

Ring-Expansion and Ring-Opening of Phosphorus-Containing Heterocycles

by

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Abstract

This thesis describes the synthesis of phosphorus-rich heterocyclic frameworks through the ring-expansion of cyclic phosphanes, which we demonstrate as a method to access structure-colour correlation and switchability as well as newly accessible P_3C and P_3CO frameworks. Investigations into the synthesis of and physical properties of hybrid phosphonate-siloxane heterocycles for the design of new P-O-Si-O polymers through ROP are also described, alongside investigations into the electronic and steric stabilization of phosphonate moieties with the goal of minimizing dynamic covalent behaviour in phosphonate-containing rings and polymers.

Chapter 1 gives an overview of silicon and phosphorus chemistry from elements to heterocycles, covering ring expansions and ring-opening polymerizations of silicon and phosphorus heterocycles, and reviewing strategies to accessing new main group polymers.

Chapter 2 describes the acid-mediated ring-expansion of sterically encumbered cyclic phosphanes with nitriles, the structural characterization of the bent rings, and the change of the electronic structure induced by the ring-bending which allows for a charge transfer to occur.

Chapter 3 describes the investigation into the substrate scope of acid-mediated ring-expansion of $(t\text{-BuP})_3$, which was found to be limited to substrates which bear an exocyclic nitrogen which acts as a Lewis base to activate substrates upon protonation. Structural characterization of cationic and neutral cycloaddition products of xylyl isonitrile and *tert*-butyl isocyanate, the latter of which forms a novel P_3CO framework, are described, as are electronic effects on substrate specificity and a discussion of substrates which did not provide selective addition.

Chapter 4 describes the synthesis and characterization of hybrid phosphonate-siloxane heterocycles, and their physical characterization as relevant to accessing the ability of the rings

to undergo thermal ROP. Rings lacking kinetic stabilization are found to be dynamic in solution. The least sterically hindered of these rings were found to form polymeric material upon heating, while more sterically hindered derivatives did not undergo ROP. Our preliminary studies into preventing observed dynamic behaviour through electronic and steric modification of phosphonate moieties are also described.

Chapter 5 provides an outlook for the work in this thesis, with an overview of potential routes for future studies.

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protons except H1 have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.2557(7), P2-P3 2.2247(7), P1-N1 1.7767(16), P3-C1 1.8190(19), N1-C1 1.311(2), C1-C2 1.468(3), N1-H1 0.860, O2_1-H1 1.984, P1-C38 1.8295(19), P2-C23 1.8410(19), P3-C8 1.8318(19); P1-N1-C1 123.15(13), P3-C1-N1 114.76(14), P1-P2-P3 85.76(2), P2-P1-N1 89.70(5), P2-P3-C1 92.35(6), P2-P3-C8 104.12(7), C1-P3-C8 111.56(9), P2-P1-C38 110.61(7), N1-P1-C38 101.40(8), P3-P2-C23 102.11(6), P1-P2-C23 114.04(6)..... 265

Figure A.77 Solid state molecular structure of [1_{Dipp}]⁺ (R' = Me). Thermal ellipsoids are drawn at the 50% probability level. Dipp substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.2387(6), P2-P3 2.2360(5), P1-N1 1.781(1), P3-C1 1.816(1), C1-N1 1.299(2), C1-C2 1.491(2), N1-H1 0.85(2), O1-H1 1.89(2), P1-C27 1.831(1), P2-C15 1.848(1), P3-C3 1.836(1); P1-N1-C1 121.58(9), P3-C1-N1 117.8(1), P1-P2-P3 86.98(2), P2-P1-N1 90.53(4), P2-P3-C1 91.13(4), N1-P1-C27 104.52(6), P2-P1-C27 105.82(4), C1-P3-C3 105.57(6), P2-P3-C3 111.54(4), P1-P2-C15 103.96(5), P3-P2-C15 110.46(5). 266

Figure A.78 Solid state molecular structure of [1_{Dipp}]⁺ (R' = Ph). Thermal ellipsoids are drawn at the 50% probability level. Dipp substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.243(1), P3-P2 2.212(1), P1-N1 1.790(2), P3-C1 1.822(3), C1-N1 1.312(4), C1-C2 1.473(3), N1-H1 0.87(4), P1-C8 1.838(3), P2-C20 1.854(3), P3-C32 1.842(4), O2-H1 2.04(4); P1-N1-C1 124.0(2), P3-C1-N1 115.8(2), P2-P1-N1 91.23(8), P2-P3-C1 93.98(9), P3-P2-P1 88.53(4), P2-P1-C8 104.6(1), N1-P1-C8 104.7(1), P2-P3-C32 105.80(9), C1-P3-C32 112.4(1), P1-P2-C20 107.61(9), P3-P2-C20 103.55(9). 267

Figure A.79 Solid state molecular structure of [1_{Mes}]⁺ (R' = Me). Thermal ellipsoids are drawn at the 50% probability level. Mes substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.237(3), P2-P3 2.192(3), P1-N1 1.778(8), P3-C1 1.782(8), C1-N1 1.309(9), C1-C2 1.50(1), N1-H1 0.88, O1-H1 1.993, P1-C21 1.835(7), P2-C12 1.849(7), P3-C3 1.825(6); P1-N1-C1 127.4(6), P3-C1-N1 118.8(6), P1-P2-P3 95.5(1), P2-P1-N1 95.4(2), P2-P3-C1 98.6(3), N1-P1-C21

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Figure A.80 Solid state molecular structure of $[1_{\text{Mes}}]^+$ ($R' = \text{Ph}$). Thermal ellipsoids are drawn at the 50% probability level. Mes substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P3-P2 2.238(1), P1-P2 2.206(1), P3-N1 1.772(2), P1-C1 1.804(2), C1-N1 1.309(4), C1-C2 1.475(3), N1-H1 0.87(3), P3-C8 1.830(3), P2-C17 1.844(2), P1-C26 1.823(3), H1-O1 1.92(3); P3-N1-C1 126.3(2), P1-C1-N1 118.8(2), P2-P3-N1 95.34(8), P2-P1-C1 97.42(9), P1-P2-P3 93.42(4), P2-P3-C8 100.68(8), N1-P3-C8 106.6(1), P2-P1-C26 110.44(9), C1-P1-C26 105.1(1), P3-P2-C17 104.64(8), P1-P2-C17 103.39(8). 269

Figure A.81 Solid state molecular structure of $[1_{\text{tBu}}]$ ($R' = \text{Ph}$). Thermal ellipsoids are drawn at the 50% probability level, and all protons except H1 and CH_2Cl_2 protons have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P2-P3 2.2086(6), P1-P3 2.1958(6), P2-N1 1.768(2), P1-C1 1.817(2), C1-N1 1.311(2), C1-C4 1.469(2), N1-H1 0.87(3), P2-C5 1.870(2), P3-C2 1.891(2), P1-C6 1.893(2), H1-O1 1.88(3); P2-N1-C1 125.8(1), P1-C1-N1 120.0(1), P3-P2-N1 97.35(5), P3-P1-C1 98.65(6), P1-P3-P2 95.30(2), P3-P2-C5 105.31(6), N1-P2-C5 102.37(8), P3-P1-C6 105.24(6), C1-P1-C6 106.27(8), P2-P3-C2 99.62(6), P1-P3-C2 101.07(6). 270

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Chapter 1. Introduction

1.1 Research Objectives

The aim of the research described in this thesis is to develop synthetic routes to new main group heterocycles and polymeric materials. The insertion of unsaturated substrates into cyclic phosphanes, the formation of electronically-modified cyclic and polymeric phosphonates, and the development of routes to hybrid siloxane-phosphonate polymers have been explored.

This introductory chapter serves to provide an overview on phosphorus and silicon, their transformations to chemical reagents and heterocycles, the chemistry of cyclic phosphanes, and main group polymers with particular focus on strategies to synthesize polysiloxanes and polyphosphonates to give context to the chapters of this thesis. Each chapter contains a detailed introduction associated with the work reported along with further relevant background information.

1.2 The origins of silicon and phosphorus

All elements heavier than hydrogen are born in the stars. Initially, the fusion (known in astrophysics as “burning”) of hydrogen in massive stars forms helium, inducing gravitational compression of the core and exponentially increasing the heat and pressure within the core to burn their new chemical fuels in successive stages: He, C, Ne, O, and then Si.¹ It is towards the end of a star’s life (≥ 8 solar masses),² after which H, He, and C have been largely spent, that the explosive burning of Ne yields temperatures high enough to overcome electrostatic repulsion associated with higher Z elements. This forms the only stable phosphorus nuclide, ^{31}P , *via* the capture of a neutron at ^{30}Si at a total yield of 2.5% relative to all other products of explosive Ne burning.^{1, 3} Once Ne fuel has been spent, the burning of previously-formed oxygen yields vast amounts of ^{28}Si (nearly 34% of reaction yield) alongside ^{32}S .¹ It is during a star’s death, *via* supernova, that phosphorus,

silicon, and other elements are dispersed into the interstellar medium,² and commence reacting with other elements to form a host of small molecules. Phosphorus molecules formed in these interstellar environments include PO and PN,⁴ CP,⁵ HCP,⁶ CCP,⁷ and PH₃,⁸ while silicon molecules include SiO,⁹ SiS,¹⁰ SiN,¹¹ SiC_n (n = 1-4),¹²⁻¹⁵ SiNC/SiCN,¹⁶ and SiCSi.¹⁷

As temperatures cool, these molecules eventually amass as stellar clouds undergo gravitational collapse, thereby forming larger and more complex bodies of matter which form the stars, planets, and moons of our galaxies.¹⁸ While the combination of the cold vacuum of space and the slow, solid state transformations on interstellar ice grains provides an environment suitable for the stable formation of low-valent silicon and phosphorus species, on earth silicon and phosphorus exist as Si(IV) and P(V) in the form of silicate [SiO₄]⁴⁻ and phosphate [PO₄]³⁻, respectively. The following section outlines their fundamental transformations and chemistries.

1.3 Silicon: from mineral to molecule

Silicates, [SiO₄]⁴⁻, and silica, SiO₂ in the form of sand and quartz, make up the majority of the Earth's crust (90%). Silicic acid, in the form of opaline quartz, fluxes out of soil environments and becomes the dissolved source of silicon for the formation of opaline quartz exoskeletons of a host of microorganism such as diatoms, radiolaria, and others.¹⁹ The high charge of the [SiO₄]⁴⁻ unit allows for the incorporation of numerous cationic species into interstitial sites of the lattice, and numerous other species can be accessed through the catenation of multiple [SiO₄]⁴⁻ centers (Figure 1.1).²⁰

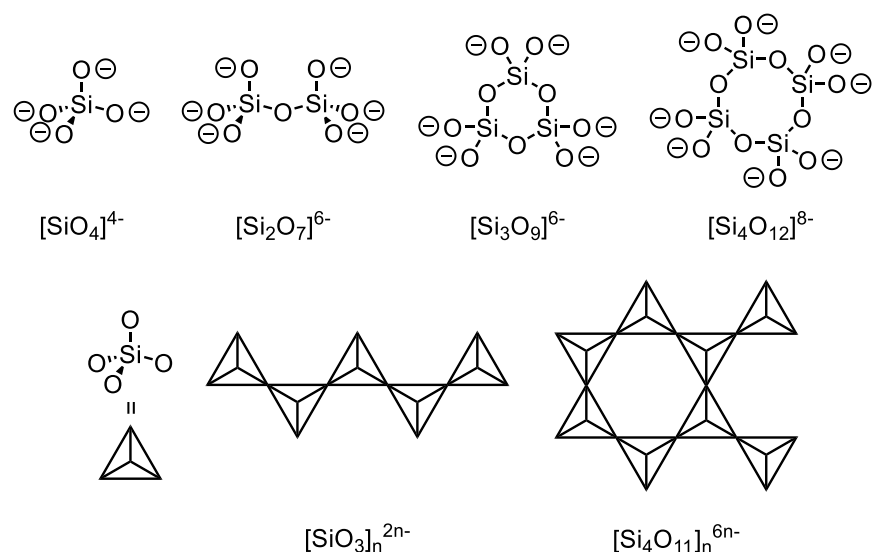


Figure 1.1 Structures of silicic acid (top left) and linear, cyclic, polymeric and branched derivatives of silicic acid commonly found in dissolved silicon sources and minerals.

Elemental silicon cannot be found naturally on earth, but is traditionally formed through the electrothermal reduction of silicon dioxide in the presence of carbon to 98% purity.²¹ However, the application of elemental silicon as a semiconductor necessitated methods for further refining silicon far beyond 98% purity (Figure 1.2). In this process, elemental silicon is reacted with hydrochloric acid to form volatile SiHCl_3 , which can be used to deposit elemental silicon by CVD at 1100 °C to afford 7N (99.9999999%) Si.²² To achieve 10N (99.999999999%) Si, the Czochralski (Cz) process is employed. Here, an ultra pure single-crystal of silicon, serving as a <100> crystal template, is precisely lowered into a molten bed of silicon and is slowly pulled out as a massive single crystal with virtually no impurities.²³ While elemental silicon holds massive value in modern technologies, halosilanes such as SiCl_4 and SiHCl_3 are also valued as readily-functionalized reagents for silicon materials, since Kipping's discovery of robust functionalization methods *via* Grignard metathesis (Figure 1.2).²⁴ They are synthesized through the direct process, in which elemental silicon is continuously reacted with hydrochloric acid and is purified by distillation of impurities such as H_4Si and H_2SiCl_2 , while

continued reaction of SiHCl_3 with HCl eventually culminates in the production of SiCl_4 .^{21, 22} A final reagent of interest is Me_2SiCl_2 , which is synthesized through Rochow's direct process (Fig 2).^{21, 25} In this process, CH_3Cl and Si^0 are reacted in the presence of catalytic amounts of CuCl to form Me_2SiCl_2 and a series of other useful partially-halogenated silanes of the form Me_xSiX_y ($x = 1, 2, \text{ or } 3; y = 4-x$).²¹

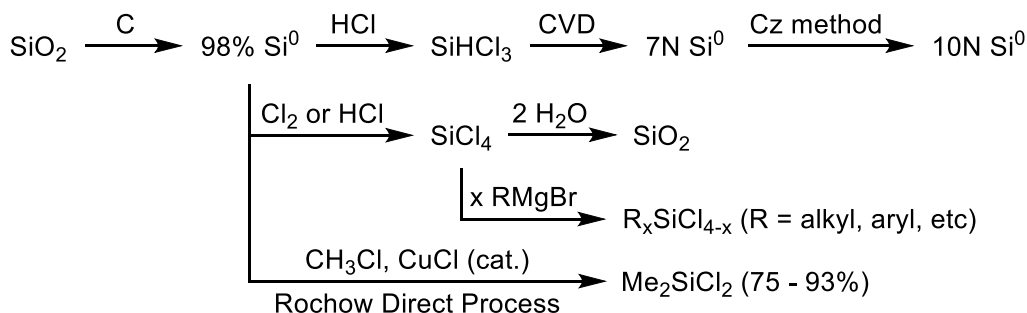


Figure 1.2 Process for the transformation of silicon dioxide to silicon products and reagents.

Me_2SiX_2 and other R_2SiX_2 compounds rapidly hydrolyze in the presence of moisture to form silanediols, $\text{R}_2\text{Si}(\text{OH})_2$, and heating these diols affords linear and cyclic species of the form $(\text{R}_2\text{Si}-\text{O})_n$ (n = number of repeat units) composed of Si-O single bonds (initially labelled by Kipping as silicoketones,²⁶ or “silicones”, the name is a misnomer but has nonetheless remained as the identifier for such materials).²¹ Of the cyclic oligomers of $(\text{R}_2\text{Si}-\text{O})_n$ formed through the driving hydrolysis of R_2SiCl_2 , tetramers are most common ($n = 4$), though higher order rings up to $n = 6$ are synthesized in the hydrolysis of Me_2SiCl_2 in <10 % yield. To prevent confusion, common nomenclature has been established for cyclic species, with the R_2SiO monomer unit is referred to as D; for example, $[\text{Me}_2\text{Si}-\text{O}]_3$ is referred to as D_3^{Me} , while $[\text{Ph}_2\text{Si}-\text{O}]_4$ is referred to as D_4^{Ph} (Figure 1.3). Eight-membered D_4 siloxanes are the most commonly formed ring structures in the synthesis of cyclic siloxanes compared to higher order ring structures, while D_3 species such as D_3^{Me} and D_3^{Ph} are generally far more strained and prone to undergo spontaneous

ring-opening polymerization upon heating.²¹ The polymerization of cyclic siloxanes will be discussed in more detail in section 1.10.1.

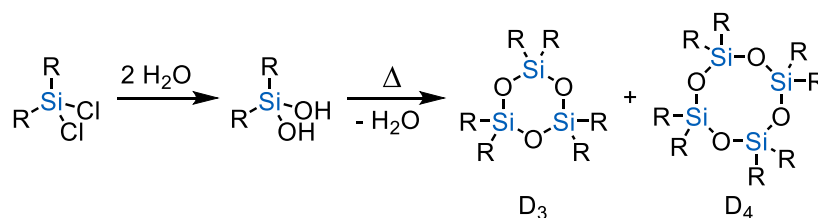


Figure 1.3 Synthesis of D₃ and D₄ cyclic siloxanes through the hydrolysis of R₂SiCl₂

1.4 Phosphorus: from mineral to molecule

Phosphorus exists on Earth largely in the form of apatite, [Ca₁₀(PO₄)₆X₂] (X = F, Cl, OH). The first element of the global phosphorus cycle,²⁷ apatite is weathered, dissolved, and is taken up by plants and oceanic algae. It is then made into linear, cyclic, and organic phosphates (Figure 1.4), which make their way into the bottom of the food chain, while also maintaining a flux between mineralization in the ocean where it is stored as sedimented or dissolved inorganic phosphate. This cycle fundamentally allows for life on earth, as phosphate makes up the key component of the polyphosphoester backbone of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), serves as the energetic currency of living cells as adenosine triphosphate (ATP), and forms the bulk of mammalian skeletons and teeth in the form of hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] interspersed in protein matrices, fundamentally lending to their strength.²⁸

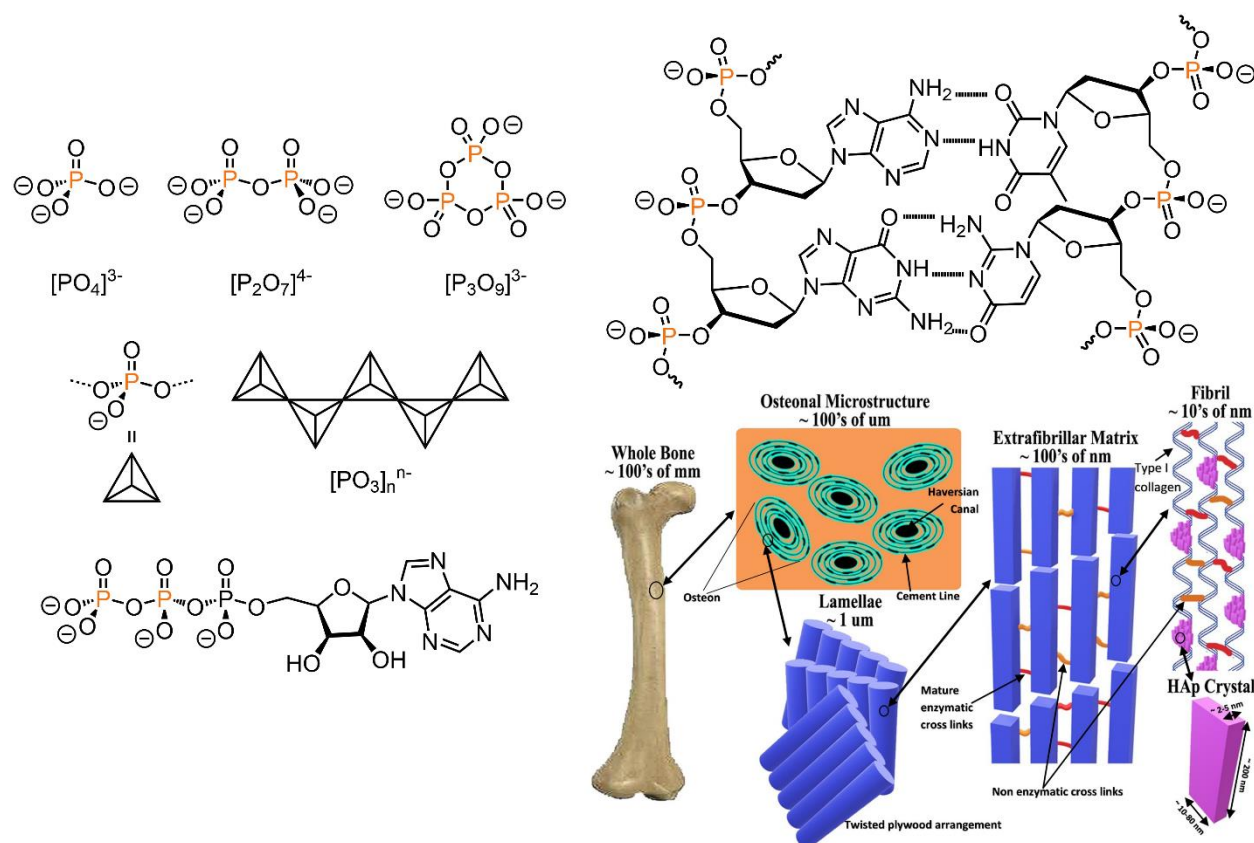


Figure 1.4: Structures of the phosphate anion PO_4^{3-} (top left), linear and cyclic phosphates (left, top and middle), adenosine triphosphate (ATP, bottom left), deoxyribonucleic acid (top right), and the hierarchical structure of bone displaying hydroxyapatite (HAp) interspersed in collagen proteins (bottom left, reproduced from ref. 28).

While phosphate may serve as Nature's main phosphorus source, so too does it serve as the main phosphorus feedstock in modern society. Over 90% of mined phosphate rock is processed through a "wet process" by reaction with mineral acids to form phosphoric acid and fertilizers.²⁹ However, the extended applicability of phosphorus requires greater synthetic accessibility found only in elemental phosphorus. Elemental phosphorus was first discovered in 1669 AD when German alchemist Hennig Brandt, searching for a liquid that could turn silver into gold, heated urine to dryness, aged the remaining black residue, and then heated the material in the presence of sand until all volatiles and oils distilled off. What remained was a glowing white waxy solid which

Brandt called *kaltes feuer* (cold fire). It was found that this process formed white phosphorus, P₄, through the process $4 \text{ NaPO}_3 + 10 \text{ C} + 2 \text{ SiO}_2 \rightarrow 2 \text{ Na}_2\text{SiO}_3 + 10 \text{ CO} + \text{P}_4$,²⁹ with the glowing phenomenon stemming from the exposure of P₄ to oxygen.³⁰ Today white phosphorus is synthesized through the reaction of apatite with SiO₂ and coke carbon at 1600 °C to form gaseous P₂ which subsequently condenses as the stable P₄ allotrope.³¹ P₄ processing follows a few main streams (Figure 1.5): firstly, transformed into red phosphorus for use in pyrotechnics, match-lighting, and precursors to metal phosphide nanomaterials; hydrolysis and oxidation to form phosphoric acids and phosphoric acid anhydrides, respectively; and oxidation by halogens to form halophosphines like PX₃ and PX₅, which serve as starting reagents for commodity organophosphorus chemicals.^{29, 31} Further transformations to P₄ can also be done to access the other allotropes of phosphorus, which bear unique bonding schemes to expand beyond molecular P₄ units and form a variety of 2D and 3D structures with unique material properties.³²

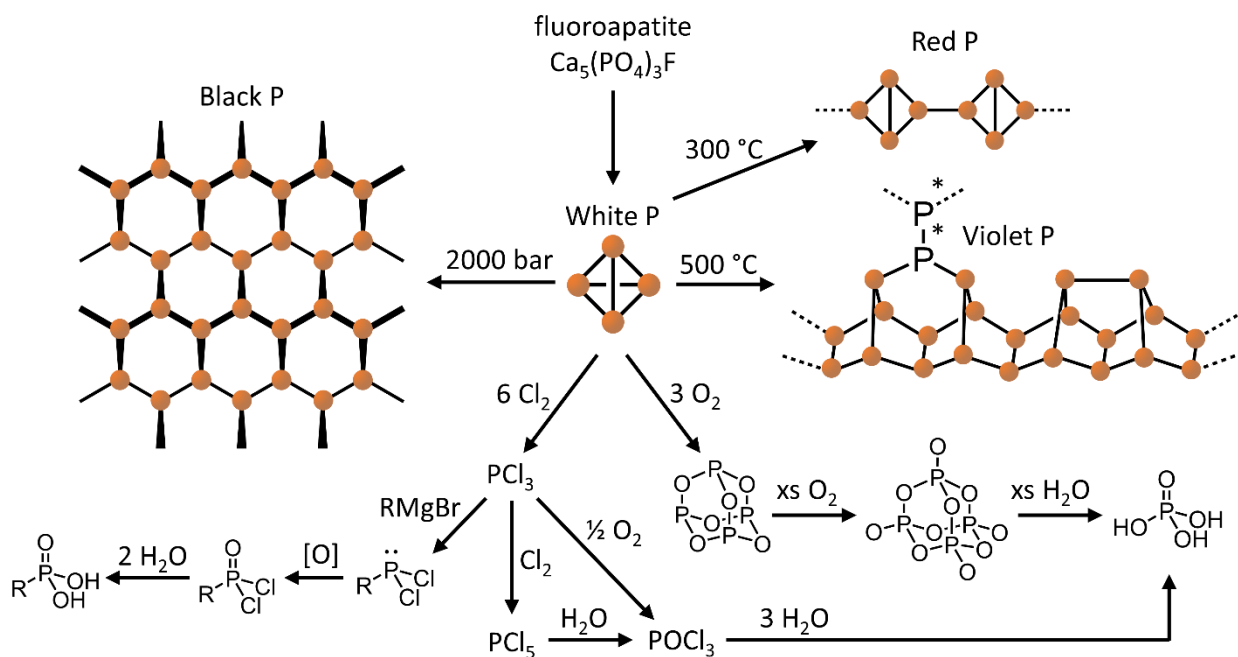


Figure 1.5 Synthesis of phosphorus allotropes, and synthetic transformations from white phosphorus, P₄, for other phosphorus reagents and chemicals as relevant to the work within this thesis.

