parent dihydropyrene **43** and its *t*-butylated analogue **45** have poor quantum yields of photoopening reactions, 0.006 and 0.0015 respectively. Activators such as [e]-Annelation or addition of a carbonyl group at the 2- or 4- positions of the dihydropyrene, accelerate the photoopening reaction. We were not sure if dicyano DHP **86,** without any activator would open or not. The photoopening reaction was quite slow; however it did open and equilibrated to a photostationary state, CPD:DHP 60:40. An NMR sample of the dihydropyrene **86** in $CDCl_3$ was irradiated overnight before the photostationary state was reached. No decomposition of the dihydropyrene was observed in the chlorinated solvent. Diethynyl DHP **236** showed a similar behavior, however the photostationary state (CPD: DHP 60:40) was reached relatively rapidly.




**86**

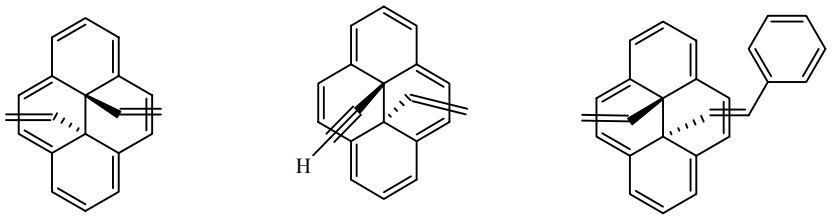



**236**

Robb[82], using high level *ab initio* calculations, has shown that the photoopening reaction of the parent DHP **43** occurs through a conical intersection between a biradical excited state and the ground state. For a highly efficient DHP based photochrome, this biradical excited state needs to be populated. However, calculations suggest that the radical excited state is not the lowest energy excited state. Moreover, excitation to this biradical excited state is symmetry forbidden.

Stabilization of the biradical excited state or destabilization of the highly populated zwitterionic excited state is expected to accelerate the photoopening reaction of dihydropyrene based switches. It could be possible that the biradical excited state of the dihydropyrene **236**, bearing a radical stabilizing ethynyl group, is more highly populated than that of **86** which is responsible for its relatively fast photoopening. Introduction of phenyl or additional ethynyl groups (DHPs **139**, **141** and **257**) at the termini of the ethynyl substituents shuts down the photoopening reaction. The exception is the dimer **254** which will be discussed later. We are not sure what factors are responsible for this behavior.

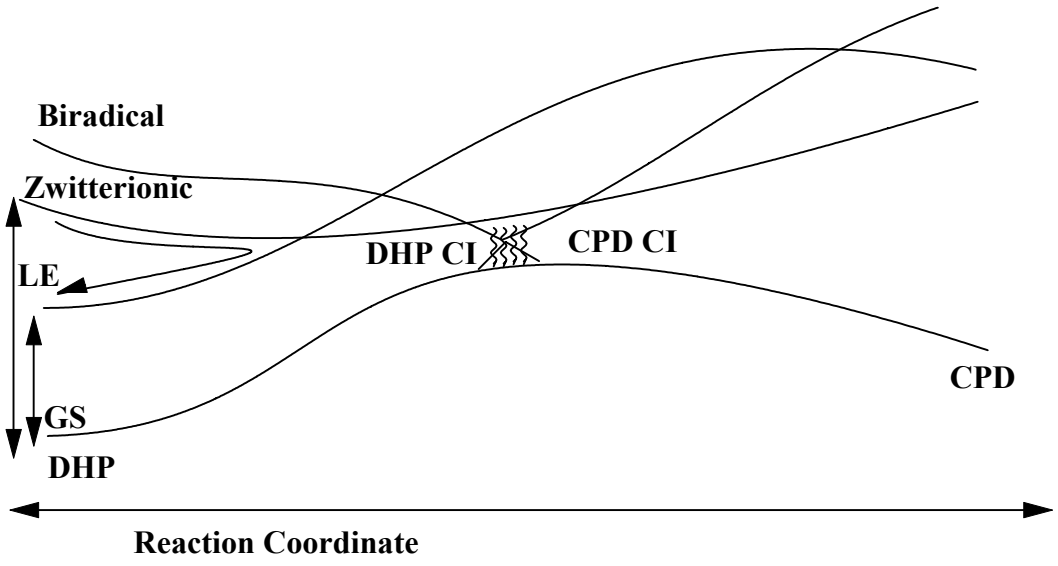
### 4.1.2 DHPs with alkyl substituted internal vinyl groups




**167** **238** **241**

Divinyl DHP **167** failed to open to any appreciable extent and it decomposes on prolonged irradiation. The unsymmetrical DHPs containing a vinyl group such as **238** and **241** failed to open at all, however no decomposition was observed. Once again the exception to this generalization is the dimer **254**.

**Figure 4.3 Outline of the proposed mechanism for the DHP/CPD photochromism**




**CI = Conical Intersection**
**LE = Locally Excited**
**GS = Ground State**

A vinyl group is as good as an ethynyl group in terms of stabilizing a radical. On the basis of this fact, divinyl DHP **167** was expected to open as fast as **236**; however this is not the case. This strongly suggests that the population of the biradical excited state is not the only factor. Robb[82] has shown that there are two different conical intersections along the CPD-DHP isomerization reaction coordinate namely CPD CI and DHP CI residing on the CPD and DHP sides of potential energy surfaces respectively (Figure 4.3). A decay of the excited state at the CPD CI can lead to both photo products, i.e., CPD and DHP ground states where as DHP CI decays only to DHP GS. It could be possible that excited states of DHPs **236** and **167** are decaying from different conical intersections.

Alternatively, if both DHPs are decaying from a common CPD CI then probably the relative stability of CPDs and DHPs is playing a major role. As mentioned earlier in Chapter 3 that the diethynyl CPD **235** is more stable than the vinyl counterpart which may be a driving force for the excited state arising from divinyl DHP **236** to drop into the diethynyl CPD **235** with a greater probability than in the case of divinyl CPD **166**.

DHP **199** containing a *trans* methyl substituted vinyl group failed to open at all, whereas DHP **164,** which contains a *cis*-methyl group, quantitatively opens to the cyclophanediene **162**. The opening rate is roughly 1% of that of benzo DHP **47**. Visible opening of diisobutenyl DHP **179**, containing two methyl groups, although four times faster than the parent **43**, was four times slower than that the benzo DHP **47**. The fast opening of the dihydropyrenes containing *cis* substituted olefinic groups, **164** and **179** can be attributed to the steric instability of the dihydropyrenes (see Chapter 3) which drives CPD CI to decay into CPDs **162** and **178** respectively with a higher probability.

### 4.1.3 Distyryl DHPs 205-207

In the styryl CPD series, a trend is seen quite analogous to the alkyl substituted vinyl CPDs series. The all *cis*-DHP **205** opens at a rate ~15% of that of benzo DHP **47,** whereas the unsymmetrical DHP **206** opens at a much slower rate and forms a photostationary state. The all *trans*-isomer **207** failed to open at all. The difference in the behavior can be explained either by the steric instability factor (similar to one described for **164** and **179**) or by the visible light closing of the corresponding cyclophanedienes.

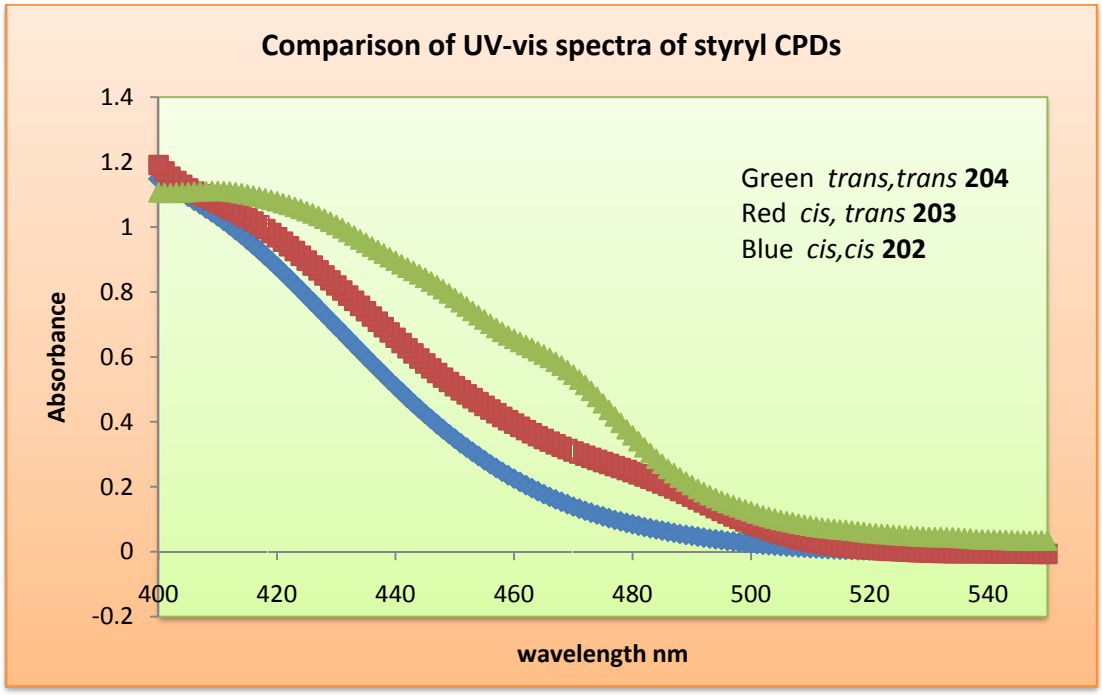
#### 4.1.3.1 Visible light closing of the CPDs *E/Z* 203 and *E/E* 204.

When a cyclophanediene has a tail which extends to the visible region of the absorption spectrum around 480 nm then there is a possibility that during the visible opening experiment of a dihydropyrene, the open form converts back to the closed dihydropyrene form. *trans*-Styryl CPD **204** shows a tail in the UV-vis spectrum ~ 550 nm, thus it may be possible that the DHP **207** opens to the cyclophanediene but closes back to the DHP at a much faster rate under the experimental conditions. An orange filter with cut-off wavelength 490 nm was used which is not sufficient to completely stop the absorption of the CPD **204** (see Figure 4.4). In a control experiment, irradiating a sample of the *t*-distyryl CPD **204** under the experimental conditions (visible light with orange filter) converted it into DHP **207** which is quite consistent with our proposed hypothesis. Irradiation of a sample of the dihydropyrene using a 590 nm cut-off red filter also failed to generate the open form.

The *cis, trans*-DHP **206**, upon photoirradiation, forms a photostationary state. This is not surprising because the corresponding open form **203** shows a small absorption beyond 490 nm in its UV-vis spectrum (Figure 4.4). The all *cis*-CPD **202** does not absorb

beyond 490 nm and thus the DHP **205** is expected to open completely and this is observed upon photoirradiation.

**Figure 4.4 Combined UV-vis spectrum of styryl CPDs 202, 203 and 204**




### 4.1.4 *Para* substituted styryl DHPs

A comparison of photoopening of the unsubstituted styryl DHPs **205-207** with those of *para* substituted DHPs reveal that:

1. For the all *cis* styryl isomers, a nitro group at the *para* position decelerates the photoopening reaction whereas a methyl or a methoxy group accelerates it relative to unsubstituted analogue.

2. The amount of the open form in the photostationary states for the unsymmetrical isomers **214**, **222** and **230** increases on going from electron withdrawing substituent to electron donating substituents

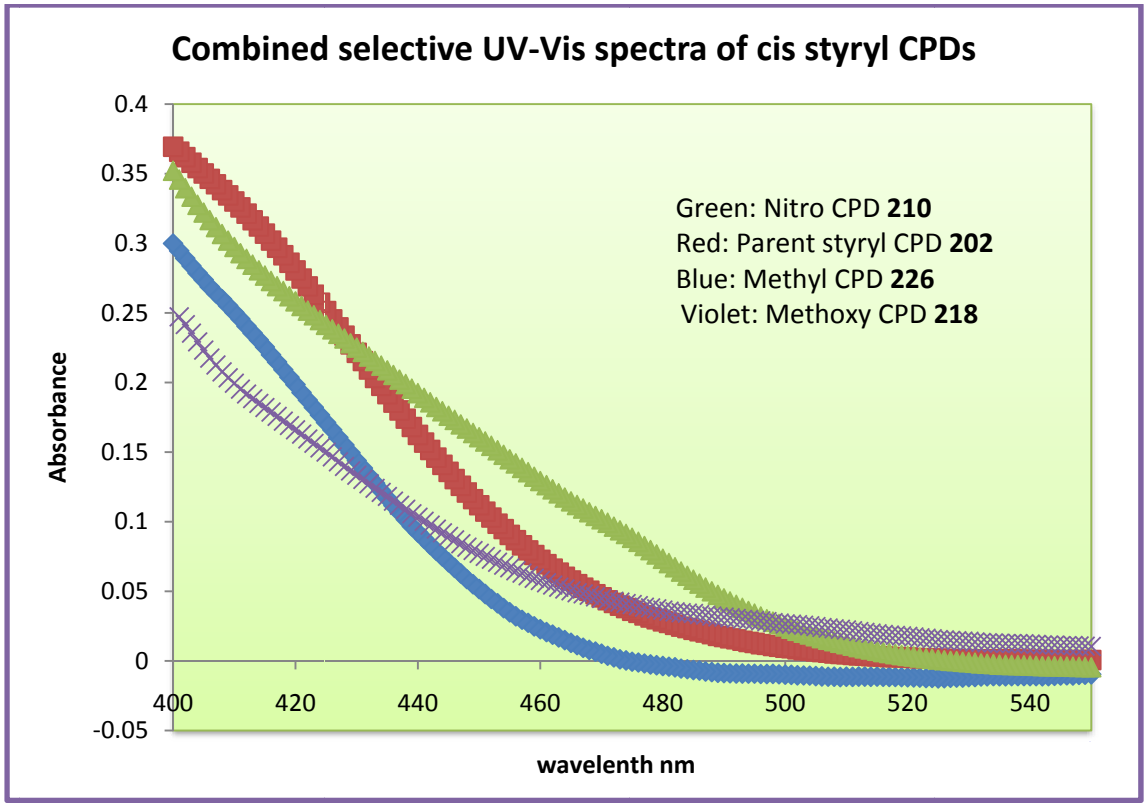
3. The all *trans* isomers failed to open in all cases.

Although quantitative measurement of the rate of photoopening of **213** could not be made (because of its poor solubility), qualitatively, its photoopening is slower than the non substituted styryl DHP **205**. On the other hand, DHPs with a virtually electron neutral methyl group or with an electron donating methoxy groups open faster than the non-substituted styryl DHP **205**. This is explained below.

#### 4.1.4.1 A shift in the UV-Vis absorption spectrum

Introduction of a methyl or a methoxy group at the *para* position of the *cis*-styryl group shifts the tail of the UV-vis absorption spectrum to a shorter wavelength (blue shift), ~ 470 nm (Figure 4.5) whereas the nitro group shifts it towards the red (~ 520 nm) compared to the parent non substituted styryl CPD **202** (~ 495 nm).

**Figure 4.5 Combined UV-vis spectrum of *cis*-styryl CPDs 202, 210 and 226 in $CH_2Cl_2$**




Based on the absorption spectrum of cyclophanedienes, it is expected that the methyl substituted DHP **229** should open faster than **205** which, in turn, should open faster than **213** and this is quite consistent with the experimental results.

### 4.1.4.2 Electronic effects on the stability of photo exited states.

As mentioned earlier, Robb[82] has shown by high level *ab initio* calculations that a DHP based photoswitch can photo open effectively provided the biradical excited state is highly populated compared to the normal zwitterionic one. Both methyl and methoxy groups are good at stabilizing radicals and can make the radicaloid excited state lower in energy and accelerate the photoopening reaction. However, a similar explanation cannot

be given for a nitro group because a nitro group is also a radical stabilizer and would be expected to accelerate the photoopening reaction.

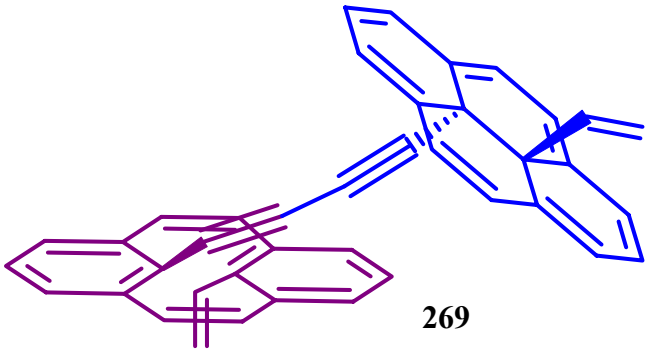
### 4.1.5 Naphthoyl DHPs 248 and 250

A carbonyl functional group at the 2- and 4- positions of dihydropyrene is known to increase the photoopening rate.[67] Robinson[35] has shown that a naphthoyl group at the 2-position of a DHP has the most profound effect, thus we synthesized the naphthoyl derivative of the most thermally robust photoswitch **179** and studied its photochemical properties. The naphthoylation enhanced the photoopening rate by approximately two orders of magnitude. Naphthoyl diisobutenyl DHP **248** was almost 25 times faster than BDHP **47**. This relative rate should be adopted with caution because there could be large errors due to very short irradiation interval, i.e., a few seconds. Moreover, in a comparable time, BDHP was open less than 4%, a level of accuracy not provided through analysis of the NMR spectrum. The naphthoyl group probably stabilizes the radical excited state by delocalizing it over the π system and thus increases the photoopening rate.

Naphthoyl divinyl DHP **250**, quite contrary to its non naphthoylated analogue **167**, is quite stable to irradiation and opens at a rate comparable to BDHP **47**. This stability could be due to the short time required for the photoopening. Divinyl **250** forms a photostationary state in cyclohexane whereas in DCM or toluene, it opens completely. Formation of the solvent dependant photostationary state has already been reported in the cases of naphthoylated DHPs.[35]

### 4.1.6 Dimer 254

Dimer **254**, despite the fact that it contains a vinyl and a butadiynyl internal group opens under visible opening conditions. Formation of the mono open product **269** can easily be seen by monitoring the NMR spectrum, however prolonged irradiation yielded a pale yellow colorless precipitate which could be the fully open form, however, we failed to obtain an NMR spectrum. Photoopening of the dimer was quite slow.



**269**

Another common factor among all the compounds, which fully opened or showed exceptional behavior, was the upfield shift of the DHP protons in their $^{1}$H NMR spectra, examples include the all *cis* isomers of vinyl substituted dihydropyrenes and the dimer **254**. In the dimer, protons were shielded by 0.3-0.5 ppm in comparison to the monomer **237**. We are not sure if this upfield shift is an accident or it has some implications in understanding the photoopening process.

In conclusion, most of the compounds studied either failed to open or formed a photostationary state. However, some generalization could be made:

1. Dihydropyrenes **86** and **236** containing internal nitrile and ethynyl groups respectively (sp carbons substituents) formed photostationary states (60: 40 open: closed), however any extension of the internal alkyne substituents (DHPs **139**, **141** and **257)** shuts down the photoopening except in the case of DHP **254**.

2. The all *cis* isomers of the internal olefinic dihydropyrenes (**164, 205, 213, 221**, **229**) opened to 100% completion.
3. The unsymmetrical (geometrical) isomers of internal styryl/*p*-substituted styryl dihydropyrenes (**206, 214, 222** and **230**) formed photostationary states.
4. The all *trans* isomers of the internal olefinic dihydropyrenes (**190, 199, 207, 215, 223** and **231**) failed to open at all.
5. Dihydropyrenes containing one or two internal ethenyl (vinyl) group such as **167**, **238** and **241** practically failed to open.

## 4.2 UV Closing

Cyclophanedienes **85** (dicyano)**, 229** (*p*-methoxystyryl) and **249** (naphthoyl diisobutenyl) were studied for the UV isomerization into the corresponding dihydropyrenes and comparative rates are given in Table

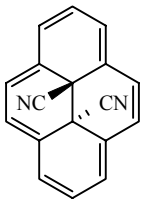
**Table 4.2 UV closing comparison of cyclophanedienes**

| | |
|---|---|
| Benzo CPD **53** | 1 |
| Dicyano CPD **85** | 0.6 |
| *p*-Methyl-styryl CPD **229** | 1 |
| Naphthoyl CPD **249** | 1.2 |

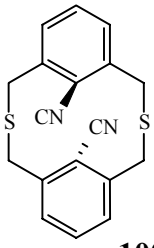
The UV closing rates of the cyclophanedienes were quite comparable to that of benzo CPD **53.** Dicyano CPD **85** isomerized slower than benzo CPD **53** whereas naphthoyl CPD **249** closed slightly faster. Robinson[35] and Bandyopadhyay[83] have concluded in a similar study that the UV isomerization rates of cyclophanedienes are generally quite comparable.

# Chapter 5: X-Ray Structure Analyses

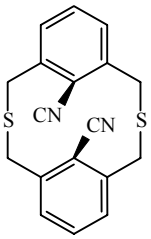
X-ray crystallography is the most reliable method for characterizing the atomic structure of materials as it gives information about the size and shape of molecules and complexes, as well as bond lengths and types of chemical bond. X-ray crystallography generally discerns materials which appear quite similar by other experiments (spectroscopic techniques). The technique besides providing insight into the structures of molecules, has also guided the direction of new research, e.g., the X-ray structure of ferrocene initiated scientific studies of sandwich compounds.[84] The following compounds were studied by X-ray crystallography as a part of this thesis research and the data was obtained by Dr Brendan Twamley (University of Idaho).



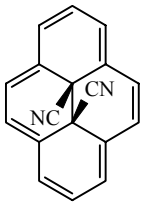

**86**



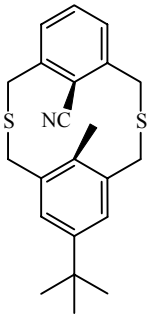

**100**



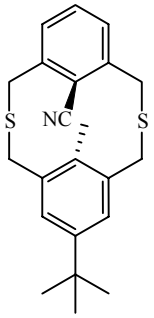

**108**



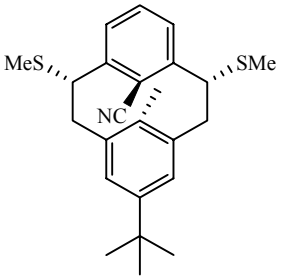

**117**



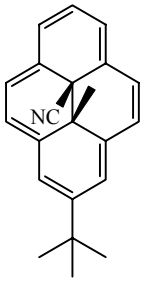

**130**



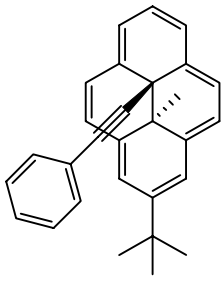

**131**



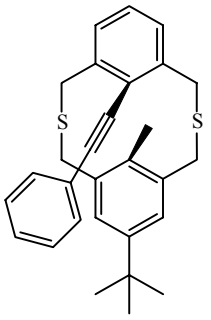

**134**



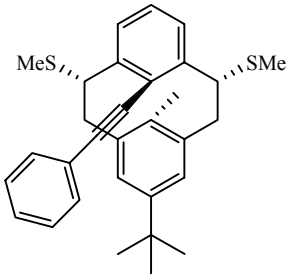

**136**



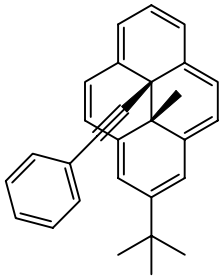
**139**



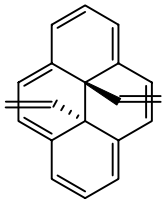

**145**



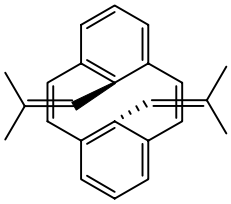

**146**



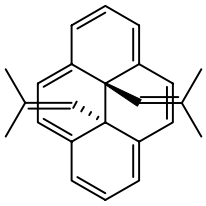
**148**



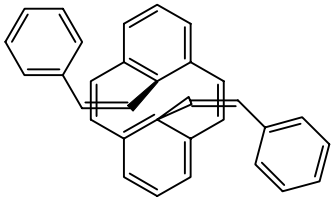
**167**



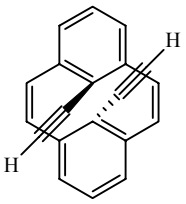
**178**



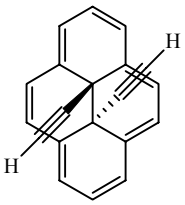
**179**



**202**




**235**

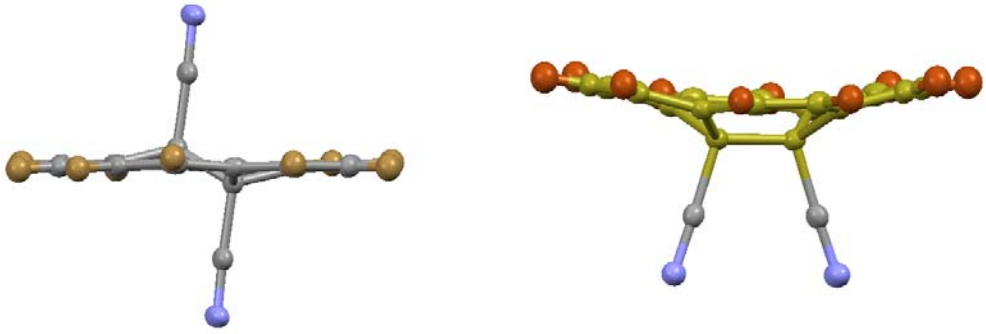



**236**

## 5.1 Dicyano DHPs 86 and 117.

It has already been stated that X-ray crystallography can discriminate molecules which appear quite similar by other spectroscopic techniques; examples are the *cis* and *trans* isomers of dicyanodihydropyrene, **117** and **86,** respectively. Both isomers have an equal number of peaks in each of their the $^{1}H$ and $^{13}C$ NMR spectra. Moreover, 2D NMR techniques fail to indicate the relative orientation of the cyano groups. An X-ray structure was obtained for each isomer (Figure 5-1) and the geometry was thus confirmed unambiguously.

**Figure 5.1 Molecular diagrams of dicyano DHPs 86 (left) and 117 (right) derived from X-ray structures**



## 5.2 *Cis*-dihydropyrenes

*cis*-Dicyano DHP **117,** as shown by its X-ray structure (Figure 5.1), is a saucer shaped molecule, a characteristic of *cis*-dihydropyrenes. A similar structure was also found for *cis*-phenylethyl DHP **148** (Figure 5.2, left) and *cis*-cyano-methyl DHP **136** (Figure 5.2, right).

**Figure 5.2 Molecular diagrams of *cis*-phenylethynyl/methyl DHP 148 (left) and *cis*-cyano/methyl DHP 136 (right) derived from X-ray structures**

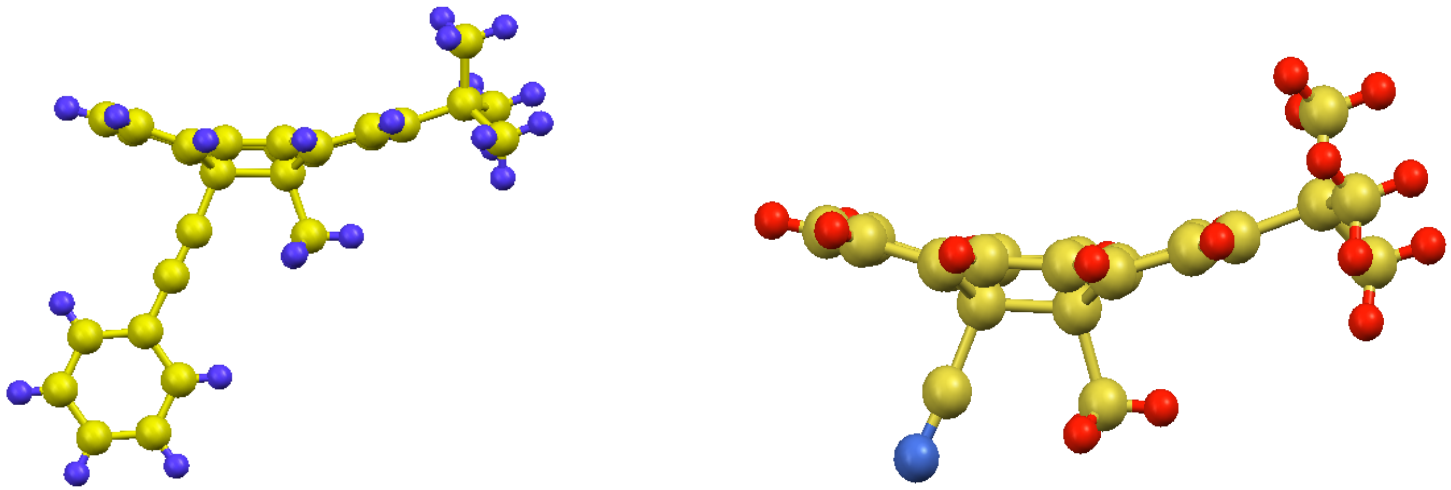


**Figure 5.3 Molecular structures of *trans*-phenylethynyl/methyl DHP 139 and *trans*-diethynyl DHP 236 derived from X-ray structures**

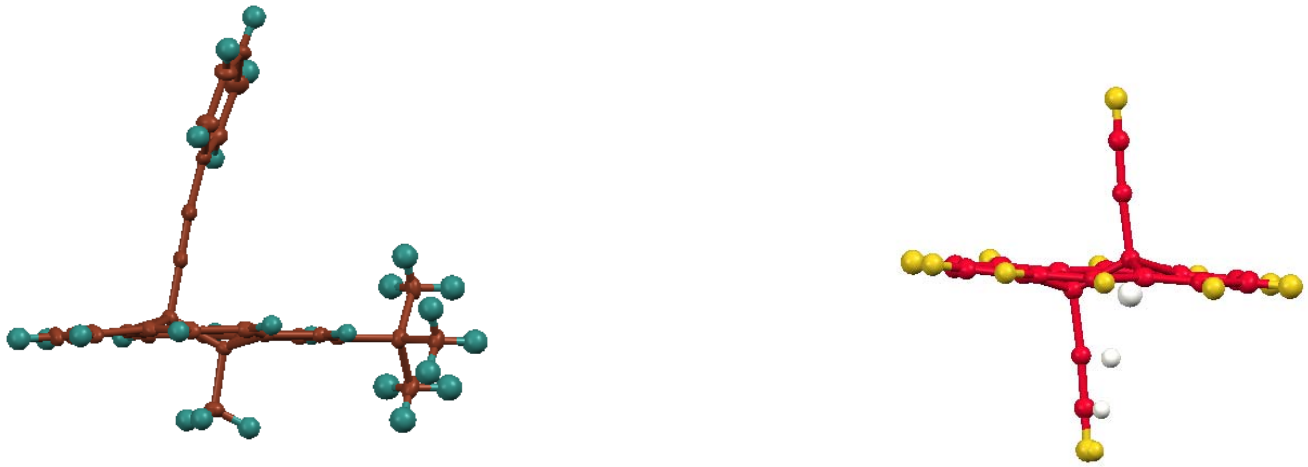
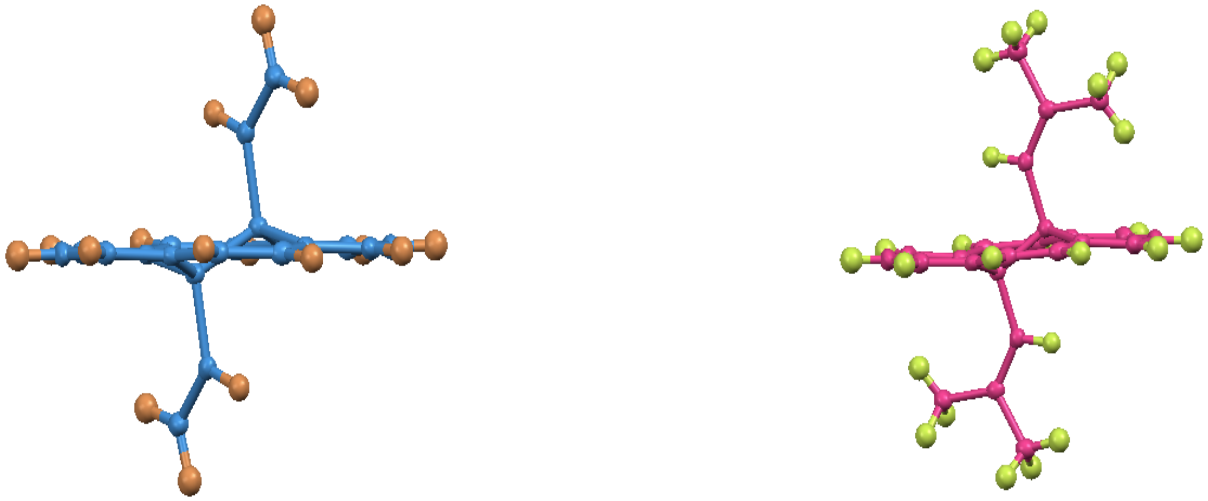


**Figure 5.4 Molecular diagrams of divinyl DHP 167 (left) and diisobutenyl DHP 179 (right) derived from X-ray structures**



### 5.3 *Trans* dihydropyrenes

The X-ray structures of the *trans*-dihydropyrenes not only indicate the orientation of the internal groups but they also give mechanistic insight into the thermal return reaction.

The *trans* dihydropyrene nuclei of dicyano DHP **86** (Figure 5.1 left), phenylethynyl/methyl DHP **139** (Figure 5.3 right), divinyl DHP **167** (Figure 5.4 left) and diethynyl DHP **236** (Figure 5.3 right) did not show any appreciable deviation from planarity probably because of the linear and sterically less demanding internal groups. However in the cases of internal diisobutenyl DHP **179**, the dihydropyrene skeleton was significantly stepped which suggests a reason for the slow thermal return of the cyclophanediene **178** (for details, see Chapter 3, pg 128).

### 5.4 Cyclophanedienes

Cyclophanedienes are thermally unstable compounds; moreover, they also convert to dihydropyrenes photochemically using the common household tungsten bulb. Thus, the crystal growth and the analysis are not trivial. We synthesized some thermally stable cyclophanedienes and thus we decided to obtain X-ray structures. The X-ray structures of diethynyl CPD **235** (Figure 5.5), distyryl CPD **202** (Figure 5.6 right) and diisobutenyl CPD **178** (Figure 5.6 left) were obtained which not only proved the stepped nature of the cyclophanediene but also gave valuable information regarding the mechanism of the thermal return. Cyclophanediene **235** showed better conjugation of the phenyl rings with sterically less demanding ethynyl groups. This conjugation is probably a reason for the high thermal stability of the CPD (for details: see Chapter 3, pg 127).

**Figure 5.5 Molecular diagram of diethynyl CPD 235 derived from X-ray structure**

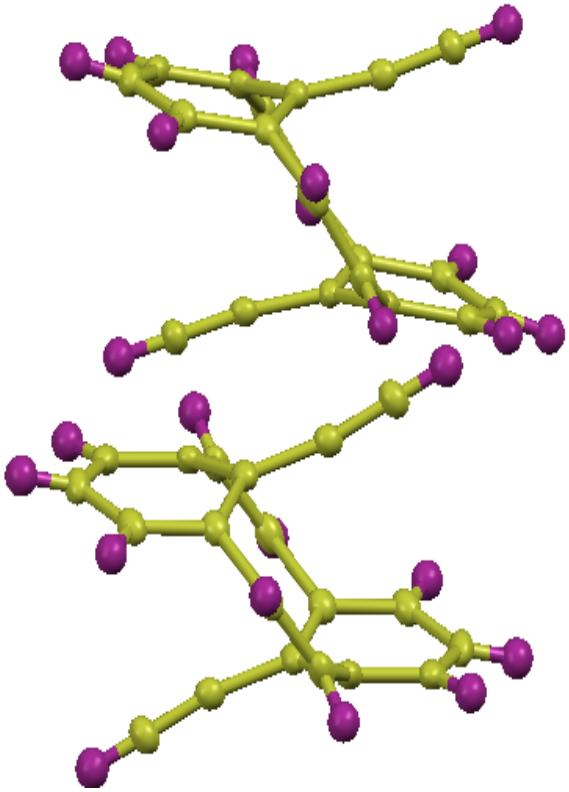
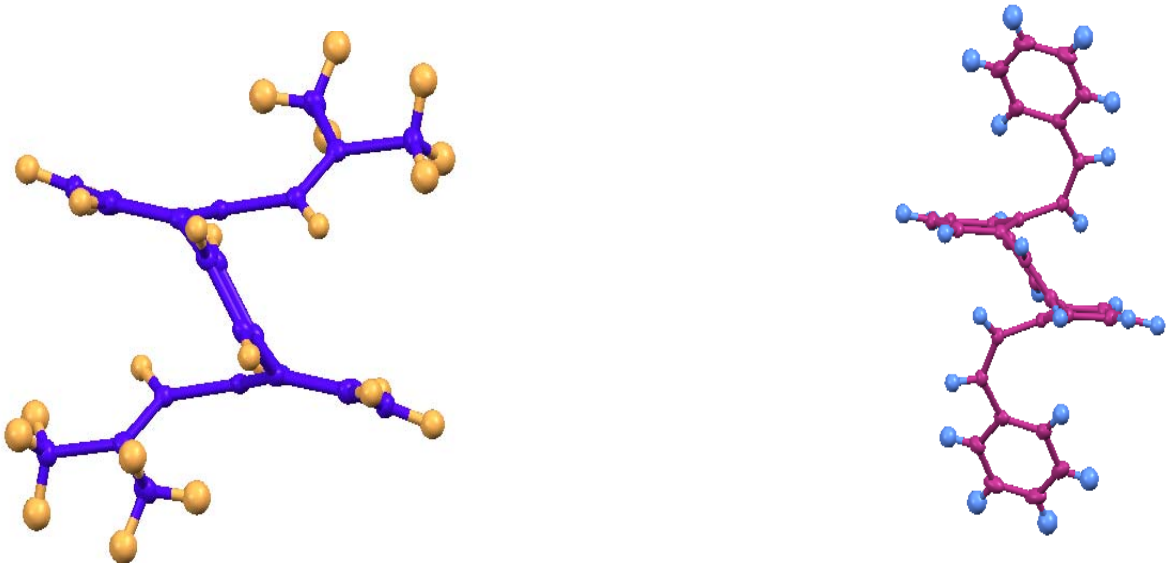
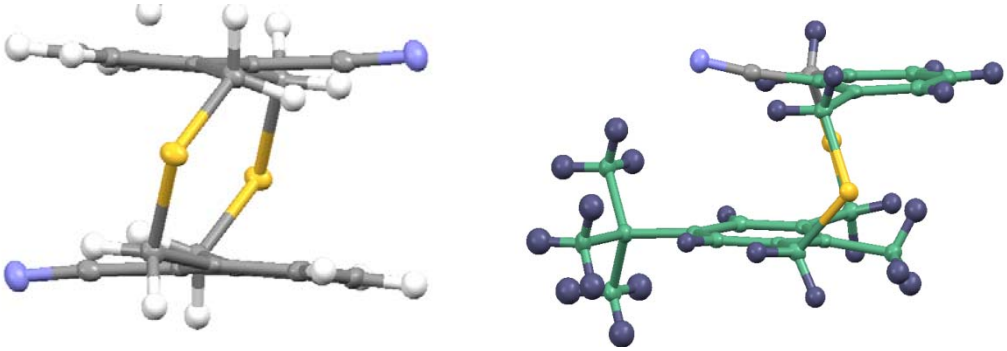


**Figure 5.6 Molecular diagrams of diisobutenyl CPD 178 (left) and distyryl CPD 202 (right) derived from X-ray structures**



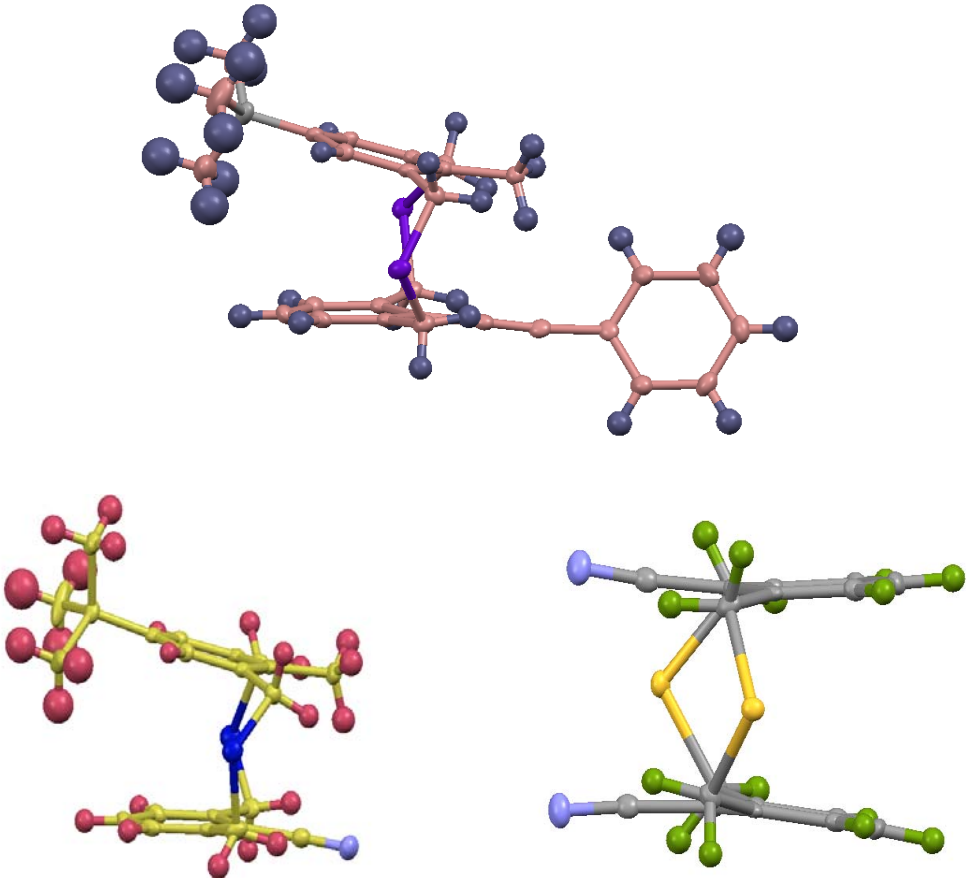
## 5.5 *Anti*-thiacyclophanes

**Figure 5.7 Molecular diagrams of dicyano-*anti*-thiacyclophane 100 and cyano-methyl-*anti*-thiacyclophane 131 derived from X-ray structures**



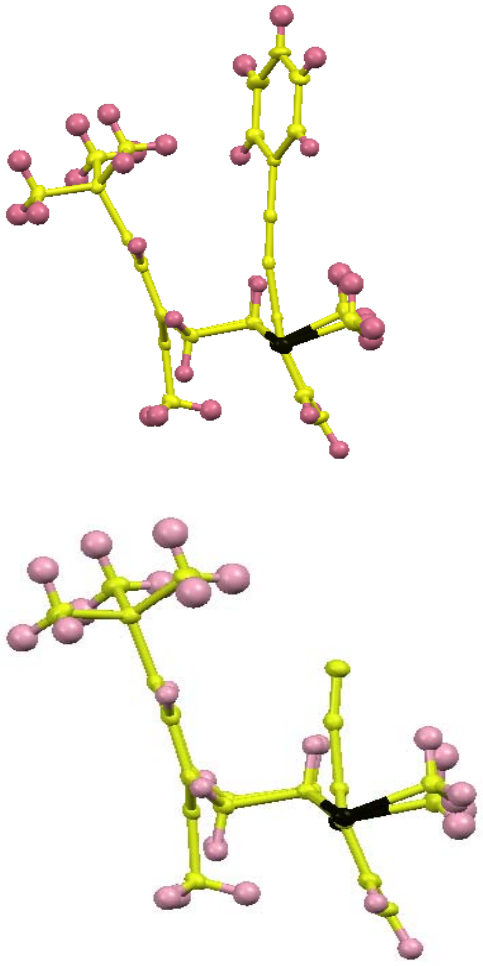
A comparison of dicyano *anti*-thiacyclophane **100** and cyano-methyl *anti*-thiacyclophanes **131** in their X-ray structures (Figure 5.7) does not indicate any observable difference in bond lengths and inter-plane distance. Generally, with increasing steric bulk at the internal positions, the phenyl rings of the thiacyclophane nucleus bend away from the planarity so as to minimize the steric interaction. However a nitrile group is not significantly different from a methyl group which explains why the structures are similar.

**Figure 5.8 Molecular diagrams of phenylethynyl/methyl-*syn*-thiacyclophane 145 (top), cyano-methyl-*syn*-thiacyclophane 130 (bottom right), dicyano-*syn*-thiacyclophane 108 (bottom left) derived from X-ray structures**



*Syn*-thiacyclophanes, on the other hand, show considerable differences in the inter-plane distances among the three cyclophanes studied, dicyano **108**, cyano-methyl **130** and phenylethynyl/methyl **145**. The deviation from planarity in dicyano *syn*-thiacyclophane **108** is much less than that for cyano-methyl **130** and phenylethynyl/methyl **145**. However, this difference is believed to arise not from the internal groups but from the *tert*-butyl group present at C-6.

**Figure 5.9 Molecular diagrams of phenylethynyl/methylcyclophane 146 (top) and cyano-methylcyclophane 134 (bottom) derived from X-ray structures**



## 5.6 Thiomethylcyclophanes

The NMR data of the pure isomers of different thiomethylcyclophane (dicyano **114**, cyano-methyl **134**, phenylethynyl/methyl **146**, diformyl **174** and divinyl **171**) was indicative of the di-equatorial orientation of the thiomethyl groups. In order to confirm this assignment, X-ray structure for cyano-methyl cyclophane **134** and phenylethynyl/methyl thiomethyl-cyclophane **146** were obtained (Figure 5.9) which is quite consistent with our supposition.

# Chapter 6: Conclusions

## 6.1 Synthesis

Synthesis of a series of cyclophanedienes with different internal groups was accomplished successfully. CPDs **85** (dicyano), **127** (cyano-methyl) and **138** (phenylethynyl/methyl) were synthesized in 25-35% overall yield from bis-bromomethyl starting material via thiacyclophane-thiomethylcyclophane intermediates. Diformyl CPD **152** and bis(hydroxymethyl) CPD **159** were obtained by the reduction of dicyano CPD **85** and diformyl CPD **152** respectively. Cyclophanedienes with internal olefinic (substituted/non-substituted) groups such as alkylvinyl (**162, 178** and **198**), butadienyl (**184**, **185** and **186**), styryl (**202, 203** and **204**), nitro-substituted styryl (**210, 211** and **212**), methoxy-substituted styryl (**218, 219** and **220**) and methyl substituted styryl (**226, 227** and **228**) were synthesized in moderate to good yields starting from dicyano thiomethylcyclophane **99** i.e functional group interconversions in **99** followed by Hoffmann elimination. Internal ethynyl substituted cyclophanedienes **235** and **237** were also synthesized by this route. Two other routes for the synthesis of the internal olefinic CPDs were also developed; FGIs in cyclophanedienes, and FGIs in dicyano thiacyclophane **100** followed by Wittig rearrangement-Hoffmann elimination sequence; although these routes provided lower yields

Phenylethynyl DHPs **141** and **247** were obtained by the Sonogashira coupling of diethynyl DHP **236**. The Eglinton coupling reaction was used to achieve butadiynyl DHPs **257** and **254**. Naphthoyl DHPs **248** and **250** were synthesized by the Friedel-Crafts acylation reaction of DHP **179** and **167** respectively.

### 6.2 Thermal isomerization of cyclophanedienes

Dicyano CPD **85** was quite stable towards its thermal isomerization to the dihydropyrene **86** and showed a calculated half life of ~36 years at room temperature, a number three orders of magnitude higher than that of benzo CPD **53** (7.3 days). Cyano-methyl (**127)**, phenylethynyl/methyl (**138)** and diformyl CPDs **(152**) showed half lives less than a month at 20 $^{o}$C. Cyclophanedienes with internal ethynyl and substituted vinyl groups were quite stable thermally and showed half lives of several years (1-16 years) at room temperature. Substituents on the internal vinyl group have quite remarkable effects on the half lives of cyclophanedienes, e.g. $\tau_{1/2}$ at 100 $^{o}$C for divinyl CPD **166** (7 min), *cis*-dipropenyl CPD **162** (94 min), diisobutenyl CPD **178** (270 min). CPDs with *cis* substituted internal vinyl groups were thermally more stable than their *trans* counterparts, e.g. $\tau_{1/2}$ at 100 $^{o}$C for *cis*-**162** and *trans*-**198** propenyl CPDs are 94 and 15 min respectively. Electron withdrawing substituents ($NO_2$) accelerate whereas electron donating (MeO, Me) decelerate the thermal return reaction of all the geometrical isomers of *p*-substituted styryl CPDs. Naphthoyl CPDs **249** and **251** isomerized at rates about 6-12 faster than their non-naphthoylated analogues **178** and **166** respectively.

### 6.3 Thermal rearrangement of dihydropyrenes

The [1,5]-sigmatropic rearrangement of internal nitrile (DHPs **86** and **128**) and formyl (DHP **153**) groups were observed**.** The sigmatropic rearrangement of nitrile in **86** was quite favourable in $CDCl_3$ ($E_{act}$ 23.4 kcal/mol) compared to benzene ($E_{act}$ 28.6 kcal/mol). The sigmatropic rearrangement of nitrile in the unsymmetrical DHP **128** was much more facile when compared with dicyano DHP **86**. Formyl groups showed a much higher migration aptitude and $E_{act}$ is estimated to be < 20 kcal/mol in any solvents.

### 6.4 Photochemical isomerization

Disubstituted vinyl (**179**) and *cis* substituted vinyl DHPs (**164, 205, 213, 221** and **229**) opened completely; however their opening rates although much faster than parent **43** were 4-6 times slower than the benzo DHP **47,** a standard for comparison**.** Dicyano DHP **86,** diethynyl DHP **236** and the unsymmetrical isomers of internal olefinic DHPs (**206, 214, 222** and **230**) formed photostationary states (pss) in the photoopening experiment. DHPs with internal ethenyl (**167, 238** and **241**), substituted ethynyl (**139, 141** and **247**) and *trans* substituted vinyl (**199, 207, 215, 223** and **231**) groups failed to open in visible light irradiation experiment. In brief, introduction of a *trans* substituent on the internal olefinic group did not assist in photoopening whereas a *cis* substituent or both *cis* and *trans* substituents favoured photoopening of dihydropyrenes. Moreover, introduction of an electron withdrawing substituent on the internal styryl group decelerated the visible opening reaction (DHPs **213** and **214**) whereas electron donating groups accelerated it (DHPs **221** and **222**). Naphthoyl DHP **250** opened at rates quite comparable to that of benzo DHP **47** whereas naphthoyl diisobutenyl DHP **248** opened about 25 times faster than the benzo DHP and is one of the best new photochromes yet.

The following table gives a brief summary of the thermal and photochemical data of all the compounds.

**Table 6.1. Summary of half lives of cyclophanedienes and visible opening time of their corresponding dihydropyrenes**

| No. | Cyclophanediene | $\tau_{1/2}$ (100 $^{o}$C)* | Dihydropyrene | Visible opening time |
|---|---|---|---|---|
| 1 | **85** | 5 h | **86** | Overnight[#] |
| 2 | **178** | 4.5 h | **179** | 13 min |
| 3 | **162** | 94 min | **164** | 3 h |
| 4 | **235** | 124 min | **236** | 7 h[#] |
| 5 | **218** | 130 min | **221** | 17 min |
| 6 | **226** | 132 min | **229** | 17 min |
| 7 | **186** | 115 min | **192** | Isomerized to **190** |
| 8 | **202** | 91 min | **205** | 20 min |
| 9 | **185** | 82 min | **191** | Isomerized to **190** |
| 10 | **219** | 92 min | **222** | 43 min[#] |
| 11 | **203** | 73 min | **206** | 66 min[#] |
| 12 | **227** | 87 min | **230** | 50 min[#] |
| 13 | **220** | 64 min | **223** | Failed to open |
| 14 | **249** | 43 min | **248** | 4-5 s |
| 15 | **210** | 77 min | **213** | 30 min |
| 16 | **211** | 59 min | **214** | ~ 3h[#] |
| 17 | **228** | 63 min | **231** | Failed to open |

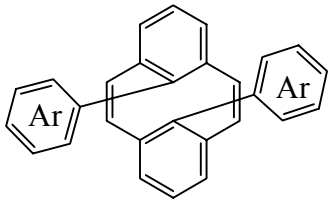
| | | | | |
|---|---|---|---|---|
| 18 | **212** | 55 min | **215** | Failed to open |
| 19 | **184** | 45 min | **190** | Failed to open |
| 20 | **204** | 40 min | **207** | Failed to open |
| 21 | **237** | 24 min | **238** | Failed to open |
| 22 | **240** | 23 min | **241** | Failed to open |
| 23 | **198** | ~15 min | **199** | Failed to open |
| 24 | **166** | 7.7 min | **167** | Slow (dec) |
| 25 | **138** | 15.2 h (50 $^{o}$C) | **139** | Failed to open |
| 26 | **127** (benzene) | 6.7 h (50 $^{o}$C) | **128** | Unstable (dec.) |
| 27 | **152** | 4.2 h (50 $^{o}$C) | **153** | Decomposes |
| 28 | **127** $CDCl_3$ | 5.2 h (50 $^{o}$C) | **128** | Unstable (dec.) |
| 29 | **251** | 3 h (50 $^{o}$C) | **250** | 2 min |
| 30 | **158** | ~ 1 h (20 $^{o}$C) | **159** | Decomposes |
| 31 | | | **141** | Failed to open |
| 32 | | | **247** | Failed to open |
| 33 | | | **257** | Failed to open |
| 34 | | | **254** | ~ 3h |
| 35 | | | **151** | Failed to open |

$^{\#}$ Photostationary state was formed ***** Errors estimated are less than 5%

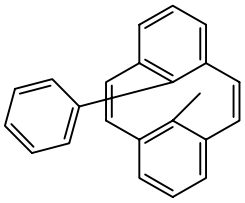
**6.5 Future Work**

A series of thermally stable cyclophanedienes have been synthesized during the course of this project, however there is still a great potential of research in this field both from a mechanistic and a practical application (commercial) point of view. Substituted

vinyl cyclophanedienes have shown a good compromise between the thermal stability and photoopening. However a closely related series in which the internal vinyl group is a part of aromatic ring e.g. diphenyl CPD **270** or similar compounds with other internal aromatic rings such as furan, thiophene and pyridine needs to be studied. Monophenyl photoswitch **271** has already been made and studied, however the previous synthesis of **270** failed probably because of steric overcrowding[85]. However, if it could be made, we believe that **270** would behave quite differently (compare dicyano **85** and cyano-methyl **127**). Synthesis of **270** and similar compounds is challenging because of increased steric crowding at the internal positions.

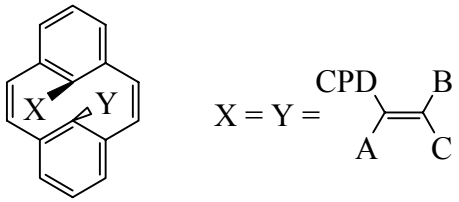



**270**



**271**

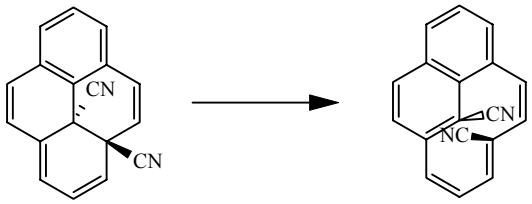
We synthesized several substituted vinyl cyclophanedienes but none of them had a strong electron donating or electron withdrawing group attached directly (groups A, B and C in **272**) to the vinyl group. A study of these vinyl cyclophanedienes would give further insight into the relative contribution of steric and electronic effects absent in this study.




**272**

All the olefinic CPDs studied contained hydrogen as group A (CPD **272**). Introduction of methyl, phenyl and styryl groups at this position may have some strong favourable steric effects. Diisobutenyl pair **178/179** (B and C are methyl groups in **272**) showed great thermal stability because of the steric contributions from the methyl groups, however replacement of the methyl groups with ethyl, isopropyl, *t*-butyl would be an interesting project to see the upper limit of steric tolerance.

In the substituted styryl series, electronic effects were studied only at the *para* position; however a study of electronic and steric effects at the *ortho* and *meta* positions would help in designing more sophisticated photoswitches.




**124** **273**

We realized that the products of sigmatropic rearrangement (dicyano **124**, cyano-methyl **137**) can also behave as a photoswitch because they still contains a hexadiene moiety. An example of the reaction is shown above. The reaction would be an uphill process, as expected, however by modeling the reaction, suitable substituents may be found to favour this process. Once it is successful it will help in multimode high density storage devices with both permanent and erasable memories CPD → DHP → mig. prod. → mig. open etc.

Investigation of the captodative effect in the Woodward-Hoffmann forbidden reaction and the sigmatropic rearrangements would aid in understanding the mechanism of these reactions as well as in designing the multimode photoswitches mentioned above.

# Chapter 7: Experimental

## 7.1 General experimental conditions

Melting points were determined on a Reichert 7905 melting point apparatus integrated to an Omega Engineering model 199 Chromel-alumel thermocouple. $^{1}H$ and $^{13}C$ NMR spectra were recorded, unless otherwise specified, on a Bruker Avance 500 MHz spectrometer (500.1 MHz for $^{1}H$, 125.7 MHz for $^{13}C$). Spectra were calibrated based on the solvent residual peak (5.32 and 54.00 ppm for $CD_2Cl_2$, 7.26 and 77.23 ppm for $CDCl_3$, 7.16 and 128.39 ppm for $C_6D_6$). NMR assignments were made on the basis of 2D COSY/NOESY experiments for $^{1}H$ and HSQC and HMBC experiments for $^{13}C$. The numbering for the structures shown in experimental is for NMR peak identification. H-1,2 means H-1 and H-2; H-1/2 means H-1 or H-2; H-1-3 means H-1, H-2 and H-3. Expanded data sets were used to obtain coupling constant data. Kinetic data were obtained using a Bruker AC 300 MHz or Bruker AV 300 MHz (unless otherwise specified) spectrometer.

Infrared spectra, calibrated with polystyrene, were recorded on a Thermo Nicolet IR 200 spectrometer as KBr pellets or thin film from dichloromethane on NaCl plates and only the major bands are reported. UV-vis spectra were recorded on a Cary 5 UV-vis-NIR spectrometer. Units of $\varepsilon_{max}$ are L $mol^{-1}$ $cm^{-1}$. Mass spectra were recorded on a Finnigan 3300 gas chromatography-mass spectroscopy system using methane as a carrier gas for chemical ionization or electron impact (EI) at 70 eV. Exact mass measurements were obtained on a Kratos Concept-H instrument using perfluorokerosene as the standard. Elemental analyses were performed by Canadian Microanalytical Services Ltd., Vancouver, B.C. All evaporation were carried out under reduced pressure on a rotary

evaporator, or by using an oil pump and liquid nitrogen condenser. Silica gel refers to Merck silica gel, 60-200 mesh. Alumina refers to Aldrich Aluminum oxide, activated neutral, Brockmann I, standard grade, ~ 150 mesh. Tetrahydrofuran (THF) was dried by distillation from potassium benzophenone ketyl. DCM and DMF were dried over calcium hydride. Toluene was used directly without drying; water contents less than 0.03%. Salts used in the Wittig reaction, except methyl triphenylphosphonium bromide and ethyl triphenylphosphonium bromide, were prepared according to the literature procedure and confirmed by their spectral data.

### 7.2 General procedure for crystal growth

10-20 mg of the sample was dissolved in 2-3 ml of an organic solvent (DCM for **100**, **108**, **86**, **117**, **235**, **236**, **134**; cyclohexane for **130**, **131**, **134**, **167**, **178**; isopropanol for **148**: acetone for **179**, and benzene for **136**) and the solvent was allowed to evaporate slowly. In the cases of thiacyclophanes **130** and **131,** cyclohexane was heated to boiling and the resulting solution, when cooled down to room temperature, yielded nice crystals instantly. Crystals of Phenylethynyl/ methyl DHP **139** were obtained when methanolic solution (5 mg in 4-5 ml) was placed in a freezer for a week.

### 7.3 Experimental conditions for X-ray crystallographic studies

Crystals of the compound were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data was collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Absorption corrections were applied using SADABS. The structure was solved by direct methods and refined by least squares

method on $F^2$ using the SHELXTL program package. All non-hydrogen atoms were refined anisotropically.

### 7.4 General procedure for S-Methylation

Mixed isomers of thiomethyl-*m*-cyclophane (1.00 mmol) in dry $CH_2Cl_2$ (20 mL) was added slowly to $(MeO)_2CHBF_4$[59] (80% oil, 600 mg, 3 mmol) at -78 $^oC$ with stirring under nitrogen. The mixture was then stirred at 20 $^oC$ for 3 h. The $CH_2Cl_2$ was decanted and ethyl acetate (40 mL) was added and stirring (trituration) was continued for a further 3 h. Decantation followed by more ethyl acetate and stirring was used if required. The white precipitate was then collected and dried to give bis-sulfonium salt in greater than 90% yield (unless otherwise specified). This was used directly in the next step.

### 7.5 General procedure for the Hoffmann elimination

[Note: to avoid photochemical conversion of the cyclophanediene product to the dihydropyrene, these operations should be carried out under minimal light] *t*-BuOK (280 mg, 2.50 mmol) was added to a stirred suspension of mixed isomers of bis-sulfonium salt (1 mmol), in THF (25 mL) under argon at 20 $^oC$. After stirring for 30 minutes, water (unless otherwise specified) was added and then dichloromethane (120 mL). The extract was washed, dried and evaporated. The residue was chromatographed over silica gel to give 50-90% yield of cyclophanediene(s).

### 7.6 General procedure for the thermal isomerization of cyclophanedienes to dihydropyrenes

Cyclophanediene (5-25 mg) in toluene (1-2 mL) was sealed in a glass tube under argon and heated at 100 $^oC$ until it isomerized completely to the dihydropyrene. The

reaction was monitored by $^{1}H$ NMR spectroscopy. No *cis-trans* isomerization of the internal olefinic substituents was observed during the thermal return experiment. Dicyano DHP **86** and cyano-methyl DHP **128** were obtained by photochemical isomerization. Bis(hydroxymethyl) dihydropyrene **160** was obtained from the bis(hydroxymethyl) CPD **159** at room temperature.

## 7.7 General procedure for Wittig reaction

### 7.7.1 Procedure A

BuLi (1.6 mL of 2.5M in hexanes, 4.0 mmol) was added dropwise to a suspension of alkyl triphenylphosphonium bromide (3.22 mmol) in THF (20 mL) under argon at 0 $^{o}C$ and the mixture was stirred for 20 minutes. After that time, a clear and orange to red solution was obtained. To this solution, diformylthiomethylcyclophane **174** (1.46 mmol) was added and the reaction mixture was allowed to stir for 1.5 h and then quenched with water. The resulting solution was extracted with $CH_2Cl_2$ (4 x 20 mL), dried over anhydrous $MgSO_4$ and evaporated. The crude mixture was chromatographed over silica gel.

### 7.7.2 Procedure B

*t*-BuOK (14.3 mmol) was added to a suspension of alkyl triphenylphosphonium bromide (10.2 mmol) in THF (40 mL) under argon at room temperature and the solution was stirred for 20 minutes. After that time, a clear and dark orange red solution was obtained. To this solution, diformylthiomethylcyclophane **174** (4 mmol) was added and the reaction mixture was allowed to stir for an hour at room temperature and then quenched with water. The resulting solution was extracted with $CH_2Cl_2$ (4 x 40 mL),

dried over anhydrous $MgSO_4$ and evaporated. The crude mixture was chromatographed over silica gel.

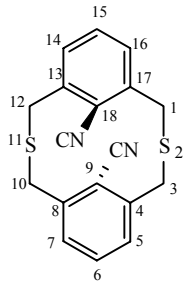
## 7.8 General procedure for photoopening (NMR)

1-2 mg of the dihydropyrene sample was dissolved in NMR solvent. The NMR tube was capped and wrapped with Teflon film. The sample was irradiated with light using a 500W household tungsten-halogen lamp (8500 lumens) as the light source and a 490 nm cut off filter. Irradiation was continued until color faded or a photo stationary state is reached. Irradiation was stopped after 16 h if no change is observed in the $^1H$ NMR spectrum.

## 7.9 Syntheses

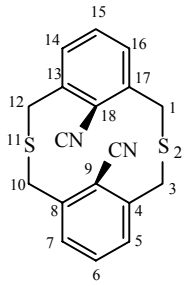
### 9,18-Dicyano-2,11-dithia[3.3]cyclophane

The bis(bromomethyl)nitrile[54] **102** (28.0 g, 97 mmol) in de-aerated benzene (700 mL) in one dropping funnel was added at the same drop rate (~ 1 every 2-3 seconds) as $Na_2S.9H_2O$ (23.2 g, 97 mmol) in de-aerated water (700 mL) in a second funnel to a mixture of vigorously stirred ethanol (95%, 2333 mL) and water (367 mL) under nitrogen. The addition took about 8 hours. The solvent was then evaporated and the residue was dissolved in $CH_2Cl_2$ and washed with water. The organic layer was washed, dried and evaporated, and the residue was chromatographed on silica gel using $CH_2Cl_2$-hexanes (6:4) as eluant.




***anti* -100**

Eluted first was 3.3 g (21%) of *anti*-**100** as colorless crystals from dichloromethane: mp ~ 220 $^{o}$C dec; $^{1}$H NMR ($CDCl_3$) δ 7.66-7.60 (m, 6H, ArH), 3.94 and 3.88 (AB, *J* = 14.4 Hz, 8H, -$CH_2$-); $^{13}$C NMR ($CDCl_3$) δ 140.80 (C-4,8,13,17), 134.44 (C-6,15), 130.73 (C-5,7,14,16), 115.38 (CN), 114.53 (C-9,18), 32.19 (C-1,3,10,12); IR ν (KBr) 2216, 1588,1464, 1445, 1408, 1237, 810, 801, 752 $cm^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ ($\varepsilon_{max}$) 305 nm (3400); EI MS *m/z* 322 ($M^+$). X-Ray structure- see Appendix A

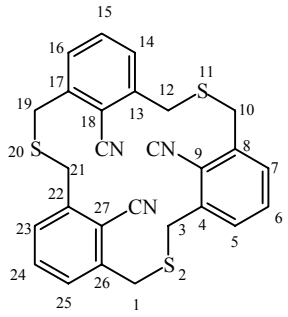



***syn* -108**

Eluted second was 3.4 g (22%) of *syn*-**108** as colorless crystals from dichloromethane: mp ~ 220 $^{o}$C dec; $^{1}$H NMR ($CDCl_3$) δ 7.15 (triplet, *J* = ~ 7.3 Hz, 4H, H-5,7,14,16), 7.07 (triplet, *J* = ~ 7.3Hz, 2H, H-6,15), 4.55 and 3.81 (AB, *J* = 15.5 Hz, 8H, -$CH_2$-); $^{13}$C NMR ($CDCl_3$) δ 141.96 (C-4,8,13,17), 132.97 (C-6,15), 129.51(C-5,7,14,16), 116.69 (CN), 113.13 (C-9,18), 35.90 (C-1,3,10,12); IR ν (KBr) 2212, 1590, 1466, 1452,

1414, 794, 751 $cm^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ ($\varepsilon_{max}$) 298 nm (5800); EI MS *m/z* 322 ($M^+$). X-Ray structure: see Appendix A

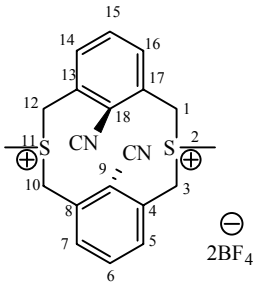
**9,18,27-Tricyano-2,11,20-trithia[3.3.3]metacyclophane 109**



**109**

Eluted third was 3.2 g (21%) of the trimer **109** as colorless crystals from dichloromethane: mp ~ 220 $^oC$ dec. $^1H$ NMR δ 7.46-7.39 (m, 9H, ArH), 3.79 (s, 12H, $-CH_2-$); $^{13}C$ NMR δ 141.78 (C-4,8), 132.73 (C-6,15), 128.61 (C-5,7), 115.19 (CN), 114.05 (C-9), 33.78 (C-1,3); IR ν (KBr) 2213, 1590, 1466, 795, 754 $cm^{-1}$; UV-Vis ($CH_2Cl_2$) $\lambda_{max}$ nm $\varepsilon_{max}$ 295 (4700); EI MS *m/z* 483 ($M^+$).

**Bis-sulfonium salt 110**

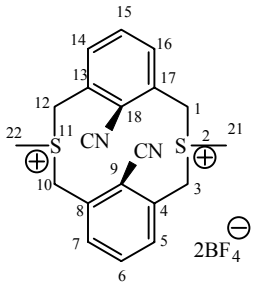


**110**

*anti*-Thiacyclophane **100** (400 mg, 1.24 mmol) in dry $CH_2Cl_2$ (15 mL) was added slowly to $(MeO)_2CHBF_4$ (80% oil, 550 mg, 2.7 mmol) at -78 $^oC$ with stirring under nitrogen. The mixture was then stirred at 20 $^oC$ for 3 h. The $CH_2Cl_2$ was decanted and

ethyl acetate (40 mL) was added and stirring (trituration) was continued for a further 3 h. The white precipitate was then collected and dried to give 650 mg (quant.) of bis-sulfonium salt **110**. This was used directly in the next step. $^1$H NMR (DMSO-$d_6$) δ 8.14-8.12 (m, 2H), 7.98-7.97 (m, 4H), 5.14 and 4.27 (AB, $J$ = 14.7 Hz, 4H –$CH_2$-), 5.01 and 4.92 (AB, $J$ = 14.1Hz, 4H, -$CH_2$-), 3.46 (s, 6H, -$CH_3$).

**Bis-sulfonium salt 115**




**115**

*syn*-Thiacyclophane **108** under the same conditions used for the synthesis of **110** gave the sulfonium salt **115** in quantitative yield.

$^1$H NMR (DMSO-$d_6$) δ 8.0-7.8 (m), 7.52 (s), 7.48 (t, $J$ = 7.8 Hz), 7.26 (d, $J$ = 7.7 Hz), 7.20-7.12 (m), 5.44 (d, $J$ = 14.0 Hz), 5.19 (s), 5.15-5.05 (m), 4.22 and 4.11 (AB, $J$ = 15 Hz), 3.45-3.40 (m), 3.32 (br s).

**2, 10-Bis(thiomethyl)-8,16-dicyano-*anti*-[2.2]cyclophane**

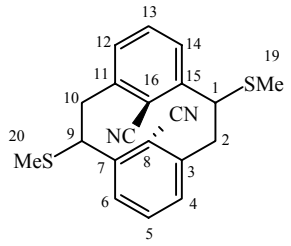
*t*-BuOK (330 mg, 2.94 mmol) was added to a stirred suspension of mixed isomers of salt **110** (600 mg, 1.15 mmol) in THF (25 mL) under argon at 20 $^o$C. After stirring for 3 h, water was added and then dichloromethane (120 mL). The extract was washed, dried and evaporated. The residue was chromatographed over silica gel using $CH_2Cl_2$-hexane

(6:4) as eluant to give 385 mg (98%) of product **99** as a mixture of isomers, EI MS *m/z* 350 ($M^+$, 100%). These could be used directly in the next step.

**Mixture of *anti* isomers**

$^1$H NMR ($CDCl_3$) δ 8.14-8.12 (m), 8.07-8.04 (m), 7.7 -7.40 (m), 6.64 (s), 6.23 (d, *J* = 9.0 Hz), 5.89-5.85 (m), 5.67 (s), 5.29, 5.26 (s), 4.69-4.65 (m), 4.44-4.41 (m), 4.21-4.16 (m), 3.77-3.71 (m), 3.57-3.34 (m), 2.95-2.89 (m), 2.53, 2.39, 2.35, 2.20, 2.19, 2.18, 2.17, 2.16 (s).

For characterization, re-chromatography yielded a single isomer of **99**, in which the 1,9-thiomethyl groups are pseudo-equatorial (48%).

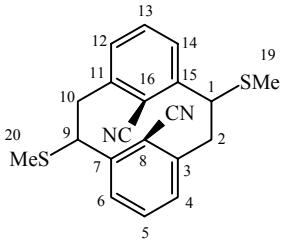



**99**

mp ~ 215 dec. $^1$H NMR ($CDCl_3$) δ 8.05-8.03 (m, 2H, H-6,14), 7.58-7.56 (m, 4H, H-4,5,12,13), 4.17 (dd, *J* = 11.5, 3.6 Hz, 2H, H-1,9), 3.53 (dd, *J* = 12.8, 3.6 Hz, 2H, H-$2_{eq}$,$10_{eq}$), 2.87 (dd, *J* = 12.8, 11.5 Hz, 2H, H-$2_{ax}$,$10_{ax}$), 2.17 (s, 6H, -SMe); $^{13}$C NMR ($CDCl_3$) δ 141.00 (C-3,11), 140.29 (C-7,15), 134.56 (C-5,13), 130.78 (C-4,12), 127.31 (C-6,14), 119.75 (C-8,16), 114.92 (CN), 54.54 (C-1,9), 44.60 (C-2,10), 15.82 ($CH_3$); IR ν (KBr) 2215, 1579, 1460, 1440, 1431, 806, 766, 743, 580, 497 $cm^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ ($\varepsilon_{max}$) 303 nm (1270); EI MS *m/z* 350 ($M^+$); HR MS Calcd for $C_{20}H_{18}N_2S_2$: 350.0911. Found: 350.0902. Anal. Calcd: C,68.55; H, 5.18; N, 8.00. Found: C, 67.69; H, 5.24; N,7.79.

**Mixture of *cis*-isomers 114**

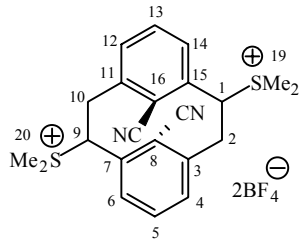
Bis-sulfonium salt **115** under the Stevens rearrangement conditions gave < 10% yield of the *syn*-cyclophane **114** as a mixture of isomers along with ~ 90% yield of the *anti*-isomers **99**. Column chromatography over silica gel using hexanes: DCM 4:6 eluted *trans*-isomers **99**. Hexanes: DCM 3:7 eluted **114** as a mixture of *syn*-isomers




**114**

$^1$H NMR ($CDCl_3$) δ 8.12-8.09 (m), 8.04-8.01 (m), 7.60-7.40 (m), 7.21 (d, *J* = 7.4 Hz), 7.16 (d, *J* = 7.7 Hz), 7.14 (d, *J* = 7.5 Hz), 6.91 (t, *J* = 7.4 Hz), 6.83 (t, *J* = 7.6 Hz), 6.73 (t, *J* = 7.5 Hz), 6.60 (d, *J* = 7.6 Hz), 6.49 (d, *J* = 7.4 Hz), 520-5.14 (m), 4.54 (d, *J* = 15.4 Hz), 4.25-4.14 (m), 3.82-3.72 (m), 3.55-3.38 (m), 2.91-2.61 (m), 2.43-2.37 (dd, *J* = 14.1, 8.0 Hz), 2.21, 2.19, 2.17, 2.16, 2.15, 2.14, 2.13 (s).

**2, 10-Bis(thiomethyl)-8,16-dicyano-*anti*-[2.2]cyclophane bis-sulfonium salt 111**

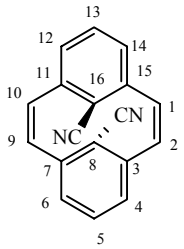



**111**

Using procedure 7.3 and the pure 1,9-diequatorial-thiomethyl isomer of **99** (350 mg, 1.00 mmol) gave the product **111** as a single isomer, $^1$H NMR (DMSO-$d_6$) δ 8.18-

7.81 (m, 6H, ArH), 4.92 (dd, *J* = 11.5, 3.6 Hz, 2H, H-1,9), 4.01 (dd, *J* = 12.8, 3.6 Hz, 2H, H-$2_{eq}$,$10_{eq}$) and 3.19 (~ t, *J* = ~ 12 Hz, 2H, H-$2_{ax}$,$10_{ax}$ ), 3.46 and 3.07 (s, 6H, - $SMe_2$).

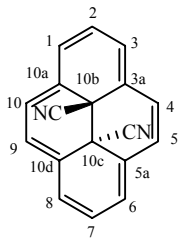
**8,16-Dicyano-*anti*-[2.2]metacyclophane-1,9-diene 85**




**85**

Using procedure 7.4 and then column chromatography over silica gel using $CH_2Cl_2$ as eluant gave (190 mg, 0.75 mmol, 75%) of cyclophanediene **85** as colorless crystals, which on attempted mp determination converts into DHP **86** and migration products: $^1$H NMR δ 7.54 (t, *J* = 7.6 Hz, 2H, H-5,13), 7.01 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 6.63 (s, 4H, H-1,2,9,10); $^{13}$C NMR δ 140.66 (C-3,7,11,15), 135.91 (C-5,13), 134.81 (C-1,2,9,10), 128.52 (C-4,6,12,14), 120.11 (C-8,16), 115.81 (CN); IR ν (KBr) 2215, 1560, 1442, 859, 810, 757, 570 $cm^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ ($\varepsilon_{max}$) 225 (30,000), 282 (9800), 330 (4800), 367(1600); EI MS *m/z* 254 ($M^+$); HR MS Calcd for $C_{18}H_{10}N_2$: 254.0843. Found: 254.0833.

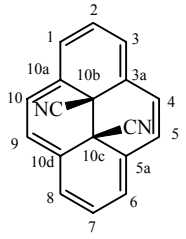
***trans*-10b,10c-Dicyano-10b,10c-dihydropyrene 86.**




**86**

Irradiation of a solution of cyclophanediene **85** in $CH_2Cl_2$ (concentration is not critical, 5 mg/mL is convenient) with a UV source with output 254 nm quickly converts **85** in to **86** quantitatively; however, **86** slowly converts thermally in to **124**, even at room temperature (see below), and so irradiation should not be continued unnecessarily. Careful evaporation of the dichloromethane yields green crystals of product **86**. On attempted mp determination, these turn colorless (from ~ 70 $^{o}$C up, depending upon the rate of heating, and finally melt at 142-144 $^{o}$C, corresponding to **124**). Slow evaporation (in dark) from $CH_2Cl_2$ yielded X-ray suitable crystals of **86**. (see Appendix A); $^{1}$H NMR δ 8.97 (s, 4H, H-4,5,9,10), 8.83 (d, *J* = 7.8 Hz, 4H, H-1,3,6,8), 8.37 (t, *J* = 7.8 Hz, 2H, H-2,7); $^{13}$C NMR δ 127.45 (C-3a,5a,10a,10d), 126.71 (C-4,5,9,10), 126.30 (C-2,7), 125.46 (C-1,3,6,8), 108.64 (CN), 30.76 (C-10b,10c). IR ν (KBr) 2227, 1351, 1254, 974, 930, 855, 767, 620 cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ ($\varepsilon_{max}$) 331 (87,300), 367 (34,300), 442 (6400), 528 (80), 599 (130), 640 (770); EI MS *m/z* 254 ($M^+$); HR MS Calcd for $C_{18}H_{10}N_2$: 254.0843. Found: 254.0832. Anal. Calcd: C, 85.02; H, 3.96; N, 11.02. Found: C, 84.22; H, 4.07; N, 10.91.

***cis*-10b,10c-Dicyano-10b,10c-dihydropyrene 117.**

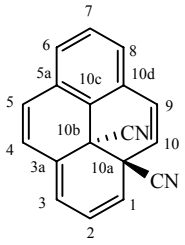



**117**

If a mixture of *syn*-and *anti*-cyclophane **114** and **99** is employed in the S-methylation and Hoffmann elimination reaction sequence, then *cis*-DHP **117** is obtained in a 5% yield along with > 90% of dicyano CPD **85**. The *cis*-dihydropyrene **117** was

obtained as dark green crystals from dichloromethane, mp 192 $^{o}$C (dec); $^{1}$H NMR ($CDCl_3$) δ 8.97 (4H, s, H-4,5,9,10), 8.66 ( 4H, d, *J* = 7.8 Hz, H-1,3,6,8), 8.10 (2H, t, *J* = 7.8 Hz, H-2,7); $^{13}$C NMR ($CDCl_3$) δ 129.22 (C-4,5,9,10), 126.14 (C-1,3,6,8), 124.97 (C-3a,5a,10a,10d), 124.04 (C-2,7), 115.28 (CN), 33.15 ( C-10b,10c); IR ν (KBr) 3046, 2925, 2227, 1654, 1593, 1261, 970, 852, 630 cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ ($\varepsilon_{max}$) 331 (67100), 360 (21600), 438 (5700), 635 (670); EI MS *m/z* 254 ($M^+$); HR MS Calcd for $C_{18}H_{10}N_2$: 254.0843. Found: 254.0839. Anal. Calcd: C, 85.02; H, 3.96; N, 11.02. Found: C, 80.83; H, 3.93; N, 9.77.

***trans*-10a,10b-Dicyano-10a,10b-dihydropyrene 124.**

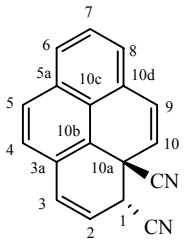



**124**

Dihydropyrene **86** (10mg) was sealed in a glass tube under argon and heated at 70 $^{o}$C for 30 min (or until completely colorless), which quantitatively converted it into colorless **124**; evaporation gave crystals: mp 143-145 $^{o}$C; $^{1}$H NMR δ 7.35 (t, *J* = 7.7 Hz, 1H, H-7), 7.16 (dd, *J* = 7.7, 1.1 Hz, 1H, H-8), 7.13 (dd, *J* = 7.7, 1.0 Hz, 1H, H-6), 6.91 (d, *J* = 9.2 Hz, 1H, H-9), 6.60-6.57 (m, 2H, H-2,5), 6.43 (d, *J* = 9.7 Hz, 1H, H-4), 6.30 (dd, *J* = 5.7, 0.6 Hz, 1H, H-3), 6.17 (d, *J* = 9.2 Hz, 1H, H-10), 6.09 (d, *J* = 9.2 Hz, 1H, H-1); $^{13}$C NMR δ 132.74 (C-3a,9), 132.13 (C-5a), 131.82 (C-10a), 130.81 (C-2), 130.75 (C-7), 129.74 (C- 5), 128.55 (C-6), 127.73 (C-8), 125.49 (C-4), 125.06 (C-10), 124.42 (C-10c), 124.32 (C-3), 124.09 (C-1), 116.65 (10b-CN), 116.15 (10c-CN), 42.68 (C-10b), 40.63

(C-10a); IR ν (KBr) 2227, 1578, 1467, 974, 909, 882, 828, 801, 757, 731, 708 $cm^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ ($\varepsilon_{max}$) 257 (22,000), 298 (5400), 311 (5400), 333 (5100), 348 (4300), 368 (3500), 385 (4100), 405 (2800); EI MS *m/z* 254 ($M^+$); HR MS Calculated for $C_{18}H_{10}N_2$: 254.0843. Found: 254.0834. Anal. Calcd: C, 85.02; H, 3.96; N, 11.02. Found: C, 82.49; H, 4.46; N, 10.05.

***trans*-1,10a-Dicyano-1,10a-dihydropyrene 125**




**125**

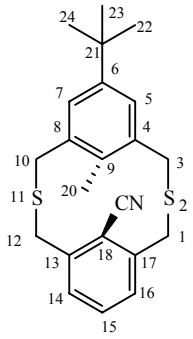
Dihydropyrene **86** (10 mg) in $CDCl_3$ (0.8 ml) was sealed in a glass tube under argon and heated at 70 $^oC$ for 4 days, which converted it into **125**. Evaporation gave colorless solid which decomposed on attempted chromatography but was pure enough to obtain the following data:

$^1H$ NMR ($CDCl_3$) δ 7.86 (d , *J* = 8.4 Hz, 1H, H-5), 7.74 (dd *J* = 0.9, 8.3 Hz, 1Hz, 1H, H-6), 7.45 (dd, *J* = 7, 8.4 Hz, 1H, H-7) , 7.41 (d, *J* = 8.3 Hz, 1H, H-4), 7.32 (dd, *J* = 6.9, 0.8 Hz, 1H, H-8), 7.08 (d, *J* = 9.5 Hz, 1H, H-9), 7.05 (d, *J* = 9.4 Hz, 1H, H-3), 6.11 (dd , *J* = 9.4, 6.2 Hz, 1H, H-2), 6.04 (1H, d, *J* = 9.5 Hz, H-10), 3.92 (dd , *J* = 6.2, 0.6 Hz, 1H, H-1); $^{13}C$ NMR ($CDCl_3$) δ 133.36 (C-5a), 133.15 (C-9), 132.87 (C-3), 129.91 (C-3a), 129.87 (C-5), 129.36 (C-6), 128.40 (C-10d), 127.53 (C-7), 126.95 (C-8), 126.55 (C-10c), 126.24 (C-4), 121.55 (C-10b), 120.84 (C-10), 117.92 (10a-CN), 117.62 (C-2), 114.53 (1-CN), 34.9 (C-10a), 29.9 (C-1); IR ν (KBr) 3055, 2918, 2224, 1590, 1503, 924,

905, 841, 789, 766, 690, 656 $cm^{-1}$ UV (dichloromethane) $\lambda_{max}$, nm ($\varepsilon_{max}$) 262 (29700), 272 (37900), 342 (4420), 354 (4330), 373 (2200), 407 sh (240); EI MS *m/z* 254 ($M^+$) HR MS calcd for $C_{18}H_{10}N_2$: 254.0843. Found: 254.0829.

**6-*t*-Butyl-18-Cyano-9-methyl-2,11-dithia[3.3]metacyclophanes 130 and 131**

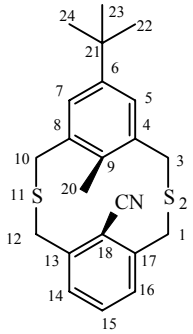
A solution of 2,6-bis(bromomethyl)benzonitrile[54] **102** (4.4 g, 15.2 mmol) and 2,6 bis-thiomethyl-4-*tert*-butyltoluene[64] **129** (3.80 g, 15.2 mmol) in de-aerated benzene (700 mL) was added drop wise to ethanolic KOH solution { prepare by adding KOH (4.83 g) in de-aerated water (230 mL) and ethanol (2090 mL) followed by addition of sodium borohydride (0.9 g)} under nitrogen. The drop rate was crucial (~ 1 every 3-4 seconds) and the addition took 44 hours. The solvent was then evaporated and the residue was dissolved in DCM and extracted with water, dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel using $CH_2Cl_2$-hexanes 3.5: 6.5 as eluant to give 1.9 g (5.17 mmol, 34%) of **131** as colorless crystals




**131**

from cyclohexane: mp 147-148 $^oC$; $^1$H-NMR ($CDCl_3$) δ 7.42-7.45 (m, 3H, H-14,15,16), 7.43 (s, 2H, H-5,7), 3.92 and 3.72 (AB, *J* = 14.4 Hz, 4H, H-1,12), 3.82 and 3.74 (AB, *J* = 14.0 Hz , 4H, H-3,10), 1.43 (s, 3H, Me), 1.39 (s, 9H, $C(C\underline{H}_3)_3$); $^{13}$C NMR δ 149.34 (C-6), 141.54 (C-13,17), 136.58 (C-9), 133.46 (C-4,8), 131.89 (C-15), 129.57 (C-14,16), 128.16

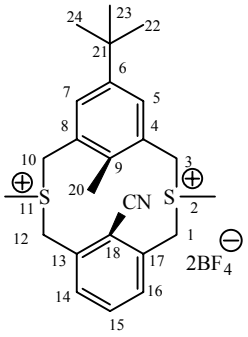
(C-5,7), 115.38 (CN), 115.12 (C-18), 34.58 (<u>C</u>($CH_3$)$_3$), 33.01 (C-3,10), 31.62 (C-1,12), 31.26 (C(<u>C</u>$H_3$)$_3$), 15.37 (C-20); IR ν (KBr) 3027, 2954, 2217, 1588, 1483, 1464, 1417, 1236, 877, 804, 794, 755 $cm^{-1}$; UV(cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 297 (1410), 307 (1390); EI MS *m/z* 367 (100); HR MS Calcd for $C_{22}H_{25}NS_2$: 367.1428. Found: 367.1413. Anal. Calcd: C, 71.89; H, 6.86; N, 3.81. Found: C, 71.52; H, 6.87; N, 3.69.



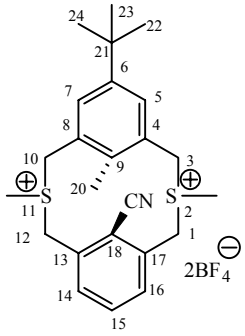

**130**

Eluted second using $CH_2Cl_2$-hexanes 4.5:5.5 was 1.9 g (4.90 mmol, 32%) of the *syn*-thiacyclophane **130** as colorless crystals from cyclohexane, mp 166-167 $^oC$; $^1H$ NMR ($CDCl_3$) δ 7.07 (br s. 3H, H-14-16), 6.96 (s, 2H, H-5,7), 4.36 and 3.75 (AB, *J* = 15.1 Hz, 4H, H-1,12), 4.36 and 3.67(AB, *J* = 15 Hz, 4H, H-3,10), 2.56 (s, 3H, Me), 1.18 (s, 9H, C(C<u>H</u>$_3$)$_3$); $^{13}C$ NMR δ 147.41 (C-6), 142.54 (C-13,17), 135.85 (C-4,8), 132.88 (C-15), 132.21 (C-9), 128.72 (C-14,16), 126.29 (C-5,7), 117.72 (CN), 111.65 (C-18), 35.79 (C-1,12), 34.94 (C-3,10), 34.27 (<u>C</u>($CH_3$)$_3$), 31.17 (C(<u>C</u>$H_3$)$_3$), 17.00 (C-20); IR ν (KBr) 3040, 2962, 2214, 1592, 1478, 1225, 1185, 871, 746 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 292 (2320), 311 (1210); EI MS m/z 367 ($M^+$); HR MS Calcd for $C_{22}H_{25}NS_2$: 367.1428. Found: 367.1419. Anal. Calcd: C, 71.89; H, 6.86; N, 3.81. Found: C, 71.56; H, 6.52; N, 3.70.

**Sulfonium salt 132/132a**




**132**

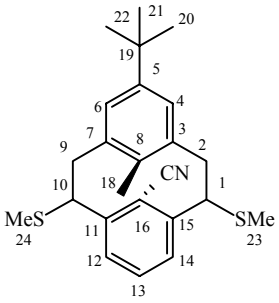



**132a**

*syn*-Thiacyclophane **130** (1.4g, 3.8 mmol) in dry $CH_2Cl_2$ (12 mL) was added slowly to $(MeO)_2CHBF_4$ (80% oil, 2.0 g, 9.8 mmol) at -78 $^oC$ with stirring under nitrogen. The mixture was then stirred at 20 $^oC$ for 3 h. The $CH_2Cl_2$ was decanted and ethyl acetate (50 mL) was added and stirring (trituration) was continued for a further 3 h. The white precipitate was then collected and dried to give 2.0 g (quant.) of bis-sulfonium salt **132**. This was used directly in the next step. $^1$H NMR (DMSO-$d_6$) δ 7.45-7.58 (m), 7.23-7.17 (m), 6.94 (d, $J$ = 8.1 Hz), 5.37-4.73 (m), 3.27-3.25 (m), 2.67, 2.69 (2 s), 1.12, 1.14, 1.18 (3 s).

*anti*-Thiacyclophane **131** under similar conditions gave bis-sulfonium salt **132a** in quantitative yield. $^1$H NMR (DMSO-$d_6$). δ 8.14-8.13 (m), 7.74-7.69 (m), 7.61-7.53 (m), 5.35-5.31 (m), 5.16 (d, $J$ = 13.1 Hz), 4.99-4.93 (m), 4.85-4.81 (m), 4.64 (d), 4.34 (d, $J$ = 14.2 Hz), 4.10 (d, $J$ = 14.5 Hz), 3.84 (s), 3.38 (s), 3.33 (s), 2.94 (s), 2.34 (s), 1.98 (s), 1.34 (s), 1.27 (s), 1.17 (s).

**1,10-Bis(thiomethyl)-5-$^{t}$butyl-16-cyano-8-methyl-*anti*-[2,2]metacyclophane 134**




**134**

*t*-BuOK (0.87 g, 7.7 mmol) was added to a stirred suspension of mixed isomers of salt **132a** (2g, 3.5 mmol) in THF (35 mL) under argon at 20 $^{o}$C. After stirring for 3 h, water was added and then dichloromethane (120 mL). The extract was washed, dried and evaporated. The residue was chromatographed over silica gel using $CH_2Cl_2$-hexane (3.5: 6.5) to give 1.27 g of product **134** as a mixture of isomers, EI MS *m/z* 395 ($M^+$). These could be used directly in the next step.

**Mixture of *anti*-thiomethylcyclophane isomers 134**

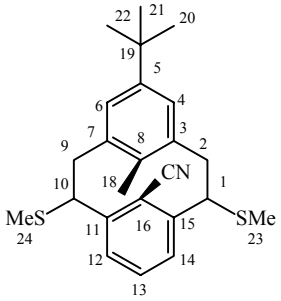
$^1$H NMR ($CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz), 7.92-7.84 (d), 7.58-7.21 (m), 7.08 (d, *J* = 8.3 Hz), 6.2(s), 5.9 (s), 5.02 (d, *J* = 11.2 Hz), 4.54-4.48 (m), 4.32-4.28 (dd, *J* = 11.3, 4.4 Hz), 4.10-4.06 (dd, *J* = 11.2, 4.2 Hz) , 3.74-3.70 (m), 3.55 (d, *J* = 2.1 Hz), 3.32-3.23 (m), 2.70-2.62 (m), 2.46, 2.35, 2.27 (3 singlet), 2.13 (m), 2.08 (s), 1.84-1.81 (m), 1.70 (s), 1.34, 1.32, 1.17 (3s), 0.54, 0.51, 0.49 (3 singlet).

For characterization, re-chromatography yielded 170 mg **(**12%) of a single isomer of **134** in which the 1,10-thiomethyl groups are pseudo-equatorial: mp 139-140 $^{o}$C; $^1$H NMR ($CDCl_3$) δ 7.97 (d, *J* = 7.7 , 2H, H-12,14), 7.39 (t, *J* = 7.7, 1H, H-13), 7.28 (s, 2H, C-4,6), 4.09 (dd, *J* = 11.2, 4.2 Hz, 2H, H-1,10), 2.67 (dd, *J* = 12.6, 4.2, 2H, H-$2_{eq}$, $9_{eq}$), 2.67 (dd, *J* = 11.4, 12.6 Hz, 2H, H-$2_{ax}$,$9_{ax}$), 2.13 (s, 6H, S-Me) , 1.33 (s, 9H,

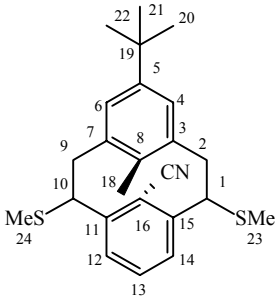
C(C<u>H</u>$_3$)$_3$), 0.54 (s, 3H, Me); $^{13}$C NMR δ 150.23 (C-5), 140.88 (C-8), 140.33 (C-11,15), 134.89 (C-3,7), 130.77 (C-13), 126.63 (C-12,14), 126.35 (C-4,6), 119.58 (C-16), 114.40 (CN), 54.8 (C-1,10), 42.75 (C-2,9), 34.23 (<u>C</u>(CH$_3$)$_3$, 31.25 (C(<u>C</u>H$_3$)$_3$), 15.52 (S-Me), 14.49 (C-17); IR ν (KBr) 3049, 2951, 2864, 2216, 1598, 1479, 1455, 866, 792, 743, 578 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 274 (3040), 295 (3530); EI MS *m/z* 395(M$^+$, 100%); HR MS Calcd for $C_{24}H_{29}NS_2$: 395.1741. Found: 395.1747. Anal. Calcd: C, 72.86; H, 7.39; N, 3.54. Found: C, 72.41; H, 7.02; N, 3.50.

**Mixture of *syn*- and *anti*-thiomethylcyclophanes 133 and 134**

Sulfonium salt **132** under the Stevens rearrangement conditions gave a mixture of and *anti*-thiomethylcyclophanes which gave following $^1$H NMR data.



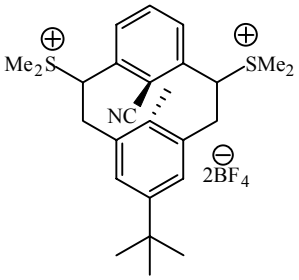

**133**




**134**

$^1$H NMR ($CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz), 7.88 (d, *J* = 7.7 Hz), 7.84 (d, *J* = 1.8 Hz), 7.42-7.25 (m), 7.12 (d, *J* = 7.6 Hz), 6.90-6.75 (m), 6.53 (d), 6.47 (d), 6.42 (m), 6.29, 6.17, 6.11, 6.02 (4 singlet), 5.04-4.97 (m), 4.88 (t, *J* = 8.6 Hz), 4.53-4.47 (m), 4.12-3.24 (m), 2.80-2.60 (m), 2.40-2.35 (m), 2.22-2.14 (6 singlets), 1.38, 1.35, 1.32, 1.02, 0.97 (5 singlets), 0.54, 0.51, 0.49 (3 singlets).

**Bis-sulfonium salt 135**



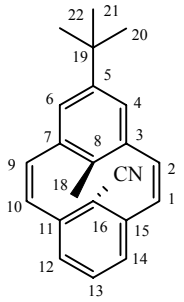

**135**

Using procedure 7.3, cyclophane **134** (2.8 g, 7.00 mmol) and Borch reagent (4.50 g, 22 mmol) in DCM (25 mL) gave 77%.(3.24 g, 5.39 mmol) yield of an air sensitive bis-sulfonium salt **135**.

$^1$H NMR (DMSO-$d_6$) δ 8.00 (t, $J$ = 8.0 Hz), 7.91-7.84 (m), 7.75-7.61 (m), 7.51 (d, $J$ = 11.5 Hz), 7.49 (s), 7.37-7.27 (m), 7.09-7.05 (m), 6.60, 6.40 (s), 5.57 (d, $J$ = 5.5 Hz), 5.43 (d, $J$ = 3.0 Hz), 5.54, 5.37 (s), 4.74-4.66 (m), 4.25 (d, $J$ = 2.8 Hz), 3.45-3.3 (m), 3.05 (d, $J$ = 8.0 Hz), 2.96, 2.90, 2.84, 2.81, 2.59 (5 singlet), 1.33-1.31, 1.22, 1.04 (5 singlet), 0.69, 0.63, 0.56 ( 3 singlet)

If a mixture of **133** and **134** was used, the salt showed following $^1$H NMR data: $^1$H NMR (DMSO-$d_6$) δ 8.02 (d, $J$ = 7.9 Hz), 7.91-7.85 (m), 7.75-7.62 (m), 7.49, 7.50 (singlets), 7.35-7.27 (m), 7.22-7.12 (m), 7.08 (t, $J$ = 6.5 Hz), 6.63, 6.60 (s), 5.84-5.54 (m), 4.85-4.74 (m), 4.73-4.67 (m), 3.45-3.30 (m), 3.10-2.92 (m), 1.34-1.30 (singlets), 1.11, 1.04, 0.97, 0.69, 0.63, 0.56 (s).

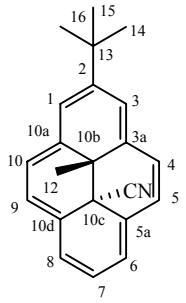
**5-(*tert*-Butyl)-16-cyano-8-methyl-*anti*-[2.2]metacyclophane-1,9-diene 127**




**127**

Using procedure 7.4, a reaction of *t*-BuOK (0.87 g 7.7 mmol) and sulfonium salt **135** (2.0 g, 3.35 mmol) in THF (35 mL) followed by column chromatography using $CH_2Cl_2$-hexanes 4:6 as eluant gave 710 mg (70% yield) of **127** as colorless crystals from cyclohexane, which on attempted mp determination converts into DHP **128** and the migration product **137**: $^1$H NMR ($CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 1H, H-13), 6.85 (d, *J* = 7.5 Hz, 2H, H-12,14), 6.79 (s, 2H, H-4,6), 6.62 (d, *J* = 11.3 Hz, 2H, H-2,9), 6.30 (d, *J* = 11.3 Hz, 2H, H-1,10), 1.57 (s, 3H, Me), 1.31 (s, 9H, -C(C<u>H</u>$_3$)$_3$); $^{13}$C NMR ($CDCl_3$) δ 154.04 (C-5), 141.46 (C-8), 140.95 (C-11,15), 137.71 (C-2,9), 136.24 (C-3,7), 133.30 (C-13), 129.95 (C-1,10), 126.64 (C-12,14), 124.64 (C-4,6), 120.02 (C-16), 115.92 (CN), 34.45 (-<u>C</u>(CH$_3$)$_3$), 31.51 (-C(<u>C</u>H$_3$)$_3$), 19.84 (C-18); IR ν (KBr) 3048, 3009, 2964, 2904, 2867, 2215, 1571, 1476, 1443, 1217, 1154, 873, 843, 808, 768, 679, 660, 583, 556, 490 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 225 (31100), 287 (12440), 337 (14970), 375 (6800); EI MS *m/z* 299 ($M^+$); HR MS Calcd for $C_{22}H_{21}N$: 299.1674. Found: 299.1669; Anal. Calcd: C, 88.25; H, 7.07; N, 4.68. Found: C, 86.79; H, 6.96; N, 4.34.

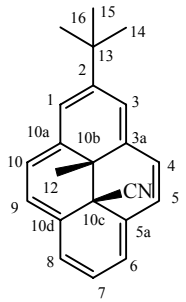
**2-(*tert*-Butyl)-10c-cyano-10b-methyl-*trans*-10b,10c-dihydropyrene 128**




**128**

Irradiation of an NMR sample of cyclophanediene **127** in benzene with a UV source with output 254 nm quickly converts **127** in to **128** in ~ 75% yield as a dark green solid: $^{1}$H NMR ($CDCl_3$) δ 8.56 (s, 2H, H-1,3), 8.42 (AB, *J* = 7.9 Hz, 4H, H-4,5,9,10), 8.30 (d, *J* = 7.8 Hz, 2H, H-6,8), 7.75 (t, *J* = 7.8 Hz, H-7), 1.49 (s, 9H, -C(C$\underline{H}_3)_3$, $^{t}$-Bu), -3.97 (s, 3H, Me); $^{13}$C NMR ($CDCl_3$) δ 150.01 (C-2), 140.02 (C-10a,3a), 126.26 (C-5,9), 125.66 (C-5a,10d), 124.72 (C-6,8), 124.52 (C-4,10), 122.80 (C-7), 122.45 (C-1,3), 112.74 (CN), 36.56 (-$\underline{C}(CH_3)_3$), 33.20 (C-10c), 32.00 (-C($\underline{C}H_3)_3$), 30.2 (C-10b), 12.03 (C-12); IR ν (thin film) 3040, 2964, 2867, 2217, 1601, 1576, 1478, 1463, 1231, 965, 878, 843, 825, 757, 736, 716 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 203 (50300), 274 (7500), 339 (43600), 377 (5600), 463 (3340), 533 (40), 575 (105), 600 (50).

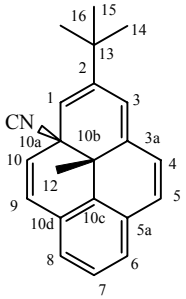
**2-(*tert*-Butyl)-10c-cyano-10b-methyl-*cis*-10b,10c-dihydropyrene 136**




**136**

When the sulfonium salt mixture (obtained from the cyclophanes **133** and **134**) was employed in the Hoffmann elimination, it gave 60% yield of the *cis*-DHP **136**. The product was purified by column chromatography using hexanes-$CH_2Cl_2$ 55: 45 as dark green crystals from benzene: mp 108-109 $^oC$; $^1H$ NMR ($CDCl_3$) δ 8.86 & 8.78 (AB, *J* = 8.4 Hz, 4H, H-4,5,9,10), 8.50 (d, *J* = 7.8 Hz, 2H, H-6,8), 8.42 (s, 2H, H-1,3), 7.88 (t, *J* = 7.8 Hz, 1H, H-7), 1.62 (s , 9H, -C(C$\underline{H}_3)_3$), -1.60 (s, 3H, Me); $^{13}C$ NMR ($CDCl_3$) δ 145.10 (C-2), 139.32 (3a,10a), 129.64 (C-5,9), 128.08 (C-4,10), 125.09 (C-6,8), 122.87 (C-5a,10d), 121.39 (C-1,3), 121.25 (C-7), 115.82 (CN), 37.77 (C-12), 35.74 (-$\underline{C}(CH_3)_3$), 35.18 (C-10c), 31.87 (-C($\underline{C}H_3)_3$), 30.95 (C-10b); IR ν (KBr) 2960, 2865, 2214, 1235, 818 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 245 (4250), 275 (2710), 334 (85800), 340 (49300), 361 (41300), 404 (3890), 447 (10670), 515 (80), 556 (160), 614 (264); EI MS *m/z* 299 ($M^+$) HR MS Calcd for $C_{22}H_{21}N$: 299.1674. Found: 299.1670; Anal. Calcd: C, 88.25; H, 7.07; N, 4.68. Found: C, 85.41; H, 7.00; N, 4.44.

**2-(*tert*-Butyl)-10a-cyano-10b-methyl-*trans*-10a,10b-dihydropyrene 137**



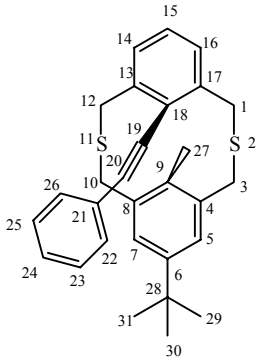

**137**

Cyclophanediene **127** (10 mg) was sealed in a glass tube under argon and heated at 70 $^oC$ for 3 hours (or until completely colorless), which quantitatively converted it into colorless crystals of **137**; evaporation gave crystals: mp 82-84 $^oC$; $^1H$ NMR ($CDCl_3$) δ 7.18 (dd, *J* = 7.6, 1H, H-7), 7.04 (m, 2H, H-6,8), 6.72 (d, *J* = 9.1, 1H, H-9), 6.50 & 6.34

(AB, $J$ = 9.5, 1H , H-4,5), 6.13 (s, 1H, H-3), 5.99 (d, $J$ = 9.1 Hz, 1H, H-10), 5.53 (s, 1H, H-1), 1.157 (s, 3H, Me), 1.153 (s, 9H, -C(C<u>H</u>$_3$)$_3$); $^{13}$C NMR ($CDCl_3$) δ 150.61 (C-2), 143.22 (C-3a), 136.17 (C-10c), 131.67 (C-5a), 130.86 (C-10d), 128.98 (C-5), 127.75 (C-7), 127.39 (C-6), 126.83 (C-8), 126.57 (C-4), 125.65 (C-10), 121.52 (CN), 121.48 (C-3), 113.74 (C-1), 43.17 (C-10b), 40.84 (C-10a), 34.69 (-<u>C</u>(CH$_3$)$_3$), 28.88 (-C(<u>C</u>H$_3$)$_3$), 17.44 (C-12); IR ν (KBr) 3038, 2961, 2904, 2867, 2217, 1625, 1577, 1477, 1465, 1367, 1210, 966, 865, 825, 813, 756, 746, 661 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 259 nm (12200), 273 (8870), 289 (4380), 301 (4520), 315 (3870), 339 (3660), 353 (3750); EI MS *m/z* 299 ($M^+$) HR MS Calcd for $C_{22}H_{21}N$: 299.1674. Found: 299.1674; Anal. Calcd: C, 88.25; H, 7.07; N, 4.68. Found: C, 84.13; H, 6.84; N, 4.32.

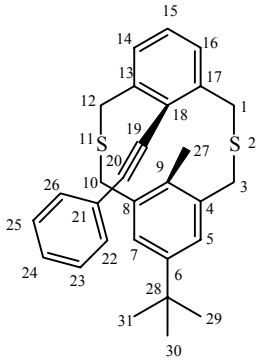
**6-(*tert*-Butyl)-9-methyl-18-phenylethynyl-2,11-dithia[3.3]metacyclophanes 142 and 145**

A solution of bis-bromomethyl-2-phenylethynylbenzene (3.9 g, 10.7 mmol) and 2,6 bis-thiomethyl-4-*tert*-butyltoluene (2.57 g, 10.7 mmol) in deaerated benzene (500 ml) was added drop wise to ethanolic KOH solution {prepare by adding KOH (3.4 g) in deaerated water (160 mL) and ethanol (1470 mL) followed by addition of sodium borohydride (0.64 g)}. Drop rate was very crucial, optimum result were obtained with a drop per 5-6 second and this addition took 56 hours. The solvent was then evaporated and the residue was dissolved in DCM and extracted with water, dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel using $CH_2Cl_2$-hexanes 1.5: 8.5 as eluant.



**142**

Eluted first was 700 mg (1.58 mmol, 15%) of *anti* **142** as colorless crystals from cyclohexane: mp 148-149 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 7.43 (m, 2H, H-22, 26), 7.40 (d, *J* = 7.6 Hz, 2H, H-14,16), 7.33-7.31 (m, 3H, H-23,24,25), 7.27 (s, 2H, H-5,7), 7.22 (t, *J* = 7.6 Hz, 1H, H-15), 4.16 and 3.72 (AB, *J* = 14.1 Hz, 4H, H-1, 12), 3.76 (AB, *J* = 13.9 Hz, 4H, H-3,10), 1.42 (s, 3H, Me), 0.98 (s, 9H, -C(C$\underline{H}_3)_3$.); $^{13}$C NMR ($CDCl_3$) δ 148.26 (C-6), 139.26 (C-13,17), 135.90 (C-9), 134.14 (C-4,8), 131.64 (C-22,26), 129.07 (C-14,16), 128.51 (C-23,25), 128.45 (C-24), 127.84 (C-15), 127.32 (C-5,7), 125.74 (C-18), 123.97 (C-21), 100.19 (C-20), 86.19 (C-19), 34.08 (-$\underline{C}(CH_3)_3$), 32.4 (C-3,10), 32.13 (C-1,12), 31.08(-C($\underline{C}H_3)_3$), 15.27 (C-27); IR ν (KBr) 3057, 2959, 2904, 2862, 1594, 1477, 1488,1440, 756. 7477, 691 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 288 (10100) 303 (11700), 318 (11900); EI MS *m/z* 442 ($M^+$); HR MS calculated for $C_{29}H_{30}S_2$: 442.1788. Found: 442.1779; Anal. Calcd: C, 78.68; H, 6.83. Found: C, 75.81; H, 7.0.

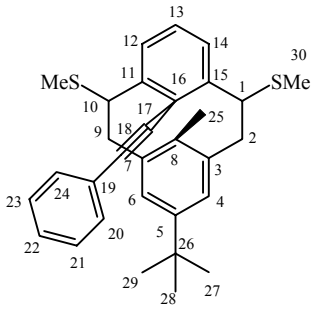


**145**

Eluted second was 2.2 g (4.77 mmol, 47%) of *syn*-**145** as colorless crystals from cyclohexane, mp 170-171 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 7.62 (dd, *J* = 7.8, 1.8 Hz, 2H, H-22,26), 7.40-7.44 (m, 3H, H-23,24,25), 7.02 (d, *J* = 7.6, 2H, H-14,16), 7.01 (s, 2H, H-5,7), 6.86 (t, *J* = 7.6 Hz, 1H, H-15), 4.65 and 3.67 (AB, *J* = 14.8 Hz, 4H, H-1,12), 4.41 and 3.62 (AB, *J* = 14.8 Hz, 4H, H-3,10), 2.54 (s, 3H, Me) 1.22 (s, 9H, -C(C$\underline{H}_3$)$_3$); $^{13}$C NMR ($CDCl_3$) δ 147.15 (C-6), 140.41 (C-13,17), 136.01 (C-4,8), 132.15 (C-9), 131.41 (C-22,26), 129.01 (C-15), 128.84 (C-23,25), 128.75 (C-24), 128.04 (C-14,16), 126.02 (C-5,7), 123.56 (C-21), 121.65 (C-18), 99.15 (C-20), 87.83 (C-19), 35.75 (C-1,12), 34.74 (C-3,10), 34.34 (-$\underline{C}$(CH$_3$)$_3$), 31.29 (-C($\underline{C}$H$_3$)$_3$), 17.15 (C-27); IR ν (thin film, KBr) 3057, 2961, 2906, 2864, 1596, 1489, 1478, 1461, 1361, 1261, 872, 792, 755, 748, 691 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 258 (16100), 297 (13600), 319 (11000); EI MS *m/z* 442 ($M^+$); HR MS Calcd for $C_{29}H_{30}S_2$: 442.1788. Found: 442.1786; Anal. Calcd: C, 78.68; H, 6.83. Found: C, 77.71; H, 6.54.

**1,10-Bis(thiomethyl)- 5-$^{t}$butyl-8-methyl-16-phenylethynyl-*anti*-[2,2]metacyclophane 146**

BuLi (2.5 mmol) was added dropwise to a solution of mixed thiacyclophanes **142** and **145** (300 mg, 0.68 mmol) in dry THF (30 mL) at 0 $^{o}$C. The solution was allowed to warm up to room temperature over 10 minutes where dark purple solution turned pale yellow. MeI (0.4 mL, mmol) was added and allowed to stir for another 10 minutes. The reaction was quenched using water (5 mL) and then extracted with dichloromethane (3 x 25 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated. The residue was chromatographed over silica gel using $CH_2Cl_2$-hexanes (12:88) as eluant to afford 290 mg (80%) of **146** as a mixture of isomers. Re-chromatography yielded 150 mg of a single isomer of **146** in which the 1,10 thiomethyl groups are pseudo-equatorial.




**146**

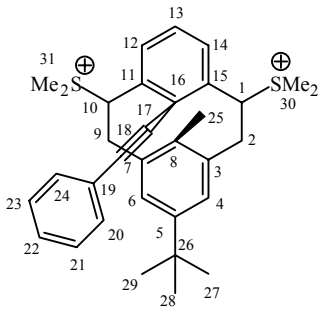
mp 203-204 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H, H-12,14), 7.28 (tt, *J* = 6.4, 1.5 Hz, 1H, H-22), 7.27-7.17 (m, 4H, H-20,21,23,24), 7.21 (t, *J* = 7.6 Hz, 1H, H-13), 7.14 (s, 2H, H-4,6), 4.45 (dd, *J* = 11.4, 4.1 Hz, 2H, H-$1_{ax}$,$10_{ax}$), 3.24 (dd, *J* = 12.4, 4.1 Hz, 2H, H-$2_{eq}$,$9_{eq}$), 2.74 (dd, *J* = 12.2, 11.6 Hz, 2H, H-$2_{ax}$,$9_{ax}$), 2.18 (s, 6H, S-Me), 0.91 (s, 9H, -C(C$\underline{H}_3$)$_3$), 0.63 (s, 3H, Me); $^{13}$C NMR ( $CDCl_3$) δ 148.44 (C-5), 140.02 (C-8), 138.83 (C-11,15), 135.19 (C-3,7), 131.66 (C-13), 130.21 (C-16), 128.31 (C-22), 127.29, 128.48 (C-20,21,23,24), 125.78 (C-12,14), 125.15 (C-4,6), 123.63 (C-19), 92.78

(C-18), 86.17 (C-17), 54.63 (C-1,10), 43.50 (C-2,9), 34.05 (-$\underline{C}(CH_3)_3$), 31.23 (-C($\underline{C}H_3)_3$), 15.89 (C-30,31), 14.93 (C-25); IR (thin film, KBr) 3044, 2952, 2913, 1596, 1490, 1425, 754, 745, 690 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 280 (13000), 293 (13500), 320 (12600); EI MS *m/z* 470 ($M^+$); HR MS Calcd for $C_{31}H_{34}S_2$: 470.2102. Found: 470.2104. Anal. Calcd: C, 79.09; H, 7.28. Found: C, 79.35; H, 7.01.

A mixture of *syn*- and *anti* isomers showed following NMR data:

$^1$H NMR ($CDCl_3$) δ 7.8 (d, *J* = 7.6 Hz), 7.7 (br s), 7.6-7.5 (m), 7.4-7.2 (m), 7.1-7.0 (m), 6.91 (d, *J* = 7.5 Hz), 6.8 (t, *J* = 7.6 Hz), 6.6 (t, *J* = 7.6 Hz), 6.4 (d, *J* = 7.3 Hz), 6.3, 6.2 (br s), 6.35 (s), 5.4 (m), 5.23 (t, *J* = 8.7 Hz), 5.15 (t, *J* = 8.4 Hz), 4.8 (d, *J* = 14.1 Hz), 4.44 (dd, *J* = 11.3, 4.1 Hz), 4.35 (d, *J* = 15.0 Hz), 4.1-3.9 (m), 3.7 (t, *J* = 13.4 Hz), 3.3 (m), 3.1 (t, *J* = 11.7 Hz), 2.7 (t, *J* = 11.6 Hz), 2.5 (s), 2.2 (four singlets), 1.17 (s), 1.12 (s), 0.92 (s), 0.64 ( s).

**1, 10-Bis(thiomethyl)-8-methyl-16-phenylethynyl-*anti*-[2.2]metacyclophane bis-sulfonium salt 147**



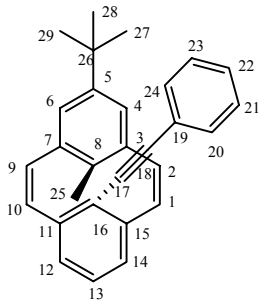

**147**

Using procedure 7.3, the pure 1,10-diequatorial-thiomethyl isomer of **146** (1 g, 2.12 mmol) on reaction with Borch reagent (1 g, 4.8 mmol) in $CH_2Cl_2$ (7 mL) gave the product as a single isomer (1.4g, quantitative): $^1$H NMR (DMSO-$d_6$) δ 7.87 (d, *J* = 7.8 Hz, 2H, H-12,14), 7.58 (dd *J* = 7.8, 2.3 Hz, 2H, H-20,24), 7.47 (t, *J* = 7.76 Hz, 1H, H-

13), 7.41 (m, 3H, H-21-23), 7.35 (s, 2H, H-4,6), 4.66 (dd, *J* = 12.0, 4.2 Hz, 2H, H-$1_{ax}$,$10_{ax}$), 3.60 (dd, *J* = 12, 4.2 Hz, 2H, H-$2_{eq}$,$9_{eq}$), 3.46 (s, 6H, S-$Me_2$), 3.17 (triplet, *J* = 12 Hz, 2H, H-$2_{ax}$,$9_{ax}$), 3.04 (s, 6H, S-$Me_2$), 0.89 (s, 9H, -C(C$\underline{H}_3$)$_3$), 0.75 (s, 3H, Me).

When the mixture of cyclophane isomers **146** were used in the *S*-methylation, following NMR data was obtained: $^1$H NMR (DMSO-$d_6$) δ 7.88-7.34 (m), 7.0-6.8 (m), 6.6 (br s), 5.83-5.55 (m), 4.8-4.6 (m), 4.04-3.00 (m), 2.26, 1.98 (s), 1.18, 0.78 (9 singlets).

**5-(*tert*-Butyl)-8-methyl-16-phenylethynyl-*anti*-[2.2]metacyclophane-1,9-diene 138**



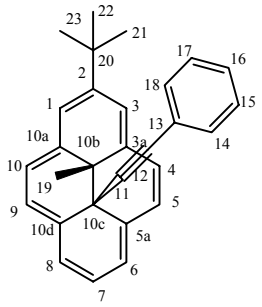

**138**

Using procedure 7.4, a reaction of sulfonium salt **147** (300 mg, 0.45 mmol) and *t*-BuOK (120 mg, 1.07 mmol) in THF (10 mL) followed by chromatography over silica gel in a jacketed column using hexanes: $CH_2Cl_2$ (80: 20) as eluant gave **138** (quantitative) as colorless crystals, which on attempted mp determination converts into DHP **139**: $^1$H NMR ($C_6D_6$) δ 7.28 (dd, *J* = 7.1, 1.5 Hz, 2H, H-20,24), 6.92-6.98 (m, 3H, H-21-23), 6.86 (t, *J* = 7.4 Hz, 1H, H-13), 6.73 (s, 2H, H-4,6), 6.54 (d *J* = 7.4 Hz, 2H, H-12,14), 6.42 and 6.23 (AB, *J* = 11.3 Hz, 2H, H-1,2,9,10), 1.83 (s, 3H, Me), 0.93 (s, 9H, -C(C$\underline{H}_3$)$_3$); $^{13}$C NMR ($C_6D_6$) δ 150.90 (C-5)**,** 142.47 (C-8), 141.15 (C-11,15), 138.11 (C-3,7), 135.40 (C-2,9), 132.30 (C-20,24), 131.99 (C-1,10), 131.13 (C-16), 129.79 (C-13), 128.68 (C-21,23), 128.12 (C-22), 126.32 (C-12,14), 125.47 (C-19), 123.68 (C-4,6), 95.85 (C-18), 91.03 (C-17), 34.19 (-$\underline{C}$(CH$_3$)$_3$), 31.72 (-C($\underline{C}$H$_3$)$_3$), 20.76 (C-25); IR ν (thin film) 3041, 3004, 2867,

2962, 1597, 1491, 1442, 871, 772, 757, 737, 690, 673 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 288 nm (13500), 339 (15000), 377 (6700);

$^1$H NMR ($CDCl_3$) δ 7.25-7.23 (m, 5H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.4 Hz, 2H), 6.58 (s, 2H), 6.49 (d, *J* = 11.3 Hz, 2H), 6.36 (d *J* = 11.3 Hz, 2H), 1.65 (s, 3H, Me), 0.80 (s, 9H, $C(C\underline{H}_3)_3$, $^{t}$-Bu); $^{13}$C NMR ($CDCl_3$) δ 150.58, 141.70, 137.42, 131.34, 130.23, 129.39, 128.26, 127.80, 125.90, 124.61, 123.07, 95.13 (sp), 89.98 (sp), 33.03 (C-26), 30.67 (-$C(C\underline{H}_3)_3$) 20.22 (Me).

**2-(*tert*-Butyl)-10b-methyl-10c-phenylethynyl-*trans*-10b,10c-dihydropyrene 139**

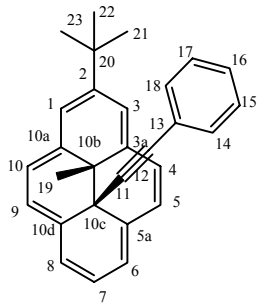



**139**

*t*-BuOK (140 mg, 1.2 mmol) was added to a stirred suspension of mixed isomers of bis-sulfonium salt **147** (350 mg, 0.52 mmol), in THF (10 mL) under argon at 20 $^{o}$C. After refluxing for 6 h, water was added and then dichloromethane (90 mL). The extract was washed, dried over $MgSO_4$ and evaporated. The residue was chromatographed over silica gel using hexanes: $CH_2Cl_2$ (85:15) as eluant to give 160 mg (85%) of the dihydropyrene **139** as green crystals from methanol: mp 112-113 $^{o}$C; $^1$H NMR ($CDCl_3$) δ 8.72 and 8.65 (AB, *J* = 7.8 Hz, 2H, H-4,5,9,10), 8.69 (s , 2H, H-1,3), 8.62 (d, *J* = 7.8 Hz, 2H, H-6,8), 8.07 (t, *J* = 7.8 Hz, 1H, H-7), 6.83 (tt, *J* = 7.8, 1.8 Hz, 1H, H-16), 6.72 (dd, *J* = 7.8, 7.5 Hz, 2H, H-15,17), 6.04 (dd, *J* = 7.4, 1.8 Hz, 2H, H-14,18), 1.74 (s, 9H, -

C(C<u>H</u>$_3$)$_3$), -4.00 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) δ 148.15 (C-2), 139.95 (C-3a,10a), 131.08 (C-14,18), 130.06 (C-5a,10d), 127.39 (C-15,17), 125.11 (C-5,9), 126.99 (C-16), 123.46 (C-4,10), 123.33 (C-6,8), 122.49 (C-13), 121.95 (C-7), 121.30 (C-1,3), 84.61 (C-12) 75.41 (C-11), 36.41 (-<u>C</u>(CH$_3$)$_3$), 32.13 (-C(<u>C</u>H$_3$)$_3$), 31.18 (C-10b), 30.48 (C-10c), 12.86 (C-19); IR ν ( thin film) 3036, 2963, 1597, 1489, 1478, 1442, 1230, 874, 822, 755, 737, 691, 682, 628 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 250 (41200), 339 (1.64x10$^5$), 377 (73200), 467 (14900), 577 (380), 639 (300); EI MS 374 ($M^+$); HR MS Calcd for $C_{29}H_{26}$: 374.2034. Found: 374.2036. Anal. Calcd: C, 93; H, 7. Found: C, 91.47; H, 7.21.

**2-(*tert*-Butyl)-10b-methyl-10c-phenylethynyl- *cis*-10b,10c-dihydropyrene 148**

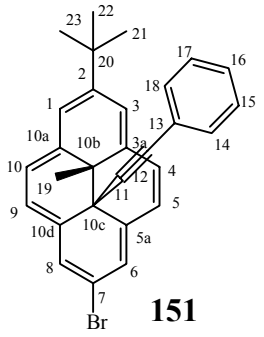



**148**

Mixed isomers of sulfonium salts (**147**) in the Hoffmann elimination (procedure and quantities same as for **139**) gave an 8% yield of the *cis*-DHP **148**. The product was purified by column chromatography using hexane-DCM 8: 2 to give dark green crystals from isopropanol: mp 159-160 $^o$C; $^1$H NMR ($CDCl_3$) δ 8.85-8.78 (AB, *J* = 8.3, 2H, H-4,5,9,10), 8.40 (d, *J* = 7.6, 2H, H-6,8), 8.39 (s, 2H, H-1,3), 7.75 (t, *J* = 7.6 Hz, 1H, H-7), 7.01-6.97 (m, 3H, H-15-17), 6.67 (dd, *J* = 7.2, 1.2 Hz, 2H, H-14,18), 1.65 (s, 9H, -C(C<u>H</u>$_3$)$_3$), -1.55 (s, 3H, Me); $^{13}$C NMR ($CDCl_3$) δ 143.61 (C-2), 139.38 (C-10a,3a), 131.10 (C-14,18), 129.50 (C-5a,10d), 129.14 (C-5,9), 127.84 (C-15,17), 127.82 (C-4,10),

127.33 (C-16), 124.08 (C-6,8), 123.27 (C-13), 120.67 (C-1,3), 112.14 (C-7), 89.61 (C-11), 77.38 (C-12), 36.25 (C-19), 35.51 (-$\underline{C}(CH_3)_3$), 32.90 (C-10c), 32.03 (C-10b), 31.99 (-C($\underline{C}H_3)_3$); IR ν (KBr) 3022, 2973, 2863, 1594, 1486, 1438, 1234, 874, 867, 822, 755, 690, 647, 632 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 342 (5.07 x $10^4$), 364 (38200), 428 (6755) 447 (13200), 591 (130), 614 nm (160); EI MS *m/z* 374 ($M^+$); HR MS Calcd for $C_{29}H_{26}$: 374.2034. Found: 374.2033. Anal. Calcd: C, 93; H, 7. Found: C, 90.27; H, 7.05.

**7-Bromo-2-(*tert*-butyl)-10b-methyl-10c-(2-phenylethynyl)-*trans*-10b,10c-dihydropyrene 151**

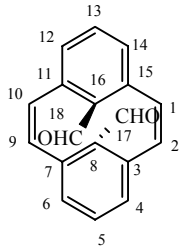



**151**

NBS (24 mg, 0.135 mmol) in DMF (4 mL) was added drop wise to a solution of DHP **139** (50 mg, 0.134 mmol) in $CH_2Cl_2$ (20 mL) at 0 $^oC$ and stirred at room temperature for one hour. Reaction mixture was poured into hexanes (200 mL) in a separatory funnel and washed with 4x50 ml of water. The organic green layer was dried over $MgSO_4$ and evaporated. Column chromatography over silica using $CH_2Cl_2$: hexanes (15: 85) as eluant gave the bromo DHP **151** (40 mg, 0.09 mmol, 66%) as green crystals from cyclohexane: mp 120-121 $^oC$; $^1H$ NMR ($CDCl_3$) δ 8.72 (s, 2H, H-6,8), 8.67 (s, 2H, H-1,3), 8.62 (s, 4H, H-4,5,9,10), 6.84 (tt, *J* = 7.5, 1.5 Hz, 1H, H-16), 6.74 (dd, *J* = 7.8, 7.5 Hz, 2H, H-15,17), 6.06 (dd, *J* = 7.8, 1.5 Hz, 2H, H-14,18), 1.72 (s, 9H, -C(C$\underline{H}_3)_3$), -3.95 (s, 3H, Me); $^{13}C$ NMR ($CDCl_3$) δ 148.74 (C-2). 139.99 (C-3a,10a), 131.09 (C-14,18),

130.12 (C-5a,10d), 127.47 (C-15,17), 127.24 (C-16), 125.53 (C-6,8), 124.63 (C-4,10), 124.31 (C-5,9), 122.45 (C-1,3), 122.18 (C-13), 116.72 (C-7), 75.49, 83.70 (C-11,12), 36.49 (-$\underline{C}(CH_3)_3$), 32.01 (-C($\underline{C}H_3)_3$), 31.48 (C-10b), 29.38 (C-10c), 12.84 (C-19); IR ν (thin film) 3043, 2963, 1596,1489, 1462, 1230, 879, 827, 755, 738, 691, 682 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 343 (24030), 379 (33970), 475 (10360), 581 (290), 640 (340); EI MS *m/z* 452 ($M^+$); HR MS Calcd for $C_{29}H_{25}Br$: 452.1139. Found: 452.1130. Calcd. Anal: C, 76.82; H, 5.55. Found: C, 77.35; H, 5.80.

**8,16-Diformyl-*anti*-[2.2]metacyclophane-1,9-diene 152**

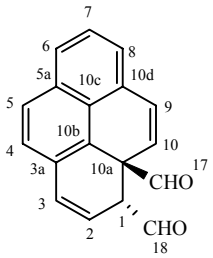



**152**

DIBAL (2.5 mmol, 2.5 ml of 1 M solution in cyclohexane) was added dropwise to a solution of dicyano CPD **85** (250 mg, 1 mmol) in dry dichloromethane (12 mL) at room temperature, over a period of 6 minutes. It was stirred for 5 h at room temperature, after which it was slowly added to methanol (5 mL) and stirred for half an hour. Then HCl (10 mL, 1M) was added carefully and the resulting solution was extracted with dichloromethane (3 x 30 mL). The organic layer was dried over anhydrous $MgSO_4$, evaporated and column chromatographed over silica using ethyl acetate: DCM (1:9) as eluant to yield 8,16-diformylcyclophanediene **152** (146 mg, 56%) as colorless crystals from methanol, which on attempted mp determination converts into migration products **155**: $^1$H NMR ($CDCl_3$) δ 9.35 (s, 2H, H-17,18), 7.39 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.85 (d,

*J* = 7.4 Hz, 4H, H-4,6,12,14), 6.73 (s, 4H, H-1,2,9,10); $^{13}$C NMR ($CDCl_3$) δ 185.77 (C-17,18), 145.41(C-8,16), 140.03 (C-3,7,11,15), 135.35 (C-1,2,9,10), 135.29 (C-5,13), 128.84 (C-4,6,12,14); IR ν (KBr) 3056, 3011, 2924, 2869, 2768, 1712, 1683, 1559, 1445, 1222, 1181, 816, 761, 628 $cm^{-1}$; UV (dichloromethane), $\lambda_{max}$ nm ($\varepsilon_{max}$) 245 nm (8500), 274 (8600), 338 (4150), 345 (4130), 395 sh (1500); EI MS *m/z* 260 ($M^+$).

**1,10a-Diformyl-*trans*-1,10a-dihydropyrene 155**



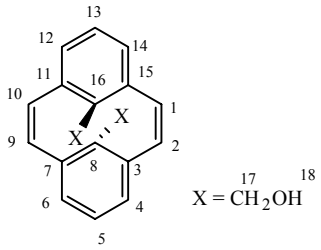

**155**

Cyclophanediene **152** (10 mg) in $CDCl_3$ (1 mL) was sealed in a glass tube under argon and heated at 70 $^oC$ for 1 h, which converted it into **155**. Evaporation gave colorless solid which decomposed on attempted chromatography but was pure enough to obtain the following data:

$^1$H NMR ($CDCl_3$) δ 9.71 (d, *J* = 3.4 Hz, 1H, H-18), 9.34 (s, 1H, H-17), 7.69 (d, *J* = 8.3 Hz, 1H, H-5), 7.61 (d, *J* = 8.4 Hz, 1H, H-6), 7.32 (dd, *J* = 6.9, 8.4 Hz, 1H, H-7), 7.28 (d, *J* = 8.3 Hz, 1H, H-4), 7.11 (d, *J* = 6.8 Hz, 1H, H-8), 6.9 (d, *J* = 9.6 Hz, 1H, H-9), 6.7 (d, *J* = 9.9 Hz, 1H, H-3), 5.91 (dd, *J* = 9.6, 6.2 Hz, 1H, H-2), 5.68 (d, *J* = 9.6 Hz, 1H, H-10), 3.76 (dd, *J* = 6.3, 3.5 Hz, 1H, H-1); $^{13}$C NMR ($CDCl_3$) δ 198.74 (C-18), 190.97(C-17), 133.50 (C-5a), 132.94 (C-9), 131.29 (C-3), 131.16 (C-3a), 130.45 (C-10d), 128.62 (C-6), 128.41 (C-10c), 128.23 (C-5), 127.14 (C-7), 126.10 (C-4), 125.59 (C-10b), 125.25 (C-8), 122.71 (C-10), 122.02 (C-2), 55.93 (C-10a), 51.08 (C-1); IR ν (thin film) 3048, 2927,

2820, 2721, 1719, 1685, 1590, 1569, 1502, 1174, 842, 770, 734 $cm^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 208 (850) , 243 (13500), 274 (24600), 322 (3600), 322 (3600), 338 ( 4100), 402 (2130 ), 470 *sh* (460); EI MS *m/z* 260 ($M^+$)

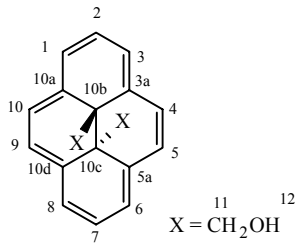
**8,16-Bis(hydroxymethyl)-*anti*-[2.2]metacyclophane-1,9-diene 159**




**159**

$NaBH_4$ (9 mg, 0.236 mmol) was added to a solution of diformylcyclophanediene **152** (18 mg, 0.0692 mmol) in methanol (4 mL) at room temperature under argon and stirred for five minutes, then quenched with HCl (0.5 mL of 1M solution). The resulting solution was extracted between dichloromethane and water. The organic layer was dried over $MgSO_4$ and evaporated in cold to give 17 mg (0.0644 mmol, 93%) of **159** as colorless solid, which on attempted mp determination converts into DHP **160** and pyrene **112**: $^1$H NMR ($CDCl_3$) δ 7.21 (t, *J* = 7.4 Hz, H-5,13), the OH protons are not located, 6.80 (d, *J* = 7.4 Hz, H-4,6,12,14), 6.48 (s, 4H, H-1,2,9,10), 3.80 (s, 2H, H-17,19); $^{13}$C NMR ($CDCl_3$) δ 148.2 (C-8,16), 136.7 (C-3,7,11,15), 133.43 (C-1,2,9,10), 130.00 (C-5,13), 127.33 (C-4,6,12,14), 62.73 (C-17,19); IR ν (thin film) 3049, 2921, 1653, 1438, 1265, 997, 772, 735 $cm^{-1}$; UV (dichloromethane) $\lambda_{max}$ ($\varepsilon_{max}$) 236 (11400), 276 (8500) EI MS 202 ($M^+$- $C_2H_6O_2$).

**10b,10c-Bis(hydroxymethyl)-*trans*-10b,10c-dihydropyrene 160**




**160**

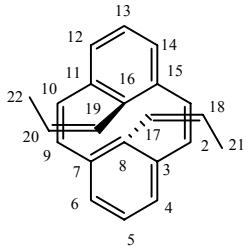
An NMR sample of cyclophanediene **159** was held at room temperature which converted it into dihydropyrene **160** in ~ 80% yield. If the sample was held for longer time, the dihydropyrene gradually decomposed into pyrene **112**: $^{1}$H NMR ($CDCl_3$) δ 8.80 (s, 4H, H-4,5,9,10), 8.74 (d, *J* = 7.5 Hz, 4H, H-1,3,6,8), 8.07 (t, *J* = 7.6 Hz, 2H, H-2,7), -1.77 (d, *J* = 7.1 Hz , 4H, 11, 13), -2.1 (t, *J* = 7.1 Hz, 2H, H-12,14); $^{13}$C NMR ($CDCl_3$) δ 132.59 (C-3a,5a,10a,10d), 125.90 (C-1,3,6,8), 125.31 (C-4,5,9,10), 124.07 (C-2,7), 61.25 (C-11,13), 34.01 (C-10b,10c); IR ν (thin film) 3048, 2924, 1338, 1261, 852, 630 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 243 (8000), 388 (4200), 482 (950), 636 (40).

**8,16-Bis(prop-1-enyl)-*anti*-[2.2]metacyclophane-1,9-dienes 162 and 163**

BuLi (0.35 mL of 2.5M in hexanes, 0.9 mmol) was added dropwise to a suspension of ethyltriphenylphosphonium bromide (240 mg, 0.65 mmol) in THF (5 mL) under argon at 0 $^{o}$C and the mixture was stirred for 20 minutes. After that time, clear and orange to red solution was obtained. At -30 $^{o}$C, diformylcyclophanediene **152** (70 mg, 0.269 mmol) was added and the reaction mixture was allowed to warm to room temperature over 30 minutes and then quenched with water. The resulting solution was extracted with $CH_2Cl_2$ (4 x 20 mL), dried over anhydrous $MgSO_4$ and evaporated. The crude mixture was chromatographed over silica gel. Hexanes eluted firstly pyrene **112**

and then 8,16-dipropenyl cyclophanedienes as a mixture of **162** and **163** (40 mg, 0.14 mmol, 52%).

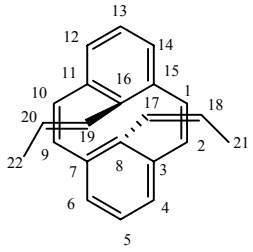
**8,16-Bis((1*Z*)-Prop-1-enyl)-*anti*-[2.2]metacyclophane-1,9-diene 162 (major isomer)**




**162**

The melting point could not be determined because the sample was a mixture of isomers. $^{1}$H NMR ($CDCl_3$) δ 6.94 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.46 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.12 (qd, *J* = 12.0, 1.8 Hz, 2H, H-17,19), 6.09 (s, 4H, H-1,2,9,10), 5.23 (qd, *J* = 12.0, 7.2 Hz, 2H, H-18,20), 1.55 (dd, *J* = 7.3, 1.8 Hz , 6H, H-21,22); $^{13}$C NMR ($CDCl_3$) δ 142.31 (C-8,16), 136.88 (C-3,7,11,15), 131.98 (C-1,2,9,10), 129.37 (C-17,19), 128.20 (C-5,13), 125.98 (C-18,20), 125.45 (C-4,6,12,14), 15.35 (C-21,22); IR ν (thin film) 3036, 3001, 2930, 2848, 1599, 1561, 1434, 962, 929, 858, 842, 771, 711, 665 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 215 (25000), 243 (26200), 277 (11500), 340 (~ 2500); EI MS *m/z* 284 ($M^+$); HR MS Calcd for $C_{22}H_{20}$: 284.1565. Found: 284.1562.

**16-((1*E*)-Prop-1-enyl)-8-((1*Z*)prop-1-enyl)-*anti*-[2.2]metacyclophane-1,9-diene 163 (minor isomer)**




**163**

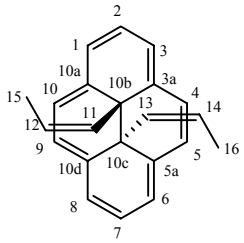
The melting point could not be determined because the sample was a mixture of isomers. $^{1}$H NMR ($CDCl_3$) 6.98 (t, *J* = 7.4 Hz, 1H, H-13), 6.86 (t, *J* = 7.4 Hz, 1H, H-5), 6.44 (d, *J* = 7.4 Hz, 2H, H-12,14), 6.42 (d, *J* = 7.4 Hz, 2H, H-4,6), 6.11(AB*, 4H, H-1,2,9,10), 5.94 (dq, *J* = 15.4, 6.7 Hz, H-20), 1.57 (dd, *J* = 1.9 Hz, *J* = 6.6 Hz, 3H, H-21), 1.52 (dd, *J* = 6.6, 1.6 Hz, 3H, H-22) H-17-19*; $^{13}$C- NMR ($CDCl_3$) δ 145.92 (C-8), 141.30 (C-16), 137.40 (C-11,15), 135.10 (C-3,7), 132.56 (C-2,9), 131.80 (C-17), 130.80 (C-19), 129.77 (C-20), 128.49 (C-13), 127.76 (C-5), 126.16 (C-4,6), 125.35 (C-12,14), 18.23 (C-22), 15.32 (C-21), C-1,10,18*

*Indicates when peaks are not distinct (overlapped by the major isomer)

**Closed isomers**

Using procedure 7.5, a mixture of cyclophanedienes **162** and **163** (10 mg) was converted into a mixture of dihydropyrenes **164** and **165**.

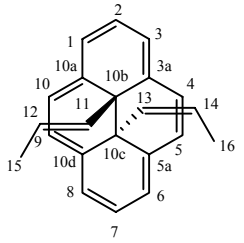
**10b,10c-Bis((1*Z*)prop-1-enyl)-*trans*-10b,10c-dihydropyrene 164 (major isomer)**




**164**

The melting point could not be determined because the sample was a mixture of isomers. $^{1}$H NMR ($CDCl_3$) δ 8.64 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 8.63 (s, 4H, H-4,5,9,10), 8.05 (t, *J* = 7.6 Hz, 2H, H-2,7), 3.21 (qd, *J* = 12.4, 7.3 Hz, 2H, H-12, 14), 0.33 (dd, *J* = 7.3, 1.8 Hz, 6H, H-15,16), 0.09 (qd, *J* = 12.4, 1.8 Hz, 2H, H-11,13); $^{13}$C- NMR ($CDCl_3$) δ 135.27 (C-3a,5a,10a,10d), 126.07 (C-4,5,9,10), 125.35 (C-1,3,6,8), 123.61 (C-12,14), 123.59 (C-2,7), 121.87 (C-11,13), 11.45 (C-15,16); EI MS *m/z* 284 ($M^+$). HR MS Calcd for $C_{22}H_{20}$: 284.1565. Found: 284.1557.

**10b-((1*E*)prop-1-enyl)-10c-((1*Z*)prop-1-enyl)-*trans*-10b,10c-dihydropyrene 165**

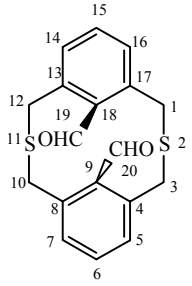



**165**

The melting point could not be determined because the sample was a mixture of isomers. $^{1}$H NMR ($CDCl_3$) δ 8.71 (d, *J* = 7.7 Hz, 2H, H-4,10), 8.67 (d, *J* = 7.6 Hz, 2H, H-6,8), 8.66 (d, *J* = 7.6 Hz, 2H, H-5,9), 8.58 (d, *J* = 7.7 Hz, 2H, H-1,3), 8.07 (t, *J* = 7.8 Hz, 1H, H-7), 8.02 (t, *J* = 7.7 Hz, 1H, H-2), 3.14 (qd, *J* = 12.4, 7.3 Hz, 1H, H-14), 2.36 (qd, *J* = 15.1, 6.5 Hz, 1H, H-12), 0.32 (dd, *J* = 7.2, 1.8 Hz, 3H, H-15), 0.17 (dd, *J* = 6.7, 1.5 Hz,

3H, H-16), 0.15 (m, 2H, H-11,13); $^{13}$C- NMR ($CDCl_3$) δ 135.15 (C-5a,10d), 134.77 (C-10a,3a), 126.10 (C-5,9), 125.21 (C-4,10), 125.10 (C-6,8), 124.24 (C-1,3), 123.44 (C-2), 123.39 (C-7), 123.00 (C-13), 122.81 (C-14), 120.62 (C-11), 120.32 (C-12), 16.41 (C-15), 11.09 (C-16); IR ν (KBr) 3018, 2923, 2852, 1365, 836, 797, 692 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 346 nm (46600), 369 (12700), 390 (21100), 482 (4500), 626 (120); Calcd Anal.: C, 92.91; H, 7.09. Found: C, 82.91; H, 7.10.

***anti*-9,18-Diformyl-2,11-dithia-[3.3]metacyclophane 168**

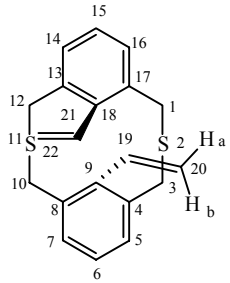



**168**

DIBAL (5 mL of 1M solution in hexane, 5 mmol) was added dropwise over three minutes to a solution of dicyano-*anti*-thiacyclophane **100** (500 mg, 1.55 mmol) in dichloromethane (10 mL) at room temperature under argon. The reaction mixture was allowed to stir for 3.5 hours and then cooled to 0 $^{o}$C, treated with excess methanol and stirred for 30 minutes. Then 1N HCl (10 mL) was added and the reaction was stirred for 1hr. The resulting solution was extracted between dichloromethane and water. The organic layer was dried over $K_2CO_3$ and evaporated. Column chromatography over silica using dichloromethane gave 452 mg (1.38 mmol, 89%) of **168** as colorless crystals from dichloromethane: mp ~ 150 $^{o}$C dec. $^{1}$H NMR ($CDCl_3$) δ 9.93 (s, 2H, H-19,20), 7.40 (s, 6H, H-5,6,7,14,15,16), 4.32 and 3.79 (AB, *J* = 14.6 Hz, 4H, H-1,3,10,12); $^{13}$C NMR ($CDCl_3$) δ 191.49 (C-19,20), 140.20 (C-9,18), 135.07 (C-4,8,13,17), 132.88 (C-6,15),

132.18 (C-5,7,14,16), 30.50 (C-1,3,10,12); IR ν (KBr) 3061, 3019, 2903, 2773, 1683, 1584, 1572, 1461, 1401, 1172, 1295, 884, 831, 800, 741 $cm^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 235 (12930), 314 (3350).

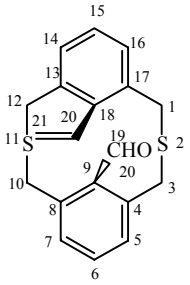
***anti*-9,18-Diethenyl-2,11-dithia-[3.3]metacyclophane 170**




**170**

Using procedure 7.6 A, a reaction of diformylthiacyclophane **168** (480 mg, 1.46 mmol) with ylide {prepared by reaction of BuLi (1.6 mL of 2.5 M in hexanes, 4 mmol) and methyltriphenylphosphonium bromide (1.15 g, 3.22 mmol) in THF (20 mL)} followed by column chromatography using hexanes: dichloromethane (7:3) as eluant gave divinylthiacyclophane **170** (87.6%) as colorless crystals from cyclohexane: mp ~ 184 $^{o}$C dec. $^{1}$H NMR ($CDCl_3$) δ 7.35 (d, *J* = 7.6 Hz, 4H, H-5,7,14,16), 7.17 (t, *J* = 7.6 Hz, 2H, H-6,15), 5.93 (dd, *J* = 17.8, 11.3 Hz, 2H, H-19,21(-<u>CH</u>=$CH_2$)), 5.16 (dd, *J* = 11.3, 2.1 Hz, 2H, H-20a,22a*), 4.68 (dd, *J* = 17.8, 2.1Hz, 2H, H-22b,20b*), 3.79 and 3.64 (AB, *J* = 14 Hz, 4H, H-1,3,10,12); $^{13}$C NMR ($CDCl_3$) δ 142.08 (C-9,18), 134.84 (C-4,8,13,17), 134.72 (C-19,21), 130.07 (C-5,7,14,16), 127.09 (C-6,15), 120.34 (C-20,22), 31.94 (C-1,3,10,12); IR ν (KBr) 3080, 2924, 1458, 924, 762 $cm^{-1}$; UV (cyclohexane), $\lambda_{max}$ nm, ($\varepsilon_{max}$) 215 (33500), 247 (11000); EI MS *m/z* 324 ($M^+$); HR MS Calcd for $C_{20}H_{20}S_2$ 324.1006. Found: 324.1005; Anal. Calcd: C, 74.02; H, 6.21. Found: C, 73.66; H, 6.23.

* “a" stands for the *trans*-vinyl protons whereas “b” stands for the *cis*-vinyl proton.

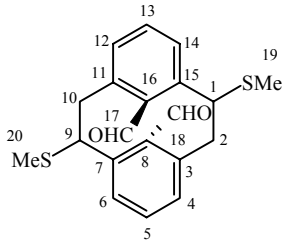



**169**

Hexanes:dichloromethane 4:6 eluted **169** (8%) as colorless crystals from cyclohexane: mp 169-171 $^{o}$C**;** H NMR($CDCl_3$) δ 9.82 (s, 1H, -C<u>H</u>O), 7.41 (m, 3H, H-5,6,7), 7.33 (d, *J* = 7.6 Hz, 2H, H-14,16), 7.20 (t, *J* = 7.6 Hz, 1H, H-15), 6.00 (dd, *J* = 17.8, 11.3 Hz, 1H, H-20 (-<u>CH</u>=$CH_2$)), 5.22 (dd, *J* = 11.4, 1.9 Hz, 1H, H-21a), 4.78 (dd, *J* = 17.7, 1.9 Hz, 1H, H-21b), 4.27 and 3.72 (AB, *J* = 14.6 Hz, 2H, H-3,10), 3.80 and 3.72 (AB, *J* = 14.1 Hz, 1H, H-1,12); $^{13}$C NMR ($CDCl_3$) δ 191.81 (CHO), 141.61 (C-18), 139.88 (C-4,8), 135.83 (C-9), 134.82 (C-13,17), 133.86 (C-20), 132.28 (C-6), 131.77 (C-5,7), 130.41 (C-14,16), 127.49 (C-15), 121.04 (C-21), 32.20 (C-1,12), 30.09 (C-3,10); IR ν (KBr) 3080, 2938, 2908, 2780, 1679, 1587, 1464, 1009, 940, 771, 751 $cm^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 231 (17500), 306 sh (1900); EI MS 326 ($M^{+}$); Anal. Calcd: C, 69.90; H, 5.55. Found: C, 69.25; H, 5.71.

* “a" stands for the *trans*-vinyl protons whereas “b” stands for the *cis*-vinyl proton.

**2, 10-Bis(thiomethyl)-8,16-diformyl-*anti*-[2.2]metacyclophane 174**



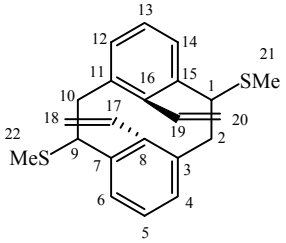

**174**

DIBAL (20 mL of 1M solution in hexane, 20 mmol) was added dropwise over three minutes to a solution of dicyano-*anti*-thiomethylcyclophane **99** (2.3 g, 6.55 mmol) in dichloromethane (60 mL) at room temperature under argon. The reaction mixture was allowed to stir for 2.5 h and then cooled to 0 $^{o}$C, treated with excess methanol and stirred for 30 minutes. Then 0.35 N HCl (100 mL) was added and stirred for 1hr. The resulting solution was extracted between dichloromethane and water. The organic layer was dried over $K_2CO_3$ and evaporated. Column chromatography over silica gel using hexanes-dichloromethane 2:8 gave 2.05 g (5.76 mmol, 88%) of **174** as a mixture of isomers, EI MS *m/z* 356 ($M^+$). These could be used directly in the next step. For characterization, a single isomer of **174**, in which the 1,9-thiomethyl groups are pseudo-equatorial was purified by careful column chromatography: mp 187-192 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 8.95 (s, 2H, H-17,18), 8.00 (dd, *J* = 7.6, 1.0 Hz, 2H, H-6,14), 7.36 (t, *J* = 7.6 Hz, 2H, H-5,13), 7.27 (dd, *J* = 7.5 Hz, 1.0 Hz, 2H, H-4,12), 5.15 (dd, *J* = 11.4, 5.0 Hz, 2H, H-$1_{ax}$,$9_{ax}$), 3.36 (dd, *J* = 12.8, 5.0 Hz, 2H, H-$2_{eq}$,$10_{eq}$), 3.21 (dd, *J* = 12.8, 11.4 Hz, 2H, H-$2_{ax}$,$10_{ax}$), 2.19 (s, 6H, -SMe); $^{13}$C NMR ($CDCl_3$) δ 188.74 (CHO), 143.49 (C-7,15), 142.94 ( C-3,11), 141.15 (C-8,16), 133.28 (C-5,13), 131.24 (C-4,12), 127.04 (C-6,14), 50.89 (C-1,9), 42.23 (C-2,10), 15.82 (SMe); IR ν (KBr) 2890, 2889, 2786, 1682, 1580, 1445, 1208, 880, 789,

738, 707 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 227 (5100), 259 (3500), 297 (800); EI MS *m/z* 356 ($M^+$); HR MS Calcd for $C_{20}H_{20}O_2S_2$: 356.0904. Found: 356.0902. Anal. Calcd: C, 67.38; H, 5.65. Found: C, 67.41; H, 5.57.

Mixture of isomers gave following NMR data: $^1H$ NMR ($CDCl_3$) δ 9.04, 8.94, 8.91, 8.75 (4s), 8.04 (d, *J* = 7.8 Hz ), 7.98 (d, *J* = 7.3 Hz), 7.5-7.2 (m), 5.14 (dd, *J* = 11.4, 5.0 Hz), 4.83(dd, *J* = 11.4, 4.8 Hz), 4.63 (dd, *J* = 7.1, 1.2 Hz), 4.48 (dd, *J* = 11.2, 4.7 Hz), 4.36 (dd, *J* = 14.0, 7.1 Hz), 3.50 (dd, *J* = 12.4, 11.6 Hz) 3.37-3.33 (m), 3.20 (t), 2.19-2.18 (3 s, S-Me).

**2,10-Bis(thiomethyl)-8,16-diethenyl-*anti*-[2.2]metacyclophane 171**




**171**

Using procedure 7.6 A, a reaction of diformylthiomethylcyclophane **174** (1.5 g, 4.21 mmol) with an ylide {prepared by reaction of BuLi (5.3 mL of 2.5M in hexanes, 13.25 mmol) and methyltriphenylphosphonium bromide (3.6 g, 10.08 mmol) in THF (40 mL)} followed by column chromatography using hexanes: dichloromethane (7:3) as eluant gave divinylthiomethylcyclophane **171** (93%) as a mixture of isomers, EI MS *m/z* 352 ($M^+$).

**Procedure B: Wittig rearrangement.**

BuLi (0.9 mL, 2.5M solution in hexanes, 2.25 mmol) was added dropwise to the solution of 9,18-divinylthiacyclophane **170** (250 mg, 0.77 mmol) in THF (12 mL) at 0 $^oC$

under argon and brought to room temperature over ten minutes where dark brown solution turned yellow. MeI (excess, 0.5 mL) was added to this reaction mixture and stirred for another 10 minutes. The reaction was quenched with water and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated to give desired product **171** (250 mg, 0.71 mmol, 92%) as a mixture of isomers.

**Mixture of isomers**

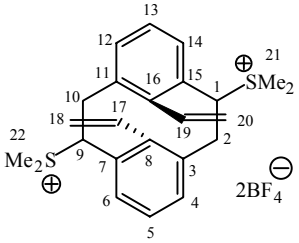
$^1$H NMR ($CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz)7.80 (d, *J* = 7.7 Hz), 7.67-7.62 (m), 7.53-7.51 (m), 7.45-7.42 (m), 7.20-7.16 (m), 7.08-7.05 (m), 6.94 (t, *J* = 7.4 Hz), 4.80-4.60 (complex m), 4.52-4.40 (m), 4.28-4.25 (m), 4.11-4.08 (m), 3.08-3.04 (m), 2.87 (t, *J* = 12.0 Hz), 2.66 (t, *J* = 12.1 Hz), 2.12, 2.08 (s).

These could be used directly in the next step. For characterization, a single isomer of **171**, in which the 1,9-thiomethyl groups are pseudo-equatorial was purified by re-chromatography.

mp 228-229 $^o$C; $^1$H NMR ($CDCl_3$) δ 7.81 (dd, *J* = 7.6, 1.1 Hz, 2H, H-6,14), 7.18 (dd, *J* = 7.5, 1.0 Hz, 2H, H-4,12), 7.07 (t, *J* = 7.5 Hz, 2H, H-5,13), 4.76 and 4.43 (m, 4H, H-19,20,17,18), 4.27 (dd, *J* = 11.6, 4.2 Hz, 2H, H-1,9), 3.06 (dd, *J* = 12.6, 4.2 Hz, 2H, H-$2_{eq}$,$10_{eq}$), 2.66 (dd, *J* = 12.1, 11.9 Hz, 2H, H-$2_{ax}$,$10_{ax}$), 2.13 (s, 3H, SMe); $^{13}$C NMR ($CDCl_3$) δ 147.02 ( C-8,16), 135.70 (C-7,15), 135.24 (C-3,11), 134.98 (C-17, 19), 128.93(C-4,12), 126.62 (C-5,13), 125.37 (C-6,14), 120.57(C-18,20), 53.20 (C-1,9), 43.27 (C-2,10), 15.34 (C-21,22); IR ν (KBr) 3078, 2960, 2909, 1438, 1397, 994, 930, 771, 748 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 227 (17300), 288 (3986); EI MS *m/z* 352

($M^+$); HR MS Calcd for $C_{22}H_{24}S_2$: 352.1319. Found: 352.1319. Anal. Calcd: C, 74.95; H, 6.86. Found: C, 74.48; H, 6.91.

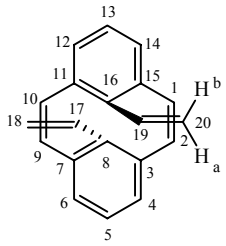
**1,10-Bis(thiomethyl)-8-16-divinyl-*anti*-[2.2]metacyclophane bis-sulfonium salt 172**




**172**

Using procedure 7.3, mixed isomers **171** (360 mg, 1 mmol) on reaction with Borch reagent (80% oil, 580 mg, 2.86 mmol) in $CH_2Cl_2$ (14 mL) gave the sulfonium salt **172** in 79% yield : $^1$H NMR (DMSO-$d_6$) δ 7.72 (d, $J$ = 7.8 Hz), 7.58 (d, $J$ = 7.4 Hz), 7.54 (d, $J$ = 7.3 Hz), 7.41 (d, $J$ = 7.6 Hz), 7.28 (t, $J$ = 7.6 Hz), 7.13 (t, $J$ = 7.4 Hz), 5.2-4.6 (m), 3.46-3.05 (m), 2.90, 2.87(s).

**8,16-Divinyl-*anti*-[2.2]metacyclophane-1,9-diene 166**

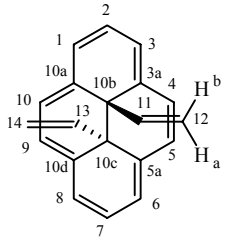



**166**

Using procedure 7.4, a reaction of bis-sulfonium salt **172** (440 mg, 0.791 mmol) and *t*-BuOK (250 mg, 2.23 mmol) in THF (14 mL) followed by column chromatography over silica gel using hexanes as eluant gave **166 (**90%) as colorless crystals from cyclohexane, which on attempted mp determination isomerizes into DHP **167**: $^1$H NMR

($CDCl_3$) δ 7.07 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.60 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.38 (s, 4H, H-1,2,9,10), 6.32 (dd, *J* = 17.4, 11.0 Hz, 2H, H-17,19) 5.47 (dd, *J* = 17.4, 1.8 Hz, 2H, H-18,20b), 4.84 (dd, *J* = 11.0, 1.8 Hz, 2H, H-18,20a); $^{13}$C NMR ($CDCl_3$) δ 146.42 (C-8,16), 135.83 (3,7,11,15), 135.20 (C-17,19), 133.23 (C-1,2,9,10), 129.54 (C-5,13), 126.68 (C-4,6,12,14), 118.90 (C-18,20); IR ν (KBr) 3077, 3049, 3004, 1618, 1436, 1397, 993, 903, 861, 807, 764, 605 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 202 (51700), 242 (33170), 279 (12370), 339 (11000), 377 (5710), 390 sh (2100); EI MS *m/z* 256 ($M^+$), 229 ($M^+$ -27), 202(100%, $M^+$ - 54); HR MS Calcd for $C_{20}H_{16}$: 256.1252. Found: 256.1255. Calcd. Anal: C, 93.70; H, 6.30. Found: C, 93.51; H, 6.41.

**10b,10c-Divinyl-*trans*-10b,10c-dihydropyrene 167**

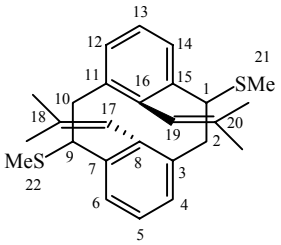



**167**

Using procedure 7.5, DHP **167** was obtained from cyclophanediene **166** in quantitative yield as dark green crystals from cyclohexane: mp 163-165 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 8.79 (s, 4H, H-4,5,9,10), 8.65 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 8.08 (t, *J* = 7.6 Hz, 2H, H-2,7), 2.67 (dd, *J* = 10.3, 1.4 Hz, 2H, H-12,14b), 2.06 (dd, *J* = 17.0, 1.5 Hz, 2H, H-12,14a), 0.50 (dd, *J* = 17.0, 10.3 Hz, 2H, H-11,13); $^{13}$C NMR ($CDCl_3$) δ 133.81 (3a,5a,10a,10d), 128.57 (C-11,13), 125.47 (C-4,5,9,10), 124.42 (C-1,3,6,8), 123.79 (C-2,7), 109.83 (C-12,14), 36.12 (C-10b,10c); IR ν (KBr) 3032, 3007, 1621, 1399, 1295, 912, 841 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 339 (71300), 377 (30000), 462 (5600),

608 (100); EI MS *m/z* 256 ($M^+$), 229 ($M^+$ - 27, 100%), 202. HR MS Calcd for $C_{20}H_{16}$: 256.1252. Found: 256.1251. Calcd. Anal: C, 93.70; H, 6.30. Found: C, 93.92; H, 6.57.

**2,10-Bis(thiomethyl)-8,16-bis(2-methyl-1-preopenyl)-*anti*-[2.2]-cyclophane 176**

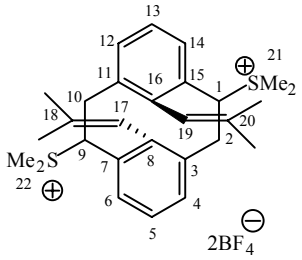



**176**

Using procedure 7.6 B, a reaction of diformylthiomethylcyclophane **174** (1.0 g, 2.81 mmol) with an ylide {prepared by reaction of *t*-BuOK (2.0 g, 18.6 mmol) and isopropyl triphenylphosphonium bromide (2.75 g, 7.14 mmol) in THF (25 mL)} followed by column chromatography using hexanes: dichloromethane (7:3) as eluant gave diisobutenylthiomethylcyclophane **176** (61%) as a mixture of isomers, EI MS *m/z* 408 ($M^+$). These could be used directly in the next step: $^1$H NMR ($CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz), 7.735 (d, *J* = 7.6 Hz), 7.733 (d, *J* = 7.6 Hz), 7.19 (m), 7.06 (t, *J* = 7.5 Hz), 6.94 (t, *J* = 7.4 Hz), 4.04 (br s), 3.98 (dd, *J* = 11.4, 4.0 Hz), 3.92 (dd, *J* = 11.5, 4.0 Hz), 3.80, 3.69 (br singlets), 3.03 (dd, *J* = 12.1, 4.0 Hz), 2.59 (t, *J* = 11.8 Hz), 2.51 (t, *J* = 11.8 Hz), 2.12, 2.07 (two singlets), 1.43, 1.40, 1.39, 1.07, 0.97, 0.88 (six singlets); $^{13}$C NMR ($CDCl_3$) δ 145.77, 144.66, 143.68, 137.45, 137.37, 136.36, 136.21, 136.10, 135.81, 134.86, 134.49, 134.39, 134.36, 134.21, 128.57, 128.04, 128.43, 128.18, 126.05, 125.93, 125.77, 125.36, 125.32, 124.70, 122.48, 122.19, 122.08, 121.997, 53.30, 53.12, 43.87, 43.47, 32.15, 29.92, 29.58, 25.47, 25.27, 25.14, 22.91, 18.70, 18.57, 18.20, 16.11, 15.62, 14.33; IR ν (KBr) 3047, 2962, 2923, 2853, 1654, 1437, 1376, 833, 777, 731, 720 $cm^{-1}$;

UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 230 nm sh (33400); EI MS *m/z* 408 ($M^+$); HR MS Calcd: 408.1945. Found: 408.1950.

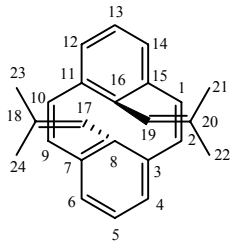
**8,16-Bis(2-methyl-1-propenyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane sulfonium salt 177**




**177**

Using procedure 7.3, mixed isomers **176** (700 mg, 1.716 mmol) on reaction with Borch reagent ((80% oil, 1.50 g, 7.4 mmol) in $CH_2Cl_2$ (15 mL) gave the sulfonium salt **177** as a mixture of isomers in 71% yield: $^1$H NMR (DMSO-$d_6$) δ 7.71 (d, *J* = 7.8 Hz), 7.61 (d, *J* = 7.3 Hz), 7.50 (d, *J* = 7.2 Hz), 7.43 (m), 7.29 (t, *J* = 7.6 Hz), 7.14 (t, *J* = 7.4 Hz), 4.56 (dd, *J* = 11.6, 3.8 Hz), 4.41 (dd, *J* = 11.6, 4.0 Hz), 4.22 (s), 3.92 (br s), 3.54 (br s), 3.45 (dd, *J* = 12.1, 3.9 Hz), 3.38 (dd, *J* = 12.1, 3.9 Hz), 3.32 (s, SMe), 2.88 (t), 2.83, 2.82 (singlets), 1.52, 1.49, 1.47, 1.13, 1.03, 0.86 (six broad singlets).

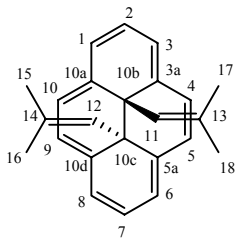
**8,16-Bis(2-methylprop-1-enyl)-*anti*-[2.2]metacyclophane-1,9-diene 178**




**178**

Using procedure 7.4, a reaction of bis-sulfonium salt **177** (640 mg, 1.05 mmol) and *t*-BuOK (400 mg, 3.57 mmol) in THF (25 mL) followed by column chromatography over silica gel using hexanes as eluant gave **178** (96%) as colorless crystals from cyclohexane, which on attempted mp determination isomerizes into DHP **179**: $^{1}$H NMR ($CDCl_3$) δ 7.04 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.60 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.26 (s, 4H, H-1,2,9,10), 5.70 (m, 2H, H-17,19), 1.57 (two overlapping doublets, 12H, Me); $^{13}$C NMR ($CDCl_3$) δ 142.80 (C-8,16), 137.45 (C-3,7,11,15), 135.17 (C-18,20), 132.14 (C-1,2,9,10), 127.71 (C-5,13), 125.71 (C-4,6,12,14), 125.47 (C-17,19), 20.64, 26.81 (C-21,22,23,2,4); IR ν (KBr) 3045, 3011, 2956, 2892, 1637, 1444, 1434, 1052, 827, 763, 656, 637 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 229 nm (46000), 254 sh ( 16900), 299 sh (2400), 355 (2800) EI MS *m/z* 312 ($M^+$), 257 ($M^+$ - isobutenyl), 202 (100%); HR MS Calcd for $C_{24}H_{24}$: 312.1878. Found: 312.1876. Calcd. Anal: C, 92.26; H, 7.74. Found: C, 92.00; H, 7.83.

**10b,10c-Bis(2-methylprop-1-enyl)-*trans*-10b,10c-dihydropyrene 179**

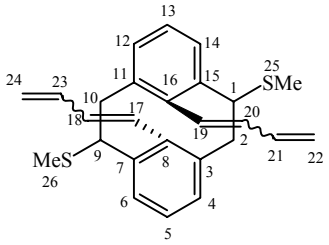



**179**

Using procedure 7.5, DHP **179** was obtained in quantitative yield from diisobutenyl CPD **178** as orange crystals: mp ~ 142-143 $^{o}$C dec; decomposed product's mp 175-177 $^{o}$C; $^{1}$H NMR ($CDCl_3$); δ 8.55 (d, *J* = 7.5 Hz, 4H, H-1,3,6,8), 8.51 (s, 4H, H-4,5,9,10), 7.93 (t, *J* = 7.5 Hz, 2H, H- 2,7), 0.17 (d, *J* = 1.1 Hz, 6H, H-15,17), 0.14 (d, *J* =

1.3 Hz, 6H, H-16,18), -0.16 (m, 2H, H-11,12); $^{13}$C NMR ($CDCl_3$) δ 135.75 (C-3a,5a,10a,10d), 130.73 (C-13,14), 125.89 ( C-4,5,9,10), 125.34 (C-1,3,6,8), 123.10 (C-2,7), 116.18 (C-11,12), 36.22 (C-10b,10c), 28.24 (C-15,18), 16.16 (C-16,17); IR ν (KBr) 3020, 2967, 2920, 1654, 1648, 1637, 838, 826, 764 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 205 (32300), 243 (12000), 349 (44400), 371 (14500), 395 (27000), 494 (4200), 644 (130); EI MS *m/z* 312 ($M^+$), 257 ($M^+$ - isobutenyl), 202 (100%); HR MS Calcd for $C_{24}H_{24}$: 312.1878. Found: 312.1876. Calcd. Anal: C, 92.26; H, 7.74. Found: C, 85.88; H, 7.21.

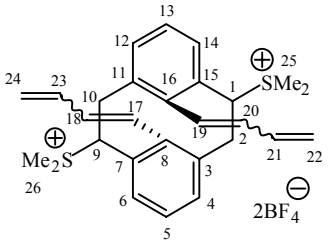
**8,16-Bis(buta-1,3-dienyl)-1,9-bis(thiomethyl)-*anti*-[2.2]-cyclophane 180**




**180**

Using procedure 7.6 A, a reaction of diformylthiomethylcyclophane **174** (600 g, 1.68 mmol) with an ylide {prepared by reaction of BuLi (1.7 mL of 2.5M in hexanes, 4.25 mmol) and allyl triphenylphosphonium bromide (1.5 g, 3.24 mmol) in THF (20 mL)} followed by column chromatography using hexanes: dichloromethane (7:3) as eluant gave cyclophane **180** (52%) was obtained as a mixture of isomers by column chromatography using hexanes-DCM 70:30. These could be used directly in the next step: $^1$H NMR ($CDCl_3$) δ 7.88-7.79 (m), 7.25-7.07 (m), 6.0-5.90 (m), 5.68-5.38 (m), 5.03-4.95 (m), 4.87-4.83 (m), 4.72 (d, *J* = 15.8 Hz), 4.31-4.27 (m), 4.13 (d, *J* = 9.7 Hz), 4.01 (dd, *J* = 11.5, 4.1 Hz), 3.07 (dd, *J* = 12.8, 4.0 Hz), 2.70 (t, *J* = 12.0 Hz), 2.54 (t, *J* = 12.0 Hz), 2.50 (t, *J* = 12.0 Hz), 2.17, 2.10, 2.04 (s).

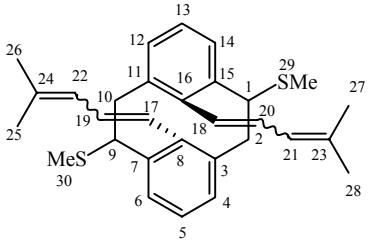
**8,16-Bis(buta-1,3-dienyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane-bis-sulfonium salt 182**



**182**

Using procedure 7.3, mixed isomers **180** (320 mg, 0.8 mmol) on reaction with Borch reagent ((80% oil, 0.6 g, 3 mmol) in $CH_2Cl_2$ (20 mL) gave 160 mg (0.225 mmol, 33%) of sulfonium salt **182**. The reaction conditions were not optimized. $^1$H NMR (DMSO-$d_6$) 7.67 (d, $J$ = 7.4 Hz), 7.63 (d, $J$ = 7.4 Hz), 7.58 (d, $J$ = 7.6 Hz), 7.53 (t, $J$ = 7.0 Hz), 7.37 (t, $J$ = 7.6 Hz), 7.29 (t, $J$ = 7.5 Hz), 5.82 (t, $J$ = 10.2 Hz), 5.62-5.50 (m), 5.24 (d, $J$ = 16.6 Hz), 5.06 (d, $J$ = 10.3 Hz), 4.64 (dd, $J$ = 11.4, 3.7 Hz), 4.27 (d, $J$ = 11.5 Hz), 4.02 (AB, $J$ = 14.3, 7.2 Hz), 3.52-3.47 (m), 3.35-3.29 (4 s), 2.89 (s), 2.82, 2.80, 2.78 (s)

**8,16-Bis(4-methylpenta-1,3-dienyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane 188**

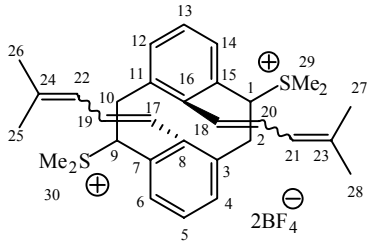


**188**

Using procedure 7.6 B, a reaction of diformylthiomethylcyclophane **174** (680 mg, 1.91 mmol) with an ylide {prepared by reaction of *t*-BuOK (1.60 g, 14.3 mmol) and 3-methylbut-2-enyl triphenylphosphonium bromide (4.2 g, 10.2 mmol) in THF (40 mL)}

followed by column chromatography using hexanes: DCM 75:25 gave the desired product **188** (67%) as a mixture of isomers, $^1$H NMR ($CDCl_3$) δ 7.88-7.78 (m), 7.24-6.89 (m), 5.86-5.56 (m), 5.50-5.40 (m), 5.15-4.91 (m), 4.70-4.56 (m), 4.40-4.32 (m), 4.10-3.95 (m), 3.10-3.00 (m), 2.91-2.83 (m), 2.70-2.50 (m), 2.28 (t, *J* = 11.4 Hz), 2.19, 2.18 (s), 2.13, 2.09 (3 s), 2.06, 2.04, 2.03 (3 s), 1.74, 1.61, 1.60 (br s), 1.53, 1.51 (br s) ); EI MS *m/z* 460 ($M^+$). HR MS Calcd for $C_{30}H_{36}S_2$: 460.2258. Found: 460.2257.

**8,16-Bis(4-methylpenta-1,3-dienyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane sulfonium salt 189**



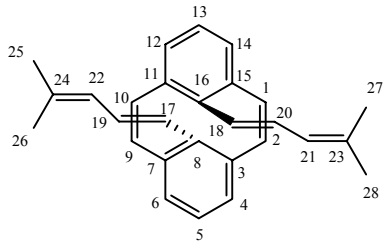

**189**

Using procedure 7.3, mixed isomers **188** (0.55 g, 1.19 mmol) on reaction with Borch reagent ((80% oil, 0.9 g, 4.4 mmol) in $CH_2Cl_2$ (8 mL) gave 320 mg (0.48 mmol, 41%) of bis-sulfonium salt **189**: $^1$H NMR (DMSO-$d_6$) 7.77-7.32 (m), 7.26 (t, *J* = 7.6 Hz), 7.10 (t, *J* = 7.5 Hz), 6.08-5.92 (m), 5.82-5.71(m), 5.06 (t, *J* = 12.2 Hz), 4.93-4.74 (m), 4.63-4.42 (m), 4.18 (d, *J* = 11.2 Hz), 4.12 (d, *J* = 11.7 Hz) 4.02 (AB, *J* = 14.2, 7.0 Hz), 3.9 (d, *J* = 11.2 Hz), 3.52-3.10 (m), 3.32-3.29 ( overlapping singlets), 2.91-2.76 (6 s), 1.75, 1.64, 1.62, 1.57, 1.55, 1.52 (br s).

**8,16-Bis(4-methylpent-1,3-dienyl)-*anti*-[2.2]metacyclophane-1,9-dienes 184-186**

Using procedure 7.4, a reaction of bis-sulfonium salt **189** (300 mg, 1.05 mmol) and *t*-BuOK (400 mg, 3.57 mmol) in THF (20 mL) gave a mixture of cyclophanedienes. The mixture was chromatographed over silica gel using hexanes: DCM 19: 1. Eluted first from column was a mixture of **184** and **185**, and then last the *cis*-isomer **186**.

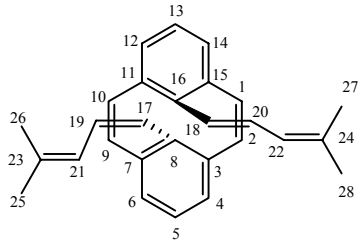
**8,16-Bis((1*E*) 4-methyl-penta-1,3-dienyl)-*anti*-[2.2]metacyclophane-1,9-diene 184**




**184**

The melting point could not be determined because the sample was a mixture of isomers. $^{1}$H NMR ($CD_2Cl_2$) δ 6.98 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.80 (dd, *J* = 15.3, 11.0 Hz, 2H, H-19,20), 6.53 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.38 (s, 4H, H-1,2,9,10), 6.09 (d, *J* = 15.4 Hz, 2H, H-17,18), 5.60 (dm, *J* = 10.8 Hz, 2H, H-21,22), 1.78 (s, 6H, H-25,28), 1.72 (s, 6H, H-26,27); $^{13}$C NMR ($CD_2Cl_2$) δ 145.99 (C-8,16), 136.44 (C-3,7,11,15), 136.32 (C-23,24), 133.50 (C-1,2,9,10), 130.85 (C-19,20), 129.81 (C-17,18), 128.99 (C-5,13), 127.14 (C-21,22), 126.94 (C-4,6,12,14), 26.45 (C-25,28), 18.71 (C-26,27); EI MS *m/z* 364 ($M^+$); HR MS Calcd for $C_{28}H_{28}$: 364.2191, Found: 364.2195; Anal. Calcd: C, 92.26; H, 7.74. Found: C, 90.78; H, 7.82.

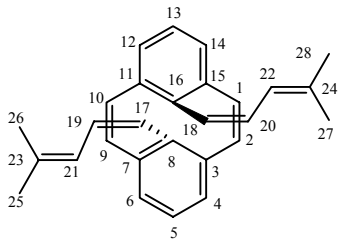
**16-Bis((1*E*)-4-methyl-penta-1,3-dienyl)-8-((1*Z*)-4-methyl-penta-1,3-dienyl)-*anti*-[2.2]metacyclophane-1,9-diene 185**




**185**

The melting point could not be determined because the sample was a mixture of isomers. $^{1}$H NMR ($CD_2Cl_2$) δ 7.09 (t, *J* = 7.4 Hz, 1H, H-13), 6.99 (t, *J* = 7.4 Hz, 1H, H-5), 6.75 (dd, *J* = 15.2, 11.0 Hz, 1H, H-20), 6.58 (d, *J* = 7.4 Hz, 2H, H-12,14), 6.57 (d, *J* = 7.4 Hz, 2H, H-4,6), 6.30 (AB, *J* = 11.4 Hz, 4H, H-1,2,9,10), 6.04 (d, *J* = 15.4 Hz, 1H, H-18), 5.98 (m, 1H, H-21), 5.83 (dd, *J* = 12.4, 11.8 Hz, 1H, H-19), 5.79 (d, *J* = 12.4 Hz, 1H, H-17), 5.60 (dm, *J* = 12.5 Hz, 1H, H-22), 1.78 (s, 3H, H-28), 1.74 (s, 3H, H-25), 1.72 (s, 3H, H-27), 1.71 (s, 3H, H-26); $^{13}$C NMR ($CD_2Cl_2$) δ 147.10 (C-8), 142.36 (C-16), 138.18 (C-11,15), 137.41 (C-23), 136.51 (C-24), 136.20 (C-3,7), 133.10 (C-2,9), 133.01 (C-1,10), 130.93 (C-20), 129.81 (C-13), 129.57 (C-18), 128.36 (C-5), 127.13 (C-22), 126.89 (C-4,6), 126.87 (C-17), 126.42 (C-19), 126.40 (C-12,14), 123.42 (C-21), 26.64 (C-25), 26.45 (C-28), 18.71 (C-27), 18.55 (C-26).

**8,16-Bis((1*Z*)-4-methyl-penta-1,3-dienyl)-*anti*-[2.2]metacyclophane-1,9-diene 186**



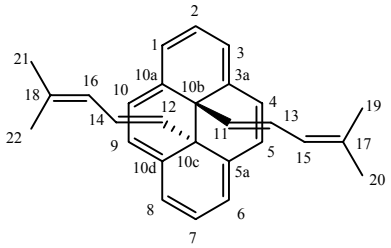
**186**

The melting point could not be determined because the sample was a mixture of isomers. $^{1}$H NMR ($CD_2Cl_2$) δ 7.10 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.63 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.24 (s, 4H, H-1,2,9,10), 5.97 (m, 2H, H-21,22), 5.76 (m, 4H, H-17-20), 1.74 (s, 6H, H-25,28), 1.71 (s, 6H, H-26,27); $^{13}$C NMR ($CD_2Cl_2$) δ 143.43 (C-8,16), 137.92 (C-3,7,11,15), 137.56 (C-23,24), 132.55 (C-1,2,9,10), 129.21 (C-5,13), 126.60, 126.46 (C-17-20), 126.30 (C-4,6,12,14), 26.64 (C-25,28), 18.55 (C-26,27); IR (mix) ν (KBr) 3041, 3002, 2965, 2910, 1636, 1560, 426, 1375, 952, 786, 777, 750 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ ($\varepsilon_{max}$) 246 (27900), 284 (32600), 390 (5000), 406 sh (4800).

**Dihydropyrenes 190-192**

A mixture of cyclophanedienes **184-186** (45 mg) in toluene-$d_8$ (6 mL) was sealed in a glass tube under argon and heated at 110 $^{o}$C for 2 h, which converted it into a mixture of dihydropyrenes **190-192**. The mixture was chromatographed over silica gel using hexanes-DCM 9: 1 as eluant. Eluted first was the all *trans*-isomer **190,** then **191** and finally all *cis*-**192**.

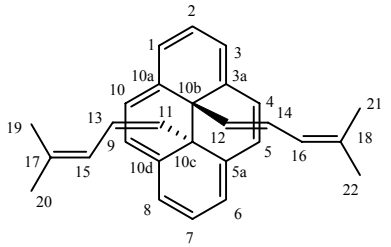
**10b,10c-Bis((1*E*)-4-methylpenta-1,3-dienyl)-*trans*-10b,10c-dihydropyrene 190**



**190**

mp 188-190 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 8.76 (s, 4H, H-4,5,9,10), 8.63 (d, *J* = 7.8 Hz, 4H, H-1,3,6,8), 8.06 (t, *J* = 7.7 Hz, 2H, H-2,7), 4.04 (dm, *J* = 10.9 Hz, 2H, H-15,16), 2.95 (dd, *J* = 15.0, 10.8 Hz, 2H, H-13,14), 1.15, 1.10 (s, 12H, Me), 0.22 (d, *J* = 15.0 Hz, 2H, H-11,12); $^{13}$C NMR ($CDCl_3$) δ 134.39 (C-3a,5a,10a,10d), 133.51 (C-17,18), 125.29 (C-4,5,9,10), 124.20 (C-1,3,6,8), 123.84 (C-15,16), 123.66 (C-2,7), 121.75 (C-11,12), 121.38 (C-13,14), 35.75 (C-10b,10c), 25.51, 18.00 ( 19-22); IR ν (KBr) 3053, 3029, 3003, 1654, 1648, 1441, 1376, 956, 843, 710 cm$^{-1}$ ; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 247 (76200), 338 (78300), 380 (27900), 469 (7900), 609 (135) EI MS *m/z* 364 ($M^+$); HR MS Calcd for $C_{28}H_{28}$: 364.2191. Found: 364.2195.

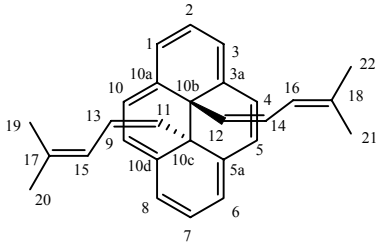
**10b-((1*E*-4-Methylpenta-1,3-dienyl)-10c-((1*Z*)-4-methylpenta-1,3-dienyl-*trans*-10b,10c-dihydropyrene 191**



**191**

The melting point could not be determined because of contamination from **192**. $^{1}$H NMR ($CDCl_3$) δ 8.70 (AB, *J* = 7.7 Hz, 4H, H-4,5,9,10), 8.69 (d, *J* = 7.6 Hz, 2H, H-6,8), 8.60 (d, *J* = 7.8 Hz, 2H, H-1,3), 8.08 (t, *J* = 7.7 Hz, 1H, H-7), 8.04 (t, *J* = 7.8 Hz, 1H, H-2), 4.50 (dm, *J* = 12, 1.3 Hz, 1H, H-15), 4.06 (dm, *J* = 10.8 Hz 1H, H-16), 3.84 (t, *J* = 12.3 Hz, 1H, H-13), 3.03 (dd, *J* = 15.0, 10.8 Hz, 1H, H-14), 1.52, 1.00 (br s, 6H, H-19,20), 1.16. 1.11 (s, 6H, H-21,22), 0.23 (d, *J* = 15.0 Hz, 1H, H-12), 0.01 (d, *J* = 12.4 Hz, 1H, H-11); $^{13}$C NMR 135.93 (C-17,18), 135.31 (C-5a,10d), 134.80 (3a,10a), 126.30 (C-5,9), 125.36 (C-4,10), 125.09 (C-6,8), 124.40 (C-1,3), 123.78 (C-2), 123.84 (C-16), 123.24 (C-7), 122.72 (C-13), 121.92 (C-14), 120.76 (C-12), 119.99 (C-11), 119.36 (C-15), 37.77 (C-10b), 34.75 (C-10c), 26.54, 17.08 (C-19,20), 25.52, 18.03 (C-21,22); IR ν (KBr) 3030, 3003, 2926, 2853, 1654, 1438, 1374, 955, 843, 838, 714, 645 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 250 nm (54800), 344 (56400), 389 (30400), 475 (6058 ), 614 (120).

**10b,10c-Bis((1*Z*)-4-methylpenta-1,3-dienyl)-*trans*-10b,10c-dihydropyrene 192**

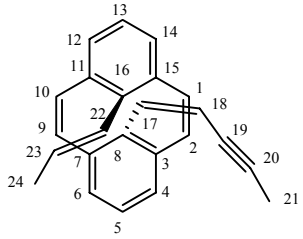



**192**

The melting point could not be determined because of contamination from **191.** $^{1}$H NMR ($CDCl_3$) δ 8.65 (d, *J* = 7.7 Hz, 4H, H-1,3,6,8), 8.62 (s, 4H, H-4,5,9,10), 8.08 (2H, H-2,7), 4.53 (dm, *J* = 12.2, 1.4 Hz, 2H, H-15,16), 3.90 (dd, *J* = 12.2 Hz, 2H, H-13,14), 1.52, 1.01 (s, 12H, Me), -0.02 (d, *J* = 12.5 Hz, 2H, H-11,12); $^{13}$C NMR ($CDCl_3$) δ 136.06 (C-17,18), 135.88 (C-3a,5a,10a,10d), 126.31 (C-4,5,9,10), 125.36 (C-1,3,6,8),

123.53 (C-2,7), 123.31 (C-13,14), 119.39 (C-15,16), 119.01 (C-11,12), 36.62 (C-10b,10c), 26.55, 17.11 (C-19-22); IR ν (KBr) 3023, 2965, 1647, 1654, 1438, 1374, 836, 729 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 251 (42900), 347 (38200), 392 (20100), 486 (5000), 627 (137).

**(Pent-1-ene-3-ynl)-*anti*-[2.2]metacyclophane-1,9-dienes**




**196**

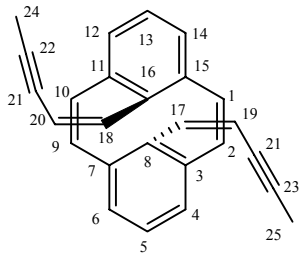
BuLi (1.20 mmol, 0.55 mL of 2.25 M in hexanes) was added dropwise to a suspension of 2-butynyl triphenylphosphonium bromide (300 mg, 0.8 mmol) in THF (8 mL) at room temperature under argon and allowed to stir for 20 minutes. The reaction mixture was cooled to -20 to -30 $^{o}$C and diformyl cyclophanediene **174** (120 mg, 0.47 mmol) was added. The reaction mixture was brought to room temperature over 30 minutes and then quenched with acid (15 mL of 1.5 M aq. HCl solution) and extracted with hexanes, dried and evaporated. The crude product was column chromatographed over silica using hexanes as eluant to give a mixture of CPDs **194**, **196** and **198** (20 mg).