1.5 Phosphinidenes and cyclic phosphanes

Naturally occurring phosphorus species on earth exist as tetracoordinate molecules in the P^V oxidation state, and stable synthetic species up to the mid 1900s were largely composed of tricoordinate P^{III} phosphines (PR_3) used for metal complexes and tetracoordinate P^V organophosphorus compounds for the formation of olefins through oxygen transfer such as Wittig reagents and esterified phosphonates.^{33, 34} However the discovery of low-valent phosphorus species gave way to a new chapter of phosphorus chemistry and challenged long-held beliefs on the ability of heavy main group elements to form multiple bonds. In 1877, Kohler and Michaelis condensed $PhPH_2$ and $PhPCl_2$ to form a crystalline material which by elemental analysis they characterized as $Ph-P=P-Ph$, or “phosphobenzene” (named as the phosphorus derivative of azobenzene, $Ph-N=N-Ph$).³⁵ This proposal was bold for the time period it was proposed in, for Pitzer and Mulliken put forth the “classical double bond rule” – wherein elements with a principal quantum number greater than 2 cannot form $(p-p)\pi$ multiple bonds – as late as the 1950s.^{36, 37} However, Michaelis and Rothe’s hypothesis was proven wrong years later, as mass spectrometry³⁸ and crystallography³⁹ showed that the reaction instead produced cyclic phosphanes $(PhP)_n$ ($n = 4-6$). This demonstrated that Michaelis and Rothe, unbeknownst to them, formed a new low-valent species *in situ* which subsequently oligomerized. This may potentially have been a phosphinidene, $R-P:$ a neutral, monocoordinate, monovalent species with six valence electrons that is isolobal to the neutral methylene CR_2 moiety (or, more correctly, the $R-C$ anion)⁴⁰ and exists as a triplet in the ground state in accordance with Hund’s rules of maximum multiplicity (Figure 1.6). Due to their electron deficient state, phosphinidenes undergo a host of reactivities including metal coordination,^{41, 42} Lewis base coordination,⁴³ and insertion into unsaturated substrates,⁴⁴ C–H bonds,⁴⁵ and N–H bonds.⁴⁶

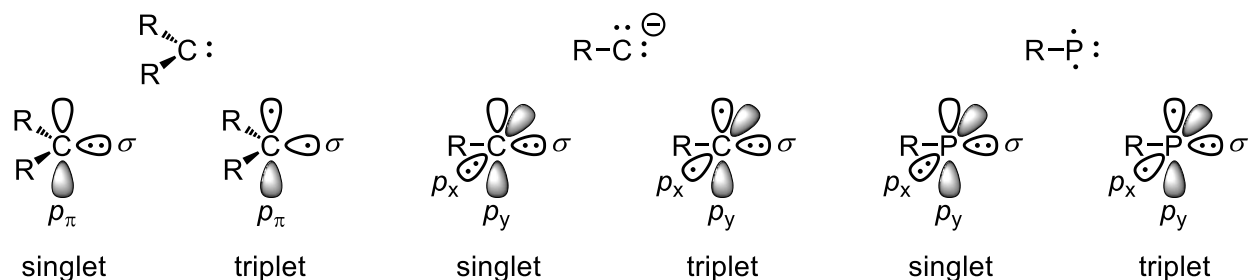


Figure 1.6 Comparison of electronic structure of carbenes and phosphinidenes.

In the absence of reactive partners, free phosphinidenes lacking sufficient steric stabilization do not exist in the monomeric state and instead oligomerize into homoleptic cyclic phosphanes, $(RP)_n$, harkening back to the initial investigation of Köhler and Michaelis.³⁵ Studies on cyclic phosphanes were extensive from the 1960s through the 1980s, as the development of ^{31}P NMR spectroscopy allowed for the decisive characterization of phosphorus materials compared to the previous use of elemental analysis and mass spectrometry (both of which could not determine connectivity and stereochemistry for species with ≥ 2 phosphorus atoms). The syntheses, structural features, and fundamental reactivity of cyclic phosphanes will be reviewed herein in the scope of thesis; for more exhaustive reviews, the reader is directed to seminal reviews on cyclic phosphanes by Baudler^{47, 48} and a recent review by Hering-Junghans.⁴⁹

Cyclic phosphanes are synthesized through a host of routes, which either may be specific for a specific type of $(RP)_n$ ring size or form a variety of ring sizes. Kinetic stabilization is a key factor to the formation of $(RP)_n$ rings. Phosphorus species with very little steric impact can form larger membered rings (see for example, the thermolysis of P_2H_4 to form cyclic oligomers from $(\text{HP})_3$ to $(\text{HP})_{10}$),⁴⁷ while species bearing alkyl or aryl groups are generally limited to forming ring species between $(RP)_3$ to $(RP)_6$. Structurally, cyclic phosphane substituents take on a defined stereochemistry that allowed for their definitive characterization by ^{31}P NMR spectroscopy.⁴⁸ For

example, (RP)₃ rings such as (tBuP)₃ have *tert*-butyl groups that take on a chair-like *cis,trans,trans* conformation which results in an AB₂ spin pattern in ³¹P NMR spectra, while (RP)₄ rings exhibit an all *trans* conformation that results in a singlet. (RP)₅ species take on a conformation in which all phosphorus substituents except two lie *trans* to one another (resulting in a very complex ³¹P NMR spin pattern), whilst (RP)₆ rings have an all *trans* configuration that generates a singlet.

A host of synthetic methodologies exist which yield pure cyclic phosphanes and mixtures of multiple ring sizes.⁴⁸ The first major method for forming cyclic phosphanes, by Köhler and Michaelis, was through dehydrochlorination to form (PhP)₅ through the condensation reaction of PhPH₂ and PhPCl₂,³⁵ which has since been used to form a variety of cyclic phosphanes.⁴⁹ However, the overwhelming majority of cyclic phosphanes have been generated through reductive methods, in which R₂PCl₂ is reacted with an alkali or alkaline earth reducing agent to yield a variety of cyclic phosphanes (Figure 1.7). For example, (tBuP)₃ can be formed by refluxing tBuPCl₂ with magnesium turnings in THF, extracting the formed (tBuP)₃/(tBuP)₄ mixture from MgCl₂ with *n*-pentane, and purifying by fractionally distilling (tBuP)₃ from (tBuP)₄.⁵⁰ Contrarily, (tBuP)₄ can be selectively synthesized by refluxing tBuPCl₂ with sodium in dioxane.⁵¹ Recent work has led to new reductive methods that extend beyond conventional elemental alkali and alkaline earth reactions. Cossairt and Cummins reported the radical-mediated formation of (MesP)₃ through dehalogenation of MesBr with {Ti[N(tBu)(Ar)]₃} and the subsequent Mes-radical reduction of P₄. This forms MesP in situ which selectively oligomerizes to (MesP)₃.⁵² Velian and Cummins reported that the reduction of {(Me₃Si)₂N}PCl₂ with [(THF)₃Mg(anthracene)] in THF to generate MgCl₂ and re-aromatized anthracene yielded a mixture of {(Me₃Si)₂N}P(anthracene) and [(Me₃Si)₂N}P]₃. However, running the reaction in Et₂O resulted in the selective formation of [(Me₃Si)₂N}P]₃.⁵³ Weigand and coworkers formed tetra-cationic cyclic phosphane

$[(^i\text{Pr}_2\text{Im}^{\text{Me}})\text{P}]_4[\text{OTf}]_4$ through the reduction of $[(^i\text{Pr}_2\text{Im}^{\text{Me}})\text{PCL}_2][\text{OTf}]$ with 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine.⁵⁴ Reduction of the cationic dichlorophosphine with Mg resulted in incomplete reduction, while the additional entropy gained from reduction with 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (namely, the formation of 2 eq. of Me_3SiCl (TMSCl) and one equivalent of pyrazine) allowed for complete reduction to the cyclic tetraphosphane. Finally, Hering-Junghans and coworkers have reported a phospho-Wittig approach, used by Protasiewicz for the synthesis of phosphalkenes,⁵⁵ to synthesize aryl-substituted cyclic phosphanes.⁵⁶ Cyclic phosphanes are formed from a mixture of ArPX_2 ($\text{X} = \text{Cl}, \text{Br}$), PMe_3 , and Zn in a 1/2.5/5 ratio,

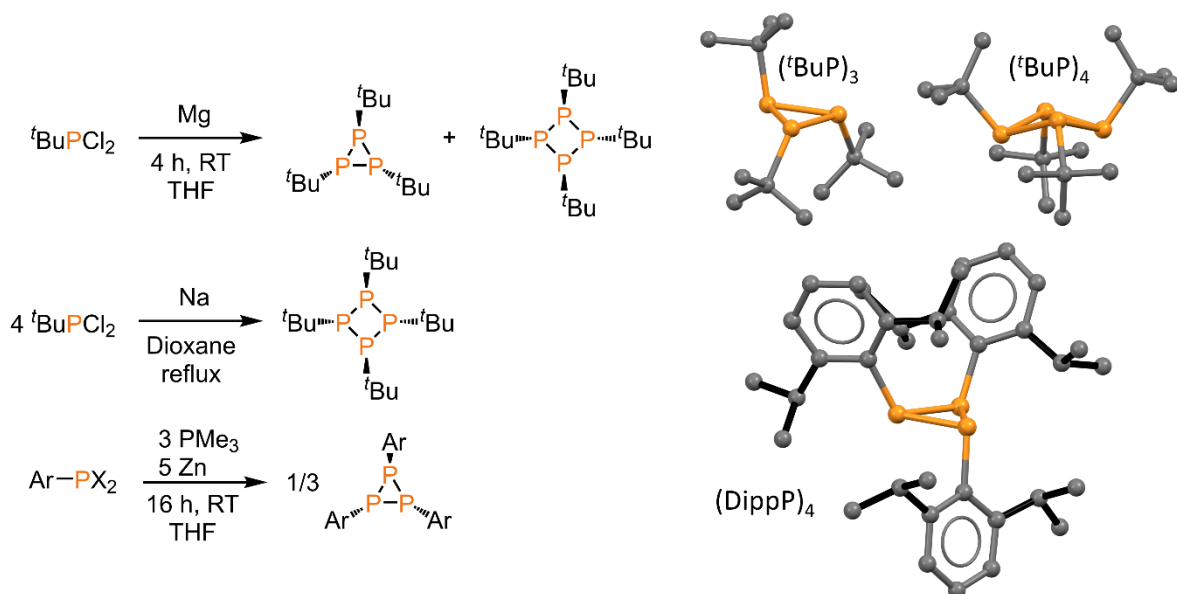


Figure 1.7 Reductive methods for the synthesis of prototypical cyclic phosphanes $(^t\text{BuP})_3$ and $(^t\text{BuP})_4$ (left, top and middle), aryltriphosphanes $(\text{ArP})_3$ (bottom left), and prototypical single-crystal X-ray structures of $(^t\text{BuP})_3$, $(^t\text{BuP})_4$, and $(\text{DippP})_3$ demonstrating $(\text{RP})_3$ and $(\text{RP})_4$ solid state structures (right). Hydrogen atoms have been removed for clarity.

resulting in the *in situ* formation of a masked phosphinidene, ArP-PMe_3 , which decomposes to selectively afford cyclic triphosphanes $(\text{ArP})_3$ ($\text{Ar} = \text{Mes}$, Dipp , and Tripp) (Figure 1.7).⁵⁶

Whilst reductive methods have allowed for the selective and high yielding synthesis of cyclic phosphanes, they suffer from the use of air and moisture sensitive halophosphines and

highly reactive alkali metals, and reductions must generally be done at large scales due to the low molecular weight of elemental alkali metals. Consequently, catalytic methods have since arisen that afford various cyclic phosphanes with high specificity and at more approachable scales than reductive methods. Stephan and coworkers initially reported that heating 1% of $[\text{Cp}^*\text{Zr}(\mu\text{-H})_3\text{M}]$ ($\text{M} = \text{Li}, \text{K}$) catalyst with RPH_2 ($\text{R} = \text{Ph}, \text{Cy}, \text{Mes}$) at $80\text{ }^\circ\text{C}$ for 72-96 h yielded $(\text{RP})_5$ rings.⁵⁷ The reaction was found to proceed through the dehydrocoupling of phosphines leading to on-metal $(\text{RP})_3$ ligation, followed by release of the $(\text{RP})_3$ ligand and oligomerization to $(\text{RP})_5$ at higher temperatures. Stephan subsequently reported the dehydrocoupling of PhPH_2 with 10% $\text{B}(p\text{-C}_6\text{F}_4\text{H})_3$ at $130\text{ }^\circ\text{C}$ over 5 days to form $(\text{PhP})_5$ in quantitative yield, a reaction which likewise could be exploited for transfer hydrogenation of imines and alkenes present in the reaction medium.⁵⁸ This transfer hydrogenation inspired Manners and coworkers to use hydrogen acceptors such as imines as stoichiometric, sacrificial substrates in the dehydrocoupling of RPH_2 in the presence of 10% $t\text{BuOK}$.⁵⁹ Here, the Brønsted base abstracts a proton from RPH_2 and results in a cycle of nucleophilic attack at the hydrogen acceptor by the phosphide, followed by subsequent protonation of the hydrogen acceptor and release of coupled phosphines; this catalytic cycle is able to access $(\text{PhP})_5$ and $(\text{CyP})_4$ in 63% and 29% yield, respectively (Figure 1.8).

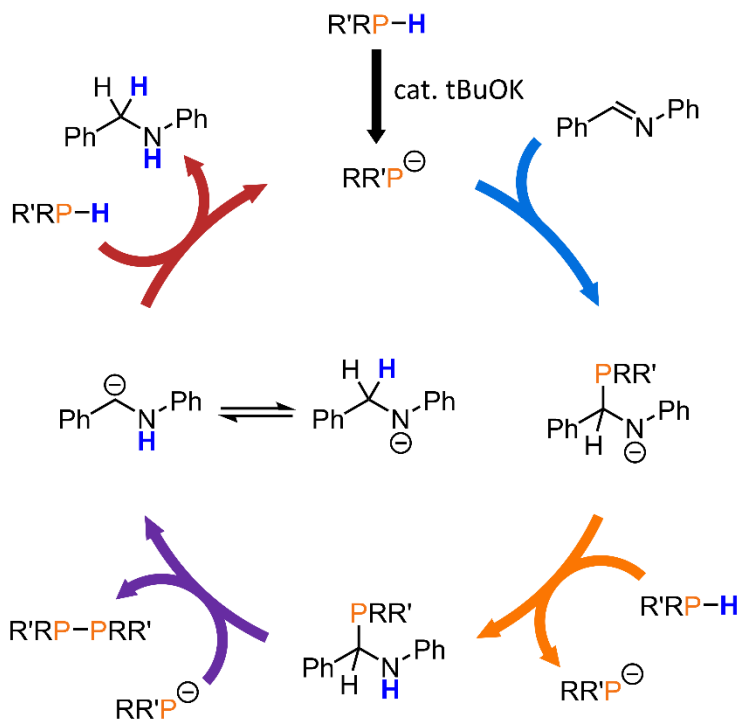


Figure 1.8 Catalytic cycle of non-metal P–P bond formation using a base and sacrificial hydrogen accepting imine, which can be applied to cyclic phosphane formation where $R = \text{Ph}$, Cy and $R' = \text{H}$.

Of note in the synthesis of cyclic phosphanes is the effect of sterics on the size of rings $(\text{RP})_n$ that may be formed. Phosphorus species bearing Dipp and Tripp substituents selectively form $(\text{RP})_3$ rings compared to phosphorus species bearing $t\text{Bu}$ groups which form $(\text{RP})_3/(\text{RP})_4$ mixtures, due to the increased kinetic stability provided by sterically demanding aryl groups. Pushing kinetic stability further than Dipp and Tripp prevents the oligomerization of phosphinidenes into cyclic species entirely, as exemplified by Yoshifuji and coworkers who discovered the first phosphobenzene by increasing steric bulk through the use of the 2,4,6-tri-*tert*-butylphenyl (aka super mesityl, or Mes^*) substituent. Reduction of Mes^*PCl_2 with Mg resulted in the first formal $\text{P}=\text{P}$ double bond $\text{Mes}^*-\text{P}=\text{P}-\text{Mes}^*$ (Fig 9).⁶⁰ This motif demonstrated the lowest oligomer of phosphinidene until very recently, when Bertrand and coworkers used a rigid 1,3,2 diazaphospholidine scaffold with extreme steric demand to generate the first and only free

phosphinidene at room temperature (Figure 1.9).⁶¹ Due to the high degree of donation from the diazaphospholidine phosphorus into the phosphinidene phosphorus on account of lone pair repulsion from the neighbouring nitrogen atoms in the diazaphospholidine scaffold, the free phosphinidene exists in the singlet state, and has been found to be electrophilic through accepting

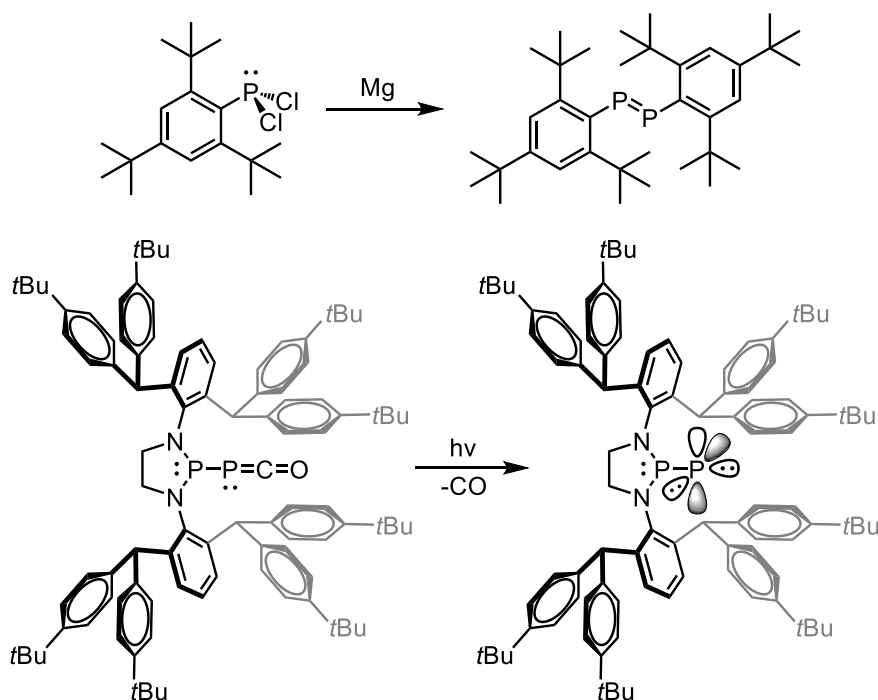


Figure 1.9 Yoshifuji's phosphobenzene (top) and Bertrand's free phosphinidene (bottom).
electrons into the empty *p*-orbital which persists due to the singlet configuration.⁶²

1.6 Fundamental reactivity of cyclic phosphanes

The reactivity of cyclic phosphanes has been well established since their full spectroscopic and crystallographic characterization. Early fundamental studies investigated the oxidation of (RP)_n (*n* = 3-5) rings, demonstrating that cyclic phosphanes could react with oxygen to form exocyclic monoxides, while (RP)_n (*n* = 4, 5) rings formed exocyclic monosulfides in the presence of S₈.⁵⁰ The reactivity of cyclophosphanes such as (tBuP)₃ with alkali metals generally results in the cleavage of P-P bonds to form open chain phosphides such as K(tBu)P-P(tBu)K.⁶³ However,

with stoichiometric control, monometallated tricyclophosphanes can be isolated.⁶⁴ The coordination chemistry of $(RP)_n$ with transition metals is also well established, forming various monometallated, bimetalated, and bridged complexes with metal carbonyls.^{65, 66}

Another aspect to the reactivity of cyclic phosphanes is ring-expansion via the insertion of main group fragments. Elemental sulfur and selenium can insert into cyclophosphanes in endocyclic fashion to yield P_3E rings and other P–E clusters ($E = S, Se$).⁴⁸ Group 13 complexes such as $(AlCp^*)_4$ and $(Ga[C(SiMe_3)])_4$ react cleanly to insert an RE^+ fragment into the ring.^{67, 68} This reactivity was mimicked in the insertion of $TiCp_2$ into $(tBuP)_3$ and $(AdP)_3$, though insertion of the titanocene into $(ArP)_3$ derivatives resulted in ring fragmentation and the formation of η^2 -diphosphene complexes $[Cp_2Ti(P_2Ar_2)]$.⁵⁶ Work by Burford and coworkers provided a new perspective to the reactivity of cyclic phosphanes when reacted with various triflate cations (Figure 1.10).⁶⁹⁻⁷¹ Reactions of $(tBuP)_3$ with $MeOTf$ form the stable three-membered phosphonium $[P_3tBu_3Me][OTf]$, while $[PMe_2][OTf]$ and $[PPh_2][OTf]$ insert into $(tBuP)_3$ and $(tBuP)_4$ to form stable $[(P_n tBu_n)(PR_2)][OTf]$ ($n = 3, 4$) phosphonium salts. In the presence of $[TMS][OTf]$, $(tBuP)_3$ was instead converted into $(tBuP)_4$ as opposed to forming a TMS-bound phosphonium as seen in the reaction with $MeOTf$; this was proposed to occur through the formation of $tBu-P=P-tBu$, which dimerizes to form $(tBuP)_4$, and the $[tBuP-TMS][OTf]$ adduct, which subsequently dissociates into free $TMSOTf$ and $tBuP$ (which undergoes subsequent dimerizations to $(tBuP)_4$).