**16-((1*E*)-Propenyl)-8-((1*Z*)-pent-1-ene-3-ynl)-*anti*-[2.2]metacyclophane-1,9-diene 196**

The melting point was not determined because the sample was a mixture of products. $^{1}$H NMR ($CDCl_3$) δ 7.17 (t, *J* = 7.4 Hz, 1H, H-5), 6.97 (t, *J* = 7.4 Hz, H-13), 6.62 (d, *J* = 7.4 Hz, H-4,6), 6.58 (d, *J* = 7.4 Hz, 2H, H-12,14), 6.33 (s, 4H, H-1,2,9,10), 6.28 (d, *J* = 11.7 Hz, 1H, H-17), 5.99 (m, 2H, H-22,23), 5.12 (d, *J* = 11.7 Hz, 1H, H-18),

1.74 (m, 3H, H-21), 1.56 (m, 3H, H-24); $^{13}$C NMR ($CDCl_3$) δ 146.23 (C-16), 140.99 (C-8), 137.80 (C-3,7), 137.73 (C-17), 135.23 (C-11,15), 132.81 (C-2,9), 132.39 (C-1,10), 130.76, 130.65 (C-22,23), 130.02 (C-5), 127.98 (C-13), 126.87 (C-12,14), 125.84 (C-4,6), 109.66 (C-18), 91.28 (C-20), 80.00 (C-19), 18.84 (C-24), 4.88 (C-21).

**8,16-Bis((1*Z*)-pent-1-ene-3-ynl)-*anti*-[2.2]metacyclophane-1,9-diene 194**



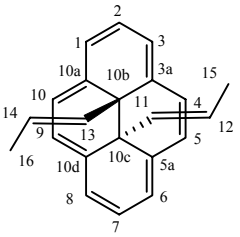

**194**

$^1$H NMR ($CDCl_3$) δ 7.09 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.65 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.34 (s, 4H, H-1,2,9,10), 6.30 (d, *J* = 11.8 Hz, 2H, H-17,18) 5.12 (dq, *J* = 11.8, 2.5 Hz, 2H, H-19,20), 1.96 (d, *J* = 2.6 Hz, 6H, Me); $^{13}$C NMR ($CDCl_3$) δ 142.30 (C-8,16), 137.40 (C-3,7,11,15), 133.73 (C-17,18), 132.22 (C-1,2,9,10), 129.76 (C-5,13), 126.10 (C-4,6,12,14), 109.96 (C-19,20), 92.04 (C-23,24), 80.04 (C-21,22), 4.91 (C-25,26); IR ν (thin film) 3044, 2958, 2924, 2852, 1722, 1683, 1436, 1374, 1262, 1095, 785, 768, 738 cm$^{-1}$; UV (cyclohexane), $\lambda_{max}$ nm ($\varepsilon_{max}$), 257 (14100), tails up to 500 nm)

**(Pent-1-ene-3-ynl)-10b,10c-*trans*-dihydropyrenes 195, 197 and prop-1-enyl-10b,10c-*trans*-dihydropyrene 199**

Cyclophanediene mixture (**194**, **196** and **198**) was converted to the dihydropyrene mixture (**195**, **197** and **199**). The mixture was column chromatographed over silica gel using hexane-DCM 9:1. Eluted first was 3 mg of DHP **199** as a dark green solid. Eluted second was DHP **197** and the last was DHP **195**.

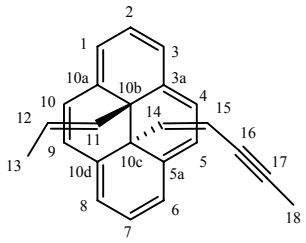
**10b,10c-Bis((1*E*)-propenyl)-10b,10c-dihydropyrene 199**




**199**

$^{1}$H NMR ($CDCl_3$) δ 8.73 (s, 4H, H-4,5,9,10), 8.60 (d, *J* = 7.5 Hz, 4H, 1,3,6,8), 8.04 (t, *J* = 7.6 Hz, 2H, H-2,7), 2.26 (dq, *J* = 15.1, 6.5 Hz, 2H, H-12,14), 0.14 (s, 6H, H-15,16), 0.06 (dq, *J* = 15.1, 1.6 Hz, 2H, H-11,13); $^{13}$C- NMR ($CDCl_3$) δ 134.76 (C-3a,5a,10a,10d), 125.17 (C-4,5,9,10), 124.05 (C-1,3,6,8), 123.45 (C-2,7), 121.26 (C-11,13), 119.97 (C-12,14), 35.56 (C-10b,10c); UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 274 (7000), 343 (55800), 383 (22700), 468 (4300), 609 (110).

**10b-((1*E*)-Propenyl)-10c-((1*Z*)pent-1-ene-3-ynyl)-*trans*-10b,10c-dihydropyrene 197**



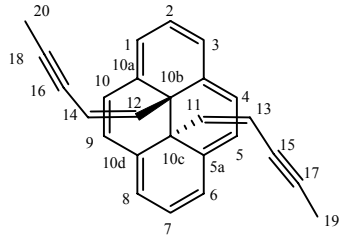

**197**

The melting point determination failed because the product was contaminated with **195**. $^{1}$H NMR ($CDCl_3$) δ 8.71 (s, 4H, H-4,5,9,10), 8.69 (d, *J* = 7.8 Hz, 2H, H-6,8), 8.55 (d, *J* = 7.7 Hz, 2H, H-1,3), 8.10 (t, *J* = 7.8 Hz, 1H, H-7), 8.00 (t, *J* = 7.7 Hz, 1H, H-2), 3.18 (dq, *J* = 12.3, 2.7 Hz, 1H, H-15), 2.38 (dq, *J* = 15.5, 6.0 Hz, 1H, H-12), 1.94 (d, *J* = 3.0 Hz, 3H, H-18), 0.26 (d, *J* = 12.4 Hz, 1H, H-14), 0.18 (d, *J* = 6 Hz, 3H, H-13), 0.16 (d*, 1H, H-11); $^{13}$C NMR ($CDCl_3$) δ 134.80 (C-3a,10a), 132.57 (C-5a,10d), 131.09

(C-14), 126.58 (C-5,9), 125.71 (C-6,8), 125.02 (C-4,10), 123.97 (C-1,3), 123.56 (C-2), 123.50 (C-7), 120.64 (C-12), 120.38 (C-11), 105.43 (C-15), 92.18, 75.31 (C-16,17), 36.63 (C-10b), 35.84 (C-10c), 16.70 (C-13), 4.77 (C-18); IR ν (thin film) 3030, 2957, 2924, 2852, 1727, 1445, 1376, 1348, 1262, 960, 842, 805, 739, 717; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 232 (17600), 275 (7300), 343 (60100), 385 (22500), 471 (5200), 608 (130) ; EI MS *m/z* 308 ($M^+$). HR MS Calcd for $C_{24}H_{20}$: 308.1565. Found:308.1570.

* Coupling constant is not clear due to the overlap of peaks.

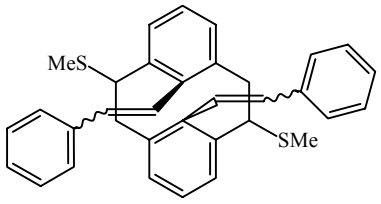
**10b,10c-Bis((1*Z*)pent-1-ene-3-ynyl)-*trans*-10b,10c-dihydropyrene 195**




**195**

The melting point determination failed because the product was contaminated with **197.** $^1$H NMR ($CDCl_3$) δ 8.69 (s, 4H, H-4,5,9,10), 8.63 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 8.06 (t, *J* = 7.6 Hz, 2H, H-2,7), 3.25 (dq, *J* = 12.3, 2.7 Hz, 2H, H-13,14), 1.93 (d, *J* = 2.4 Hz, 6H, H-19,20), 0.38 (d, *J* = 12.3 Hz, 2H, H-11,12); $^{13}$C NMR ($CDCl_3$) δ 132.71 (C-3a,5a,10a,10d), 130.11 (C-11,12), 126.40 (C-4,5,9,10), 125.66 (C-1,3,6,8), 123.66 (C-2,7), 106.02 (C-13,14), 92.50, 75.26 (C-15-18), 36.80 (C-10b,10c), 4.78 (C-19,20); IR ν (KBr) 3003, 2924, 2853, 1637, 1560, 1458, 1261, 1099, 1024, 844, 803; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 234 (28500), 278 (10700), 346 (54000), 387 (19800), 475 (5300), 616 (130) ); EI MS *m/z* 332 ($M^+$). HR MS Calcd for $C_{26}H_{20}$: 332.1565. Found 332.1559.

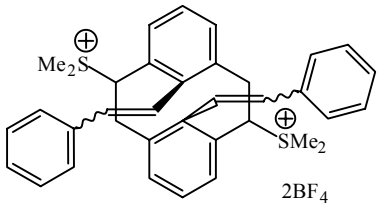
**8,16-Bis(2-phenylethenyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane 200**




**200**

Using procedure 7.6 B, a reaction of diformylthiomethylcyclophane **174** (1.4 g, 3.93 mmol) with an ylide {prepared by reaction of *t*-BuOK (4.0 g, 35.72 mmol) and benzyl triphenylphosphonium bromide (5.0 g, 11.54 mmol) in THF (30 mL)} followed by column chromatography using hexanes:dichloromethane (7:3) delivered 400 mg (0.8 mmol, 20%) of distyrylthiomethylcyclophane **200** as a mixture of isomers: EI MS *m/z* 504 ($M^+$); $^1$H NMR ($CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz), 7.96 (d, *J* = 8.0 Hz), 7.91 (d, *J* = 7.6 Hz), 7.84 (d, *J* = 7.6 Hz), 7.4-6.9 (m), 6.34-6.27 (m), 5.93 (d, *J* = 12.4 Hz), 5.88 (d, *J* = 12.4 Hz), 5.73 (d, *J* = 16.4 Hz), 5.22 (d, *J* = 16.4 Hz), 5.16 (d, *J* = 16.4 Hz) 4.4-4.0 (m), 3.1-3.0 (m), 2.73-2.53 (m), 2.19, 2.18 (s), 1.61, 1.38, 1.37 (3 singlets); EI MS *m/z* 504 (M+), 409 (100), HRMS Calcd for $C_{34}H_{32}S_2$: 504.1945. Found: 504.1938.

**8,16-Bis(2-phenylethenyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane sulfonium salt 201**




**201**

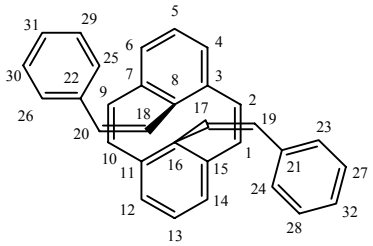
Using procedure 7.3, mixed isomers **200** (600 mg, 1.19 mmol) on reaction with Borch reagent ((80% oil, 1g, 4.94 mmol) in $CH_2Cl_2$ (10 mL) gave 700 mg (0.99 mmol,

83%) of bis-sulfonium salt **201**: $^1$H NMR (DMSO-$d_6$) δ 7.75-7.18 (m), 7.08-6.96 (m), 6.37-5.91 (m), 5.33 (d, *J* = 16.4 Hz), 4.54 (m), 4.28-3.95 (m), 3.48-3.37 (m), 3.29-3.15 (singlets) 2.98-2.80 (singlets), 2.27, 2.29 (s), 2.14, 1.96 (s).

**8,16-Bis(2-phenylethenyl)-*anti*-[2.2]metacyclophane-1,9-dienes 202-204**

Using procedure 7.4, a reaction of bis-sulfonium salt **201** (650 mg, 0.93 mmol) and *t*-BuOK (500 mg, 4.46 mmol) in THF (10 mL) gave a mixture of cyclophanedienes. The product mixture was purified by column chromatography using hexanes-dichloromethane 85: 15 as eluant.

**8,16-Bis((1*Z*)-2-phenylethenyl)-*anti*-[2.2]metacyclophane-1,9-diene 202**



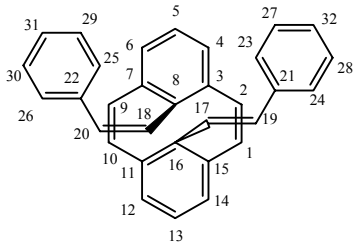

**202**

Eluted first was 152 mg (41%) of *cis,cis*-distyrylcyclophanediene **202** as pale yellow crystals from cyclohexane, which on melting point determination converts into DHP **205**: $^1$H NMR ($CD_2Cl_2$) δ 7.18 (t, *J* = 7.4 Hz, 2H, H-5,13), 7.05 (m, 6H, H-27-32), 6.78 (m, 4H, 23-26), 6.59 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 5.96 (d, *J* = 12.4 Hz, 2H, H-19,20), 5.84 (s, 4H, 1,2,9,10), 5.80 (d, *J* = 12.4 Hz, 2H, H-17,18); $^{13}$C NMR ($CD_2Cl_2$) δ 141.94 (C-8,16), 139.14 (C-21,22), 138.55 (3,7,11,15), 132.69 (C-1,2,9,10), 131.60 (C-19,20), 130.22 (C-5,13), 129.97 (C-17,18), 128.81 (C-23-26), 128.20 (C-31,32), 126.79 (C-27-30), 126.56 (C-4,6,12,14); IR ν (KBr) 3077, 3050, 3005, 1596, 1492, 1448, 1432, 961, 795, 769, 736, 702, 696, 646, 597 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 257

(28900), 280 (23900), 389 (3700); EI MS *m/z* 408 ($M^+$), 305 ($M^+$ - styryl); HR MS Calcd for $C_{32}H_{24}$: 408.1878. Found: 408.1884. Anal. Calcd: C, 94.08; H, 5.92. Found: C, 93.21; H, 6.04.

$^1$H NMR ($CDCl_3$) δ 7.2-7.1 (m, 6H, H-27-32), 7.16 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.81 (m, 4H, H-23-26), 6.56 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 5.97 (d, *J* = 12.4 Hz, 2H, H-19,20), 5.84 (d, *J* = 12.4 Hz, 2H, H-17,18), 5.80 (s, 4H, H-1,2,9,10); $^{13}$C NMR ($CDCl_3$) δ 141.54 (C-8,16), 138.80 (C-21,22), 138.19 (C-3,7,11,15), 132.35 (C-1,2,9,10), 131.54 (C-19,20), 129.45 (C-17,18), 128.50 (C-23-26), 127.33 (C-5,13), 126.14 (C-4,6,12,14).

**8-((1*E*)-2-Phenylethenyl)-16-((1*Z*)-2-phenylethenyl)-*anti*-[2.2]metacyclophane-1,9-diene 203**

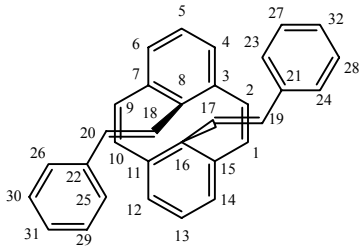



**203**

Eluted second was 132 mg (35.4%) of the unsymmetrical isomer **203** as pale yellow crystals from cyclohexane, which on attempted melting point determination converts into DHP **206**: $^1$H NMR ($CDCl_3$) δ 7.24-7.0 (m, 8H, 23,24, 27-32), 7.13 (t, *J* = 7.4 Hz, 1H, H-13), 6.84 (m, 2H, H-25,26), 7.00 (t, *J* = 7.4 Hz, 1H, H-5), 6.77 (AB, *J* = 16.3 Hz, H-17,19), 6.72 (d, *J* = 7.4 Hz, 2H, H-12,14), 6.45 (d, *J* = 7.4 Hz, 2H, H-4,6), 6.33 (d, *J* = 11.4 Hz, H-1,10), 6.06 (d, *J* = 12.5 Hz, 1H, H-20), 5.97 (d, *J* = 11.4 Hz, 2H, H-2,9), 5.92 (d, *J* = 12.5 Hz, 1H, H-18); $^{13}$C- NMR ($CDCl_3$) δ 146.12 (C-16), 140.07 (C-

8), 138.83 (C-22), 138.59 (C-3,7), 138.11 (C-21), 136.24 (C-11,15), 133.28 (C-19), 132.96 (C-1,10), 132.74 (C-2,9), 131.54 (C-20), 130.29 (C-5), 129.52 (C-18), 128.82 (C-13), 128.75 (C-17), 128.55 (25,26), 126.80 (C-12,14), 126.33 (C-4,6); IR ν (thin film) 3020, 1597, 1574, 1493, 1448, 960, 793, 763, 737, 691 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 252 (29300), 282 (26500), 408 (1600); EI MS *m/z* 408 ($M^+$), 305 ($M^+$ - styryl); HR MS Calcd for $C_{32}H_{24}$: 408.1878. Found: 408.1884.

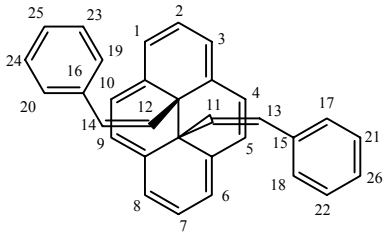
**8,16-Bis((1*E*)-2-phenylethenyl)-*anti*-[2.2]metacyclophane-1,9-diene 204**




**204**

Eluted third was 67 mg (18%) of *trans, trans*-distyryl CPD **204**, which on melting point determination converts into DHP **207**: $^1$H NMR ($CDCl_3$) δ 7.22-7.02 (m, 10H, H-23-32), 7.0 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.86 (s, 4H, H-17-20), 6.62 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.48 (s, 4H, H-1,2,9,10); $^{13}$C NMR ($CDCl_3$) δ 144.58 (C-8,16), 138.18 (C-21,22), 136.66 (C-3,7,11,15), 133.61 (C-19,20), 133.28 (C-1,2,9,10), 129.29 (C-5,13), 128.82 (C-17,18), 127.40 (C-31,32), 126.98 (C-4,6,12,14), 126.78 (C-27,28,29,30), 126.49 (C-23,24,25,26); IR ν (KBr) 3026, 1598, 1492, 1447, 959, 838, 774, 763, 736, 690 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 258 ( 33000), 284 (33400), 308 (30300), 411 sh (1900).

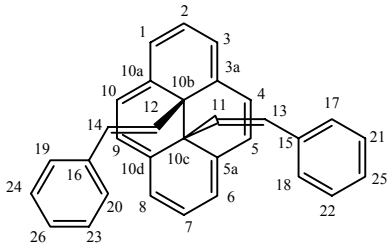
**10b,10c-Bis((1*Z*)-2-phenylvinyl)-*trans*-10b,10c-dihydropyrene 205**



**205**

Using procedure 7.5, *cis*-styryl DHP **205** was obtained from the *cis*-styryl CPD **202** as orange crystals from cyclohexane, mp 152-154 $^{o}$C; $^{1}$H NMR ($CD_2Cl_2$) δ 8.26 (s, 4H, H-4,5,9,10), 8.21 (d, *J* = 7.5 Hz, 4H, H-1,3,6,8), 7.78 (t, *J* = 7.5 Hz, 2H, H-2,7), 7.15 (tt, *J* = 6.5, 1.1 Hz, 2H, H-25,26), 7.03 (m, 4H, H-21-24), 6.02 (m, 4H, H-17-20), 4.21 (d, *J* = 12.6 Hz, 2H, 13,14), 0.28 (d, *J* = 12.6 Hz, 2H, H-11,12); $^{13}$C NMR ($CD_2Cl_2$) δ 136.79 (C-15,16), 134.17 (C-3a,5a,10a,10d), 128.76 (C-17-20), 127.48 (C-13,14), 126.92 (C-4,5,9,10), 126.36 (C-21-26), 125.72 (C-1,3,6,8), 124.12 (C-2,7), 122.47 (C-11,12), 36.72 (C-10b,10c); IR ν (KBr) 3024, 844, 830, 694, 609 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 351 nm (56400), 369 (15300), 395 (25700), 487 (5100), 624 (95); EI MS *m/z* 408 ($M^+$); HR MS Calcd for $C_{32}H_{24}$: 408.1878. Found: 408.1887. Anal. Calcd: C, 94.08; H, 5.92. Found: C, 93.90; H, 6.02.

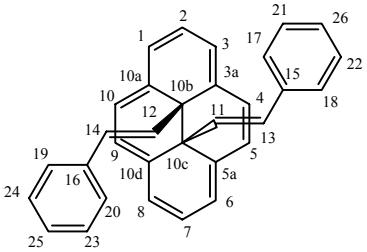
**10b-((1*E*)-2-Phenylvinyl)-10c-((1*Z*)-2-phenylvinyl)-*trans*-10b,10c-dihydropyrene 206**



**206**

*cis, trans*-Styryl DHP **206** could not be crystallized (oily film) which resulted in failure to determine melting point. $^{1}$H NMR ($CDCl_3$) δ 8.72 (d, *J* = 7.7 Hz, 2H, H-4,10), 8.64 (d, *J* = 7.7 Hz, 2H, H-1,3), 8.41 (d, *J* = 7.7 Hz, 2H, H-5,9), 8.27 (d, *J* = 7.7 Hz, 2H, H-6,8), 8.08 (t, *J* = 7.6 Hz, 1H, H-2), 7.81 (t, *J* = 7.7 Hz, 1H, H-7), 7.18 (tt, *J* = 7.4, 1.0 Hz, 1H, H-25), 7.09 (dd, *J* = 7.6, 7.4 Hz, 2H, H-21,22), 6.72 (m, 3H, H-23,24,26), 6.11 (dd, *J* = 7.8, 0.9 Hz, 2H, H-17,18), 5.99 (dd, *J* = 7.8, 1.4 Hz, 2H, H-19,20), 4.31 (d, *J* = 12.9 Hz, 1H, H-13), 3.22 (d, *J* = 15.8 Hz, 1H, H-14), 0.83 (d, *J* = 15.9 Hz, H-12), 0.41 (d, *J* = 12.9 Hz, 1H, H-11); $^{13}$C-NMR ($CDCl_3$) δ 136.50 (C-15), 136.29 (C-16), 134.02 (C-3a,10a), 133.68 (C-5a,10d), 128.55 (C-17,18), 127.79 (C-23,24), 127.17 (C-13), 126.94 (C-5,9), 126.55 (C-26), 126.07 (C-21,22,25), 125.78 (C-6,8), 125.60 (C-19,20), 125.29 (C-4,10), 124.84 (C-14), 124.19 (C-1,3), 123.96 (C-7), 123.73 (C-2), 122.57 (C-11), 120.18 (C-12), 37.29 (C-10b), 15.03(C-10c); IR ν (thin film) 3028, 1733, 1597, 1490, 1441, 1355, 1070, 958, 836, 738, 693, 599 $cm^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 256 nm (20000), 348 (54800), 389 (25300), 478 (5780), 609 (106).

**10b,10c-Bis((1*E*)-2-phenylvinyl)-*trans*-10b,10c-dihydropyrene 207**

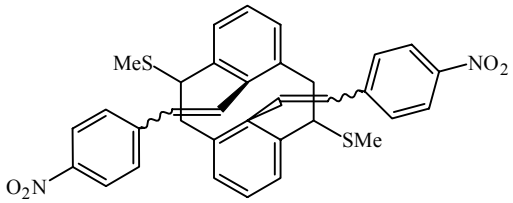



**207**

Using procedure 7.5, the all *trans*-styryl DHP **207** was obtained from CPD **204** as dark green crystals from cyclohexane, mp 232-234 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 8.85 (s, 4H, H-4,5,9,10), 8.67 (d, *J* = 7.7 Hz, 4H, H-1,3,6,8), 8.08 (t, *J* = 7.7 Hz, 2H, H-2,7), 6.75 (m,

6H, H-21-26), 6.03 (dd, *J* = 8.0, 2.5 Hz, 4H, H-17-20), 3.22 (d, *J* = 15.8 Hz, 2H, H-13,14), 0.87 (d, *J* = 15.8 Hz, 2H, H-11,12); $^{13}$C NMR ($CDCl_3$) δ 136.28 (C-15,16), 133.93 (C-3a,5a,10a,10d), 127.85 (C-21-24), 126.62 (C-25,26), 125.66 (C-17,20), 125.63 (C-4,5,9,10), 124.58 (C-1,3,6,8), 124.56 (C-13,14), 123.97 (C-2,7), 120.82 (C-11,12), 35.91 (C-10b,10c); IR ν (KBr) 3027, 1654, 1636, 1492, 1447, 959, 838, 774, 735, 717, 690 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 257 nm (47900), 342 (58000), 380 (26400), 466 (5770), 597 (165).

**8,16-Bis(2-(4-nitro-phenyl)ethenyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane 208**

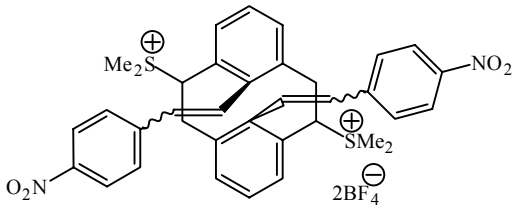



**208**

To a suspension of 4-nitrobenzyl triphenylphosphonium bromide (4 g, 8.37 mmol) in toluene (50 mL), potassium *tert*-butoxide (1.3g, 11.6 mmol) was added and heated at 50 $^{o}$C for 1hour and then 8,16-diformylthiomethylcyclophane **174** (1 g, 2.81 mmol) was added. The mixture was heated to reflux over a period of 6 h and stirred overnight. Toluene was evaporated and the crude was extracted between water and dichloromethane (5 x 40 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and evaporated. The residue was chromatographed over silica gel using dichloromethane-hexane (55: 45) to give 0.9 gram (1.51 mmol, 54%) of yellow orange **208** as a mixture of isomers.

$^1$H NMR ($CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz), 7.99 (m), 7.94 (d, *J* = 8.6 Hz), 7.90-7.76 (m), 7.42-7.05 (m), 6.51-6.31 (m), 6.02-5.90 (m), 5.42-5.20 (m), 4.43-4.23 (m), 3.96-3.85 (m), 3.17-3.05 (m), 2.98 (dd, *J* = 12.5, 3.9 Hz), 2.87 (t, *J* = 12.2 Hz), 2.68 (t, *J* = 12.5 Hz), 2.55-2.45 (m), 2.17, 2.11 (4s), 1.63 (s), 1.62 (s), 1.52 (s), 1.47 (s), 1.46 (s); HRMS Calcd for $C_{34}H_{30}N_2O_4S_2$: 594.1647. Found: 594.1657.

**8,16-Bis(2-(4-nitro-phenyl)ethenyl)-1,9-bis-(thiomethyl)-*anti*-[2.2]metacyclophane sulfonium salt 209**



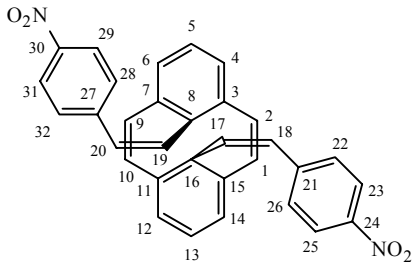

**209**

Using procedure 7.3, mixed isomers **208** (900 mg, 1.50 mmol) on reaction with Borch reagent ((80% oil, 0.9 g, 4.44 mmol) in $CH_2Cl_2$ (22 mL) gave 1.20 g (quantitative) of bis-sulfonium salt **209**: $^1$H NMR (DMSO-$d_6$) δ 8.22 (m), 7.89-7.39 (m), 6.61-6.19 (m), 4.60-4.54 (m), 4.32 (d, *J* = 12.6 Hz), 4.18 (d, *J* = 12.4 Hz), 3.44-3.32 (m), 3.26 (s), 3.25 (s), 3.23 (s), 3.20 (s), 2.95 (s), 2.94 (s), 2.92 (s), 2.87 (s), 2.81 (s).

**Bis-2-(4-nitrophenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-dienes 210-212**

Using procedure 7.4, a reaction of bis-sulfonium salt **209** (1.20 g) and *t*-BuOK (600 mg, 5.35 mmol) in THF (10 mL) gave a mixture of cyclophanedienes **210-212**. The residue was chromatographed over silica gel using hexanes: DCM 60: 40.

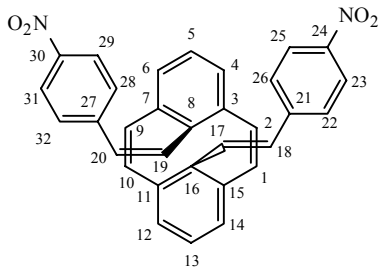
**8,16-Bis((1*Z*)-2-(4-nitrophenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-diene 210**



**210**

Eluted first was semi-pure **210** (~75% pure) which was purified by washing with $CH_2Cl_2$ to yield 88 mg (23%) of the all *cis* isomer as orange crystals, which on attempted melting point determination converts into DHP **213**: $^1$H NMR ($CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 4H, H-23,25,29,31), 7.23 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.91 (d, *J* = 8.8 Hz, 4H, H-22,26,28,32), 6.60 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.00 (s, 4H, H-17-20), 5.84 (s, 4H, H-1,2,9,10); $^{13}$C-NMR ($CDCl_3$) δ 146.22 (C-24,30), 145.83 (C-21,27), 140.80 (C-8,16), 138.15 (C-3,7,11,15), 132.56 (C-18,20), 132.51 (C-1,2,9,10), 130.88 (C-5,13), 129.42 (C-17,19), 129.18 (C-22,26,28,32), 126.56 (C-4,6,12,14), 123.30 (C-23,25,29,31); IR ν (KBr) 3045, 3008, 1592, 1512, 1339, 1106, 884, 855, 797, 772, 712 $cm^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 254 (14900), 342 (16400), 423 sh (5800); EI MS *m/z* 498 ($M^+$), 350 ($M^+$ - $NO_2$-styryl), 202 ($M^+$ - $2NO_2$ styryl); HR MS Calcd for $C_{32}H_{22}N_2O_4$: 498.1579. Found: 498.1593; Anal. Calcd: C, 76.78; H, 4.83. Found: C, 72.75; H, 4.19.

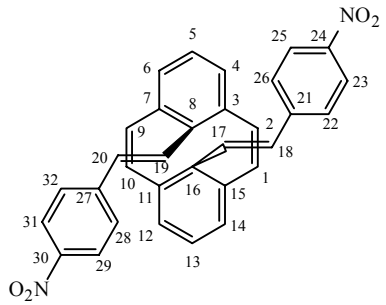
**16-((1*E*)-2-(4-Nitrophenyl)vinyl)-8-((1*Z*)-2-(4-nitrophenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-diene 211**




**211**

Eluted second was 175 mg (45%) of the unsymmetrical isomer **211** as orange red crystals from dichloromethane, which on attempted melting point determination converts into DHP **214**: $^{1}$H NMR ($CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 2H, H-29,31), 7.96 (d, *J* = 8.8 Hz, 2H, H-23,25), 7.30 (d, *J* = 8.8 Hz, 2H, H-28,32), 7.20 (t, *J* = 7.4 Hz, 1H, H-5), 6.98 (t, *J* = 7.4 Hz, 1H, H-13), 6.96 (d, *J* = 8.8 Hz, 2H, H-22,26), 6.95 (d, *J* = 16.2 Hz, 1H, H-19), 6.86 (d, *J* = 16.2 Hz, 1H, H-20), 6.76 (d, *J* = 7.4 Hz, 2H, H-4,6), 6.45 (d, *J* = 7.4 Hz, 2H, H-12,14), 6.38 (d, *J* = 11.4 Hz, 2H, H-2,9), 6.10 (s, 2H, H-17,18), 6.00 (d, *J* = 11.4 Hz, 2H, H-1,10); $^{13}$C NMR ($CDCl_3$) δ 146.71 (C-30), 146.25 (C-24), 145.75 (C-21), 144.33 (C-27), 144.81 (C-8), 139.611 (C-16), 138.55 (C-11,15), 136.92 (C-3,7), 133.25 (C-2,9), 132.98 (C-1,10), 132.69 (C-18 ), 132.27 (C-19), 130.93 (C-13), 130.67 (C-20), 130.13 (C-5), 129.60 (C-17), 129.19 (C-22,26), 127.13 (C-4,6), 126.88 (C-28,32), 126.64 (C-12,14), 124.05 (C-29,31), 123.35 (C-23,25); IR ν (KBr) 3007, 1592, 1512, 1339, 1108, 855, 795, 772, 711 $cm^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 258 (32100), 340 (25000), 435 sh (9300).

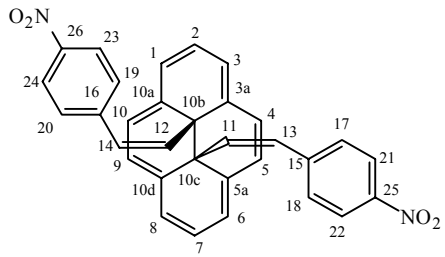
**8,16-Bis((1*E*)-2-(4-nitrophenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-diene 212**



**212**

Eluted third was 86 mg (22%) of the all *trans*-isomer **212** as red crystals, which on attempted melting point determination converts into *trans*-DHP **215**: $^{1}$H NMR ($CDCl_3$) δ 8.17 (d, *J* = 8.8 Hz, 4H, H-23,25,29,31), 7.35 (d, *J* = 8.8 Hz, 4H, H-22,26,28,32), 7.05 (d, *J* = 16.2 Hz, 2H, H-17,19), 7.00 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.96 (d, *J* = 16.2 Hz, 2H, H-18,20), 6.63 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.55 (s, 4H, H-1,2,9,10); $^{13}$C NMR ($CDCl_3$) δ 146.84 (C-24,30), 144.44 (C-21,27), 143.72 (C-8,16), 137.40 (C-3,7,11,15), 133.76 (C-1,2,9,10), 132.54 (C-17,19), 131.10 (C-18,20), 130.30 (C-5,13), 127.27 (C-4,6,12,14), 126.95 (C-22,26,28,32), 124.14 (C-23,25,29,31); IR ν (KBr) 3046, 1588, 1507, 1335, 1108, 965, 863, 817, 761, 745, 688 $cm^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 240 (27000), 258 (25400), 285 sh (18100), 369 (28800), 444 sh (13400).

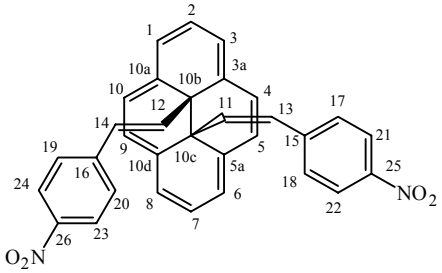
**10b,10c-Bis((1*Z*)-2-(4-nitrophenyl)vinyl)-*trans*-10b,10c-dihydropyrene 213**



**213**

Using procedure 7.5, *cis*-DHP **213** was obtained from CPD **210** as orange crystals from dichloromethane mp 243-244 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 8.28 (s, 4H, H-4,5,9,10), 8.25 (d, *J* = 7.5 Hz, 4H, H-1,3,6,8), 7.94 (d, *J* = 8.6 Hz, 4H, H-21-24), 7.86 (t, *J* = 7.6 Hz, 2H, H-2,7), 6.20 (dd, *J* = 8.7, 0.8 Hz, 4H, H-17-20), 4.18 (d, *J* = 13.2 Hz, 2H, H-13,14), 0.38 (d, *J* = 13.2 Hz, 2H, H-11,12); $^{13}$C NMR ($CDCl_3$) δ 146.60 (C-25,26), 143.78 (C-15,16), 133.40 (C-3a,5a,10a,10d), 129.19 (C-17-20), 126.91 (C-4,5,9,10), 125.91 (C-1,3,6,8), 125.24 (C-13,14), 124.26 (C-2,7), 123.35 (C-11,12), 121.36 (C-21-24), 36.12 (C-10b,10c); IR ν (KBr) 3074, 3036, 1598, 1515, 1341, 1107, 854, 842 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 281 (19500), 348 (46700), 397 (19500), 484 (5160); EI MS *m/z* 498 ($M^+$). HR MS Calcd for $C_{32}H_{22}N_2O_4$: 498.1580. Found: 498.1586.

**10b-((1*E*)-2-(4-Nitrophenyl)vinyl)-10c-((1*Z*)-2-(4-nitrophenyl)vinyl)-*trans*-10b,10c-dihydropyrene 214**

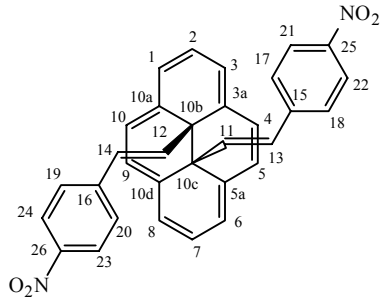



**214**

Using procedure 7.5, the unsymmetrical DHP **214** was obtained from CPD **211** as olive green crystals from dichloromethane mp 214-216 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 8.75 (d, *J* = 7.8 Hz, 2H, H-4,10), 8.68 (d, *J* = 7.7 Hz, 2H, H-1,3), 8.40 (d, *J* = 7.8 Hz, 2H, H-5,9), 8.29 (d, *J* = 7.7 Hz, 2H, H-6,8), 8.12 (t, *J* = 7.7 Hz, 1H, H-2), 7.97 (d, *J* = 8.6 Hz, 2H, H-21,22), 7.88 (t, *J* = 7.7 Hz, 1H, H-7), 7.56 (d, *J* = 9.0 Hz, 2H, H-23,24), 6.26 (d, *J* = 8.7

Hz, 2H, H-17,18), 6.08 (d, *J* = 9.0 Hz, 2H, H-19,20), 4.23 (d, *J* = 13.1 Hz, 1H, H-13), 3.25 (d, *J* = 15.8 Hz, 1H, H-14), 0.96 (d, *J* = 15.8 Hz, 1H, H-12), 0.46 (d, *J* = 13.1 Hz, 1H, H-11); $^{13}$C NMR ($CDCl_3$) δ 146.66 (C-25), 146.23 (C-26), 143.76 (C-15), 142.65 (C-16), 133.49 (C-3a,10a), 133.08 (C-5a,10d), 129.24 (C-17,18), 127.19 (C-5,9), 126.09 (C-19,20), 126.06 (C-6,8), 125.59 (C-4,10), 125.11 (C-12), 125.01 (C-13), 124.77 (C-1,3), 124.38 (C-2), 124.30 (C-7), 123.87 (C-11), 123.55 (C-14), 123.25 (C-23,24), 121.40 (C-21,22), 37.39 (C-10b), 34.78 (C-10c); IR ν (KBr) 3031, 1595, 1512, 1341, 846 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 228 (32100), 344 (65800), 387 (25800), 481 (6860), 606 (125).

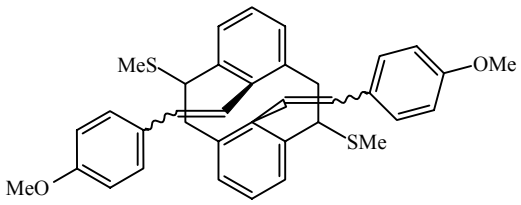
**10b,10c-Bis((1*E*)-2-(4-nitrophenylvinyl)-*trans*-10b,10c-dihydropyrene 215**




**215**

Using procedure 7.5, *trans*-DHP **215** was obtained from CPD **212** as dark green crystals from cyclohexane, mp 275-276 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 8.88 (s, 4H, H-4,5,9,10), 8.71 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 8.13 (t, *J* = 7.6 Hz, 2H, H-2,7), 7.60 (d, *J* = 8.8 Hz, 4H, H-21-24), 6.12 (d, *J* = 8.9 Hz, 4H, H-17-20), 3.28 (d, *J* = 15.7 Hz, 2H, H-13,14), 1.05 (d, *J* = 15.8 Hz, 2H, H-11,12); IR ν (KBr) 3032, 1513, 1340, 1109, 850 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 228 (16700), 340 (45900), 375 (16300), 473 (4800).

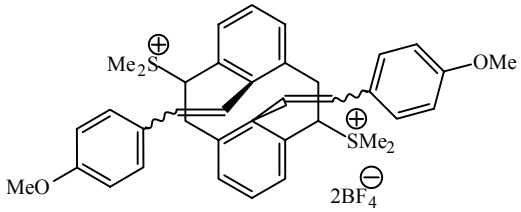
**8,16-Bis((2-(4-methoxyphenyl)ethenyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane 216**




**216**

Using the same procedure as for the synthesis of **208** except warming the reaction to 80 $^{o}$C overnight gave the cyclophane **216** (50%) as a mixture of isomers. column chromatography over silica gel using dichloromethane-hexane 4:6 eluted the desired products as pale yellow solid: $^{1}$H NMR ($CDCl_3$) 7.95-7.80 (m), 7.29-7.20 (m), 7.04-6.98 (m), 6.85-6.80 (m), 6.47-6.43 (m), 6.23 (d, *J* = 8.8 Hz), 6.18 (d, *J* = 9.0 Hz), 5.85-5.62 (m), 5.09-5.0 (m), 4.36 (dd), 4.09-3.93 (m), 3.801, 3.80, 3.798 (3 s), 3.66, 3.65 (s), 3.63, 3.62 (3s), 3.12-3.00 (m), 2.91 (t), 2.72 (AB, *J* = 12 Hz), 2.59-2.50 (m), 2.17, 2.16, 2.10, 2.09, 1.64, 1.63, 1.52, 1.45, 1.44 (9 s) ); EI MS *m/z* 564 ($M^+$); HR MS Calcd for $C_{36}H_{36}O_2S_2$: 564.2157. Found:564.2169.

**8,16-Bis((2-(4-methoxyphenyl)ethenyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane sulfonium salt 217**



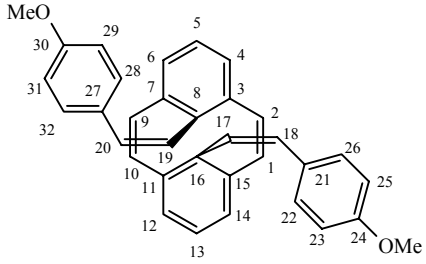

**217**

Using procedure 7.3, mixed isomers **216** (200 mg, 0.35 mmol) on reaction with Borch reagent (80% oil, 0.5 g, 2.44 mmol) in $CH_2Cl_2$ (5 mL) gave 275 mg (quantitative) of bis-sulfonium salt **217**: $^1$H NMR (DMSO-$d_6$) 7.84-7.34 (m), 7.25-7.17 (m), 6.99-6.91 (m), 6.63-6.55 (m), 6.28-5.88 (m), 4.62-4.52 (m), 3.77, 3.62 (2 s), 3.48-3.20 (6 s), 2.97, 2.94, 2.92 (3 s), 2.36, 2.34, 2.24, 2.23, 1.99 (5 s).

**Bis-2-(4-methoxyphenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-dienes 218-220**

Using procedure 7.4, a reaction of bis-sulfonium salt **217** (200 mg, 0.26 mmol) and *t*-BuOK (250 mg, 2.23 mmol) in THF (10 mL) gave a mixture of cyclophanedienes **218-220**. The residue was chromatographed over silica gel using hexanes: DCM 60:40.

**8,16-Bis((1*Z*)-2-(4-methoxyphenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-diene 218**

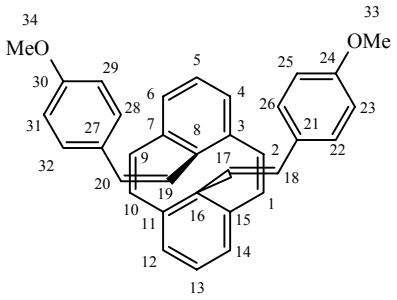



**218**

Eluted first was 19 mg of **218** (0.04 mmol, 16%) as colorless crystals, which on attempted melting point determination converts into DHP **221**: $^1$H NMR ($CDCl_3$) δ 7.15 (t, *J* = 7.3 Hz, 2H, H-5,13), 6.74 (d, *J* = 8.7 Hz, 4H, H-22,26,28,32), 6.61 (d, *J* = 8.7 Hz, 4H, H-23,25,29,31), 6.57 (d, *J* = 7.3 Hz, 4H, H-4,6,12,14), 5.91 (d, *J* = 12.4 Hz, 2H, H-18,20), 5.86 (s, 4H, H-1,2,9,10), 5.73 (d, *J* = 12.4 Hz, 2H, H-17,19), 3.74 (s, 6H, H-33,34); $^{13}$C NMR ($CDCl_3$) δ 158.26 (C-24,30), 141.89 (C-8,16), 138.18 (C-3,7,11,15), 132.37 (C-1,2,9,10), 131.36 (C-21,27), 130.86 (C-18,20), 129.71 (C-22,26,28,32), 129.56 (C-5,13), 128.25 (C-17,19), 126.16 (C-4,6,12,14), 113.32 (C-23,25,29,31), 55.34 (C-

33,34); IR ν (KBr) 3003, 2835, 1605, 1509, 1458, 1303, 1252, 1178, 1032, 832, 812, 784, 739, 517 $cm^{-1}$; UV (DCM) $\lambda_{max}$ nm ($\varepsilon_{max}$) 228 (46400), 257 (46100), 372 sh (4160); EI MS *m/z* 468 ($M^+$); HR MS Calcd for $C_{34}H_{28}O_2$: 468.2089. Found: 468.2095.

**16-((1*E*)-2-(4-Methoxyphenyl)vinyl)-8-((1*Z*)-2-(4-methoxyphenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-diene 219**

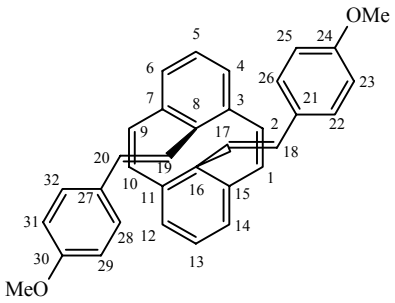



**219**

Eluted second was 57 mg (0.12 mmol, 47%) of the unsymmetrical isomer **219** as pale yellow solid, which on attempted melting point determination converts into DHP **222**: $^1$H NMR ($CDCl_3$) δ 7.17 (d, *J* = 8.8 Hz, 2H, H-22,26), 7.09 (t, *J* = 7.4 Hz, 1H, H-13), 7.02 (t, *J* = 7.3 Hz, 1H, H-5), 6.82 (d, *J* = 8.8 Hz, 2H, H-23,25), 6.78 (d, *J* = 8.7 Hz, 2H, H-28,32), 6.69 (d, *J* = 7.4 Hz, 2H, H-12,14), 6.68 (AB hidden, 2H, H-17,18), 6.65 (d, *J* = 8.6 Hz, 2H, H-29,31), 6.46 (d, *J* = 7.4 Hz, 2H, H-4,6), 6.32 (d, *J* = 11.3 Hz, 2H, H-1,10), 6.00 (d, *J* = 11.3 Hz, 2H, H-2,9), 5.98 (d, *J* = 12.3 Hz, 1H, H-20), 5.79 (d, *J* = 12.3 Hz, 1H, H-19), 3.82 (s, 3H, H-33), 3.75 (s, 3H, H-34); $^{13}$C NMR ($CDCl_3$) δ 159.20 (C-24), 158.28 (C-30), 146.48 (C-16), 140.32 (C-8), 138.64 (C-3,7), 135.89 (C-11,15), 133.05 (C-2,9), 132.83 (C-18), 132.47 (C-2,9), 131.33 (C-27), 131.10 (C-21), 131.00 (C-17), 130.06 (C-5), 129.78 (C-28,32), 128.01 (C-13), 128.28 (C-19), 128.01 (C-22,26), 126.73 (C-12,14), 126.30 (C-4,6), 113.97 (C-23,25), 113.34 (C-29,31), 55.47 (C-33),

55.33 (C-34); IR ν (KBr) 3031, 3001, 2834, 1604, 1509, 1465, 1250, 1175, 1033, 832, 812, 783 $cm^{-1}$; UV (DCM) $\lambda_{max}$ nm ($\varepsilon_{max}$) 227 (44600), 257 (50000), 283 (36300), 417 sh (4900).

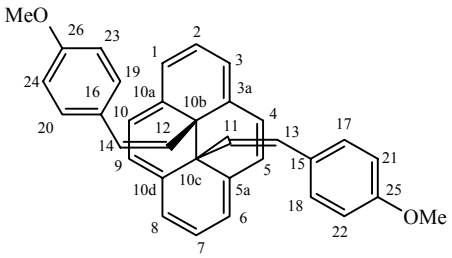
**8,16-Bis((1*E*)-2-(4-methoxyphenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-diene 220**




**220**

Eluted third was 27 mg (0.057 mmol, 22%) of the all *trans*-isomer **220** pale yellow crystals, which on attempted melting point determination converts into DHP **223**: $^{1}$H NMR ($CDCl_3$) δ 7.20 (d, *J* = 8.8 Hz, 4H, H-22,26,28,32), 6.98 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.84 (d, *J* = 8.8 Hz, 4H, H-23,25,29,31), 6.76 (AB, hidden, 4H, H-17-20), 6.60 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.45 (s, 4H, H-1,2,9,10), 3.83 (s, 6H, OMe); $^{13}$C NMR ($CDCl_3$) δ 159.24 (C-24,30), 144.84 (C-8,16), 136.41 (C-3,7,11,15), 133.14 (C-18,20), 133.11 (C-1,2,910), 131.22 (C-21,27), 128.85 (C-23,25,29,31), 128.28 (C-5,13), 128.01 (C-22,26,28,32), 127.04 (C-17,19), 126.86 (C-4,6,12,14), 55.49 (C-33,34); IR ν (KBr) 3031, 3001, 2833, 1604, 1509, 1465, 1438, 1250, 1174, 1034, 966, 810, 770, 753 $cm^{-1}$; UV (DCM) $\lambda_{max}$ nm ($\varepsilon_{max}$) 228 (50600), 263 (45700), 417 sh (6200).

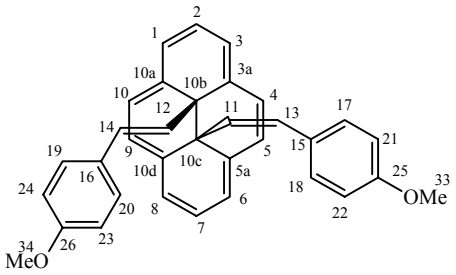
**10b,10c-Bis((1*Z*)-2-(4-methoxyphenyl)vinyl)-*trans*-10b,10c-dihydropyrene 221**




**221**

Using procedure 7.5, methoxy-styryl DHP **221** was obtained from CPD **218** as orange crystals from DCM, $^{1}$H NMR ($CD_2Cl_2$) δ 8.28 (s, 4H, H-4,5,9,10), 8.24 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 7.79 (t, *J* = 7.6 Hz, 2H, H-2,7), 6.59 (d, *J* = 8.6 Hz, 4H, H-21-24), 5.92 (d, *J* = 8.6 Hz, 4H, H-17-20), 4.12 (d, *J* = 12.8 Hz, 2H, H-13,14), 3.83 (OMe), 0.25 (d, *J* = 12.8 Hz, 2H, H-11,12); $^{13}$C NMR ($CD_2Cl_2$) δ 158.56 (C-25,26), 134.33 (3a,5a,10a,10d), 129.75 (C-17-20), 129.12 (C-15,16), 127.26 (C-13,14), 126.79 (C-4,5,9,10), 125.67 (C-1,3,6,8), 124.02 (C-2,7), 122.94 (C-11,12), 111.82 (C-21,24), 55.74 (OMe), 36.83 (10b,10c); IR ν (thin film) 3030, 2834, 1605, 1574, 1507, 1463, 1243, 1174, 1034, 960, 860, 814, 737, 704 cm$^{-1}$; UV (DCM) $\lambda_{max}$ nm ($\varepsilon_{max}$) 228 (34600), 351 (47100), 394 (25200), 486 (5500), 619 (140); EI MS *m/z* 468 ($M^+$); HR MS Calcd for $C_{34}H_{28}O_2$: 468.2089. Found: 468.2094. Anal. Calcd: C, 87.15; H, 6.02. Found: C, 82.66; H, 6.20.

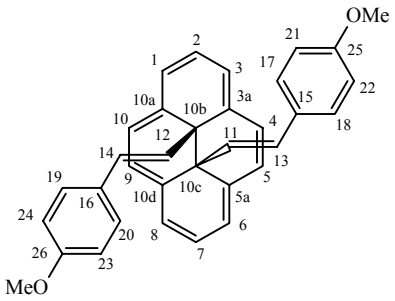
**10b-((1*E*)-2-(4-Methoxyphenyl)vinyl)-10c-((1*Z*)-2-(4-methoxyphenyl)vinyl)-*trans*-10b,10c-dihydropyrene 222**




**222**

Using procedure 7.5, methoxy-styryl DHP **222** was obtained from CPD **219** as olive green solid. Melting point could not be determined because of contamination from **223**. $^{1}$H NMR ($CD_2Cl_2$) δ 8.72 (d, *J* = 7.7 Hz, 2H, H-4,10), 8.64 (d, *J* = 7.7 Hz, 2H, 1,3), 8.44 (d, *J* = 7.7 Hz, 2H, H-5,9), 8.31 (d, *J* = 7.7 Hz, 2H, H-6,8), 8.06 (t, *J* = 7.7 Hz, 1H, H- 2), 7.83 (t, *J* = 7.7 Hz, 1H, H-7), 6.62 (d, *J* = 8.5 Hz, 2H, H-21,22), 6.25 (d, *J* = 8.8 Hz, 2H, H-23,24), 5.98 (d, *J* = 8.4Hz, 2H, H-17,18), 5.89 (d, *J* = 8.8 Hz, 2H, H-19,20), 4.20 (d, *J* = 12.8 Hz, 1H, H-13), 3.84 (s, 3H, H-33), 3.48 (s, 3H, H-34), 3.15 (d, *J* = 15.8 Hz, 1H, H-14), 0.65 (d, *J* = 15.8 Hz, 1H, H-12), 0.33 (d, *J* =12.8 Hz, 1H, H-11); $^{13}$C NMR ($CD_2Cl_2$) δ 158.96 (C-26), 158.57 (C-25), 134.40 (C-3a,10a), 134.09 (C-5a,10d), 129.83 (C-17,18), 127.16 (C-5,9), 127.06 (C-13), 126.79 (C-19,20), 126.01 (C-6,8), 125.67 (C-4,10), 124.43 (C-1,3), 124.25 (C-14), 124.17 (C-7), 123.90 (C-2), 123.41 (C-11), 118.33 (C-12), 113.59 (C-23,24), 111.85 (C-21,22), 55.72 (C-33), 55.47 (C-34), 37.67 (C-10b), 35.55 (C-10c); IR ν (thin film) 3030, 2834, 1606, 1509, 1464, 1440, 1244, 1174, 1034, 959, 842, 815, 736, 704 cm$^{-1}$; UV (DCM) $\lambda_{max}$ nm ($\varepsilon_{max}$) 225 (24300), 264 (32300), 346 (42100), 387 (21200), 472 (5400), 607 (120).

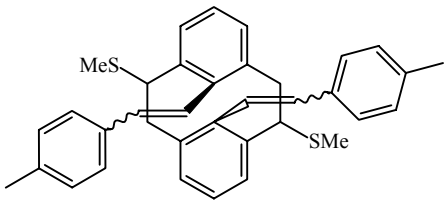
**10b,10c-Bis((1*E*)-2-(4-methoxyphenylvinyl)-*trans*-10b,10c-dihydropyrene 223**




**223**

Using procedure 7.5, methoxy-styryl DHP **223** was obtained from CPD **220** as dark green solid, **223** could not be crystallized (oily film) which resulted in failure to determine the melting point. $^{1}$H NMR ($CD_2Cl_2$) δ 8.88 (s, 4H, H-4,5,9,10), 8.70 (d, *J* = 7.7 Hz, 4H, 1,3,6,8), 8.10 (t, *J* = 7.7 Hz, 2H, H-2,7), 6.28 (d, *J* = 8.8 Hz, 4H, H-21-24), 5.95 (d, *J* = 8.8 Hz, 4H, H-17-20), 3.51 (OMe), 3.17 (d, *J* = 15.8 Hz, 2H, H-13,14), 0.70 (d, *J* = 15.8 Hz, 2H, H-11,12); $^{13}$C NMR ($CD_2Cl_2$) δ 159.01 (C-25,26), 134.48 (C-3a,5a,10a,10d), 129.83 (C-15,16), 126.84 (C-17-20), 125.98 (C-4,5,9,10), 124.80 (C1,3,6,8), 124.21 (C-13,14), 124.17 (C-2,7), 118.98 (C-11,12), 113.63 (C-21-24), 55.49 (OMe), 36.35 (C-10b,10c); IR ν (thin film) 3030, 2834, 1606, 1509, 1464, 1440, 1244, 1174, 1034, 959, 842, 815, 736, 704 cm$^{-1}$; UV (DCM) $\lambda_{max}$ nm ($\varepsilon_{max}$) 225 (31000), 265 (40200), 343 (46800), 382 (22400), 470 (6400), 606 (130).

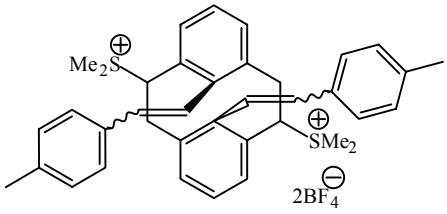
**8,16-Bis(2-(4-methylphenyl)ethenyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane 224**




**224**

Using procedure 7.6 B, a reaction of diformylthiomethylcyclophane **174** (0.8 g, 2.25 mmol) with an ylide {prepared by reaction of *t*-BuOK (1.70 g, 15.12 mmol) and 4-methylbenzyl triphenylphosphonium bromide (4.5 g, 10 mmol) in THF (45 mL)} followed by column chromatography using hexanes: dichloromethane (7:3) eluted 685 mg of **224** (1.27 mmol, 57%) as a mixture of isomers: $^1$H NMR ($CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz), 7.84 (d, *J* = 7.7 Hz), 7.83-7.80 (m), 7.44-6.94 (m), 6.76-6.69 (m), 6.24 (d, *J* = 8.2 Hz), 6.20 (d, *J* = 8.2 Hz), 6.16 (d, *J* = 8.6 Hz), 6.14 (d, *J* = 8.3 Hz), 6.10 (d, *J* = 8.2 Hz), 5.92 (d, *J* = 12.3 Hz), 5.87 (d, *J* = 12.4 Hz), 5.82 (d, *J* = 12.4 Hz), 5.68 (d, *J* = 16.3 Hz), 5.23 (d, *J* = 16.3 Hz), 5.10 (d, *J* = 16.3 Hz), 4.35 (dd, *J* = 11.5, 4.0 Hz), 4.15-3.95 (m), 3.14-2.87 (m), 2.75-2.51 (m), 2.36, 2.32, 2.28, 2.26 (4s), 2.17, 2.16, 2.15, 2.12, 2.11, 2.10 (s), 2.03 (s), 1.61, 1.60, 1.42, 1.40 (s) ); EI MS *m/z* 532 ($M^+$); HR MS Calcd for $C_{36}H_{36}S_2$: 532.2258. Found: 532.2253.

**8,16-Bis(2-(4-methylphenyl)ethenyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane sulfonium salt 225**




**225**

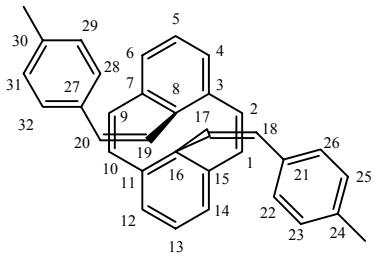
Using procedure 7.3, mixed isomers **224** (650 mg, 1.21 mmol) on reaction with Borch reagent (80% oil, 1.0 g, 4.84 mmol) in $CH_2Cl_2$ (7 mL) gave 510 mg (0.69 mmol, 57%) of bis-sulfonium salt **225**: $^1$H NMR (DMSO-$d_6$) δ 7.83 (d, *J* = 7.7 Hz), 7.75 (d, *J* = 7.6 Hz), 7.71-7.50 (m), 7.47 (t, *J* = 7.6 Hz), 7.20-7.10 (m), 6.86-6.76 (m), 6.24-6.05 (m),

6.00-5.87 (m), 5.46 (d, *J* = 16.4 Hz), 5.30 (d, *J* = 16.6 Hz), 4.53 (br d), 4.26-3.97 (m), 3.30, 3.22, 3.21, 3.20, 3.18 (s), 2.98-2.78 (m), 2.30, 2.28 (3 s), 2.18, 2.10, 1.96 (4 s).

**Bis-2-(4-methylphenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-dienes 226-228**

Using procedure 7.4, a reaction of bis-sulfonium salt **225** (470 mg, 0.63 mmol) and *t*-BuOK (200 mg, 1.79 mmol) in THF (8 mL) gave a mixture of cyclophanedienes **226-228**. The residue was chromatographed over silica gel using hexanes: DCM 90:10.

**8,16-Bis((1*Z*)-2-(4-methylphenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-diene 226**

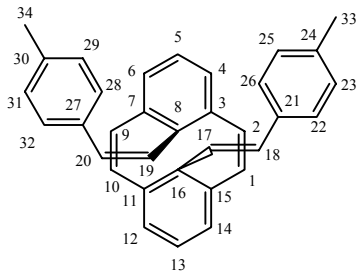



**226**

Eluted first was 116 mg of **226** (0.27 mmol, 42%) as colorless crystals which on attempted melting point determination converts into DHP **229**: $^{1}$H NMR ($CDCl_3$) δ 7.16 (t, *J* = 7.3 Hz, 2H, H-5,13), 6.88 (d, *J* = 8.0 Hz, 4H, H-23,25,29,31), 6.70 (d, *J* = 8.0 Hz, 4H, H-22,26,28,32), 6.57 (d, *J* = 7.3 Hz, 4H, H-4,6,12,14), 5.94 (d, *J* = 12.4 Hz, 2H, H-18,20), 5.85 (s, 4H, H-1,2,9,10), 5.78 (d, *J* = 12.4 Hz, 2H, H-17.19), 2.25 (s, 6H, Me); $^{13}$C NMR (CDCl3) δ 141.81 (C-8,16), 138.18 (C-3,7,11,15), 136.01 (C-24,30). 135.84 (C-21,27), 132.37 (C-1,2,9,10), 131.31 (C-18,20), 129.62 (C-5,13), 128.87 (C-17,19), 128.57 (C-23,25,29,31), 128.40 (C-22,26,28,32), 126.13 (C-4,6,12,14), 21.36 (C-33,34); IR ν (KBr) 3041, 3015, 3003, 1560, 1508, 1370, 1405, 1151, 859, 817, 782, 749, 737, 594 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 257 (30100), 277 (24000), 392 (3300); EI MS

*m/z* 436 ($M^+$); HR MS Calcd for $C_{34}H_{28}$: 436.2191. Found: 436.2205; Anal. Calcd: C, 93.54; H, 6.46. Found: C, 92.80; H, 6.46.

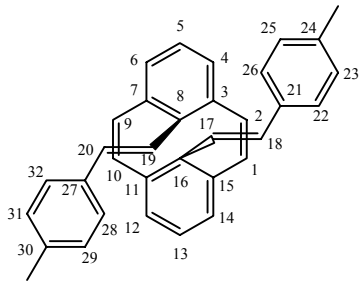
**16-((1*E*)-2-(4-Methylphenyl)vinyl)-8-((1*Z*)-2-(4-methylphenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-diene 227**




**227**

Eluted second was 105 mg (24 mmol, 38%) of the unsymmetrical isomer **227** as pale yellow crystals from cyclohexane, which on attempted melting point determination converts into DHP **230**: $^1$H NMR ($CDCl_3$) δ 7.12 (d, *J* = 8.3 Hz, 2H, H-22,26), 7.10 (t, *J* = 7.5 Hz, 1H, H-13), 7.08 (d, *J* = 8.4 Hz, 2H, H-23,25), 7.01 (t, *J* = 7.4 Hz, 1H, H-5), 6.90 (d, *J* = 8.0 Hz, 2H, H-29,31), 6.74 (m, 4H, H-17,18,28,32), 6.71 (d, *J* = 7.4 Hz, 2H, H-12,14), 6.47 (d, *J* = 7.4 Hz, 2H, H-4,6), 6.33 (d, *J* = 11.3 Hz, 2H, H-1,10), 6.02 (d, *J* = 12.3 Hz, H-20), 6.00 (d, *J* = 11.4 Hz, 2H, H-2,9), 5.83 (d, *J* = 12.3 Hz, 1H, H-19). 2.34 (s, 3H, H-33), 2.26 (s, 3H, H-34); $^{13}$C NMR (CDCl3) δ 146.34 (C-16), 140.24 (C-8), 137.16 (C-24), 138.58 (C-3,7), 136.09 (C-30), 136.07 (C-11,15), 135.78 (C-27), 133.20 (C-18), 132.98 (C-1,10), 132.64 (C-2,9), 131.47 (C-20), 130.17 (C-5), 129.20 (C-13), 128.90 (C-19), 128.62 (C-29,31), 128.46 (C-28,32), 127.84 (C-17), 126.75 (C-12,14), 126.73 (C-22,26), 126.30 (C-4,6), 21.48 (C-33), 21.38 (C-34) IR ν (thin film) 3045, 3019, 3005, 1510, 1436, 1265, 963, 868, 816, 805, 786, 777, 746, 702, 647 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 252 (60000), 280 (48400), 413 sh (6600).

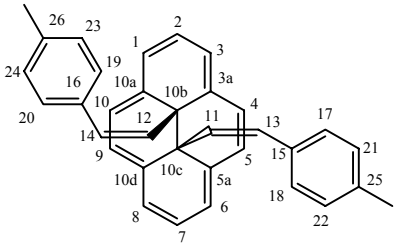
**8,16-Bis((1*E*)-2-(4-methylphenyl)vinyl)-*anti*-[2.2]metacyclophane-1,9-diene 228**



**228**

Eluted third was 30 mg (0.07 mmol, 11%) of the all *trans*-isomer **228** as pale yellow crystals which on attempted melting point determination converts into DHP **231**: $^{1}$H NMR ($CDCl_3$) δ 7.16 (AB, *J* = 8.1 Hz, 4H, H-22,26,28,32), 7.10 (AB, *J* = 8.1 Hz, 4H, H-23,25,29,31), 6.98 (t, *J* = 7.3 Hz, 2H, H-5,13), 6.81 (AB, *J* = 16.2, 4H, H-17-20), 6.60 (d, *J* = 7.3 Hz, 4H, H-4,6,12,14), 6.46 (s, 4H, H-1,2,9,10) 2.34 (s, 6H, Me); $^{13}$C NMR (CDCl3) δ 144.70 (C-8,16), 137.21 (C-24,30), 136.53 (C-3,7,11,15), 135.47 (C-21,27), 133.52 (C-18,20), 133.19 (C-1,2,9,10), 129.23 (C-23,25,29,31), 129.06 (C-5,13), 127.93 (C-17,19), 126.90 (C-4,6,12,14), 126.72 (C-22,26,28,32). 21.49 (C-33,34, Me) ; IR ν (KBr) 3045, 3022, 3003, 1560, 1513, 1458, 1429, 960, 797, 755, 653, 631 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 257 (53500), 285 (53000), 313 (48700), 410 sh (6100).

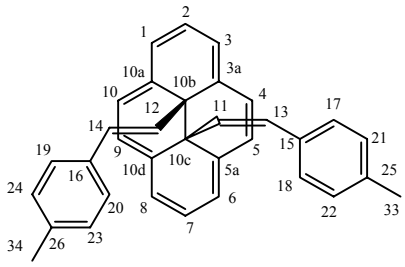
**10b,10c-Bis((1*Z*)-2-(4-methylphenyl)vinyl)-*trans*-10b,10c-dihydropyrene 229**



**229**

Using procedure 7.5, *cis*-styryl DHP **229** was obtained from CPD **226** as orange crystals from cyclohexane, $^{1}$H NMR ($CD_2Cl_2$) δ 8.25 (s, 4H, H-4,5,9,10), 8.22 (d, *J* = 7.5 Hz, 4H, H-1,3,6,8), 7.78 (t, *J* = 7.5 Hz, 2H, H-2,7), 6.84 (d, *J* = 7.6 Hz, 4H, H-21-24), 5.89 (d, *J* = 7.5 Hz, 4H, H-17-20), 4.17 (d, *J* = 12.9 Hz, 2H, H-13,14), 2.34 (s, 6H, Me) 0.25 (d, *J* = 12.9 Hz, 2H, H-11,12); $^{13}$C NMR ($CD_2Cl_2$) δ 135.84 (C-25,26), 134.19 (C-3a,5a,10a,10d), 133.70 (C-15,16), 128.60 (17-20), 127.51 (C-13,14), 127.01 (C-21-24), 126.88 (C-4,5,9,10), 125.71 (C-1,3,6,8), 124.04 (C-2,7), 122.47 (C-11,12), 36.72 (C-10b,10c), 21.47 (Me); IR ν (KBr) 3038, 3019, 1507, 1345, 860, 836, 607 cm$^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 227 (37500), 353 (68800), 396 (33300), 490 (6300), 624 (130); EI MS *m/z* 436 ($M^+$); HR MS Calcd for $C_{34}H_{28}$: 436.2191. Found: 436.2197; Anal. Calcd: C, 93.54; H, 6.46. Found: C, 88.69; H, 6.78.

**10b-((1*E*)-2-(4-Methylphenyl)vinyl)-10c-((1*Z*)-2-(4-methylphenyl)vinyl)-*trans*-10b,10c-dihydropyrene 230**

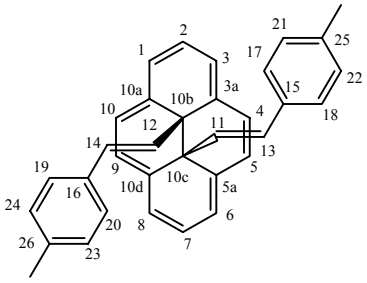



**230**

Using procedure 7.5, *p*-methyl-styryl DHP **230** was obtained from CPD **227** as olive green solid. The dihydropyrene **230** could not be crystallized (oily film) which resulted in failure to determine the melting point. $^{1}$H NMR ($CD_2Cl_2$) δ 8.72 (d, *J* =7.7 Hz, 2H, H-4,10), 8.63 (d, *J* = 7.7 Hz, 2H, H-1,3), 8.41 (d, *J* = 7.7 Hz, 2H, H-5,9), 8.28 (d, *J* =

7.7 Hz, 2H, H-6,8), 8.06 (t, *J* = 7.7 Hz, 1H, H-2), 7.82 (t, *J* = 7.7 Hz, 1H, H-7), 6.89 (d, *J* = 7.7 Hz, 2H, H-21,22), 6.51 (d, *J* = 8.1, 2H, H-23,24), 5.95 (d, *J* = 7.4 Hz, 2H, H-17,18), 5.84 (d, *J* = 8.3 Hz, 2H, H-19,20), 4.22 (d, *J* = 12.8 Hz, 1H, H-13), 3.17 (d, *J* = 15.9 Hz, 1H, H-14), 2.36 (s, 3H, H-33), 1.96 (s, 3H, H-34), 0.73 (d, *J* = 15.9 Hz, 1H, H-12), 0.32 (d, *J* = 12.9 Hz, 1H, H-11); $^{13}$C NMR ($CD_2Cl_2$) δ 136.94 (C-26), 135.91 (C-25), 134.43 (C-3a,10a), 134.10 (C-5a,10d), 133.69 (C-15), 133.57 (C-16), 128.87 (C-23,24), 128.70 (C-17,18), 127.38 (C-13), 127.27 (C-5,9), 127.08 (C-21,22), 126.10 (C-6,8), 125.53 (C-19,20), 124.89 (C-14), 124.44 (C-1,3), 124.31 (C-7), 123.92 (C-2), 122.94 (C-11), 119.57 (C-12), 37.67 (C-10b), 35.47 (C-10c), 21.49 (C-33), 21.03 (C-34); IR ν (thin film) 3025, 2921, 2851, 1637, 1512, 1458, 1123, 962, 840, 801, 711 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 227 (24500), 257 (28900), 347 (42900), 387 (19100), 478 (4300), 607 (100).

**10b,10c-Bis((1*E*)-2-(4-methylphenylvinyl)-*trans*-10b,10c-dihydropyrene 231**

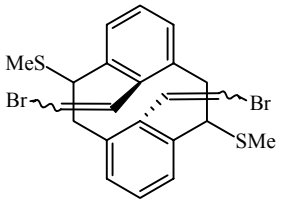



**231**

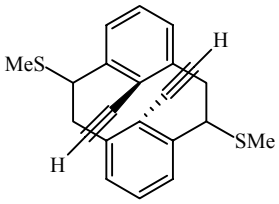
Using procedure 7.5, *trans*-styryl DHP **231** was obtained from CPD **228** as dark green solid. DHP **231** could not be crystallized (oily film) which resulted in failure to determine the melting point. $^1$H NMR ($CD_2Cl_2$) δ 8.88 (s, 4H, H-4,5,9,10), 8.69 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 8.10 (t, *J* = 7.6 Hz, 2H, H-2,7), 6.55 (d, *J* = 8.2 Hz, 4H, H-21-24), 5.89 (d, *J* = 8.2 Hz, 4H, H-17-20), 3.19 (d, *J* = 15.8 Hz, 2H, H-13,14), 1.99 (s, Me), 0.79

(d, *J* = 15.8 Hz, 2H, H-11,12); $^{13}$C NMR ($CD_2Cl_2$) δ 137.00 (C-25,26), 134.39 (C-3a,5a,10a,10d), 133.54 (C-15,16), 128.90 (C-21-24), 126.00 (C-4,5,9,10), 125.60 (C-17-20), 124.85 (C-1,3,6,8), 124.67 (C-13,14), 124.25 (C-2,7), 120.13 (C-11,12), 36.33 (C-10b,10c) 21.04 (Me); IR ν (KBr) 3025, 2921, 2851, 1637, 1512, 1458, 962, 840, 801, 711 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 227 (19100), 259 (33700), 343 (40300), 380 (21000), 468 (5400), 593 (170) ;

**8,16-Bis(ethynyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane 233**




**232**



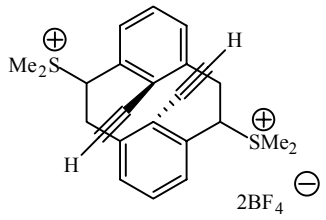

**233**

Using procedure 7.6 B, a reaction of diformylthiomethylcyclophane **174** (1.0 g, 2.81 mmol) with an ylide {prepared by reaction of *t*-BuOK (3.0 g, 26.8 mmol) and bromomethyl triphenylphosphonium bromide (2.76 g, 6.3 mmol) in THF (25 mL)} followed by column chromatography using hexanes: dichloromethane (7:3) eluted 600 mg of **232/233** as a mixture of isomers.

$^1$H NMR ($CDCl_3$ ) δ 7.86 (d, *J* = 7.6 Hz), 7.84 (d, *J* = 7.7 Hz), 7.67-7.62 (m), 7.55-7.52 (m), 7.47-7.41 (m), 7.30-7.25 (m), 7.19 (t, *J* = 7.5 Hz), 7.06 (t, *J* = 7.3 Hz), 5.83-5.73 (m), 4.58 (d, *J* = 7.8 Hz), 4.54 (d, *J* = 7.6 Hz), 3.89 (dd, *J* = 11.5, 4.0 Hz), 3.80 (dd, *J* = 711.5, 3.9 Hz), 3.17-3.13 (m), 2.55 (t, *J* = 12.5 Hz), 2.44 (t, *J* = 12.1 Hz), 2.17, 2.15, 2.12, 2.10 (4 s); $^{13}$C NMR ($CDCl_3$) δ 144.44, 143.02, 141.72, 141.24, 136.12, 135.9, 135.87, 134.94, 133.17, 132.70, 132.27, 132.14, 132.12, 132.04, 131.42, 130.21, 129.76, 129.58, 129.18, 128.93, 128.75, 128.65, 128.47, 128.36, 127.97, 127.89, 127.59, 127.50,

127.26, 127.07, 126.30, 125.92, 125.20, 124.89, 123.49, 110.24, 109.47, 109.32, 109.04, 108.96, 87.24, 54.02, 53.53, 53.31, 52.96, 50.72, 46.15, 44.12, 44.05, 43.59, 29.9, 28.4, 22.89, 21.09, 17.56, 16.86, 16.95, 15.90, 15.62, 14.31.

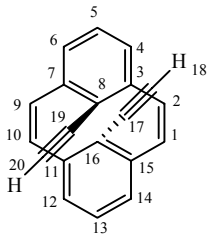
**8,16-Bis(ethynyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane sulfonium salts 233**




**234**

Using procedure 7.3, mixed isomers of **232**/**233** (600 mg) on reaction with Borch reagent (80% oil, 1.0 g, 4.84 mmol) in $CH_2Cl_2$ (7 mL) gave 600 mg of bis-sulfonium salt **234**: $^1$H NMR (DMSO-$d_6$) δ 7.81 (d, $J$ = 7.8 Hz), 7.69 (d, $J$ = 7.5 Hz), 7.62 (d, $J$ = 7.6 Hz), 7.52 (d, $J$ = 7.6 Hz), 7.41 (t, $J$ = 7.6 Hz), 7.27 (t, $J$ = 7.2 Hz), 6.41 (d, $J$ = 7.6 Hz), 6.36 (d, $J$ = 7.8 Hz), 6.25 (d, $J$ = 8.0 Hz), 5.08 (d, $J$ = 7.7 Hz), 4.74 (d, $J$ = 7.8 Hz), 4.57 (dd, $J$ = 11.2, 3.3 Hz), 4.48-4.42 (m), 3.55-3.50 (m), 3.33, 3.32 (2s), 2.86, 2.84 (s), 2.93-2.74 (m).

**8,16-Diethynyl-*anti*-[2.2]metacyclophane-1,9-diene 235**



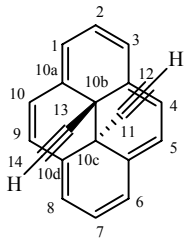

**235**

Using procedure 7.4, a reaction of bis-sulfonium salt **234** (650 mg, 1.18 mmol) and *t*-BuOK (600 mg, 5.35mmol) in THF (20 mL) followed by colunm chromatographed

over silica gel using hexane-$CH_2Cl_2$ 90: 10 gave diethynyl CPD **235 (**100 mg, 0.4 mmol). Other products include **237** and **240** in variable quantities.

On attempted melting point determination, diethynyl CPD **235** isomerizes into diethynyl DHP **236**. $^1$H NMR ($CDCl_3$) δ 7.19 (t, *J* = 7.5 Hz, 2H, H-5,13), 6.75 (d, *J* = 7.5 Hz, 4H, H-4,6,12,14), 6.49 (s, 4H, H-1,2,9,10), 2.84 (H-18,20); $^{13}$C NMR ($CDCl_3$) δ 141.11 (C-3,7,11,15), 133.86 (C-1,2,9,10), 131.44 (C-5,13), 129.78 (C-8,16), 126.45 (C-4,6,12,14), 83.39 (C-18,20), 81.84 (C-17,19); IR ν (KBr) 3293, 3050, 3005, 2578, 1727, 1427, 1262, 857, 805, 755, 655 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 235 (35800), 281 (12900); EI MS *m/z* 252 ($M^+$, 100%); HR MS Calcd for $C_{20}H_{12}$: 252.0939. Found: 252.0923.

**10b,10c-Diethynyl-*trans*-10b,10c-dihydropyrene 236**

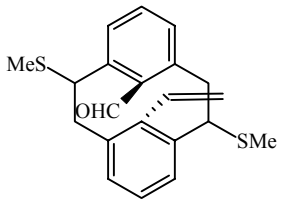



**236**

Using procedure 7.5, diethynyl DHP **236** was obtained from diethynyl CPD **235** as dark green crystals from DCM, mp 245-250 $^o$C (dec); $^1$H NMR ($CDCl_3$) δ 8.88 (s, 4H, H-4,5,9,10), 8.74 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 8.27 (t , *J* = 7.7 Hz, 2H, H-2,7), -0.09 (s, 2H, H-12,14); $^{13}$C NMR ($CDCl_3$) δ 132.89 (C-3a,5a,10a,10d), 125.54 (C-4,5,9,10), 124.58 (C-2,7), 123.83 (C-1,3,6,8), 75.36 (C-11,13), 65.00 (C-12,14), 30.00 (C-10b, 10c); IR ν (KBr) 3264, 3042, 1654, 1353, 845, 756, 662 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 223 (2900), 229 (7900), 336 (9700), 372 (42700), 399 (4400), 452 (7200), 535

(100), 596 (130), 639 (210); EI MS *m/z* 252 ($M^+$); HR MS Calcd for $C_{20}H_{12}$: 252.0939. Found. 252.0923: Calcd. Anal: C, 95.21; H, 4.79. Found: C, 94.15; H, 4.91.

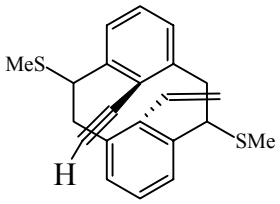
**1,9-Bis(thiomethyl)-8-formyl-16-vinyl-*anti*-[2.2]metacyclophane 264**



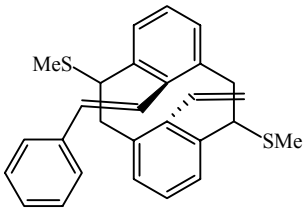

**264**

BuLi (2.4 mL of 2.5M in hexanes, 6 mmol) was added dropwise to a suspension of methyl triphenylphosphonium bromide (3.6 g, 10.08 mmol) in THF (40 mL) under argon at 0 $^oC$ and the mixture was stirred for 20 minutes at room temperature. To this solution, diformylcyclophane **174** (1.5 g, 4.21 mmol) was added and the reaction mixture was allowed to stir for 1.5 h and then quenched with water. The resulting solution was extracted with $CH_2Cl_2$ (4 x 40 mL), dried over anhydrous $MgSO_4$ and evaporated. The crude mixture was chromatographed over silica gel using hexane: dichloromethane (7:3) to give mono vinyl thiomethylcyclophane **264** (690 mg, 1.95 mmol, 46%) as a mixture of isomers.

$^1H$ NMR ($CDCl_3$) 8.92 (s), 8.72 (s), 8.07-7.72 (m), 7.41-7.07 (m), 5.12 (dd, $J$ = 11.4, 5.0 Hz), 4.99 (dd, $J$ = 11.6, 4.6 Hz), 4.85-4.45 (m), 4.35-4.25 (m), 4.16-4.07 (m), 3.39-3.09 (m), 2.96-2.54 (m), 2.16, 2.15, 2.146, 2.137, 2.135, 2.131, 2.124, 2.119 (singlets); HR MS Calcd for $C_{21}H_{22}OS_2$: 354.1112. Found: 354.1107.




**265**

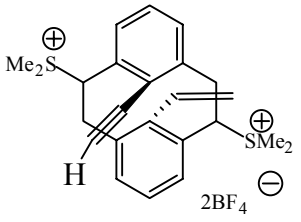



**266**

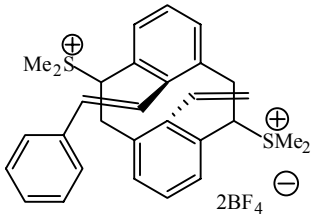
Using procedure 7.6 B, a reaction of diformylthiomethylcyclophane **174** (0.6 g, 1.7 mmol) with an ylide {prepared by reaction of *t*-BuOK (1.1 g, 10 mmol) and bromomethyl triphenylphosphonium bromide (1.6 g, 3.7 mmol) in THF (25 mL)} followed by column chromatography using hexanes: dichloromethane (7:3) eluted 360 mg of **265** and **266** as a mixture of isomers.

$^1$H NMR ($CDCl_3$) δ 7.88-7.86 (m), 7.84 (d, *J* = 7.6 Hz), 7.78 (d, *J* = 7.6 Hz), 7.75 (m), 7.69 (dd, *J* = 7.7, 1.8 Hz), 7.63 (m), 7.43 (t, *J* = 7.6 Hz), 7.37-6.97 (m), 5.81 (d, *J* = 16.4 Hz), 5.72 (d, *J* = 16.4 Hz), 5.27 (d, *J* = 16.3 Hz), 5.16 (d, *J* = 16.4 Hz), 4.86-3.86 (m), 3.4-2.65 (m), 2.59 (dd, *J* = 11.8 Hz)), 2.15-217 (9 singlets); EI MS *m/z* 428($M^+$, **266**), 350($M^+$, **265**); HR MS, Calcd for $C_{28}H_{28}S_2$: 428.1632. Found: 428.1633. Calcd for $C_{22}H_{22}S_2$: 350.1162. Found: 350.1161.

**Thiomethylcyclophane sulfonium salts 267 and 268**




**267**




**268**

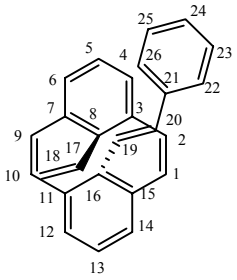
Using procedure 7.3, mixed isomers of **265** and **266** (300 mg) on reaction with Borch reagent (80% oil, 0.5 g, 2.47 mmol) in $CH_2Cl_2$ (5 mL) gave 280mg of bis-

sulfonium salts **267** and **268**, $^1$H NMR (DMSO-$d_6$) δ 7.80-7.15 (m), 5.95 (two doublets, *J* = 16.4 Hz), 5.53 (d, *J* = 16.4 Hz), 5.36 (d, *J* = 16.4 Hz), 5.13-4.53 (m), 4.42 (two doublets, *J* = 11.3 Hz), 4.22 (m), 3.6-3.0 (m), 3.3 (s), 2.9 (s).

**Unsymmetrical cyclophanedienes with internal vinyl groups**

Using procedure 7.4, a reaction of bis-sulfonium salt mixture of **267** and **268** (280 mg) and *t*-BuOK (420 mg, 3.75 mmol) in THF (8 mL) followed by colunm chromatography over silica gel using hexane-$CH_2Cl_2$ 95: 5 first eluted the 8-styryl-16-vinyl cyclophanediene **240** (~ 17%) as colorless crystals from cyclohexane which on attempted melting point determination converts into DHP **241**.

**16-((1*E*)-2-Phenylvinyl)-8-vinyl-*anti*-[2.2]metacyclophane-1,9-diene 240**



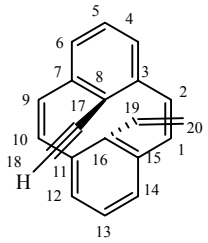

**240**

$^1$H NMR ($CDCl_3$) δ 7.29 (m, 2H, H-23,25), 7.24 (dd, *J* = 7.0, 1.5 Hz, 2H, H-22,26), 7.20 (tt, *J* = 7.0, 1.5 Hz, 1H, H-24), 7.08 (t, *J* = 7.4 Hz, 1H, H-13), 6.99 (t, *J* = 7.4 Hz, 1H, H-5), 6.81 (AB, *J* = 16.1, 2H, H-19,20), 6.64 (d, *J* = 7.4 Hz, 2H, H-12,14), 6.58 (d, *J* = 7.4 Hz, 2H, H-4,6), 6.43 (AB, *J* = 11.45, 4H, H-1,2,9,10), 6.39 (dd, *J* = 17.5, 11.0 Hz, 1H, H-17(-CH=$CH_2$)), 5.49 (dd, *J* = 17.4, 1.7Hz, 1H, H–18b*), 4.88 (dd, *J* = 11, 1.7 Hz, 1H, H-18a*); $^{13}$C NMR ($CDCl_3$) δ 145.72 (C-16), 145.25 (C-8), 138.16 (C-21), 136.32 (C-11,15), 136.18 (C-3,7), 135.36 (C-17), 133.64 (C-20), 133.43, 133.09 (C-1,2,9,10), 129.41 (C-5), 129.35 (C-13), 128.66 (C-19), 128.48 (C-23,25), 127.38 (C-24),

126.88 (C-4,6), 126.80 (C-22,26), 126.78 (C-12,14), 118.76 (C-18); IR ν (KBr) 3044, 3007, 1741, 1449, 964, 909, 805, 758, 769, 692 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 261 (28500), 275 (26300), 400 sh (4000); EI MS *m/z* 332 ($M^+$), 227 ($M^+$ - styryl), 202 (100); HR MS Calcd for $C_{26}H_{20}$: 332.1565. Found: 332.1568.

* "a" stands for the *trans*-vinyl protons whereas "b" stands for the *cis*-vinyl proton.

**8-Ethynyl-16-vinyl-*anti*-[2.2]metacyclophane-1,9-diene 237**

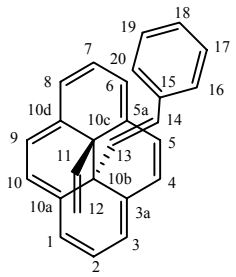



**237**

Hexanes: DCM (92:08) eluted 8-ethynyl-16-vinyl cyclophanediene **237** (~20%) as colorless crystals which on attempted melting point determination converts into DHP **238**: $^1$H NMR ($CDCl_3$) δ 7.19 (t, *J* = 7.4 Hz, 1H, H-5), 7.06 (t, *J* = 7.4 Hz, 1H, H-13), 6.69 (d, *J* = 7.3 Hz, 2H, H-12,14), 6.67 (d, *J* = 7.2 Hz, 2H, H-4,6), 6.56 (d, *J* = 11.4 Hz, 2H, H-1,10), 6.34 (d, *J* = 11.4 Hz, 2H, H-2,9), 6.33 (dd, *J* = 17.3, 11.0 Hz, 1H, H-19, (-CH=$CH_2$)), 5.46 (dd, *J* = 17.4, 1.7 Hz, 1H, H-20b*), 4.81 (dd, *J* = 11.0, 1.7 Hz, 1H, H-20a*), 2.81 (s, H-18); $^{13}$C NMR ($CDCl_3$) δ 147.88 (C-16), 141.03 (C-33,7), 136 (C-1,10), 134.77 (C-19), 131.26 (C-5), 131.13 (C-2,9), 129.73 (C-13), 128.81 (C-8), 127.08 (C-12,14), 126.20 (C-4,6), 118.75 (C-20), 82.28, 81.96 (C-17,18); IR ν (KBr) 3303, 3047, 3005, 2580, 1615, 1427, 908, 860, 804, 768, 755, 653, 597 $cm^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 239 (24000), 281 (10900), 355 sh (2800); EI MS *m/z* 254 ($M^+$); HR MS Calcd for $C_{20}H_{14}$: 254.1095. Found: 254.1094.

* "a" stands for the *trans*-vinyl protons whereas "b" stands for the *cis*-vinyl proton.

**10b-((1*E*)-2-Phenylvinyl)-10c-vinyl-*trans*-10b,10c-dihydropyrene 241**

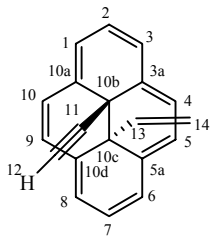



**241**

Using procedure 7.5, vinyl-styryl DHP **241** was obtained from CPD **240** as dark green crystals from cyclohexane, mp 147-148 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 8.83 (AB, *J* = 7.9 Hz, 4H, H-4,5,9,10), 8.68 (d, *J* = 7.7 Hz, 2H, H-1,3), 8.65 (d, *J* = 7.7 Hz, 2H, H-6,8), 8.10 (t, *J* = 7.5 Hz, 1H, H–2), 8.08 (t, *J* = 7.5 Hz, 1H, H-7), 6.73 (m, 3H, H-17,18,19), 6.03 (dd, *J* = 7.5, 1.7 Hz, 2H, H-16,20), 3.21 (d, *J* = 15.6 Hz, 1H, H-14), 2.70 (dd, *J* = 10.3, 1.4 Hz, 1H, H-12a*), 2.08 (dd, *J* = 17.0, 1.5 Hz, 1H, H-12b*), 0.84 ( d, *J* = 16.1 Hz, 1H, H-13), 0.54 (dd, *J* = 17.0, 10.3 Hz, 1H, H-11(-CH=$CH_2$)); $^{13}$C- NMR ($CDCl_3$) δ 136.22 (C-15), 133.93 (C-5a,10d), 133.76 (C-3a,10a), 128.64 (C-11), 127.83 (C-17,19), 126.62 (C-18), 125.63 (C-16,20), 125.57, 125.52 (C-4,5,9,10), 124.54 (C-6,8), 124.45 (C-14), 123.87 (C-2,7), 120.70 (C-13), 109.85 (C-12), 36.37 (C-10c), 35.61(C-10b); IR ν (KBr) 3028, 959, 917, 839, 744, 691; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 253 (18900), 341 (73700), 466 (6400), 609 (110); EI MS *m/z* 332 ($M^+$), 227($M^+$ - styryl, 100%); HR MS Calcd for $C_{26}H_{20}$: 332.1565. Found: 332.1565. Calcd. Anal: C, 93.94; H, 6.06. Found: C, 92.27; H, 6.26.

* "a" stands for the *trans*-vinyl protons whereas "b" stands for the *cis*-vinyl proton.

**10b-Ethynyl-10c-vinyl-*trans*-10b,10c-dihydropyrene 238**

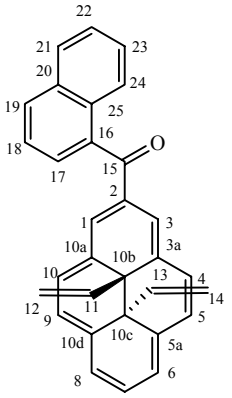



**238**

Using procedure 7.5, vinyl-ethynyl DHP **238** was obtained from CPD **237** as dark green crystals from cyclohexane, mp 216-217 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ 8.91 (AB, *J* = 7.8 Hz, 2H, H-5,9), 8.80 (AB, *J* = 7.8 Hz, H-4,10), 8.70 (overlapping doublets, 4H, H-1,3,6,8), 8.21 (t, *J* = 7.7 Hz, 1H, H-2), 8.17 (t, *J* = 7.7 Hz, 1H, H-7), 2.74 (dd, *J* = 10.3, 1.3 Hz, 1H, H-14a*), 2.16 (dd, *J* = 16.9, 1.3 Hz, 1H, H-14b*), 0.49 (dd, *J* = 16.9, 10.3 Hz, 1H, H-13 (-CH=$CH_2$)), -0.14 (s, H-12); $^{13}$C NMR ($CDCl_3$) δ 135.20 (C-5a,10a), 131.40 (C-3a,10a), 126.13 (C-13), 125.70 (C-5,9), 125.39 (C-4,10), 124.83 (C-7), 124.63, 123.65 (C-1,3,6,8), 123.57 (C-2), 111.27 (C-14), 77.73 (C-11), 63.44 (C-12), 36.86 (C-10c), 29.47 (C-10b); IR ν (KBr) 3267, 3036, ~ 2560, 841, 632 $cm^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 232 (6500), 338 (67000), 375 (29500), 458 (5900), 525 (50), 595 (120), 637 (70); EI MS *m/z* 254 ($M^+$); HR MS Calcd for $C_{20}H_{14}$: 254.1095. Found: 254.1090. Calcd. Anal: C, 94.45; H, 5.55. Found: C, 92.22; H, 5.70.

* "a" stands for the *trans*-vinyl protons whereas "b" stands for the *cis*-vinyl proton.

**10b,10c-Divinyl-2-(1-naphthoyl)-*trans*-10b,10c-dihydropyrene 250**




**250**

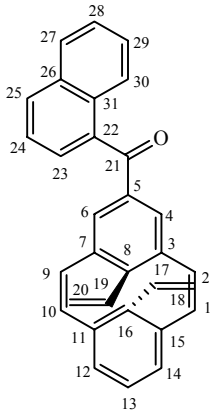
To avoid photo isomerization of the product, this reaction was carried out under minimal light. 15,16-Divinyldihydropyrene **167** (60 mg, 0.234 mmol) and naphthoyl chloride (300 mg, 1.574 mmol) were stirred in DCM (10 mL) for 15 minutes. $AlCl_3$ (160 mg, 1.198 mmol) was added and the reaction mixture was stirred for 10 seconds and then quenched with water. The resulting solution was extracted with DCM (3 x 25 mL), dried over $MgSO_4$ and evaporated. The crude was column chromatographed over silica gel to give the naphthoylated product **250** (65 mg, 0.16 mmol, 67%) as dark maroon solid from dichloromethane.

$^1$H NMR ($CDCl_3$) δ 9.13 (s, 2H, H-1,3), 8.86 (d, *J* = 7.8 Hz, 2H, H-4,10), 8.72 (d, *J* = 7.8 Hz, 2H, H-5,9), 8.58 (d, *J* = 7.7 Hz, 2H, H-6,8), 8.09-8.16 (m, 3H, H-7,19,24), 8.00 (br d, *J* = 8.3 Hz, 1H, H-21), 7.79 (dd, *J* = 7, 1.0 Hz, 1H, H-17), 7.63 (dd , *J* = 8.1, 7.1 Hz, 1H, H-18), 7.56 ( dt, *J* = 7.0, 0.9 Hz, 1H, H-22), 7.44 (dt, *J* = 7.0, 1.1 Hz, 1H, H-23), 2.85 (dd, *J* = 10.4, 1.0 Hz, 1H, H-14a*), 2.80 (dd, *J* = 10.3, 1.0 Hz, 1H, H-12a), 2.27 (dd, *J* = 17.0, 1.0, 1H, H-12b), 2.22 (dd, *J* = 17.0, 1.0 Hz, 1H, H-14b*), 0.83 (dd, *J* = 17.0, 10.3 Hz, 1H, H-11), 0.74 (dd, *J* = 17.0, 10.3 Hz, H-13); $^{13}$C NMR ($CDCl_3$) δ 199.07 (C-15), 138.05 (C-2), 137.73 (C-10d,5a), 134.02 (C-20), 132.54 (C-10a,3a), 131.53 (C-

25), 131.90 (C-19), 130.29 (C-4,10), 128.86 (C-13), 128.63 (C-21), 128.47 (C-11), 127.93 (C-17), 127.24 (C-23), 127.07 (C-7), 126.63 (C-22), 126.60 (C-1,3), 126.31 (C-24), 125.93 (C-5,9), 124.93 (C-6,8), 124.80 (C-18), 110.90 (C-14), 110.83 (C-12), 37.19 (C-10c), 36.75 (C-10b); IR ν (KBr) 3042, 1637, 1544, 1507, 1462, 1401, 1308, 1236, 1185, 1136, 890, 832, 785 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 222 (75000), 350 (80200), 373 (20000), 397 (25500), 508 (11600), 600 (350), 664 (470); EI MS *m/z* 410 ($M^+$); HR MS Calcd for $C_{31}H_{22}O$: 410.1670. Found: 410.1679.

* "a" stands for the *trans*-vinyl protons whereas "b" stands for the *cis*-vinyl proton. C-16 is not clear, probably at δ 137.75.

**5-(1-Naphthoyl)-8,16-divinyl-*anti*-[2.2]metacyclophane-1,9-diene 251**

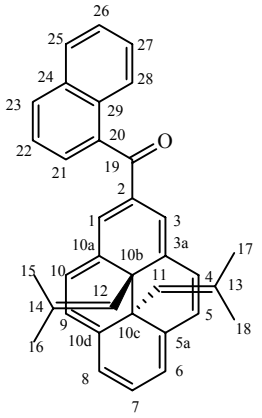



**251**

Using procedure 5.7, cyclophanediene **251** was obtained quantitatively from the dihydropyrene **250** . On attempted melting point determination, it converts into DHP **250**: $^1$H NMR ($CDCl_3$) δ 8.07 (dd, *J* = 7.8, 2.3 Hz, 1H, H-30), 7.98 (m, 1H, H-25), 7.92 (dd, *J* = 7.3, 2.3 Hz, 1H, H-27), 7.53-7.51 (m, 4H, H-23,24,28,29), 7.16 (s, 2H, H-4,6), 7.13 (t, *J* = 7.4 Hz, 1H, H-13), 6.60 (d, *J* = 7.4 Hz, 2H, H-12,14), 6.45 (dd, *J* = 17.4, 11.1 Hz, 1H, H-17), 6.38 (AB, *J* = 11.2, 4H, H-1,2,9,10), 6.37 (m, 1H, H-19), 5.64 (dd, *J* = 17.5, 1.7

Hz, 1H, H-20b), 5.56 (dd, *J* = 17.5, 1.5 Hz, 1H, H-18b), 4.98 (dd, *J* = 11.0, 1.5 Hz, 1H, H-18a*), 4.97 (dd, *J* = 11.1, 1.5 Hz, 1H, H-20a); $^{13}$C NMR ($CDCl_3$) δ 196.90 (C-21), 152.58 (C-8), 144.41 (C-16), 139.32 (C-5), 137.16 (C-22), 136.32 (C-11,15), 135.94 (C-3,7), 134.89 (C-17), 134.40 (C-19), 133.90 (C-26), 133.62 (C-1,10), 132.93 (C-2,9), 131.08 (C-31), 130.95 (C-25), 130.59 (C-13), 129.16 (C-4,6), 128.59 (C-27), 127.27 (C-29), 126.93 (C-23), 126.76 (C-12,14), 126.63 (C-28), 125.89 (C-30), 124.66 (C-24), 120.87 (C-20), 119.26 (C-18); IR ν (Thin film) 3049, 2924, 2853, 1732, 1651, 1564, 1462, 1291, 806, 785, 768, 741 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 222 (18200), 228 (43700), 250 (36300), 329 (8400), 408 (4200).

**10b,10c-Bis(3-methyl-1-propenyl)-2-(1-Naphthoyl)-*trans*-10b,10c-dihydropyrene 248**

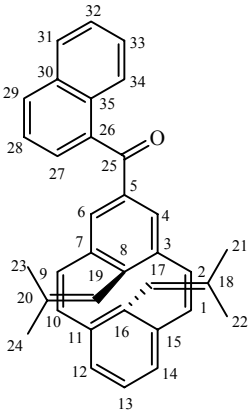



**248**

Procedure same as for the synthesis of **250** except that the reaction time is 3 s instead of 10 s: mp 179-180 $^{o}$C; $^{1}$H NMR ($CD_2Cl_2$) δ 9.04 (s, 2H, H-1,3), 8.63 (AB, *J* = 7.8 Hz, 2H, H- 4,10), 8.52 (d, *J* = 7.8 Hz, 2H, H- 6,8), 8.45 (AB, *J* = 7.8 Hz, H-5,9), 8.06 (m, 4H, H-7,23,25,28), 7.79 (dd, *J* = 7.0, 1.2 Hz, 1H, H-21), 7.65 (dd, *J* = 7.0 Hz, 1H, H-22), 7.55 (td, *J* = 6.8, 1.2 Hz, 1H, H-26), 7.44 (td, *J* = 6.7, 1.3 Hz, 1H, H-27), 0.28, 0.272 (d, *J* = 1.2 Hz, 6H, H-15,16), 0.27 (d, *J* = 1.2 Hz, 3H, H-17), 0.21 (septet, *J* = 1.2 Hz, 1H,

H-12), 0.19 (br s, 3H, H-18), 0.15 (septet, $J$ = 1.2 Hz, H-11); $^{13}$C NMR ($CD_2Cl_2$) δ 198.30 (C-19), 140.39 (C-5a,10d), 138.85 (C-20), 134.87 (C-3a,10a), 134.43 (C-24), 132.40 (C-14), 132.27 (C-13), 131.72 (C-29), 131.60 (C-4,10), 131.00 (C-23), 129.03 (C-25), 127.71 (C-1,3), 127.64 (C-21), 127.40 (C-7), 126.96 (C-26), 126.79 (C-5,9), 126.51 (C-27), 126.32 (C-6,8), 125.30 (C-22), 117.19 (C-12), 115.63 (C-11), 37.85 (C-10c), 37.19 (C-10b), 28.37 (C-17), 28.05, 16.44 (C-15,16), 16.54 (C-18)*; IR ν (thin film) 3046, 2963, 2924, 2853, 1637,1591, 1507, 1461, 1304, 1235, 1185, 1136, 1057, 1028, 883, 829, 785, 736 702, 631 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 228 (20400), 361 (16800), 397 (5590), 421 (6480), 557 (3320), 631 (284); EI MS *m/z* 466 ($M^+$); HR MS Calcd: 466.2297. Found: 466.2294. Calcd. Anal: C, 90.09; H, 6.48. Found: C, 88.49; H, 6.55.

C-2 is not clear probably overlapping with the signal at δ 140.39.



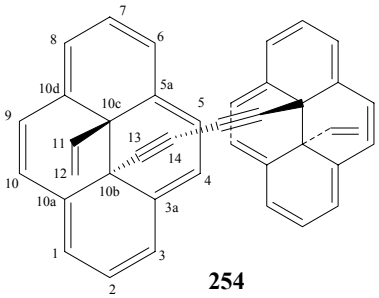

**249**

Using procedure 5.7, cyclophanediene **249** was obtained quantitatively from the dihydropyrene **248**. On attempted melting point determination transforms into DHP **248**: $^1$H NMR ($CD_2Cl_2$) δ 8.00 (m, 2H, H-31,34), 7.94 (dd, $J$ = 7.0, 1.3 Hz, 1H, H-29), 7.52 (m, 4H, H-27,28,32,33), 7.18 (s, 2H, H-4,6), 7.10 (t, $J$ = 7.4 Hz, 1H, H-13), 6.62 (d, $J$ =

7.4 Hz, H-12,14), 6.25, 6.32 (AB, *J* = 11.4 Hz, 4H, H-1,2,9,10), 5.83 (septet, *J* = 1.4 Hz, H-17), 5.82 (septet *J* = 1.4 Hz, 1H, H-19), 1.63 (d, *J* = 1.4 Hz, 3H, H-24), 1.62 (d, *J* = 1.4 Hz, 3H, H-23), 1.61 (d, *J* = 1.4 Hz, 3H, H-21), 1.55 (d, *J* = 1.4 Hz, 3H, H- 22); $^{13}$C NMR ($CD_2Cl_2$) δ 197.43 (CO), 150.56 (C-8), 142.06 (C-16), 139.92 (C-20), 138.93 (C-11,15), 138.61 (C-3,7), 138.60 (C-26), 138.52 (C-5), 135.06 (C-30), 133.52 (C-1,10), 132.69 (C-2,9), 132.12 (C-35), 131.60 (C-31/C-34), 129.86 (C-13), 129.58 (C-29), 129.10 (C-4,6), 128.17, 127.62, 125.69 (C-27,28,32,33) 126.86 (C-31/34), 126.86 (C-12,14), 126.18 (C-17,19), 28.08, 27.90 (C-21,24), 21.95 (C-23), 21.60 (C-22); IR ν (thin film) 3048, 2971, 2927, 1652, 1591, 1507, 1461, 1292, 1234, 1186, 1127, 1056, 1028, 1008, 966, 853, 782, 736; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 231 (24000), 247 (23300), 281 (14500), 325 (6900), 396 sh (3200); EI MS *m/z* 466 ($M^+$); HR MS calculated: 466.2297. Found: 466.2294.

**10b-[4-(10b-Vinyl(10b,10c-dihydropyrene-10c-yl))buta-1,3-diynyl]-10c-vinyl-10b,10c-dihydropyrene 254**

$Cu(OAc)_2$ (90 mg, 0.5 mmol) was added to a solution of 15-vinyl-16-ethynyldihydropyrne **237** (15 mg) in pyridine: methanol (6 mL:6 mL) solvent mixture. The reaction mixture was heated overnight at 80 $^{o}$C, cooled to room temperature, solvent was evaporated under vacuum. The crude mixture was chromatographed over silica gel using dichloromethane: hexane (2: 8) to give the dimer **254** (14 mg, 94%) as dark green crystals from benzene.

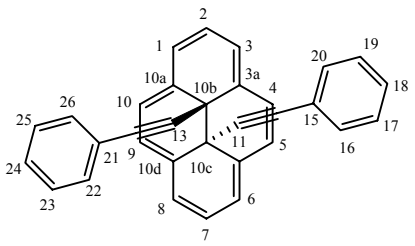


**254**

mp 208-240 $^{o}$C (dec.) $^{1}$H NMR ($CD_2Cl_2$) δ 8.60 (d, *J* = 7.7 Hz, 4H, H-5,9), 8.47 (d, *J* = 7.7 Hz, 4H, H-4,10), 8.46 (d, *J* = 7.6 Hz, 4H, H-6,8), 8.38 (d, *J* = 7.8 Hz, 4H, H-1,3), 7.98 (t, *J* = 7.7 Hz, 2H, H-7), 7.93 (t, *J* = 7.8 Hz, 2H, H-2), 2.53 (dd, *J* = 10.4, 1.4 Hz, 2H, H-12a*), 1.92 (dd, *J* = 16.9, 1.4 Hz, 2H, H-12b*), 0.16 (dd, *J* = 16.9, 10.3 Hz, 2H, H-11); $^{13}$C NMR ($CD_2Cl_2$) δ 135.03 (C-5a,10d), 130.32 (C-3a, 10a), 125.93 (C-11), 125.82 (C-5,9), 125.54 (C-4,10), 125.17 (C-7), 124.73 (C-6,8), 123.60 (C-1,3), 123.56 (C-2), 111.30 (C-12), 70.90, 58.95 (C-13,14), 36.57 (C-10c), 30.44 (C-10b); IR ν (KBr) 3035, 1624, 1401, 1349, 917, 838, 743, 685, 630 cm$^{-1}$; UV (DCM) $\lambda_{max}$ nm ($\varepsilon_{max}$) 232 (11900), 338 (79300), 377 (32500), 461 (7600), 534 (30), 595 (80), 638 (70); HR MS Calcd for $C_{20}H_{14}$: 506.2034. Found: 506.2038; Calcd. Anal: C, 94.82; H, 5.18. Found: C, 90.11; H, 5.14.

* "a" stands for the *cis*-vinyl proton whereas "b" denotes the *trans*-vinyl proton.

**10b,10c-Bis(2-phenylethynyl)-*trans*-10b,10c-dihydropyrene**

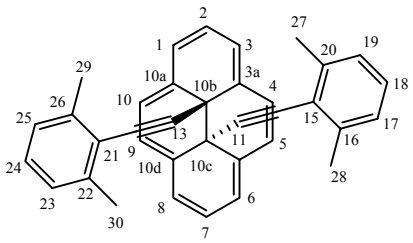


**141**

Dichloro-bis-triphenylphosphine palladium (II) (90 mg, 0.13 mmol ) and CuBr (30 mg, 0.2 mmol) were added to a solution of iodobenzene (300 mg, 1.47 mmol) and phenyl acetylene (30 mg, 0.29 mmol) in 2.5 mL triethylamine under argon at room temperature. The solution was stirred at 80 $^{o}$C for 20 min and then 15,16-diethynyldihydropyrene **235** (40 mg, 0.08 mmol) was added and stirring was continued for another 20 minutes. The reaction mixture was cooled to room temperature and TEA evaporated. The crude mixture was extracted between dichloromethane and water. The organic layer was washed three times with aq $NaHCO_3$ solution, dried over $MgSO_4$ and evaporated. The product mix was chromatographed over silica gel using hexane: dichloromethane (80: 20) to give the desired prod **141** (42 mg, 66%) as dark green crystals from benzene.

mp 192-193 $^{o}$C; $^{1}$H NMR ($CD_2Cl_2$) δ 8.92 (s, 4H, H-4,5,9,10), 8.76 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 8.27 (t, *J* = 7.7 Hz, 2H, H-2,7), 6.89 (tt, *J* = 7.5, 1.3 Hz, 2H, H-18,24), 6.78 (m, 4H, H-17,19,23,25), 6.06 (dd, *J* = 8.4, 1.4 Hz, 4H, H-16,20,22,26); $^{13}$C NMR ($CD_2Cl_2$) δ 133.66 (C-3a,5a,10a,10d), 131.11 (C-16,20,22,26), 128.09 (C-17,19,23,25), 128.04 (C-18,24), 125.91 (C-4,5,9,10), 124.65 (C-2,7), 123.95 (C-1,3,6,8), 121.89 (C-15,21), 81.55 (C-11,13), 76.96 (C-12,14), 31.66 (C-10b,10c); IR ν (KBr) 3053, 3037, 1596, 1489, 1442, 1351, 1251, 1029, 837, 755, 693, 618 cm$^{-1}$; UV (DCM) $\lambda_{max}$ nm ($\varepsilon_{max}$) 245 (35000), 253 (35200), 339 (53000), 375 (30000), 456 (5800), 597 (70), 641 (100); Calcd. Anal: C, 95.01; H, 499. Found: C, 92.63; H, 5.48. HR MS Calcd for $C_{32}H_{20}$: 404.1565. Found: 404.1549.

**10b,10c-bis[2-(2,6-dimethylphenyl)ethynyl]-10b,10c-dihydropyrene**

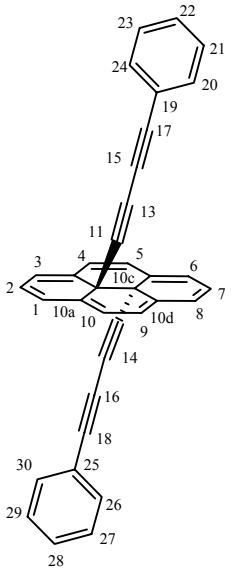



**247**

Dichloro-bis-triphenylphosphine palladium (II) (20 mg, 0.03 mmol) and CuBr (10 mg, 0.068 mmol) were added to a solution of 2,6-dimethyliodobenzene (46 mg, 0.198 mmol) and 15,16-diethynyldihydropyrene **235** (40 mg, 0.08 mmol) in 2 mL triethylamine under argon at room temperature. The solution was stirred at 90 $^{o}$C for 1.5 h, cooled to room temperature and TEA evaporated. The crude mixture was extracted between dichloromethane and water. The organic layer was washed three times with aq $NaHCO_3$ solution, dried over $MgSO_4$ and evaporated. The product mix was chromatographed over silica gel using hexane: dichloromethane (80: 20) to give the desired prod **247** (15 mg, 20%) as dark green crystals from benzene.

$^{1}$H NMR ($CDCl_3$) δ 8.88 (s, 4H, H-4,5,9,10), 8.71 (d, *J* = 7.7 Hz, 4H, H-1,3,6,8), 8.21 (t, *J* = 7.7 Hz, 2H, H-2,7), 6.46 (d, *J* = 7.5 Hz, 4H, H-17,19,23,25), 6.63 (t, *J* = 7.5 Hz, 2H, H-18,24), 1.17 (s, 12H, Me); $^{13}$C NMR ($CDCl_3$) δ 139.74 (C-16,20,22,26), 133.85 (C-3a,5a,10a,10d), 126.89 (C-18,24), 125.87 (C-17,19,23,25), 125.44 (4,5,9,10), 124.07 (C-2,7), 123.43 (1,3,6,8), 121.62 (C-15,21), 89.56, 74.44 (sp carbons), 31.53 (C-10b,10c), 29.92 (Me).

**10b,10c-Bis(4-phenylbutadiyny)-*trans*-10b,10c-dihydropyrene 257**




**257**

$Cu(OAc)_2$ (500 mg , 2.76 mmol) was added to a solution of phenylacetylene (0.3 g, 0.29 mmol) and diethynyl DHP **235** (10 mg, 0.02 mm0l) in pyridine (30 mL). The reaction mixture was heated at 50 $^{o}$C for 16 h, cooled to room temperature and the solvent was evaporated under vacuum. The crude mixture was chromatographed over silica. hexanes eluted 1,4-diphenylbutadiyne. Dichloromethane: hexane (3: 7) eluted 5 mg of the desired product **257** as green crystals from benzene.

mp ~ 325 $^{o}$C (dec); $^{1}$H NMR ($CD_2Cl_2$) δ 8.94 (s, 4H, H-4,5,9,10), 8.78 (d, *J* = 7.7 Hz, 4H, H-1,3,6,8), 8.32 (t, *J* = 7.7 Hz, 2H, H-2,7), 7.19 (tt, *J* = 7.5, 1.4 Hz, 2H, H-22,28), 7.09 (dd, *J* = 8.0, 7.6 Hz, 4H, H-21,23,27,29), 6.99 (dd, *J* = 8.1, 1.4 Hz, 4H, H-20,24,26,30); $^{13}$C- NMR ($CD_2Cl_2$) δ 132.68 (C-22,24,26,30), 132.39 (C-3a,5a,10a,10d), 129.67 (C-22,28), 128.76 (C-21,23,27,29), 126.19 (C-4,5,9,10), 125.23 (C-2,7), 124.33 (C-1,3,6,8), 76.44 (C-17,18), 74.93, 72.32, 62.15 (C-11-16); IR ν (KBr) 1489, 1441, 837, 750, 685 cm$^{-1}$; UV (dichloromethane) $\lambda_{max}$ nm ($\varepsilon_{max}$) 229 (40100), 266 (25100), 281

(25600), 298 (17600), 340 (36400), 378 (16700), 457 (4440), 640 (170); EI MS *m/z* 452 ($M^+$). HR MS Calcd for $C_{36}H_{20}$: 452.1565. Found: 452.1554; Anal. Calcd: C, 95.55; H, 4.45. Found: C, 89.89; H, 4.16.

**References**


1. Feringa, B. L. *Molecular Switches*, Wiley-VCH, Weinheim, **2001**.
2. Micheau, J-C.; Yokoyama, Y. *J. Phys. Org. Chem*. **2007**, *20*, 801-1020 and references therein.
3. (a)Waldeck, D. H.; Beratan, D. N. *Science* **1993**, *261*, 576-577; Tour, J. M.; Schumm, J. S. *J. Am. Chem. Soc*. **1991**, *113*, 7064-7066; (b) Patil, A. O.; Heegar, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183-200 and references therein. Hu, J.; Odom, T. W.; Lieber, C.M. *Acc. Chem. Res*. **1999**, *32*, 434-445; (c) Feringa, B. L.; Jager, W. F.; de Lange, B. *Tetrahedron* **1993**, *49*, 8267-8310; (d). Willner, I.; Willner, B. *J. Mater. Chem*. **1998**, *8*, 2543-2556 and references therein.
4. Bouas-Laurent, H.; Durr, H. *Pure Appl. Chem*. **2001,** *73,* 639-665; (b) *Photochromism*: *Molecules and Systems*, ed. by H. Durr, H. Bouas-Laurent, Elsevier, Amsterdam, **2003**.
5. Ferri, V.; Elbing, M.; Pace, G.; Dickey, M. D.; Zharnikov, M.; Samori, P.; Mayor, M.; Rampi, M. A. *Angew. Chem. Int. Ed*. **2008**, *47*, 3407-3409.
6. (a) Ichihara, K.; Namada, N.; Kato, S.; Shinohara, I. *J Polymer Sci., Polym. Chem. Ed.* **1984,** *22*, 121-128; (b) Ichihara, K.; Namada, N.; Kato, S.; Shinohara, I. *J. Polymer Sci., Polym. Chem. Ed* **1983**, *21*, 1551-1555; (c) Balasubrabamaman, D.; Subramani, S.; Kumar, C. *Nature*, **1975**, *254,* 252-254;
7. Irie, M.; Tanaka, H., *Macromolecules*, **1983**, *16*, 210-214.
8. Delaire, J. A.; Nakatani, K. *Chem. Rev*. **2000**, *100*, 1817-1845.
9. Sakagami, S.; Koga, T.; Takase, A. *Liquid crystals*, **2000**, *27,* 1551-1554.

**10.** Barachevsky, V. A.; Crano, J. C.; Guglielmetti, R. J. *Org. Photochromic Thermochromic Compd.* **1999**, 267-314. Plenum Publishing Corp., New York N.Y.

**11.** Reddy, C. D.; Ramamurthy, V. *J. Org. Chem*. **1987,** *52,* 5521-5528.

**12.** Noakas, J. E.; Culp, R. A. US Pat. (**1985**) *4*,507,226.

**13.** Irie, M., *J. Am. Chem. Soc*. **1983**, *105*, 2078-2079.

**14.** Lomoth, R.; Haupl, T.; Johanssen, O.; Hammarstrom, L. *Chem. Eur. J*, **2002**, *8*, 102-109.

**15.** Stookey, S.D. US patent 3252374, Corning Glass Works, **1962**.

**16.** IUPAC *Compendium of Chemical Terminology*, 2nd Edition, **1997**.

**17.** Bouas-Laurent, H.; Castellan, A.; Desvergne, J-P. *Pure Appl. Chem*. **1980,** *52*, 2633-2648.

**18.** Sauter, von H.; Hoerster, H.; Prinzbach, H. *Angew. Chem*. **1973**, *85*, 1106-1107.

**19.** Ansari, F. L.; Qureshi, R.; Qureshi, M. L. *Electrocyclic Reactions* 1st ed. Wiley VCH Weinheim, **1999.**

**20.** Stobbe, H. *Ber*. **1905**, *38*, 3673-3682.

**21.** Yokoyama,Y.; Uchida, S.; Sugawara, Y.; Kurita, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3100-3107.

**22.** Fischer, E.; Hirshberg, Y. *J. Chem. Soc*. **1952**, 4522-4524.

**23.** Berkovic, G. *Chem. Rev*. **2000**, *100*, 1741-1753.

**24.** Irie, M. *Chem. Rev*., **2000**, *100*, 1685-1716.

**25.** Takeshita, M.; Irie, M. *J. Chem. Soc. Chem. Comm*. **1996**, 1807-1808.

**26.** Tanifuji, N.; Irie, M.; Matsuda, K. *Chem. Lett*. **2005**, *34*, 1580-1581

**27.** Gilat, S.L.; Kawai, S. H.; Lehn, J. M. *Chem. Eur. J*. **1995**, *1*, 275-284

**28.** Samachetty, H. D.; Branda, N. R., *Pure Appl. Chem*. **2006**, *78*, 2351-2359.

**29.** Mitchell, R.H.; Brkic, Z.; Sauro, V. A.; Berg, D. J. *J. Am. Chem. Soc.,* **2003**, *125*, 7581-7585.

**30.** Blattman, H. R.; Meuch, D.; Heilbronner, E.; Molyneux, R. G.; Bookelheide, V. J. *J. Am. Chem. Soc*. **1965**, *87*, 130-131.

**31.** Boekelheide, V. J.; Phillips, J. *J. Am. Chem. Soc*. **1967**, *89*, 1695-1704.

**32.** Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc*. **1974**, *96*, 1547-1553

**33.** Tashiro, M.; Yamato, T*, J. Am. Chem. Soc.* **1982**, *104*, 3701-3707.

**34.** Sheepwash, M. A. L.; Mitchell, R. H.; Bohne, C. *J. Am. Chem. Soc*., **2002**. *124*, 4693-4700.

**35.** Robinson, S. G., Ph.D. Thesis, University of Victoria, **2008**.

**36.** Mitchell, R. H.; Boekelheide, V. *Tet. Lett*, **1970**, *11*, 1197-1202

**37.** Ayub, K.; Zhang, R.; Robinson, S. G.; Twamley, B.; Williams, R. V.; Mitchell, R. H. *J. Org. Chem.* **2008**, *73*, 451-456.

**38.** Mitchell, R. H.; Ward, T. R.; Chen, Y.; Weerawana, S. A.; Dibble, P. W.; Marsella, M. J.; Almutairi, A.; Wang, Z. Q. *J. Am. Chem. Soc*. **2003**, *125*, 2974-2988.

**39.** Mitchell, R. H.; Brkic, Z.; Sauro, V. A.; Berg, D. J. *J. Am. Chem. Soc*. **2003,** *125*, 7581-7585; Mitchell, R. H.; Yan, J. S. H.; Dingle, T. W. *J. Am. Chem. Soc*. **1982**, *104*, 2551-2559; Cerfontain, H.; Koeberg-Tedler, A.; Bakker, B. H.; Mitchell, R. H.; Tashiro, M. *Leibigs Ann./Recueil* **1997**, 873-878; Mitchell, R. H.; Fan, W.; Lau, D. Y. K.; Berg, D. J. *J. Org. Chem.* **2004**, *69*, 549-554; Mitchell, R. H. *Eur.*

*J. Org. Chem*. **1999**, 2695-2703. Blattman, H. R.; Schmidt, W. *Tetrahedron*, **1970**, *26*, 5885-5899.

**40.** Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim Germany, **1970**; Schmidt, W. *Helv. Chem. Acta*. **1971**, 54, 862-868.

**41.** Williams, R. V.; Edwards, W. D.; Mitchell, R. H.; Robinson, S. G. *J. Am. Chem. Soc*. **2005,** *127*, 16207-16214.

**42.** Baldwin, J. E. *Org. Chem.* **1977,** *35*, 273.

**43.** Jarzecki, A. A.; Gajewski, J.; Davidson, E. R. *J. Am. Chem. Soc.* **1999,** *121*, 6928-6935.

**44.** Borden, W. T. *Mol. Phys*. **2002**, *100*, 337-347.

**45.** Pryor, W. A. Free Radicals, McGraw Hill. New York. 1960. March, J. *Advanced Org. Chem.* 4th Ed. Wiley Interscience, New York, **1992**, 186-195.

**46.** Henry, D. J.; Parkinson, C, J.; Mayer, P. M.; Radom, L. *J. Phys. Chem. A,* **2001**, *105*, 6750-6756.

**47.** Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem*. **1987**, *52*, 3062-3072. Bordwell, F. G.; Zhang, X.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1992,** *114*, 7623-7629.

**48.** Song, K.; Liu, L.; Guo, Q. *J. Org. Chem*. **2003**, *68*, 4604-4607.

**49.** Berman, E.; Fox, R. E.; Thomson, F. D. *J. Am. Chem. Soc*. **1959**, *81*, 5605-5608

**50.** Kobatake, S.; Terakawa, Y. *Chem. Comm*. **2007**, *17*, 1698-1700.

**51.** Morimitsu, K.; Kobatake, S.; Irie, M. *Mol. Cryst. Liq. Cryst*. **2005**, *431*, 151-154.

**52.** Pu, S.; Zheng, C.; Le, Z.; Liu, G.; Fan, C. *Tetrahedron*, **2008**, *64*, 2576-2585.

**53.** Wittig, G.; Lohmann, L. *Ann*. **1942**, *550*, 260

**54.** Stevens, T. S.; Creighton, E. M.; Gordon, A. B.; MacNicol, M. *J. Chem. Soc*. **1928**, 3193-3197..

**55.** Bruhin, J.; Gerson, F.; Martin, W. B.; Novotny, H. *J. Am. Chem. Soc*. **1988**, *110*, 6377-6384.

**56.** Sandmeyer, T. *Ber. Dtsch. Chem. Ges*. **1884**, *17*, 1633-1635.

**57.** Bodwell, G. J.; Houghton, T. J.; Koury, H. E.; Yarlagadda, B. *Synlett*, **1995**, 751-752.

**58.** Vogtle, F.; Zuber, M.; Neumann, P. *Z. Naturforsch.* **1971**, *26b*, 707-709.

**59.** Borch, R. F. *J. Org. Chem*. **1969**, *34*, 627-629.

**60.** Lai, Y.; Eu, H. *J. Chem. Soc. Perkin Trans. 1,* **1993**, 233-237.

**61.** Boekelheide, V.; Sturm, E. *J. Am. Chem. Soc.* **1969**, *91*, 902.

**62.** Boekelheide, V,; Hylton, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 3669.

**63.** Kitagawa, F.; Murase, M.; Kitamura, N. *J. Org. Chem*. **2002,** *67*, 2524-2531

**64.** Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 1543-1552

**65.** Lai, Y-H.; Zhou, Z-L. *J. Org. Chem*. **1994**, *59*, 8275-8278.

**66.** Cao, D.; Kolshorn, H.; Meier, H. *Tetrahedron Lett*. **1996**, *37*, 4487-4490.

**67.** Sheepwash, M. A. L.; Mitchell, R. H.; Bohne, C. *J. Am. Chem. Soc*. **2002**, *124*, 4693-4700.

**68.** Brady, O. L; Eksmie, G. V. *Analyst* 1926, *51*, 77-78; (b) *Chemistry in context*, 4th Edition, **2000**, Graham Hill and John Holman.

**69.** For isopropyl triphenylphosphonium bromide, procedure was adopted from Brovema, S.; Duar, Y. *J. Am. Chem. Soc*. **1990**, *112*, 5830-5837. Other

phosphonium bromides were obtained by heating triphenyl phosphine and allylic/benzylic bromide in toluene at 100 $^{o}$C overnight.

**70.** Glaser, C. *Ann* **1870**, *154*, 159; Glaser, C. *Ber*. **1869,** *2*, 422-424.

**71.** PC MODEL for Windows Version 8.50.0, September 2003, Sereena Software.

**72.** Otero, M.; Herranz, M. A.; Seoane, C.; Martin, N.; Garin, J.; Orduna, J.; Alcala, R.; Villlacampa, B. *Tetrahedron*, **2002,** *58*, 7463-7475.

**73.** Lamture, J. B.; Suryawanshi, S. N.; Nayak, U. R. *Indian Journal of Chemistry, Section B: Organic Chemistry Including Medicinal Chemistry*, **1981**, *20B*, 957-959.

**74.** Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tet. Lett*. **1975**, 4467-4470.

**75.** Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature*, **2007**, *446*, 778-781.

**76.** Pieroni, O.; Houben, J. L.; Fissi, A.; Costantino, P.; Ciardelli, F. J. Am. Chem. Soc, 1980, 102, 5913-5915.

**77.** Eglington, G.; Galbraith, A. R. *J. Chem. Soc.* **1959**, 889-896.

**78.** Yu, T.; Fu, Y.; Liu, L.; Guo, Q. *J. Org. Chem*. **2006**, *71*, 6157-6164.

**79.** Megamedov, N. A.; Ruggiero, P. L.; Tang, Y. *J. Am. Chem. Soc*. **2004**, **126**, 1624-1625.

**80.** Nonoshita, K.; Banno, H.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc*. **1990**, 112, 316-322. and references therein.

**81.** Bury, A.; Bougeard, P.; Corker, S. J.; Johnson, M, D.; Perlmann, M.; *J Chem Soc Perkin Trans II,* **1982**, 1367-1372.

**82.** Boggio-Pasqua, M.; Bearpark, M. J.; Bobb, M. A. *J. Org. Chem.* **2007**, *72*, 4497-4503.

**83.** Bandyopadhyay, S. PhD thesis, University of Victoria, **2004**.

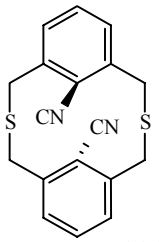
**84.** Dunitz, J.D.; Orgel, L. E.; Rich, A. *Acta Crystallographica*, **1956**, *9,* 373-375.

**85.** Anker, W., Ph.D. Thesis, University of Victoria, **1982**.

**X-ray structure reports**

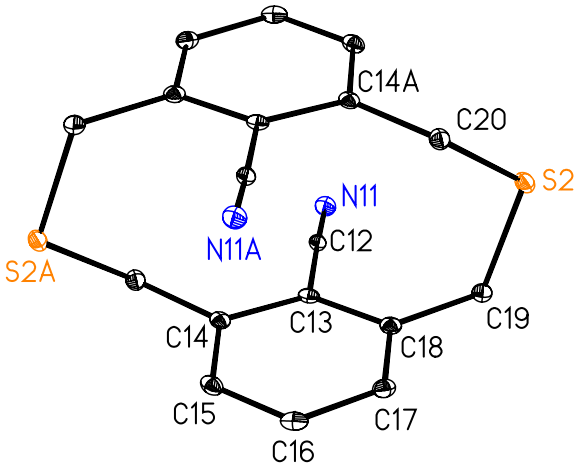
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

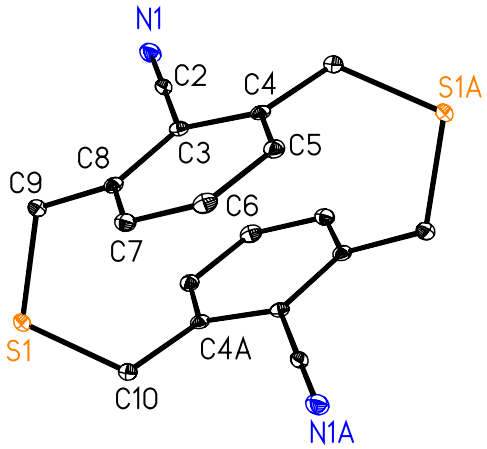
**X-ray structure for *anti*-dithiacyclophane 100**




**100**

Brendan Twamley




Project name : bt906

5-30-06

**Experimental:**

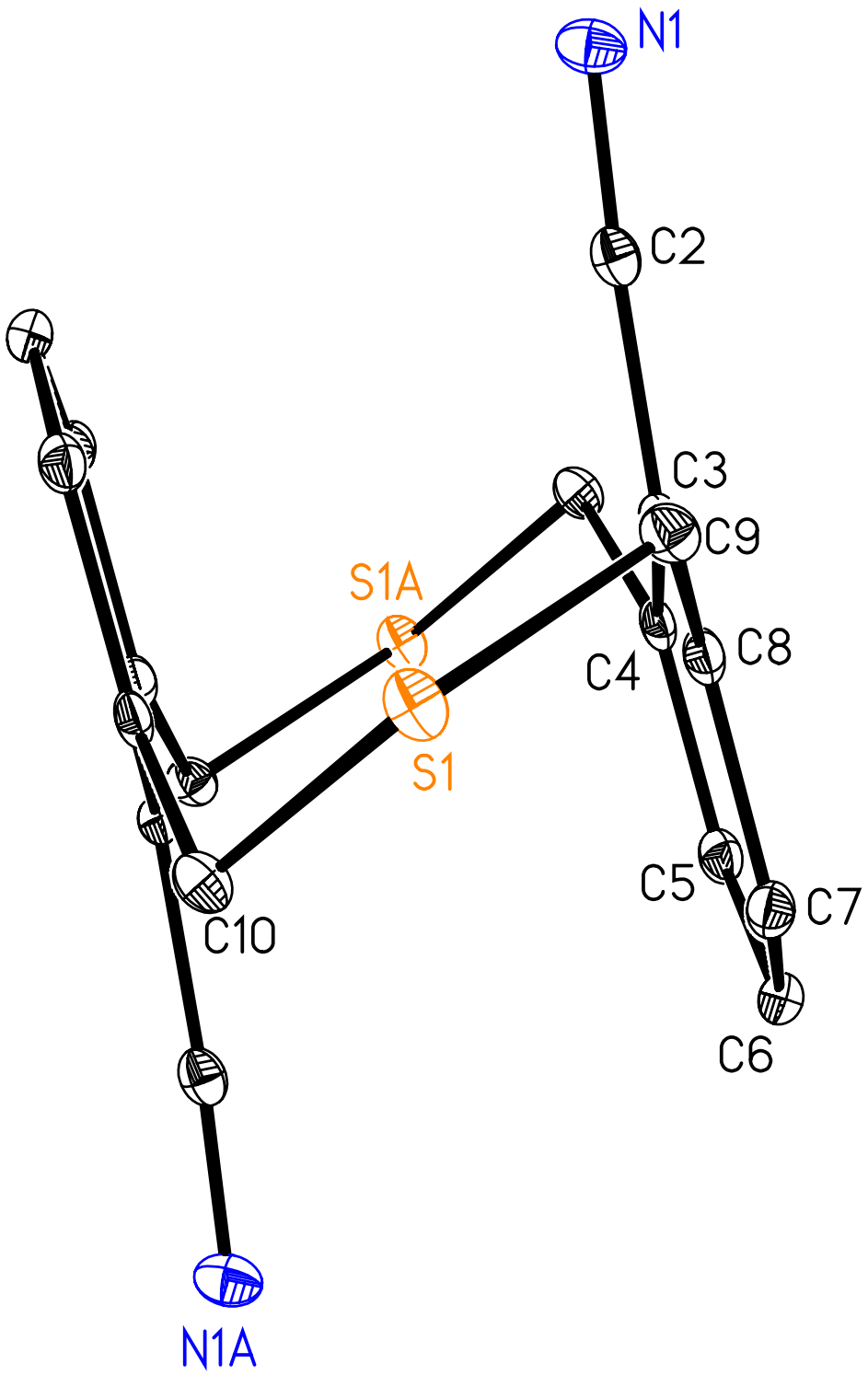
Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a MiTeGen fiber and data were collected at 89(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 30 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[1] software and refined using SAINTPlus[2] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[3] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[4] The structure was solved in the space group P-1 (# 2) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[1] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2001**.
[2] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[3] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[4] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.


N1
C2
C3
C9
S1A
S1
C4
C8
C5
C7
C6
C10
N1A

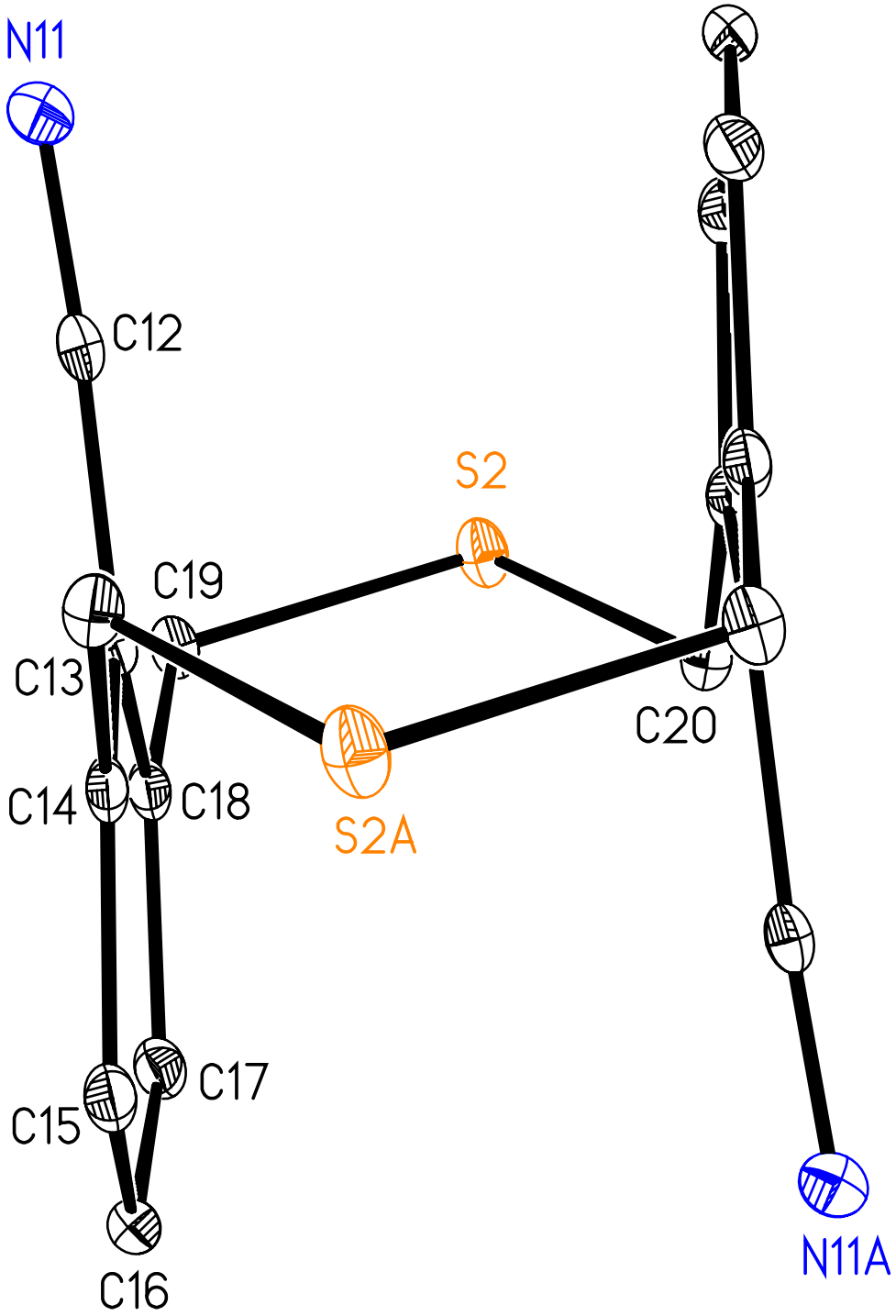

N11
C12
S2
C19
C13
C20
C14
C18
S2A
C17
C15
C16
N11A

**Table A. 1 Crystal data and structure refinement for 100 (C18 H14 N2 S2).**

| | | |
|---|---|---|
| Identification code | bt906 | |
| Empirical formula | C18 H14 N2 S2 | |
| Formula weight | 322.43 | |
| Temperature | 89(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 6.8155(10) Å | α = 99.458(2)°. |
| | b = 7.8620(12) Å | β = 96.368(2)°. |
| | c = 14.322(2) Å | γ = 106.897(2)°. |
| Volume | 714.01(19) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.500 $Mg/m^3$ | |
| Absorption coefficient | 0.369 $mm^{-1}$ | |
| F(000) | 336 | |
| Crystal size | 0.20 x 0.17 x 0.05 $mm^3$ | |
| Crystal color and habit | colorlessplate | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 1.46 to 25.25°. | |
| Index ranges | -8<=h<=8, -9<=k<=9, -17<=l<=17 | |
| Reflections collected | 10494 | |
| Independent reflections | 2595 [R(int) = 0.0194] | |
| Completeness to theta = 25.25° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9818 and 0.9298 | |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2595 / 0 / 199 | |
| Goodness-of-fit on $F^2$ | 1.062 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0312, wR2 = 0.0791 | |
| R indices (all data) | R1 = 0.0341, wR2 = 0.0821 | |
| Largest diff. peak and hole | 0.431 and -0.189 $e.Å^{-3}$ | |

**Table A. 2 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 100 (bt 906)**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(2) | 1243(2) | -2342(2) | 4019(1) | 14(1) |
| C(3) | 1828(2) | -448(2) | 4483(1) | 12(1) |
| C(4) | 2772(2) | 82(2) | 5454(1) | 13(1) |
| C(5) | 3513(2) | 1931(2) | 5861(1) | 15(1) |
| C(6) | 3265(3) | 3195(2) | 5325(1) | 16(1) |
| C(7) | 2207(2) | 2646(2) | 4387(1) | 15(1) |
| C(8) | 1448(2) | 811(2) | 3952(1) | 13(1) |
| C(9) | 185(3) | 169(2) | 2958(1) | 15(1) |
| C(10) | -2834(3) | 1334(2) | 3958(1) | 15(1) |
| C(12) | 2082(2) | 2578(2) | -442(1) | 13(1) |
| C(13) | 2542(2) | 4504(2) | -72(1) | 12(1) |
| C(14) | 2982(2) | 5726(2) | -690(1) | 13(1) |
| C(15) | 3174(2) | 7535(2) | -332(1) | 16(1) |
| C(16) | 3029(3) | 8115(2) | 618(1) | 16(1) |
| C(17) | 2748(2) | 6919(2) | 1238(1) | 16(1) |
| C(18) | 2481(2) | 5085(2) | 904(1) | 14(1) |
| C(19) | 2170(3) | 3778(2) | 1570(1) | 15(1) |
| C(20) | 6761(3) | 4906(2) | 1711(1) | 15(1) |
| N(1) | 857(2) | -3832(2) | 3639(1) | 19(1) |
| N(11) | 1618(2) | 1039(2) | -732(1) | 17(1) |
| S(1) | -2155(1) | 872(1) | 2770(1) | 16(1) |
| S(2) | 4577(1) | 3440(1) | 2127(1) | 18(1) |

**Table A. 3 Bond lengths [Å] and angles [°] for 100 (bt 906).**

| | | | |
|---|---|---|---|
| C(2)-N(1) | 1.148(2) | C(18)-C(19) | 1.500(2) |
| C(2)-C(3) | 1.445(2) | C(19)-S(2) | 1.8524(17) |
| C(3)-C(8) | 1.407(2) | C(19)-H(19A) | 0.9900 |
| C(3)-C(4) | 1.407(2) | C(19)-H(19B) | 0.9900 |
| C(4)-C(5) | 1.391(2) | C(20)-C(14)#2 | 1.512(2) |
| C(4)-C(10)#1 | 1.509(2) | C(20)-S(2) | 1.8233(17) |
| C(5)-C(6) | 1.388(2) | C(20)-H(20A) | 0.9900 |
| C(5)-H(5) | 0.9500 | C(20)-H(20B) | 0.9900 |
| C(6)-C(7) | 1.386(2) | | |
| C(6)-H(6) | 0.9500 | N(1)-C(2)-C(3) | 177.22(17) |
| C(7)-C(8) | 1.392(2) | C(8)-C(3)-C(4) | 121.90(15) |
| C(7)-H(7) | 0.9500 | C(8)-C(3)-C(2) | 119.27(15) |
| C(8)-C(9) | 1.503(2) | C(4)-C(3)-C(2) | 118.82(14) |
| C(9)-S(1) | 1.8405(17) | C(5)-C(4)-C(3) | 117.89(15) |
| C(9)-H(9A) | 0.9900 | C(5)-C(4)-C(10)#1 | 121.80(15) |
| C(9)-H(9B) | 0.9900 | C(3)-C(4)-C(10)#1 | 120.18(14) |
| C(10)-C(4)#1 | 1.509(2) | C(6)-C(5)-C(4) | 120.50(16) |
| C(10)-S(1) | 1.8203(17) | C(6)-C(5)-H(5) | 119.7 |
| C(10)-H(10A) | 0.9900 | C(4)-C(5)-H(5) | 119.7 |
| C(10)-H(10B) | 0.9900 | C(7)-C(6)-C(5) | 120.95(15) |
| C(12)-N(11) | 1.149(2) | C(7)-C(6)-H(6) | 119.5 |
| C(12)-C(13) | 1.448(2) | C(5)-C(6)-H(6) | 119.5 |
| C(13)-C(14) | 1.402(2) | C(6)-C(7)-C(8) | 120.40(15) |
| C(13)-C(18) | 1.406(2) | C(6)-C(7)-H(7) | 119.8 |
| C(14)-C(15) | 1.393(2) | C(8)-C(7)-H(7) | 119.8 |
| C(14)-C(20)#2 | 1.512(2) | C(7)-C(8)-C(3) | 118.03(15) |
| C(15)-C(16) | 1.385(2) | C(7)-C(8)-C(9) | 121.56(15) |
| C(15)-H(15) | 0.9500 | C(3)-C(8)-C(9) | 120.37(14) |
| C(16)-C(17) | 1.385(2) | C(8)-C(9)-S(1) | 115.99(11) |
| C(16)-H(16) | 0.9500 | C(8)-C(9)-H(9A) | 108.3 |
| C(17)-C(18) | 1.394(2) | S(1)-C(9)-H(9A) | 108.3 |
| C(17)-H(17) | 0.9500 | C(8)-C(9)-H(9B) | 108.3 |

| | | | |
|---|---|---|---|
| S(1)-C(9)-H(9B) | 108.3 | C(14)#2-C(20)-H(20B) | 108.3 |
| H(9A)-C(9)-H(9B) | 107.4 | S(2)-C(20)-H(20B) | 108.3 |
| C(4)#1-C(10)-S(1) | 114.75(11) | H(20A)-C(20)-H(20B) | 107.4 |
| C(4)#1-C(10)-H(10A) | 108.6 | C(10)-S(1)-C(9) | 105.06(8) |
| S(1)-C(10)-H(10A) | 108.6 | C(20)-S(2)-C(19) | 107.68(8) |
| C(4)#1-C(10)-H(10B) | 108.6 | | |
| S(1)-C(10)-H(10B) | 108.6 | | |
| H(10A)-C(10)-H(10B) | 107.6 | | |
| N(11)-C(12)-C(13) | 176.69(17) | | |
| C(14)-C(13)-C(18) | 121.92(15) | | |
| C(14)-C(13)-C(12) | 119.86(15) | | |
| C(18)-C(13)-C(12) | 118.20(14) | | |
| C(15)-C(14)-C(13) | 117.87(15) | | |
| C(15)-C(14)-C(20)#2 | 121.24(15) | | |
| C(13)-C(14)-C(20)#2 | 120.89(14) | | |
| C(16)-C(15)-C(14) | 120.72(15) | | |
| C(16)-C(15)-H(15) | 119.6 | | |
| C(14)-C(15)-H(15) | 119.6 | | |
| C(17)-C(16)-C(15) | 120.71(15) | | |
| C(17)-C(16)-H(16) | 119.6 | | |
| C(15)-C(16)-H(16) | 119.6 | | |
| C(16)-C(17)-C(18) | 120.46(16) | | |
| C(16)-C(17)-H(17) | 119.8 | | |
| C(18)-C(17)-H(17) | 119.8 | | |
| C(17)-C(18)-C(13) | 118.03(15) | | |
| C(17)-C(18)-C(19) | 120.88(15) | | |
| C(13)-C(18)-C(19) | 121.08(15) | | |
| C(18)-C(19)-S(2) | 115.16(11) | | |
| C(18)-C(19)-H(19A) | 108.5 | | |
| S(2)-C(19)-H(19A) | 108.5 | | |
| C(18)-C(19)-H(19B) | 108.5 | | |
| S(2)-C(19)-H(19B) | 108.5 | | |
| H(19A)-C(19)-H(19B) | 107.5 | | |
| C(14)#2-C(20)-S(2) | 115.73(11) | | |
| C(14)#2-C(20)-H(20A) | 108.3 | | |
| S(2)-C(20)-H(20A) | 108.3 | | |

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z+1  #2 -x+1,-y+1,-z

**Table A. 4 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 100 (bt 906).**

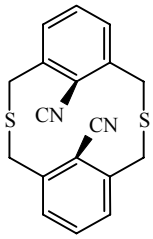
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(2) | 13(1) | 19(1) | 14(1) | 6(1) | 3(1) | 8(1) |
| C(3) | 9(1) | 12(1) | 15(1) | 3(1) | 4(1) | 4(1) |
| C(4) | 8(1) | 17(1) | 17(1) | 5(1) | 5(1) | 6(1) |
| C(5) | 10(1) | 18(1) | 15(1) | 2(1) | 2(1) | 5(1) |
| C(6) | 12(1) | 13(1) | 21(1) | 2(1) | 5(1) | 2(1) |
| C(7) | 13(1) | 15(1) | 20(1) | 7(1) | 5(1) | 5(1) |
| C(8) | 10(1) | 16(1) | 16(1) | 5(1) | 5(1) | 5(1) |
| C(9) | 17(1) | 16(1) | 16(1) | 6(1) | 4(1) | 8(1) |
| C(10) | 15(1) | 19(1) | 14(1) | 4(1) | 3(1) | 9(1) |
| C(12) | 10(1) | 19(1) | 13(1) | 6(1) | 2(1) | 7(1) |
| C(13) | 9(1) | 13(1) | 16(1) | 3(1) | 0(1) | 5(1) |
| C(14) | 7(1) | 15(1) | 16(1) | 5(1) | 0(1) | 4(1) |
| C(15) | 11(1) | 16(1) | 22(1) | 8(1) | 1(1) | 4(1) |
| C(16) | 12(1) | 12(1) | 24(1) | 1(1) | 2(1) | 5(1) |
| C(17) | 13(1) | 18(1) | 16(1) | 1(1) | 2(1) | 7(1) |
| C(18) | 9(1) | 17(1) | 17(1) | 4(1) | 1(1) | 5(1) |
| C(19) | 13(1) | 19(1) | 16(1) | 5(1) | 3(1) | 7(1) |
| C(20) | 13(1) | 16(1) | 15(1) | 5(1) | 2(1) | 4(1) |
| N(1) | 23(1) | 17(1) | 19(1) | 2(1) | 1(1) | 10(1) |
| N(11) | 19(1) | 16(1) | 18(1) | 5(1) | 4(1) | 8(1) |
| S(1) | 15(1) | 22(1) | 13(1) | 6(1) | 2(1) | 9(1) |
| S(2) | 15(1) | 22(1) | 20(1) | 12(1) | 5(1) | 7(1) |

**Table A. 5 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for 100 (bt 906).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5) | 4194 | 2331 | 6510 | 17 |
| H(6) | 3827 | 4454 | 5604 | 19 |
| H(7) | 1999 | 3528 | 4040 | 18 |
| H(9A) | -247 | -1175 | 2801 | 18 |
| H(9B) | 1092 | 617 | 2499 | 18 |
| H(10A) | -1865 | 2522 | 4317 | 18 |
| H(10B) | -4252 | 1441 | 3885 | 18 |
| H(15) | 3405 | 8380 | -743 | 19 |
| H(16) | 3125 | 9346 | 846 | 20 |
| H(17) | 2736 | 7352 | 1897 | 19 |
| H(19A) | 1217 | 2587 | 1208 | 18 |
| H(19B) | 1478 | 4218 | 2087 | 18 |
| H(20A) | 6599 | 6129 | 1772 | 18 |
| H(20B) | 8056 | 5029 | 2143 | 18 |

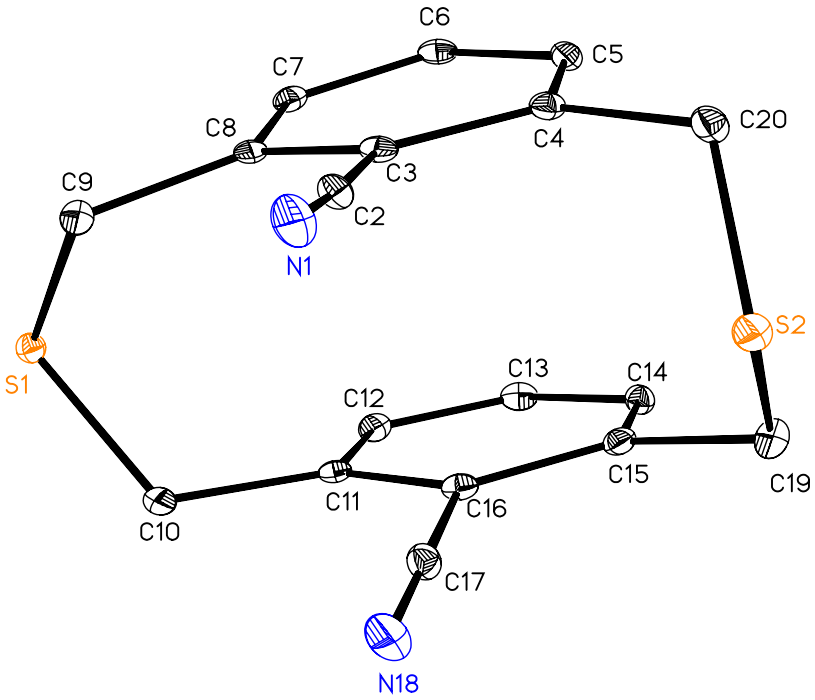
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for *syn*-dithiacyclophane 108**




**108**

Brendan Twamley




Project name : bt908t

5-31-06

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a MiTeGen fiber and data for **1** were collected at 89(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 5 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[5] software. The data were rotationally twinned and were deconvoluted using CELL_NOW[6] giving a two component twin relationship: 179.9° rotation about the reciprocal axis 1.000, 0.006, -0.995, with a refined twinning ratio of 0.285(1). The matrix used to relate both orientations to the first domain are:

0.383 0.003 -0.621

0.006 -1.000 -0.007

-1.375 0.000 -0.383

Each cell component was refined using SAINTPlus[7] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using TWINABS.[8] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[9] The structure was solved in the space group P2(1)/n (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No

---

[5] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2002**.
[6] CELL_NOW: Sheldrick, G.M., **2002**.
[7] SAINTPlus: v. 6.45a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2001**.
[8] TWINABS: v.1.05, an empirical absorption correction program, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2002**.
[9] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2003**.

decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

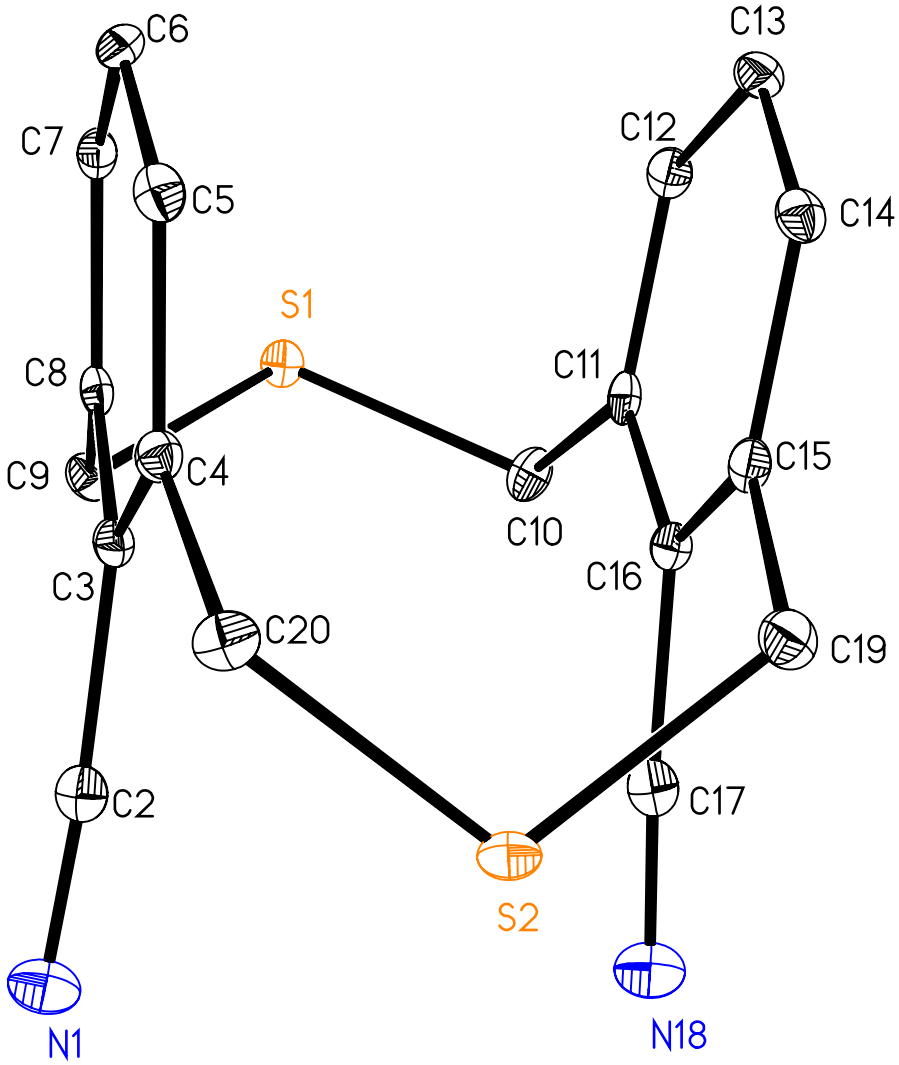


**Table A. 6 Crystal data and structure refinement for 108 (C18 H14 N2 S2)**

| | | |
|---|---|---|
| Identification code | bt908t | |
| Empirical formula | C18 H14 N2 S2 | |
| Formula weight | 322.43 | |
| Temperature | 89(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 8.653(2) Å | α = 90°. |
| | b = 14.262(4) Å | β = 100.058(4)°. |
| | c = 11.980(3) Å | γ = 90°. |
| Volume | 1455.7(6) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.471 $Mg/m^3$ | |
| Absorption coefficient | 0.362 $mm^{-1}$ | |
| F(000) | 672 | |
| Crystal size | 0.55 x 0.21 x 0.12 $mm^3$ | |
| Crystal color and habit | colorlessblock | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 2.24 to 25.25°. | |
| Index ranges | -10<=h<=10, 0<=k<=17, 0<=l<=14 | |
| Reflections collected | 34520 | |
| Independent reflections | 3182 [R(int) = 0.0000] | |
| Completeness to theta = 25.25° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9578 and 0.8256 | |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3182 / 0 / 200 | |
| Goodness-of-fit on $F^2$ | 1.083 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0332, wR2 = 0.0831 | |
| R indices (all data) | R1 = 0.0389, wR2 = 0.0851 | |
| Largest diff. peak and hole | 0.344 and -0.266 $e.Å^{-3}$ | |

**Table A. 7 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for 108 (bt 908t)**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(2) | 8843(2) | 2107(1) | 3950(2) | 14(1) |
| C(3) | 7771(2) | 2734(1) | 4374(1) | 12(1) |
| C(4) | 7985(2) | 3705(1) | 4302(2) | 12(1) |
| C(5) | 7076(2) | 4285(1) | 4838(1) | 13(1) |
| C(6) | 5955(2) | 3912(1) | 5413(2) | 14(1) |
| C(7) | 5682(2) | 2967(1) | 5406(2) | 13(1) |
| C(8) | 6569(2) | 2356(1) | 4874(1) | 11(1) |
| C(9) | 6185(2) | 1326(1) | 4810(2) | 14(1) |
| C(10) | 3917(2) | 1387(1) | 2764(2) | 16(1) |
| C(11) | 4044(2) | 2418(1) | 2541(1) | 13(1) |
| C(12) | 2984(2) | 3032(1) | 2891(2) | 14(1) |
| C(13) | 3121(2) | 3980(1) | 2748(2) | 15(1) |
| C(14) | 4357(2) | 4343(1) | 2290(1) | 13(1) |
| C(15) | 5445(2) | 3757(1) | 1938(2) | 13(1) |
| C(16) | 5226(2) | 2786(1) | 2014(2) | 13(1) |
| C(17) | 6193(2) | 2146(1) | 1508(2) | 16(1) |
| C(19) | 6810(2) | 4185(1) | 1496(2) | 17(1) |
| C(20) | 9096(2) | 4123(1) | 3616(2) | 16(1) |
| N(1) | 9733(2) | 1608(1) | 3671(1) | 21(1) |
| N(18) | 6859(2) | 1614(1) | 1063(1) | 22(1) |
| S(1) | 4136(1) | 1079(1) | 4255(1) | 13(1) |
| S(2) | 8771(1) | 3774(1) | 2126(1) | 15(1) |

**Table A. 8 Bond lengths [Å] and angles [°] for 108 (bt 908t)**

| | | | |
|---|---|---|---|
| C(2)-N(1) | 1.140(2) | C(4)-C(20) | 1.494(2) |
| C(2)-C(3) | 1.443(2) | C(5)-C(6) | 1.389(2) |
| C(3)-C(8) | 1.395(2) | C(5)-H(5) | 0.9500 |
| C(3)-C(4) | 1.402(2) | C(6)-C(7) | 1.368(2) |
| C(4)-C(5) | 1.375(2) | C(6)-H(6) | 0.9500 |

| | | | |
|---|---|---|---|
| C(7)-C(8) | 1.387(2) | C(4)-C(5)-C(6) | 120.46(16) |
| C(7)-H(7) | 0.9500 | C(4)-C(5)-H(5) | 119.8 |
| C(8)-C(9) | 1.505(2) | C(6)-C(5)-H(5) | 119.8 |
| C(9)-S(1) | 1.8165(18) | C(7)-C(6)-C(5) | 120.60(16) |
| C(9)-H(9A) | 0.9900 | C(7)-C(6)-H(6) | 119.7 |
| C(9)-H(9B) | 0.9900 | C(5)-C(6)-H(6) | 119.7 |
| C(10)-C(11) | 1.502(2) | C(6)-C(7)-C(8) | 120.80(16) |
| C(10)-S(1) | 1.8162(19) | C(6)-C(7)-H(7) | 119.6 |
| C(10)-H(10A) | 0.9900 | C(8)-C(7)-H(7) | 119.6 |
| C(10)-H(10B) | 0.9900 | C(7)-C(8)-C(3) | 117.95(16) |
| C(11)-C(12) | 1.385(2) | C(7)-C(8)-C(9) | 120.10(15) |
| C(11)-C(16) | 1.395(2) | C(3)-C(8)-C(9) | 121.91(15) |
| C(12)-C(13) | 1.371(2) | C(8)-C(9)-S(1) | 113.61(12) |
| C(12)-H(12) | 0.9500 | C(8)-C(9)-H(9A) | 108.8 |
| C(13)-C(14) | 1.385(2) | S(1)-C(9)-H(9A) | 108.8 |
| C(13)-H(13) | 0.9500 | C(8)-C(9)-H(9B) | 108.8 |
| C(14)-C(15) | 1.379(2) | S(1)-C(9)-H(9B) | 108.8 |
| C(14)-H(14) | 0.9500 | H(9A)-C(9)-H(9B) | 107.7 |
| C(15)-C(16) | 1.402(2) | C(11)-C(10)-S(1) | 114.39(12) |
| C(15)-C(19) | 1.506(2) | C(11)-C(10)-H(10A) | 108.7 |
| C(16)-C(17) | 1.442(2) | S(1)-C(10)-H(10A) | 108.7 |
| C(17)-N(18) | 1.141(2) | C(11)-C(10)-H(10B) | 108.7 |
| C(19)-S(2) | 1.8292(19) | S(1)-C(10)-H(10B) | 108.7 |
| C(19)-H(19A) | 0.9900 | H(10A)-C(10)-H(10B) | 107.6 |
| C(19)-H(19B) | 0.9900 | C(12)-C(11)-C(16) | 118.37(16) |
| C(20)-S(2) | 1.8279(18) | C(12)-C(11)-C(10) | 119.51(16) |
| C(20)-H(20A) | 0.9900 | C(16)-C(11)-C(10) | 122.09(16) |
| C(20)-H(20B) | 0.9900 | C(13)-C(12)-C(11) | 120.63(17) |
| | | C(13)-C(12)-H(12) | 119.7 |
| N(1)-C(2)-C(3) | 176.4(2) | C(11)-C(12)-H(12) | 119.7 |
| C(8)-C(3)-C(4) | 121.58(16) | C(12)-C(13)-C(14) | 120.56(17) |
| C(8)-C(3)-C(2) | 119.05(15) | C(12)-C(13)-H(13) | 119.7 |
| C(4)-C(3)-C(2) | 119.35(15) | C(14)-C(13)-H(13) | 119.7 |
| C(5)-C(4)-C(3) | 118.21(16) | C(15)-C(14)-C(13) | 120.64(16) |
| C(5)-C(4)-C(20) | 119.51(16) | C(15)-C(14)-H(14) | 119.7 |
| C(3)-C(4)-C(20) | 122.20(15) | C(13)-C(14)-H(14) | 119.7 |

| | | | |
|---|---|---|---|
| C(14)-C(15)-C(16) | 118.14(16) | S(2)-C(19)-H(19B) | 108.1 |
| C(14)-C(15)-C(19) | 118.77(16) | H(19A)-C(19)-H(19B) | 107.3 |
| C(16)-C(15)-C(19) | 123.09(16) | C(4)-C(20)-S(2) | 115.12(12) |
| C(11)-C(16)-C(15) | 121.28(16) | C(4)-C(20)-H(20A) | 108.5 |
| C(11)-C(16)-C(17) | 118.46(16) | S(2)-C(20)-H(20A) | 108.5 |
| C(15)-C(16)-C(17) | 120.22(16) | C(4)-C(20)-H(20B) | 108.5 |
| N(18)-C(17)-C(16) | 175.00(19) | S(2)-C(20)-H(20B) | 108.5 |
| C(15)-C(19)-S(2) | 116.93(13) | H(20A)-C(20)-H(20B) | 107.5 |
| C(15)-C(19)-H(19A) | 108.1 | C(10)-S(1)-C(9) | 103.90(8) |
| S(2)-C(19)-H(19A) | 108.1 | C(20)-S(2)-C(19) | 106.82(9) |
| C(15)-C(19)-H(19B) | 108.1 | | |

**Table A. 9 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 108 (bt 908t)**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(2) | 14(1) | 13(1) | 16(1) | 0(1) | 2(1) | -4(1) |
| C(3) | 10(1) | 14(1) | 11(1) | -1(1) | -1(1) | 0(1) |
| C(4) | 11(1) | 14(1) | 11(1) | -1(1) | 1(1) | -1(1) |
| C(5) | 13(1) | 11(1) | 15(1) | 0(1) | 0(1) | -2(1) |
| C(6) | 14(1) | 17(1) | 10(1) | -4(1) | 2(1) | 2(1) |
| C(7) | 10(1) | 18(1) | 10(1) | 2(1) | 1(1) | -1(1) |
| C(8) | 10(1) | 13(1) | 10(1) | 1(1) | -3(1) | 0(1) |
| C(9) | 11(1) | 14(1) | 17(1) | 3(1) | 2(1) | 0(1) |
| C(10) | 20(1) | 15(1) | 12(1) | -1(1) | 2(1) | -5(1) |
| C(11) | 14(1) | 15(1) | 8(1) | 1(1) | -3(1) | -2(1) |
| C(12) | 11(1) | 19(1) | 13(1) | 2(1) | 2(1) | -2(1) |
| C(13) | 11(1) | 18(1) | 15(1) | -1(1) | 1(1) | 3(1) |
| C(14) | 15(1) | 10(1) | 15(1) | 1(1) | 1(1) | 0(1) |
| C(15) | 13(1) | 16(1) | 10(1) | 2(1) | 1(1) | -1(1) |
| C(16) | 13(1) | 15(1) | 10(1) | -1(1) | 0(1) | 1(1) |
| C(17) | 14(1) | 14(1) | 18(1) | 2(1) | 1(1) | -4(1) |
| C(19) | 16(1) | 17(1) | 18(1) | 5(1) | 5(1) | 1(1) |
| C(20) | 16(1) | 15(1) | 17(1) | -2(1) | 5(1) | -3(1) |

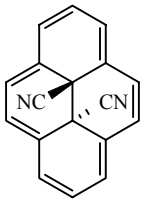
| | | | | | | |
|---|---|---|---|---|---|---|
| N(1) | 20(1) | 14(1) | 29(1) | -1(1) | 9(1) | 0(1) |
| N(18) | 22(1) | 17(1) | 29(1) | -4(1) | 8(1) | -2(1) |
| S(1) | 13(1) | 13(1) | 14(1) | 2(1) | 2(1) | -3(1) |
| S(2) | 13(1) | 16(1) | 17(1) | -1(1) | 6(1) | 0(1) |

**Table A. 10 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for 108 (bt 908t)**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5) | 7215 | 4945 | 4815 | 16 |
| H(6) | 5373 | 4317 | 5813 | 17 |
| H(7) | 4876 | 2726 | 5771 | 15 |
| H(9A) | 6458 | 1052 | 5578 | 17 |
| H(9B) | 6844 | 1015 | 4321 | 17 |
| H(10A) | 4732 | 1053 | 2432 | 19 |
| H(10B) | 2881 | 1162 | 2371 | 19 |
| H(12) | 2154 | 2794 | 3233 | 17 |
| H(13) | 2363 | 4392 | 2965 | 18 |
| H(14) | 4456 | 5003 | 2217 | 16 |
| H(19A) | 6775 | 4872 | 1605 | 20 |
| H(19B) | 6659 | 4068 | 669 | 20 |
| H(20A) | 10178 | 3945 | 3967 | 19 |
| H(20B) | 9020 | 4814 | 3655 | 19 |

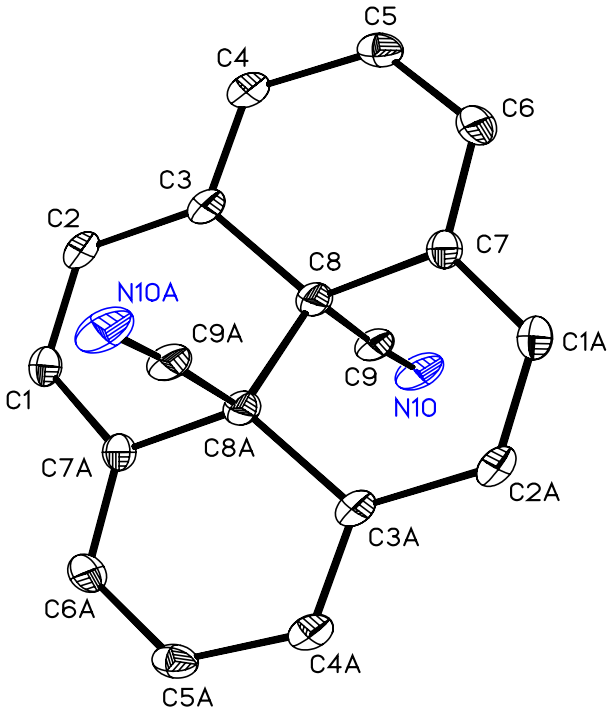
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for dicyano DHP 86**




**86**

Brendan Twamley




Project name : bt953

8-15-06

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 50 seconds, and a partial sphere of data was collected. A total of 953 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[10] software and refined using SAINTPlus[11] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[12] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[13] The structure was solved in the space group Pbca (# 61) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[10] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2001**.
[11] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[12] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[13] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Table A. 11 Crystal data and structure refinement for DHP 86 (C18 H10 N2)**

| | | |
|---|---|---|
| Identification code | bt953 | |
| Empirical formula | C18 H10 N2 | |
| Formula weight | 254.28 | |
| Temperature | 90(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pbca | |
| Unit cell dimensions | a = 7.8663(12) Å | α = 90°. |
| | b = 11.7838(18) Å | β = 90°. |
| | c = 13.402(2) Å | γ = 90°. |
| Volume | 1242.3(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.360 $Mg/m^3$ | |
| Absorption coefficient | 0.081 $mm^{-1}$ | |
| F(000) | 528 | |
| Crystal size | 0.41 x 0.38 x 0.08 $mm^3$ | |
| Crystal color and habit | greenplate | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 3.04 to 25.23°. | |
| Index ranges | -6<=h<=9, -14<=k<=14, -9<=l<=16 | |
| Reflections collected | 7085 | |
| Independent reflections | 1126 [R(int) = 0.0378] | |
| Completeness to theta = 25.23° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.993 and 0.963 | |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1126 / 0 / 91 | |
| Goodness-of-fit on $F^2$ | 1.043 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0450, wR2 = 0.1103 | |
| R indices (all data) | R1 = 0.0579, wR2 = 0.1182 | |
| Largest diff. peak and hole | 0.295 and -0.226 $e.Å^{-3}$ | |

**Table A. 12 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for 86 (bt 953).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | -2339(2) | 8555(2) | 356(1) | 25(1) |
| C(2) | -957(2) | 8213(2) | 927(1) | 24(1) |
| C(3) | 552(2) | 8839(2) | 976(1) | 22(1) |
| C(4) | 1974(2) | 8545(2) | 1521(1) | 25(1) |
| C(5) | 3439(3) | 9215(2) | 1510(1) | 27(1) |
| C(6) | 3589(2) | 10166(2) | 909(1) | 26(1) |
| C(7) | 2266(2) | 10541(2) | 314(1) | 23(1) |
| C(8) | 522(2) | 10008(2) | 481(1) | 22(1) |
| C(9) | -381(2) | 10795(2) | 1199(1) | 25(1) |
| N(10) | -993(2) | 11388(1) | 1771(1) | 35(1) |

**Table A. 13 Bond lengths [Å] and angles [°] for 86 (bt 953)**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.389(3) | C(8)-C(8)#1 | 1.529(4) |
| C(1)-C(7)#1 | 1.394(3) | C(9)-N(10) | 1.144(2) |
| C(1)-H(1) | 0.9500 | | |
| C(2)-C(3) | 1.399(3) | C(2)-C(1)-C(7)#1 | 122.96(18) |
| C(2)-H(2) | 0.9500 | C(2)-C(1)-H(1) | 118.5 |
| C(3)-C(4) | 1.380(3) | C(7)#1-C(1)-H(1) | 118.5 |
| C(3)-C(8) | 1.529(3) | C(1)-C(2)-C(3) | 122.45(17) |
| C(4)-C(5) | 1.398(3) | C(1)-C(2)-H(2) | 118.8 |
| C(4)-H(4) | 0.9500 | C(3)-C(2)-H(2) | 118.8 |
| C(5)-C(6) | 1.385(3) | C(4)-C(3)-C(2) | 125.42(17) |
| C(5)-H(5) | 0.9500 | C(4)-C(3)-C(8) | 117.93(16) |
| C(6)-C(7) | 1.384(3) | C(2)-C(3)-C(8) | 116.23(16) |
| C(6)-H(6) | 0.9500 | C(3)-C(4)-C(5) | 121.38(18) |
| C(7)-C(1)#1 | 1.394(3) | C(3)-C(4)-H(4) | 119.3 |
| C(7)-C(8) | 1.525(3) | C(5)-C(4)-H(4) | 119.3 |
| C(8)-C(9) | 1.513(3) | C(6)-C(5)-C(4) | 122.27(18) |

| | |
|---|---|
| C(6)-C(5)-H(5) | 118.9 |
| C(4)-C(5)-H(5) | 118.9 |
| C(7)-C(6)-C(5) | 121.95(18) |
| C(7)-C(6)-H(6) | 119.0 |
| C(5)-C(6)-H(6) | 119.0 |
| C(6)-C(7)-C(1)#1 | 125.73(18) |
| C(6)-C(7)-C(8) | 117.42(17) |
| C(1)#1-C(7)-C(8) | 116.51(17) |
| C(9)-C(8)-C(7) | 105.25(15) |
| C(9)-C(8)-C(8)#1 | 106.98(18) |
| C(7)-C(8)-C(8)#1 | 111.39(18) |
| C(9)-C(8)-C(3) | 106.47(14) |
| C(7)-C(8)-C(3) | 114.90(15) |
| C(8)#1-C(8)-C(3) | 111.25(19) |
| N(10)-C(9)-C(8) | 176.6(2) |

---

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z

**Table A. 14 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 86 bt953.**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 26(1) | 22(1) | 26(1) | -3(1) | 7(1) | -7(1) |
| C(2) | 34(1) | 15(1) | 21(1) | 0(1) | 8(1) | 0(1) |
| C(3) | 30(1) | 17(1) | 18(1) | 0(1) | 6(1) | 2(1) |
| C(4) | 35(1) | 22(1) | 18(1) | 1(1) | 4(1) | 4(1) |
| C(5) | 29(1) | 31(1) | 21(1) | -3(1) | -2(1) | 4(1) |
| C(6) | 24(1) | 30(1) | 24(1) | -6(1) | 2(1) | -3(1) |
| C(7) | 26(1) | 20(1) | 22(1) | -5(1) | 2(1) | -3(1) |
| C(8) | 25(1) | 20(1) | 21(1) | 1(1) | 1(1) | -1(1) |
| C(9) | 31(1) | 21(1) | 23(1) | 3(1) | 2(1) | 2(1) |
| N(10) | 51(1) | 26(1) | 27(1) | 0(1) | 7(1) | 11(1) |

**Table A. 15 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for 86 (bt 953).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | -3381 | 8156 | 426 | 30 |
| H(2) | -1040 | 7528 | 1297 | 28 |
| H(4) | 1956 | 7872 | 1911 | 30 |
| H(5) | 4365 | 9011 | 1928 | 32 |
| H(6) | 4632 | 10573 | 905 | 31 |

**Table A. 16 Hydrogen bonds for 86 (bt953) [Å and °].**

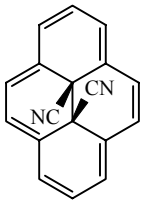
| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| C(4)-H(4)...N(10)#2 | 0.95 | 2.60 | 3.507(3) | 160.1 |

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z #2 -x,y-1/2,-z+1/2

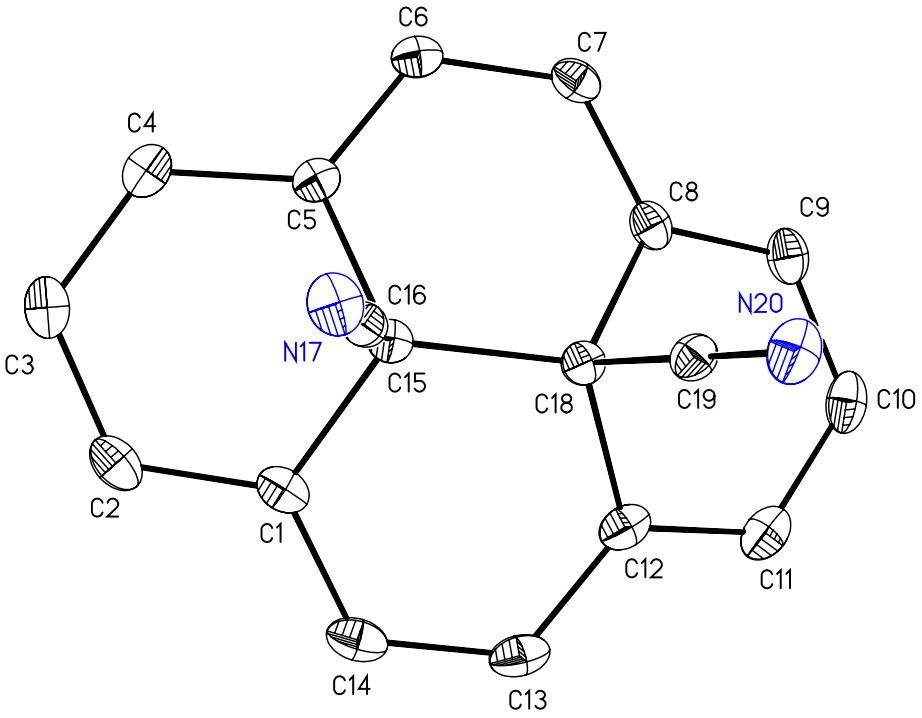
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for *cis*-dicyano DHP 117**




**117**

Brendan Twamley




Project name : Bt1105

5-9-07

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans 0.3 ° per frame for 30 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[14] software and refined using SAINTPlus[15] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[16] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[17] The structure was solved in the space group Pbca (# 61) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[14] SMART: v. 5.632, Bruker AXS, Madison, WI, **2005**.
[15] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[16] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[17] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Table A. 17 Crystal data and structure refinement for 117 (C18 H10 N2).**

| | | |
|---|---|---|
| Identification code | bt1105 | |
| Empirical formula | C18 H10 N2 | |
| Formula weight | 254.28 | |
| Temperature | 90(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pbca | |
| Unit cell dimensions | a = 13.0508(6) Å | α = 90°. |
| | b = 11.7608(6) Å | β = 90°. |
| | c = 16.0871(8) Å | γ = 90°. |
| Volume | 2469.2(2) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.368 $Mg/m^3$ | |
| Absorption coefficient | 0.082 $mm^{-1}$ | |
| F(000) | 1056 | |
| Crystal size | 0.45 x 0.33 x 0.03 $mm^3$ | |
| Crystal color and habit | green fragment | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 2.53 to 25.25°. | |
| Index ranges | -15<=h<=15, -14<=k<=14, -19<=l<=19 | |
| Reflections collected | 35893 | |
| Independent reflections | 2234 [R(int) = 0.0599] | |
| Completeness to theta = 25.25° | 99.9% | |
| Absorption correction | None | |
| Max. andmin. transmission | 0.993 and 0.964 | |
| Solution method | XS, SHELXTL v. 6.14 (Bruker, 2003) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2234 / 0 / 181 | |
| Goodness-of-fit on $F^2$ | 1.036 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0334, wR2 = 0.0861 | |
| R indices (all data) | R1 = 0.0436, wR2 = 0.0906 | |
| Largest diff. peak and hole | 0.248 and -0.147 $e.Å^{-3}$ | |

**Table A. 18 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 117 (bt 1105).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | -371(1) | 6469(1) | 2834(1) | 25(1) |
| C(2) | -225(1) | 5967(1) | 2066(1) | 29(1) |
| C(3) | 687(1) | 5439(1) | 1840(1) | 29(1) |
| C(4) | 1460(1) | 5279(1) | 2418(1) | 27(1) |
| C(5) | 1407(1) | 5729(1) | 3217(1) | 22(1) |
| C(6) | 2064(1) | 5417(1) | 3852(1) | 24(1) |
| C(7) | 1860(1) | 5632(1) | 4683(1) | 26(1) |
| C(8) | 983(1) | 6187(1) | 4951(1) | 24(1) |
| C(9) | 650(1) | 6188(1) | 5773(1) | 29(1) |
| C(10) | -292(1) | 6630(1) | 5999(1) | 32(1) |
| C(11) | -1001(1) | 6974(1) | 5405(1) | 31(1) |
| C(12) | -775(1) | 7002(1) | 4565(1) | 26(1) |
| C(13) | -1502(1) | 7125(1) | 3940(1) | 31(1) |
| C(14) | -1312(1) | 6868(1) | 3119(1) | 30(1) |
| C(15) | 591(1) | 6653(1) | 3371(1) | 21(1) |
| C(16) | 1080(1) | 7670(1) | 2984(1) | 22(1) |
| N(17) | 1480(1) | 8422(1) | 2668(1) | 28(1) |
| C(18) | 371(1) | 6926(1) | 4336(1) | 22(1) |
| C(19) | 753(1) | 8092(1) | 4529(1) | 22(1) |
| N(20) | 1045(1) | 8978(1) | 4707(1) | 31(1) |

**Table A. 19 Bond lengths [Å] and angles [°] for 117 (bt 1105)**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.383(2) | | |
| C(1)-C(14) | 1.392(2) | C(2)-C(1)-C(14) | 124.00(13) |
| C(1)-C(15) | 1.5385(18) | C(2)-C(1)-C(15) | 116.69(12) |
| C(2)-C(3) | 1.390(2) | C(14)-C(1)-C(15) | 119.19(12) |
| C(2)-H(2) | 0.9500 | C(1)-C(2)-C(3) | 122.76(13) |
| C(3)-C(4) | 1.385(2) | C(1)-C(2)-H(2) | 118.6 |
| C(3)-H(3) | 0.9500 | C(3)-C(2)-H(2) | 118.6 |
| C(4)-C(5) | 1.3924(19) | C(4)-C(3)-C(2) | 120.63(13) |
| C(4)-H(4) | 0.9500 | C(4)-C(3)-H(3) | 119.7 |
| C(5)-C(6) | 1.3821(19) | C(2)-C(3)-H(3) | 119.7 |
| C(5)-C(15) | 1.5411(18) | C(3)-C(4)-C(5) | 122.13(13) |
| C(6)-C(7) | 1.386(2) | C(3)-C(4)-H(4) | 118.9 |
| C(6)-H(6) | 0.9500 | C(5)-C(4)-H(4) | 118.9 |
| C(7)-C(8) | 1.3859(19) | C(6)-C(5)-C(4) | 123.38(13) |
| C(7)-H(7) | 0.9500 | C(6)-C(5)-C(15) | 119.84(12) |
| C(8)-C(9) | 1.391(2) | C(4)-C(5)-C(15) | 116.74(12) |
| C(8)-C(18) | 1.5412(19) | C(5)-C(6)-C(7) | 122.99(13) |
| C(9)-C(10) | 1.384(2) | C(5)-C(6)-H(6) | 118.5 |
| C(9)-H(9) | 0.9500 | C(7)-C(6)-H(6) | 118.5 |
| C(10)-C(11) | 1.391(2) | C(8)-C(7)-C(6) | 123.01(13) |
| C(10)-H(10) | 0.9500 | C(8)-C(7)-H(7) | 118.5 |
| C(11)-C(12) | 1.385(2) | C(6)-C(7)-H(7) | 118.5 |
| C(11)-H(11) | 0.9500 | C(7)-C(8)-C(9) | 123.68(13) |
| C(12)-C(13) | 1.389(2) | C(7)-C(8)-C(18) | 119.57(12) |
| C(12)-C(18) | 1.5426(18) | C(9)-C(8)-C(18) | 116.58(12) |
| C(13)-C(14) | 1.378(2) | C(10)-C(9)-C(8) | 121.90(14) |
| C(13)-H(13) | 0.9500 | C(10)-C(9)-H(9) | 119.0 |
| C(14)-H(14) | 0.9500 | C(8)-C(9)-H(9) | 119.0 |
| C(15)-C(16) | 1.4903(18) | C(9)-C(10)-C(11) | 121.32(13) |
| C(15)-C(18) | 1.6116(19) | C(9)-C(10)-H(10) | 119.3 |
| C(16)-N(17) | 1.1472(17) | C(11)-C(10)-H(10) | 119.3 |
| C(18)-C(19) | 1.4920(19) | C(12)-C(11)-C(10) | 122.42(14) |
| C(19)-N(20) | 1.1462(17) | C(12)-C(11)-H(11) | 118.8 |

| | |
|---|---|
| C(10)-C(11)-H(11) | 118.8 |
| C(11)-C(12)-C(13) | 124.27(13) |
| C(11)-C(12)-C(18) | 115.99(13) |
| C(13)-C(12)-C(18) | 119.71(13) |
| C(14)-C(13)-C(12) | 123.17(13) |
| C(14)-C(13)-H(13) | 118.4 |
| C(12)-C(13)-H(13) | 118.4 |
| C(13)-C(14)-C(1) | 123.28(13) |
| C(13)-C(14)-H(14) | 118.4 |
| C(1)-C(14)-H(14) | 118.4 |
| C(16)-C(15)-C(1) | 103.20(11) |
| C(16)-C(15)-C(5) | 101.76(10) |
| C(1)-C(15)-C(5) | 112.00(11) |
| C(16)-C(15)-C(18) | 108.57(10) |
| C(1)-C(15)-C(18) | 114.98(11) |
| C(5)-C(15)-C(18) | 114.69(11) |
| N(17)-C(16)-C(15) | 177.16(14) |
| C(19)-C(18)-C(8) | 102.17(10) |
| C(19)-C(18)-C(12) | 102.76(11) |
| C(8)-C(18)-C(12) | 112.48(11) |
| C(19)-C(18)-C(15) | 108.91(11) |
| C(8)-C(18)-C(15) | 114.46(11) |
| C(12)-C(18)-C(15) | 114.51(11) |
| N(20)-C(19)-C(18) | 177.63(14) |

**Table A. 20 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 117 (bt 1105).**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 24(1) | 20(1) | 29(1) | 5(1) | -6(1) | -4(1) |
| C(2) | 33(1) | 25(1) | 29(1) | 5(1) | -10(1) | -9(1) |
| C(3) | 42(1) | 23(1) | 23(1) | 1(1) | 1(1) | -8(1) |
| C(4) | 31(1) | 21(1) | 29(1) | 1(1) | 7(1) | -2(1) |
| C(5) | 20(1) | 19(1) | 26(1) | 2(1) | 4(1) | -3(1) |
| C(6) | 20(1) | 20(1) | 32(1) | 2(1) | 1(1) | -1(1) |
| C(7) | 25(1) | 22(1) | 30(1) | 2(1) | -7(1) | -2(1) |
| C(8) | 28(1) | 20(1) | 24(1) | -1(1) | -4(1) | -5(1) |
| C(9) | 40(1) | 23(1) | 25(1) | -2(1) | -2(1) | -6(1) |
| C(10) | 44(1) | 24(1) | 27(1) | -5(1) | 9(1) | -12(1) |
| C(11) | 30(1) | 24(1) | 40(1) | -6(1) | 12(1) | -6(1) |
| C(12) | 23(1) | 18(1) | 37(1) | -2(1) | 6(1) | -2(1) |
| C(13) | 20(1) | 25(1) | 47(1) | 1(1) | 3(1) | 1(1) |
| C(14) | 23(1) | 26(1) | 42(1) | 6(1) | -8(1) | -2(1) |
| C(15) | 20(1) | 19(1) | 24(1) | 1(1) | -1(1) | -2(1) |
| C(16) | 21(1) | 22(1) | 22(1) | -2(1) | -3(1) | 1(1) |
| N(17) | 32(1) | 24(1) | 26(1) | 1(1) | -1(1) | -5(1) |
| C(18) | 21(1) | 19(1) | 24(1) | -1(1) | 0(1) | -2(1) |
| C(19) | 20(1) | 24(1) | 23(1) | 0(1) | 4(1) | -1(1) |
| N(20) | 35(1) | 26(1) | 31(1) | -3(1) | 7(1) | -7(1) |

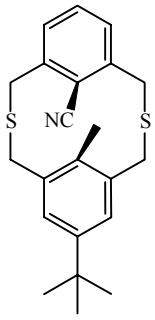
**Table A. 21 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for 117 (bt 1105).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | -771 | 5984 | 1675 | 35 |
| H(3) | 780 | 5185 | 1285 | 35 |
| H(4) | 2046 | 4848 | 2264 | 32 |
| H(6) | 2683 | 5039 | 3712 | 29 |
| H(7) | 2343 | 5388 | 5087 | 31 |
| H(9) | 1081 | 5875 | 6190 | 35 |
| H(10) | -457 | 6700 | 6572 | 38 |
| H(11) | -1665 | 7199 | 5583 | 37 |
| H(13) | -2162 | 7400 | 4087 | 37 |
| H(14) | -1849 | 6969 | 2728 | 36 |

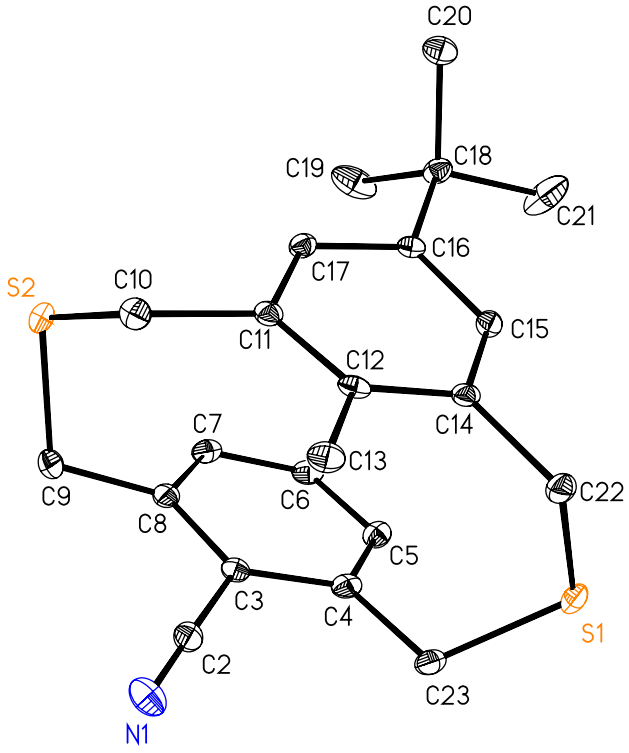
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray Structure Report for *syn*-thiacyclophane 130**

Brendan Twamley




**130**




Project name : bt907t

5-30-06

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a MiTeGen fiber and data for **1** were collected at 89(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 30 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[18] software. The data were rotationally twinned and were deconvoluted using CELL_NOW[19] giving a two component twin relationship: 180° rotation about the reciprocal axis 0.001, -0.003, 1.000, with a refined twinning ratio of 0.447(1). The matrix used to relate the second orientation to the first domain is:

-0.999 0.000 0.001

-0.001 -1.000 -0.006

0.909 0.002 0.999

Each cell component was refined using SAINTPlus[20] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using TWINABS.[21] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[22] The structure was solved in the space group P2(1)/c (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically.