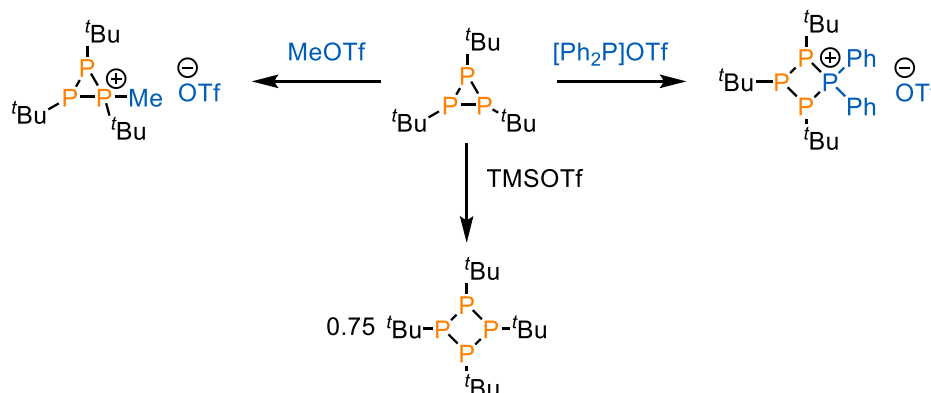


Figure 1.10 Fundamental reactions of (*t*BuP)₃ with triflate salts, demonstrating adduct formation, insertion, and ring equilibration.

These fundamental insertion reactions provided a clue that insertions into cyclic phosphanes could also be achieved by sufficiently polar or cationic substrates. This was verified when our lab reported the cycloaddition reaction of nitriles to (*t*BuP)₃ through either ring or nitrile activation by HOTf (Figure 1.11).⁷² Deprotonation with NEt₃ yields neutral 1-aza-2,3,4-triphosphenes, which were only previously observed upon decomposition of a tungsten-stabilized (PPh)₃ transfer reagent in the presence of a nitrile to form a P₃CN ring with two flanking W(CO)₅ units (Figure 1.11).⁷³ While [P₃*t*Bu₃H][OTf] was not isolable from the reaction of (*t*BuP)₃ and HOTf due to selective formation of [P₄*t*Bu₄H][OTf],⁷¹ an initial protonation event either at (*t*BuP)₃ or RCN (R = Me, Ph, etc.) provides enough reactivity to preferentially form the P₃CN cation in the presence of excess nitrile. It was also found that [MeCNMe][OTf] was able to rapidly insert into (*t*BuP)₃, suggesting that the activation of nitriles by triflic acid may provide a favourable thermodynamic route to insertion. Of significance is the ability to insert of nitriles to (*t*BuP)₃ using catalytic amounts of Lewis acid Ph₃SbClOTf, which was also found to convert (*t*BuP)₃ to (*t*BuP)₄ when nitrile was not present in the reaction mixture.

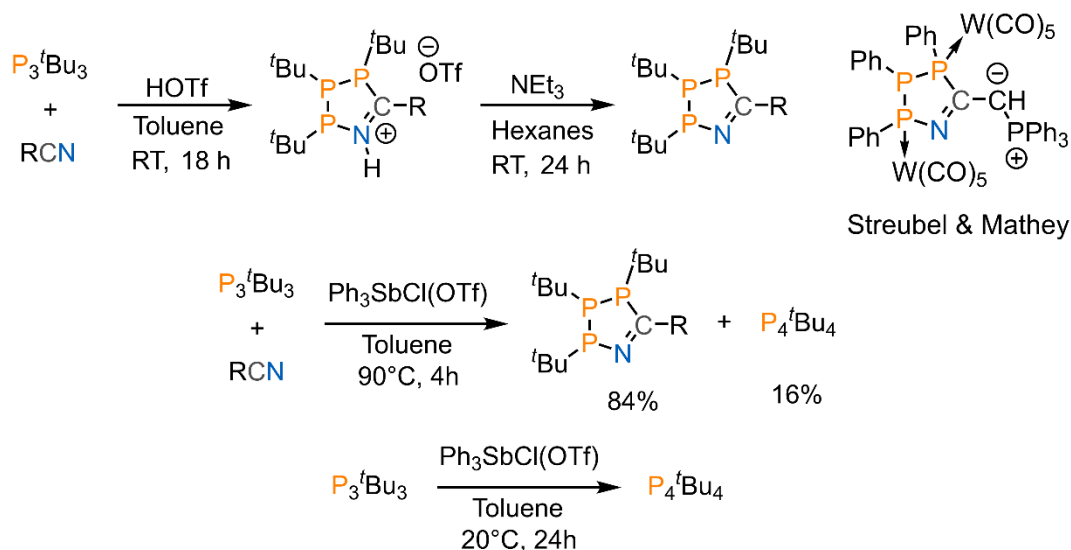


Figure 1.11 Synthesis of cationic and neutral 1-aza-2,3,4-triphospholenes from $(^tBuP)_3$ and nitriles (top), catalytic formation of 1-aza-2,3,4-triphospholenes using Lewis acid (middle), and Lewis-acid catalyzed transformation of $(^tBuP)_3$ to $(^tBuP)_4$ (bottom).

Activation of cyclic phosphanes with MeOTf helps to facilitate insertion reactions, wherein $[P_3^tBu_3Me][OTf]$ is capable of inserting nitriles and isonitriles given its high strain (Figure 1.12), while $[P_4^tBu_4Me][OTf]$ was found to slowly insert isonitriles.⁷⁴ In monitoring the reaction of $[P_3^tBu_3Me][OTf]$ with MeCN it was found that pseudo first-order rate constants were obtained, and Eyring analysis of the rates as a function of temperature yielded a positive activation enthalpy and negative activation entropy.⁷⁴ This was found to be consistent with an associative rate-determining step, suggesting a nucleophilic attack by nitriles or isonitriles at phosphorus atoms neighbouring cationic tetravalent phosphorus centres and resulting in the formation of linear phosphorus species akin to those observed by Burford and coworkers in the ring-opening of $[P_3^tBu_3Me][OTf]$ with DMAP (Figure 1.12).⁷⁵ Such species bear terminal trivalent phosphorus atoms which are then capable of back-biting onto the empty *p*-orbital of the carbon atom associated with the nitrile/isonitrile, formally closing the ring.

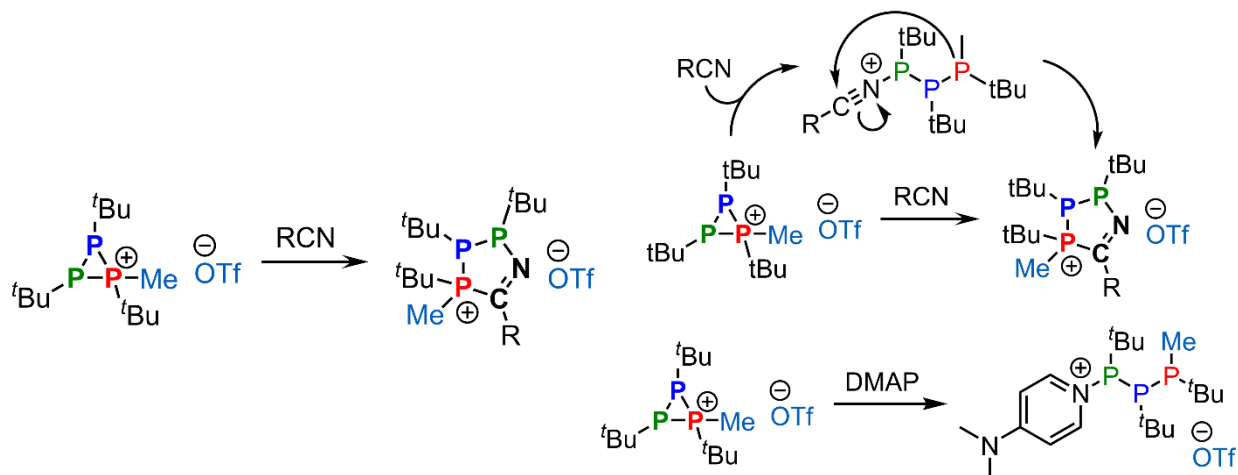


Figure 1.12 Insertion of nitriles into $[P_3^+tBu_3Me]$ cation (left) and the proposed mechanism of insertion (top right) akin to previously reported $[P_3^+tBu_3Me]$ activation (bottom right).

1.7 P–O heterocycles: cyclic phosphates and phosphonates

The reaction of white phosphorus with oxygen first results in the formation of P_4O_6 , which further reacts to form P_4O_{10} (Figure 1.5). The hydrolysis of P_4O_{10} results in the formation of phosphoric acid, H_3PO_4 , which is also made through the acid etching of calcium phosphate rock (Figure 1.5). This acid is capable of undergoing condensation reactions to yield condensed phosphates of the type $[P_2O_7]^{4-}$, $[P_3O_{10}]^{5-}$, and longer linear phosphates (Figure 1.4), which may be further condensed to undergo branching or cyclization. In the latter case, these heterocycles – also known as *metaphosphates* – form a variety of heterocycles from $[P_3O_9]^{3-}$, $[P_4O_{12}]^{4-}$, and $[P_6O_{18}]^{6-}$. The replacement of O^-M^+ (M = alkali, alkaline earth metal, etc) on cyclic metaphosphates by organic substituents results in neutral cyclic phosphonates of the form $[RP(O)-O]_x$ (R = organic substituent, x = 2-6). Also referred to as phosphonic anhydrides, cyclic phosphonates were discovered in 1892 by Michaelis and Rothe through the heating of phosphonic acids and phosphonic dichlorides, which produced mixtures of glassy solids and white crystalline material from which glassy solids were discarded while the crystalline materials were identified as stable monomeric RPO_2 species according to elemental analyses (it would be later corrected as

having been the six-membered cyclic phosphonate).⁷⁶ These heterocycles were then mentioned in the literature of the late 1950s⁷⁷ and early 1960s,⁷⁸ but lacked robust spectroscopic and structural characterization to verify their structure and stereochemistry. They were structurally characterized for the first time in 1970 by Andrianov and coworkers, who reported the solid state structure of $[(\text{Et}_2\text{N})\text{P}(\text{O})-\text{O}]_3$ which was shown to crystallize as an all *cis* derivative and a *cis,trans,trans* derivative in separate single-crystals (Figure 1.13b).^{79,80} While single crystals of $[(\text{Et}_2\text{N})\text{P}(\text{O})-\text{O}]_3$ were obtained, the synthesis of these heterocycles were not reported. Notably, cyclic phosphonate $[\text{}^n\text{PrP}(\text{O})-\text{O}]_3$ was synthesized by Wissman in 1980 for its use as a coupling agent in peptide synthesis.⁸¹ The synthesis of $[\text{}^n\text{PrP}(\text{O})-\text{O}]_3$ was performed by adding a stoichiometric amount of water to stirring *n*-propylphosphonic dichloride and heating to release hydrochloric acid, however the material was not characterized beyond boiling point and a measurement of the chlorine content through an unreported method. $[\text{}^n\text{PrP}(\text{O})-\text{O}]_3$ would go on to be commercialized as T3P®,^{82,83} and is sold at a massive scale per year through multiple vendors despite little being known about its chemical structure. Mahmood and Shreeve would report the synthesis of $[(\text{C}_2\text{F}_5)\text{P}(\text{O})-\text{O}]_3$ in 1986 *via* the oxidation of $(\text{C}_2\text{F}_5)\text{PCl}_2$ with NO_2 at 25 °C with complete spectroscopic characterization, though it is uncertain whether this synthesis would be applicable to other substrates.⁸⁴

The first purposeful synthetic study of cyclic phosphonates was conducted by Fuchs and Schmidbaur in 1995, using Wissman's method of stoichiometric water addition to synthesize $[\text{MeP}(\text{O})-\text{O}]_3$ and $[\text{EtP}(\text{O})-\text{O}]_3$ and the condensation of phosphonic dichlorides and phosphonic acids to synthesize $[\text{}^i\text{PrP}(\text{O})-\text{O}]_3$, $[\text{}^t\text{BuP}(\text{O})-\text{O}]_3$, and $[\text{PhP}(\text{O})-\text{O}]_3$. These materials were characterized by NMR spectroscopy and ESI-MS, and the study provided a few key pieces of structural knowledge: firstly, that for substituents such as methyl and *tert*-butyl the presence of a single set of resonances in the ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra reveal the rings have a C_{3v}

all-*cis* structure; secondly, the presence of an AB₂ spin system in ³¹P{¹H} NMR spectra reveal that [RP(O)–O]₃ (R = Et, ⁱPr, and Ph) rings have a C_s *cis,trans,trans* structure; and finally that the presence of [RP(O)–O]₄ and [RP(O)–O]₆ species were confirmed by ESI-MS measurements, and likewise purity of some species could not be confirmed by NMR spectroscopic characterization on account of the presence of multiple phosphorus species in ³¹P{¹H} NMR spectra.

Diemert and coworkers subsequently reported the reproducible synthesis of cyclic phosphonates through the condensation of RPOCl₂ and RPO(OTMS)₂ to yield crystalline [RP(O)–O]₃ species (R = ^tBu, *o*-Tol, Mes).⁸⁵ In this case, ³¹P{¹H} NMR spectra revealed that [^tBuP(O)–O]₃ and [(*o*-Tol)P(O)–O]₃ display AB₂ spin systems in CDCl₃ and C₆D₆, respectively, while [MesP(O)–O]₃ displayed a singlet in CDCl₃. The spin system of [^tBuP(O)–O]₃ was verified through crystallography (Figure 1.13c), as well as the crystallographic product of hydrolysis, [^tBu₃P₃O₇]²⁻. The report also looks into the mechanism of peptide synthesis, traditionally done with T3P®, using [^tBuP(O)–O]₃ instead; however, it was found that by the end of the reaction the [^tBu₃P₃O₇]²⁻ diacid and the peptide of interest were formed, suggesting that the diacid is the principle by-product of the reaction. Further structural evidence of AB₂-type cyclic anhydrides was found by Karaghiosoff and coworkers, after the accidental exposure of *o*-MeOPh–PCl₂ to moisture during storage resulted in the co-crystallization of *o*-MeOPh–PCl₂ with the corresponding cyclic phosphonate [(*o*-MeOPh)P(O)–O]₃ (Figure 1.13d).⁸⁶

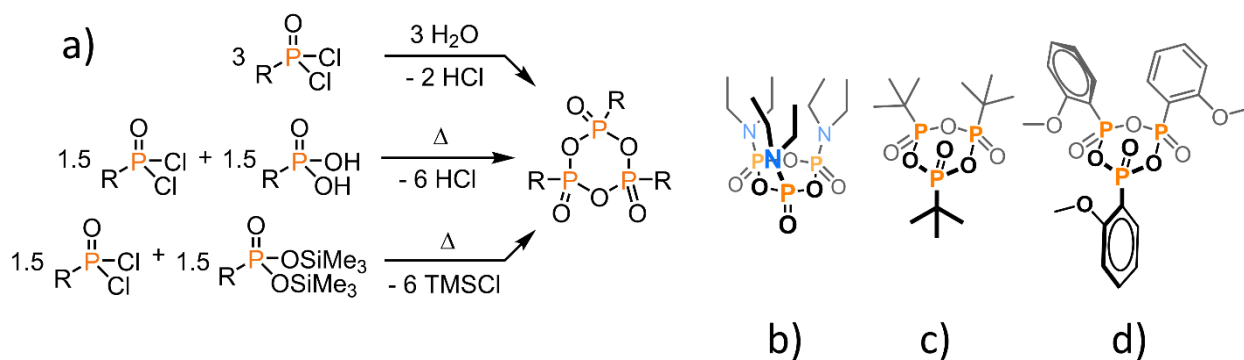


Figure 1.13 Synthetic methods reported for the synthesis of cyclic phosphonates (a), and crystallized cyclic phosphonates with either an all-*cis* C_{3v} configuration (b) or *cis,trans,trans* C_3 configuration (c,d).

The story of cyclic phosphonates has been slowly built up in non-linear fashion, and while the results reported are robust it should be noted that the most thorough investigation of these heterocycles was done through NMR spectroscopy on 200 MHz instruments and ESI-MS measurements in methanol, which is non-inert in its interactions with cyclic phosphonates. Given this, our lab elected to conduct a comprehensive study of cyclic phosphonates for the purpose of exploring their polymerization (to be discussed *vide infra*).⁸⁷ Here, cyclic phosphonates $[RP(O)-O]_3$ ($R = \text{Ph}, p\text{-}^t\text{BuPh}, \text{Mes}, p\text{-}^t\text{BuMes}$) were synthesized *via* the condensation of $RPOCl_2$ and $RPO(OH)_2$ upon heating in toluene for 4 hours (Figure 1.14a). Allowing the toluene solutions to cool to 5 °C or conventionally crystallizing the rings through layering CH_2Cl_2 or toluene solutions with pentane or hexanes afforded single crystals of $[RP(O)-O]_3$ ($R = \text{Ph}, p\text{-}^t\text{BuPh}, \text{Mes}, p\text{-}^t\text{BuMes}$), which all crystallized as *cis,trans,trans* AB_2 ring systems (Figure 1.14b). $[\text{PhP}(O)-O]_3$ did not crystallize as single-crystals suitable for diffraction, but instead its higher oligomer $[\text{PhP}(O)-O]_6$ (Figure 1.14b) crystallized in small amounts. The crystallization of a higher oligomer supports the suggestion that cyclic phosphonates exist in equilibrium between different ring species in solution. The presence of larger oligomers are likely the cause of unknown singlets present in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for species lacking kinetic stabilization, such as $[\text{PhP}(O)-O]_3$ and

[^tBuP(O)–O]₃. Of note is the discovery that Diemert's report that the singlet present in the ³¹P{¹H} NMR spectrum (81 MHz) of [MesP(O)–O]₃ is actually a distorted triplet characteristic of AB₂ spin systems in which the ratio of ν/J is <1, as revealed by the ³¹P{¹H} NMR spectrum at 162 MHz (Figure 1.14c). The dynamic nature of the equilibrium was verified through mixing [PhP(O)–O]₃ and [MesP(O)–O]₃ in CDCl₃, which resulted in complex NMR spectra and ESI-MS results associated with mixed {[PhP(O)–O]_x[MesP(O)–O]_y} rings (x = 1, 2; y = 3-x). Also of note for these rings is their behaviour in differential scanning calorimetry experiments, demonstrating an initial melt endotherm and small exotherm in the first heating, characteristic of a ring-opening event, following by a glass transition, *T_g*, in the subsequent cooling and heating cycles. This is suggestive of a ring-opening polymerization, and the resultant polyphosphonate polymers will be discussed *vide infra*.

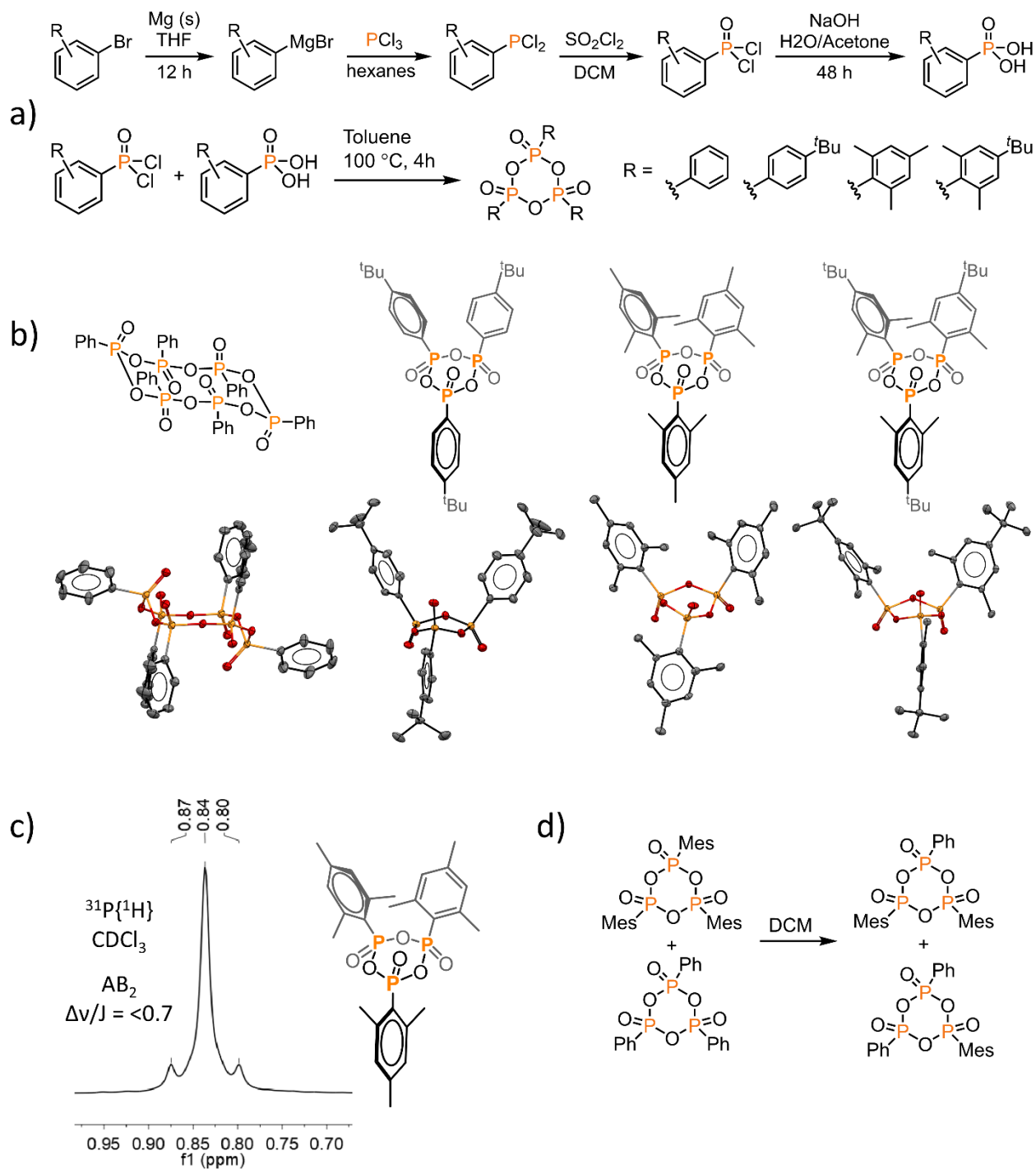


Figure 1.14 Synthetic methodology to access aryl-substituted cyclic phosphonates (a); single-crystal X-ray structures of $[\text{PhP}(\text{O})\text{-O}]_6$, $[(\text{tBuPh})\text{P}(\text{O})\text{-O}]_3$, $[\text{MesP}(\text{O})\text{-O}]_3$, and $[(\text{tBuMes})\text{P}(\text{O})\text{-O}]_3$; prototypical example of complex AB_2 spin patterns observed for aryl-substituted cyclic phosphonates; scheme of the mixture formed from combining $[\text{MesP}(\text{O})\text{-O}]_3$ and $[\text{PhP}(\text{O})\text{-O}]_3$.

1.8 Main Group Polymers

Conventional organic polymers, made of carbon, oxygen, and nitrogen, have long found uses across all of modern society spanning textiles, packaging, and electronics, and a host of other applications.^{88, 89} This has historically been on account of their easily sourced monomer materials, simple preparation, high processability, and lightweight constitution (minimizing the weight of packaging has recently become a clever strategy for reducing fuel usage). Main group polymers with main group elements in their backbone have comparatively been seen as chemical curiosities, though they have begun to be applied across various facets of industry and society due to the unique electronic properties imparted by their inherently polar E–E' bonds. Bonds between main group elements are often stronger and more resistant to free-radical cleavage, are longer and thereby impart greater flexibility, and bear different electronic properties than carbon-based materials.

Despite their potential, main group polymers are largely a boutique and emergent field, as methods commonly used for the formation of organic polymers do not easily translate to inorganic polymers. Addition polymerization between unsaturated monomers, converting energetically weak multiple bonds to stronger single bonds, is a favourable method for chain growth polymerization (Figure 1.15). This proves difficult for main group multiple bonds, which are either too reactive to polymerize controllably (e.g. $\text{P}\equiv\text{N}$),⁵³ or cannot form without substantial steric protection which prohibits polymerization in most circumstances.^{90, 91} Notably, acyclic diene metathesis (ADMET) methods have been discovered for $\text{Ge}=\text{Ge}$ double bonds, though the polymer formed has a relatively low degree of polymerization due to solubility constraints of the bulky monomers used therein.⁹² Step-growth methods (Figure 1.15) such as Wurtz coupling or polycondensations require high purity monomers to achieve high molecular weight polymers.