---

[18] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2002**.
[19] CELL_NOW: Sheldrick, G.M., **2002**.
[20] SAINTPlus: v. 6.45a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2001**.
[21] TWINABS: v.1.05, an empirical absorption correction program, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2002**.
[22] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2003**.

No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

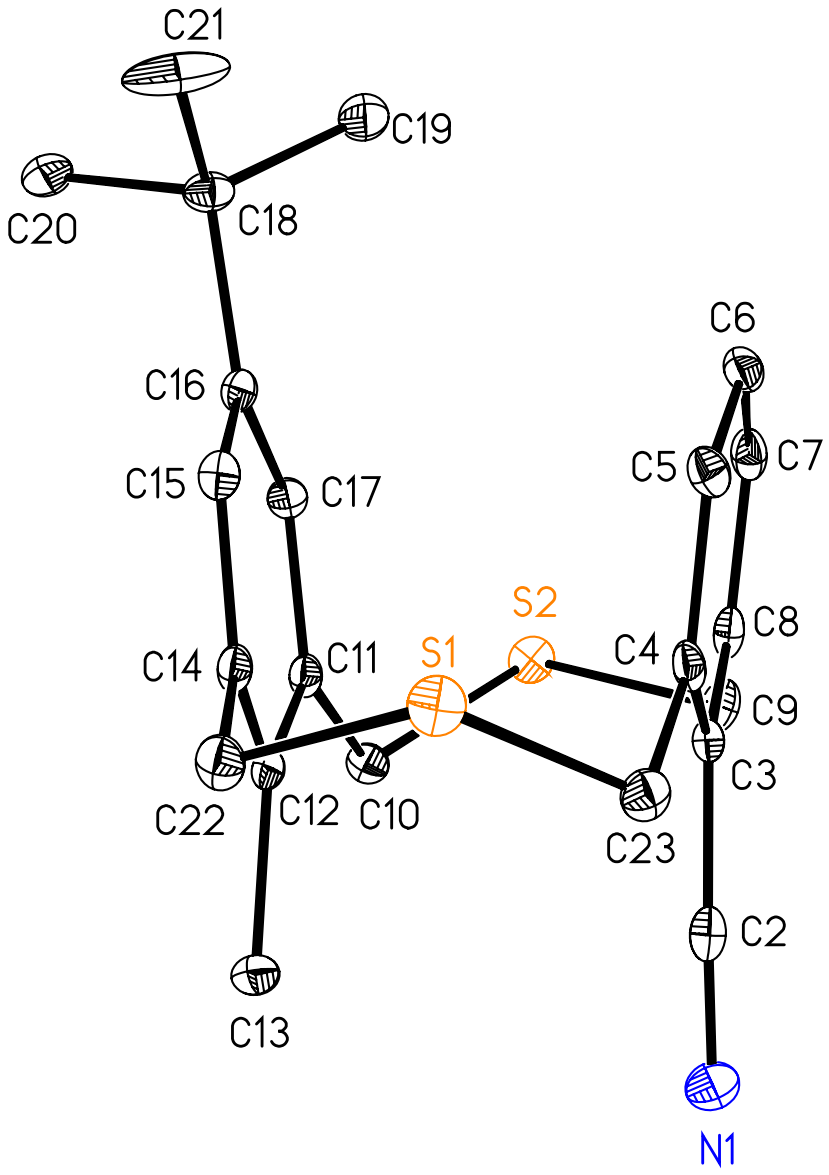


**Table A. 22 Crystal data and structure refinement for 130 (C22 H25 N S2).**

| | | |
|---|---|---|
| Identification code | bt907t | |
| Empirical formula | C22 H25 N S2 | |
| Formula weight | 367.55 | |
| Temperature | 89(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 7.1512(13) Å | α = 90°. |
| | b = 15.903(3) Å | β = 100.734(3)°. |
| | c = 17.304(3) Å | γ = 90°. |
| Volume | 1933.5(6) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.263 $Mg/m^3$ | |
| Absorption coefficient | 0.280 $mm^{-1}$ | |
| F(000) | 784 | |
| Crystal size | 0.33 x 0.13 x 0.08 $mm^3$ | |
| Crystal color and habit | colorless plate | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 1.75 to 25.25°. | |
| Index ranges | -8<=h<=8, 0<=k<=19, 0<=l<=20 | |
| Reflections collected | 40892 | |
| Independent reflections | 5056 [R(int) = 0.0000] | |
| Completeness to theta = 25.25° | 99.8% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9780 and 0.9133 | |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5056 / 6 / 231 | |
| Goodness-of-fit on $F^2$ | 0.997 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0411, wR2 = 0.1122 | |
| R indices (all data) | R1 = 0.0500, wR2 = 0.1155 | |
| Largest diff. peak and hole | 0.332 and -0.236 $e.Å^{-3}$ | |

**Table A. 23 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 130 (bt 907t).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(2) | 1296(3) | -637(1) | 3969(1) | 20(1) |
| C(3) | 534(3) | -277(1) | 3207(1) | 16(1) |
| C(4) | 423(3) | -772(1) | 2531(1) | 18(1) |
| C(5) | -482(3) | -437(1) | 1823(1) | 19(1) |
| C(6) | -1239(3) | 364(1) | 1780(1) | 20(1) |
| C(7) | -1017(3) | 864(1) | 2447(1) | 20(1) |
| C(8) | -99(3) | 560(1) | 3167(1) | 19(1) |
| C(9) | 288(3) | 1126(1) | 3873(1) | 23(1) |
| C(10) | 4288(3) | 1260(1) | 3840(1) | 21(1) |
| C(11) | 4402(3) | 837(1) | 3063(1) | 16(1) |
| C(12) | 4967(3) | -4(1) | 3025(1) | 16(1) |
| C(13) | 5886(3) | -477(1) | 3765(1) | 22(1) |
| C(14) | 4711(3) | -382(1) | 2284(1) | 17(1) |
| C(15) | 4146(3) | 91(1) | 1606(1) | 18(1) |
| C(16) | 3787(3) | 948(1) | 1630(1) | 16(1) |
| C(17) | 3871(3) | 1294(1) | 2374(1) | 16(1) |
| C(18) | 3323(3) | 1505(1) | 899(1) | 20(1) |
| C(19) | 1525(3) | 2024(2) | 910(2) | 38(1) |
| C(20) | 4985(3) | 2107(1) | 891(1) | 25(1) |
| C(21) | 3041(5) | 993(2) | 137(1) | 48(1) |
| C(22) | 4949(3) | -1317(1) | 2185(1) | 22(1) |
| C(23) | 1264(3) | -1648(1) | 2570(1) | 21(1) |
| N(1) | 1853(3) | -934(1) | 4571(1) | 29(1) |
| S(1) | 2711(1) | -1870(1) | 1829(1) | 22(1) |
| S(2) | 2160(1) | 1899(1) | 3833(1) | 21(1) |

**Table A. 24 Bond lengths [Å] and angles [°] for 130 (bt 907t)**

| | | | |
|---|---|---|---|
| C(2)-N(1) | 1.144(3) | C(17)-H(17) | 0.9500 |
| C(2)-C(3) | 1.448(3) | C(18)-C(20) | 1.529(3) |
| C(3)-C(4) | 1.400(3) | C(18)-C(21) | 1.530(3) |
| C(3)-C(8) | 1.404(3) | C(18)-C(19) | 1.531(3) |
| C(4)-C(5) | 1.380(3) | C(19)-H(19A) | 0.9800 |
| C(4)-C(23) | 1.514(3) | C(19)-H(19B) | 0.9800 |
| C(5)-C(6) | 1.380(3) | C(19)-H(19C) | 0.9800 |
| C(5)-H(5) | 0.9500 | C(20)-H(20A) | 0.9800 |
| C(6)-C(7) | 1.387(3) | C(20)-H(20B) | 0.9800 |
| C(6)-H(6) | 0.9500 | C(20)-H(20C) | 0.9800 |
| C(7)-C(8) | 1.383(3) | C(21)-H(21A) | 0.9800 |
| C(7)-H(7) | 0.9500 | C(21)-H(21B) | 0.9800 |
| C(8)-C(9) | 1.502(3) | C(21)-H(21C) | 0.9800 |
| C(9)-S(2) | 1.828(2) | C(22)-S(1) | 1.830(2) |
| C(9)-H(9A) | 0.9900 | C(22)-H(22A) | 0.9900 |
| C(9)-H(9B) | 0.9900 | C(22)-H(22B) | 0.9900 |
| C(10)-C(11) | 1.520(3) | C(23)-S(1) | 1.826(2) |
| C(10)-S(2) | 1.828(2) | C(23)-H(23A) | 0.9900 |
| C(10)-H(10A) | 0.9900 | C(23)-H(23B) | 0.9900 |
| C(10)-H(10B) | 0.9900 | | |
| C(11)-C(17) | 1.387(3) | N(1)-C(2)-C(3) | 178.1(2) |
| C(11)-C(12) | 1.403(3) | C(4)-C(3)-C(8) | 121.57(19) |
| C(12)-C(14) | 1.397(3) | C(4)-C(3)-C(2) | 119.50(18) |
| C(12)-C(13) | 1.524(3) | C(8)-C(3)-C(2) | 118.93(19) |
| C(13)-H(13A) | 0.9800 | C(5)-C(4)-C(3) | 117.99(18) |
| C(13)-H(13B) | 0.9800 | C(5)-C(4)-C(23) | 120.78(19) |
| C(13)-H(13C) | 0.9800 | C(3)-C(4)-C(23) | 121.24(18) |
| C(14)-C(15) | 1.389(3) | C(6)-C(5)-C(4) | 121.2(2) |
| C(14)-C(22) | 1.510(3) | C(6)-C(5)-H(5) | 119.4 |
| C(15)-C(16) | 1.388(3) | C(4)-C(5)-H(5) | 119.4 |
| C(15)-H(15) | 0.9500 | C(5)-C(6)-C(7) | 120.1(2) |
| C(16)-C(17) | 1.390(3) | C(5)-C(6)-H(6) | 120.0 |
| C(16)-C(18) | 1.530(3) | C(7)-C(6)-H(6) | 120.0 |

| | |
|---|---|
| C(8)-C(7)-C(6) | 120.73(19) |
| C(8)-C(7)-H(7) | 119.6 |
| C(6)-C(7)-H(7) | 119.6 |
| C(7)-C(8)-C(3) | 118.09(19) |
| C(7)-C(8)-C(9) | 120.57(19) |
| C(3)-C(8)-C(9) | 121.27(19) |
| C(8)-C(9)-S(2) | 113.39(14) |
| C(8)-C(9)-H(9A) | 108.9 |
| S(2)-C(9)-H(9A) | 108.9 |
| C(8)-C(9)-H(9B) | 108.9 |
| S(2)-C(9)-H(9B) | 108.9 |
| H(9A)-C(9)-H(9B) | 107.7 |
| C(11)-C(10)-S(2) | 114.95(14) |
| C(11)-C(10)-H(10A) | 108.5 |
| S(2)-C(10)-H(10A) | 108.5 |
| C(11)-C(10)-H(10B) | 108.5 |
| S(2)-C(10)-H(10B) | 108.5 |
| H(10A)-C(10)-H(10B) | 107.5 |
| C(17)-C(11)-C(12) | 119.63(19) |
| C(17)-C(11)-C(10) | 118.53(18) |
| C(12)-C(11)-C(10) | 121.81(18) |
| C(14)-C(12)-C(11) | 117.57(18) |
| C(14)-C(12)-C(13) | 121.42(18) |
| C(11)-C(12)-C(13) | 120.98(19) |
| C(12)-C(13)-H(13A) | 109.5 |
| C(12)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(12)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(15)-C(14)-C(12) | 120.72(19) |
| C(15)-C(14)-C(22) | 117.32(19) |
| C(12)-C(14)-C(22) | 121.91(18) |
| C(16)-C(15)-C(14) | 122.13(19) |
| C(16)-C(15)-H(15) | 118.9 |
| S(1)-C(22)-H(22B) | 108.8 |
| C(14)-C(15)-H(15) | 118.9 |
| C(15)-C(16)-C(17) | 116.13(18) |
| C(15)-C(16)-C(18) | 123.78(18) |
| C(17)-C(16)-C(18) | 120.09(18) |
| C(11)-C(17)-C(16) | 123.08(19) |
| C(11)-C(17)-H(17) | 118.5 |
| C(16)-C(17)-H(17) | 118.5 |
| C(20)-C(18)-C(16) | 108.77(17) |
| C(20)-C(18)-C(21) | 107.59(19) |
| C(16)-C(18)-C(21) | 112.23(18) |
| C(20)-C(18)-C(19) | 108.57(18) |
| C(16)-C(18)-C(19) | 110.84(17) |
| C(21)-C(18)-C(19) | 108.7(2) |
| C(18)-C(19)-H(19A) | 109.5 |
| C(18)-C(19)-H(19B) | 109.5 |
| H(19A)-C(19)-H(19B) | 109.5 |
| C(18)-C(19)-H(19C) | 109.5 |
| H(19A)-C(19)-H(19C) | 109.5 |
| H(19B)-C(19)-H(19C) | 109.5 |
| C(18)-C(20)-H(20A) | 109.5 |
| C(18)-C(20)-H(20B) | 109.5 |
| H(20A)-C(20)-H(20B) | 109.5 |
| C(18)-C(20)-H(20C) | 109.5 |
| H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 |
| C(18)-C(21)-H(21A) | 109.5 |
| C(18)-C(21)-H(21B) | 109.5 |
| H(21A)-C(21)-H(21B) | 109.5 |
| C(18)-C(21)-H(21C) | 109.5 |
| H(21A)-C(21)-H(21C) | 109.5 |
| H(21B)-C(21)-H(21C) | 109.5 |
| C(14)-C(22)-S(1) | 113.67(14) |
| C(14)-C(22)-H(22A) | 108.8 |
| S(1)-C(22)-H(22A) | 108.8 |
| C(14)-C(22)-H(22B) | 108.8 |
| C(4)-C(23)-H(23B) | 108.6 |

| | | | |
|---|---|---|---|
| H(22A)-C(22)-H(22B) | 107.7 | S(1)-C(23)-H(23B) | 108.6 |
| C(4)-C(23)-S(1) | 114.72(14) | H(23A)-C(23)-H(23B) | 107.6 |
| C(4)-C(23)-H(23A) | 108.6 | C(23)-S(1)-C(22) | 104.20(10) |
| S(1)-C(23)-H(23A) | 108.6 | C(10)-S(2)-C(9) | 103.96(10) |

**Table A. 25 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 130 (bt907t).**

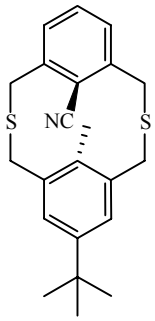
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(2) | 19(1) | 21(1) | 22(1) | -2(1) | 6(1) | -2(1) |
| C(3) | 10(1) | 18(1) | 19(1) | 1(1) | 3(1) | -2(1) |
| C(4) | 10(1) | 17(1) | 27(1) | 1(1) | 3(1) | -3(1) |
| C(5) | 15(1) | 19(1) | 23(1) | -2(1) | 1(1) | -2(1) |
| C(6) | 14(1) | 21(1) | 24(1) | 4(1) | 0(1) | -2(1) |
| C(7) | 14(1) | 14(1) | 34(1) | 2(1) | 8(1) | 2(1) |
| C(8) | 14(1) | 18(1) | 27(1) | -2(1) | 10(1) | -3(1) |
| C(9) | 24(1) | 24(1) | 26(1) | -5(1) | 14(1) | -2(1) |
| C(10) | 19(1) | 23(1) | 19(1) | 1(1) | 2(1) | -1(1) |
| C(11) | 13(1) | 17(1) | 20(1) | 0(1) | 5(1) | -2(1) |
| C(12) | 12(1) | 18(1) | 20(1) | 5(1) | 4(1) | -2(1) |
| C(13) | 22(1) | 21(1) | 21(1) | 7(1) | 3(1) | 1(1) |
| C(14) | 13(1) | 14(1) | 25(1) | 2(1) | 8(1) | 0(1) |
| C(15) | 17(1) | 18(1) | 20(1) | -2(1) | 5(1) | -2(1) |
| C(16) | 14(1) | 16(1) | 19(1) | 2(1) | 4(1) | -4(1) |
| C(17) | 17(1) | 13(1) | 20(1) | 1(1) | 4(1) | 0(1) |
| C(18) | 25(1) | 16(1) | 17(1) | 2(1) | 1(1) | -2(1) |
| C(19) | 27(1) | 47(2) | 39(2) | 26(1) | 8(1) | 7(1) |
| C(20) | 28(1) | 23(1) | 23(1) | 8(1) | 5(1) | 0(1) |
| C(21) | 100(2) | 22(1) | 16(1) | 2(1) | -8(1) | -11(1) |
| C(22) | 21(1) | 15(1) | 30(1) | 1(1) | 8(1) | 3(1) |
| C(23) | 21(1) | 14(1) | 26(1) | 2(1) | 5(1) | -2(1) |
| N(1) | 29(1) | 38(1) | 21(1) | 4(1) | 6(1) | 1(1) |
| S(1) | 26(1) | 14(1) | 26(1) | -5(1) | 6(1) | 0(1) |
| S(2) | 27(1) | 16(1) | 22(1) | -6(1) | 6(1) | -1(1) |

**Table A. 26 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for 130 (bt 907t).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5) | -585 | -764 | 1358 | 23 |
| H(6) | -1912 | 572 | 1292 | 24 |
| H(7) | -1501 | 1422 | 2409 | 24 |
| H(9A) | 660 | 777 | 4351 | 28 |
| H(9B) | -899 | 1426 | 3919 | 28 |
| H(10A) | 5422 | 1623 | 3993 | 25 |
| H(10B) | 4341 | 821 | 4249 | 25 |
| H(13A) | 4924 | -823 | 3950 | 32 |
| H(13B) | 6419 | -74 | 4175 | 32 |
| H(13C) | 6904 | -839 | 3645 | 32 |
| H(15) | 4000 | -180 | 1109 | 21 |
| H(17) | 3549 | 1870 | 2412 | 20 |
| H(19A) | 1271 | 2385 | 443 | 56 |
| H(19B) | 1710 | 2374 | 1384 | 56 |
| H(19C) | 443 | 1646 | 909 | 56 |
| H(20A) | 6120 | 1785 | 834 | 37 |
| H(20B) | 5240 | 2425 | 1384 | 37 |
| H(20C) | 4661 | 2498 | 448 | 37 |
| H(21A) | 1991 | 596 | 128 | 72 |
| H(21B) | 4211 | 683 | 109 | 72 |
| H(21C) | 2742 | 1374 | -315 | 72 |
| H(22A) | 5554 | -1559 | 2698 | 26 |
| H(22B) | 5819 | -1412 | 1811 | 26 |
| H(23A) | 212 | -2061 | 2512 | 25 |
| H(23B) | 2059 | -1730 | 3098 | 25 |

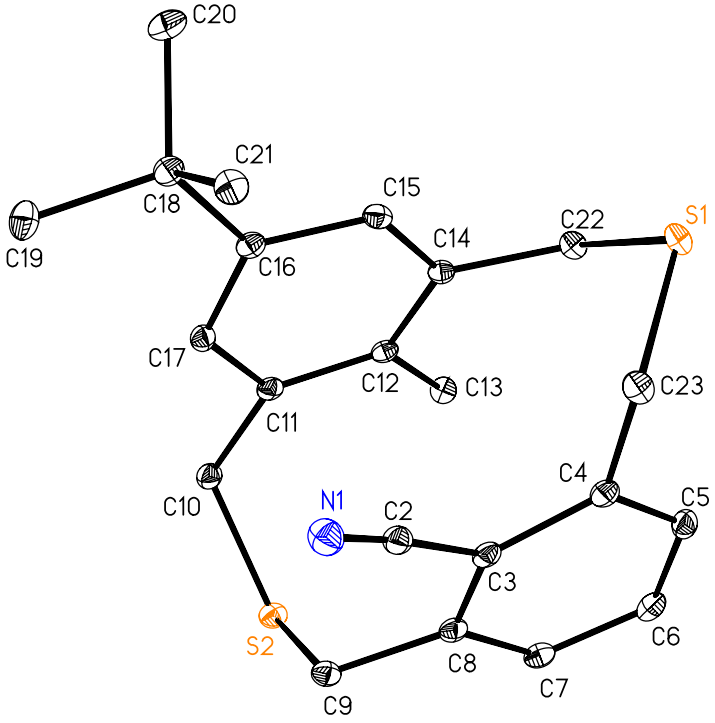
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for *anti*-thiacyclophane 131**




**131**

Brendan Twamley




Project name : bt909

5-31-06

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a MiTeGen fiber and data were collected at 89(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 10 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[23] software and refined using SAINTPlus[24] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[25] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[26] The structure was solved in the space group C2/c (# 15) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[23] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2001**.
[24] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[25] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[26] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

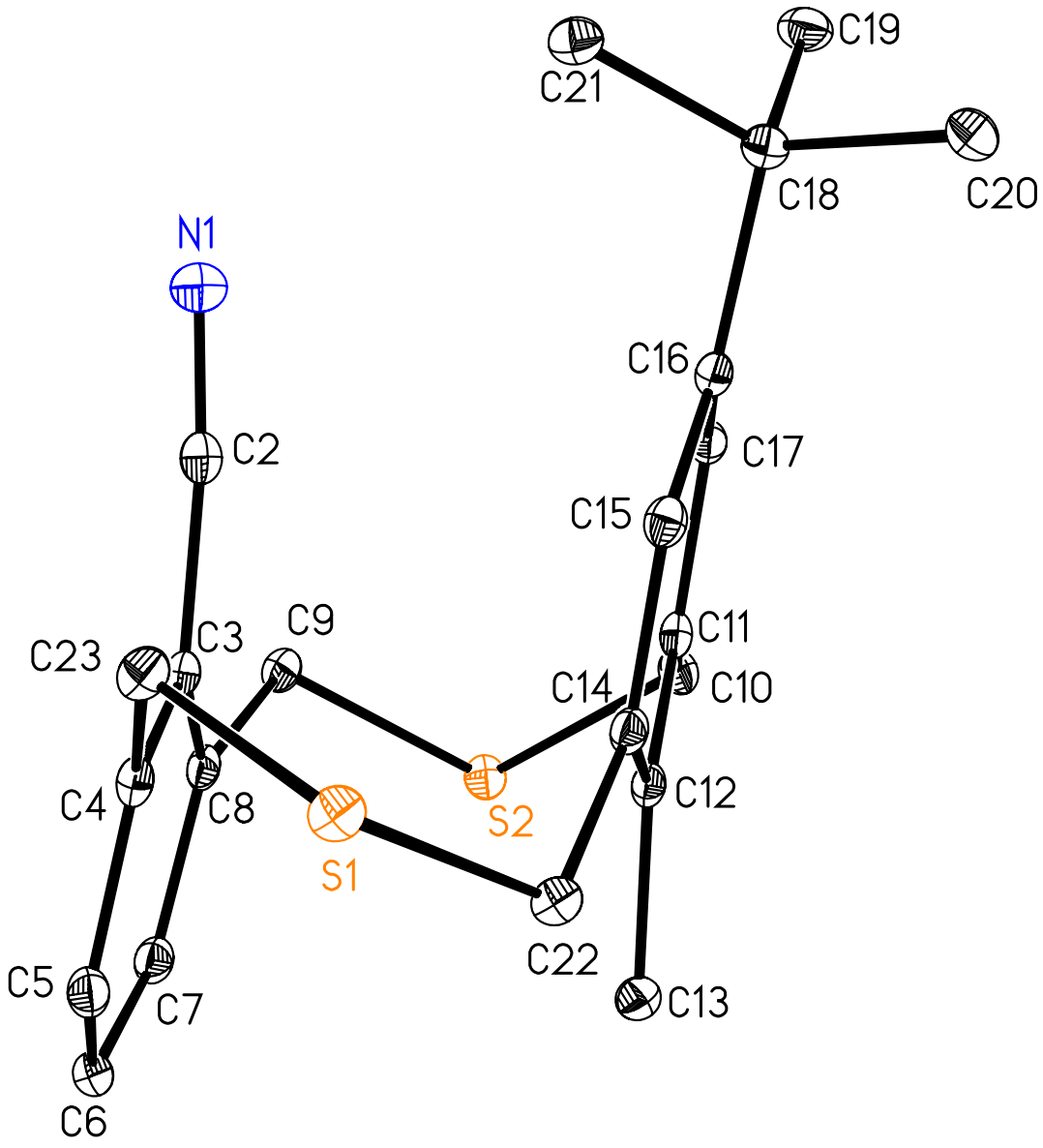

C19
C21
C18
C20
N1
C16
C2
C17
C15
C9
C11
C23
C3
C14
C10
C4
C8
S2
C12
S1
C22
C5
C7
C13
C6

**Table A. 27 Crystal data and structure refinement for 131 (C22 H25 N S2).**

| | |
|---|---|
| Identification code | bt909 |
| Empirical formula | C22 H25 N S2 |
| Formula weight | 367.55 |
| Temperature | 89(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | a = 29.829(4) Å α = 90°.<br>b = 7.2157(9) Å β = 122.036(1)°.<br>c = 20.565(3) Å γ = 90°. |
| Volume | 3752.3(9) $Å^3$ |
| Z | 8 |
| Density (calculated) | 1.301 $Mg/m^3$ |
| Absorption coefficient | 0.288 $mm^{-1}$ |
| F(000) | 1568 |
| Crystal size | 0.48 x 0.25 x 0.19 $mm^3$ |
| Crystal color and habit | colorlessblock |
| Diffractometer | Bruker/Siemens SMART APEX |
| Theta range for data collection | 1.61 to 25.25°. |
| Index ranges | -35<=h<=35, -8<=k<=8, -24<=l<=24 |
| Reflections collected | 27816 |
| Independent reflections | 3403 [R(int) = 0.0221] |
| Completeness to theta = 25.25° | 100.0% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9473 and 0.8740 |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3403 / 0 / 230 |
| Goodness-of-fit on $F^2$ | 1.084 |
| Final R indices [I>2sigma(I)] | R1 = 0.0291, wR2 = 0.0770 |
| R indices (all data) | R1 = 0.0307, wR2 = 0.0784 |
| Largest diff. peak and hole | 0.352 and -0.215 $e.Å^{-3}$ |

**Table A. 28 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 131 (bt 909).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(2) | 1761(1) | 936(2) | 4797(1) | 16(1) |
| C(3) | 1501(1) | 721(2) | 5221(1) | 15(1) |
| C(4) | 993(1) | -74(2) | 4854(1) | 16(1) |
| C(5) | 785(1) | -509(2) | 5301(1) | 18(1) |
| C(6) | 1071(1) | -173(2) | 6084(1) | 18(1) |
| C(7) | 1555(1) | 731(2) | 6426(1) | 17(1) |
| C(8) | 1771(1) | 1242(2) | 5995(1) | 15(1) |
| C(9) | 2266(1) | 2410(2) | 6354(1) | 16(1) |
| C(10) | 1903(1) | 6199(2) | 5879(1) | 16(1) |
| C(11) | 1472(1) | 5507(2) | 5098(1) | 14(1) |
| C(12) | 989(1) | 4780(2) | 4945(1) | 14(1) |
| C(13) | 844(1) | 4796(2) | 5545(1) | 16(1) |
| C(14) | 642(1) | 4034(2) | 4213(1) | 14(1) |
| C(15) | 746(1) | 4226(2) | 3635(1) | 15(1) |
| C(16) | 1203(1) | 5108(2) | 3759(1) | 14(1) |
| C(17) | 1568(1) | 5666(2) | 4506(1) | 14(1) |
| C(18) | 1286(1) | 5383(2) | 3092(1) | 16(1) |
| C(19) | 1813(1) | 6349(2) | 3351(1) | 21(1) |
| C(20) | 837(1) | 6604(2) | 2478(1) | 22(1) |
| C(21) | 1281(1) | 3487(2) | 2745(1) | 18(1) |
| C(22) | 160(1) | 2950(2) | 4062(1) | 16(1) |
| C(23) | 675(1) | -346(2) | 3998(1) | 18(1) |
| N(1) | 1985(1) | 963(2) | 4484(1) | 22(1) |
| S(1) | 30(1) | 804(1) | 3522(1) | 17(1) |
| S(2) | 2175(1) | 4623(1) | 6699(1) | 16(1) |

**Table A. 29 Bond lengths [Å] and angles [°] for 131 (bt 909)**

| | | | |
|---|---|---|---|
| C(2)-N(1) | 1.1472(19) | C(18)-C(19) | 1.5339(19) |
| C(2)-C(3) | 1.4495(19) | C(18)-C(21) | 1.5388(19) |
| C(3)-C(8) | 1.4011(19) | C(18)-C(20) | 1.5401(19) |
| C(3)-C(4) | 1.408(2) | C(19)-H(19A) | 0.9800 |
| C(4)-C(5) | 1.389(2) | C(19)-H(19B) | 0.9800 |
| C(4)-C(23) | 1.5059(19) | C(19)-H(19C) | 0.9800 |
| C(5)-C(6) | 1.388(2) | C(20)-H(20A) | 0.9800 |
| C(5)-H(5) | 0.9500 | C(20)-H(20B) | 0.9800 |
| C(6)-C(7) | 1.388(2) | C(20)-H(20C) | 0.9800 |
| C(6)-H(6) | 0.9500 | C(21)-H(21A) | 0.9800 |
| C(7)-C(8) | 1.3946(19) | C(21)-H(21B) | 0.9800 |
| C(7)-H(7) | 0.9500 | C(21)-H(21C) | 0.9800 |
| C(8)-C(9) | 1.5096(19) | C(22)-S(1) | 1.8234(14) |
| C(9)-S(2) | 1.8252(14) | C(22)-H(22A) | 0.9900 |
| C(9)-H(9A) | 0.9900 | C(22)-H(22B) | 0.9900 |
| C(9)-H(9B) | 0.9900 | C(23)-S(1) | 1.8301(14) |
| C(10)-C(11) | 1.5132(18) | C(23)-H(23A) | 0.9900 |
| C(10)-S(2) | 1.8287(14) | C(23)-H(23B) | 0.9900 |
| C(10)-H(10A) | 0.9900 | | |
| C(10)-H(10B) | 0.9900 | N(1)-C(2)-C(3) | 174.33(15) |
| C(11)-C(17) | 1.3961(19) | C(8)-C(3)-C(4) | 121.67(12) |
| C(11)-C(12) | 1.4038(19) | C(8)-C(3)-C(2) | 119.04(12) |
| C(12)-C(14) | 1.4062(19) | C(4)-C(3)-C(2) | 119.24(12) |
| C(12)-C(13) | 1.5088(18) | C(5)-C(4)-C(3) | 117.93(13) |
| C(13)-H(13A) | 0.9800 | C(5)-C(4)-C(23) | 121.22(13) |
| C(13)-H(13B) | 0.9800 | C(3)-C(4)-C(23) | 120.77(12) |
| C(13)-H(13C) | 0.9800 | C(6)-C(5)-C(4) | 120.92(13) |
| C(14)-C(15) | 1.3872(19) | C(6)-C(5)-H(5) | 119.5 |
| C(14)-C(22) | 1.5173(18) | C(4)-C(5)-H(5) | 119.5 |
| C(15)-C(16) | 1.3978(19) | C(7)-C(6)-C(5) | 120.23(13) |
| C(15)-H(15) | 0.9500 | C(7)-C(6)-H(6) | 119.9 |
| C(16)-C(17) | 1.3901(19) | C(5)-C(6)-H(6) | 119.9 |
| C(16)-C(18) | 1.5319(18) | C(6)-C(7)-C(8) | 120.63(13) |
| C(17)-H(17) | 0.9500 | C(6)-C(7)-H(7) | 119.7 |

| | | | |
|---|---|---|---|
| C(8)-C(7)-H(7) | 119.7 | C(17)-C(16)-C(18) | 123.11(12) |
| C(7)-C(8)-C(3) | 118.05(13) | C(15)-C(16)-C(18) | 120.05(12) |
| C(7)-C(8)-C(9) | 119.89(12) | C(16)-C(17)-C(11) | 122.42(12) |
| C(3)-C(8)-C(9) | 121.98(12) | C(16)-C(17)-H(17) | 118.8 |
| C(8)-C(9)-S(2) | 111.71(9) | C(11)-C(17)-H(17) | 118.8 |
| C(8)-C(9)-H(9A) | 109.3 | C(16)-C(18)-C(19) | 111.81(11) |
| S(2)-C(9)-H(9A) | 109.3 | C(16)-C(18)-C(21) | 109.49(11) |
| C(8)-C(9)-H(9B) | 109.3 | C(19)-C(18)-C(21) | 108.76(11) |
| S(2)-C(9)-H(9B) | 109.3 | C(16)-C(18)-C(20) | 108.86(11) |
| H(9A)-C(9)-H(9B) | 107.9 | C(19)-C(18)-C(20) | 108.11(12) |
| C(11)-C(10)-S(2) | 119.07(10) | C(21)-C(18)-C(20) | 109.79(11) |
| C(11)-C(10)-H(10A) | 107.5 | C(18)-C(19)-H(19A) | 109.5 |
| S(2)-C(10)-H(10A) | 107.5 | C(18)-C(19)-H(19B) | 109.5 |
| C(11)-C(10)-H(10B) | 107.5 | H(19A)-C(19)-H(19B) | 109.5 |
| S(2)-C(10)-H(10B) | 107.5 | C(18)-C(19)-H(19C) | 109.5 |
| H(10A)-C(10)-H(10B) | 107.0 | H(19A)-C(19)-H(19C) | 109.5 |
| C(17)-C(11)-C(12) | 119.81(12) | H(19B)-C(19)-H(19C) | 109.5 |
| C(17)-C(11)-C(10) | 116.61(12) | C(18)-C(20)-H(20A) | 109.5 |
| C(12)-C(11)-C(10) | 123.56(12) | C(18)-C(20)-H(20B) | 109.5 |
| C(11)-C(12)-C(14) | 117.93(12) | H(20A)-C(20)-H(20B) | 109.5 |
| C(11)-C(12)-C(13) | 121.38(12) | C(18)-C(20)-H(20C) | 109.5 |
| C(14)-C(12)-C(13) | 120.69(12) | H(20A)-C(20)-H(20C) | 109.5 |
| C(12)-C(13)-H(13A) | 109.5 | H(20B)-C(20)-H(20C) | 109.5 |
| C(12)-C(13)-H(13B) | 109.5 | C(18)-C(21)-H(21A) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 | C(18)-C(21)-H(21B) | 109.5 |
| C(12)-C(13)-H(13C) | 109.5 | H(21A)-C(21)-H(21B) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 | C(18)-C(21)-H(21C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 | H(21A)-C(21)-H(21C) | 109.5 |
| C(15)-C(14)-C(12) | 120.46(12) | H(21B)-C(21)-H(21C) | 109.5 |
| C(15)-C(14)-C(22) | 119.73(12) | C(14)-C(22)-S(1) | 115.76(9) |
| C(12)-C(14)-C(22) | 119.77(12) | C(14)-C(22)-H(22A) | 108.3 |
| C(14)-C(15)-C(16) | 121.92(13) | C(14)-C(22)-H(22B) | 108.3 |
| C(14)-C(15)-H(15) | 119.0 | S(1)-C(22)-H(22B) | 108.3 |
| C(16)-C(15)-H(15) | 119.0 | H(22A)-C(22)-H(22B) | 107.4 |
| C(17)-C(16)-C(15) | 116.82(12) | C(4)-C(23)-S(1) | 113.47(10) |
| | | S(1)-C(23)-H(23B) | 108.9 |

| | | | |
|---|---|---|---|
| C(4)-C(23)-H(23A) | 108.9 | H(23A)-C(23)-H(23B) | 107.7 |
| S(1)-C(23)-H(23A) | 108.9 | C(22)-S(1)-C(23) | 103.62(6) |
| S(1)-C(22)-H(22A) | 108.3 | C(9)-S(2)-C(10) | 105.68(6) |
| C(4)-C(23)-H(23B) | 108.9 | | |

**Table A. 30 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 131 (bt 909).**

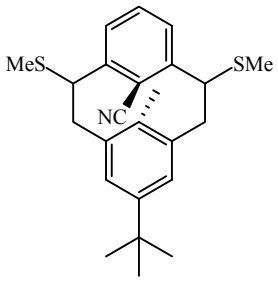
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(2) | 16(1) | 14(1) | 16(1) | 0(1) | 6(1) | 0(1) |
| C(3) | 17(1) | 11(1) | 18(1) | 3(1) | 10(1) | 4(1) |
| C(4) | 18(1) | 11(1) | 19(1) | 1(1) | 9(1) | 3(1) |
| C(5) | 16(1) | 13(1) | 25(1) | 1(1) | 12(1) | 0(1) |
| C(6) | 23(1) | 14(1) | 23(1) | 5(1) | 16(1) | 4(1) |
| C(7) | 21(1) | 15(1) | 17(1) | 2(1) | 10(1) | 5(1) |
| C(8) | 16(1) | 11(1) | 19(1) | 2(1) | 9(1) | 4(1) |
| C(9) | 15(1) | 16(1) | 17(1) | 0(1) | 8(1) | 3(1) |
| C(10) | 18(1) | 14(1) | 15(1) | 0(1) | 7(1) | -2(1) |
| C(11) | 16(1) | 9(1) | 15(1) | 1(1) | 7(1) | 2(1) |
| C(12) | 16(1) | 11(1) | 15(1) | 2(1) | 8(1) | 4(1) |
| C(13) | 17(1) | 16(1) | 17(1) | -1(1) | 10(1) | 0(1) |
| C(14) | 13(1) | 12(1) | 16(1) | 2(1) | 7(1) | 3(1) |
| C(15) | 14(1) | 14(1) | 13(1) | 0(1) | 5(1) | 2(1) |
| C(16) | 16(1) | 12(1) | 16(1) | 1(1) | 9(1) | 3(1) |
| C(17) | 14(1) | 12(1) | 18(1) | 1(1) | 9(1) | 1(1) |
| C(18) | 18(1) | 16(1) | 15(1) | 1(1) | 10(1) | 1(1) |
| C(19) | 25(1) | 21(1) | 23(1) | -2(1) | 17(1) | -4(1) |
| C(20) | 27(1) | 23(1) | 17(1) | 5(1) | 13(1) | 5(1) |
| C(21) | 19(1) | 20(1) | 17(1) | -2(1) | 11(1) | -1(1) |
| C(22) | 15(1) | 17(1) | 16(1) | -2(1) | 8(1) | 0(1) |
| C(23) | 17(1) | 18(1) | 20(1) | -3(1) | 10(1) | 0(1) |
| N(1) | 21(1) | 26(1) | 21(1) | 0(1) | 12(1) | 0(1) |
| S(1) | 13(1) | 18(1) | 17(1) | -4(1) | 6(1) | -3(1) |
| S(2) | 19(1) | 16(1) | 12(1) | -1(1) | 6(1) | 0(1) |

**Table A. 31 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for 131 (bt 909).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5) | 443 | -1043 | 5066 | 21 |
| H(6) | 935 | -563 | 6388 | 22 |
| H(7) | 1740 | 1005 | 6959 | 21 |
| H(9A) | 2364 | 2641 | 5971 | 20 |
| H(9B) | 2560 | 1724 | 6788 | 20 |
| H(10A) | 1763 | 7297 | 6003 | 20 |
| H(10B) | 2200 | 6631 | 5833 | 20 |
| H(13A) | 480 | 5245 | 5315 | 25 |
| H(13B) | 1086 | 5616 | 5967 | 25 |
| H(13C) | 871 | 3537 | 5741 | 25 |
| H(15) | 501 | 3744 | 3140 | 18 |
| H(17) | 1895 | 6174 | 4617 | 17 |
| H(19A) | 1813 | 7586 | 3548 | 31 |
| H(19B) | 1859 | 6461 | 2915 | 31 |
| H(19C) | 2105 | 5618 | 3757 | 31 |
| H(20A) | 495 | 6022 | 2311 | 32 |
| H(20B) | 878 | 6740 | 2038 | 32 |
| H(20C) | 851 | 7828 | 2695 | 32 |
| H(21A) | 1564 | 2707 | 3141 | 27 |
| H(21B) | 1338 | 3663 | 2322 | 27 |
| H(21C) | 939 | 2885 | 2553 | 27 |
| H(22A) | -155 | 3760 | 3779 | 19 |
| H(22B) | 202 | 2648 | 4561 | 19 |
| H(23A) | 620 | -1690 | 3886 | 22 |
| H(23B) | 879 | 137 | 3781 | 22 |

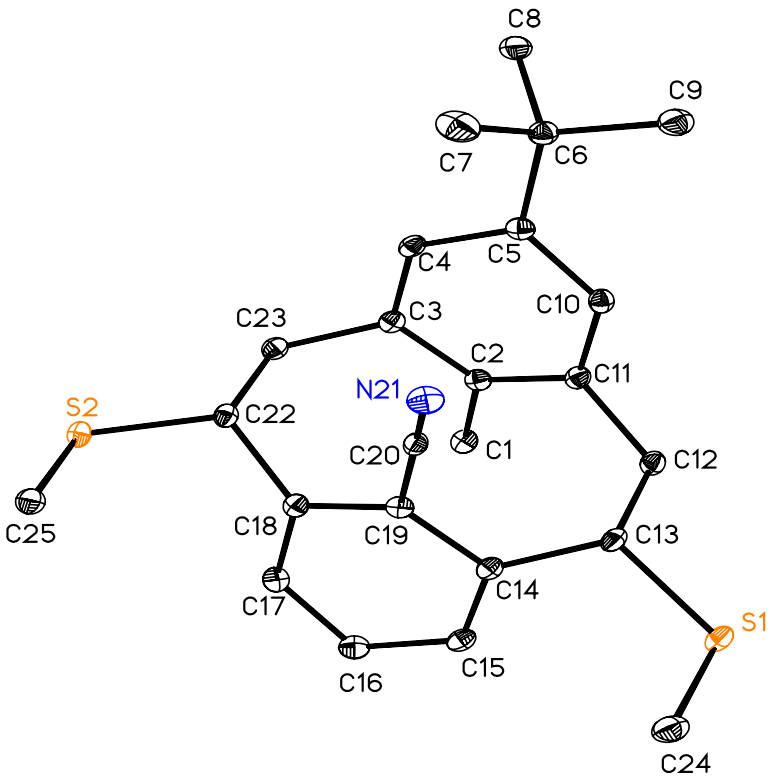
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for thiomethylcyclophane 134**




**134**

Brendan Twamley




Project name : bt960

8-21-06

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 89(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 10 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[27] software and refined using SAINTPlus[28] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[29] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[30] The structure was solved in the space group P2(1)/c (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[27] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2001**.
[28] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[29] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[30] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Table A. 32 Crystal data and structure refinement for 134 (C24 H29 N S2).**

| | | |
|---|---|---|
| Identification code | bt960 | |
| Empirical formula | C24 H29 N S2 | |
| Formula weight | 395.60 | |
| Temperature | 89(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 12.1190(10) Å | α = 90°. |
| | b = 10.0317(8) Å | β = 104.752(1)°. |
| | c = 18.1594(14) Å | γ = 90°. |
| Volume | 2134.9(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.231 $Mg/m^3$ | |
| Absorption coefficient | 0.258 $mm^{-1}$ | |
| F(000) | 848 | |
| Crystal size | 0.52 x 0.41 x 0.25 $mm^3$ | |
| Crystal color and habit | colorless block | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 1.74 to 25.25°. | |
| Index ranges | -14<=h<=14, -12<=k<=12, -21<=l<=21 | |
| Reflections collected | 31239 | |
| Independent reflections | 3858 [R(int) = 0.0277] | |
| Completeness to theta = 25.25° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9383 and 0.8775 | |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3858 / 0 / 250 | |
| Goodness-of-fit on $F^2$ | 1.042 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0340, wR2 = 0.0853 | |
| R indices (all data) | R1 = 0.0364, wR2 = 0.0870 | |
| Largest diff. peak and hole | 0.459 and -0.175 $e.Å^{-3}$ | |

**Table A. 33 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 134 (bt 960)**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 4936(1) | 7620(2) | 8212(1) | 19(1) |
| C(2) | 5979(1) | 8167(2) | 8005(1) | 16(1) |
| C(3) | 6336(1) | 9490(2) | 8184(1) | 16(1) |
| C(4) | 7136(1) | 10056(2) | 7849(1) | 16(1) |
| C(5) | 7655(1) | 9337(2) | 7370(1) | 17(1) |
| C(6) | 8476(1) | 10050(2) | 6984(1) | 19(1) |
| C(7) | 9475(2) | 10637(2) | 7594(1) | 32(1) |
| C(8) | 7842(2) | 11191(2) | 6493(1) | 25(1) |
| C(9) | 8957(2) | 9118(2) | 6475(1) | 26(1) |
| C(10) | 7443(1) | 7971(2) | 7319(1) | 17(1) |
| C(11) | 6645(1) | 7370(2) | 7649(1) | 17(1) |
| C(12) | 6670(1) | 5869(2) | 7756(1) | 19(1) |
| C(13) | 7531(1) | 5463(2) | 8530(1) | 18(1) |
| C(14) | 7219(1) | 6126(2) | 9202(1) | 16(1) |
| C(15) | 6494(1) | 5567(2) | 9600(1) | 18(1) |
| C(16) | 6064(1) | 6339(2) | 10100(1) | 20(1) |
| C(17) | 6229(1) | 7707(2) | 10137(1) | 18(1) |
| C(18) | 6944(1) | 8310(2) | 9745(1) | 16(1) |
| C(19) | 7540(1) | 7467(2) | 9360(1) | 15(1) |
| C(20) | 8530(1) | 7970(2) | 9140(1) | 15(1) |
| C(22) | 6965(1) | 9803(2) | 9605(1) | 16(1) |
| C(23) | 6057(1) | 10196(2) | 8853(1) | 17(1) |
| C(24) | 8590(2) | 3324(2) | 9431(1) | 27(1) |
| C(25) | 7975(1) | 10372(2) | 11095(1) | 21(1) |
| N(21) | 9391(1) | 8299(1) | 9045(1) | 22(1) |
| S(1) | 7529(1) | 3651(1) | 8554(1) | 23(1) |
| S(2) | 6709(1) | 10819(1) | 10373(1) | 18(1) |

**Table A. 34 Bond lengths [Å] and angles [°] for 134 (bt 960)**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.510(2) | C(14)-C(15) | 1.390(2) |
| C(1)-H(1A) | 0.9800 | C(14)-C(19) | 1.409(2) |
| C(1)-H(1B) | 0.9800 | C(15)-C(16) | 1.391(2) |
| C(1)-H(1C) | 0.9800 | C(15)-H(15) | 0.9500 |
| C(2)-C(11) | 1.405(2) | C(16)-C(17) | 1.386(2) |
| C(2)-C(3) | 1.408(2) | C(16)-H(16) | 0.9500 |
| C(3)-C(4) | 1.390(2) | C(17)-C(18) | 1.393(2) |
| C(3)-C(23) | 1.518(2) | C(17)-H(17) | 0.9500 |
| C(4)-C(5) | 1.397(2) | C(18)-C(19) | 1.408(2) |
| C(4)-H(4) | 0.9500 | C(18)-C(22) | 1.521(2) |
| C(5)-C(10) | 1.393(2) | C(19)-C(20) | 1.449(2) |
| C(5)-C(6) | 1.532(2) | C(20)-N(21) | 1.148(2) |
| C(6)-C(9) | 1.531(2) | C(22)-C(23) | 1.571(2) |
| C(6)-C(8) | 1.532(2) | C(22)-S(2) | 1.8169(15) |
| C(6)-C(7) | 1.535(2) | C(22)-H(22A) | 1.0000 |
| C(7)-H(7A) | 0.9800 | C(23)-H(23A) | 0.9900 |
| C(7)-H(7B) | 0.9800 | C(23)-H(23B) | 0.9900 |
| C(7)-H(7C) | 0.9800 | C(24)-S(1) | 1.8044(18) |
| C(8)-H(8A) | 0.9800 | C(24)-H(24A) | 0.9800 |
| C(8)-H(8B) | 0.9800 | C(24)-H(24B) | 0.9800 |
| C(8)-H(8C) | 0.9800 | C(24)-H(24C) | 0.9800 |
| C(9)-H(9A) | 0.9800 | C(25)-S(2) | 1.8024(16) |
| C(9)-H(9B) | 0.9800 | C(25)-H(25A) | 0.9800 |
| C(9)-H(9C) | 0.9800 | C(25)-H(25B) | 0.9800 |
| C(10)-C(11) | 1.398(2) | C(25)-H(25C) | 0.9800 |
| C(10)-H(10) | 0.9500 | | |
| C(11)-C(12) | 1.517(2) | C(2)-C(1)-H(1A) | 109.5 |
| C(12)-C(13) | 1.576(2) | C(2)-C(1)-H(1B) | 109.5 |
| C(12)-H(12A) | 0.9900 | H(1A)-C(1)-H(1B) | 109.5 |
| C(12)-H(12B) | 0.9900 | C(2)-C(1)-H(1C) | 109.5 |
| C(13)-C(14) | 1.519(2) | H(1A)-C(1)-H(1C) | 109.5 |
| C(13)-S(1) | 1.8180(15) | H(1B)-C(1)-H(1C) | 109.5 |
| C(13)-H(13) | 1.0000 | C(11)-C(2)-C(3) | 117.58(14) |

| | | | |
|---|---|---|---|
| C(11)-C(2)-C(1) | 121.54(14) | C(5)-C(10)-H(10) | 118.9 |
| C(3)-C(2)-C(1) | 120.85(14) | C(11)-C(10)-H(10) | 118.9 |
| C(4)-C(3)-C(2) | 119.52(14) | C(10)-C(11)-C(2) | 119.54(14) |
| C(4)-C(3)-C(23) | 118.81(13) | C(10)-C(11)-C(12) | 119.32(14) |
| C(2)-C(3)-C(23) | 120.39(13) | C(2)-C(11)-C(12) | 120.05(14) |
| C(3)-C(4)-C(5) | 122.40(14) | C(11)-C(12)-C(13) | 110.94(12) |
| C(3)-C(4)-H(4) | 118.8 | C(11)-C(12)-H(12A) | 109.5 |
| C(5)-C(4)-H(4) | 118.8 | C(13)-C(12)-H(12A) | 109.5 |
| C(10)-C(5)-C(4) | 116.41(14) | C(11)-C(12)-H(12B) | 109.5 |
| C(10)-C(5)-C(6) | 123.99(14) | C(13)-C(12)-H(12B) | 109.5 |
| C(4)-C(5)-C(6) | 119.44(14) | H(12A)-C(12)-H(12B) | 108.0 |
| C(9)-C(6)-C(8) | 108.49(13) | C(14)-C(13)-C(12) | 111.07(12) |
| C(9)-C(6)-C(5) | 112.49(13) | C(14)-C(13)-S(1) | 114.63(11) |
| C(8)-C(6)-C(5) | 109.06(13) | C(12)-C(13)-S(1) | 105.94(10) |
| C(9)-C(6)-C(7) | 108.53(14) | C(14)-C(13)-H(13) | 108.3 |
| C(8)-C(6)-C(7) | 108.68(14) | C(12)-C(13)-H(13) | 108.3 |
| C(5)-C(6)-C(7) | 109.53(13) | S(1)-C(13)-H(13) | 108.3 |
| C(6)-C(7)-H(7A) | 109.5 | C(15)-C(14)-C(19) | 117.25(14) |
| C(6)-C(7)-H(7B) | 109.5 | C(15)-C(14)-C(13) | 124.06(14) |
| H(7A)-C(7)-H(7B) | 109.5 | C(19)-C(14)-C(13) | 117.97(13) |
| C(6)-C(7)-H(7C) | 109.5 | C(14)-C(15)-C(16) | 120.34(14) |
| H(7A)-C(7)-H(7C) | 109.5 | C(14)-C(15)-H(15) | 119.8 |
| H(7B)-C(7)-H(7C) | 109.5 | C(16)-C(15)-H(15) | 119.8 |
| C(6)-C(8)-H(8A) | 109.5 | C(17)-C(16)-C(15) | 120.68(14) |
| C(6)-C(8)-H(8B) | 109.5 | C(17)-C(16)-H(16) | 119.7 |
| H(8A)-C(8)-H(8B) | 109.5 | C(15)-C(16)-H(16) | 119.7 |
| C(6)-C(8)-H(8C) | 109.5 | C(16)-C(17)-C(18) | 120.41(14) |
| H(8A)-C(8)-H(8C) | 109.5 | C(16)-C(17)-H(17) | 119.8 |
| H(8B)-C(8)-H(8C) | 109.5 | C(18)-C(17)-H(17) | 119.8 |
| C(6)-C(9)-H(9A) | 109.5 | C(17)-C(18)-C(19) | 117.22(14) |
| C(6)-C(9)-H(9B) | 109.5 | C(17)-C(18)-C(22) | 123.58(13) |
| H(9A)-C(9)-H(9B) | 109.5 | C(19)-C(18)-C(22) | 118.42(13) |
| C(6)-C(9)-H(9C) | 109.5 | C(14)-C(19)-C(18) | 121.64(13) |
| H(9A)-C(9)-H(9C) | 109.5 | C(14)-C(19)-C(20) | 118.75(13) |
| H(9B)-C(9)-H(9C) | 109.5 | C(18)-C(19)-C(20) | 119.59(13) |
| C(5)-C(10)-C(11) | 122.14(14) | N(21)-C(20)-C(19) | 171.71(16) |

| | |
|---|---|
| C(18)-C(22)-C(23) | 110.75(12) |
| C(18)-C(22)-S(2) | 114.25(11) |
| C(23)-C(22)-S(2) | 107.93(10) |
| C(18)-C(22)-H(22A) | 107.9 |
| C(23)-C(22)-H(22A) | 107.9 |
| S(2)-C(22)-H(22A) | 107.9 |
| C(3)-C(23)-C(22) | 109.23(12) |
| C(3)-C(23)-H(23A) | 109.8 |
| C(22)-C(23)-H(23A) | 109.8 |
| C(3)-C(23)-H(23B) | 109.8 |
| C(22)-C(23)-H(23B) | 109.8 |
| H(23A)-C(23)-H(23B) | 108.3 |
| S(1)-C(24)-H(24A) | 109.5 |
| S(1)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| S(1)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| S(2)-C(25)-H(25A) | 109.5 |
| S(2)-C(25)-H(25B) | 109.5 |
| H(25A)-C(25)-H(25B) | 109.5 |
| S(2)-C(25)-H(25C) | 109.5 |
| H(25A)-C(25)-H(25C) | 109.5 |
| H(25B)-C(25)-H(25C) | 109.5 |
| C(24)-S(1)-C(13) | 101.41(8) |
| C(25)-S(2)-C(22) | 97.93(7) |

**Table A. 35 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 134 (bt 960).**

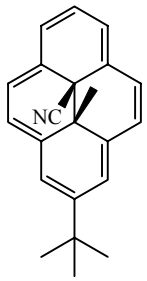
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 15(1) | 19(1) | 22(1) | -1(1) | 2(1) | -2(1) |
| C(2) | 14(1) | 18(1) | 15(1) | 1(1) | 0(1) | -1(1) |
| C(3) | 13(1) | 16(1) | 17(1) | 1(1) | 1(1) | 3(1) |
| C(4) | 16(1) | 13(1) | 18(1) | 1(1) | 1(1) | 1(1) |
| C(5) | 14(1) | 19(1) | 15(1) | 2(1) | 0(1) | 1(1) |
| C(6) | 19(1) | 19(1) | 20(1) | 1(1) | 6(1) | -1(1) |
| C(7) | 25(1) | 42(1) | 28(1) | 1(1) | 6(1) | -14(1) |
| C(8) | 32(1) | 20(1) | 27(1) | 5(1) | 14(1) | 4(1) |
| C(9) | 26(1) | 23(1) | 32(1) | 4(1) | 15(1) | 3(1) |
| C(10) | 16(1) | 17(1) | 16(1) | -1(1) | 3(1) | 2(1) |
| C(11) | 18(1) | 16(1) | 16(1) | -1(1) | 0(1) | -2(1) |
| C(12) | 21(1) | 16(1) | 20(1) | -3(1) | 6(1) | -2(1) |
| C(13) | 19(1) | 11(1) | 24(1) | -1(1) | 8(1) | -1(1) |
| C(14) | 13(1) | 14(1) | 19(1) | 0(1) | 2(1) | 1(1) |
| C(15) | 16(1) | 14(1) | 24(1) | 1(1) | 4(1) | -2(1) |
| C(16) | 15(1) | 22(1) | 23(1) | 2(1) | 7(1) | -3(1) |
| C(17) | 14(1) | 21(1) | 19(1) | -2(1) | 5(1) | 1(1) |
| C(18) | 13(1) | 16(1) | 16(1) | -1(1) | 0(1) | -1(1) |
| C(19) | 12(1) | 17(1) | 16(1) | 2(1) | 2(1) | -1(1) |
| C(20) | 17(1) | 13(1) | 16(1) | -1(1) | 3(1) | 1(1) |
| C(22) | 14(1) | 16(1) | 19(1) | -2(1) | 6(1) | -1(1) |
| C(23) | 16(1) | 16(1) | 20(1) | 0(1) | 5(1) | 1(1) |
| C(24) | 28(1) | 22(1) | 32(1) | 6(1) | 11(1) | 5(1) |
| C(25) | 21(1) | 20(1) | 20(1) | -1(1) | 4(1) | -2(1) |
| N(21) | 17(1) | 24(1) | 26(1) | 2(1) | 6(1) | -2(1) |
| S(1) | 29(1) | 13(1) | 27(1) | -1(1) | 8(1) | 0(1) |
| S(2) | 17(1) | 17(1) | 21(1) | -4(1) | 6(1) | 0(1) |

**Table A. 36 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for 134 (bt 960).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 4632 | 6866 | 7879 | 29 |
| H(1B) | 4354 | 8319 | 8148 | 29 |
| H(1C) | 5144 | 7320 | 8743 | 29 |
| H(4) | 7338 | 10965 | 7951 | 20 |
| H(7A) | 10007 | 11078 | 7346 | 48 |
| H(7B) | 9872 | 9920 | 7923 | 48 |
| H(7C) | 9184 | 11288 | 7900 | 48 |
| H(8A) | 7549 | 11813 | 6815 | 37 |
| H(8B) | 7203 | 10828 | 6099 | 37 |
| H(8C) | 8366 | 11661 | 6252 | 37 |
| H(9A) | 8327 | 8703 | 6097 | 38 |
| H(9B) | 9420 | 8423 | 6788 | 38 |
| H(9C) | 9433 | 9630 | 6214 | 38 |
| H(10) | 7853 | 7430 | 7050 | 20 |
| H(12A) | 6900 | 5438 | 7328 | 23 |
| H(12B) | 5896 | 5549 | 7753 | 23 |
| H(13) | 8311 | 5769 | 8517 | 21 |
| H(15) | 6291 | 4652 | 9530 | 22 |
| H(16) | 5653 | 5924 | 10418 | 23 |
| H(17) | 5852 | 8236 | 10432 | 21 |
| H(22A) | 7737 | 10037 | 9540 | 19 |
| H(23A) | 5285 | 9935 | 8891 | 21 |
| H(23B) | 6064 | 11173 | 8778 | 21 |
| H(24A) | 8316 | 3648 | 9862 | 40 |
| H(24B) | 9301 | 3784 | 9423 | 40 |
| H(24C) | 8731 | 2362 | 9484 | 40 |
| H(25A) | 7991 | 9405 | 11172 | 31 |
| H(25B) | 7970 | 10822 | 11573 | 31 |
| H(25C) | 8652 | 10646 | 10931 | 31 |

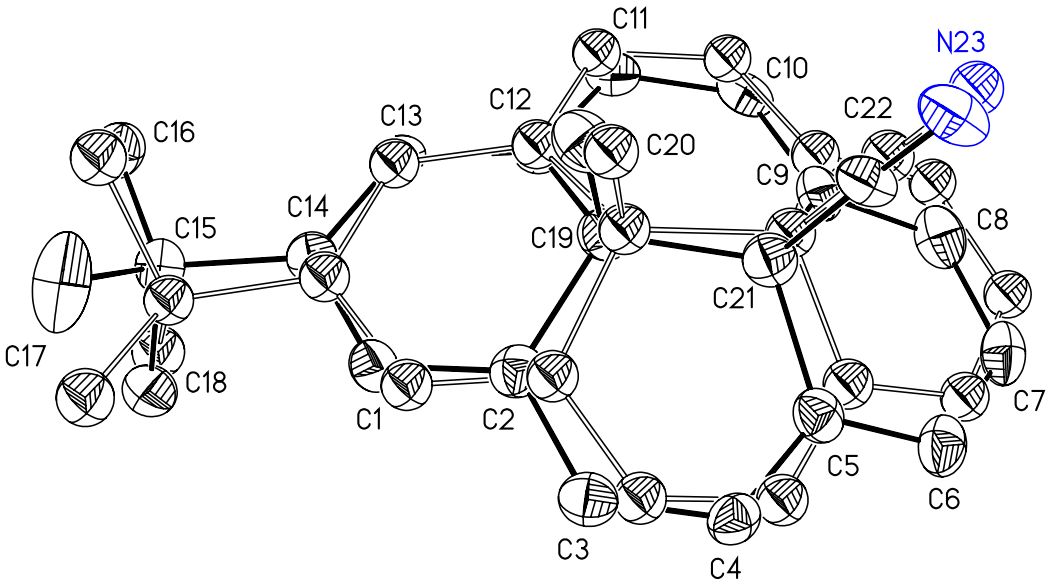
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for *cis*-cyano-methyl DHP 136**




**136**

Brendan Twamley




Project name : Bt1019

12-15-06

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans 0.3 ° per frame for 60 seconds, and a total of 2366 frames were collected. Cell parameters were retrieved using SMART[31] software and refined using SAINTPlus[32] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[33] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[34] The structure was solved in the space group P2(1)/c (# 14) by analysis of systematic absences. The data exhibited whole molecule disorder and was refined in two positions with occupancies of 85:15%. The first moiety was refined anisotropically, the second held isotropic. Coordinates for the second moiety were generated from the major moiety and were refined as a rigid group. Restraints were applied to the tBu bond lengths of the minor moiety to stabilize the refinement. The diffraction was very weak and the data were truncated to a resolution of 0.93 Å. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

---

[31] SMART: v. 5.632, Bruker AXS, Madison, WI, **2005**.
[32] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[33] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[34] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

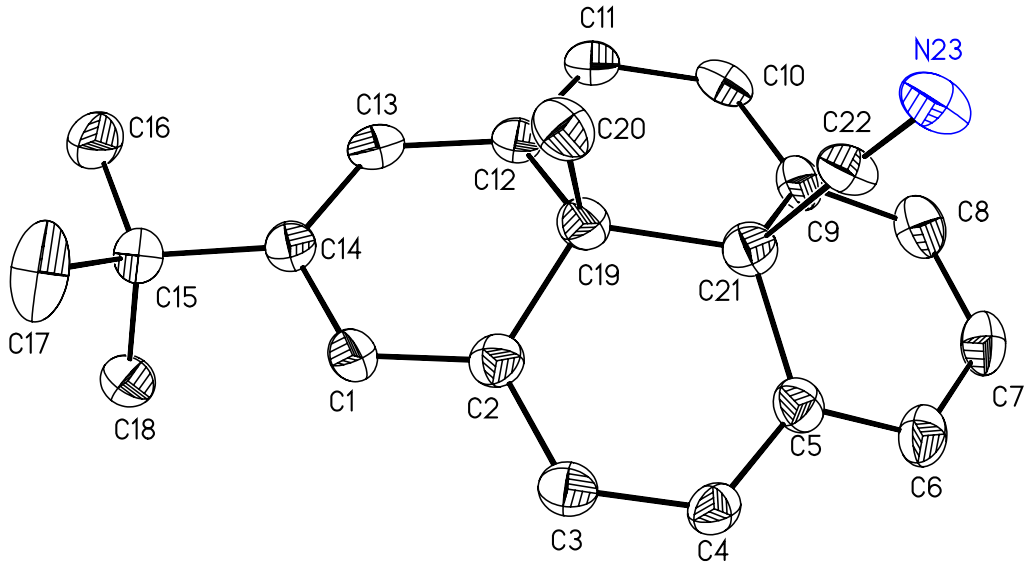



Figure 1a. Thermal ellipsoid plot (30%) of the major moiety in 1 (85%). This moiety was refined anisotropically.

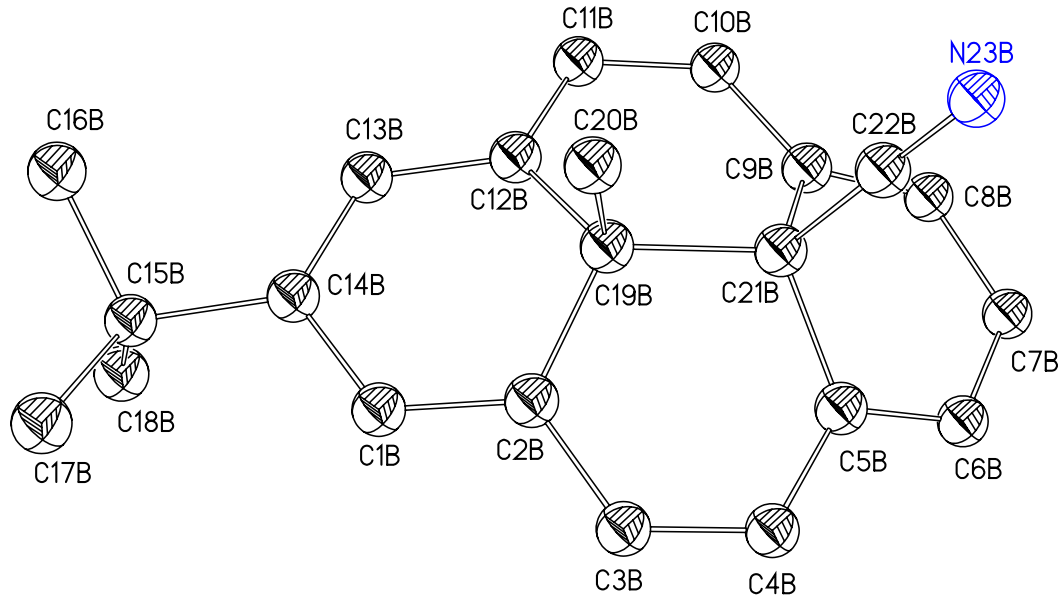



Figure 1b. Thermal ellipsoid plot (30%) of the minor moiety in 1 (15%). This moiety was refined isotropically using coordinates from the major moiety.

**Table A. 37 Crystal data and structure refinement for 136**

| | | |
|---|---|---|
| Identification code | bt1019 | |
| Empirical formula | C22 H21 N | |
| Formula weight | 299.40 | |
| Temperature | 90(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 14.2537(11) Å | α = 90°. |
| | b = 8.6909(7) Å | β = 104.395(2)°. |
| | c = 13.8551(11) Å | γ = 90°. |
| Volume | 1662.4(2) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.196 $Mg/m^3$ | |
| Absorption coefficient | 0.069 $mm^{-1}$ | |
| F(000) | 640 | |
| Crystal size | 0.44 x 0.25 x 0.10 $mm^3$ | |
| Crystal color and habit | brown/green block | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 2.77 to 22.50°. | |
| Index ranges | -15<=h<=15, -9<=k<=9, -14<=l<=14 | |
| Reflections collected | 17683 | |
| Independent reflections | 2169 [R(int) = 0.0413] | |
| Completeness to theta = 22.50° | 99.7% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.992 and 0.979 | |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2169 / 6 / 231 | |
| Goodness-of-fit on $F^2$ | 1.085 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0737, wR2 = 0.1938 | |
| R indices (all data) | R1 = 0.0911, wR2 = 0.2083 | |
| Largest diff. peak and hole | 0.296 and -0.194 $e.Å^{-3}$ | |

**Table A. 38 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for 136 (bt 1019).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 2113(3) | 7888(5) | 4896(3) | 46(1) |
| C(2) | 2720(3) | 9004(5) | 5410(3) | 44(1) |
| C(3) | 3321(3) | 8761(5) | 6369(3) | 45(1) |
| C(4) | 4124(3) | 9639(5) | 6745(3) | 41(1) |
| C(5) | 4418(3) | 10856(5) | 6229(3) | 43(1) |
| C(6) | 5332(3) | 11475(5) | 6475(4) | 51(1) |
| C(7) | 5652(3) | 12516(6) | 5860(4) | 52(1) |
| C(8) | 5089(4) | 12855(6) | 4924(4) | 54(1) |
| C(9) | 4154(3) | 12280(5) | 4574(3) | 44(1) |
| C(10) | 3614(3) | 12371(5) | 3589(3) | 45(1) |
| C(11) | 2799(3) | 11481(5) | 3219(3) | 44(1) |
| C(12) | 2460(3) | 10441(5) | 3799(3) | 41(1) |
| C(13) | 1841(3) | 9240(6) | 3364(3) | 46(1) |
| C(14) | 1638(3) | 7980(5) | 3878(3) | 48(1) |
| C(15) | 1017(3) | 6622(6) | 3361(4) | 55(1) |
| C(16) | 546(4) | 6899(6) | 2299(4) | 73(2) |
| C(17) | 252(4) | 6313(9) | 3930(5) | 93(2) |
| C(18) | 1694(5) | 5205(7) | 3429(5) | 67(2) |
| C(19) | 2716(3) | 10586(5) | 4919(3) | 44(1) |
| C(20) | 1829(3) | 11405(6) | 5162(4) | 51(1) |
| C(21) | 3672(3) | 11609(5) | 5354(3) | 46(1) |
| C(22) | 3404(4) | 13081(5) | 5796(4) | 46(1) |
| N(23) | 3249(4) | 14250(5) | 6122(4) | 58(1) |
| C(15B) | 1068(12) | 6605(19) | 3773(13) | 40 |
| C(14B) | 1678(10) | 8036(16) | 4167(11) | 40 |
| C(1B) | 2284(10) | 8051(15) | 5141(10) | 40 |
| C(2B) | 2892(9) | 9241(15) | 5534(8) | 40 |
| C(3B) | 3611(11) | 9106(17) | 6430(9) | 40 |
| C(4B) | 4397(11) | 10058(18) | 6667(9) | 40 |

| | | | | |
|---|---|---|---|---|
| C(5B) | 4552(9) | 11259(15) | 6050(9) | 40 |
| C(6B) | 5434(9) | 11949(17) | 6142(11) | 40 |
| C(7B) | 5611(9) | 12966(17) | 5429(13) | 40 |
| C(8B) | 4921(10) | 13202(16) | 4543(12) | 40 |
| C(9B) | 4006(10) | 12544(15) | 4348(10) | 40 |
| C(10B) | 3347(12) | 12525(18) | 3425(10) | 40 |
| C(11B) | 2555(11) | 11561(18) | 3203(10) | 40 |
| C(12B) | 2356(9) | 10540(16) | 3882(9) | 40 |
| C(13B) | 1747(9) | 9270(18) | 3567(10) | 40 |
| C(19B) | 2761(8) | 10801(14) | 4989(9) | 40 |
| C(20B) | 1930(9) | 11569(17) | 5364(14) | 40 |
| C(21B) | 3709(8) | 11947(13) | 5242(9) | 40 |
| C(22B) | 3443(10) | 13401(14) | 5706(13) | 40 |
| N(23B) | 3290(12) | 14587(16) | 6024(17) | 40 |
| C(16B) | 170(16) | 7180(30) | 3015(17) | 50 |
| C(17B) | 728(19) | 5730(30) | 4572(17) | 50 |
| C(18B) | 1610(30) | 5550(50) | 3230(30) | 50 |

**Table A. 39 Bond lengths [Å] and angles [°] for 136 (bt 1019).**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.375(6) | C(16)-H(16B) | 0.9800 |
| C(1)-C(14) | 1.406(6) | C(16)-H(16C) | 0.9800 |
| C(1)-H(1A) | 0.9500 | C(17)-H(17A) | 0.9800 |
| C(2)-C(3) | 1.407(6) | C(17)-H(17B) | 0.9800 |
| C(2)-C(19) | 1.533(6) | C(17)-H(17C) | 0.9800 |
| C(3)-C(4) | 1.367(6) | C(18)-H(18A) | 0.9800 |
| C(3)-H(3A) | 0.9500 | C(18)-H(18B) | 0.9800 |
| C(4)-C(5) | 1.398(6) | C(18)-H(18C) | 0.9800 |
| C(4)-H(4A) | 0.9500 | C(19)-C(20) | 1.558(6) |
| C(5)-C(6) | 1.373(6) | C(19)-C(21) | 1.614(6) |
| C(5)-C(21) | 1.544(6) | C(20)-H(20A) | 0.9800 |
| C(6)-C(7) | 1.394(7) | C(20)-H(20B) | 0.9800 |
| C(6)-H(6A) | 0.9500 | C(20)-H(20C) | 0.9800 |
| C(7)-C(8) | 1.377(7) | C(21)-C(22) | 1.508(6) |
| C(7)-H(7A) | 0.9500 | C(22)-N(23) | 1.155(5) |
| C(8)-C(9) | 1.393(7) | C(15B)-C(18B) | 1.515(19) |
| C(8)-H(8A) | 0.9500 | C(15B)-C(17B) | 1.519(17) |
| C(9)-C(10) | 1.393(6) | C(15B)-C(16B) | 1.523(17) |
| C(9)-C(21) | 1.532(6) | C(15B)-C(14B) | 1.5381 |
| C(10)-C(11) | 1.384(6) | C(14B)-C(13B) | 1.3759 |
| C(10)-H(10A) | 0.9500 | C(14B)-C(1B) | 1.4098 |
| C(11)-C(12) | 1.374(6) | C(1B)-C(2B) | 1.3719 |
| C(11)-H(11A) | 0.9500 | C(1B)-H(1BA) | 0.9500 |
| C(12)-C(13) | 1.402(6) | C(2B)-C(3B) | 1.4043 |
| C(12)-C(19) | 1.509(6) | C(2B)-C(19B) | 1.5409 |
| C(13)-C(14) | 1.376(6) | C(3B)-C(4B) | 1.3644 |
| C(13)-H(13A) | 0.9500 | C(3B)-H(3BA) | 0.9500 |
| C(14)-C(15) | 1.542(6) | C(4B)-C(5B) | 1.4015 |
| C(15)-C(16) | 1.477(7) | C(4B)-H(4BA) | 0.9500 |
| C(15)-C(17) | 1.521(7) | C(5B)-C(6B) | 1.3691 |
| C(15)-C(18) | 1.552(7) | C(5B)-C(21B) | 1.5449 |
| C(16)-H(16A) | 0.9800 | C(6B)-C(7B) | 1.3946 |

| | | | |
|---|---|---|---|
| C(6B)-H(6BA) | 0.9500 | C(3)-C(2)-C(19) | 119.2(4) |
| C(7B)-C(8B) | 1.3838 | C(4)-C(3)-C(2) | 122.2(4) |
| C(7B)-H(7BA) | 0.9500 | C(4)-C(3)-H(3A) | 118.9 |
| C(8B)-C(9B) | 1.3874 | C(2)-C(3)-H(3A) | 118.9 |
| C(8B)-H(8BA) | 0.9500 | C(3)-C(4)-C(5) | 123.8(4) |
| C(9B)-C(10B) | 1.3862 | C(3)-C(4)-H(4A) | 118.1 |
| C(9B)-C(21B) | 1.4985 | C(5)-C(4)-H(4A) | 118.1 |
| C(10B)-C(11B) | 1.3780 | C(6)-C(5)-C(4) | 123.8(4) |
| C(10B)-H(10B) | 0.9500 | C(6)-C(5)-C(21) | 117.0(4) |
| C(11B)-C(12B) | 1.3731 | C(4)-C(5)-C(21) | 119.2(4) |
| C(11B)-H(11B) | 0.9500 | C(5)-C(6)-C(7) | 122.5(4) |
| C(12B)-C(13B) | 1.4047 | C(5)-C(6)-H(6A) | 118.8 |
| C(12B)-C(19B) | 1.5160 | C(7)-C(6)-H(6A) | 118.8 |
| C(13B)-H(13B) | 0.9500 | C(8)-C(7)-C(6) | 120.8(4) |
| C(19B)-C(20B) | 1.5571 | C(8)-C(7)-H(7A) | 119.6 |
| C(19B)-C(21B) | 1.6444 | C(6)-C(7)-H(7A) | 119.6 |
| C(20B)-H(20D) | 0.9800 | C(7)-C(8)-C(9) | 122.3(4) |
| C(20B)-H(20E) | 0.9800 | C(7)-C(8)-H(8A) | 118.9 |
| C(20B)-H(20F) | 0.9800 | C(9)-C(8)-H(8A) | 118.9 |
| C(21B)-C(22B) | 1.5075 | C(10)-C(9)-C(8) | 124.6(4) |
| C(22B)-N(23B) | 1.1628 | C(10)-C(9)-C(21) | 118.6(4) |
| C(16B)-H(16D) | 0.9800 | C(8)-C(9)-C(21) | 116.7(4) |
| C(16B)-H(16E) | 0.9800 | C(11)-C(10)-C(9) | 122.6(4) |
| C(16B)-H(16F) | 0.9800 | C(11)-C(10)-H(10A) | 118.7 |
| C(17B)-H(17D) | 0.9800 | C(9)-C(10)-H(10A) | 118.7 |
| C(17B)-H(17E) | 0.9800 | C(12)-C(11)-C(10) | 122.5(4) |
| C(17B)-H(17F) | 0.9800 | C(12)-C(11)-H(11A) | 118.8 |
| C(18B)-H(18D) | 0.9800 | C(10)-C(11)-H(11A) | 118.8 |
| C(18B)-H(18E) | 0.9800 | C(11)-C(12)-C(13) | 120.9(4) |
| C(18B)-H(18F) | 0.9800 | C(11)-C(12)-C(19) | 121.1(4) |
| | | C(13)-C(12)-C(19) | 118.0(4) |
| C(2)-C(1)-C(14) | 124.3(4) | C(14)-C(13)-C(12) | 124.1(4) |
| C(2)-C(1)-H(1A) | 117.9 | C(14)-C(13)-H(13A) | 117.9 |
| C(14)-C(1)-H(1A) | 117.9 | C(12)-C(13)-H(13A) | 117.9 |
| C(1)-C(2)-C(3) | 122.7(4) | C(13)-C(14)-C(1) | 117.0(4) |
| C(1)-C(2)-C(19) | 118.1(4) | C(13)-C(14)-C(15) | 122.6(4) |

| | | | |
|---|---|---|---|
| C(1)-C(14)-C(15) | 120.0(4) | C(4B)-C(3B)-H(3BA) | 118.8 |
| C(16)-C(15)-C(17) | 109.7(5) | C(2B)-C(3B)-H(3BA) | 118.8 |
| C(16)-C(15)-C(14) | 113.9(4) | C(3B)-C(4B)-C(5B) | 123.3 |
| C(17)-C(15)-C(14) | 107.2(4) | C(3B)-C(4B)-H(4BA) | 118.3 |
| C(16)-C(15)-C(18) | 108.2(5) | C(5B)-C(4B)-H(4BA) | 118.3 |
| C(17)-C(15)-C(18) | 110.1(5) | C(6B)-C(5B)-C(4B) | 123.4 |
| C(14)-C(15)-C(18) | 107.6(4) | C(6B)-C(5B)-C(21B) | 115.4 |
| C(12)-C(19)-C(2) | 110.8(3) | C(4B)-C(5B)-C(21B) | 121.2 |
| C(12)-C(19)-C(20) | 105.0(3) | C(5B)-C(6B)-C(7B) | 122.4 |
| C(2)-C(19)-C(20) | 103.2(3) | C(5B)-C(6B)-H(6BA) | 118.8 |
| C(12)-C(19)-C(21) | 113.3(3) | C(7B)-C(6B)-H(6BA) | 118.8 |
| C(2)-C(19)-C(21) | 114.8(3) | C(8B)-C(7B)-C(6B) | 120.5 |
| C(20)-C(19)-C(21) | 108.9(3) | C(8B)-C(7B)-H(7BA) | 119.8 |
| C(22)-C(21)-C(9) | 99.6(3) | C(6B)-C(7B)-H(7BA) | 119.8 |
| C(22)-C(21)-C(5) | 103.6(3) | C(7B)-C(8B)-C(9B) | 122.6 |
| C(9)-C(21)-C(5) | 111.9(4) | C(7B)-C(8B)-H(8BA) | 118.7 |
| C(22)-C(21)-C(19) | 110.1(3) | C(9B)-C(8B)-H(8BA) | 118.7 |
| C(9)-C(21)-C(19) | 115.5(3) | C(10B)-C(9B)-C(8B) | 125.0 |
| C(5)-C(21)-C(19) | 114.3(3) | C(10B)-C(9B)-C(21B) | 119.5 |
| N(23)-C(22)-C(21) | 175.8(5) | C(8B)-C(9B)-C(21B) | 115.3 |
| C(18B)-C(15B)-C(17B) | 110.7(19) | C(11B)-C(10B)-C(9B) | 122.9 |
| C(18B)-C(15B)-C(16B) | 107.2(19) | C(11B)-C(10B)-H(10B) | 118.6 |
| C(17B)-C(15B)-C(16B) | 107.5(16) | C(9B)-C(10B)-H(10B) | 118.6 |
| C(18B)-C(15B)-C(14B) | 111(2) | C(12B)-C(11B)-C(10B) | 122.5 |
| C(17B)-C(15B)-C(14B) | 113.7(12) | C(12B)-C(11B)-H(11B) | 118.7 |
| C(16B)-C(15B)-C(14B) | 106.6(11) | C(10B)-C(11B)-H(11B) | 118.7 |
| C(13B)-C(14B)-C(1B) | 116.9 | C(11B)-C(12B)-C(13B) | 120.8 |
| C(13B)-C(14B)-C(15B) | 122.3 | C(11B)-C(12B)-C(19B) | 120.3 |
| C(1B)-C(14B)-C(15B) | 120.3 | C(13B)-C(12B)-C(19B) | 118.9 |
| C(2B)-C(1B)-C(14B) | 124.3 | C(14B)-C(13B)-C(12B) | 123.8 |
| C(2B)-C(1B)-H(1BA) | 117.8 | C(14B)-C(13B)-H(13B) | 118.1 |
| C(14B)-C(1B)-H(1BA) | 117.8 | C(12B)-C(13B)-H(13B) | 118.1 |
| C(1B)-C(2B)-C(3B) | 122.6 | C(12B)-C(19B)-C(2B) | 109.5 |
| C(1B)-C(2B)-C(19B) | 118.7 | C(12B)-C(19B)-C(20B) | 105.8 |
| C(3B)-C(2B)-C(19B) | 118.6 | C(2B)-C(19B)-C(20B) | 102.9 |
| C(4B)-C(3B)-C(2B) | 122.5 | C(12B)-C(19B)-C(21B) | 113.1 |

| | |
|---|---|
| C(2B)-C(19B)-C(21B) | 115.8 |
| C(20B)-C(19B)-C(21B) | 108.8 |
| C(19B)-C(20B)-H(20D) | 109.5 |
| C(19B)-C(20B)-H(20E) | 109.5 |
| H(20D)-C(20B)-H(20E) | 109.5 |
| C(19B)-C(20B)-H(20F) | 109.5 |
| H(20D)-C(20B)-H(20F) | 109.5 |
| H(20E)-C(20B)-H(20F) | 109.5 |
| C(9B)-C(21B)-C(22B) | 102.4 |
| C(9B)-C(21B)-C(5B) | 113.8 |
| C(22B)-C(21B)-C(5B) | 104.4 |
| C(9B)-C(21B)-C(19B) | 114.8 |
| C(22B)-C(21B)-C(19B) | 108.6 |
| C(5B)-C(21B)-C(19B) | 111.7 |
| N(23B)-C(22B)-C(21B) | 174.3 |
| C(15B)-C(16B)-H(16D) | 109.5 |
| C(15B)-C(16B)-H(16E) | 109.5 |
| H(16D)-C(16B)-H(16E) | 109.5 |
| C(15B)-C(16B)-H(16F) | 109.5 |
| H(16D)-C(16B)-H(16F) | 109.5 |
| H(16E)-C(16B)-H(16F) | 109.5 |
| C(15B)-C(17B)-H(17D) | 109.5 |
| C(15B)-C(17B)-H(17E) | 109.5 |
| H(17D)-C(17B)-H(17E) | 109.5 |
| C(15B)-C(17B)-H(17F) | 109.5 |
| H(17D)-C(17B)-H(17F) | 109.5 |
| H(17E)-C(17B)-H(17F) | 109.5 |
| C(15B)-C(18B)-H(18D) | 109.5 |
| C(15B)-C(18B)-H(18E) | 109.5 |
| H(18D)-C(18B)-H(18E) | 109.5 |
| C(15B)-C(18B)-H(18F) | 109.5 |
| H(18D)-C(18B)-H(18F) | 109.5 |
| H(18E)-C(18B)-H(18F) | 109.5 |

**Table A. 40 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 136 (bt1019).**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 42(3) | 41(2) | 54(3) | 7(2) | 10(2) | -6(2) |
| C(2) | 38(2) | 48(3) | 46(2) | 3(2) | 11(2) | 2(2) |
| C(3) | 49(3) | 47(3) | 42(2) | 4(2) | 15(2) | 2(2) |
| C(4) | 44(3) | 42(2) | 35(2) | -6(2) | 4(2) | 5(2) |
| C(5) | 51(3) | 36(2) | 42(2) | -6(2) | 14(2) | 0(2) |
| C(6) | 46(3) | 47(3) | 58(3) | -16(2) | 9(2) | -2(2) |
| C(7) | 42(3) | 51(3) | 63(3) | -15(2) | 16(2) | -12(2) |
| C(8) | 56(3) | 49(3) | 64(3) | -8(2) | 28(3) | -8(2) |
| C(9) | 48(3) | 34(2) | 52(3) | -9(2) | 18(2) | -3(2) |
| C(10) | 57(3) | 33(2) | 52(3) | 10(2) | 27(2) | 8(2) |
| C(11) | 44(3) | 44(3) | 44(2) | 6(2) | 12(2) | 9(2) |
| C(12) | 39(2) | 36(2) | 47(2) | 1(2) | 8(2) | 6(2) |
| C(13) | 42(3) | 51(3) | 43(3) | 5(2) | 5(2) | 11(2) |
| C(14) | 40(2) | 41(3) | 60(3) | 2(2) | 5(2) | 2(2) |
| C(15) | 47(3) | 50(3) | 61(3) | 4(3) | 4(3) | -7(2) |
| C(16) | 67(3) | 55(3) | 79(4) | -8(3) | -14(3) | -2(3) |
| C(17) | 72(4) | 117(5) | 95(5) | -40(4) | 31(3) | -38(4) |
| C(18) | 66(4) | 42(4) | 81(5) | 4(3) | -3(4) | 0(3) |
| C(19) | 44(2) | 42(3) | 47(3) | 6(2) | 12(2) | -2(2) |
| C(20) | 57(3) | 44(3) | 58(3) | -3(2) | 22(2) | 3(2) |
| C(21) | 51(3) | 47(3) | 40(2) | 2(2) | 13(2) | -1(2) |
| C(22) | 57(3) | 35(3) | 47(3) | 5(2) | 16(2) | 8(2) |
| N(23) | 84(3) | 40(3) | 55(3) | 6(2) | 26(2) | 8(2) |

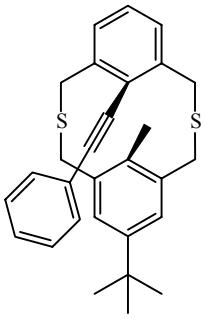
**Table A. 41 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for 136 (bt 1019).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 2007 | 6997 | 5251 | 55 |
| H(3A) | 3164 | 7959 | 6768 | 55 |
| H(4A) | 4505 | 9409 | 7395 | 49 |
| H(6A) | 5764 | 11183 | 7087 | 61 |
| H(7A) | 6265 | 12998 | 6090 | 62 |
| H(8A) | 5347 | 13504 | 4502 | 65 |
| H(10A) | 3814 | 13072 | 3153 | 54 |
| H(11A) | 2461 | 11593 | 2540 | 53 |
| H(13A) | 1544 | 9300 | 2671 | 56 |
| H(16A) | 110 | 7785 | 2240 | 109 |
| H(16B) | 173 | 5987 | 2016 | 109 |
| H(16C) | 1041 | 7108 | 1936 | 109 |
| H(17A) | -136 | 7244 | 3932 | 140 |
| H(17B) | 568 | 6023 | 4617 | 140 |
| H(17C) | -171 | 5474 | 3608 | 140 |
| H(18A) | 2197 | 5428 | 3079 | 100 |
| H(18B) | 1314 | 4314 | 3122 | 100 |
| H(18C) | 1997 | 4981 | 4131 | 100 |
| H(20A) | 1742 | 12420 | 4844 | 77 |
| H(20B) | 1941 | 11525 | 5885 | 77 |
| H(20C) | 1245 | 10784 | 4908 | 77 |
| H(1BA) | 2271 | 7180 | 5552 | 48 |
| H(3BA) | 3549 | 8324 | 6889 | 48 |
| H(4BA) | 4862 | 9898 | 7281 | 48 |
| H(6BA) | 5943 | 11727 | 6712 | 48 |
| H(7BA) | 6210 | 13501 | 5552 | 48 |
| H(8BA) | 5080 | 13839 | 4050 | 48 |
| H(10B) | 3446 | 13206 | 2923 | 48 |
| H(11B) | 2130 | 11605 | 2556 | 48 |

| | | | | |
|---|---|---|---|---|
| H(13B) | 1361 | 9263 | 2901 | 48 |
| H(20D) | 1374 | 10869 | 5252 | 60 |
| H(20E) | 1735 | 12529 | 4997 | 60 |
| H(20F) | 2157 | 11793 | 6077 | 60 |
| H(16D) | 365 | 7873 | 2543 | 75 |
| H(16E) | -251 | 7724 | 3360 | 75 |
| H(16F) | -180 | 6296 | 2652 | 75 |
| H(17D) | 283 | 4908 | 4261 | 75 |
| H(17E) | 394 | 6434 | 4926 | 75 |
| H(17F) | 1288 | 5276 | 5045 | 75 |
| H(18D) | 1289 | 4543 | 3130 | 75 |
| H(18E) | 2277 | 5428 | 3620 | 75 |
| H(18F) | 1605 | 5998 | 2577 | 75 |

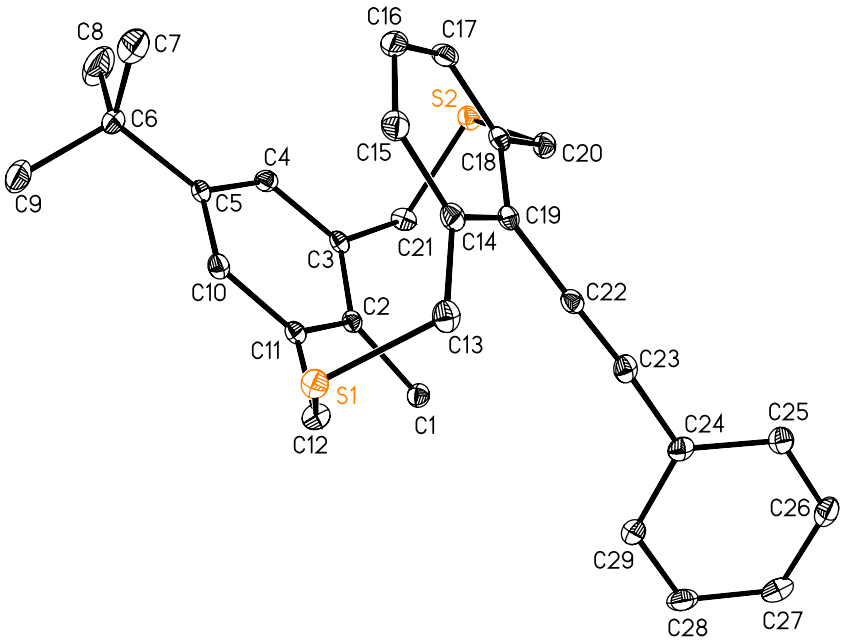
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray report for *syn*-thiacyclophane 145**




**145**

Brendan Twamley




Project name : bt830

11-29-05

**Experimental:**

A crystal of compound **1** was removed from the flask and covered with a layer of hydrocarbon oil. A suitable fragment was selected, attached to a MiTeGen fiber and placed in the low-temperature nitrogen stream.[35] Data for **1** were collected at 89(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 10 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[36] software and refined using SAINTPlus[37] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[38] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[39] The structure was solved in the chiral space group P2(1) (# 4) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

[35] Hope, H. *Prog. Inorg. Chem.*, **1994**, *41*, 1.
[36] SMART: v.5.626, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2002**.
[37] SAINTPlus: v. 6.45a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2003**.
[38] SADABS: v.2.01, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[39] SHELXTL: v. 6.10, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2001**.

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

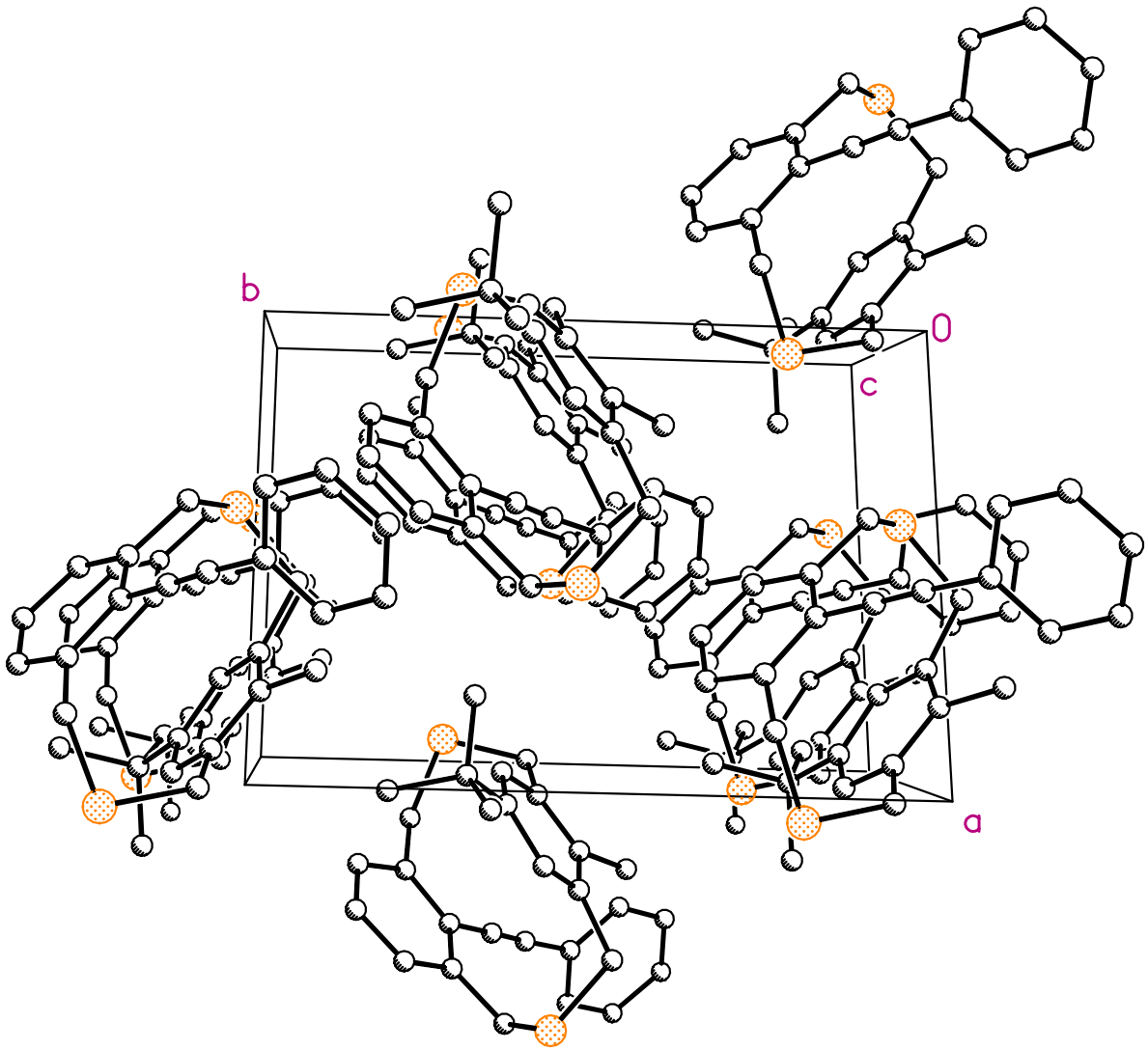

b
0
c
a

**Table A. 42 Crystal data and structure refinement for 145 (C29 H30 S2).**

| | | |
|---|---|---|
| Identification code | bt830 | |
| Empirical formula | C29 H30 S2 | |
| Formula weight | 442.65 | |
| Temperature | 89(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1) | |
| Unit cell dimensions | a = 9.7279(14) Å | α = 90°. |
| | b = 12.5775(17) Å | β = 116.703(2)°. |
| | c = 10.6452(15) Å | γ = 90°. |
| Volume | 1163.6(3) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.263 $Mg/m^3$ | |
| Absorption coefficient | 0.243 $mm^{-1}$ | |
| F(000) | 472 | |
| Crystal size | 0.36 x 0.32 x 0.22 $mm^3$ | |
| Crystal color and habit | colorless needle | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 2.14 to 25.25°. | |
| Index ranges | -11<=h<=11, -15<=k<=15, -12<=l<=12 | |
| Reflections collected | 17126 | |
| Independent reflections | 4196 [R(int) = 0.0204] | |
| Completeness to theta = 25.25° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.946 and 0.914 | |
| Solution method | XS, Bruker SHELXTL v. 6.12 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4196 / 1 / 284 | |
| Goodness-of-fit on $F^2$ | 1.047 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0311, wR2 = 0.0864 | |
| R indices (all data) | R1 = 0.0313, wR2 = 0.0867 | |
| Absolute structure parameter | 0.03(5) | |
| Largest diff. peak and hole | 0.559 and -0.212 $e.Å^{-3}$ | |

**Table A. 43 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 145 (bt 830)**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 2315(2) | 4066(2) | 9404(2) | 19(1) |
| C(2) | 1836(2) | 4881(1) | 8235(2) | 16(1) |
| C(3) | 2607(2) | 4934(1) | 7399(2) | 17(1) |
| C(4) | 2003(2) | 5532(2) | 6162(2) | 18(1) |
| C(5) | 667(2) | 6126(2) | 5749(2) | 17(1) |
| C(6) | -29(2) | 6775(2) | 4377(2) | 25(1) |
| C(7) | 360(3) | 7964(2) | 4771(3) | 47(1) |
| C(8) | 612(3) | 6445(3) | 3369(3) | 51(1) |
| C(9) | -1773(3) | 6684(2) | 3640(2) | 38(1) |
| C(10) | 21(2) | 6167(2) | 6679(2) | 18(1) |
| C(11) | 580(2) | 5566(1) | 7908(2) | 16(1) |
| C(12) | -149(2) | 5694(2) | 8901(2) | 20(1) |
| C(13) | 1352(2) | 7539(2) | 10493(2) | 22(1) |
| C(14) | 2481(2) | 7608(2) | 9888(2) | 20(1) |
| C(15) | 2282(2) | 8373(2) | 8875(2) | 24(1) |
| C(16) | 3221(2) | 8389(2) | 8217(2) | 23(1) |
| C(17) | 4346(2) | 7614(2) | 8526(2) | 23(1) |
| C(18) | 4603(2) | 6845(1) | 9540(2) | 19(1) |
| C(19) | 3698(2) | 6877(1) | 10278(2) | 17(1) |
| C(20) | 5813(2) | 5999(2) | 9837(2) | 22(1) |
| C(21) | 4149(2) | 4396(2) | 7836(2) | 21(1) |
| C(22) | 4015(2) | 6158(2) | 11435(2) | 18(1) |
| C(23) | 4295(2) | 5573(2) | 12412(2) | 20(1) |
| C(24) | 4601(2) | 4775(2) | 13483(2) | 19(1) |
| C(25) | 5988(2) | 4771(2) | 14733(2) | 25(1) |
| C(26) | 6314(2) | 3944(2) | 15680(2) | 27(1) |
| C(27) | 5286(3) | 3117(2) | 15425(2) | 27(1) |
| C(28) | 3904(3) | 3125(2) | 14204(2) | 30(1) |
| C(29) | 3548(2) | 3956(2) | 13250(2) | 25(1) |
| S(1) | -548(1) | 7051(1) | 9243(1) | 20(1) |
| S(2) | 5729(1) | 5336(1) | 8282(1) | 21(1) |

**Table A. 44 Bond lengths [Å] and angles [°] for 145 (bt 830)**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.516(3) | C(13)-S(1) | 1.832(2) |
| C(1)-H(1A) | 0.9800 | C(13)-H(13A) | 0.9900 |
| C(1)-H(1B) | 0.9800 | C(13)-H(13B) | 0.9900 |
| C(1)-H(1C) | 0.9800 | C(14)-C(15) | 1.393(3) |
| C(2)-C(3) | 1.400(3) | C(14)-C(19) | 1.407(3) |
| C(2)-C(11) | 1.405(2) | C(15)-C(16) | 1.378(3) |
| C(3)-C(4) | 1.396(3) | C(15)-H(15) | 0.9500 |
| C(3)-C(21) | 1.516(3) | C(16)-C(17) | 1.391(3) |
| C(4)-C(5) | 1.388(3) | C(16)-H(16) | 0.9500 |
| C(4)-H(4) | 0.9500 | C(17)-C(18) | 1.386(3) |
| C(5)-C(10) | 1.392(3) | C(17)-H(17) | 0.9500 |
| C(5)-C(6) | 1.539(3) | C(18)-C(19) | 1.419(3) |
| C(6)-C(9) | 1.520(3) | C(18)-C(20) | 1.511(3) |
| C(6)-C(8) | 1.521(3) | C(19)-C(22) | 1.445(3) |
| C(6)-C(7) | 1.553(4) | C(20)-S(2) | 1.8230(19) |
| C(7)-H(7A) | 0.9800 | C(20)-H(20A) | 0.9900 |
| C(7)-H(7B) | 0.9800 | C(20)-H(20B) | 0.9900 |
| C(7)-H(7C) | 0.9800 | C(21)-S(2) | 1.825(2) |
| C(8)-H(8A) | 0.9800 | C(21)-H(21A) | 0.9900 |
| C(8)-H(8B) | 0.9800 | C(21)-H(21B) | 0.9900 |
| C(8)-H(8C) | 0.9800 | C(22)-C(23) | 1.201(3) |
| C(9)-H(9A) | 0.9800 | C(23)-C(24) | 1.447(3) |
| C(9)-H(9B) | 0.9800 | C(24)-C(29) | 1.394(3) |
| C(9)-H(9C) | 0.9800 | C(24)-C(25) | 1.406(3) |
| C(10)-C(11) | 1.393(3) | C(25)-C(26) | 1.382(3) |
| C(10)-H(10) | 0.9500 | C(25)-H(25) | 0.9500 |
| C(11)-C(12) | 1.522(2) | C(26)-C(27) | 1.383(3) |
| C(12)-S(1) | 1.8227(19) | C(26)-H(26) | 0.9500 |
| C(12)-H(12A) | 0.9900 | C(27)-C(28) | 1.388(3) |
| C(12)-H(12B) | 0.9900 | C(27)-H(27) | 0.9500 |
| C(13)-C(14) | 1.504(3) | C(28)-C(29) | 1.389(3) |

| | | | |
|---|---|---|---|
| C(28)-H(28) | 0.9500 | C(6)-C(8)-H(8C) | 109.5 |
| C(29)-H(29) | 0.9500 | H(8A)-C(8)-H(8C) | 109.5 |
| | | H(8B)-C(8)-H(8C) | 109.5 |
| C(2)-C(1)-H(1A) | 109.5 | C(6)-C(9)-H(9A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 | C(6)-C(9)-H(9B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 | H(9A)-C(9)-H(9B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 | C(6)-C(9)-H(9C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 | H(9A)-C(9)-H(9C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 | H(9B)-C(9)-H(9C) | 109.5 |
| C(3)-C(2)-C(11) | 117.94(16) | C(11)-C(10)-C(5) | 122.53(17) |
| C(3)-C(2)-C(1) | 119.98(16) | C(11)-C(10)-H(10) | 118.7 |
| C(11)-C(2)-C(1) | 122.01(16) | C(5)-C(10)-H(10) | 118.7 |
| C(4)-C(3)-C(2) | 120.45(16) | C(10)-C(11)-C(2) | 119.61(16) |
| C(4)-C(3)-C(21) | 117.95(16) | C(10)-C(11)-C(12) | 119.19(16) |
| C(2)-C(3)-C(21) | 121.53(16) | C(2)-C(11)-C(12) | 121.16(16) |
| C(5)-C(4)-C(3) | 121.71(17) | C(11)-C(12)-S(1) | 116.42(13) |
| C(5)-C(4)-H(4) | 119.1 | C(11)-C(12)-H(12A) | 108.2 |
| C(3)-C(4)-H(4) | 119.1 | S(1)-C(12)-H(12A) | 108.2 |
| C(4)-C(5)-C(10) | 116.92(16) | C(11)-C(12)-H(12B) | 108.2 |
| C(4)-C(5)-C(6) | 122.39(16) | S(1)-C(12)-H(12B) | 108.2 |
| C(10)-C(5)-C(6) | 120.57(17) | H(12A)-C(12)-H(12B) | 107.3 |
| C(9)-C(6)-C(8) | 109.4(2) | C(14)-C(13)-S(1) | 113.61(13) |
| C(9)-C(6)-C(5) | 111.25(17) | C(14)-C(13)-H(13A) | 108.8 |
| C(8)-C(6)-C(5) | 112.30(18) | S(1)-C(13)-H(13A) | 108.8 |
| C(9)-C(6)-C(7) | 107.0(2) | C(14)-C(13)-H(13B) | 108.8 |
| C(8)-C(6)-C(7) | 109.0(2) | S(1)-C(13)-H(13B) | 108.8 |
| C(5)-C(6)-C(7) | 107.73(17) | H(13A)-C(13)-H(13B) | 107.7 |
| C(6)-C(7)-H(7A) | 109.5 | C(15)-C(14)-C(19) | 119.00(18) |
| C(6)-C(7)-H(7B) | 109.5 | C(15)-C(14)-C(13) | 119.81(18) |
| H(7A)-C(7)-H(7B) | 109.5 | C(19)-C(14)-C(13) | 121.12(17) |
| C(6)-C(7)-H(7C) | 109.5 | C(16)-C(15)-C(14) | 120.71(19) |
| H(7A)-C(7)-H(7C) | 109.5 | C(16)-C(15)-H(15) | 119.6 |
| H(7B)-C(7)-H(7C) | 109.5 | C(14)-C(15)-H(15) | 119.6 |
| C(6)-C(8)-H(8A) | 109.5 | C(15)-C(16)-C(17) | 120.05(18) |
| C(6)-C(8)-H(8B) | 109.5 | C(15)-C(16)-H(16) | 120.0 |
| H(8A)-C(8)-H(8B) | 109.5 | C(17)-C(16)-H(16) | 120.0 |

| | | | |
|---|---|---|---|
| C(18)-C(17)-C(16) | 121.36(18) | C(29)-C(28)-H(28) | 119.7 |
| C(18)-C(17)-H(17) | 119.3 | C(27)-C(28)-H(28) | 119.7 |
| C(16)-C(17)-H(17) | 119.3 | C(28)-C(29)-C(24) | 120.23(19) |
| C(17)-C(18)-C(19) | 118.17(17) | C(28)-C(29)-H(29) | 119.9 |
| C(17)-C(18)-C(20) | 120.35(17) | C(24)-C(29)-H(29) | 119.9 |
| C(19)-C(18)-C(20) | 121.49(17) | C(12)-S(1)-C(13) | 102.90(9) |
| C(14)-C(19)-C(18) | 120.32(17) | C(20)-S(2)-C(21) | 102.79(9) |
| C(14)-C(19)-C(22) | 119.24(17) | | |
| C(18)-C(19)-C(22) | 120.44(17) | | |
| C(18)-C(20)-S(2) | 114.78(13) | | |
| C(18)-C(20)-H(20A) | 108.6 | | |
| S(2)-C(20)-H(20A) | 108.6 | | |
| C(18)-C(20)-H(20B) | 108.6 | | |
| S(2)-C(20)-H(20B) | 108.6 | | |
| H(20A)-C(20)-H(20B) | 107.5 | | |
| C(3)-C(21)-S(2) | 113.12(13) | | |
| C(3)-C(21)-H(21A) | 109.0 | | |
| S(2)-C(21)-H(21A) | 109.0 | | |
| C(3)-C(21)-H(21B) | 109.0 | | |
| S(2)-C(21)-H(21B) | 109.0 | | |
| H(21A)-C(21)-H(21B) | 107.8 | | |
| C(23)-C(22)-C(19) | 178.9(2) | | |
| C(22)-C(23)-C(24) | 173.82(19) | | |
| C(29)-C(24)-C(25) | 118.84(18) | | |
| C(29)-C(24)-C(23) | 119.83(18) | | |
| C(25)-C(24)-C(23) | 121.23(17) | | |
| C(26)-C(25)-C(24) | 120.06(19) | | |
| C(26)-C(25)-H(25) | 120.0 | | |
| C(24)-C(25)-H(25) | 120.0 | | |
| C(25)-C(26)-C(27) | 120.92(19) | | |
| C(25)-C(26)-H(26) | 119.5 | | |
| C(27)-C(26)-H(26) | 119.5 | | |
| C(26)-C(27)-C(28) | 119.31(19) | | |
| C(26)-C(27)-H(27) | 120.3 | | |
| C(28)-C(27)-H(27) | 120.3 | | |
| C(29)-C(28)-C(27) | 120.6(2) | | |

**Table A. 45 Anisotropic displacement parameters ($Å^2 x 10^3$) for 145 (bt 830).**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 21(1) | 18(1) | 18(1) | 0(1) | 7(1) | 0(1) |
| C(2) | 15(1) | 15(1) | 16(1) | -2(1) | 5(1) | -2(1) |
| C(3) | 14(1) | 17(1) | 17(1) | -4(1) | 4(1) | -4(1) |
| C(4) | 20(1) | 20(1) | 17(1) | -2(1) | 10(1) | -3(1) |
| C(5) | 14(1) | 19(1) | 14(1) | -2(1) | 3(1) | -5(1) |
| C(6) | 21(1) | 34(1) | 18(1) | 7(1) | 7(1) | -1(1) |
| C(7) | 44(1) | 44(2) | 38(1) | 15(1) | 5(1) | -4(1) |
| C(8) | 47(2) | 81(2) | 29(1) | 18(1) | 20(1) | 14(1) |
| C(9) | 29(1) | 59(2) | 23(1) | 15(1) | 10(1) | 6(1) |
| C(10) | 14(1) | 21(1) | 18(1) | 0(1) | 5(1) | 1(1) |
| C(11) | 14(1) | 16(1) | 16(1) | -3(1) | 5(1) | -3(1) |
| C(12) | 25(1) | 17(1) | 21(1) | 0(1) | 12(1) | 2(1) |
| C(13) | 22(1) | 24(1) | 20(1) | -5(1) | 9(1) | 1(1) |
| C(14) | 20(1) | 18(1) | 18(1) | -6(1) | 7(1) | -4(1) |
| C(15) | 25(1) | 18(1) | 23(1) | -1(1) | 7(1) | -1(1) |
| C(16) | 28(1) | 17(1) | 21(1) | 1(1) | 8(1) | -6(1) |
| C(17) | 24(1) | 23(1) | 22(1) | -4(1) | 11(1) | -10(1) |
| C(18) | 18(1) | 19(1) | 17(1) | -5(1) | 5(1) | -7(1) |
| C(19) | 19(1) | 17(1) | 14(1) | -5(1) | 5(1) | -6(1) |
| C(20) | 21(1) | 26(1) | 18(1) | -3(1) | 8(1) | -2(1) |
| C(21) | 21(1) | 18(1) | 26(1) | -2(1) | 13(1) | 0(1) |
| C(22) | 17(1) | 17(1) | 18(1) | -5(1) | 7(1) | -4(1) |
| C(23) | 22(1) | 22(1) | 17(1) | -6(1) | 9(1) | 0(1) |
| C(24) | 26(1) | 19(1) | 18(1) | -4(1) | 14(1) | 0(1) |
| C(25) | 27(1) | 25(1) | 21(1) | -2(1) | 10(1) | -5(1) |
| C(26) | 27(1) | 33(1) | 18(1) | 3(1) | 8(1) | 5(1) |
| C(27) | 38(1) | 25(1) | 27(1) | 6(1) | 22(1) | 3(1) |
| C(28) | 40(1) | 29(1) | 28(1) | 0(1) | 22(1) | -11(1) |
| C(29) | 26(1) | 31(1) | 18(1) | -2(1) | 10(1) | -6(1) |
| S(1) | 18(1) | 22(1) | 20(1) | 0(1) | 10(1) | 4(1) |
| S(2) | 16(1) | 28(1) | 20(1) | -3(1) | 10(1) | -1(1) |

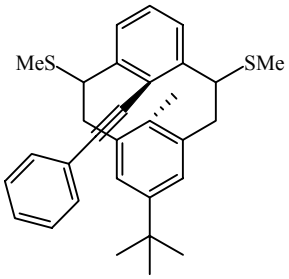
**Table A. 46 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for 145 (bt 830).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 2367 | 3362 | 9034 | 29 |
| H(1B) | 1559 | 4054 | 9777 | 29 |
| H(1C) | 3327 | 4255 | 10158 | 29 |
| H(4) | 2519 | 5532 | 5587 | 22 |
| H(7A) | -69 | 8187 | 5404 | 70 |
| H(7B) | -85 | 8398 | 3916 | 70 |
| H(7C) | 1480 | 8057 | 5242 | 70 |
| H(8A) | 1730 | 6549 | 3821 | 77 |
| H(8B) | 142 | 6879 | 2515 | 77 |
| H(8C) | 378 | 5693 | 3122 | 77 |
| H(9A) | -2065 | 5942 | 3368 | 57 |
| H(9B) | -2187 | 7133 | 2798 | 57 |
| H(9C) | -2190 | 6917 | 4278 | 57 |
| H(10) | -834 | 6623 | 6467 | 22 |
| H(12A) | 542 | 5361 | 9811 | 24 |
| H(12B) | -1128 | 5291 | 8508 | 24 |
| H(13A) | 1235 | 8254 | 10823 | 27 |
| H(13B) | 1776 | 7061 | 11320 | 27 |
| H(15) | 1491 | 8889 | 8635 | 28 |
| H(16) | 3100 | 8930 | 7553 | 28 |
| H(17) | 4951 | 7611 | 8031 | 27 |
| H(20A) | 5705 | 5456 | 10461 | 26 |
| H(20B) | 6841 | 6329 | 10354 | 26 |
| H(21A) | 4086 | 3935 | 7058 | 25 |
| H(21B) | 4371 | 3936 | 8659 | 25 |
| H(25) | 6701 | 5337 | 14927 | 30 |
| H(26) | 7257 | 3945 | 16519 | 32 |

| | | | | |
|---|---|---|---|---|
| H(27) | 5524 | 2549 | 16077 | 33 |
| H(28) | 3195 | 2557 | 14020 | 36 |
| H(29) | 2582 | 3967 | 12434 | 30 |

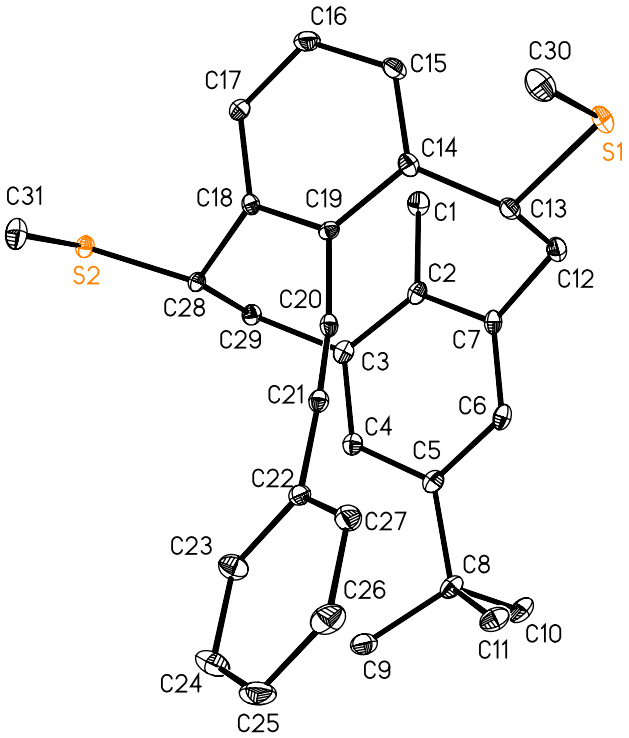
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for thiomethylcyclophane 146**




**146**

Brendan Twamley




Project name : bt958

8-20-06

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a MiTeGen fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 10 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[40] software and refined using SAINTPlus[41] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[42] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[43] The structure was solved in the space group P2(1)/c (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[40] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2001**.
[41] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[42] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[43] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Table A. 47 Crystal data and structure refinement for 146 (C31H34S2)**

| | | |
|---|---|---|
| Identification code | bt958 | |
| Empirical formula | C31 H34 S2 | |
| Formula weight | 470.70 | |
| Temperature | 90(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 12.1876(19) Å | α = 90°. |
| | b = 21.210(3) Å | β = 110.925(2)°. |
| | c = 10.6355(17) Å | γ = 90°. |
| Volume | 2567.9(7) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.218 $Mg/m^3$ | |
| Absorption coefficient | 0.225 $mm^{-1}$ | |
| F(000) | 1008 | |
| Crystal size | 0.50 x 0.43 x 0.09 $mm^3$ | |
| Crystal color and habit | colorless plate | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 1.79 to 25.25°. | |
| Index ranges | -14<=h<=14, -25<=k<=25, -12<=l<=12 | |
| Reflections collected | 37760 | |
| Independent reflections | 4658 [R(int) = 0.0331] | |
| Completeness to theta = 25.25° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9801 and 0.8960 | |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4658 / 0 / 304 | |
| Goodness-of-fit on $F^2$ | 1.086 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0380, wR2 = 0.0904 | |
| R indices (all data) | R1 = 0.0414, wR2 = 0.0924 | |
| Largest diff. peak and hole | 0.434 and -0.221 $e.Å^{-3}$ | |

**Table A. 48 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for 146 (bt 958).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 6564(2) | 6329(1) | -404(2) | 20(1) |
| C(2) | 6872(1) | 5874(1) | 766(2) | 16(1) |
| C(3) | 5999(1) | 5573(1) | 1119(2) | 15(1) |
| C(4) | 6286(1) | 5047(1) | 1963(2) | 16(1) |
| C(5) | 7433(1) | 4824(1) | 2532(2) | 16(1) |
| C(6) | 8310(1) | 5209(1) | 2376(2) | 16(1) |
| C(7) | 8052(1) | 5740(1) | 1554(2) | 16(1) |
| C(8) | 7756(1) | 4200(1) | 3301(2) | 19(1) |
| C(9) | 6731(2) | 3911(1) | 3616(2) | 24(1) |
| C(10) | 8124(2) | 3731(1) | 2423(2) | 23(1) |
| C(11) | 8790(2) | 4287(1) | 4642(2) | 22(1) |
| C(12) | 8996(1) | 6229(1) | 1703(2) | 18(1) |
| C(13) | 8995(1) | 6741(1) | 2772(2) | 16(1) |
| C(14) | 7814(1) | 7068(1) | 2406(2) | 15(1) |
| C(15) | 7509(2) | 7608(1) | 1622(2) | 19(1) |
| C(16) | 6350(2) | 7814(1) | 1121(2) | 21(1) |
| C(17) | 5465(1) | 7439(1) | 1253(2) | 17(1) |
| C(18) | 5734(1) | 6888(1) | 2006(2) | 14(1) |
| C(19) | 6929(1) | 6755(1) | 2733(2) | 13(1) |
| C(20) | 7236(1) | 6308(1) | 3814(2) | 13(1) |
| C(21) | 7456(1) | 6010(1) | 4833(2) | 14(1) |
| C(22) | 7653(1) | 5664(1) | 6047(2) | 14(1) |
| C(23) | 6805(2) | 5243(1) | 6132(2) | 22(1) |
| C(24) | 6990(2) | 4904(1) | 7299(2) | 30(1) |
| C(25) | 8013(2) | 4983(1) | 8399(2) | 29(1) |
| C(26) | 8853(2) | 5407(1) | 8335(2) | 27(1) |
| C(27) | 8678(2) | 5745(1) | 7166(2) | 20(1) |
| C(28) | 4830(1) | 6378(1) | 1897(2) | 14(1) |
| C(29) | 4808(1) | 5880(1) | 795(2) | 16(1) |
| C(30) | 10178(2) | 7743(1) | 4338(2) | 25(1) |

| | | | | |
|---|---|---|---|---|
| C(31) | 3479(2) | 7074(1) | 2992(2) | 26(1) |
| S(1) | 10221(1) | 7267(1) | 2956(1) | 19(1) |
| S(2) | 3334(1) | 6666(1) | 1457(1) | 16(1) |

**Table A. 49 Bond lengths [Å] and angles [°] for 146 (bt 958)**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.512(2) | C(12)-H(12A) | 0.9900 |
| C(1)-H(1A) | 0.9800 | C(12)-H(12B) | 0.9900 |
| C(1)-H(1B) | 0.9800 | C(13)-C(14) | 1.517(2) |
| C(1)-H(1C) | 0.9800 | C(13)-S(1) | 1.8187(16) |
| C(2)-C(3) | 1.402(2) | C(13)-H(13) | 1.0000 |
| C(2)-C(7) | 1.412(2) | C(14)-C(15) | 1.388(2) |
| C(3)-C(4) | 1.397(2) | C(14)-C(19) | 1.411(2) |
| C(3)-C(29) | 1.514(2) | C(15)-C(16) | 1.389(2) |
| C(4)-C(5) | 1.392(2) | C(15)-H(15) | 0.9500 |
| C(4)-H(4) | 0.9500 | C(16)-C(17) | 1.387(2) |
| C(5)-C(6) | 1.401(2) | C(16)-H(16) | 0.9500 |
| C(5)-C(8) | 1.532(2) | C(17)-C(18) | 1.388(2) |
| C(6)-C(7) | 1.390(2) | C(17)-H(17) | 0.9500 |
| C(6)-H(6) | 0.9500 | C(18)-C(19) | 1.413(2) |
| C(7)-C(12) | 1.515(2) | C(18)-C(28) | 1.520(2) |
| C(8)-C(9) | 1.532(2) | C(19)-C(20) | 1.434(2) |
| C(8)-C(10) | 1.537(2) | C(20)-C(21) | 1.199(2) |
| C(8)-C(11) | 1.541(2) | C(21)-C(22) | 1.429(2) |
| C(9)-H(9A) | 0.9800 | C(22)-C(23) | 1.393(2) |
| C(9)-H(9B) | 0.9800 | C(22)-C(27) | 1.394(2) |
| C(9)-H(9C) | 0.9800 | C(23)-C(24) | 1.382(2) |
| C(10)-H(10A) | 0.9800 | C(23)-H(23) | 0.9500 |
| C(10)-H(10B) | 0.9800 | C(24)-C(25) | 1.382(3) |
| C(10)-H(10C) | 0.9800 | C(24)-H(24) | 0.9500 |
| C(11)-H(11A) | 0.9800 | C(25)-C(26) | 1.381(3) |
| C(11)-H(11B) | 0.9800 | C(25)-H(25) | 0.9500 |
| C(11)-H(11C) | 0.9800 | C(26)-C(27) | 1.385(2) |
| C(12)-C(13) | 1.573(2) | C(26)-H(26) | 0.9500 |

| | | | |
|---|---|---|---|
| C(27)-H(27) | 0.9500 | C(6)-C(7)-C(2) | 119.35(15) |
| C(28)-C(29) | 1.570(2) | C(6)-C(7)-C(12) | 119.71(14) |
| C(28)-S(2) | 1.8185(15) | C(2)-C(7)-C(12) | 119.93(14) |
| C(28)-H(28) | 1.0000 | C(9)-C(8)-C(5) | 112.84(13) |
| C(29)-H(29A) | 0.9900 | C(9)-C(8)-C(10) | 108.16(14) |
| C(29)-H(29B) | 0.9900 | C(5)-C(8)-C(10) | 108.09(13) |
| C(30)-S(1) | 1.7993(18) | C(9)-C(8)-C(11) | 107.85(14) |
| C(30)-H(30A) | 0.9800 | C(5)-C(8)-C(11) | 111.13(13) |
| C(30)-H(30B) | 0.9800 | C(10)-C(8)-C(11) | 108.67(13) |
| C(30)-H(30C) | 0.9800 | C(8)-C(9)-H(9A) | 109.5 |
| C(31)-S(2) | 1.7993(18) | C(8)-C(9)-H(9B) | 109.5 |
| C(31)-H(31A) | 0.9800 | H(9A)-C(9)-H(9B) | 109.5 |
| C(31)-H(31B) | 0.9800 | C(8)-C(9)-H(9C) | 109.5 |
| C(31)-H(31C) | 0.9800 | H(9A)-C(9)-H(9C) | 109.5 |
| | | H(9B)-C(9)-H(9C) | 109.5 |
| C(2)-C(1)-H(1A) | 109.5 | C(8)-C(10)-H(10A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 | C(8)-C(10)-H(10B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 | H(10A)-C(10)-H(10B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 | C(8)-C(10)-H(10C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 | H(10A)-C(10)-H(10C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 | H(10B)-C(10)-H(10C) | 109.5 |
| C(3)-C(2)-C(7) | 117.34(14) | C(8)-C(11)-H(11A) | 109.5 |
| C(3)-C(2)-C(1) | 121.47(14) | C(8)-C(11)-H(11B) | 109.5 |
| C(7)-C(2)-C(1) | 121.19(14) | H(11A)-C(11)-H(11B) | 109.5 |
| C(4)-C(3)-C(2) | 119.75(14) | C(8)-C(11)-H(11C) | 109.5 |
| C(4)-C(3)-C(29) | 119.32(14) | H(11A)-C(11)-H(11C) | 109.5 |
| C(2)-C(3)-C(29) | 120.06(14) | H(11B)-C(11)-H(11C) | 109.5 |
| C(5)-C(4)-C(3) | 122.15(15) | C(7)-C(12)-C(13) | 110.61(12) |
| C(5)-C(4)-H(4) | 118.9 | C(7)-C(12)-H(12A) | 109.5 |
| C(3)-C(4)-H(4) | 118.9 | C(13)-C(12)-H(12A) | 109.5 |
| C(4)-C(5)-C(6) | 116.20(14) | C(7)-C(12)-H(12B) | 109.5 |
| C(4)-C(5)-C(8) | 123.44(14) | C(13)-C(12)-H(12B) | 109.5 |
| C(6)-C(5)-C(8) | 120.36(14) | H(12A)-C(12)-H(12B) | 108.1 |
| C(7)-C(6)-C(5) | 122.36(15) | C(14)-C(13)-C(12) | 112.09(13) |
| C(7)-C(6)-H(6) | 118.8 | C(14)-C(13)-S(1) | 114.54(11) |
| C(5)-C(6)-H(6) | 118.8 | C(12)-C(13)-S(1) | 106.73(10) |

| | | | |
|---|---|---|---|
| C(14)-C(13)-H(13) | 107.7 | C(25)-C(26)-H(26) | 119.9 |
| C(12)-C(13)-H(13) | 107.7 | C(27)-C(26)-H(26) | 119.9 |
| S(1)-C(13)-H(13) | 107.7 | C(26)-C(27)-C(22) | 120.33(16) |
| C(15)-C(14)-C(19) | 118.16(14) | C(26)-C(27)-H(27) | 119.8 |
| C(15)-C(14)-C(13) | 123.87(14) | C(22)-C(27)-H(27) | 119.8 |
| C(19)-C(14)-C(13) | 117.40(14) | C(18)-C(28)-C(29) | 110.74(12) |
| C(14)-C(15)-C(16) | 120.46(15) | C(18)-C(28)-S(2) | 114.38(11) |
| C(14)-C(15)-H(15) | 119.8 | C(29)-C(28)-S(2) | 106.62(10) |
| C(16)-C(15)-H(15) | 119.8 | C(18)-C(28)-H(28) | 108.3 |
| C(17)-C(16)-C(15) | 120.16(15) | C(29)-C(28)-H(28) | 108.3 |
| C(17)-C(16)-H(16) | 119.9 | S(2)-C(28)-H(28) | 108.3 |
| C(15)-C(16)-H(16) | 119.9 | C(3)-C(29)-C(28) | 111.08(12) |
| C(16)-C(17)-C(18) | 120.57(15) | C(3)-C(29)-H(29A) | 109.4 |
| C(16)-C(17)-H(17) | 119.7 | C(28)-C(29)-H(29A) | 109.4 |
| C(18)-C(17)-H(17) | 119.7 | C(3)-C(29)-H(29B) | 109.4 |
| C(17)-C(18)-C(19) | 118.00(14) | C(28)-C(29)-H(29B) | 109.4 |
| C(17)-C(18)-C(28) | 122.72(14) | H(29A)-C(29)-H(29B) | 108.0 |
| C(19)-C(18)-C(28) | 118.48(13) | S(1)-C(30)-H(30A) | 109.5 |
| C(14)-C(19)-C(18) | 120.02(14) | S(1)-C(30)-H(30B) | 109.5 |
| C(14)-C(19)-C(20) | 120.37(14) | H(30A)-C(30)-H(30B) | 109.5 |
| C(18)-C(19)-C(20) | 119.60(14) | S(1)-C(30)-H(30C) | 109.5 |
| C(21)-C(20)-C(19) | 169.68(16) | H(30A)-C(30)-H(30C) | 109.5 |
| C(20)-C(21)-C(22) | 176.74(16) | H(30B)-C(30)-H(30C) | 109.5 |
| C(23)-C(22)-C(27) | 118.95(15) | S(2)-C(31)-H(31A) | 109.5 |
| C(23)-C(22)-C(21) | 119.87(14) | S(2)-C(31)-H(31B) | 109.5 |
| C(27)-C(22)-C(21) | 121.17(15) | H(31A)-C(31)-H(31B) | 109.5 |
| C(24)-C(23)-C(22) | 120.29(16) | S(2)-C(31)-H(31C) | 109.5 |
| C(24)-C(23)-H(23) | 119.9 | H(31A)-C(31)-H(31C) | 109.5 |
| C(22)-C(23)-H(23) | 119.9 | H(31B)-C(31)-H(31C) | 109.5 |
| C(25)-C(24)-C(23) | 120.41(17) | C(30)-S(1)-C(13) | 99.74(8) |
| C(25)-C(24)-H(24) | 119.8 | C(31)-S(2)-C(28) | 99.45(8) |
| C(23)-C(24)-H(24) | 119.8 | | |
| C(26)-C(25)-C(24) | 119.83(16) | | |
| C(26)-C(25)-H(25) | 120.1 | | |
| C(24)-C(25)-H(25) | 120.1 | | |
| C(25)-C(26)-C(27) | 120.18(17) | | |

**Table A. 50 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 146 (bt 958).**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 19(1) | 27(1) | 14(1) | 1(1) | 5(1) | 2(1) |
| C(2) | 18(1) | 17(1) | 14(1) | -4(1) | 5(1) | 2(1) |
| C(3) | 14(1) | 17(1) | 12(1) | -5(1) | 1(1) | 0(1) |
| C(4) | 15(1) | 15(1) | 16(1) | -4(1) | 5(1) | -1(1) |
| C(5) | 17(1) | 15(1) | 14(1) | -5(1) | 4(1) | 1(1) |
| C(6) | 13(1) | 20(1) | 15(1) | -5(1) | 3(1) | 3(1) |
| C(7) | 16(1) | 20(1) | 15(1) | -5(1) | 8(1) | 1(1) |
| C(8) | 16(1) | 17(1) | 19(1) | -1(1) | 1(1) | 2(1) |
| C(9) | 23(1) | 20(1) | 26(1) | 5(1) | 5(1) | 1(1) |
| C(10) | 21(1) | 18(1) | 26(1) | -4(1) | 3(1) | 4(1) |
| C(11) | 22(1) | 19(1) | 20(1) | 1(1) | 0(1) | 3(1) |
| C(12) | 16(1) | 23(1) | 18(1) | 1(1) | 8(1) | 1(1) |
| C(13) | 13(1) | 19(1) | 16(1) | 3(1) | 6(1) | -2(1) |
| C(14) | 14(1) | 18(1) | 13(1) | -1(1) | 4(1) | -2(1) |
| C(15) | 18(1) | 19(1) | 21(1) | 3(1) | 7(1) | -4(1) |
| C(16) | 22(1) | 17(1) | 22(1) | 6(1) | 6(1) | 1(1) |
| C(17) | 15(1) | 18(1) | 18(1) | 3(1) | 5(1) | 3(1) |
| C(18) | 15(1) | 15(1) | 12(1) | -1(1) | 6(1) | 0(1) |
| C(19) | 16(1) | 11(1) | 12(1) | -1(1) | 5(1) | 1(1) |
| C(20) | 11(1) | 14(1) | 15(1) | -3(1) | 5(1) | -1(1) |
| C(21) | 13(1) | 15(1) | 15(1) | -2(1) | 6(1) | 0(1) |
| C(22) | 17(1) | 14(1) | 13(1) | 1(1) | 7(1) | 3(1) |
| C(23) | 23(1) | 22(1) | 20(1) | 1(1) | 6(1) | -3(1) |
| C(24) | 37(1) | 25(1) | 30(1) | 6(1) | 17(1) | -7(1) |
| C(25) | 43(1) | 26(1) | 21(1) | 10(1) | 14(1) | 6(1) |
| C(26) | 28(1) | 31(1) | 17(1) | 4(1) | 2(1) | 7(1) |
| C(27) | 19(1) | 22(1) | 20(1) | 2(1) | 6(1) | 0(1) |
| C(28) | 10(1) | 15(1) | 14(1) | 2(1) | 3(1) | 2(1) |
| C(29) | 14(1) | 17(1) | 15(1) | 0(1) | 3(1) | 1(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(30) | 25(1) | 30(1) | 21(1) | -3(1) | 8(1) | -7(1) |
| C(31) | 22(1) | 30(1) | 27(1) | -7(1) | 11(1) | 2(1) |
| S(1) | 14(1) | 24(1) | 20(1) | 0(1) | 7(1) | -5(1) |
| S(2) | 12(1) | 18(1) | 18(1) | 1(1) | 4(1) | 2(1) |

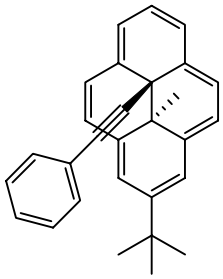
**Table A. 51 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for 146 (bt 958).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 6415 | 6747 | -108 | 31 |
| H(1B) | 5859 | 6180 | -1130 | 31 |
| H(1C) | 7219 | 6354 | -731 | 31 |
| H(4) | 5679 | 4834 | 2156 | 19 |
| H(6) | 9110 | 5104 | 2850 | 20 |
| H(9A) | 6983 | 3515 | 4106 | 36 |
| H(9B) | 6075 | 3829 | 2773 | 36 |
| H(9C) | 6477 | 4205 | 4169 | 36 |
| H(10A) | 8749 | 3917 | 2166 | 35 |
| H(10B) | 7446 | 3634 | 1611 | 35 |
| H(10C) | 8411 | 3342 | 2932 | 35 |
| H(11A) | 9492 | 4414 | 4461 | 33 |
| H(11B) | 8943 | 3888 | 5141 | 33 |
| H(11C) | 8592 | 4613 | 5179 | 33 |
| H(12A) | 8856 | 6434 | 824 | 22 |
| H(12B) | 9774 | 6021 | 1990 | 22 |
| H(13) | 9157 | 6522 | 3653 | 19 |
| H(15) | 8096 | 7839 | 1427 | 23 |
| H(16) | 6164 | 8212 | 688 | 25 |
| H(17) | 4667 | 7560 | 823 | 21 |
| H(23) | 6095 | 5189 | 5384 | 27 |
| H(24) | 6411 | 4614 | 7346 | 35 |
| H(25) | 8138 | 4747 | 9198 | 35 |

| | | | | |
|---|---|---|---|---|
| H(26) | 9552 | 5466 | 9094 | 32 |
| H(27) | 9260 | 6035 | 7126 | 24 |
| H(28) | 5056 | 6156 | 2784 | 16 |
| H(29A) | 4215 | 5552 | 741 | 19 |
| H(29B) | 4578 | 6090 | -93 | 19 |
| H(30A) | 9441 | 7981 | 4060 | 38 |
| H(30B) | 10843 | 8036 | 4608 | 38 |
| H(30C) | 10228 | 7470 | 5100 | 38 |
| H(31A) | 3764 | 6781 | 3751 | 38 |
| H(31B) | 2712 | 7242 | 2932 | 38 |
| H(31C) | 4038 | 7422 | 3127 | 38 |

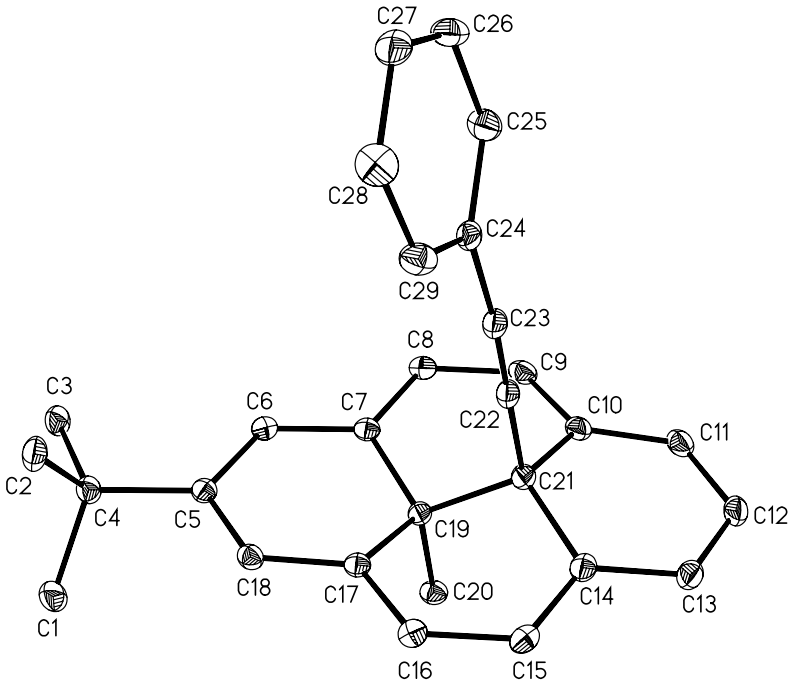
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for phenylethynyl DHP 139**



**139**

Brendan Twamley




Project name : bt914

6-10-06

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 89(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 30 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[44] software and refined using SAINTPlus[45] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[46] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[47] The structure was solved in the space group Pbca (# 61) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[44] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2001**.
[45] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[46] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[47] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Table A. 52 Crystal data and structure refinement for 139**

| | | |
|---|---|---|
| Identification code | bt914 | |
| Empirical formula | C29 H26 | |
| Formula weight | 374.50 | |
| Temperature | 89(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhomibc | |
| Space group | Pbca | |
| Unit cell dimensions | a = 15.3244(16) Å | α = 90°. |
| | b = 13.3476(14) Å | β = 90°. |
| | c = 20.633(2) Å | γ = 90°. |
| Volume | 4220.4(7) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.179 $Mg/m^3$ | |
| Absorption coefficient | 0.066 $mm^{-1}$ | |
| F(000) | 1600 | |
| Crystal size | 0.55 x 0.26 x 0.04 $mm^3$ | |
| Crystal color and habit | greenplate | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 1.97 to 25.24°. | |
| Index ranges | -18<=h<=18, -16<=k<=16, -24<=l<=24 | |
| Reflections collected | 62517 | |
| Independent reflections | 3818 [R(int) = 0.0380] | |
| Completeness to theta = 25.24° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9974 and 0.9644 | |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3818 / 0 / 266 | |
| Goodness-of-fit on $F^2$ | 1.033 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0390, wR2 = 0.0926 | |
| R indices (all data) | R1 = 0.0463, wR2 = 0.0973 | |
| Largest diff. peak and hole | 0.277 and -0.170 $e.Å^{-3}$ | |

**Table A. 53 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 139 (bt 914).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 4199(1) | 6279(1) | 4972(1) | 31(1) |
| C(2) | 4701(1) | 5679(1) | 3881(1) | 28(1) |
| C(3) | 4870(1) | 7467(1) | 4184(1) | 27(1) |
| C(4) | 4277(1) | 6548(1) | 4250(1) | 23(1) |
| C(5) | 3359(1) | 6732(1) | 3979(1) | 19(1) |
| C(6) | 3133(1) | 7615(1) | 3664(1) | 19(1) |
| C(7) | 2295(1) | 7798(1) | 3423(1) | 19(1) |
| C(8) | 2063(1) | 8648(1) | 3076(1) | 22(1) |
| C(9) | 1210(1) | 8796(1) | 2848(1) | 25(1) |
| C(10) | 582(1) | 8054(1) | 2873(1) | 23(1) |
| C(11) | -298(1) | 8178(1) | 2708(1) | 28(1) |
| C(12) | -903(1) | 7420(1) | 2797(1) | 30(1) |
| C(13) | -676(1) | 6501(1) | 3077(1) | 26(1) |
| C(14) | 169(1) | 6284(1) | 3261(1) | 22(1) |
| C(15) | 423(1) | 5417(1) | 3595(1) | 22(1) |
| C(16) | 1265(1) | 5284(1) | 3819(1) | 21(1) |
| C(17) | 1892(1) | 6054(1) | 3801(1) | 18(1) |
| C(18) | 2737(1) | 5952(1) | 4018(1) | 20(1) |
| C(19) | 1572(1) | 7088(1) | 3615(1) | 18(1) |
| C(20) | 1154(1) | 7537(1) | 4238(1) | 22(1) |
| C(21) | 898(1) | 7006(1) | 3065(1) | 20(1) |
| C(22) | 1330(1) | 6564(1) | 2482(1) | 22(1) |
| C(23) | 1673(1) | 6204(1) | 2016(1) | 24(1) |
| C(24) | 2143(1) | 5756(1) | 1486(1) | 21(1) |
| C(25) | 2386(1) | 6313(1) | 945(1) | 28(1) |
| C(26) | 2898(1) | 5891(1) | 464(1) | 31(1) |
| C(27) | 3183(1) | 4917(1) | 517(1) | 29(1) |
| C(28) | 2939(1) | 4354(1) | 1046(1) | 33(1) |
| C(29) | 2411(1) | 4761(1) | 1523(1) | 27(1) |

**Table A. 54 Bond lengths [Å] and angles [°] for 139 (bt 914)**

| | | | |
|---|---|---|---|
| C(1)-C(4) | 1.5370(19) | C(14)-C(21) | 1.5303(19) |
| C(1)-H(1A) | 0.9800 | C(15)-C(16) | 1.3826(19) |
| C(1)-H(1B) | 0.9800 | C(15)-H(15) | 0.9500 |
| C(1)-H(1C) | 0.9800 | C(16)-C(17) | 1.4063(18) |
| C(2)-C(4) | 1.532(2) | C(16)-H(16) | 0.9500 |
| C(2)-H(2A) | 0.9800 | C(17)-C(18) | 1.3774(18) |
| C(2)-H(2B) | 0.9800 | C(17)-C(19) | 1.5140(18) |
| C(2)-H(2C) | 0.9800 | C(18)-H(18) | 0.9500 |
| C(3)-C(4) | 1.5328(19) | C(19)-C(21) | 1.5390(17) |
| C(3)-H(3A) | 0.9800 | C(19)-C(20) | 1.5565(17) |
| C(3)-H(3B) | 0.9800 | C(20)-H(20A) | 0.9800 |
| C(3)-H(3C) | 0.9800 | C(20)-H(20B) | 0.9800 |
| C(4)-C(5) | 1.5333(18) | C(20)-H(20C) | 0.9800 |
| C(5)-C(6) | 1.3902(18) | C(21)-C(22) | 1.4937(18) |
| C(5)-C(18) | 1.4147(18) | C(22)-C(23) | 1.1967(19) |
| C(6)-C(7) | 1.3985(18) | C(23)-C(24) | 1.4399(19) |
| C(6)-H(6) | 0.9500 | C(24)-C(25) | 1.392(2) |
| C(7)-C(8) | 1.3883(18) | C(24)-C(29) | 1.392(2) |
| C(7)-C(19) | 1.5116(18) | C(25)-C(26) | 1.384(2) |
| C(8)-C(9) | 1.4031(19) | C(25)-H(25) | 0.9500 |
| C(8)-H(8) | 0.9500 | C(26)-C(27) | 1.377(2) |
| C(9)-C(10) | 1.383(2) | C(26)-H(26) | 0.9500 |
| C(9)-H(9) | 0.9500 | C(27)-C(28) | 1.376(2) |
| C(10)-C(11) | 1.4001(19) | C(27)-H(27) | 0.9500 |
| C(10)-C(21) | 1.5321(19) | C(28)-C(29) | 1.385(2) |
| C(11)-C(12) | 1.384(2) | C(28)-H(28) | 0.9500 |
| C(11)-H(11) | 0.9500 | C(29)-H(29) | 0.9500 |
| C(12)-C(13) | 1.400(2) | | |
| C(12)-H(12) | 0.9500 | C(4)-C(1)-H(1A) | 109.5 |
| C(13)-C(14) | 1.3798(19) | C(4)-C(1)-H(1B) | 109.5 |
| C(13)-H(13) | 0.9500 | H(1A)-C(1)-H(1B) | 109.5 |
| C(14)-C(15) | 1.401(2) | C(4)-C(1)-H(1C) | 109.5 |

| | | | |
|---|---|---|---|
| H(1A)-C(1)-H(1C) | 109.5 | C(9)-C(10)-C(21) | 116.34(12) |
| H(1B)-C(1)-H(1C) | 109.5 | C(11)-C(10)-C(21) | 118.38(13) |
| C(4)-C(2)-H(2A) | 109.5 | C(12)-C(11)-C(10) | 121.73(14) |
| C(4)-C(2)-H(2B) | 109.5 | C(12)-C(11)-H(11) | 119.1 |
| H(2A)-C(2)-H(2B) | 109.5 | C(10)-C(11)-H(11) | 119.1 |
| C(4)-C(2)-H(2C) | 109.5 | C(11)-C(12)-C(13) | 121.97(13) |
| H(2A)-C(2)-H(2C) | 109.5 | C(11)-C(12)-H(12) | 119.0 |
| H(2B)-C(2)-H(2C) | 109.5 | C(13)-C(12)-H(12) | 119.0 |
| C(4)-C(3)-H(3A) | 109.5 | C(14)-C(13)-C(12) | 121.98(14) |
| C(4)-C(3)-H(3B) | 109.5 | C(14)-C(13)-H(13) | 119.0 |
| H(3A)-C(3)-H(3B) | 109.5 | C(12)-C(13)-H(13) | 119.0 |
| C(4)-C(3)-H(3C) | 109.5 | C(13)-C(14)-C(15) | 124.66(13) |
| H(3A)-C(3)-H(3C) | 109.5 | C(13)-C(14)-C(21) | 118.72(13) |
| H(3B)-C(3)-H(3C) | 109.5 | C(15)-C(14)-C(21) | 116.55(11) |
| C(2)-C(4)-C(3) | 108.05(11) | C(16)-C(15)-C(14) | 122.01(12) |
| C(2)-C(4)-C(5) | 109.18(11) | C(16)-C(15)-H(15) | 119.0 |
| C(3)-C(4)-C(5) | 112.47(11) | C(14)-C(15)-H(15) | 119.0 |
| C(2)-C(4)-C(1) | 109.77(12) | C(15)-C(16)-C(17) | 122.33(13) |
| C(3)-C(4)-C(1) | 108.69(11) | C(15)-C(16)-H(16) | 118.8 |
| C(5)-C(4)-C(1) | 108.66(11) | C(17)-C(16)-H(16) | 118.8 |
| C(6)-C(5)-C(18) | 118.86(12) | C(18)-C(17)-C(16) | 124.18(12) |
| C(6)-C(5)-C(4) | 122.38(12) | C(18)-C(17)-C(19) | 118.48(11) |
| C(18)-C(5)-C(4) | 118.65(11) | C(16)-C(17)-C(19) | 116.81(11) |
| C(5)-C(6)-C(7) | 122.91(12) | C(17)-C(18)-C(5) | 122.89(12) |
| C(5)-C(6)-H(6) | 118.5 | C(17)-C(18)-H(18) | 118.6 |
| C(7)-C(6)-H(6) | 118.5 | C(5)-C(18)-H(18) | 118.6 |
| C(8)-C(7)-C(6) | 124.19(12) | C(7)-C(19)-C(17) | 113.64(10) |
| C(8)-C(7)-C(19) | 117.37(11) | C(7)-C(19)-C(21) | 110.03(10) |
| C(6)-C(7)-C(19) | 118.07(11) | C(17)-C(19)-C(21) | 109.87(10) |
| C(7)-C(8)-C(9) | 121.86(13) | C(7)-C(19)-C(20) | 106.06(10) |
| C(7)-C(8)-H(8) | 119.1 | C(17)-C(19)-C(20) | 105.97(10) |
| C(9)-C(8)-H(8) | 119.1 | C(21)-C(19)-C(20) | 111.16(10) |
| C(10)-C(9)-C(8) | 122.30(13) | C(19)-C(20)-H(20A) | 109.5 |
| C(10)-C(9)-H(9) | 118.8 | C(19)-C(20)-H(20B) | 109.5 |
| C(8)-C(9)-H(9) | 118.8 | H(20A)-C(20)-H(20B) | 109.5 |
| C(9)-C(10)-C(11) | 125.20(13) | C(19)-C(20)-H(20C) | 109.5 |

| | |
|---|---|
| H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 |
| C(22)-C(21)-C(14) | 106.71(11) |
| C(22)-C(21)-C(10) | 107.08(11) |
| C(14)-C(21)-C(10) | 114.32(11) |
| C(22)-C(21)-C(19) | 108.97(10) |
| C(14)-C(21)-C(19) | 109.81(11) |
| C(10)-C(21)-C(19) | 109.77(11) |
| C(23)-C(22)-C(21) | 179.58(16) |
| C(22)-C(23)-C(24) | 175.58(14) |
| C(25)-C(24)-C(29) | 118.34(13) |
| C(25)-C(24)-C(23) | 121.45(13) |
| C(29)-C(24)-C(23) | 120.10(13) |
| C(26)-C(25)-C(24) | 120.64(14) |
| C(26)-C(25)-H(25) | 119.7 |
| C(24)-C(25)-H(25) | 119.7 |
| C(27)-C(26)-C(25) | 120.39(14) |
| C(27)-C(26)-H(26) | 119.8 |
| C(25)-C(26)-H(26) | 119.8 |
| C(28)-C(27)-C(26) | 119.59(13) |
| C(28)-C(27)-H(27) | 120.2 |
| C(26)-C(27)-H(27) | 120.2 |
| C(27)-C(28)-C(29) | 120.47(14) |
| C(27)-C(28)-H(28) | 119.8 |
| C(29)-C(28)-H(28) | 119.8 |
| C(28)-C(29)-C(24) | 120.50(13) |
| C(28)-C(29)-H(29) | 119.8 |
| C(24)-C(29)-H(29) | 119.8 |

**Table A. 55 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 139 (bt 914).**

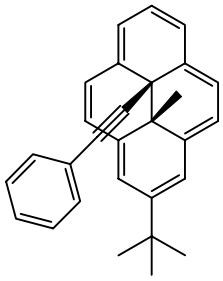
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 26(1) | 38(1) | 28(1) | 7(1) | -9(1) | -6(1) |
| C(2) | 18(1) | 28(1) | 39(1) | 3(1) | -4(1) | 1(1) |
| C(3) | 21(1) | 31(1) | 30(1) | 3(1) | -7(1) | -5(1) |
| C(4) | 20(1) | 24(1) | 24(1) | 3(1) | -4(1) | -2(1) |
| C(5) | 19(1) | 22(1) | 16(1) | -2(1) | 0(1) | -1(1) |
| C(6) | 21(1) | 18(1) | 18(1) | -2(1) | 1(1) | -2(1) |
| C(7) | 22(1) | 19(1) | 15(1) | -3(1) | 2(1) | 1(1) |
| C(8) | 25(1) | 22(1) | 20(1) | 1(1) | 3(1) | 0(1) |
| C(9) | 29(1) | 25(1) | 21(1) | 6(1) | 3(1) | 8(1) |
| C(10) | 23(1) | 31(1) | 16(1) | 2(1) | 2(1) | 6(1) |
| C(11) | 26(1) | 38(1) | 21(1) | 6(1) | 0(1) | 12(1) |
| C(12) | 18(1) | 49(1) | 22(1) | 1(1) | -1(1) | 7(1) |
| C(13) | 19(1) | 39(1) | 22(1) | -3(1) | 1(1) | -1(1) |
| C(14) | 19(1) | 30(1) | 18(1) | -5(1) | 2(1) | 0(1) |
| C(15) | 20(1) | 24(1) | 24(1) | -3(1) | 3(1) | -4(1) |
| C(16) | 22(1) | 19(1) | 23(1) | -1(1) | 2(1) | 0(1) |
| C(17) | 20(1) | 19(1) | 15(1) | -2(1) | 2(1) | 1(1) |
| C(18) | 22(1) | 18(1) | 19(1) | 2(1) | 0(1) | 3(1) |
| C(19) | 16(1) | 20(1) | 16(1) | -1(1) | 1(1) | 2(1) |
| C(20) | 25(1) | 22(1) | 19(1) | -1(1) | 3(1) | 2(1) |
| C(21) | 17(1) | 26(1) | 18(1) | 0(1) | 1(1) | 3(1) |
| C(22) | 16(1) | 29(1) | 21(1) | -1(1) | -3(1) | 0(1) |
| C(23) | 16(1) | 33(1) | 21(1) | -2(1) | -2(1) | 0(1) |
| C(24) | 16(1) | 30(1) | 18(1) | -4(1) | -2(1) | 0(1) |
| C(25) | 32(1) | 27(1) | 24(1) | 1(1) | 2(1) | 8(1) |
| C(26) | 34(1) | 38(1) | 21(1) | 2(1) | 6(1) | 2(1) |
| C(27) | 28(1) | 36(1) | 24(1) | -11(1) | 3(1) | 4(1) |
| C(28) | 41(1) | 22(1) | 34(1) | -7(1) | 0(1) | 3(1) |
| C(29) | 32(1) | 26(1) | 24(1) | 0(1) | 0(1) | -8(1) |

**Table A. 56 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for 139 (bt 914).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 3821 | 5691 | 5022 | 46 |
| H(1B) | 3948 | 6846 | 5209 | 46 |
| H(1C) | 4779 | 6127 | 5146 | 46 |
| H(2A) | 4350 | 5072 | 3938 | 42 |
| H(2B) | 5290 | 5564 | 4049 | 42 |
| H(2C) | 4733 | 5846 | 3419 | 42 |
| H(3A) | 5442 | 7320 | 4373 | 41 |
| H(3B) | 4606 | 8036 | 4410 | 41 |
| H(3C) | 4941 | 7633 | 3724 | 41 |
| H(6) | 3567 | 8117 | 3610 | 23 |
| H(8) | 2493 | 9142 | 2990 | 27 |
| H(9) | 1059 | 9429 | 2669 | 30 |
| H(11) | -485 | 8799 | 2530 | 34 |
| H(12) | -1489 | 7527 | 2664 | 35 |
| H(13) | -1118 | 6012 | 3143 | 32 |
| H(15) | 4 | 4906 | 3668 | 27 |
| H(16) | 1426 | 4651 | 3992 | 25 |
| H(18) | 2910 | 5330 | 4202 | 24 |
| H(20A) | 1593 | 7569 | 4583 | 33 |
| H(20B) | 668 | 7112 | 4379 | 33 |
| H(20C) | 937 | 8213 | 4146 | 33 |
| H(25) | 2199 | 6988 | 905 | 34 |
| H(26) | 3053 | 6277 | 94 | 37 |
| H(27) | 3545 | 4634 | 191 | 35 |
| H(28) | 3135 | 3681 | 1085 | 39 |
| H(29) | 2229 | 4358 | 1878 | 33 |

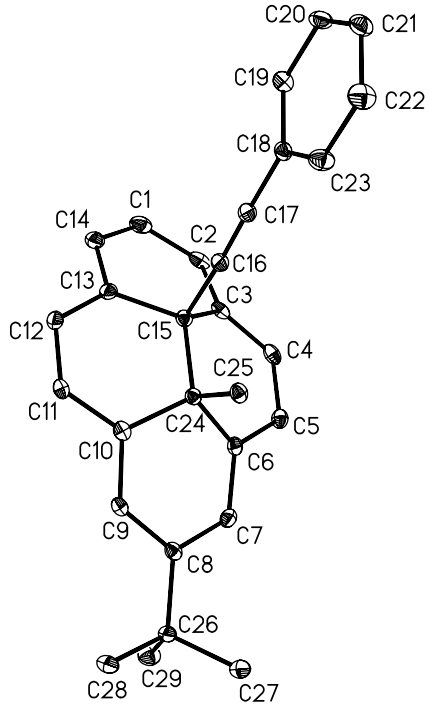
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for *cis*-phenylethynyl/methyl DHP 148**



**148**

Brendan Twamley




Project name : bt956

8-17-06

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 89(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 10 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[48] software and refined using SAINTPlus[49] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[50] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[51] The structure was solved in the space group P2(1)2(1)2(1) (# 19) by analysis of systematic absences. The structure was refined as a racemic twin. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[48] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2001**.
[49] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[50] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[51] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Table A. 57 Crystal data and structure refinement for 148**

| | | |
|---|---|---|
| Identification code | bt956 | |
| Empirical formula | C29 H26 | |
| Formula weight | 374.50 | |
| Temperature | 89(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2(1) | |
| Unit cell dimensions | a = 8.1094(6) Å | α = 90°. |
| | b = 13.9234(11) Å | β = 90°. |
| | c = 18.4052(14) Å | γ = 90°. |
| Volume | 2078.1(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.197 $Mg/m^3$ | |
| Absorption coefficient | 0.067 $mm^{-1}$ | |
| F(000) | 800 | |
| Crystal size | 0.50 x 0.34 x 0.15 $mm^3$ | |
| Crystal color and habit | red needle | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 1.83 to 25.25°. | |
| Index ranges | -9<=h<=9, -16<=k<=16, -22<=l<=22 | |
| Reflections collected | 30885 | |
| Independent reflections | 2163 [R(int) = 0.0279] | |
| Completeness to theta = 25.25° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9900 and 0.9671 | |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2163 / 0 / 267 | |
| Goodness-of-fit on $F^2$ | 1.096 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0369, wR2 = 0.0923 | |
| R indices (all data) | R1 = 0.0377, wR2 = 0.0929 | |
| Largest diff. peak and hole | 0.231 and -0.144 $e.Å^{-3}$ | |

**Table A. 58 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 148 (bt 956).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 623(3) | 11085(2) | 3344(1) | 28(1) |
| C(2) | 2214(3) | 11460(2) | 3369(1) | 24(1) |
| C(3) | 3560(3) | 10966(2) | 3107(1) | 20(1) |
| C(4) | 5090(3) | 11399(2) | 3005(1) | 21(1) |
| C(5) | 6253(3) | 11055(2) | 2526(1) | 21(1) |
| C(6) | 5975(3) | 10225(2) | 2114(1) | 18(1) |
| C(7) | 6871(3) | 10040(2) | 1488(1) | 20(1) |
| C(8) | 6456(3) | 9304(2) | 996(1) | 18(1) |
| C(9) | 5008(3) | 8796(1) | 1122(1) | 17(1) |
| C(10) | 4011(3) | 8935(1) | 1735(1) | 17(1) |
| C(11) | 2438(3) | 8556(2) | 1766(1) | 19(1) |
| C(12) | 1247(3) | 8906(2) | 2240(1) | 21(1) |
| C(13) | 1563(3) | 9661(2) | 2711(1) | 20(1) |
| C(14) | 306(3) | 10216(2) | 3003(1) | 25(1) |
| C(15) | 3353(3) | 9890(2) | 2925(1) | 17(1) |
| C(16) | 3503(3) | 9424(2) | 3653(1) | 19(1) |
| C(17) | 3525(3) | 9081(2) | 4246(1) | 20(1) |
| C(18) | 3593(3) | 8667(2) | 4964(1) | 20(1) |
| C(19) | 2557(3) | 9012(2) | 5513(1) | 23(1) |
| C(20) | 2657(3) | 8636(2) | 6209(1) | 26(1) |
| C(21) | 3782(3) | 7916(2) | 6364(1) | 29(1) |
| C(22) | 4800(3) | 7564(2) | 5824(1) | 33(1) |
| C(23) | 4704(3) | 7937(2) | 5125(1) | 28(1) |
| C(24) | 4735(3) | 9482(1) | 2375(1) | 16(1) |
| C(25) | 5823(3) | 8723(2) | 2774(1) | 20(1) |
| C(26) | 7467(3) | 9177(2) | 299(1) | 19(1) |
| C(27) | 9310(3) | 9095(2) | 487(1) | 26(1) |
| C(28) | 6989(3) | 8264(2) | -115(1) | 26(1) |
| C(29) | 7180(3) | 10049(2) | -195(1) | 28(1) |

**Table A. 59 Bond lengths [Å] and angles [°] for 148 (bt 956)**

| | | | |
|---|---|---|---|
| C(1)-C(14) | 1.386(4) | C(18)-C(19) | 1.399(3) |
| C(1)-C(2) | 1.393(4) | C(19)-C(20) | 1.386(3) |
| C(1)-H(1) | 0.9500 | C(19)-H(19) | 0.9500 |
| C(2)-C(3) | 1.378(3) | C(20)-C(21) | 1.385(4) |
| C(2)-H(2) | 0.9500 | C(20)-H(20) | 0.9500 |
| C(3)-C(4) | 1.392(3) | C(21)-C(22) | 1.382(4) |
| C(3)-C(15) | 1.544(3) | C(21)-H(21) | 0.9500 |
| C(4)-C(5) | 1.377(3) | C(22)-C(23) | 1.389(3) |
| C(4)-H(4) | 0.9500 | C(22)-H(22) | 0.9500 |
| C(5)-C(6) | 1.400(3) | C(23)-H(23) | 0.9500 |
| C(5)-H(5) | 0.9500 | C(24)-C(25) | 1.560(3) |
| C(6)-C(7) | 1.385(3) | C(25)-H(25A) | 0.9800 |
| C(6)-C(24) | 1.522(3) | C(25)-H(25B) | 0.9800 |
| C(7)-C(8) | 1.409(3) | C(25)-H(25C) | 0.9800 |
| C(7)-H(7) | 0.9500 | C(26)-C(28) | 1.533(3) |
| C(8)-C(9) | 1.391(3) | C(26)-C(29) | 1.534(3) |
| C(8)-C(26) | 1.532(3) | C(26)-C(27) | 1.538(3) |
| C(9)-C(10) | 1.401(3) | C(27)-H(27A) | 0.9800 |
| C(9)-H(9) | 0.9500 | C(27)-H(27B) | 0.9800 |
| C(10)-C(11) | 1.381(3) | C(27)-H(27C) | 0.9800 |
| C(10)-C(24) | 1.521(3) | C(28)-H(28A) | 0.9800 |
| C(11)-C(12) | 1.389(3) | C(28)-H(28B) | 0.9800 |
| C(11)-H(11) | 0.9500 | C(28)-H(28C) | 0.9800 |
| C(12)-C(13) | 1.387(3) | C(29)-H(29A) | 0.9800 |
| C(12)-H(12) | 0.9500 | C(29)-H(29B) | 0.9800 |
| C(13)-C(14) | 1.387(3) | C(29)-H(29C) | 0.9800 |
| C(13)-C(15) | 1.538(3) | | |
| C(14)-H(14) | 0.9500 | C(14)-C(1)-C(2) | 121.0(2) |
| C(15)-C(16) | 1.493(3) | C(14)-C(1)-H(1) | 119.5 |
| C(15)-C(24) | 1.614(3) | C(2)-C(1)-H(1) | 119.5 |
| C(16)-C(17) | 1.193(3) | C(3)-C(2)-C(1) | 122.3(2) |
| C(17)-C(18) | 1.442(3) | C(3)-C(2)-H(2) | 118.9 |
| C(18)-C(23) | 1.391(3) | C(1)-C(2)-H(2) | 118.9 |

| | | | |
|---|---|---|---|
| C(2)-C(3)-C(4) | 122.5(2) | C(16)-C(15)-C(13) | 102.50(17) |
| C(2)-C(3)-C(15) | 118.3(2) | C(16)-C(15)-C(3) | 102.65(16) |
| C(4)-C(3)-C(15) | 119.2(2) | C(13)-C(15)-C(3) | 111.06(18) |
| C(5)-C(4)-C(3) | 123.09(19) | C(16)-C(15)-C(24) | 110.68(17) |
| C(5)-C(4)-H(4) | 118.5 | C(13)-C(15)-C(24) | 114.94(16) |
| C(3)-C(4)-H(4) | 118.5 | C(3)-C(15)-C(24) | 113.72(18) |
| C(4)-C(5)-C(6) | 121.6(2) | C(17)-C(16)-C(15) | 175.6(2) |
| C(4)-C(5)-H(5) | 119.2 | C(16)-C(17)-C(18) | 178.7(2) |
| C(6)-C(5)-H(5) | 119.2 | C(23)-C(18)-C(19) | 119.1(2) |
| C(7)-C(6)-C(5) | 121.3(2) | C(23)-C(18)-C(17) | 120.8(2) |
| C(7)-C(6)-C(24) | 118.86(18) | C(19)-C(18)-C(17) | 120.1(2) |
| C(5)-C(6)-C(24) | 119.78(19) | C(20)-C(19)-C(18) | 120.1(2) |
| C(6)-C(7)-C(8) | 123.0(2) | C(20)-C(19)-H(19) | 119.9 |
| C(6)-C(7)-H(7) | 118.5 | C(18)-C(19)-H(19) | 119.9 |
| C(8)-C(7)-H(7) | 118.5 | C(19)-C(20)-C(21) | 120.2(2) |
| C(9)-C(8)-C(7) | 117.64(19) | C(19)-C(20)-H(20) | 119.9 |
| C(9)-C(8)-C(26) | 122.21(18) | C(21)-C(20)-H(20) | 119.9 |
| C(7)-C(8)-C(26) | 119.66(19) | C(22)-C(21)-C(20) | 120.1(2) |
| C(8)-C(9)-C(10) | 123.49(19) | C(22)-C(21)-H(21) | 119.9 |
| C(8)-C(9)-H(9) | 118.3 | C(20)-C(21)-H(21) | 119.9 |
| C(10)-C(9)-H(9) | 118.3 | C(21)-C(22)-C(23) | 120.0(2) |
| C(11)-C(10)-C(9) | 120.95(19) | C(21)-C(22)-H(22) | 120.0 |
| C(11)-C(10)-C(24) | 120.99(19) | C(23)-C(22)-H(22) | 120.0 |
| C(9)-C(10)-C(24) | 118.02(19) | C(22)-C(23)-C(18) | 120.4(2) |
| C(10)-C(11)-C(12) | 122.30(19) | C(22)-C(23)-H(23) | 119.8 |
| C(10)-C(11)-H(11) | 118.9 | C(18)-C(23)-H(23) | 119.8 |
| C(12)-C(11)-H(11) | 118.9 | C(10)-C(24)-C(6) | 110.56(17) |
| C(13)-C(12)-C(11) | 122.0(2) | C(10)-C(24)-C(25) | 104.13(16) |
| C(13)-C(12)-H(12) | 119.0 | C(6)-C(24)-C(25) | 103.61(17) |
| C(11)-C(12)-H(12) | 119.0 | C(10)-C(24)-C(15) | 113.25(17) |
| C(12)-C(13)-C(14) | 121.9(2) | C(6)-C(24)-C(15) | 114.69(16) |
| C(12)-C(13)-C(15) | 119.47(19) | C(25)-C(24)-C(15) | 109.61(16) |
| C(14)-C(13)-C(15) | 118.62(19) | C(24)-C(25)-H(25A) | 109.5 |
| C(1)-C(14)-C(13) | 121.7(2) | C(24)-C(25)-H(25B) | 109.5 |
| C(1)-C(14)-H(14) | 119.2 | H(25A)-C(25)-H(25B) | 109.5 |
| C(13)-C(14)-H(14) | 119.2 | C(24)-C(25)-H(25C) | 109.5 |

| | |
|---|---|
| H(25A)-C(25)-H(25C) | 109.5 |
| H(25B)-C(25)-H(25C) | 109.5 |
| C(8)-C(26)-C(28) | 112.13(18) |
| C(8)-C(26)-C(29) | 108.89(17) |
| C(28)-C(26)-C(29) | 108.89(18) |
| C(8)-C(26)-C(27) | 109.88(17) |
| C(28)-C(26)-C(27) | 107.21(19) |
| C(29)-C(26)-C(27) | 109.82(19) |
| C(26)-C(27)-H(27A) | 109.5 |
| C(26)-C(27)-H(27B) | 109.5 |
| H(27A)-C(27)-H(27B) | 109.5 |
| C(26)-C(27)-H(27C) | 109.5 |
| H(27A)-C(27)-H(27C) | 109.5 |
| H(27B)-C(27)-H(27C) | 109.5 |
| C(26)-C(28)-H(28A) | 109.5 |
| C(26)-C(28)-H(28B) | 109.5 |
| H(28A)-C(28)-H(28B) | 109.5 |
| C(26)-C(28)-H(28C) | 109.5 |
| H(28A)-C(28)-H(28C) | 109.5 |
| H(28B)-C(28)-H(28C) | 109.5 |
| C(26)-C(29)-H(29A) | 109.5 |
| C(26)-C(29)-H(29B) | 109.5 |
| H(29A)-C(29)-H(29B) | 109.5 |
| C(26)-C(29)-H(29C) | 109.5 |
| H(29A)-C(29)-H(29C) | 109.5 |
| H(29B)-C(29)-H(29C) | 109.5 |

**Table A. 60 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 148 (bt 956).**

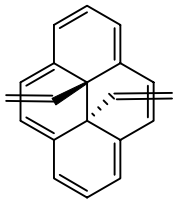
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 28(1) | 35(1) | 20(1) | -1(1) | 4(1) | 11(1) |
| C(2) | 34(1) | 23(1) | 14(1) | -1(1) | 1(1) | 8(1) |
| C(3) | 29(1) | 18(1) | 12(1) | 0(1) | -2(1) | 3(1) |
| C(4) | 31(1) | 14(1) | 18(1) | -2(1) | -6(1) | 1(1) |
| C(5) | 21(1) | 18(1) | 23(1) | 1(1) | -3(1) | -3(1) |
| C(6) | 17(1) | 19(1) | 18(1) | 1(1) | -4(1) | 2(1) |
| C(7) | 16(1) | 21(1) | 22(1) | 2(1) | -1(1) | -3(1) |
| C(8) | 20(1) | 18(1) | 16(1) | 1(1) | -3(1) | 4(1) |
| C(9) | 21(1) | 16(1) | 15(1) | -1(1) | -3(1) | 2(1) |
| C(10) | 21(1) | 12(1) | 18(1) | 1(1) | -3(1) | 3(1) |
| C(11) | 21(1) | 17(1) | 17(1) | -2(1) | -4(1) | -1(1) |
| C(12) | 17(1) | 27(1) | 19(1) | 2(1) | -2(1) | -3(1) |
| C(13) | 18(1) | 25(1) | 17(1) | 5(1) | 1(1) | -2(1) |
| C(14) | 22(1) | 35(1) | 18(1) | 2(1) | 1(1) | 3(1) |
| C(15) | 18(1) | 18(1) | 16(1) | 1(1) | -1(1) | 1(1) |
| C(16) | 20(1) | 19(1) | 19(1) | -3(1) | 0(1) | -1(1) |
| C(17) | 21(1) | 19(1) | 20(1) | -2(1) | 0(1) | -1(1) |
| C(18) | 22(1) | 20(1) | 17(1) | 0(1) | -2(1) | -5(1) |
| C(19) | 26(1) | 22(1) | 21(1) | -1(1) | -1(1) | 2(1) |
| C(20) | 31(1) | 30(1) | 18(1) | -3(1) | 7(1) | -2(1) |
| C(21) | 35(1) | 32(1) | 20(1) | 7(1) | -2(1) | -2(1) |
| C(22) | 36(1) | 31(1) | 33(1) | 9(1) | 0(1) | 10(1) |
| C(23) | 31(1) | 29(1) | 25(1) | 2(1) | 5(1) | 7(1) |
| C(24) | 17(1) | 17(1) | 16(1) | 0(1) | -1(1) | 1(1) |
| C(25) | 20(1) | 20(1) | 19(1) | -1(1) | -4(1) | 4(1) |
| C(26) | 19(1) | 24(1) | 15(1) | 0(1) | 2(1) | 1(1) |
| C(27) | 23(1) | 34(1) | 22(1) | -1(1) | 3(1) | 2(1) |
| C(28) | 28(1) | 31(1) | 18(1) | -3(1) | 4(1) | 1(1) |
| C(29) | 31(1) | 31(1) | 23(1) | 7(1) | 2(1) | 2(1) |

**Table A. 61 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for 148 (bt 956).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | -258 | 11428 | 3563 | 33 |
| H(2) | 2376 | 12079 | 3575 | 28 |
| H(4) | 5344 | 11957 | 3280 | 25 |
| H(5) | 7267 | 11389 | 2473 | 25 |
| H(7) | 7809 | 10427 | 1387 | 24 |
| H(9) | 4677 | 8330 | 774 | 20 |
| H(11) | 2161 | 8037 | 1454 | 22 |
| H(12) | 183 | 8620 | 2241 | 25 |
| H(14) | -800 | 9996 | 2968 | 30 |
| H(19) | 1783 | 9506 | 5409 | 28 |
| H(20) | 1952 | 8872 | 6580 | 32 |
| H(21) | 3854 | 7664 | 6842 | 35 |
| H(22) | 5566 | 7067 | 5930 | 40 |
| H(23) | 5402 | 7691 | 4755 | 34 |
| H(25A) | 5123 | 8200 | 2952 | 29 |
| H(25B) | 6384 | 9028 | 3185 | 29 |
| H(25C) | 6644 | 8466 | 2435 | 29 |
| H(27A) | 9495 | 8518 | 780 | 39 |
| H(27B) | 9654 | 9664 | 762 | 39 |
| H(27C) | 9955 | 9052 | 38 | 39 |
| H(28A) | 7167 | 7702 | 197 | 38 |
| H(28B) | 7670 | 8207 | -553 | 38 |
| H(28C) | 5824 | 8297 | -254 | 38 |
| H(29A) | 7829 | 9976 | -641 | 42 |
| H(29B) | 7522 | 10635 | 59 | 42 |
| H(29C) | 6007 | 10093 | -319 | 42 |

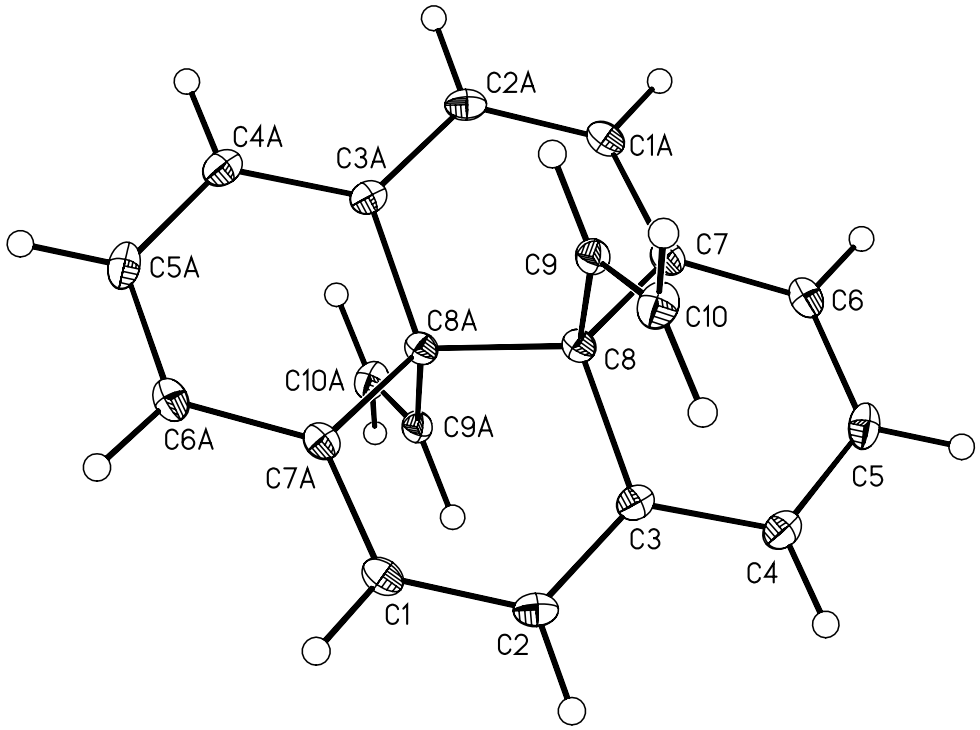
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for divinyl DHP 167**



**167**

Brendan Twamley




Project name : Bt1160

8-9-07

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans 0.3 ° per frame for 10 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[52] software and refined using SAINTPlus[53] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[54] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[55] The structure was solved in the space group Pbca (# 61) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[52] SMART: v. 5.632, Bruker AXS, Madison, WI, **2005**.
[53] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[54] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[55] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Table A. 62 Crystal data and structure refinement for Divinyl-DHP 167.**

| | | |
|---|---|---|
| Identification code | bt1160 | |
| Empirical formula | C20 H16 | |
| Formula weight | 256.33 | |
| Temperature | 90(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pbca | |
| Unit cell dimensions | a = 12.1187(7) Å | α = 90°. |
| | b = 7.1498(4) Å | β = 90°. |
| | c = 15.2530(9) Å | γ = 90°. |
| Volume | 1321.62(13) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.288 $Mg/m^3$ | |
| Absorption coefficient | 0.073 $mm^{-1}$ | |
| F(000) | 544 | |
| Crystal size | 0.34 x 0.26 x 0.06 $mm^3$ | |
| Crystal color and habit | colorless plate | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 2.67 to 25.25°. | |
| Index ranges | -14<=h<=14, -8<=k<=8, -18<=l<=18 | |
| Reflections collected | 19365 | |
| Independent reflections | 1203 [R(int) = 0.0425] | |
| Completeness to theta = 25.25° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.991 and 0.971 | |
| Solution method | XS, SHELXTL v. 6.14 (Bruker, 2003) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1203 / 0 / 91 | |
| Goodness-of-fit on $F^2$ | 1.097 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0496, wR2 = 0.1302 | |
| R indices (all data) | R1 = 0.0537, wR2 = 0.1343 | |
| Largest diff. peak and hole | 0.395 and -0.207 $e.Å^{-3}$ | |

**Table A. 63 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 167 (bt 1160).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 5552(1) | 13128(2) | 682(1) | 20(1) |
| C(2) | 4914(1) | 12227(2) | 1311(1) | 20(1) |
| C(3) | 4527(1) | 10401(2) | 1192(1) | 17(1) |
| C(4) | 3872(1) | 9444(2) | 1789(1) | 21(1) |
| C(5) | 3456(1) | 7671(2) | 1605(1) | 23(1) |
| C(6) | 3624(1) | 6802(2) | 796(1) | 21(1) |
| C(7) | 4275(1) | 7623(2) | 152(1) | 17(1) |
| C(8) | 4957(1) | 9342(2) | 398(1) | 16(1) |
| C(9) | 6103(1) | 8525(2) | 625(1) | 17(1) |
| C(10) | 6611(1) | 8599(2) | 1389(1) | 22(1) |

**Table A. 64 Bond lengths [Å] and angles [°] for 167 (bt 1160).**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.391(2) | C(5)-C(4)-H(4) | 119.3 |
| C(1)-C(7)#1 | 1.396(2) | C(4)-C(5)-C(6) | 122.08(14) |
| C(1)-H(1) | 0.9500 | C(4)-C(5)-H(5) | 119.0 |
| C(2)-C(3) | 1.399(2) | C(6)-C(5)-H(5) | 119.0 |
| C(2)-H(2) | 0.9500 | C(7)-C(6)-C(5) | 121.32(14) |
| C(3)-C(4) | 1.390(2) | C(7)-C(6)-H(6) | 119.3 |
| C(3)-C(8) | 1.5197(19) | C(5)-C(6)-H(6) | 119.3 |
| C(4)-C(5) | 1.393(2) | C(6)-C(7)-C(1)#1 | 124.55(14) |
| C(4)-H(4) | 0.9500 | C(6)-C(7)-C(8) | 118.17(13) |
| C(5)-C(6) | 1.395(2) | C(1)#1-C(7)-C(8) | 116.90(13) |
| C(5)-H(5) | 0.9500 | C(3)-C(8)-C(7) | 114.31(11) |
| C(6)-C(7) | 1.391(2) | C(3)-C(8)-C(8)#1 | 110.29(14) |
| C(6)-H(6) | 0.9500 | C(7)-C(8)-C(8)#1 | 109.55(14) |
| C(7)-C(1)#1 | 1.396(2) | C(3)-C(8)-C(9) | 108.51(11) |
| C(7)-C(8) | 1.5280(19) | C(7)-C(8)-C(9) | 103.71(11) |
| C(8)-C(8)#1 | 1.540(3) | C(8)#1-C(8)-C(9) | 110.26(14) |
| C(8)-C(9) | 1.5467(19) | C(10)-C(9)-C(8) | 127.01(13) |
| C(9)-C(10) | 1.319(2) | C(10)-C(9)-H(9) | 116.5 |
| C(9)-H(9) | 0.9500 | C(8)-C(9)-H(9) | 116.5 |
| C(10)-H(10A) | 0.9500 | C(9)-C(10)-H(10A) | 120.0 |
| C(10)-H(10B) | 0.9500 | C(9)-C(10)-H(10B) | 120.0 |
| | | H(10A)-C(10)-H(10B) | 120.0 |
| C(2)-C(1)-C(7)#1 | 122.25(14) | | |
| C(2)-C(1)-H(1) | 118.9 | | |
| C(7)#1-C(1)-H(1) | 118.9 | | |
| C(1)-C(2)-C(3) | 121.90(13) | | |
| C(1)-C(2)-H(2) | 119.1 | | |
| C(3)-C(2)-H(2) | 119.1 | | |
| C(4)-C(3)-C(2) | 124.43(14) | | |
| C(4)-C(3)-C(8) | 118.22(13) | | |
| C(2)-C(3)-C(8) | 117.03(13) | | |
| C(3)-C(4)-C(5) | 121.49(14) | | |
| C(3)-C(4)-H(4) | 119.3 | | |

**Table A. 65 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for bt1160 (167).**

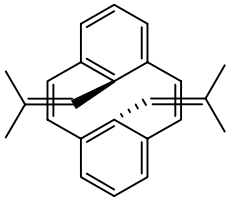
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 19(1) | 16(1) | 24(1) | -1(1) | -5(1) | 0(1) |
| C(2) | 19(1) | 21(1) | 19(1) | -5(1) | -3(1) | 4(1) |
| C(3) | 15(1) | 22(1) | 14(1) | 0(1) | -2(1) | 4(1) |
| C(4) | 19(1) | 27(1) | 17(1) | 2(1) | 0(1) | 6(1) |
| C(5) | 17(1) | 29(1) | 22(1) | 10(1) | 2(1) | 0(1) |
| C(6) | 17(1) | 18(1) | 27(1) | 4(1) | -3(1) | -1(1) |
| C(7) | 15(1) | 16(1) | 21(1) | 2(1) | -3(1) | 2(1) |
| C(8) | 15(1) | 15(1) | 18(1) | 0(1) | -1(1) | 0(1) |
| C(9) | 16(1) | 16(1) | 20(1) | 1(1) | 3(1) | 0(1) |
| C(10) | 17(1) | 28(1) | 21(1) | 4(1) | 0(1) | 2(1) |

**Table A. 66 Hydrogen coordinates ( $x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for 167 (bt1160).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 5882 | 14294 | 825 | 23 |
| H(2) | 4735 | 12870 | 1837 | 24 |
| H(4) | 3704 | 10011 | 2337 | 25 |
| H(5) | 3045 | 7034 | 2042 | 27 |
| H(6) | 3286 | 5627 | 684 | 25 |
| H(9) | 6483 | 7902 | 165 | 21 |
| H(10A) | 6269 | 9205 | 1872 | 26 |
| H(10B) | 7319 | 8047 | 1456 | 26 |

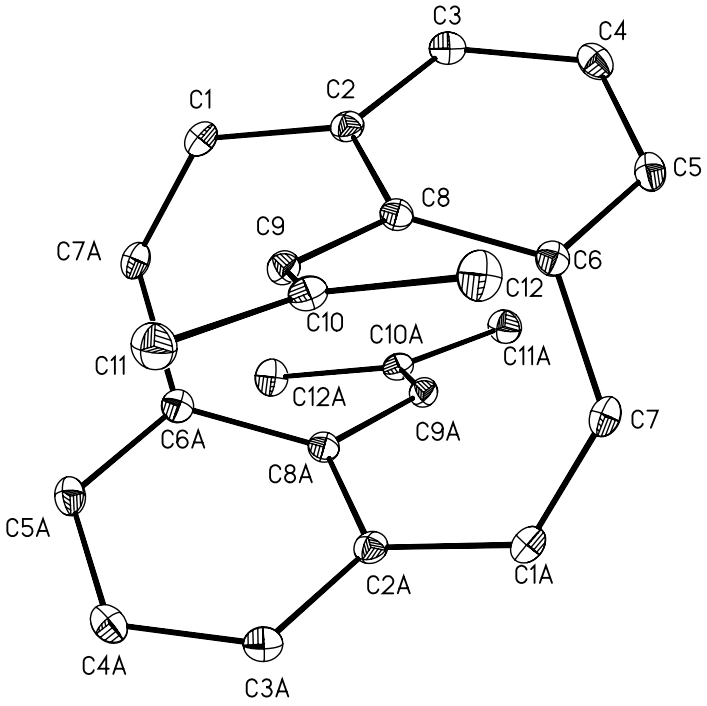
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for diisobutenyl CPD 178**



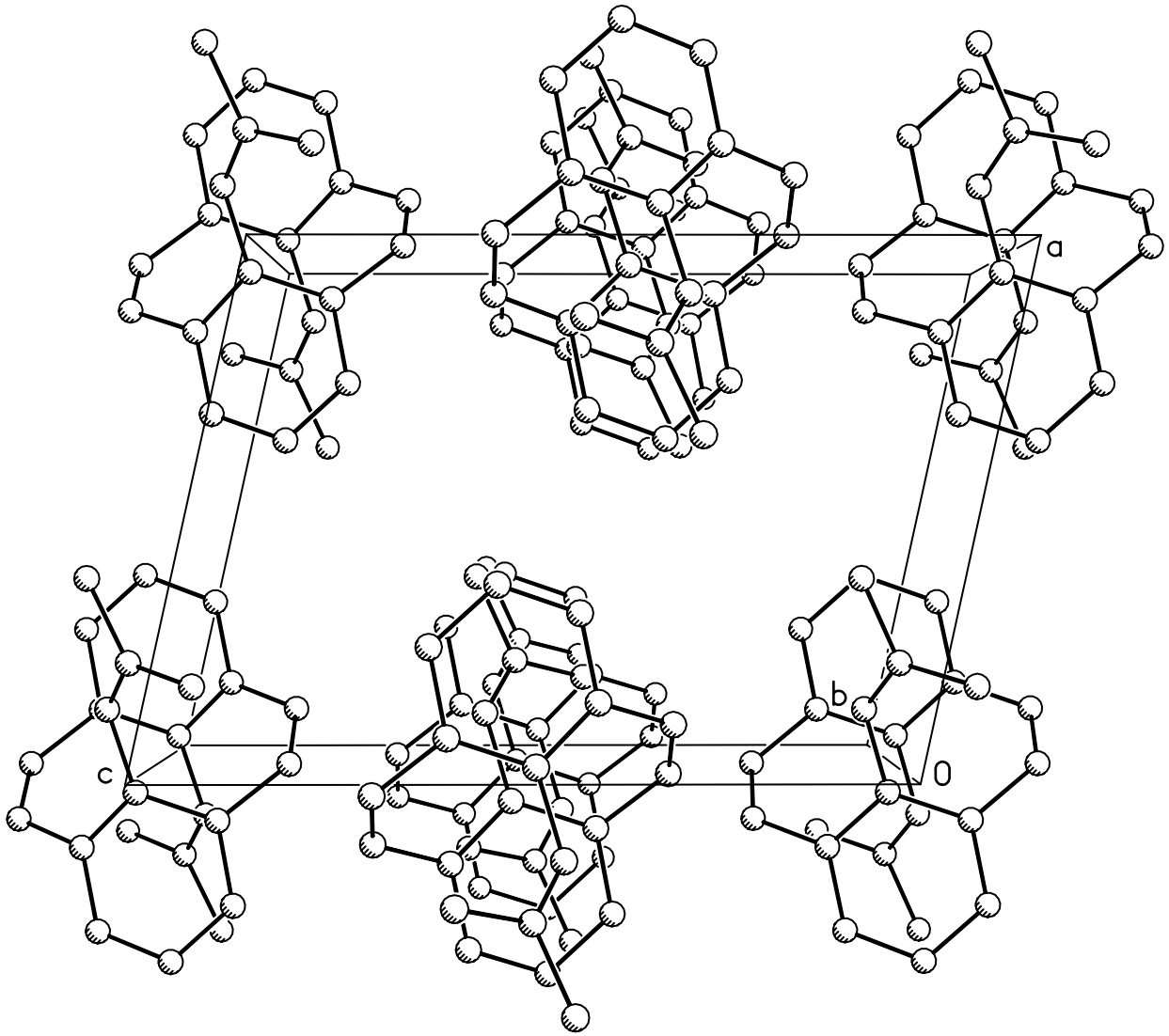
**178**

Brendan Twamley




Project name : Bt1173

8-29-07


a
b
c
0

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans 0.3 ° per frame for 5 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.77 Å. Cell parameters were retrieved using SMART[56] software and refined using SAINTPlus[57] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[58] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[59] The structure was solved in the space group P2(1)/c (# 14) by analysis of systematic absences. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[56] SMART: v. 5.632, Bruker AXS, Madison, WI, **2005**.
[57] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[58] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[59] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Table A. 67 Crystal data and structure refinement for 178 (C24 H24)**

| | |
|---|---|
| Identification code | bt1173 |
| Empirical formula | C24 H24 |
| Formula weight | 312.43 |
| Temperature | 90(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | a = 8.6932(3) Å α = 90°. |
| | b = 8.2751(3) Å β = 102.388(1)°. |
| | c = 12.2713(4) Å γ = 90°. |
| Volume | 862.21(5) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.203 $Mg/m^3$ |
| Absorption coefficient | 0.067 $mm^{-1}$ |
| F(000) | 336 |
| Crystal size | 0.44 x 0.34 x 0.15 $mm^3$ |
| Crystal color and habit | orange block |
| Diffractometer | Bruker/Siemens SMART APEX |
| Theta range for data collection | 2.40 to 27.50°. |
| Index ranges | -11<=h<=11, -10<=k<=10, -15<=l<=15 |
| Reflections collected | 12814 |
| Independent reflections | 1988 [R(int) = 0.0218] |
| Completeness to theta = 27.50° | 100.0% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.992 and 0.907 |
| Solution method | XS, SHELXTL v. 6.14 (Bruker, 2003) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1988 / 0 / 111 |
| Goodness-of-fit on $F^2$ | 1.074 |
| Final R indices [I>2sigma(I)] | R1 = 0.0438, wR2 = 0.1241 |
| R indices (all data) | R1 = 0.0468, wR2 = 0.1280 |
| Largest diff. peak and hole | 0.396 and -0.239 $e.Å^{-3}$ |

**Table A. 68 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 178 (bt 1173).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 8914(1) | -32(1) | 6724(1) | 16(1) |
| C(2) | 8454(1) | 979(1) | 5701(1) | 15(1) |
| C(3) | 6848(1) | 1122(1) | 5228(1) | 18(1) |
| C(4) | 6328(1) | 1659(1) | 4134(1) | 19(1) |
| C(5) | 7422(1) | 1831(1) | 3465(1) | 18(1) |
| C(6) | 9038(1) | 1694(1) | 3924(1) | 15(1) |
| C(7) | 10094(1) | 1298(1) | 3156(1) | 16(1) |
| C(8) | 9564(1) | 1569(1) | 5099(1) | 14(1) |
| C(9) | 11184(1) | 1941(1) | 5687(1) | 15(1) |
| C(10) | 12122(1) | 3123(1) | 5449(1) | 16(1) |
| C(11) | 13715(1) | 3387(1) | 6201(1) | 21(1) |
| C(12) | 11740(1) | 4276(1) | 4484(1) | 21(1) |

**Table A. 69 Bond lengths [Å] and angles [°] for 178 (bt 1173)**

| | | | |
|---|---|---|---|
| C(1)-C(7)#1 | 1.3452(16) | C(4)-C(3)-C(2) | 121.04(10) |
| C(1)-C(2) | 1.4905(15) | C(4)-C(3)-H(3) | 119.5 |
| C(1)-H(1) | 0.9500 | C(2)-C(3)-H(3) | 119.5 |
| C(2)-C(3) | 1.3974(15) | C(5)-C(4)-C(3) | 118.66(10) |
| C(2)-C(8) | 1.4220(15) | C(5)-C(4)-H(4) | 120.7 |
| C(3)-C(4) | 1.3936(16) | C(3)-C(4)-H(4) | 120.7 |
| C(3)-H(3) | 0.9500 | C(4)-C(5)-C(6) | 120.47(10) |
| C(4)-C(5) | 1.3915(16) | C(4)-C(5)-H(5) | 119.8 |
| C(4)-H(4) | 0.9500 | C(6)-C(5)-H(5) | 119.8 |
| C(5)-C(6) | 1.4019(15) | C(5)-C(6)-C(8) | 119.44(10) |
| C(5)-H(5) | 0.9500 | C(5)-C(6)-C(7) | 117.65(9) |
| C(6)-C(8) | 1.4188(15) | C(8)-C(6)-C(7) | 121.32(10) |
| C(6)-C(7) | 1.4862(15) | C(1)#1-C(7)-C(6) | 124.84(9) |
| C(7)-C(1)#1 | 1.3452(16) | C(1)#1-C(7)-H(7) | 117.6 |
| C(7)-H(7) | 0.9500 | C(6)-C(7)-H(7) | 117.6 |
| C(8)-C(9) | 1.4705(14) | C(6)-C(8)-C(2) | 116.49(10) |
| C(9)-C(10) | 1.3445(16) | C(6)-C(8)-C(9) | 123.29(10) |
| C(9)-H(9) | 0.9500 | C(2)-C(8)-C(9) | 120.15(9) |
| C(10)-C(12) | 1.5014(15) | C(10)-C(9)-C(8) | 127.41(10) |
| C(10)-C(11) | 1.5061(15) | C(10)-C(9)-H(9) | 116.3 |
| C(11)-H(11A) | 0.9800 | C(8)-C(9)-H(9) | 116.3 |
| C(11)-H(11B) | 0.9800 | C(9)-C(10)-C(12) | 126.26(10) |
| C(11)-H(11C) | 0.9800 | C(9)-C(10)-C(11) | 119.59(10) |
| C(12)-H(12A) | 0.9800 | C(12)-C(10)-C(11) | 114.15(10) |
| C(12)-H(12B) | 0.9800 | C(10)-C(11)-H(11A) | 109.5 |
| C(12)-H(12C) | 0.9800 | C(10)-C(11)-H(11B) | 109.5 |
| | | H(11A)-C(11)-H(11B) | 109.5 |
| C(7)#1-C(1)-C(2) | 125.37(9) | C(10)-C(11)-H(11C) | 109.5 |
| C(7)#1-C(1)-H(1) | 117.3 | H(11A)-C(11)-H(11C) | 109.5 |
| C(2)-C(1)-H(1) | 117.3 | H(11B)-C(11)-H(11C) | 109.5 |
| C(3)-C(2)-C(8) | 118.97(10) | C(10)-C(12)-H(12A) | 109.5 |
| C(3)-C(2)-C(1) | 117.46(9) | C(10)-C(12)-H(12B) | 109.5 |
| C(8)-C(2)-C(1) | 122.75(9) | H(12A)-C(12)-H(12B) | 109.5 |

| | | | |
|---|---|---|---|
| C(10)-C(12)-H(12C) | 109.5 | H(12B)-C(12)-H(12C) | 109.5 |
| H(12A)-C(12)-H(12C) | 109.5 | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1

**Table A. 70 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 178 (bt 1173)**

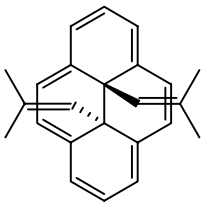
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 19(1) | 18(1) | 14(1) | -1(1) | 5(1) | -3(1) |
| C(2) | 18(1) | 13(1) | 15(1) | -2(1) | 4(1) | 0(1) |
| C(3) | 18(1) | 16(1) | 20(1) | -1(1) | 6(1) | -1(1) |
| C(4) | 16(1) | 18(1) | 23(1) | 0(1) | 1(1) | 1(1) |
| C(5) | 20(1) | 15(1) | 16(1) | 2(1) | 0(1) | 0(1) |
| C(6) | 18(1) | 12(1) | 16(1) | 1(1) | 3(1) | -1(1) |
| C(7) | 20(1) | 16(1) | 12(1) | 1(1) | 3(1) | -4(1) |
| C(8) | 17(1) | 11(1) | 15(1) | 0(1) | 3(1) | 1(1) |
| C(9) | 17(1) | 14(1) | 13(1) | -1(1) | 2(1) | 1(1) |
| C(10) | 18(1) | 16(1) | 15(1) | -3(1) | 4(1) | 1(1) |
| C(11) | 18(1) | 22(1) | 22(1) | -2(1) | 2(1) | -2(1) |
| C(12) | 23(1) | 18(1) | 21(1) | 2(1) | 4(1) | -4(1) |

**Table A. 71 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for 178 (bt 1173)**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 8470 | 241 | 7343 | 20 |
| H(3) | 6098 | 848 | 5658 | 21 |
| H(4) | 5248 | 1904 | 3852 | 23 |
| H(5) | 7072 | 2042 | 2690 | 21 |
| H(7) | 10066 | 1991 | 2535 | 20 |
| H(9) | 11617 | 1270 | 6305 | 18 |
| H(11A) | 13914 | 2543 | 6774 | 31 |
| H(11B) | 13740 | 4448 | 6559 | 31 |
| H(11C) | 14529 | 3342 | 5759 | 31 |
| H(12A) | 12276 | 3929 | 3898 | 31 |
| H(12B) | 12097 | 5364 | 4737 | 31 |
| H(12C) | 10600 | 4288 | 4189 | 31 |

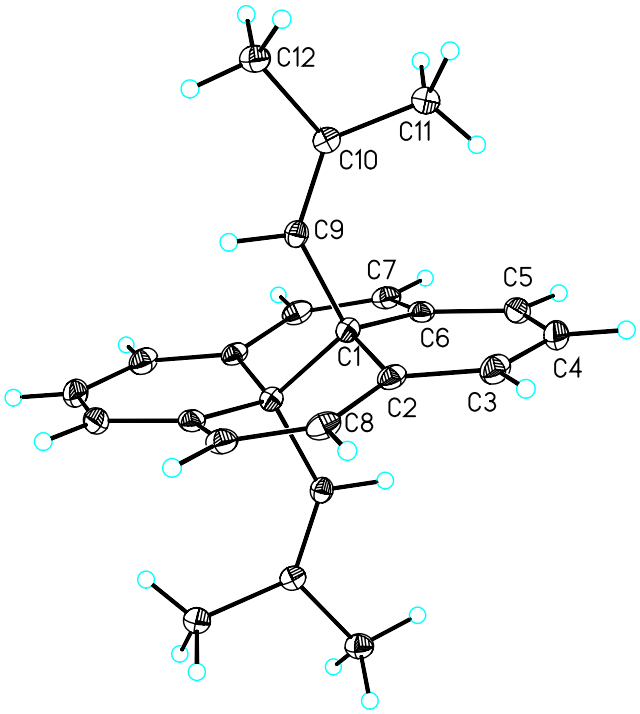
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for diisobutenyl DHP 179**



**179**

Brendan Twamley




Project name : Bt1265

3-31-0

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans 0.3 ° per frame for 30 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[60] software and refined using SAINTPlus[61] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[62] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[63] The structure was solved in the space group P2(1)/c (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms associated with C11 were refined with mild distance restraints. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[60] SMART: v. 5.632, Bruker AXS, Madison, WI, **2005**.
[61] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[62] SADABS: v.2007/4, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2007**.
[63] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Table A. 72 Crystal data and structure refinement for 179**.

| | | |
|---|---|---|
| Identification code | bt1265 | |
| Empirical formula | C24 H24 | |
| Formula weight | 312.43 | |
| Temperature | 90(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 8.9436(19) Å | α = 90°. |
| | b = 13.044(3) Å | β = 107.758(4)°. |
| | c = 7.5887(16) Å | γ = 90°. |
| Volume | 843.1(3) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.231 $Mg/m^3$ | |
| Absorption coefficient | 0.069 $mm^{-1}$ | |
| F(000) | 336 | |
| Crystal size | 0.28 x 0.13 x 0.04 $mm^3$ | |
| Crystal color and habit | orange plate | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 2.39 to 25.25°. | |
| Index ranges | -10<=h<=10, -15<=k<=15, -9<=l<=9 | |
| Reflections collected | 12281 | |
| Independent reflections | 1527 [R(int) = 0.0615] | |
| Completeness to theta = 25.25° | 100.0% | |
| Absorption correction | None | |
| Solution method | XS, SHELXTL v. 6.14 (Bruker, 2003) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1527 / 3 / 119 | |
| Goodness-of-fit on $F^2$ | 0.832 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0415, wR2 = 0.0939 | |
| R indices (all data) | R1 = 0.0659, wR2 = 0.1053 | |
| Largest diff. peak and hole | 0.274 and -0.254 $e.Å^{-3}$ | |

**Table A. 73 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 179 (bt 1265).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 4256(2) | 5213(1) | 9267(2) | 20(1) |
| C(2) | 4797(2) | 5896(1) | 7923(2) | 22(1) |
| C(3) | 3978(2) | 5864(2) | 6058(3) | 29(1) |
| C(4) | 2857(2) | 5109(2) | 5316(3) | 31(1) |
| C(5) | 2518(2) | 4343(2) | 6415(3) | 28(1) |
| C(6) | 3217(2) | 4316(1) | 8320(2) | 22(1) |
| C(7) | 3031(2) | 3523(1) | 9461(3) | 25(1) |
| C(8) | 6071(2) | 6540(1) | 8690(3) | 26(1) |
| C(9) | 3389(2) | 5923(1) | 10263(2) | 20(1) |
| C(10) | 1884(2) | 6192(1) | 9896(2) | 20(1) |
| C(11) | 497(2) | 5854(2) | 8320(3) | 27(1) |
| C(12) | 1442(2) | 6956(1) | 11144(3) | 27(1) |

**Table A. 74 Bond lengths [Å] and angles [°] for 179 (bt 1265)**

| | | | |
|---|---|---|---|
| C(1)-C(6) | 1.531(2) | C(9)-C(1)-C(1)#1 | 108.18(17) |
| C(1)-C(2) | 1.539(2) | C(3)-C(2)-C(8) | 123.87(17) |
| C(1)-C(9) | 1.545(2) | C(3)-C(2)-C(1) | 119.05(17) |
| C(1)-C(1)#1 | 1.554(3) | C(8)-C(2)-C(1) | 117.05(15) |
| C(2)-C(3) | 1.381(3) | C(2)-C(3)-C(4) | 121.79(18) |
| C(2)-C(8) | 1.393(3) | C(2)-C(3)-H(3) | 119.1 |
| C(3)-C(4) | 1.395(3) | C(4)-C(3)-H(3) | 119.1 |
| C(3)-H(3) | 0.9500 | C(5)-C(4)-C(3) | 121.66(17) |
| C(4)-C(5) | 1.393(3) | C(5)-C(4)-H(4) | 119.2 |
| C(4)-H(4) | 0.9500 | C(3)-C(4)-H(4) | 119.2 |
| C(5)-C(6) | 1.390(3) | C(6)-C(5)-C(4) | 122.04(18) |
| C(5)-H(5) | 0.9500 | C(6)-C(5)-H(5) | 119.0 |
| C(6)-C(7) | 1.391(3) | C(4)-C(5)-H(5) | 119.0 |
| C(7)-C(8)#1 | 1.390(3) | C(5)-C(6)-C(7) | 124.45(17) |
| C(7)-H(7) | 0.9500 | C(5)-C(6)-C(1) | 118.98(16) |
| C(8)-C(7)#1 | 1.390(3) | C(7)-C(6)-C(1) | 116.57(16) |
| C(8)-H(8) | 0.9500 | C(8)#1-C(7)-C(6) | 122.04(17) |
| C(9)-C(10) | 1.335(3) | C(8)#1-C(7)-H(7) | 119.0 |
| C(9)-H(9) | 0.9500 | C(6)-C(7)-H(7) | 119.0 |
| C(10)-C(11) | 1.503(3) | C(7)#1-C(8)-C(2) | 122.23(17) |
| C(10)-C(12) | 1.507(2) | C(7)#1-C(8)-H(8) | 118.9 |
| C(11)-H(11A) | 1.017(15) | C(2)-C(8)-H(8) | 118.9 |
| C(11)-H(11B) | 0.954(15) | C(10)-C(9)-C(1) | 132.87(16) |
| C(11)-H(11C) | 0.936(15) | C(10)-C(9)-H(9) | 113.6 |
| C(12)-H(12A) | 0.9800 | C(1)-C(9)-H(9) | 113.6 |
| C(12)-H(12B) | 0.9800 | C(9)-C(10)-C(11) | 128.52(17) |
| C(12)-H(12C) | 0.9800 | C(9)-C(10)-C(12) | 118.94(16) |
| | | C(11)-C(10)-C(12) | 112.52(15) |
| C(6)-C(1)-C(2) | 113.60(14) | C(10)-C(11)-H(11A) | 108.5(11) |
| C(6)-C(1)-C(9) | 111.34(14) | C(10)-C(11)-H(11B) | 111.5(11) |
| C(2)-C(1)-C(9) | 106.48(14) | H(11A)-C(11)-H(11B) | 102.6(13) |
| C(6)-C(1)-C(1)#1 | 109.06(17) | C(10)-C(11)-H(11C) | 118.3(12) |
| C(2)-C(1)-C(1)#1 | 107.99(17) | H(11A)-C(11)-H(11C) | 104.6(13) |

| | | | |
|---|---|---|---|
| H(11B)-C(11)-H(11C) | 109.9(14) | C(10)-C(12)-H(12C) | 109.5 |
| C(10)-C(12)-H(12A) | 109.5 | H(12A)-C(12)-H(12C) | 109.5 |
| C(10)-C(12)-H(12B) | 109.5 | H(12B)-C(12)-H(12C) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

**Table A. 75 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 179 (bt 1265).**

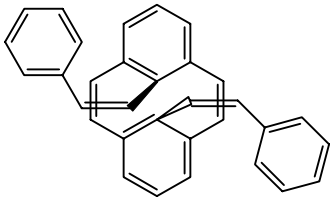
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 22(1) | 20(1) | 18(1) | 0(1) | 7(1) | 1(1) |
| C(2) | 26(1) | 20(1) | 23(1) | 1(1) | 11(1) | 7(1) |
| C(3) | 34(1) | 30(1) | 24(1) | 6(1) | 12(1) | 9(1) |
| C(4) | 30(1) | 41(1) | 20(1) | -2(1) | 3(1) | 10(1) |
| C(5) | 22(1) | 31(1) | 28(1) | -10(1) | 4(1) | 3(1) |
| C(6) | 17(1) | 22(1) | 28(1) | -6(1) | 7(1) | 2(1) |
| C(7) | 22(1) | 22(1) | 35(1) | -6(1) | 13(1) | -2(1) |
| C(8) | 32(1) | 20(1) | 32(1) | 2(1) | 19(1) | 1(1) |
| C(9) | 23(1) | 19(1) | 19(1) | -1(1) | 6(1) | -2(1) |
| C(10) | 23(1) | 17(1) | 23(1) | 1(1) | 9(1) | -1(1) |
| C(11) | 24(1) | 31(1) | 26(1) | -1(1) | 7(1) | 2(1) |
| C(12) | 25(1) | 26(1) | 30(1) | -1(1) | 10(1) | 2(1) |

**Table A. 76 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for 179 (bt 1265)**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 4183 | 6369 | 5260 | 34 |
| H(4) | 2312 | 5118 | 4028 | 37 |
| H(5) | 1787 | 3823 | 5844 | 34 |
| H(7) | 2266 | 3010 | 8962 | 30 |
| H(8) | 6337 | 7039 | 7924 | 31 |
| H(9) | 4060 | 6228 | 11355 | 24 |
| H(11A) | -130(20) | 6486(11) | 7740(30) | 32 |
| H(11B) | -240(20) | 5480(12) | 8750(20) | 32 |
| H(11C) | 690(20) | 5507(13) | 7330(30) | 32 |
| H(12A) | 704 | 6637 | 11705 | 32 |
| H(12B) | 947 | 7554 | 10418 | 32 |
| H(12C) | 2387 | 7171 | 12120 | 32 |

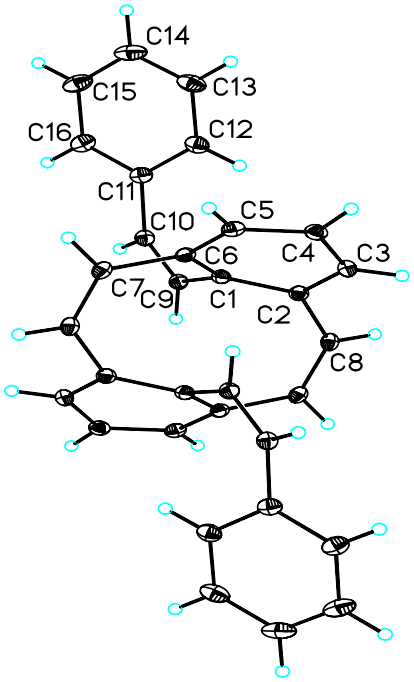
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for *cis*-styryl CPD 202**



**202**

Brendan Twamley




Project name : Bt1263

3-23-08

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans 0.3 ° per frame for 5 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.77 Å. Cell parameters were retrieved using SMART[64] software and refined using SAINTPlus[65] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[66] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[67] The structure was solved in the space group P2(1)/n (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[64] SMART: v. 5.632, Bruker AXS, Madison, WI, **2005**.
[65] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[66] SADABS: v.2007/4, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2007**.
[67] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

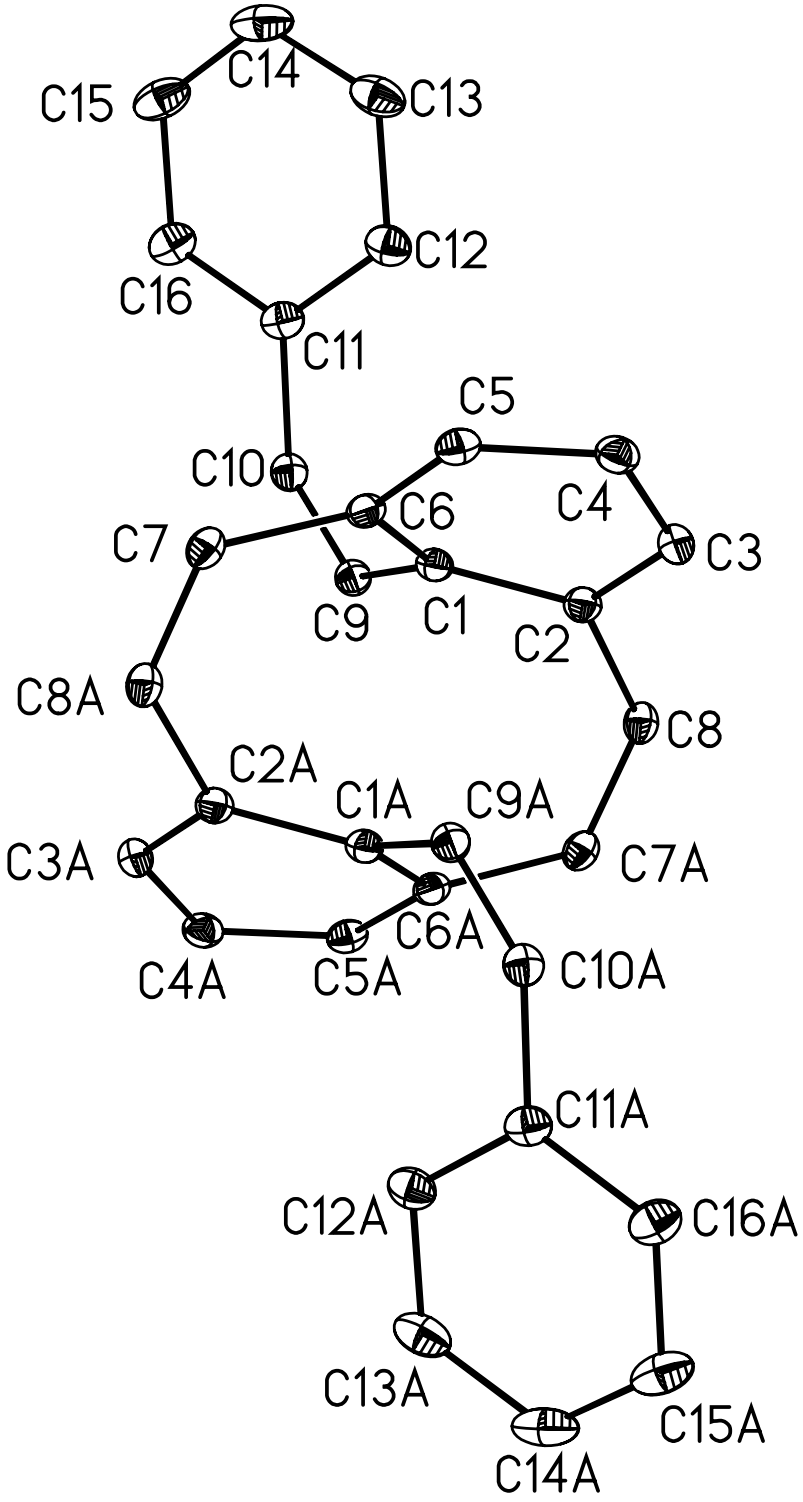

C14
C15
C13
C12
C16
C11
C5
C10
C6
C4
C7
C3
C9
C1
C2
C8A
C8
C2A
C1A
C9A
C3A
C7A
C6A
C4A
C5A
C10A
C11A
C12A
C16A
C13A
C15A
C14A

**Table A. 77 Crystal data and structure refinement for *cis*-distyryl CPD 202**

| | | |
|---|---|---|
| Identification code | bt1263 | |
| Empirical formula | C32 H24 | |
| Formula weight | 408.51 | |
| Temperature | 90(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 9.6423(3) Å | α = 90°. |
| | b = 7.3261(2) Å | β = 100.983(1)°. |
| | c = 15.3388(5) Å | γ = 90°. |
| Volume | 1063.69(6) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.275 $Mg/m^3$ | |
| Absorption coefficient | 0.072 $mm^{-1}$ | |
| F(000) | 432 | |
| Crystal size | 0.34 x 0.23 x 0.17 $mm^3$ | |
| Crystal color and habit | yellow needle | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 2.31 to 27.49°. | |
| Index ranges | -12<=h<=12, -9<=k<=9, -19<=l<=19 | |
| Reflections collected | 15817 | |
| Independent reflections | 2447 [R(int) = 0.0303] | |
| Completeness to theta = 27.49° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.984 and 0.902 | |
| Solution method | XS, SHELXTL v. 6.14 (Bruker, 2003) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2447 / 0 / 145 | |
| Goodness-of-fit on $F^2$ | 1.842 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0442, wR2 = 0.1139 | |
| R indices (all data) | R1 = 0.0525, wR2 = 0.1183 | |
| Largest diff. peak and hole | 0.302 and -0.202 $e.Å^{-3}$ | |

**Table A. 78 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 202 (bt 1263).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 9749(1) | 5278(2) | 824(1) | 19(1) |
| C(2) | 9339(1) | 7078(2) | 569(1) | 20(1) |
| C(3) | 10175(1) | 8526(2) | 970(1) | 23(1) |
| C(4) | 11459(1) | 8193(2) | 1533(1) | 23(1) |
| C(5) | 12003(1) | 6436(2) | 1598(1) | 21(1) |
| C(6) | 11189(1) | 4971(2) | 1205(1) | 19(1) |
| C(7) | 11926(1) | 3277(2) | 1017(1) | 21(1) |
| C(8) | 8215(1) | 7507(2) | -214(1) | 21(1) |
| C(9) | 8722(1) | 3756(2) | 694(1) | 20(1) |
| C(10) | 8437(1) | 2684(2) | 1344(1) | 21(1) |
| C(11) | 8984(1) | 2755(2) | 2312(1) | 23(1) |
| C(12) | 9455(1) | 4367(2) | 2768(1) | 26(1) |
| C(13) | 9921(1) | 4347(2) | 3680(1) | 33(1) |
| C(14) | 9919(2) | 2741(2) | 4159(1) | 37(1) |
| C(15) | 9426(1) | 1156(2) | 3723(1) | 35(1) |
| C(16) | 8965(1) | 1157(2) | 2810(1) | 28(1) |

**Table A. 79 Bond lengths [Å] and angles [°] for 202 (bt 1263)**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.4110(16) | C(2)-C(1)-C(6) | 117.61(11) |
| C(1)-C(6) | 1.4171(16) | C(2)-C(1)-C(9) | 121.43(10) |
| C(1)-C(9) | 1.4798(16) | C(6)-C(1)-C(9) | 120.95(10) |
| C(2)-C(3) | 1.4018(17) | C(3)-C(2)-C(1) | 118.57(11) |
| C(2)-C(8) | 1.4897(16) | C(3)-C(2)-C(8) | 117.61(11) |
| C(3)-C(4) | 1.3900(17) | C(1)-C(2)-C(8) | 122.92(11) |
| C(3)-H(3) | 0.9500 | C(4)-C(3)-C(2) | 120.65(11) |
| C(4)-C(5) | 1.3864(17) | C(4)-C(3)-H(3) | 119.7 |
| C(4)-H(4) | 0.9500 | C(2)-C(3)-H(3) | 119.7 |
| C(5)-C(6) | 1.3971(16) | C(5)-C(4)-C(3) | 119.17(11) |
| C(5)-H(5) | 0.9500 | C(5)-C(4)-H(4) | 120.4 |
| C(6)-C(7) | 1.4851(16) | C(3)-C(4)-H(4) | 120.4 |
| C(7)-C(8)#1 | 1.3422(17) | C(4)-C(5)-C(6) | 120.58(11) |
| C(7)-H(7) | 0.9500 | C(4)-C(5)-H(5) | 119.7 |
| C(8)-C(7)#1 | 1.3422(17) | C(6)-C(5)-H(5) | 119.7 |
| C(8)-H(8) | 0.9500 | C(5)-C(6)-C(1) | 118.79(11) |
| C(9)-C(10) | 1.3378(16) | C(5)-C(6)-C(7) | 118.38(11) |
| C(9)-H(9) | 0.9500 | C(1)-C(6)-C(7) | 121.32(10) |
| C(10)-C(11) | 1.4795(17) | C(8)#1-C(7)-C(6) | 124.57(11) |
| C(10)-H(10) | 0.9500 | C(8)#1-C(7)-H(7) | 117.7 |
| C(11)-C(16) | 1.3998(18) | C(6)-C(7)-H(7) | 117.7 |
| C(11)-C(12) | 1.4028(18) | C(7)#1-C(8)-C(2) | 125.43(11) |
| C(12)-C(13) | 1.3865(18) | C(7)#1-C(8)-H(8) | 117.3 |
| C(12)-H(12) | 0.9500 | C(2)-C(8)-H(8) | 117.3 |
| C(13)-C(14) | 1.387(2) | C(10)-C(9)-C(1) | 124.69(11) |
| C(13)-H(13) | 0.9500 | C(10)-C(9)-H(9) | 117.7 |
| C(14)-C(15) | 1.379(2) | C(1)-C(9)-H(9) | 117.7 |
| C(14)-H(14) | 0.9500 | C(9)-C(10)-C(11) | 130.00(11) |
| C(15)-C(16) | 1.3866(18) | C(9)-C(10)-H(10) | 115.0 |
| C(15)-H(15) | 0.9500 | C(11)-C(10)-H(10) | 115.0 |
| C(16)-H(16) | 0.9500 | C(16)-C(11)-C(12) | 117.97(12) |

| | | | |
|---|---|---|---|
| C(16)-C(11)-C(10) | 118.62(11) | C(15)-C(14)-C(13) | 119.50(13) |
| C(12)-C(11)-C(10) | 123.32(11) | C(15)-C(14)-H(14) | 120.3 |
| C(13)-C(12)-C(11) | 120.38(13) | C(13)-C(14)-H(14) | 120.3 |
| C(13)-C(12)-H(12) | 119.8 | C(14)-C(15)-C(16) | 120.27(14) |
| C(11)-C(12)-H(12) | 119.8 | C(14)-C(15)-H(15) | 119.9 |
| C(14)-C(13)-C(12) | 120.74(13) | C(16)-C(15)-H(15) | 119.9 |
| C(14)-C(13)-H(13) | 119.6 | C(15)-C(16)-C(11) | 121.11(13) |
| C(12)-C(13)-H(13) | 119.6 | C(15)-C(16)-H(16) | 119.4 |
| | | C(11)-C(16)-H(16) | 119.4 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z

**Table A. 80 Anisotropic displacement parameters ($Å^2$x $10^3$) for 202 (bt 1263).**

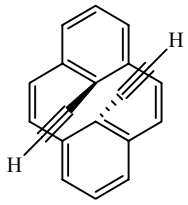
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 21(1) | 20(1) | 15(1) | -1(1) | 3(1) | -1(1) |
| C(2) | 20(1) | 22(1) | 18(1) | 0(1) | 4(1) | 1(1) |
| C(3) | 28(1) | 18(1) | 22(1) | -1(1) | 6(1) | 2(1) |
| C(4) | 28(1) | 23(1) | 18(1) | -3(1) | 3(1) | -4(1) |
| C(5) | 21(1) | 25(1) | 17(1) | 2(1) | 1(1) | -2(1) |
| C(6) | 21(1) | 20(1) | 15(1) | 2(1) | 3(1) | 0(1) |
| C(7) | 19(1) | 21(1) | 22(1) | 4(1) | 0(1) | 1(1) |
| C(8) | 19(1) | 19(1) | 25(1) | 1(1) | 2(1) | 2(1) |
| C(9) | 18(1) | 20(1) | 19(1) | -1(1) | 1(1) | 1(1) |
| C(10) | 19(1) | 21(1) | 22(1) | -1(1) | 2(1) | -1(1) |
| C(11) | 16(1) | 31(1) | 21(1) | 2(1) | 5(1) | 0(1) |
| C(12) | 21(1) | 33(1) | 25(1) | -3(1) | 7(1) | 0(1) |
| C(13) | 23(1) | 49(1) | 26(1) | -10(1) | 6(1) | 1(1) |
| C(14) | 26(1) | 66(1) | 19(1) | 2(1) | 5(1) | 3(1) |
| C(15) | 27(1) | 52(1) | 27(1) | 13(1) | 7(1) | 0(1) |
| C(16) | 22(1) | 34(1) | 27(1) | 5(1) | 6(1) | -3(1) |

**Table A. 81 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for 202 (bt 1263)**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 9860 | 9747 | 856 | 27 |
| H(4) | 11959 | 9158 | 1869 | 27 |
| H(5) | 12937 | 6226 | 1913 | 26 |
| H(7) | 12539 | 2710 | 1498 | 25 |
| H(8) | 7541 | 8411 | -138 | 26 |
| H(9) | 8228 | 3524 | 107 | 24 |
| H(10) | 7782 | 1729 | 1154 | 25 |
| H(12) | 9455 | 5478 | 2449 | 31 |
| H(13) | 10245 | 5445 | 3981 | 39 |
| H(14) | 10255 | 2734 | 4783 | 45 |
| H(15) | 9402 | 58 | 4050 | 42 |
| H(16) | 8630 | 55 | 2517 | 33 |

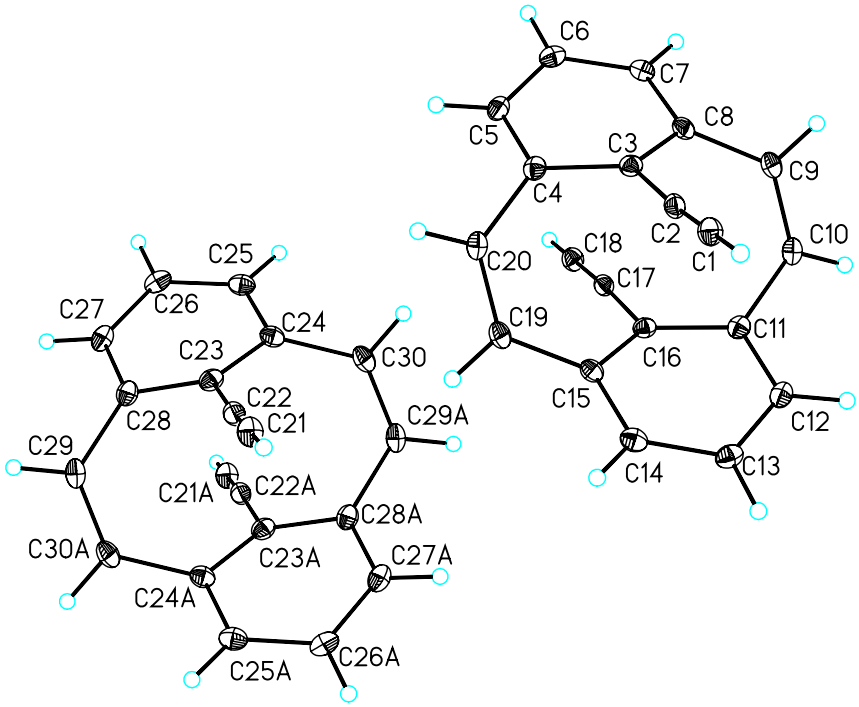
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for diethynyl CPD 235**




**235**

Brendan Twamley




Project name : Bt1220

1-17-08

**Experimental:**

Crystals of compound **1** were removed from the flask, cooled with dry ice, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans 0.3 ° per frame for 10 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[68] software and refined using SAINTPlus[69] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[70] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[71] The structure was solved in the space group P2(1)/n (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[68] SMART: v. 5.632, Bruker AXS, Madison, WI, **2005**.
[69] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[70] SADABS: v.2007/4, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2007**.
[71] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

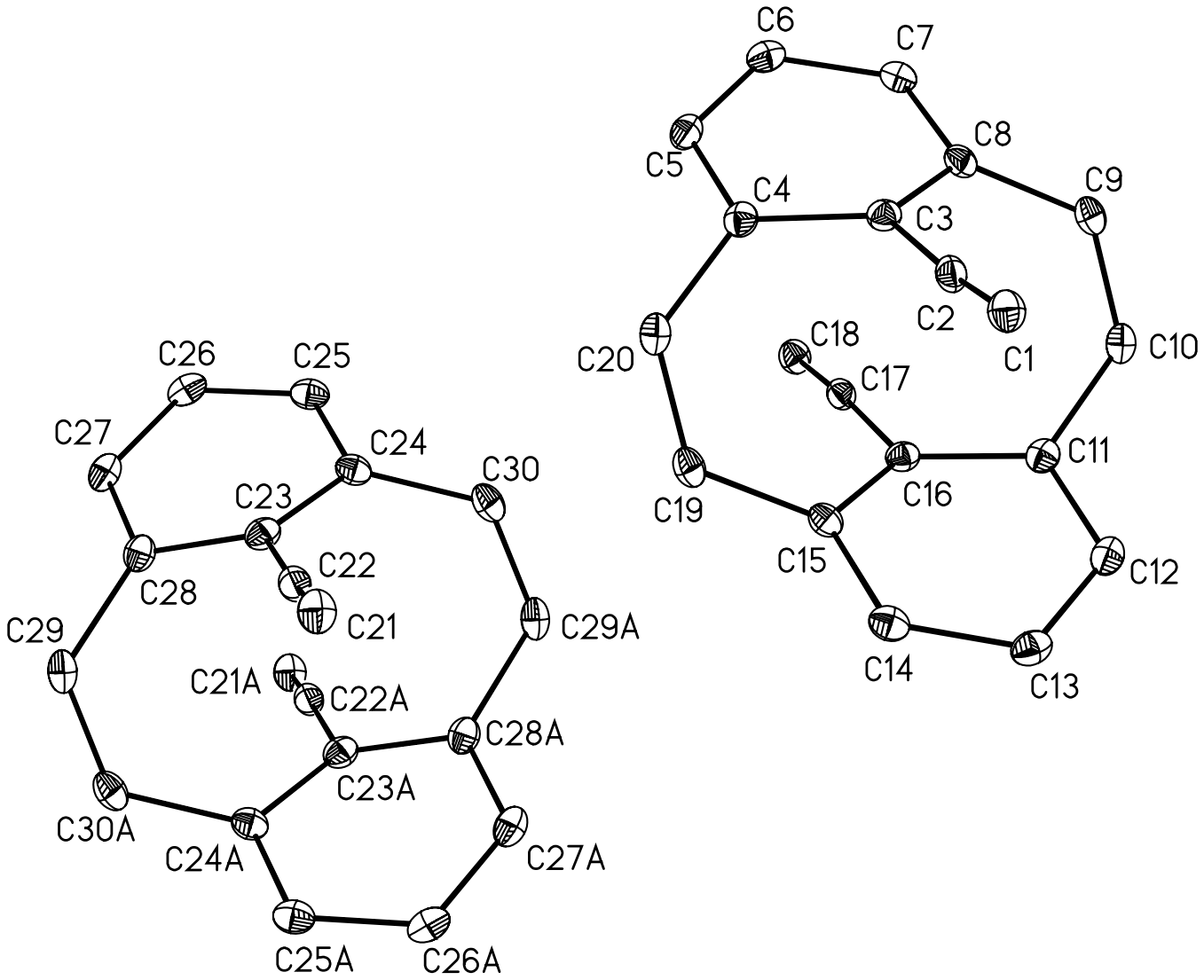

C6
C7
C8
C5
C9
C4
C3
C2
C1
C10
C20
C18
C17
C11
C19
C16
C15
C12
C14
C13
C26
C25
C27
C24
C30
C23
C22
C28
C21
C29
C29A
C21A
C22A
C28A
C23A
C30A
C24A
C27A
C25A
C26A

**Table A. 82 Crystal data and structure refinement for diethynyl CPD 235**

| | | |
|---|---|---|
| Identification code | bt1220 | |
| Empirical formula | C20 H12 | |
| Formula weight | 252.30 | |
| Temperature | 90(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 7.4416(3) Å | α = 90°. |
| | b = 19.6206(7) Å | β = 104.501(1)°. |
| | c = 13.6665(5) Å | γ = 90°. |
| Volume | 1931.86(13) $Å^3$ | |
| Z | 6 | |
| Density (calculated) | 1.301 $Mg/m^3$ | |
| Absorption coefficient | 0.074 $mm^{-1}$ | |
| F(000) | 792 | |
| Crystal size | 0.33 x 0.23 x 0.09 $mm^3$ | |
| Crystal color and habit | yellow needle | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 1.86 to 25.25°. | |
| Index ranges | -8<=h<=8, -23<=k<=23, -16<=l<=16 | |
| Reflections collected | 28655 | |
| Independent reflections | 3496 [R(int) = 0.0356] | |
| Completeness to theta = 25.25° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.990 and 0.976 | |
| Solution method | XS, SHELXTL v. 6.14 (Bruker, 2003) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3496 / 0 / 271 | |
| Goodness-of-fit on $F^2$ | 1.012 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0434, wR2 = 0.1129 | |
| R indices (all data) | R1 = 0.0544, wR2 = 0.1228 | |
| Largest diff. peak and hole | 0.258 and -0.172 $e.Å^{-3}$ | |

**Table A. 83 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for 235 (bt 1220).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 3552(2) | 539(1) | 9121(1) | 22(1) |
| C(2) | 2337(2) | 936(1) | 9104(1) | 19(1) |
| C(3) | 790(2) | 1396(1) | 8937(1) | 19(1) |
| C(4) | 909(2) | 2051(1) | 8524(1) | 19(1) |
| C(5) | -741(2) | 2392(1) | 8084(1) | 22(1) |
| C(6) | -2441(2) | 2126(1) | 8143(1) | 23(1) |
| C(7) | -2490(2) | 1569(1) | 8761(1) | 21(1) |
| C(8) | -859(2) | 1218(1) | 9219(1) | 20(1) |
| C(9) | -824(2) | 789(1) | 10117(1) | 21(1) |
| C(10) | 419(2) | 830(1) | 11019(1) | 21(1) |
| C(11) | 2193(2) | 1213(1) | 11225(1) | 19(1) |
| C(12) | 3848(2) | 884(1) | 11696(1) | 21(1) |
| C(13) | 5550(2) | 1151(1) | 11645(1) | 23(1) |
| C(14) | 5606(2) | 1696(1) | 11003(1) | 22(1) |
| C(15) | 3974(2) | 2039(1) | 10524(1) | 19(1) |
| C(16) | 2321(2) | 1862(1) | 10797(1) | 18(1) |
| C(17) | 769(2) | 2322(1) | 10612(1) | 19(1) |
| C(18) | -444(2) | 2726(1) | 10553(1) | 22(1) |
| C(19) | 3944(2) | 2470(1) | 9629(1) | 21(1) |
| C(20) | 2686(2) | 2433(1) | 8729(1) | 21(1) |
| C(21) | 6742(2) | 3986(1) | 8900(1) | 26(1) |
| C(22) | 5653(2) | 4398(1) | 9031(1) | 21(1) |
| C(23) | 4194(2) | 4882(1) | 9024(1) | 21(1) |
| C(24) | 2537(2) | 4679(1) | 9269(1) | 21(1) |
| C(25) | 957(2) | 5079(1) | 8917(1) | 23(1) |
| C(26) | 1067(2) | 5696(1) | 8438(1) | 25(1) |
| C(27) | 2793(2) | 5961(1) | 8438(1) | 24(1) |
| C(28) | 4404(2) | 5578(1) | 8786(1) | 22(1) |
| C(29) | 6224(2) | 5928(1) | 9077(1) | 24(1) |

| | | | | |
|---|---|---|---|---|
| C(30) | 2518(2) | 4143(1) | 10035(1) | 24(1) |

**Table A. 84 Bond lengths [Å] and angles [°] for 235 (bt 1220)**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.189(2) | C(18)-H(18) | 0.9500 |
| C(1)-H(1) | 0.9500 | C(19)-C(20) | 1.348(2) |
| C(2)-C(3) | 1.435(2) | C(19)-H(19A) | 0.9500 |
| C(3)-C(4) | 1.416(2) | C(20)-H(20A) | 0.9500 |
| C(3)-C(8) | 1.419(2) | C(21)-C(22) | 1.189(2) |
| C(4)-C(5) | 1.395(2) | C(21)-H(21) | 0.9500 |
| C(4)-C(20) | 1.484(2) | C(22)-C(23) | 1.440(2) |
| C(5)-C(6) | 1.389(2) | C(23)-C(24) | 1.413(2) |
| C(5)-H(5A) | 0.9500 | C(23)-C(28) | 1.421(2) |
| C(6)-C(7) | 1.388(2) | C(24)-C(25) | 1.395(2) |
| C(6)-H(6A) | 0.9500 | C(24)-C(30) | 1.487(2) |
| C(7)-C(8) | 1.399(2) | C(25)-C(26) | 1.389(2) |
| C(7)-H(7A) | 0.9500 | C(25)-H(25A) | 0.9500 |
| C(8)-C(9) | 1.485(2) | C(26)-C(27) | 1.385(2) |
| C(9)-C(10) | 1.345(2) | C(26)-H(26A) | 0.9500 |
| C(9)-H(9A) | 0.9500 | C(27)-C(28) | 1.394(2) |
| C(10)-C(11) | 1.484(2) | C(27)-H(27A) | 0.9500 |
| C(10)-H(10A) | 0.9500 | C(28)-C(29) | 1.481(2) |
| C(11)-C(12) | 1.396(2) | C(29)-C(30)#1 | 1.342(2) |
| C(11)-C(16) | 1.415(2) | C(29)-H(29A) | 0.9500 |
| C(12)-C(13) | 1.389(2) | C(30)-C(29)#1 | 1.342(2) |
| C(12)-H(12A) | 0.9500 | C(30)-H(30A) | 0.9500 |
| C(13)-C(14) | 1.389(2) | | |
| C(13)-H(13A) | 0.9500 | C(2)-C(1)-H(1) | 180.0 |
| C(14)-C(15) | 1.399(2) | C(1)-C(2)-C(3) | 172.04(16) |
| C(14)-H(14A) | 0.9500 | C(4)-C(3)-C(8) | 118.40(13) |
| C(15)-C(16) | 1.416(2) | C(4)-C(3)-C(2) | 120.44(13) |
| C(15)-C(19) | 1.483(2) | C(8)-C(3)-C(2) | 121.11(13) |
| C(16)-C(17) | 1.437(2) | C(5)-C(4)-C(3) | 118.07(14) |
| C(17)-C(18) | 1.188(2) | C(5)-C(4)-C(20) | 119.05(13) |

| | | | |
|---|---|---|---|
| C(3)-C(4)-C(20) | 121.68(14) | C(15)-C(16)-C(17) | 120.85(14) |
| C(6)-C(5)-C(4) | 120.77(14) | C(18)-C(17)-C(16) | 173.54(16) |
| C(6)-C(5)-H(5A) | 119.6 | C(17)-C(18)-H(18) | 180.0 |
| C(4)-C(5)-H(5A) | 119.6 | C(20)-C(19)-C(15) | 125.80(14) |
| C(7)-C(6)-C(5) | 119.60(14) | C(20)-C(19)-H(19A) | 117.1 |
| C(7)-C(6)-H(6A) | 120.2 | C(15)-C(19)-H(19A) | 117.1 |
| C(5)-C(6)-H(6A) | 120.2 | C(19)-C(20)-C(4) | 125.63(14) |
| C(6)-C(7)-C(8) | 120.50(14) | C(19)-C(20)-H(20A) | 117.2 |
| C(6)-C(7)-H(7A) | 119.8 | C(4)-C(20)-H(20A) | 117.2 |
| C(8)-C(7)-H(7A) | 119.8 | C(22)-C(21)-H(21) | 180.0 |
| C(7)-C(8)-C(3) | 118.08(14) | C(21)-C(22)-C(23) | 170.96(17) |
| C(7)-C(8)-C(9) | 118.86(14) | C(24)-C(23)-C(28) | 118.54(14) |
| C(3)-C(8)-C(9) | 121.78(13) | C(24)-C(23)-C(22) | 120.91(14) |
| C(10)-C(9)-C(8) | 126.10(14) | C(28)-C(23)-C(22) | 120.55(14) |
| C(10)-C(9)-H(9A) | 116.9 | C(25)-C(24)-C(23) | 118.02(15) |
| C(8)-C(9)-H(9A) | 116.9 | C(25)-C(24)-C(30) | 118.98(14) |
| C(9)-C(10)-C(11) | 125.42(14) | C(23)-C(24)-C(30) | 121.94(14) |
| C(9)-C(10)-H(10A) | 117.3 | C(26)-C(25)-C(24) | 120.60(15) |
| C(11)-C(10)-H(10A) | 117.3 | C(26)-C(25)-H(25A) | 119.7 |
| C(12)-C(11)-C(16) | 117.65(14) | C(24)-C(25)-H(25A) | 119.7 |
| C(12)-C(11)-C(10) | 119.57(13) | C(27)-C(26)-C(25) | 119.37(15) |
| C(16)-C(11)-C(10) | 121.73(13) | C(27)-C(26)-H(26A) | 120.3 |
| C(13)-C(12)-C(11) | 120.79(14) | C(25)-C(26)-H(26A) | 120.3 |
| C(13)-C(12)-H(12A) | 119.6 | C(26)-C(27)-C(28) | 121.09(15) |
| C(11)-C(12)-H(12A) | 119.6 | C(26)-C(27)-H(27A) | 119.5 |
| C(14)-C(13)-C(12) | 119.63(14) | C(28)-C(27)-H(27A) | 119.5 |
| C(14)-C(13)-H(13A) | 120.2 | C(27)-C(28)-C(23) | 117.47(15) |
| C(12)-C(13)-H(13A) | 120.2 | C(27)-C(28)-C(29) | 119.45(14) |
| C(13)-C(14)-C(15) | 120.39(15) | C(23)-C(28)-C(29) | 122.03(14) |
| C(13)-C(14)-H(14A) | 119.8 | C(30)#1-C(29)-C(28) | 125.30(14) |
| C(15)-C(14)-H(14A) | 119.8 | C(30)#1-C(29)-H(29A) | 117.4 |
| C(14)-C(15)-C(16) | 117.90(14) | C(28)-C(29)-H(29A) | 117.4 |
| C(14)-C(15)-C(19) | 119.56(14) | C(29)#1-C(30)-C(24) | 125.69(14) |
| C(16)-C(15)-C(19) | 121.51(13) | C(29)#1-C(30)-H(30A) | 117.2 |
| C(11)-C(16)-C(15) | 118.87(14) | C(24)-C(30)-H(30A) | 117.2 |
| C(11)-C(16)-C(17) | 120.25(13) | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

**Table A. 85 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 235 (bt 1220).**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 24(1) | 19(1) | 24(1) | 0(1) | 8(1) | 1(1) |
| C(2) | 24(1) | 17(1) | 18(1) | 1(1) | 7(1) | -4(1) |
| C(3) | 20(1) | 18(1) | 17(1) | -2(1) | 3(1) | 1(1) |
| C(4) | 23(1) | 20(1) | 16(1) | -1(1) | 7(1) | 1(1) |
| C(5) | 28(1) | 19(1) | 17(1) | 2(1) | 5(1) | 2(1) |
| C(6) | 21(1) | 26(1) | 19(1) | -2(1) | 2(1) | 4(1) |
| C(7) | 18(1) | 22(1) | 21(1) | -5(1) | 4(1) | -3(1) |
| C(8) | 22(1) | 15(1) | 22(1) | -4(1) | 5(1) | -2(1) |
| C(9) | 21(1) | 15(1) | 27(1) | -1(1) | 10(1) | -1(1) |
| C(10) | 23(1) | 17(1) | 24(1) | 4(1) | 11(1) | 2(1) |
| C(11) | 22(1) | 20(1) | 15(1) | -1(1) | 7(1) | 2(1) |
| C(12) | 28(1) | 18(1) | 18(1) | 1(1) | 7(1) | 4(1) |
| C(13) | 23(1) | 23(1) | 20(1) | -3(1) | 2(1) | 6(1) |
| C(14) | 20(1) | 22(1) | 23(1) | -6(1) | 6(1) | 0(1) |
| C(15) | 21(1) | 16(1) | 21(1) | -5(1) | 5(1) | -2(1) |
| C(16) | 19(1) | 19(1) | 16(1) | -2(1) | 3(1) | 1(1) |
| C(17) | 23(1) | 16(1) | 17(1) | -1(1) | 5(1) | -3(1) |
| C(18) | 24(1) | 18(1) | 25(1) | -1(1) | 7(1) | 1(1) |
| C(19) | 22(1) | 15(1) | 29(1) | 0(1) | 10(1) | 0(1) |
| C(20) | 23(1) | 18(1) | 24(1) | 4(1) | 11(1) | 2(1) |
| C(21) | 30(1) | 22(1) | 27(1) | -1(1) | 11(1) | 1(1) |
| C(22) | 24(1) | 20(1) | 20(1) | -1(1) | 7(1) | -4(1) |
| C(23) | 24(1) | 22(1) | 17(1) | -2(1) | 3(1) | 2(1) |
| C(24) | 22(1) | 19(1) | 22(1) | -6(1) | 4(1) | -2(1) |
| C(25) | 22(1) | 27(1) | 21(1) | -7(1) | 5(1) | -1(1) |
| C(26) | 24(1) | 31(1) | 18(1) | 0(1) | 3(1) | 8(1) |
| C(27) | 31(1) | 22(1) | 19(1) | 2(1) | 8(1) | 5(1) |
| C(28) | 26(1) | 22(1) | 19(1) | 1(1) | 9(1) | 2(1) |

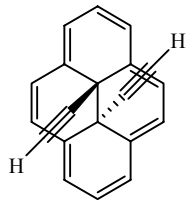
| | | | | | | |
|---|---|---|---|---|---|---|
| C(29) | 29(1) | 19(1) | 29(1) | 4(1) | 16(1) | 1(1) |
| C(30) | 23(1) | 16(1) | 35(1) | -2(1) | 11(1) | -2(1) |

**Table A. 86 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for 235 (bt 1220)**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 4522 | 221 | 9134 | 27 |
| H(5A) | -702 | 2810 | 7740 | 26 |
| H(6A) | -3563 | 2325 | 7762 | 27 |
| H(7A) | -3639 | 1425 | 8875 | 25 |
| H(9A) | -1768 | 453 | 10049 | 25 |
| H(10A) | 137 | 594 | 11569 | 25 |
| H(12A) | 3809 | 472 | 12056 | 25 |
| H(13A) | 6669 | 963 | 12046 | 27 |
| H(14A) | 6758 | 1836 | 10889 | 26 |
| H(18) | -1413 | 3048 | 10506 | 27 |
| H(19A) | 4896 | 2803 | 9695 | 25 |
| H(20A) | 2959 | 2672 | 8180 | 25 |
| H(21) | 7611 | 3657 | 8795 | 31 |
| H(25A) | -204 | 4928 | 9007 | 28 |
| H(26A) | -31 | 5935 | 8112 | 30 |
| H(27A) | 2880 | 6411 | 8198 | 29 |
| H(29A) | 6525 | 6227 | 8595 | 29 |
| H(30A) | 1529 | 3823 | 9882 | 29 |

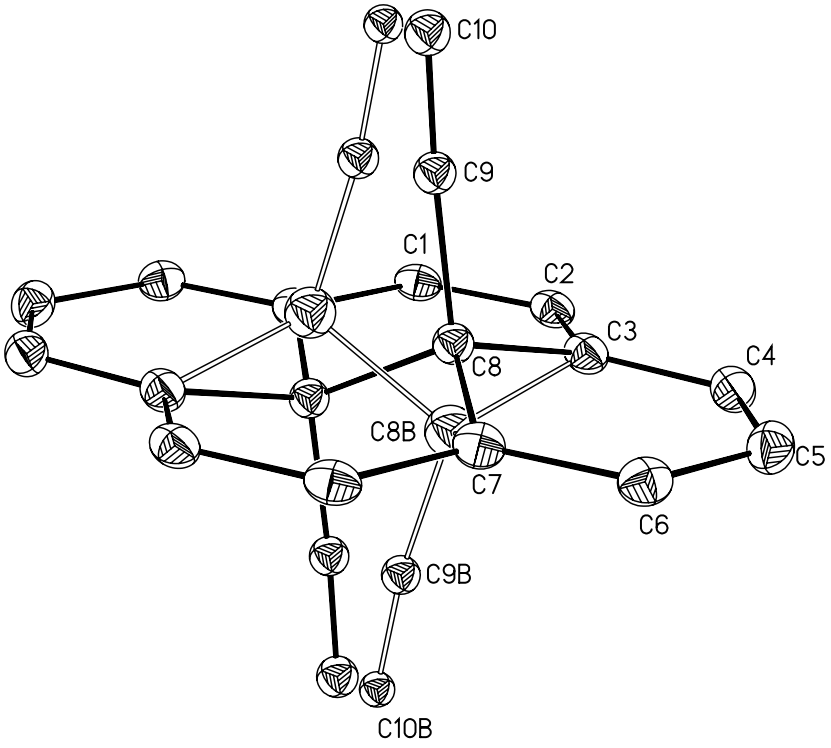
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for diethynyl DHP 236**




**236**

Brendan Twamley




Project name : Bt1228

1-26-08

**Experimental:**

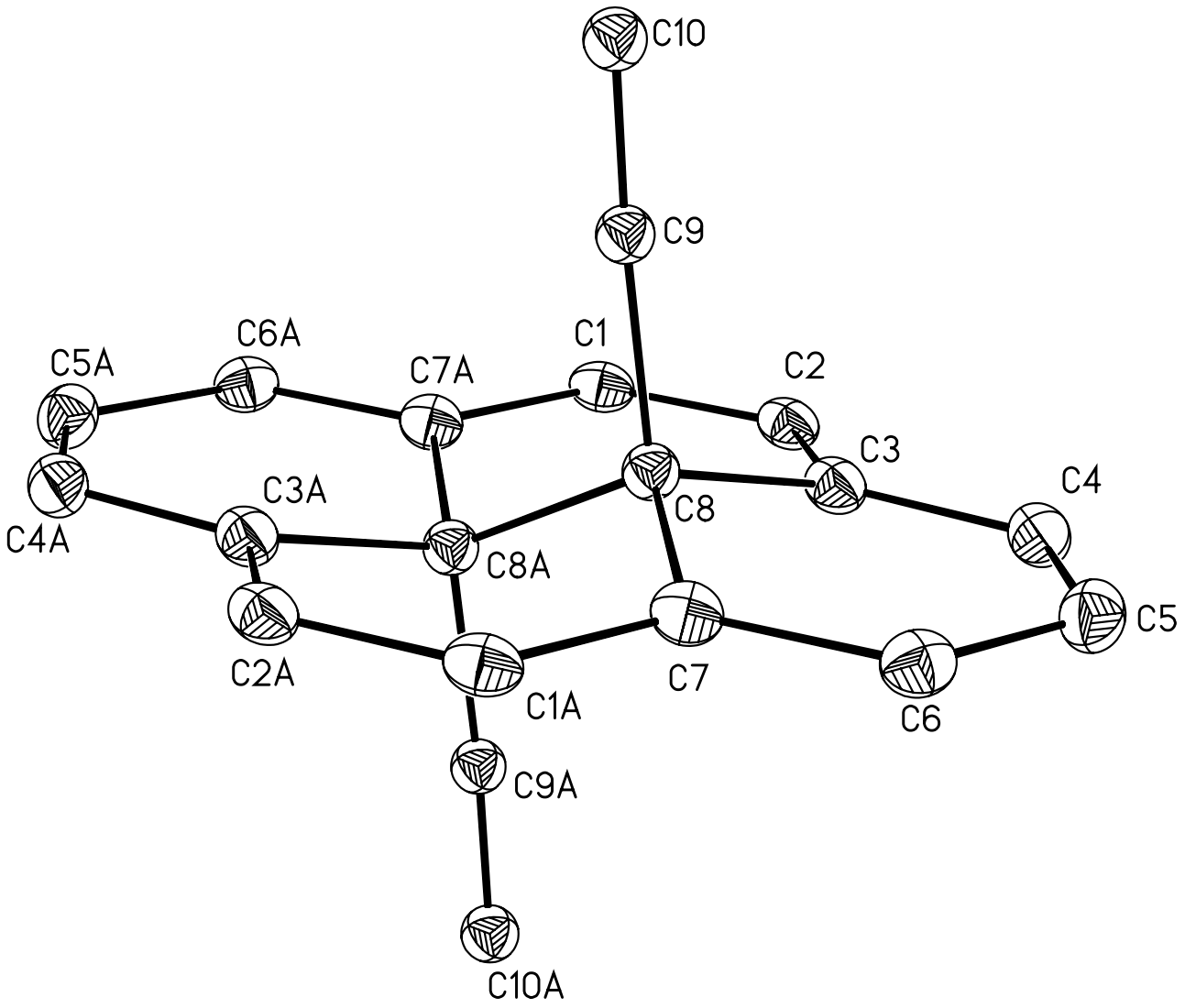
Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans 0.3 ° per frame for 30 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[72] software and refined using SAINTPlus[73] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[74] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[75] The structure was solved in the space group P2(1)/n (# 14) by analysis of systematic absences. The central diethynyl group was disordered in two positions (85:15%) and these atoms (C8, C9, C10) were held isotropic. Mild bond length restraints were used to stabilize the minor component. All other non-hydrogen atoms were refined anisotropically. Ethynyl hydrogen atoms were geometrically placed and refined with a riding model. All other hydrogen atoms were located and refined. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

---

[72] SMART: v. 5.632, Bruker AXS, Madison, WI, **2005**.
[73] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[74] SADABS: v.2007/4, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2007**.
[75] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.


C10
C9
C6A
C1
C5A
C7A
C2
C3
C4
C3A
C8
C4A
C8A
C5
C2A
C7
C1A
C6
C9A
C10A

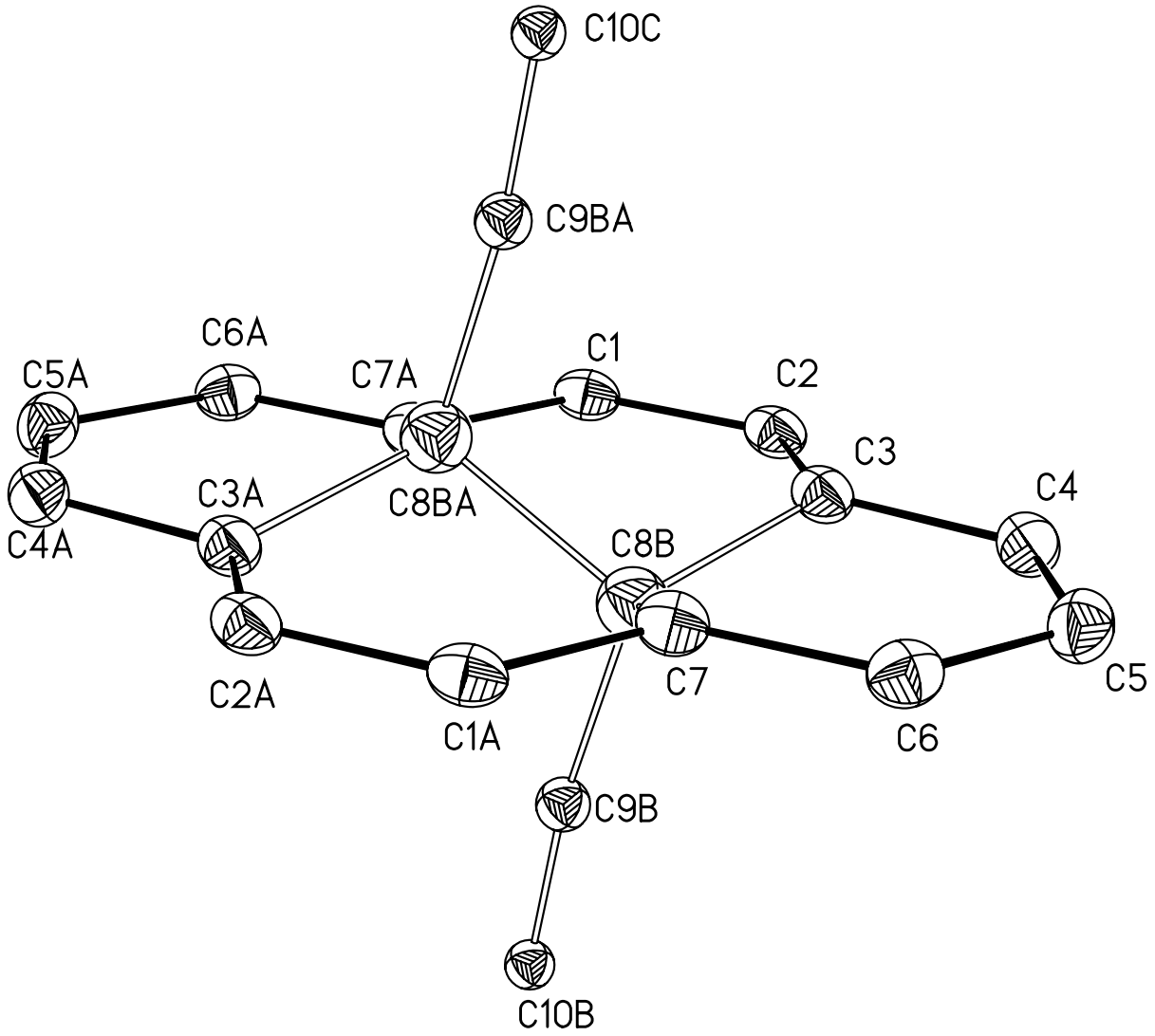

C10C
C9BA
C6A
C5A
C7A
C1
C2
C3
C4
C3A
C8BA
C4A
C8B
C2A
C1A
C7
C6
C5
C9B
C10B

**Table A. 87 Crystal data and structure refinement for diethynyl DHP 236.**

| | | |
|---|---|---|
| Identification code | bt1228 | |
| Empirical formula | C20 H12 | |
| Formula weight | 252.30 | |
| Temperature | 90(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 6.9735(5) Å | α = 90°. |
| | b = 6.8401(5) Å | β = 93.252(1)° |
| | c = 13.5036(9) Å | γ = 90°. |
| Volume | 643.08(8) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.303 $Mg/m^3$ | |
| Absorption coefficient | 0.074 $mm^{-1}$ | |
| F(000) | 264 | |
| Crystal size | 0.54 x 0.10 x 0.05 $mm^3$ | |
| Crystal color and habit | green needle | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 3.02 to 25.24°. | |
| Index ranges | -8<=h<=8, -8<=k<=8, -16<=l<=16 | |
| Reflections collected | 9506 | |
| Independent reflections | 1163 [R(int) = 0.0259] | |
| Completeness to theta = 25.24° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9963 and 0.9612 | |
| Solution method | XS, SHELXTL v. 6.14 (Bruker, 2003) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1163 / 4 / 108 | |
| Goodness-of-fit on $F^2$ | 1.058 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0395, wR2 = 0.0971 | |
| R indices (all data) | R1 = 0.0467, wR2 = 0.1026 | |
| Largest diff. peak and hole | 0.319 and -0.167 $e.Å^{-3}$ | |

**Table A. 88 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 236 (bt 1228).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 3085(2) | 1866(2) | 4635(1) | 26(1) |
| C(2) | 2019(2) | 2938(2) | 5282(1) | 26(1) |
| C(3) | 2656(2) | 4714(2) | 5688(1) | 26(1) |
| C(4) | 1639(2) | 5873(2) | 6318(1) | 28(1) |
| C(5) | 2346(2) | 7664(2) | 6667(1) | 31(1) |
| C(6) | 4069(2) | 8439(2) | 6363(1) | 28(1) |
| C(7) | 5217(2) | 7427(2) | 5732(1) | 26(1) |
| C(8) | 4763(2) | 5254(2) | 5534(1) | 22(1) |
| C(9) | 6001(2) | 4075(3) | 6249(1) | 22(1) |
| C(10) | 6935(3) | 3181(3) | 6855(2) | 25(1) |
| C(8B) | 4184(11) | 5809(11) | 5092(4) | 35(2) |
| C(9B) | 3457(13) | 6492(14) | 4080(6) | 21(2) |
| C(10B) | 2769(15) | 7169(16) | 3333(7) | 18(3) |

**Table A. 89 Bond lengths [Å] and angles [°] for 236 (bt 1228)**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.388(2) | C(4)-C(3)-C(8) | 118.08(14) |
| C(1)-C(7)#1 | 1.396(2) | C(2)-C(3)-C(8) | 116.11(13) |
| C(1)-H(1) | 0.987(17) | C(4)-C(3)-C(8B) | 115.4(3) |
| C(2)-C(3) | 1.395(2) | C(2)-C(3)-C(8B) | 115.2(3) |
| C(2)-H(2) | 0.995(16) | C(3)-C(4)-C(5) | 121.79(14) |
| C(3)-C(4) | 1.386(2) | C(3)-C(4)-H(4) | 118.7(10) |
| C(3)-C(8) | 1.541(2) | C(5)-C(4)-H(4) | 119.4(10) |
| C(3)-C(8B) | 1.563(5) | C(4)-C(5)-C(6) | 121.93(15) |
| C(4)-C(5) | 1.393(2) | C(4)-C(5)-H(5) | 117.4(10) |
| C(4)-H(4) | 0.995(17) | C(6)-C(5)-H(5) | 120.5(10) |
| C(5)-C(6) | 1.396(2) | C(7)-C(6)-C(5) | 121.84(15) |
| C(5)-H(5) | 0.996(18) | C(7)-C(6)-H(6) | 119.7(9) |
| C(6)-C(7) | 1.387(2) | C(5)-C(6)-H(6) | 118.3(9) |
| C(6)-H(6) | 0.999(18) | C(6)-C(7)-C(1)#1 | 125.18(14) |
| C(7)-C(1)#1 | 1.396(2) | C(6)-C(7)-C(8) | 117.92(13) |
| C(7)-C(8) | 1.540(2) | C(1)#1-C(7)-C(8) | 116.30(13) |
| C(7)-C(8B) | 1.556(5) | C(6)-C(7)-C(8B) | 115.5(3) |
| C(8)-C(9) | 1.495(2) | C(1)#1-C(7)-C(8B) | 115.1(2) |
| C(8)-C(8)#1 | 1.537(3) | C(9)-C(8)-C(8)#1 | 109.66(17) |
| C(9)-C(10) | 1.186(2) | C(9)-C(8)-C(7) | 107.60(13) |
| C(10)-H(10) | 0.9500 | C(8)#1-C(8)-C(7) | 109.19(16) |
| C(8B)-C(9B) | 1.506(5) | C(9)-C(8)-C(3) | 107.67(13) |
| C(8B)-C(8B)#1 | 1.617(18) | C(8)#1-C(8)-C(3) | 109.30(16) |
| C(9B)-C(10B) | 1.186(5) | C(7)-C(8)-C(3) | 113.36(13) |
| C(10B)-H(10B) | 0.9500 | C(10)-C(9)-C(8) | 176.6(2) |
| | | C(9)-C(10)-H(10) | 180.0 |
| C(2)-C(1)-C(7)#1 | 122.38(14) | C(9B)-C(8B)-C(7) | 113.9(6) |
| C(2)-C(1)-H(1) | 119.7(9) | C(9B)-C(8B)-C(3) | 114.3(6) |
| C(7)#1-C(1)-H(1) | 118.0(9) | C(7)-C(8B)-C(3) | 111.3(3) |
| C(1)-C(2)-C(3) | 122.55(14) | C(9B)-C(8B)-C(8B)#1 | 106.0(6) |
| C(1)-C(2)-H(2) | 119.5(9) | C(7)-C(8B)-C(8B)#1 | 105.4(5) |
| C(3)-C(2)-H(2) | 118.0(9) | C(3)-C(8B)-C(8B)#1 | 104.9(5) |
| C(4)-C(3)-C(2) | 125.22(14) | C(10B)-C(9B)-C(8B) | 173.0(12) |
| | | C(9B)-C(10B)-H(10B) | 180.0 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

**Table A. 90 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 236 (bt 1228).**

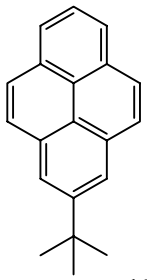
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 28(1) | 24(1) | 24(1) | 3(1) | -6(1) | -4(1) |
| C(2) | 21(1) | 32(1) | 24(1) | 7(1) | -3(1) | -4(1) |
| C(3) | 22(1) | 31(1) | 23(1) | 5(1) | -1(1) | -2(1) |
| C(4) | 22(1) | 37(1) | 25(1) | 3(1) | 0(1) | 0(1) |
| C(5) | 28(1) | 37(1) | 27(1) | -3(1) | 1(1) | 4(1) |
| C(6) | 30(1) | 28(1) | 26(1) | -1(1) | -5(1) | 1(1) |
| C(7) | 27(1) | 27(1) | 23(1) | 0(1) | -4(1) | -2(1) |

**Table A. 91 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for 236 (bt 1228).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 2630(20) | 560(30) | 4414(12) | 25(4) |
| H(2) | 760(20) | 2420(20) | 5481(11) | 26(4) |
| H(4) | 340(20) | 5430(20) | 6499(12) | 28(4) |
| H(5) | 1530(20) | 8420(30) | 7113(13) | 33(4) |
| H(6) | 4430(20) | 9790(30) | 6578(12) | 29(4) |
| H(10) | 7682 | 2464 | 7340 | 30 |
| H(10B) | 2218 | 7711 | 2735 | 22 |

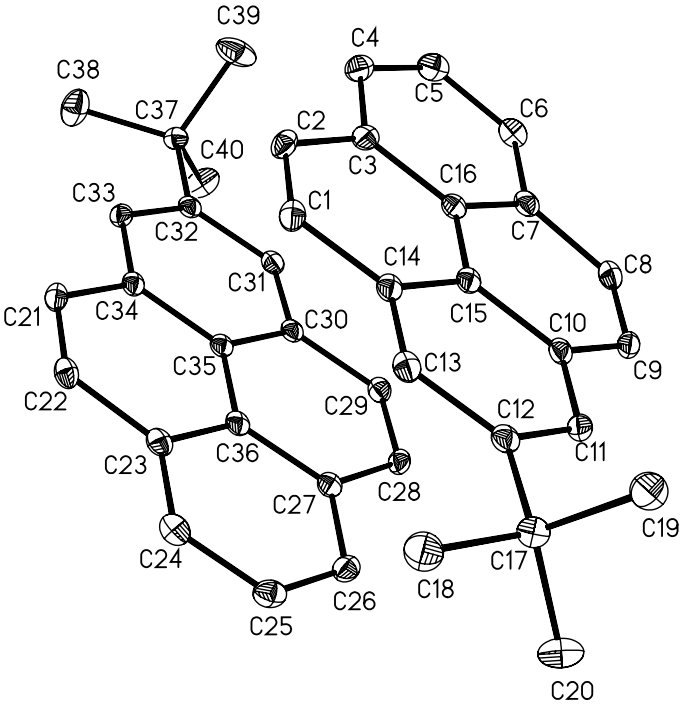
# Single-Crystal X-ray Diffraction Laboratory
# University of Idaho

**X-ray structure report for pyrene 150**



**150**

Brendan Twamley




Project name : bt957

8-18-06

**Experimental:**

Crystals of compound **1** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 5 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[76] software and refined using SAINTPlus[77] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[78] The structure was solved by direct methods and refined by least squares method on $F^2$ using the SHELXTL program package.[79] The structure was solved in the space group P2(1)/c (# 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

**Acknowledgement**

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

---

[76] SMART: v.5.630, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2001**.
[77] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[78] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.
[79] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

**Table A. 92 Crystal data and structure refinement for $^{t}$Bu-pyrene 150**

| | | |
|---|---|---|
| Identification code | bt957 | |
| Empirical formula | C20 H18 | |
| Formula weight | 258.34 | |
| Temperature | 90(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 11.5243(9) Å | α = 90°. |
| | b = 10.5760(8) Å | β = 95.2860(10)°. |
| | c = 22.9005(18) Å | γ = 90°. |
| Volume | 2779.3(4) Å$^3$ | |
| Z | 8 | |
| Density (calculated) | 1.235 Mg/m$^3$ | |
| Absorption coefficient | 0.069 mm$^{-1}$ | |
| F(000) | 1104 | |
| Crystal size | 0.50 x 0.31 x 0.28 mm$^3$ | |
| Crystal color and habit | pale yellow block | |
| Diffractometer | Bruker/Siemens SMART APEX | |
| Theta range for data collection | 1.77 to 25.25°. | |
| Index ranges | -13<=h<=13, -12<=k<=12, -27<=l<=27 | |
| Reflections collected | 41377 | |
| Independent reflections | 5033 [R(int) = 0.0329] | |
| Completeness to theta = 25.25° | 100.0% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9808 and 0.9661 | |
| Solution method | Bruker, 2003; XS, SHELXTL v. 6.14 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 5033 / 0 / 367 | |
| Goodness-of-fit on F$^2$ | 1.034 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0462, wR2 = 0.1185 | |
| R indices (all data) | R1 = 0.0546, wR2 = 0.1245 | |
| Largest diff. peak and hole | 0.352 and -0.174 e.Å$^{-3}$ | |

**Table A. 93 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for 150 (bt 957).**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 969(1) | -146(1) | 8231(1) | 21(1) |
| C(2) | 477(1) | -488(1) | 7697(1) | 22(1) |
| C(3) | 622(1) | 255(1) | 7184(1) | 20(1) |
| C(4) | 84(1) | -47(1) | 6631(1) | 24(1) |
| C(5) | 253(1) | 702(2) | 6149(1) | 26(1) |
| C(6) | 984(1) | 1747(1) | 6205(1) | 24(1) |
| C(7) | 1542(1) | 2086(1) | 6748(1) | 20(1) |
| C(8) | 2310(1) | 3155(1) | 6825(1) | 21(1) |
| C(9) | 2784(1) | 3505(1) | 7361(1) | 19(1) |
| C(10) | 2549(1) | 2820(1) | 7879(1) | 18(1) |
| C(11) | 2996(1) | 3192(1) | 8439(1) | 19(1) |
| C(12) | 2790(1) | 2504(1) | 8940(1) | 19(1) |
| C(13) | 2133(1) | 1398(1) | 8865(1) | 20(1) |
| C(14) | 1655(1) | 990(1) | 8315(1) | 19(1) |
| C(15) | 1843(1) | 1720(1) | 7812(1) | 17(1) |
| C(16) | 1337(1) | 1352(1) | 7247(1) | 18(1) |
| C(17) | 3279(1) | 2985(1) | 9545(1) | 21(1) |
| C(18) | 3147(2) | 2011(2) | 10027(1) | 31(1) |
| C(19) | 2627(1) | 4187(2) | 9691(1) | 28(1) |
| C(20) | 4580(1) | 3292(2) | 9540(1) | 31(1) |
| C(21) | 2352(1) | -3312(1) | 7800(1) | 19(1) |
| C(22) | 2883(1) | -2875(1) | 8310(1) | 20(1) |
| C(23) | 3611(1) | -1771(1) | 8332(1) | 19(1) |
| C(24) | 4192(1) | -1310(1) | 8852(1) | 22(1) |
| C(25) | 4861(1) | -221(1) | 8852(1) | 23(1) |
| C(26) | 4964(1) | 443(1) | 8337(1) | 21(1) |
| C(27) | 4412(1) | 16(1) | 7806(1) | 18(1) |
| C(28) | 4509(1) | 660(1) | 7259(1) | 19(1) |
| C(29) | 3997(1) | 203(1) | 6749(1) | 19(1) |
| C(30) | 3323(1) | -944(1) | 6725(1) | 17(1) |

| | | | | |
|---|---|---|---|---|
| C(31) | 2797(1) | -1445(1) | 6205(1) | 18(1) |
| C(32) | 2147(1) | -2560(1) | 6184(1) | 18(1) |
| C(33) | 1990(1) | -3159(1) | 6715(1) | 18(1) |
| C(34) | 2498(1) | -2696(1) | 7252(1) | 17(1) |
| C(35) | 3190(1) | -1582(1) | 7263(1) | 16(1) |
| C(36) | 3738(1) | -1112(1) | 7800(1) | 17(1) |
| C(37) | 1588(1) | -3068(1) | 5595(1) | 20(1) |
| C(38) | 1225(2) | -4450(2) | 5637(1) | 36(1) |
| C(39) | 511(2) | -2282(2) | 5405(1) | 41(1) |
| C(40) | 2434(2) | -3001(2) | 5119(1) | 34(1) |

**Table A. 94 Bond lengths [Å] and angles [°] for 150 (bt 957)**.

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.349(2) | C(11)-C(12) | 1.3971(19) |
| C(1)-C(14) | 1.441(2) | C(11)-H(11A) | 0.9500 |
| C(1)-H(1A) | 0.9500 | C(12)-C(13) | 1.396(2) |
| C(2)-C(3) | 1.436(2) | C(12)-C(17) | 1.534(2) |
| C(2)-H(2A) | 0.9500 | C(13)-C(14) | 1.396(2) |
| C(3)-C(4) | 1.395(2) | C(13)-H(13A) | 0.9500 |
| C(3)-C(16) | 1.423(2) | C(14)-C(15) | 1.4202(19) |
| C(4)-C(5) | 1.386(2) | C(15)-C(16) | 1.423(2) |
| C(4)-H(4A) | 0.9500 | C(17)-C(18) | 1.528(2) |
| C(5)-C(6) | 1.389(2) | C(17)-C(19) | 1.529(2) |
| C(5)-H(5A) | 0.9500 | C(17)-C(20) | 1.534(2) |
| C(6)-C(7) | 1.394(2) | C(18)-H(18A) | 0.9800 |
| C(6)-H(6A) | 0.9500 | C(18)-H(18B) | 0.9800 |
| C(7)-C(16) | 1.419(2) | C(18)-H(18C) | 0.9800 |
| C(7)-C(8) | 1.437(2) | C(19)-H(19A) | 0.9800 |
| C(8)-C(9) | 1.347(2) | C(19)-H(19B) | 0.9800 |
| C(8)-H(8A) | 0.9500 | C(19)-H(19C) | 0.9800 |
| C(9)-C(10) | 1.4365(19) | C(20)-H(20A) | 0.9800 |
| C(9)-H(9A) | 0.9500 | C(20)-H(20B) | 0.9800 |
| C(10)-C(11) | 1.394(2) | C(20)-H(20C) | 0.9800 |
| C(10)-C(15) | 1.4195(19) | C(21)-C(22) | 1.350(2) |

| | | | |
|---|---|---|---|
| C(21)-C(34) | 1.4371(19) | C(39)-H(39C) | 0.9800 |
| C(21)-H(21A) | 0.9500 | C(40)-H(40A) | 0.9800 |
| C(22)-C(23) | 1.436(2) | C(40)-H(40B) | 0.9800 |
| C(22)-H(22A) | 0.9500 | C(40)-H(40C) | 0.9800 |
| C(23)-C(24) | 1.398(2) | | |
| C(23)-C(36) | 1.4231(19) | C(2)-C(1)-C(14) | 121.57(13) |
| C(24)-C(25) | 1.386(2) | C(2)-C(1)-H(1A) | 119.2 |
| C(24)-H(24A) | 0.9500 | C(14)-C(1)-H(1A) | 119.2 |
| C(25)-C(26) | 1.387(2) | C(1)-C(2)-C(3) | 121.63(13) |
| C(25)-H(25A) | 0.9500 | C(1)-C(2)-H(2A) | 119.2 |
| C(26)-C(27) | 1.396(2) | C(3)-C(2)-H(2A) | 119.2 |
| C(26)-H(26A) | 0.9500 | C(4)-C(3)-C(16) | 118.95(14) |
| C(27)-C(36) | 1.4227(19) | C(4)-C(3)-C(2) | 122.83(13) |
| C(27)-C(28) | 1.4386(19) | C(16)-C(3)-C(2) | 118.21(13) |
| C(28)-C(29) | 1.349(2) | C(5)-C(4)-C(3) | 120.55(14) |
| C(28)-H(28A) | 0.9500 | C(5)-C(4)-H(4A) | 119.7 |
| C(29)-C(30) | 1.4386(19) | C(3)-C(4)-H(4A) | 119.7 |
| C(29)-H(29A) | 0.9500 | C(4)-C(5)-C(6) | 120.71(14) |
| C(30)-C(31) | 1.390(2) | C(4)-C(5)-H(5A) | 119.6 |
| C(30)-C(35) | 1.4245(19) | C(6)-C(5)-H(5A) | 119.6 |
| C(31)-C(32) | 1.396(2) | C(5)-C(6)-C(7) | 120.83(14) |
| C(31)-H(31A) | 0.9500 | C(5)-C(6)-H(6A) | 119.6 |
| C(32)-C(33) | 1.3987(19) | C(7)-C(6)-H(6A) | 119.6 |
| C(32)-C(37) | 1.5374(19) | C(6)-C(7)-C(16) | 118.76(13) |
| C(33)-C(34) | 1.3991(19) | C(6)-C(7)-C(8) | 122.74(13) |
| C(33)-H(33A) | 0.9500 | C(16)-C(7)-C(8) | 118.50(13) |
| C(34)-C(35) | 1.4219(19) | C(9)-C(8)-C(7) | 121.47(13) |
| C(35)-C(36) | 1.4207(19) | C(9)-C(8)-H(8A) | 119.3 |
| C(37)-C(39) | 1.523(2) | C(7)-C(8)-H(8A) | 119.3 |
| C(37)-C(38) | 1.526(2) | C(8)-C(9)-C(10) | 121.39(13) |
| C(37)-C(40) | 1.529(2) | C(8)-C(9)-H(9A) | 119.3 |
| C(38)-H(38A) | 0.9800 | C(10)-C(9)-H(9A) | 119.3 |
| C(38)-H(38B) | 0.9800 | C(11)-C(10)-C(15) | 119.33(13) |
| C(38)-H(38C) | 0.9800 | C(11)-C(10)-C(9) | 122.35(13) |
| C(39)-H(39A) | 0.9800 | C(15)-C(10)-C(9) | 118.32(13) |
| C(39)-H(39B) | 0.9800 | C(10)-C(11)-C(12) | 122.17(13) |

| | | | |
|---|---|---|---|
| C(10)-C(11)-H(11A) | 118.9 | C(17)-C(20)-H(20B) | 109.5 |
| C(12)-C(11)-H(11A) | 118.9 | H(20A)-C(20)-H(20B) | 109.5 |
| C(13)-C(12)-C(11) | 117.85(13) | C(17)-C(20)-H(20C) | 109.5 |
| C(13)-C(12)-C(17) | 122.60(13) | H(20A)-C(20)-H(20C) | 109.5 |
| C(11)-C(12)-C(17) | 119.55(13) | H(20B)-C(20)-H(20C) | 109.5 |
| C(14)-C(13)-C(12) | 122.29(13) | C(22)-C(21)-C(34) | 121.39(13) |
| C(14)-C(13)-H(13A) | 118.9 | C(22)-C(21)-H(21A) | 119.3 |
| C(12)-C(13)-H(13A) | 118.9 | C(34)-C(21)-H(21A) | 119.3 |
| C(13)-C(14)-C(15) | 119.13(13) | C(21)-C(22)-C(23) | 121.71(13) |
| C(13)-C(14)-C(1) | 122.95(13) | C(21)-C(22)-H(22A) | 119.1 |
| C(15)-C(14)-C(1) | 117.92(13) | C(23)-C(22)-H(22A) | 119.1 |
| C(10)-C(15)-C(14) | 119.15(13) | C(24)-C(23)-C(36) | 118.61(13) |
| C(10)-C(15)-C(16) | 120.30(13) | C(24)-C(23)-C(22) | 123.12(13) |
| C(14)-C(15)-C(16) | 120.54(13) | C(36)-C(23)-C(22) | 118.27(13) |
| C(7)-C(16)-C(15) | 119.86(13) | C(25)-C(24)-C(23) | 120.89(13) |
| C(7)-C(16)-C(3) | 120.09(13) | C(25)-C(24)-H(24A) | 119.6 |
| C(15)-C(16)-C(3) | 120.04(13) | C(23)-C(24)-H(24A) | 119.6 |
| C(18)-C(17)-C(19) | 108.48(12) | C(24)-C(25)-C(26) | 120.75(13) |
| C(18)-C(17)-C(12) | 112.14(12) | C(24)-C(25)-H(25A) | 119.6 |
| C(19)-C(17)-C(12) | 109.07(11) | C(26)-C(25)-H(25A) | 119.6 |
| C(18)-C(17)-C(20) | 108.10(12) | C(25)-C(26)-C(27) | 120.64(14) |
| C(19)-C(17)-C(20) | 109.02(13) | C(25)-C(26)-H(26A) | 119.7 |
| C(12)-C(17)-C(20) | 109.96(12) | C(27)-C(26)-H(26A) | 119.7 |
| C(17)-C(18)-H(18A) | 109.5 | C(26)-C(27)-C(36) | 118.95(13) |
| C(17)-C(18)-H(18B) | 109.5 | C(26)-C(27)-C(28) | 122.65(13) |
| H(18A)-C(18)-H(18B) | 109.5 | C(36)-C(27)-C(28) | 118.40(12) |
| C(17)-C(18)-H(18C) | 109.5 | C(29)-C(28)-C(27) | 121.37(13) |
| H(18A)-C(18)-H(18C) | 109.5 | C(29)-C(28)-H(28A) | 119.3 |
| H(18B)-C(18)-H(18C) | 109.5 | C(27)-C(28)-H(28A) | 119.3 |
| C(17)-C(19)-H(19A) | 109.5 | C(28)-C(29)-C(30) | 121.83(13) |
| C(17)-C(19)-H(19B) | 109.5 | C(28)-C(29)-H(29A) | 119.1 |
| H(19A)-C(19)-H(19B) | 109.5 | C(30)-C(29)-H(29A) | 119.1 |
| C(17)-C(19)-H(19C) | 109.5 | C(31)-C(30)-C(35) | 119.11(13) |
| H(19A)-C(19)-H(19C) | 109.5 | C(31)-C(30)-C(29) | 123.07(12) |
| H(19B)-C(19)-H(19C) | 109.5 | C(35)-C(30)-C(29) | 117.82(12) |
| C(17)-C(20)-H(20A) | 109.5 | C(30)-C(31)-C(32) | 122.84(13) |

| | | | |
|---|---|---|---|
| C(30)-C(31)-H(31A) | 118.6 | C(38)-C(37)-C(32) | 111.94(12) |
| C(32)-C(31)-H(31A) | 118.6 | C(40)-C(37)-C(32) | 111.44(12) |
| C(31)-C(32)-C(33) | 117.64(13) | C(37)-C(38)-H(38A) | 109.5 |
| C(31)-C(32)-C(37) | 120.40(12) | C(37)-C(38)-H(38B) | 109.5 |
| C(33)-C(32)-C(37) | 121.92(12) | H(38A)-C(38)-H(38B) | 109.5 |
| C(32)-C(33)-C(34) | 121.93(13) | C(37)-C(38)-H(38C) | 109.5 |
| C(32)-C(33)-H(33A) | 119.0 | H(38A)-C(38)-H(38C) | 109.5 |
| C(34)-C(33)-H(33A) | 119.0 | H(38B)-C(38)-H(38C) | 109.5 |
| C(33)-C(34)-C(35) | 119.56(12) | C(37)-C(39)-H(39A) | 109.5 |
| C(33)-C(34)-C(21) | 122.33(13) | C(37)-C(39)-H(39B) | 109.5 |
| C(35)-C(34)-C(21) | 118.10(12) | H(39A)-C(39)-H(39B) | 109.5 |
| C(36)-C(35)-C(34) | 120.58(12) | C(37)-C(39)-H(39C) | 109.5 |
| C(36)-C(35)-C(30) | 120.57(13) | H(39A)-C(39)-H(39C) | 109.5 |
| C(34)-C(35)-C(30) | 118.85(12) | H(39B)-C(39)-H(39C) | 109.5 |
| C(35)-C(36)-C(27) | 119.99(12) | C(37)-C(40)-H(40A) | 109.5 |
| C(35)-C(36)-C(23) | 119.89(13) | C(37)-C(40)-H(40B) | 109.5 |
| C(27)-C(36)-C(23) | 120.12(13) | H(40A)-C(40)-H(40B) | 109.5 |
| C(39)-C(37)-C(38) | 108.69(14) | C(37)-C(40)-H(40C) | 109.5 |
| C(39)-C(37)-C(40) | 109.13(13) | H(40A)-C(40)-H(40C) | 109.5 |
| C(38)-C(37)-C(40) | 106.61(13) | H(40B)-C(40)-H(40C) | 109.5 |
| C(39)-C(37)-C(32) | 108.95(12) | | |

**Table A. 95 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 150 (bt 957).**

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 20(1) | 17(1) | 28(1) | 1(1) | 10(1) | 1(1) |
| C(2) | 17(1) | 16(1) | 34(1) | -4(1) | 10(1) | -2(1) |
| C(3) | 14(1) | 18(1) | 29(1) | -5(1) | 6(1) | 3(1) |
| C(4) | 19(1) | 21(1) | 33(1) | -9(1) | 4(1) | 0(1) |
| C(5) | 25(1) | 29(1) | 25(1) | -8(1) | -1(1) | 3(1) |
| C(6) | 26(1) | 25(1) | 23(1) | 1(1) | 2(1) | 5(1) |
| C(7) | 18(1) | 19(1) | 24(1) | 0(1) | 3(1) | 5(1) |
| C(8) | 23(1) | 18(1) | 23(1) | 4(1) | 4(1) | 3(1) |

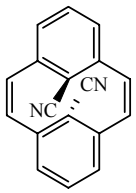
| | | | | | | |
|---|---|---|---|---|---|---|
| C(9) | 18(1) | 14(1) | 27(1) | 2(1) | 4(1) | 0(1) |
| C(10) | 15(1) | 14(1) | 24(1) | 1(1) | 4(1) | 3(1) |
| C(11) | 16(1) | 15(1) | 26(1) | 0(1) | 2(1) | 0(1) |
| C(12) | 16(1) | 19(1) | 23(1) | 0(1) | 4(1) | 4(1) |
| C(13) | 19(1) | 19(1) | 22(1) | 3(1) | 7(1) | 3(1) |
| C(14) | 15(1) | 16(1) | 25(1) | 1(1) | 6(1) | 3(1) |
| C(15) | 14(1) | 15(1) | 23(1) | -1(1) | 6(1) | 3(1) |
| C(16) | 15(1) | 17(1) | 25(1) | -2(1) | 5(1) | 5(1) |
| C(17) | 20(1) | 23(1) | 21(1) | 0(1) | 1(1) | 1(1) |
| C(18) | 37(1) | 32(1) | 23(1) | 1(1) | -3(1) | -1(1) |
| C(19) | 31(1) | 28(1) | 24(1) | -5(1) | 0(1) | 2(1) |
| C(20) | 22(1) | 46(1) | 26(1) | -4(1) | -2(1) | -2(1) |
| C(21) | 20(1) | 14(1) | 24(1) | 2(1) | 6(1) | 0(1) |
| C(22) | 23(1) | 18(1) | 19(1) | 4(1) | 7(1) | 4(1) |
| C(23) | 17(1) | 18(1) | 21(1) | 0(1) | 5(1) | 6(1) |
| C(24) | 24(1) | 25(1) | 19(1) | 2(1) | 4(1) | 5(1) |
| C(25) | 22(1) | 26(1) | 21(1) | -6(1) | -1(1) | 2(1) |
| C(26) | 17(1) | 19(1) | 28(1) | -4(1) | 3(1) | 0(1) |
| C(27) | 14(1) | 16(1) | 24(1) | -2(1) | 4(1) | 4(1) |
| C(28) | 15(1) | 15(1) | 28(1) | 1(1) | 5(1) | -1(1) |
| C(29) | 18(1) | 19(1) | 22(1) | 4(1) | 5(1) | 1(1) |
| C(30) | 14(1) | 17(1) | 21(1) | 3(1) | 4(1) | 3(1) |
| C(31) | 17(1) | 20(1) | 19(1) | 5(1) | 3(1) | 3(1) |
| C(32) | 14(1) | 18(1) | 21(1) | 1(1) | 3(1) | 4(1) |
| C(33) | 15(1) | 16(1) | 23(1) | 0(1) | 3(1) | 0(1) |
| C(34) | 15(1) | 15(1) | 21(1) | 1(1) | 5(1) | 3(1) |
| C(35) | 13(1) | 15(1) | 20(1) | 0(1) | 4(1) | 4(1) |
| C(36) | 14(1) | 16(1) | 21(1) | 0(1) | 5(1) | 5(1) |
| C(37) | 18(1) | 22(1) | 20(1) | 0(1) | 0(1) | 0(1) |
| C(38) | 55(1) | 29(1) | 24(1) | -3(1) | -1(1) | -12(1) |
| C(39) | 36(1) | 50(1) | 34(1) | -16(1) | -15(1) | 16(1) |
| C(40) | 34(1) | 44(1) | 25(1) | -8(1) | 7(1) | -11(1) |

**Table A. 96 Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for 150 (bt 957).**

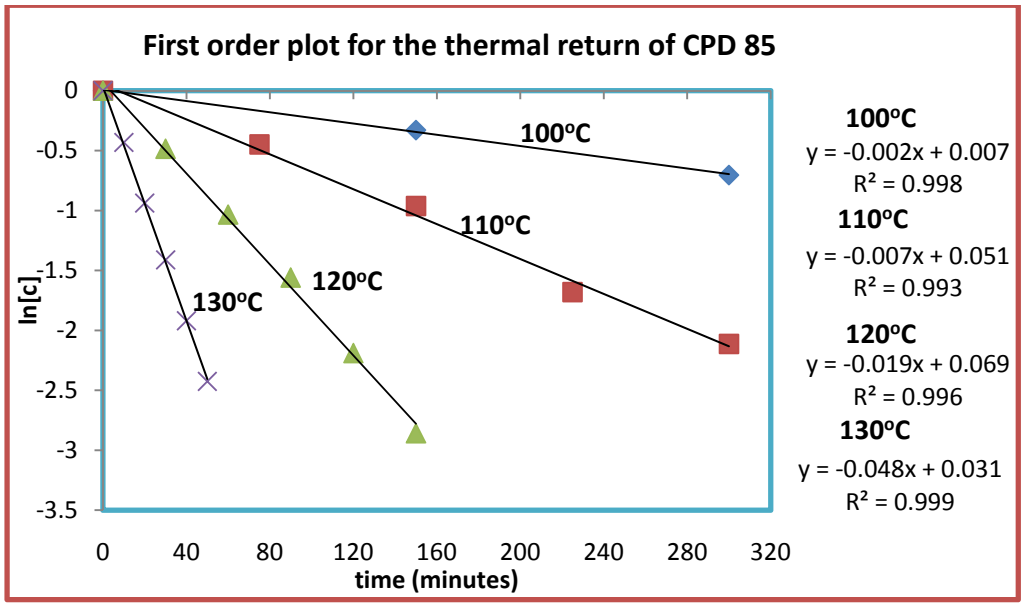
| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 860 | -667 | 8560 | 25 |
| H(2A) | 23 | -1239 | 7659 | 26 |
| H(4A) | -401 | -773 | 6584 | 29 |
| H(5A) | -137 | 499 | 5777 | 32 |
| H(6A) | 1106 | 2237 | 5868 | 29 |
| H(8A) | 2487 | 3625 | 6492 | 25 |
| H(9A) | 3284 | 4220 | 7397 | 23 |
| H(11A) | 3457 | 3937 | 8481 | 23 |
| H(13A) | 2007 | 905 | 9200 | 23 |
| H(18A) | 3502 | 2340 | 10402 | 46 |
| H(18B) | 3536 | 1224 | 9932 | 46 |
| H(18C) | 2317 | 1846 | 10057 | 46 |
| H(19A) | 2957 | 4518 | 10071 | 42 |
| H(19B) | 1801 | 3990 | 9711 | 42 |
| H(19C) | 2706 | 4822 | 9386 | 42 |
| H(20A) | 4896 | 3553 | 9933 | 47 |
| H(20B) | 4678 | 3979 | 9262 | 47 |
| H(20C) | 4996 | 2540 | 9421 | 47 |
| H(21A) | 1872 | -4042 | 7803 | 23 |
| H(22A) | 2771 | -3310 | 8664 | 24 |
| H(24A) | 4127 | -1749 | 9209 | 27 |
| H(25A) | 5253 | 75 | 9209 | 28 |
| H(26A) | 5415 | 1196 | 8347 | 25 |
| H(28A) | 4943 | 1424 | 7257 | 23 |
| H(29A) | 4083 | 651 | 6396 | 23 |
| H(31A) | 2885 | -1010 | 5849 | 22 |
| H(33A) | 1526 | -3902 | 6712 | 22 |
| H(38A) | 919 | -4753 | 5249 | 55 |
| H(38B) | 621 | -4526 | 5909 | 55 |

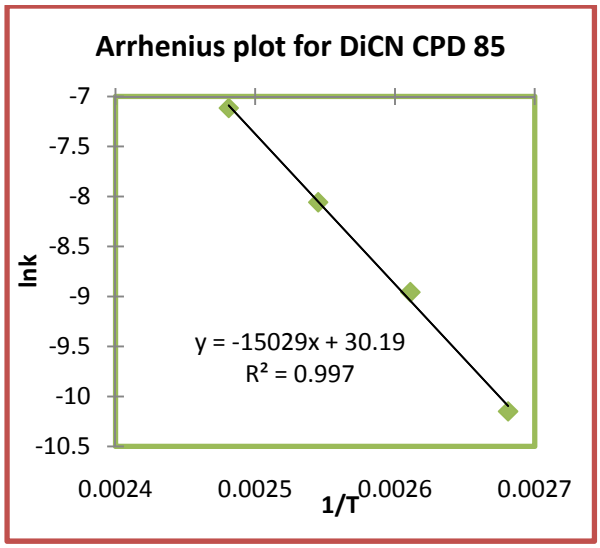
| | | | | |
|---|---|---|---|---|
| H(38C) | 1903 | -4959 | 5780 | 55 |
| H(39A) | 151 | -2597 | 5028 | 61 |
| H(39B) | 737 | -1395 | 5362 | 61 |
| H(39C) | -48 | -2347 | 5701 | 61 |
| H(40A) | 2062 | -3356 | 4753 | 51 |
| H(40B) | 3137 | -3487 | 5244 | 51 |
| H(40C) | 2645 | -2117 | 5056 | 51 |

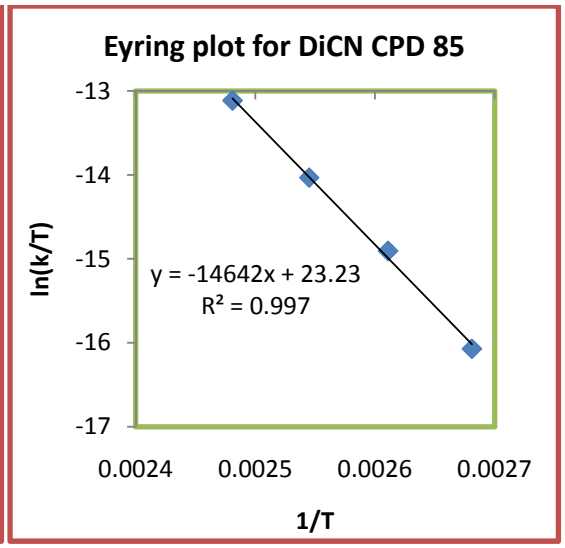
## Appendix B Thermal closing data for cyclophanedienes

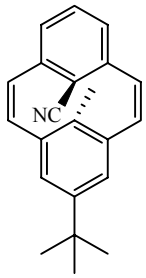



**85**

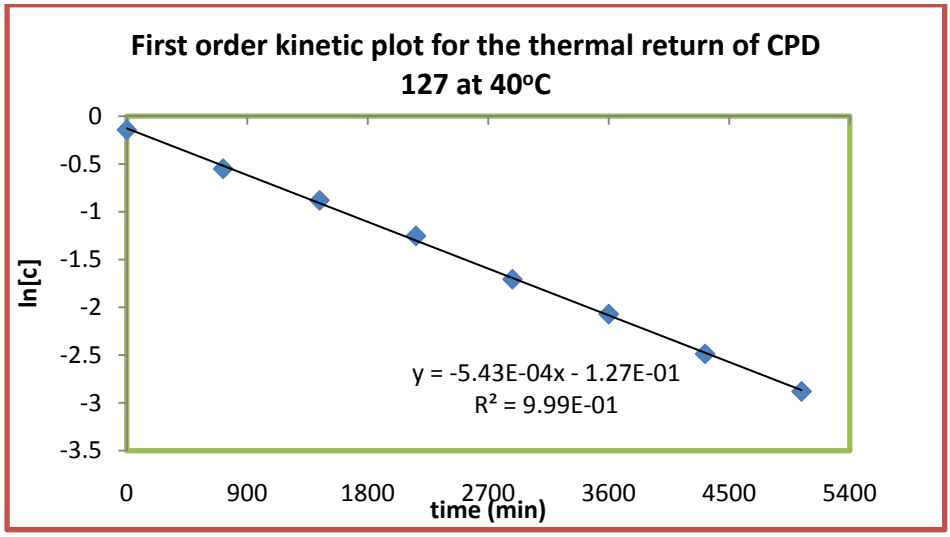


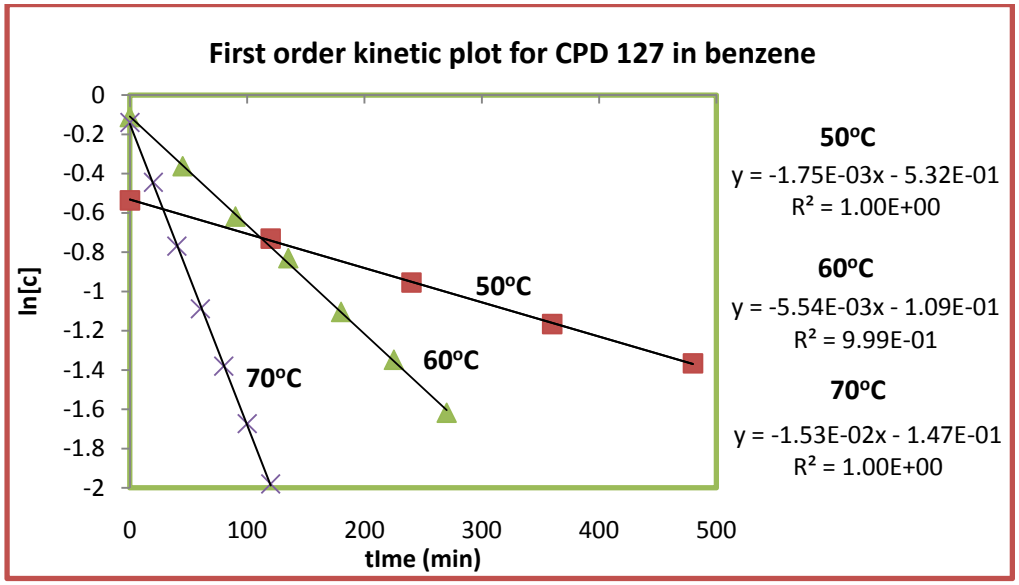



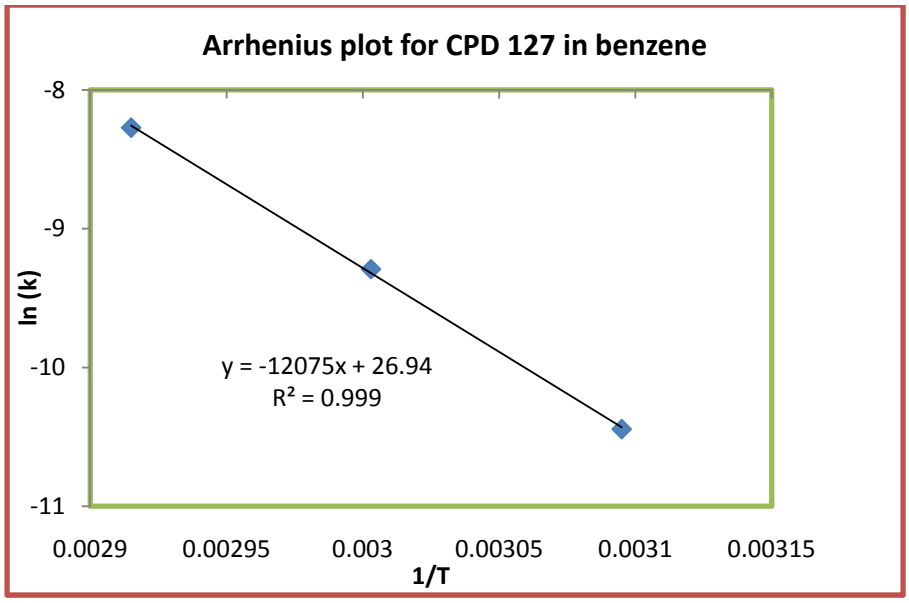



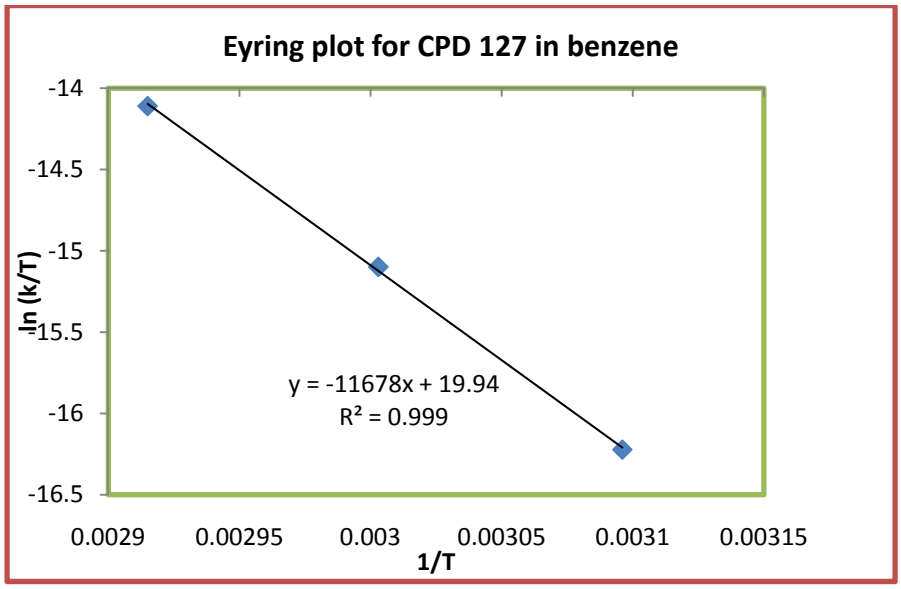

NC

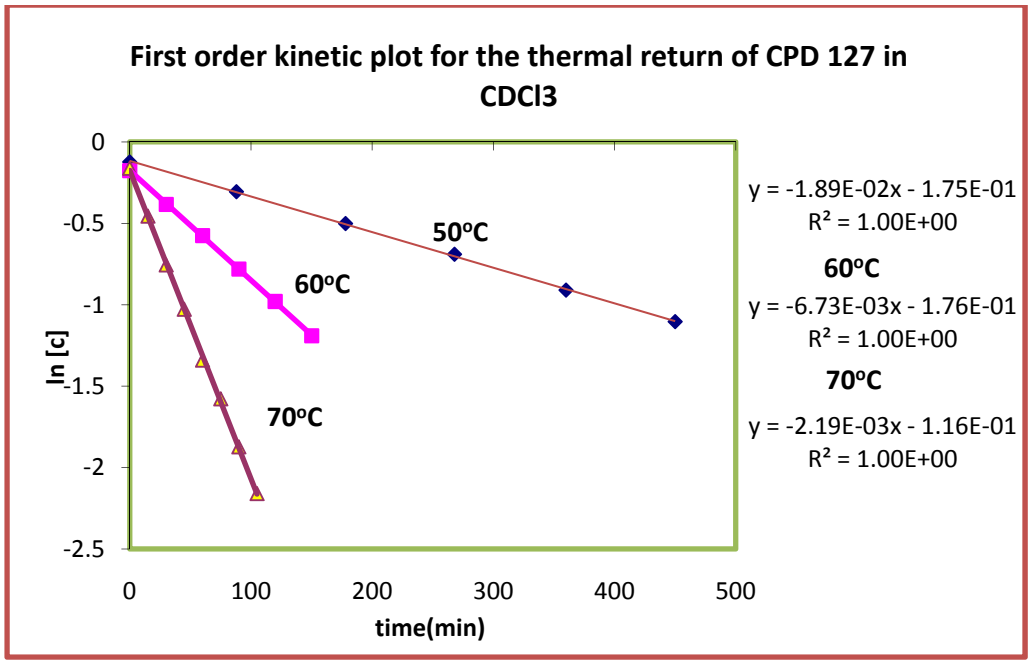
**127**

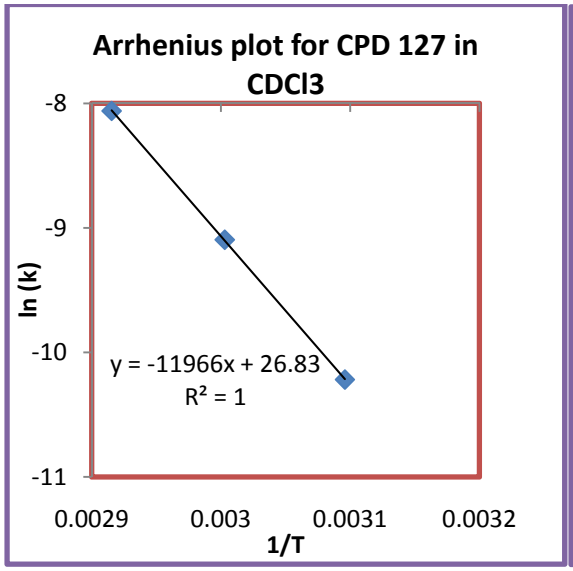

First order kinetic plot for the thermal return of CPD 127 at 40°C
ln[c]
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
0
900
1800
2700
3600
4500
5400
time (min)
y = -5.43E-04x - 1.27E-01
R² = 9.99E-01

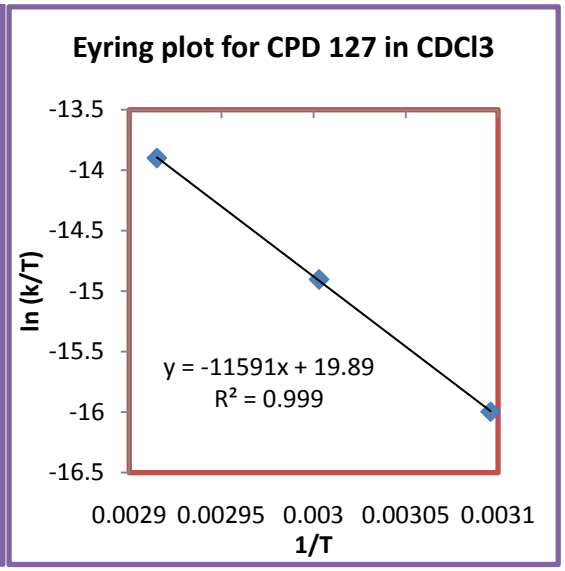

First order kinetic plot for CPD 127 in benzene
ln[c]
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-1.8
-2
0
100
200
300
400
500
tIme (min)
50°C
60°C
70°C
50°C
y = -1.75E-03x - 5.32E-01
R² = 1.00E+00
60°C
y = -5.54E-03x - 1.09E-01
R² = 9.99E-01
70°C
y = -1.53E-02x - 1.47E-01
R² = 1.00E+00

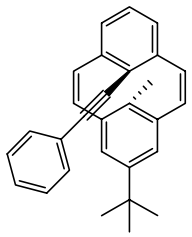

Arrhenius plot for CPD 127 in benzene
-8
-9
-10
-11
ln (k)
y = -12075x + 26.94
R² = 0.999
0.0029
0.00295
0.003
0.00305
0.0031
0.00315
1/T


Eyring plot for CPD 127 in benzene
-14
-14.5
-15
-15.5
-16
-16.5
ln (k/T)
y = -11678x + 19.94
R² = 0.999
0.0029
0.00295
0.003
0.00305
0.0031
0.00315
1/T

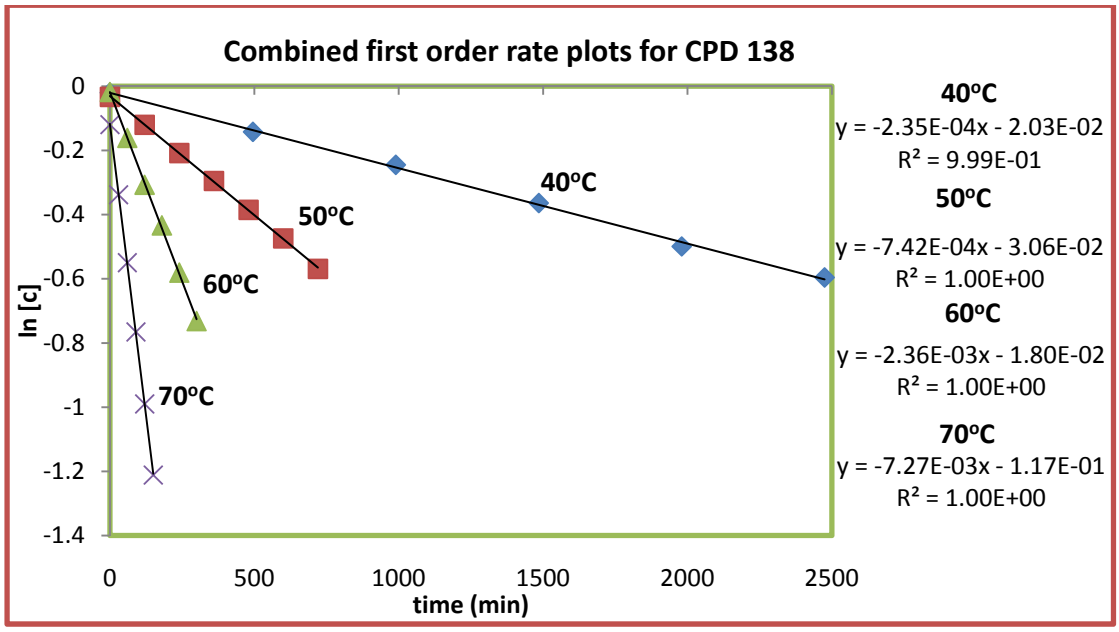

First order kinetic plot for the thermal return of CPD 127 in CDCl3
0
-0.5
-1
-1.5
-2
-2.5
ln [c]
0
100
200
300
400
500
time(min)
50°C
60°C
70°C
y = -1.89E-02x - 1.75E-01
R² = 1.00E+00
60°C
y = -6.73E-03x - 1.76E-01
R² = 1.00E+00
70°C
y = -2.19E-03x - 1.16E-01
R² = 1.00E+00

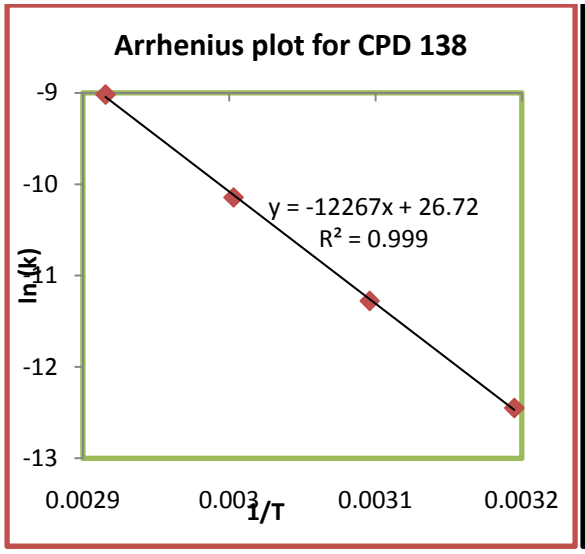

Arrhenius plot for CPD 127 in CDCl3
-8
-9
-10
-11
ln (k)
y = -11966x + 26.83
R² = 1
0.0029
0.003
0.0031
0.0032
1/T

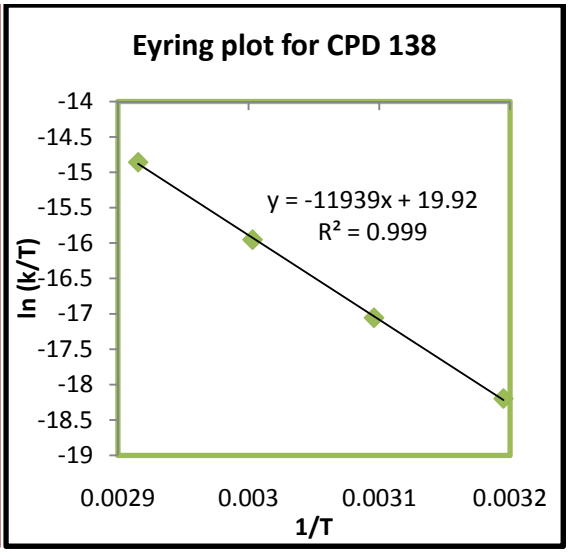

Eyring plot for CPD 127 in CDCl3
-13.5
-14
-14.5
-15
-15.5
-16
-16.5
ln (k/T)
y = -11591x + 19.89
R² = 0.999
0.0029
0.00295
0.003
0.00305
0.0031
1/T

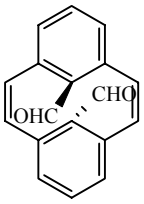


**138**

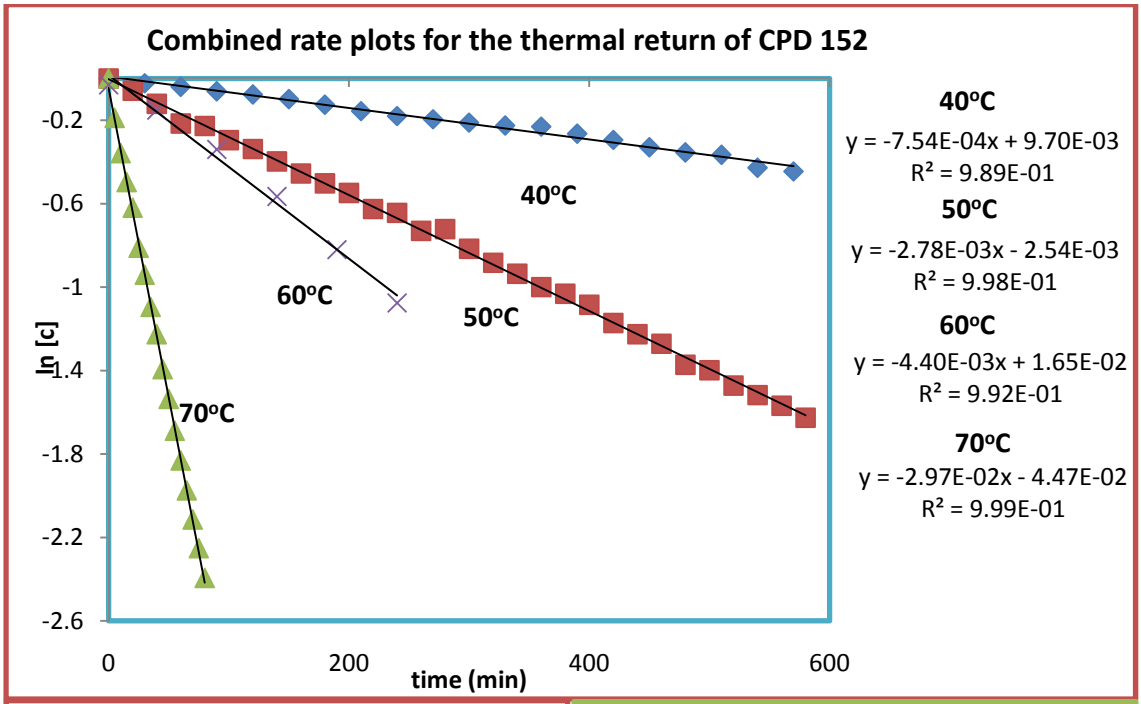

Combined first order rate plots for CPD 138
ln [c]
time (min)
40°C
50°C
60°C
70°C
y = -2.35E-04x - 2.03E-02
R² = 9.99E-01
y = -7.42E-04x - 3.06E-02
R² = 1.00E+00
y = -2.36E-03x - 1.80E-02
R² = 1.00E+00
y = -7.27E-03x - 1.17E-01
R² = 1.00E+00

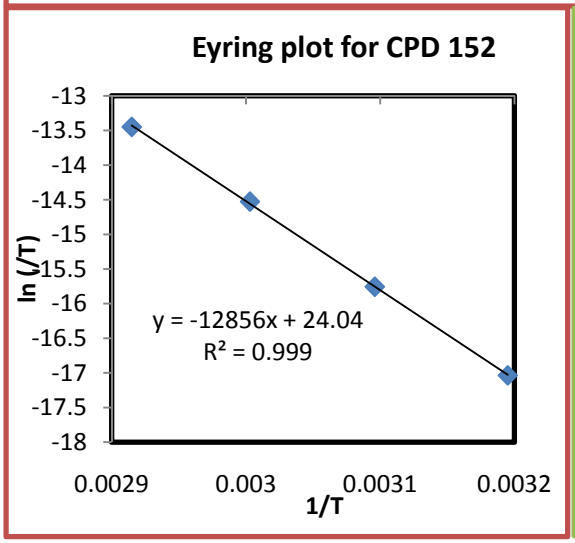

Arrhenius plot for CPD 138
ln (k)
1/T
y = -12267x + 26.72
R² = 0.999

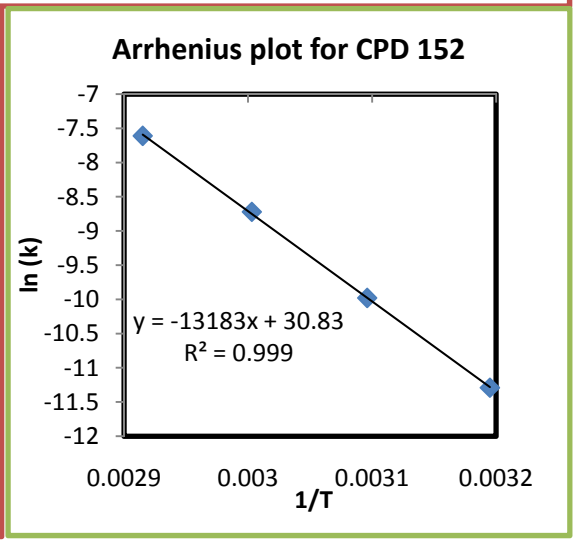

Eyring plot for CPD 138
ln (k/T)
1/T
y = -11939x + 19.92
R² = 0.999

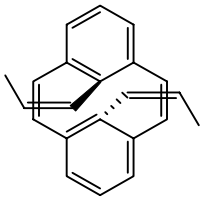

OHC
CHO

**152**

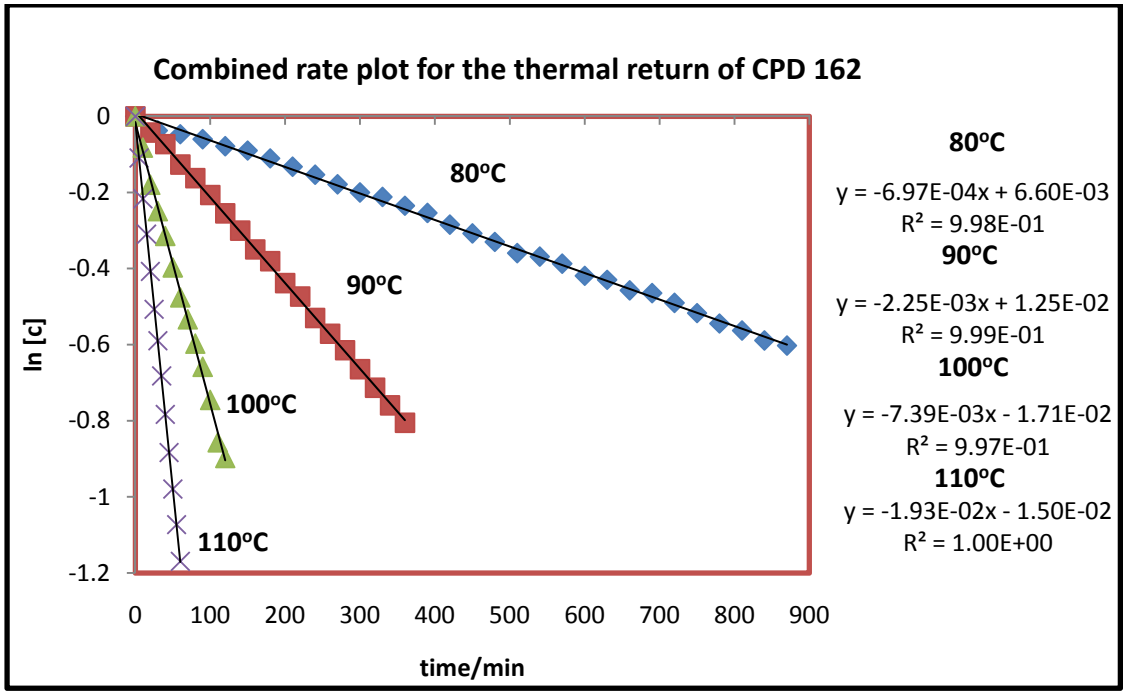

Combined rate plots for the thermal return of CPD 152
ln [c]
time (min)
40°C
60°C
50°C
70°C
40°C
y = -7.54E-04x + 9.70E-03
R² = 9.89E-01
50°C
y = -2.78E-03x - 2.54E-03
R² = 9.98E-01
60°C
y = -4.40E-03x + 1.65E-02
R² = 9.92E-01
70°C
y = -2.97E-02x - 4.47E-02
R² = 9.99E-01

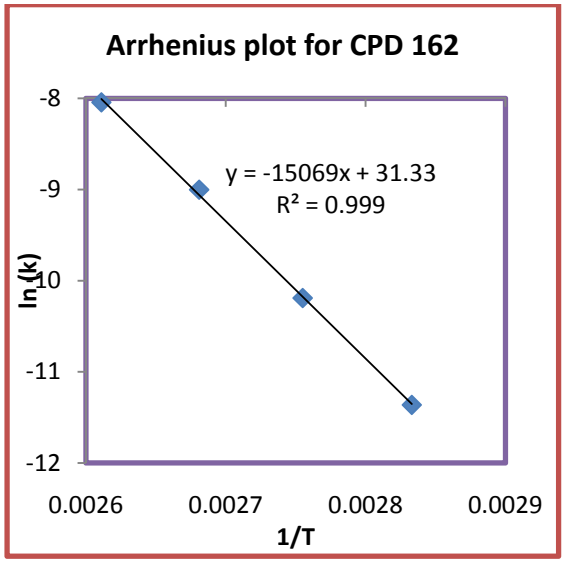

Eyring plot for CPD 152
ln (k/T)
1/T
y = -12856x + 24.04
R² = 0.999

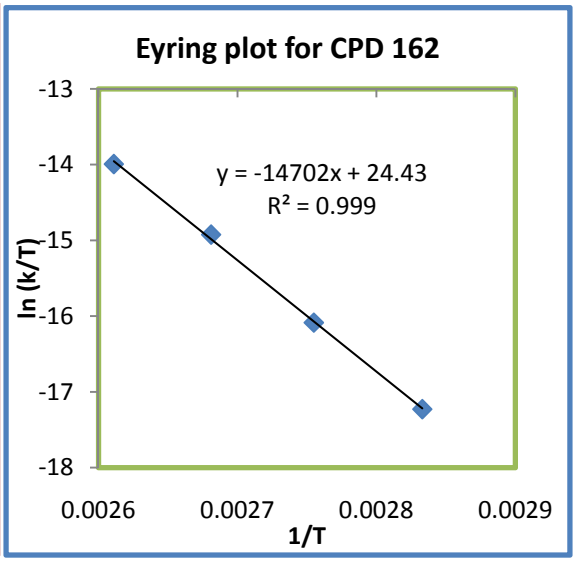

Arrhenius plot for CPD 152
ln (k)
1/T
y = -13183x + 30.83
R² = 0.999

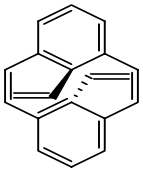


**162**

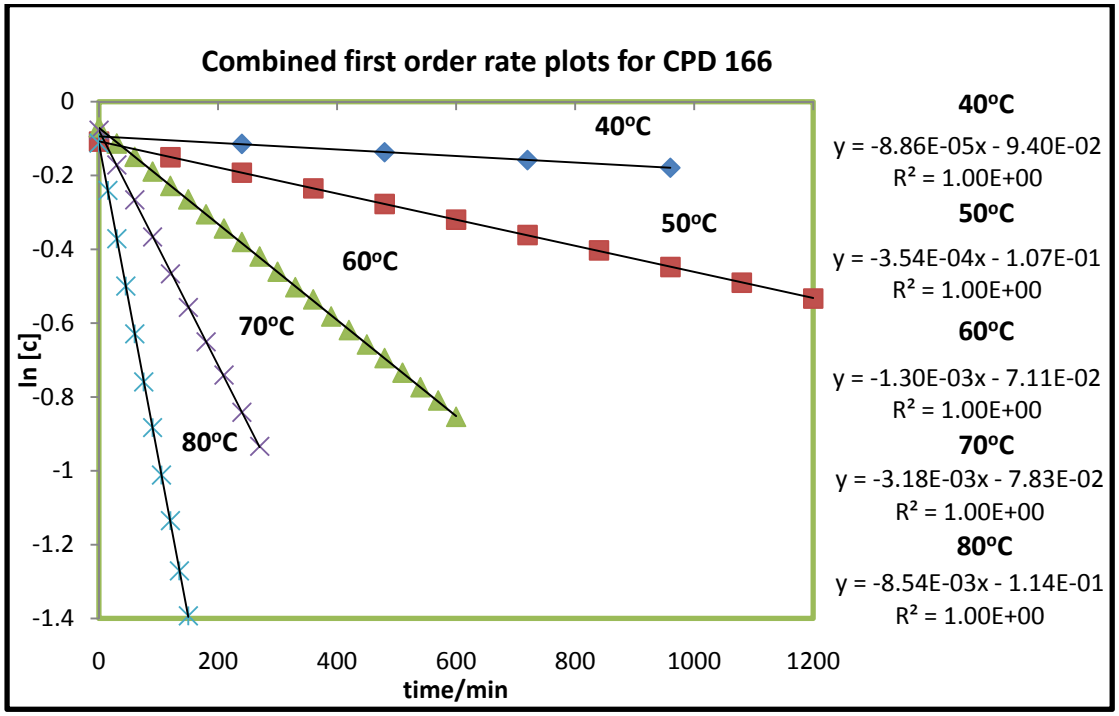

Combined rate plot for the thermal return of CPD 162
ln [c]
time/min
80°C
90°C
100°C
110°C
80°C
y = -6.97E-04x + 6.60E-03
R² = 9.98E-01
90°C
y = -2.25E-03x + 1.25E-02
R² = 9.99E-01
100°C
y = -7.39E-03x - 1.71E-02
R² = 9.97E-01
110°C
y = -1.93E-02x - 1.50E-02
R² = 1.00E+00

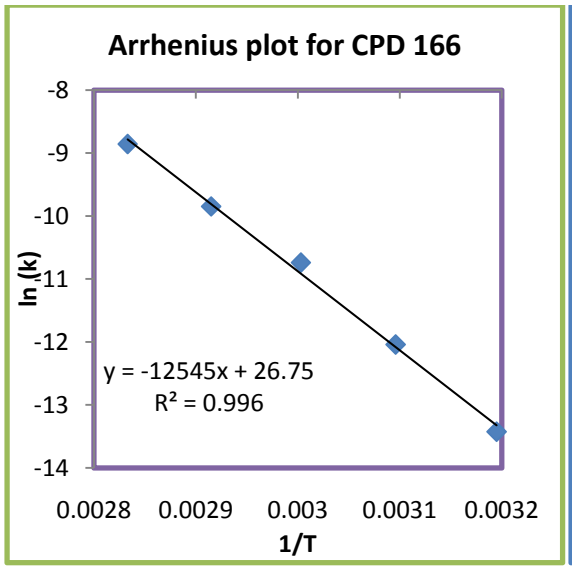

Arrhenius plot for CPD 162
ln (k)
1/T
y = -15069x + 31.33
R² = 0.999

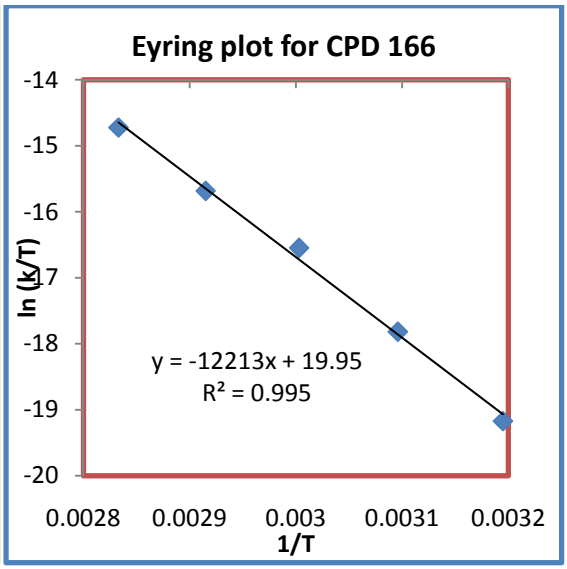

Eyring plot for CPD 162
ln (k/T)
1/T
y = -14702x + 24.43
R² = 0.999

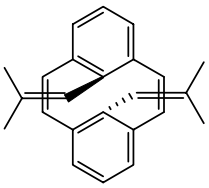


**166**

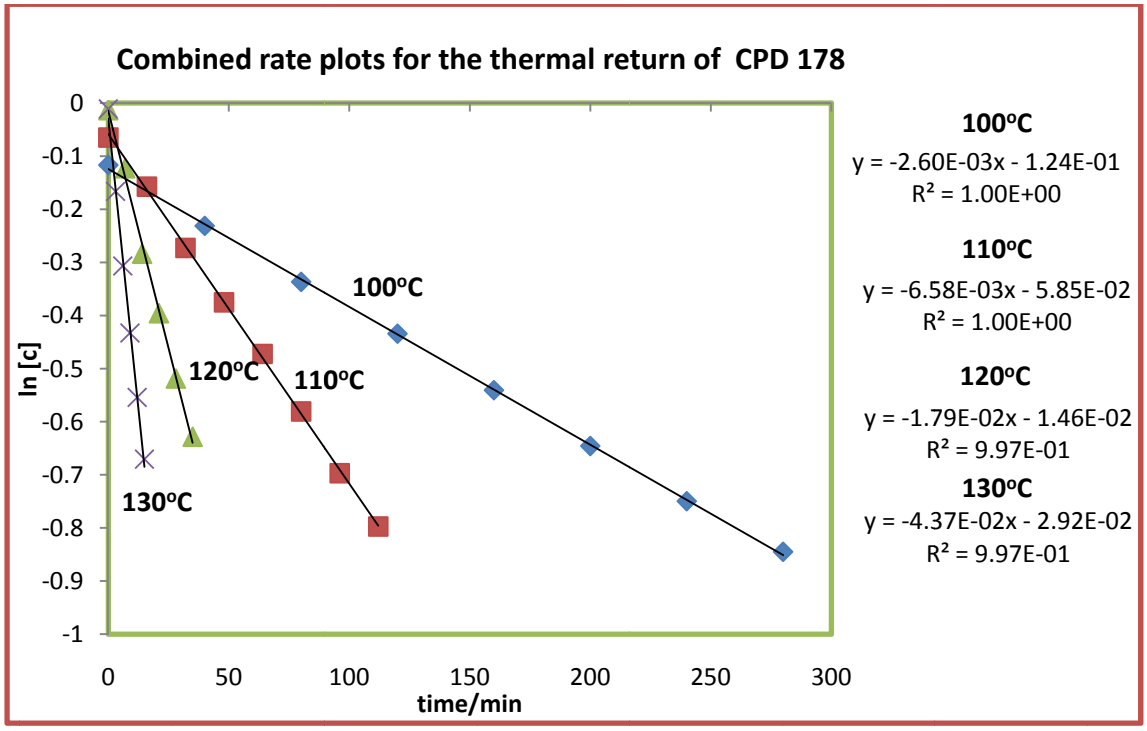

Combined first order rate plots for CPD 166
ln [c]
time/min
40°C
50°C
60°C
70°C
80°C
40°C
y = -8.86E-05x - 9.40E-02
R² = 1.00E+00
50°C
y = -3.54E-04x - 1.07E-01
R² = 1.00E+00
60°C
y = -1.30E-03x - 7.11E-02
R² = 1.00E+00
70°C
y = -3.18E-03x - 7.83E-02
R² = 1.00E+00
80°C
y = -8.54E-03x - 1.14E-01
R² = 1.00E+00

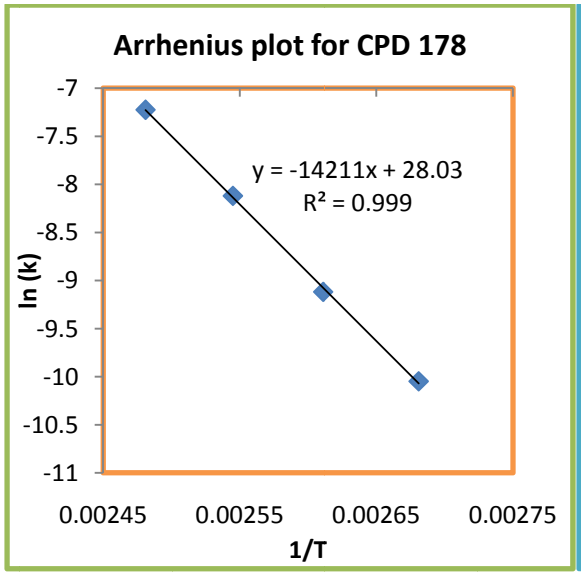

Arrhenius plot for CPD 166
ln (k)
1/T
y = -12545x + 26.75
R² = 0.996

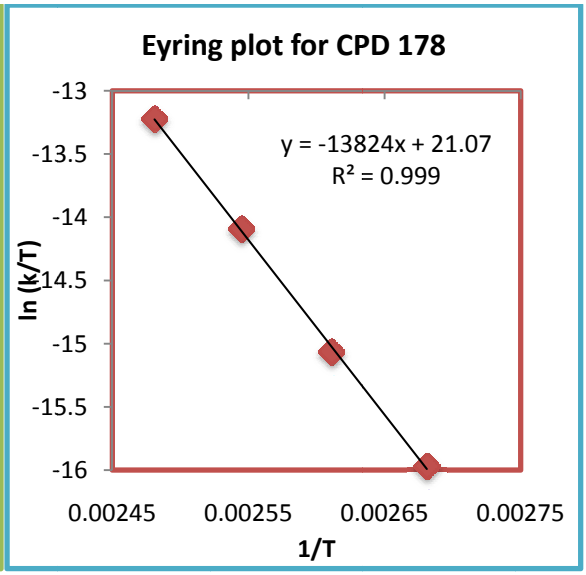

Eyring plot for CPD 166
ln (k/T)
1/T
y = -12213x + 19.95
R² = 0.995

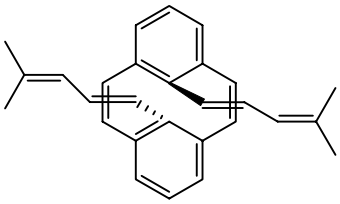


**178**

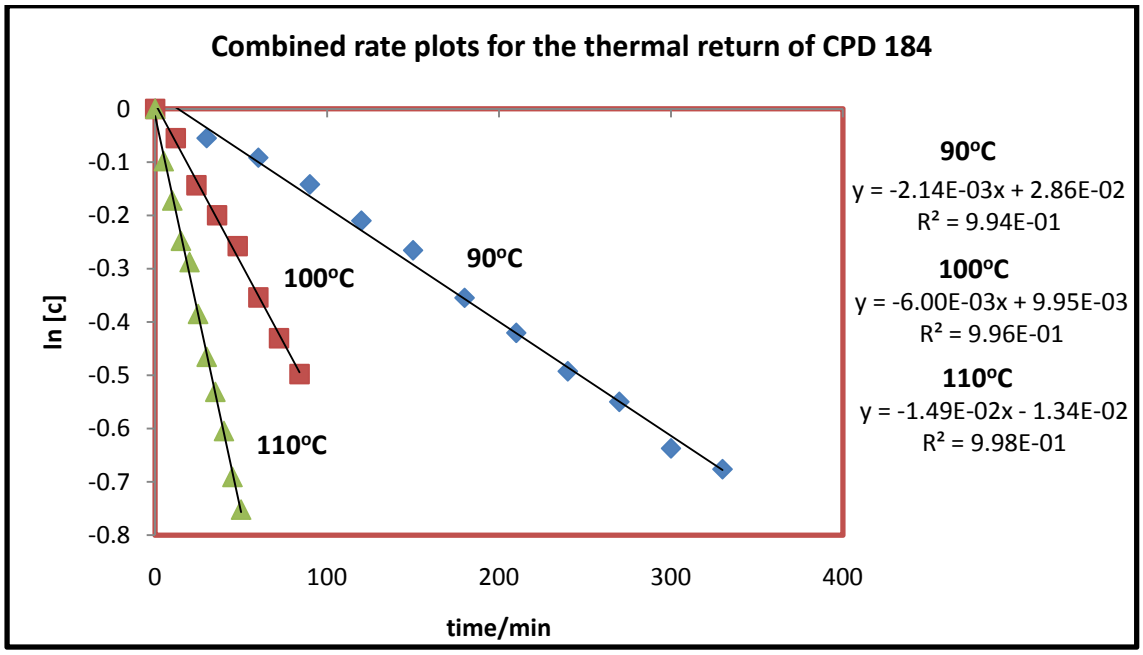

Combined rate plots for the thermal return of CPD 178
ln [c]
time/min
100°C
120°C
110°C
130°C
100°C
y = -2.60E-03x - 1.24E-01
R² = 1.00E+00
110°C
y = -6.58E-03x - 5.85E-02
R² = 1.00E+00
120°C
y = -1.79E-02x - 1.46E-02
R² = 9.97E-01
130°C
y = -4.37E-02x - 2.92E-02
R² = 9.97E-01

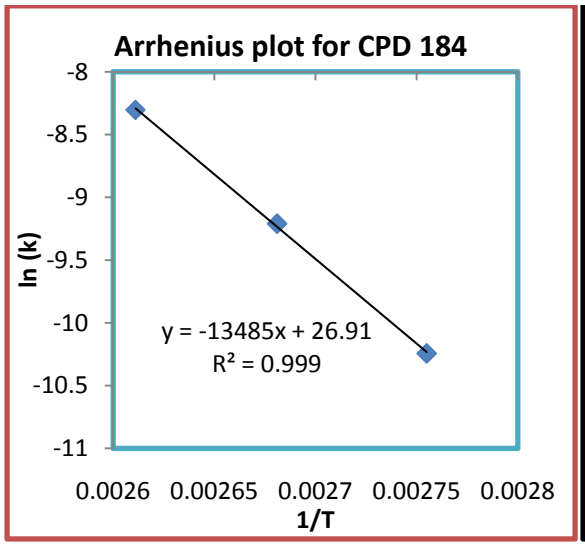

Arrhenius plot for CPD 178
ln (k)
1/T
y = -14211x + 28.03
R² = 0.999

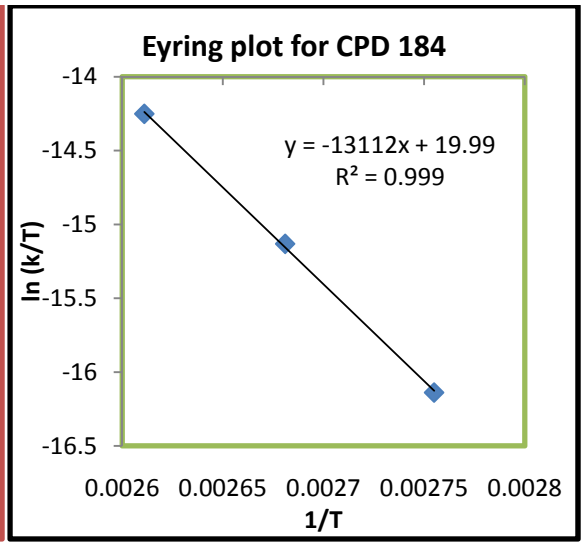

Eyring plot for CPD 178
ln (k/T)
1/T
y = -13824x + 21.07
R² = 0.999

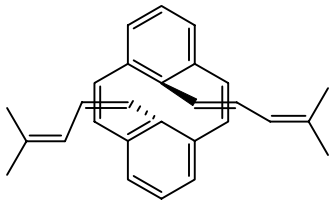


**184**

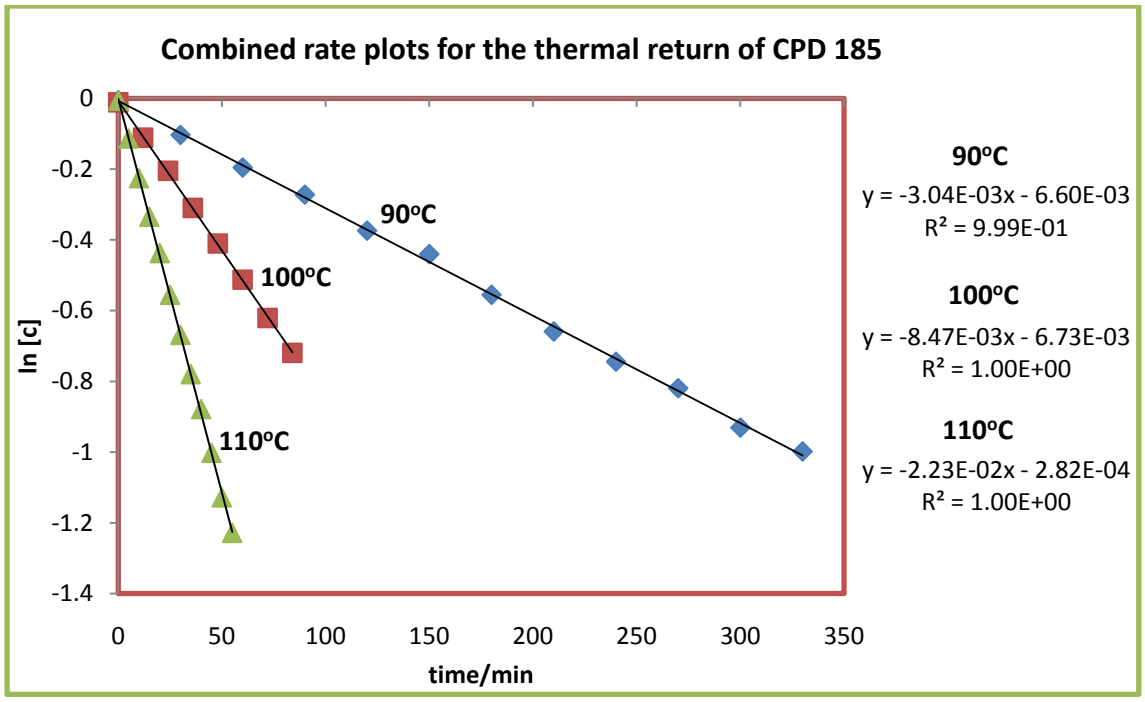

Combined rate plots for the thermal return of CPD 184
ln [c]
time/min
90°C
100°C
110°C
90°C
y = -2.14E-03x + 2.86E-02
R² = 9.94E-01
100°C
y = -6.00E-03x + 9.95E-03
R² = 9.96E-01
110°C
y = -1.49E-02x - 1.34E-02
R² = 9.98E-01

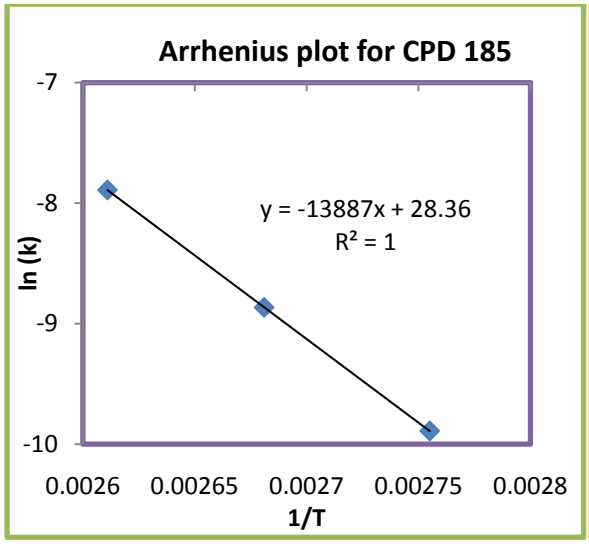

Arrhenius plot for CPD 184
ln (k)
1/T
y = -13485x + 26.91
R² = 0.999

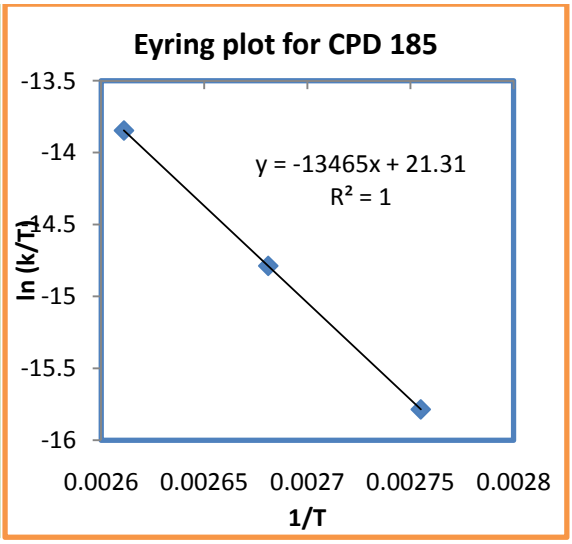

Eyring plot for CPD 184
ln (k/T)
1/T
y = -13112x + 19.99
R² = 0.999

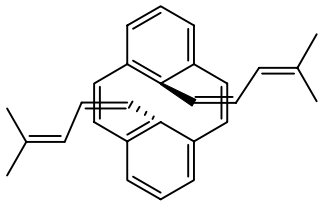


**185**

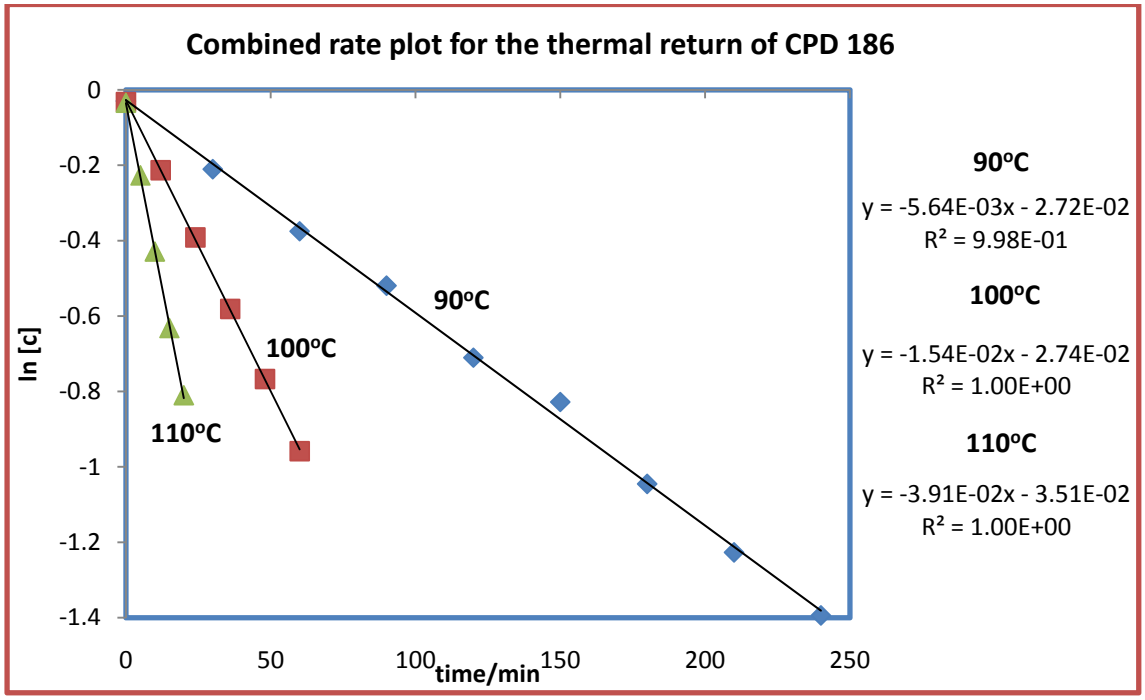

Combined rate plots for the thermal return of CPD 185
ln [c]
time/min
90°C
100°C
110°C
90°C
y = -3.04E-03x - 6.60E-03
R² = 9.99E-01
100°C
y = -8.47E-03x - 6.73E-03
R² = 1.00E+00
110°C
y = -2.23E-02x - 2.82E-04
R² = 1.00E+00

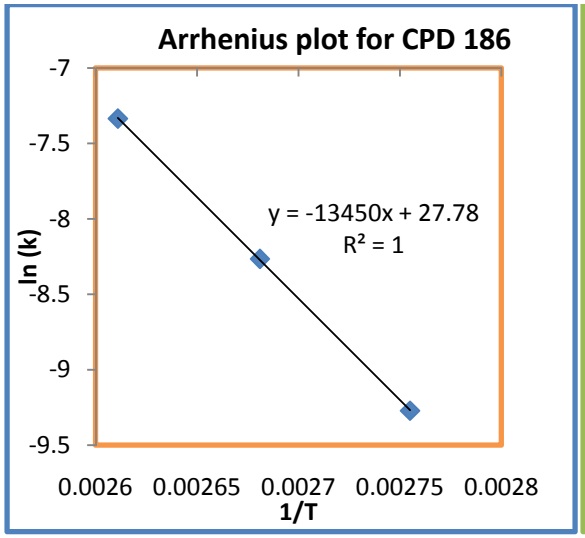

Arrhenius plot for CPD 185
ln (k)
1/T
y = -13887x + 28.36
R² = 1

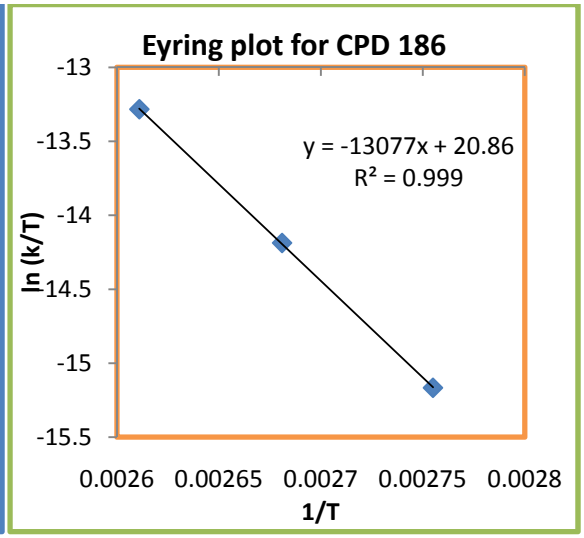

Eyring plot for CPD 185
ln (k/T)
1/T
y = -13465x + 21.31
R² = 1

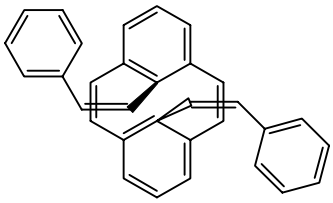


**186**

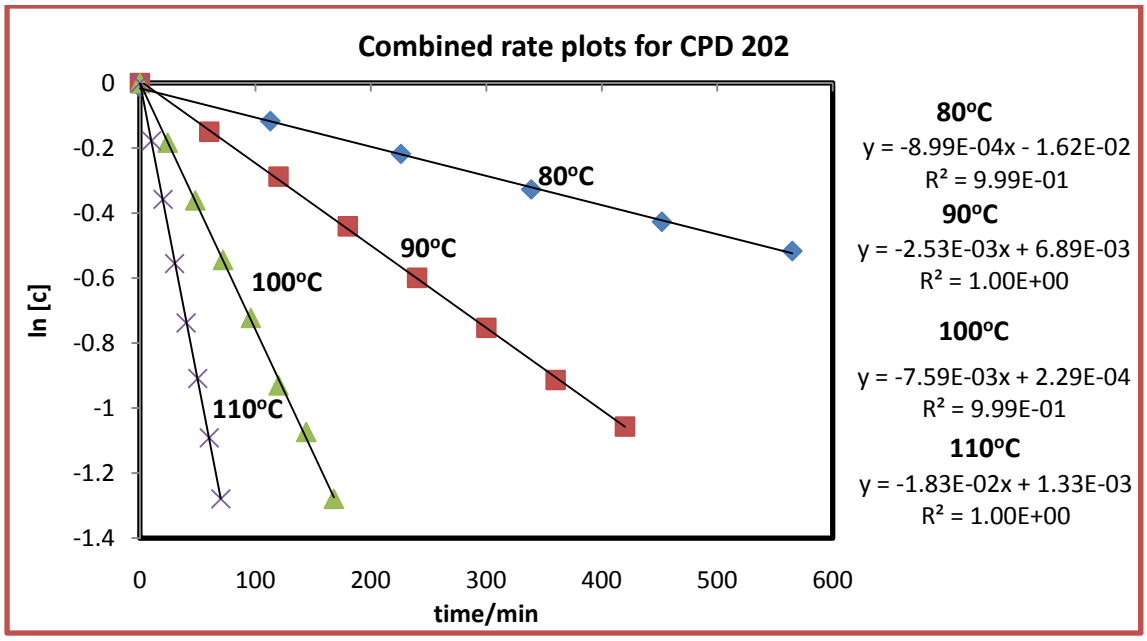

Combined rate plot for the thermal return of CPD 186
ln [c]
time/min
90°C
100°C
110°C
90°C
y = -5.64E-03x - 2.72E-02
R² = 9.98E-01
100°C
y = -1.54E-02x - 2.74E-02
R² = 1.00E+00
110°C
y = -3.91E-02x - 3.51E-02
R² = 1.00E+00

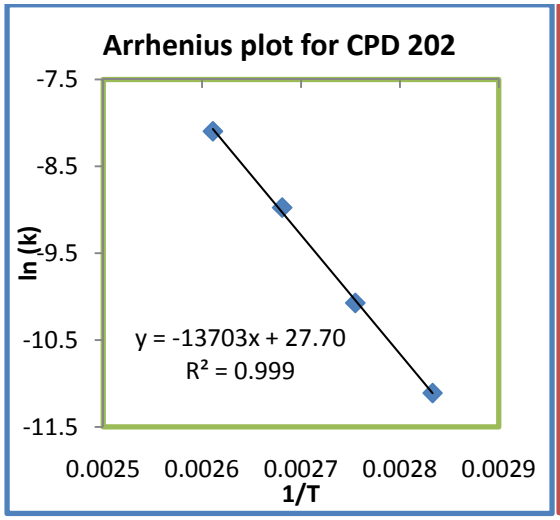

Arrhenius plot for CPD 186
ln (k)
1/T
y = -13450x + 27.78
R² = 1

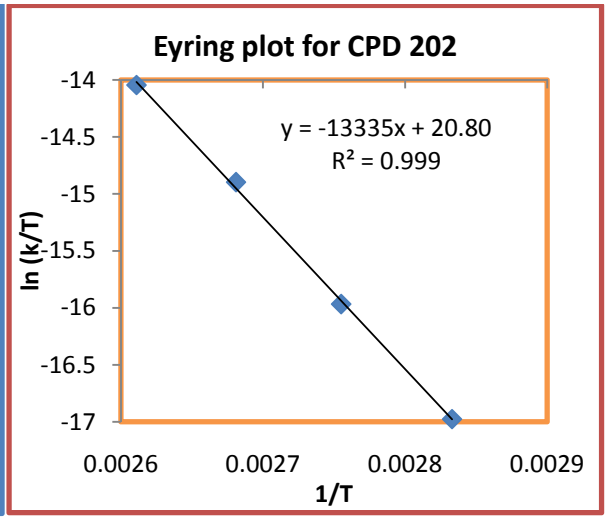

Eyring plot for CPD 186
ln (k/T)
1/T
y = -13077x + 20.86
R² = 0.999

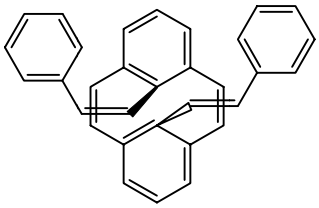


**202**

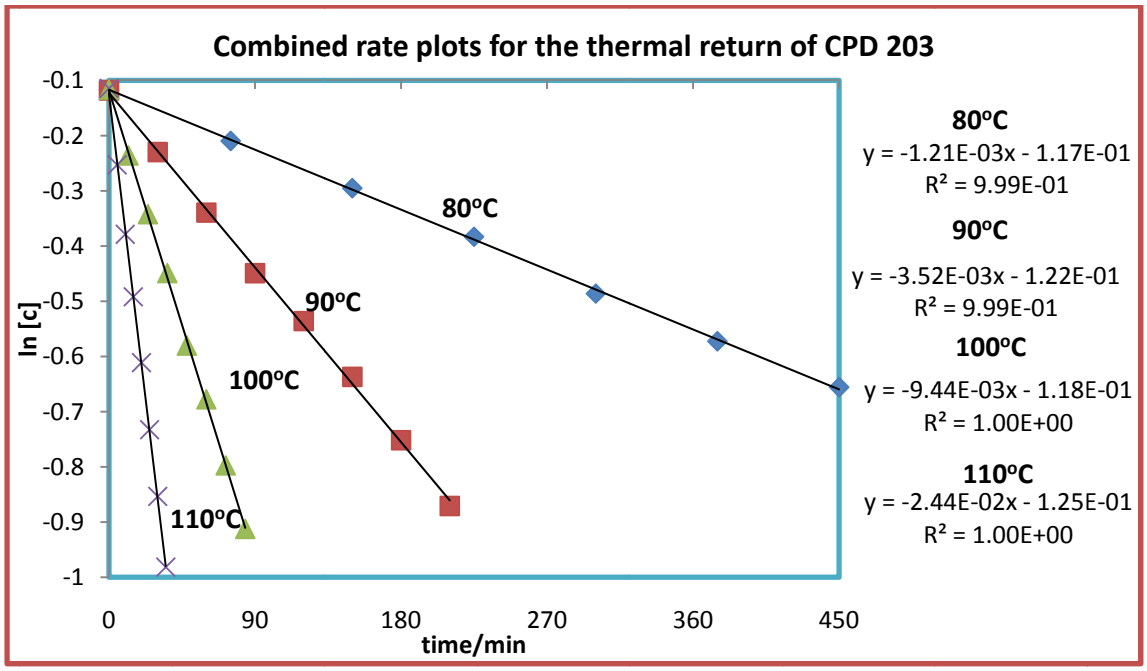

Combined rate plots for CPD 202
ln [c]
time/min
80°C
90°C
100°C
110°C
80°C
y = -8.99E-04x - 1.62E-02
R² = 9.99E-01
90°C
y = -2.53E-03x + 6.89E-03
R² = 1.00E+00
100°C
y = -7.59E-03x + 2.29E-04
R² = 9.99E-01
110°C
y = -1.83E-02x + 1.33E-03
R² = 1.00E+00

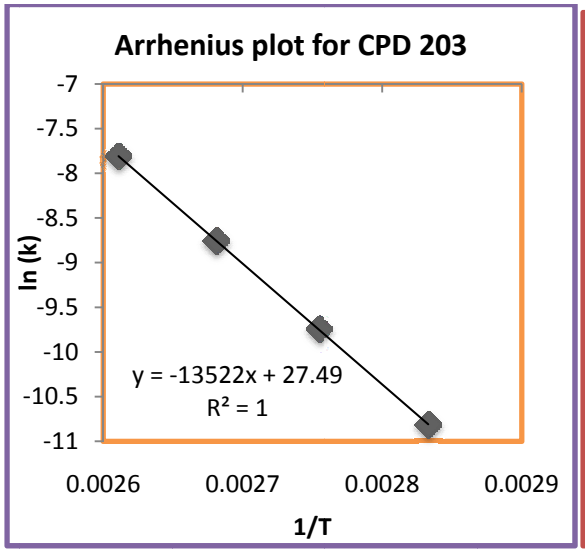

Arrhenius plot for CPD 202
ln (k)
1/T
y = -13703x + 27.70
R² = 0.999

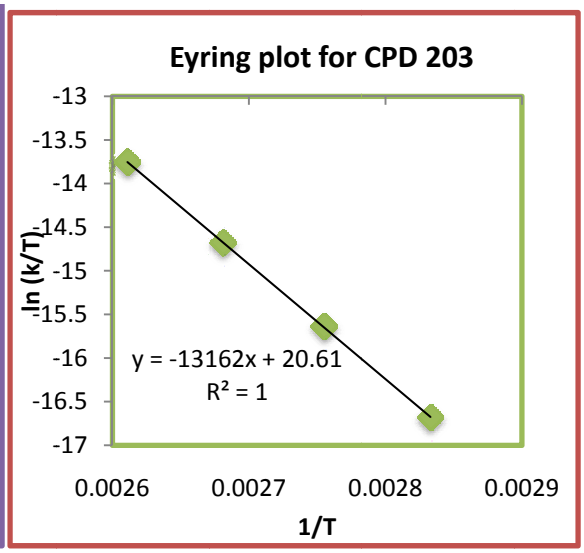

Eyring plot for CPD 202
ln (k/T)
1/T
y = -13335x + 20.80
R² = 0.999

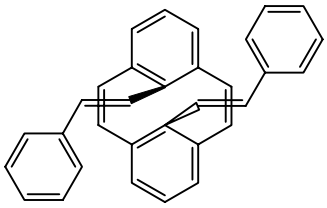


**203**

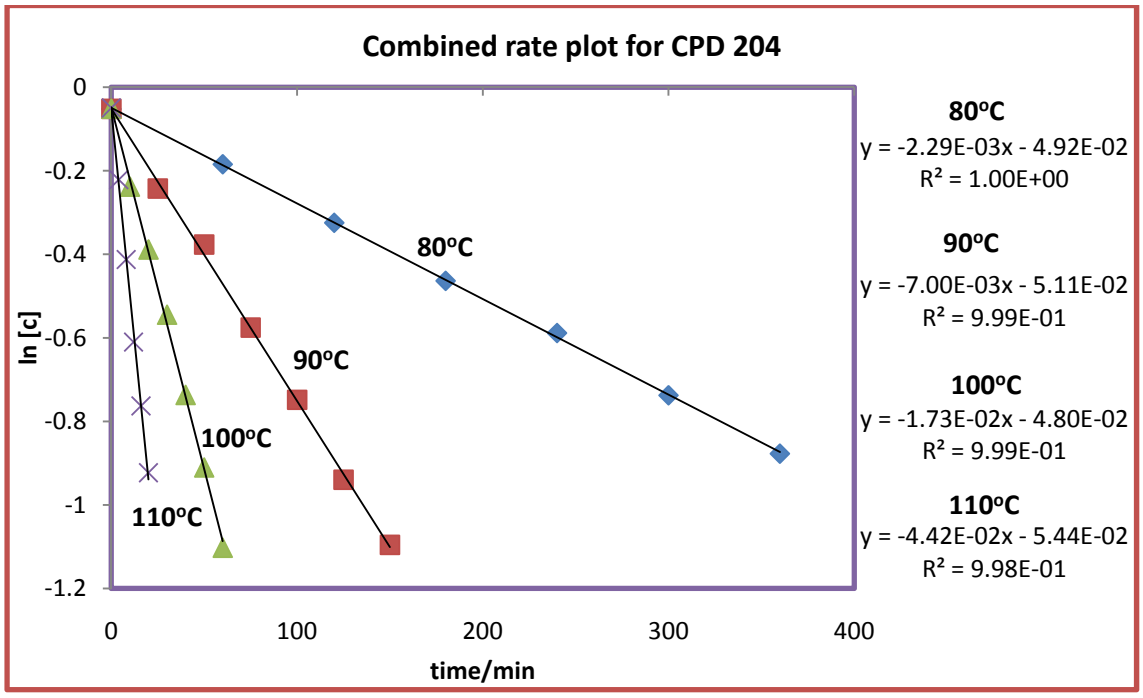

Combined rate plots for the thermal return of CPD 203
ln [c]
time/min
80°C
90°C
100°C
110°C
80°C
y = -1.21E-03x - 1.17E-01
R² = 9.99E-01
90°C
y = -3.52E-03x - 1.22E-01
R² = 9.99E-01
100°C
y = -9.44E-03x - 1.18E-01
R² = 1.00E+00
110°C
y = -2.44E-02x - 1.25E-01
R² = 1.00E+00

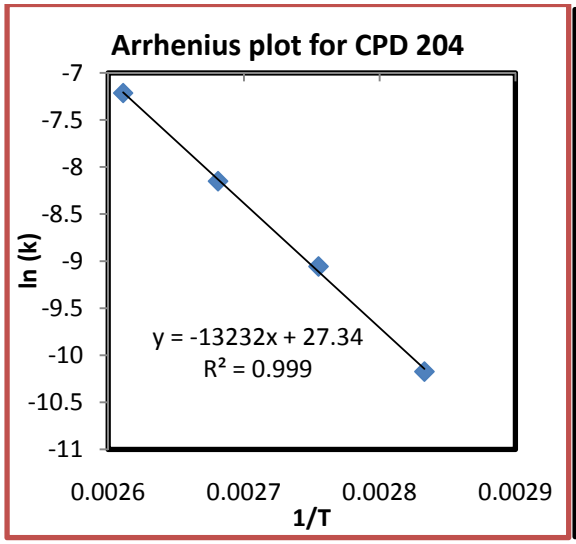

Arrhenius plot for CPD 203
ln (k)
1/T
y = -13522x + 27.49
R² = 1

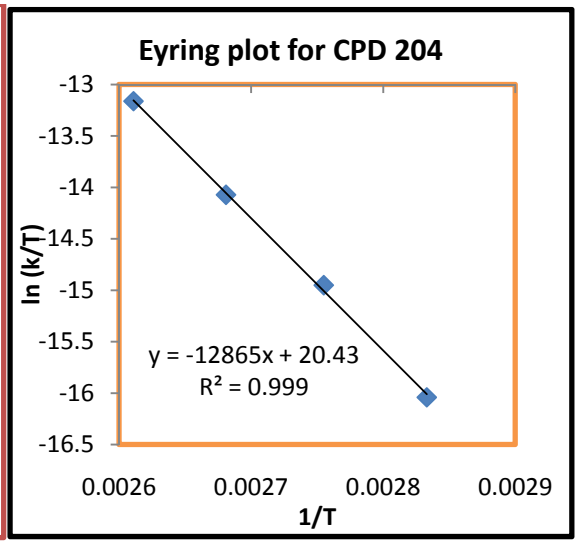

Eyring plot for CPD 203
ln (k/T)
1/T
y = -13162x + 20.61
R² = 1

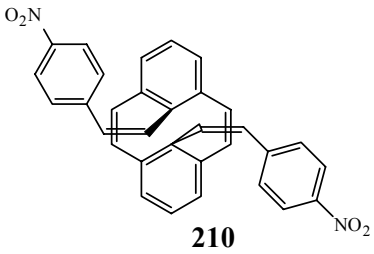


**204**

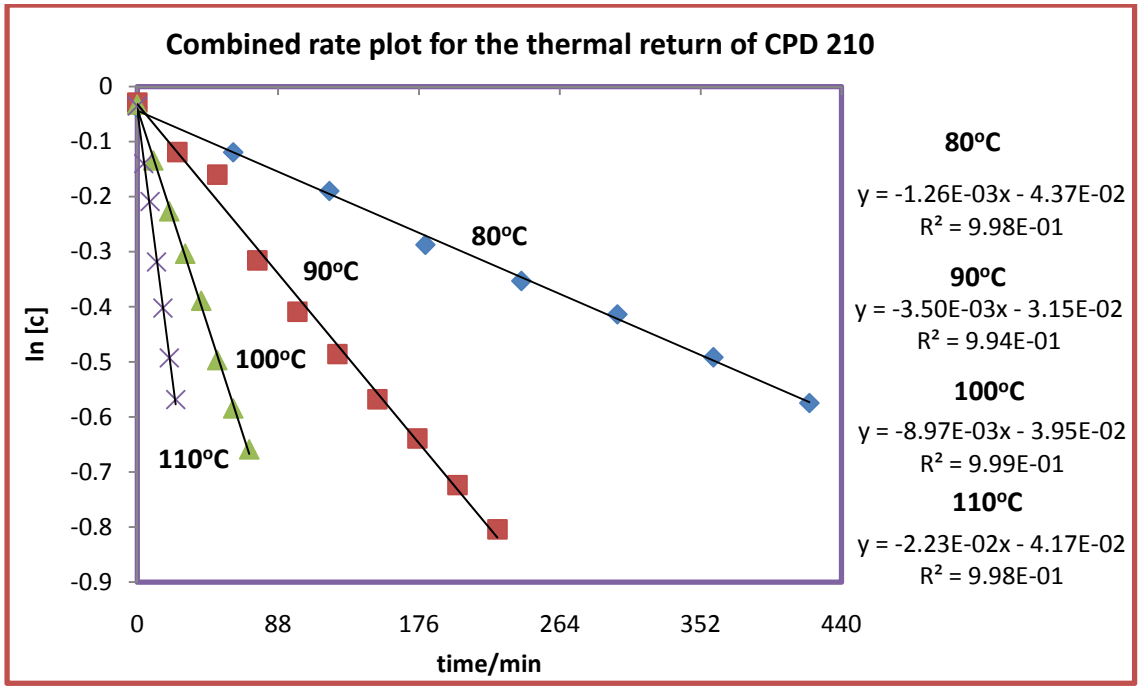

Combined rate plot for CPD 204
ln [c]
time/min
80°C
90°C
100°C
110°C
80°C
y = -2.29E-03x - 4.92E-02
R² = 1.00E+00
90°C
y = -7.00E-03x - 5.11E-02
R² = 9.99E-01
100°C
y = -1.73E-02x - 4.80E-02
R² = 9.99E-01
110°C
y = -4.42E-02x - 5.44E-02
R² = 9.98E-01

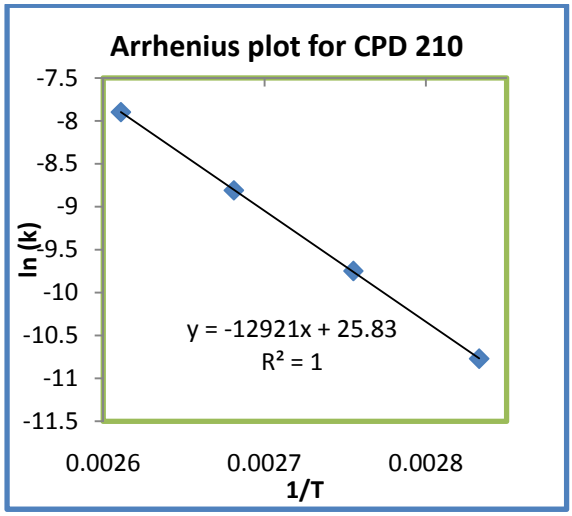

Arrhenius plot for CPD 204
ln (k)
1/T
y = -13232x + 27.34
R² = 0.999

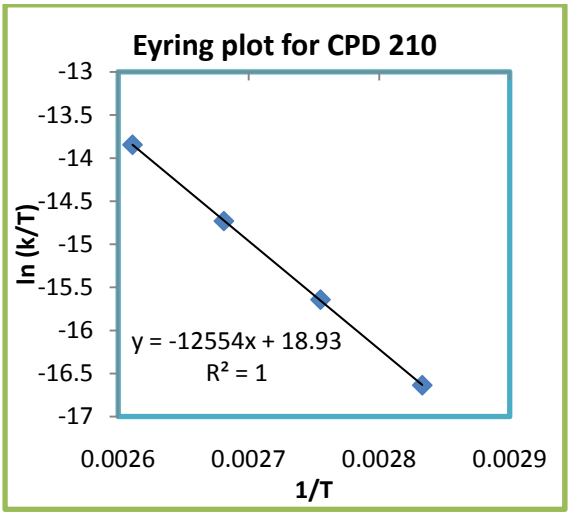

Eyring plot for CPD 204
ln (k/T)
1/T
y = -12865x + 20.43
R² = 0.999

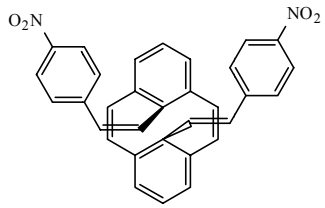

O2N
NO2

**210**

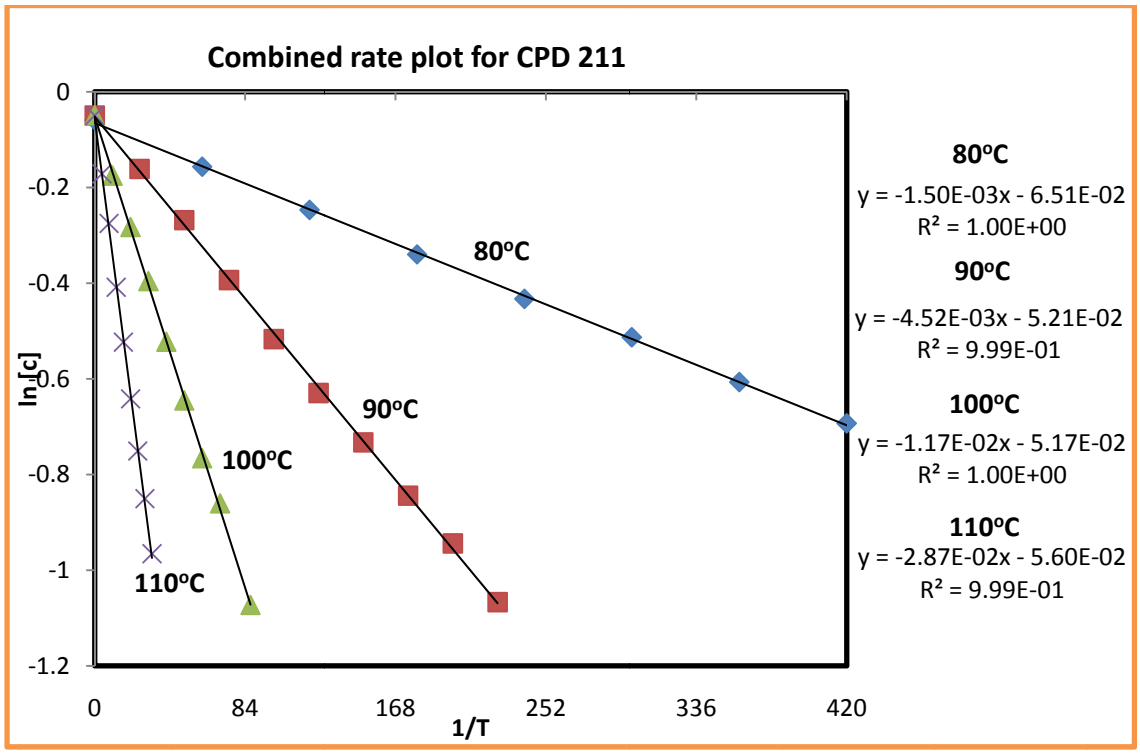

Combined rate plot for the thermal return of CPD 210
ln [c]
time/min
80°C
90°C
100°C
110°C
80°C
y = -1.26E-03x - 4.37E-02
R² = 9.98E-01
90°C
y = -3.50E-03x - 3.15E-02
R² = 9.94E-01
100°C
y = -8.97E-03x - 3.95E-02
R² = 9.99E-01
110°C
y = -2.23E-02x - 4.17E-02
R² = 9.98E-01