This can be difficult given that main group monomers are generally air or moisture sensitive, however step growth methods have been used successfully in the formation of polysiloxanes $[\text{RR}'\text{Si}-\text{O}]_n$, polytetrelanes $[\text{R}_2\text{E}]_n$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$), and polyphosphazenes $[\text{R}_2\text{P}=\text{N}]_n$.⁹³⁻⁹⁵ The discovery of catalytic dehydrocoupling methods for the formation of polysilanes in the 1980s⁹⁶ has since seen dehydrocoupling expanded into one of the most highly effective methods for the synthesis of hydrogenated monomer species (Figure 1.15), yielding polymers as diverse as polytetrelanes $[\text{R}_2\text{E}]_n$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$), polyamino- and polyphosphino-boranes $[\text{RR}'\text{E}-\text{BH}_2]_n$, polyborosiloxanes $[\text{RB}-\text{O}-\text{RR}'\text{Si}-\text{O}]_n$, and polysiloxanes $[\text{RR}'\text{Si}-\text{O}]_n$.⁹⁷⁻⁹⁹

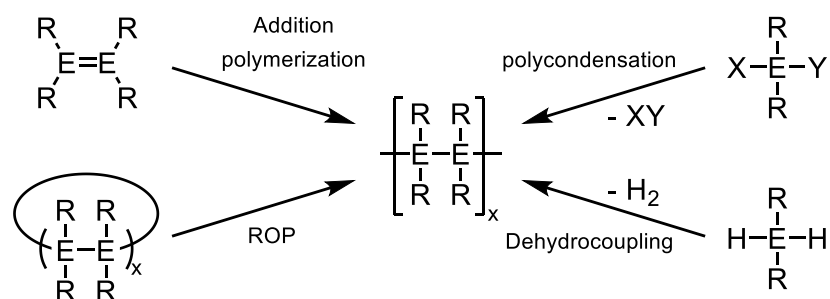


Figure 1.15 Methods for the synthesis of main group polymers.

One of the most useful polymerization methods for main group polymers, and the main focus of polymerization studies in this thesis, is ring-opening polymerization (ROP, Figure 1.15). ROP occurs when main group rings are activated either by an activator, catalyst, or heat to facilitate the ring opening reaction, forming an active chain end which can then react with other monomers, and subsequently grow the polymer chain. However, the mechanism of ROP and the ability to undergo ROP relies heavily on the monomer being considered. Firstly, thermodynamics of polymerization are considered, and described adequately by Gibbs free energy of polymerization, $\Delta G = \Delta H_p - T\Delta S_p$. For most polymerizations, ΔS_p is negative given that the increasing polymer chain length results in a decrease in degrees of freedom of the

growing polymer chain. As such, most polymerizations must be driven forward by either enthalpic preference – for example, the exothermic release of ring strain in a heterocycle, or the formation of E–E single bonds from weaker E=E double bonds – or by minimizing the temperature of the polymerization to minimize the contribution of decreasing entropy and push the polymerization equilibrium towards polymer formation.¹⁰⁰ This phenomenon is described as the *ceiling temperature*, T_c , of the polymerization, above which the entropic term outdoes the enthalpic term and results in depolymerization. Conventionally, these polymerizations are exemplified by alkene polymerizations,¹⁰¹ specifically in the ring-opening metathesis polymerization (ROMP) of cyclic alkenes,¹⁰² ring opening polymerizations of cyclic lactones,¹⁰³ and six-membered cyclic siloxanes like D_3^{Me} .²⁴ Alternatively, examples exist – generally in larger heterocycles – in which the contribution from ΔH_p is minimal due to a lack of heterocyclic strain while chain flexibility allows for an *increase* in entropy upon ring-opening. In these situations, increasing temperature emphasizes the favourable entropic term to push equilibrium from monomer toward polymerization, and hence these reactions are governed by a *floor temperature*, T_f , below which polymerization will not occur but above which polymerization is driven forward.¹⁰⁰ Examples of polymerizations that fall under this category are the thermal ring-opening of S_8 , Se_8 , and cyclooctaphenylsiloxane ($D_{4\text{Ph}}$), which all demonstrate small positive ΔH_p terms but significant ΔS_p terms,¹⁰¹ as well as the ROMP of large-membered rings bearing alkene moieties.¹⁰²

1.9 Modern Main Group Polymers

Main group polymers with inorganic backbones have begun to move out of the laboratory and into application for the unique properties their main group bonds impart. The reader is directed to two extensive reviews of main group polymers for in depth discussion on synthetic

methodologies and niche areas of main group polymer science,^{93, 95} though for the scope of this thesis a brief discussion of the key polymer families will be conducted to provide historical context.

The first main group polymer, polydichlorophosphazene $[\text{Cl}_2\text{P}=\text{N}]_n$ (Figure 1.16a), was described by Stokes in the late 19th century in serendipitous fashion while looking into the reactivity of $\text{P}_3\text{N}_3\text{Cl}_6$.¹⁰⁴ Allcock would discover routes to soluble polyphosphazenes and expand this polymer family extensively, being used for a host of material applications from o-rings to biomaterials.¹⁰⁵ To *purposely* form polymers with main group element backbones, various strategies are employed. The most logical strategy is to simply replace atoms commonplace in organic polymers, like carbon, with their heavier congeners. It is in this way that the first main family of inorganic polymers, the catenated polysilanes, polygermanes, and polystannanes, came to be (Figure 1.16b). Polysilanes were likely discovered by Kipping in 1924,¹⁰⁶ after conducting a Wurtz coupling reaction – reacting sodium metal with Ph_2SiCl_2 – to yield an insoluble crystalline material proposed to be $[\text{Ph}_2\text{Si}]_n$. West would form a far less crystalline $[(\text{PhMeSi})_x(\text{Me}_2\text{Si})_{1-x}]_n$ ($x = 0.3$ to 0.5 , $M_n = 150\text{-}300$ kDa) random copolymer in this fashion which was soluble in organic solvents and demonstrated absorbance at 330 nm, causing chain cleavage in solution, insolubility in the solid state, and making these polymers valuable for photoresists.¹⁰⁷ Polysilanes also display semiconducting properties through σ -conjugation, making these exotic conductive materials. Moving to heavier tetrrels gives polygermanes and polystannanes greater conductivity due to their enhanced polarizability and lower band gaps, though their lower bond dissociation energies result in materials much more sensitive to UV radiation and moisture and prohibits their broad investigation compared to polysilanes.¹⁰⁸

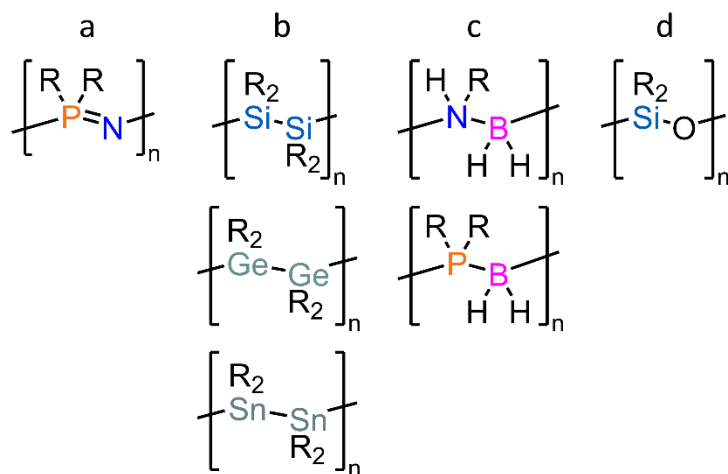


Figure 1.16 Main families of main group polymers.

Another opportunity for polymer discovery is to form isoelectronic analogies to C–C bonds found in organic polymers. In this way, Manners and coworkers pioneered the development of polyaminoboranes through the dehydropolymerization of $\text{RNH}_2\text{-BH}_3$ monomers (R = alkyl, aryl), which are formally isoelectronic to alkanes yet are inherently polar in bearing protic and hydridic hydrogens at nitrogen and boron, respectively. This inherent polarity, not present in common alkanes, allows for the dehydrogenation of these monomers at high temperature, and controlled dehydropolymerization to form well-defined, high molar mass polymeric materials through a host of catalytic methods (Figure 1.16c).^{97, 109} Aminoboranes and polyaminoboranes are especially of interest for their potential as hydrogen storage materials, given their high mass percentage of hydrogen, simple storage and handling of polymers, and potential for regeneration of monomers after hydrogen release.^{110, 111} Polyphosphinoboranes, the heavier congener of polyaminoboranes, can also be synthesized through dehydropolymerization; however, the lower polarity of the P–H bond results in more sluggish activation and the requirement for higher temperatures for polymerization, and *P*-disubstituted monomers are not polymerized (Figure 1.16c).¹¹²⁻¹¹⁷ Recently stoichiometric methods have been reported with which to conduct the dehydropolymerization of

primary and secondary phosphineboranes in mild conditions,¹¹⁸ which allows polyphosphinoboranes to be readily synthesized for a host of applications.¹¹⁹⁻¹²¹

1.10 Polysiloxanes: the prototypical main group polymer

While the main group polymers described above provide a good example of methods for strategic polymer design and the potential applications main group polymers access compared to their organic congeners, polysiloxanes (Figure 1.16d), or silicones, have found more success than almost any polymer used today. With a multibillion dollar global market and mass industrial-scale production, polysiloxanes interface with everyday life as silicone rubbers, lubricants, sealants, resins, elastomers, insulators, and permeable membranes in countless applications.^{24, 122} Polysiloxanes were first discovered by Kipping in 1901 when “Ph₂Si=O”, dubbed a “silicone” akin to the analogous carbon-based ketone, was isolated as an intractable sticky by-product of the formation of Ph₃Si–OH and was rather presciently proposed to be polymeric in nature.²⁶ They would be produced at massive scales at Dow-Corning some 40 years later.¹²³

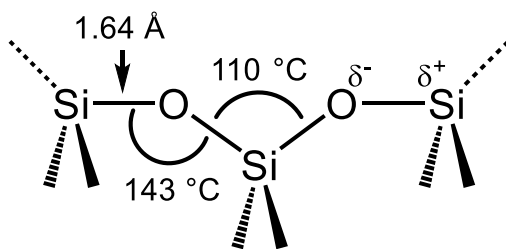


Figure 1.17 Structural representation of polysiloxanes with key bond angles, bond polarization, and bond lengths.

The valuable properties and diverse applications of polysiloxanes are intimately linked to the fundamental properties of the Si–O chemical bond and the diverse substituent chemistry that can be appended at silicon (Figure 1.17). The strength (452 kJ mol⁻¹) and length (1.64 Å) of the Si–O bond, along with the wide 143° Si–O–Si bond angles and the capacity for full 180° rotation

about Si–O bonds, result in extremely flexible and stretchable materials with low glass transition temperatures.²⁴ The fact that silicones like PDMS are generally substituted with alkyl substituents renders these polymers as quite hydrophobic despite the inherent polarity of the Si–O bond (difference in Pauling electronegativity, $\Delta\chi = 1.54$). Polysiloxanes are readily broken down in water, air, and soil when released into the natural environment²⁴ – making these polymers great alternatives to conventional hydrophobic materials which may persist through environments and food chains for centuries.¹²⁴ The siloxane linkages are extremely strong relative to most element-element single bonds, which also makes polysiloxanes impervious to breakdown by UV radiation, allowing for long lifetimes for applications. Perhaps one of the most curious properties of polysiloxanes is their transparency and high gas permeability, making these polymers excellent materials for contact lenses, biomaterials, and artificial skins.^{24, 125}

1.10.1 Synthesis of polysiloxanes

The general route to linear polysiloxanes used in industry is a two-step process. First, a chosen dichlorosilane is reacted with water to generate HCl and either linear oligomeric siloxanes with hydroxy termini or cyclic siloxanes, depending on the conditions employed.¹²⁶ In a second step, these linear or cyclic species are then subjected to either polycondensation or ROP, respectively, to form polysiloxanes (Figure 1.18a). ROP of cyclic siloxanes is the preferred route to achieving high molar mass polymers, which can be initiated with cationic or anionic species, though the success of ROP differs greatly for D₃ and D₄ cyclic species. D₃ is polymerized in living fashion by ⁿBuLi, forming polymers with little to no cyclic species present given that substantial ring strain allows for effective ring-opening of virtually all monomers and quenching of the solution affords polymers with relatively narrow PDI values (Figure 1.18b).¹²⁷ Conversely, catalytic amounts of KOH facilitate the ring-opening polymerization of D₄ at 160 °C, which

polymerizes with an entropic driving force of 6.7 kJ mol^{-1} given that the lack of strain present in these rings affords a net zero enthalpy of polymerization.¹⁰⁰ Unfortunately, the lack of strain in these species also results in chain transfer and back-biting phenomena since the rates of propagation, k_{prop} , for D_4 are on the order of the rates of chain transfer (k_{ct}) and backbiting (k_{bb}) and result in an equilibrium of cyclic siloxanes being formed and trapped in the polymer matrix in upwards of 15% (Figure 1.18c). A recent report found that back-biting equilibrium can be prevented through the coordination of alcohols to the growing anionic chain terminus, which can then be automatically quenched through decomposition of a $\text{R}_3\text{P}^i\text{Pr}$ cation and allow for complete conversion of D_4 monomers.¹²⁸ Alternatively, neutral NHC ligands have been shown to effectively polymerize D_4 through nucleophilic activation of the rings and subsequent capping/uncapping of the growing polymer chain (Figure 1.18d).¹²⁹

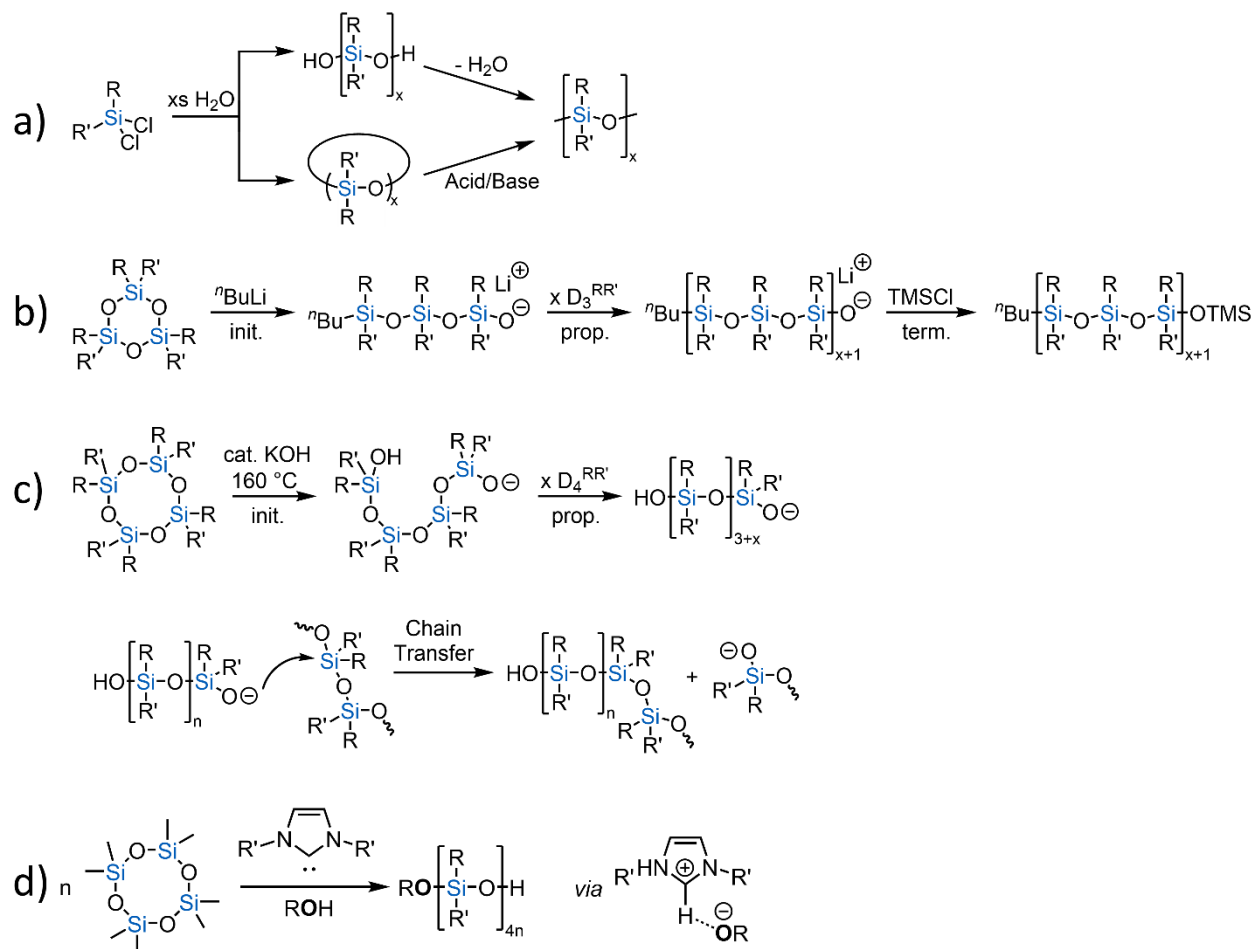


Figure 1.18 Synthetic routes to polysiloxanes using either polycondensation or ROP (a); mechanism of living anionic ROP of D3 (b); base-mediated ROP of D4 and unwanted chain-transfer mechanisms (c); and the NHC-mediated ROP of D4 (d)

A third synthetic strategy for the formation of polysiloxanes is the catalytic dehydrocoupling of hydrosilanes, which has become a valuable method for forming polysiloxanes with acid- or base-sensitive functional groups. The reaction of bis(hydrosilanes) with water or silanediols in the presence of late transition metal catalysts like Pd, Pt, or Rh has afforded stereoregular polysiloxanes and bridged $[R_2Si-R-R_2Si-O]_n$ siloxanes (Fig 19a,b).¹³⁰⁻¹³² The Piers-Rubinsztajn reaction is also a useful metal-free catalytic pathway to the dehydrocoupling synthesis of polysiloxanes. Seminal studies into the reduction of ketones with hydrosilanes in the presence

of $\text{B}(\text{C}_6\text{F}_5)_3$ (BCF) resulted in the formation of silyl ethers, which was found to proceed through formal coordination of hydride by BCF, silyl transfer to the carbonyl oxygen atom, and then following subsequent hydride transfer to the sp^2 carbon to form the silyl ether (Fig 19c). In the presence of excess hydrosilane, a second reduction of the silyl ether occurs to form a siloxane linkage. This was subsequently found to be applied to the synthesis of linear polysiloxanes through the reaction of dialkoxy and dihydrosilanes (Fig 19d), allowing for the formation of a variety of functionalized polysiloxanes, linear and dendritic polymers, crosslinked gels, and other complex structures.¹³³

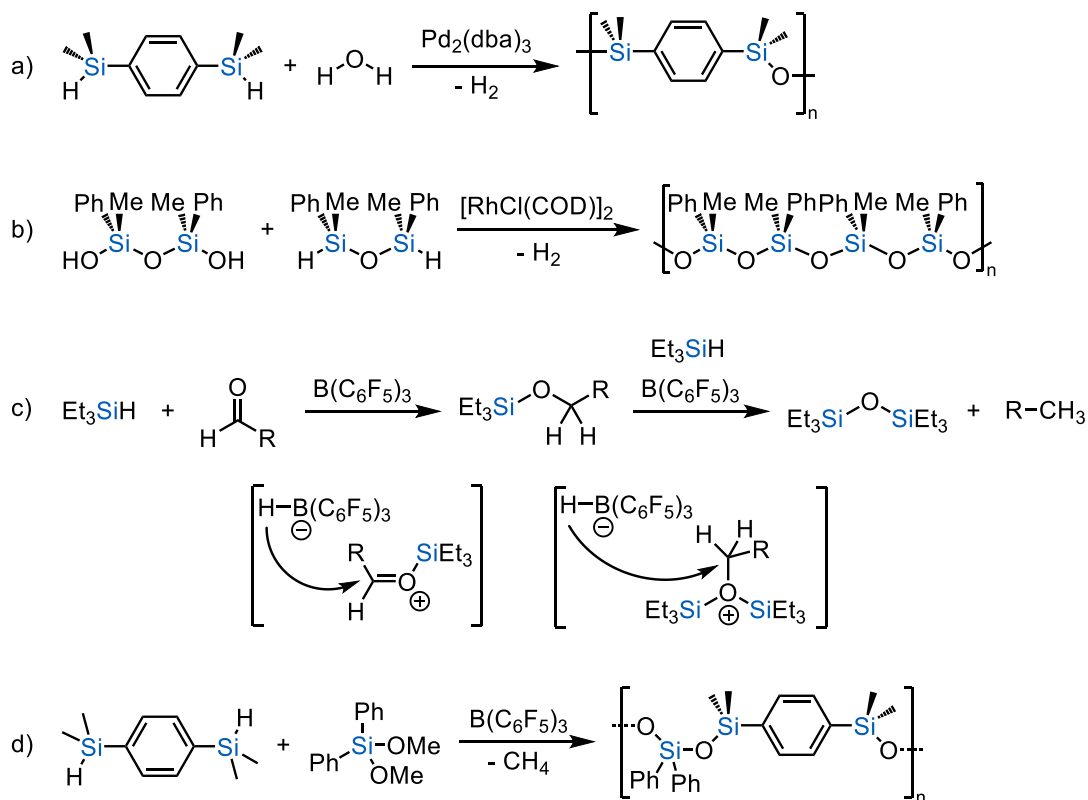


Figure 1.19 Catalytic dehydrocoupling routes to polysiloxanes materials, including metal-mediated routes with Pd(0) (a), Rh(I) (b), and through Piers-Rubinsztajn hydrosilylation reactions with catalytic $\text{B}(\text{C}_6\text{F}_5)_3$ (c and d).

1.10.2 Siloxanes as a design strategy for new main group polymers

Given their success as one of the most applied main group polymers known to date, it is sensible to look to siloxanes as a template for the rational design of new main group polymers formed through isolobal analogies to the siloxane moiety. Such materials would share a similar orbital structure as the siloxane linker but may provide different physical or electronic properties based on the elements used. Well-defined E–O (E = main group element) polymers which are isolobal to siloxanes are rare. The α and β solid state crystal structures of SO_3 crystallize as infinite polymer chains of $[\text{O}_2\text{S}-\text{O}]_n$, though rapidly depolymerize upon dissolution or heating (Figure 1.20a).²⁰ There has been substantial progress at developing diorganotelluoxane polymers $[\text{R}_2\text{Te}-\text{O}]_n$ (R = 4-alkylphenyl) by condensation with M_n spanning 10–68 kDa depending on the side chain used, though the greater atomic radius of tellurium and the inclusion of $5p$ orbitals creates a highly distorted structure with Te–O–Te bond angles of 126° and O–Te–O bond angles of 170° (Figure 1.20b).^{134–137} Sulfur-fluorine exchange (SuFEx) technologies have afforded the development of $[\text{L}_\text{C}-\text{O}-\text{SO}_2-\text{O}]_n$ (L_C = substituted aryl linker) polymers by chain growth, affording pristine control over molecular weights of this new class of material which holds promise for forming degradable inorganic main-chain polymers (Figure 1.20c).¹³⁸

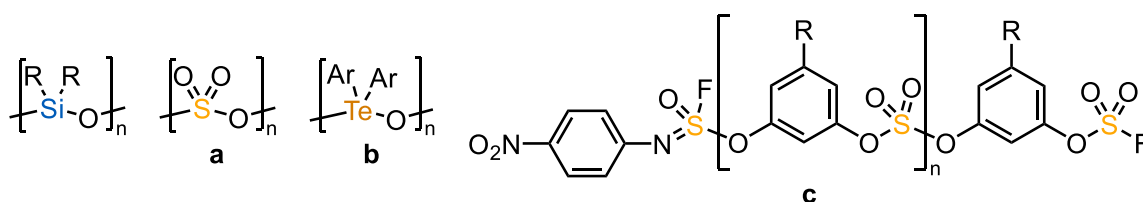


Figure 1.20 Main group polymers isolobal to polysiloxanes: poly- SO_3 (a), polytelluoxane (b), and polysulfate (c).