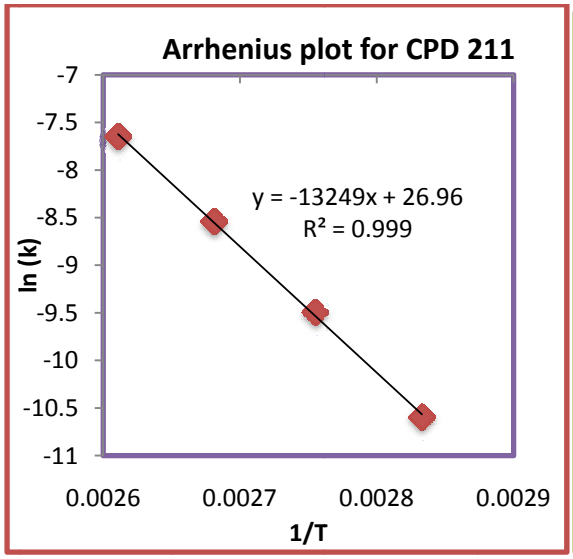

Arrhenius plot for CPD 210
ln (k)
1/T
y = -12921x + 25.83
R² = 1

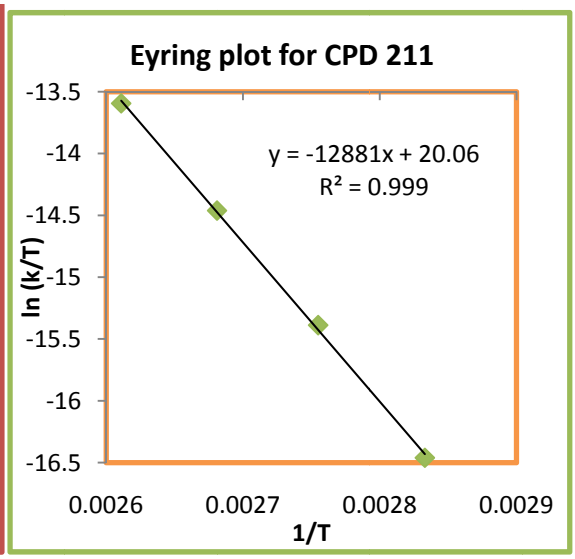

Eyring plot for CPD 210
ln (k/T)
1/T
y = -12554x + 18.93
R² = 1

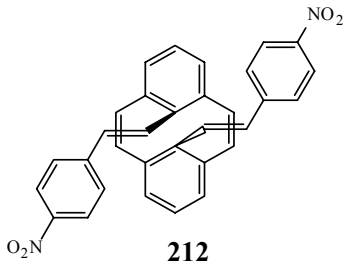

O2N
NO2

**211**

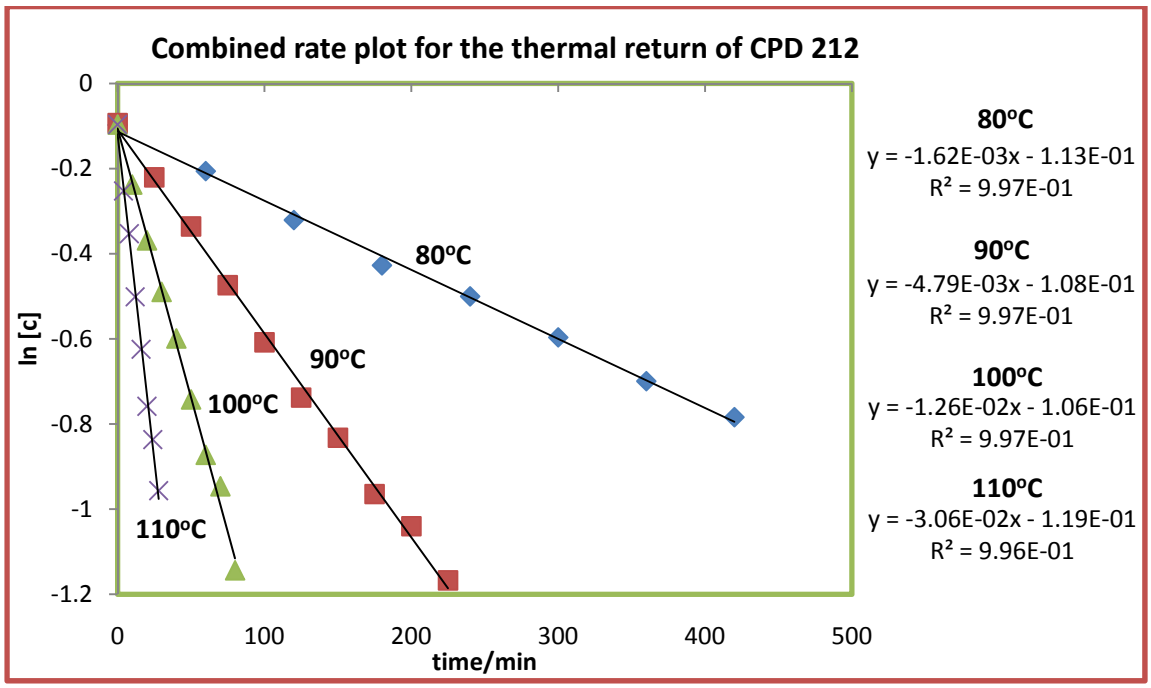

Combined rate plot for CPD 211
ln [c]
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
0
84
168
252
336
420
1/T
80°C
90°C
100°C
110°C
80°C
y = -1.50E-03x - 6.51E-02
R² = 1.00E+00
90°C
y = -4.52E-03x - 5.21E-02
R² = 9.99E-01
100°C
y = -1.17E-02x - 5.17E-02
R² = 1.00E+00
110°C
y = -2.87E-02x - 5.60E-02
R² = 9.99E-01

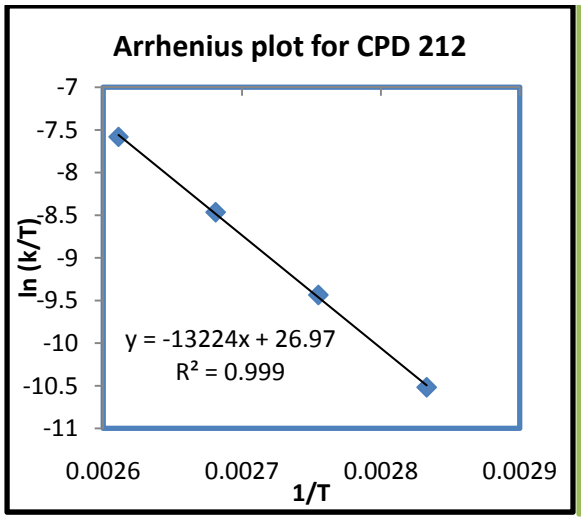

Arrhenius plot for CPD 211
ln (k)
-7
-7.5
-8
-8.5
-9
-9.5
-10
-10.5
-11
0.0026
0.0027
0.0028
0.0029
1/T
y = -13249x + 26.96
R² = 0.999

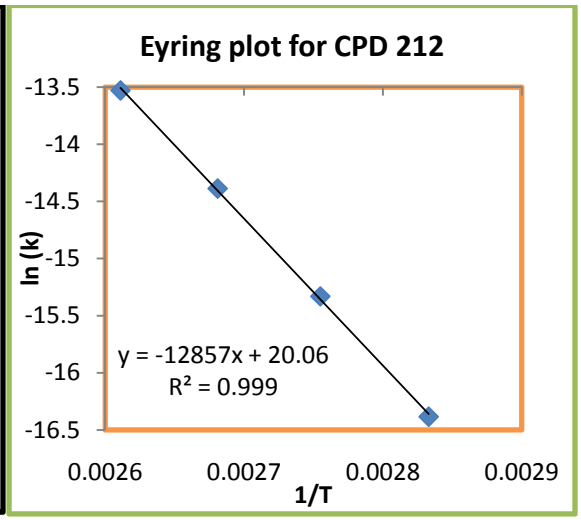

Eyring plot for CPD 211
ln (k/T)
-13.5
-14
-14.5
-15
-15.5
-16
-16.5
0.0026
0.0027
0.0028
0.0029
1/T
y = -12881x + 20.06
R² = 0.999

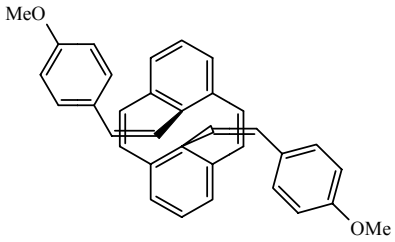

NO2
O2N

**212**

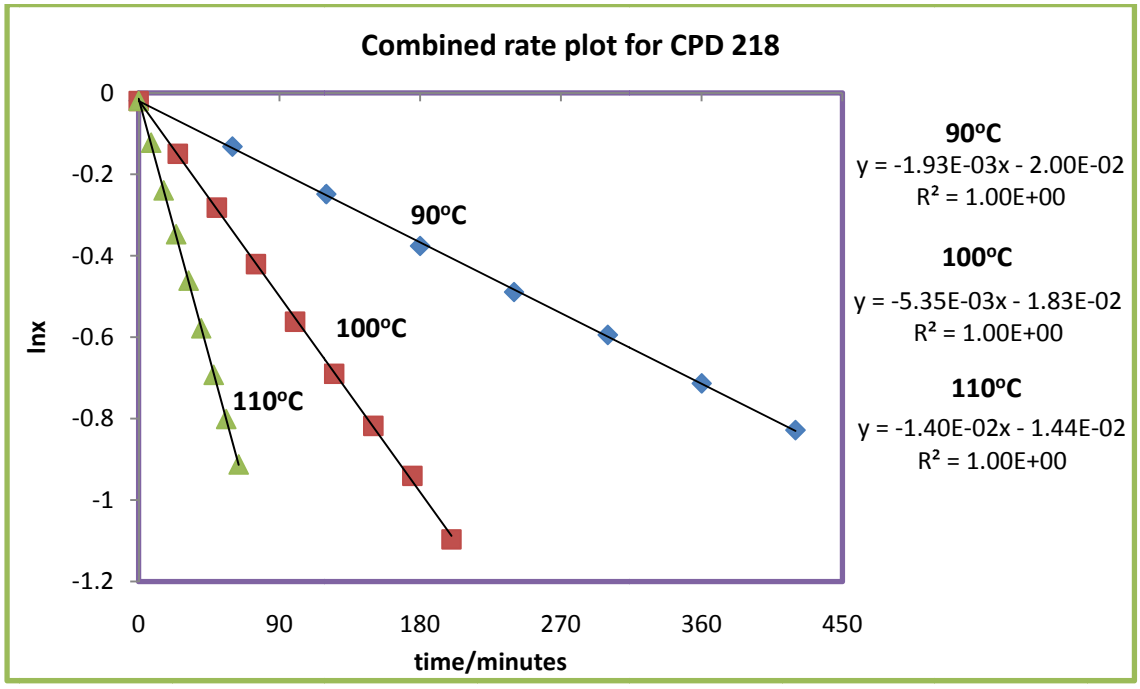

Combined rate plot for the thermal return of CPD 212
ln [c]
time/min
80°C
90°C
100°C
110°C
80°C
y = -1.62E-03x - 1.13E-01
R² = 9.97E-01
90°C
y = -4.79E-03x - 1.08E-01
R² = 9.97E-01
100°C
y = -1.26E-02x - 1.06E-01
R² = 9.97E-01
110°C
y = -3.06E-02x - 1.19E-01
R² = 9.96E-01

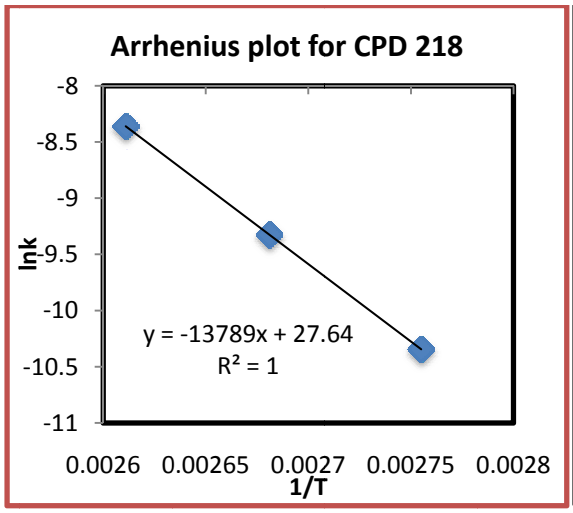

Arrhenius plot for CPD 212
ln (k/T)
1/T
y = -13224x + 26.97
R² = 0.999

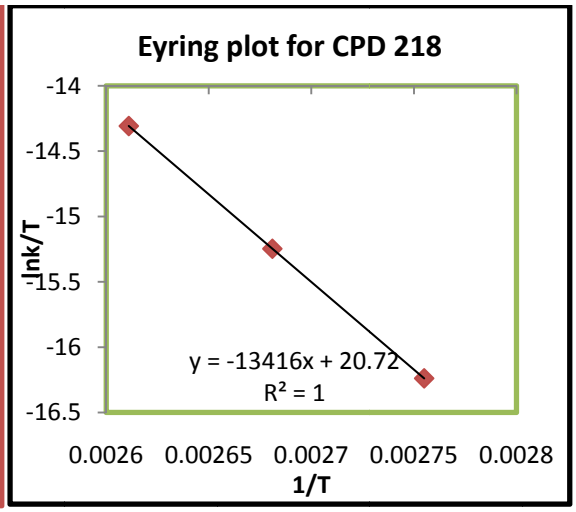

Eyring plot for CPD 212
ln (k)
1/T
y = -12857x + 20.06
R² = 0.999

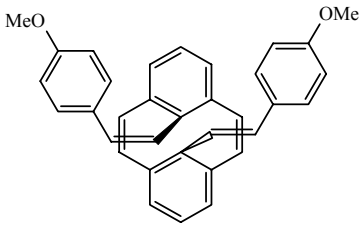

MeO
OMe

**218**

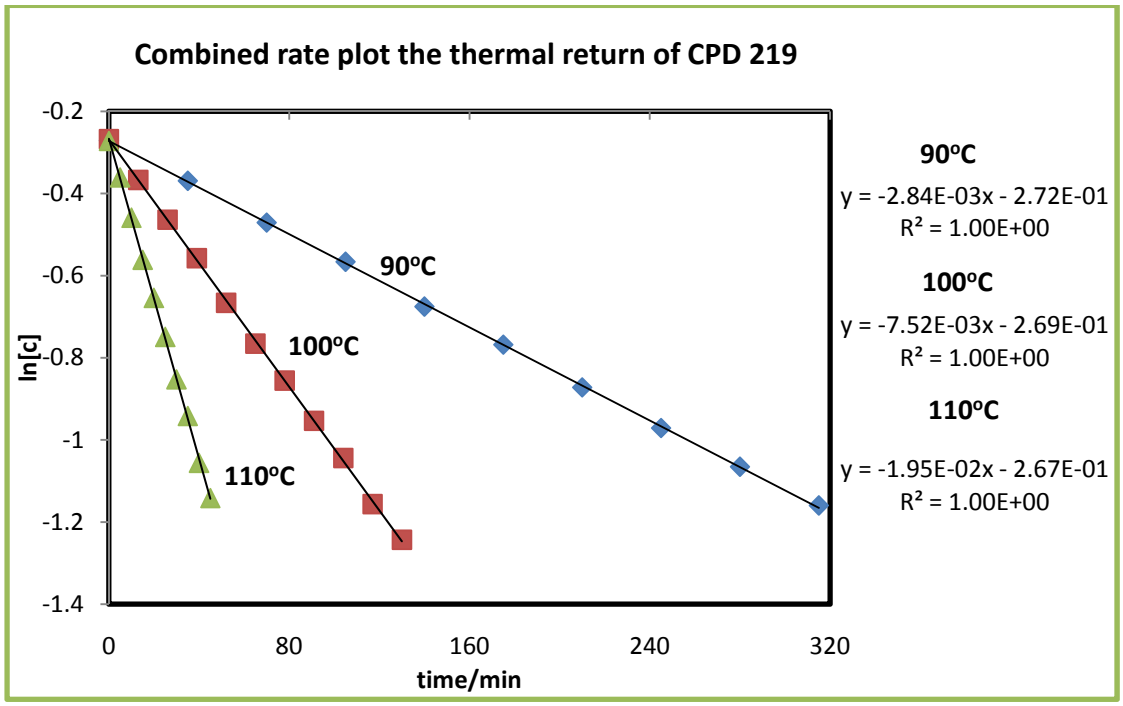

Combined rate plot for CPD 218
lnx
time/minutes
90°C
100°C
110°C
90°C
y = -1.93E-03x - 2.00E-02
R² = 1.00E+00
100°C
y = -5.35E-03x - 1.83E-02
R² = 1.00E+00
110°C
y = -1.40E-02x - 1.44E-02
R² = 1.00E+00

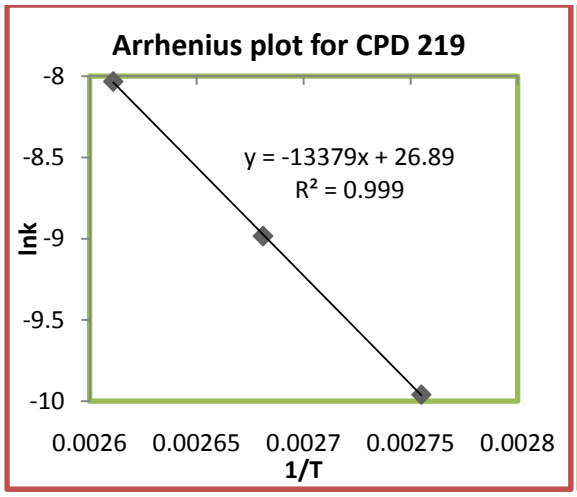

Arrhenius plot for CPD 218
lnk
1/T
y = -13789x + 27.64
R² = 1

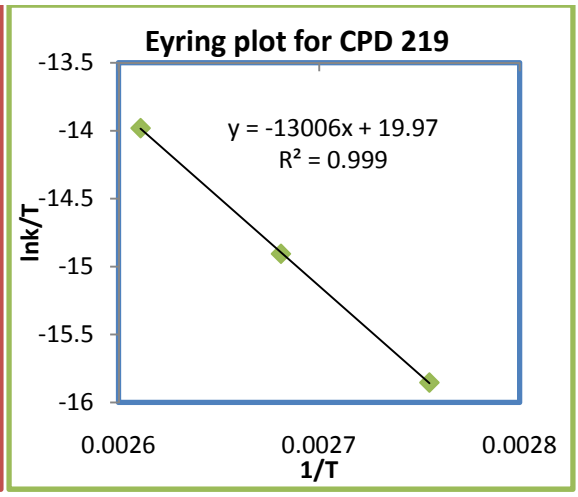

Eyring plot for CPD 218
-lnk/T
1/T
y = -13416x + 20.72
R² = 1

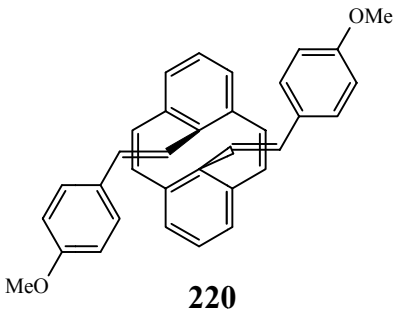

MeO
OMe

**219**

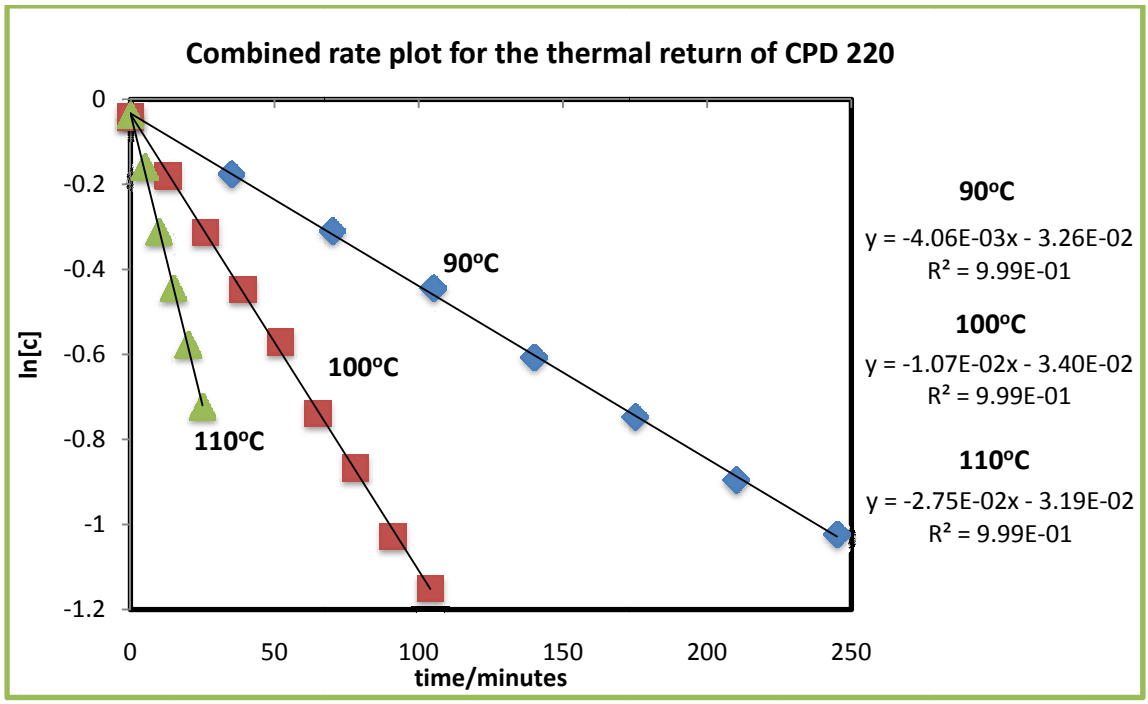

Combined rate plot the thermal return of CPD 219
ln[c]
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
0
80
160
240
320
time/min
90°C
100°C
110°C
90°C
y = -2.84E-03x - 2.72E-01
R² = 1.00E+00
100°C
y = -7.52E-03x - 2.69E-01
R² = 1.00E+00
110°C
y = -1.95E-02x - 2.67E-01
R² = 1.00E+00

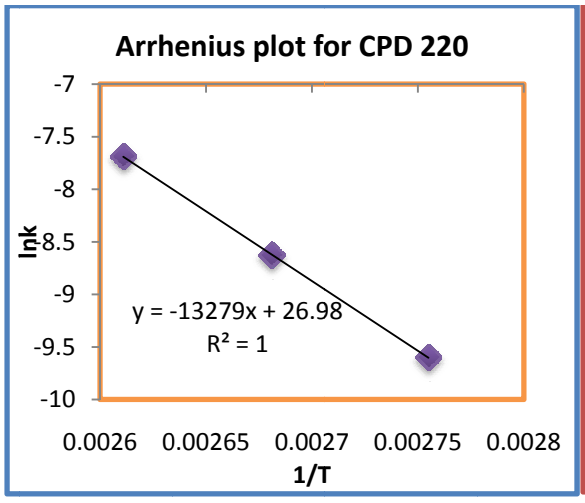

Arrhenius plot for CPD 219
lnk
-8
-8.5
-9
-9.5
-10
0.0026
0.00265
0.0027
0.00275
0.0028
1/T
y = -13379x + 26.89
R² = 0.999

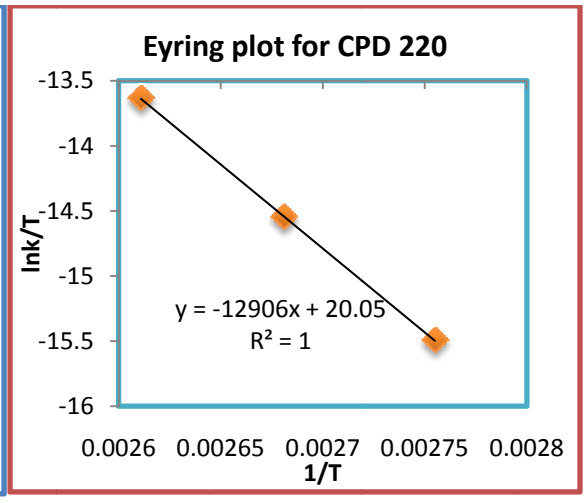

Eyring plot for CPD 219
lnk/T
-13.5
-14
-14.5
-15
-15.5
-16
0.0026
0.0027
0.0028
1/T
y = -13006x + 19.97
R² = 0.999

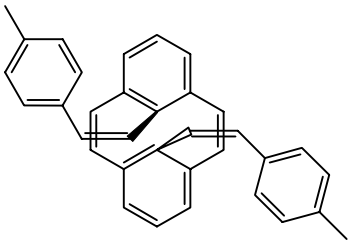

OMe
MeO

**220**

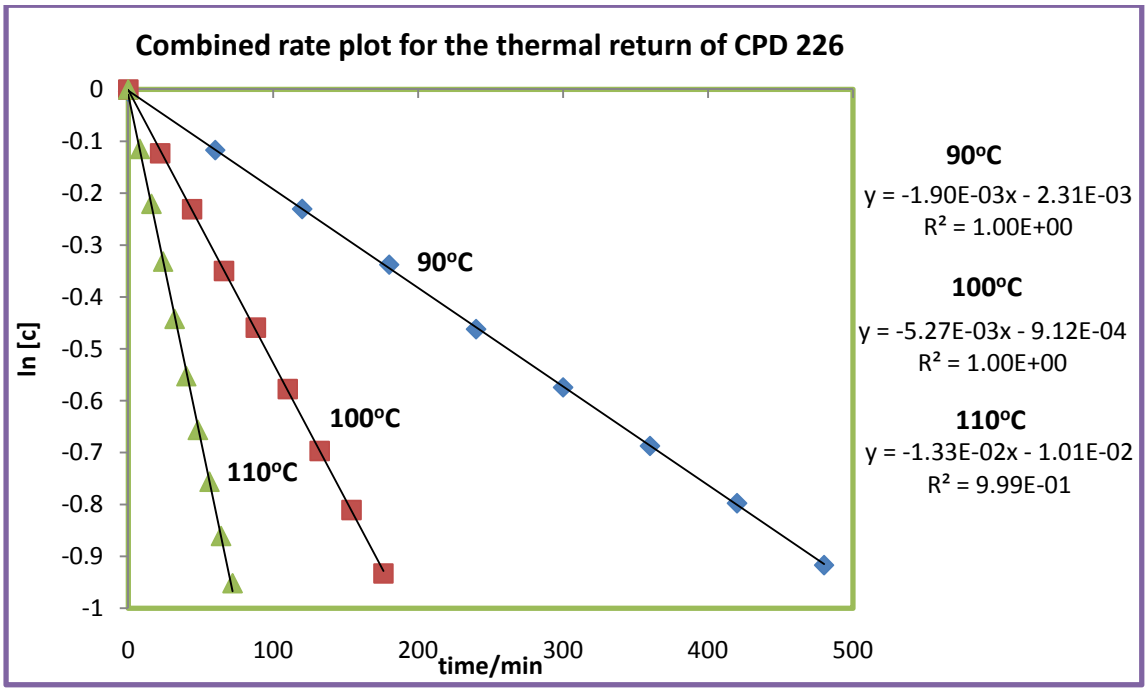

Combined rate plot for the thermal return of CPD 220
ln[c]
time/minutes
90°C
100°C
110°C
90°C
y = -4.06E-03x - 3.26E-02
R² = 9.99E-01
100°C
y = -1.07E-02x - 3.40E-02
R² = 9.99E-01
110°C
y = -2.75E-02x - 3.19E-02
R² = 9.99E-01

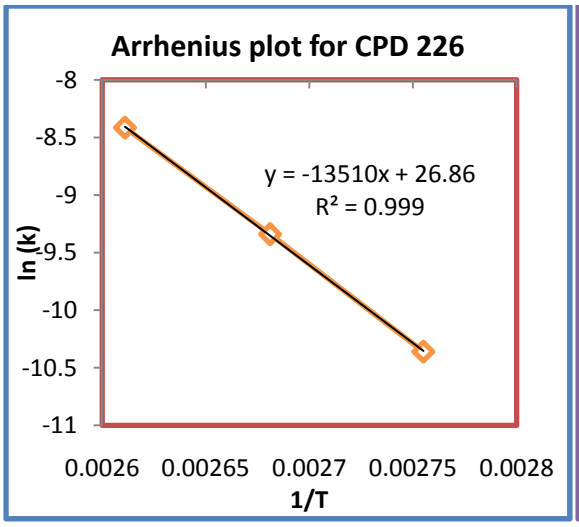

Arrhenius plot for CPD 220
lnk
1/T
y = -13279x + 26.98
R² = 1

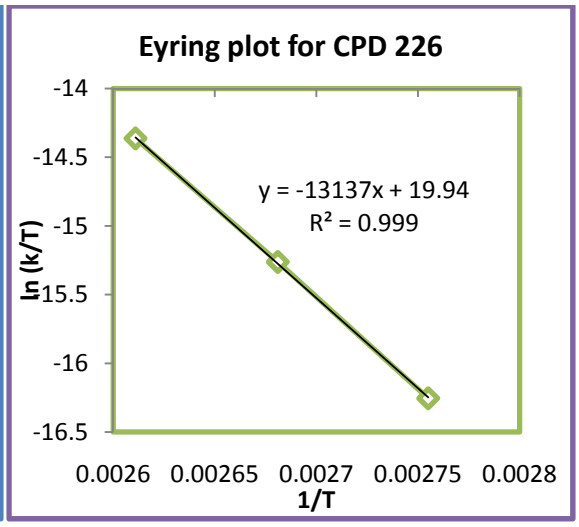

Eyring plot for CPD 220
lnk/T
1/T
y = -12906x + 20.05
R² = 1

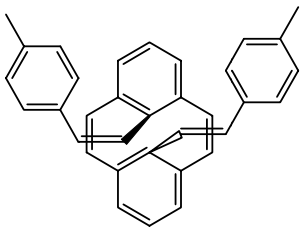


**226**

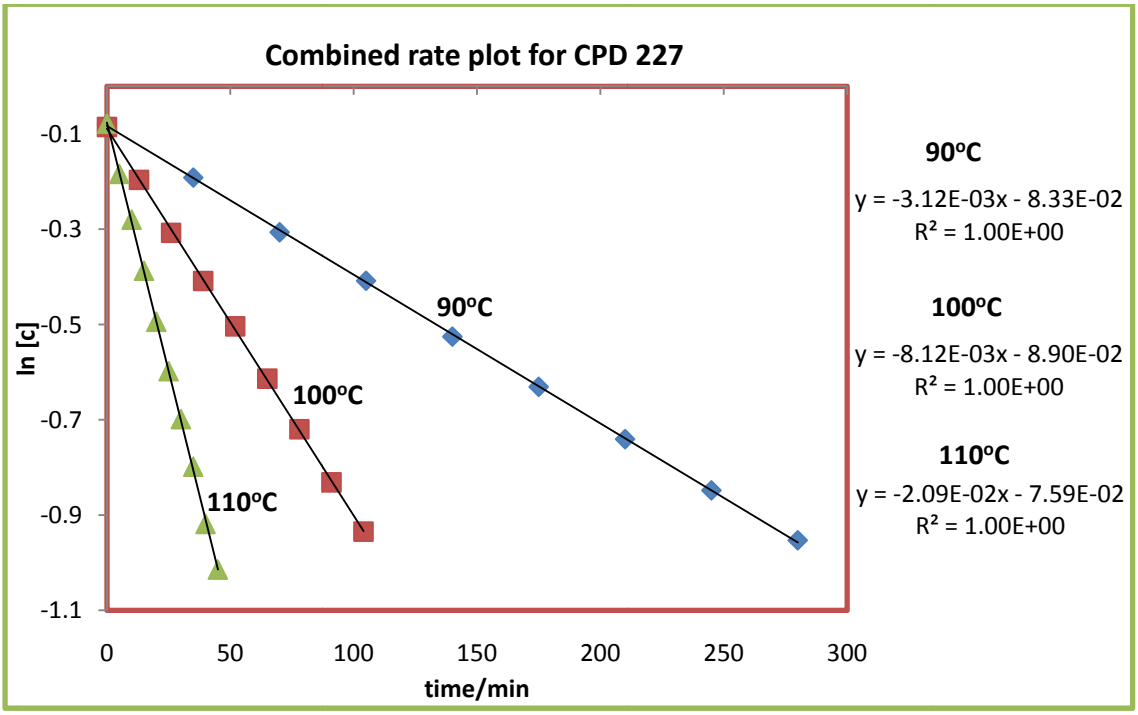

Combined rate plot for the thermal return of CPD 226
ln [c]
time/min
90°C
100°C
110°C
90°C
y = -1.90E-03x - 2.31E-03
R² = 1.00E+00
100°C
y = -5.27E-03x - 9.12E-04
R² = 1.00E+00
110°C
y = -1.33E-02x - 1.01E-02
R² = 9.99E-01

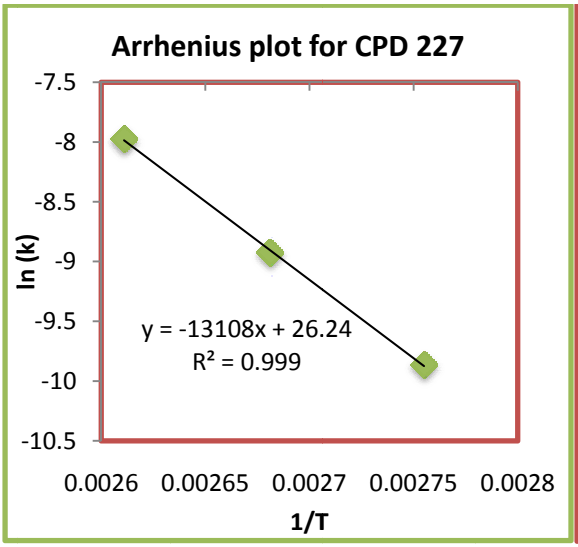

Arrhenius plot for CPD 226
ln (k)
1/T
y = -13510x + 26.86
R² = 0.999

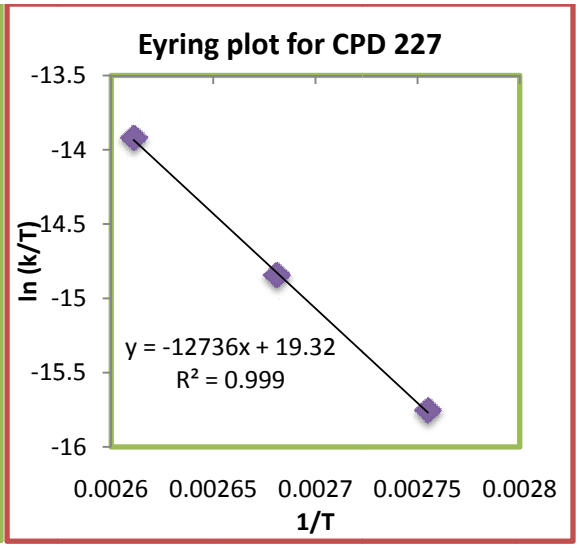

Eyring plot for CPD 226
ln (k/T)
1/T
y = -13137x + 19.94
R² = 0.999

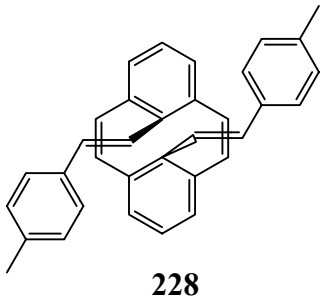


227

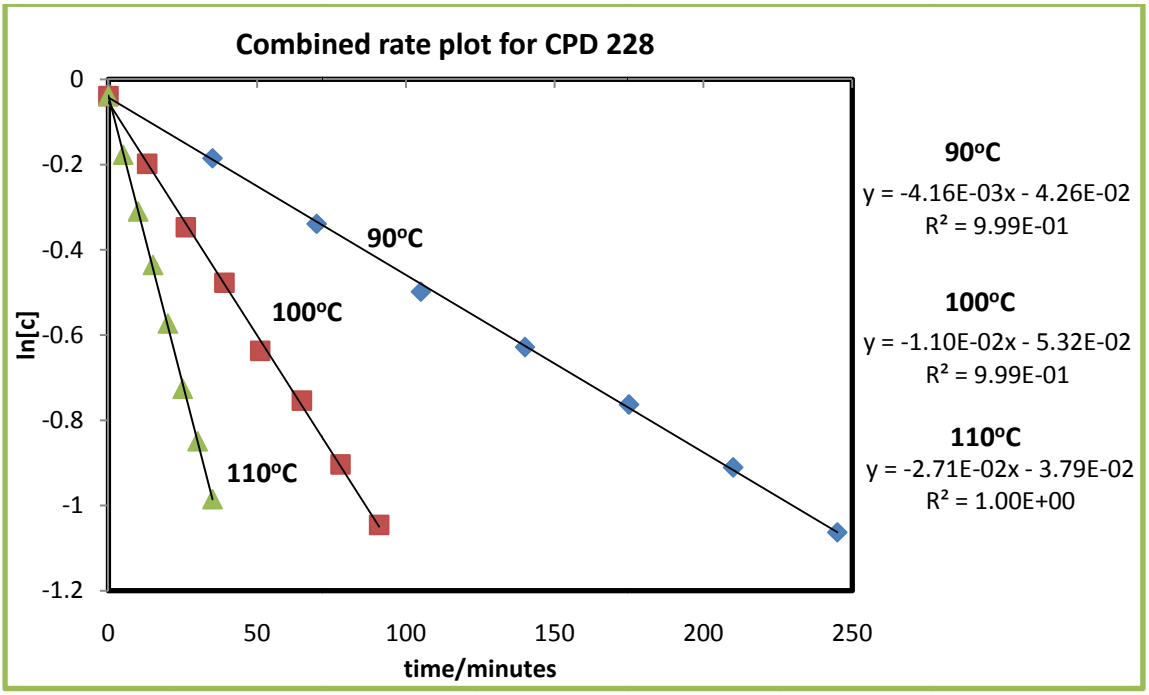

Combined rate plot for CPD 227
ln [c]
time/min
90°C
100°C
110°C
90°C
y = -3.12E-03x - 8.33E-02
R² = 1.00E+00
100°C
y = -8.12E-03x - 8.90E-02
R² = 1.00E+00
110°C
y = -2.09E-02x - 7.59E-02
R² = 1.00E+00

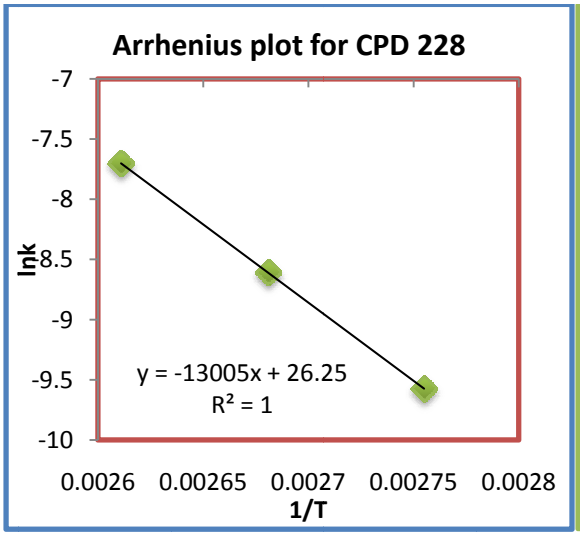

Arrhenius plot for CPD 227
ln (k)
1/T
y = -13108x + 26.24
R² = 0.999

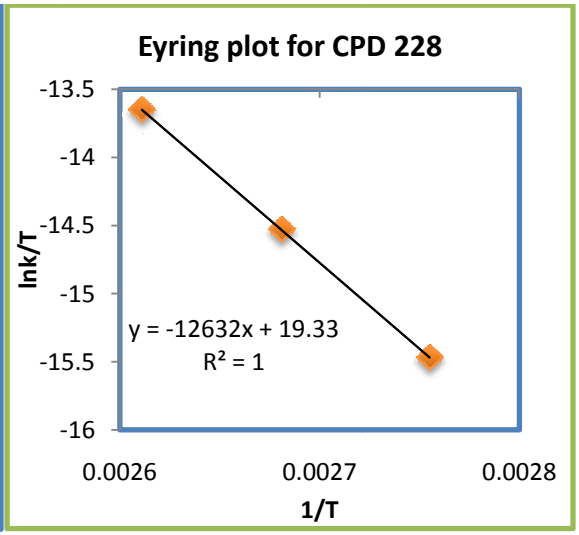

Eyring plot for CPD 227
ln (k/T)
1/T
y = -12736x + 19.32
R² = 0.999

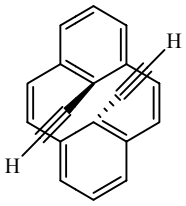


**228**

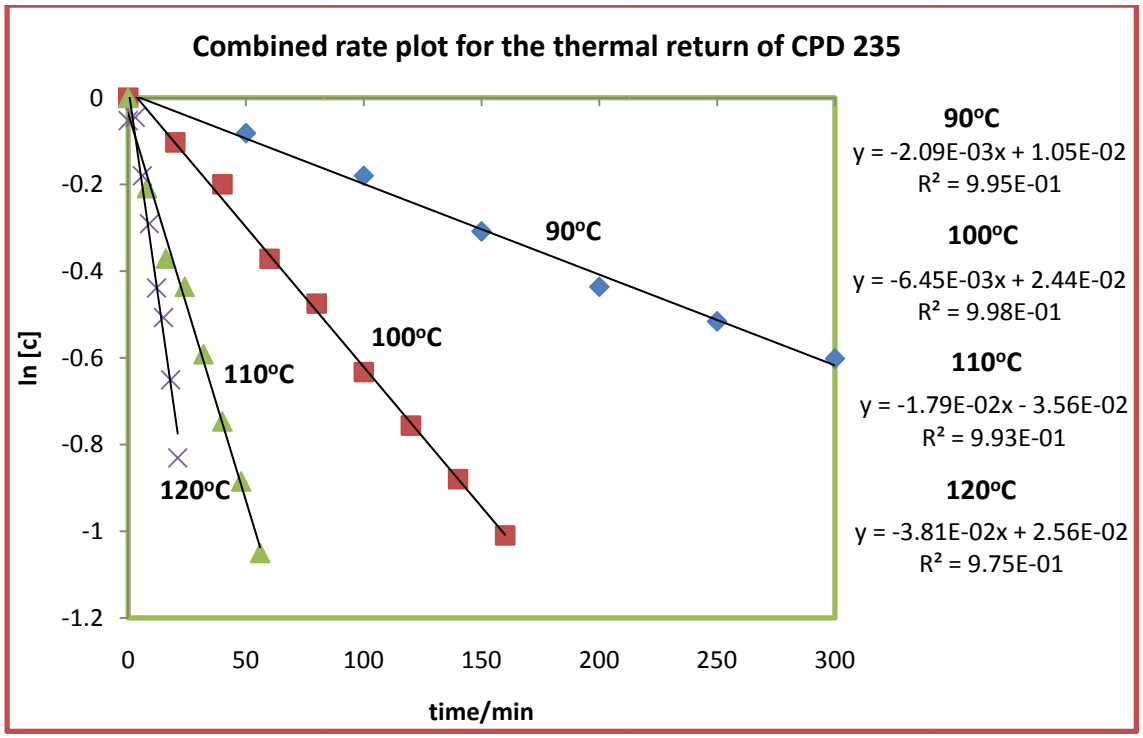

Combined rate plot for CPD 228
ln[c]
time/minutes
90°C
100°C
110°C
90°C
y = -4.16E-03x - 4.26E-02
R² = 9.99E-01
100°C
y = -1.10E-02x - 5.32E-02
R² = 9.99E-01
110°C
y = -2.71E-02x - 3.79E-02
R² = 1.00E+00

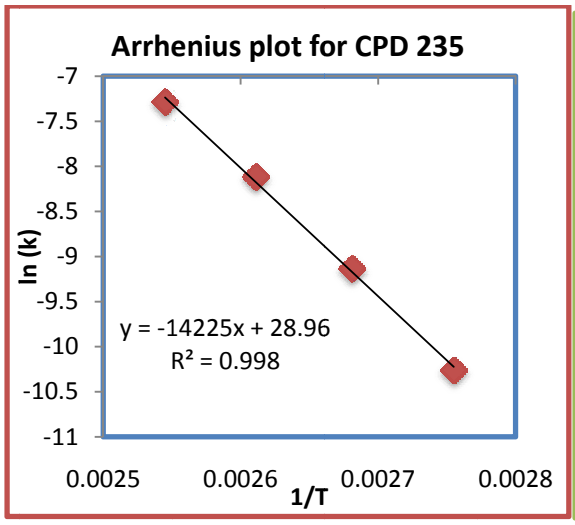

Arrhenius plot for CPD 228
lnk
1/T
y = -13005x + 26.25
R² = 1

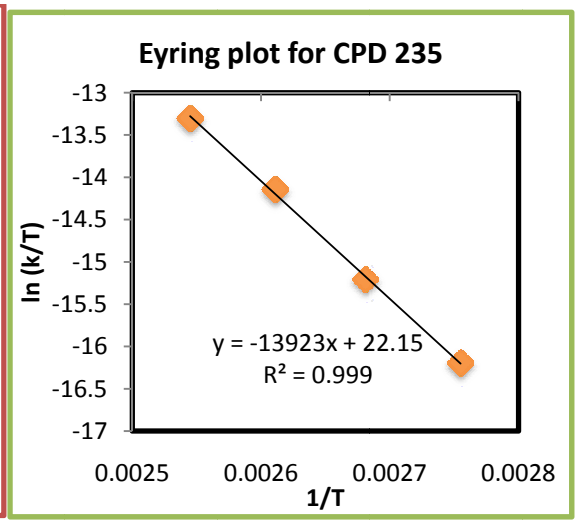

Eyring plot for CPD 228
lnk/T
1/T
y = -12632x + 19.33
R² = 1

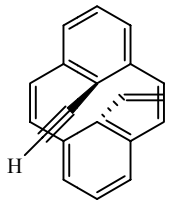

H
H

**235**

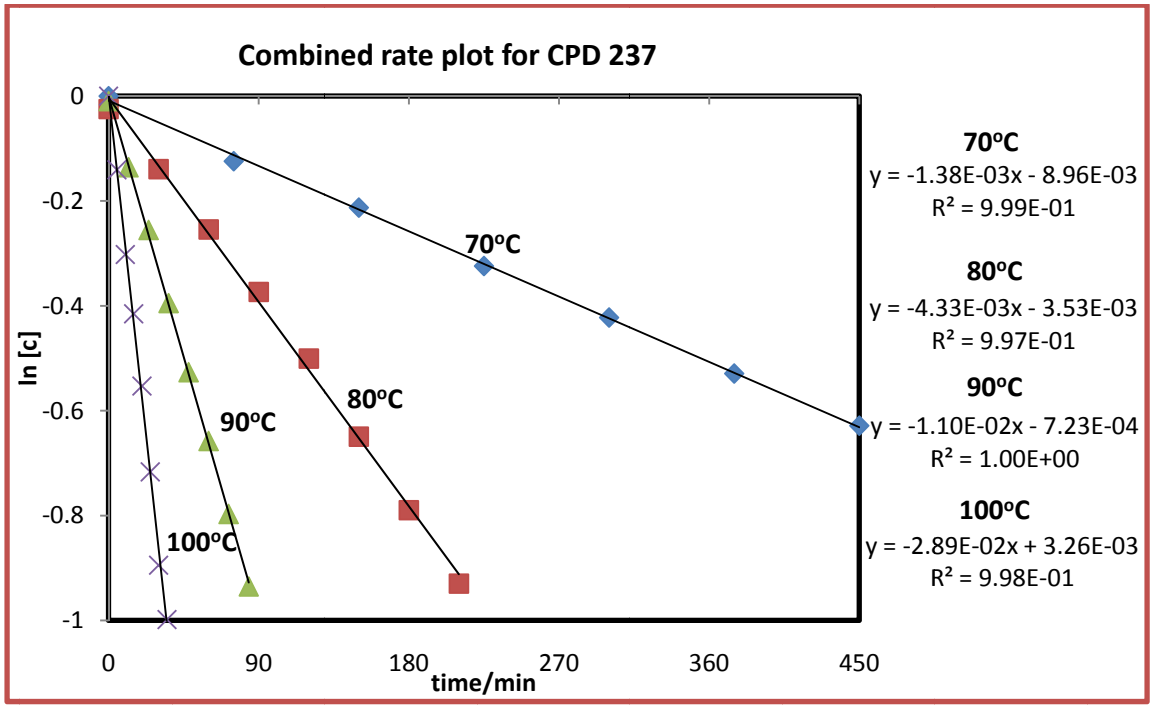

Combined rate plot for the thermal return of CPD 235
ln [c]
time/min
90°C
100°C
110°C
120°C
90°C
y = -2.09E-03x + 1.05E-02
R² = 9.95E-01
100°C
y = -6.45E-03x + 2.44E-02
R² = 9.98E-01
110°C
y = -1.79E-02x - 3.56E-02
R² = 9.93E-01
120°C
y = -3.81E-02x + 2.56E-02
R² = 9.75E-01

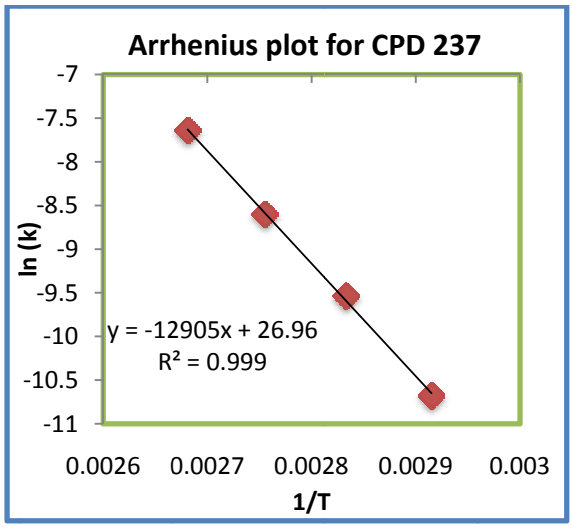

Arrhenius plot for CPD 235
ln (k)
1/T
y = -14225x + 28.96
R² = 0.998

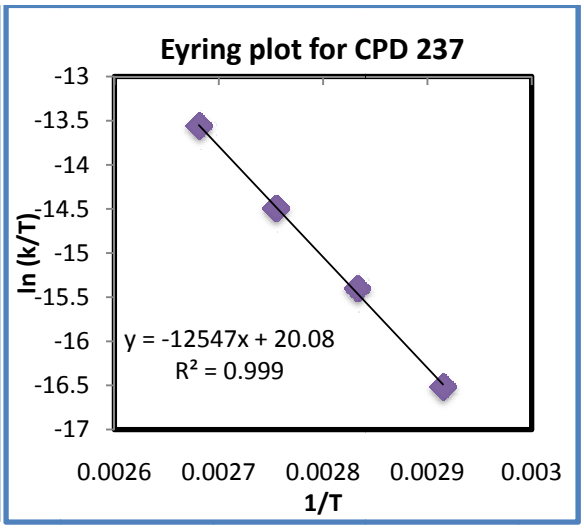

Eyring plot for CPD 235
ln (k/T)
1/T
y = -13923x + 22.15
R² = 0.999

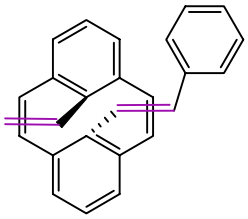

H

**237**

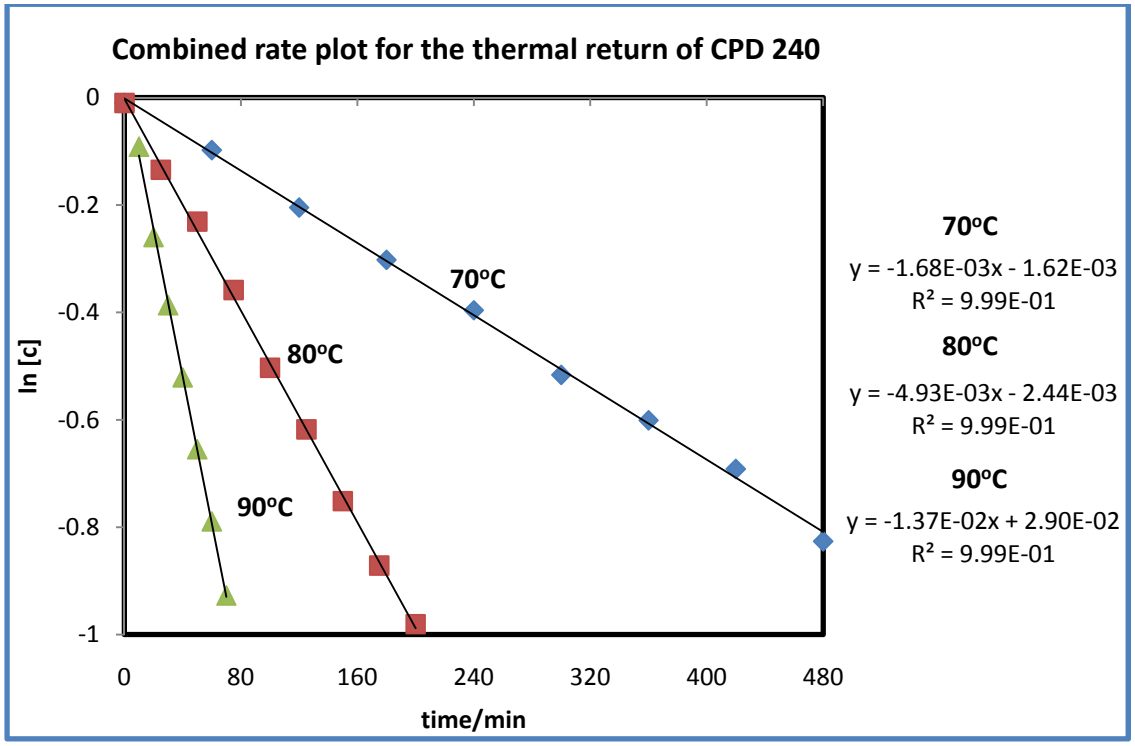

Combined rate plot for CPD 237
ln [c]
time/min
0
-0.2
-0.4
-0.6
-0.8
-1
0
90
180
270
360
450
70°C
80°C
90°C
100°C
70°C
y = -1.38E-03x - 8.96E-03
R² = 9.99E-01
80°C
y = -4.33E-03x - 3.53E-03
R² = 9.97E-01
90°C
y = -1.10E-02x - 7.23E-04
R² = 1.00E+00
100°C
y = -2.89E-02x + 3.26E-03
R² = 9.98E-01

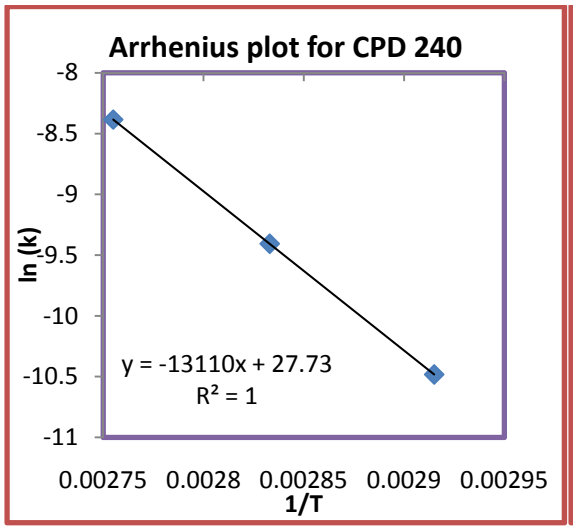

Arrhenius plot for CPD 237
ln (k)
1/T
-7
-7.5
-8
-8.5
-9
-9.5
-10
-10.5
-11
0.0026
0.0027
0.0028
0.0029
0.003
y = -12905x + 26.96
R² = 0.999

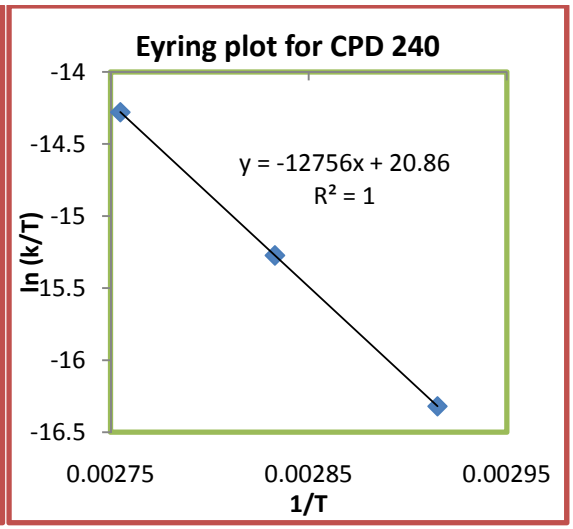

Eyring plot for CPD 237
ln (k/T)
1/T
-13
-13.5
-14
-14.5
-15
-15.5
-16
-16.5
-17
0.0026
0.0027
0.0028
0.0029
0.003
y = -12547x + 20.08
R² = 0.999

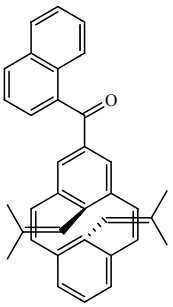


**240**

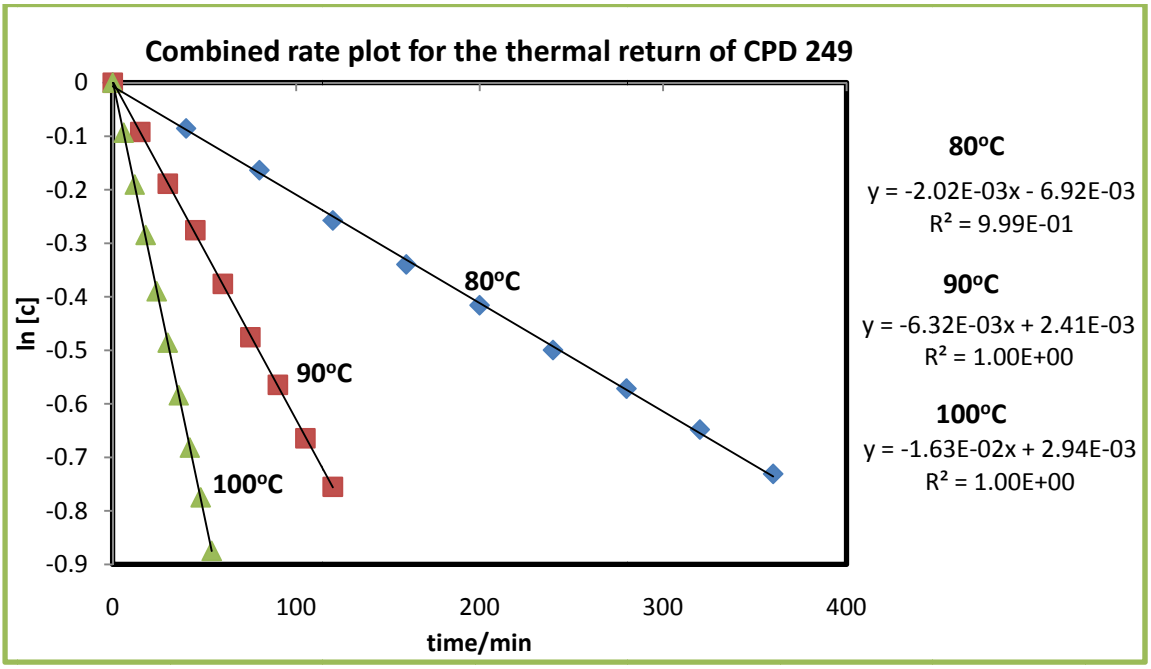

Combined rate plot for the thermal return of CPD 240
ln [c]
time/min
70°C
80°C
90°C
70°C
y = -1.68E-03x - 1.62E-03
R² = 9.99E-01
80°C
y = -4.93E-03x - 2.44E-03
R² = 9.99E-01
90°C
y = -1.37E-02x + 2.90E-02
R² = 9.99E-01

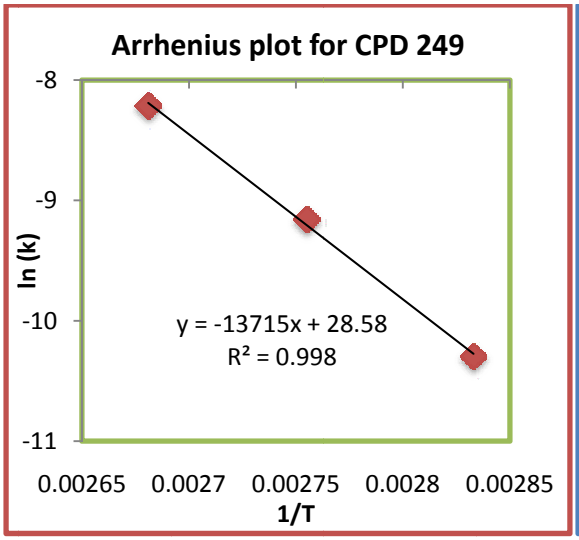

Arrhenius plot for CPD 240
ln (k)
1/T
y = -13110x + 27.73
R² = 1

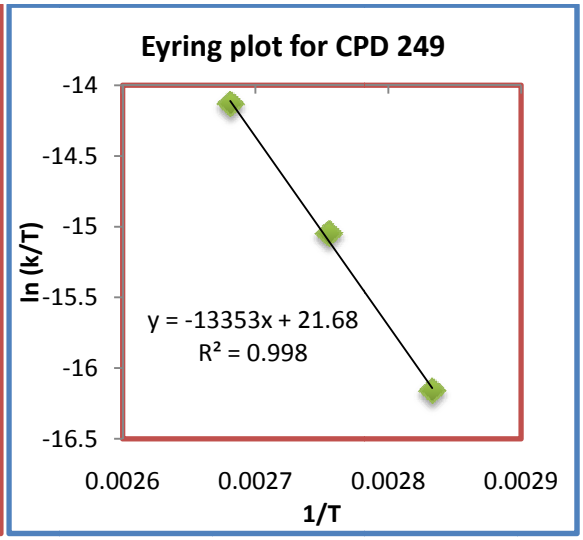

Eyring plot for CPD 240
ln (k/T)
1/T
y = -12756x + 20.86
R² = 1

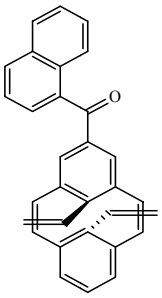


**249**

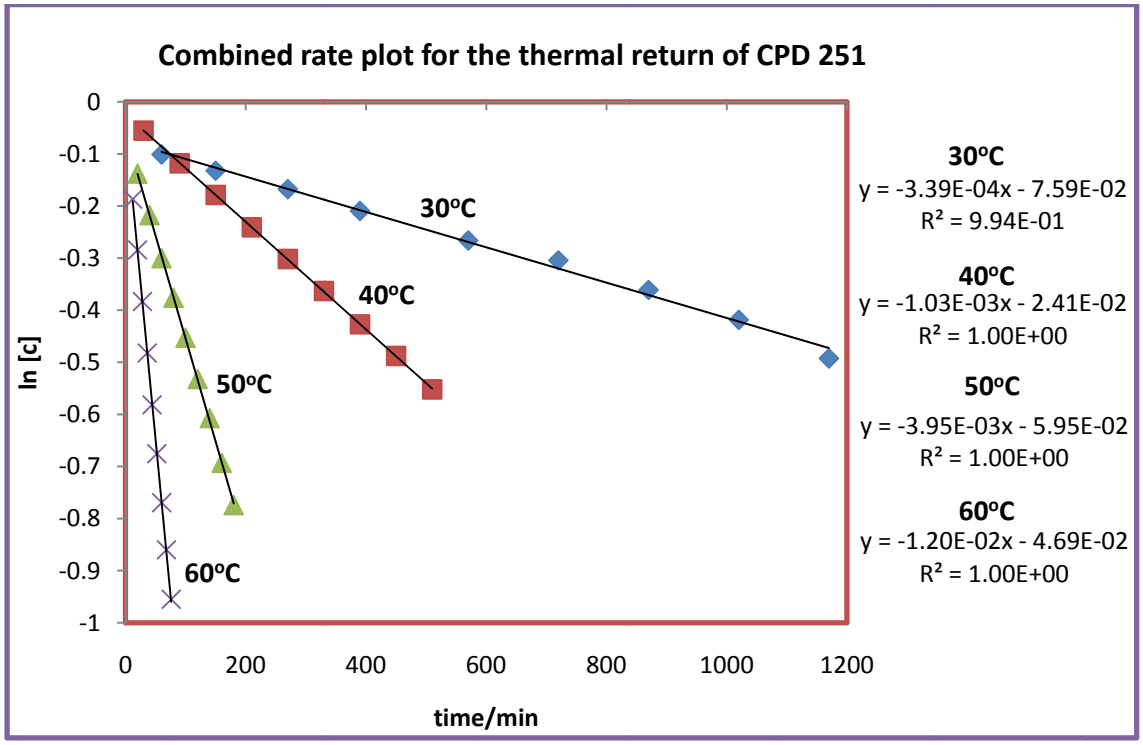

Combined rate plot for the thermal return of CPD 249
ln [c]
time/min
80°C
90°C
100°C
80°C
y = -2.02E-03x - 6.92E-03
R² = 9.99E-01
90°C
y = -6.32E-03x + 2.41E-03
R² = 1.00E+00
100°C
y = -1.63E-02x + 2.94E-03
R² = 1.00E+00

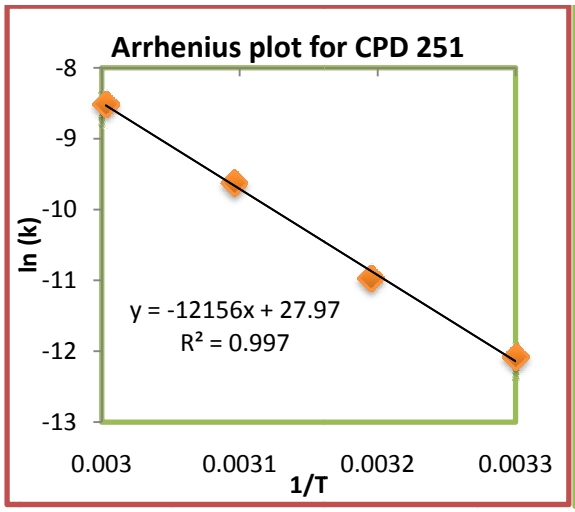

Arrhenius plot for CPD 249
ln (k)
1/T
y = -13715x + 28.58
R² = 0.998

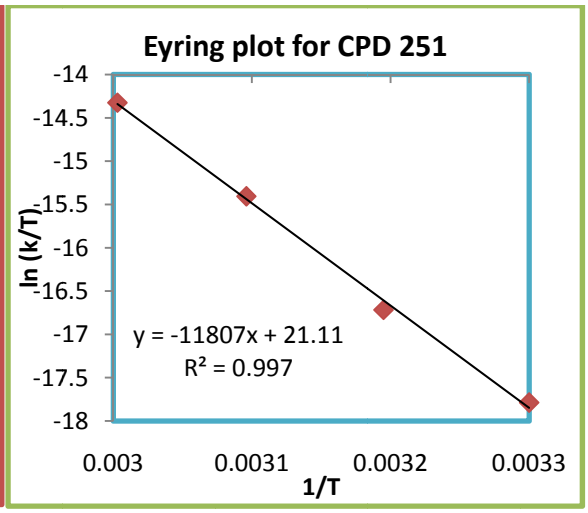

Eyring plot for CPD 249
ln (k/T)
1/T
y = -13353x + 21.68
R² = 0.998



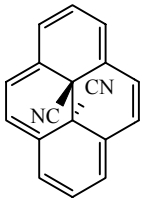
**251**


Combined rate plot for the thermal return of CPD 251
ln [c]
time/min
30°C
40°C
50°C
60°C
30°C
y = -3.39E-04x - 7.59E-02
R² = 9.94E-01
40°C
y = -1.03E-03x - 2.41E-02
R² = 1.00E+00
50°C
y = -3.95E-03x - 5.95E-02
R² = 1.00E+00
60°C
y = -1.20E-02x - 4.69E-02
R² = 1.00E+00

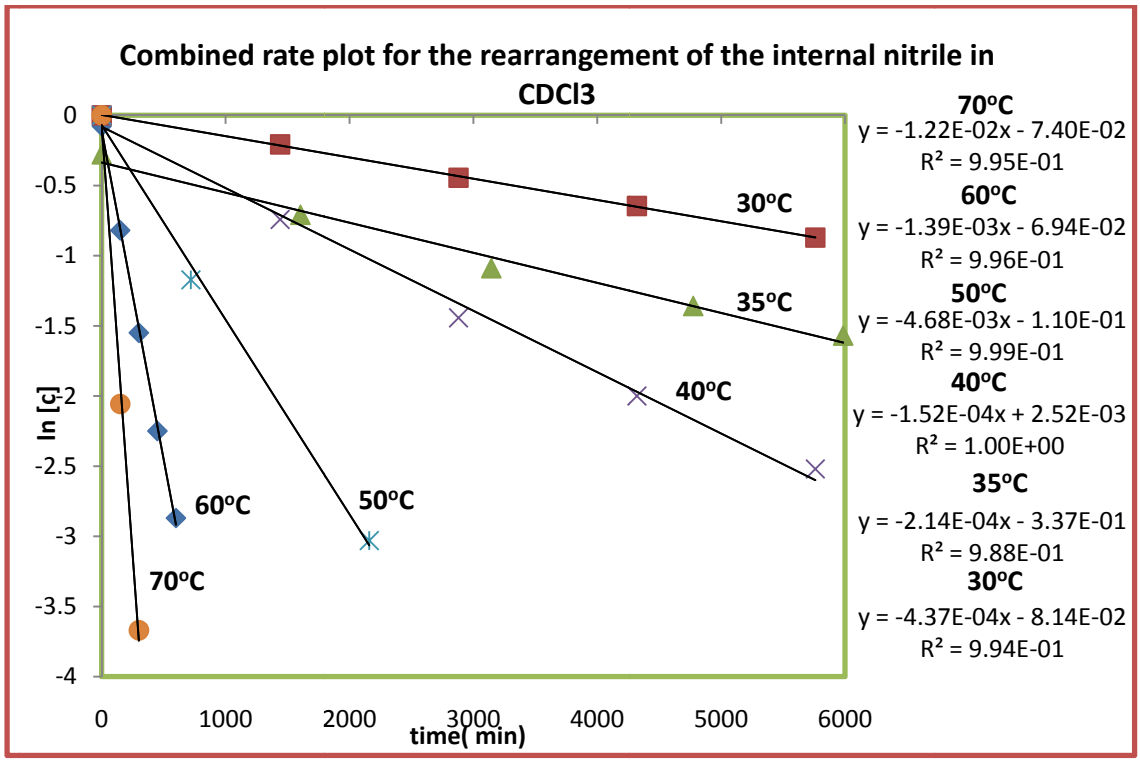

Arrhenius plot for CPD 251
ln (k)
1/T
y = -12156x + 27.97
R² = 0.997

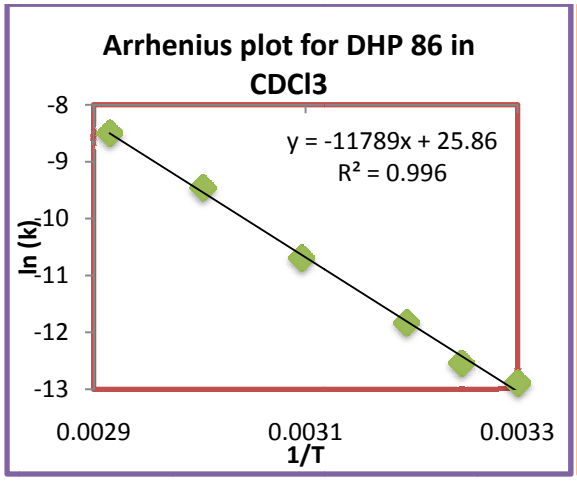

Eyring plot for CPD 251
ln (k/T)
1/T
y = -11807x + 21.11
R² = 0.997

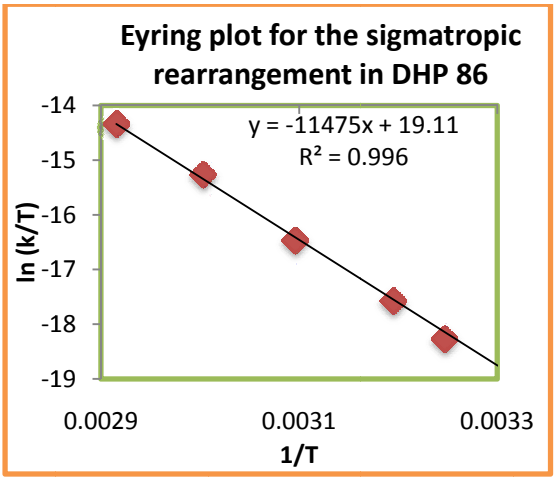
## Appendix C: Sigmatropic rearrangement data for dicyano DHP 86

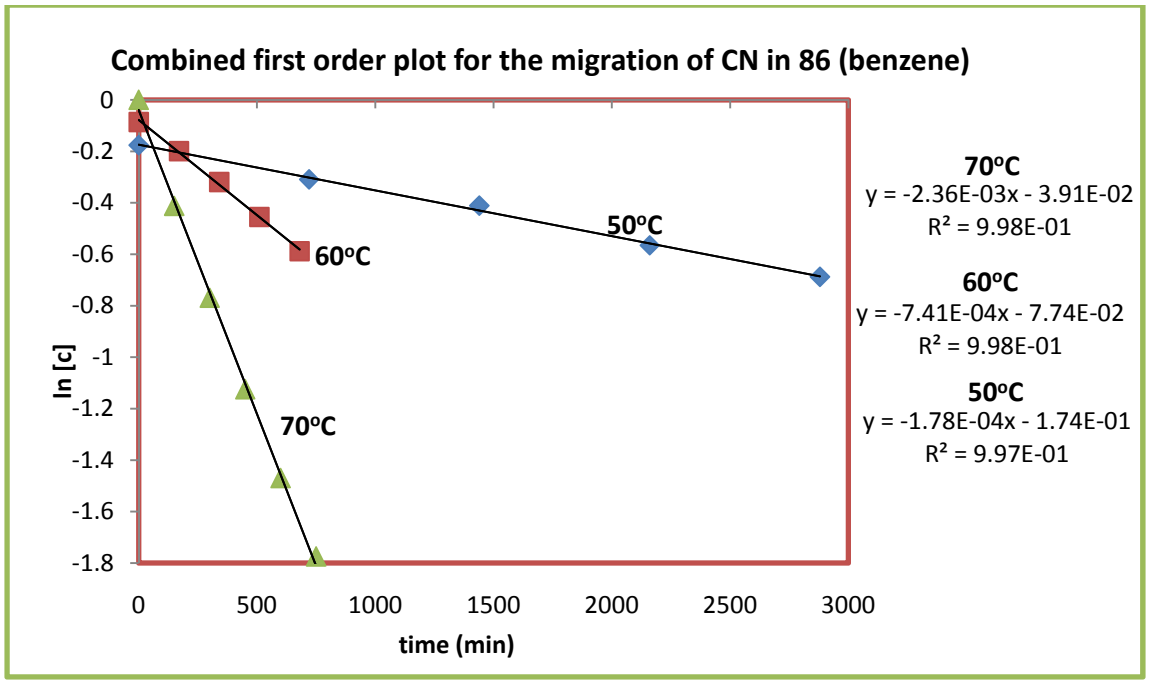


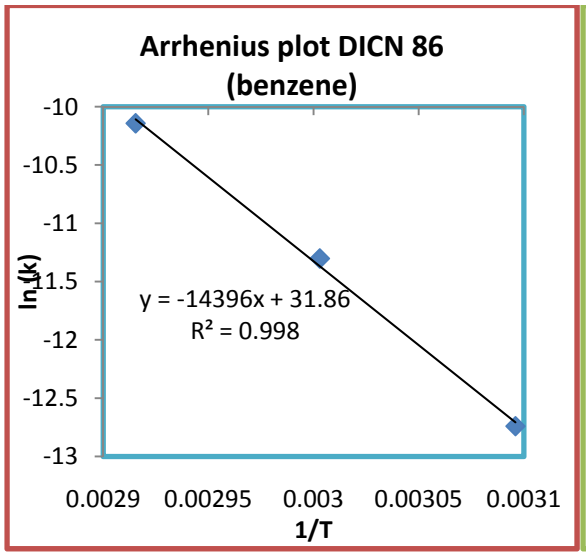

**86**

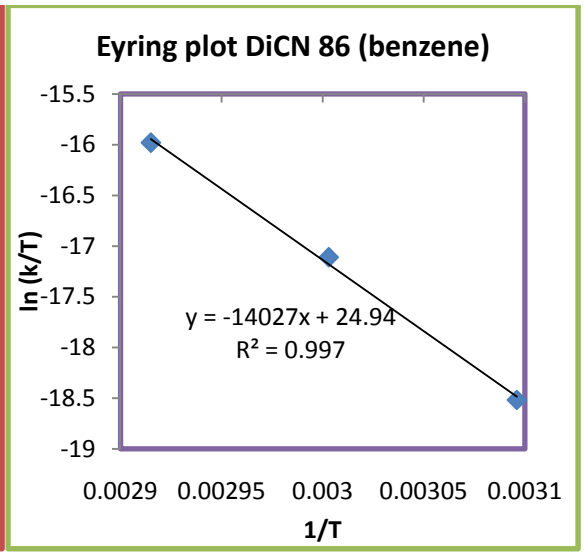


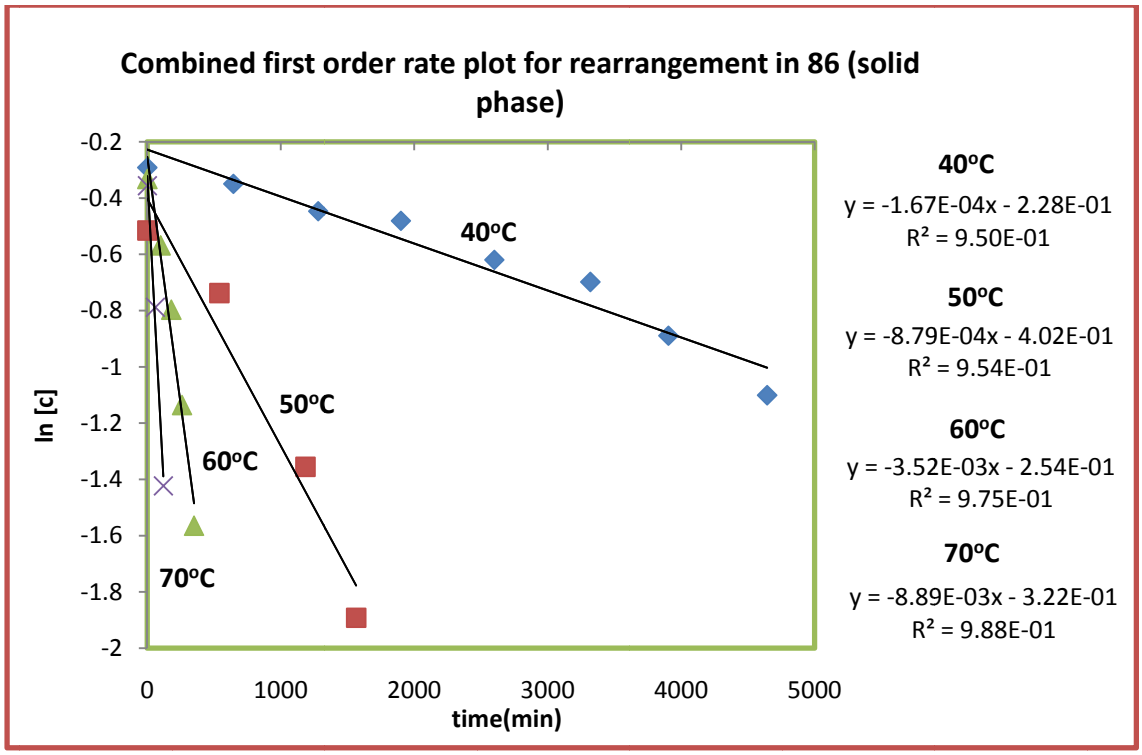



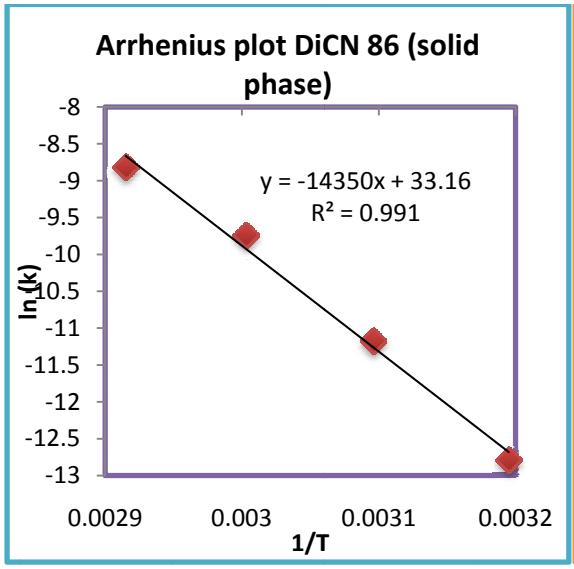



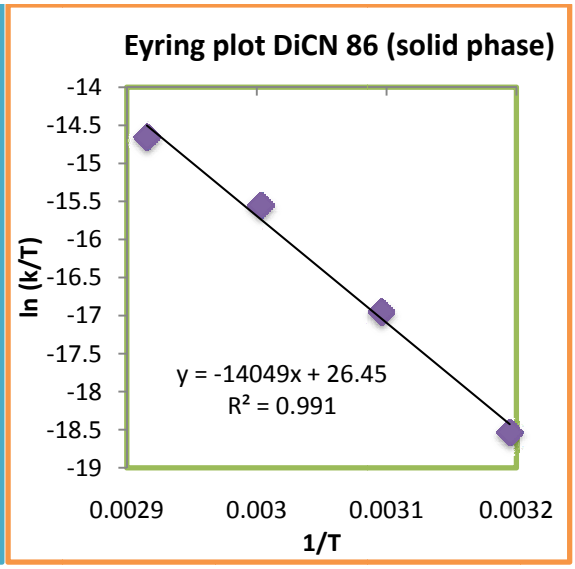

Combined first order plot for the migration of CN in 86 (benzene)
ln [c]
time (min)
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-1.8
0
500
1000
1500
2000
2500
3000
70°C
60°C
50°C
70°C
y = -2.36E-03x - 3.91E-02
R² = 9.98E-01
60°C
y = -7.41E-04x - 7.74E-02
R² = 9.98E-01
50°C
y = -1.78E-04x - 1.74E-01
R² = 9.97E-01


Arrhenius plot DICN 86 (benzene)
ln (k)
1/T
-10
-10.5
-11
-11.5
-12
-12.5
-13
0.0029
0.00295
0.003
0.00305
0.0031
y = -14396x + 31.86
R² = 0.998

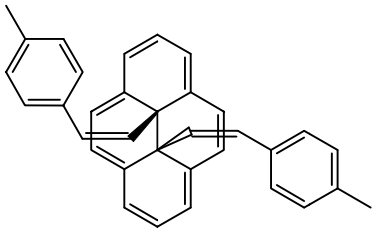

Eyring plot DiCN 86 (benzene)
ln (k/T)
1/T
-15.5
-16
-16.5
-17
-17.5
-18
-18.5
-19
0.0029
0.00295
0.003
0.00305
0.0031
y = -14027x + 24.94
R² = 0.997


Combined first order rate plot for rearrangement in 86 (solid phase)
ln [c]
time(min)
40°C
50°C
60°C
70°C
40°C
y = -1.67E-04x - 2.28E-01
R² = 9.50E-01
50°C
y = -8.79E-04x - 4.02E-01
R² = 9.54E-01
60°C
y = -3.52E-03x - 2.54E-01
R² = 9.75E-01
70°C
y = -8.89E-03x - 3.22E-01
R² = 9.88E-01

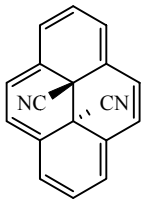

Arrhenius plot DiCN 86 (solid phase)
y = -14350x + 33.16
R² = 0.991
ln (k)
1/T


Eyring plot DiCN 86 (solid phase)
y = -14049x + 26.45
R² = 0.991
ln (k/T)
1/T

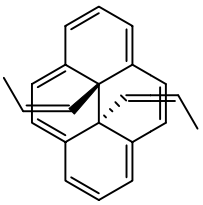
# Appendix D Photoopening data for dihydropyrenes



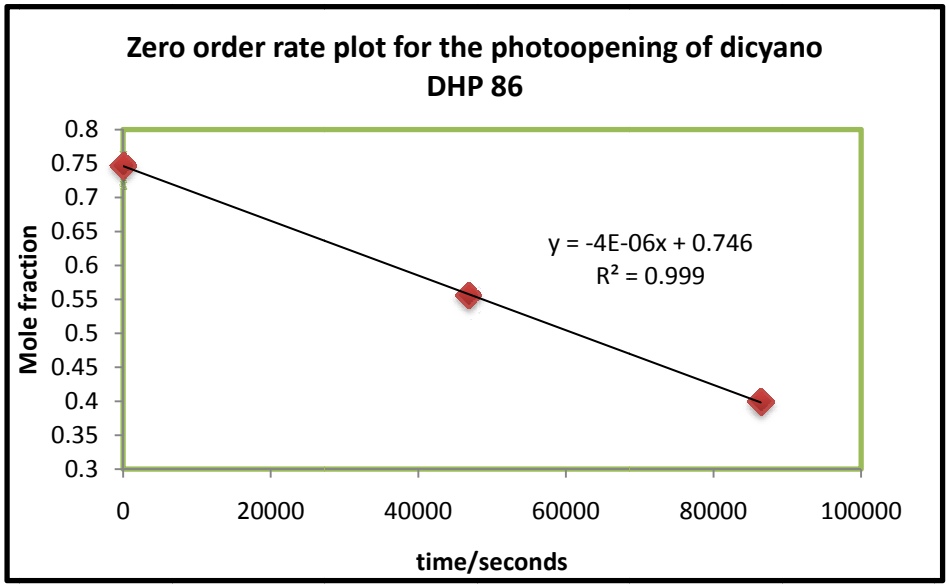
229

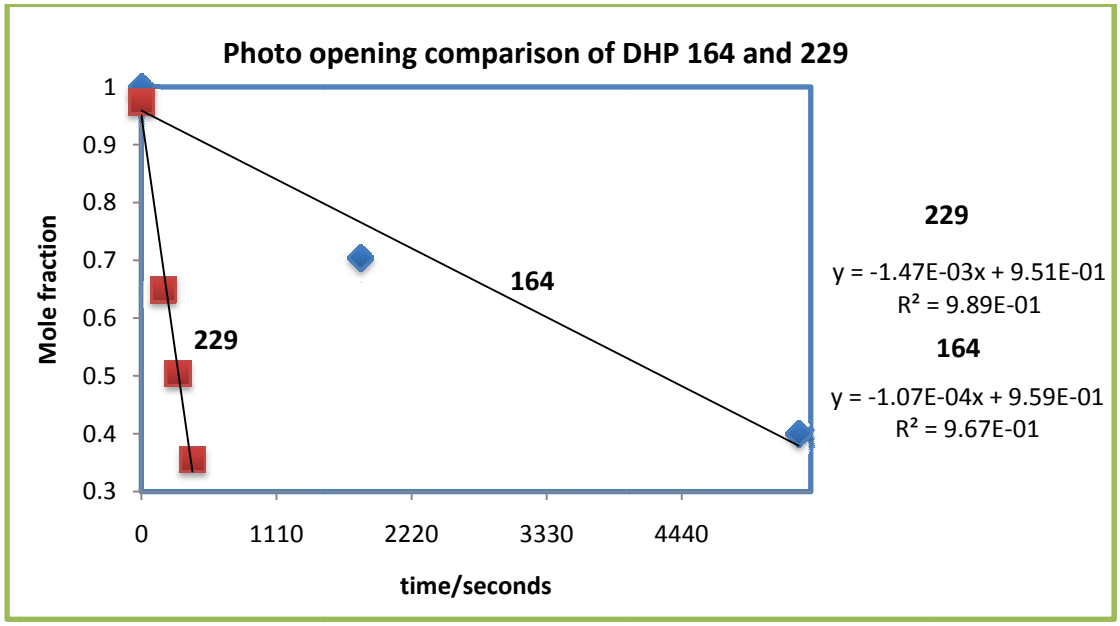


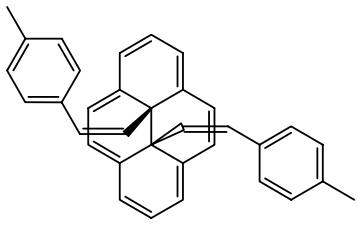

86



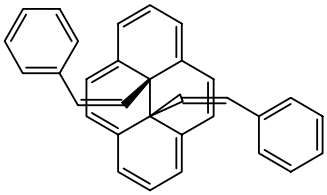
164



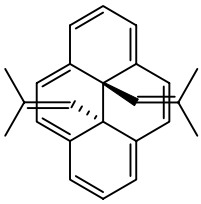





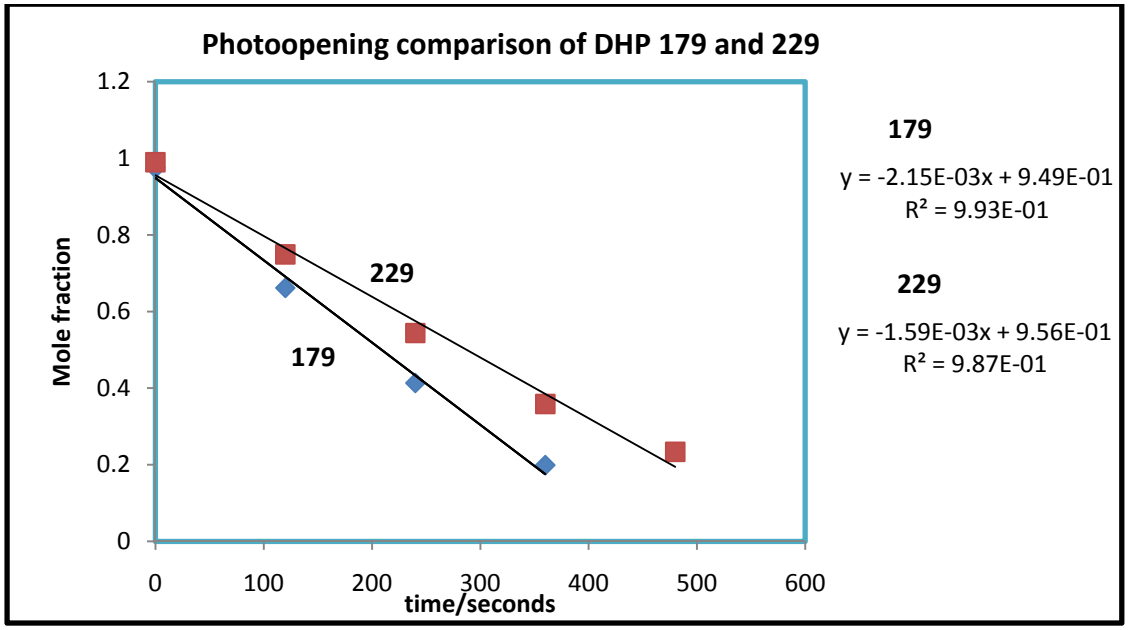
229



205



179


Photoopening comparison of DHP 179 and 229
Mole fraction
time/seconds
0
0.2
0.4
0.6
0.8
1
1.2
0
100
200
300
400
500
600
229
179
179
y = -2.15E-03x + 9.49E-01
R² = 9.93E-01
229
y = -1.59E-03x + 9.56E-01
R² = 9.87E-01

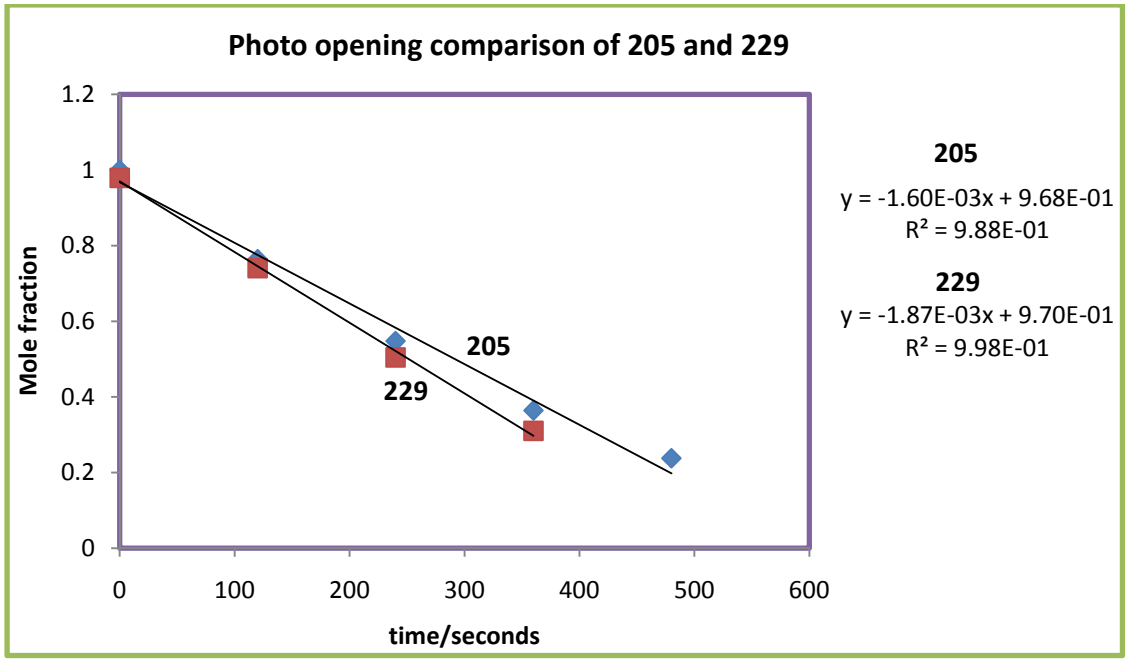
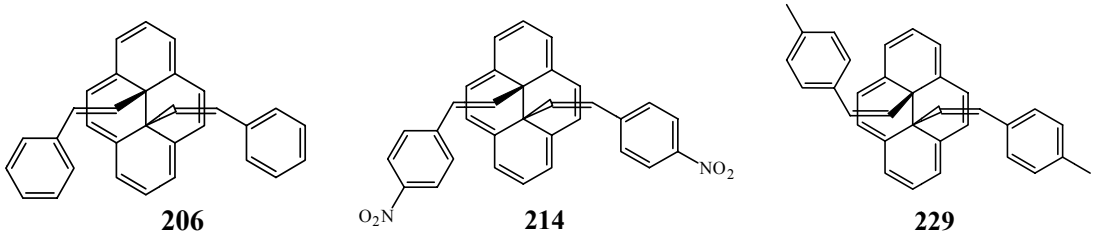


Photo opening comparison of 205 and 229
Mole fraction
time/seconds
0
0.2
0.4
0.6
0.8
1
1.2
0
100
200
300
400
500
600
205
229
205
y = -1.60E-03x + 9.68E-01
R² = 9.88E-01
229
y = -1.87E-03x + 9.70E-01
R² = 9.98E-01


206
214
229

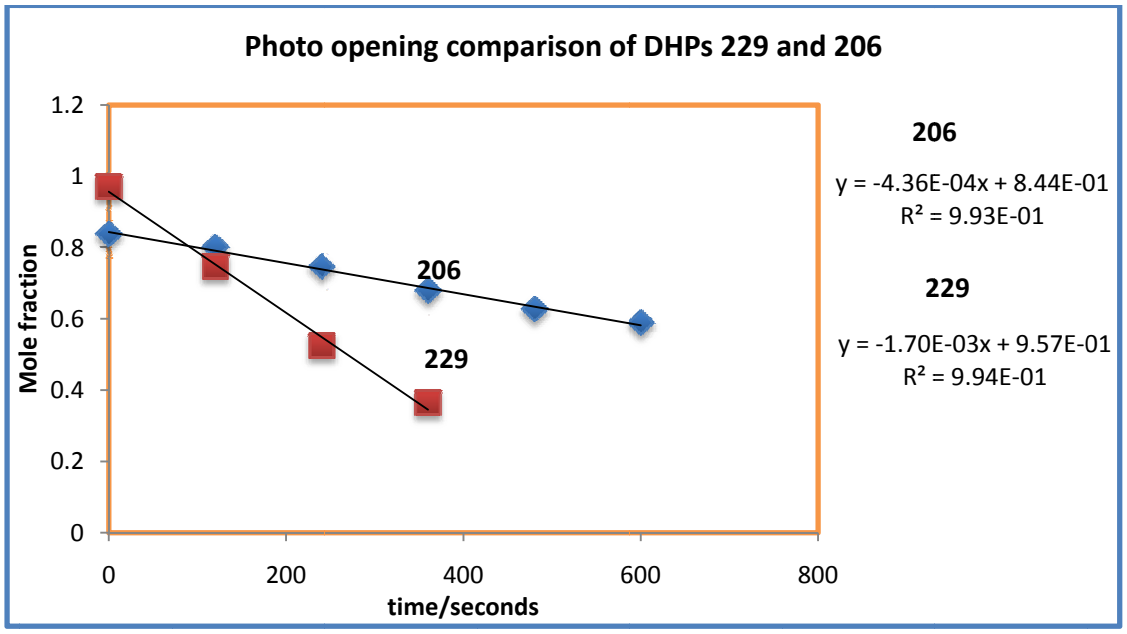


Photo opening comparison of DHPs 229 and 206
Mole fraction
time/seconds
206
229
206
y = -4.36E-04x + 8.44E-01
R² = 9.93E-01
229
y = -1.70E-03x + 9.57E-01
R² = 9.94E-01

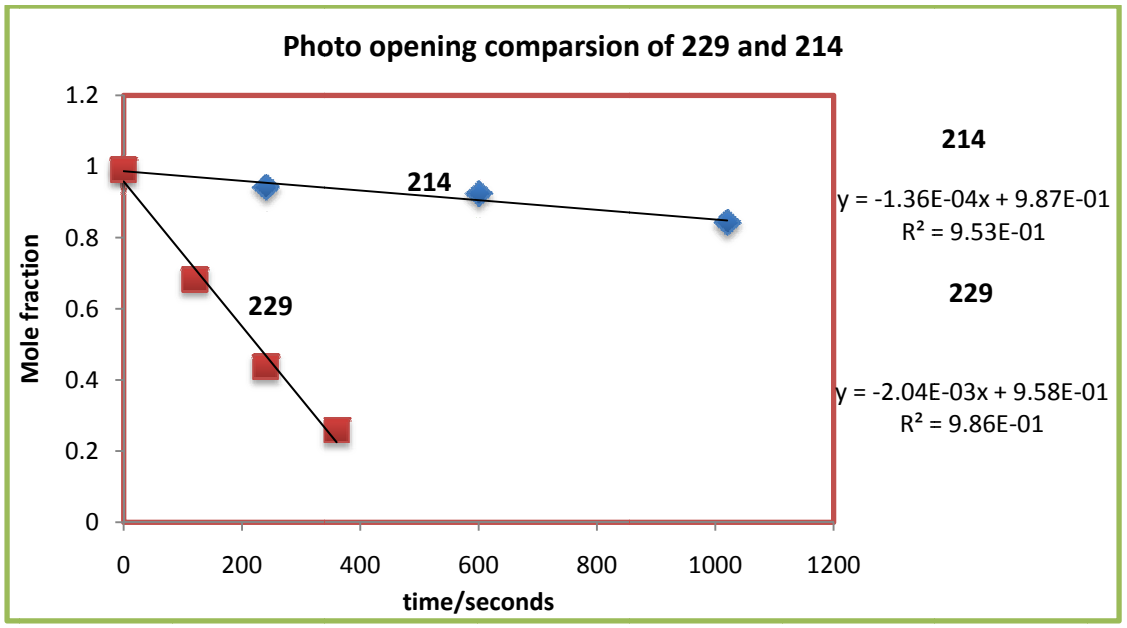
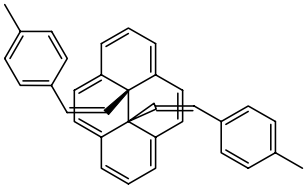
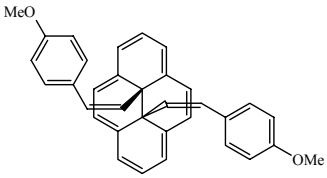


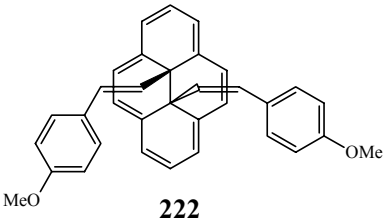
Photo opening comparsion of 229 and 214
Mole fraction
time/seconds
214
229
214
y = -1.36E-04x + 9.87E-01
R² = 9.53E-01
229
y = -2.04E-03x + 9.58E-01
R² = 9.86E-01



229


MeO
OMe

221


MeO
OMe

222

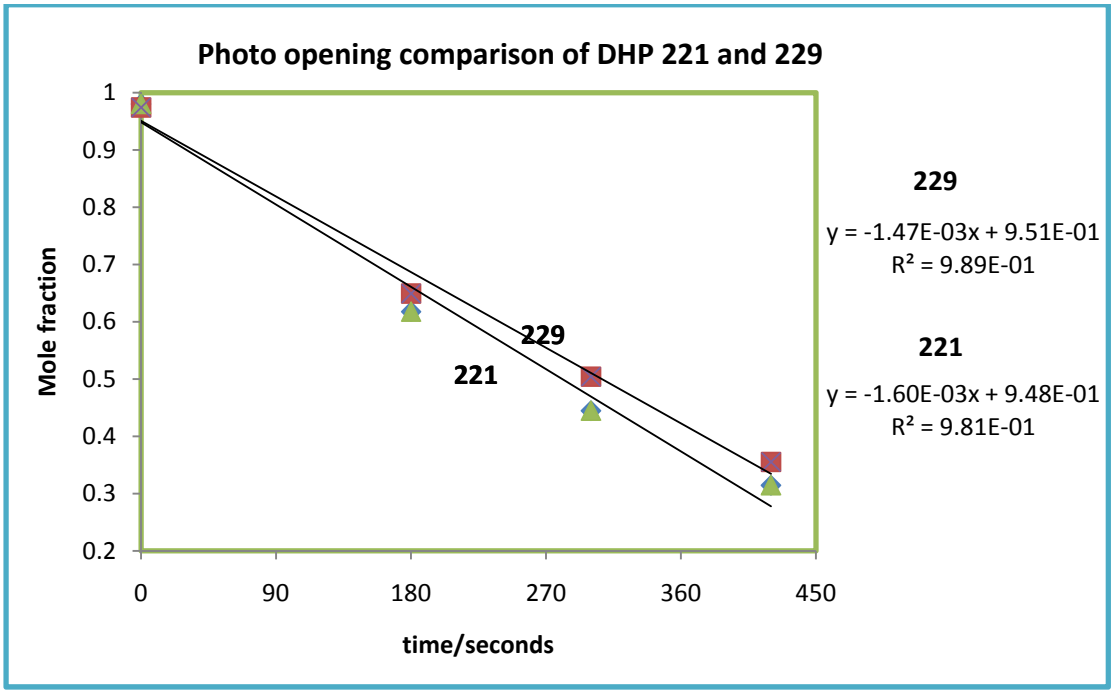


Photo opening comparison of DHP 221 and 229
Mole fraction
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
90
180
270
360
450
time/seconds
229
221
229
y = -1.47E-03x + 9.51E-01
R² = 9.89E-01
221
y = -1.60E-03x + 9.48E-01
R² = 9.81E-01

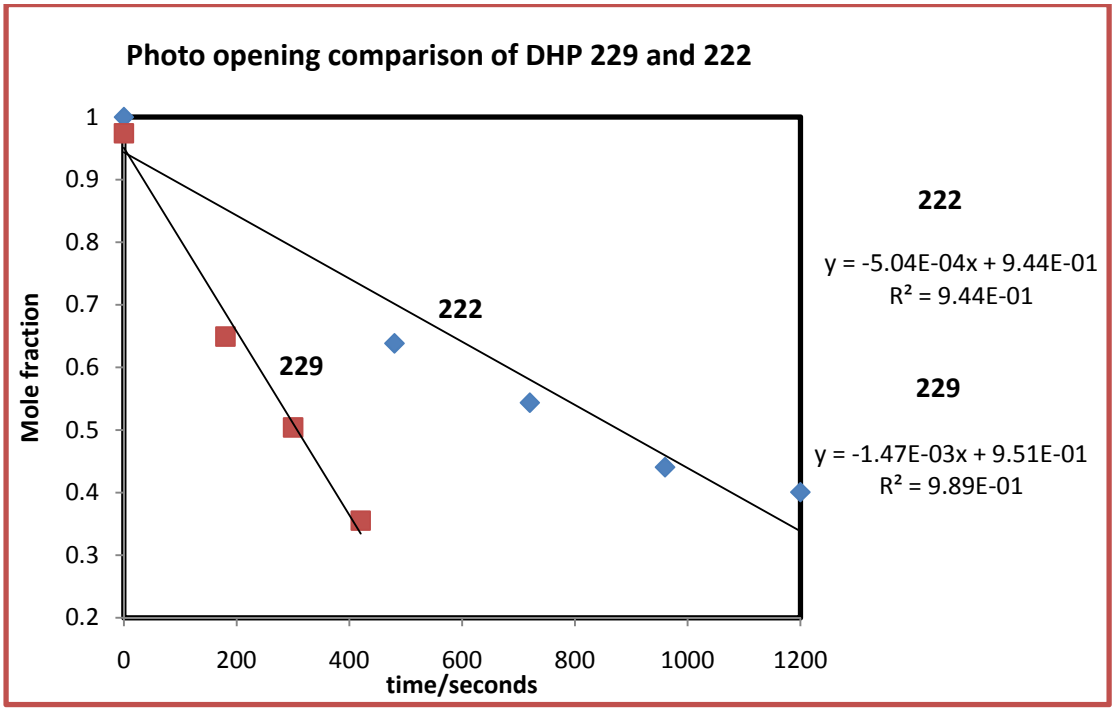
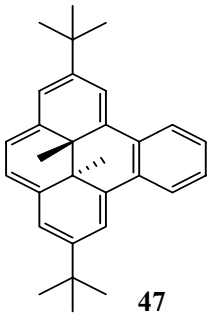
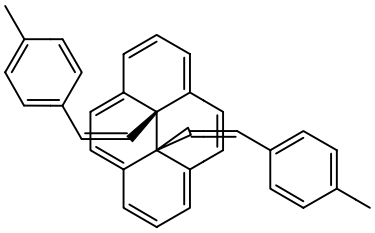


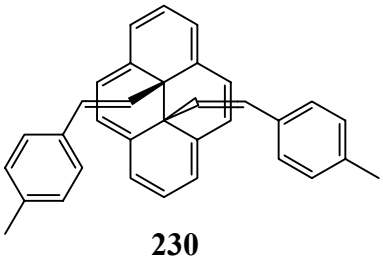
Photo opening comparison of DHP 229 and 222
Mole fraction
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
200
400
600
800
1000
1200
time/seconds
222
229
222
y = -5.04E-04x + 9.44E-01
R² = 9.44E-01
229
y = -1.47E-03x + 9.51E-01
R² = 9.89E-01



47



229



230

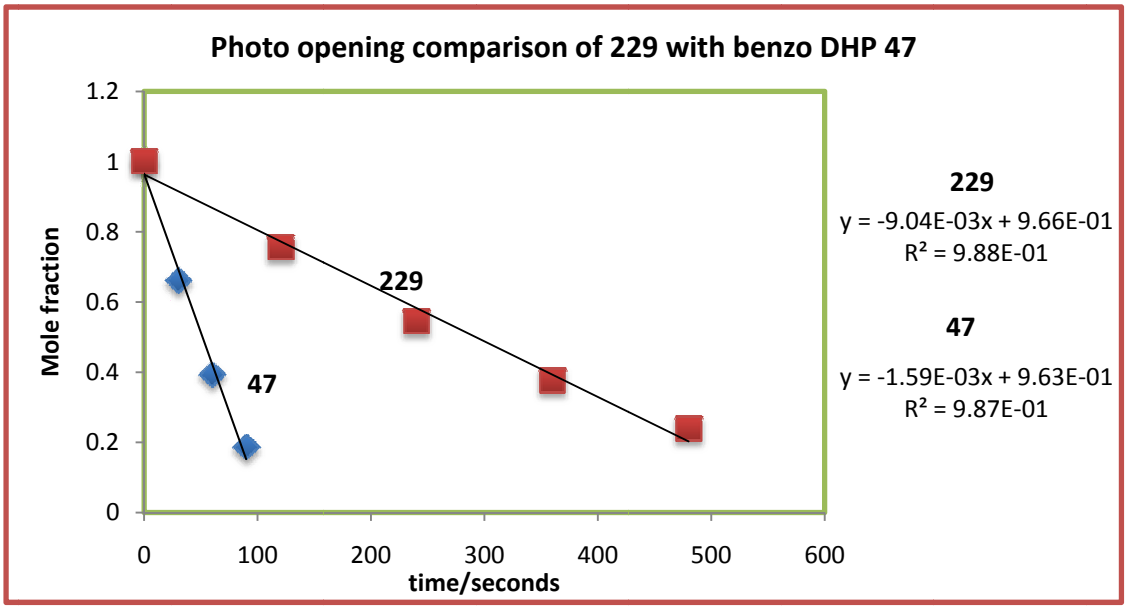


Photo opening comparison of 229 with benzo DHP 47
Mole fraction
time/seconds
229
47
229
y = -9.04E-03x + 9.66E-01
R² = 9.88E-01
47
y = -1.59E-03x + 9.63E-01
R² = 9.87E-01

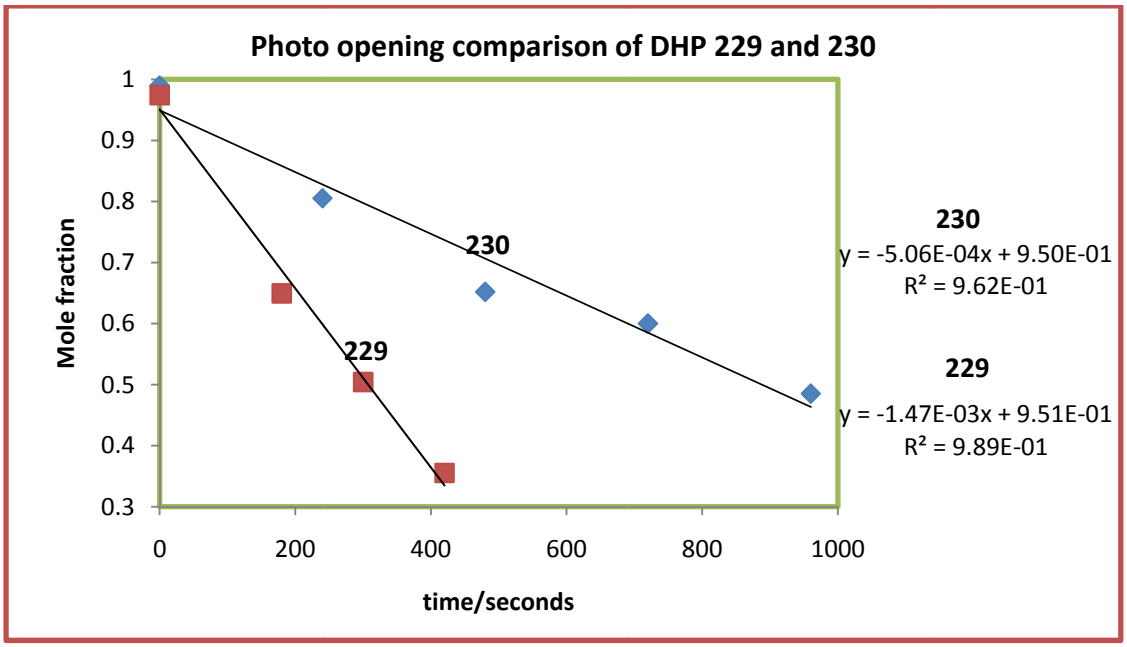
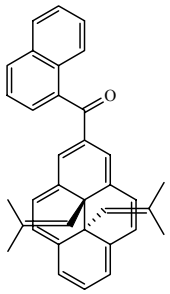
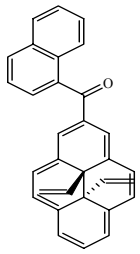


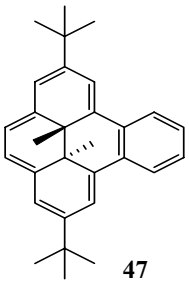
Photo opening comparison of DHP 229 and 230
Mole fraction
time/seconds
230
229
230
y = -5.06E-04x + 9.50E-01
R² = 9.62E-01
229
y = -1.47E-03x + 9.51E-01
R² = 9.89E-01



248



250



47

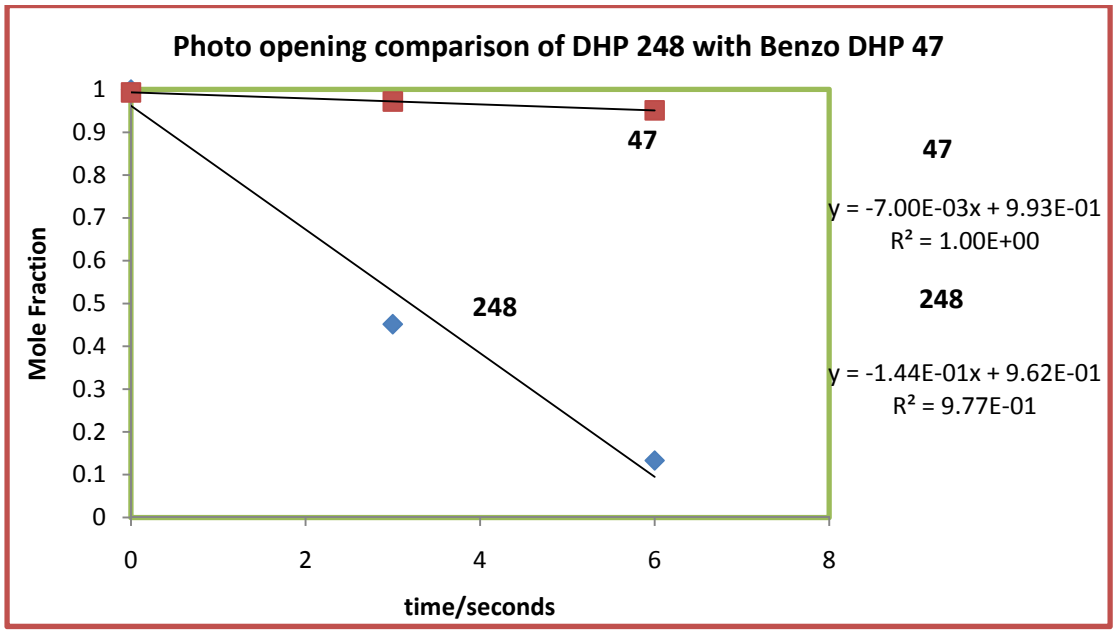


Photo opening comparison of DHP 248 with Benzo DHP 47
Mole Fraction
time/seconds
47
248
47
y = -7.00E-03x + 9.93E-01
R² = 1.00E+00
248
y = -1.44E-01x + 9.62E-01
R² = 9.77E-01

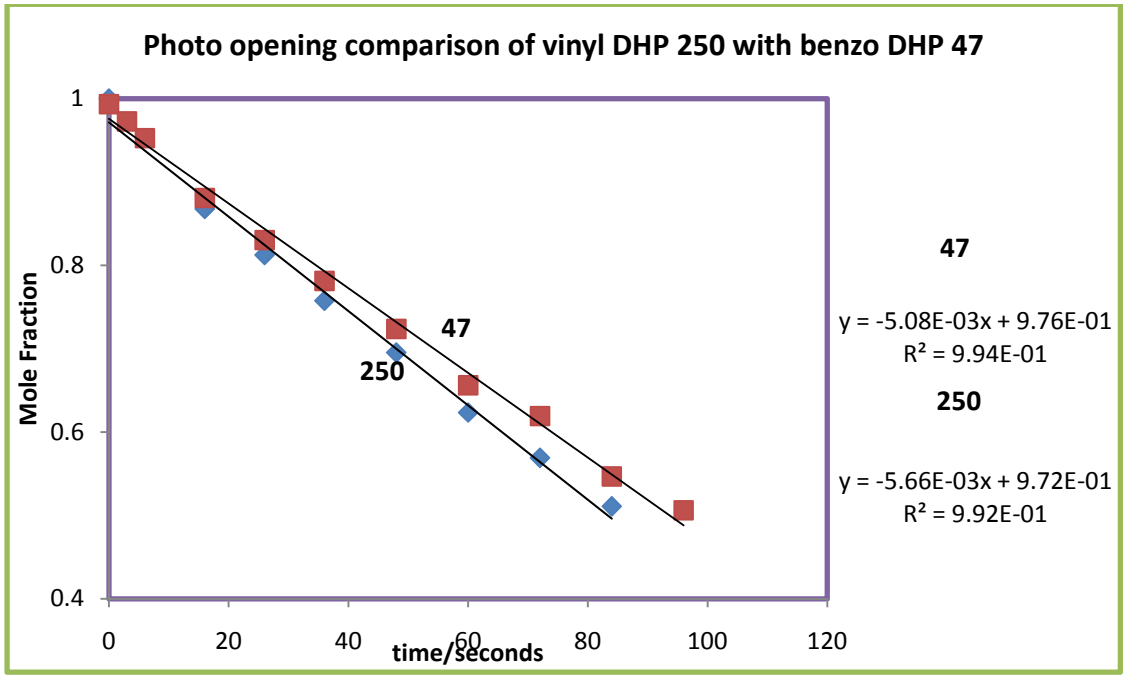
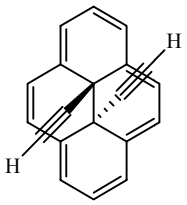
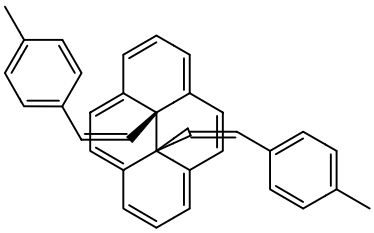


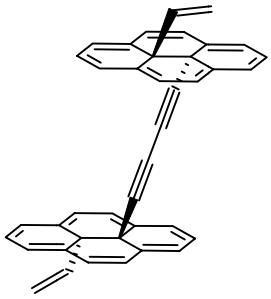
Photo opening comparison of vinyl DHP 250 with benzo DHP 47
Mole Fraction
time/seconds
47
250
47
y = -5.08E-03x + 9.76E-01
R² = 9.94E-01
250
y = -5.66E-03x + 9.72E-01
R² = 9.92E-01


H
H

236



229



254

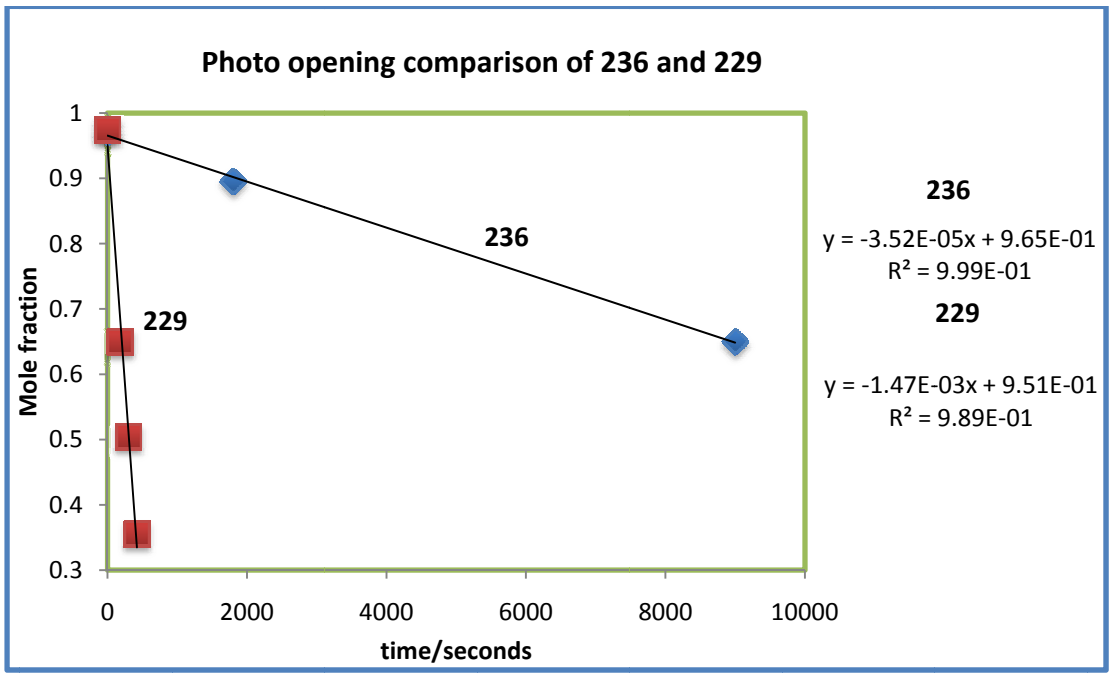
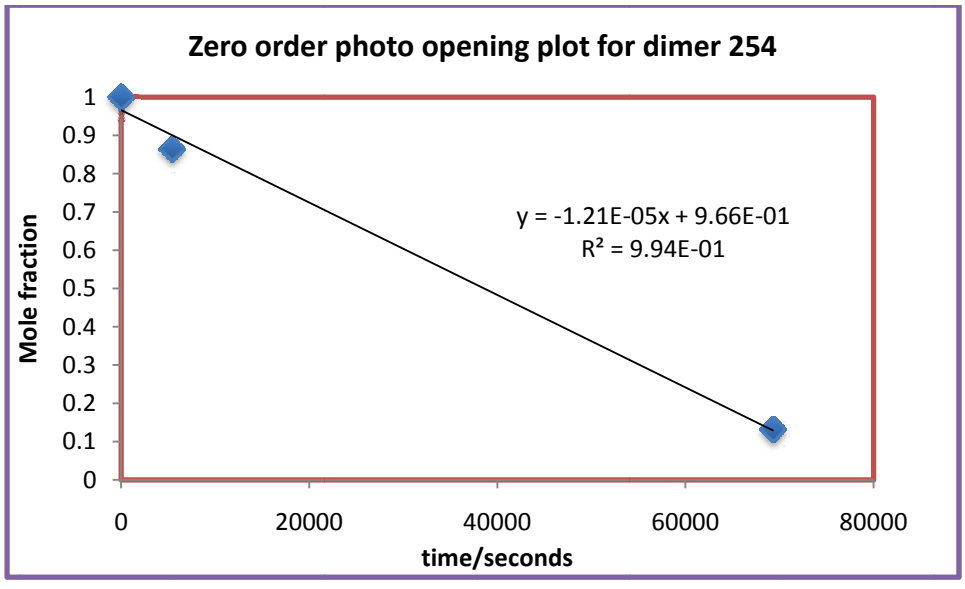
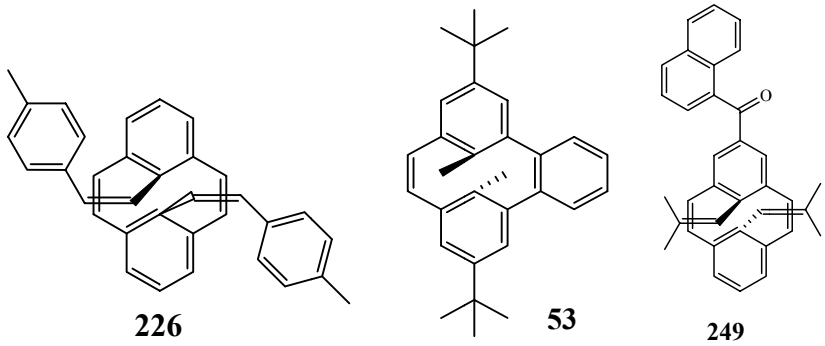


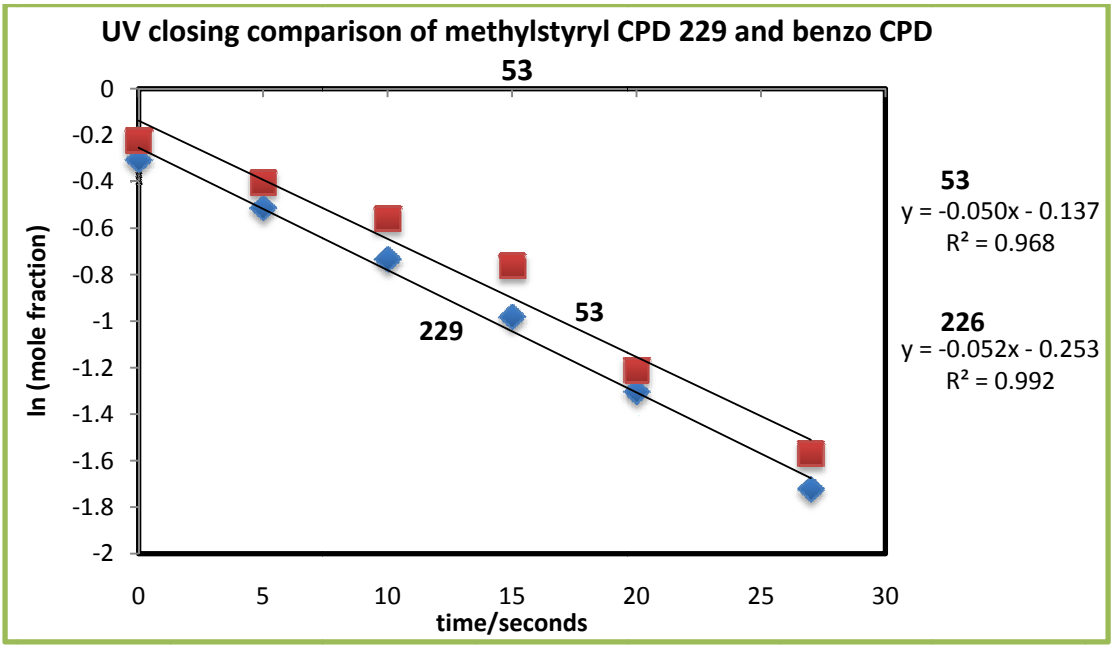
Photo opening comparison of 236 and 229
Mole fraction
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0
2000
4000
6000
8000
10000
time/seconds
236
229
236
y = -3.52E-05x + 9.65E-01
R² = 9.99E-01
229
y = -1.47E-03x + 9.51E-01
R² = 9.89E-01

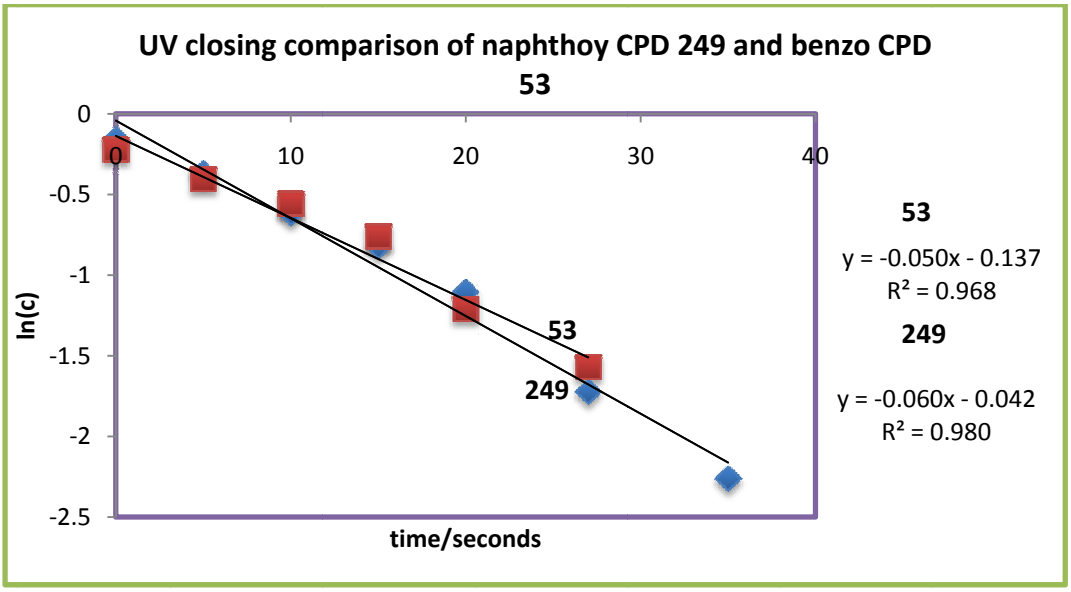

Zero order photo opening plot for dimer 254
Mole fraction
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20000
40000
60000
80000
time/seconds
y = -1.21E-05x + 9.66E-01
R² = 9.94E-01

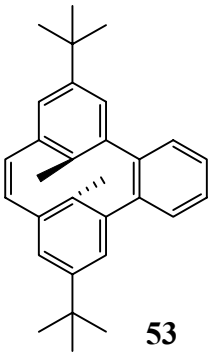
## Appendix E: UV closing data for CPDs 53, 85, 226 and 249



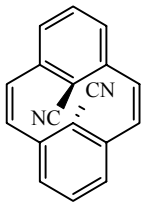

226 53 249



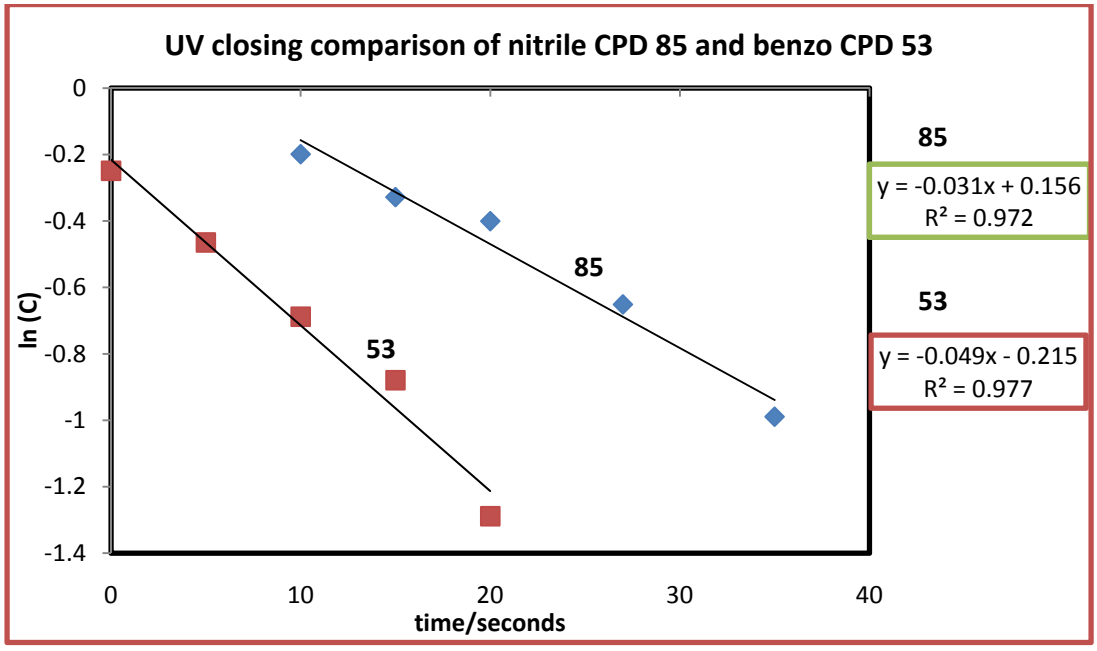





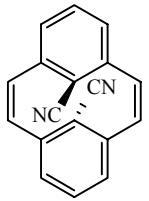
53


CN
NC

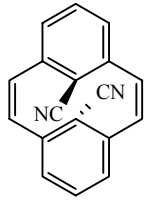
85


UV closing comparison of nitrile CPD 85 and benzo CPD 53
ln (C)
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
0
10
20
30
40
time/seconds
85
53
85
y = -0.031x + 0.156
R² = 0.972
53
y = -0.049x - 0.215
R² = 0.977

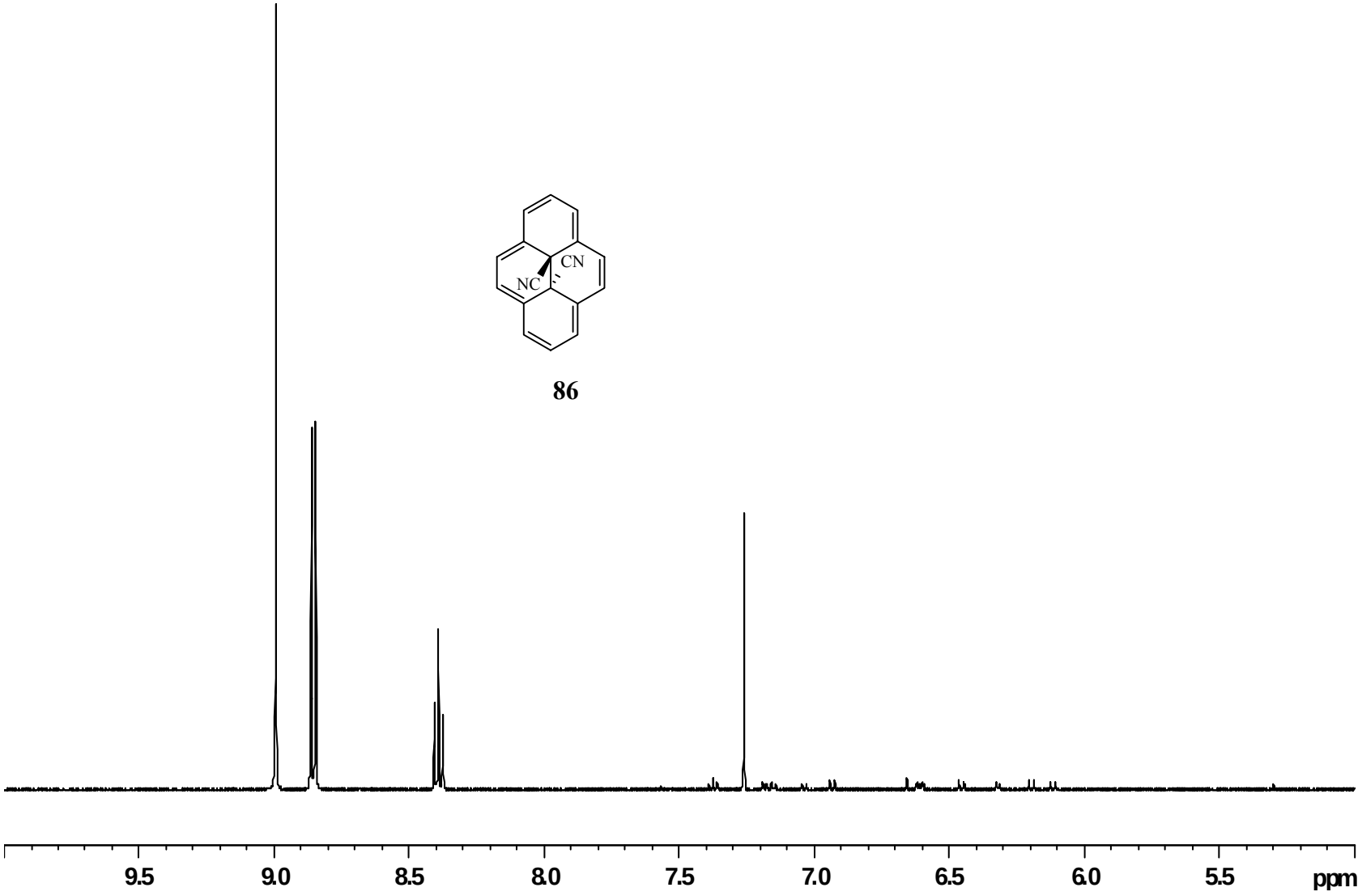
## Appendix F: NMR spectra



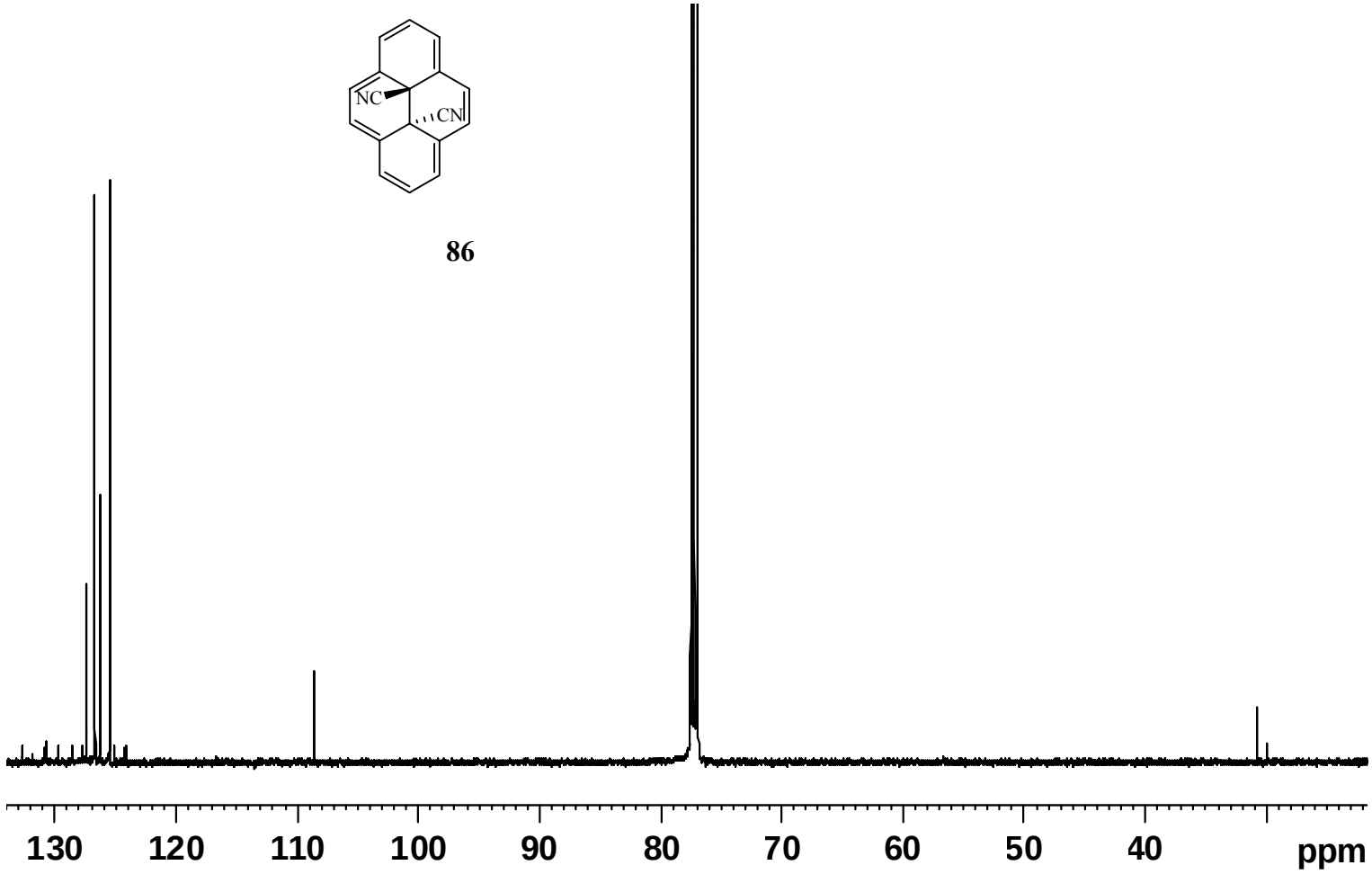

**85**



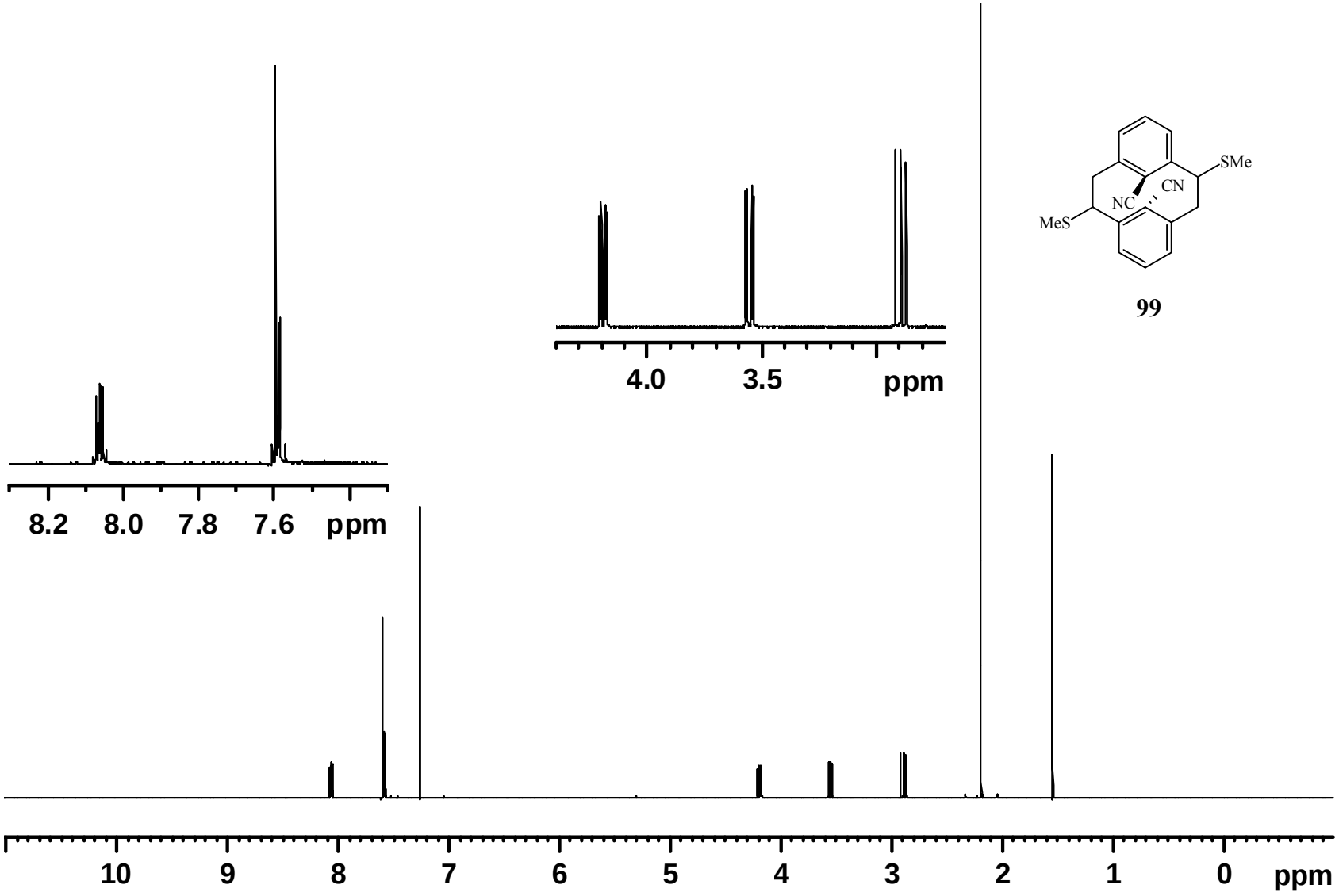

**85**




**86**



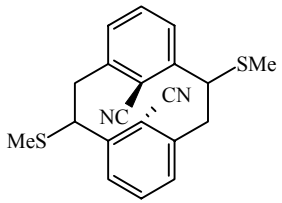

**86**



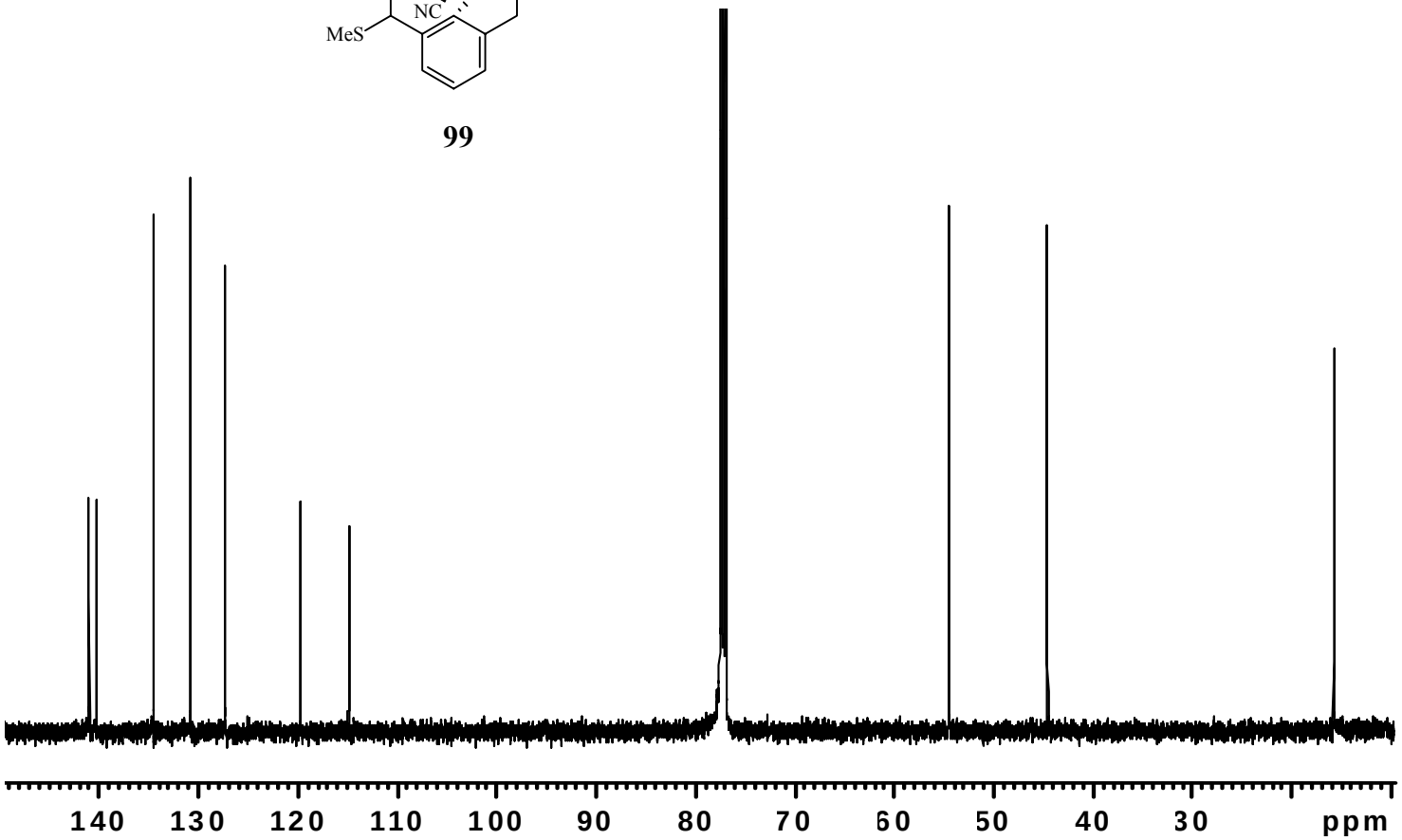


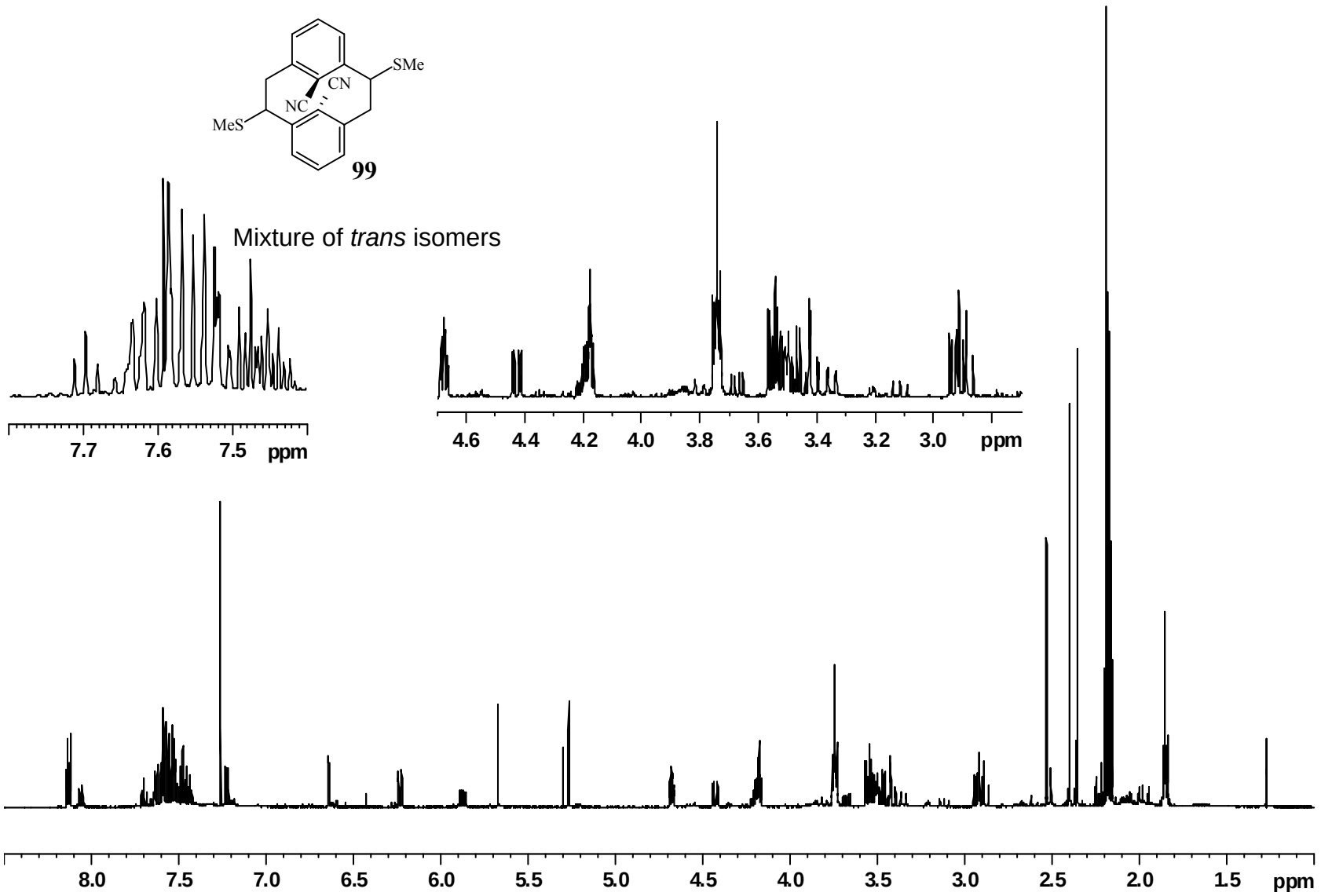


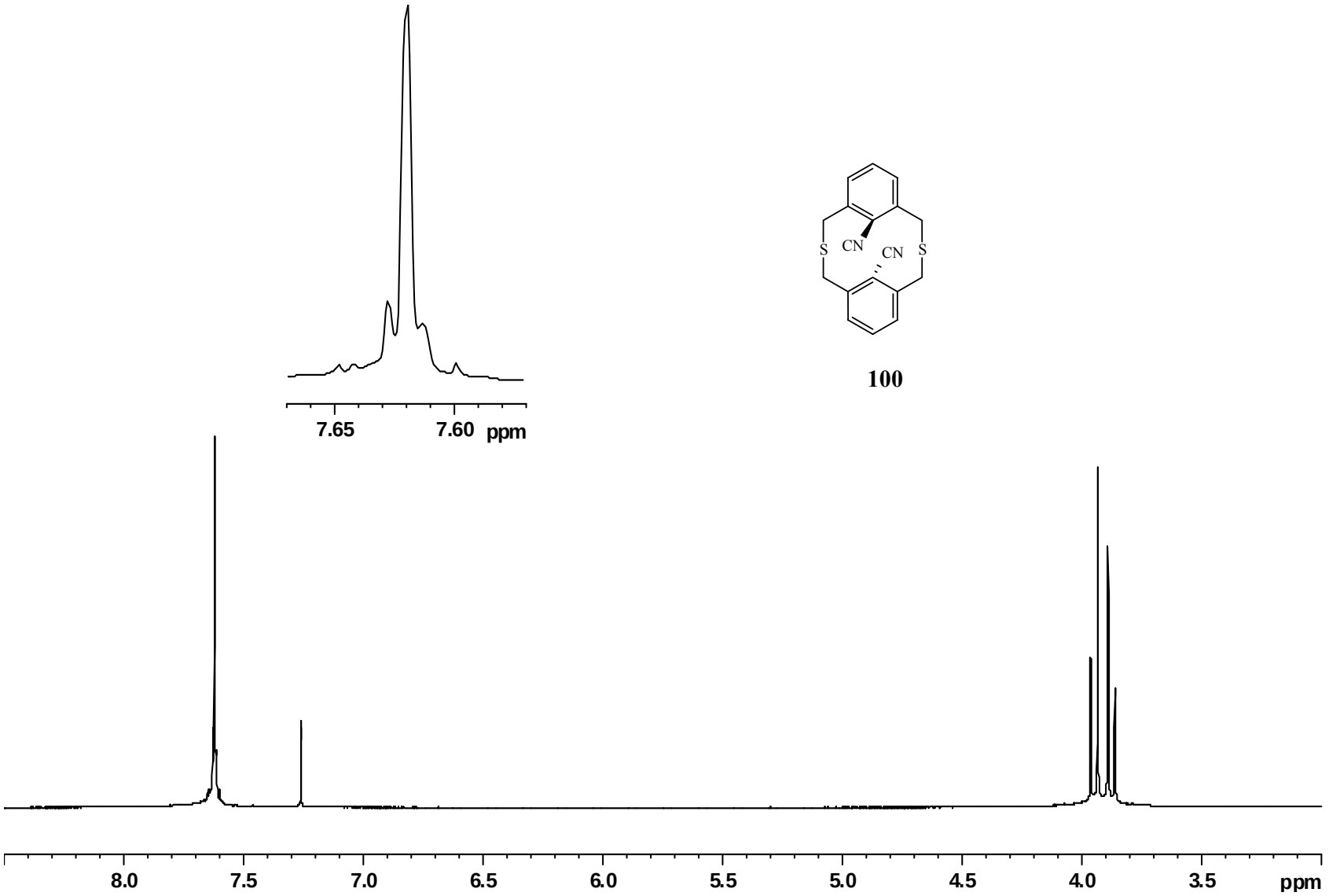
**99**



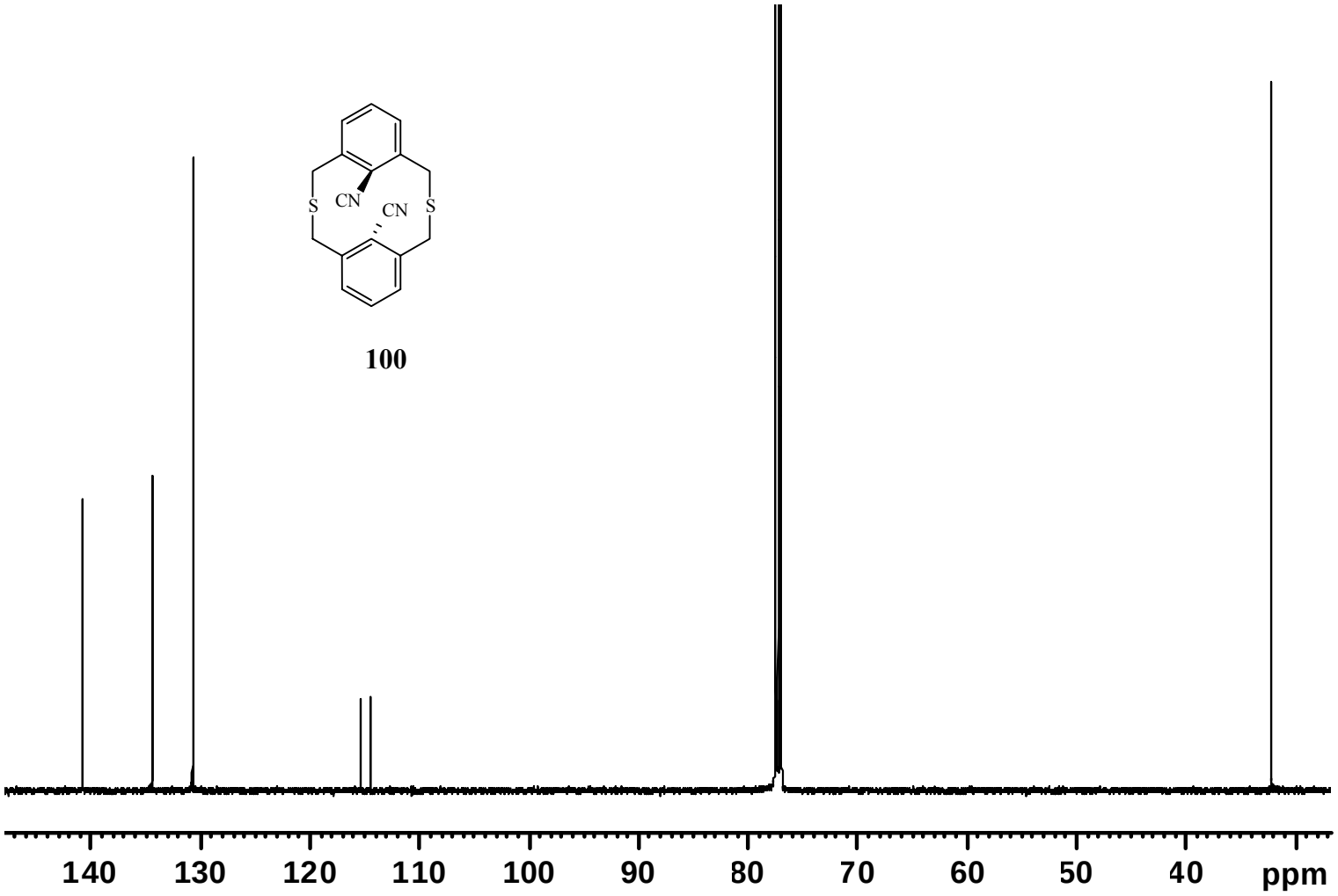

**99**



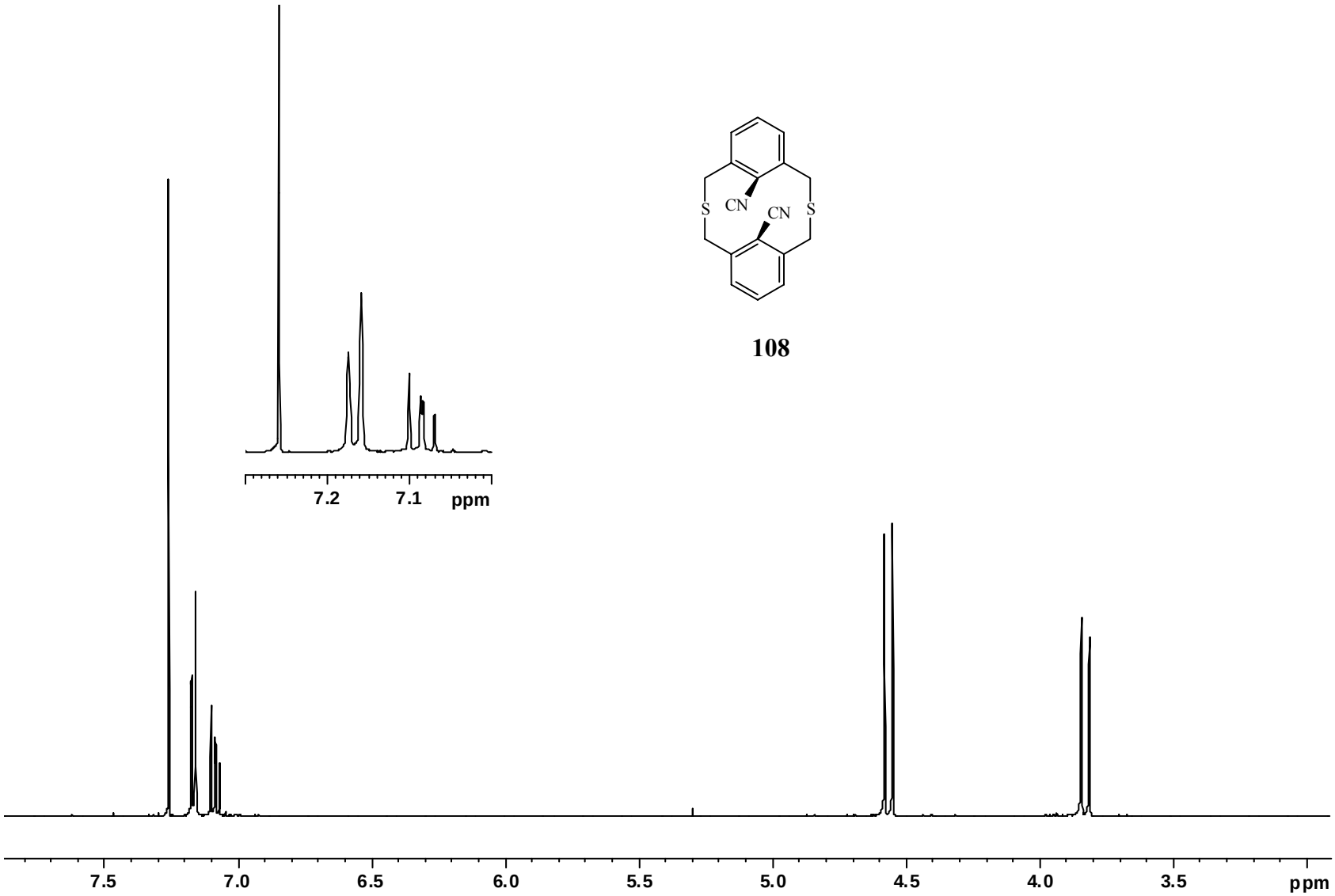

SMe
CN
NC
MeS
99
Mixture of *trans* isomers
7.7
7.6
7.5
ppm
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm



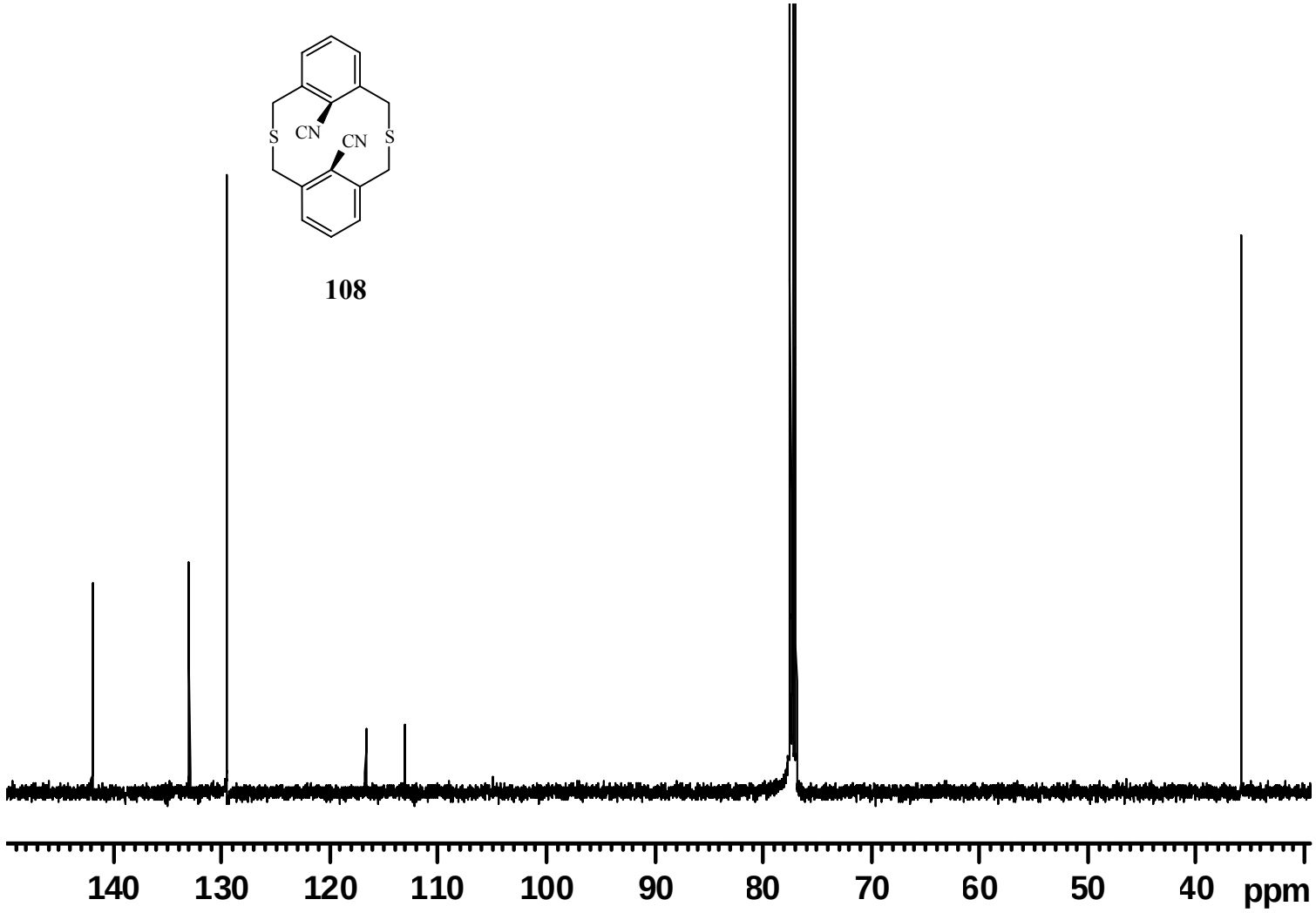

**100**



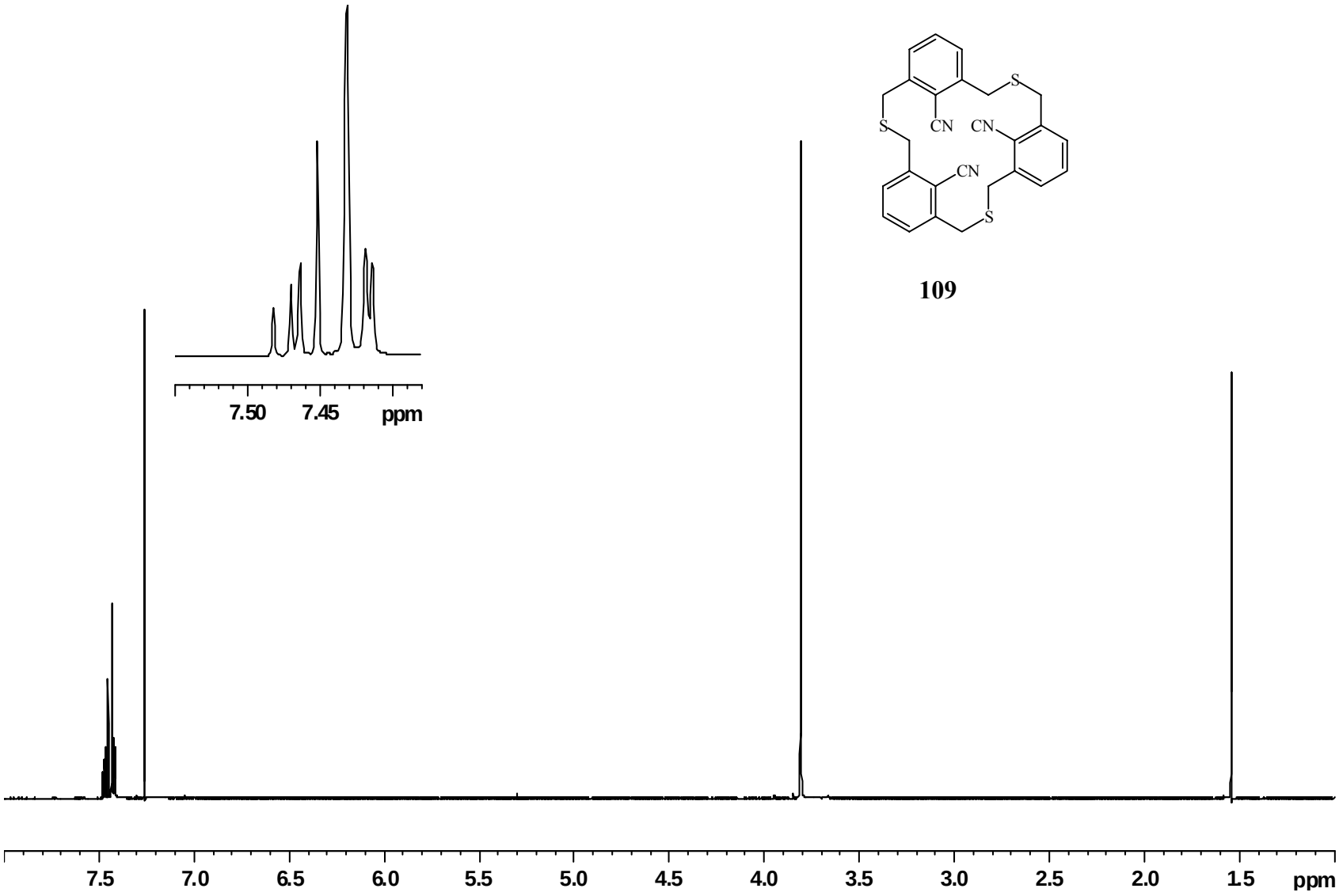

**100**

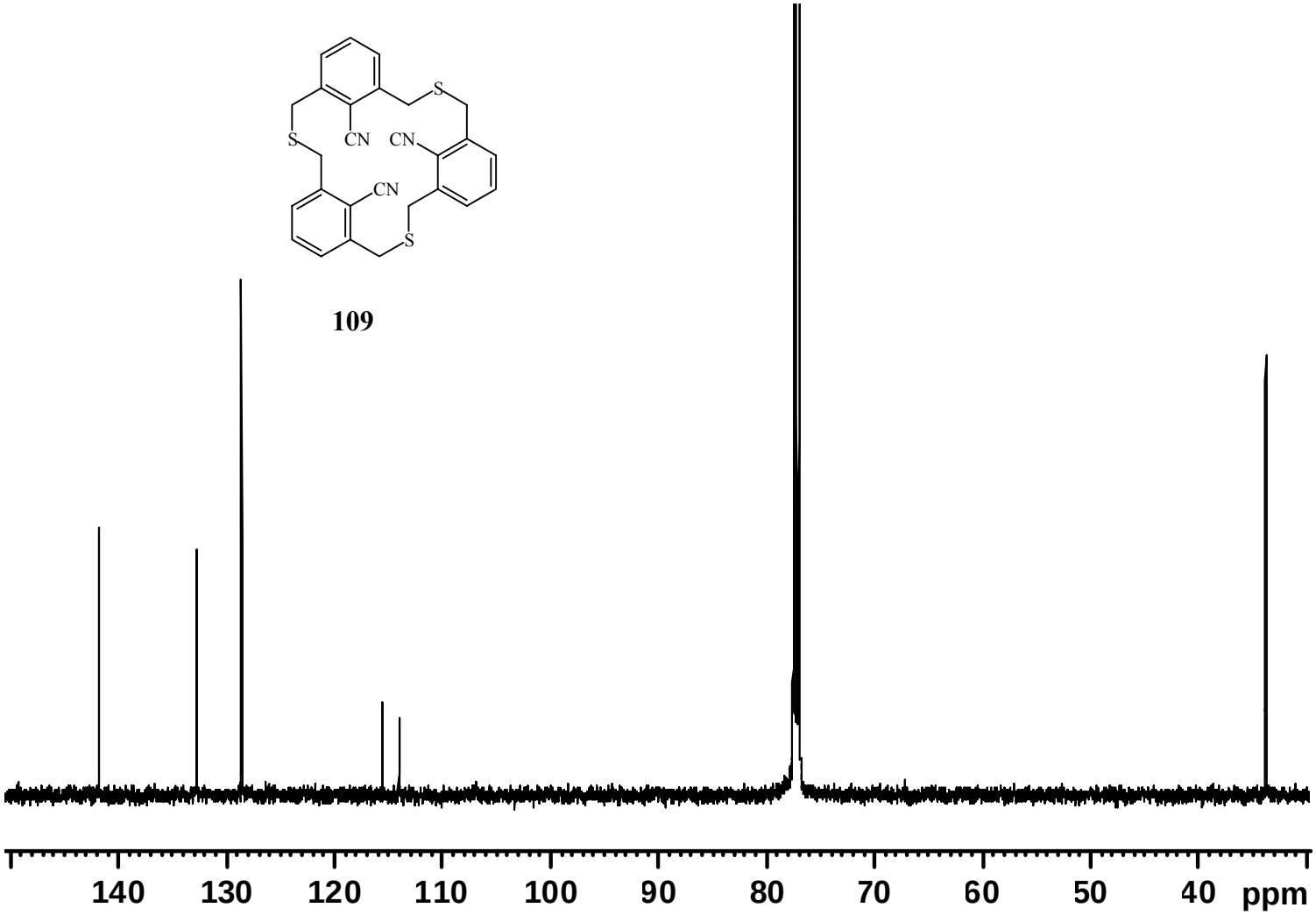



**108**

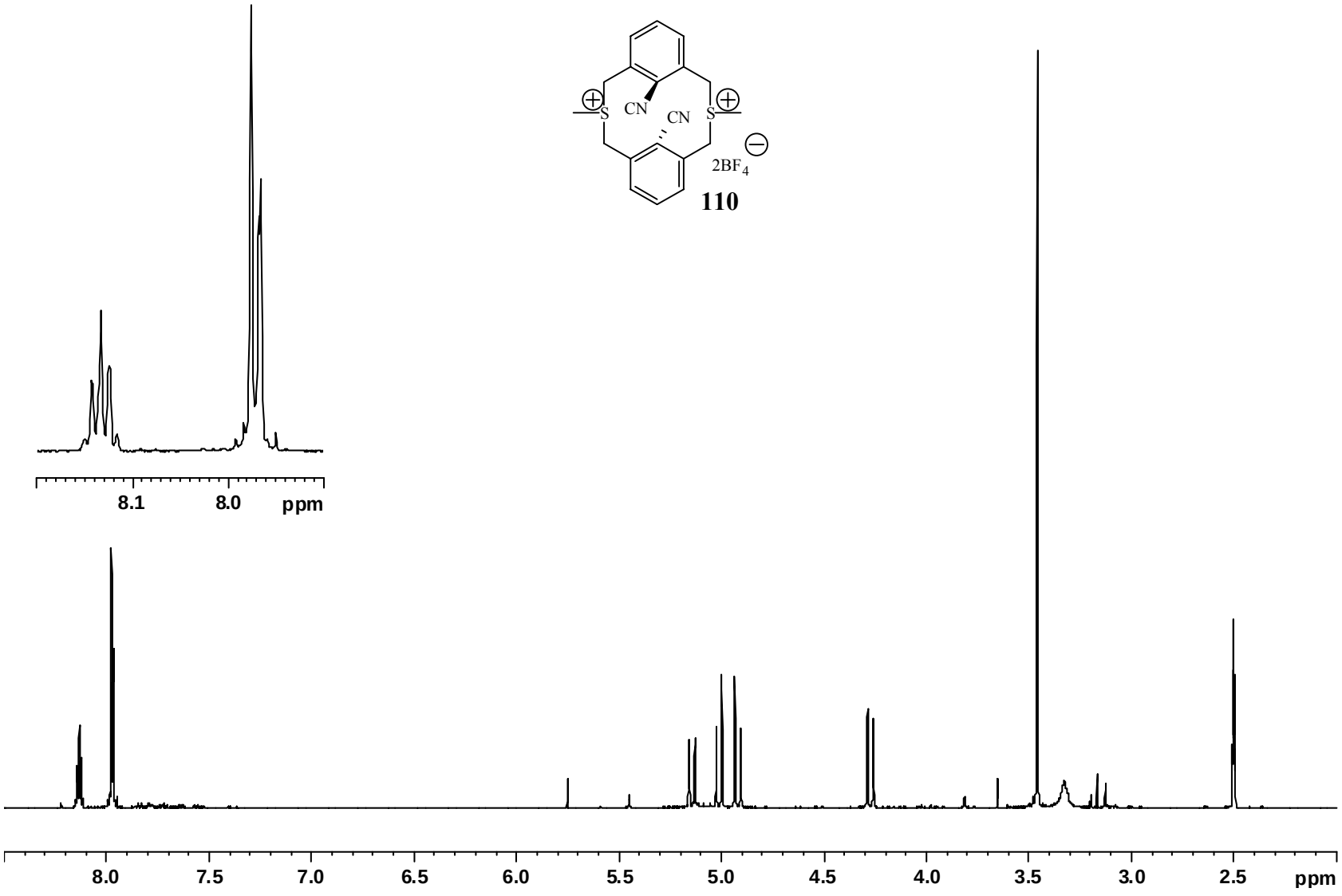



**108**

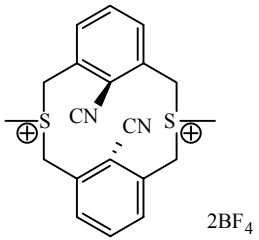

S
CN
CN
S
CN
S
109
7.50
7.45
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm



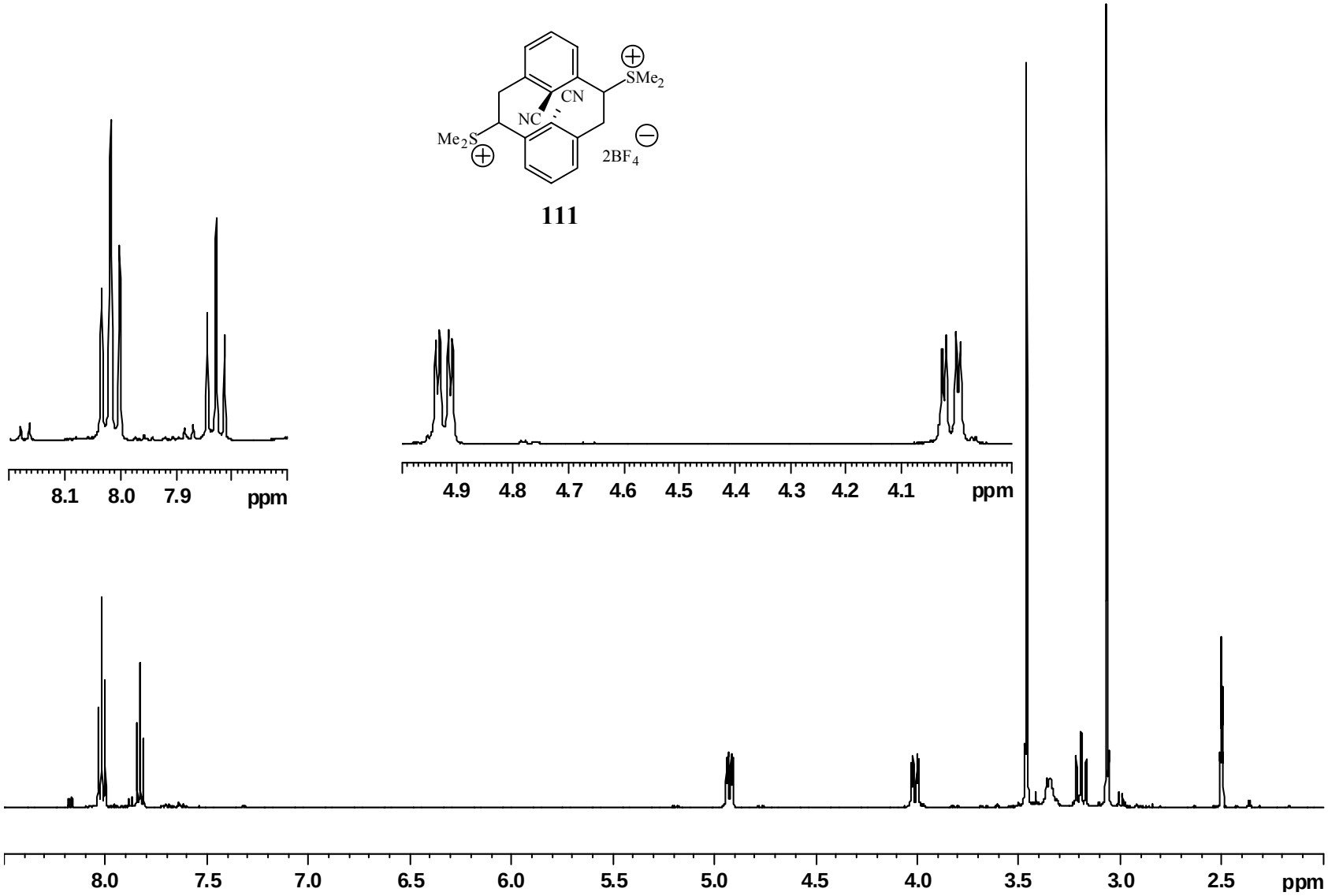

**109**



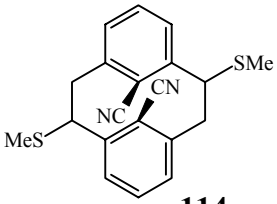

**110**




**110**

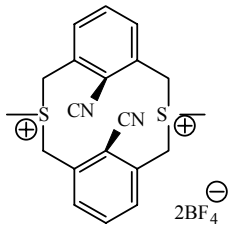

SMe2
CN
NC
Me2S
2BF4
8.1 8.0 7.9 ppm
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm

**111**

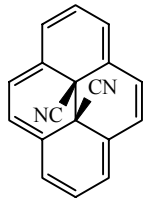



**114**

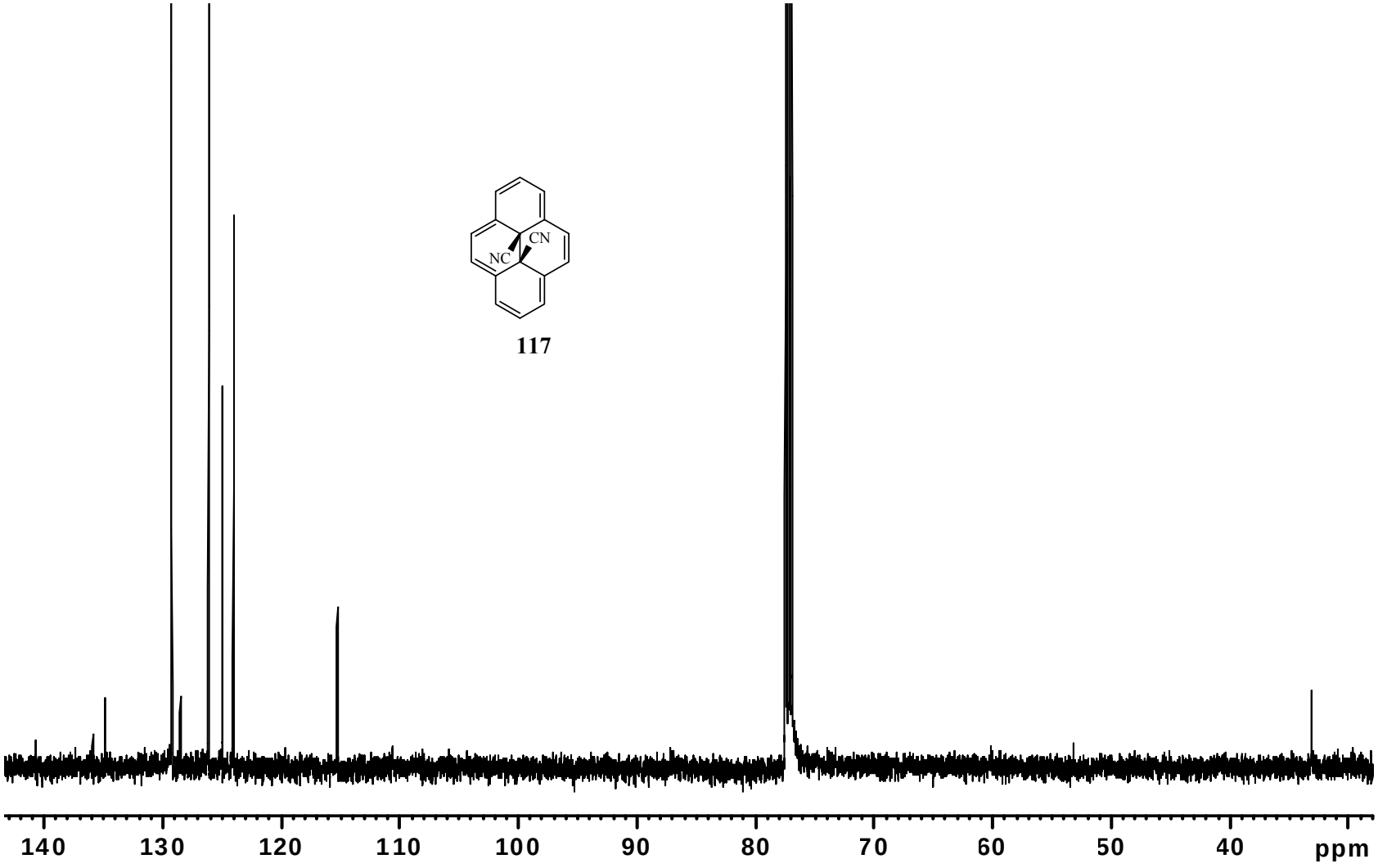
Mixture of *cis* isomers



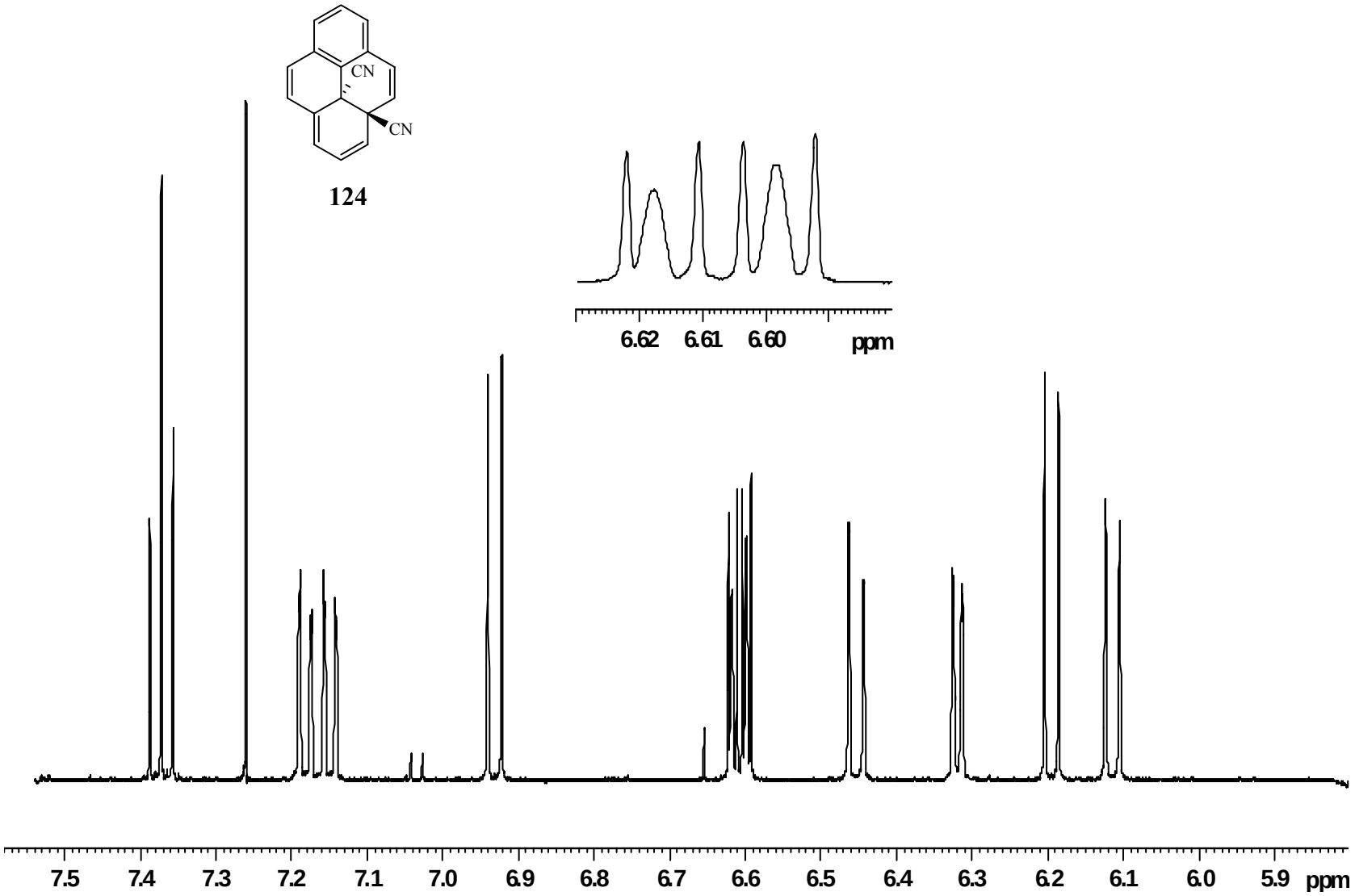

**115**

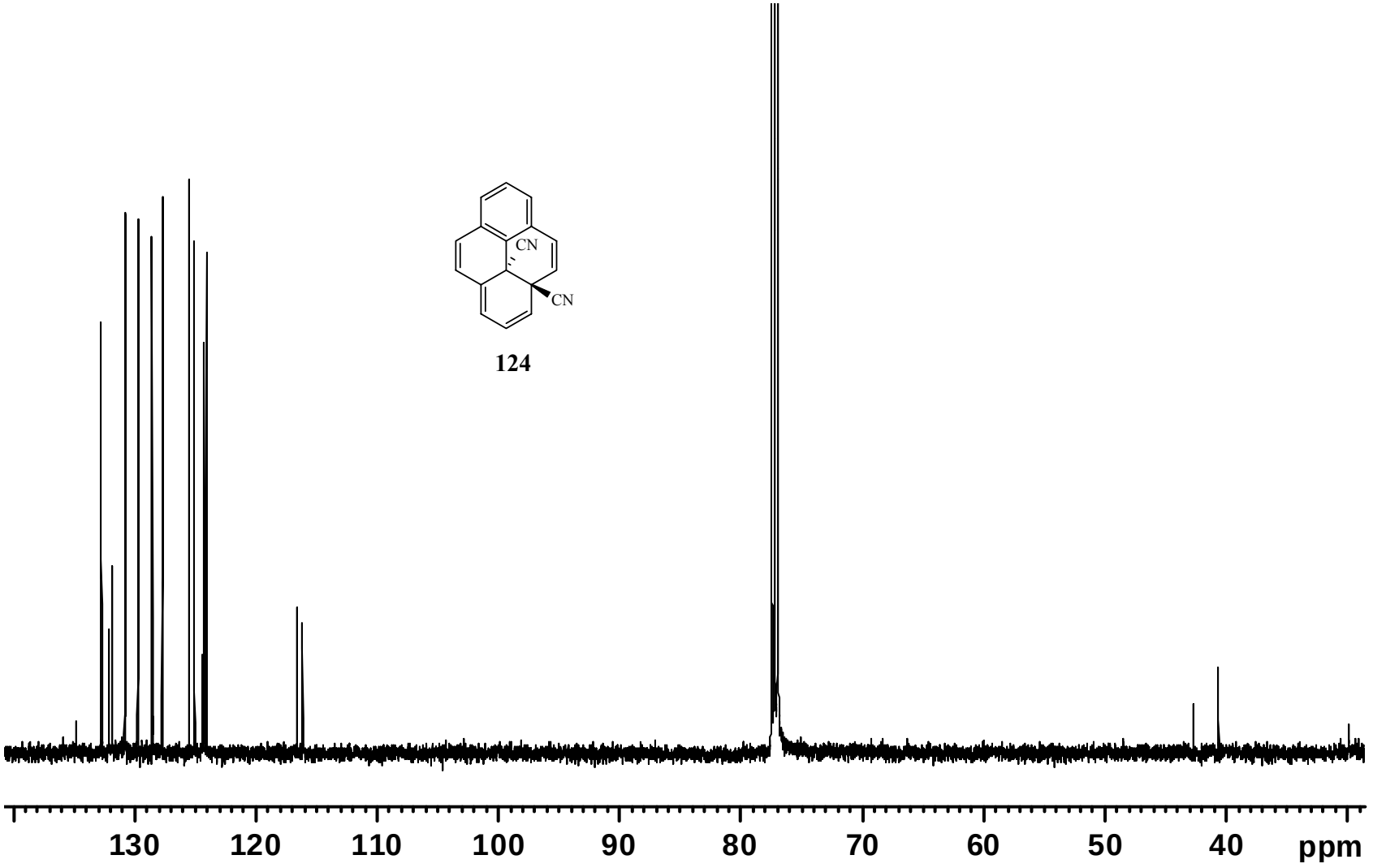



**117**

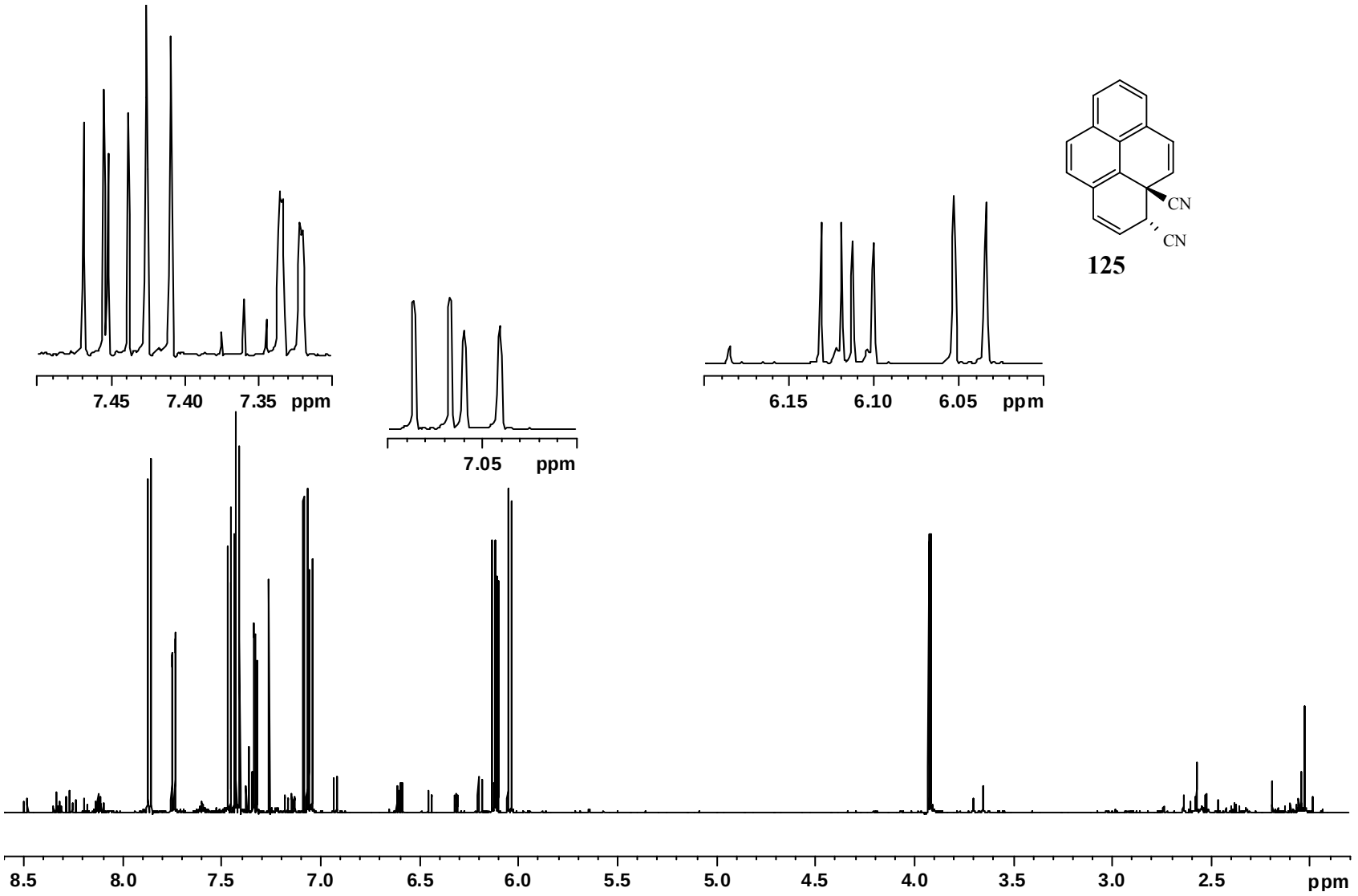


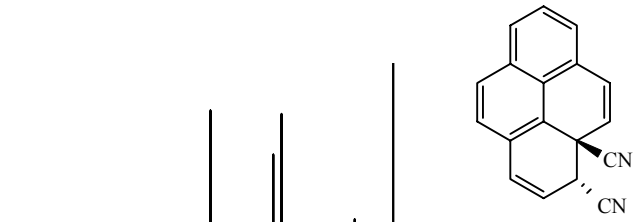

**117**


CN
CN
124
6.62
6.61
6.60
ppm
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
ppm

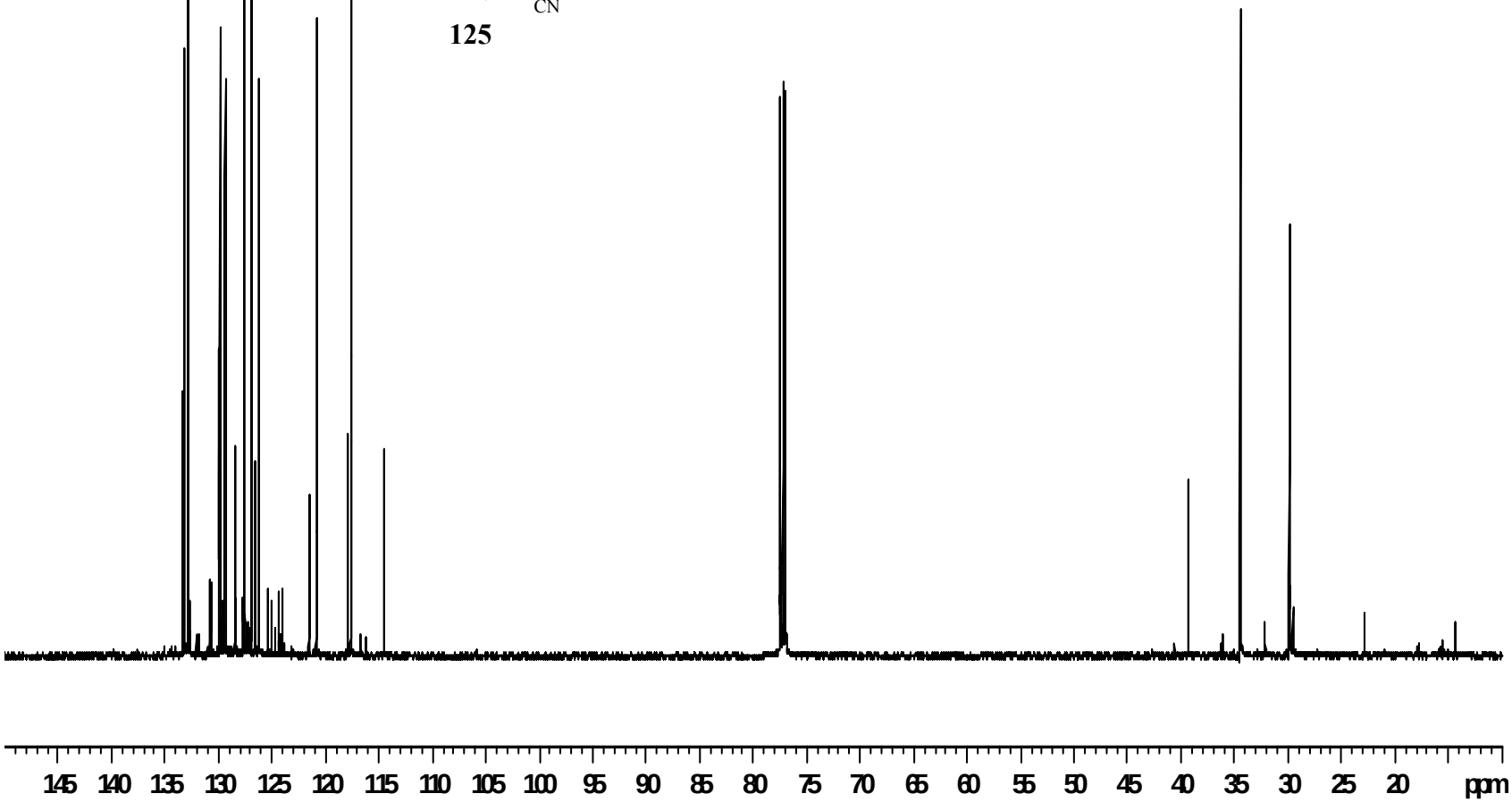


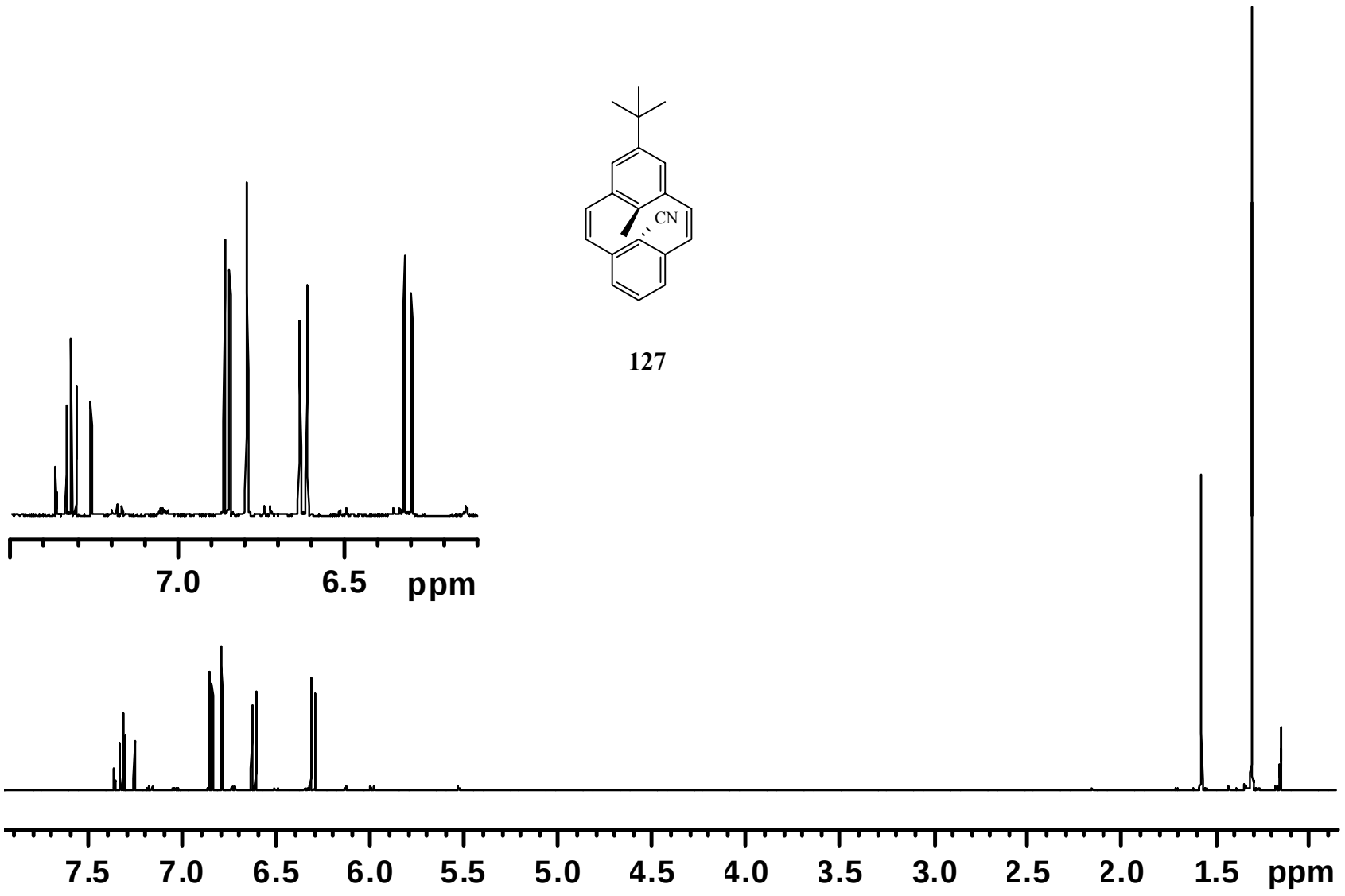

**124**


7.45
7.40
7.35
ppm
7.05
ppm
6.15
6.10
6.05
ppm
CN
CN
125
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

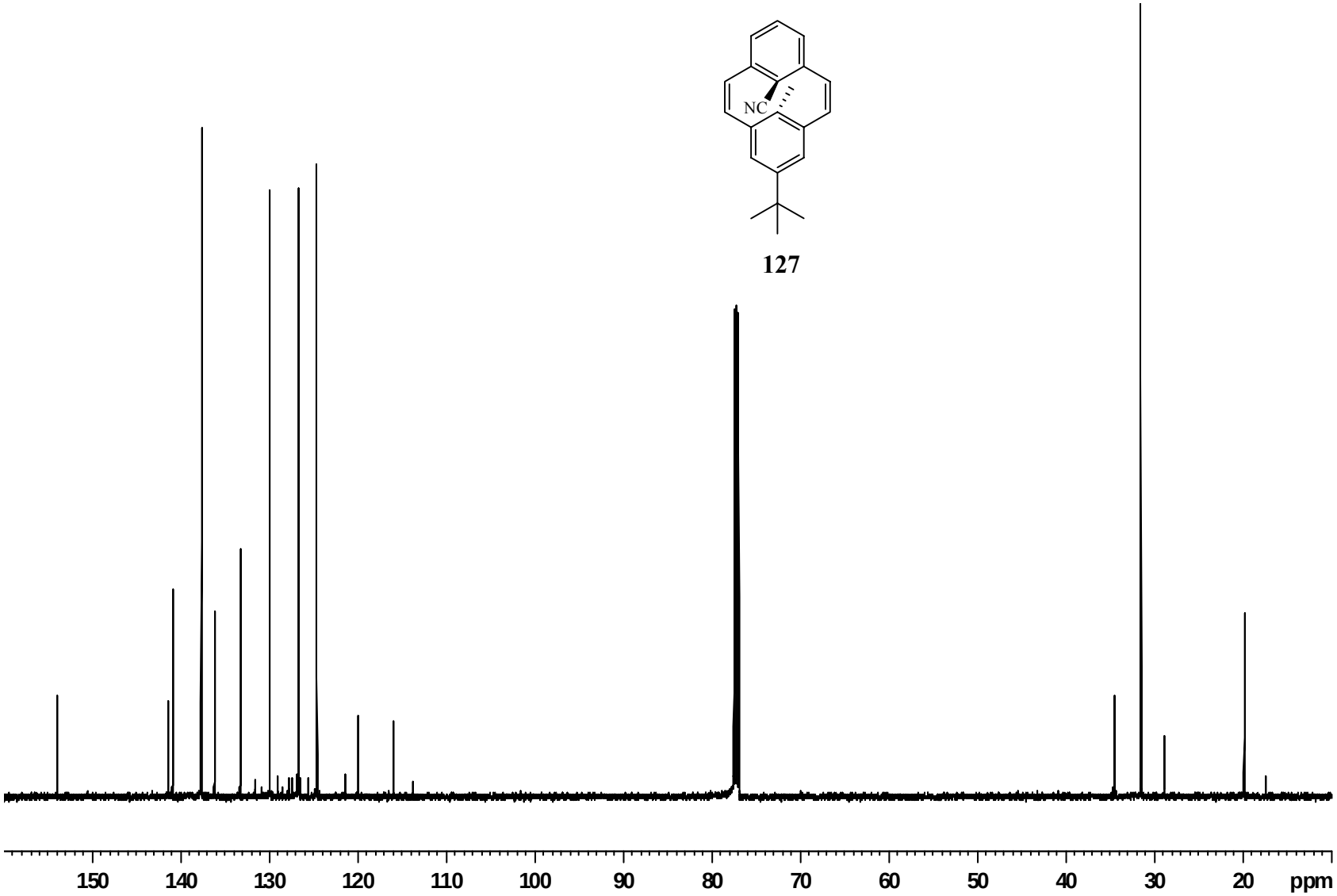

CN
CN

**125**

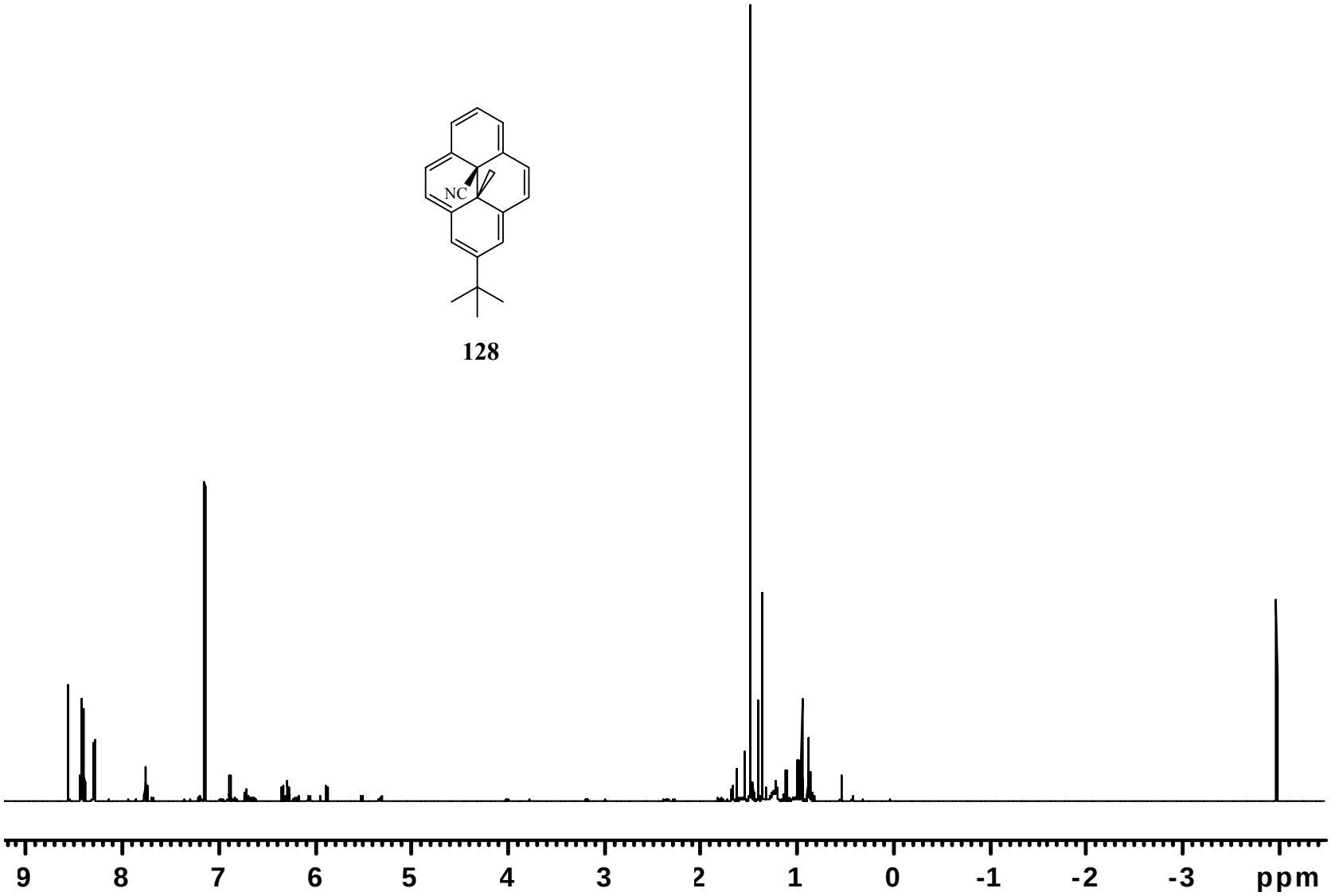

145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 ppm



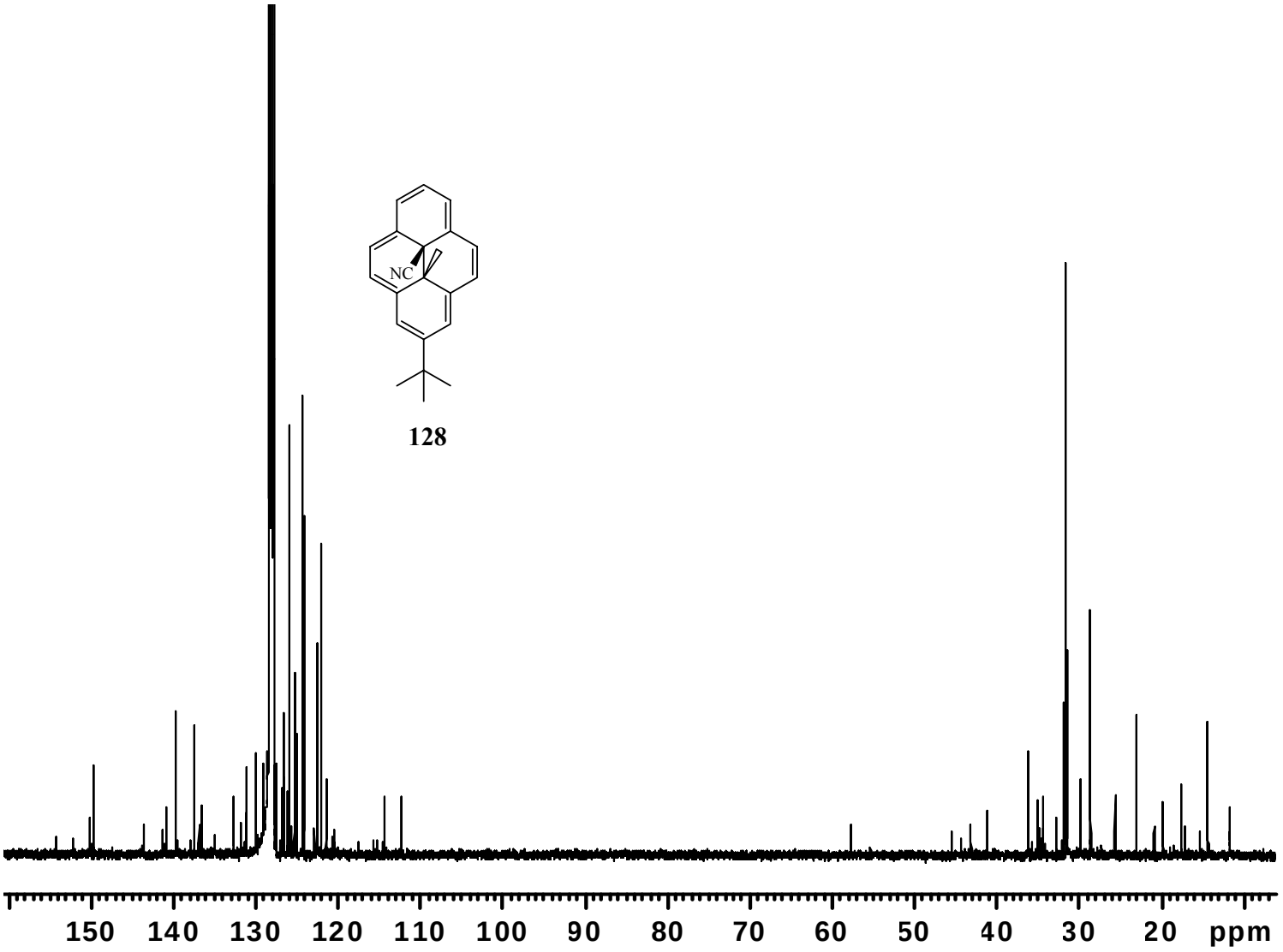

**127**



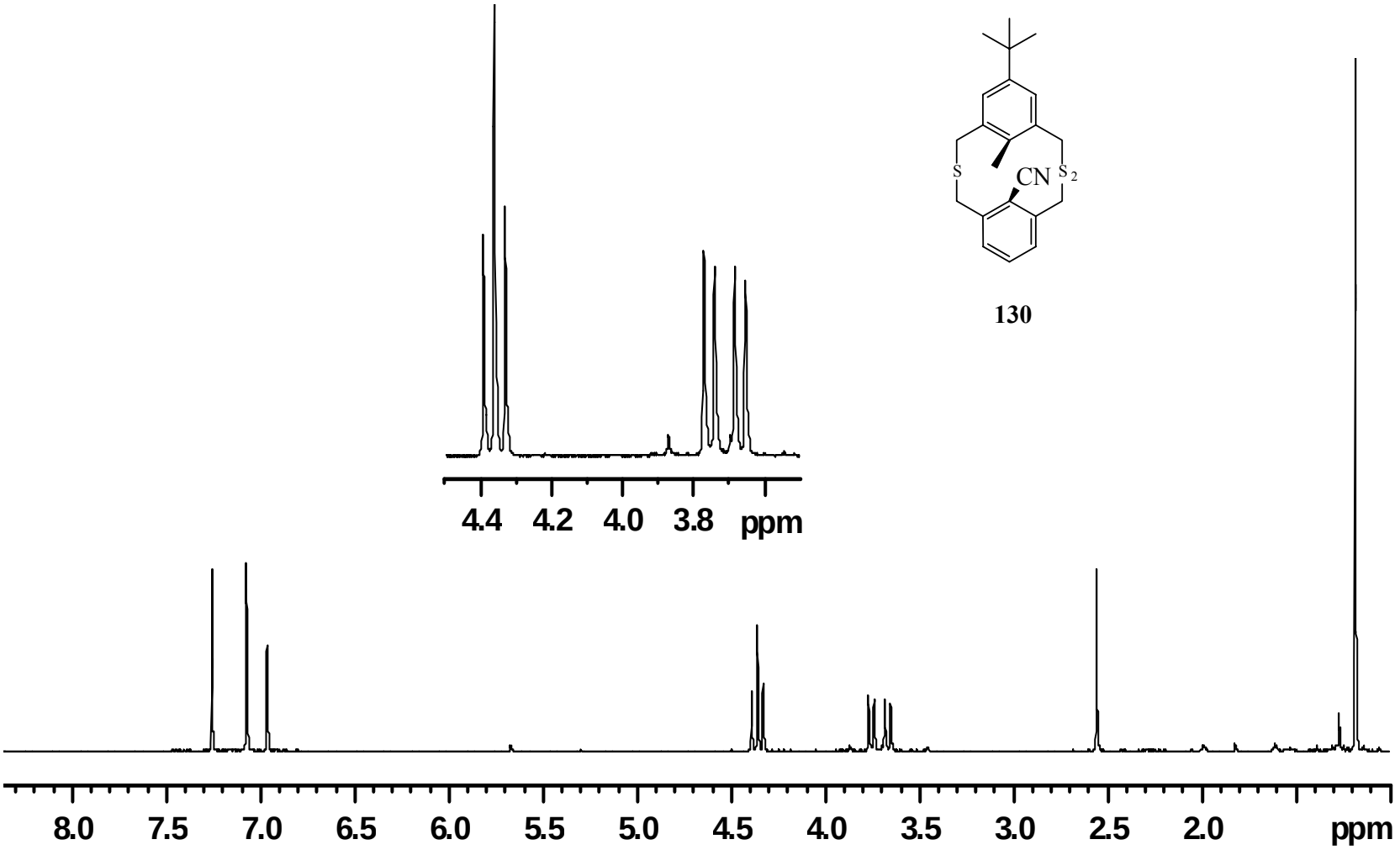

**127**



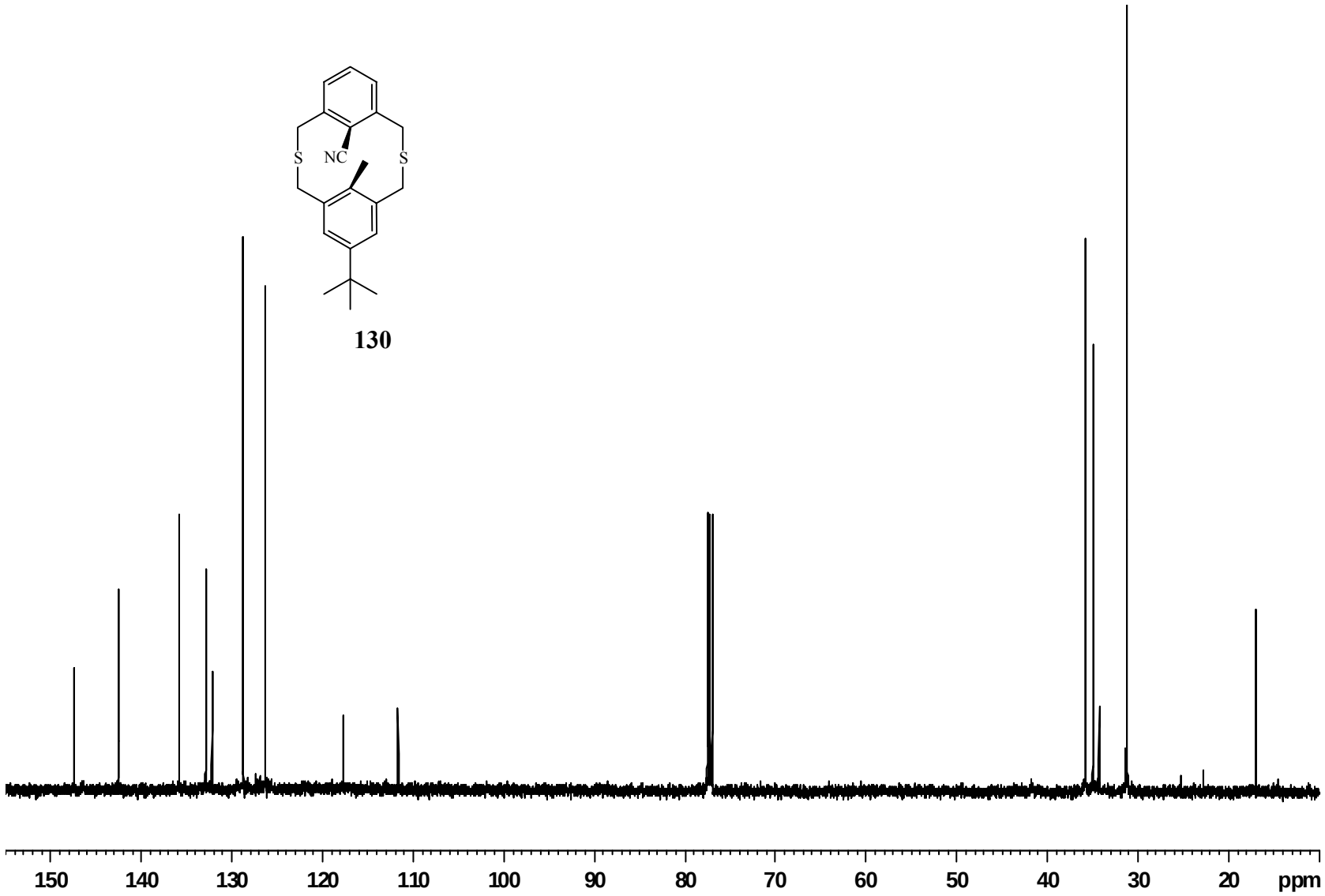

**128**



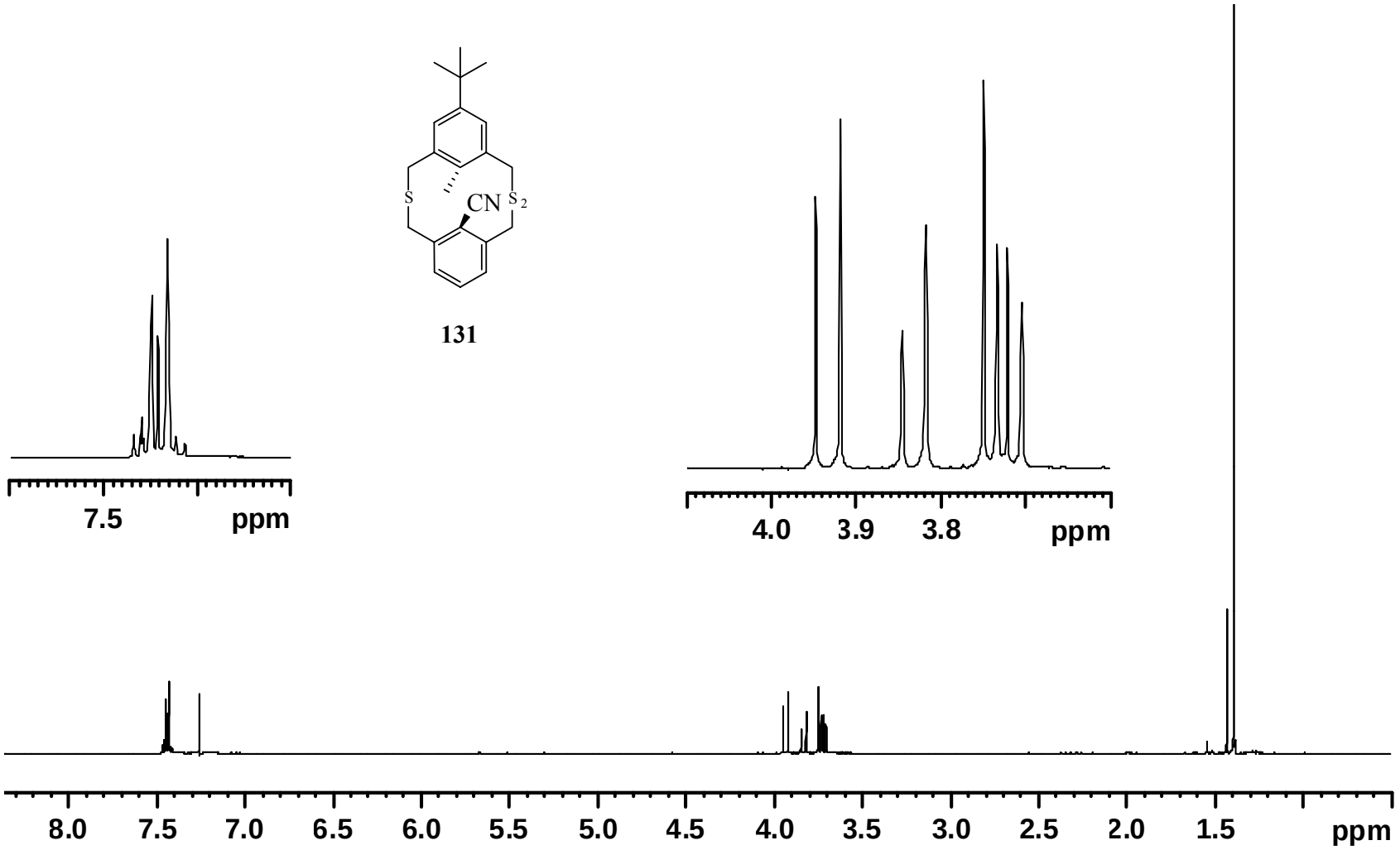

**128**

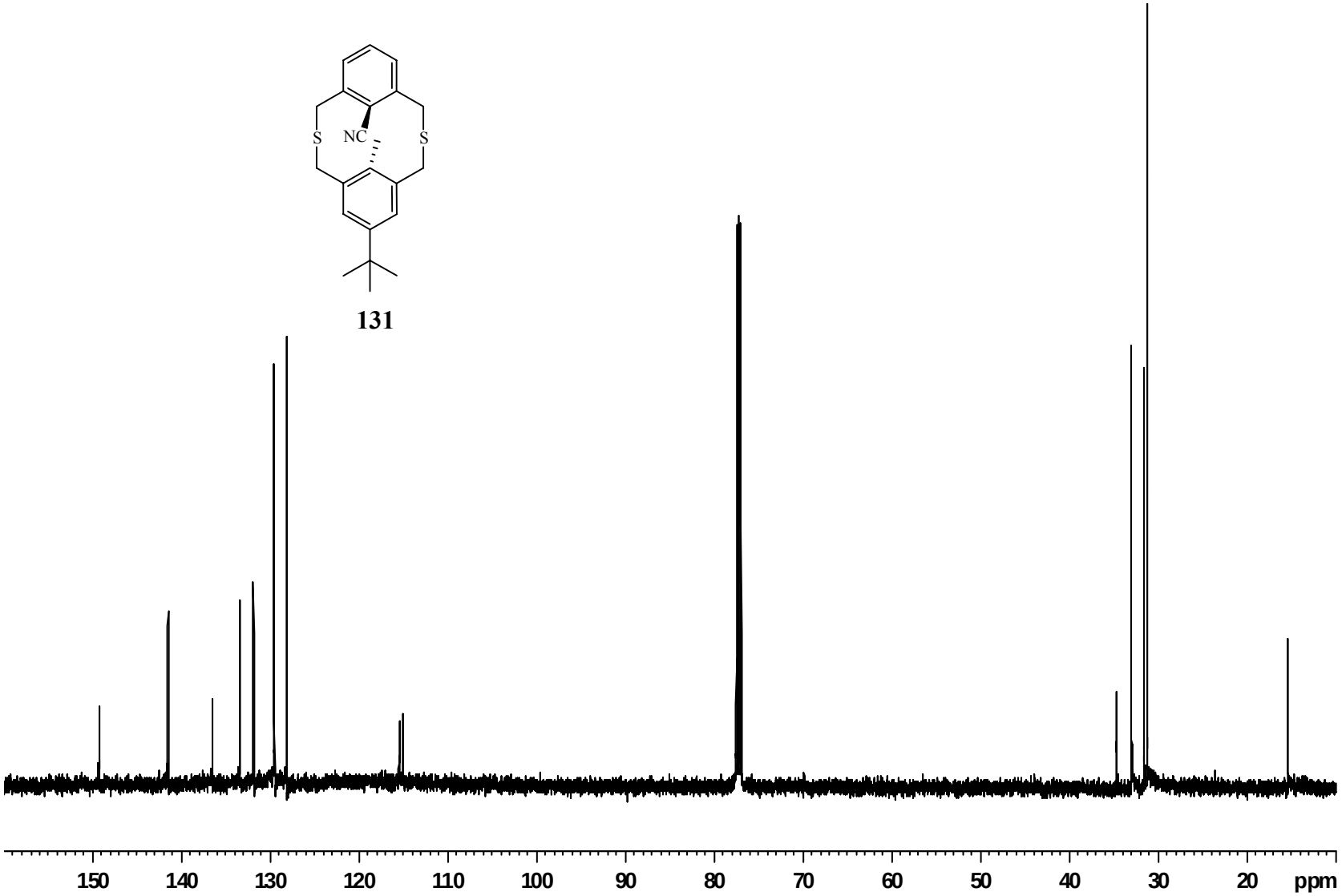



**130**

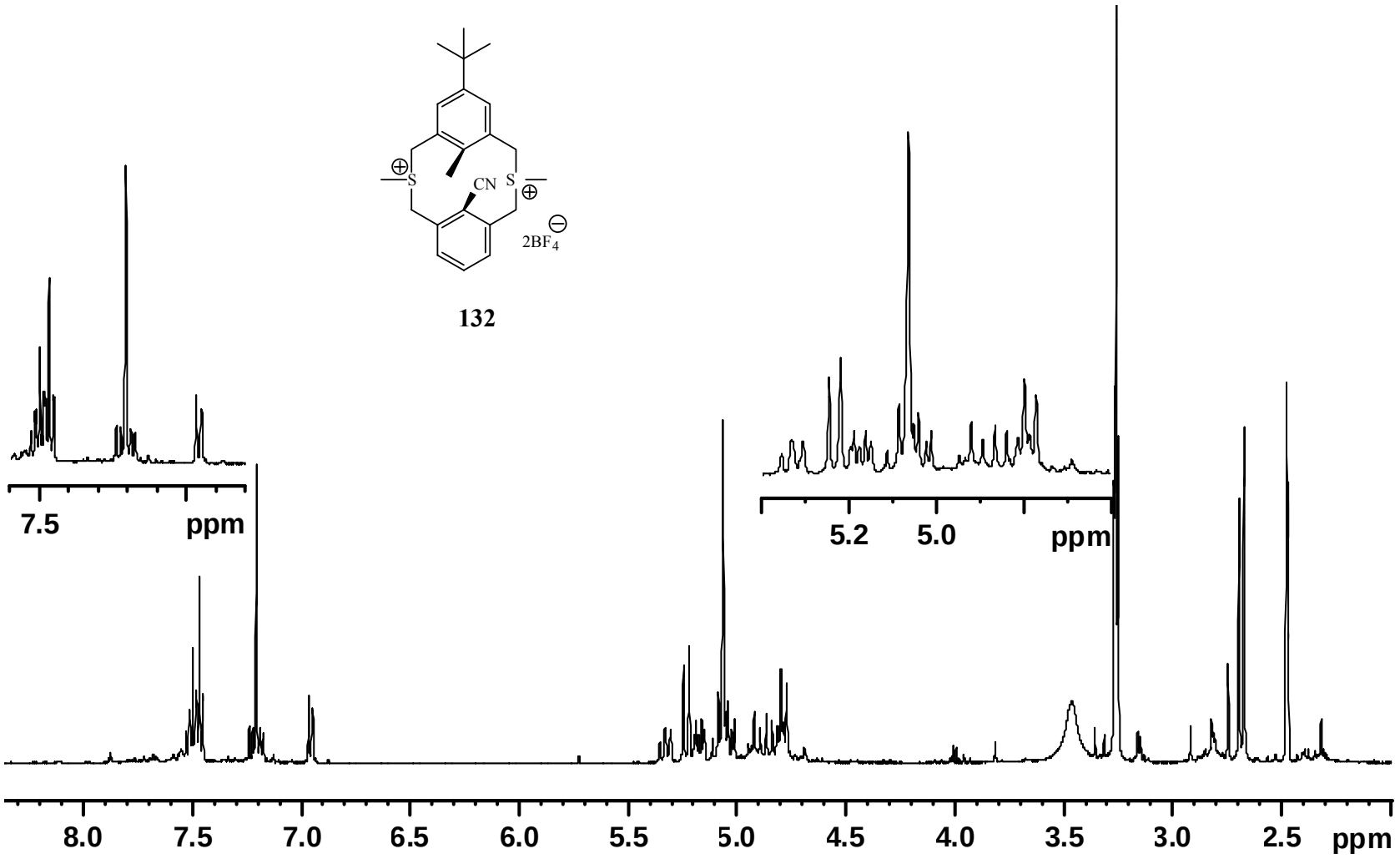



**130**

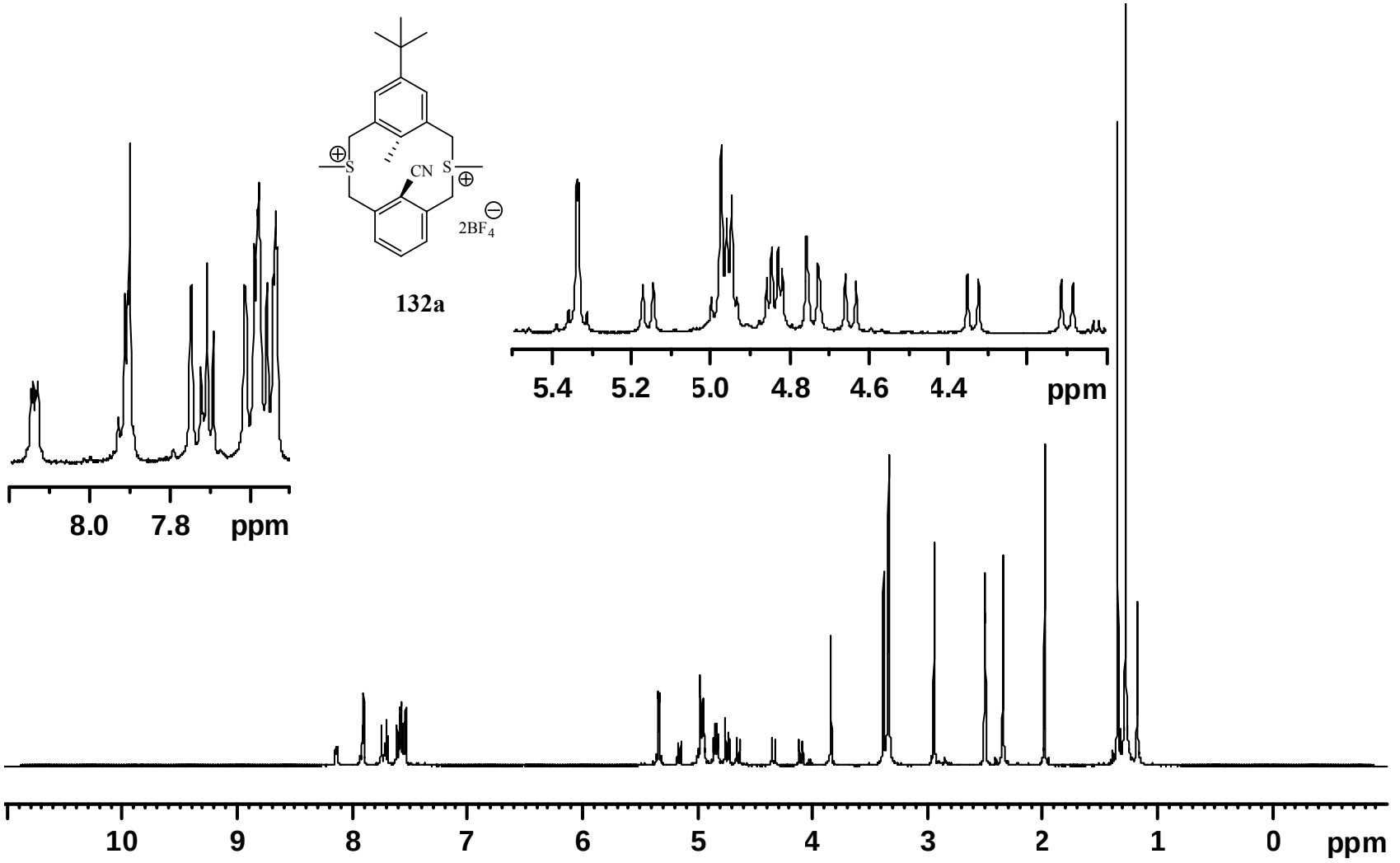

S
CN
S2
131
7.5
ppm
4.0
3.9
3.8
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm



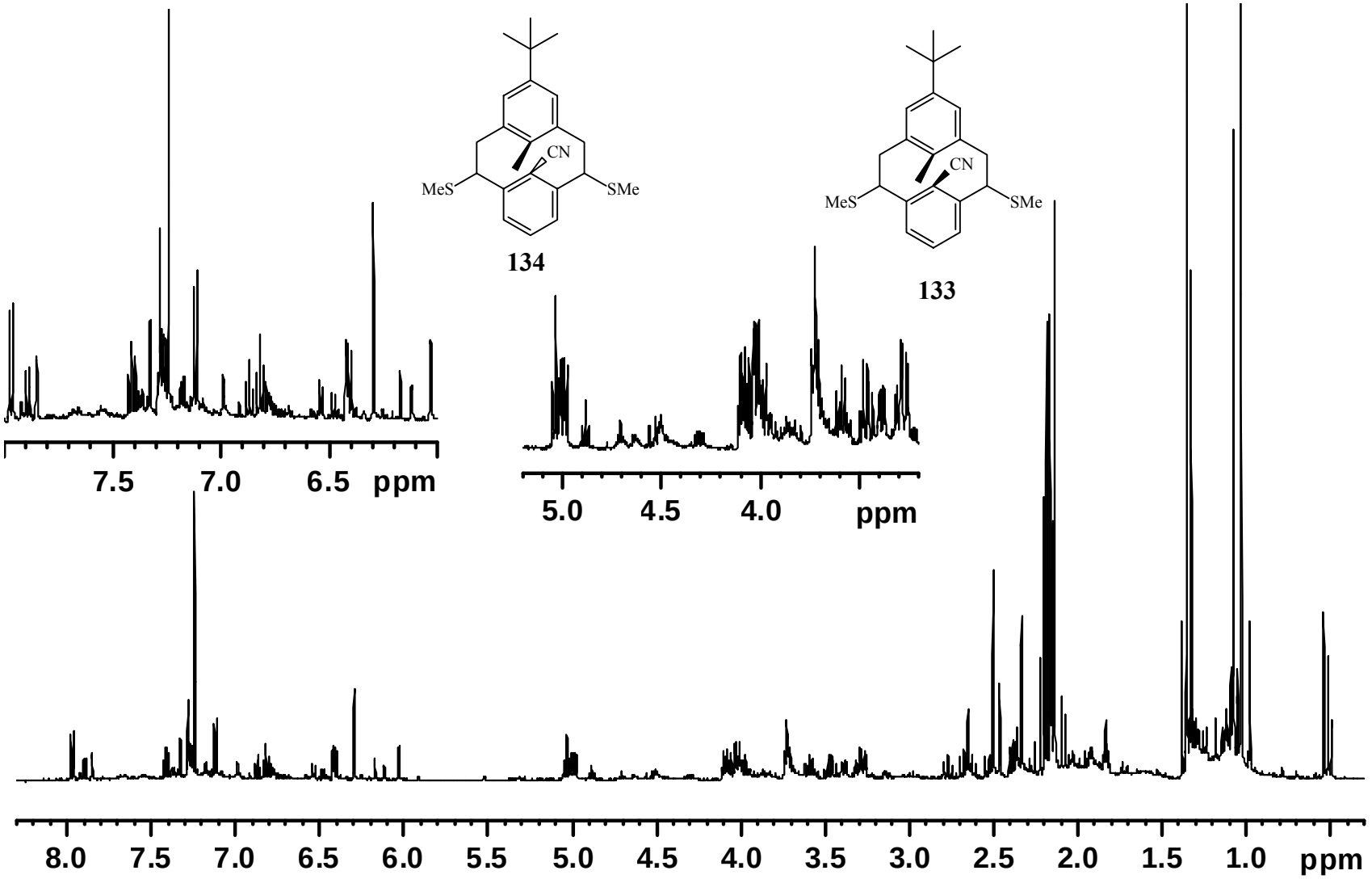

**131**

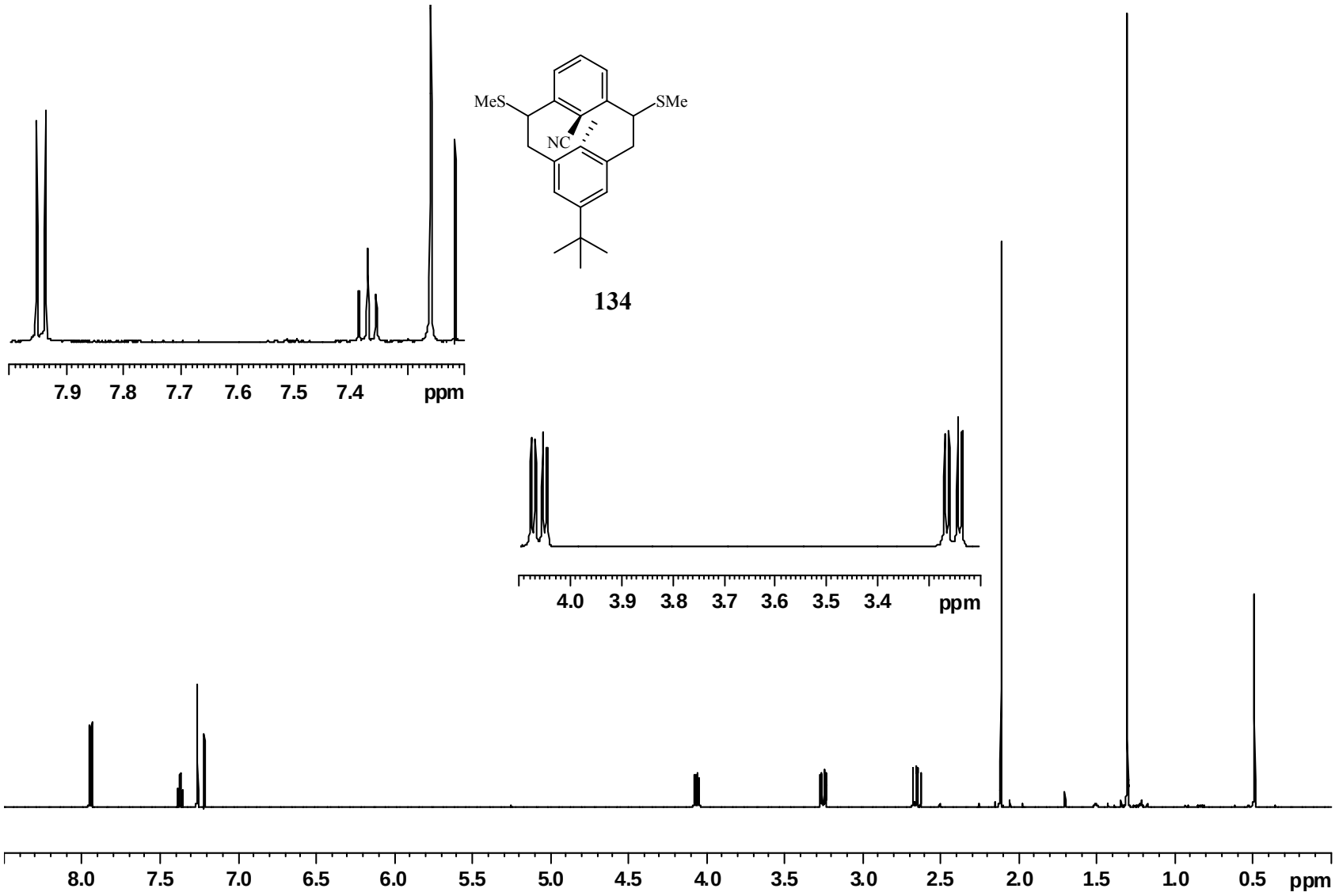



**132**

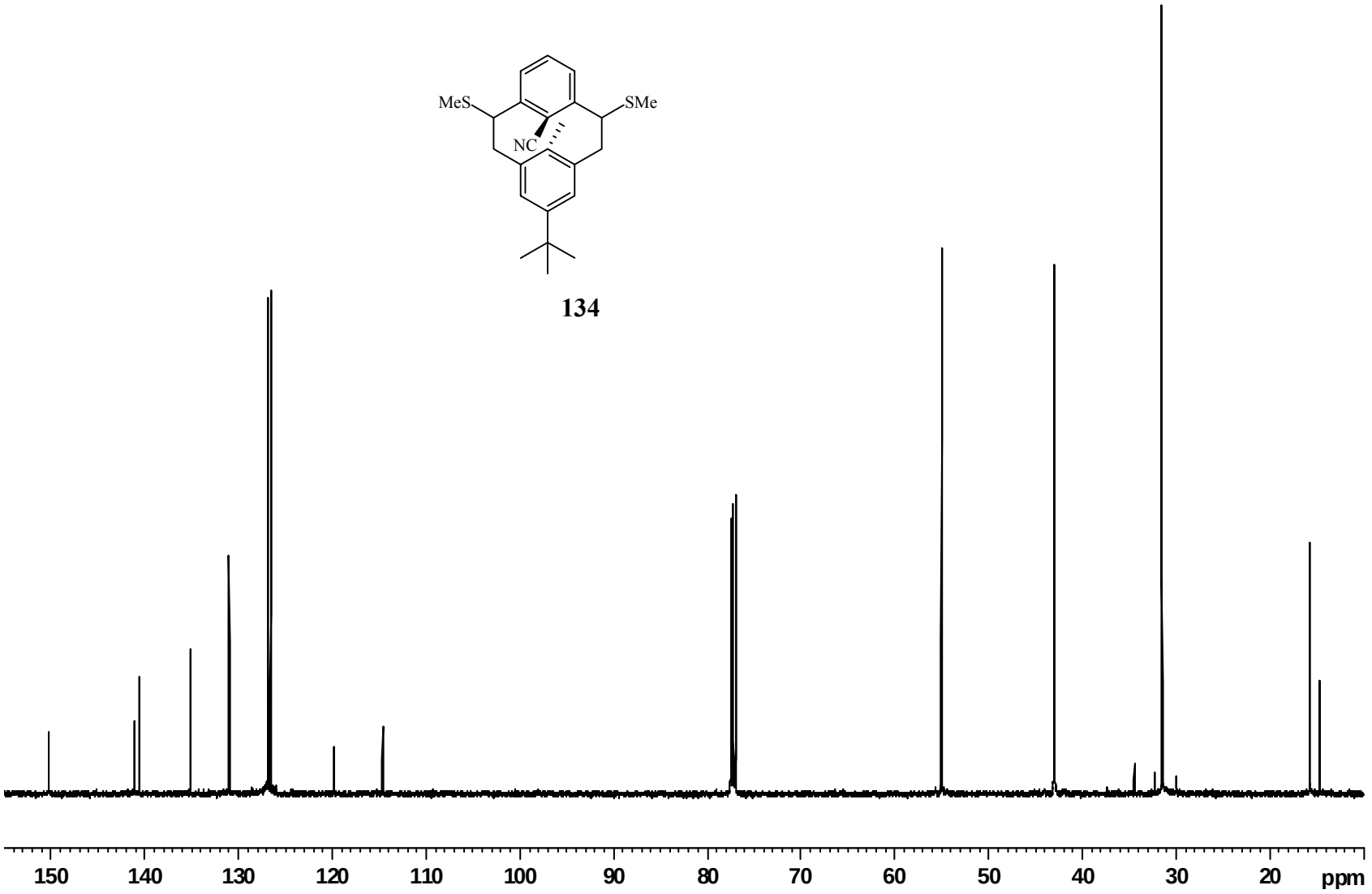



**132a**


CN
MeS
SMe
134
CN
MeS
SMe
133
7.5
7.0
6.5
ppm
5.0
4.5
4.0
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

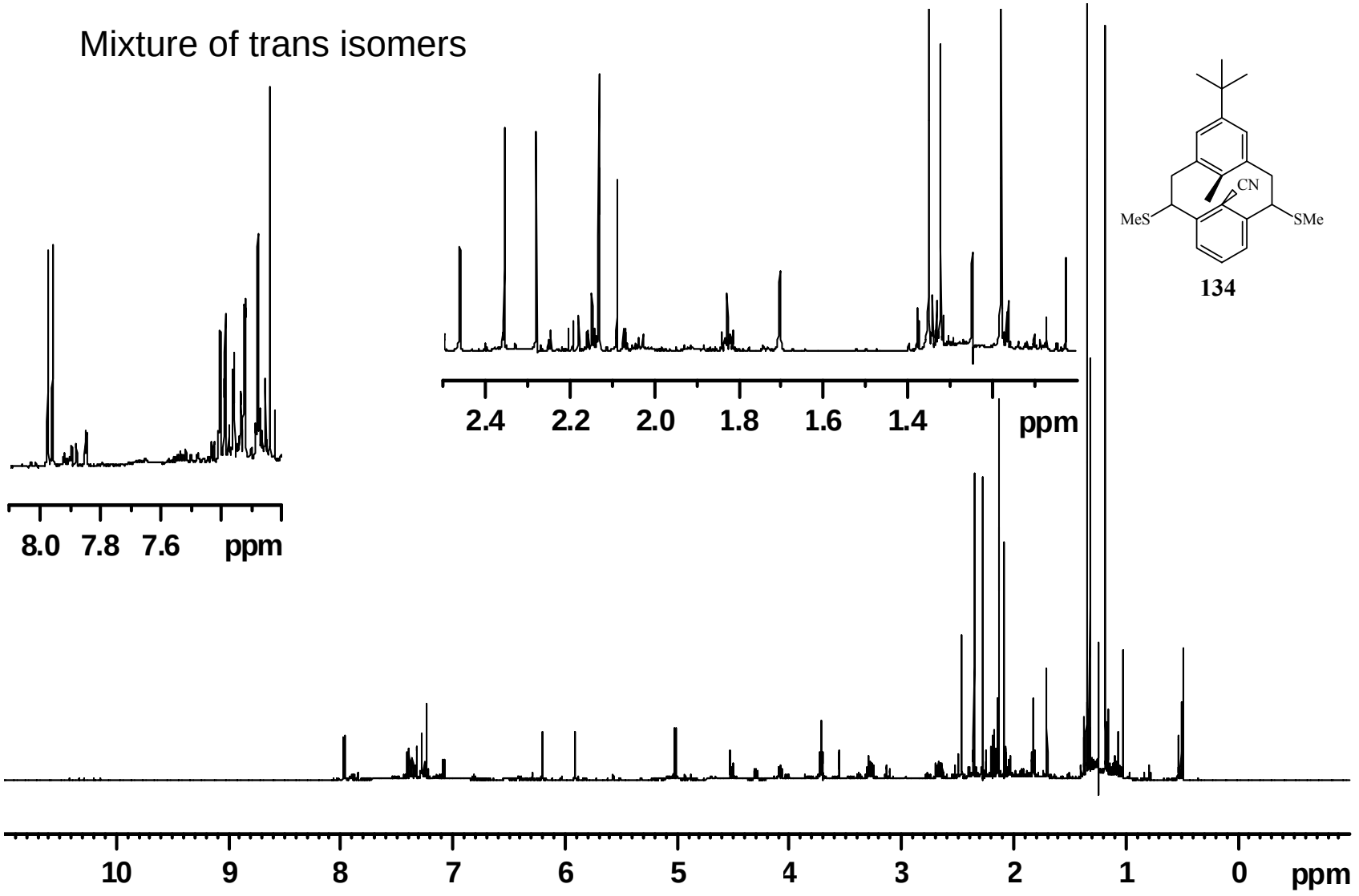

MeS
SMe
NC
7.9 7.8 7.7 7.6 7.5 7.4 ppm
4.0 3.9 3.8 3.7 3.6 3.5 3.4 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

**134**




**134**

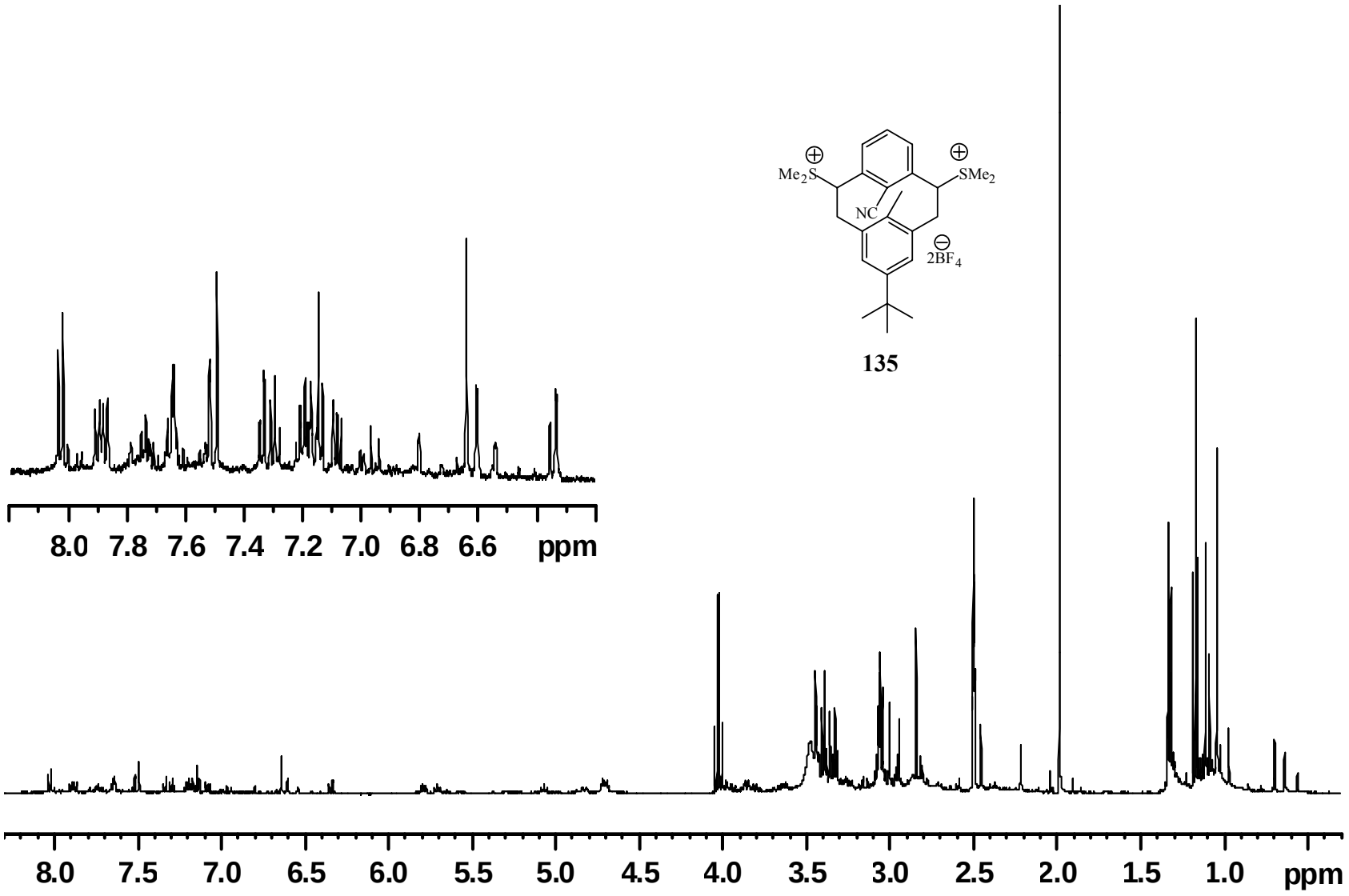
Mixture of trans isomers



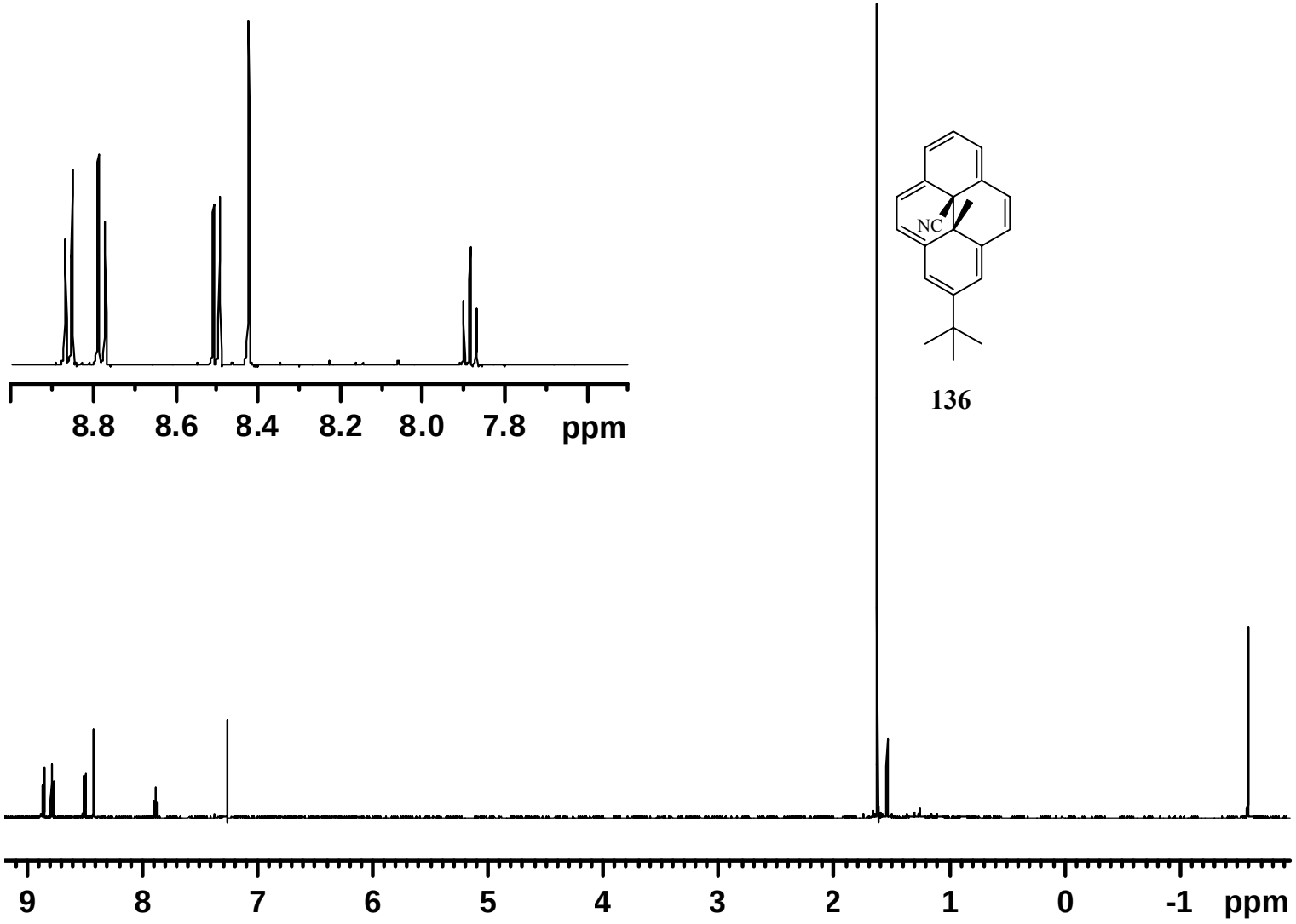


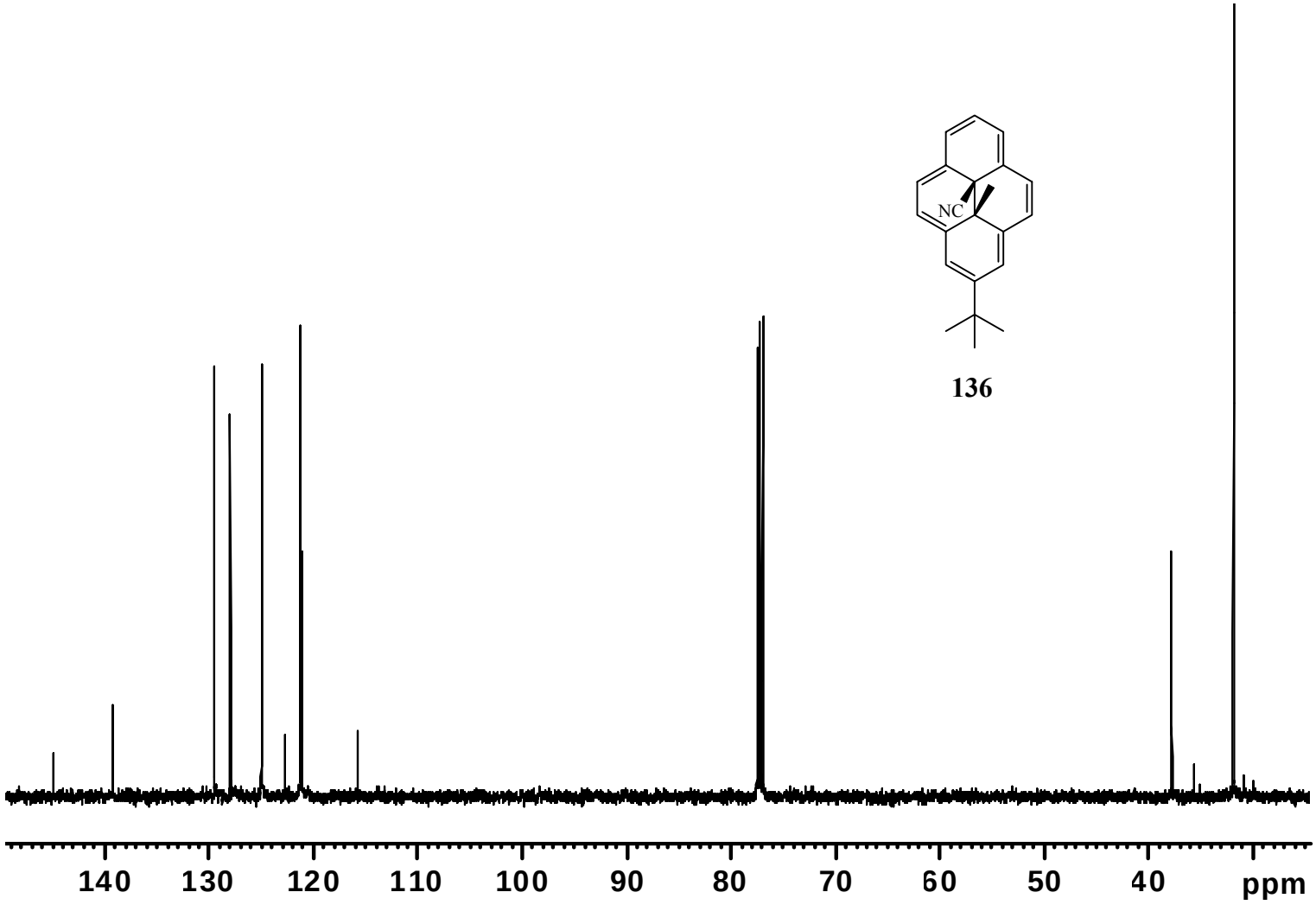


**134**

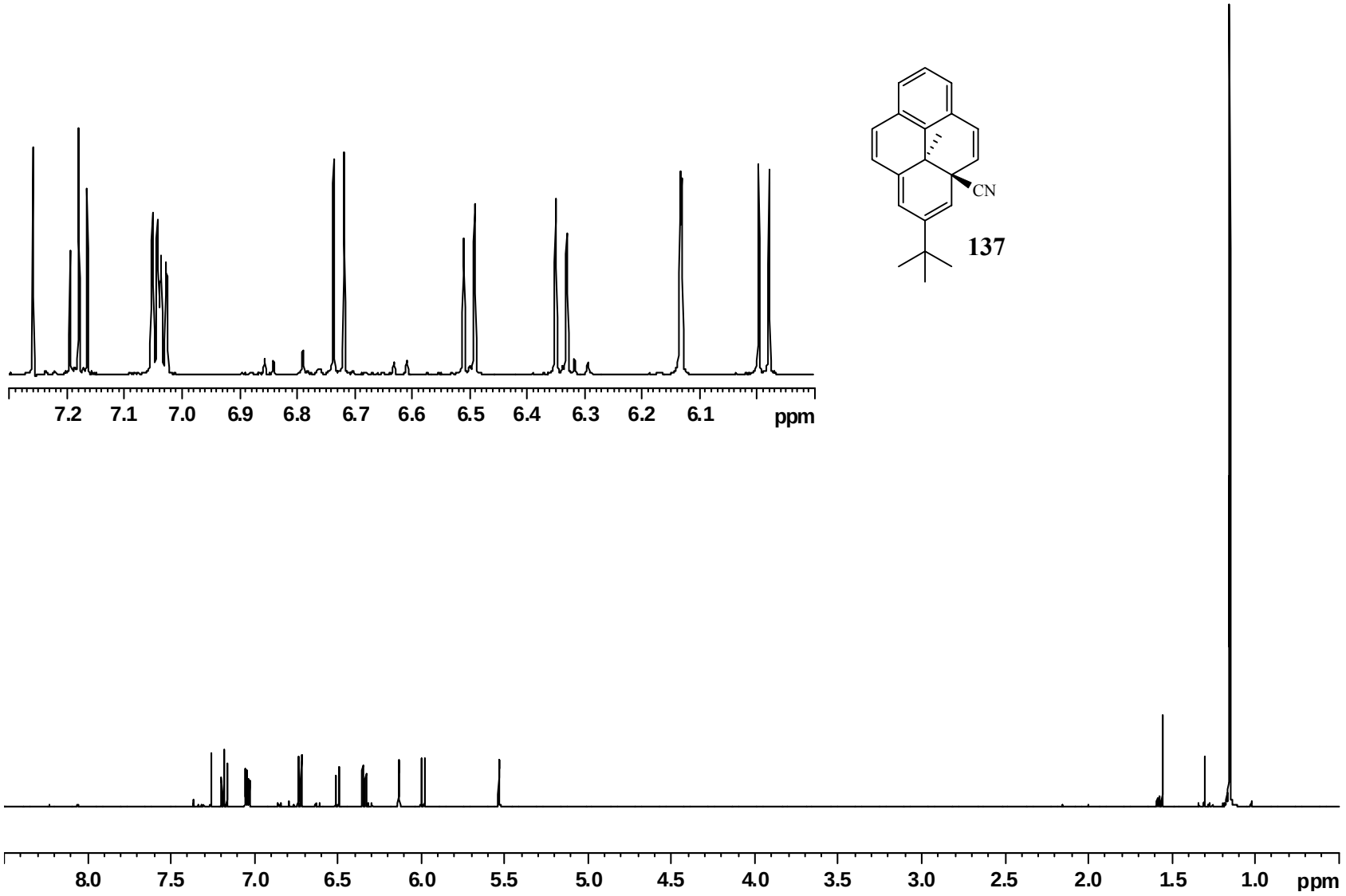

Me2S
SMe2
NC
2BF4
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

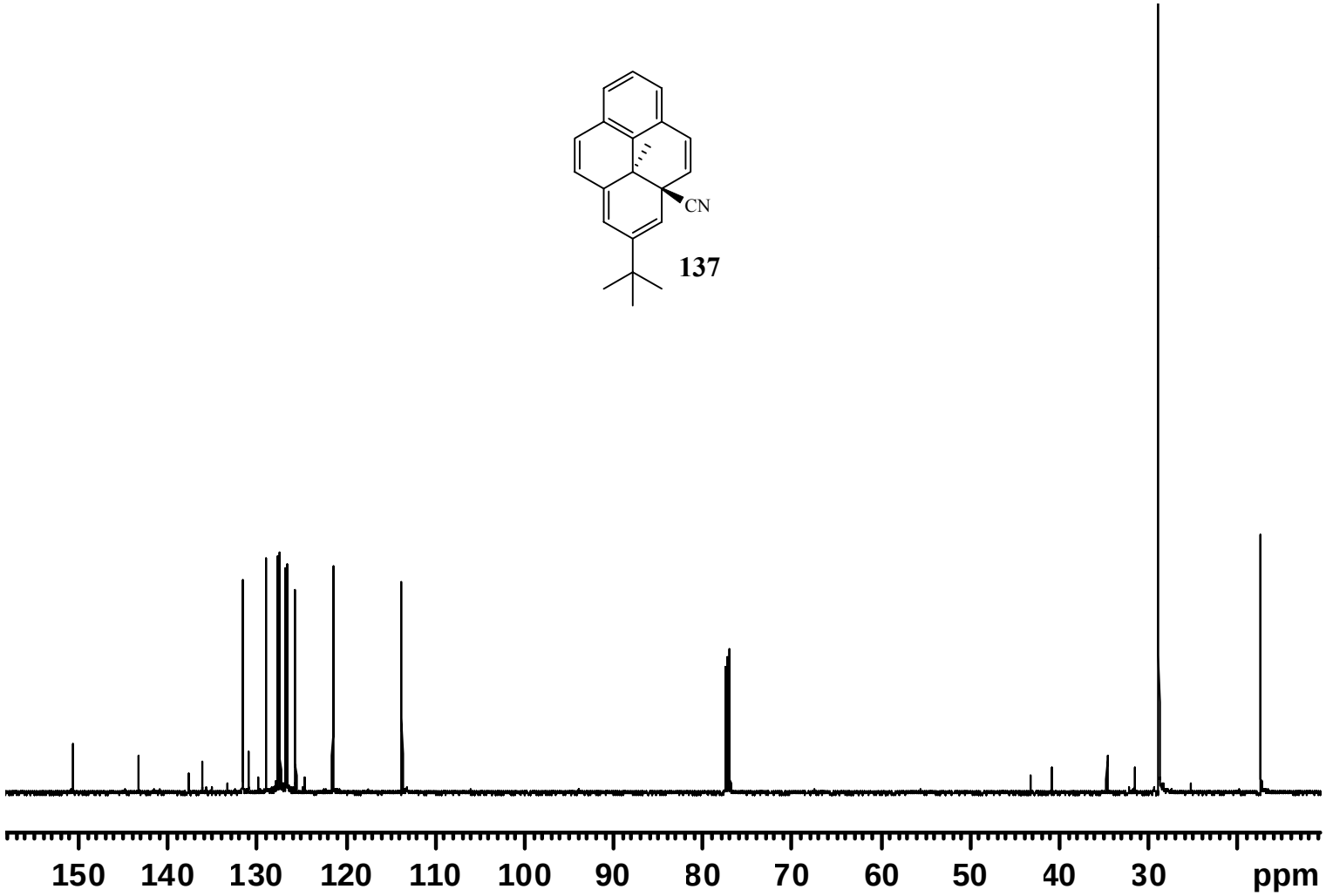
**135**

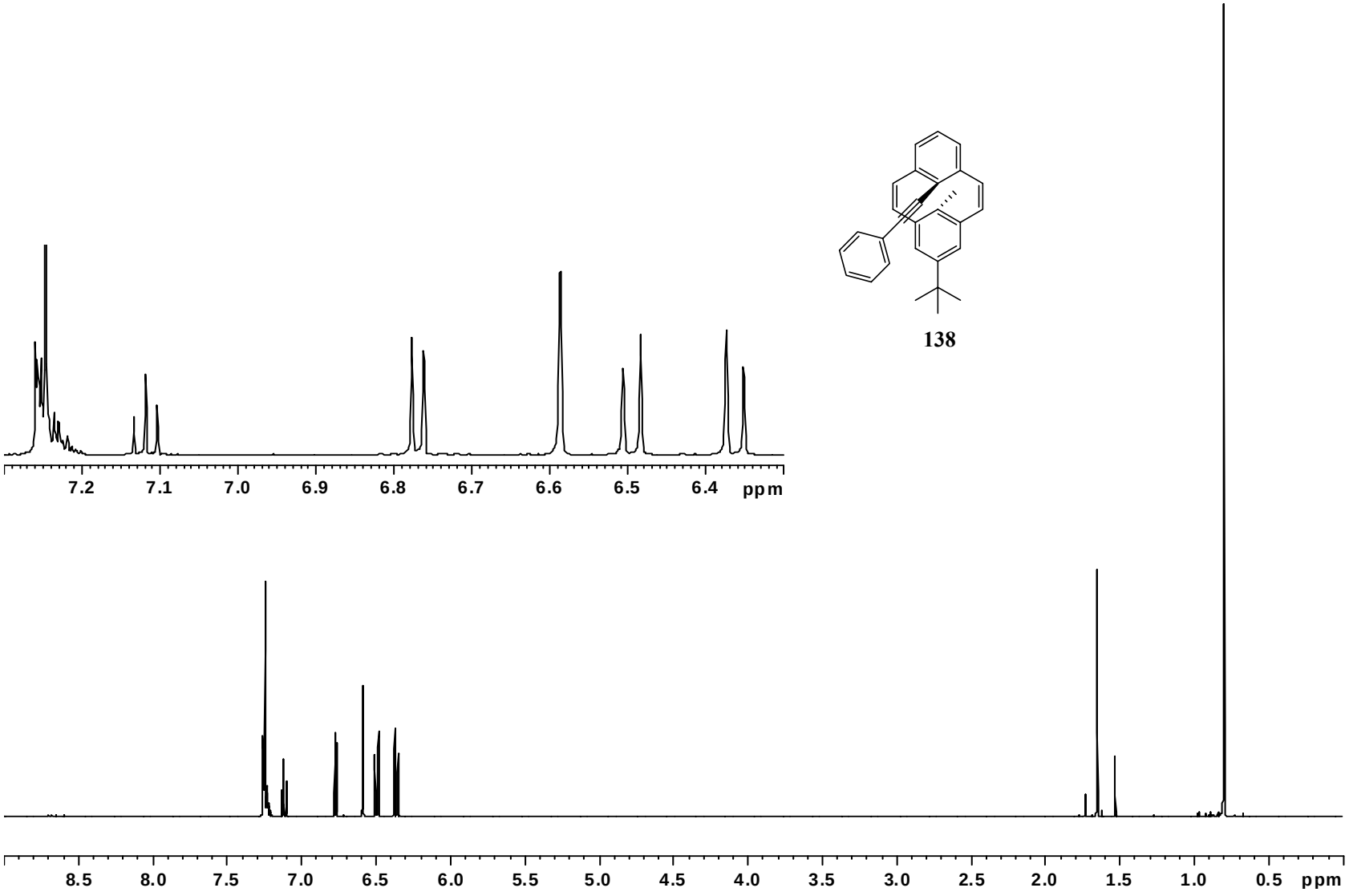

NC
136
8.8
8.6
8.4
8.2
8.0
7.8
ppm
9
8
7
6
5
4
3
2
1
0
-1
ppm



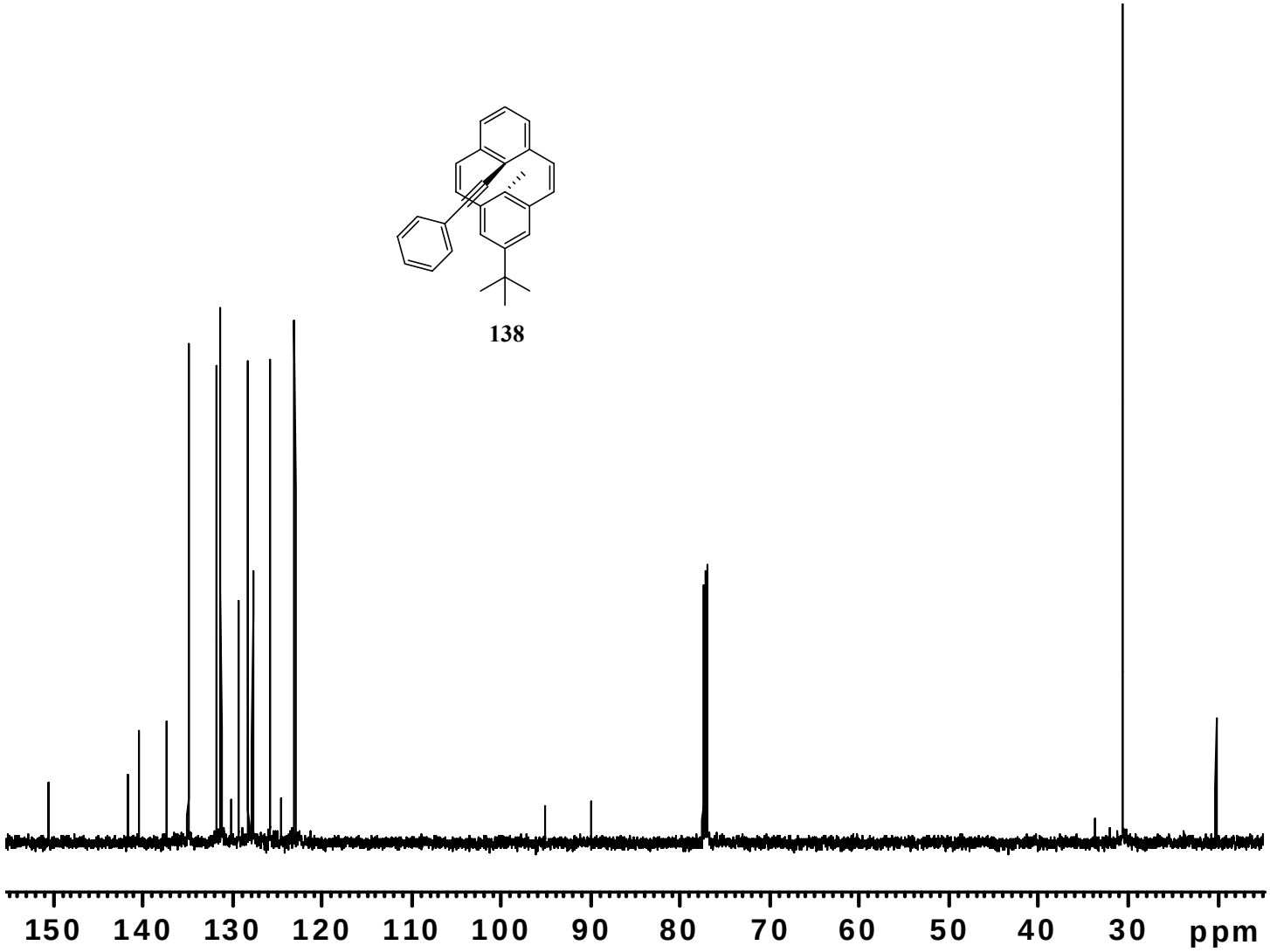

**136**


CN
137
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

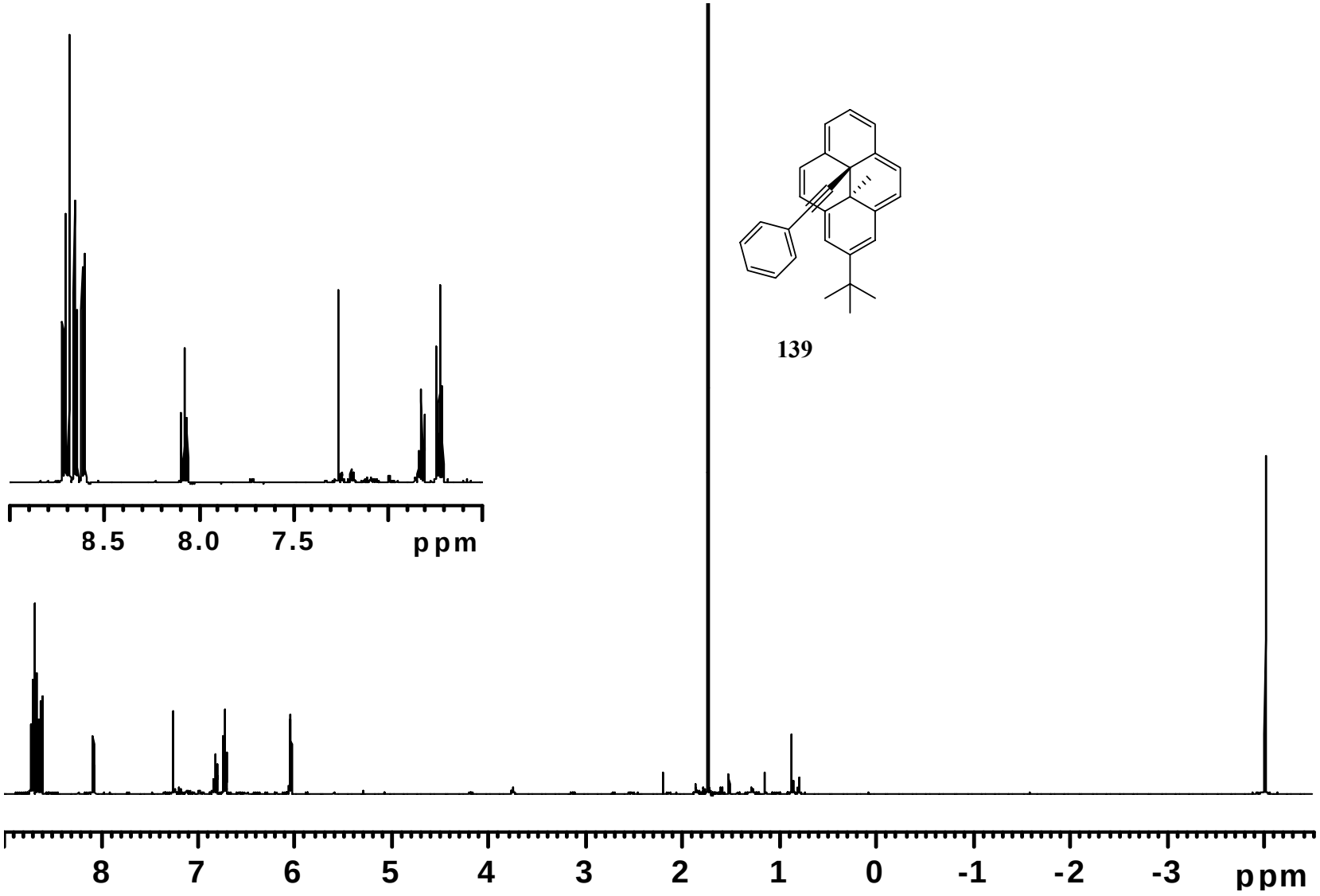

CN
137
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

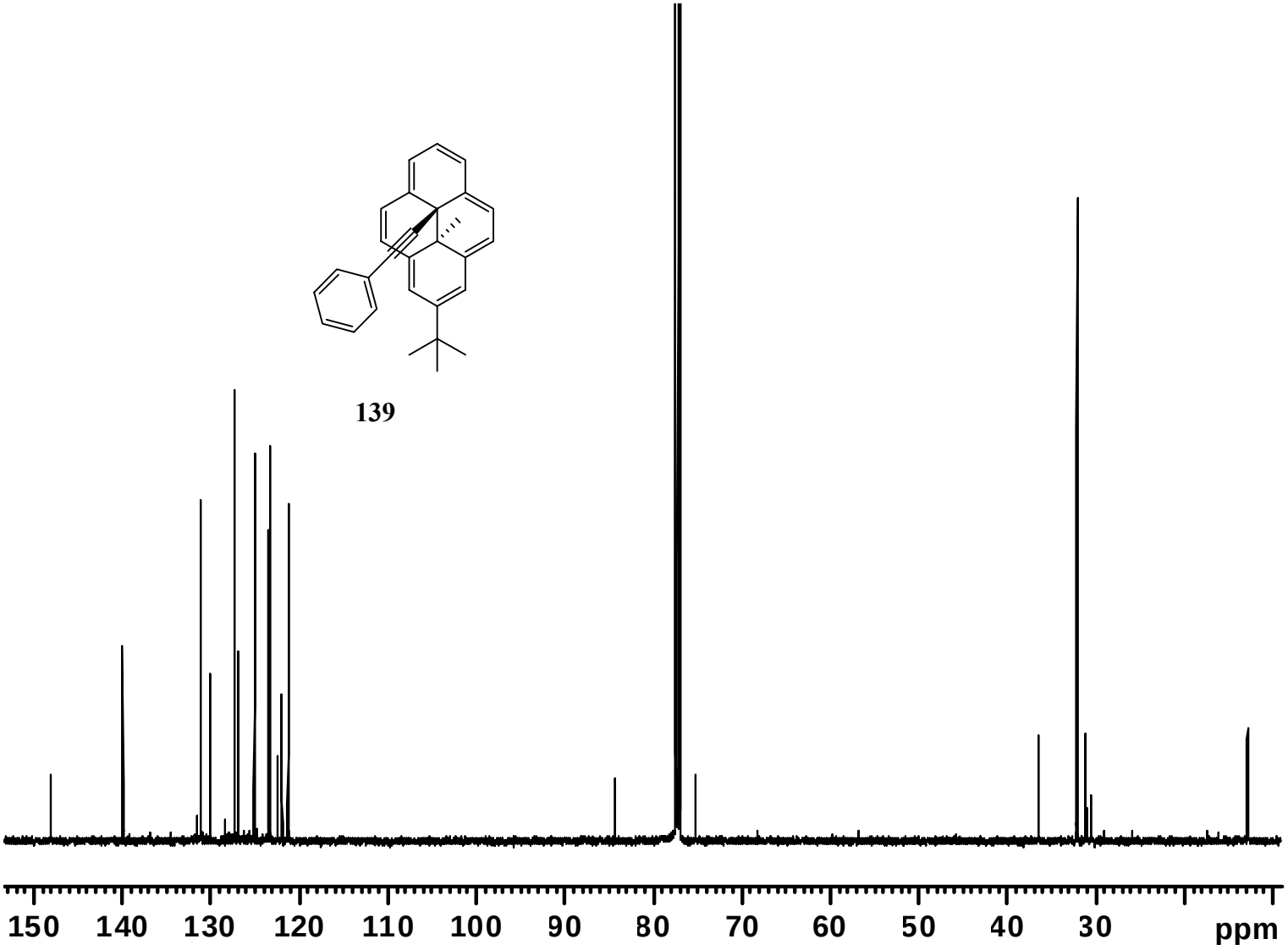
**138**



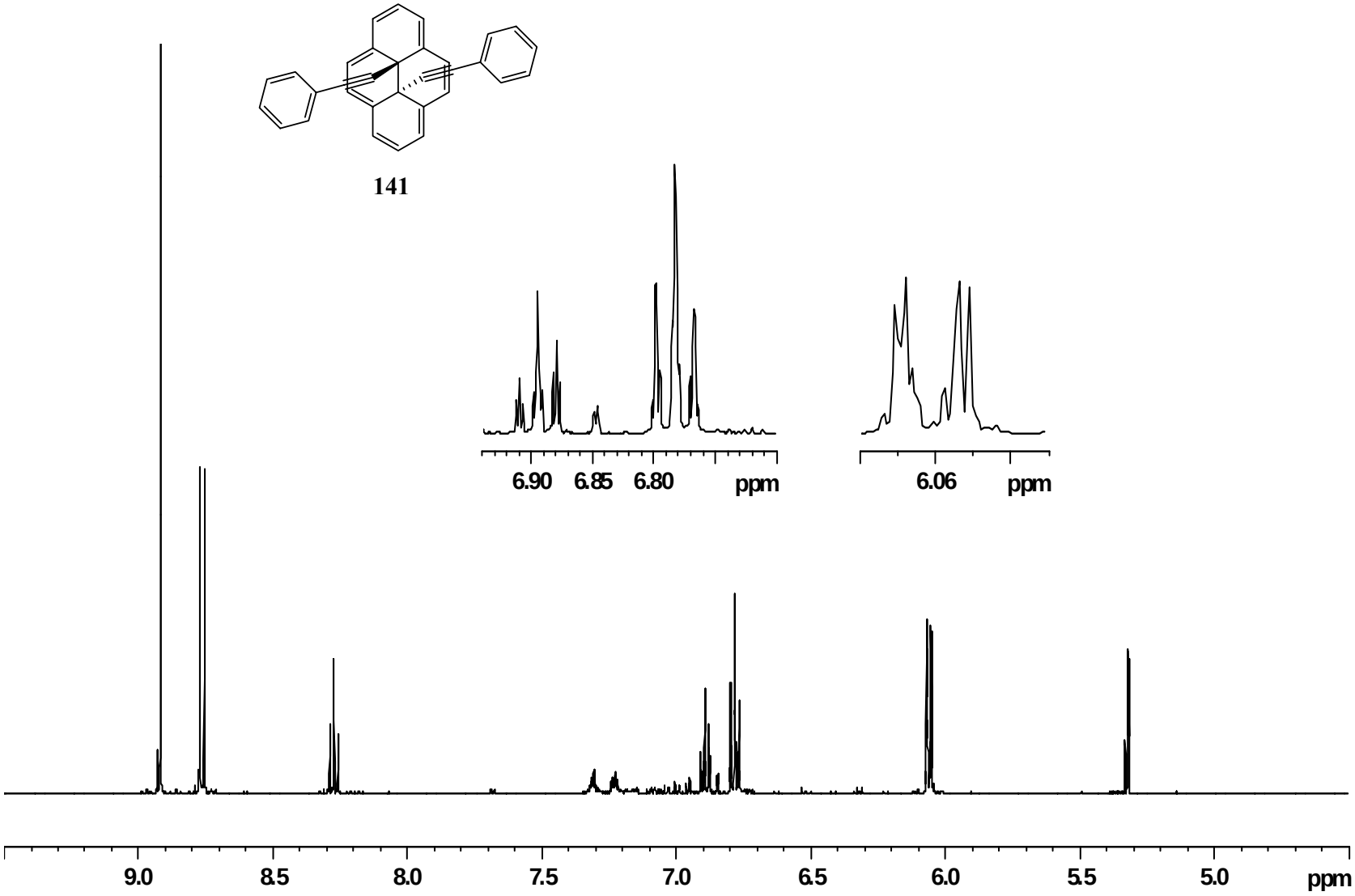

**138**

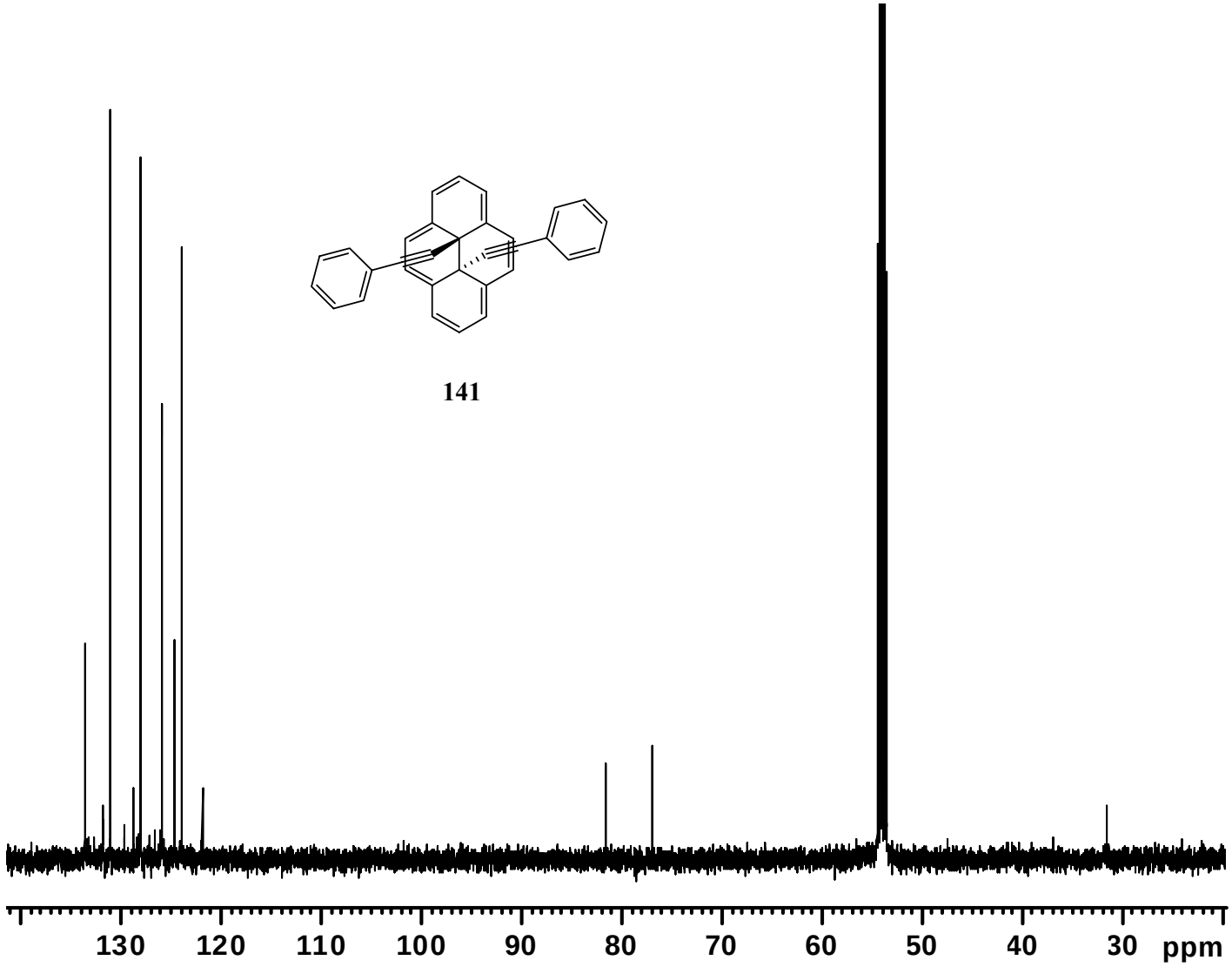



**139**

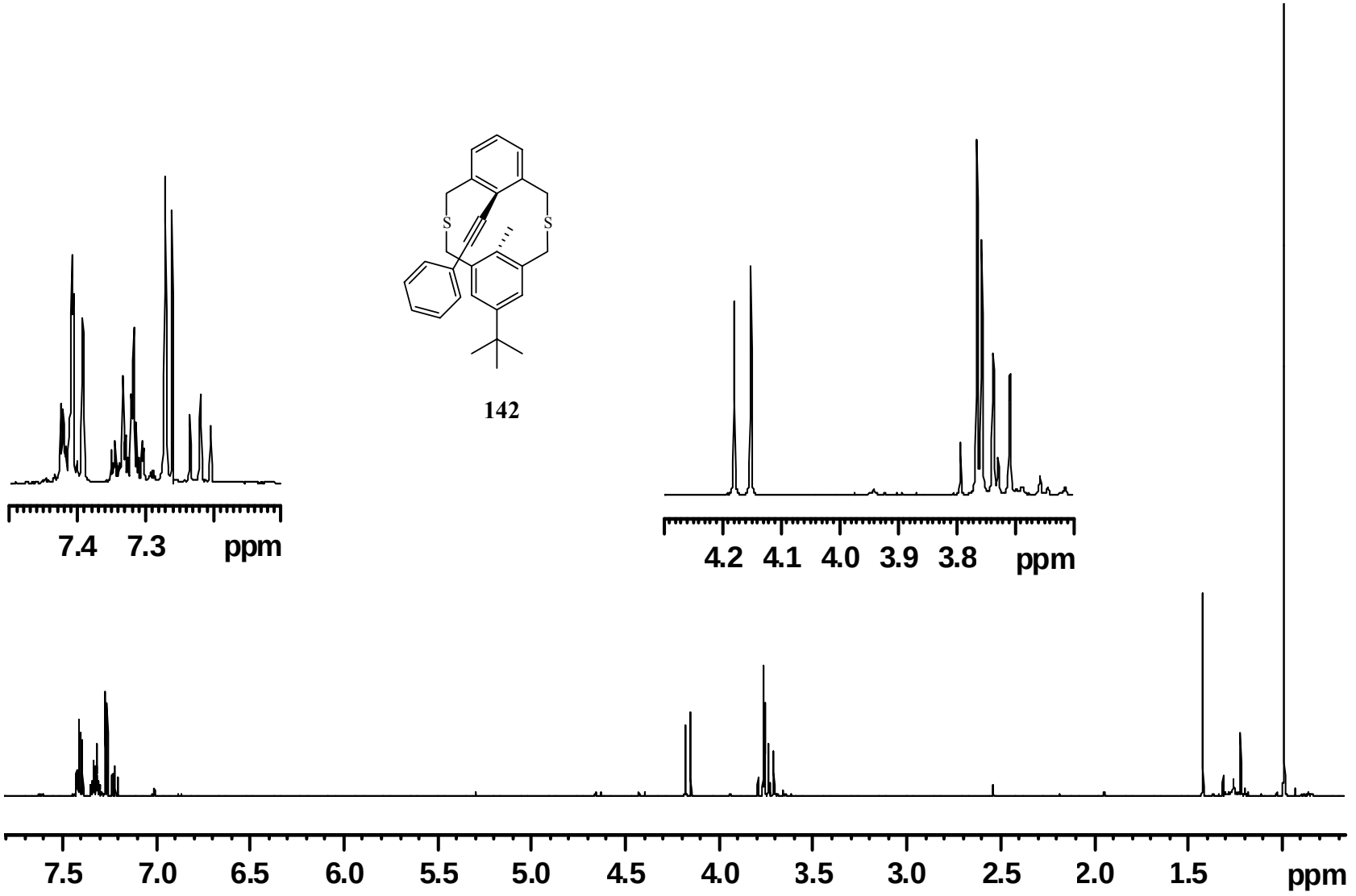


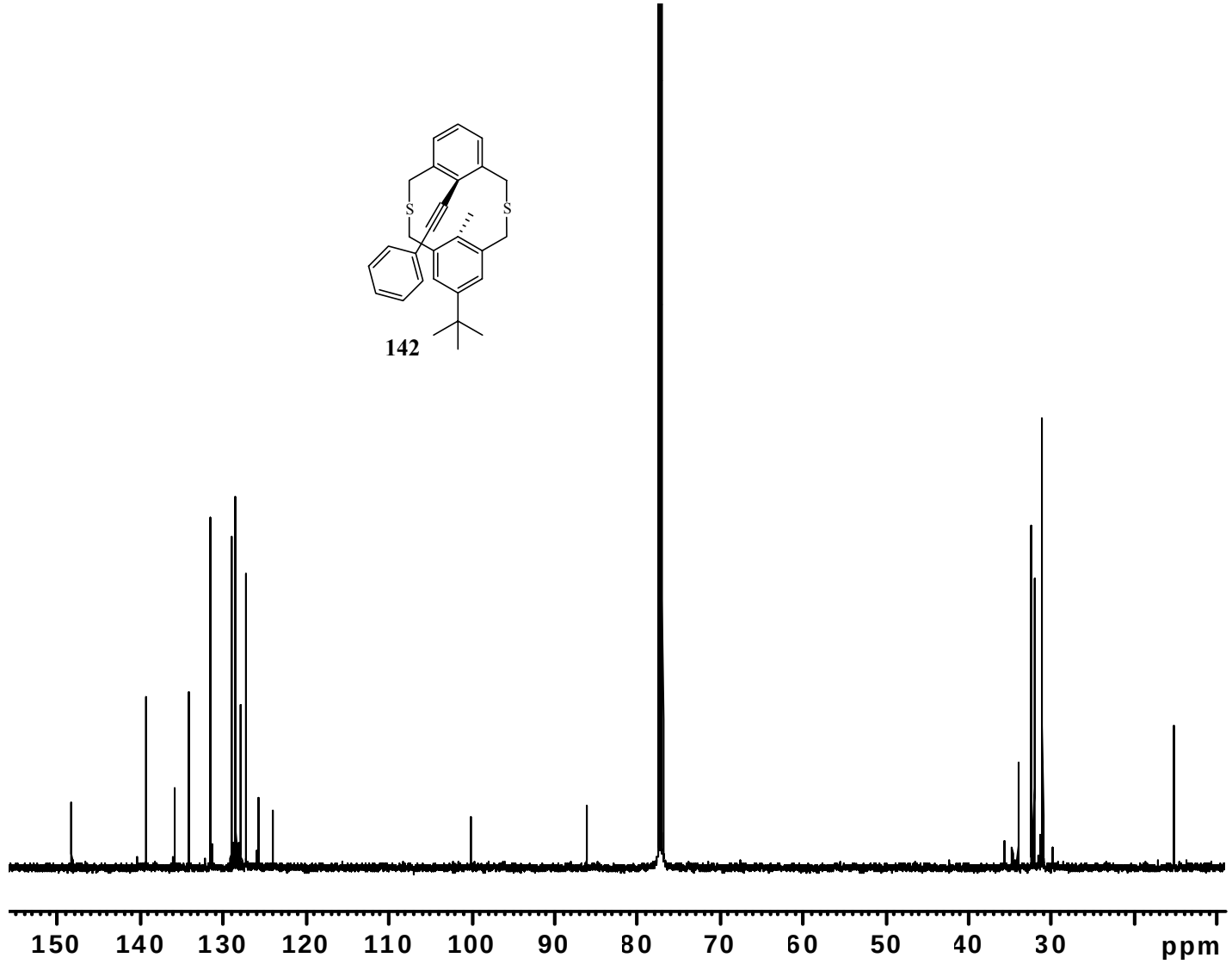

**139**

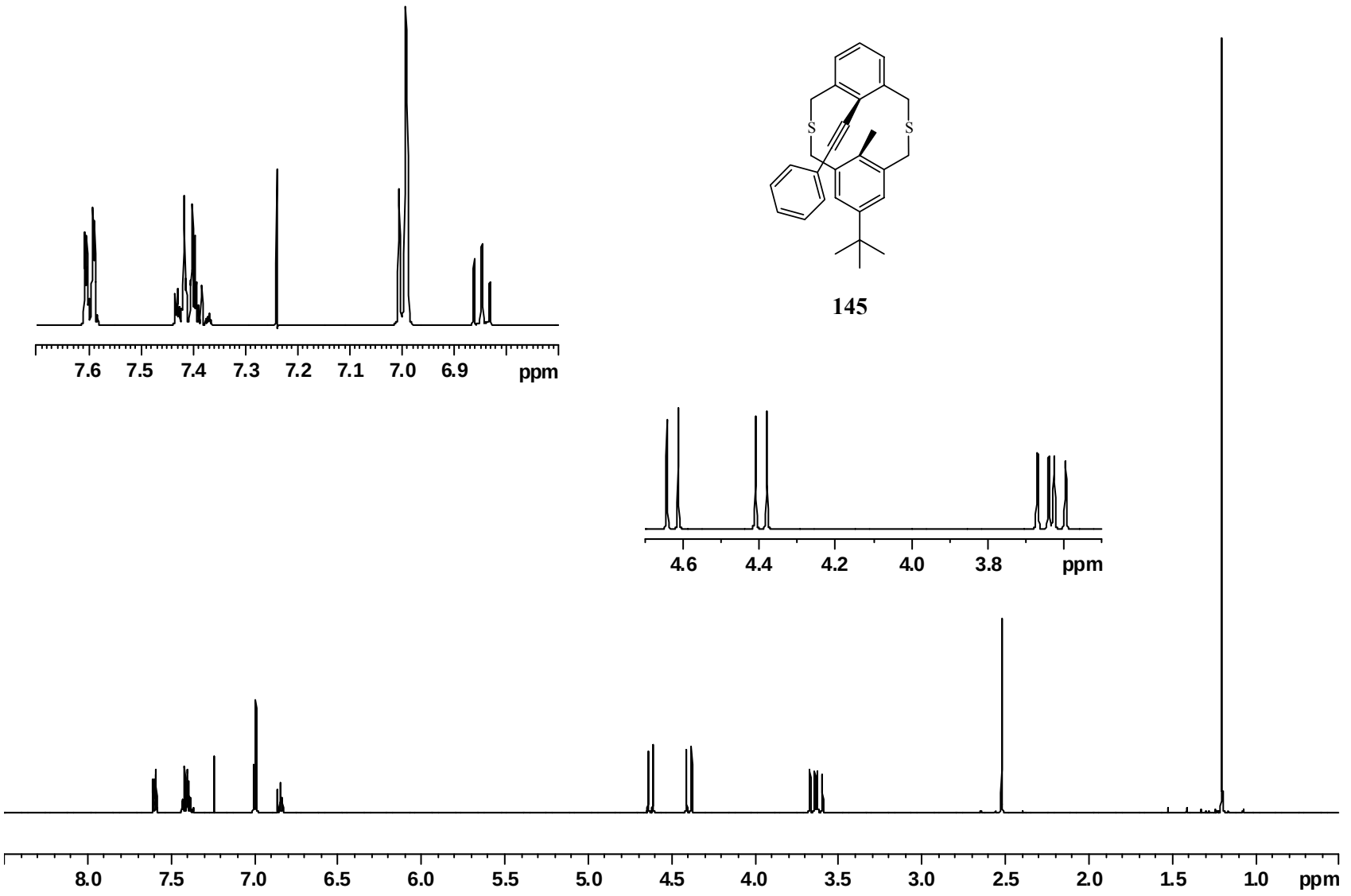

141
6.90
6.85
6.80
ppm
6.06
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm

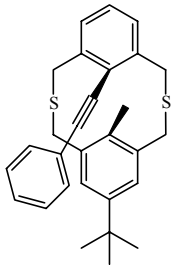



**141**

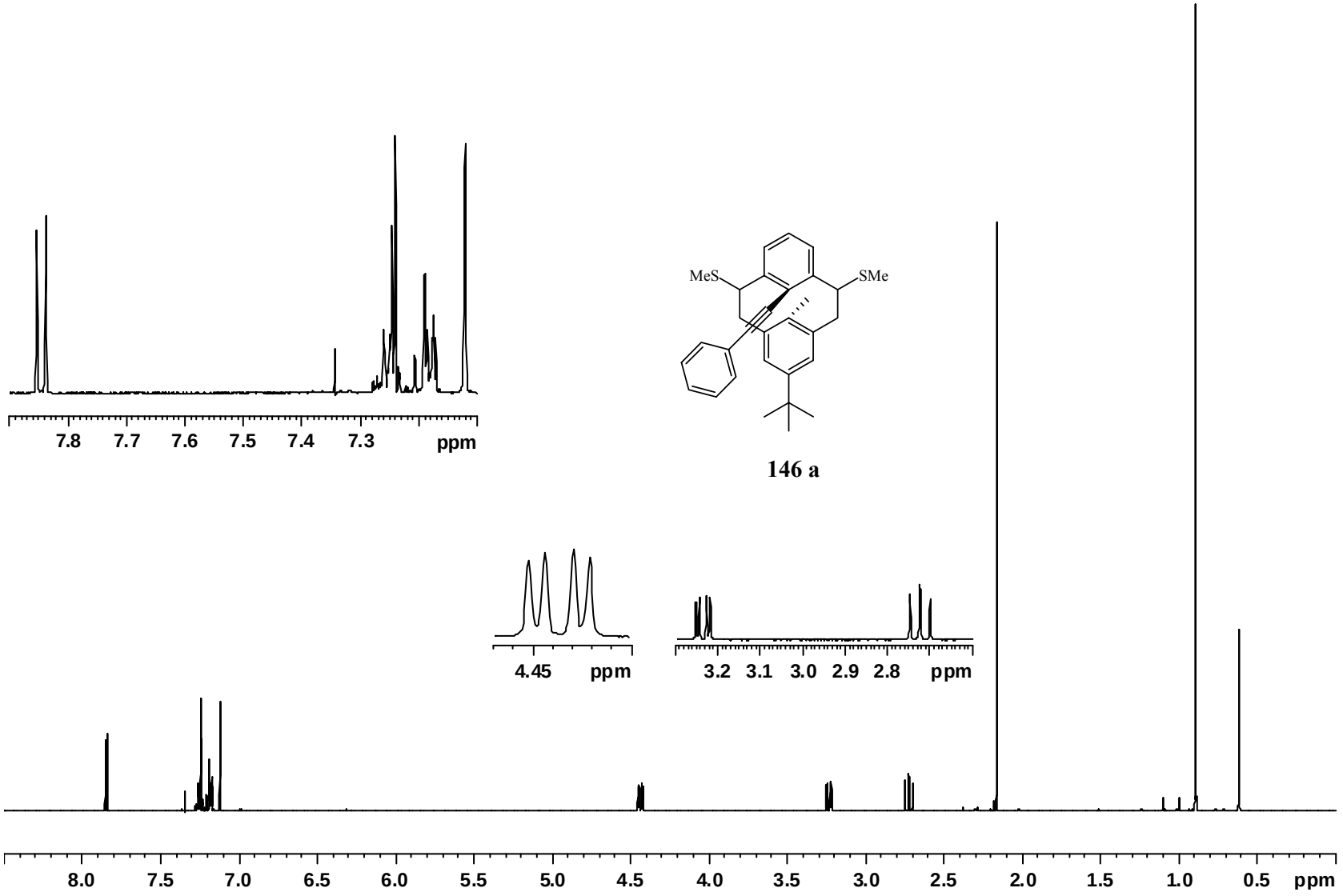

S
S
142
7.4 7.3 ppm
4.2 4.1 4.0 3.9 3.8 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm


S
S
142
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

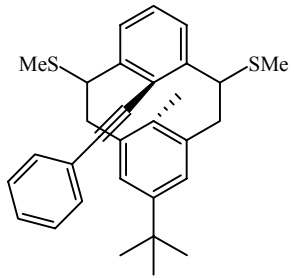

S
S
145
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 ppm
4.6 4.4 4.2 4.0 3.8 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm



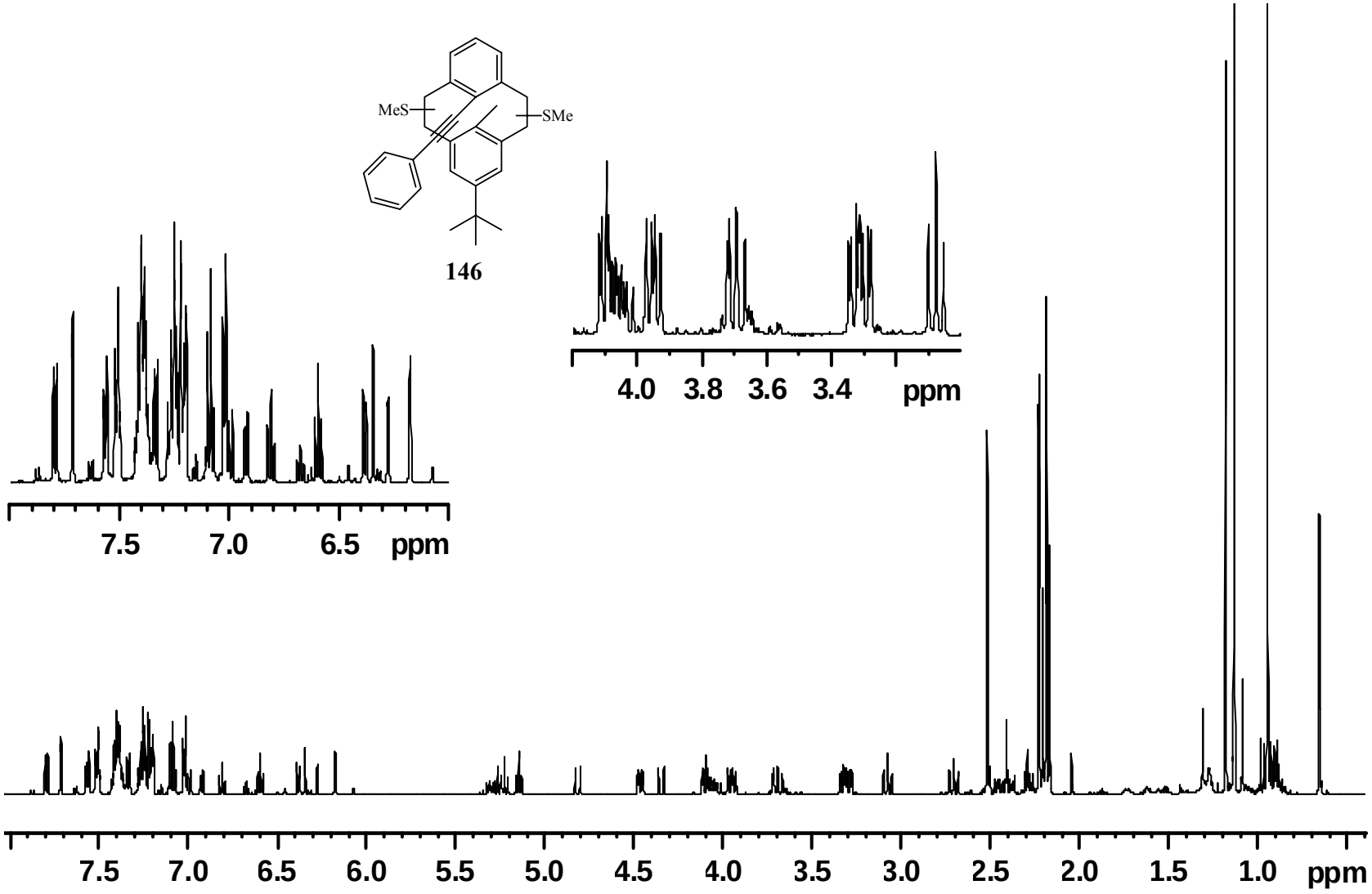

**145**

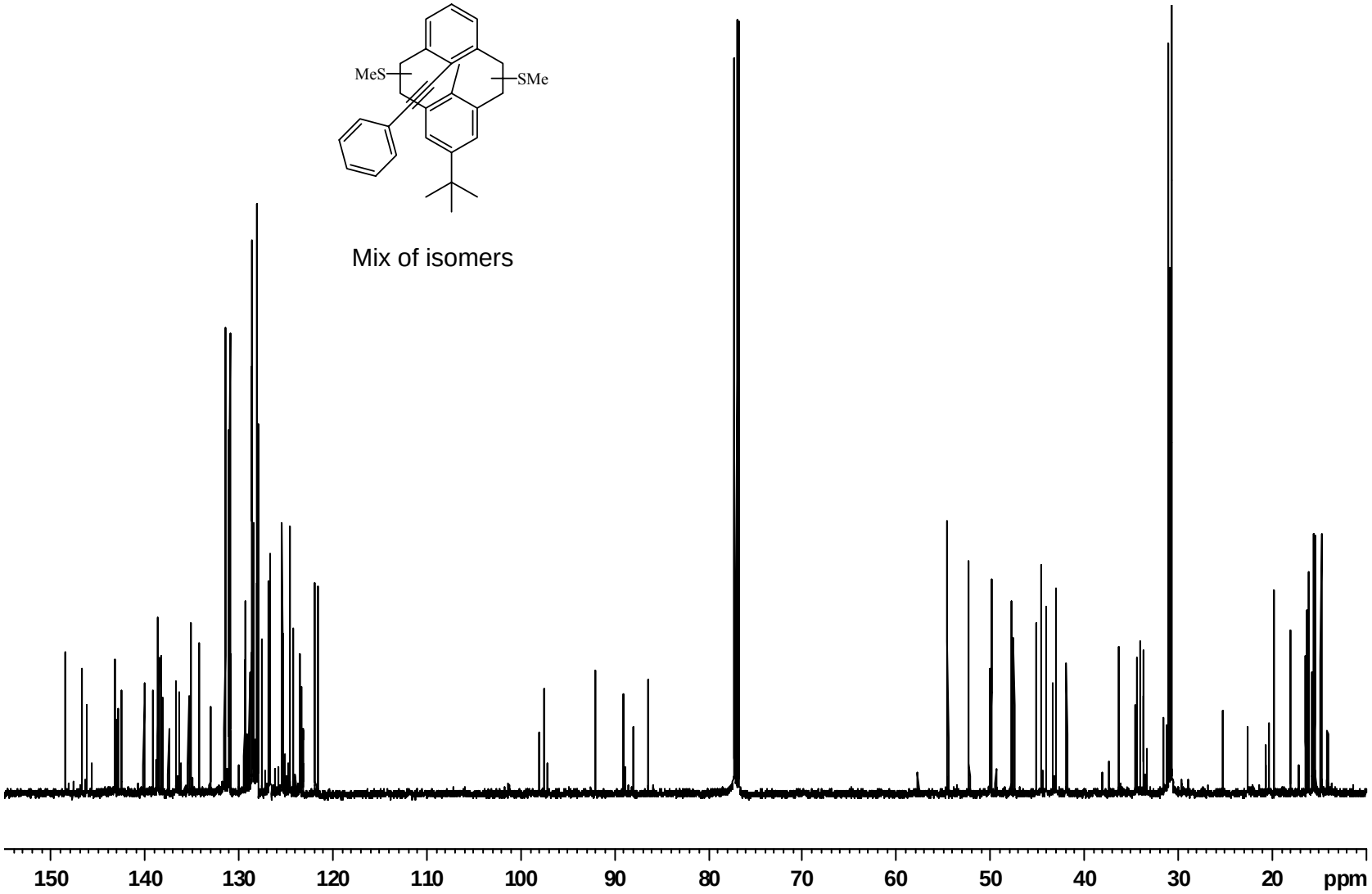

MeS
SMe
7.8 7.7 7.6 7.5 7.4 7.3 ppm
4.45 ppm
3.2 3.1 3.0 2.9 2.8 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

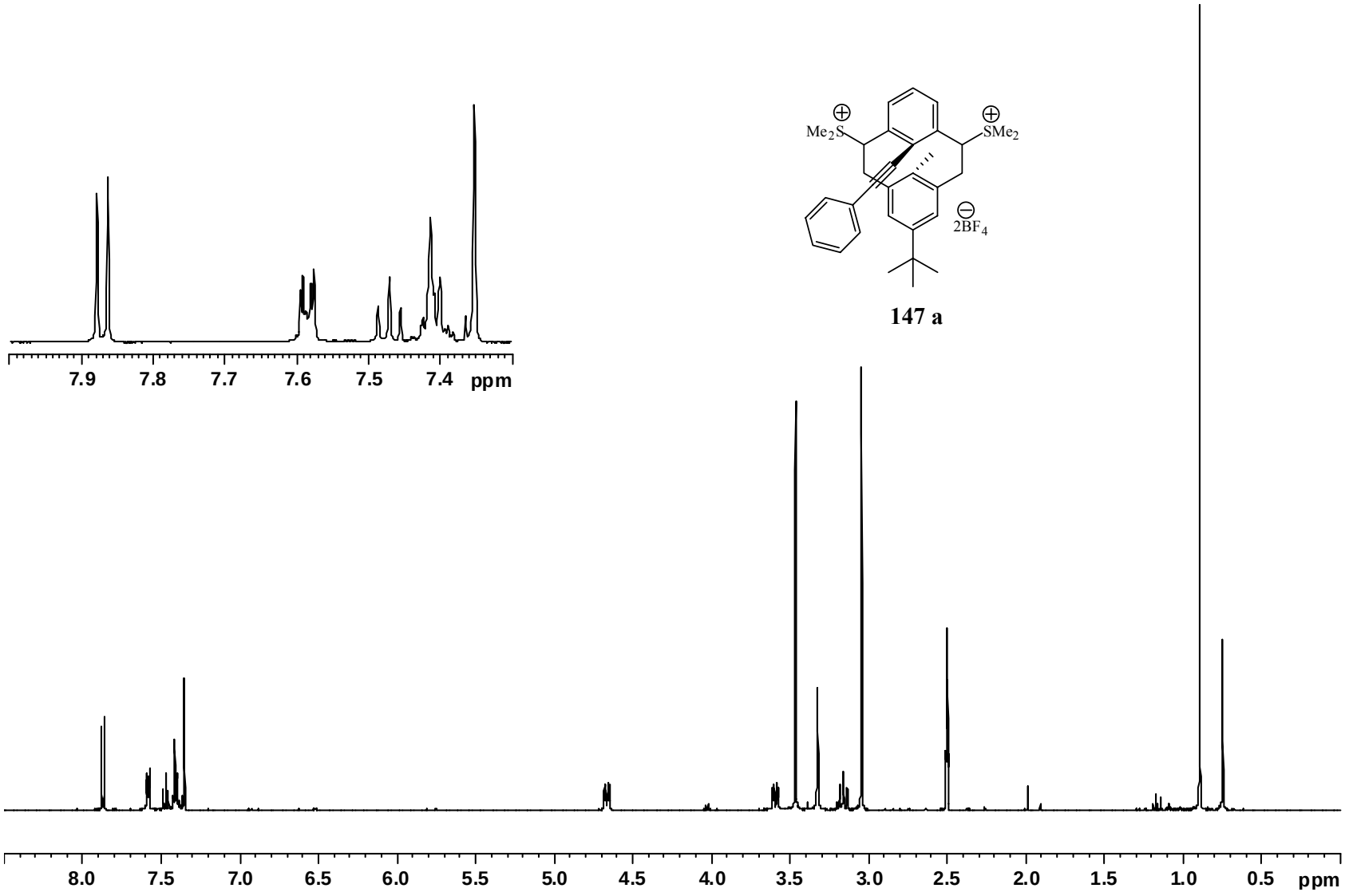
**146 a**



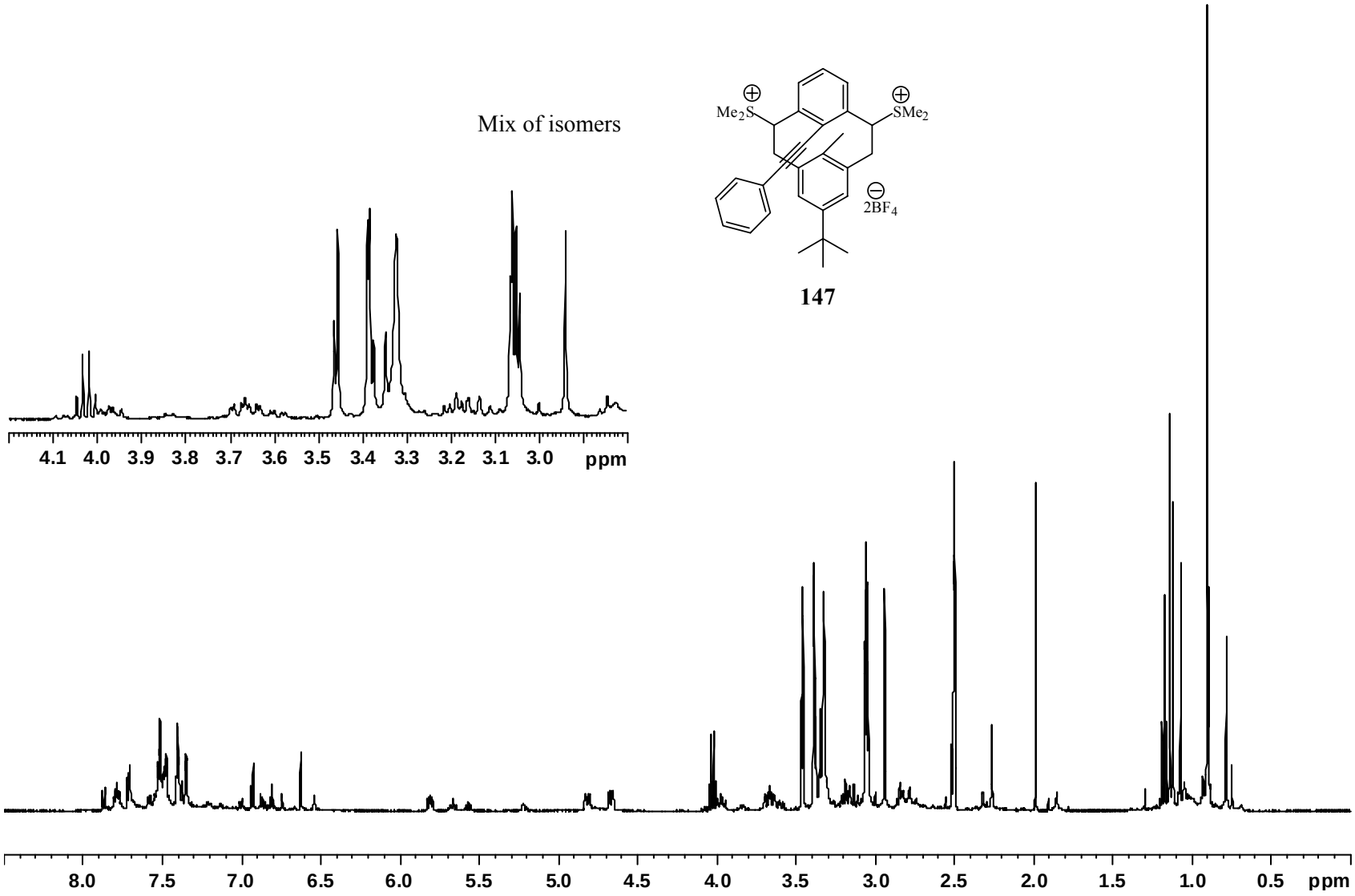

**146 a**

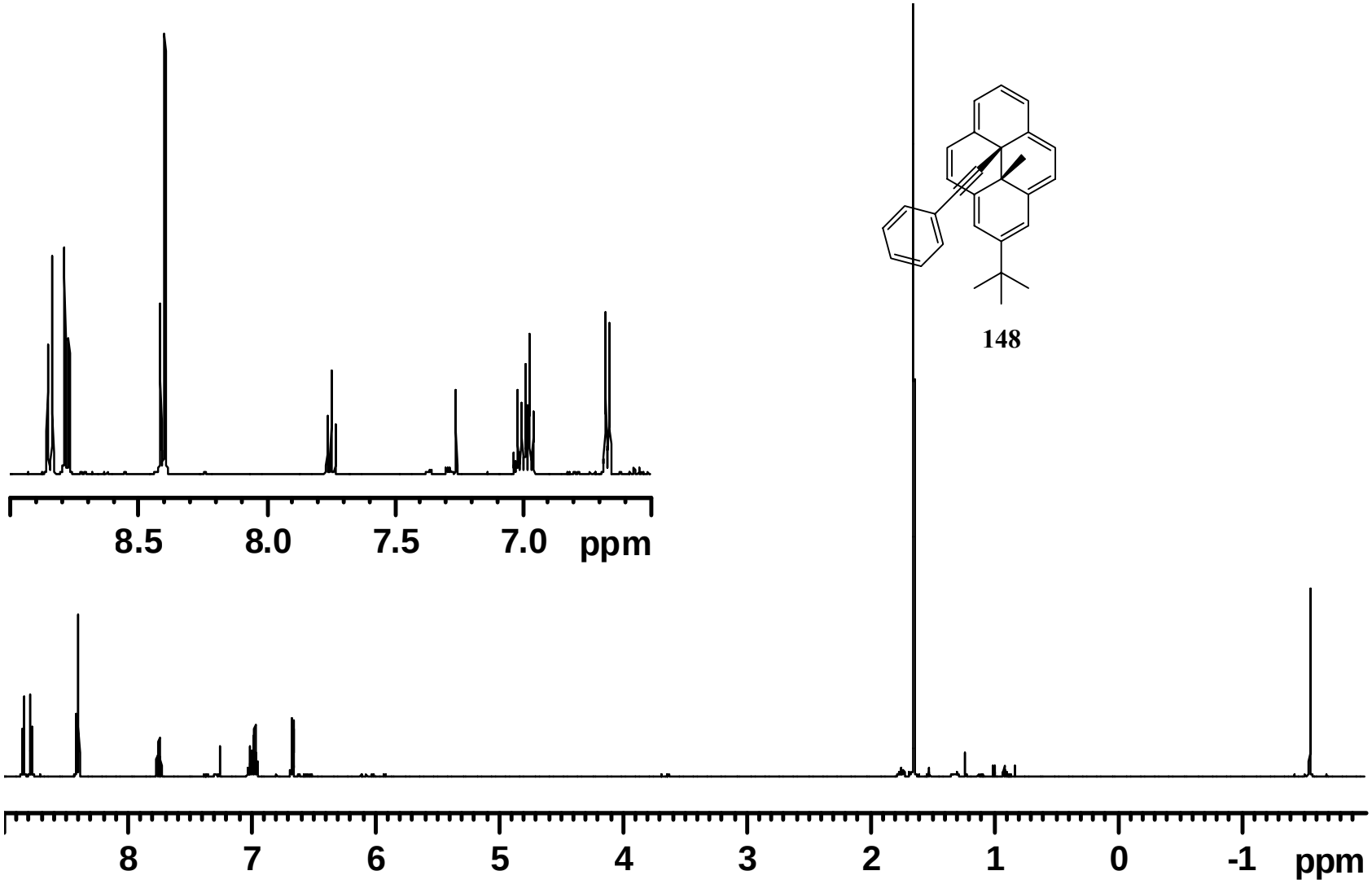

MeS
SMe
146
7.5
7.0
6.5
ppm
4.0
3.8
3.6
3.4
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


MeS
SMe
Mix of isomers
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

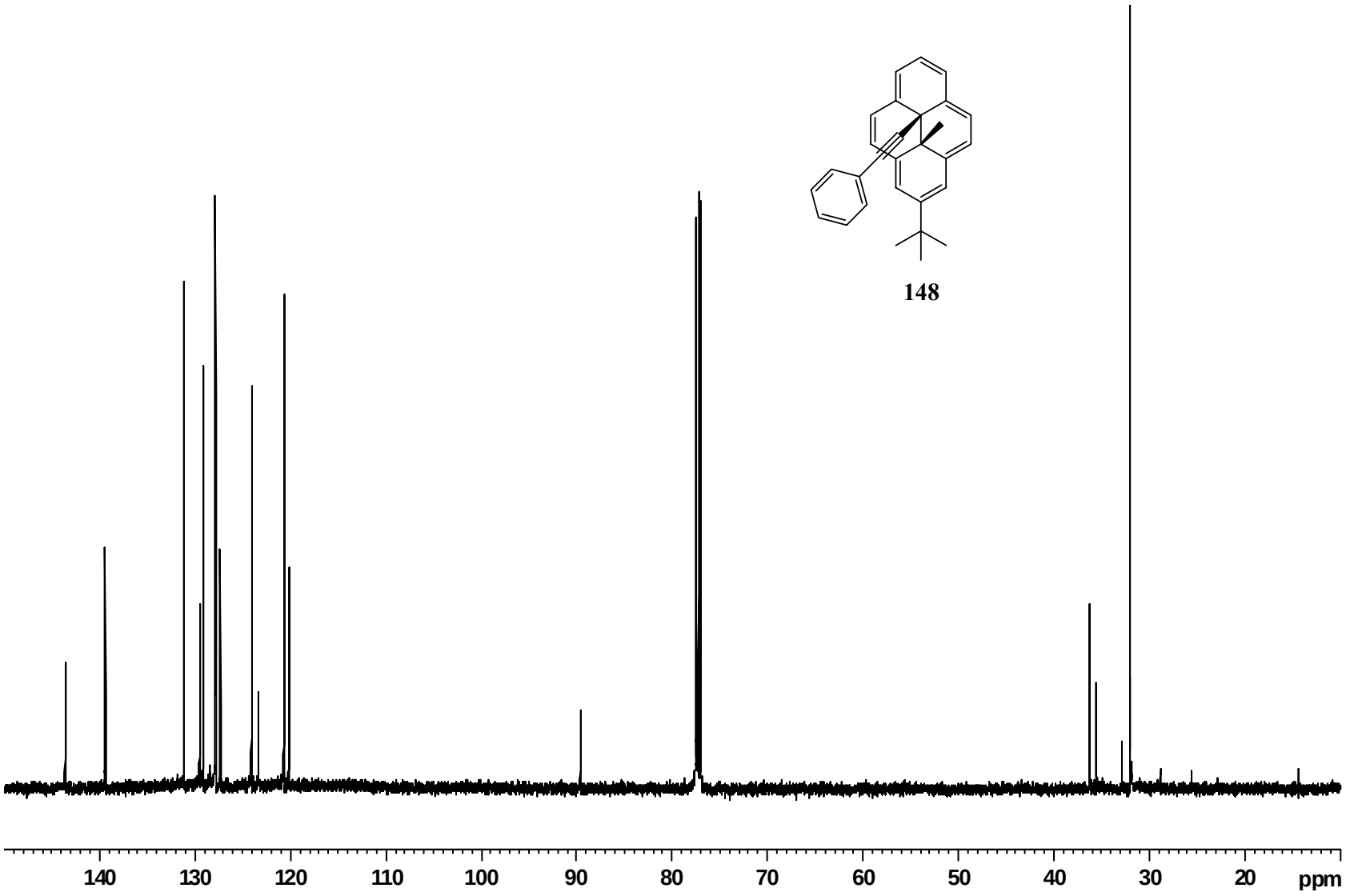

Me2S
SMe2
2BF4
7.9
7.8
7.7
7.6
7.5
7.4
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

**147 a**

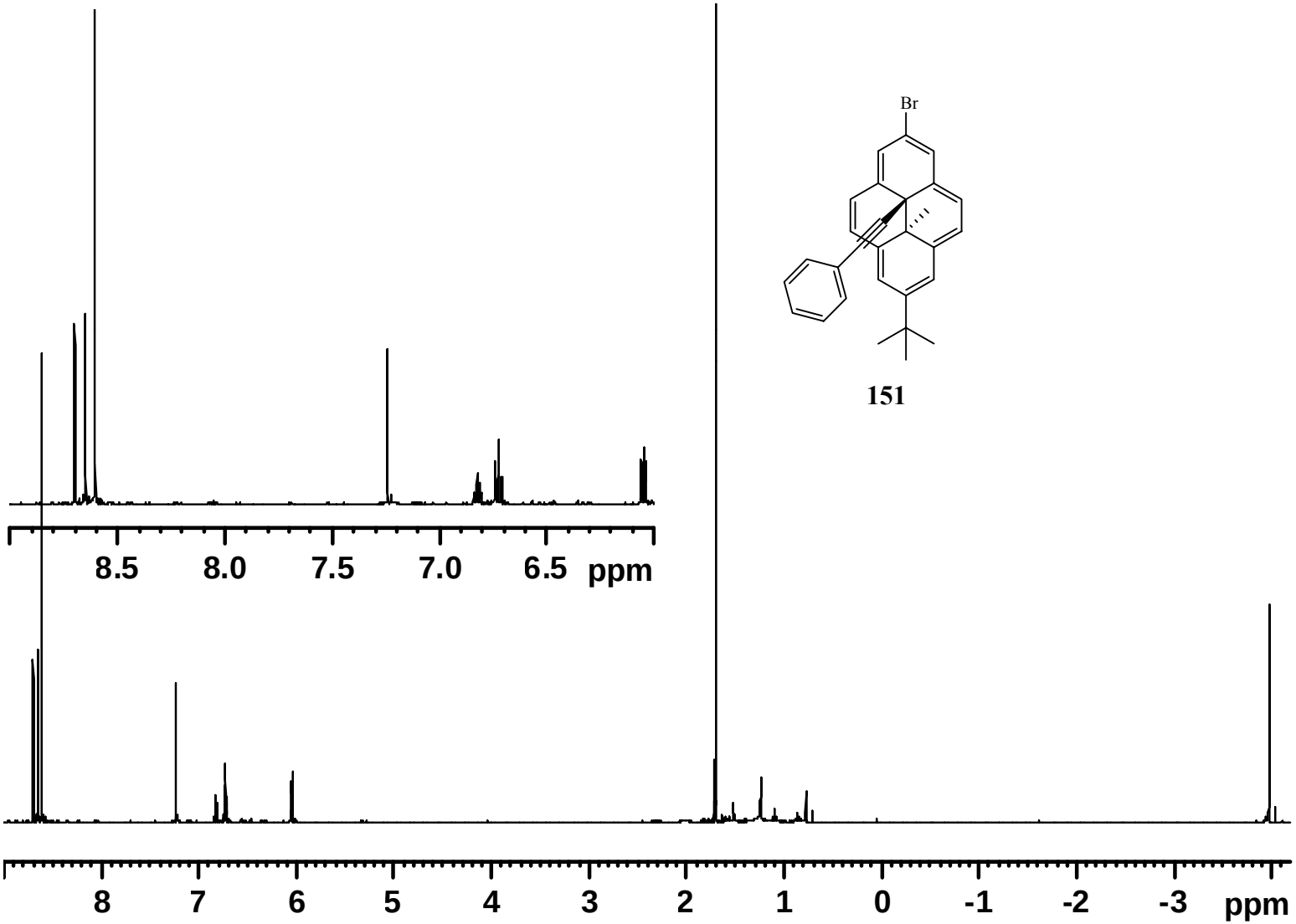

Mix of isomers
Me2S
SMe2
2BF4
147
4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



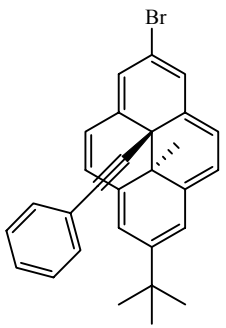

**148**



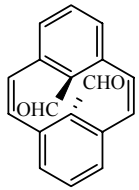

**148**



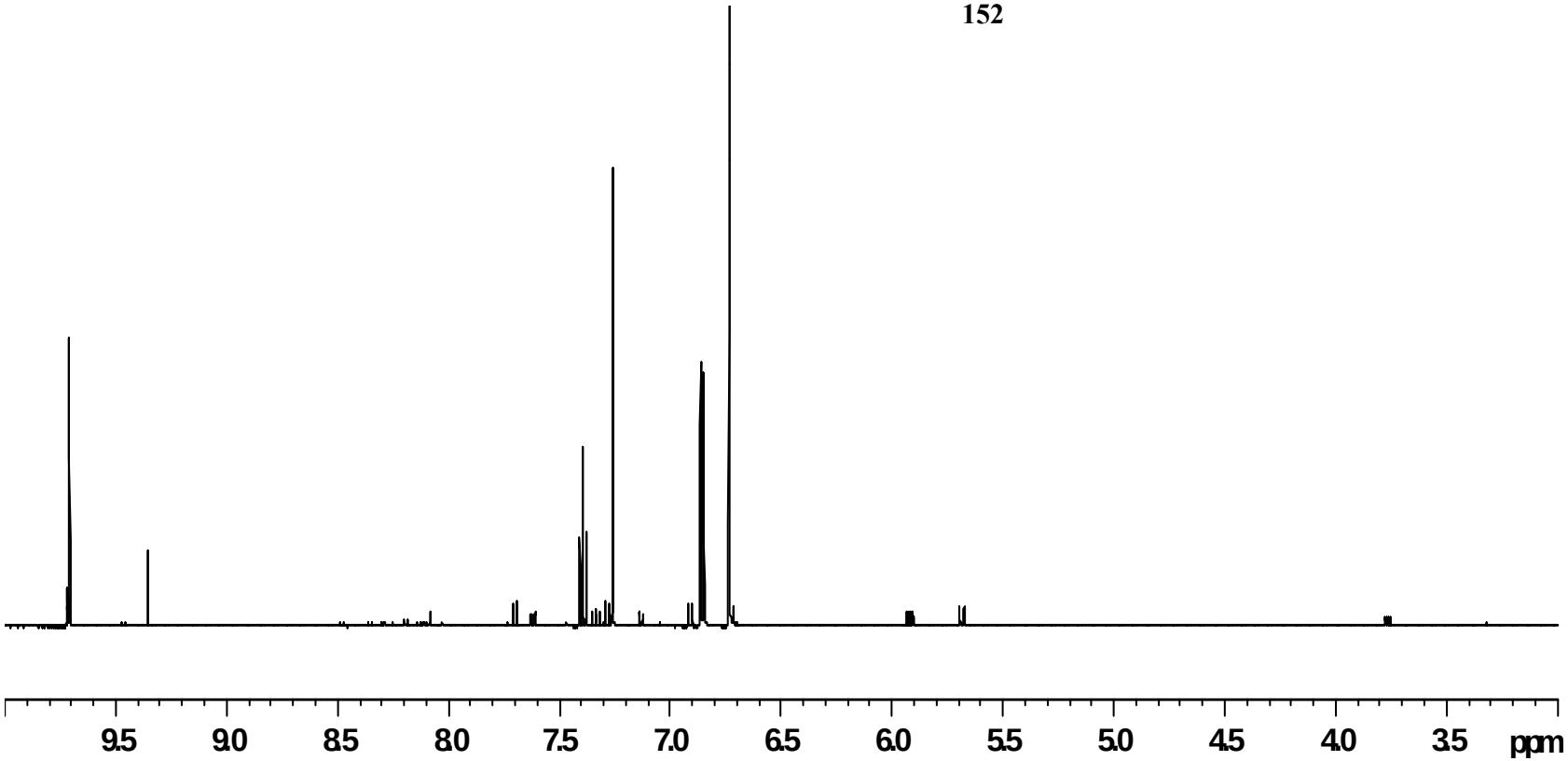

**151**

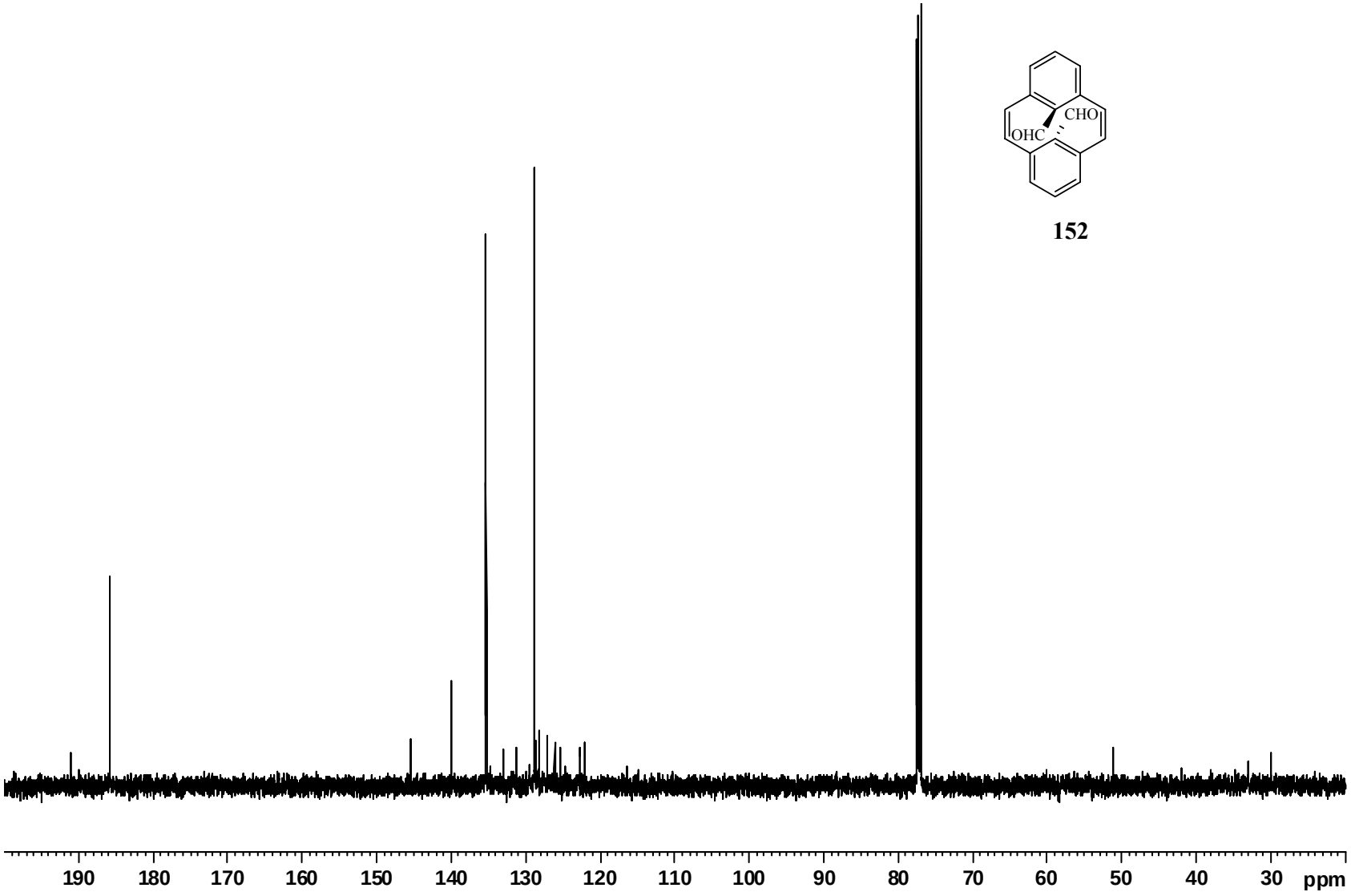



**151**

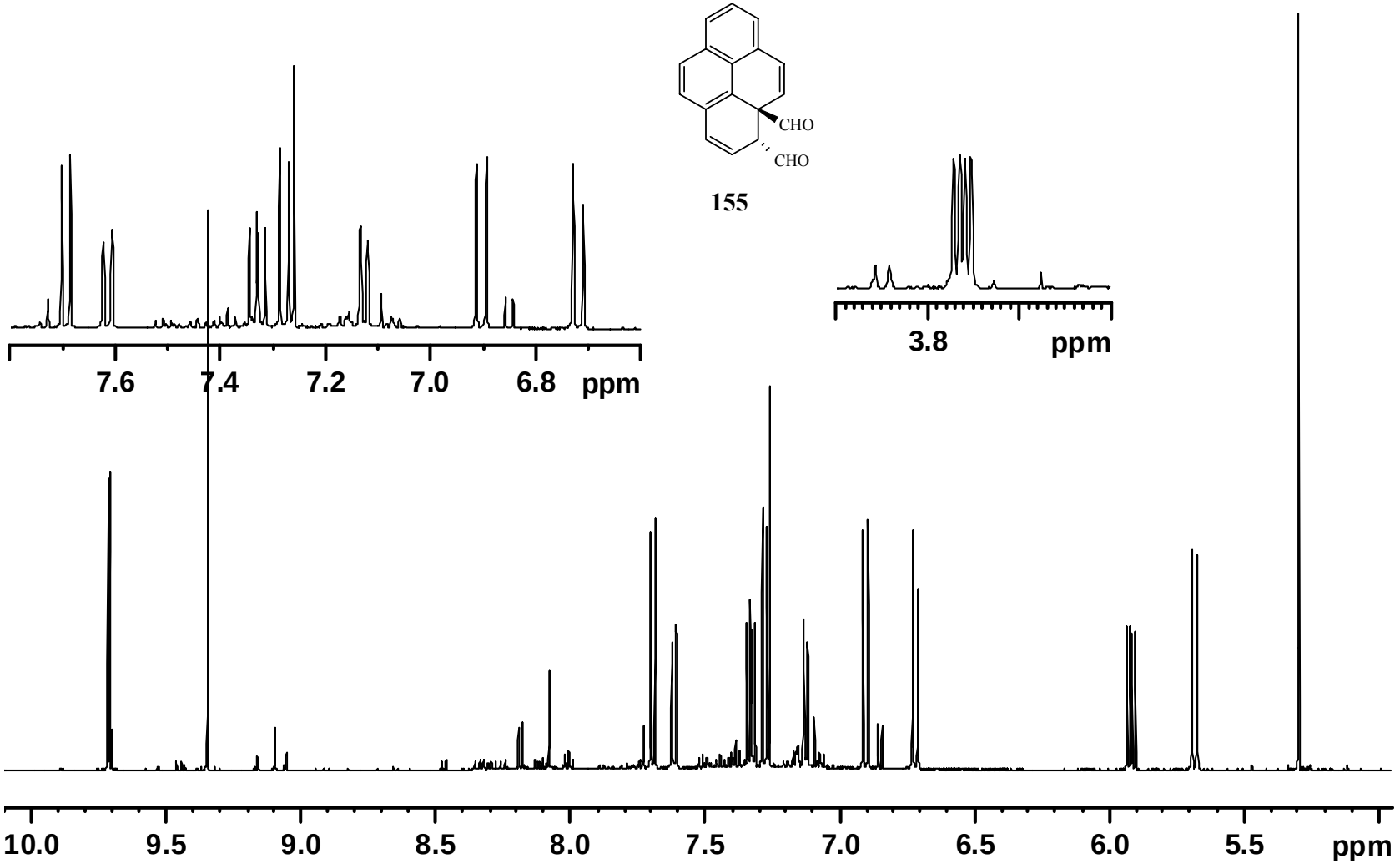


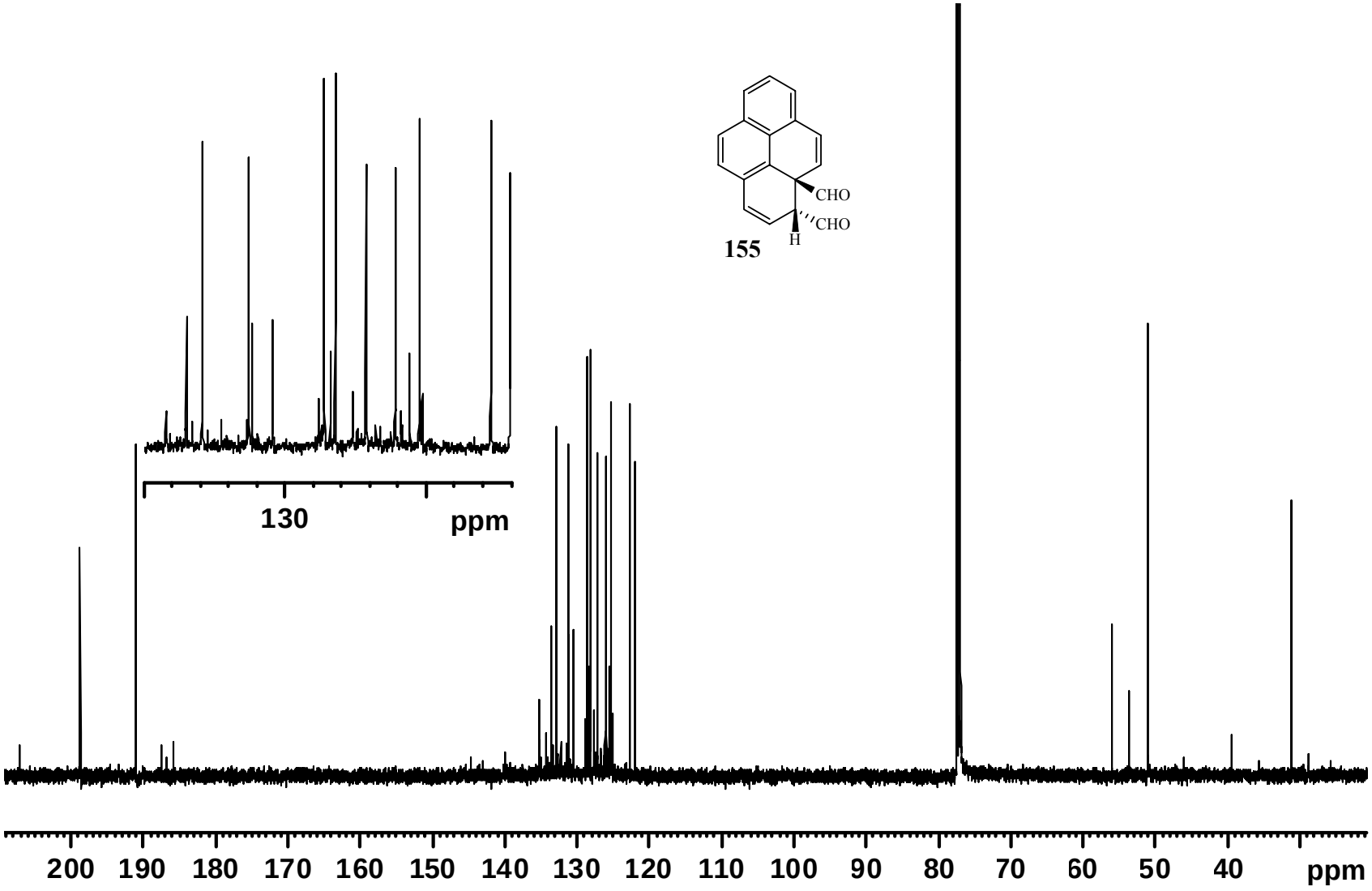

**152**

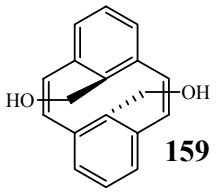



CHO
OHC
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

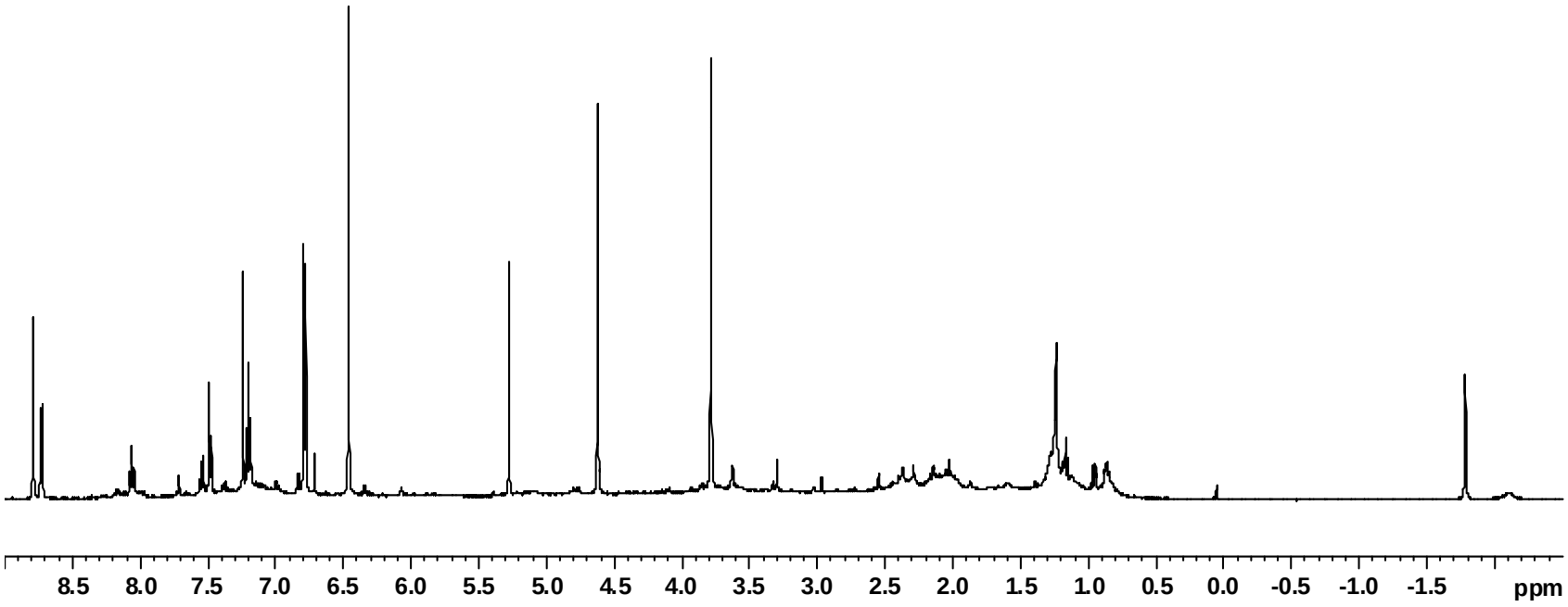
**152**

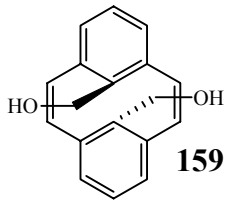

CHO
CHO
155
7.6
7.4
7.2
7.0
6.8
ppm
3.8
ppm
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
ppm


CHO
CHO
H
155
130
ppm
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm

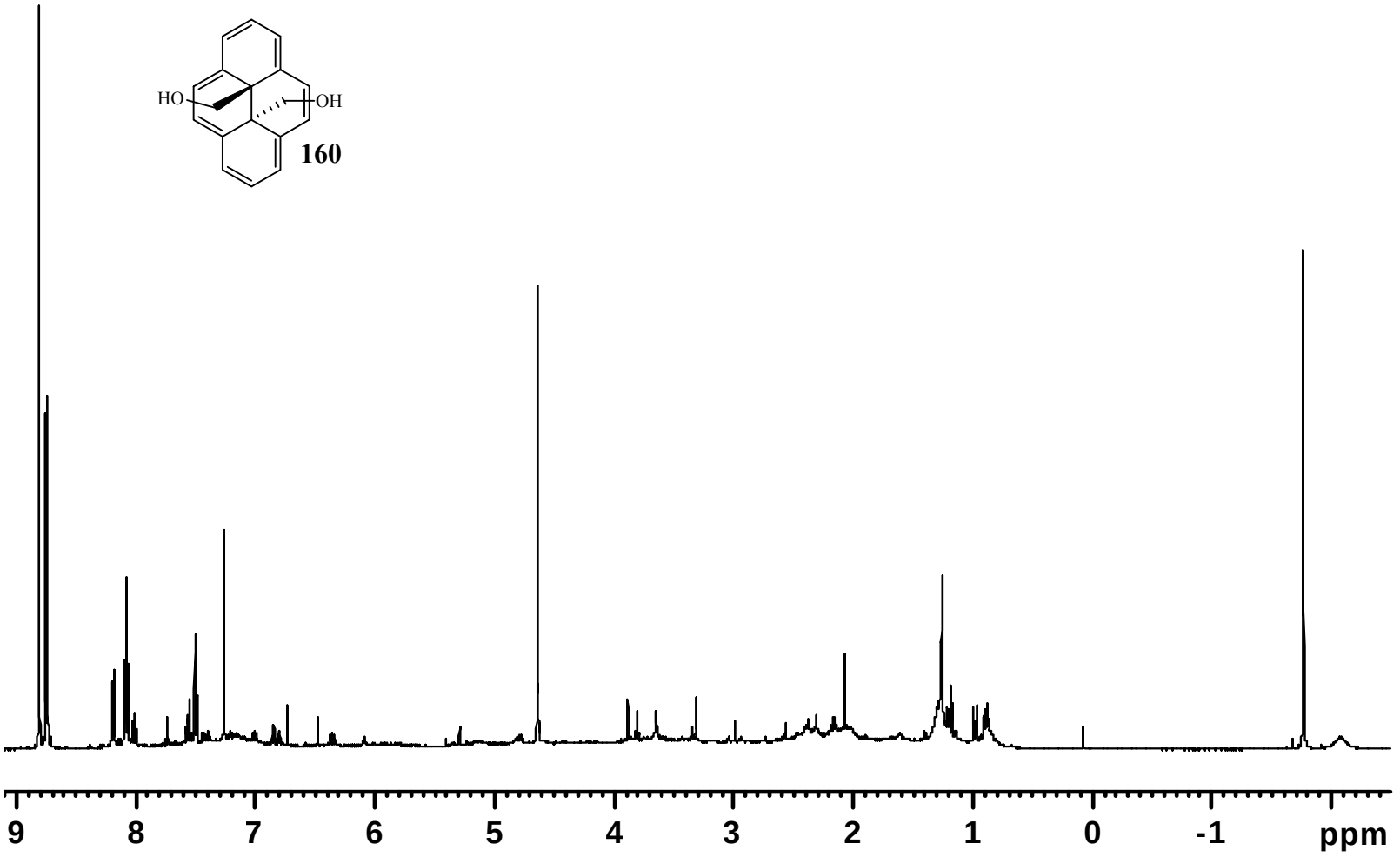


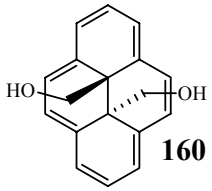

**159**



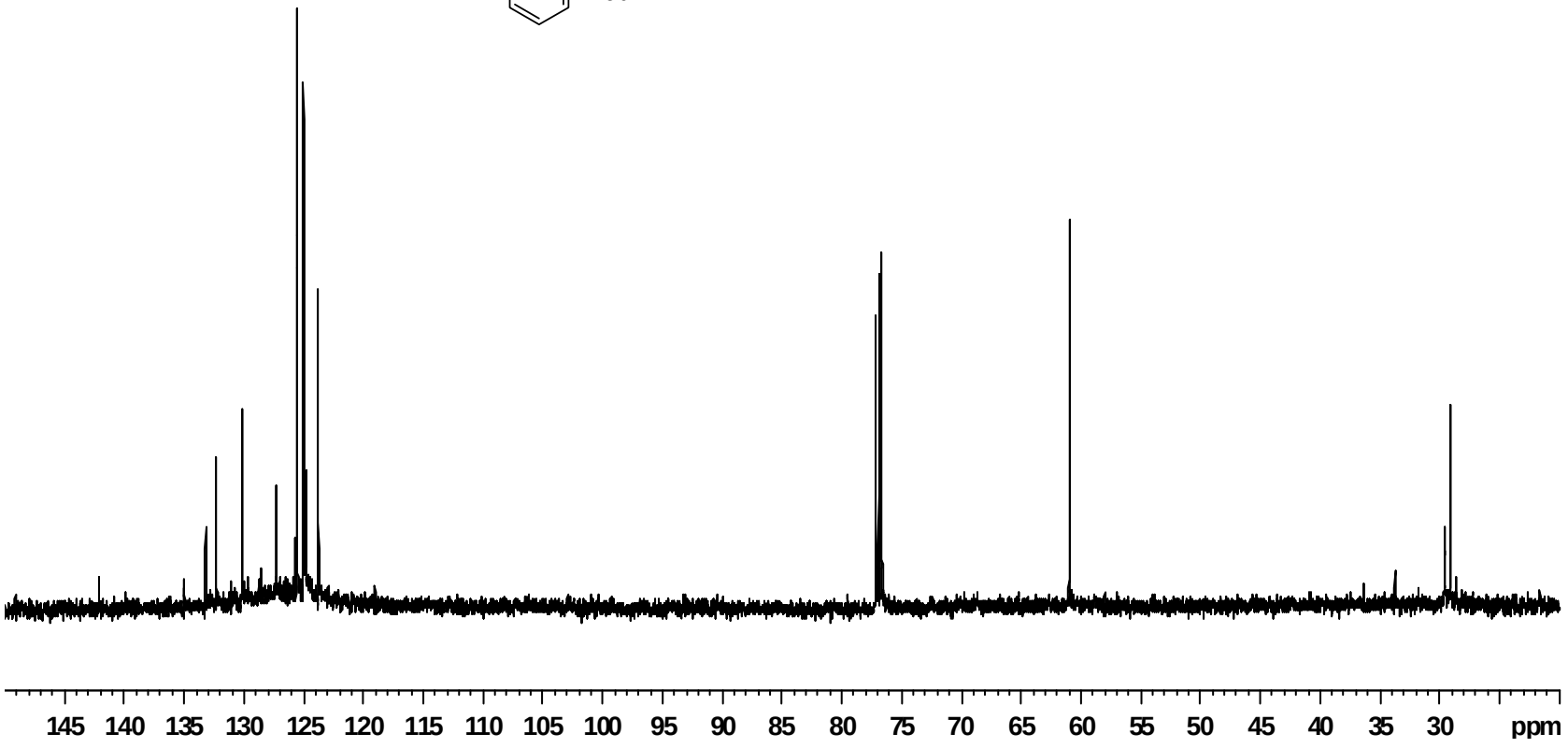


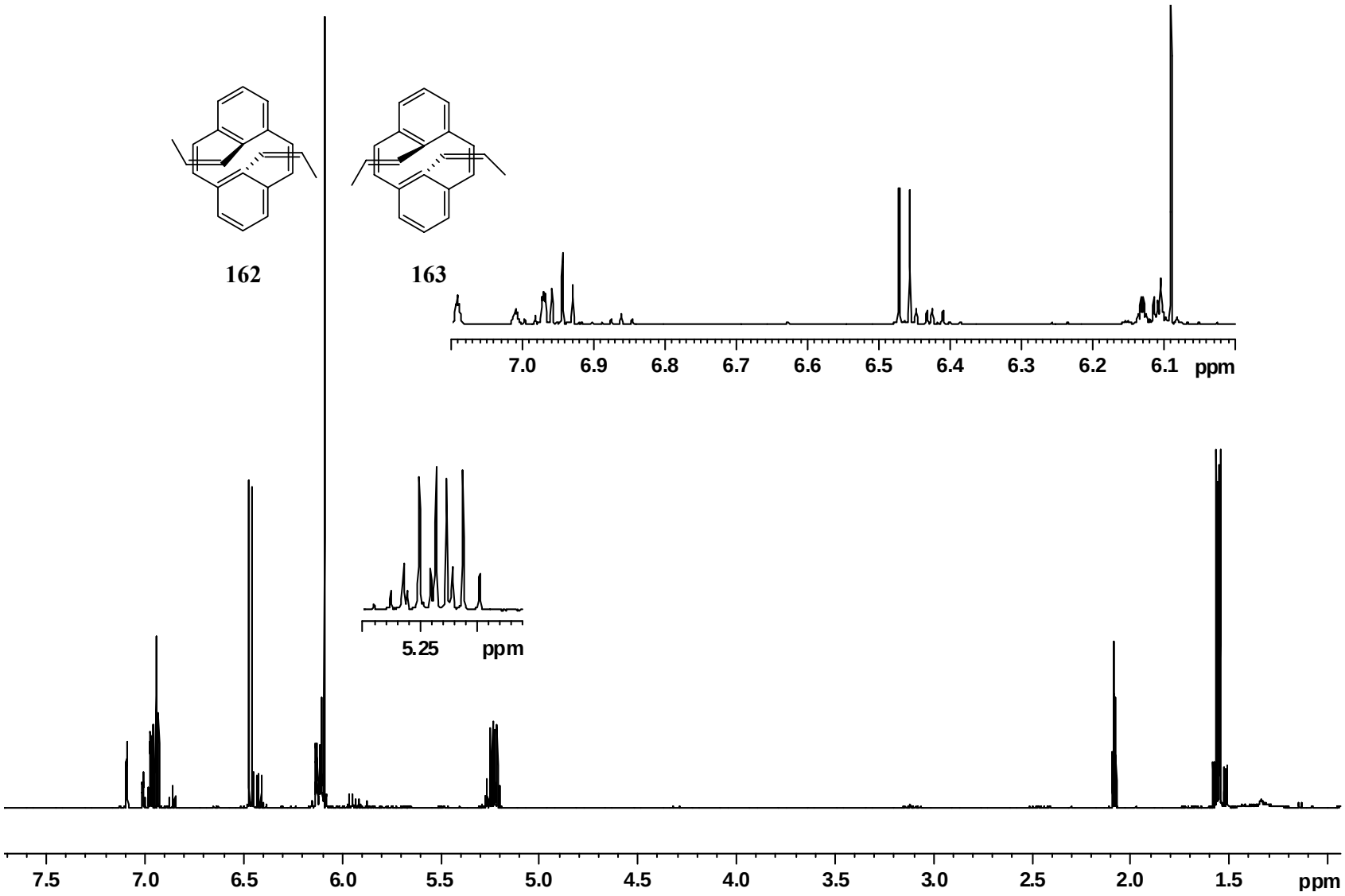

**159**

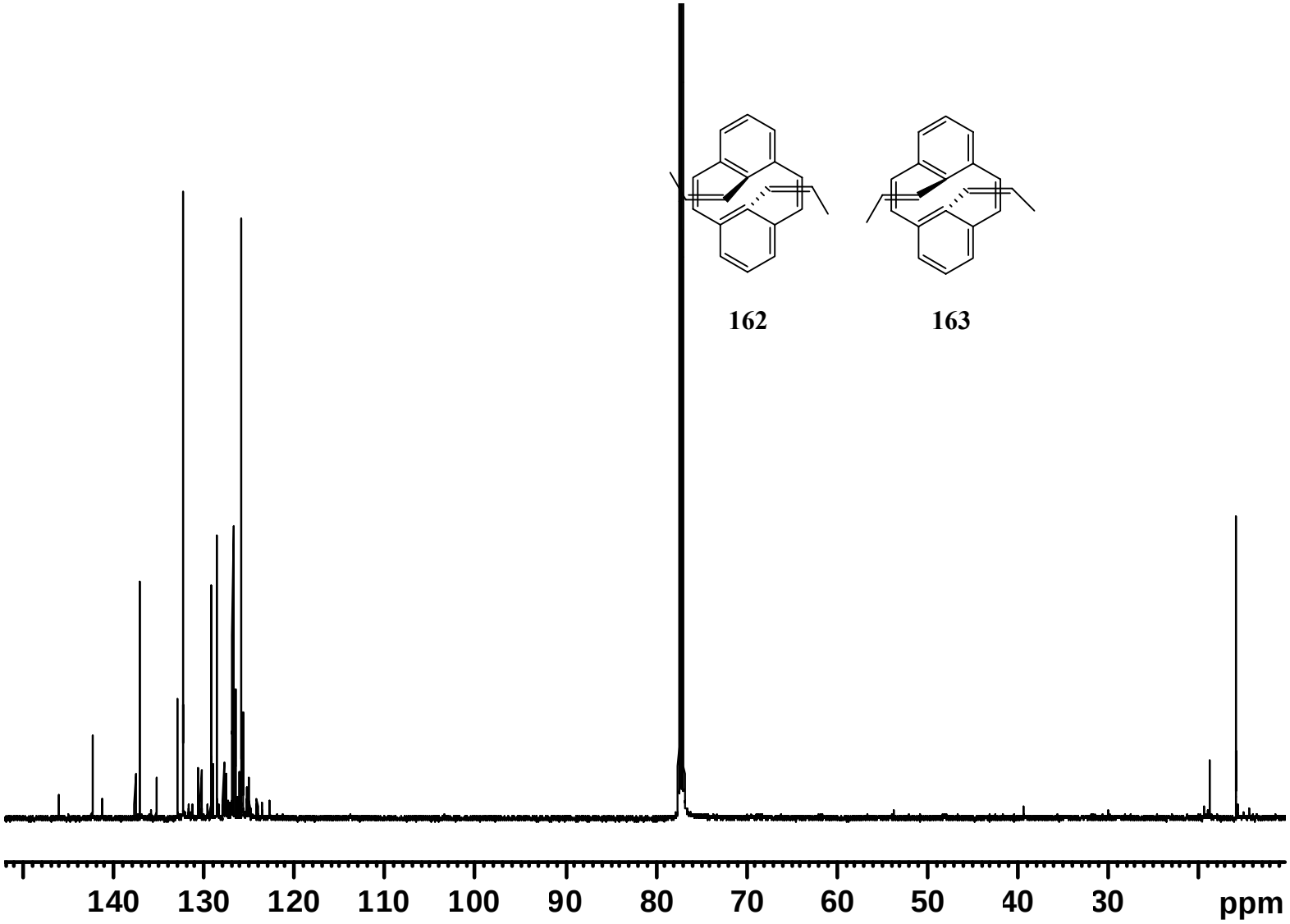

HO
OH
160
9
8
7
6
5
4
3
2
1
0
-1
ppm

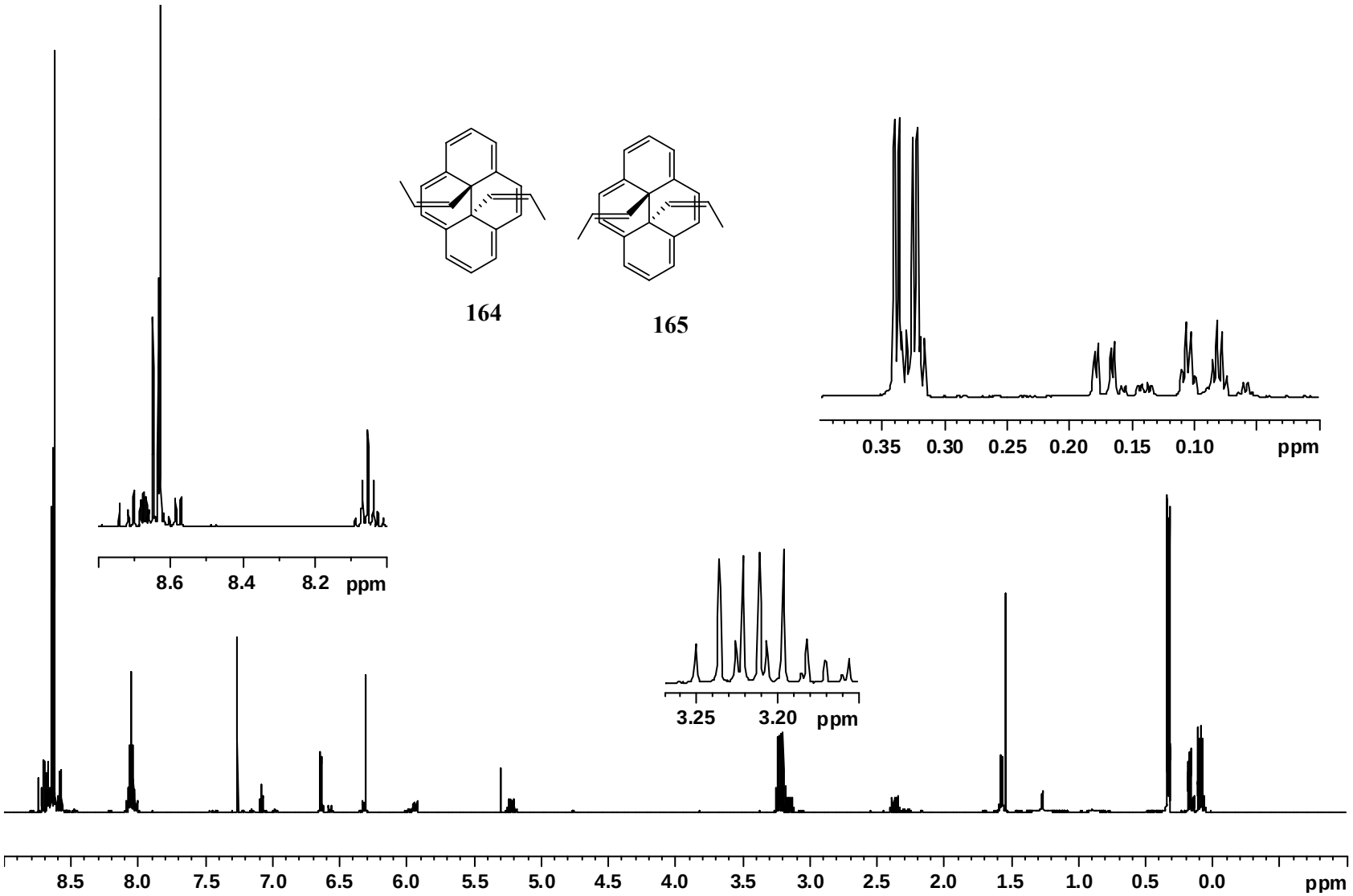

HO
OH

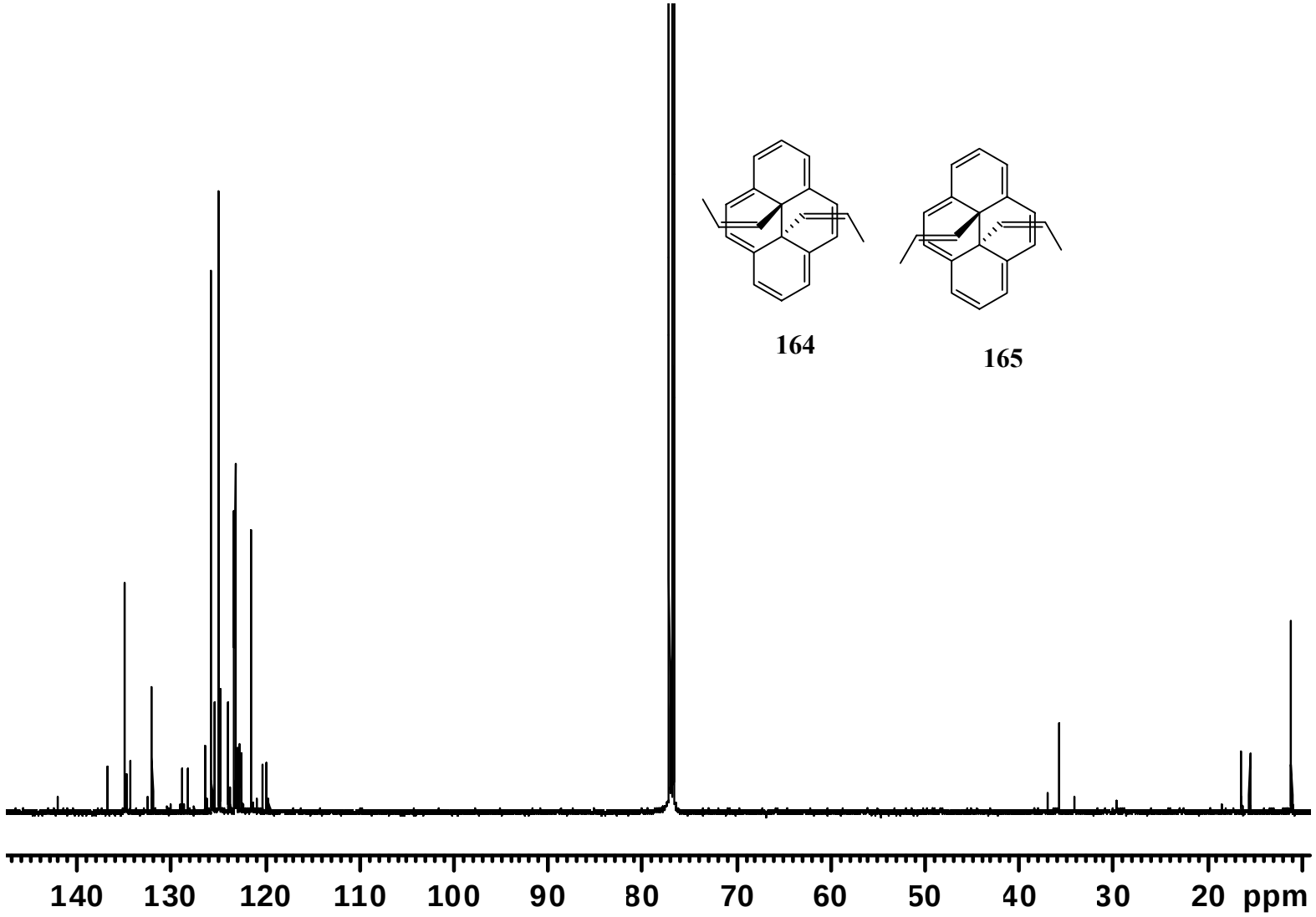
**160**


145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 ppm


162
163
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
ppm
5.25
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


162
163
140
130
120
110
100
90
80
70
60
50
40
30
ppm


164
165
0.35 0.30 0.25 0.20 0.15 0.10 ppm
8.6 8.4 8.2 ppm
3.25 3.20 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