Rational design principles would suggest attempting to form polymers with main group elements, E, and oxygen, in which E–O are of similar size and electronegativity, would provide a

more robust route to polymer development. In this respect, the potential replacement of silicon with phosphorus to form $[\text{RP}(\text{O})\text{--O}]_n$ polymers (R = alkyl, aryl, etc) would be a logical step, as phosphorus and silicon have nearly identical atomic radii (1.11 Å and 1.07 Å, respectively)¹³⁹ and have similar electronegativity. These analogies already exist in nature as polyphosphates of the form $[\text{PO}_3]_n^{n-}$ (Figure 1.21a). These macromolecules are found in prokaryotes, plants, and mammals playing a host of roles in energy storage, cell signalling, osmotic pressure regulation, phosphate removal, stress response, and recently as a candidate for COVID-19 therapeutics.¹⁴⁰⁻¹⁴⁶ Related neutral analogues to polyphosphates are polyphosphoesters $[\text{P}(\text{O})\text{R}\text{--O}\text{--C}_x\text{--O}]_n$ (R = alkyl, aryl, OR', H, or NR''R''') (Figure 1.21b), which have emerged as useful materials for biomedical applications,¹⁴⁷⁻¹⁴⁹ synthetic DNAs,^{150, 151} and flame retardants.^{152, 153} The most related P-O polymer to polysiloxanes are the polyphosphonates $[\text{P}(\text{O})\text{R}\text{--O}]_n$ (Figure 1.21c), however high molar mass polyphosphonates with satisfactory characterization were largely absent from the literature. An early report of the condensation of RPOCl_2 and $\text{RPO}(\text{OH})_2$ (R = Me, Ph) claimed to form $[\text{MeP}(\text{O})\text{--O}]_n$ and $[\text{PhP}(\text{O})\text{--O}]_n$, but materials were only characterized by elemental analysis,⁷⁸ and subsequent reports only provided evidence for oligomeric and poorly characterized materials.^{154, 155} Given their isolobal comparison to siloxanes, a feasible route to polyphosphonates could be through the ROP of cyclic phosphonates (Figure 1.21d).

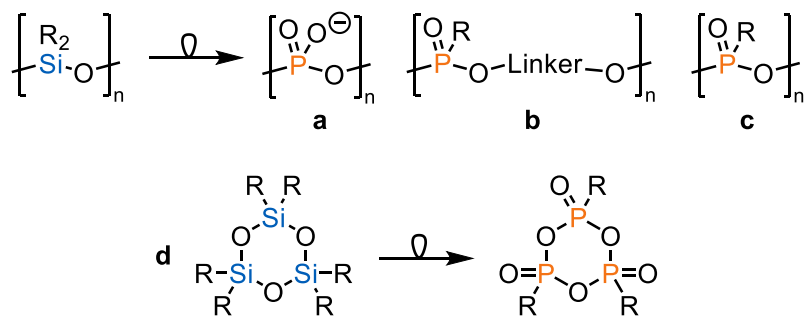


Figure 1.21 Isolobal analogies between polysiloxanes and polyphosphonates (a), polyphosphoesters (b), and polyphosphates (c), and between cyclic siloxanes and cyclic phosphonate/siloxane hybrids.

As discussed *vide supra*, our lab recently reported the complete synthesis, solution- and solid-state characterization of cyclic phosphonates (Figure 1.14, *vide supra*).⁸⁷ DSC traces of the crystalline $[\text{RP}(\text{O})\text{--O}]_3$ rings revealed intense melt endotherms in the first heating cycle succeeded by a small exotherms consistent with ring-opening of strained heterocycles; subsequent heating cycles showing glass transition deflections consistent with polymer formation. As such, our lab proceeded with large scale ROP experiments to see if the phenomena were reproducible at larger scale. These experiments produced four glassy, hydrolytically-sensitive polymers which were found to have degrees of polymerization of >70 with molar masses between 13,000 to 17,000 g mol^{-1} (as determined by MALDI-ToF MS) and significant thermal stabilities up to 310-380 °C (Figure 1.22a). The polymers, aside from the insoluble $[\text{PhP}(\text{O})\text{--O}]_n$, readily dissolve in common organic solvents (CDCl_3 , toluene, and hexanes, etc). Solution NMR experiments revealed that polymers lacking kinetic stabilization, like $[(p\text{-}^t\text{BuPh})\text{P}(\text{O})\text{--O}]_n$, depolymerize to a kinetic distribution of cyclic phosphonates, while polymers with ortho-aryl substitution ($\text{R} = \text{Mes}$, $p\text{-}^t\text{BuMes}$) have greater kinetic stability in solution and have depolymerization half lives of $t_{1/2} > 15$ days.

To verify that the formed polymers were indeed polymers with $(\text{P}\text{--O})_n$ backbones and were not the result of complex degradations of cyclic phosphonates at high temperatures, $[\text{PhP}(\text{O})\text{--O}]_n$ was reacted with the Lewis base 4-dimethylaminopyridine (DMAP) in solution. This resulted in the complete dissolution of the insoluble polymer to yield the Lewis base adduct $(\text{DMAP})\text{PhPO}_2$. These adducts are also accessible through the reaction of DMAP with $[\text{PhPO}_2]_3$ and $[\text{MesPO}_2]_3$, respectively, providing evidence that the polymers are truly polyphosphonates. Interestingly, these adducts exist in an equilibrium with the cyclotriphosphonate monomers and free DMAP, and so Lewis acids were employed to see if the Lewis base adducts could be irreversibly decomposed to

re-form free cyclotriphosphonates. Reactions with $\text{B}(\text{C}_6\text{F}_5)_3$ (BCF) resulted in the formation of push-pull adducts of the form $(\text{DMAP})\text{PhPO}_2(\text{BCF})$ (Figure 1.22b). Reactions with weaker Lewis base BPh_3 resulted in the formation of the $[\text{DMAP}][\text{BPh}_3]$ adduct, releasing the PhPO_2 fragment to form $[\text{PhPO}_2]_3$ rings. This suggests that polyphosphonates provide a rare example of polymeric materials which are recyclable to the monomer (Figure 1.22c).¹⁵⁶

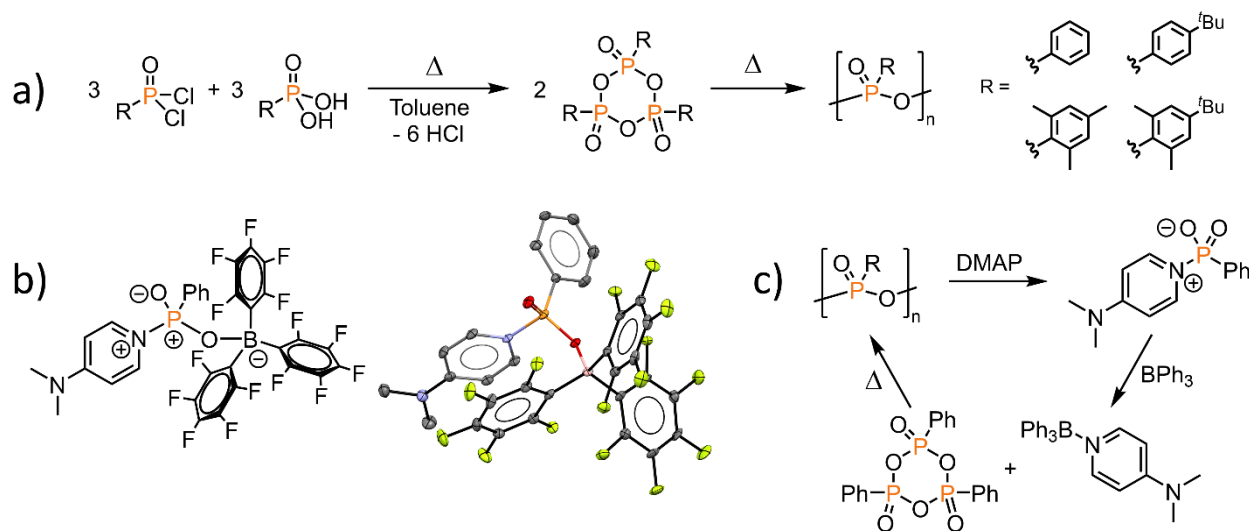


Figure 1.22 The synthesis of cyclic phosphonates and polyphosphonates (a); the structural representation and single-crystal X-ray structure of the Lewis acid-base adduct of PhPO_2 monomer of $[\text{PhP}(\text{O})\text{--O}]_n$ (b), and the closed-loop recyclability of polyphosphonates back to cyclic phosphonates by DMAP coordination and subsequent BPh_3 -induced release of RPO_2 .

The second strategy for using siloxanes as a template for new polymer development would be to form hybrid polymers of siloxanes, with backbones of the form Si--O--E--O (E = main group element), thereby incorporating the favourable physical properties of the siloxane linkage and with the properties of the chosen element incorporated into the siloxane backbone. Polyborasiloxanes $[\text{RB--O--R}_2\text{Si--O}]_n$ are a prototypical example of this design strategy. Developed in the 1940s patent literature through the treatment of PDMS with boronic and boric acids or borax,^{157, 158} the crosslinked polymeric elastomers dubbed as “Silly Putty” are valued for their composition

dependent properties, high thermal stability and heat capacity, viscoelasticity, and adhesive properties.¹⁵⁹ Well-defined linear derivatives have since been developed through condensation reactions between dichlorosilanes and boronic acids¹⁶⁰ and dehydrocoupling reactions between silanediols and boranes¹⁶¹ or between silanes and dimethylphenylboronate.⁹⁸ Our lab attempted to form such materials in similar fashion to conventional polysiloxanes *via* the formation of well-defined strained B–O–Si–O heterocycles which could undergo ROP.¹⁶² Six-membered borasiloxanes $[\text{PhB–O–R}_2\text{Si–O}]_n$ (R = Me, Ph) and eight-membered $[\text{PhB–O–Me}_2\text{Si–O–Me}_2\text{Si–O–Me}_2\text{Si–O}]_n$ were subjected to ROP through the melt in the presence of $\text{K}[\text{OSiMe}_3]$, however instead of undergoing polymerization, it was found instead that ring-disproportionation reactions occurred to form various mixed borasiloxane rings through a $\text{Me}_3\text{Si–O}^-$ mediated back-biting mechanism (Figure 1.23).¹⁶²

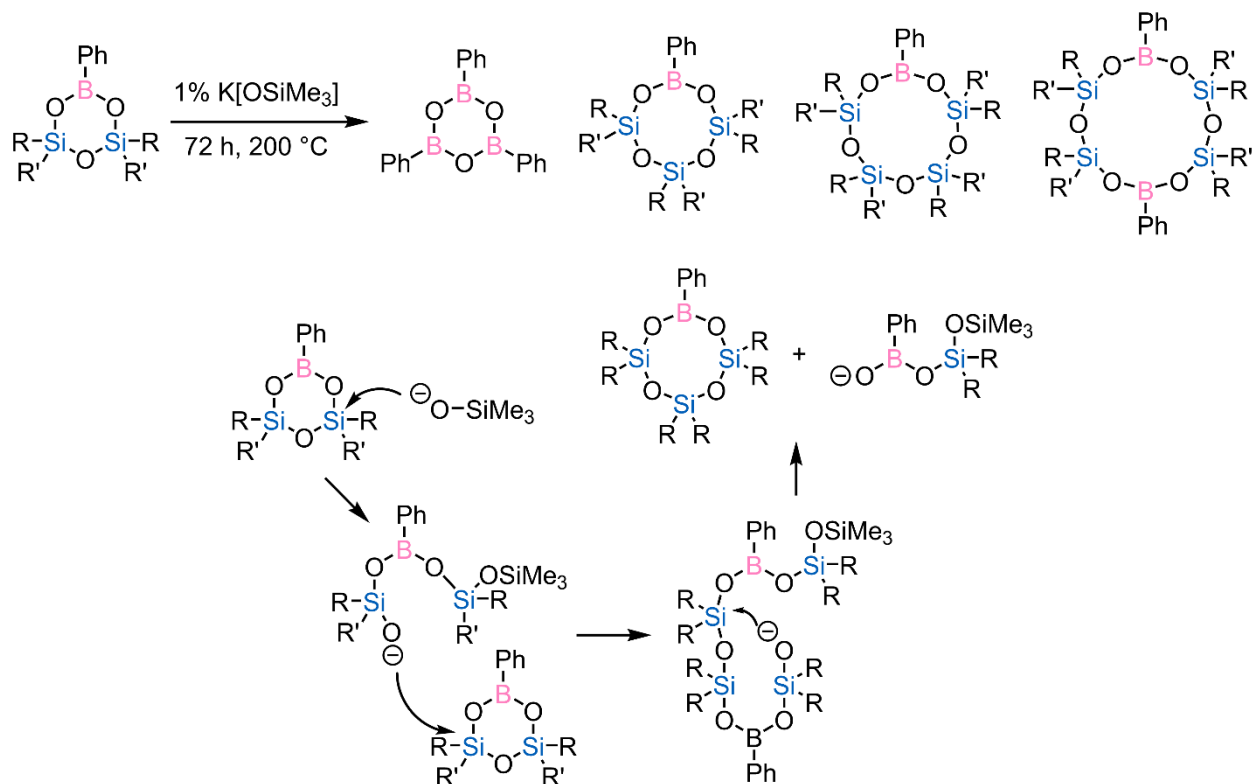


Figure 1.23 Ring-redistribution reactions for cyclic borasiloxanes in a typical ROP experiment (top), and the proposed mechanism for back-biting phenomena in experimental conditions

Another opportunity for the design of hybrid polysiloxanes would be to incorporate phosphonate linkages to form a polymer with a P–O–Si–O backbone of the form [RP(O)–O–R₂Si–O]_n. Known synergistic mechanisms between phosphorus and silicon to quench flames^{163, 164} and the high content of these elements in a P–O–Si–O main-chain polymer would make such materials excellent candidates for flame retardants akin to other main group polymers.^{121, 152, 165} A survey of the literature found that P–O–Si–O polymers have been sparsely investigated. In 1967, Kerger and Kohlhaas proposed the formation of [(CH₂=CH)P(O)–O–SiR₂–O]₂ (R = Me, Ph) heterocycles, which could undergo ring-opening polymerization at 100 °C and then subsequently be cross-linked between through vinyl linkages using AIBN (Figure 1.24a), however these materials were only characterized by elemental

analysis.¹⁶⁶ More than a decade later, Collis and coworkers reported the formation of $[\text{RP}(\text{O})\text{--O--SiPh}_2\text{--O}]_n$ ($\text{R} = \text{Me}, \text{Ph}, \text{O}^-\text{Li}^+$, or O^-Na^+) through the polycondensation reaction between $\text{RP}(\text{O})(\text{OH})_2$ and Ph_2SiCl_2 , through only oligomers of $n = 3\text{--}5$ were characterized by gel permeation chromatography (GPC) (Figure 1.24b).¹⁶⁷ Most recently, Mitova and coworkers reported a polycondensation route between dimethyl H-phosphonate and dichlorodimethylsilane,¹⁶⁸ yielding low-molecular weight polymers of $[\text{HP}(\text{O})\text{--O--SiMe}_2\text{--O}]_n$ with degrees of polymerization of $n = 28$ (molar mass ≈ 4000 g/mol by NMR peak integration) and with their material properties left unexplored (Figure 1.24c). While the original strategy of Kerger and Kohlhaas may not have been well characterized, their strategy for the ROP of a P--O--Si--O heterocycle is likened to that previously attempted in our lab for the formation of B--O--Si--O polymers.¹⁶² While B--O--Si--O heterocyclic ROP methods have previously failed for hybrid polysiloxanes synthesis, the replacement of a skeletal silicon atom in a cyclic siloxane with phosphorus may yet yield a heterocycle capable of undergoing ROP given the small difference in the covalent radii of silicon (1.11 Å) and phosphorus (1.07 Å)¹³⁹ and the established ROP methods of cyclic tri- and tetra-siloxanes.²⁴ However, akin to the case of cyclic phosphonates, cyclic phosphonosiloxanes have been reported sparsely in the literature. Most examples lack robust structural characterization,^{166, 169-171} one example was crystallized with no further characterization as a side-product of a xerogel reaction (Figure 1.24d),¹⁷² and one example was synthesized purposefully and structurally characterized, though lacked thorough spectroscopic analysis (Figure 1.24e).¹⁷³ As such, substantial work is required to better understand P--O--Si--O heterocycles if they are to be used for the formation of a new main group polymer family.

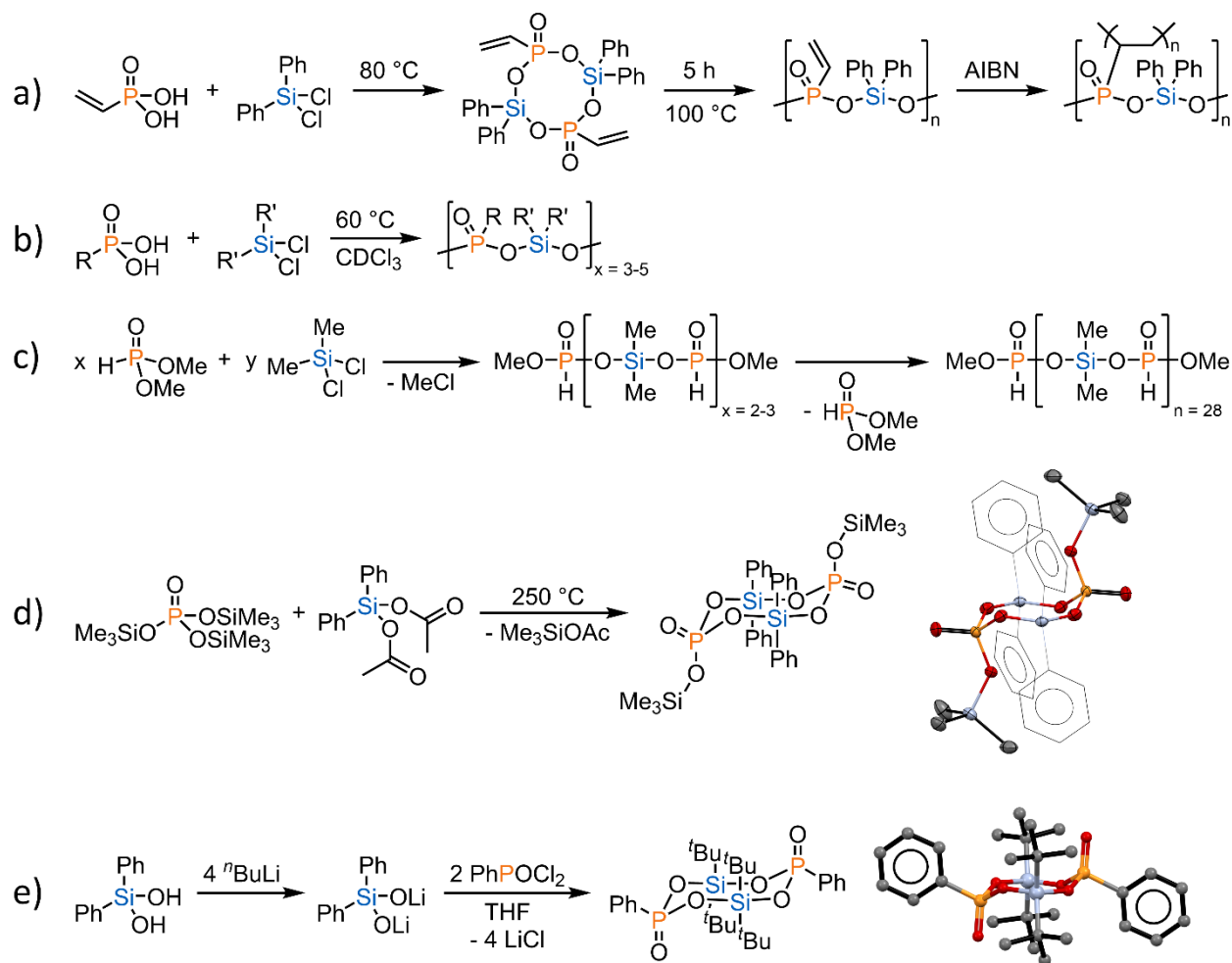


Figure 1.24 A survey of phosphonate siloxane polymeric attempts, including the ROP of cyclic phosphonate-siloxanes and subsequent cross-linking of vinyl phosphonate moieties (a); the polycondensation of phosphonic acid with dichlorosilanes (b); and the polycondensation between H-phosphonic esters and dichlorosilanes (c); as well as the synthesis and single-crystal X-ray structures of structurally characterized cyclic phosphonate-siloxane heterocycles (d,e).

1.11 Thesis outlook

This introduction has reviewed the fundamental chemistries of cyclic phosphanes and their ring expansion reactions, as well as the chemistry of cyclic phosphonates and strategies to accessing new polymer families. It is clear from this review that the newly-reported ring-expansion reactions of cyclic phosphanes require further study to access their larger applicability to inorganic

materials development, and that ring-opening polymerization reactions, such as those observed in $[\text{RP}(\text{O})\text{--O}]_3$ species, may provide a route to develop new main group polymer families.

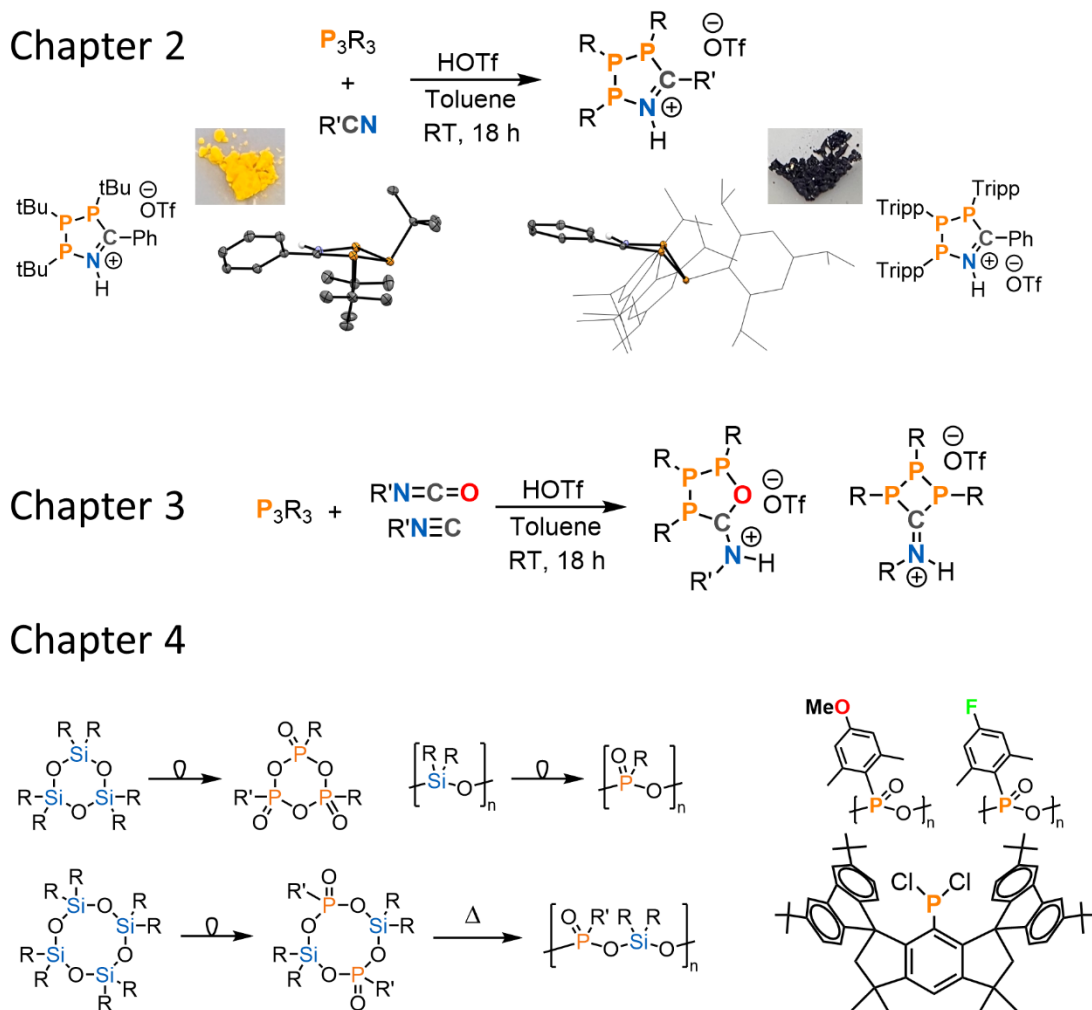


Figure 1.25 Preview of synthetic chapters 2, 3, and 4; Chapter 2 describes the ring-expansion reaction of aryl-substituted cyclic phosphanes, P_3Ar_3 ($\text{Ar} = \text{Mes}, \text{Dipp}, \text{Tripp}$) with nitriles to generate new inorganic materials with colours spanning the visible spectrum (see structure and photo inset on right) compared to yellow materials observed for ring-expansions of P_3^tBu_3 (see structure and photo inset on left); Chapter 3 describes the acid-mediated insertion of isocyanates and isonitriles into P_3^tBu_3 to form P_3C and P_3CO ring scaffolds (see Chapter 3 in Figure), and assesses the effect of electronics and heavy main group element unsaturated bonds on ring-expansion; Chapter 4 describes the synthesis and characterization of eight-membered mixed siloxane-phosphonate rings and attempts toward ring-opening polymerizations of these species, as well as progress made toward the synthesis of kinetically and electronically stabilized polyphosphonates and a sterically encumbered dichlorophosphine precursor to a phosphonate monomer.

The following chapters of this thesis look to address these gaps in the literature (Figure 1.25). The first synthetic chapter of this thesis looks to explore the applicability of the nitrile ring expansion to sterically encumbered cyclic phosphanes, which have been recently accessed in reproducible fashion (Figure 1.25, top left). We find that the same reactivity is observed, though a series of molecules which display protonation-dependent structure-colour switching were unearthed in this process (see for example, Figure 1.25 top right). The second synthetic chapter of this thesis explores the acid-mediated $P_3^tBu_3$ ring expansion reaction and its applicability to other unsaturated substrates besides nitriles, with the goal of establishing the method as a potential solution for new phosphorus heterocycle development. This method affords access to P_3C and previously unreported P_3CO cationic and neutral frameworks with isonitriles and isocyanates, respectively (see Figure 1.25, middle), while establishing electronic limitations of the aforementioned substrates as well as those of unsaturated bonds containing heavy main group elements. The third synthetic chapter of this thesis reports the first well-defined syntheses and detailed physical characterization of P-O-Si-O heterocycles, their emergent dynamic behaviour, and their potential for ROP (see Figure 1.25, bottom left). Furthermore, preliminary attempts to modify the steric and electronic environments of phosphonate moieties are reported, with the goal of designing less dynamic P-O-Si-O systems (see Figure 1.25, bottom right).

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Chapter 2. 1,3-Dipolar Cycloadditions of Nitriles with Sterically Encumbered Cyclic Triphosphanes: Synthesis and Electronic Structure of Phosphorus-rich Heterocycles with Tunable Color

Chapter 2 describes the synthesis and structure-function relationship of sterically-encumbered 1-aza-2,3,4-triphospholenium cations and their free bases. This chapter has been reproduced from M. A. Nascimento, E. A. LaPierre, B. O. Patrick, L. K. Watanabe, J. E. T. Watson, J. M. Rawson, C. Hering-Junghans,* and I. Manners.* *Submitted*.

Collaborators: Dr. Etienne LaPierre assisted in preliminary syntheses and crystallizations of P_3CN heterocycles, Dr. Lara Watanabe conducted EPR of P_3CN heterocycles, Jade Watson assisted in the synthesis of P_3CN heterocycles required for manuscript edits, Dr. Brian Patrick collected single crystal diffraction data, and Dr. Christian Hering-Junghans provided initial P_3Ar_3 material for test reactions and conducted DFT studies.

2.1 Abstract

We describe the synthesis, the solid state and electronic structures of a series of tunable 5-membered cationic and charge-neutral inorganic heterocycles featuring a P_3CN core. 1-aza-2,3,4-triphospholenium cations $[(PR)_3N(H)CR']^+$, $[1_R]^+$ ($R' = \text{Me, Ph, } p\text{-MeOPh, } p\text{-CF}_3\text{Ph}$) were formed as triflate salts by the cycloadditions of strained cyclic triphosphanes $(PR)_3$ ($R = \text{'Bu, Mesityl (Mes), 2,6-di-isopropyl-phenyl (Dipp), 2,4,6-tri-isopropyl-phenyl (Tripp)}$) with nitriles $R'CN$ ($R' = \text{Me, Ph, } p\text{-MeOPh, } p\text{-CF}_3\text{Ph}$) in the presence of triflic acid. The charge-neutral free-base analogues $(PR)_3NCR'$ (2_R) were formed by subsequent deprotonation with triethylamine and possess a typical

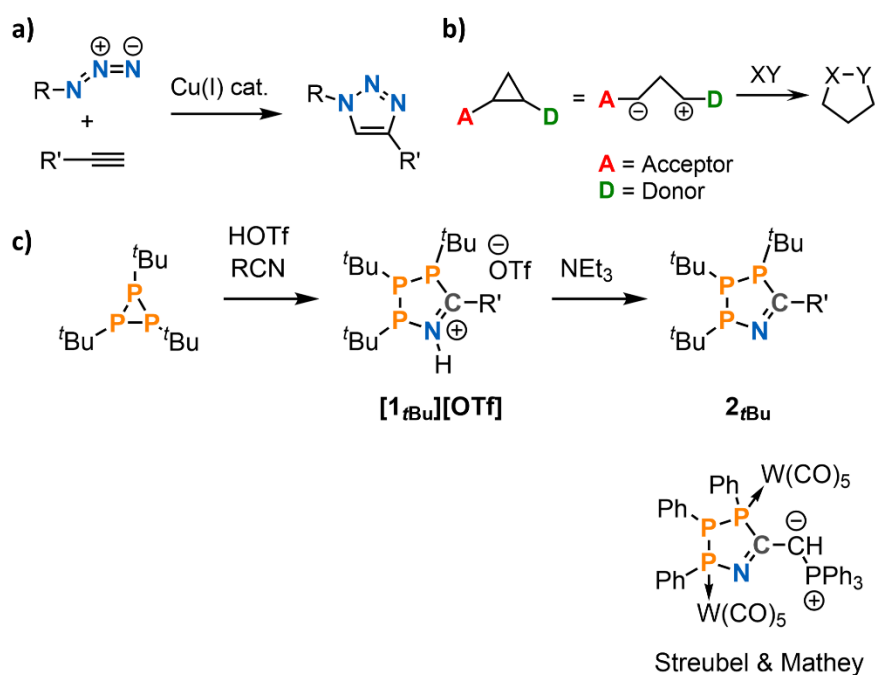
envelope geometry about the P_3CN core and yellow to orange colors in the solid state and solution depending on the phosphorus substituent. The P_3CN cores in the cationic species $[1_R]^+$ become increasingly non-planar as the steric bulk of the R group at phosphorus is increased, which results in a decrease in the HOMO-LUMO gap and distinct low-energy UV-Visible absorbance bands. This allows access to colors spanning red, blue, indigo, and magenta. TD-DFT calculations provide valuable insight into these phenomena and indicate the presence of a HOMO-LUMO charge-transfer transition from the HOMO located on the P_3 framework to the $N=C-R'$ -based LUMO in the cationic species. The cations $[1_R]^+$ represent rare examples of phosphorus-rich heterocycles with tunable color.

2.2 Introduction

Decades of intensive research into catalytic and stoichiometric organic transformations have resulted in a myriad of routes for carbon-carbon and carbon-heteroatom bond formation.¹⁻⁵ In contrast, analogous routes to bonds between main group elements are poorly developed.⁶⁻¹⁰ In most cases, reactions such as reductive coupling and salt metathesis continue to represent the state of the art in forming main group element E-E bonds, but these often involve aggressive reaction conditions that restrict the introduction of functional groups and lead to the formation of unwanted byproducts. The adaptation of well-established organic methodologies to inorganic substrates offers the possibility of new or improved routes to molecular and polymeric inorganic species with a wide range of applications.¹¹⁻¹⁵

A common atom-economic organic route to organic heterocycles is the 1,3-dipolar cycloaddition. Pioneered by Huisgen and Sharpless through reaction of azides with alkynes,^{16, 17} the reaction of azides has been expanded to nitriles,¹⁸ phosphalkynes,¹⁹⁻²² cyaphides,^{23, 24} and arsaalkynes²⁵ in the presence of copper or ruthenium catalysts, readily yielding 5-membered

heterocycles selectively with high atom-economy and yields (Scheme 2.1a). This reactivity is also mimicked in the ring expansions of vicinal donor-acceptor (DA) cyclopropanes, in which electron donating and withdrawing groups polarize a carbon-carbon bond and stabilize partial positive and negative charges, respectively (Scheme 2.1b).^{26, 27} These DA cyclopropanes react with 1,2 dipoles to yield heterocycles akin to Huisgen-Sharpless cycloadditions, and have expanded the utility and substrate scope of cycloaddition chemistry. While cycloadditions have facilitated the discovery of a variety of new molecules and reactivities in organic syntheses, their exploration for inorganic systems is limited to several investigations.²⁸⁻³⁵



Scheme 2.1 a) Prototypical Huisgen-Sharpless cycloaddition; b) generalized donor-acceptor cyclopropane ring expansion; c) cycloaddition and functionalization chemistry of $P_3^tBu_3$.

Cyclic triphosphanes, P_3R_3 , have shown potential for ring expansion chemistry as evidenced by a growing number of reported insertions and activations reactions.³⁶⁻³⁹ These results led us to the discovery of an inorganic transformation analogous to donor-acceptor cyclopropane cycloadditions, in which nitriles $R'CN$ are inserted into the P–P bonds of cyclic triphosphane

$P_3^tBu_3$ through either Brønsted or Lewis acid activation.⁴⁰ This new methodology provides a simple and rapid click-chemistry route to 1-aza-2,3,4-triphosphenium cations or 1-aza-2,3,4-triphospholene rings (Scheme 2.1c, right), for which the neutral rings were only previously reported to form in the coordination sphere of $W(CO)_5$, which could not be subsequently removed (Scheme 2.1c, bottom right).⁴¹ The cationic rings, which are accessed by cycloaddition reactions mediated by stoichiometric amounts HOTf (OTf = trifluoromethylsulfonate), are readily deprotonated (Scheme 2.1c), and can be cycled between neutral and cationic states by subsequent addition of acid or base. The cycloaddition reaction can be rendered catalytic by an appropriate Lewis acid, of which the best and most selective catalyst was found to be $SbPh_3Cl(OTf)$, while other Lewis acids such as tris(pentafluorophenyl)borane resulted in the selective formation of $P_4^tBu_4$. The $P_3^tBu_3NCR'$ rings themselves show no evidence for low-energy electronic transitions, and are either colorless or yellow as is typical of cyclic phosphanes.

This inorganic ring expansion provides a route to a class of phosphorus rich heterocycles. Such cyclic species are of general interest as OLED emitters⁴²⁻⁴⁴ and fluorophores⁴⁵⁻⁴⁷ – with examples ranging from small molecule photoswitches⁴⁸ to phosphorus analogues of common dyes.⁴⁹⁻⁵¹ Acyclic phosphorus compounds have attracted attention as dyes and pigments for many decades since phosphamethine cyanines were first reported as red crystalline solids by Dimroth in 1964, and subsequent examples exhibit colors spanning yellow, orange, and red.⁵²⁻⁵⁹ A recently reported carbene– $SiCl_2=P$ –Tripp (Tripp= 2,4,6-triisopropylphenyl) species exhibits deep blue (second from right, bottom in Figure 2.1a) or red coloration (far left, second from bottom in Figure 2.1a) depending on the carbene used.⁶⁰ Phosphoniums^{47, 61, 62} and phospholes^{48, 61-68} have also shown colors that include red, orange, green, blue, and purple, although these species achieve their color on account of large polycyclic aromatic systems appended to hyperconjugated phosphorus

centres.⁶⁹ Phosphorus radicals, as expected for most radical species, form intensely-colored compounds across the visible spectrum as well.⁷⁰⁻⁷³ However, there are few instances of color in closed-shell phosphorus-rich or catenated phosphorus species, with a unique example of a gallium-bound 1,2-diphospha-1,3-butadiene recently reported by Schulz.⁷⁴

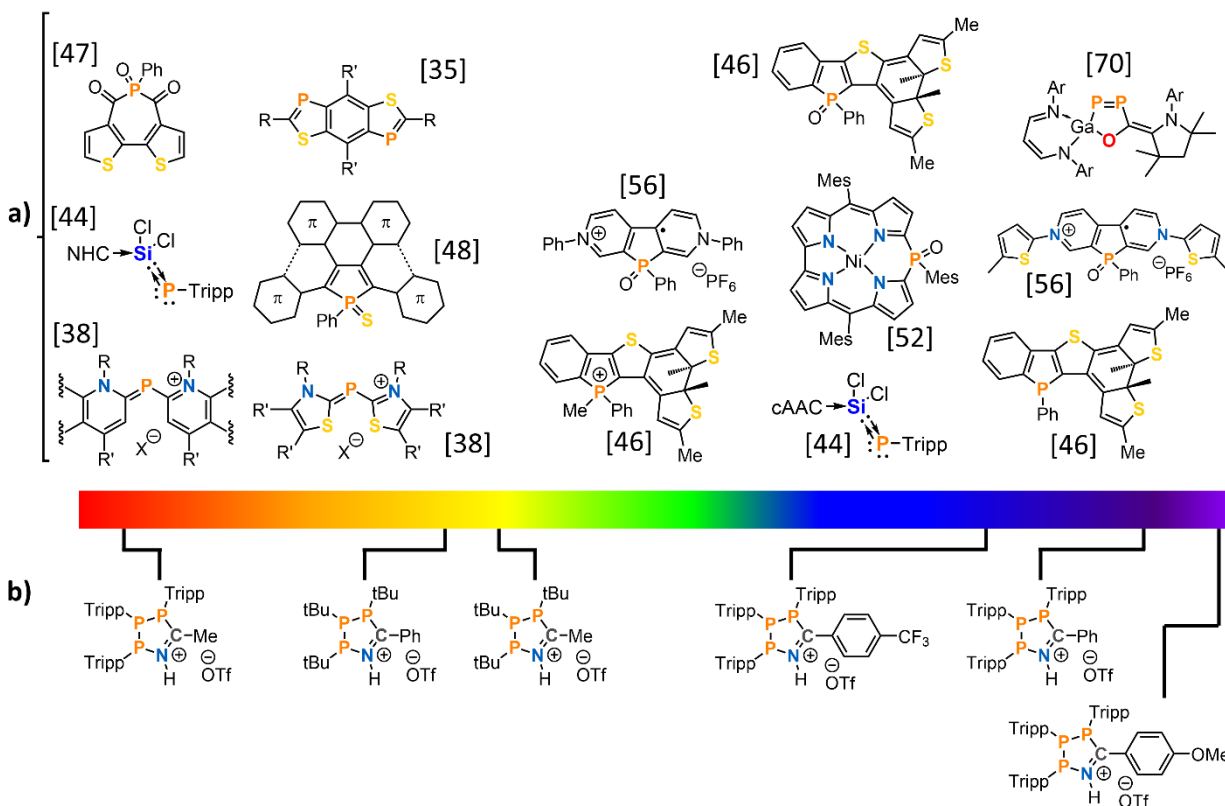
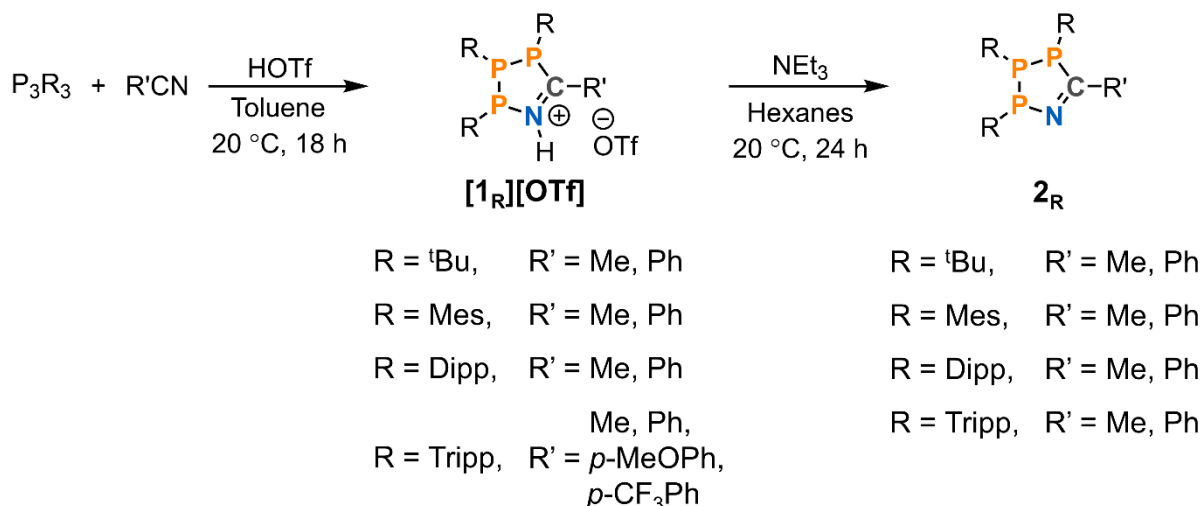


Figure 2.1 Examples of previously reported colored phosphorus species (a) and colored phosphorus species reported in this work (b), shown in line with their visible colors. References are shown in brackets beside each figure.

Recently, sterically encumbered aryl-substituted cyclic triphosphanes P_3R_3 [$R = \text{Mes}$, Dipp, and Tripp] were prepared through the reduction of RPX_2 ($X = \text{Cl}, \text{Br}$) with Zn and PMe_3 .⁷⁵ We have therefore explored whether 1,3-dipolar cycloaddition reactions could be extended to sterically encumbered cyclic phosphanes other than $P_3^t\text{Bu}_3$ to establish the steric limits of this method (Scheme 2.2). Herein we report the synthesis and detailed studies of the electronic

properties and structures of sterically encumbered 1-aza-2,3,4-triphospholeniums and their neutral 1-aza-2,3,4-triphospholene analogues (Scheme 2.2) and provide an explanation for their unusual and tunable photophysical properties.



Scheme 2.2 Synthesis of 1-aza-2,3,4-triphospholenium triflate salts and their corresponding free bases in this work with a labelling notation, where R describes the substitution at phosphorus and R' describes the nitrile substituent.

2.3 Results

2.3.1 Synthesis and NMR spectroscopic characterization of cationic and neutral P_3NC heterocycles $[\mathbf{1}_\text{R}]^+$ and $\mathbf{2}_\text{R}$

Our investigation into the effect of steric hindrance on the nitrile click chemistry of cyclic triphosphanes began with the reaction of P_3Tripp_3 with an excess of acetonitrile (MeCN) in the presence of triflic acid. P_3Tripp_3 was dissolved in a 1:1 v/v solution of toluene/MeCN to form a colorless solution. Upon subsequent addition of one equivalent of neat triflic acid at 20 °C a deep red homogeneous solution formed. This coloration was unexpected, given that analogous reactions with P_3tBu_3 yielded yellow solutions and solids (Figure 2.2). Moreover, an aliquot of the red reaction solution analyzed by ^{31}P NMR spectroscopy showed conversion to an AMX spin system

consistent with formation of the 1-aza-2,3,4-triphosphenium ring $[1_{\text{Tripp}}]^+$ ($\text{R}' = \text{Me}$) (Figure 2.2, top right). Removal of the volatiles followed by washing of the tacky residue with hexanes yielded a red powder. ^1H NMR spectra in CDCl_3 (Figure A.1, page 189) revealed inequivalent shifts for the Tripp methine environments, as well as a characteristic doublet of doublets ($J_{\text{HP}} = 10.2$ Hz, $J_{\text{HH}} = 4.6$ Hz) associated with the methyl protons arising from acetonitrile incorporation. A small broad singlet at 12.61 ppm was assigned to the H-N resonance of the protonated skeletal nitrogen center. A ^{19}F NMR spectrum taken in CDCl_3 (Figure A.2, page 190) showed a singlet at $\delta_{\text{F}} = -78.7$ ppm, typical of the triflate anion. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum taken in CDCl_3 (Figure A.3, page 191) revealed the same AMX spin system as observed in the reaction mixture, and when compared to previously synthesized $[1_{\text{tBu}}]^+$ ($\text{R}' = \text{Me}$) the most downfield peak was further shifted upfield by approximately 52 ppm, while both J_{PP} couplings are smaller than in $[1_{\text{tBu}}]^+$ ($\text{R}' = \text{Me}$) by approximately 120 Hz and 70 Hz, respectively (Figure 2.2, top left).

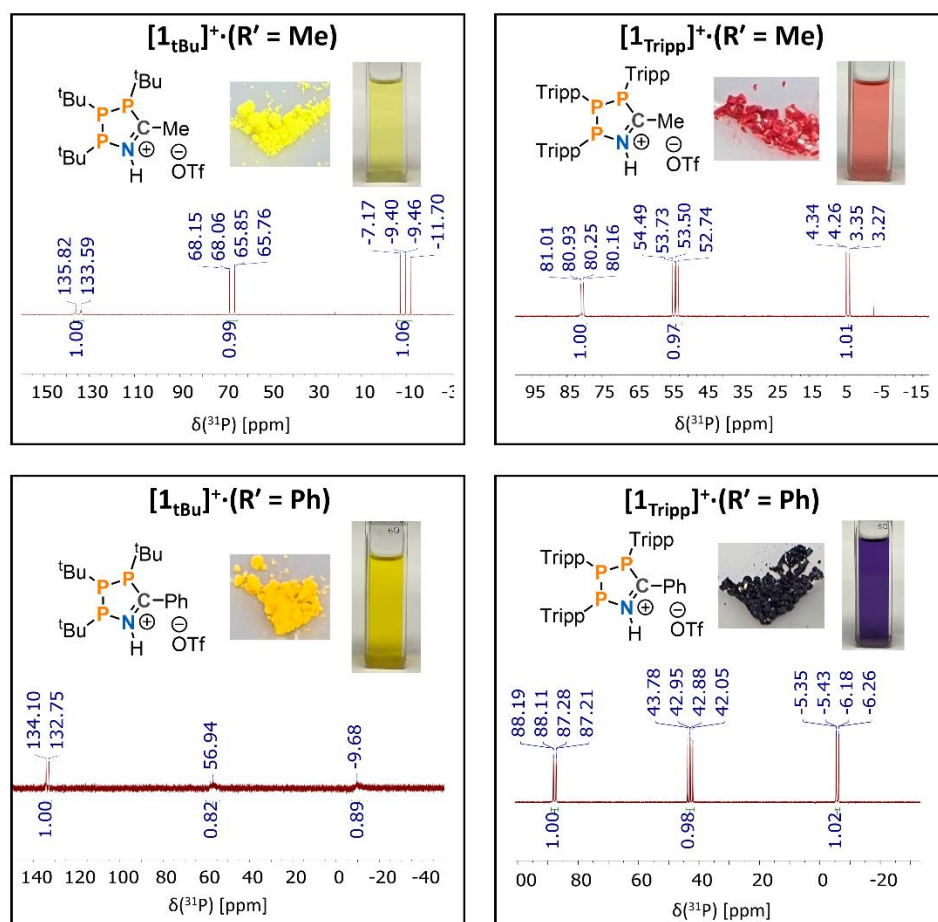


Figure 2.2 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in CDCl_3 for a comparative set of 1-aza-2,3,4-triphospholenium cations, and photographs of their $[\text{OTf}]^-$ salts in the solid state and in solution (CH_2Cl_2).

Given that P_3Tripp_3 was capable of undergoing nitrile insertion chemistry, we attempted to replicate the success of this synthetic approach using P_3Dipp_3 and P_3Mes_3 . $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Me}$) was prepared similarly and was found to be virtually identical to $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Me}$) in color with similar ^{31}P , ^1H and ^{19}F NMR spectroscopic characteristics (Figure A.23-Figure A.25, pages 213-215). In contrast, the attempted synthesis of $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Me}$) was less straightforward. After conducting a similar work-up to that for $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Me}$) and $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Me}$), a yellow powder was obtained, reminiscent in color to $[\mathbf{1}_{\text{tBu}}]^+$ ($\text{R}' = \text{Me}$). Recrystallization of the powder afforded crystals which, when dissolved in CDCl_3 , yielded the anticipated AMX $^{31}\text{P}\{^1\text{H}\}$ NMR

spectrum but also the presence of phosphorus-containing impurities characterized by resonances at -59.5 ppm (singlet, ca. 7%) and -18.9 (two peaks, ca. 2%) (Figure A.40). The impurity peaks appeared as a doublet of multiplets and the same two peaks, respectively, in the ^{31}P NMR spectrum (Figure A.39). Recrystallization of $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Me}$) by allowing a fluorobenzene/diethylether solution layered with *n*-pentane to stand for a month at -30 °C resulted in a mixture of yellow prisms of $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Me}$) and a small amount of yellow plates that were identified crystallographically as the diethylether solvate of P_6Mes_6 (Figure A.89). The latter species was previously found as a side-product of the reaction between $\text{Na}_2[\text{P}_4\text{Mes}_4]$ with $\text{Rh}(\text{COD})\text{Cl}$ by Hey-Hawkins and coworkers, which was also only characterized by single-crystal X-ray crystallography.⁷⁶ Given that P_6Mes_6 is a neutral unprotonated species with one unique phosphorus environment, we do not associate this molecule with the unknown NMR impurities and the mechanism of its formation is unclear.

Next, we synthesized the benzonitrile-derived series $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$), $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Ph}$), $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Ph}$) and $[\mathbf{1}_{\text{tBu}}]^+$ ($\text{R}' = \text{Ph}$) to provide a comparison in their properties with those of $[\mathbf{1}_{\text{R}}]^+$ ($\text{R}' = \text{Me}$). In this case P_3Tripp_3 was dissolved in a 2:1 v/v solution of toluene/PhCN to form a colorless solution. Addition of one equivalent of neat triflic acid at 20 °C led to the formation of a highly colored deep blue solution. Upon removal of volatiles, the dark blue residue of $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$) was washed with hexanes to yield a blue powder which displays an AMX spin pattern in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum virtually identical to that of $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Me}$) (Figure 2.2, bottom right). The analogous reaction was repeated with P_3Dipp_3 , again yielding a blue powder of $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Ph}$) which also displays an AMX spin pattern in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra virtually identical to $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Me}$). In the case of $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Ph}$), we obtained an orange powder as opposed to the yellow $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Me}$) that also produced an AMX spin pattern with second order effects in

the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum similar to that observed in $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Me}$), though we note that $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Ph}$) has greater stability than $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Me}$) and that the only impurities that form upon dissolution correlate to P_4Mes_4 as evidenced by ^{31}P NMR spectroscopy. Finally we synthesized $[\mathbf{1}_{\text{tBu}}]^+$ ($\text{R}' = \text{Ph}$), which was isolated as a yellow powder displaying an AMX $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with broad features (Figure 2.2, bottom left).

To probe the effect of electron-donating and electron withdrawing substituents on $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$), we used *p*-MeOC₆H₄CN and *p*-CF₃C₆H₄CN in place of PhCN to synthesize $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \textit{p}-MeOC₆H₄) and $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \textit{p}-CF₃C₆H₄), respectively. $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \textit{p}-MeOC₆H₄) formed a magenta solution with $^{31}\text{P}\{^1\text{H}\}$ NMR spectra bearing an AMX spin pattern in which the M and X nuclei are shifted upfield relative to $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$). $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \textit{p}-CF₃C₆H₄), contrarily, forms royal blue solutions with $^{31}\text{P}\{^1\text{H}\}$ NMR spectra bearing an AMX spin pattern in which the M and X nuclei are shifted downfield relative to $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$).$$$$

We explored the formation and properties of the corresponding free bases, 1-aza-2,3,4-triphosphenes $\mathbf{2}_{\text{R}}$ ($\text{R}' = \text{Me}$ and Ph), to determine if this unexpected and intriguing coloration was unique to the charged heterocycles. The free base $\mathbf{2}_{\text{Tripp}}$ ($\text{R}' = \text{Me}$) was synthesized through the addition of NEt₃ to a slurry of $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Me}$) in hexanes and was isolated as a yellow solid. ^1H NMR spectra show the absence of an N-H peak that is observed in the corresponding protonated species, while no ^{19}F NMR signal could be detected. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\mathbf{2}_{\text{tBu}}$ ($\text{R}' = \text{Me}$) also shows an AMX spin pattern with a significant upfield shift of the A and M nuclei compared to $\mathbf{2}_{\text{tBu}}$ ($\text{R}' = \text{Me}$). $\mathbf{2}_{\text{Dipp}}$ ($\text{R}' = \text{Me}$) had similar coloration to $\mathbf{2}_{\text{Tripp}}$ ($\text{R}' = \text{Me}$), while $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit a second order ABX spin pattern with the A nucleus shifting downfield to 98.6 ppm compared to the chemical shift of 82.3 ppm observed in the A nucleus of $\mathbf{2}_{\text{Tripp}}$ ($\text{R}' = \text{Me}$). $\mathbf{2}_{\text{Mes}}$ ($\text{R}' = \text{Me}$) was colorless in solution and exhibits an AMX spin pattern different to $\mathbf{2}_{\text{Dipp}}$ ($\text{R}' = \text{Me}$)

and **2_{Tripp}** (**R'** = **Me**). It also proved to be much more solution stable than the charged [**1_{Mes}**]⁺ (**R'** = **Me**), as NMR spectra collected on the solution after several weeks showed no significant change from the initial spectrum. In the case of the **2_R** (**R'** = **Ph**) series, no significant changes were observed in the ³¹P{¹H} NMR chemical shifts compared to the **2_R** (**R'** = **Me**) series. In contrast, even in the form of single crystals, **2_{Mes}** (**R'** = **Ph**) underwent partial decomposition in solution to generate an unknown impurity which appears as a singlet in ³¹P{¹H} NMR spectrum at 62.4 ppm in CDCl₃.

While free base 1-aza-2,3,4-triphospholene heterocycles are readily synthesized through deprotonation with NEt₃, these free base rings are readily and near quantitatively protonated with triflic acid to re-form the 1-aza-2,3,4-triphospholenium cations which may again be reversibly deprotonated. This ability to shuttle between cationic and free base rings provides a second route to forming these heterocycles in high purity and also provides a useful colorimetric switch as described *vide infra*.

2.3.2 X-ray Structural Characterization of the P₃NC heterocycles [**1_R**]⁺ and **2_R**

Characterization of each of the aforementioned cationic and neutral heterocycles [**1_R**]⁺ and **2_R** was performed in the solid state by single crystal X-ray diffraction to provide a structural foundation with which to attempt to rationalize the unexpected colors that were observed. Structures, key bond lengths and angles for all species can be found in **A.4 Crystallographic Details** on page 256, while representative structures of [**1_R**]⁺ (**R** = **Ph**) where **R** = Tripp, Dipp, and Mes are shown in Figure 2.3. For this discussion, we will refer to the phosphorus atoms of the central P₃CN framework as P_C (phosphorus bound to the nitrile-derived carbon atom), P_N (phosphorus bound to the nitrile nitrogen atom), and P_P for the phosphorus atom bound between P_C and P_N.

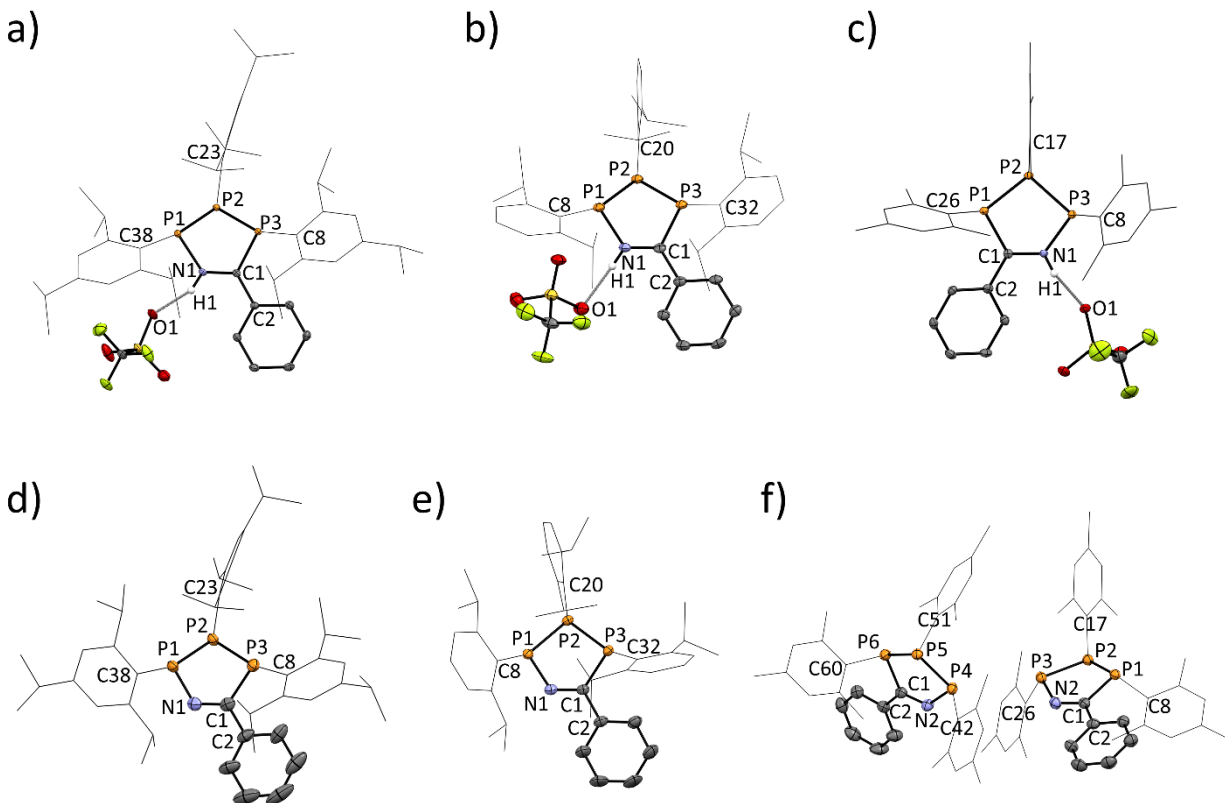


Figure 2.3 Solid-state structures of $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$) (a), $[1_{\text{Dipp}}]^+$ ($R' = \text{Ph}$) (b), $[1_{\text{Mes}}]^+$ ($R' = \text{Ph}$) (c), 2_{Tripp} ($R' = \text{Ph}$) (d), 2_{Dipp} ($R' = \text{Ph}$) (e), and 2_{Mes} ($R' = \text{Ph}$) (f). Thermal ellipsoids are drawn at the 50% probability level. Tripp, Dipp, and Mes substituents are shown in wireframe for clarity, and all hydrogen atoms except H1 in cationic rings have been omitted for clarity.

When analyzing the crystal structures of all synthesized species herein, two distinct structural features are apparent in the Dipp and Tripp series when compared to the Mes and *t*Bu series. Firstly, a clear shortening in the distance between P_N and P_C atoms in $[1_{\text{Tripp}}]^+$ and $[1_{\text{Dipp}}]^+$ ($R' = \text{Me}$ and Ph) species is observed, resulting in 4.5 - 5.5 % shorter distances compared to the analogous $[1_{\text{tBu}}]^+$ ($R' = \text{Me}$ and Ph) species (e.g. *c.f.* 3.1149(7) Å and 3.2549(6) Å for $[1_{\text{Tripp}}]^+$ and $[1_{\text{tBu}}]^+$ ($R' = \text{Ph}$), see Table A.4 page 280 for full details), which is suggestive of ring-puckering. Conversely, the free bases show no appreciable trend in lengthening or shortening of the P_N – P_C distance, indicating that this phenomenon is specific to the sterically encumbered cationic rings. Secondly, we observed a substantial bending in both $[1_{\text{Tripp}}]^+$ and $[1_{\text{Dipp}}]^+$ ($R' = \text{Me}$ and Ph)

heterocycles compared to their $[1_{tBu}]^+$ and $[1_{Mes}]^+$ congeners (Figure 2.4). The angle of bending, θ , is measured from the horizontal $P_C-C=N-P_N$ plane downward to the plane formed by the three catenated phosphorus atoms (see top of Figure 2.4). Using this parameter, $[1_{tBu}]^+$ ($R' = Me$ and **Ph**) are minimally bent, with the angles between the $P_N-P_P-P_C$ plane and the $P_N-N=C-P_C$ plane being 18.58° and 17.25° , while these angles are substantially increased to 55.73° and 48.46° in $[1_{Tripp}]^+$ ($R' = Me$ and **Ph**), respectively. Comparing between the complete set of $[1_R]^+$ ($R' = Ph$) and 2_R ($R' = Ph$), it can be seen that the change in bending angle as steric bulk is increased is greater for the $[1_R]^+$ ($R' = Ph$) series than the 2_R ($R' = Ph$) series (Figure A.90, page 280). Structural bending was also observed in $[1_{Tripp}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4$, $p\text{-CF}_3\text{C}_6\text{H}_4$), which display bending angles of 50.65° and 57.17° respectively, the latter being the most bent of the series. This substantial bending is also linked to changes in the P_N-P_C distance in these species, with $[1_{Tripp}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4\text{CN}$) displaying a 4.86% shortening and $[1_{Tripp}]^+$ ($R' = p\text{-CF}_3\text{C}_6\text{H}_4\text{CN}$) displaying a 6.76% shortening (Table A.4, page 280).

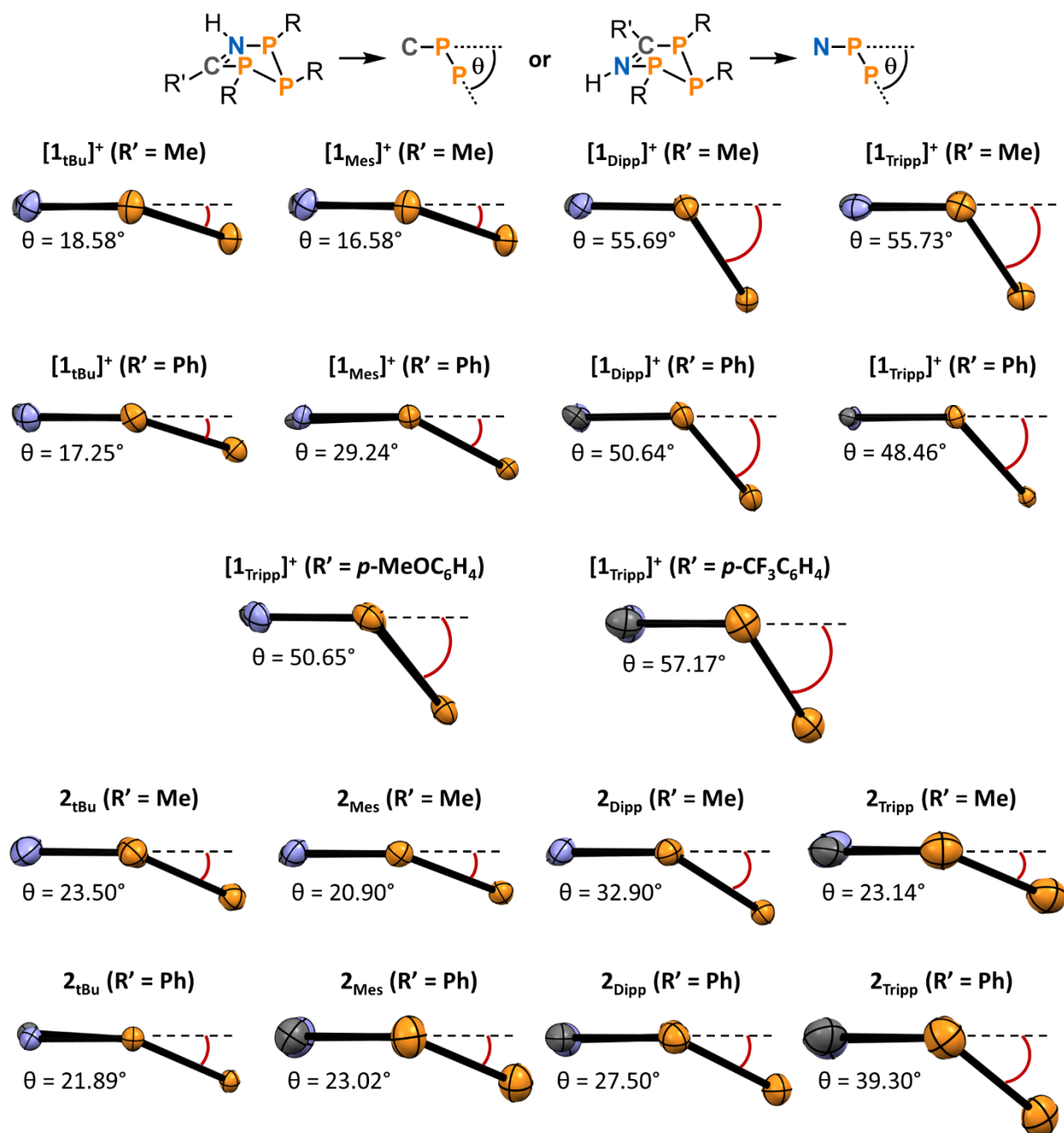


Figure 2.4 Side-on view of the central P_3CN rings in the molecular structures as determined by SC-XRD experiments of $[1\text{R}]^+$ and 2R demonstrating the angle of bending of each species (P = orange, C = grey, N = blue). View was chosen such that the bent-out-of-plane P_P atom sits to the right, and all θ values are measured from the horizontal $\text{P}_\text{C}\text{--C--N--P}_\text{N}$ plane (represented as a dotted line parallel to the bottom of the page) downward to the plane formed by the three phosphorus atoms. Thermal ellipsoids are drawn at the 50% probability level.

2.3.3 UV-Vis spectroscopic studies of $[1_R]^+$ and 2_R

UV-Visible spectra were obtained in a CH_2Cl_2 solution for each of the ring species to assess whether the observed data would be effectively correlated to the steric demands or electronics of the phosphorus substituents or the characteristics of the nitrile used. Given that we were unable to successfully crystallize an adequate amount of pure 2_{Mes} ($R' = \text{Me}$), and that $[1_{\text{Mes}}]^+$ ($R' = \text{Me}$) and 2_{Mes} ($R' = \text{Ph}$) always undergo partial decomposition in solution, even when using single crystals, UV-Vis spectra were not obtained for these species.

All compounds examined by UV-Vis spectroscopy show broad absorbance bands in the 300-400 nm region typically associated with the aryl and alkyl substituents at phosphorus (Table 2.1, λ_2). However, all cationic rings (except $[1_{\text{tBu}}]^+$ ($R' = \text{Me}$)) also show a low-energy absorbance band relative to the absorbances at 300-400 nm (Table 2.1, λ_1) which follow Beer's Law. An average bathochromic shift of 59 nm in the low-energy absorbance band is observed in $[1_R]^+$ ($R' = \text{Ph}$) compared to the absorbance of analogous $[1_R]^+$ ($R' = \text{Me}$) species, which could be attributed to increased electron conjugation involving the aromatic Ph substituent. When the steric bulk is increased at phosphorus (where $\text{tBu} < \text{Mes} < \text{Dipp} \approx \text{Tripp}$), a progressive red shift in the value of low-energy absorbance bands is also observed. Unlike $[1_R]^+$ ($R' = \text{Me}$), 2_R ($R' = \text{Me}$) showed no evidence of low-energy absorbances between 300-800 nm, while 2_R ($R' = \text{Ph}$) species showed low-energy absorbance bands that are hypsochromically shifted compared to those observed in $[1_R]^+$ ($R' = \text{Ph}$) (Table 2.1) and manifest in a shift to colorless, yellow, or orange in all species 2_R . In comparing $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$) to $[1_{\text{Tripp}}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4$ or $p\text{-CF}_3\text{C}_6\text{H}_4$), we note that $[1_{\text{Tripp}}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4$) bears a hypsochromically shifted λ_1 compared to $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$), while the λ_1 associated with $[1_{\text{Tripp}}]^+$ ($R' = p\text{-CF}_3\text{C}_6\text{H}_4$) is bathochromically shifted by 20 nm compared to $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$). When considering the Hammett parameter of the *para*-substituent

at R' it is clear that a correlation is found between an increasing Hammett parameter σ_p and an increasing wavelength of the low-energy absorbance band λ_1 ($p\text{-MeO-C}_6\text{H}_4 < p\text{-H-C}_6\text{H}_4 < p\text{-CF}_3\text{-C}_6\text{H}_4$).

Table 2.1 UV-Visible spectroscopic data in CH_2Cl_2 at 20 °C for $[\mathbf{1_R}]^+$ and $\mathbf{2_R}$

Species	λ_1 (nm)	λ_2 (nm)	ϵ_{λ_1} ($\text{L mol}^{-1} \text{cm}^{-1}$)	Species	λ_1 (nm)	λ_2 (nm)	ϵ_{λ_1} ($\text{L mol}^{-1} \text{cm}^{-1}$)
$[\mathbf{1_{tBu}}]^+$ ($R' = \text{Me}$)	—	338	20230	$\mathbf{2_{tBu}}$ ($R' = \text{Me}$)	—	345	2670
$[\mathbf{1_{Dipp}}]^+$ ($R' = \text{Me}$)	505	380	685	$\mathbf{2_{Dipp}}$ ($R' = \text{Me}$)	—	338	4020
$[\mathbf{1_{Tripp}}]^+$ ($R' = \text{Me}$)	507		790	$\mathbf{2_{Tripp}}$ ($R' = \text{Me}$)	387	331	
$[\mathbf{1_{tBu}}]^+$ ($R' = \text{Ph}$)	416	338	2310	$\mathbf{2_{tBu}}$ ($R' = \text{Ph}$)	379	312	2270
$[\mathbf{1_{Mes}}]^+$ ($R' = \text{Ph}$)	488	405		$\mathbf{2_{Dipp}}$ ($R' = \text{Ph}$)	463	346	1500
$[\mathbf{1_{Dipp}}]^+$ ($R' = \text{Ph}$)	550	348	1020	$\mathbf{2_{Tripp}}$ ($R' = \text{Ph}$)	472	335	1630
$[\mathbf{1_{Tripp}}]^+$ ($R' = \text{Ph}$)	560	331	1180				
$[\mathbf{1_{Tripp}}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4$)	555	389	1100				
$[\mathbf{1_{Tripp}}]^+$ ($R' = p\text{-CF}_3\text{C}_6\text{H}_4$)	583	332	1010				

2.3.4 DFT studies of $[\mathbf{1_R}]^+$ and $\mathbf{2_R}$

To shed further light on the unusual nature of the UV-Visible absorbances and their seemingly strong correlation to the bending angle in cations $[\mathbf{1_R}]^+$, the electronic structures of $[\mathbf{1_{Tripp}}]^+$ and $[\mathbf{1_{tBu}}]^+$ ($R' = \text{Me}$), $\mathbf{2_{Tripp}}$ and $\mathbf{2_{tBu}}$ ($R' = \text{Me}$), $[\mathbf{1_R}]^+$ ($R' = \text{Ph}$), and $\mathbf{2_R}$ ($R' = \text{Ph}$) were investigated by Time-Dependent Density Functional Theory (TD-DFT). TD-DFT calculations were performed using the B3LYP functional as well as the cc-pVTZ basis set using the respective BP86-D3/def2-SVP optimized gas-phase S^0 geometry (for complete computational details, please refer to section A.5, page 281). The UV-Vis spectra of all species were reproduced well by the calculations (e.g. compare Table A.6 and Figure A.91 to Table 2.1 and Figure A.54). The calculated lowest energy transition (λ_1) of $[\mathbf{1_R}]^+$ corresponds to a HOMO-LUMO transition, with all other transitions associated with transitions from the HOMO-1 and HOMO-2 orbitals (see section A.5.3, page 284). To better understand the generation of color in these species, it is useful to assess the differences in the HOMO and LUMO orbitals between the two classes of molecules we describe:

those of $[1_{tBu}]^+$ and $[1_{Mes}]^+$ which display blue-shifted absorbances, and those of $[1_{Dipp}]^+$ and $[1_{Tripp}]^+$ which absorb at longer wavelengths. For simplicity, we compare the $[1_{tBu}]^+$ and $[1_{Tripp}]^+$ ($R' = Ph$) species (Figure 2.5). In the case of $[1_{Tripp}]^+$ ($R' = Ph$), the HOMO is primarily composed of phosphorus-based non-bonding lone pairs orbitals and a small contribution from the C=N π system. The LUMO, comparatively, is largely π^* in character, spanning the whole benzonitrile-associated π system, including a σ^* -type contribution from Pp. Contrarily, $[1_{tBu}]^+$ ($R' = Ph$) has a HOMO similar to that of $[1_{Tripp}]^+$ ($R' = Ph$) as well as a Ph-C=N π^* -dominated LUMO, but lacks the contribution from Pp observed in $[1_{Tripp}]^+$ ($R' = Ph$). While a seemingly small difference, the change in substituent at phosphorus and the structural effects it imposes on the molecule has large consequences on the HOMO-LUMO gap in these two species. For example, Tripp substitution and the resultant ring bending in $[1_{Tripp}]^+$ ($R' = Ph$) substantially destabilizes the HOMO compared to that in $[1_{tBu}]^+$ ($R' = Ph$) while leaving the LUMO virtually identical in energy, resulting in a smaller HOMO-LUMO gap that allows a lower energy absorbance in $[1_{Tripp}]^+$ ($R' = Ph$). In the case of **2_R**, it should first be noted that deprotonation of both $[1_{Tripp}]^+$ and $[1_{tBu}]^+$ ($R' = Ph$) results in destabilization of both the HOMO and LUMO, resulting in a greater delocalization of the HOMO across the entire P_N-P-P_C framework and onto the PhCN moiety. However, Tripp substitution in **2_{Tripp}** ($R' = Ph$) results in destabilization of the HOMO but stabilization of the LUMO relative to **2_{tBu}** ($R' = Ph$), again resulting in a smaller HOMO-LUMO gap and allowing for orange coloration to occur compared to the pale yellow **2_{tBu}** ($R' = Ph$).

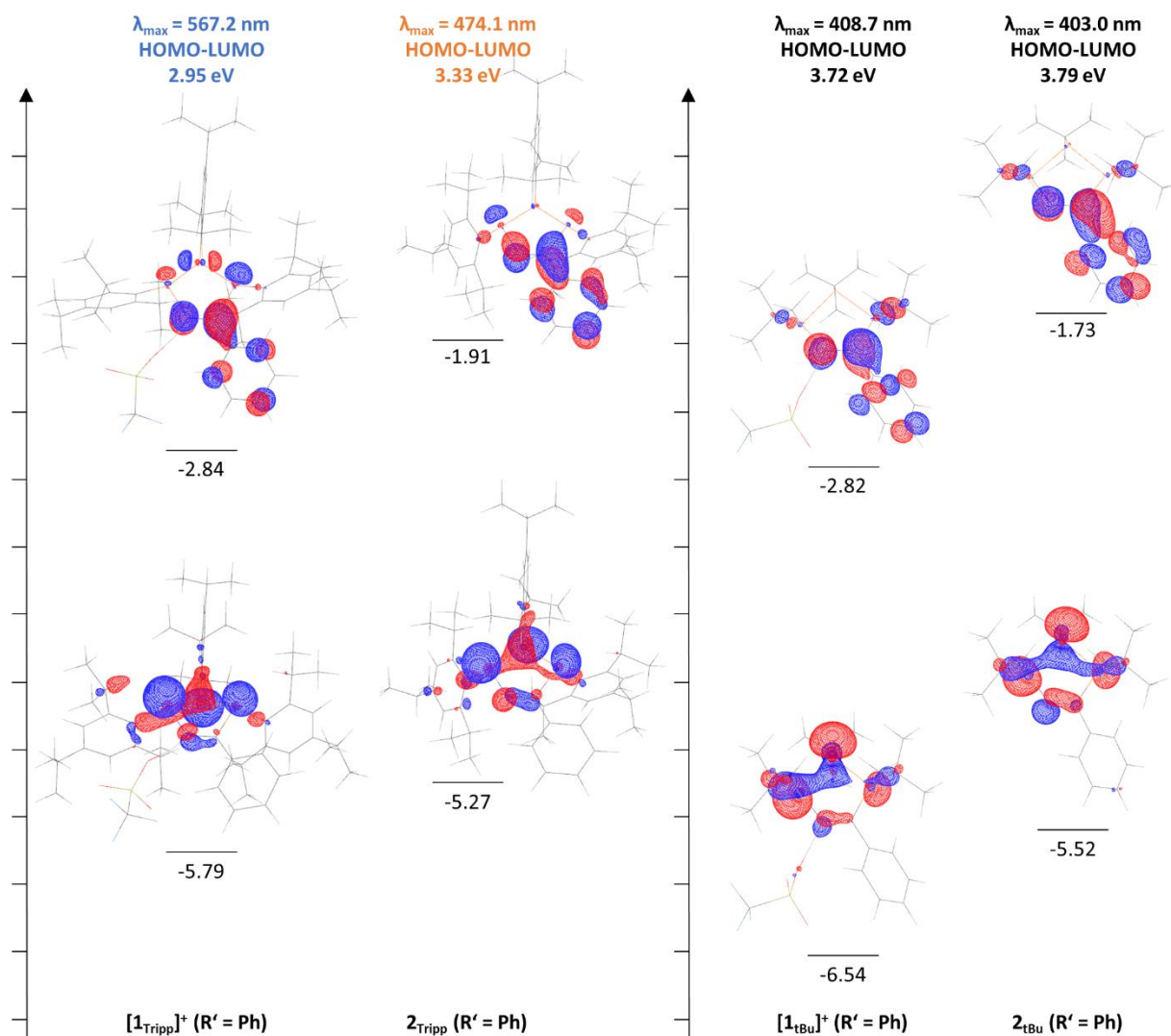


Figure 2.5 HOMO and LUMO frontier orbitals of $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$), 2_{Tripp} ($R' = \text{Ph}$), $[1_{\text{tBu}}]^+$ ($R' = \text{Ph}$), and 2_{tBu} ($R' = \text{Ph}$), with lowest-energy charge transfer energies and corresponding absorbances.

To shed light on the nature of the HOMO-LUMO transition and the resultant unexpected range of coloration, we calculated the D index of each species. The D index is used to qualitatively assess the distance of donor-acceptor electron transitions by calculating the positive and negative barycenters of the orbitals involved in an electronic transition – in this case, the HOMO and LUMO – and then subsequently calculating the distance between these two barycenters. For values greater than 2 it can be determined that charge is flowing between the two barycenters, especially in cases

molecules are not symmetric and where orbitals involved in the electronic transition have minimal spatial overlap. In this way, the D index qualitatively supports the existence of charge transfer across a molecule.^{77, 78} A comparison across the series of $[1_R]^+$ ($R' = Ph$), reveals D index values of ≥ 2.3 , which is suggestive of a HOMO-LUMO charge transfer event from the P_3 framework through to the $N(H)=C-Ph$ moiety in these species (Figure 2.6). We also observe large D values for the free bases 2_{Tripp} ($R' = Ph$) and 2_{tBu} ($R' = Ph$), while $[1_{Tripp}]^+$ ($R' = Me$), 2_{Tripp} ($R' = Me$), and 2_{tBu} ($R' = Me$) all showed D values of less than 1.4 Å. This suggests that benzonitrile-derived free bases are capable of undergoing intramolecular HOMO-LUMO charge transfer phenomena which result in unexpected color formation, while acetonitrile-derived free bases appear to computationally bear no significant HOMO-LUMO charge transfers.

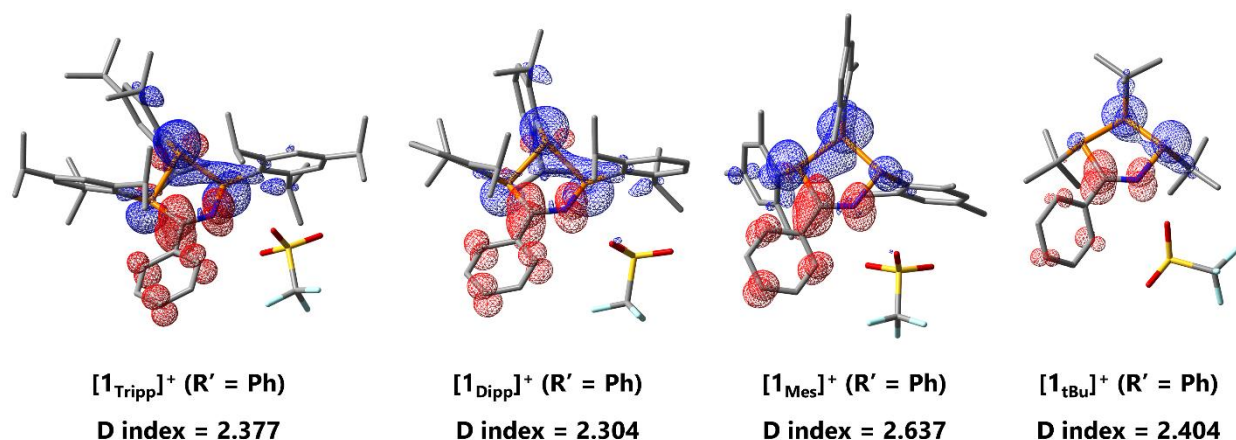


Figure 2.6 Charge density difference diagrams and D indices of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of $[1_{Tripp}]^+$, $[1_{Dipp}]^+$, $[1_{Mes}]^+$, and $[1_{tBu}]^+$ ($R' = Ph$); blue regions correspond to electron donor regions and red regions correspond to electron acceptor regions.

2.4 Discussion

A rare example of tunable coloration in phosphorus-rich main group species is described *via* intramolecular charge transfer, as demonstrated prototypically in $[1_{Tripp}]^+$. The low-energy charge transfer arises from perturbation of the HOMO-LUMO energy levels, which can be related

to the structural bending observed upon *N*-protonation of the P₃CN heterocycle and enhanced by increased steric contributions of phosphorus substituents. This is corroborated by a strong correlation between the wavelength of charge-transfer (λ_{CT} , previously labelled as λ_1) as a function of the bending angle as observed in Table 2.2 and Figure 2.7. Furthermore, solid-state UV-Vis spectra of a representative set of samples show near-identical λ_{CT} values to that of the analogous solution UV-Vis spectra (Section A.2, pp. 246, 247, 251, 252), indicating that the bending angles are similar in solution and the solid-state. Additionally, modification of the R' substituent affects the λ_{CT} as shown in Figure 2.6, presumably by modulation of the LUMO energy level. *In silico* investigations into this charge transfer phenomenon reveal that the sterically-induced bending found in [1_R]⁺ (R = Dipp, Tripp) raises the energy of the HOMO to allow for intramolecular charge transfer to occur in the visible region (see section A.5, page 281).

Table 2.2 Comparison of angle of ring bending and charge-transfer band absorbance for crystallized [1_R]⁺ and 2_R (R' = Ph) species

Species	Angle	λ_{CT}	Species	Angle	λ_{CT}
[1 _{<i>t</i>Bu}] ⁺ (R' = Ph)	17.25	419	2 _{<i>t</i>Bu} (R' = Ph)	21.89	382
[1 _{Mes}] ⁺ (R' = Ph)	29.24	488	2 _{Mes} (R' = Ph)	23.02	NA
[1 _{Dipp}] ⁺ (R' = Ph)	50.64	550	2 _{Dipp} (R' = Ph)	27.5	461
[1 _{Tripp}] ⁺ (R' = Ph)	48.46	560	2 _{Tripp} (R' = Ph)	39.3	472
[1 _{Tripp}] ⁺ (R' = <i>p</i> -MeOC ₆ H ₄)	50.65	555			
[1 _{Tripp}] ⁺ (R' = <i>p</i> -CF ₃ C ₆ H ₄)	57.17	583			

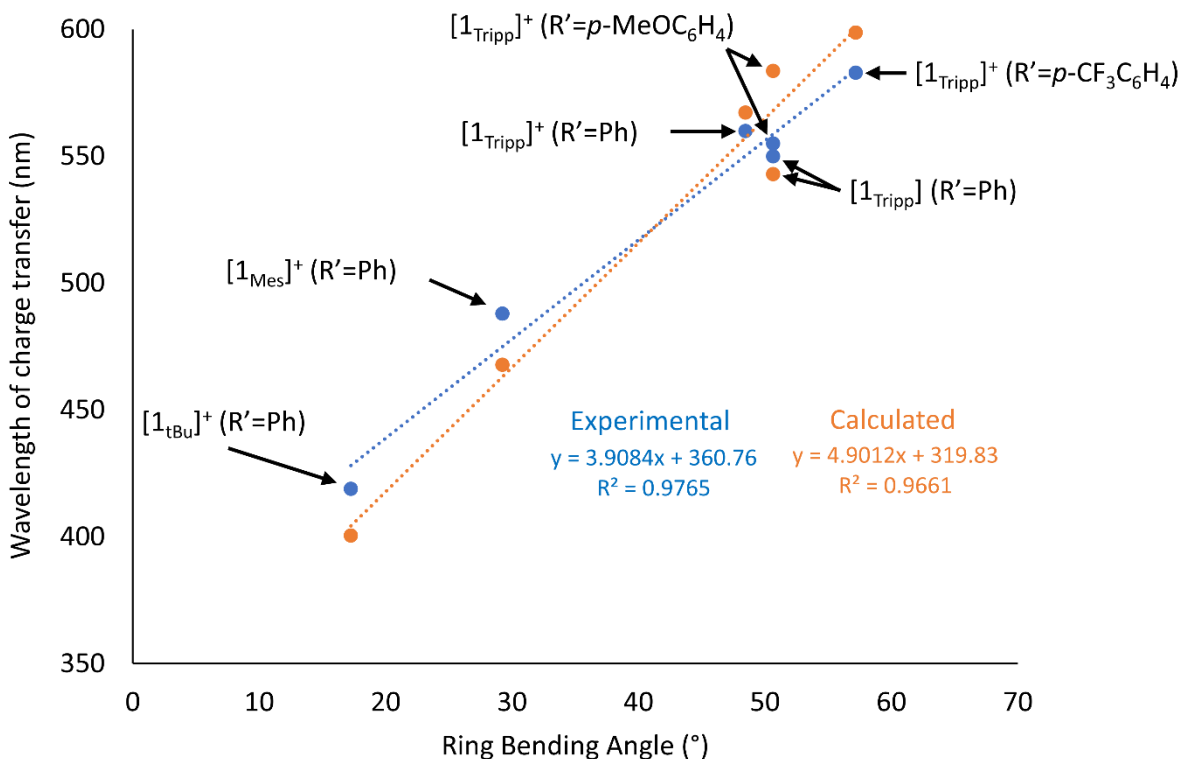


Figure 2.7 Graph depicting wavelength of charge transfer as a function of crystallographic ring-bending angle in $[1R]^+$ species both experimentally (blue) and with calculated absorbances by TD-DFT (orange).

2.5 Conclusions

Rare tunable coloration in phosphorus-rich molecules was discovered through the cycloaddition of nitriles with sterically-hindered cyclic phosphanes mediated by triflic acid. Complexes $[1R]^+$ show coloration associated with low-energy absorbance bands that become increasingly red-shifted as steric bulk at the cyclic phosphane substituent is increased. Use of benzonitrile as a substrate allows access to yellow, red, and blue colors as steric bulk at phosphorus is increased in $[1R]^+$, and coloration may be further tuned by the use of *para*-substituted aryl nitrile substrates. UV-Visible spectroscopy revealed that $[1Tripp]^+$ and $[1Dipp]^+$ have broad, red-shifted absorbance bands characteristic of low-energy gap charge transfers. Single crystal X-ray crystallography revealed increasing ring bending of $[1R]^+$ as sterics at phosphorus are increased, while $2R$ species conversely remain closer to planarity. A linear correlation was found between the

angle of ring bending and the wavelength of the low-energy absorbance bands across all benzonitrile-derived species ($R'=Ph$), indicating a relationship between ground-state structure and the photophysical properties in this family of compounds. TD-DFT calculations support an intramolecular HOMO-LUMO charge-transfer to which we ascribe the observed coloration. This unusual structure-property relationship provides a platform for the generation of color-tunable phosphorus-based materials that exhibit charge transfer phenomena.

2.6 References

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Chapter 3. Exploring the scope of the $P_3^tBu_3$ cycloaddition

Chapter 3 describes investigations into expanding the scope of $P_3^tBu_3$ insertion chemistry with unsaturated substrates beyond the currently-reported nitriles.

Collaborators: Dr. Etienne LaPierre assisted in the synthesis and crystallization of $P_3^tBu_3$ insertion reaction products, and conducted computational studies; and Dr. Brian Patrick collected single crystal diffraction data.

3.1 Abstract

We describe the investigation into the substrate scope of cyclic phosphane cycloadditions, in order to determine the wider applicability of this method for heterocyclic synthesis and discovery. Aryl isonitriles add selectively to $P_3^tBu_3$, exemplified by the addition of xylyl isonitrile in the presence of HOTf to form cationic P_3C ring **[1-H][OTf]** with an exocyclic iminium cation fragment. This ring can be deprotonated to form neutral **1**. Contrarily, *tert*-butyl isonitrile inserts unselectively, likely due to the increased nucleophilicity of the isonitrile bond. *Tert*-butyl isocyanate adds selectively to $P_3^tBu_3$ in the presence of acid, forming a novel cationic P_3CO ring **[2-H][OTf]**. This ring also bears an exocyclic cationic iminium fragment, as was observed in the xylyl isonitrile cycloaddition, and is also readily deprotonated to form neutral P_3CO ring **2**. Conversely, phenyl isocyanate adds to $P_3^tBu_3$ unselectively, likely due to the weaker basicity of the imine fragment preventing substrate activation in acidic conditions. Diisopropyl carbodiimide shows evidence for selective insertion, however, decomposition of the substrate in the presence of HOTf precludes complete cycloaddition. It was found that cycloadditions of isocyanates and diisopropyl carbodiimide to $[P_3^tBu_3Me][OTf]$ were largely unsuccessful, either requiring heating to afford

unselective reactivity or, in the case of ^tBuNCO, reacting unselectively at low temperature. Unsaturated substrates with heavier main group elements such as 1-adamantylphosphethyne, (triphenylmethyl)thionyl imide, and isopropyl isothiocyanate do not show evidence for cycloaddition chemistry with the P₃^tBu₃ scaffold. The study highlights the need for substrates with Lewis basic moieties which allow activation of the dipole, and reveals that the cycloaddition reaction scope is so far limited to certain isonitriles, isocyanates, and carbodiimides.

3.2 Introduction

Cycloaddition and ring expansions are exemplified by seminal reports by Huisgen and Sharpless^{1, 2} allowing for additions of unsaturated substrates to azide scaffolds and vicinal donor-acceptor cyclopropanes (Figure 3.1a).^{3, 4} With a high atom economy, robust activation methods, and a broad library of substituted azides, donor-acceptor cyclopropanes, and unsaturated substrates to work with, cycloadditions have allowed for countless developments in organic heterocycle development and pharmaceutical heterocyclic synthesis (Figure 3.1b), in materials chemistry as a strategy to form polymers and dendrimers (Figure 3.1c), and have even allowed for the formation of heterocycles *in vivo* to develop the field of biorthogonal chemistry (Figure 3.1d).⁵

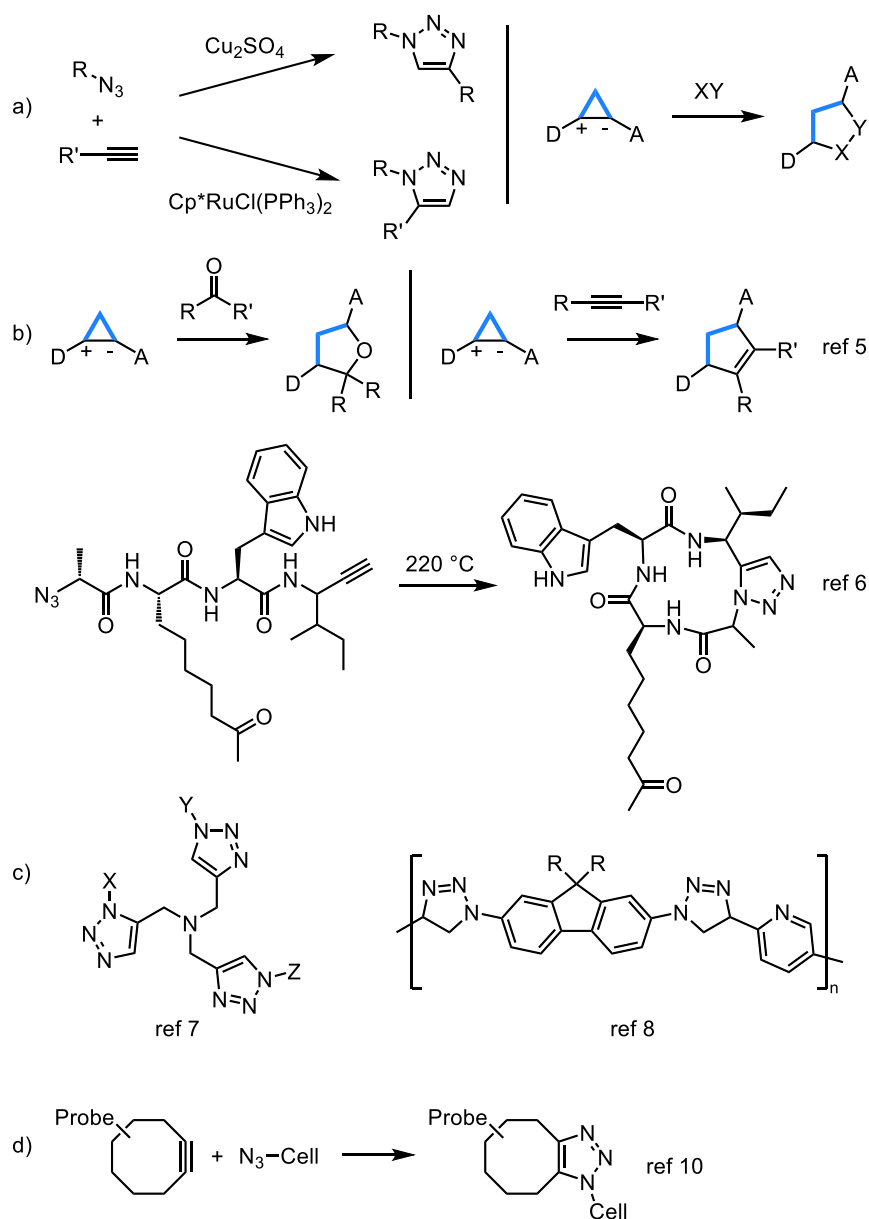


Figure 3.1 (a) Generalized examples of the azide/alkyne click cycloaddition and the donor acceptor cyclopropane cycloadditions; (b) examples of rings selectively formed through donor-acceptor cyclopropane cycloadditions and a complex macrocyclic product made by azide/alkyne cycloaddition; (c) a dendrimer/star polymer and conjugated fluorene-based polymer made by azide/alkyne cycloaddition; and (d) a generalized example of biorthogonal chemistry, specifically strain promoted azide/alkyne cycloaddition (SPAAC). References with greater surveys of scope listed throughout.

However these reaction motifs have yet to spur the same level of materials discovery in inorganic systems, with only a few examples reported in the literature⁶⁻¹³ while the majority of inorganic heterocycles the majority of main group heterocycles are synthesized through condensations and reductive couplings, atom transfer reactions, or intramolecular ring-closing phenomena.¹⁴ Our lab recently pioneered an inorganic ring expansion reaction between strained $P_3'Bu_3$ rings and nitriles, in which Brønsted or Lewis acids induce a polarization across the P–P or $C\equiv N$ bonds to allow for the cycloaddition to proceed