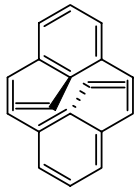





**164**

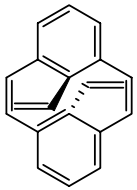


**165**

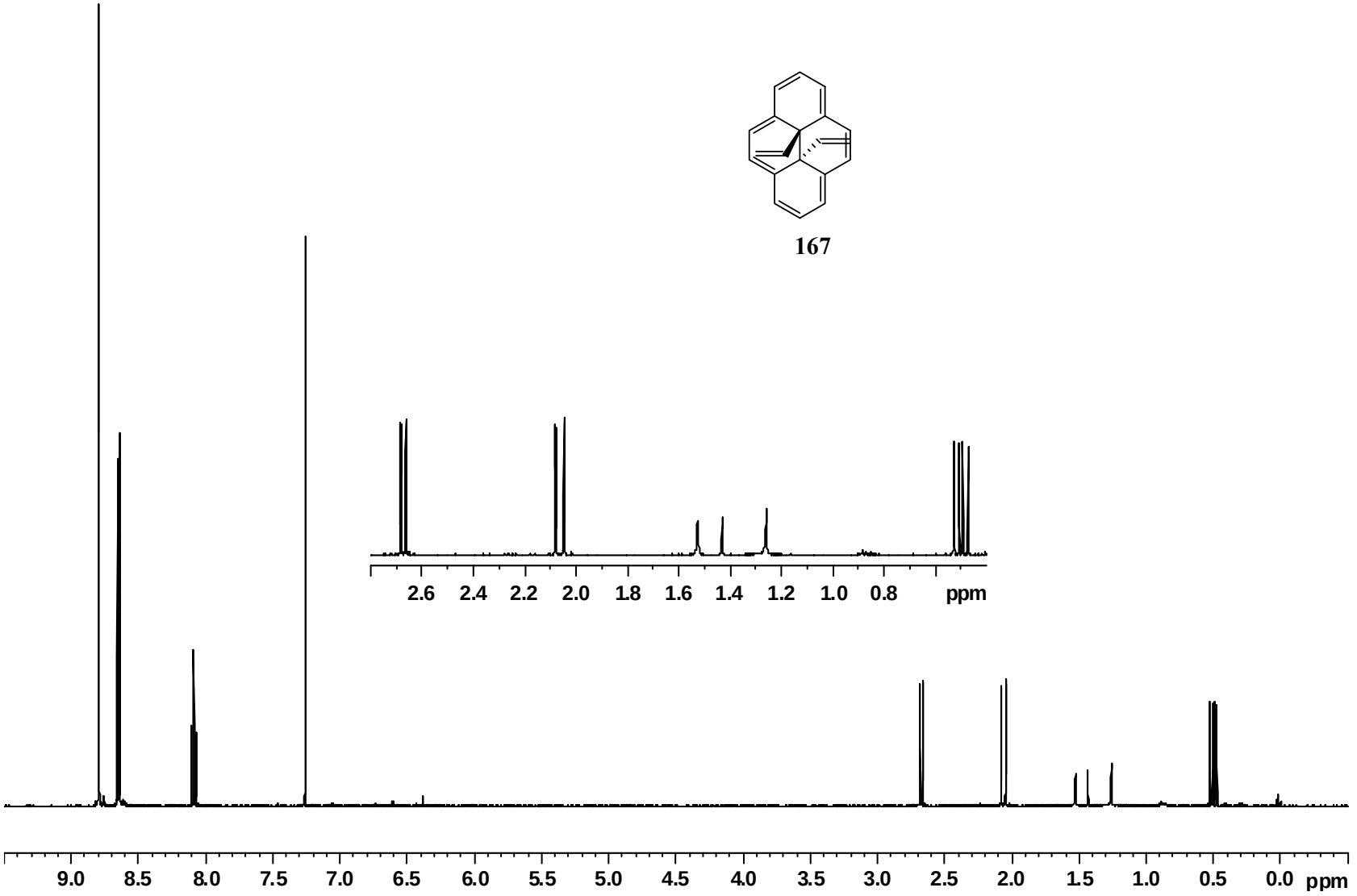


**166**

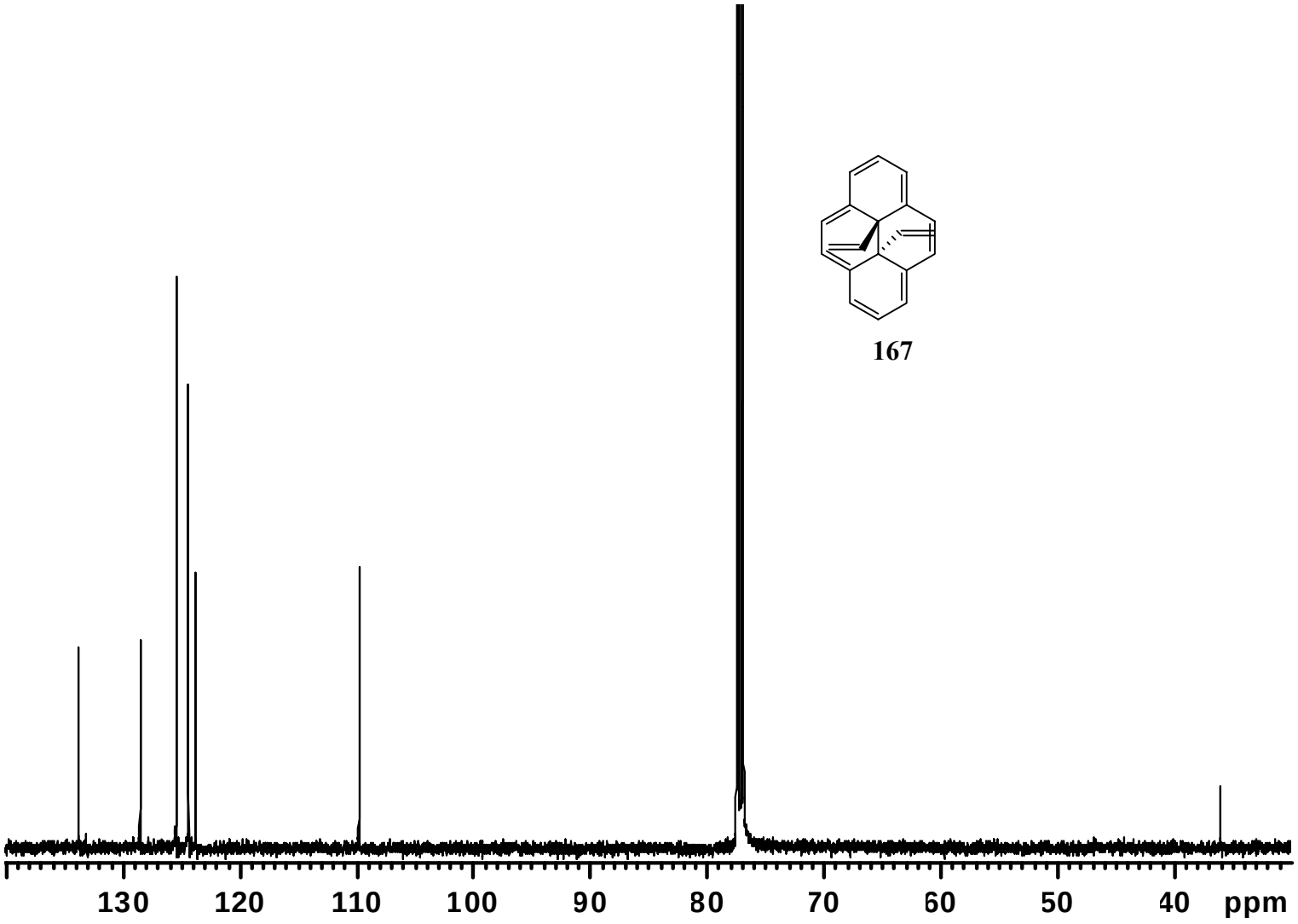

7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7
ppm



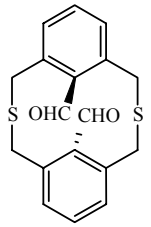
**166**


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
ppm

**167**




**167**


S OHC CHO S

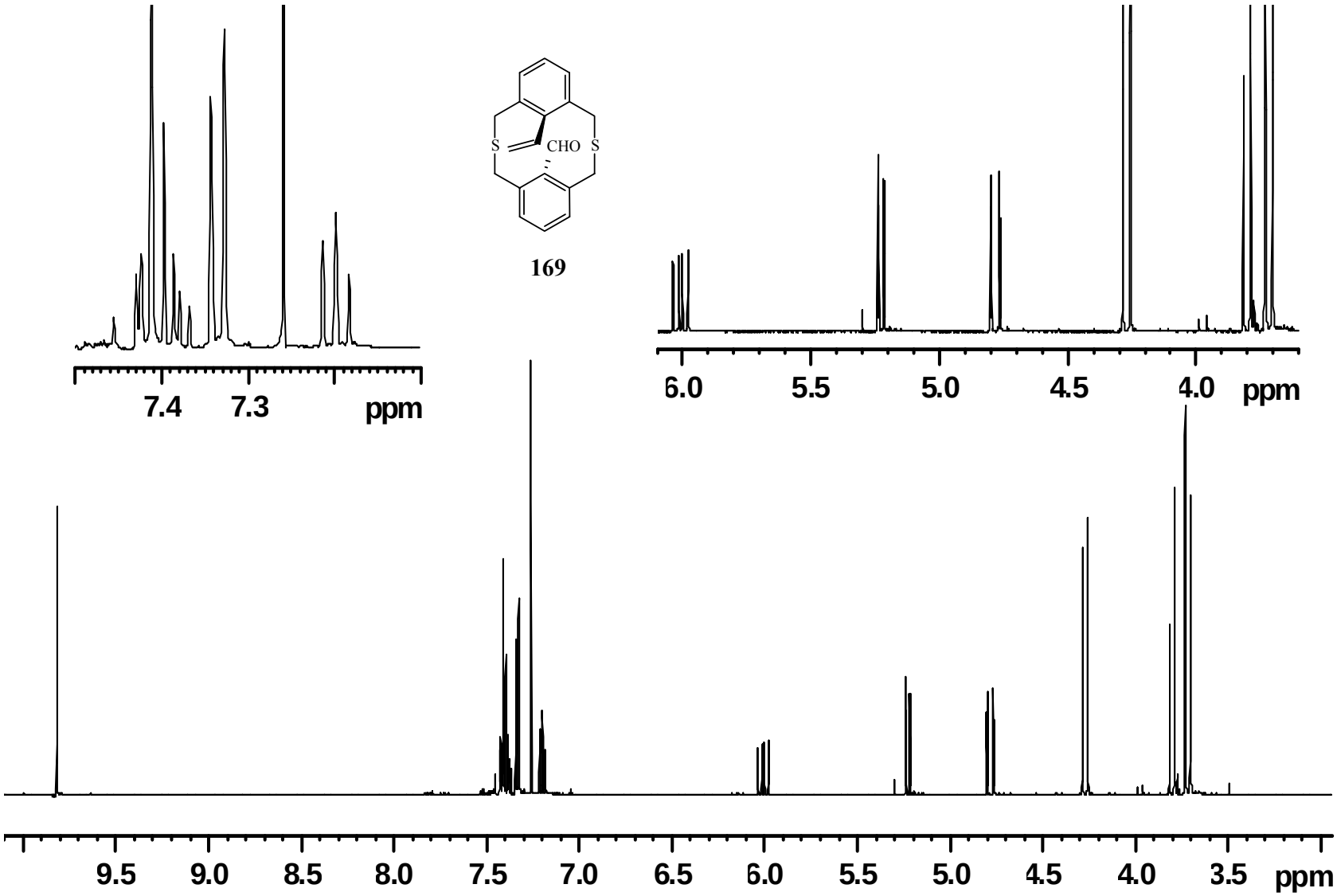
**168**


4.4 4.3 4.2 4.1 4.0 3.9 3.8 ppm
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

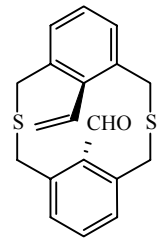

S OHC CHO S

**168**


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm

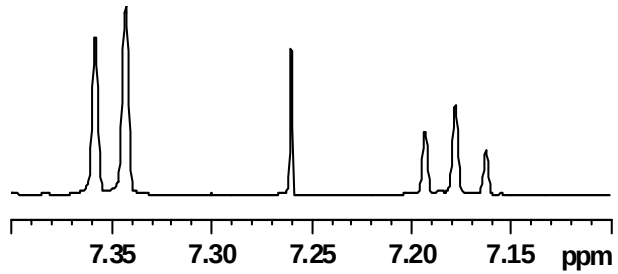

S
CHO
S
7.4
7.3
ppm
6.0
5.5
5.0
4.5
4.0
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

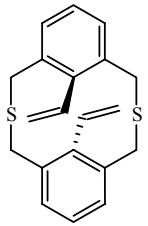
**169**


S
CHO
S

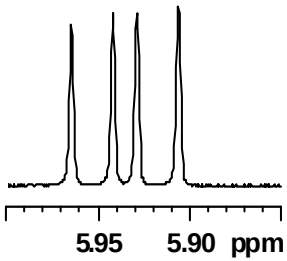
**169**


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

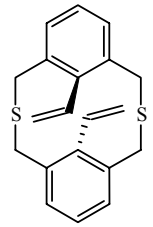

7.35
7.30
7.25
7.20
7.15
ppm


S
S

170

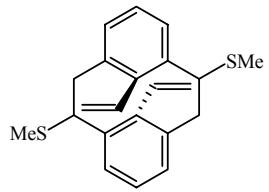

5.95
5.90
ppm


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

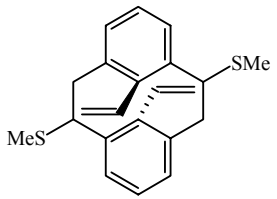

S
S

**170**


145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 ppm

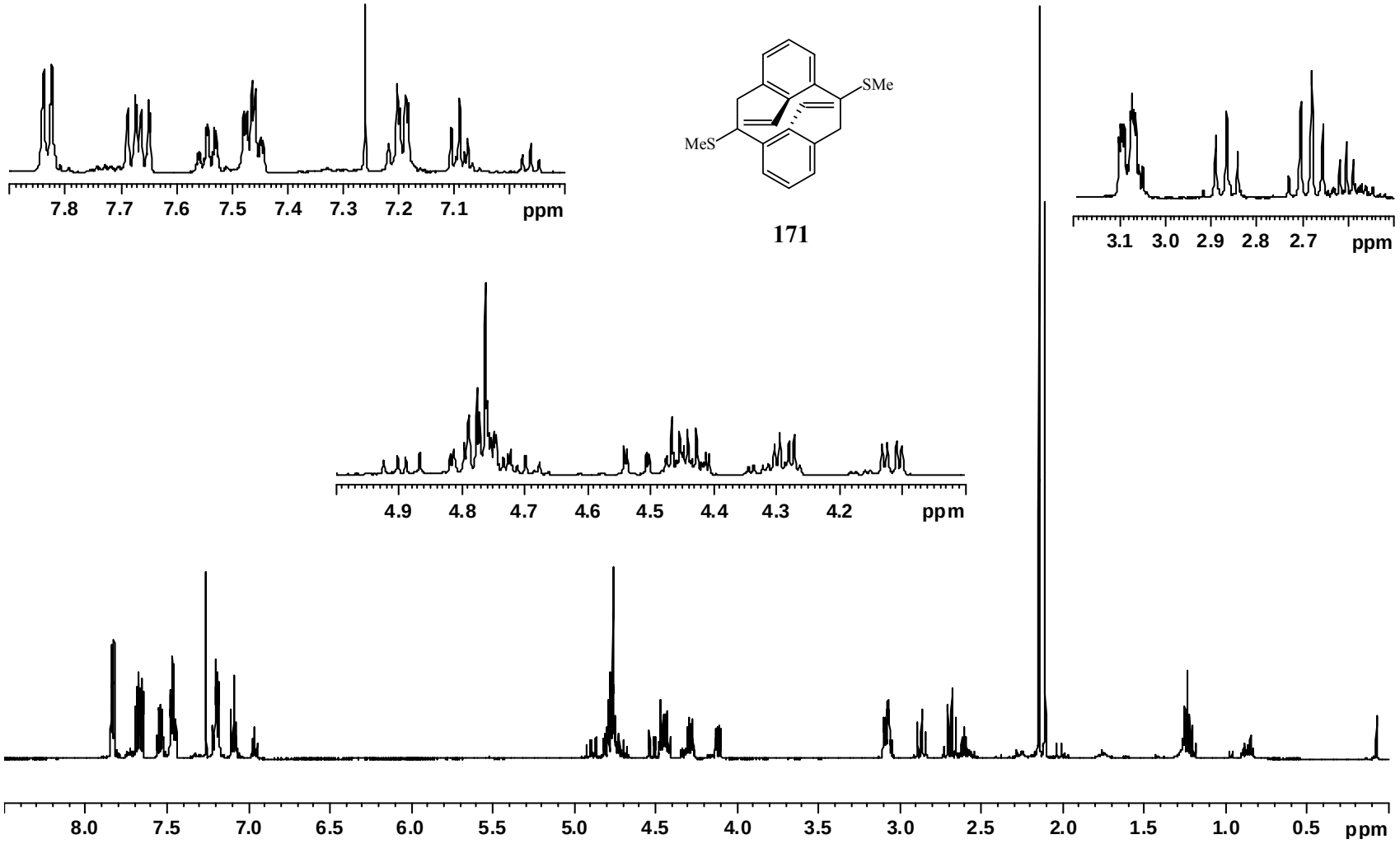



**171**

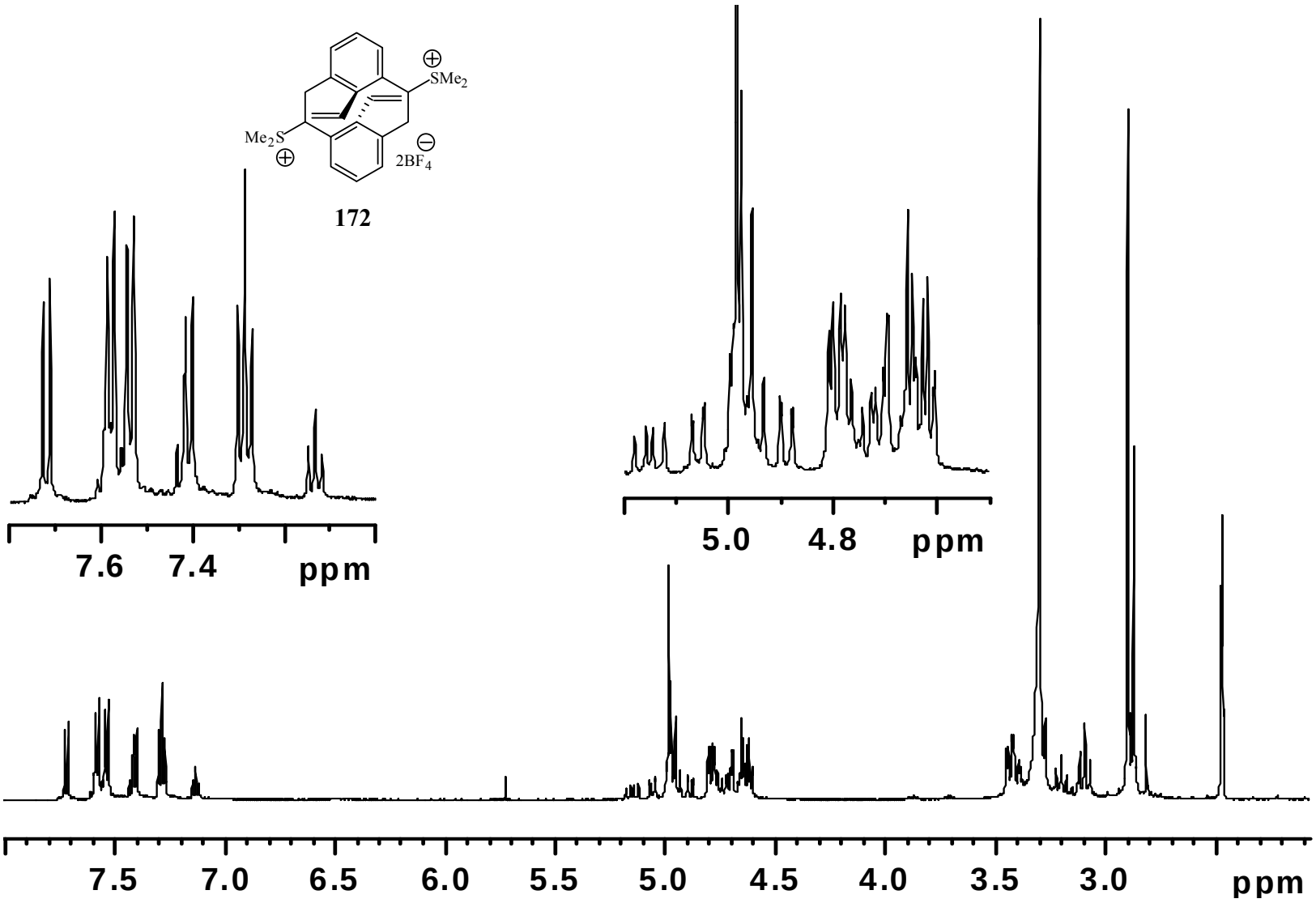



**171**

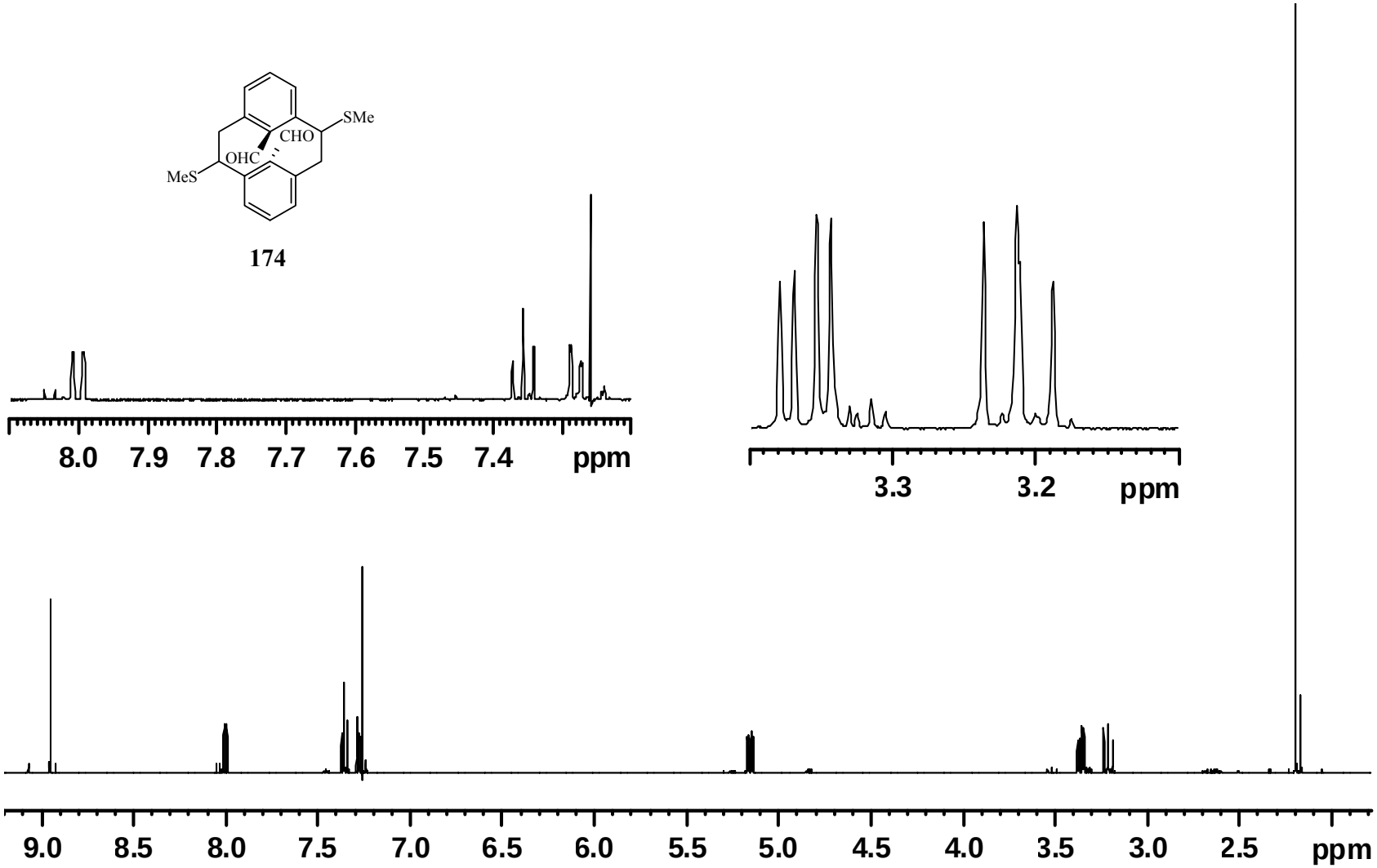
Mixture of isomers



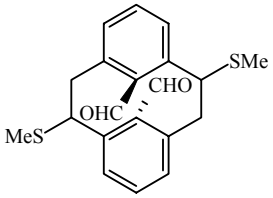

**171**




**172**

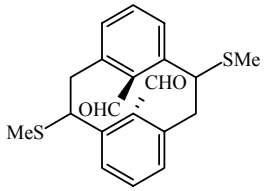

SMe
CHO
OHC
MeS
8.0 7.9 7.8 7.7 7.6 7.5 7.4 ppm
3.3 3.2 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm

**174**


SMe
CHO
OHC
MeS

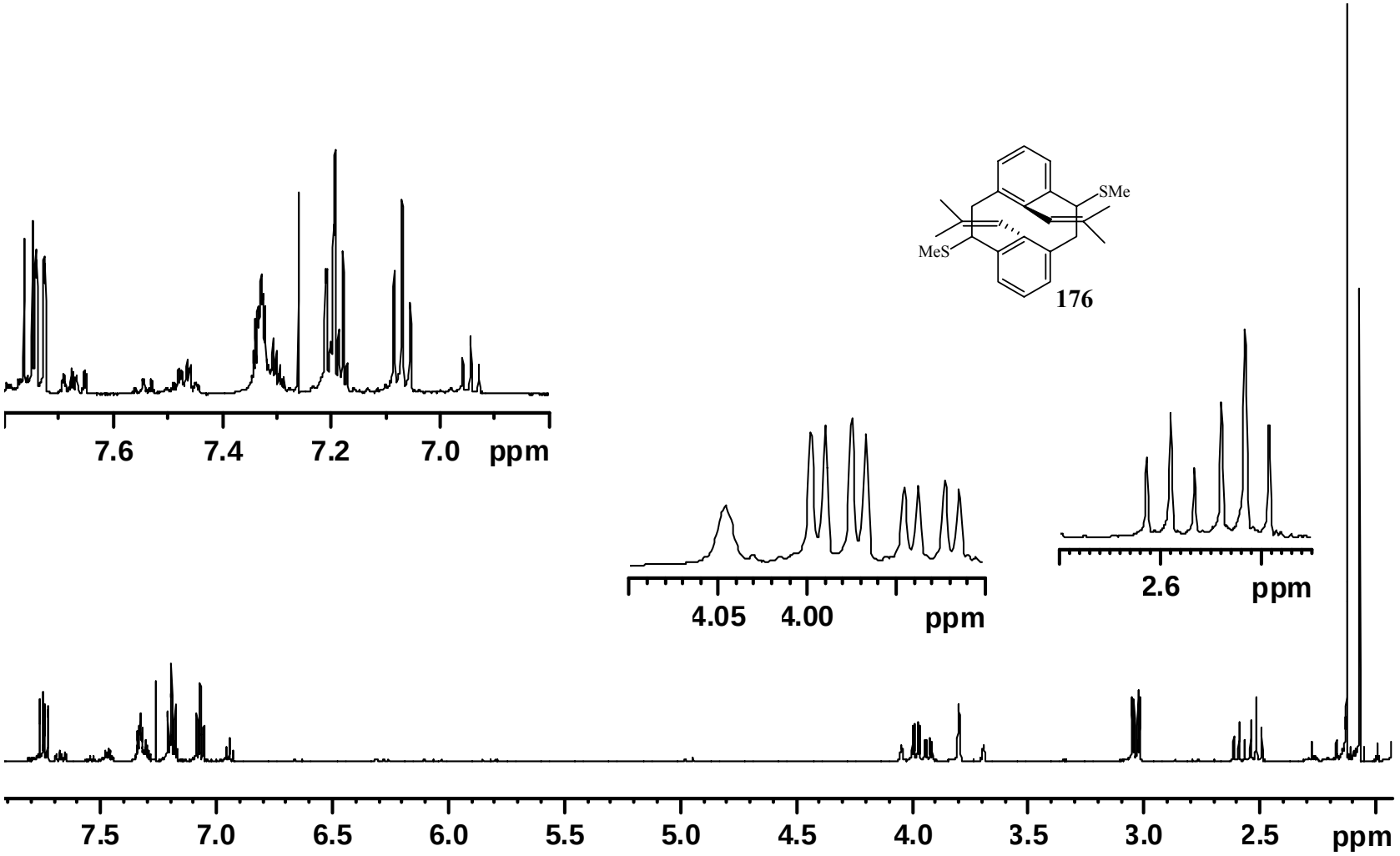
**174**

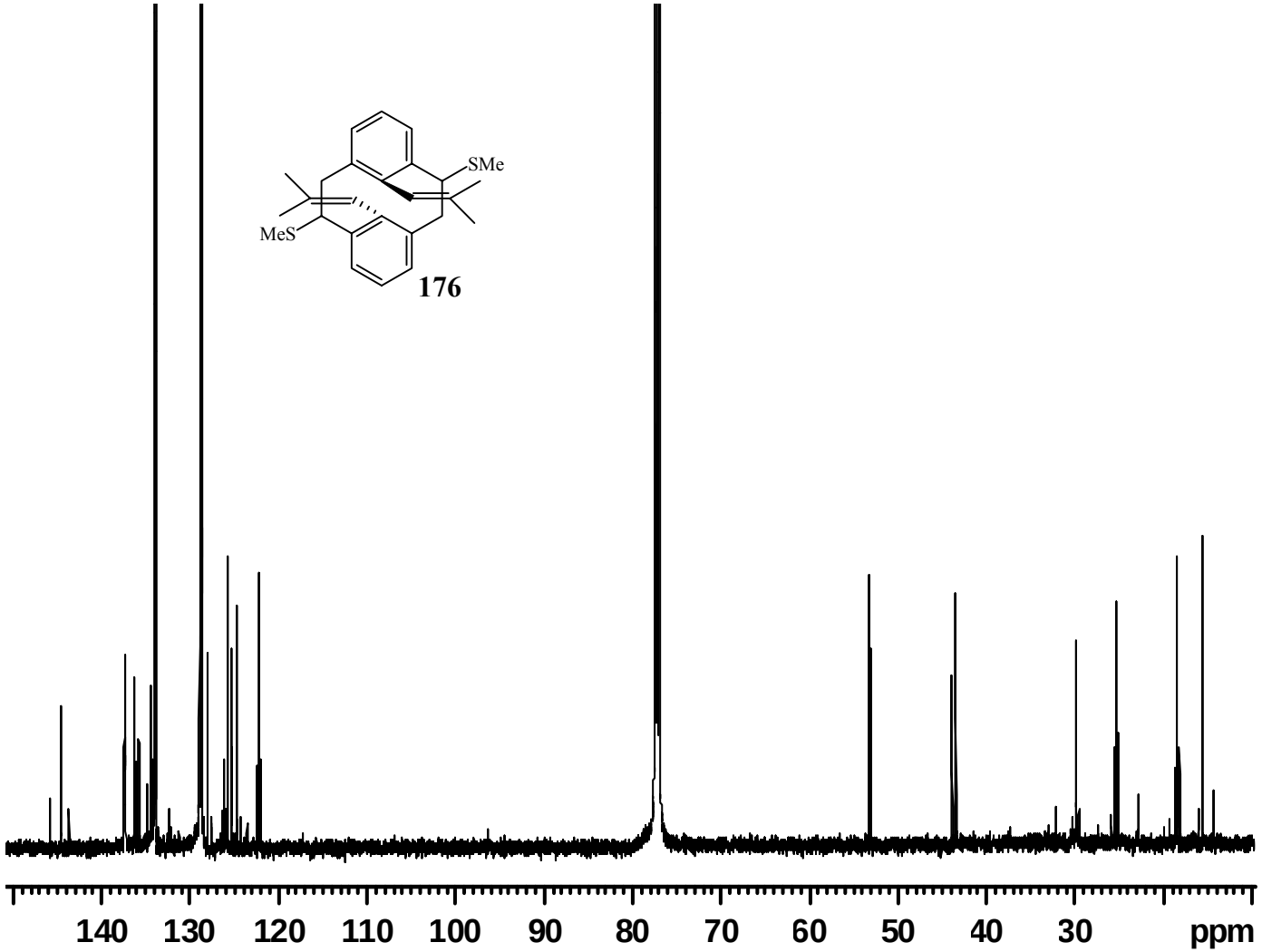

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

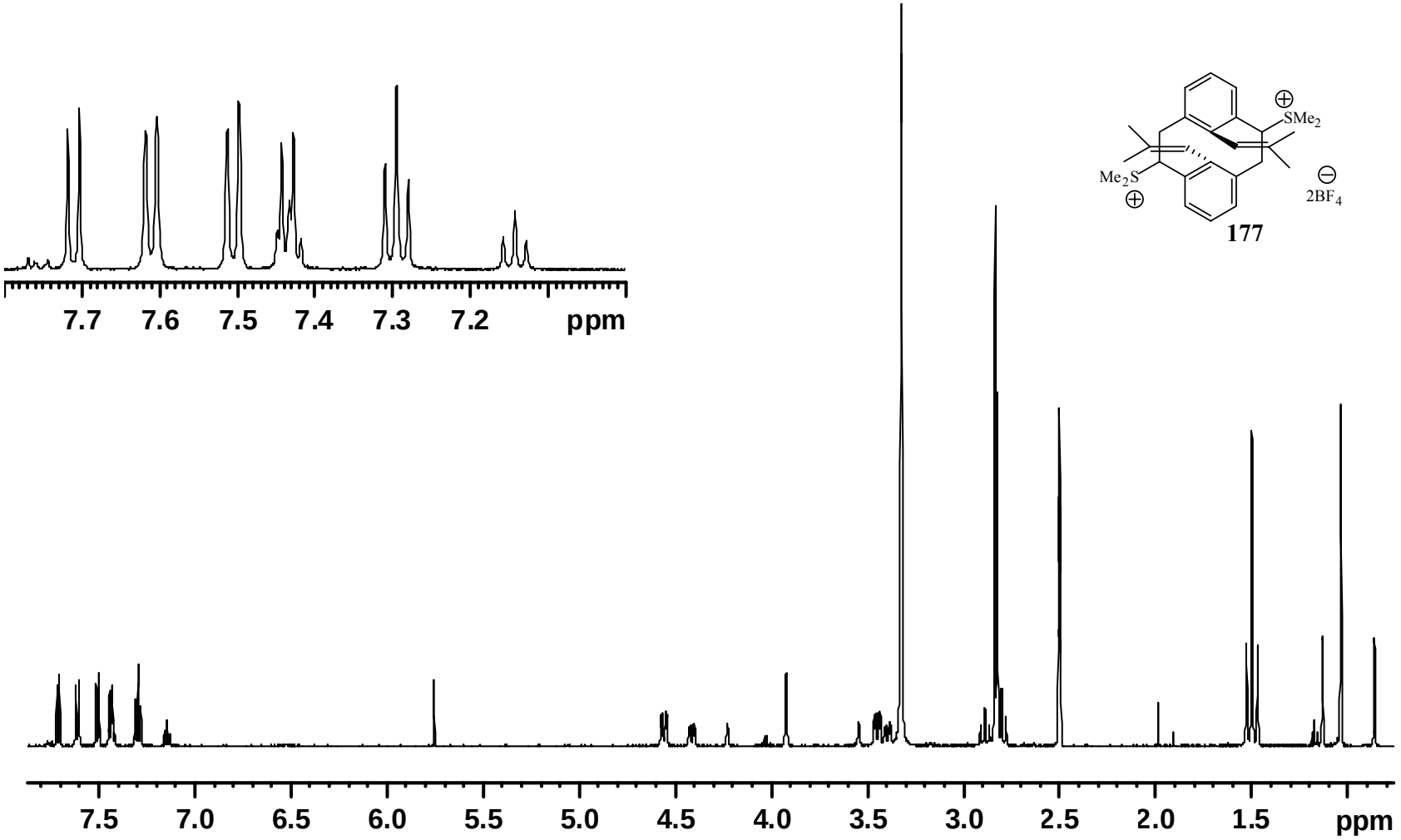

SMe
CHO
OHC
MeS

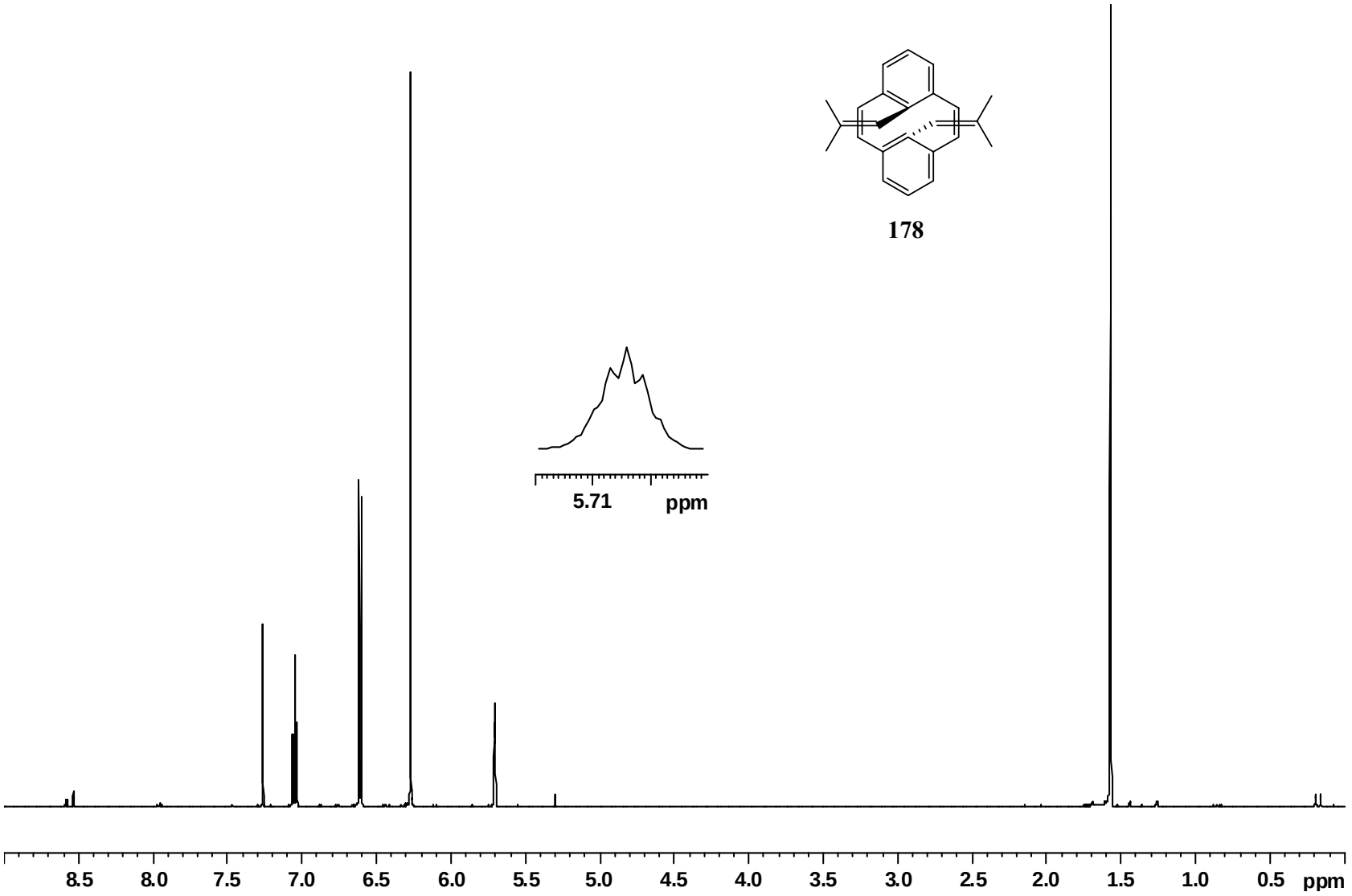
**174**

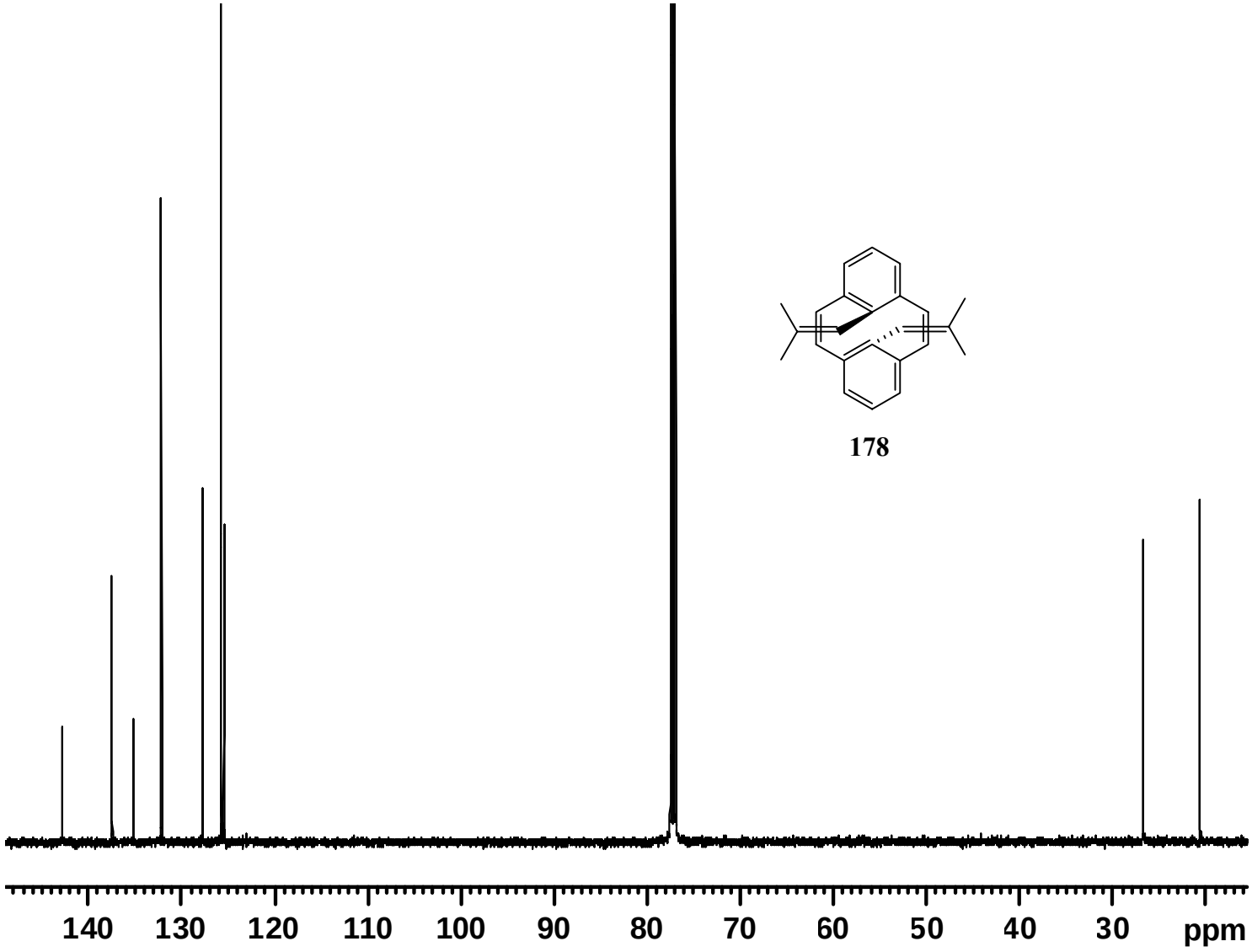

8.0
7.8
7.6
7.4
ppm
3.6
3.5
3.4
3.3
3.2
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm


SMe
MeS
176
7.6
7.4
7.2
7.0
ppm
4.05
4.00
ppm
2.6
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

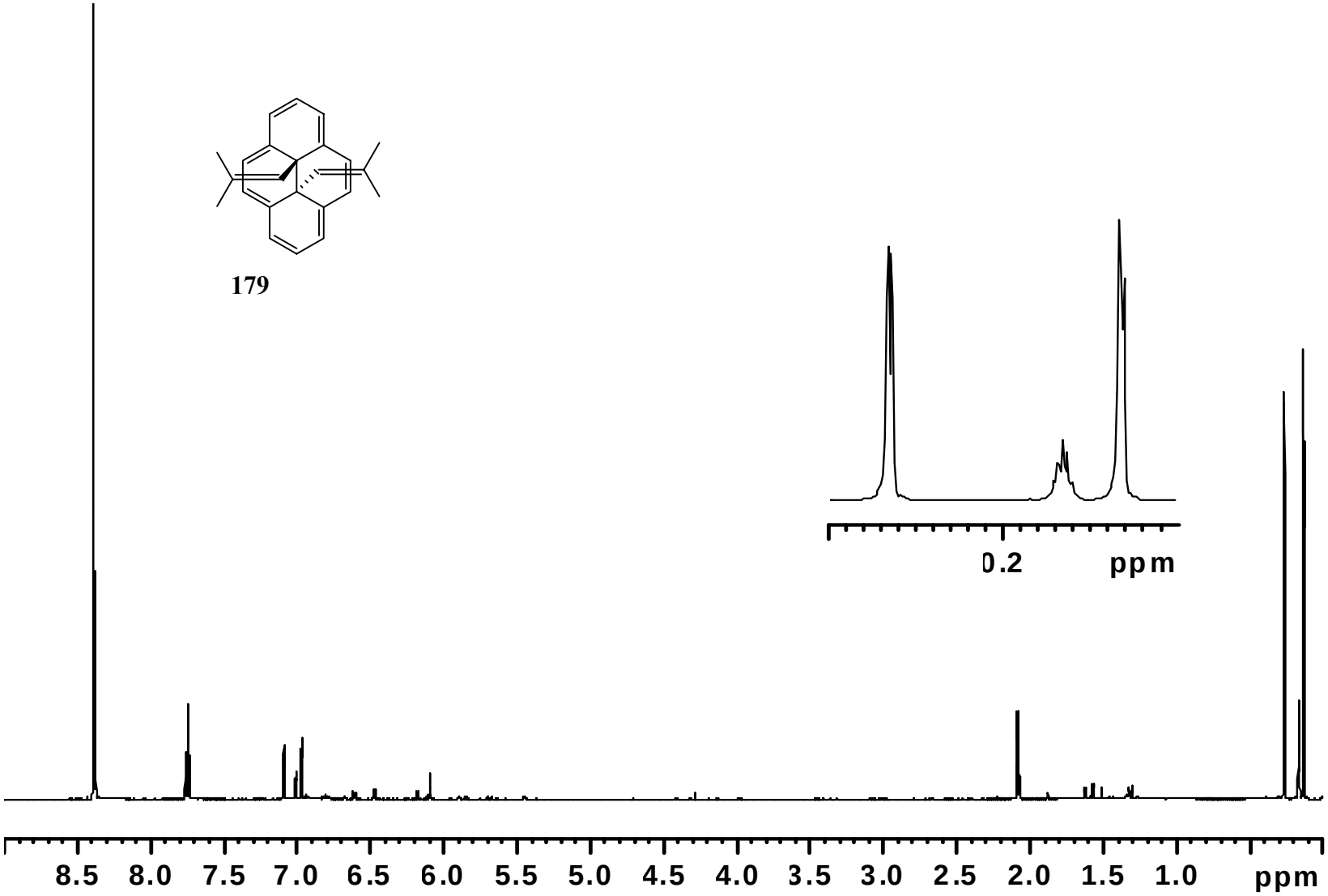

SMe
MeS
176
140
130
120
110
100
90
80
70
60
50
40
30
ppm

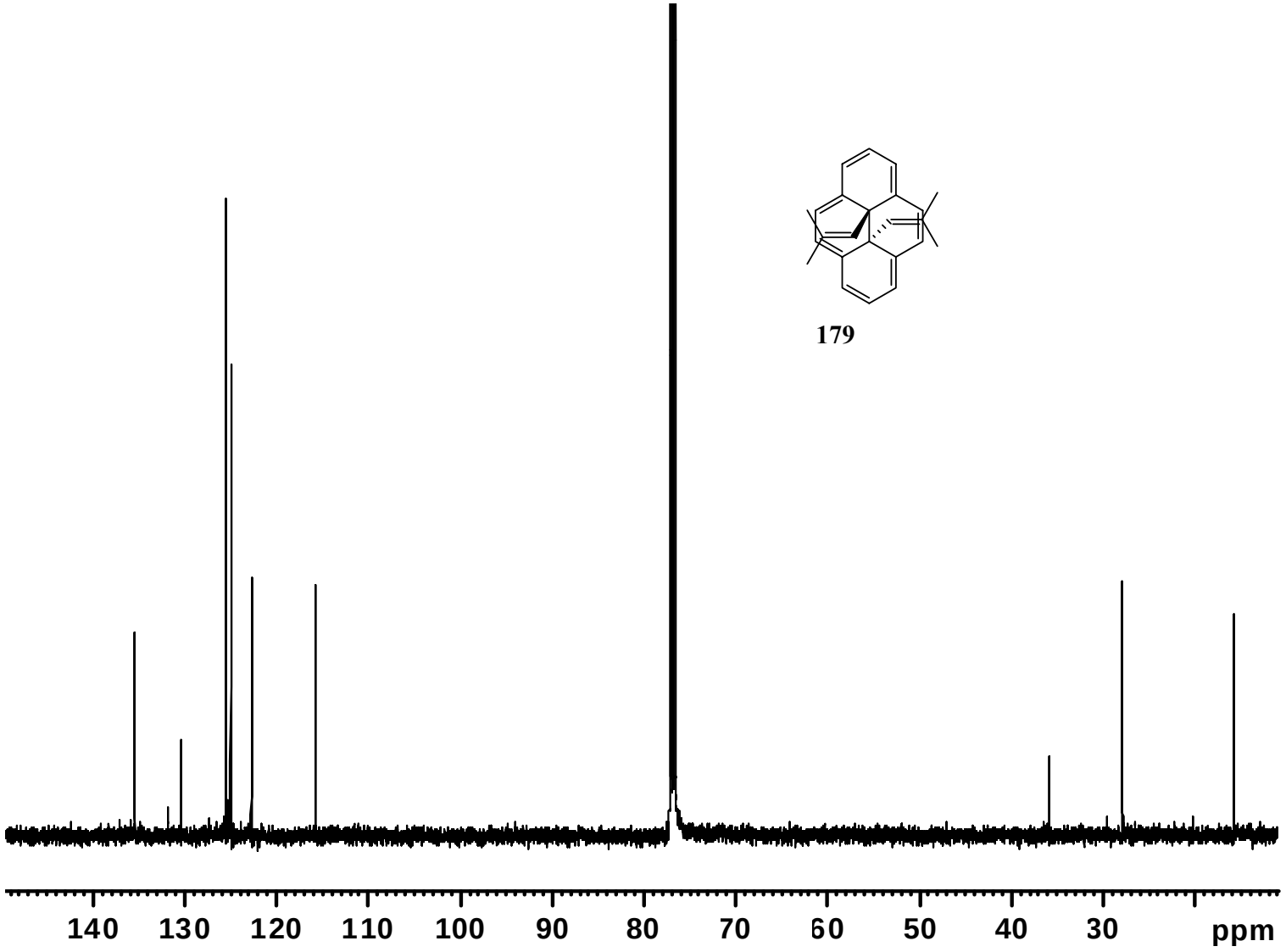

7.7
7.6
7.5
7.4
7.3
7.2
ppm
SMe2
Me2S
2BF4
177
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


178
5.71
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



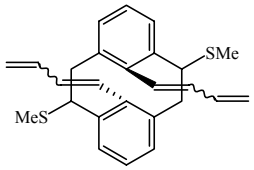

**178**


179
0.2
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

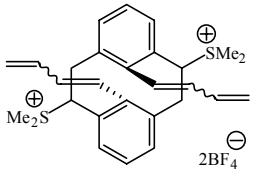




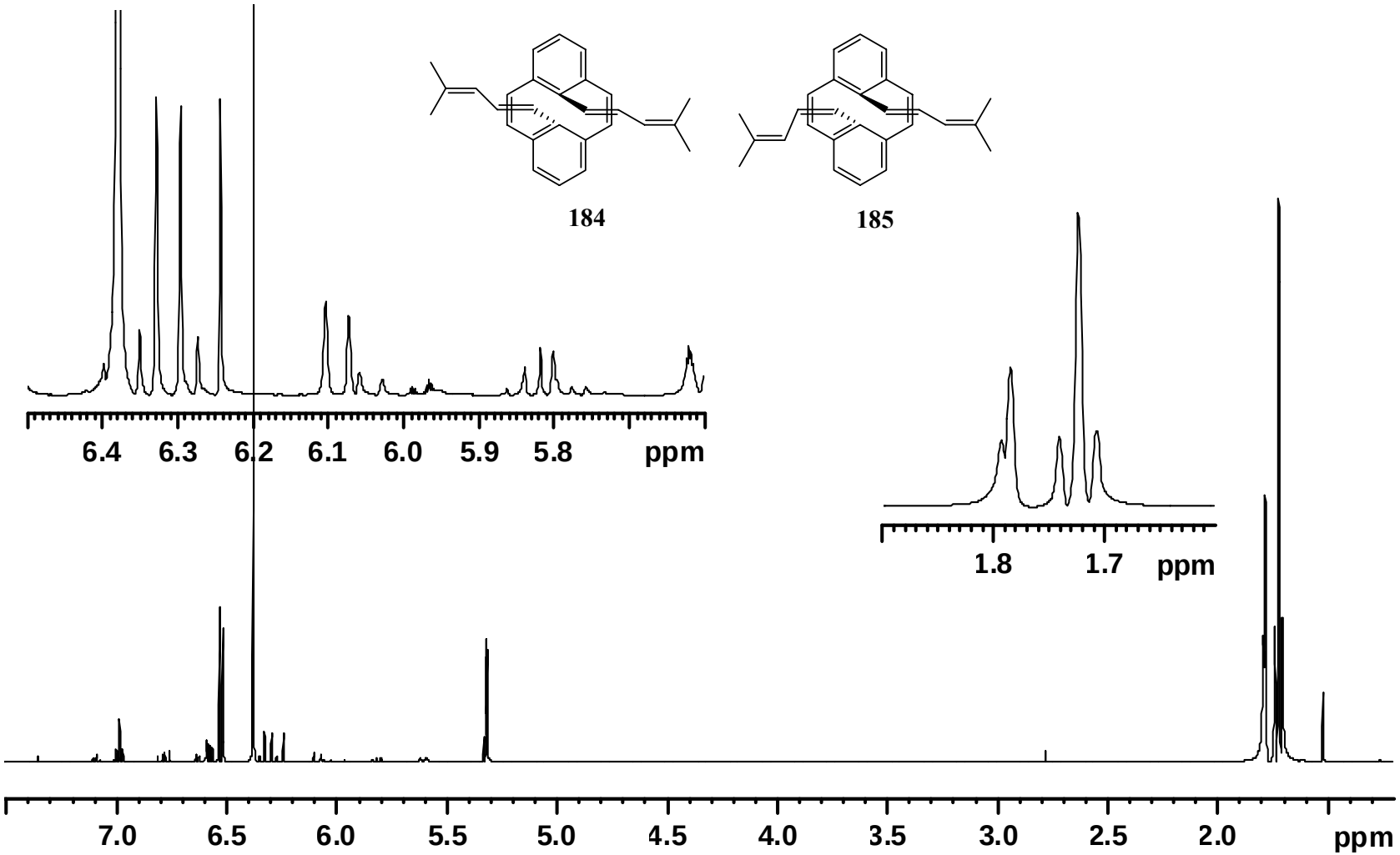

**179**

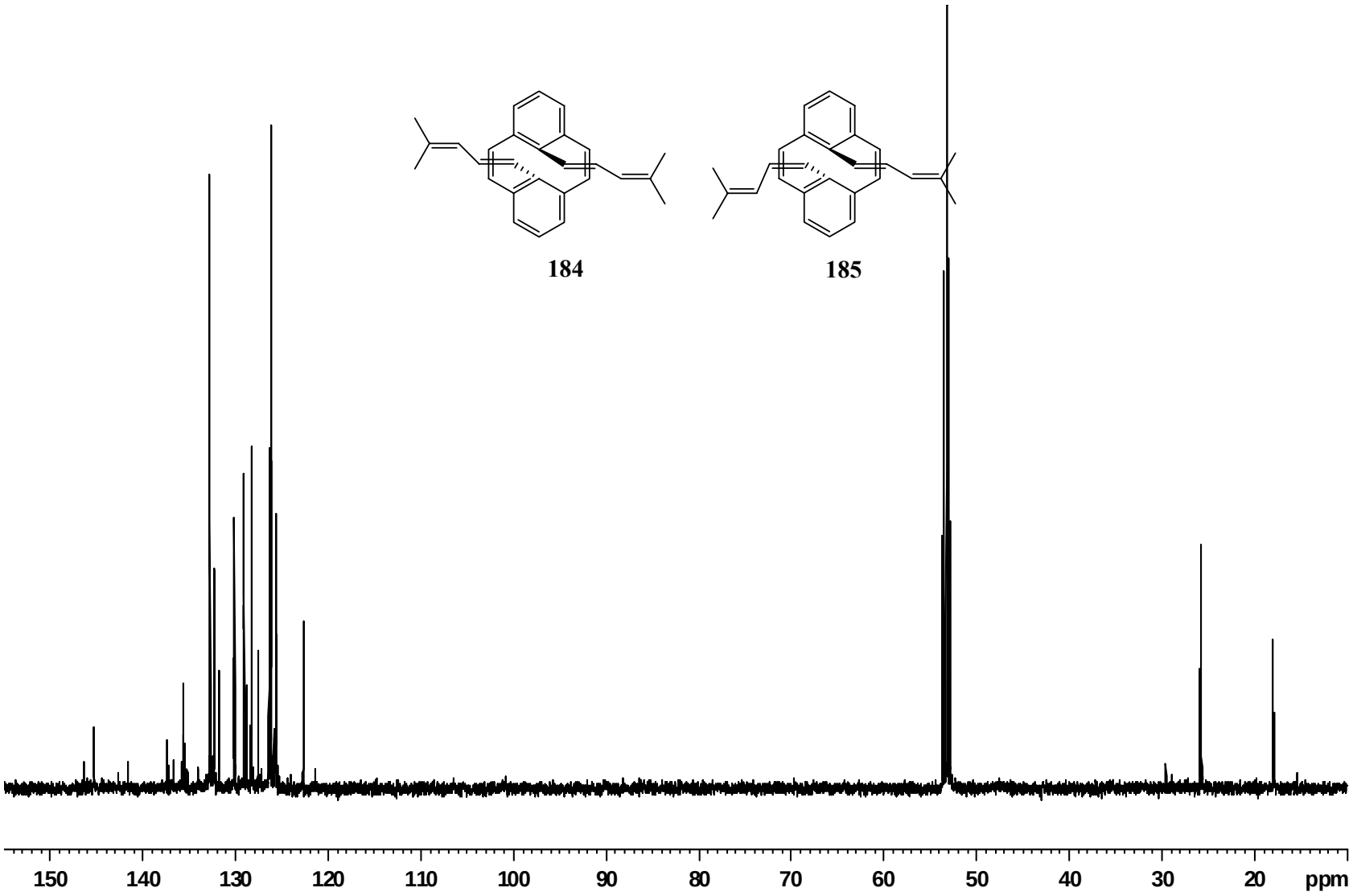


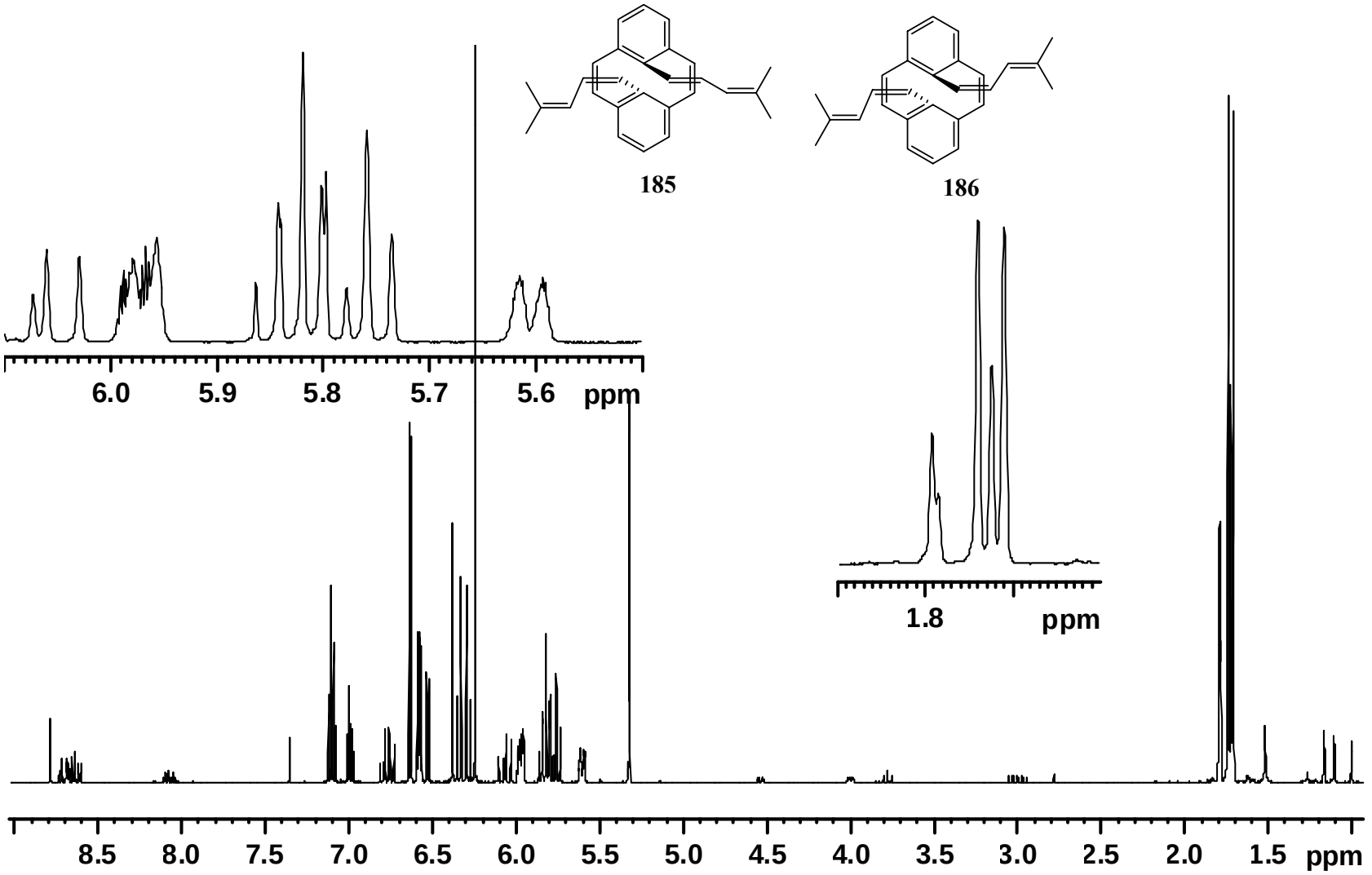

**180**

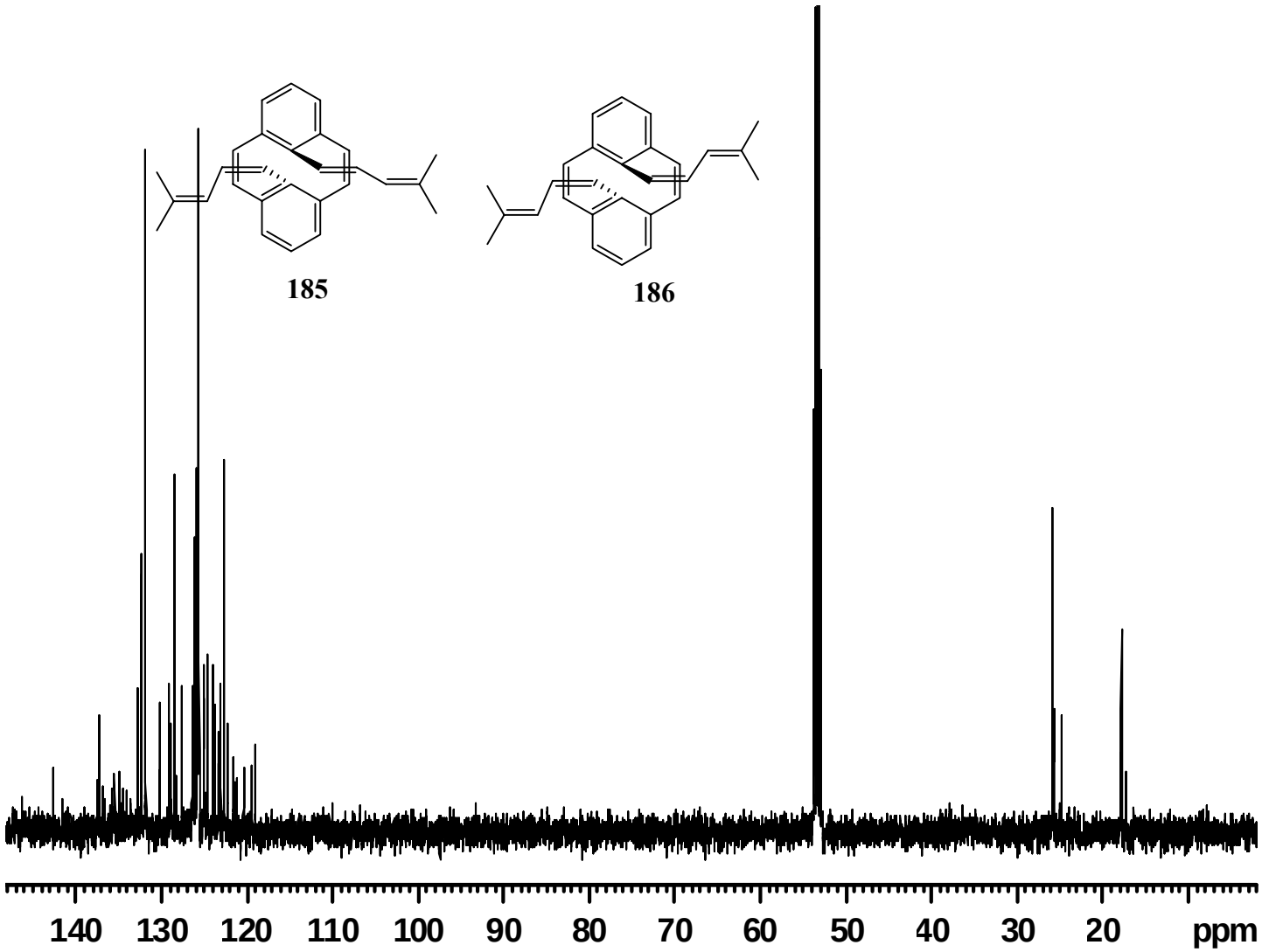


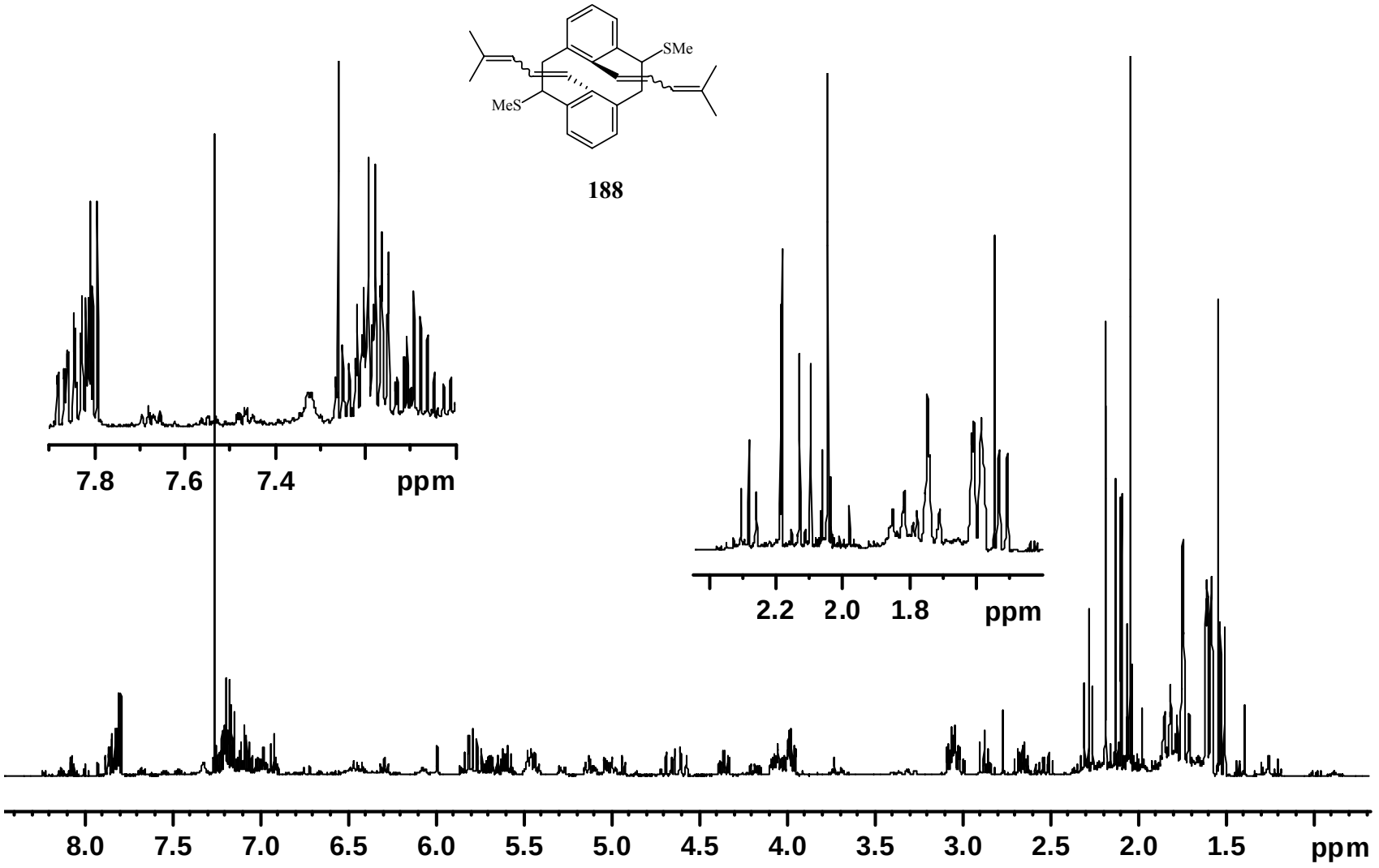

**182**

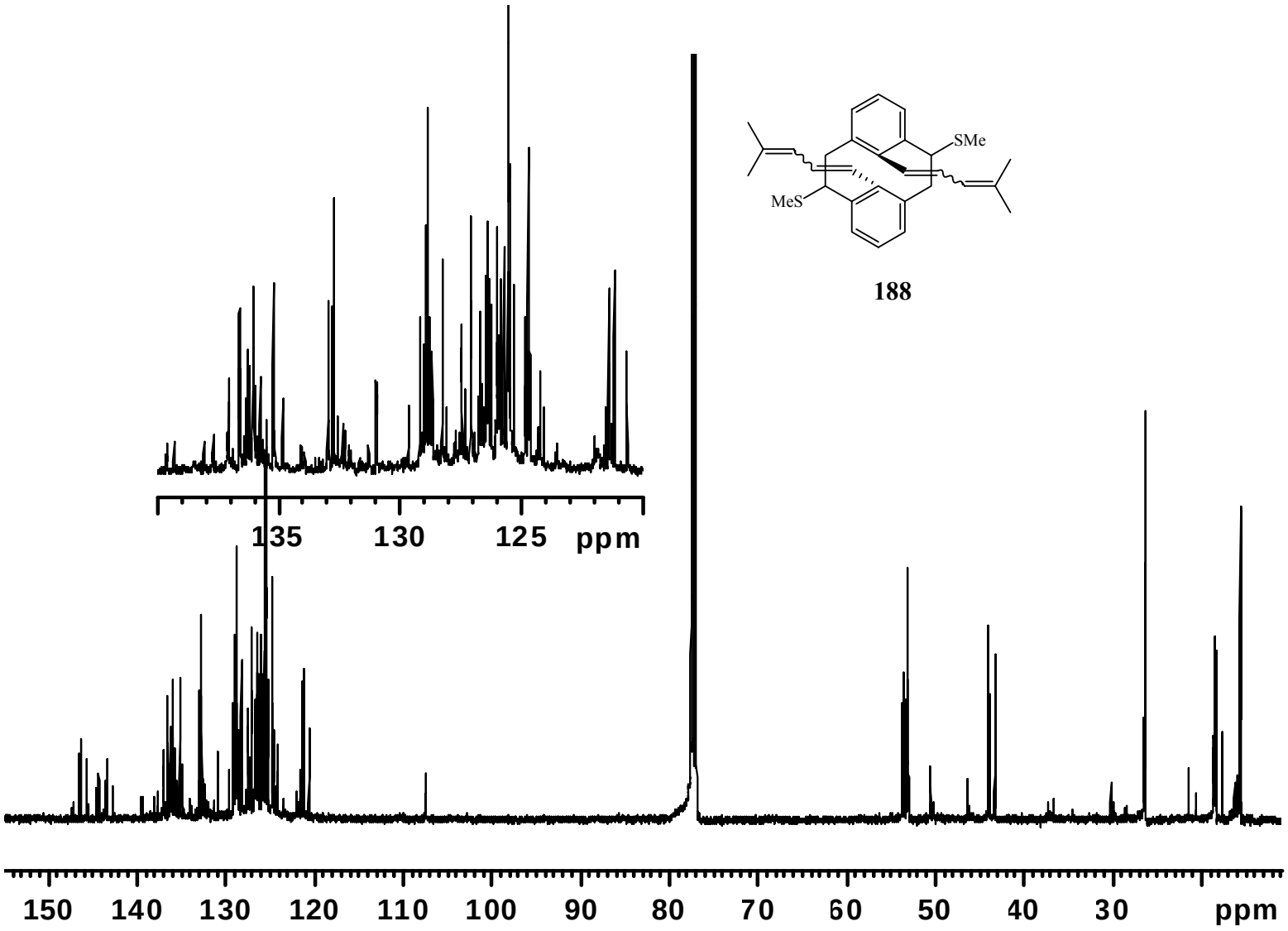

184
185
6.4
6.3
6.2
6.1
6.0
5.9
5.8
ppm
1.8
1.7
ppm
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

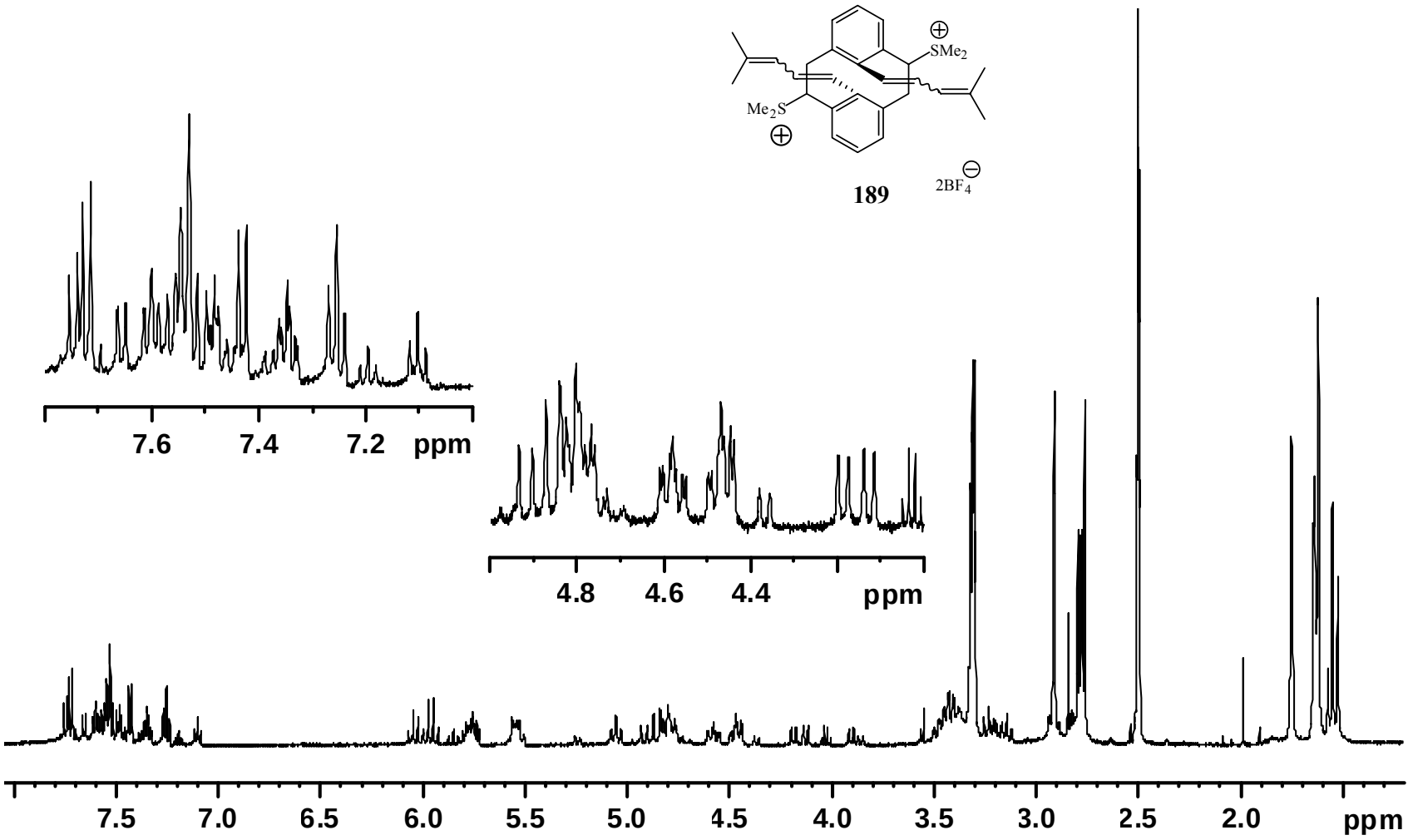

184
185
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

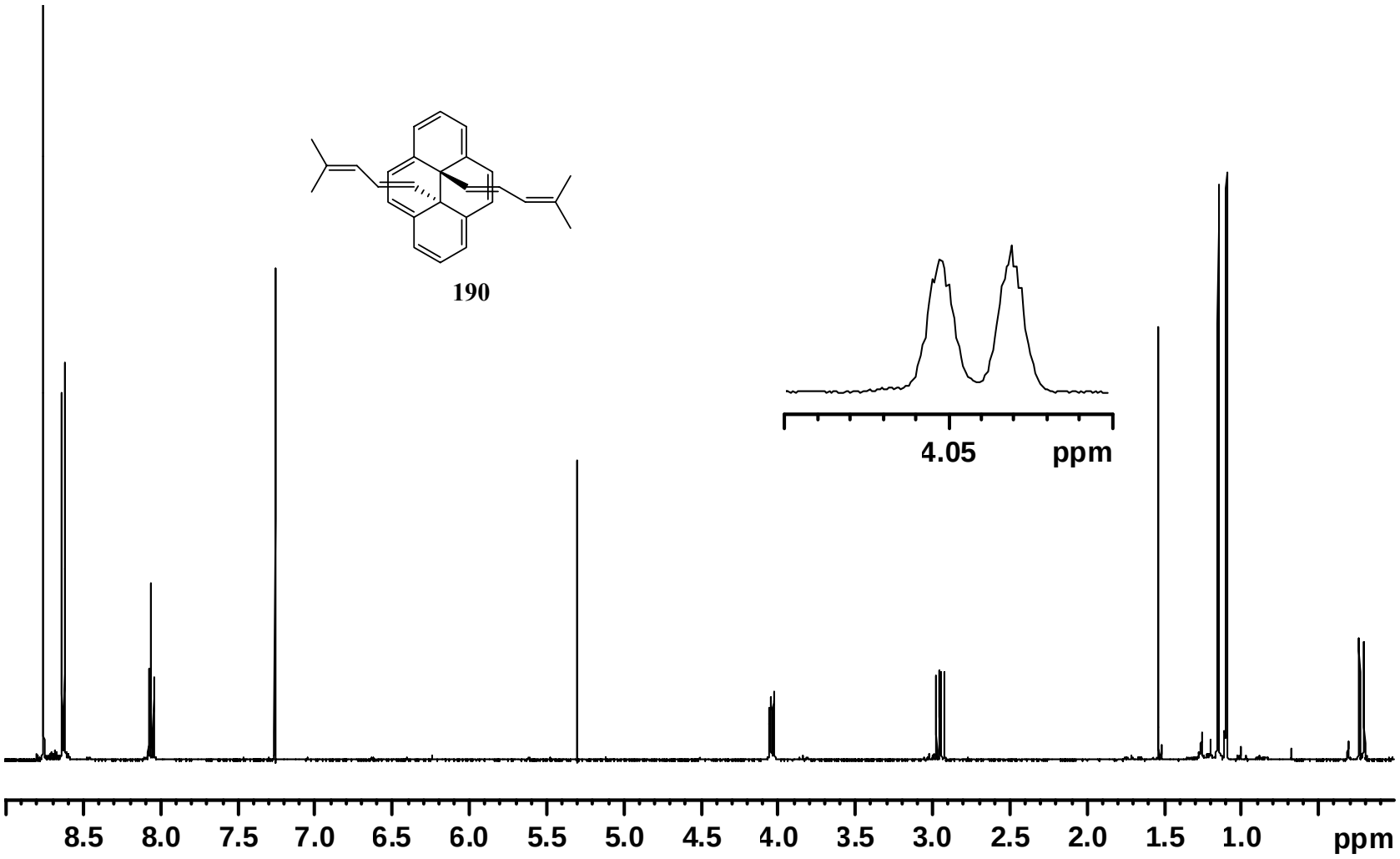

185
186
6.0
5.9
5.8
5.7
5.6
ppm
1.8
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

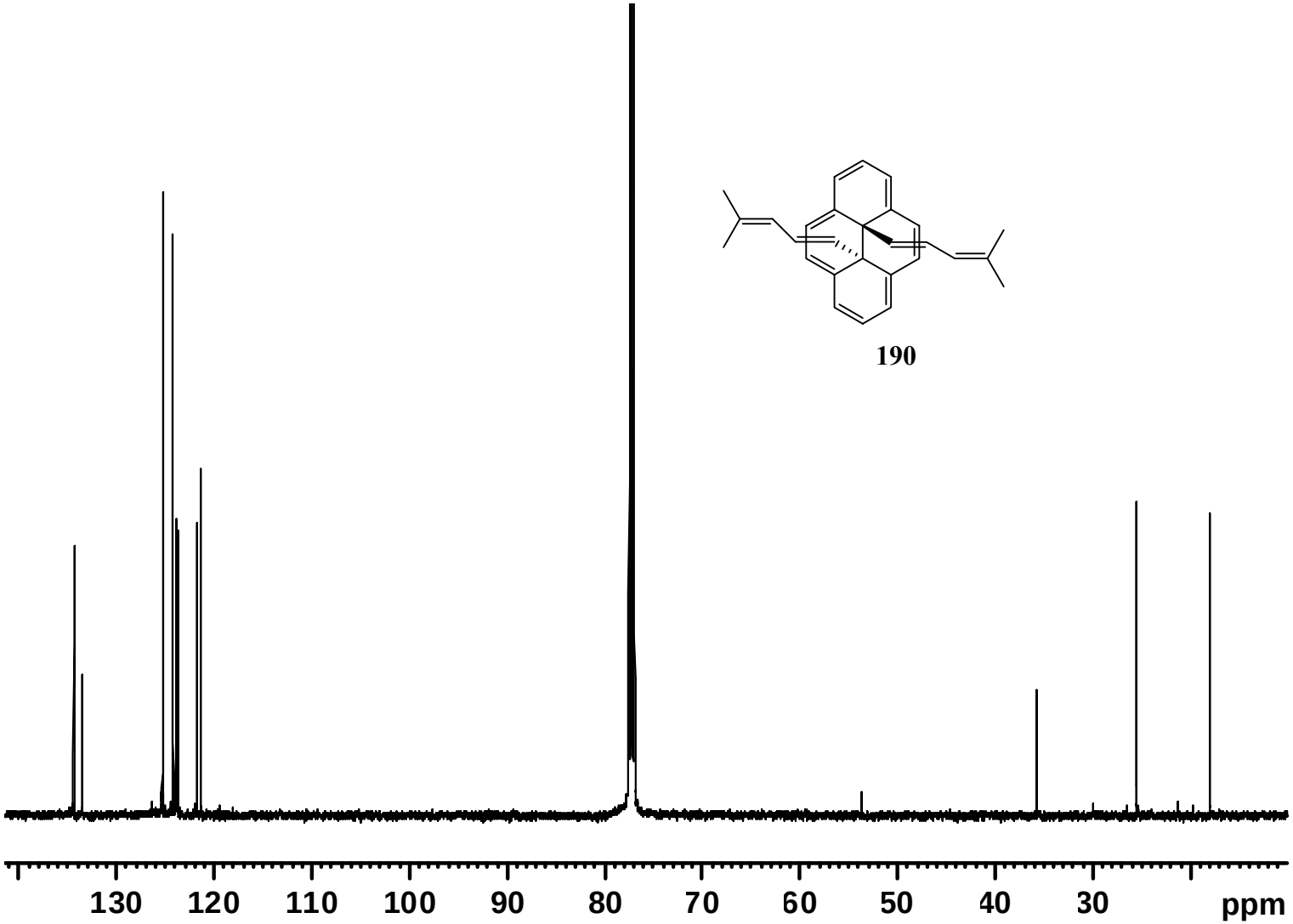

185
186
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


SMe
MeS
188
7.8
7.6
7.4
ppm
2.2
2.0
1.8
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

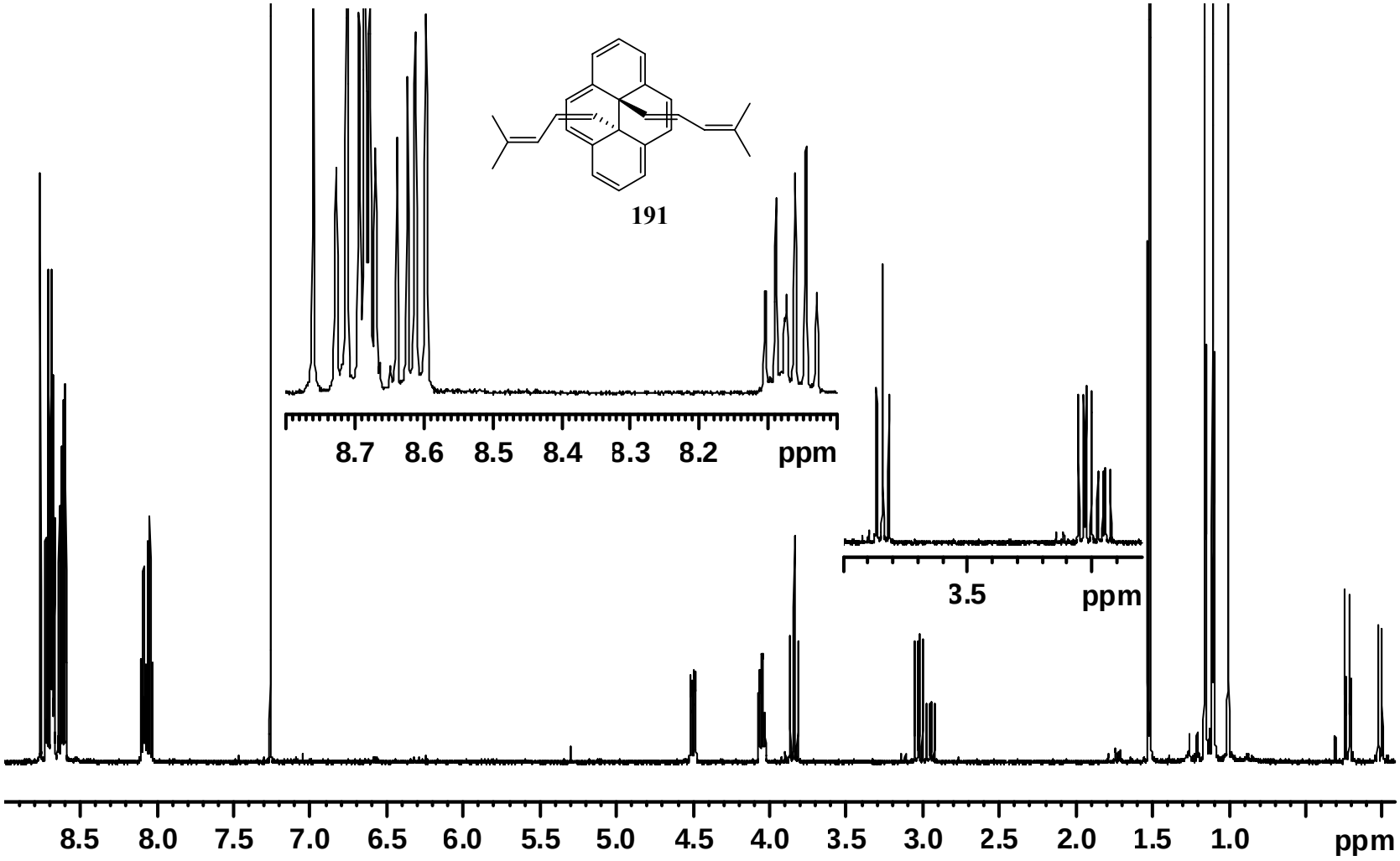

SMe
MeS
188
135
130
125
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

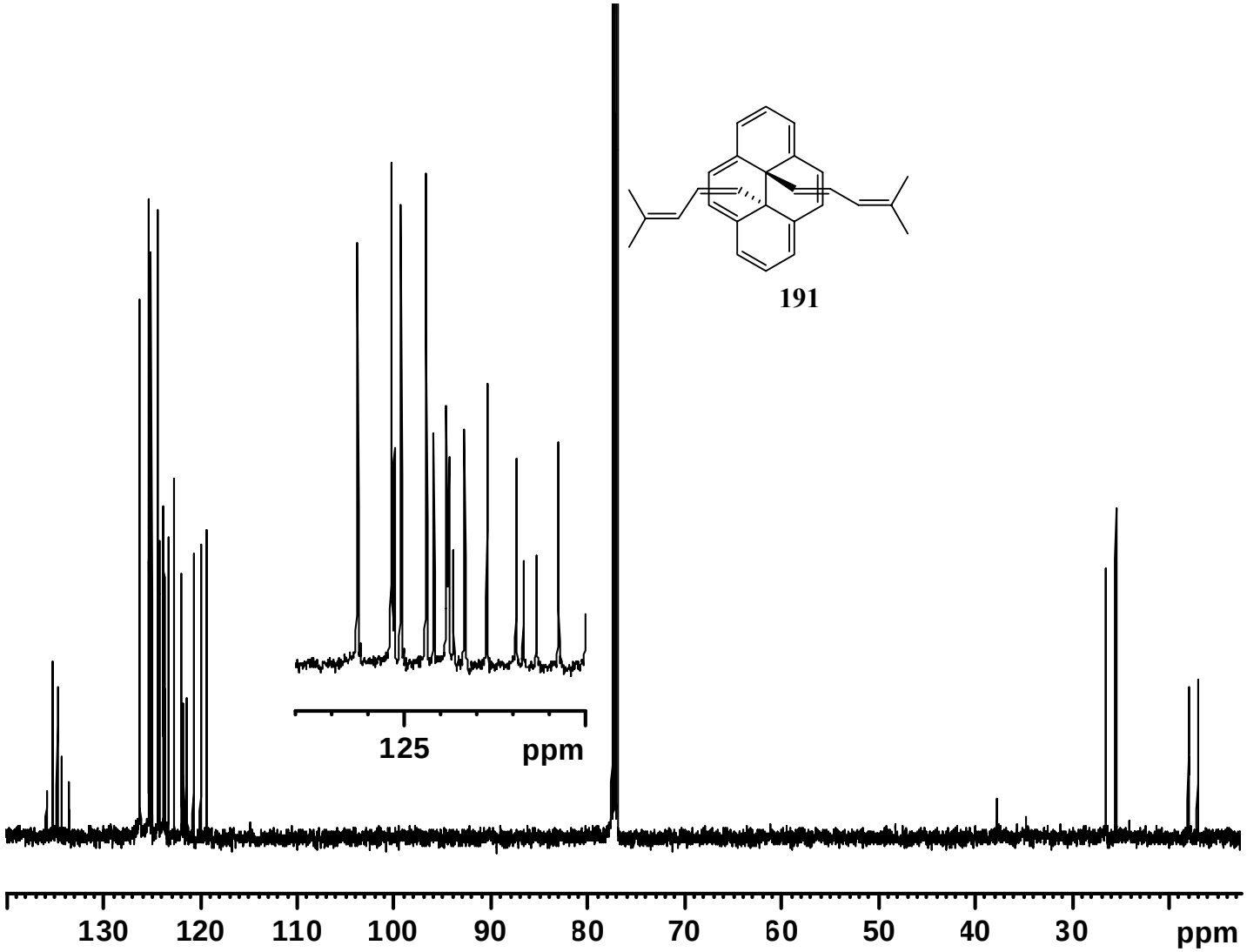

SMe2
Me2S
189
2BF4
7.6
7.4
7.2
ppm
4.8
4.6
4.4
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm


190
4.05
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

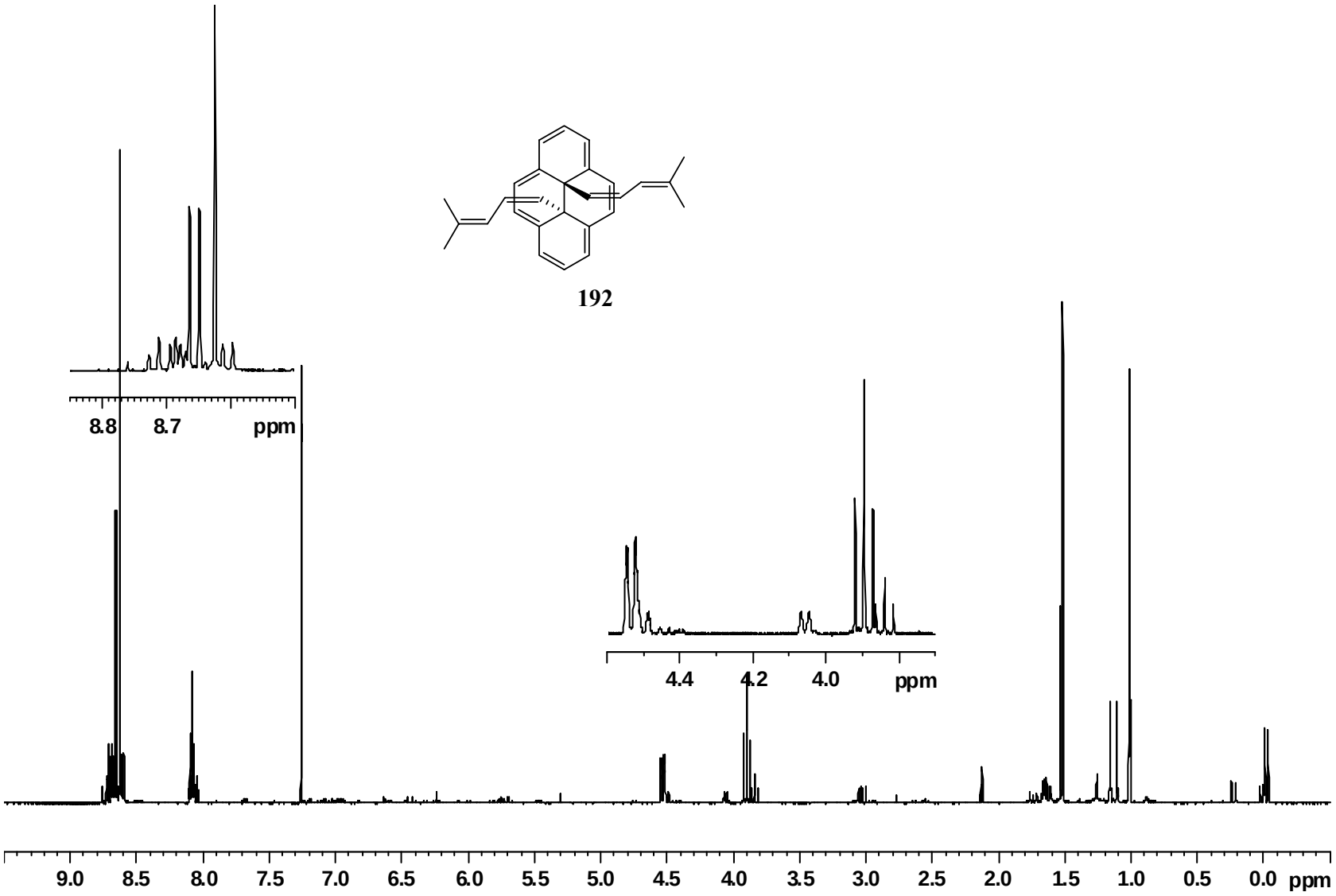



**190**

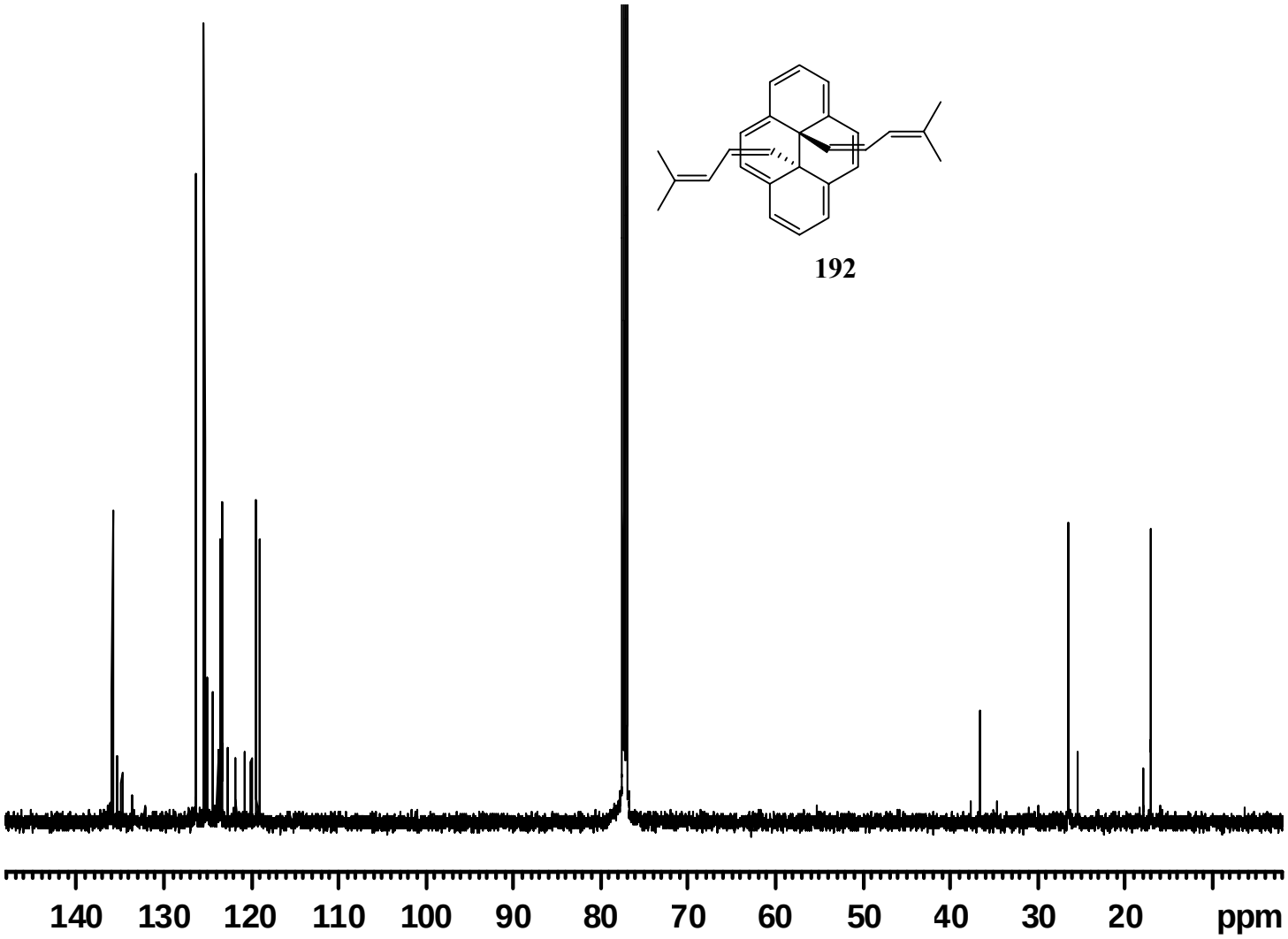

191
8.7
8.6
8.5
8.4
8.3
8.2
ppm
3.5
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm



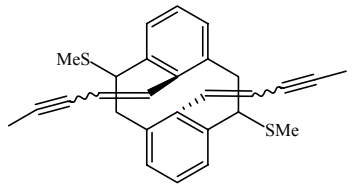

191


8.8
8.7
ppm
4.4
4.2
4.0
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

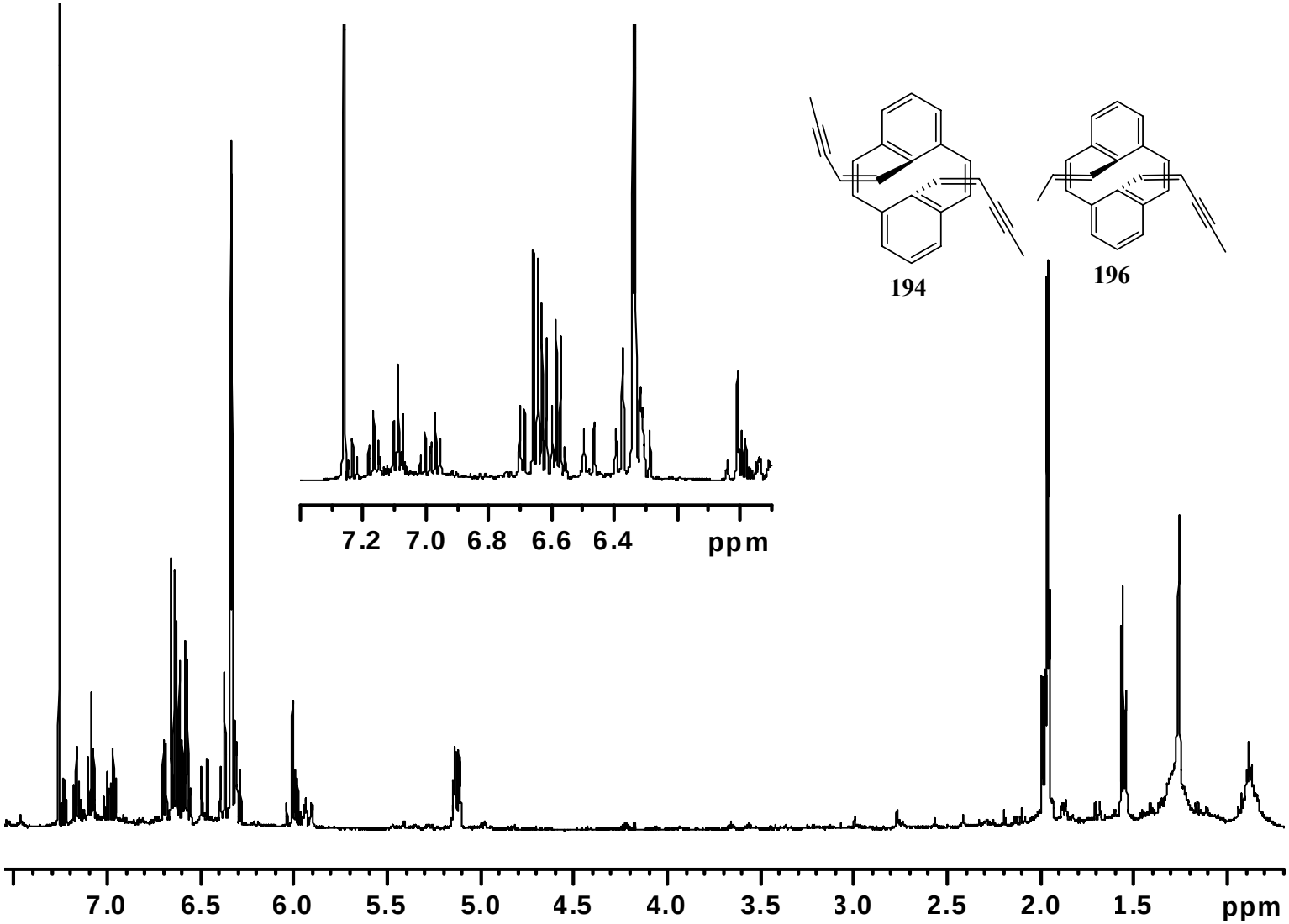
**192**

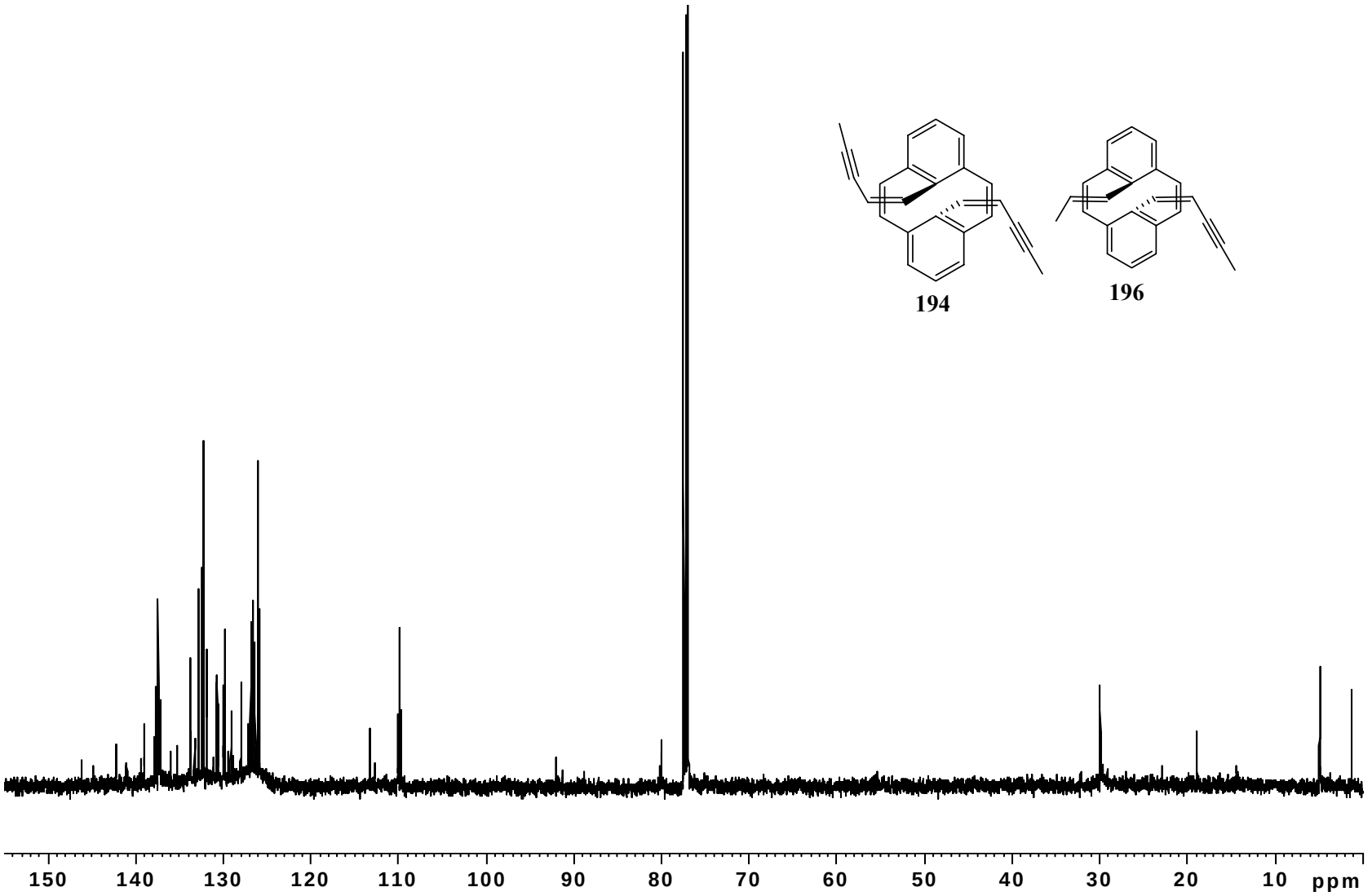


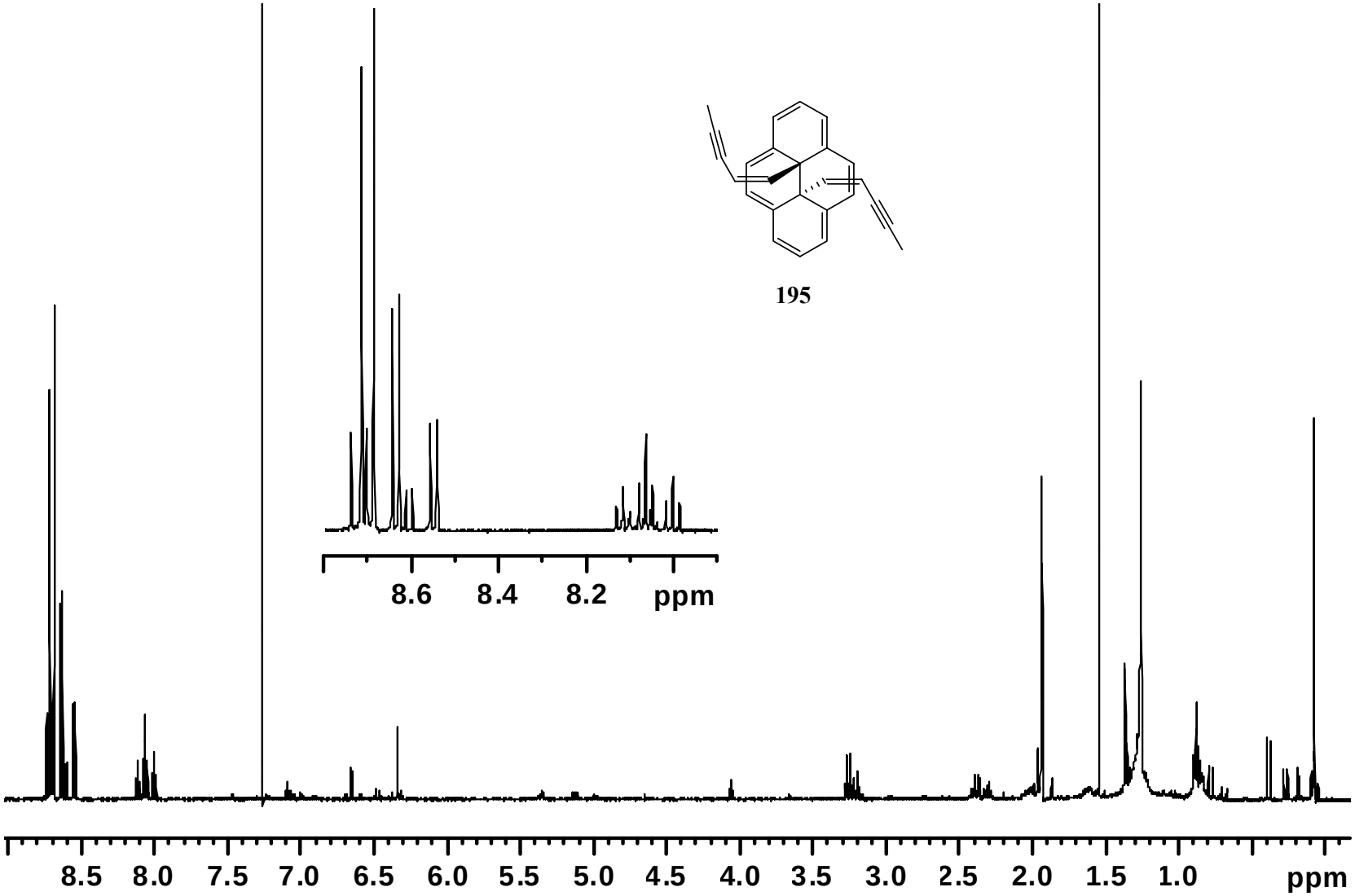

**192**



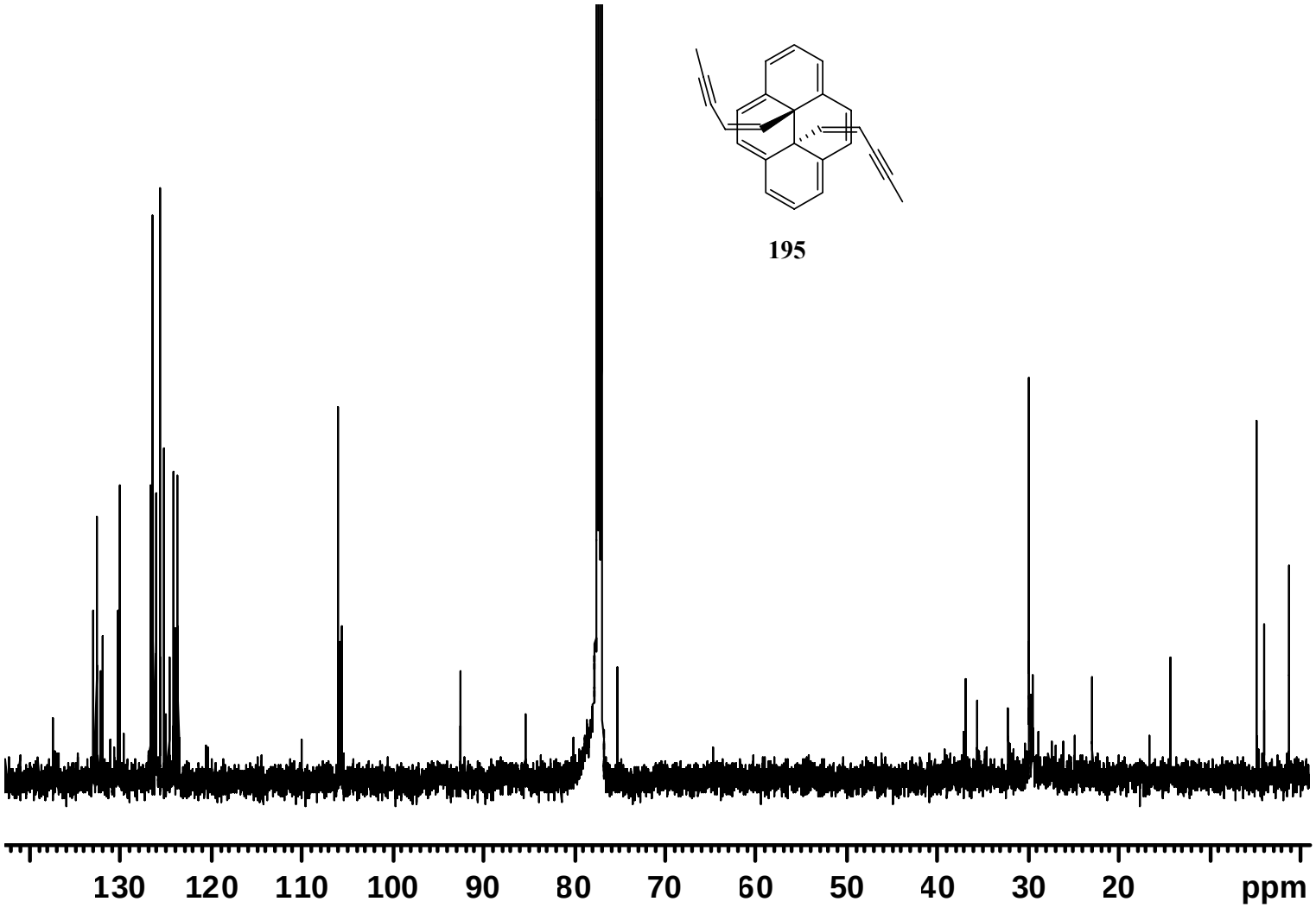

**193**


194
196
7.2 7.0 6.8 6.6 6.4 ppm
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

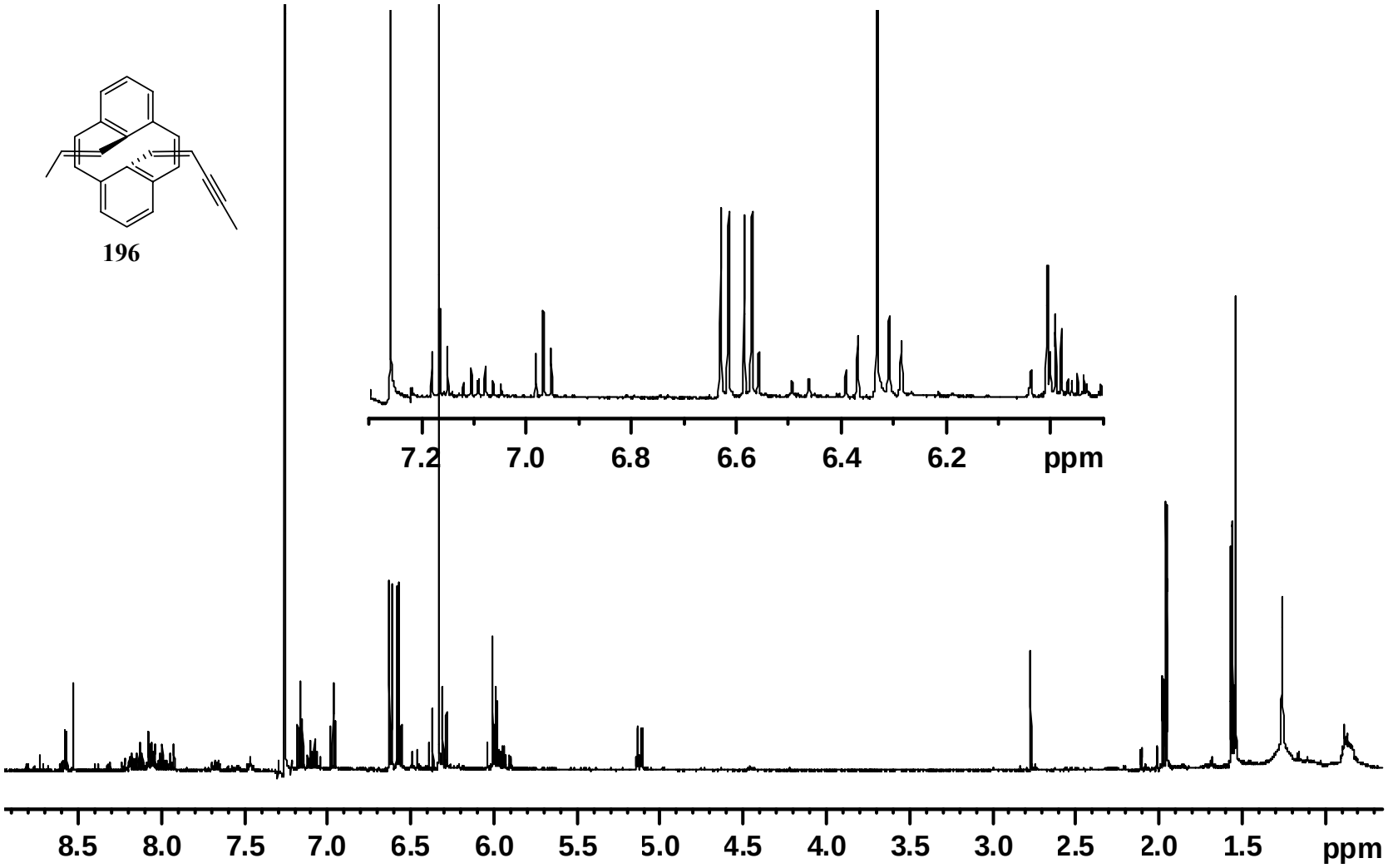

194
196
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

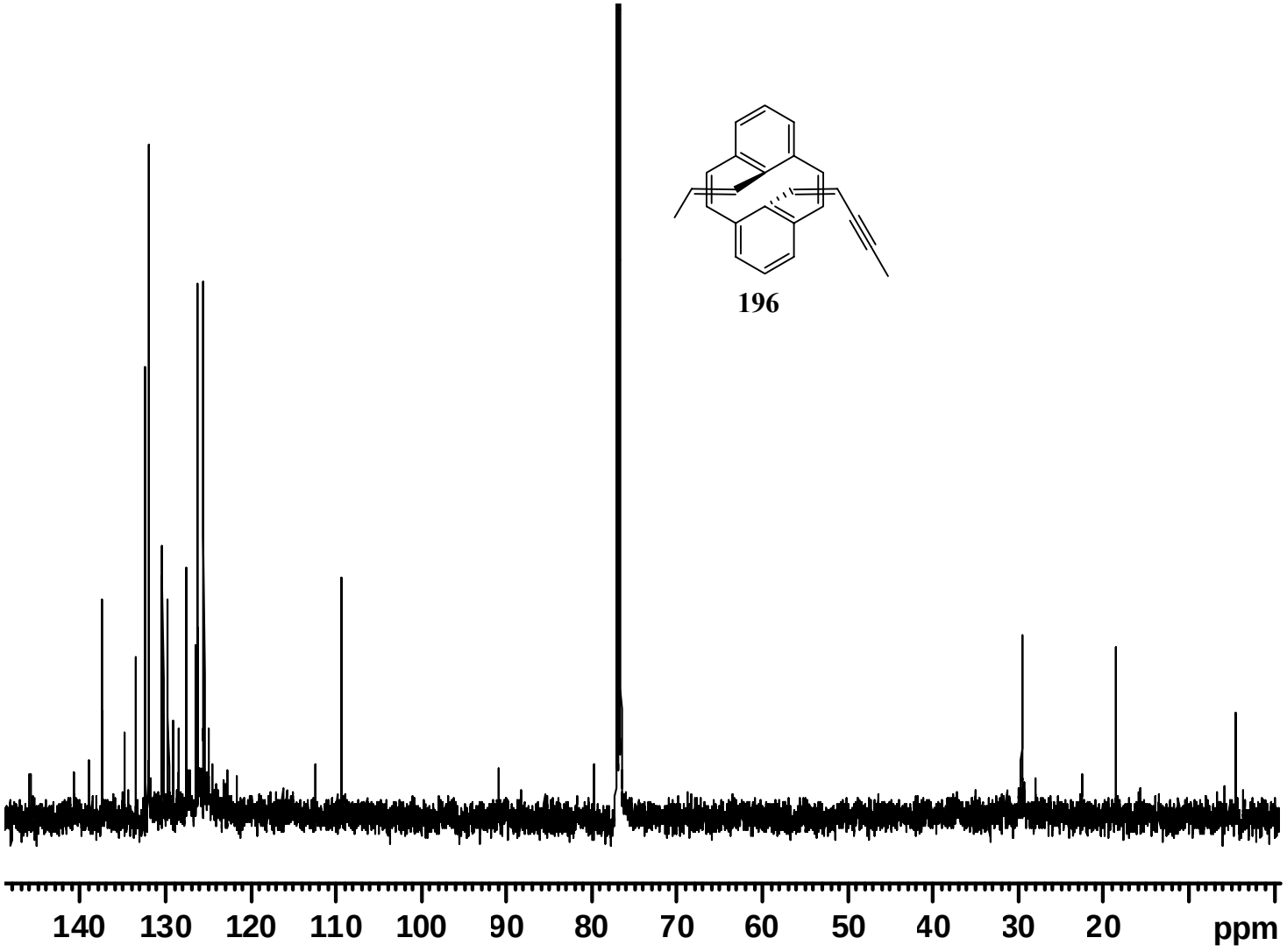



**195**

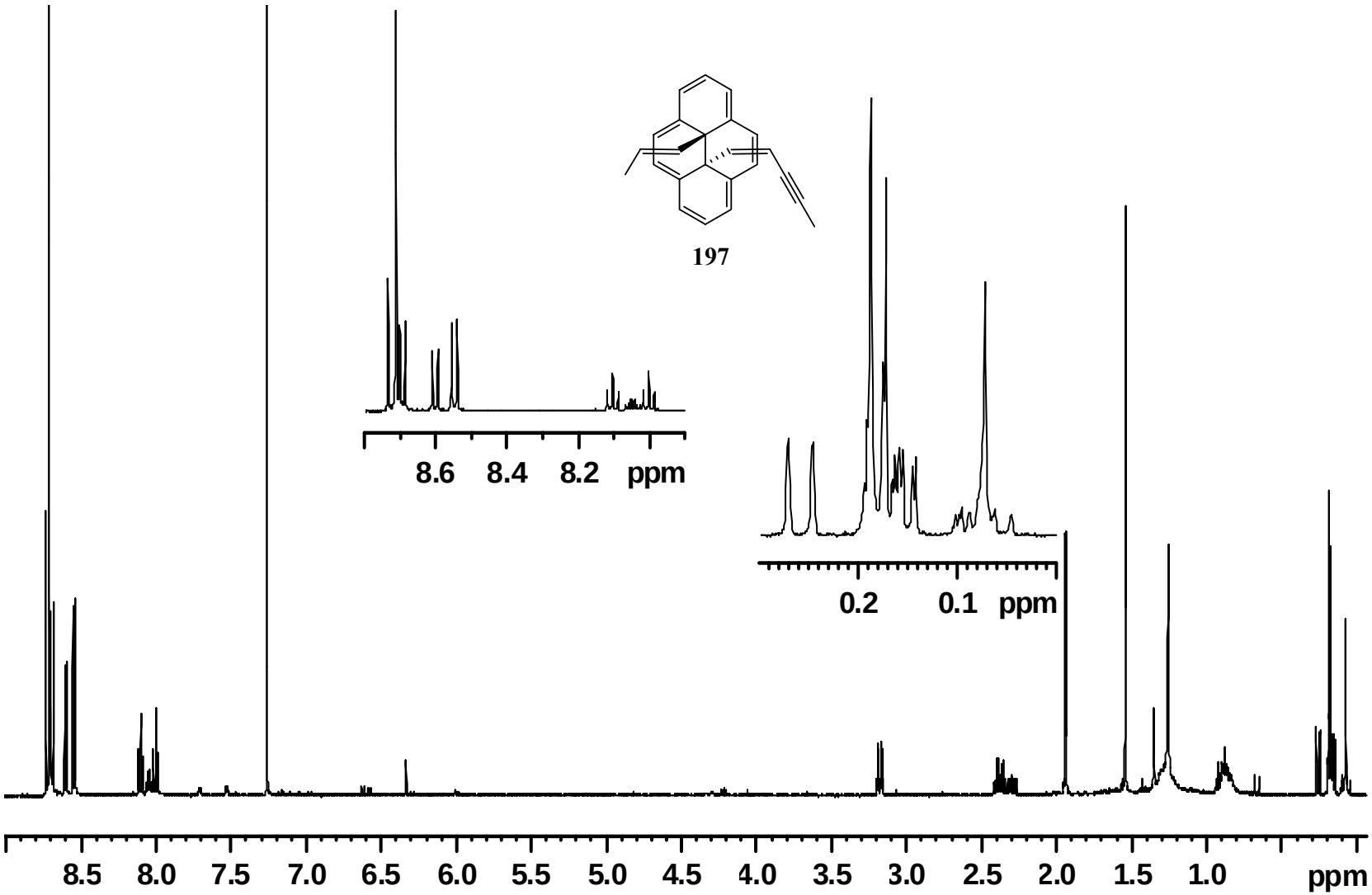


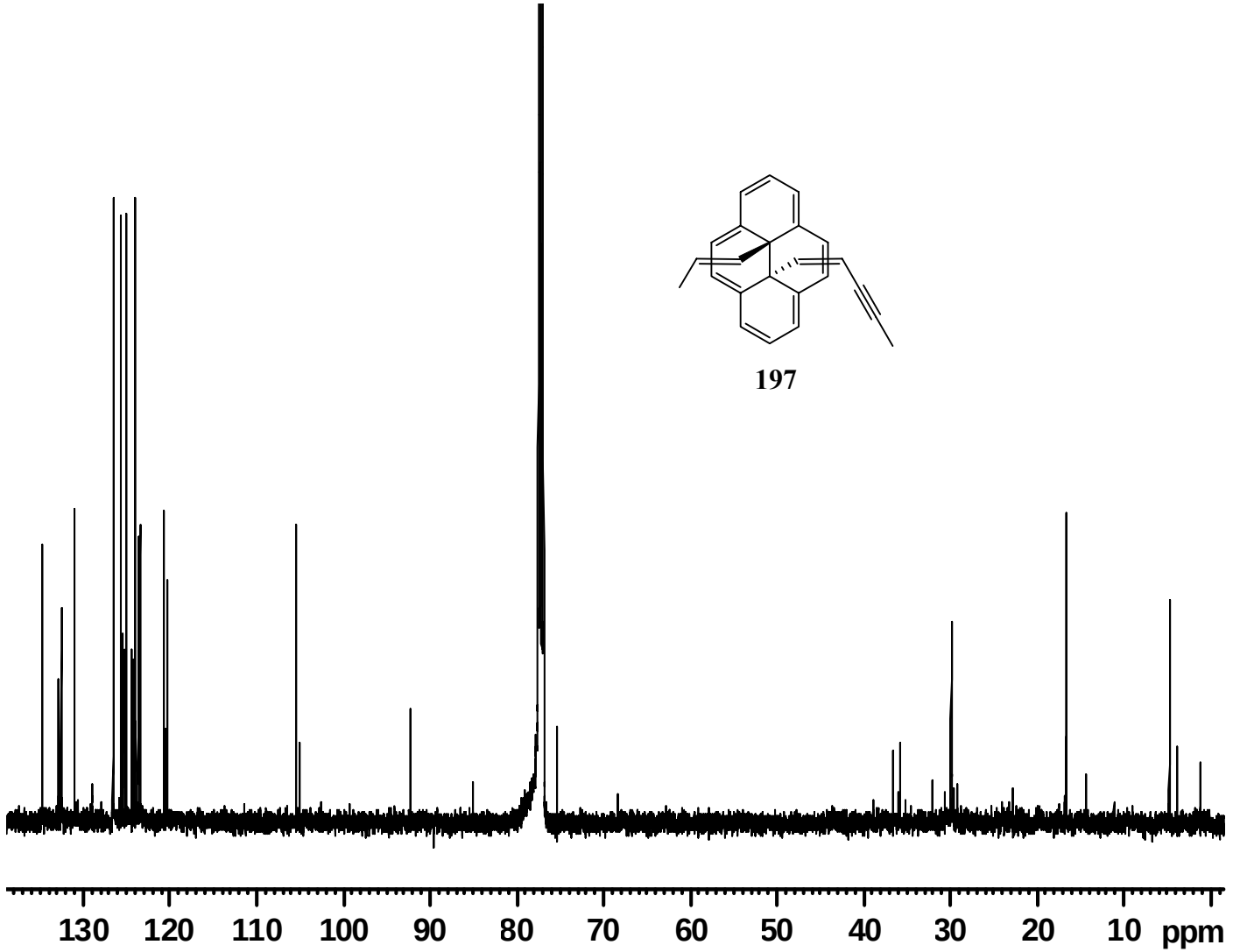

**195**


196
7.2
7.0
6.8
6.6
6.4
6.2
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

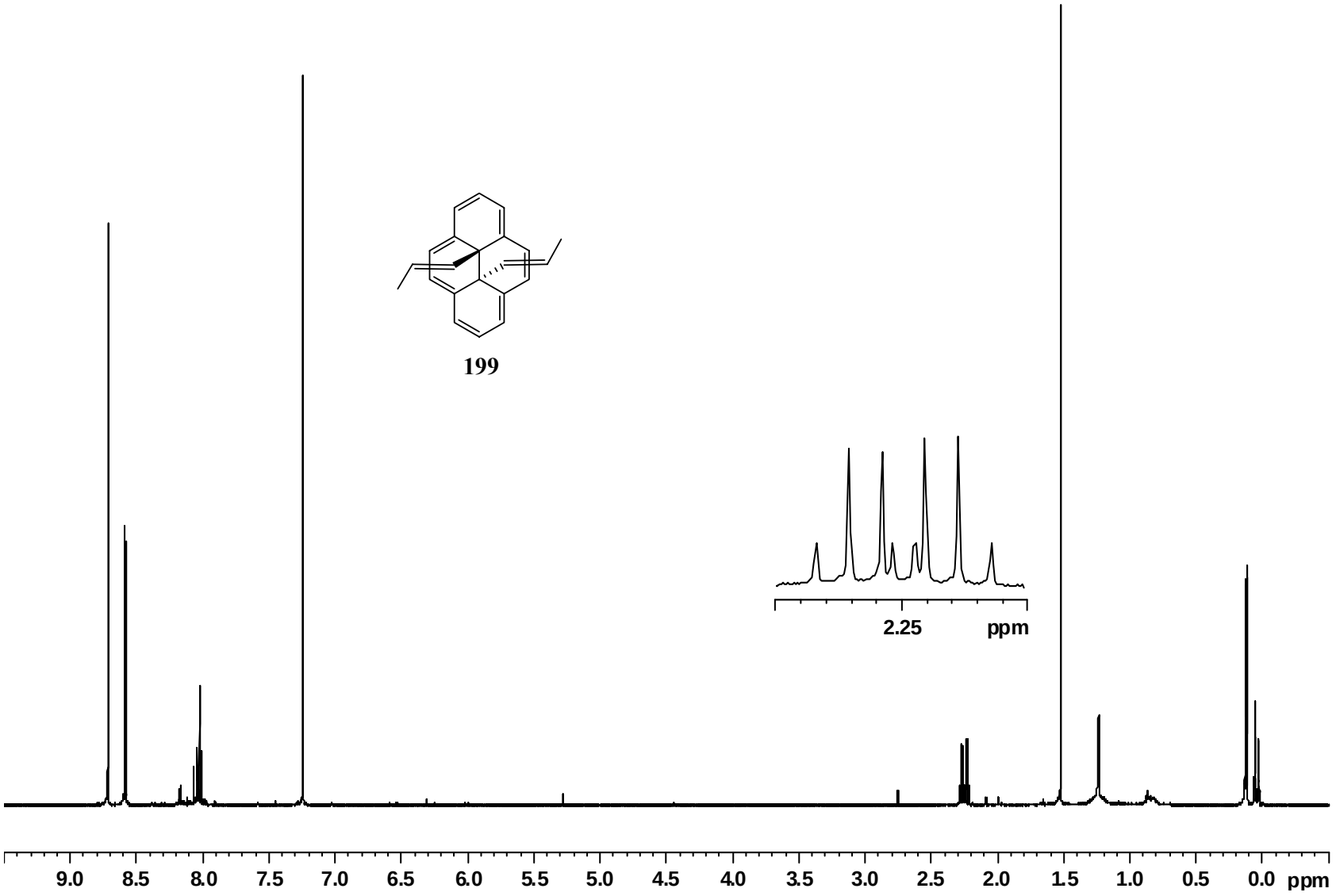


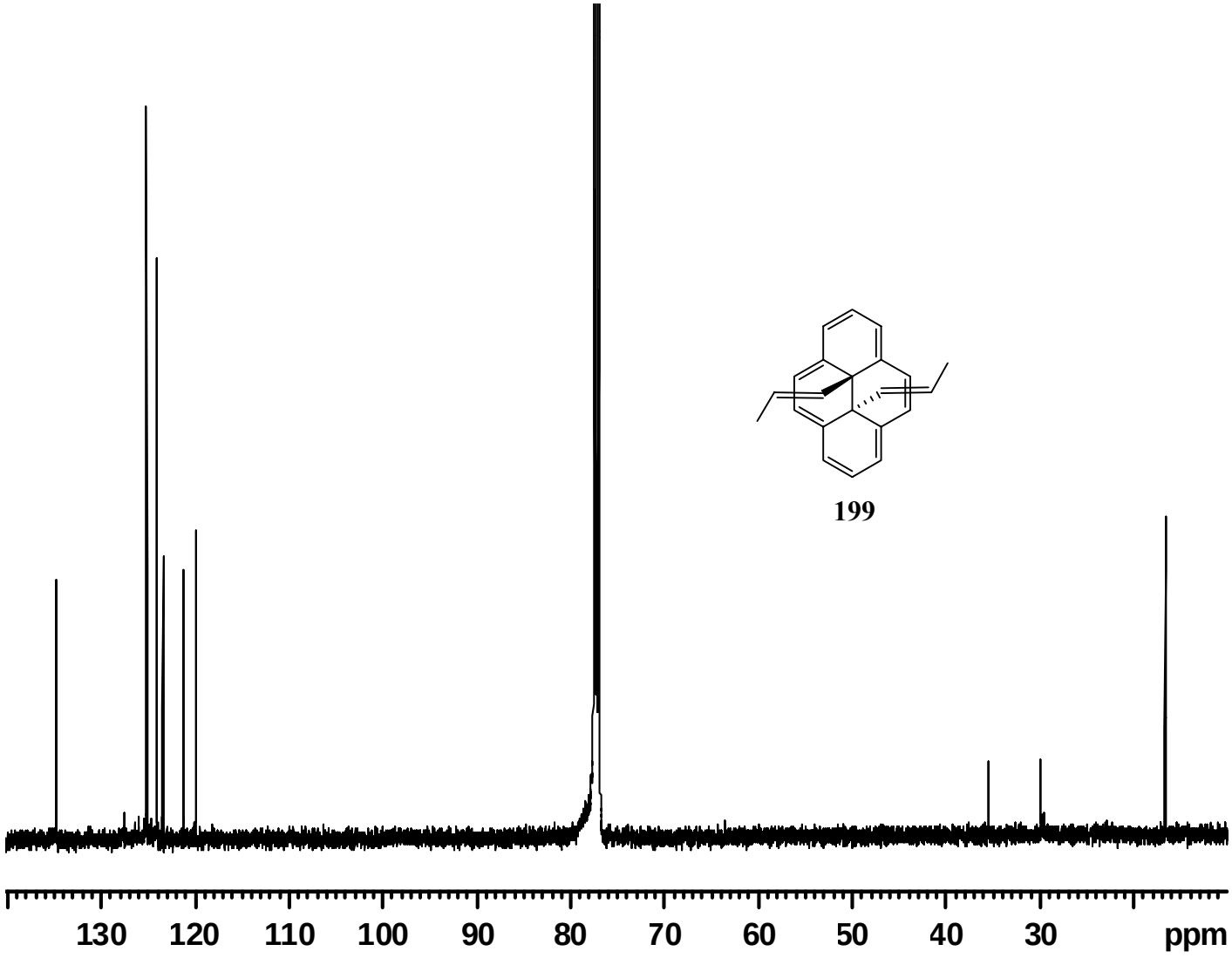

196


197
8.6
8.4
8.2
ppm
0.2
0.1
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm



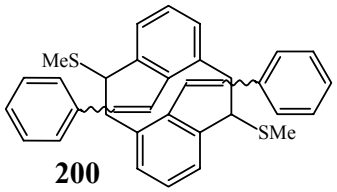

**197**


199
2.25
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

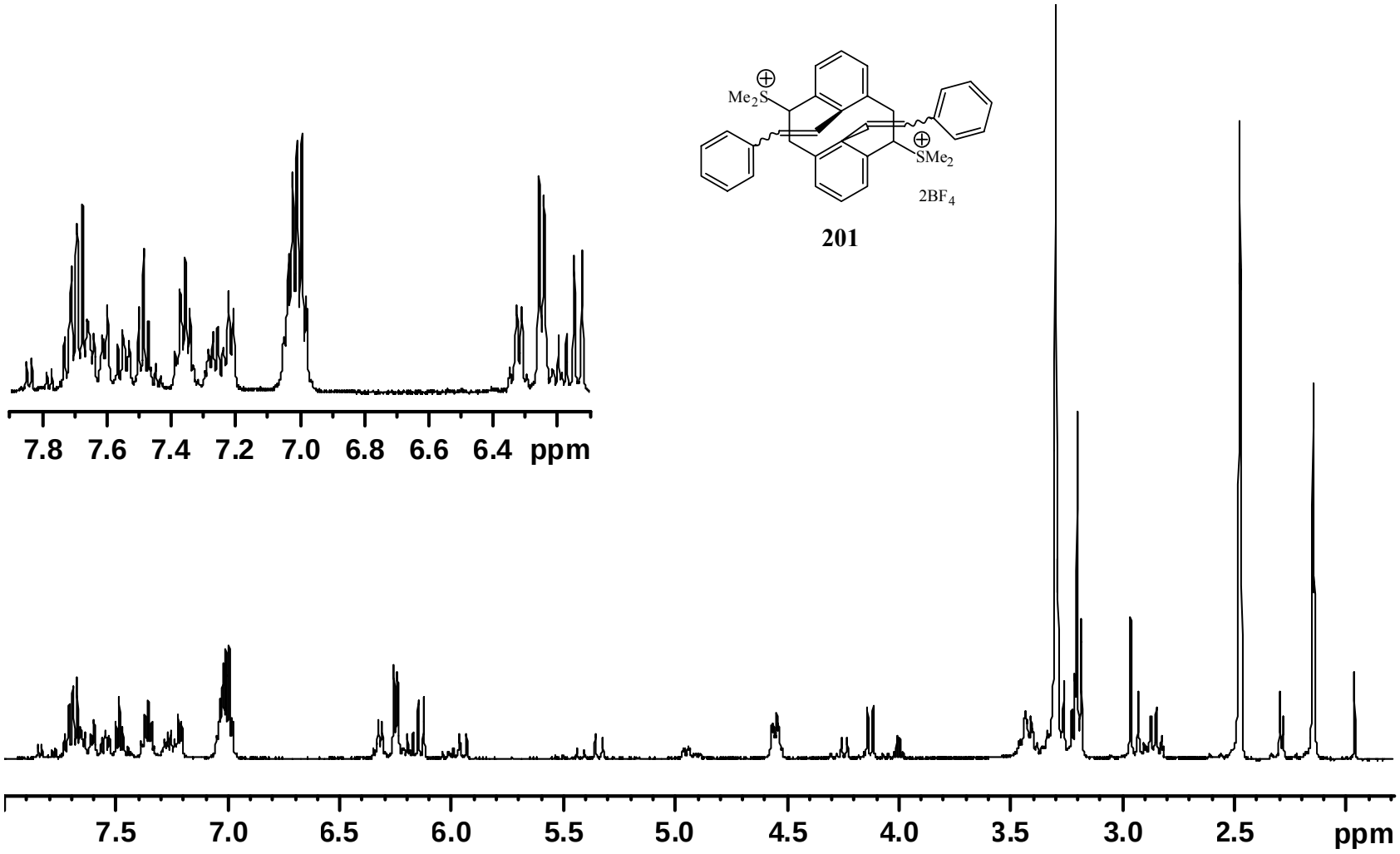




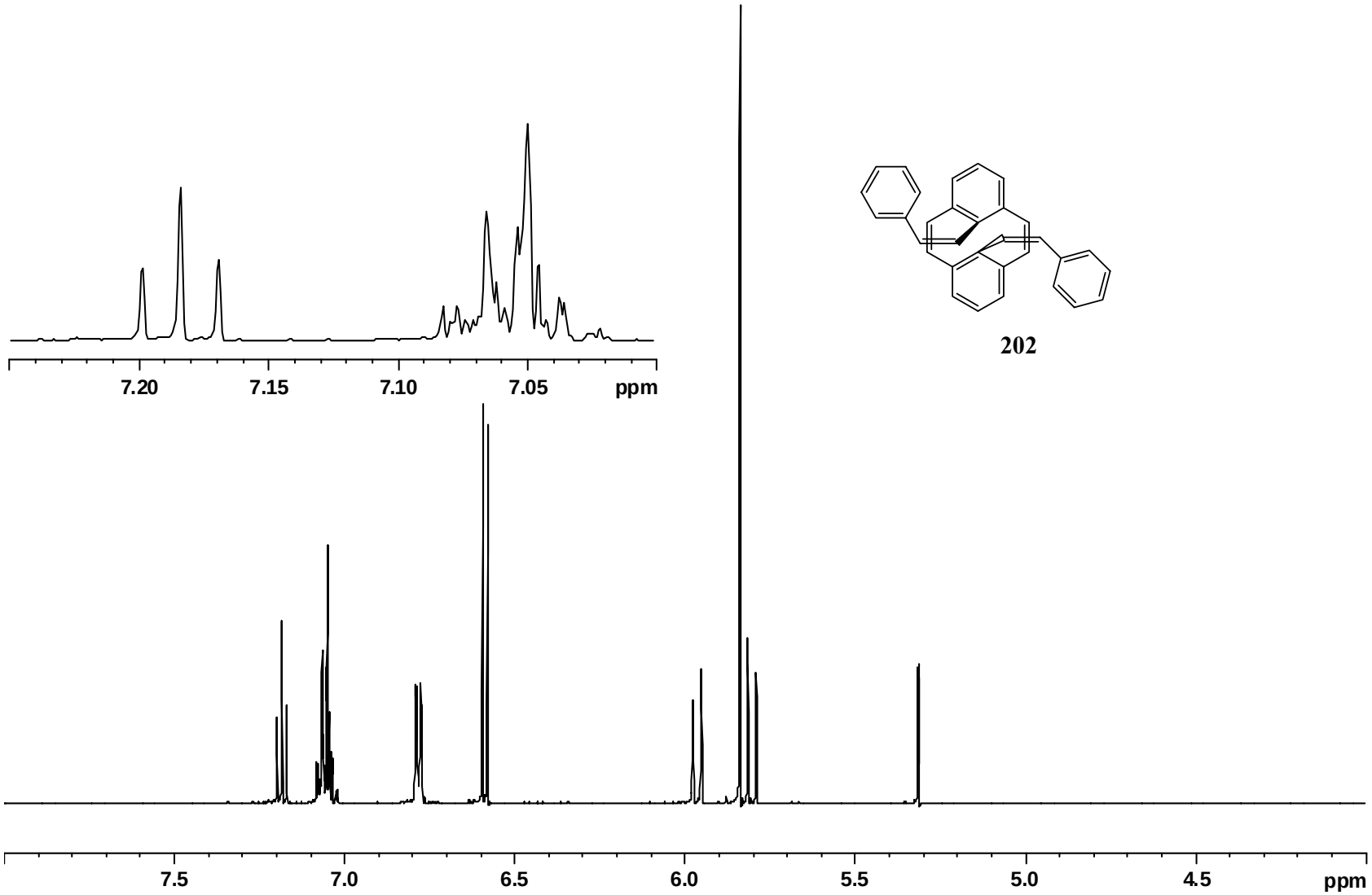

**199**



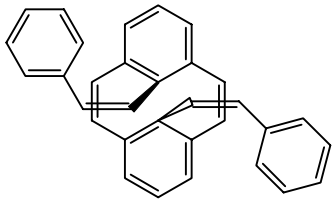

**200**


Me2S
SMe2
2BF4
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm

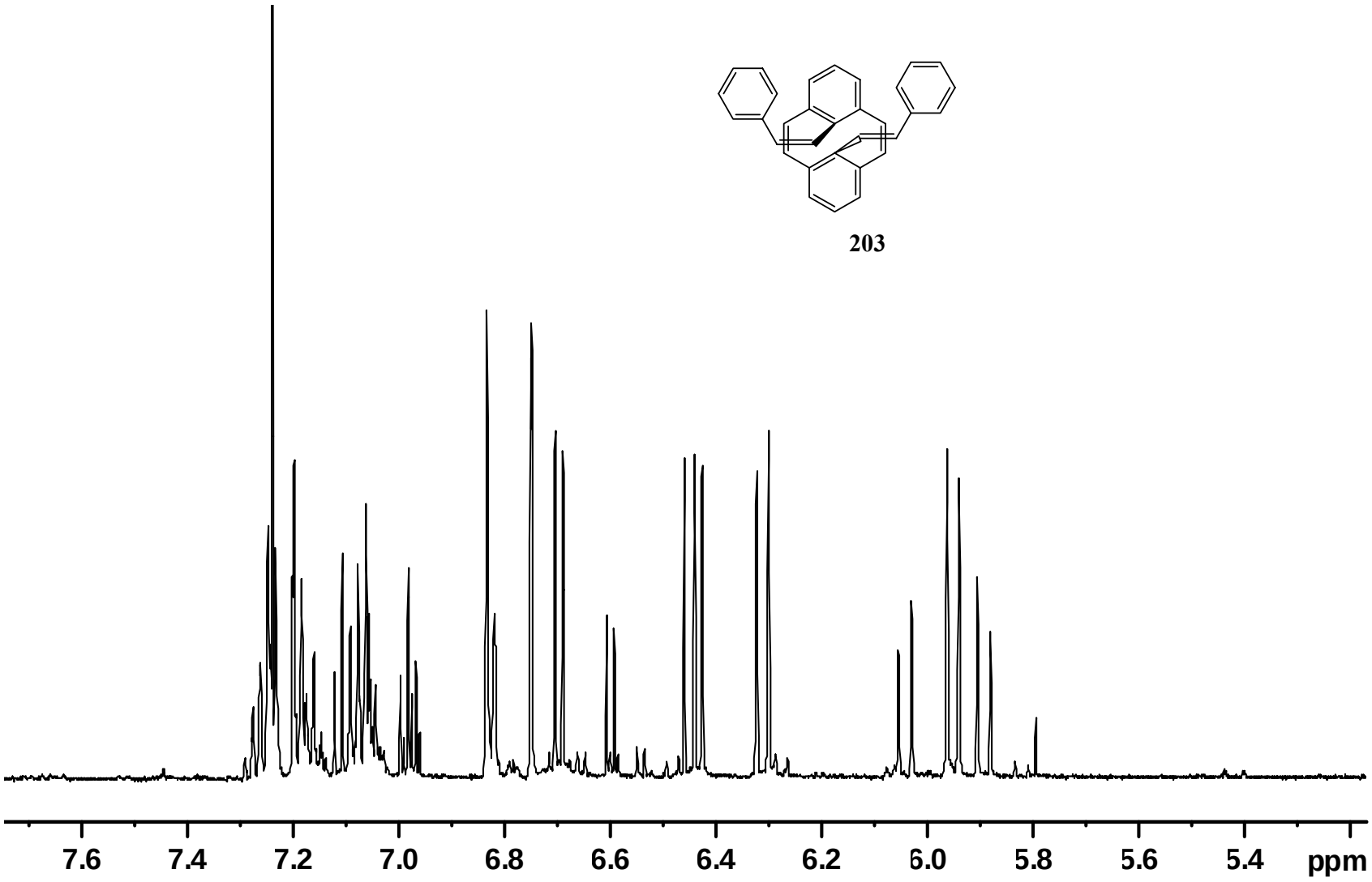
**201**



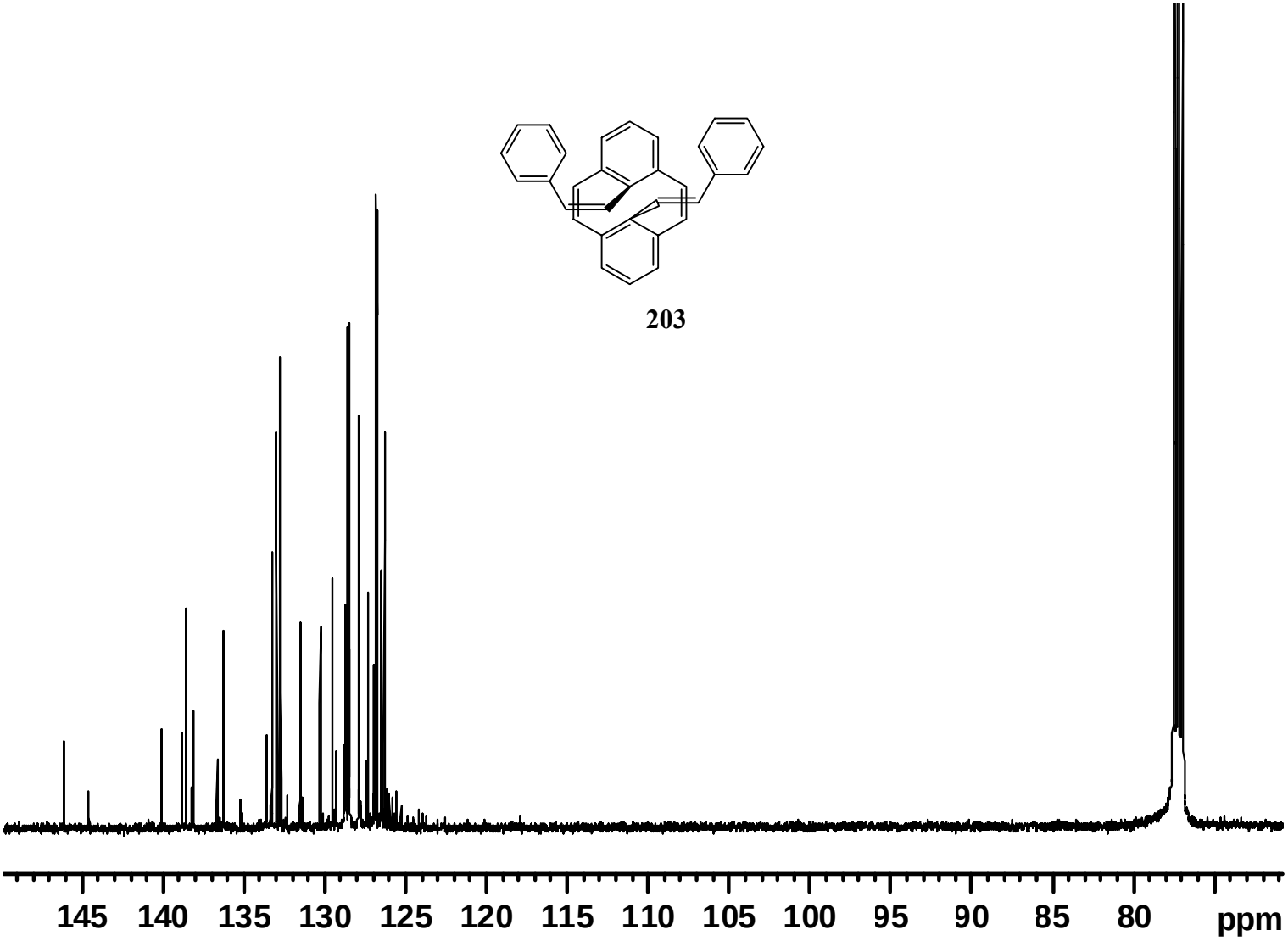

**202**



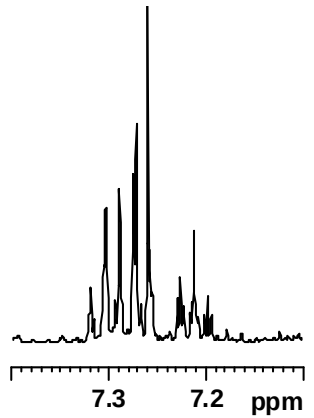
**202**

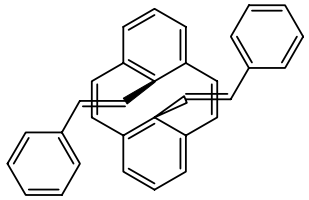



**203**

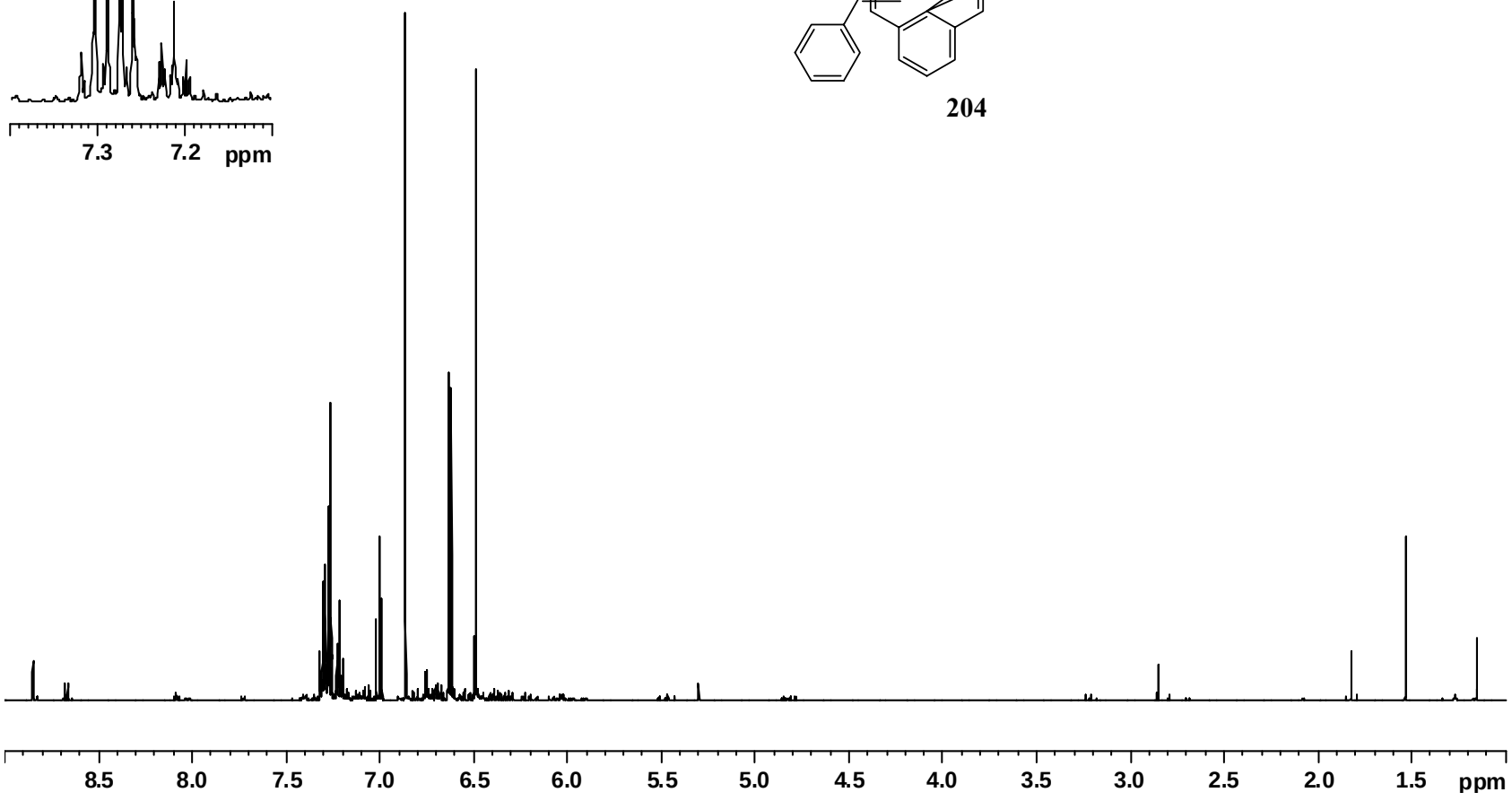


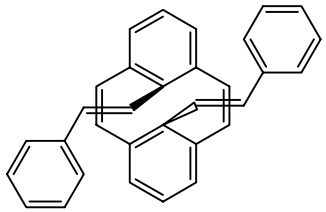

**203**



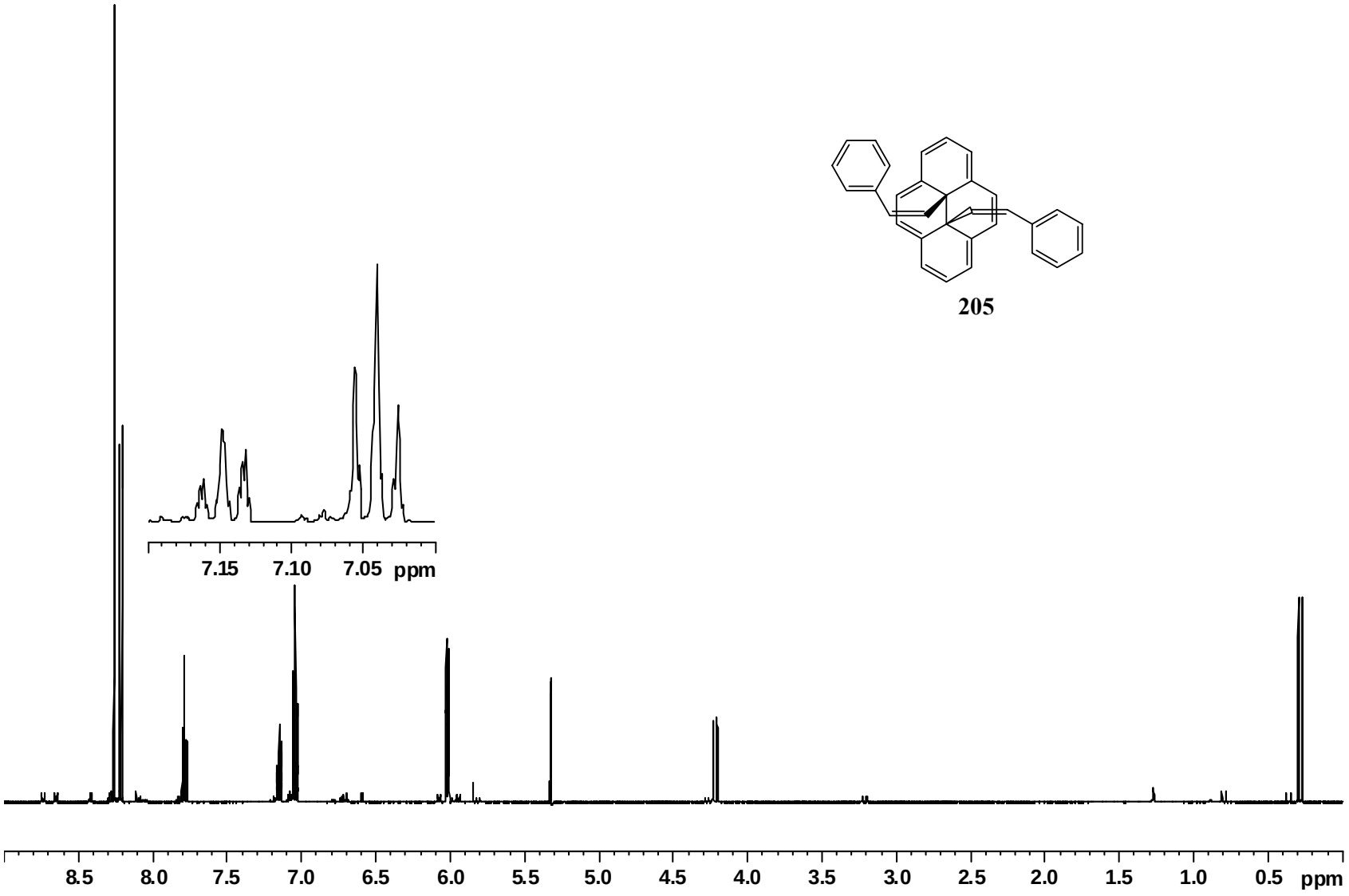



**204**

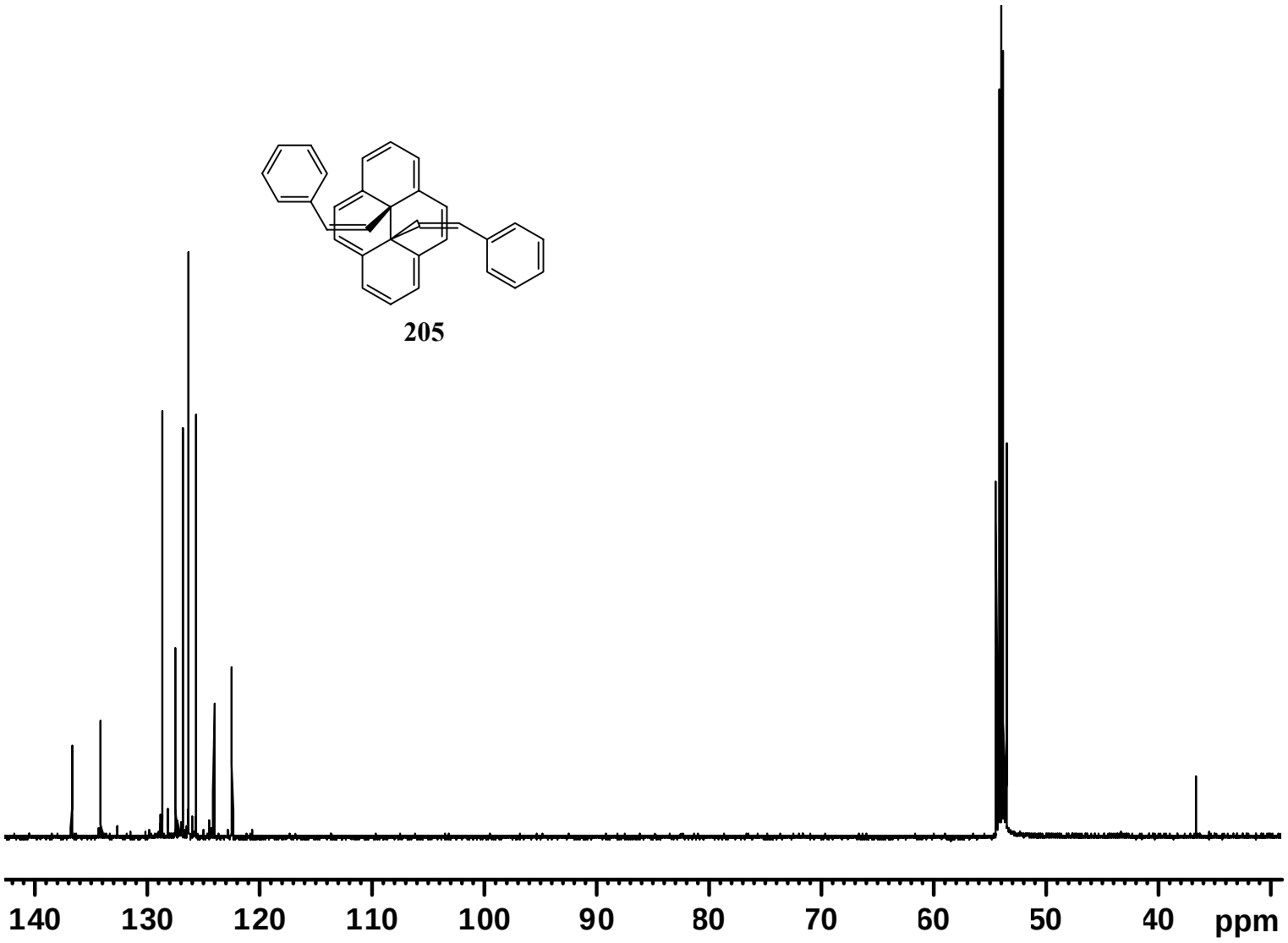




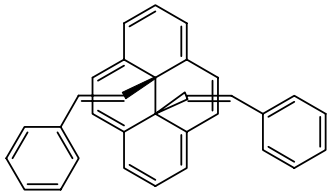
**204**



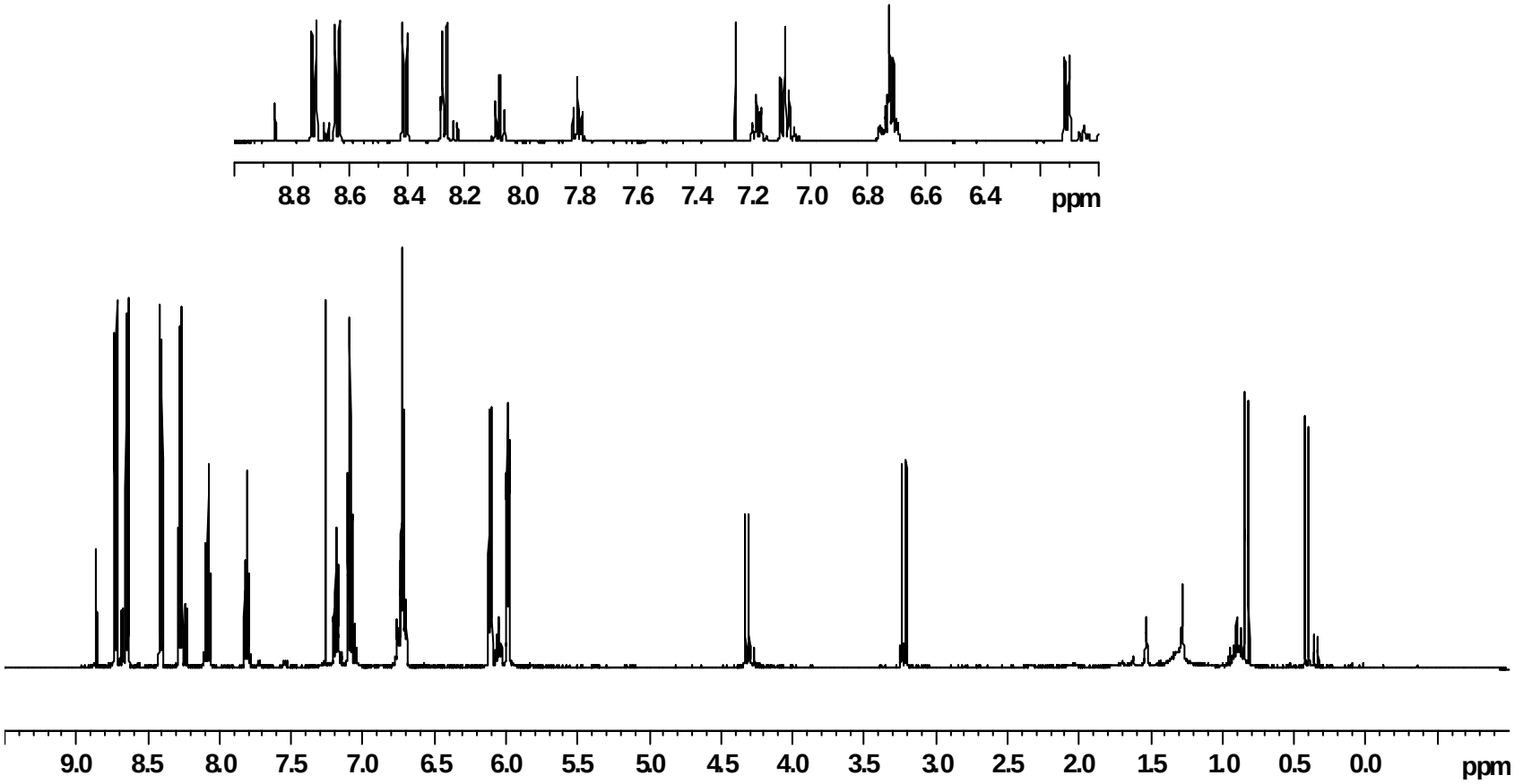

**205**

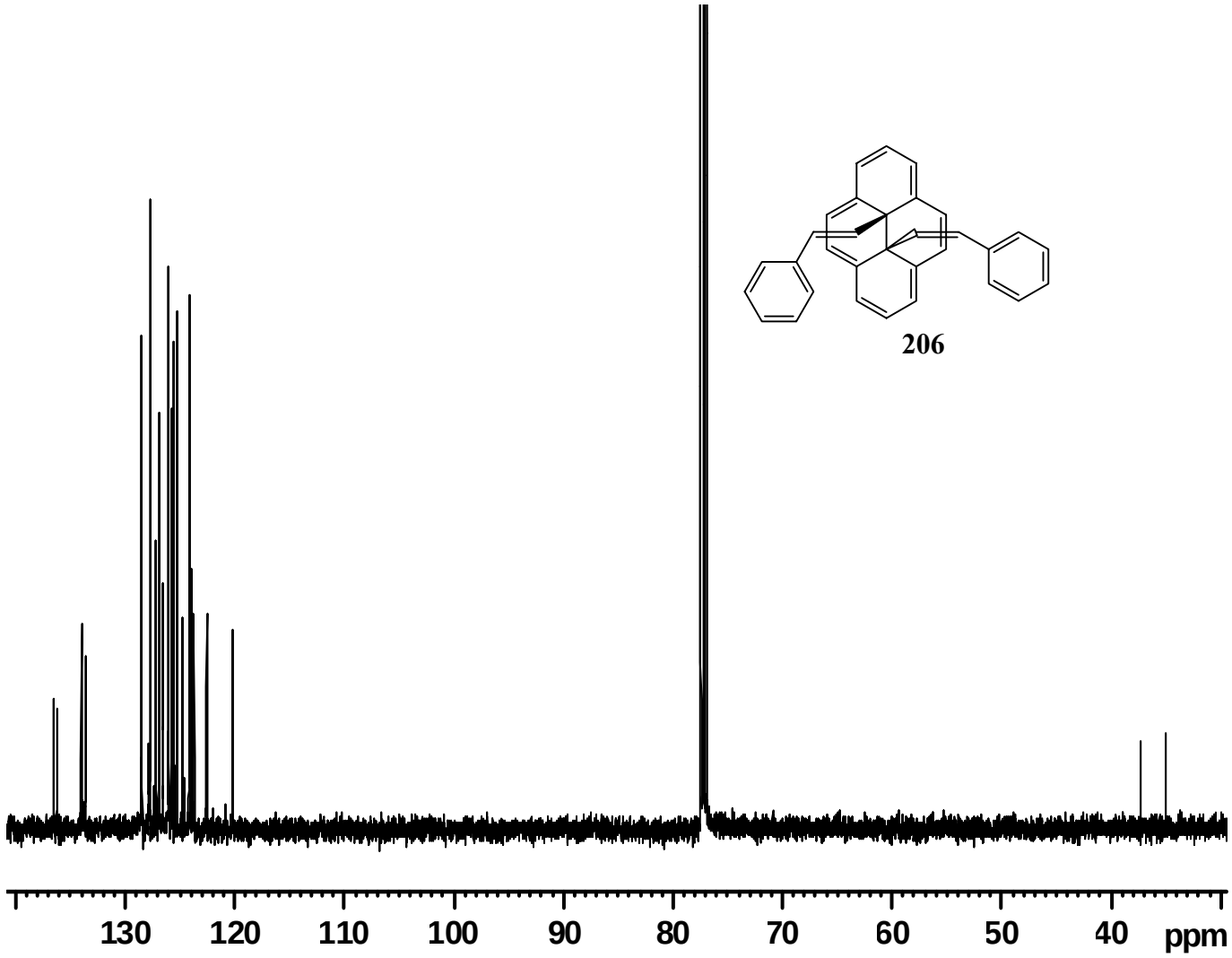



**205**

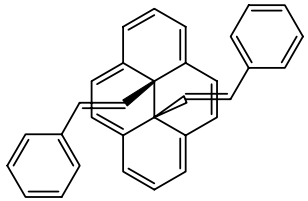


**206**


8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

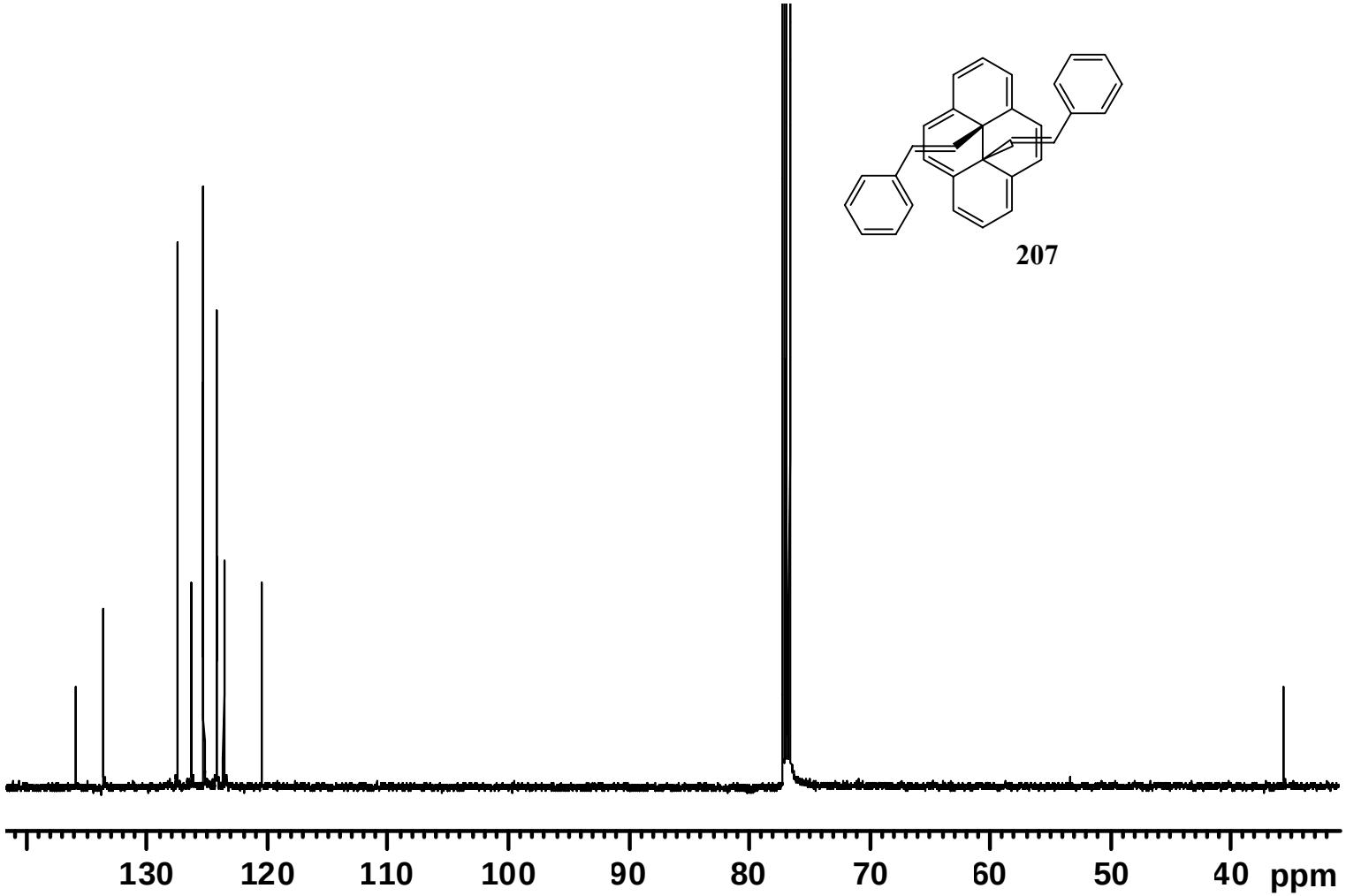



**206**

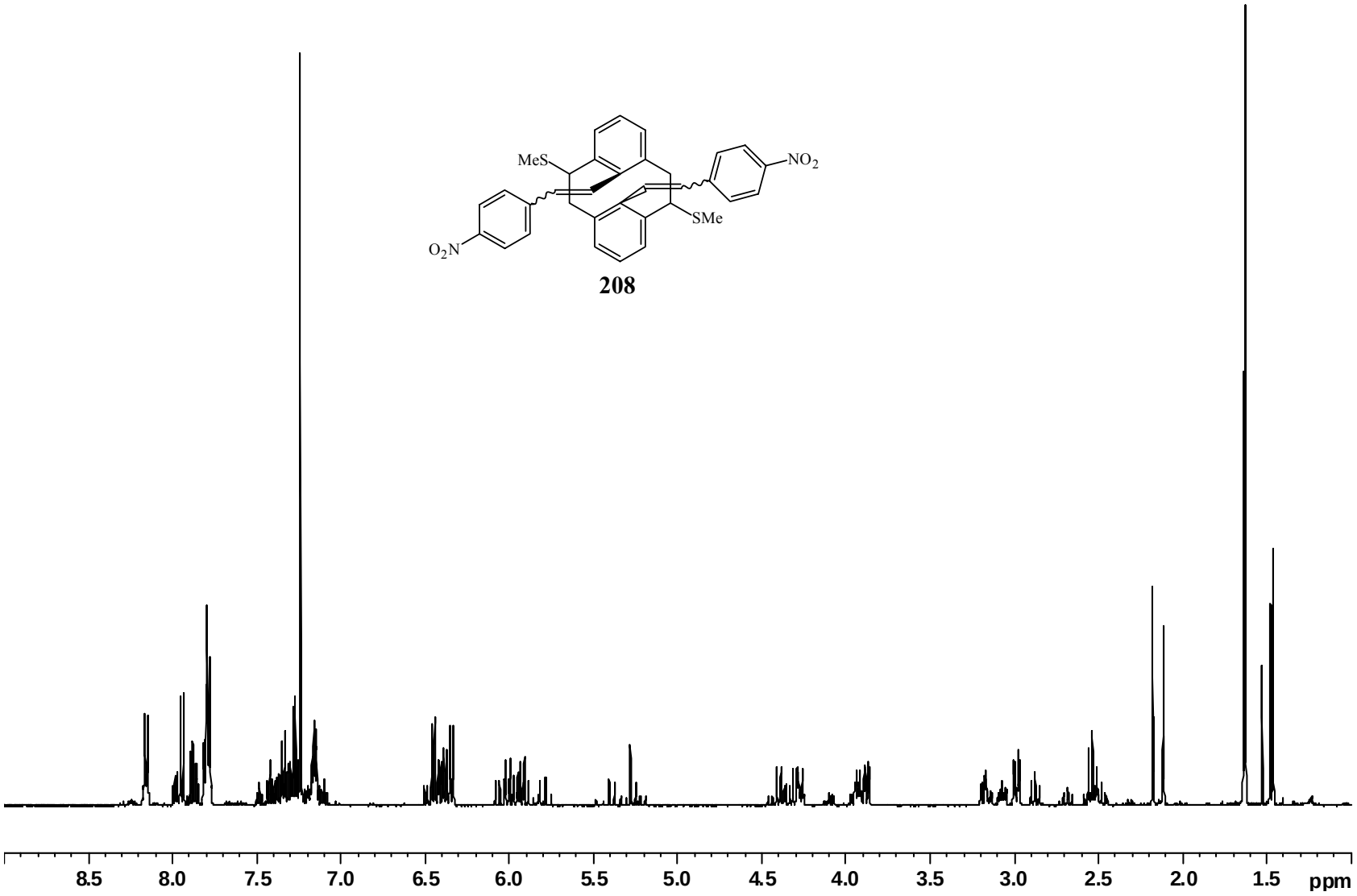


**207**

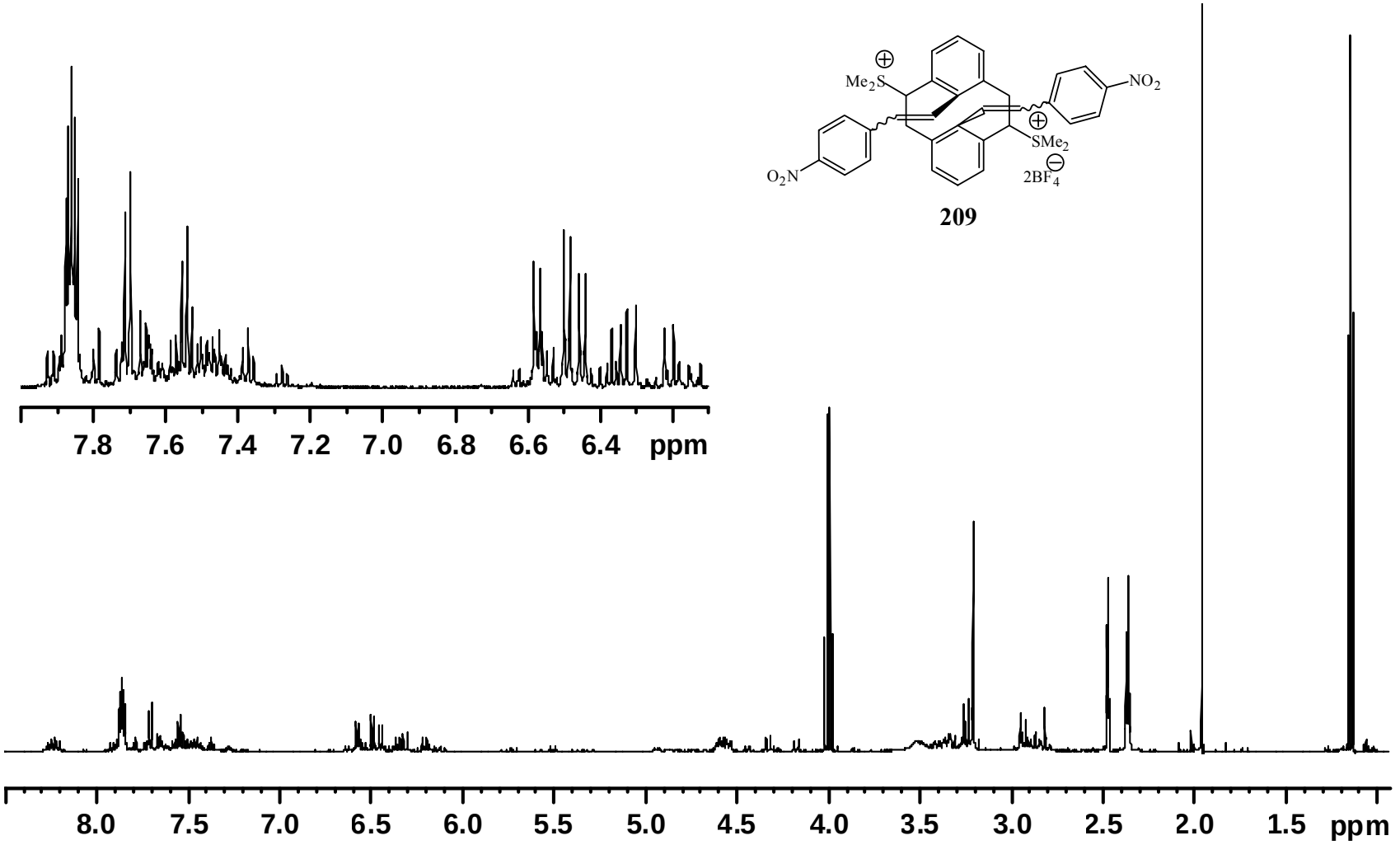

6.7
6.6
6.5
6.4
6.3
6.2
6.1
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm



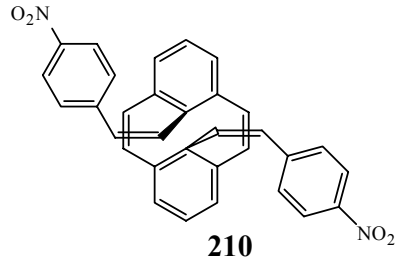

**207**



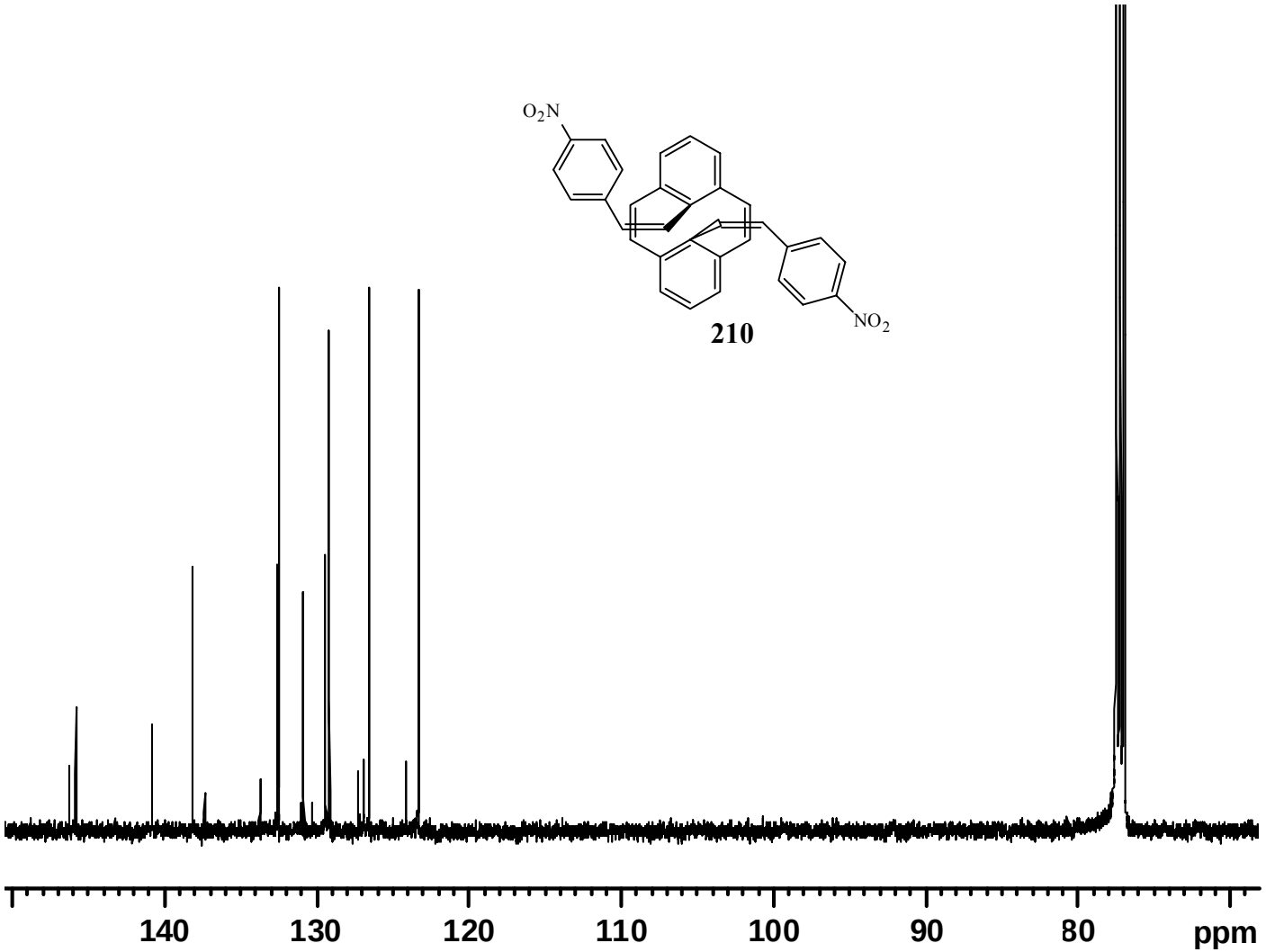

**208**

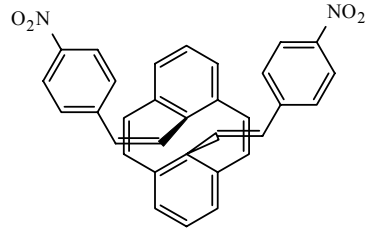

Me2S
NO2
SMe2
O2N
2BF4
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

**209**

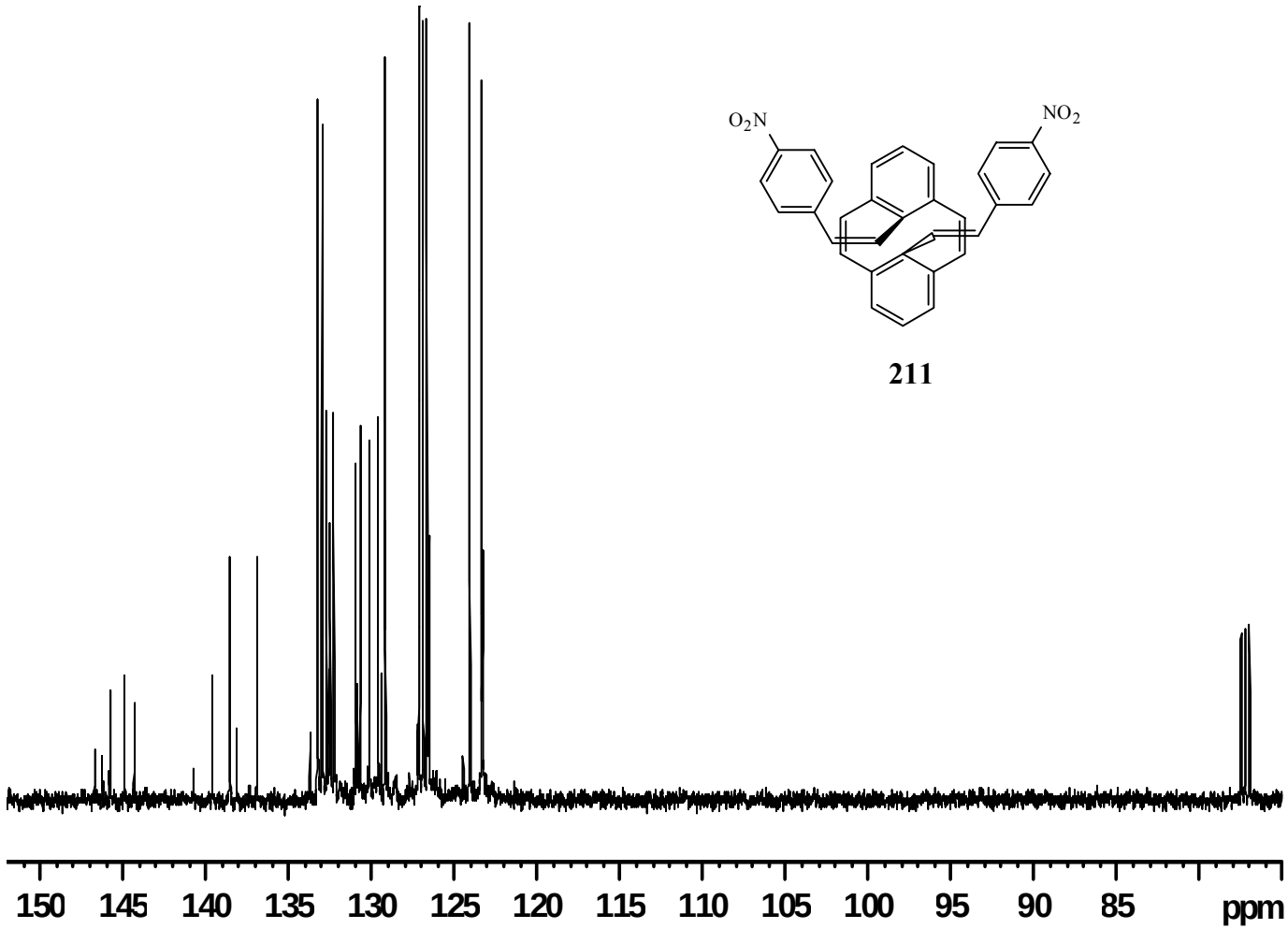



**210**

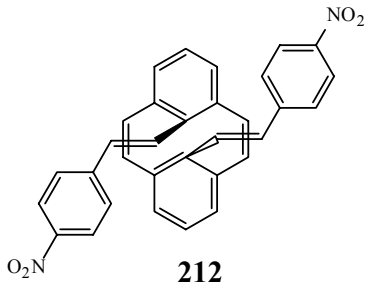

O2N
NO2
210
140
130
120
110
100
90
80
ppm



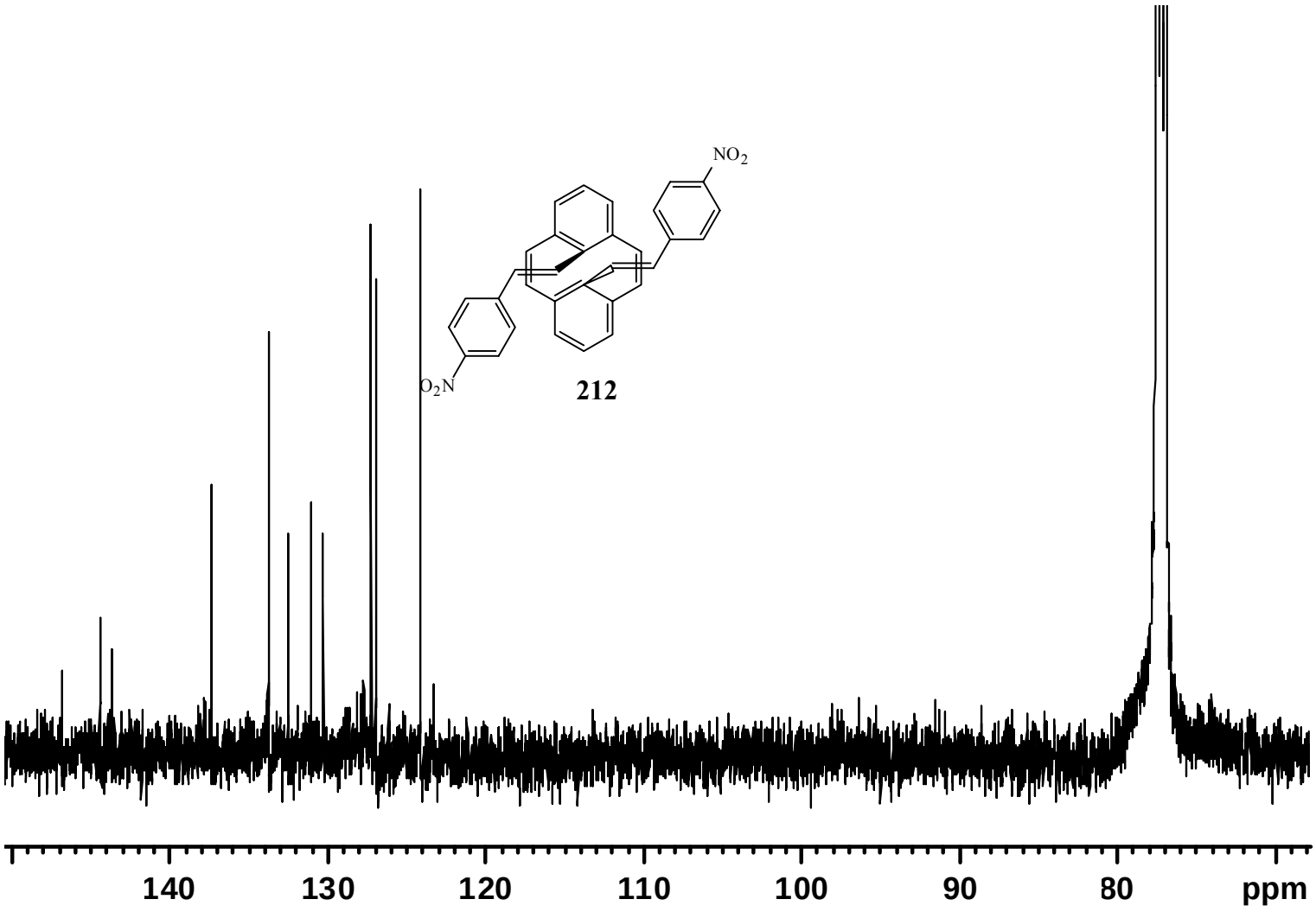

**211**

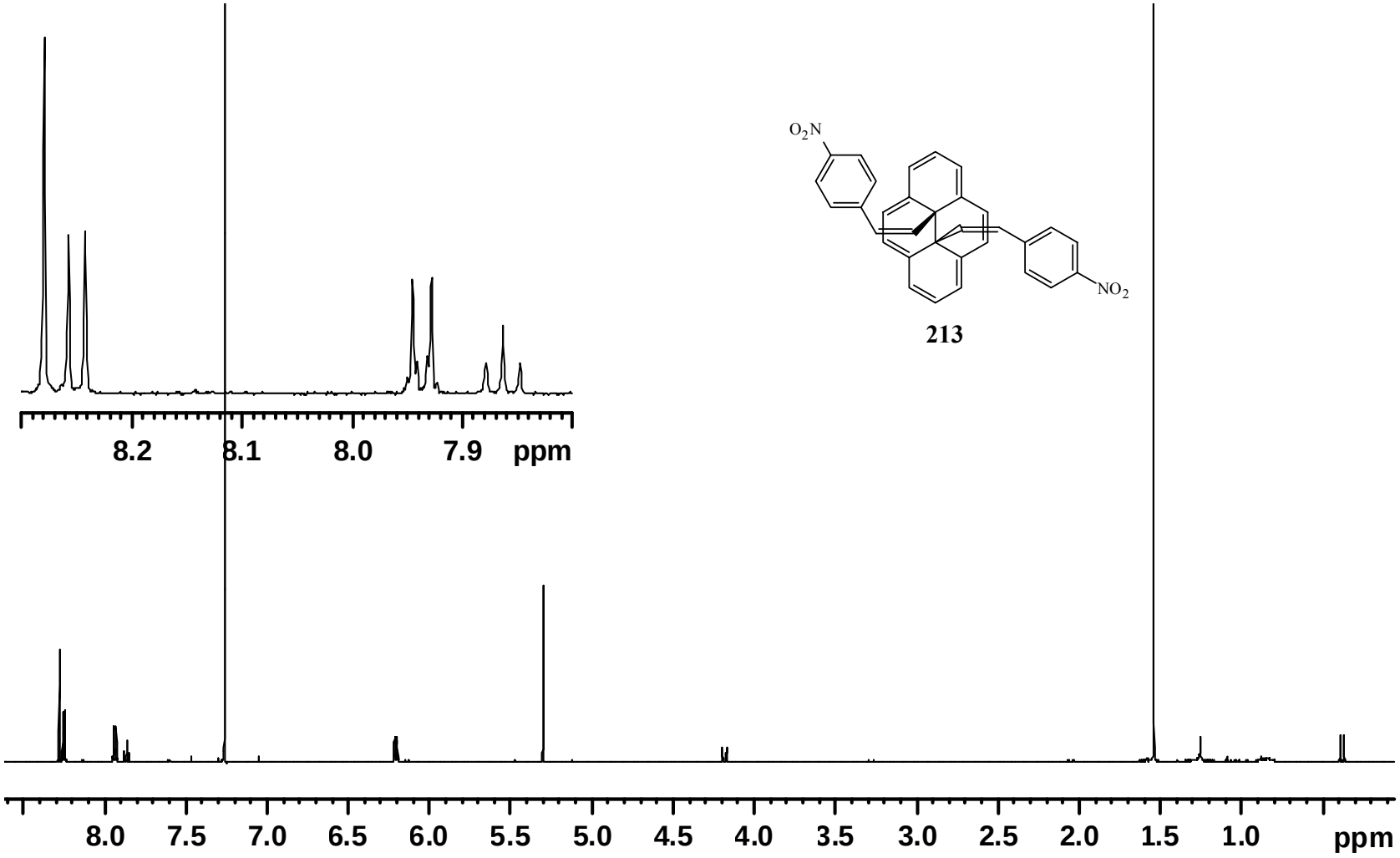



**211**



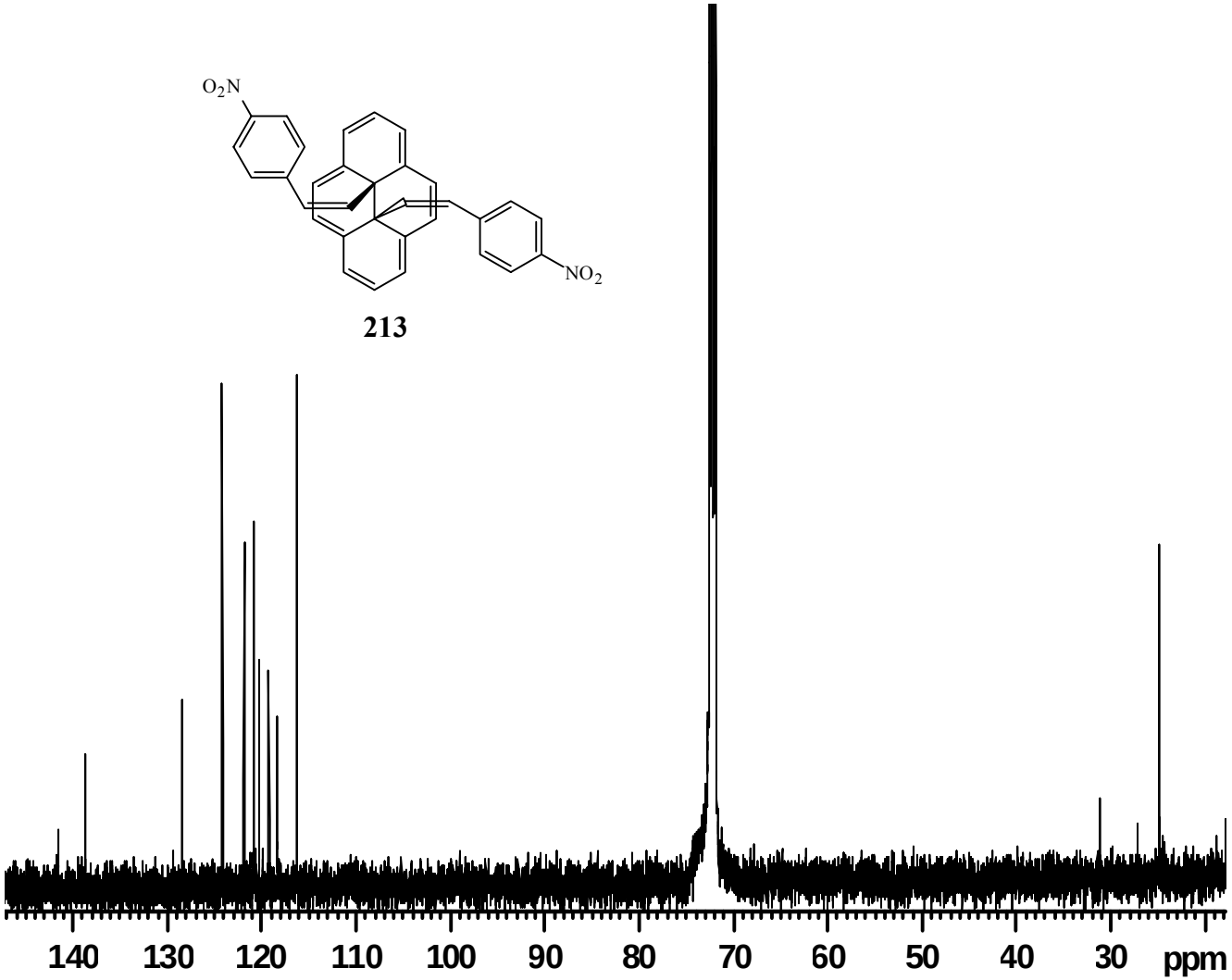

**212**


NO2
O2N
212
140
130
120
110
100
90
80
ppm

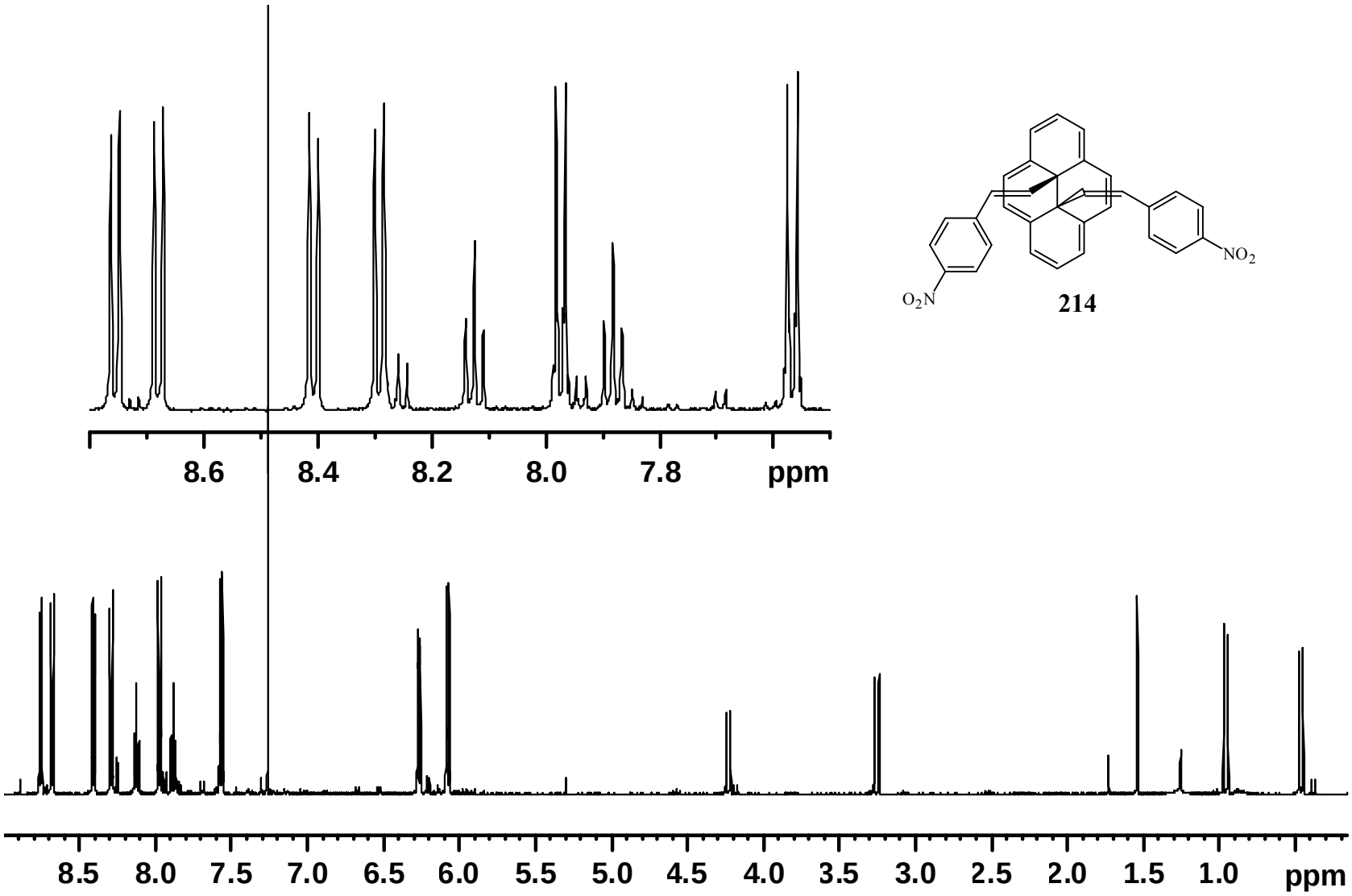

8.2
8.1
8.0
7.9
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


O2N
NO2

**213**

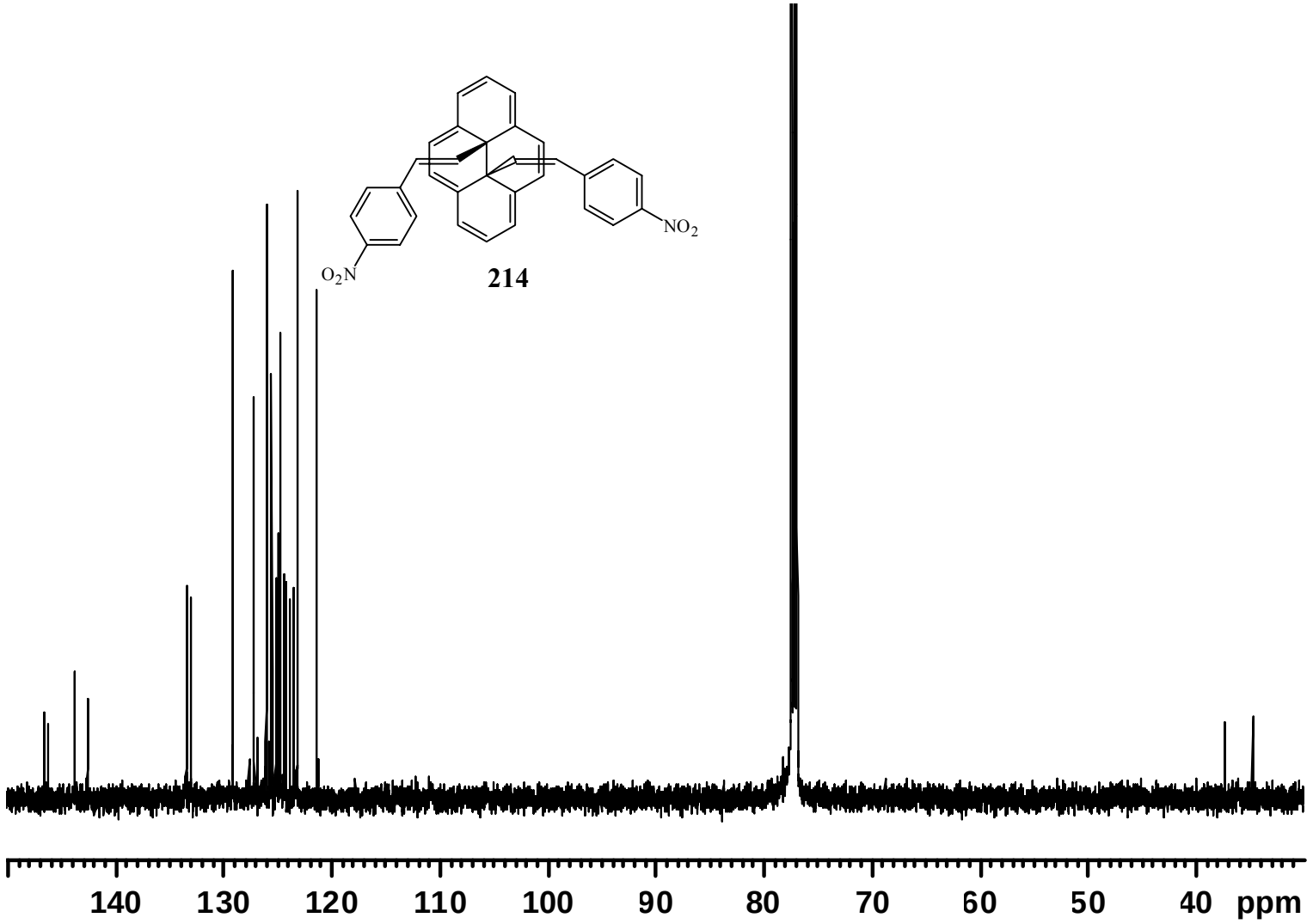


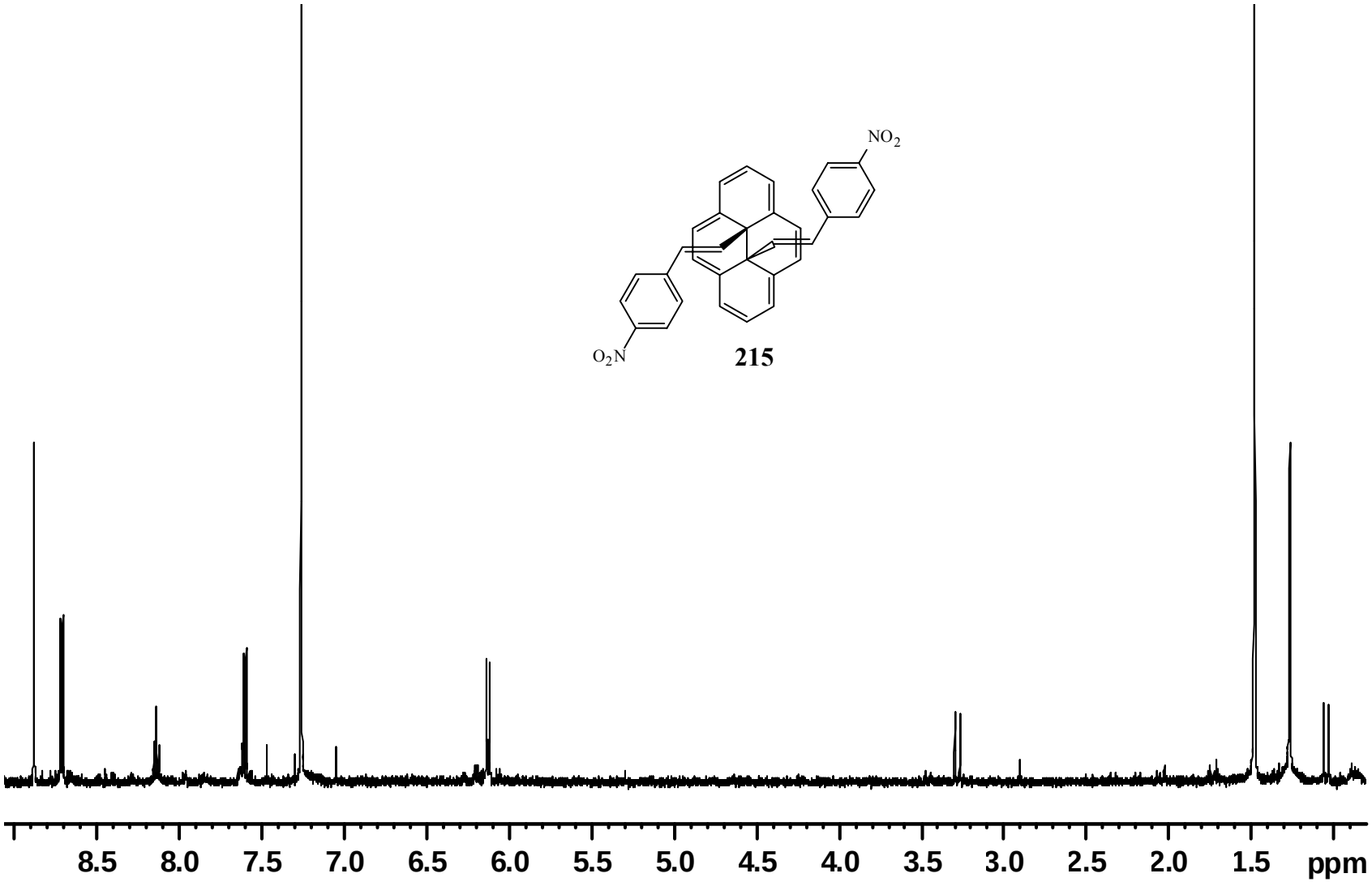

**213**


8.6
8.4
8.2
8.0
7.8
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

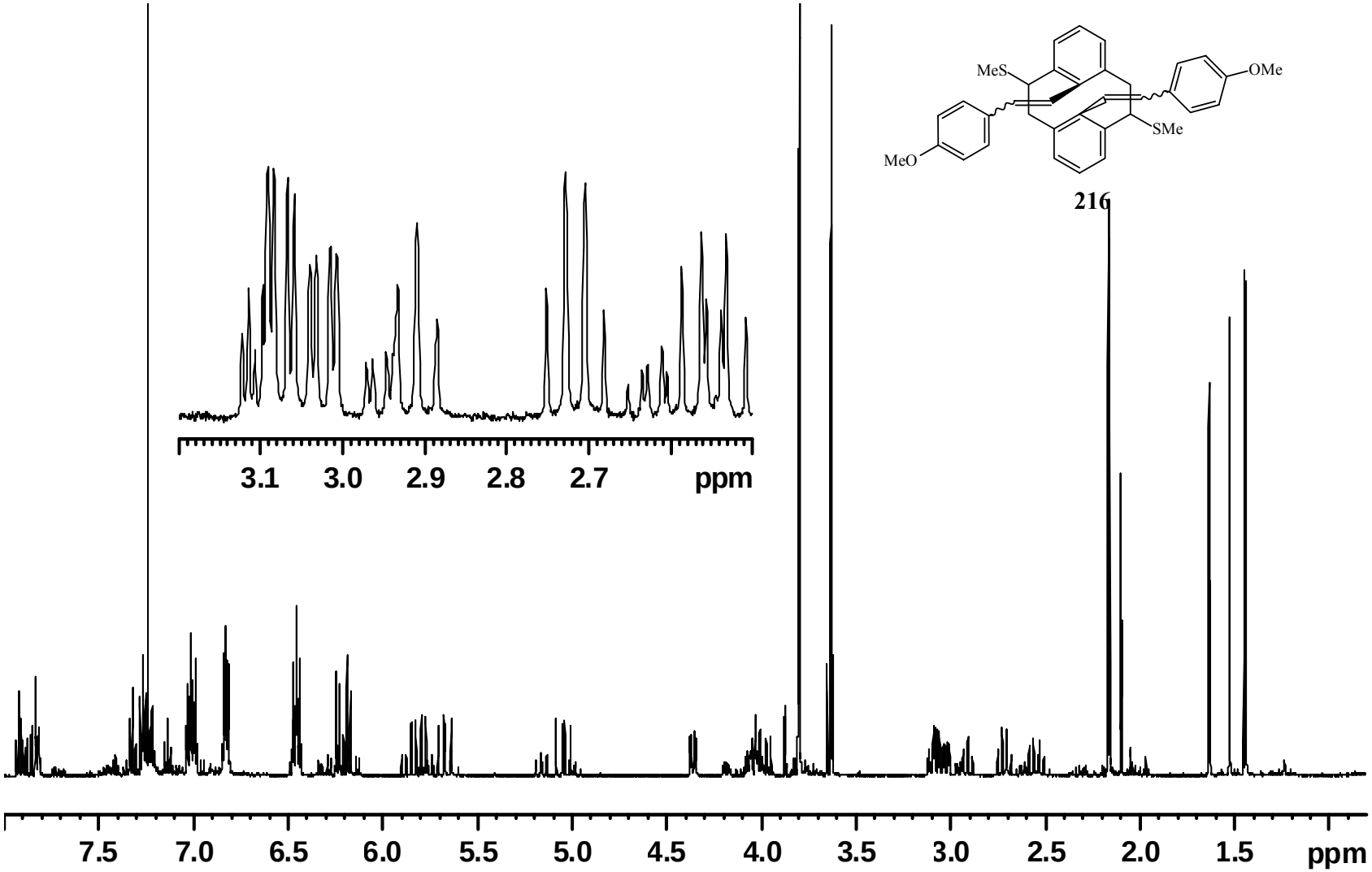

O2N
NO2

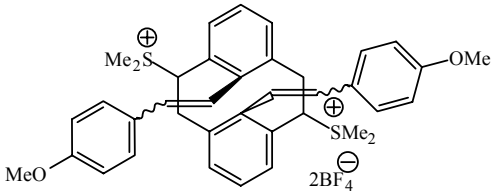
**214**


O2N
NO2
214
140
130
120
110
100
90
80
70
60
50
40
ppm

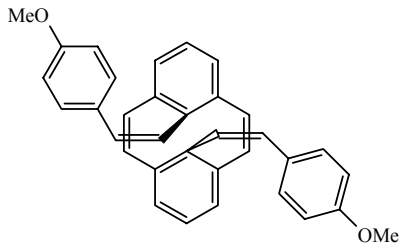



**215**

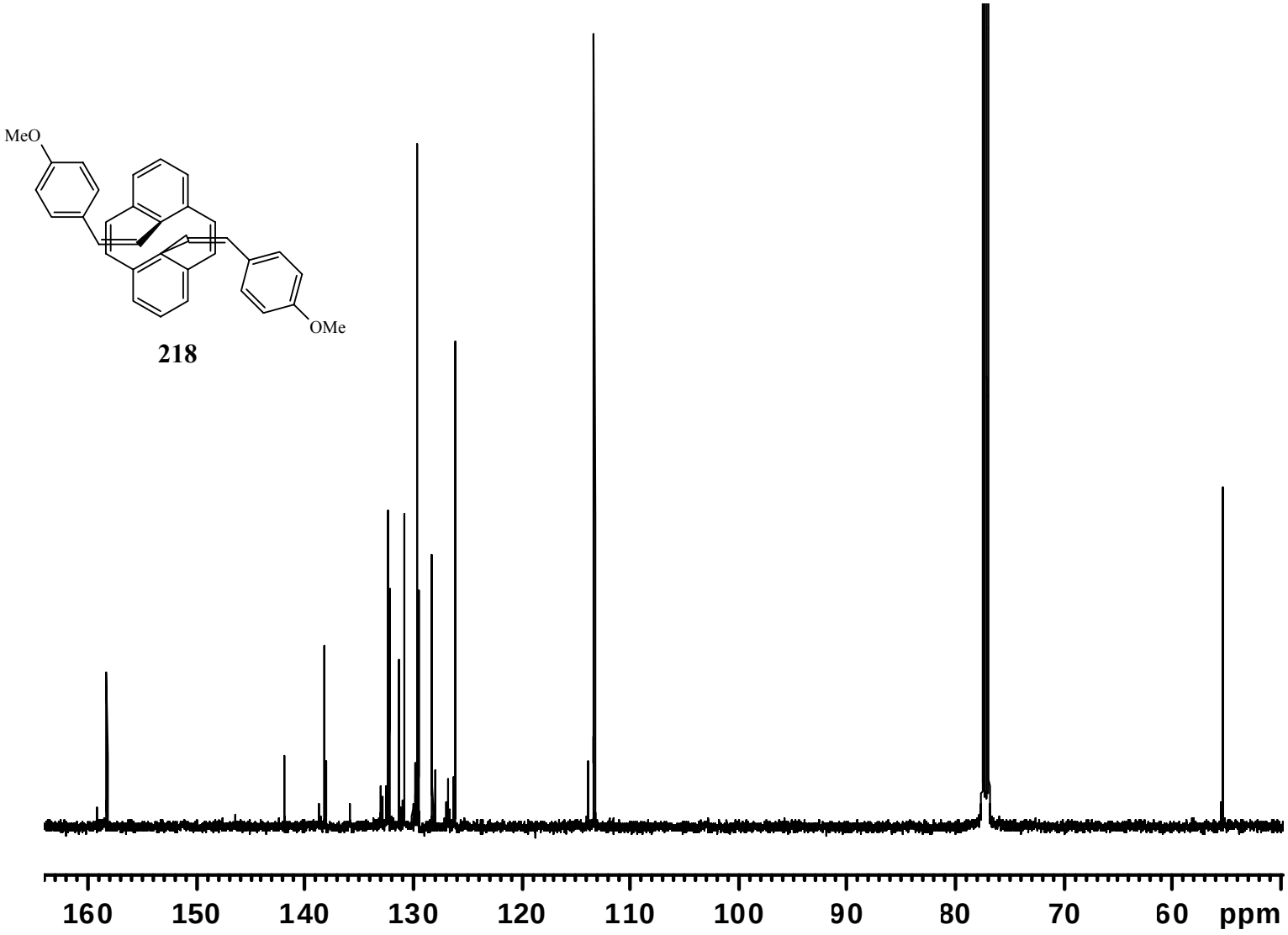

MeS
OMe
SMe
MeO
216
3.1
3.0
2.9
2.8
2.7
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm



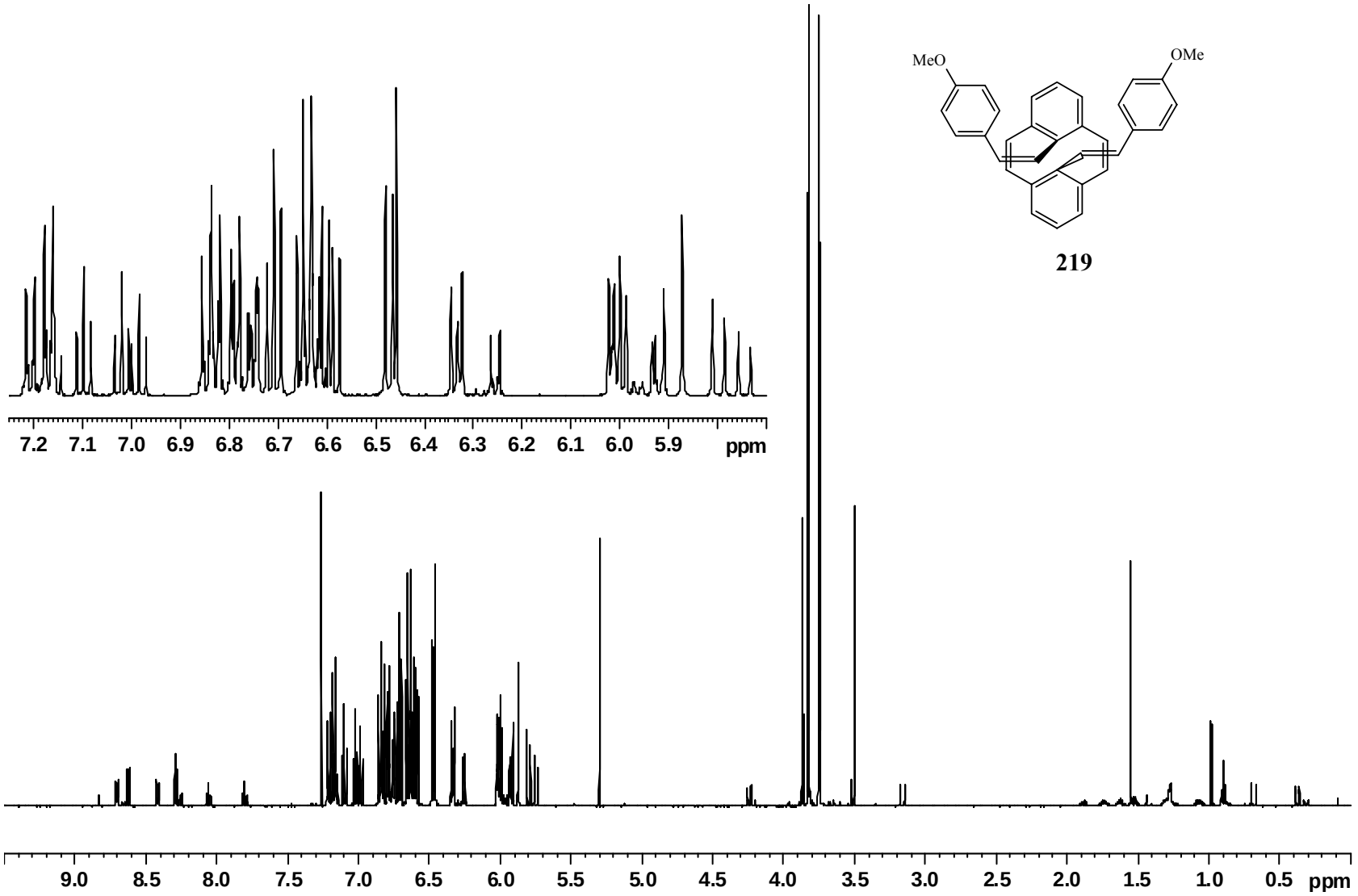

**217**



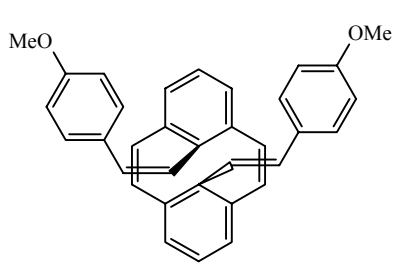

**218**



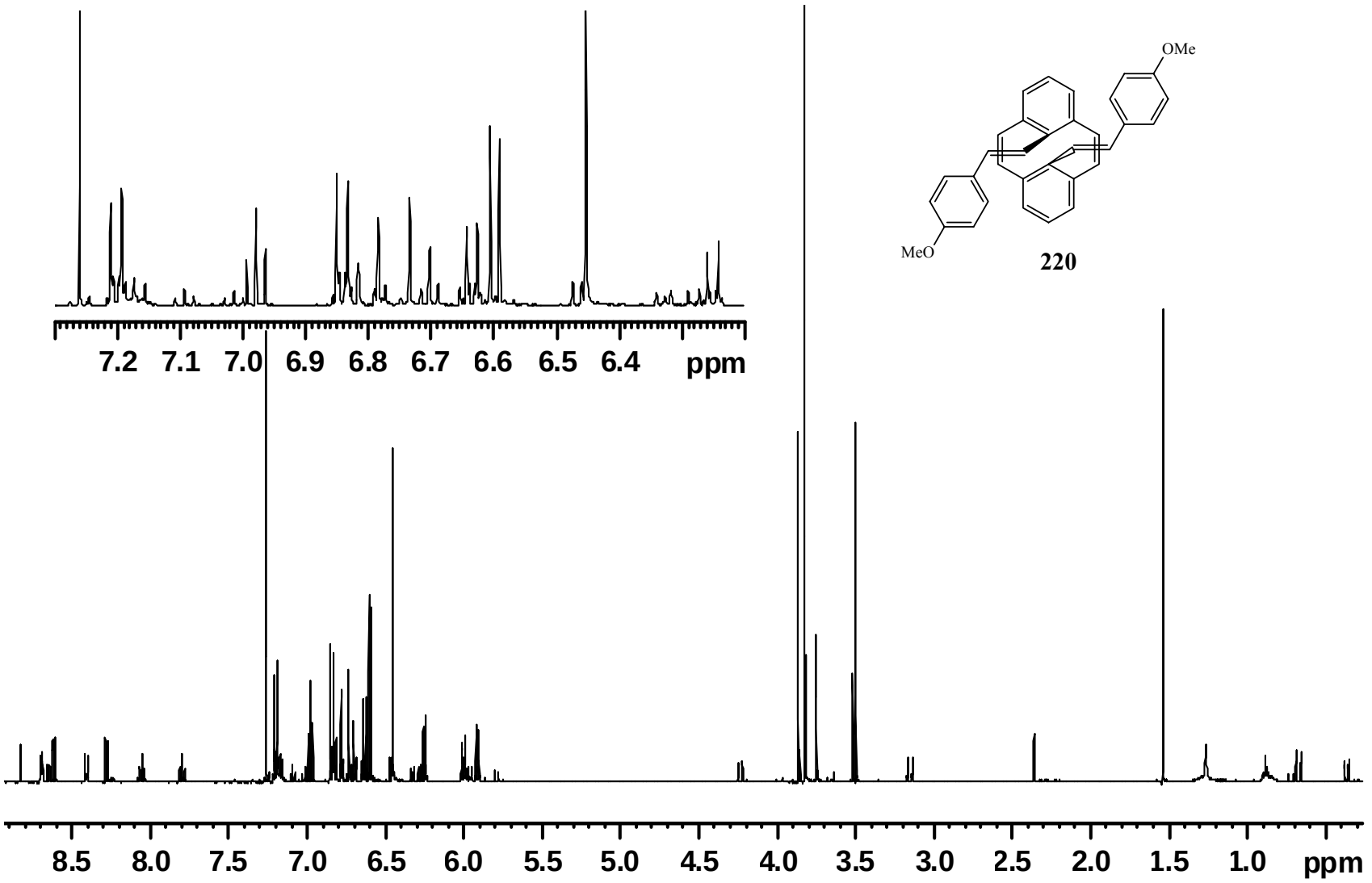

**218**

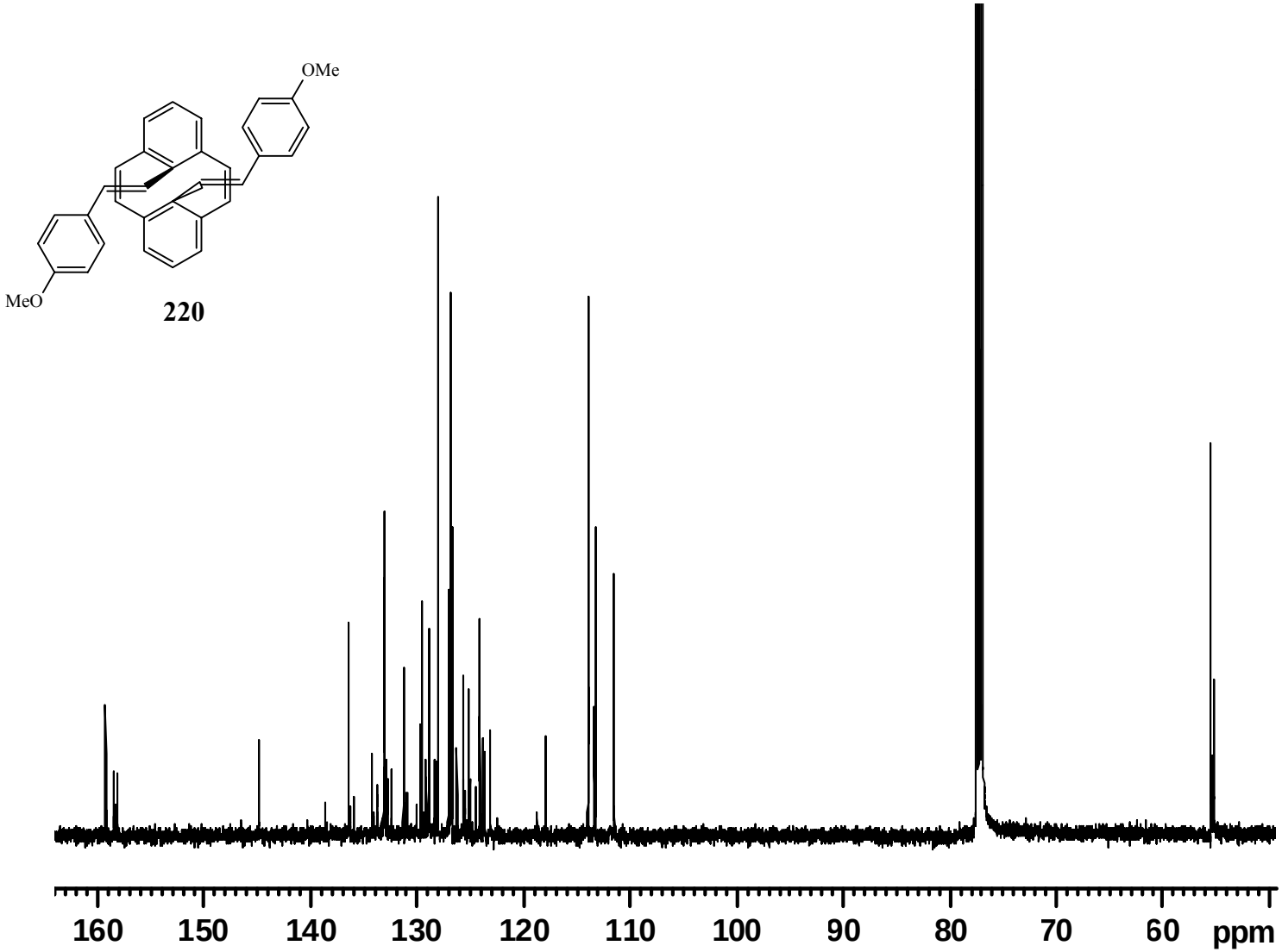

MeO
OMe
7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

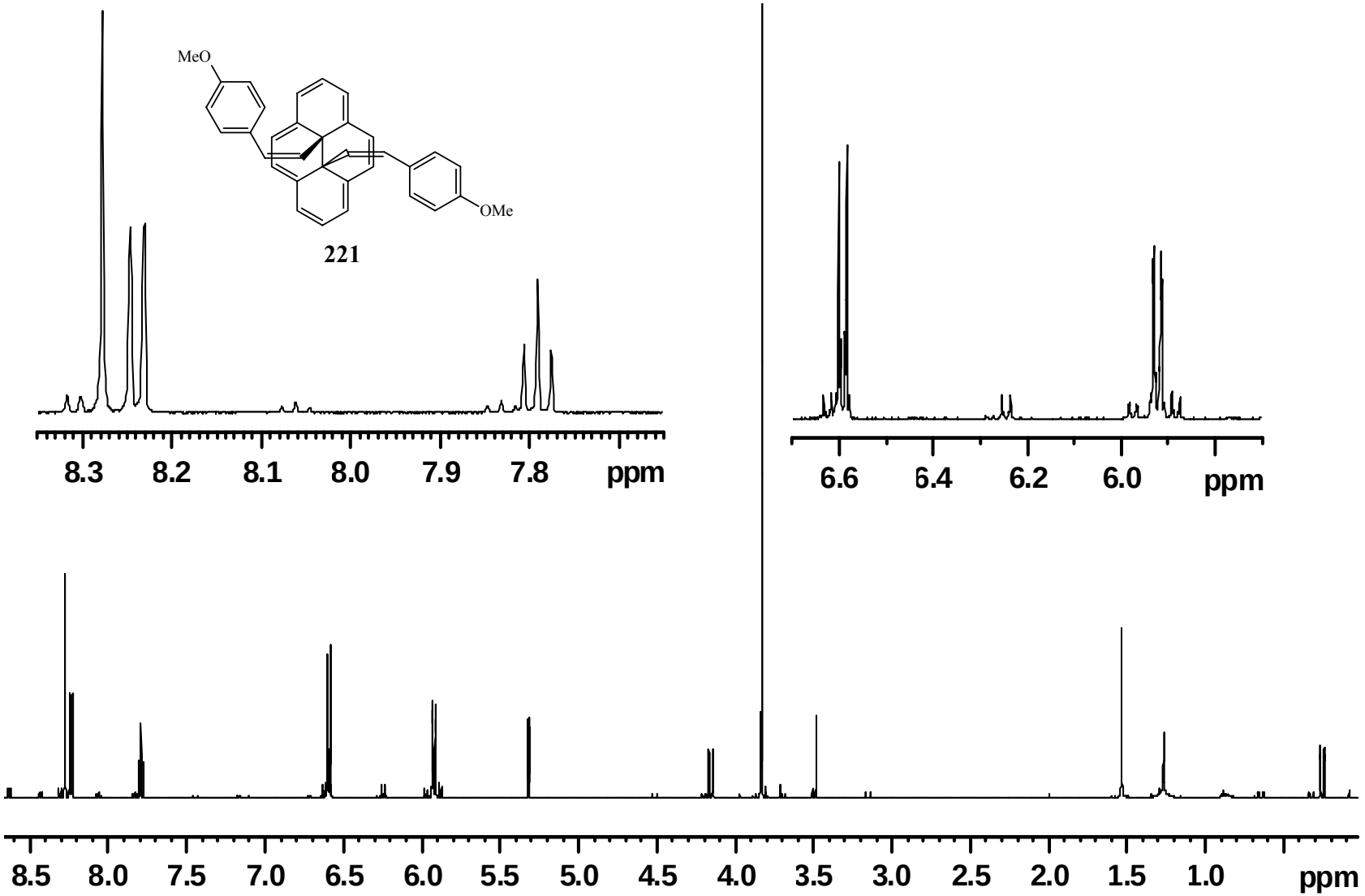
**219**

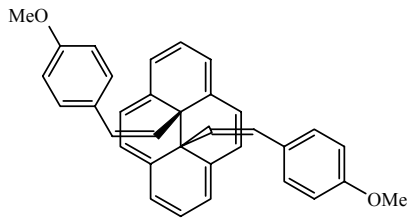



**219**

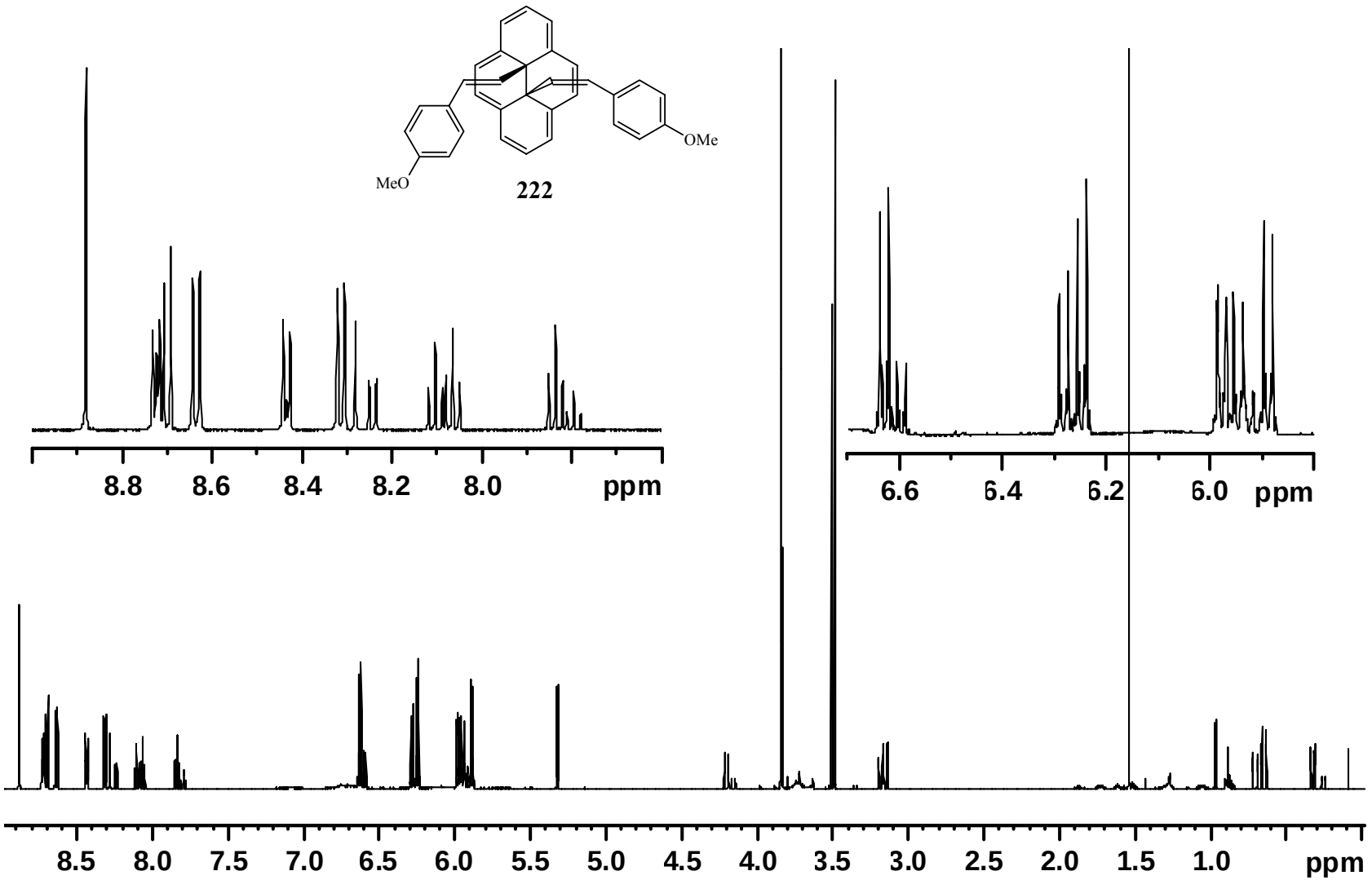

OMe
MeO
220
7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

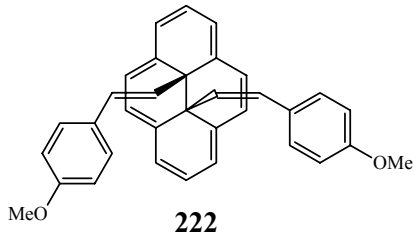

OMe
MeO
220
160
150
140
130
120
110
100
90
80
70
60
ppm


MeO
OMe
221
8.3
8.2
8.1
8.0
7.9
7.8
ppm
6.6
6.4
6.2
6.0
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

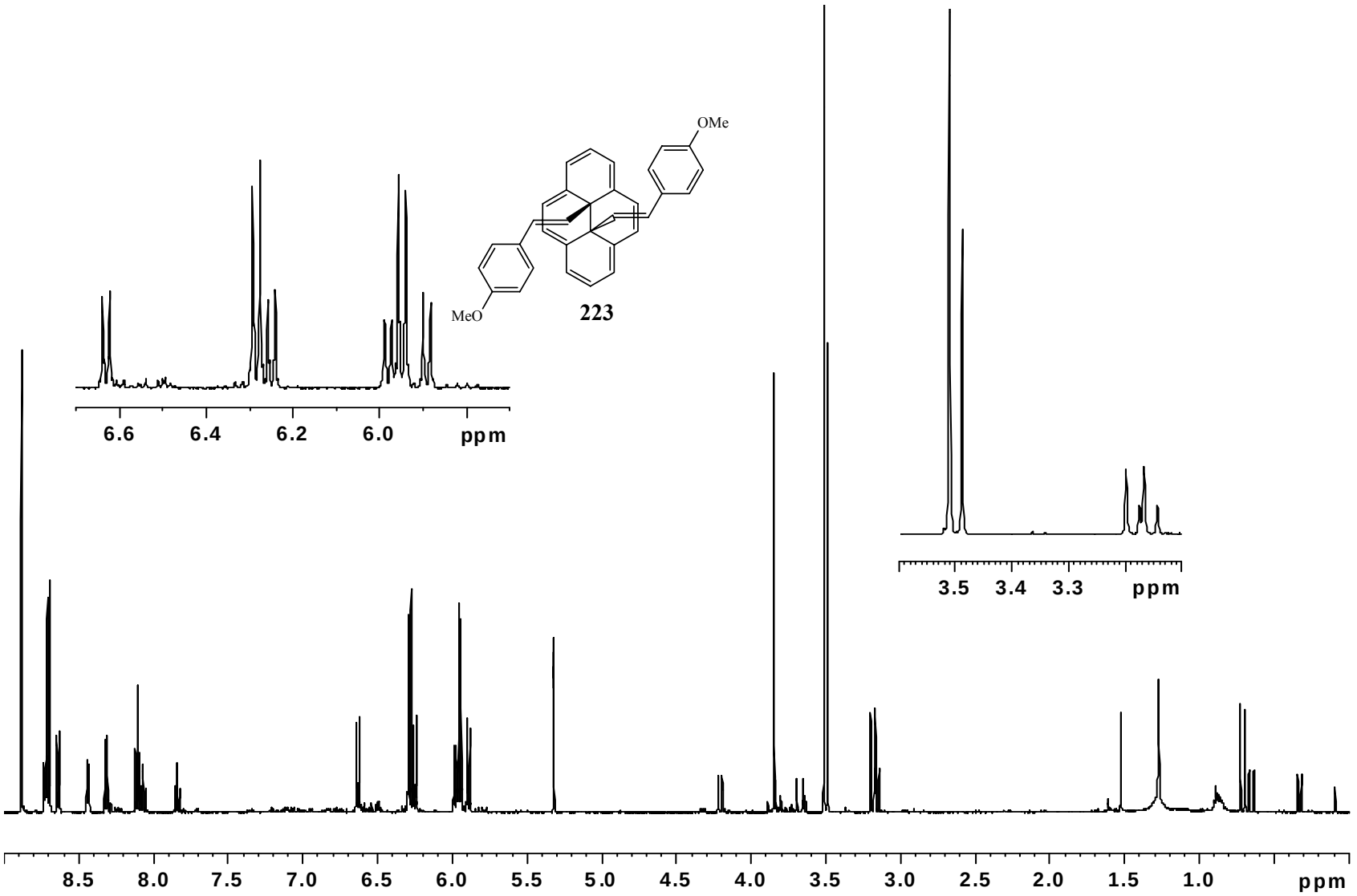


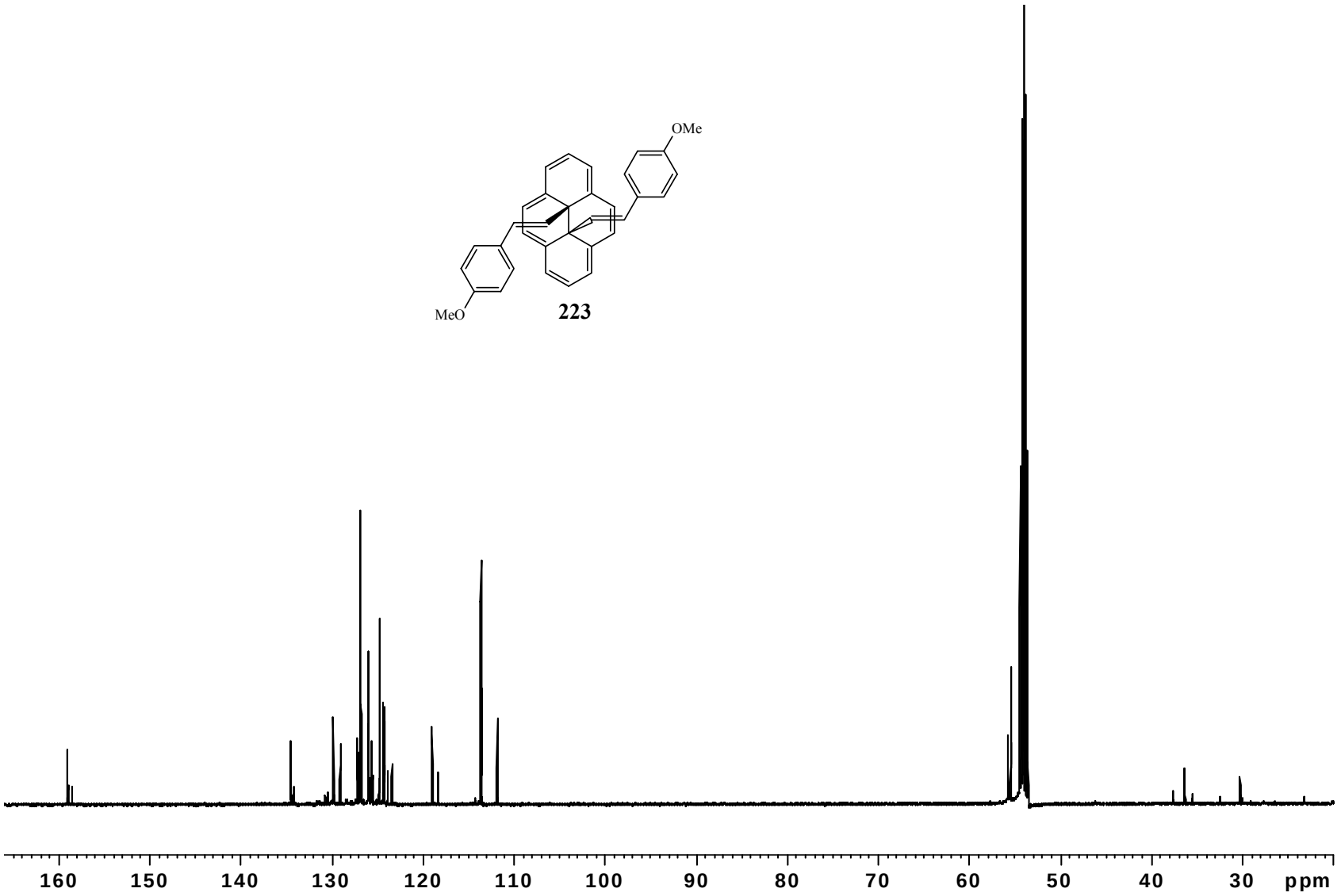

**221**


MeO
OMe
222
8.8
8.6
8.4
8.2
8.0
ppm
6.6
6.4
6.2
6.0
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

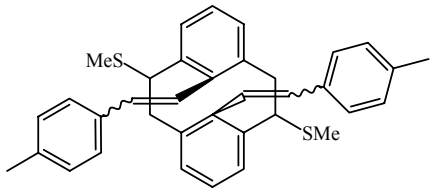



**222**

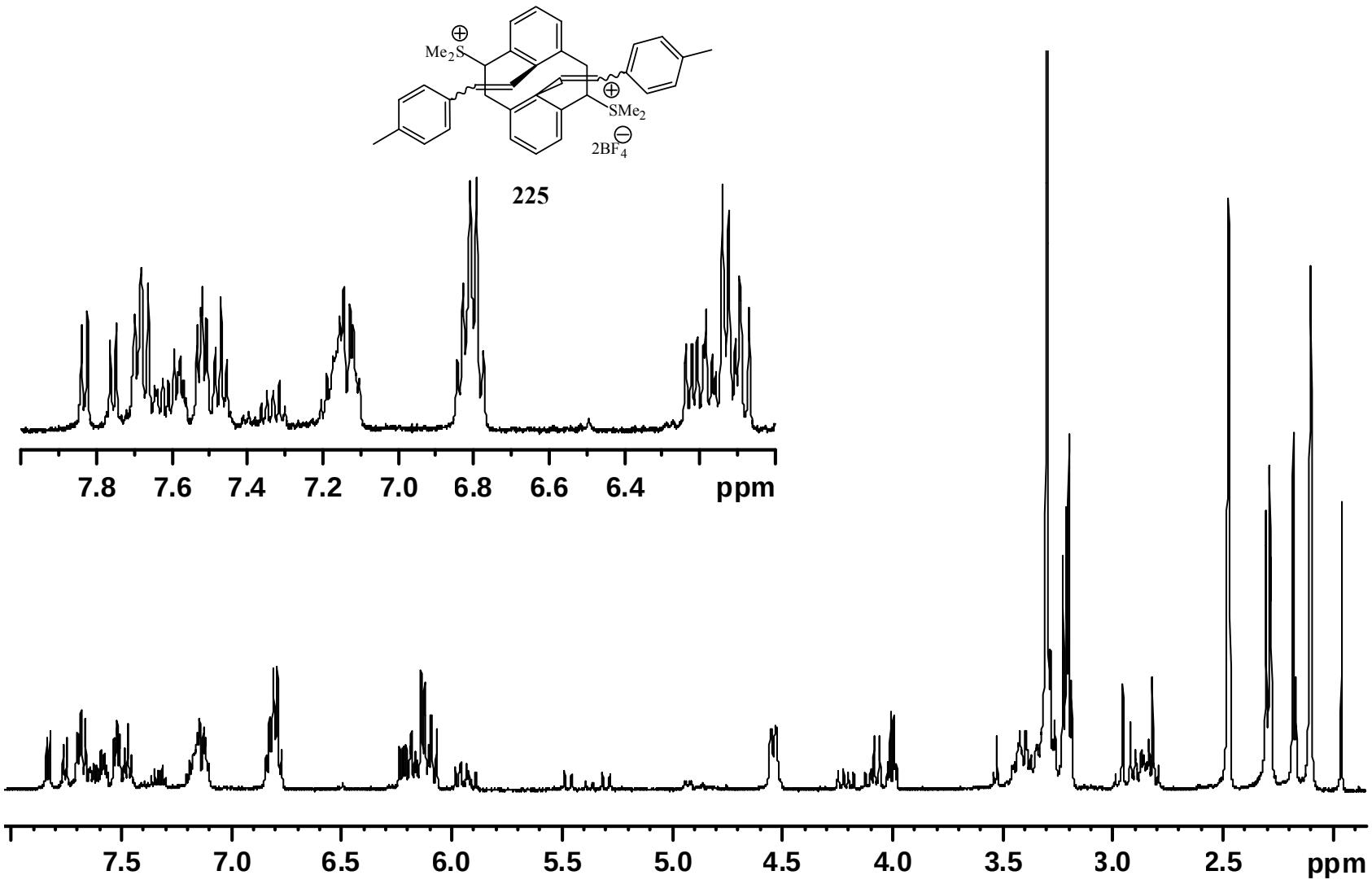

OMe
MeO
223
6.6
6.4
6.2
6.0
ppm
3.5
3.4
3.3
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

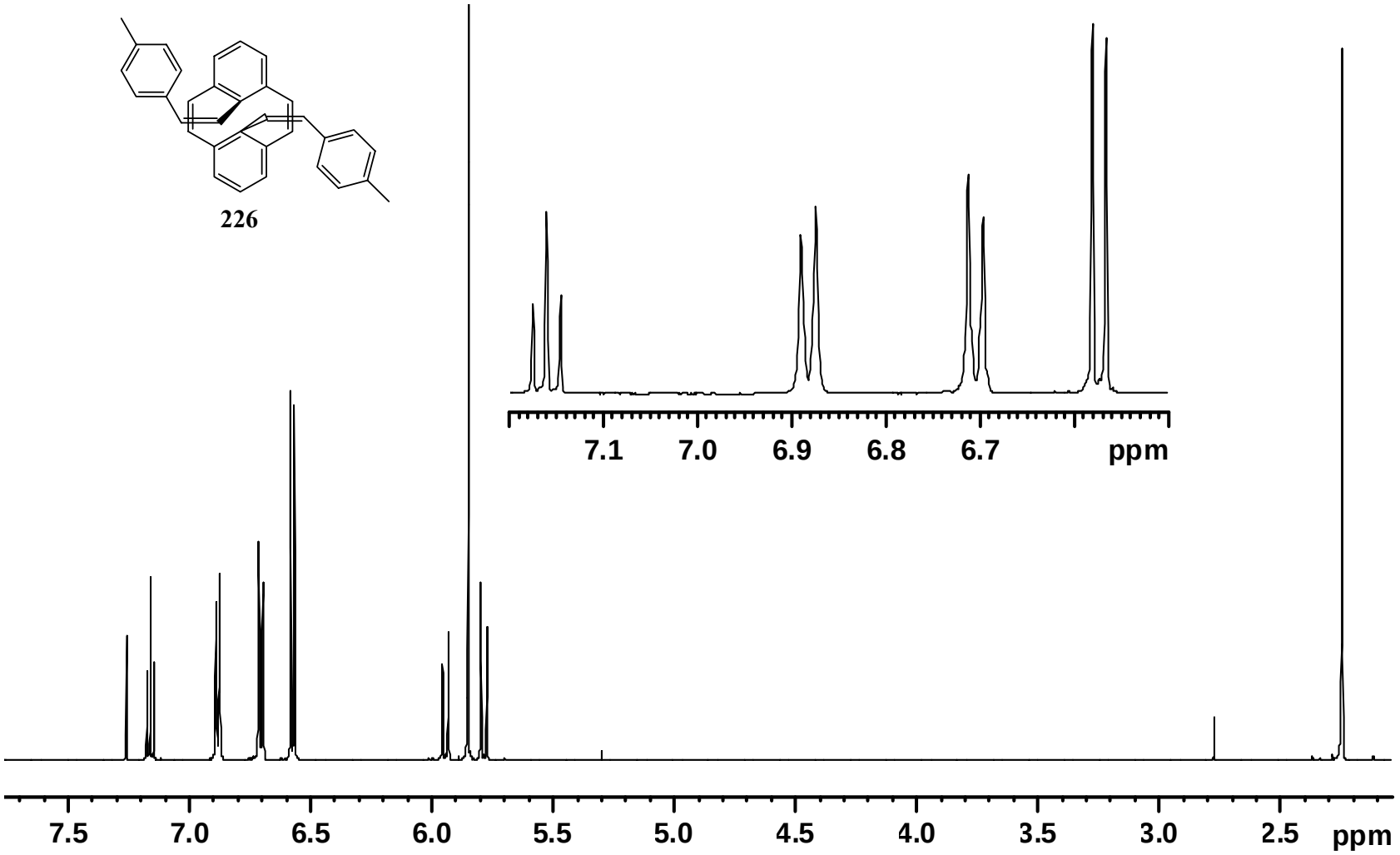


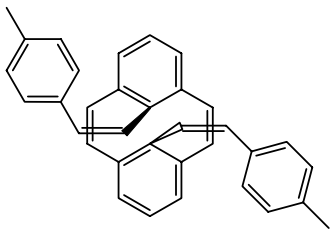

**223**



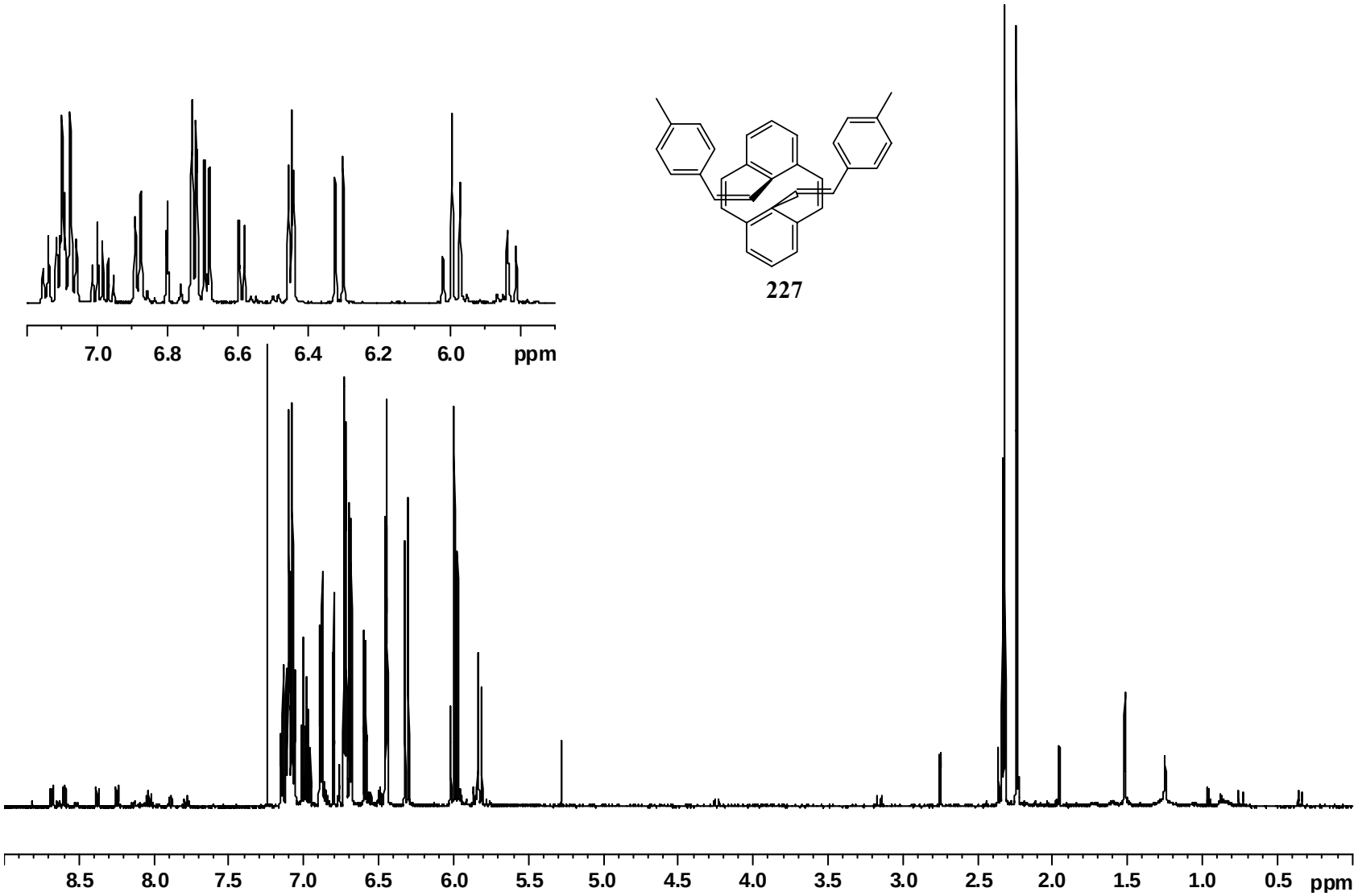

**224**

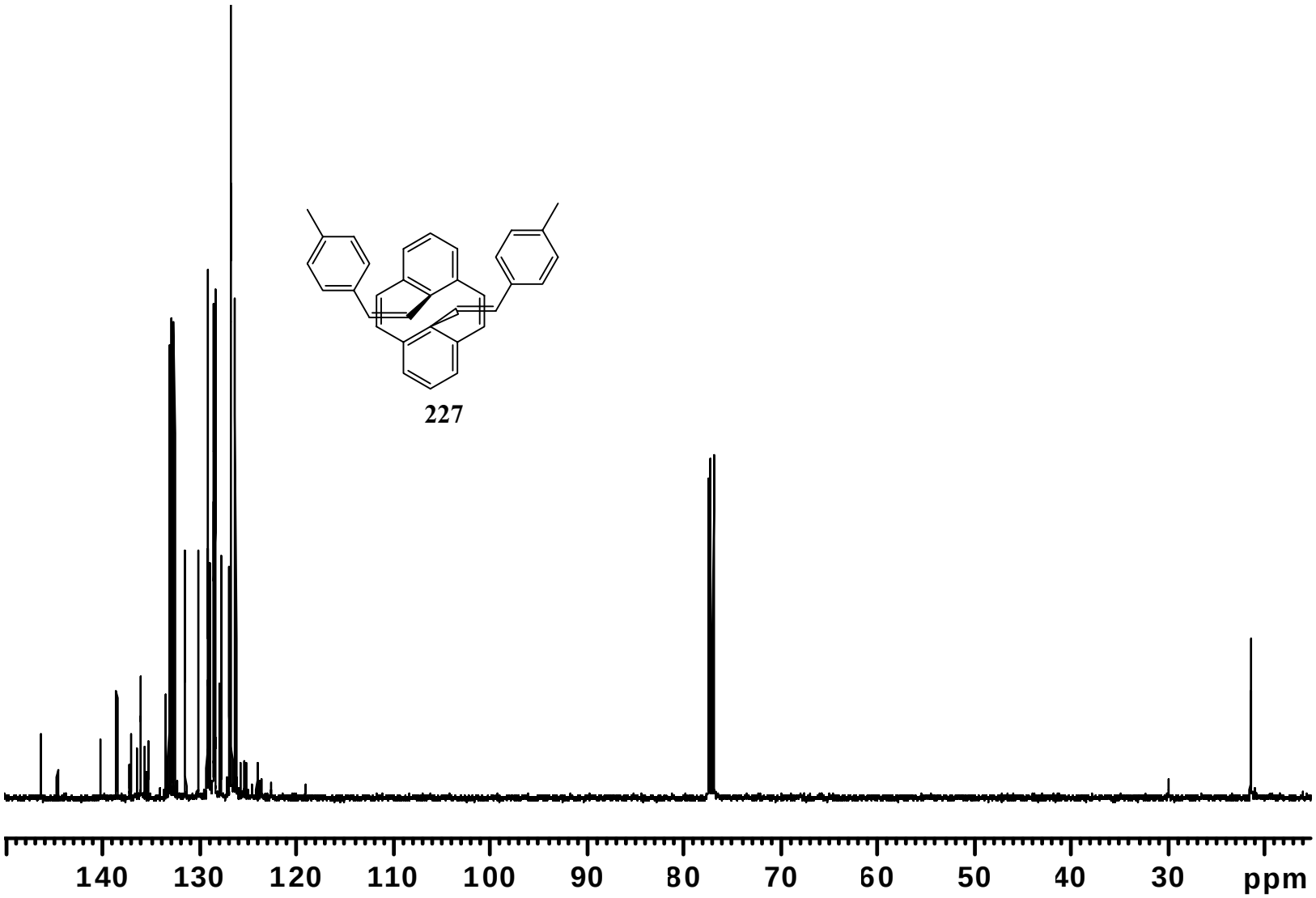

Me2S
SMe2
2BF4
225
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm


226
7.1
7.0
6.9
6.8
6.7
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

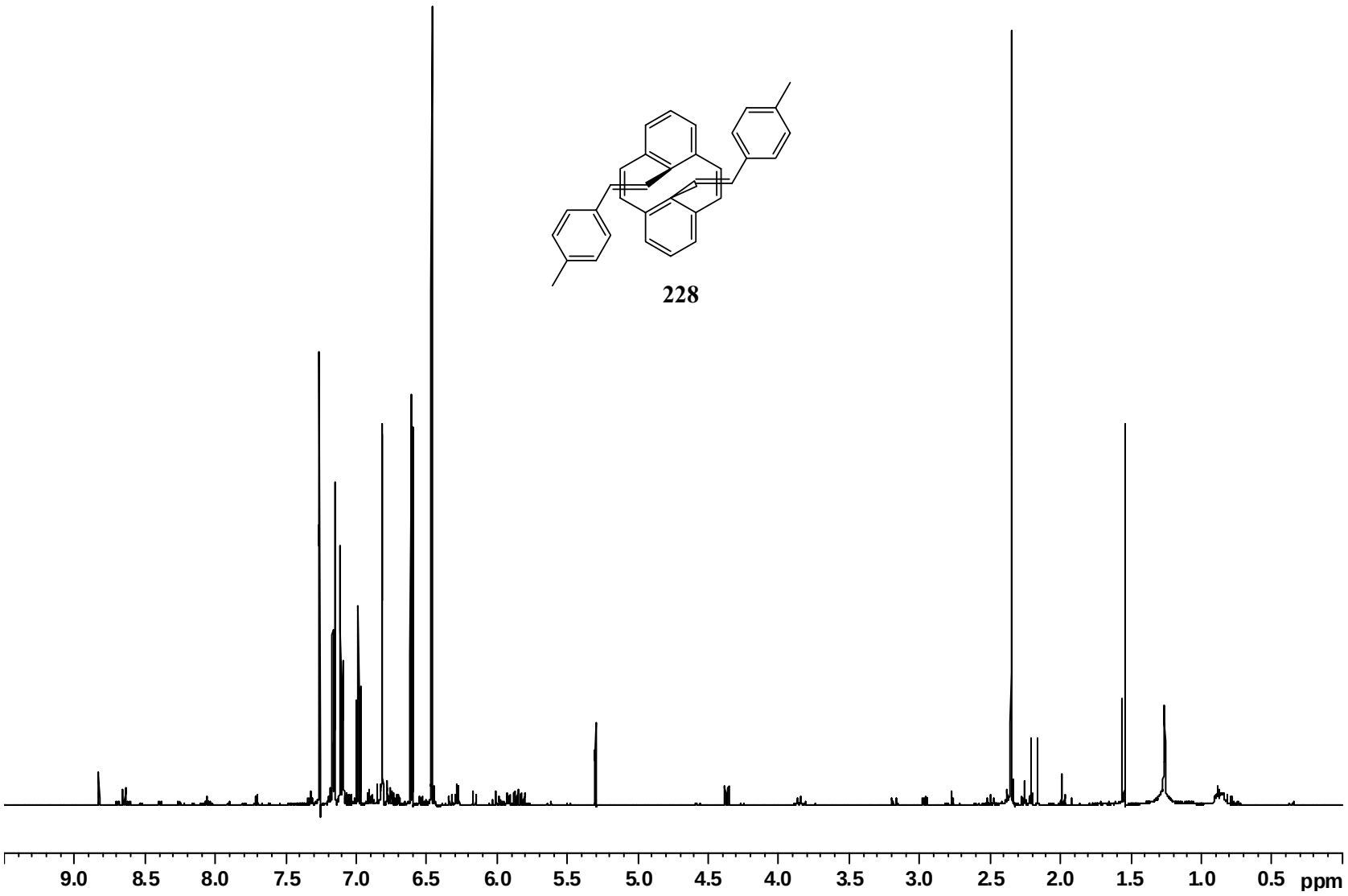


**226**

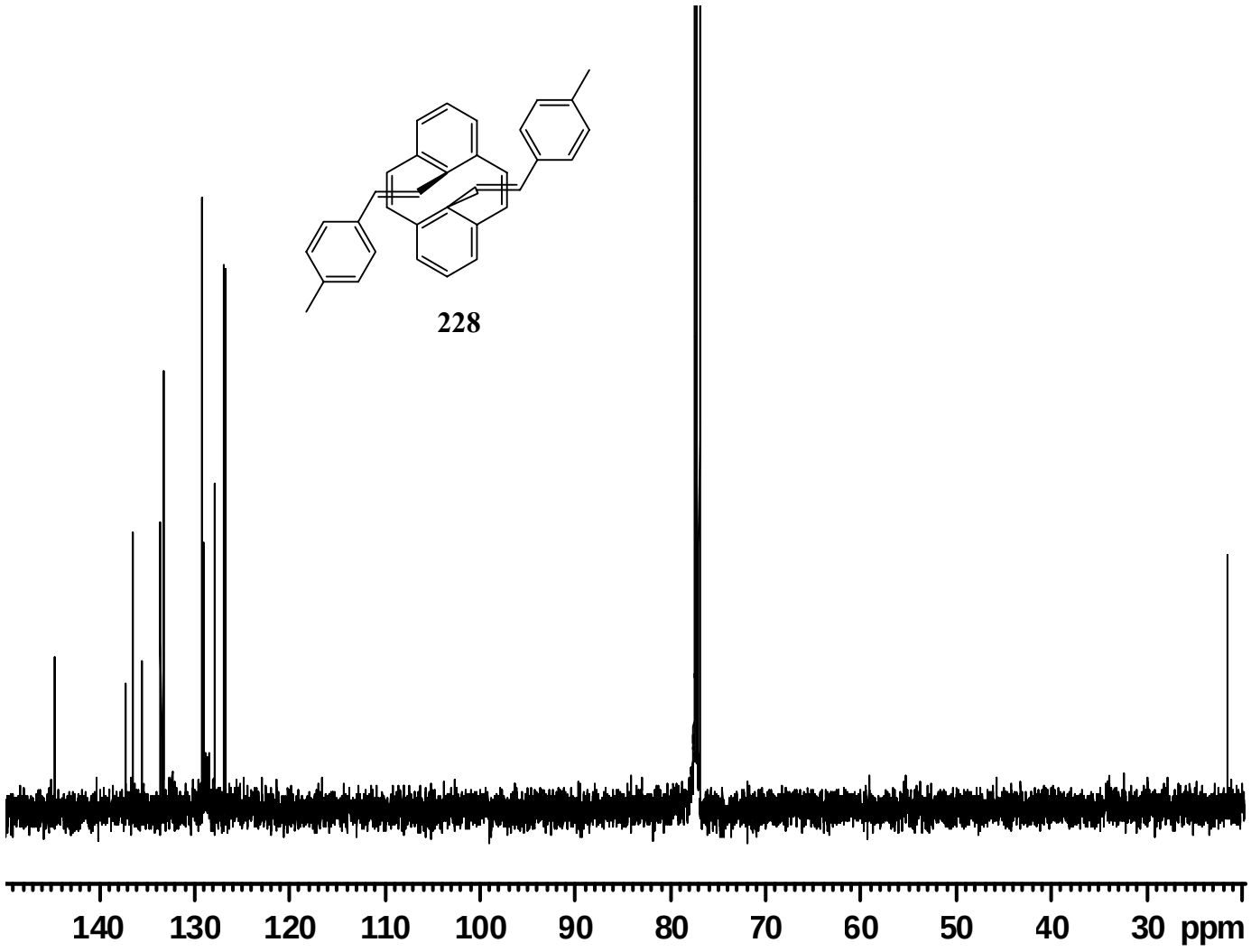

227
7.0
6.8
6.6
6.4
6.2
6.0
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



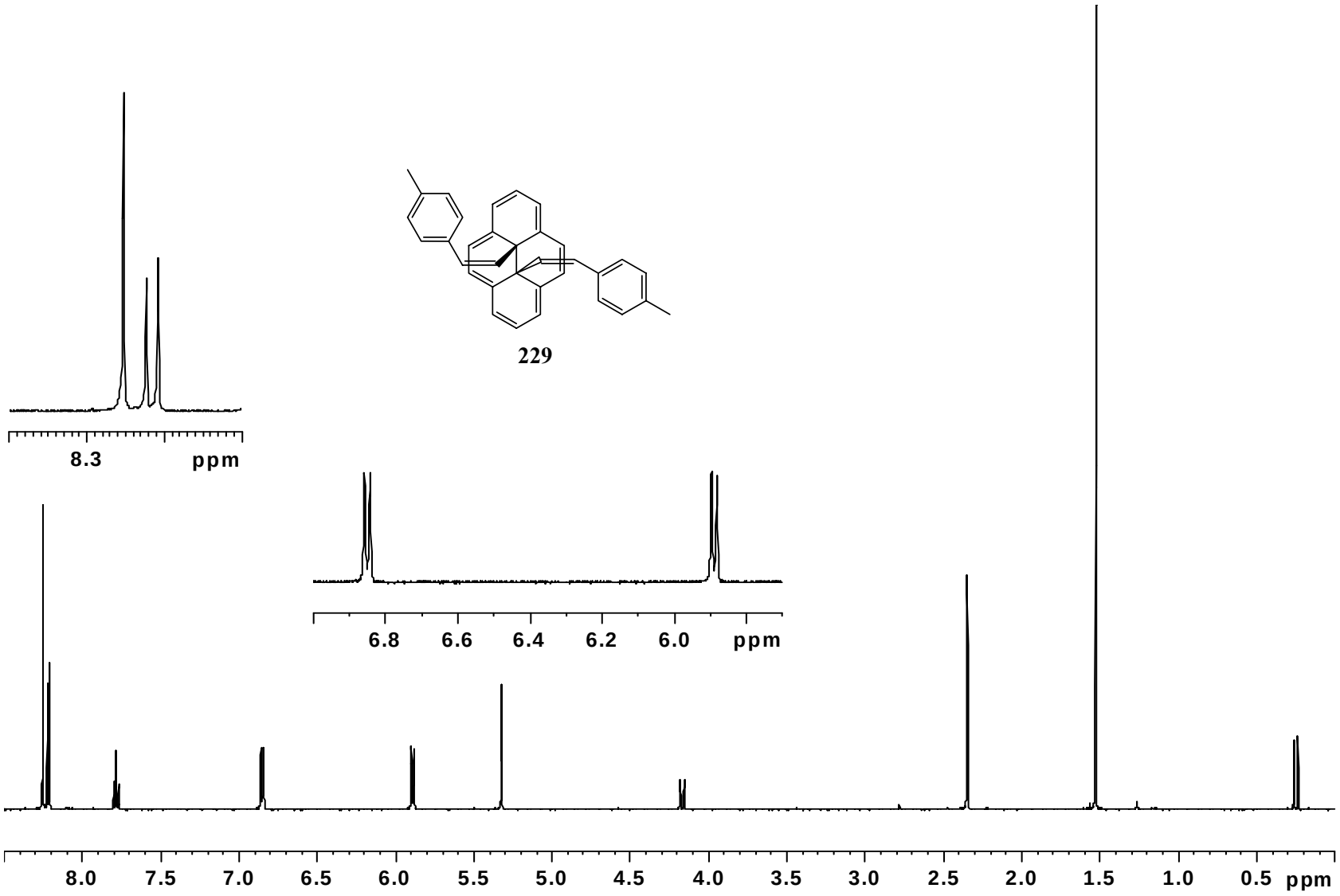

**227**



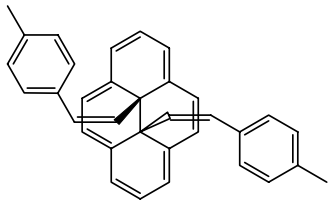

**228**



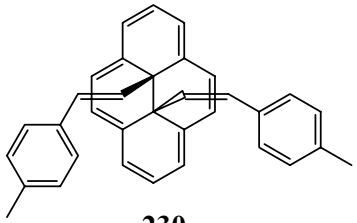

**228**


8.3
ppm
6.8
6.6
6.4
6.2
6.0
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

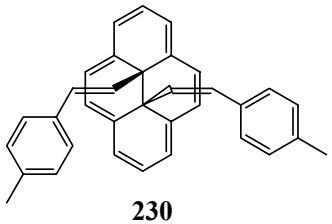
229



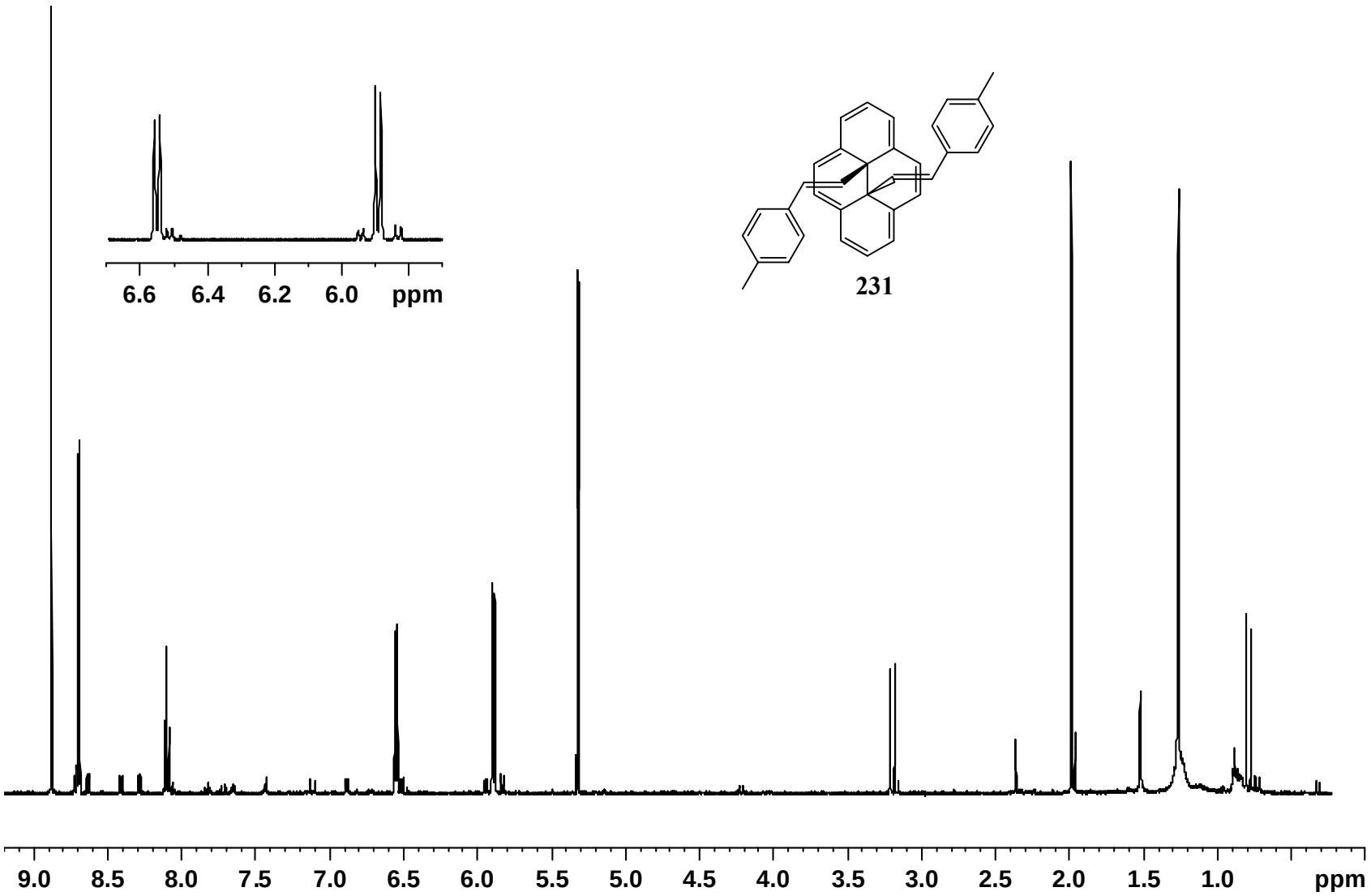
**229**

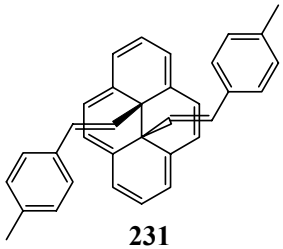


**230**

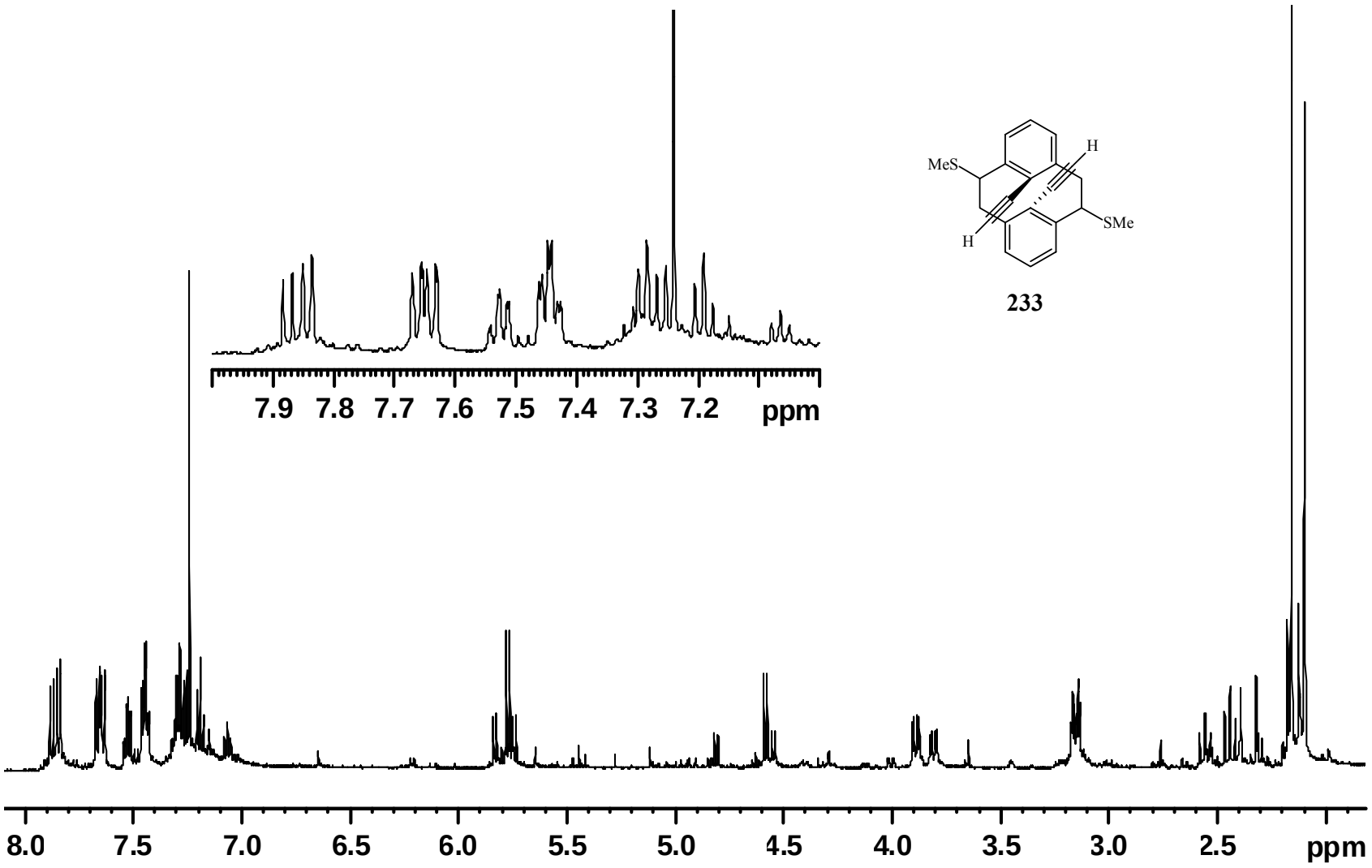


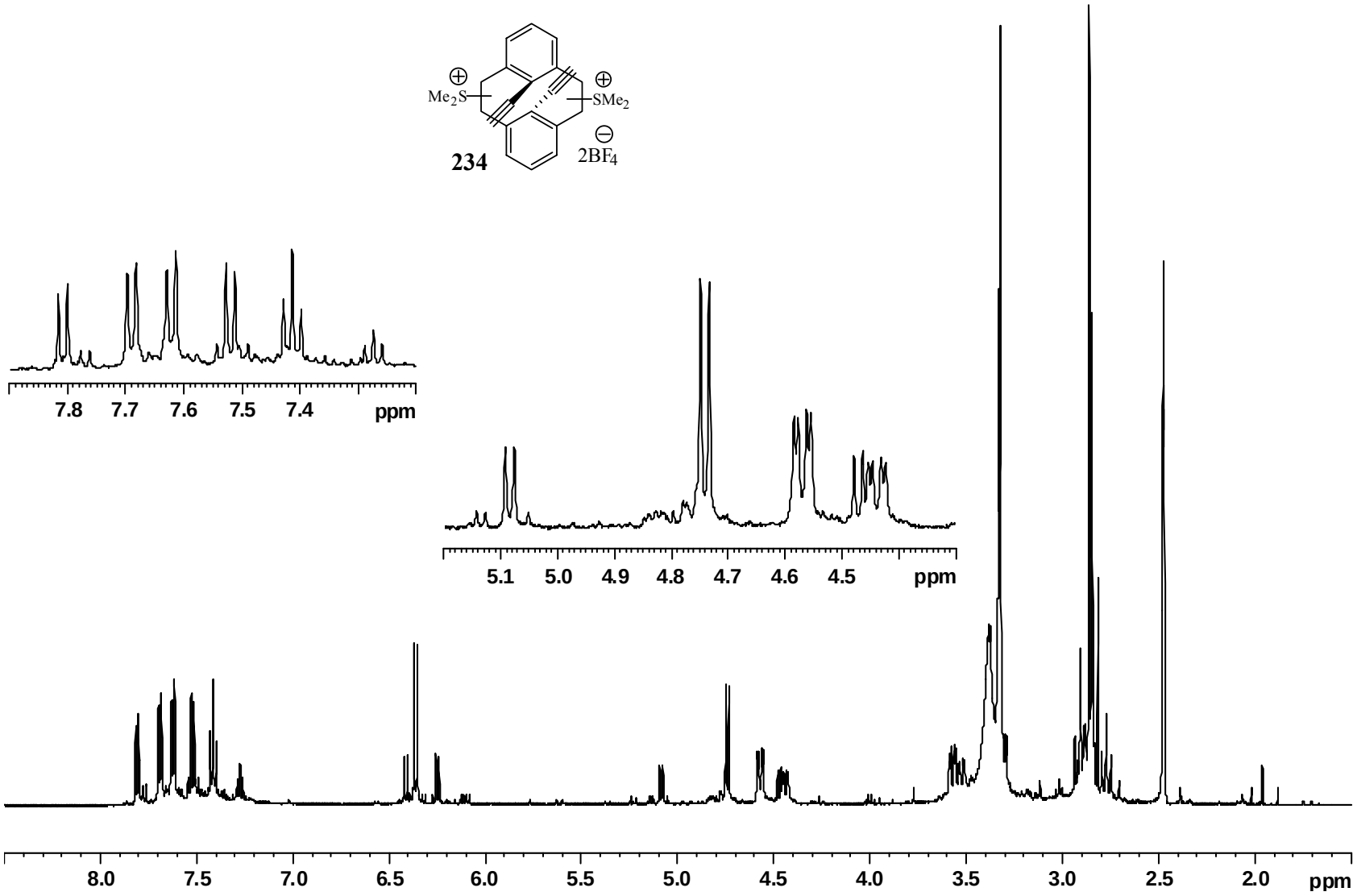
**230**

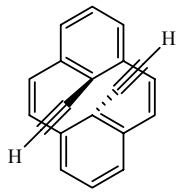

6.6
6.4
6.2
6.0
ppm
231
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm



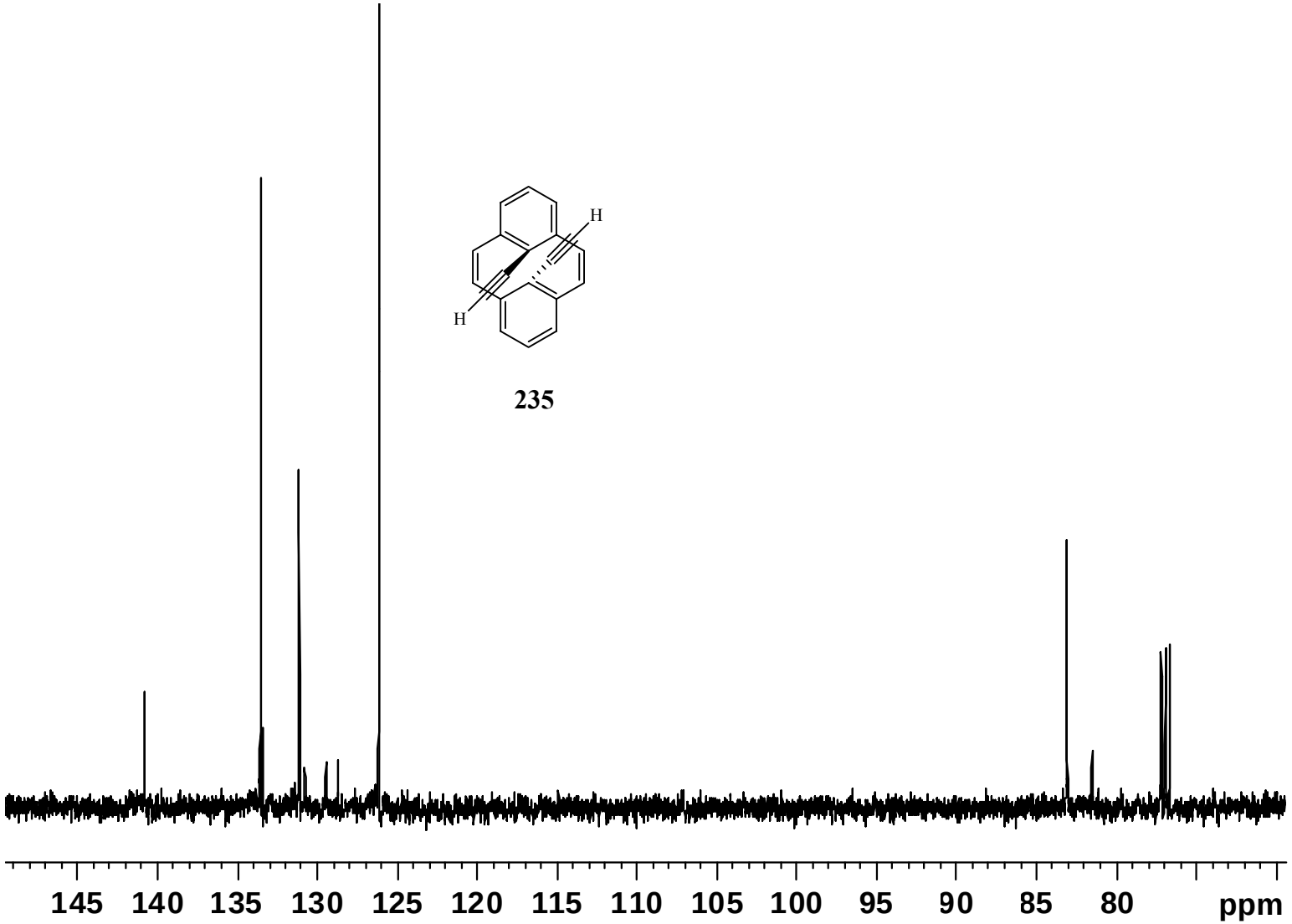
**231**


MeS
H
H
SMe
233
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm

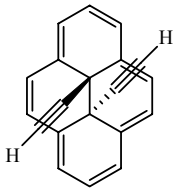

Me2S
SMe2
2BF4
234
7.8 7.7 7.6 7.5 7.4 ppm
5.1 5.0 4.9 4.8 4.7 4.6 4.5 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm



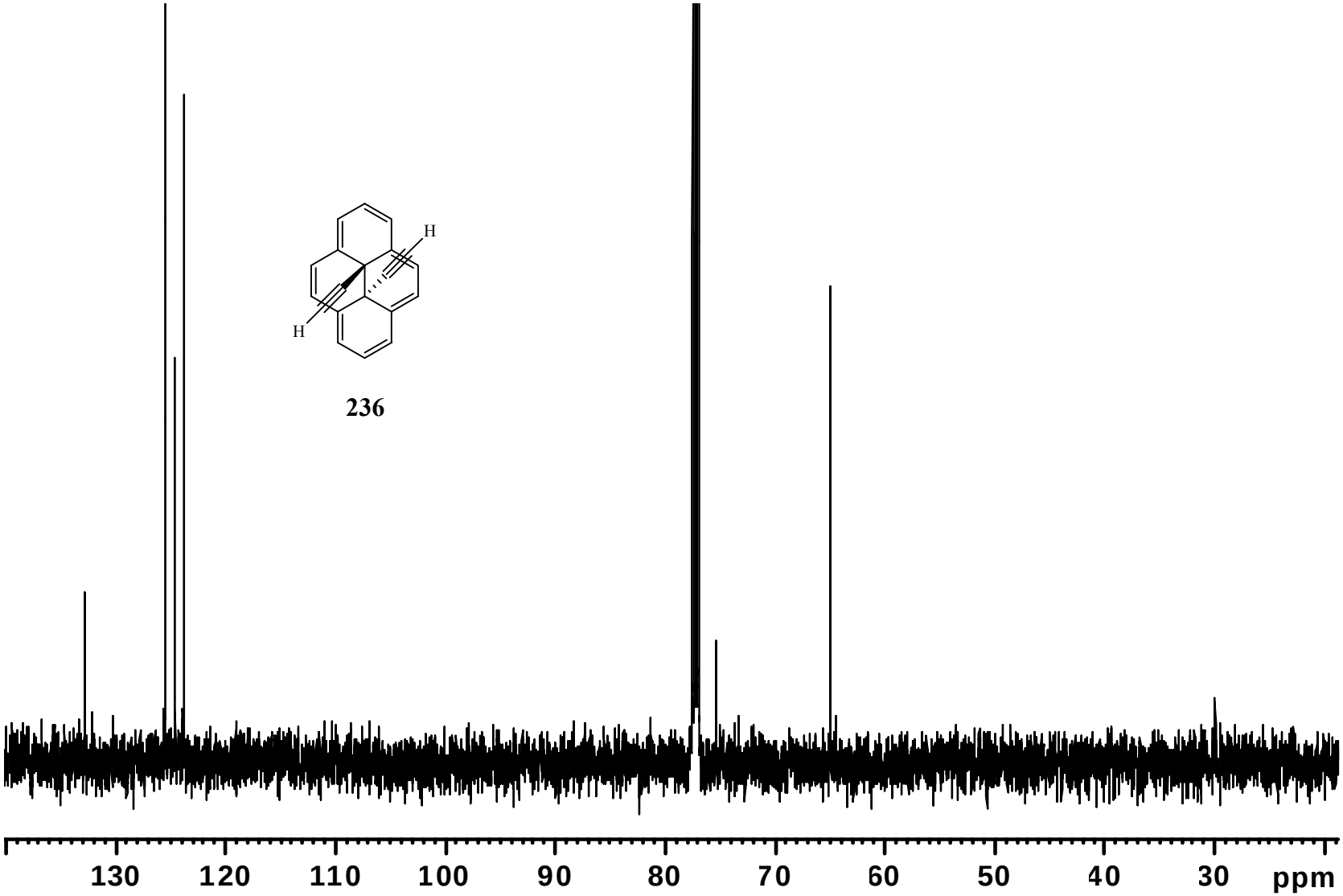

**235**



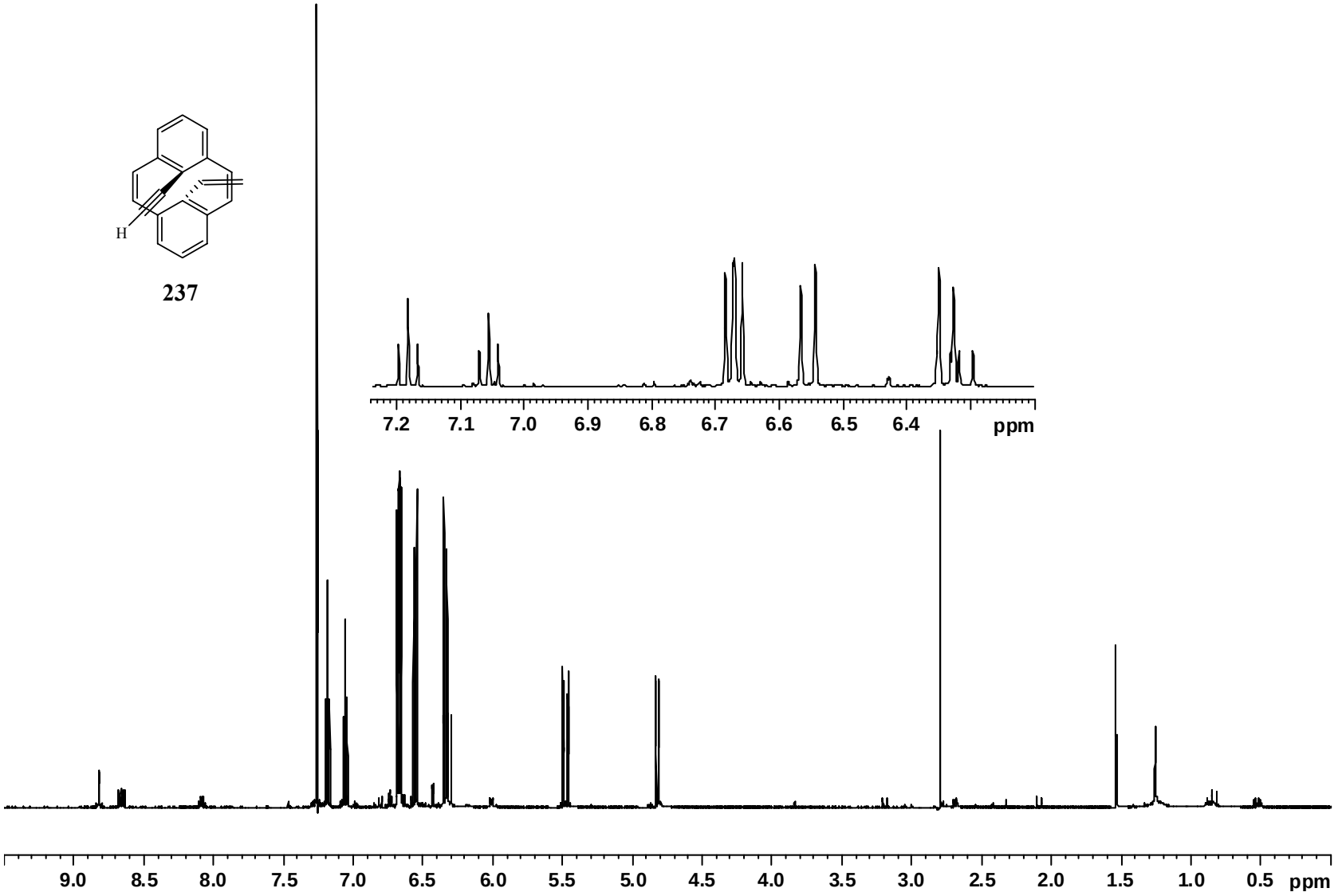

**235**

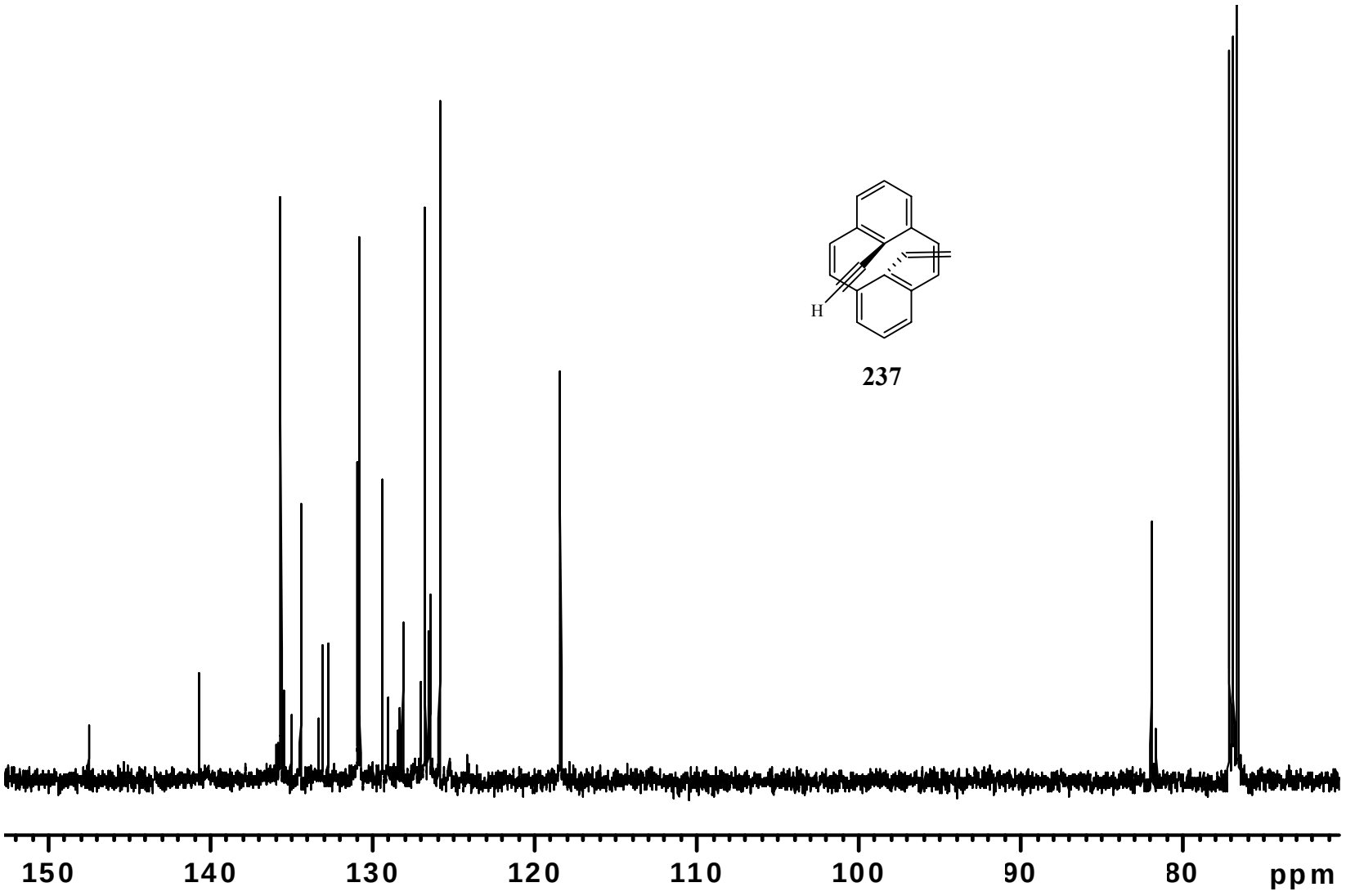



**236**

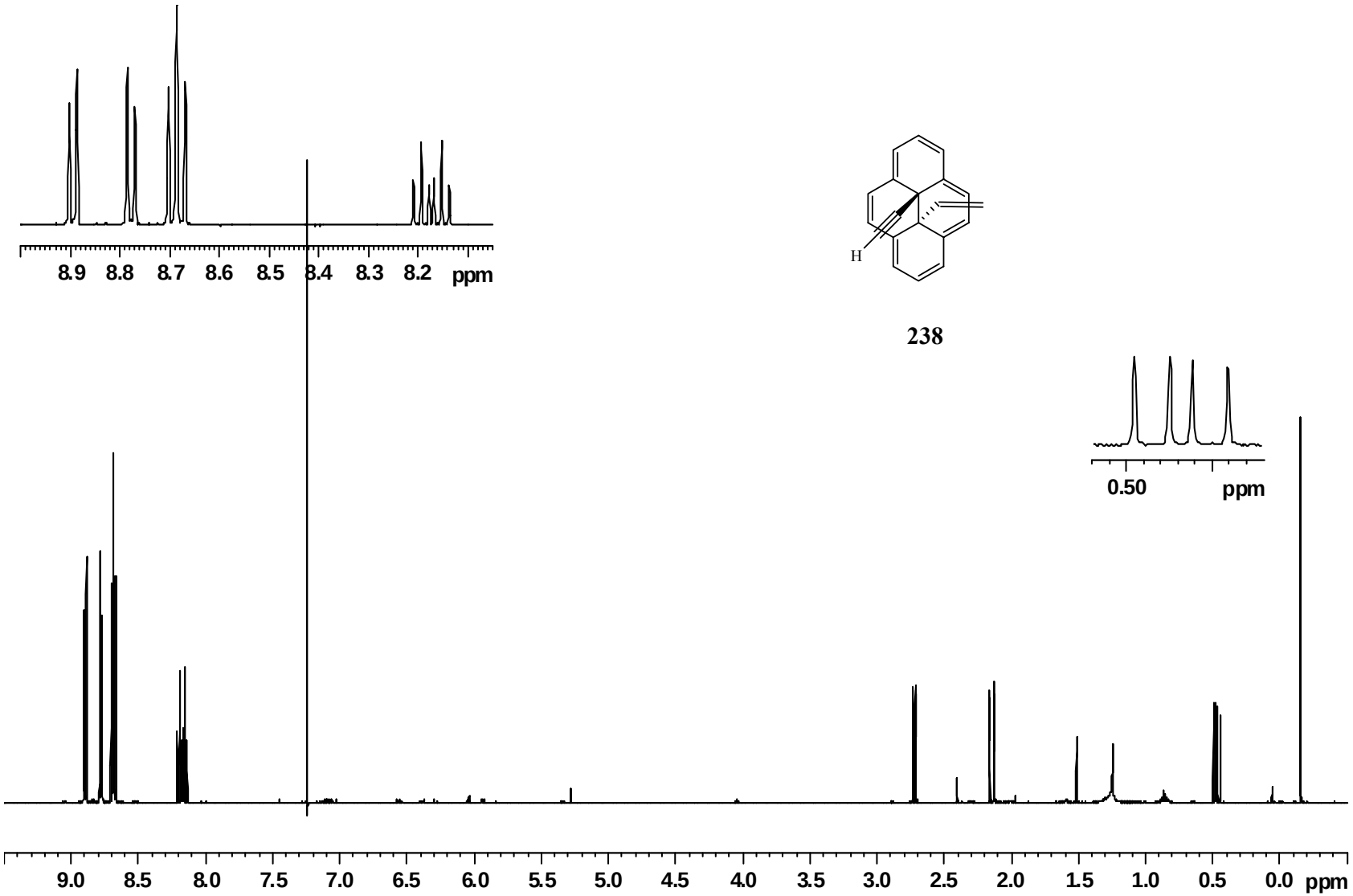



**236**

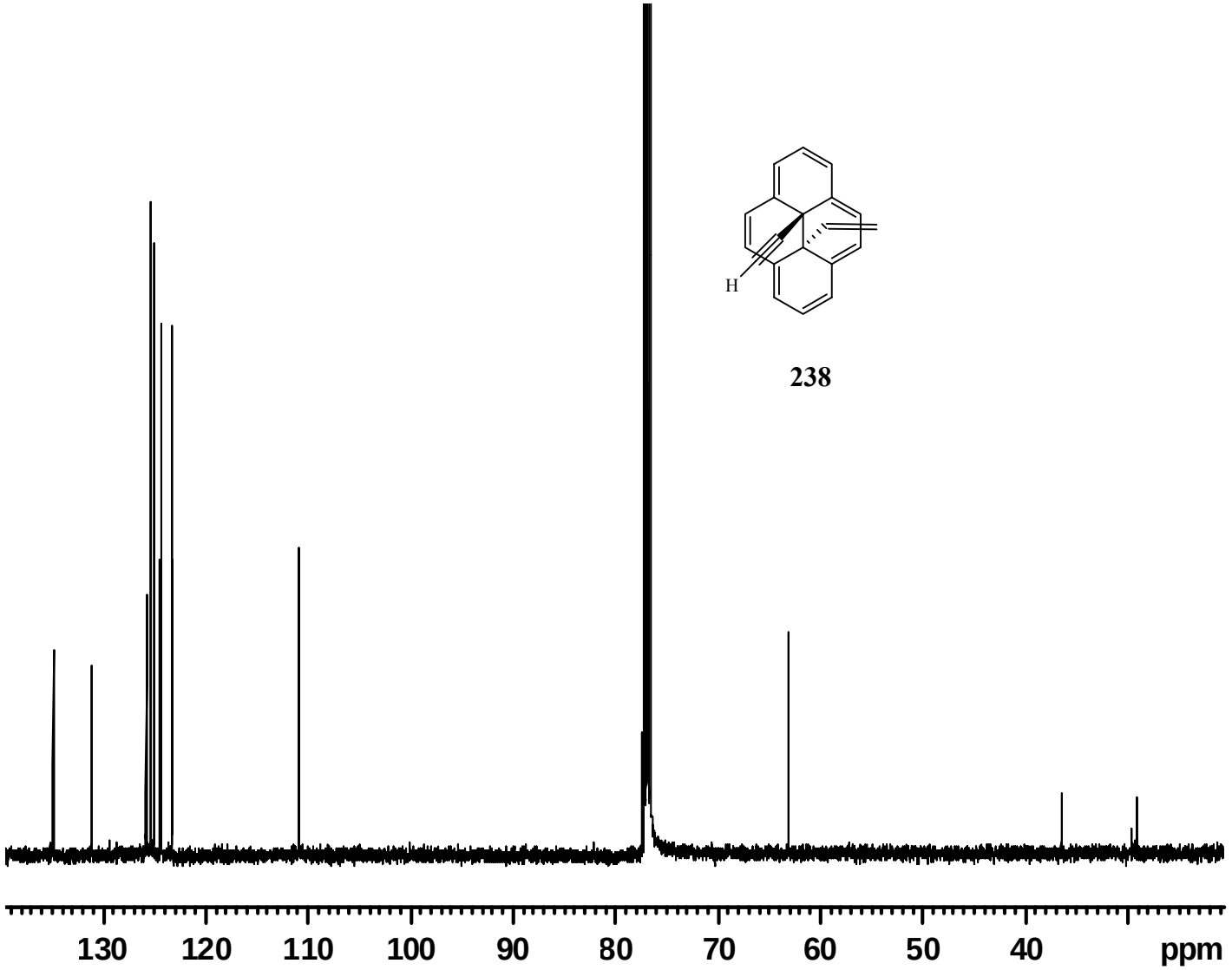

H
237
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



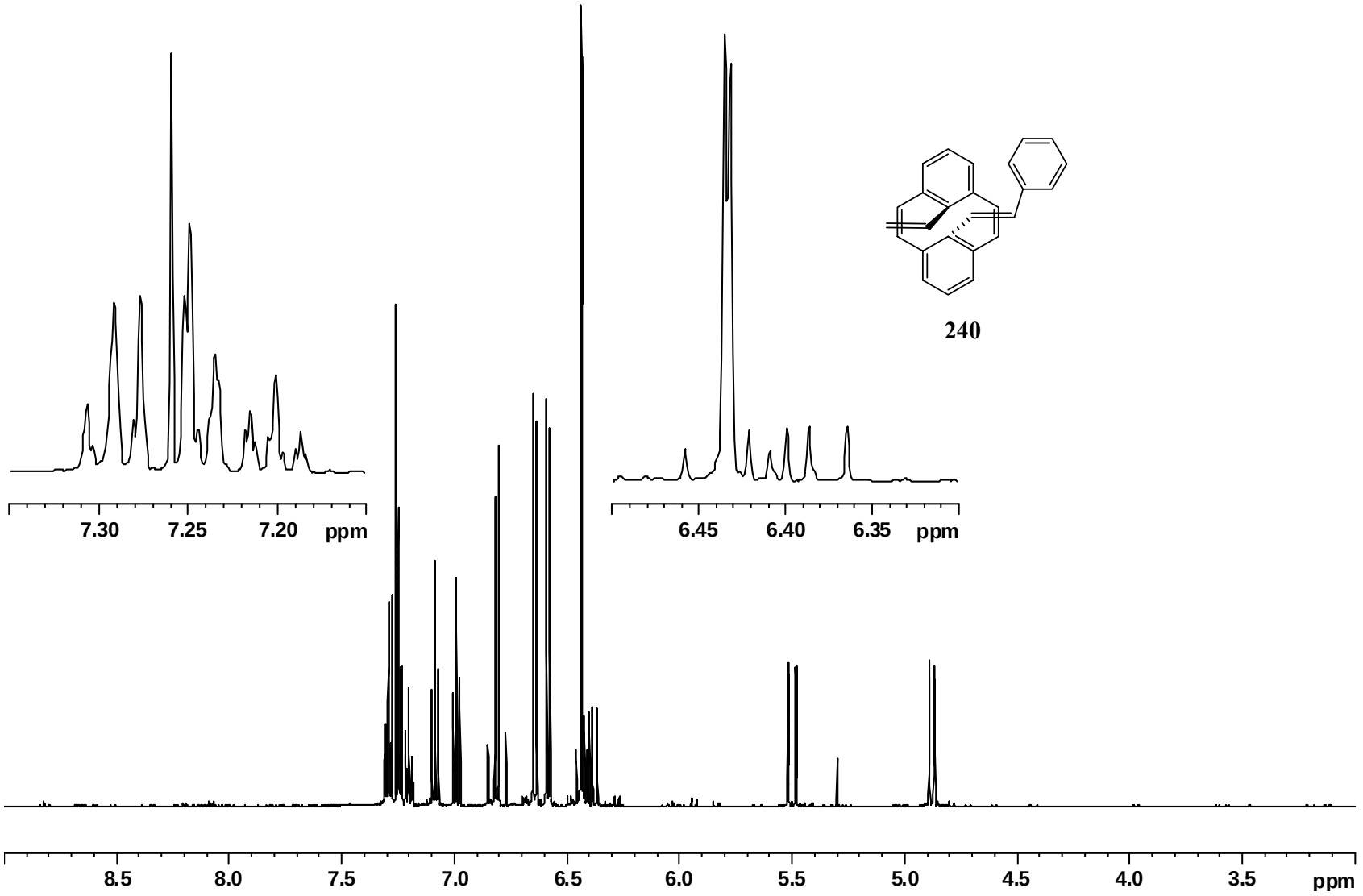

**237**


8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 ppm
H
0.50 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

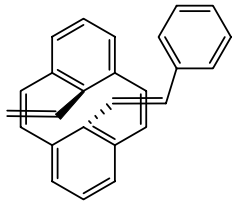
**238**




**238**

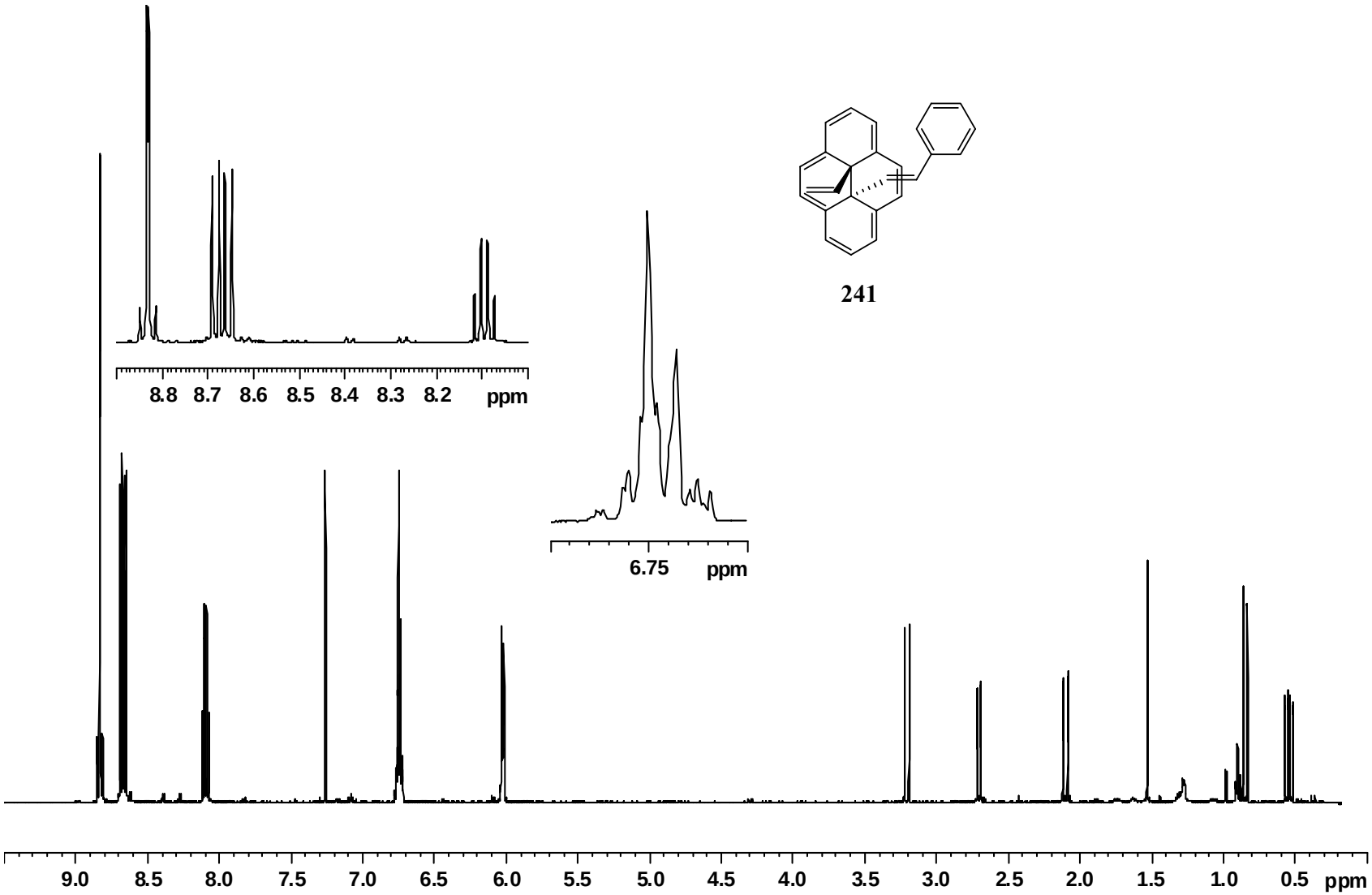



**240**

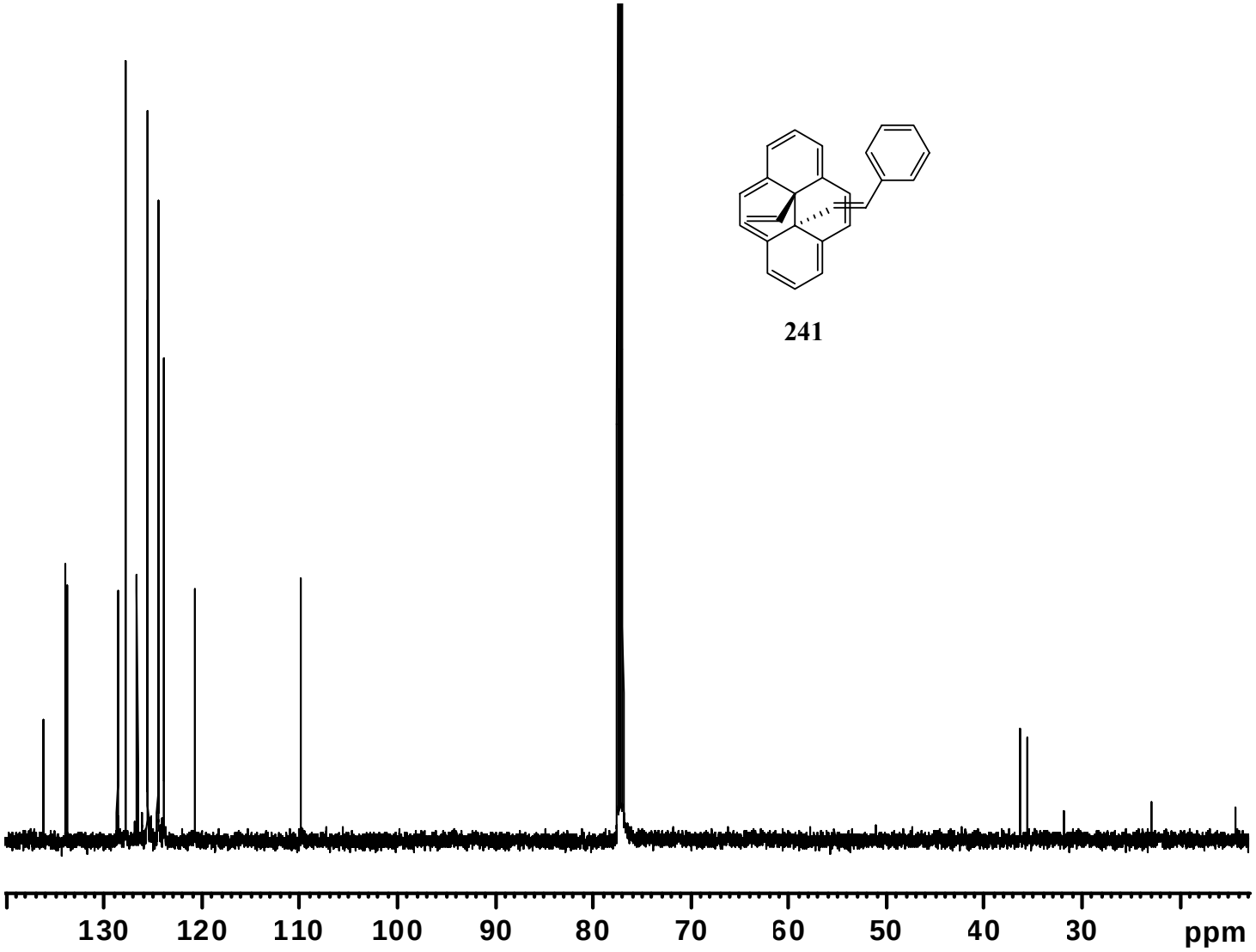


**240**

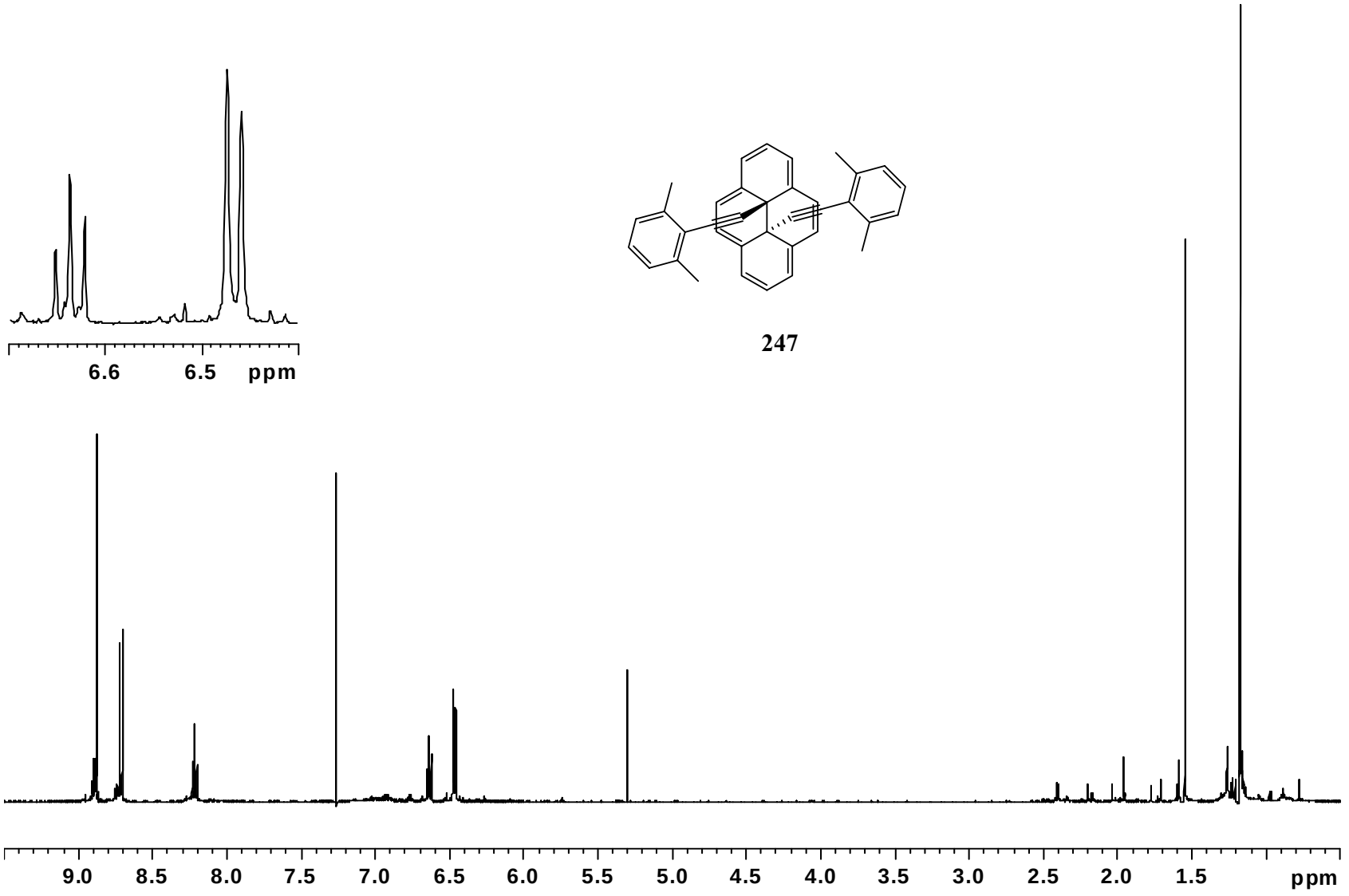

155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
ppm


8.8 8.7 8.6 8.5 8.4 8.3 8.2 ppm
6.75 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

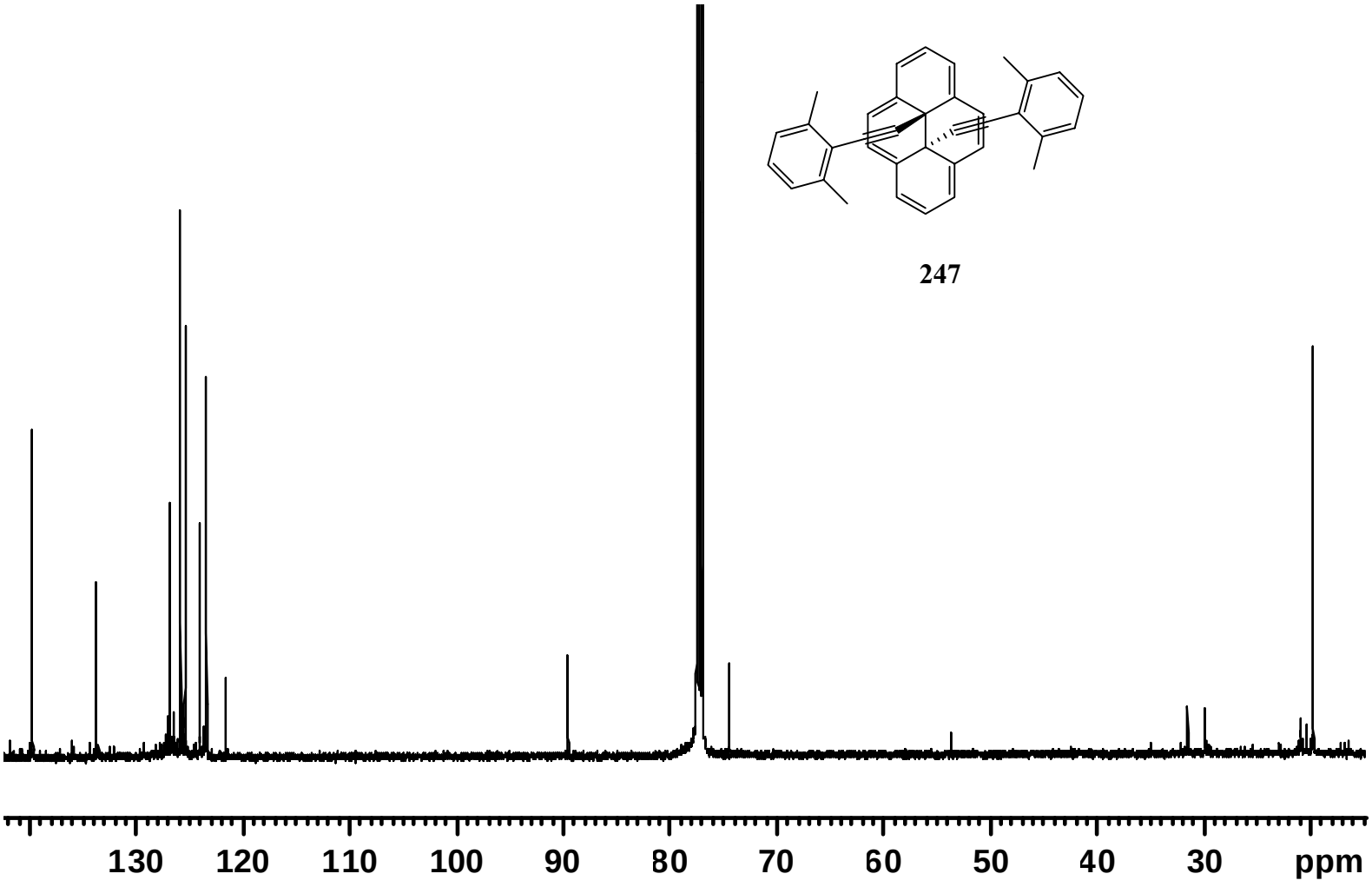
**241**



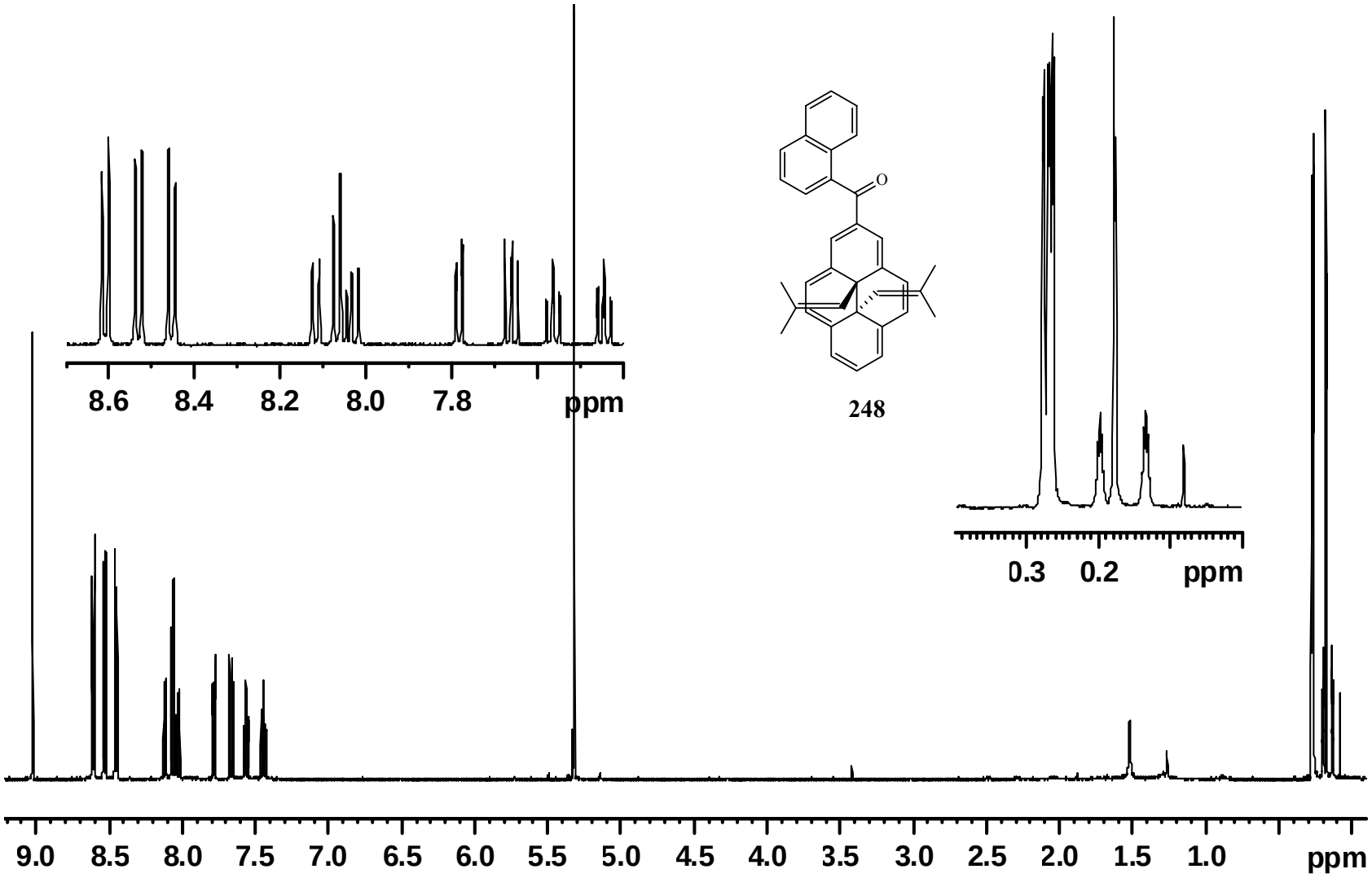

**241**

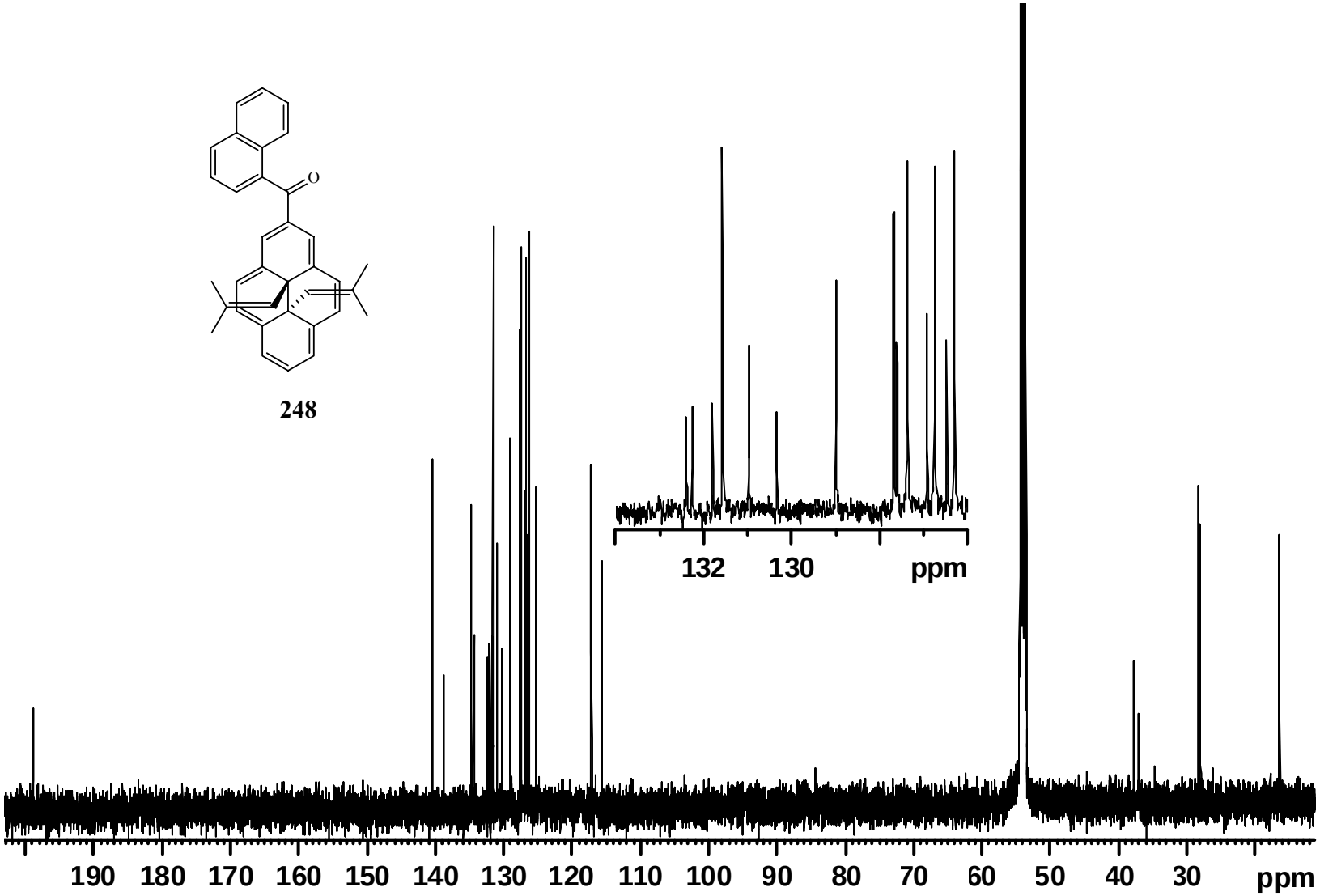


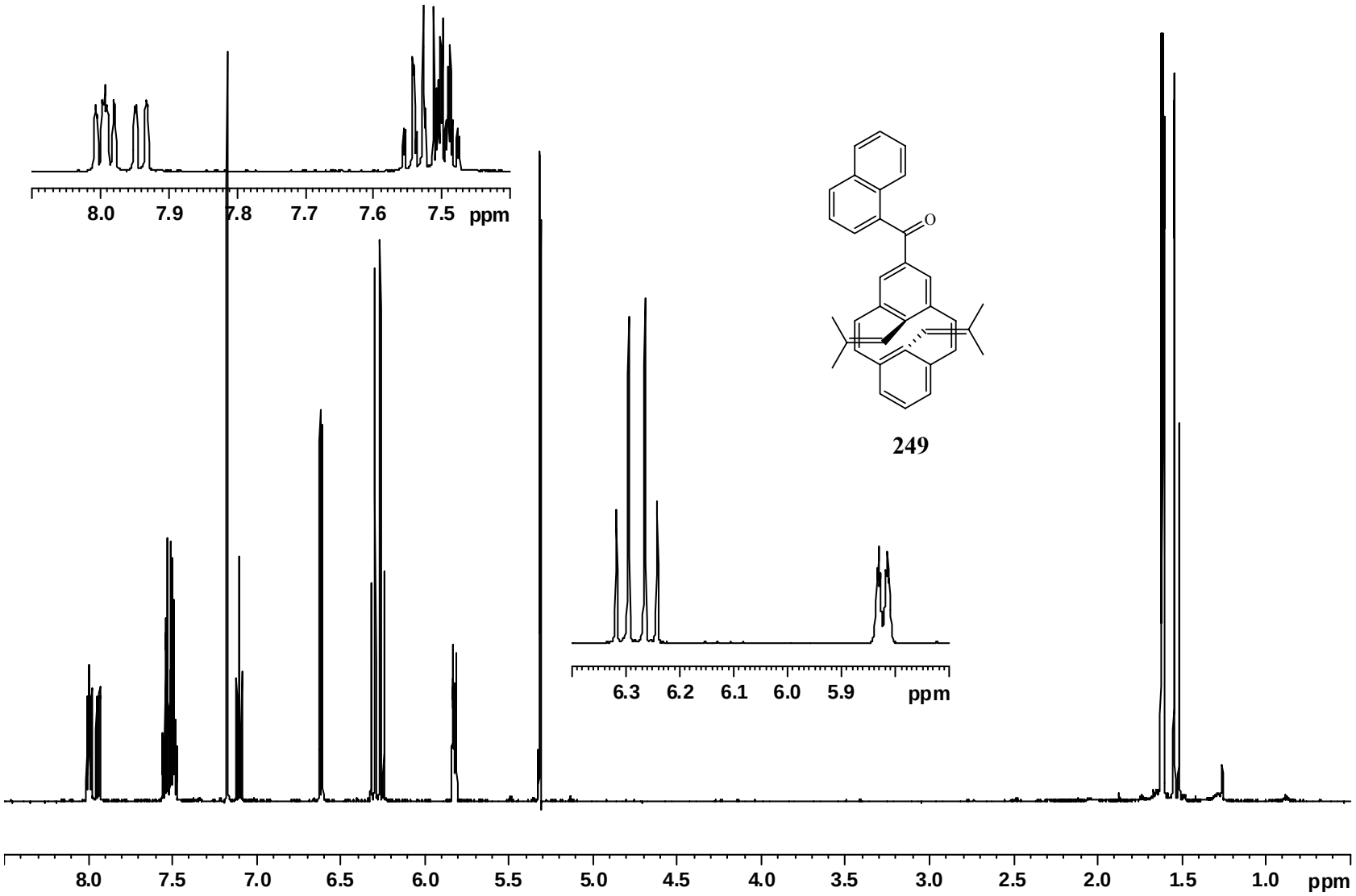

**247**

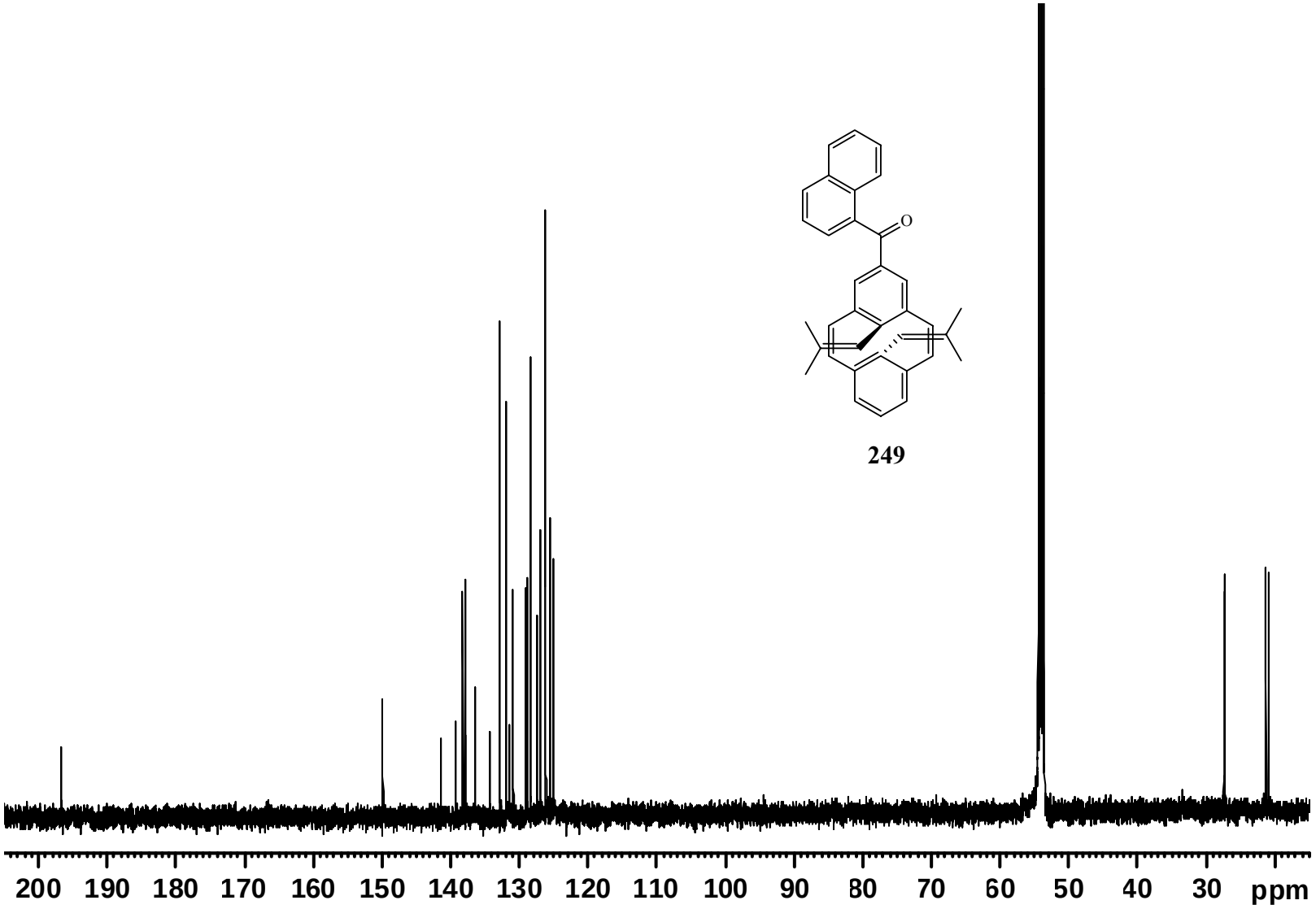



**247**

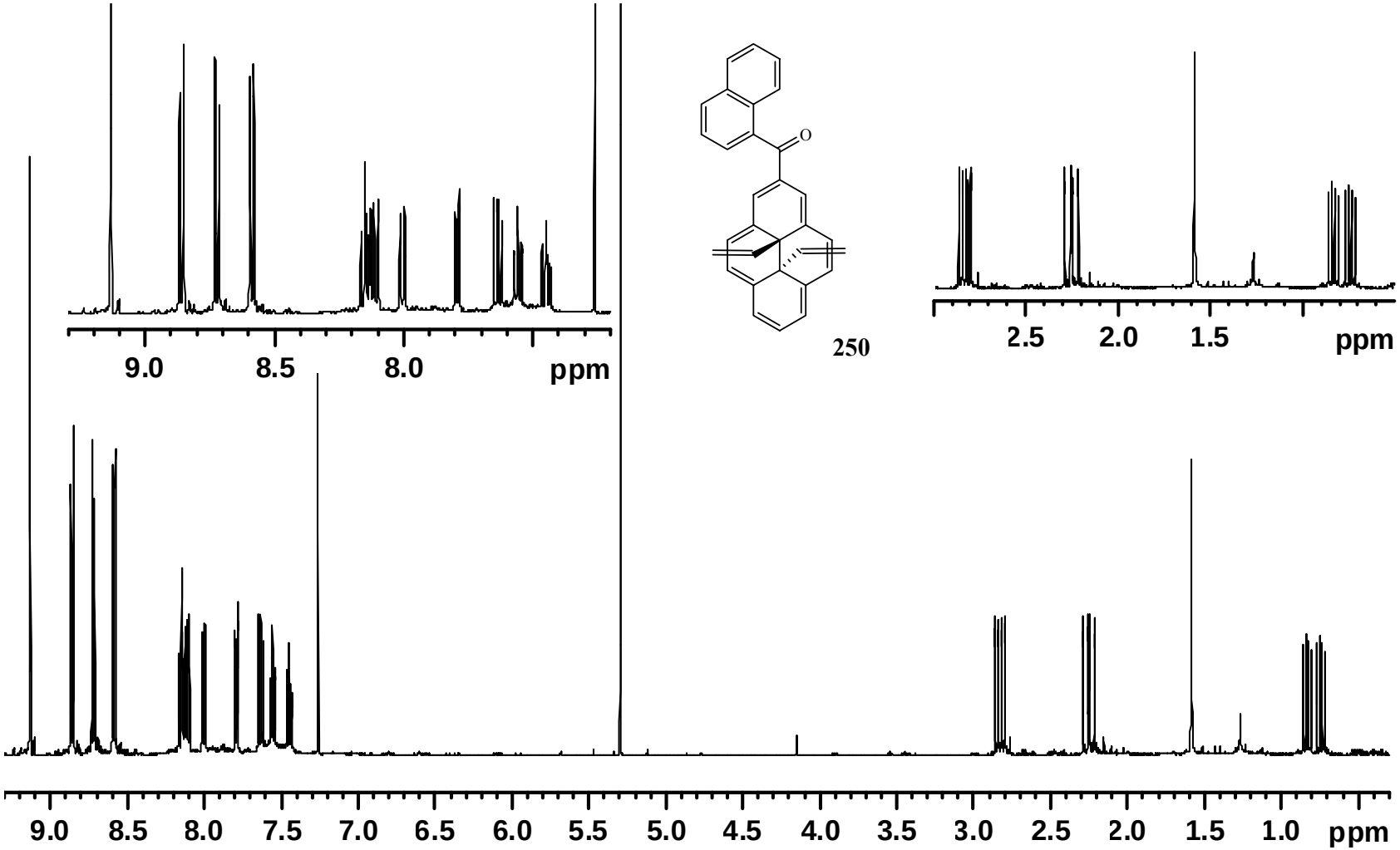

8.6
8.4
8.2
8.0
7.8
ppm
O
248
0.3
0.2
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

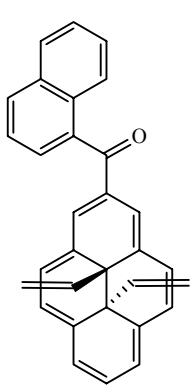

O
248
132
130
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


8.0
7.9
7.8
7.7
7.6
7.5
ppm
O
249
6.3
6.2
6.1
6.0
5.9
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

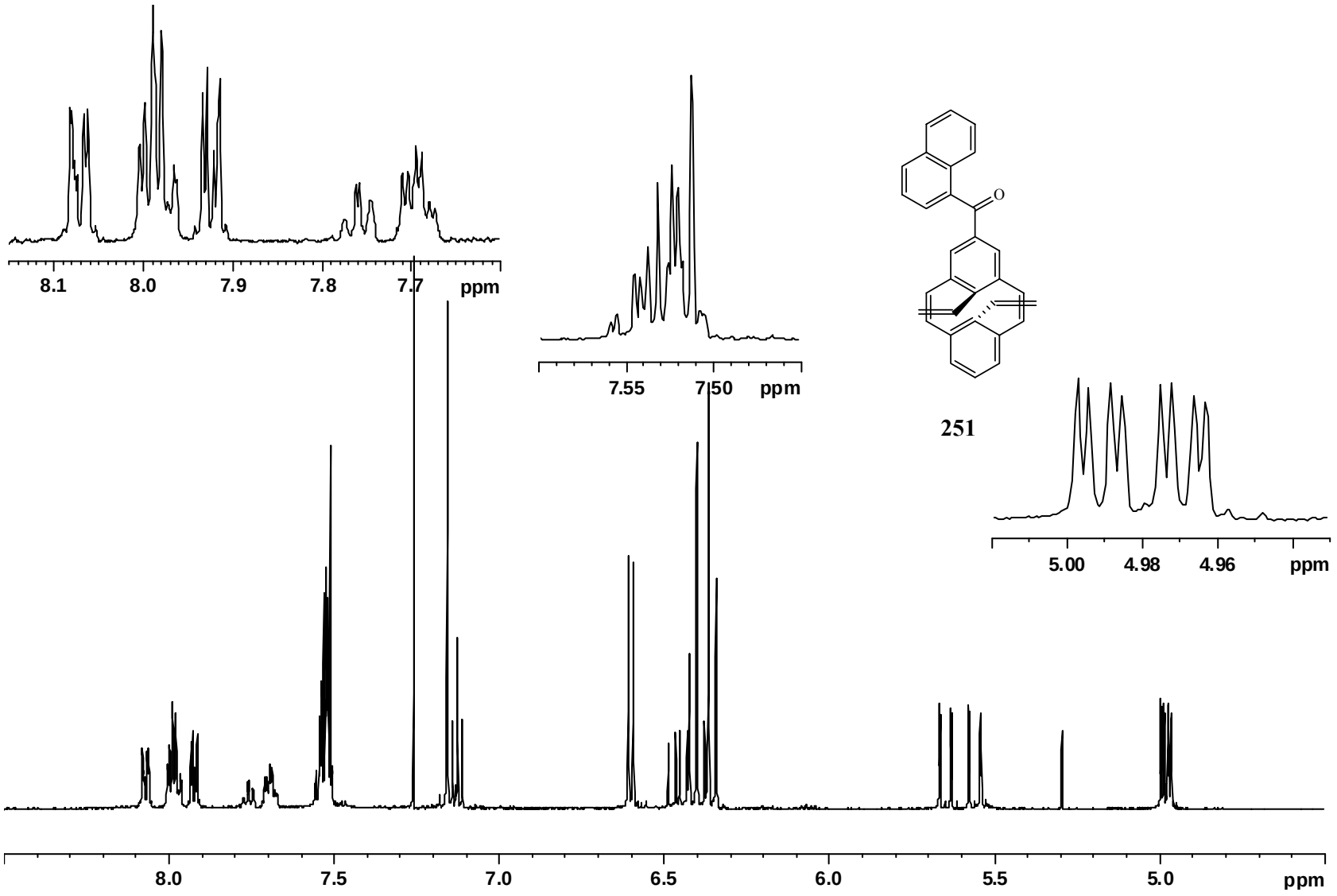

O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

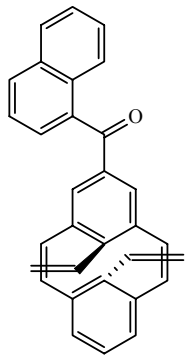
**249**


O
250
9.0
8.5
8.0
ppm
2.5
2.0
1.5
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

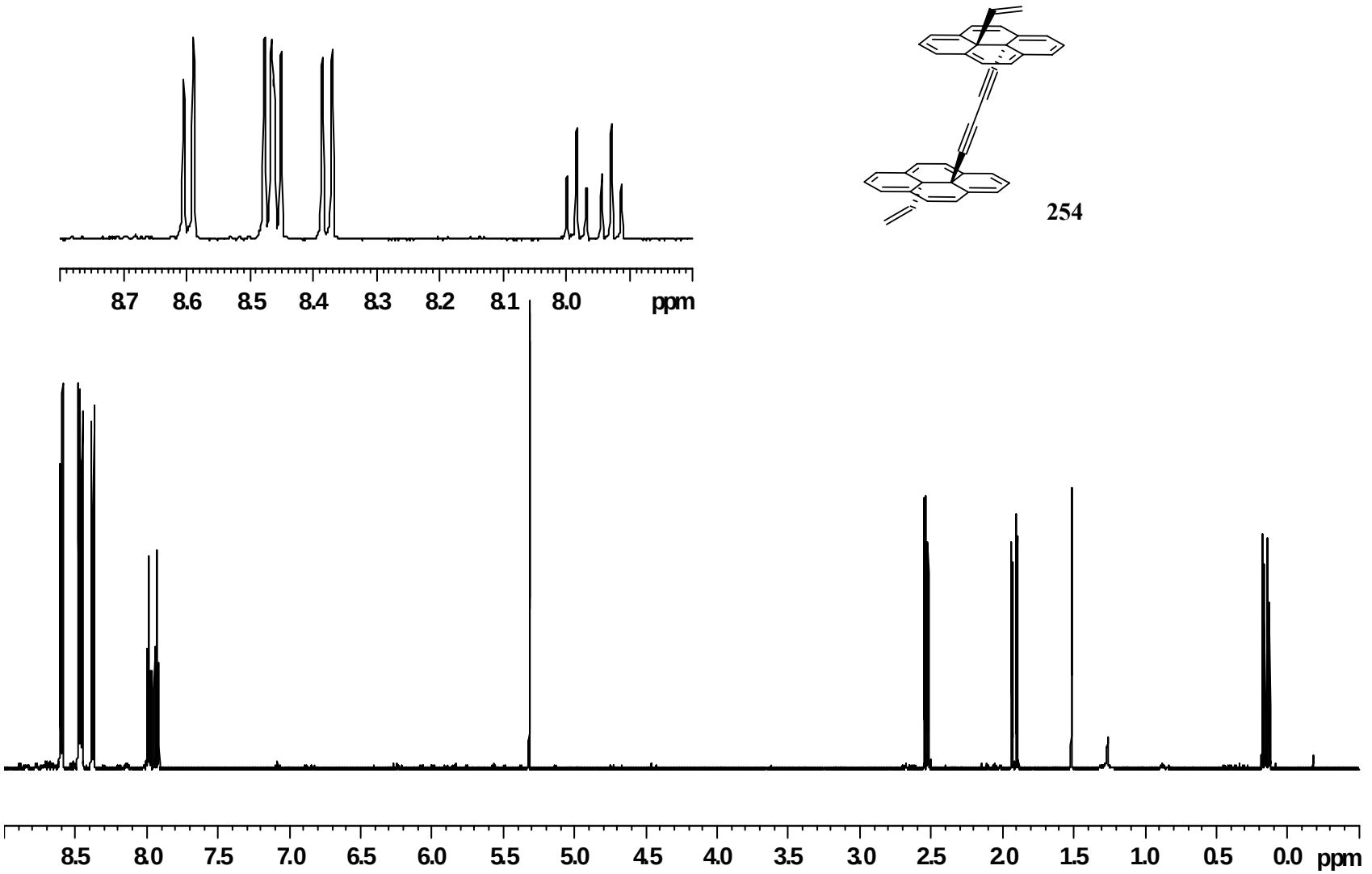



**250**

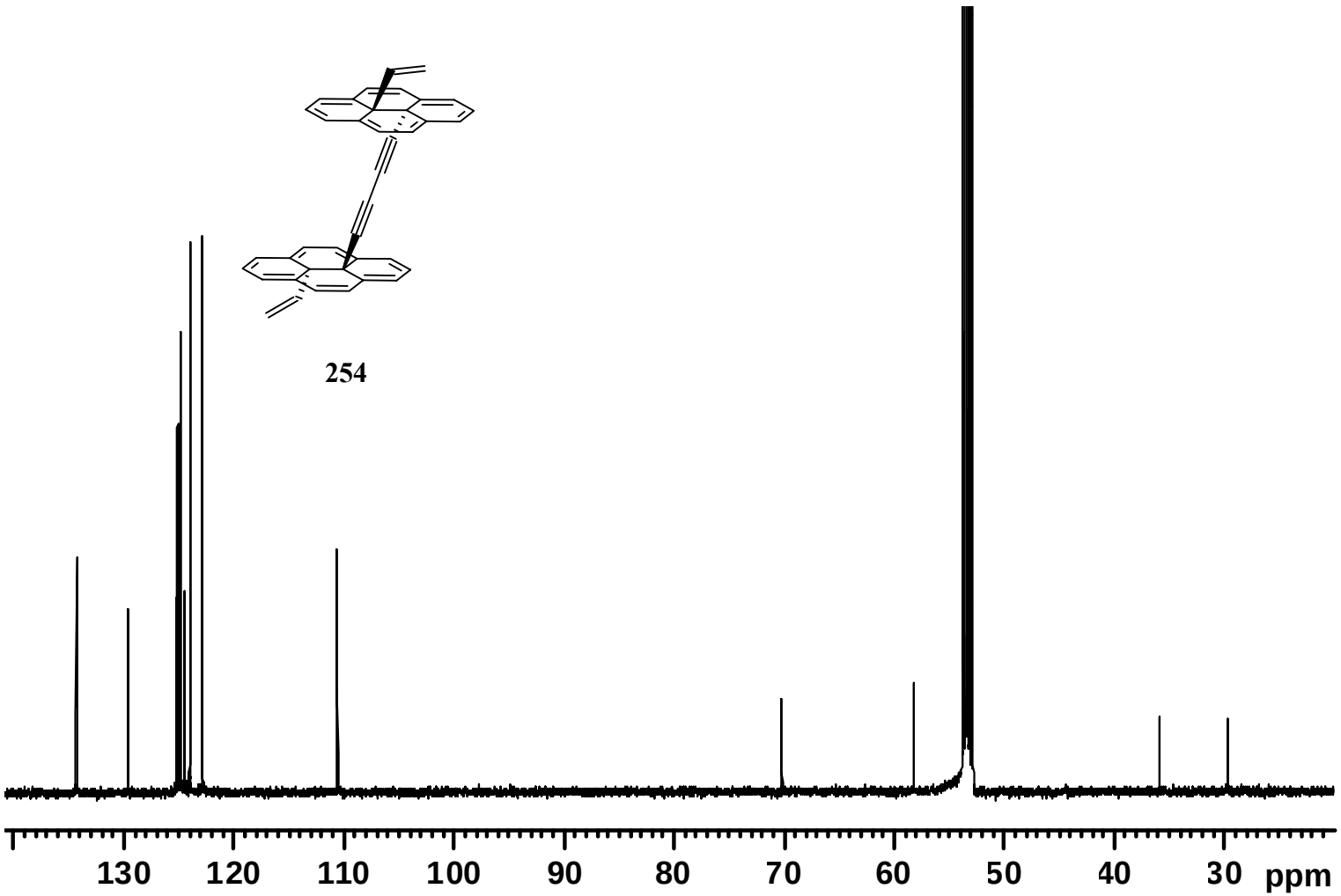

8.1
8.0
7.9
7.8
7.7
ppm
7.55
7.50
ppm
O
251
5.00
4.98
4.96
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm



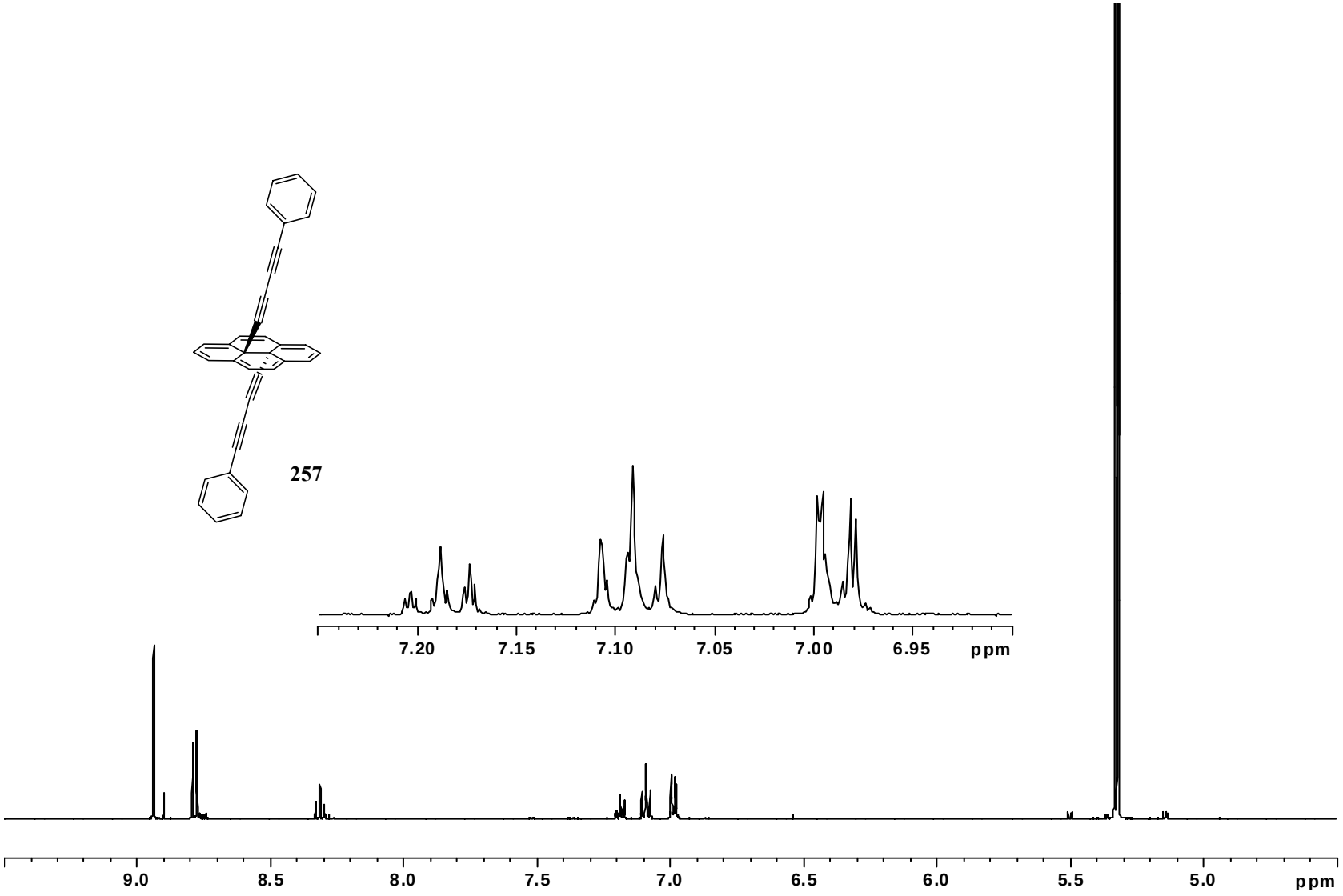

**251**

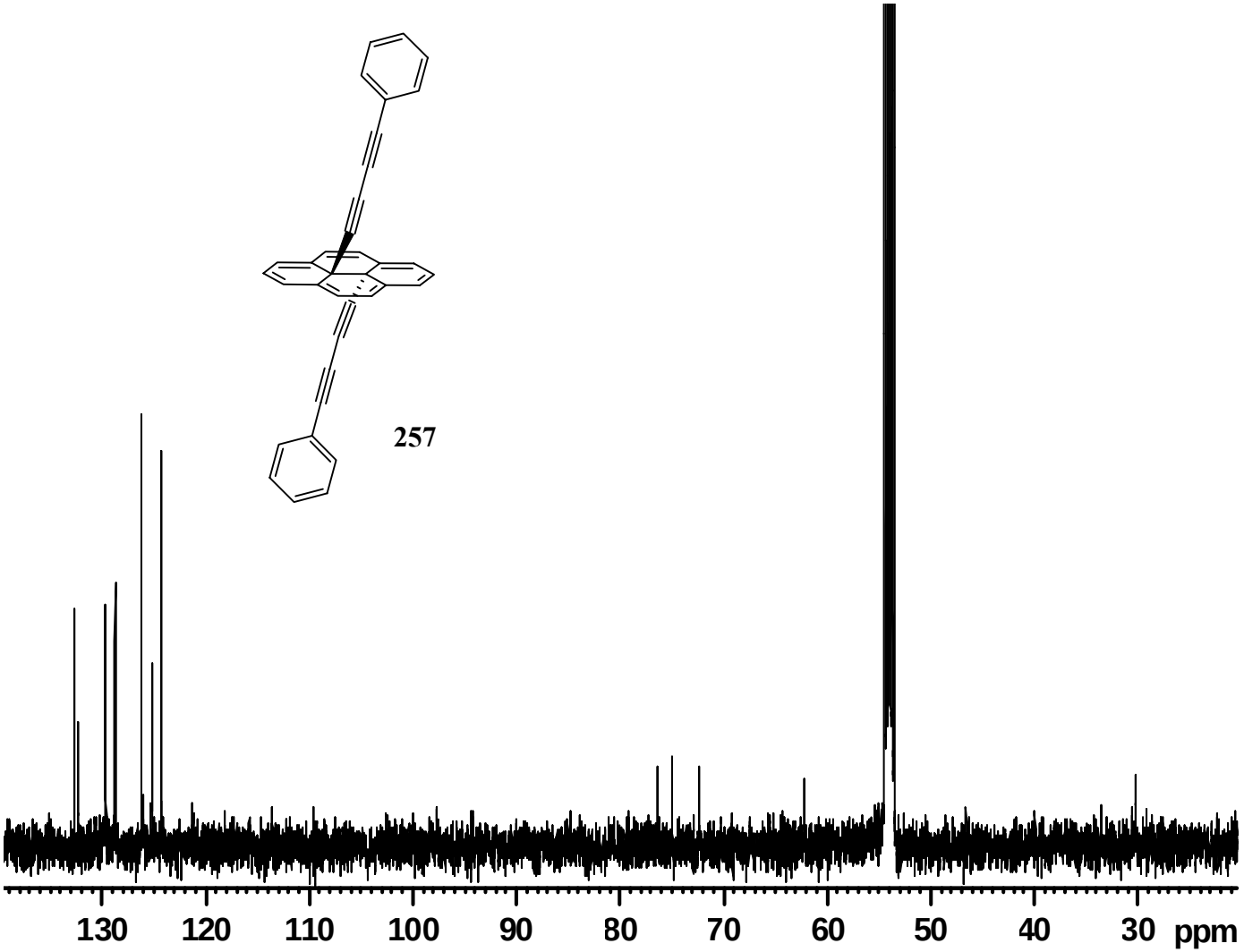

8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

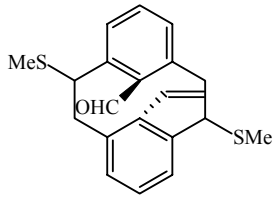
254



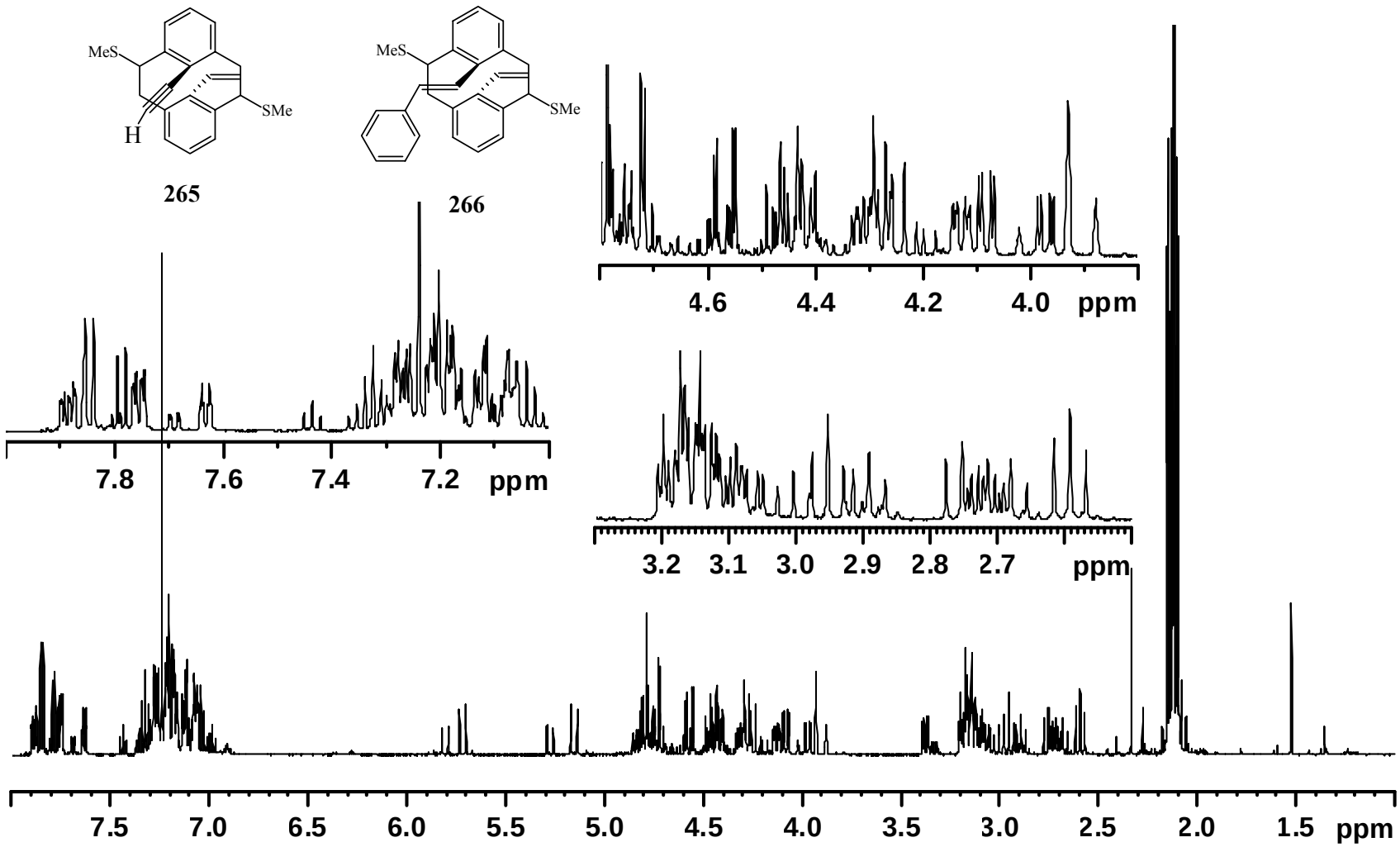

**254**

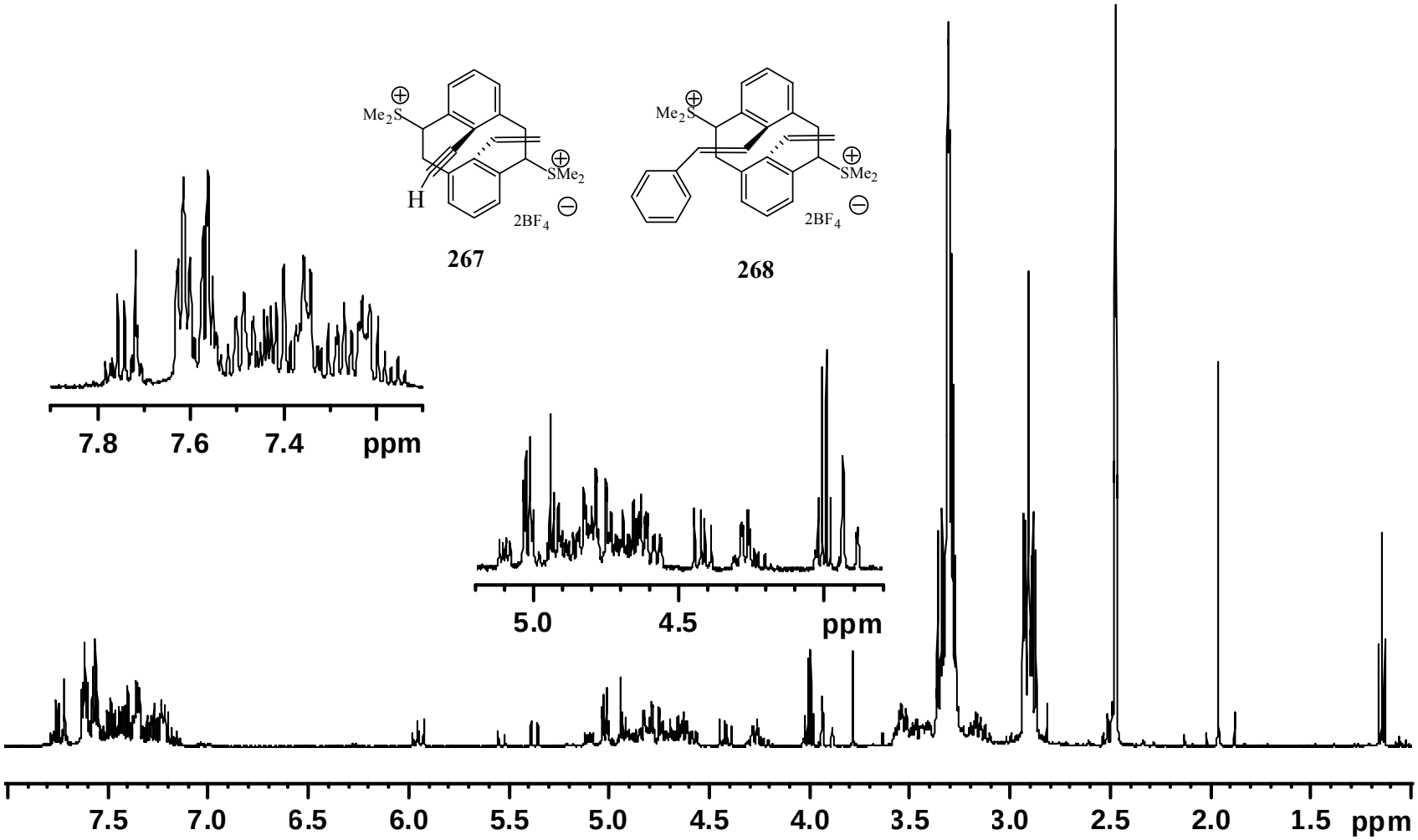

257
7.20
7.15
7.10
7.05
7.00
6.95
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm


257
130
120
110
100
90
80
70
60
50
40
30
ppm




**264**


MeS
SMe
H
265
MeS
SMe
266
7.8
7.6
7.4
7.2
ppm
4.6
4.4
4.2
4.0
ppm
3.2
3.1
3.0
2.9
2.8
2.7
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


Me2S
SMe2
H
2BF4
267
Me2S
SMe2
2BF4
268
7.8
7.6
7.4
ppm
5.0
4.5
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm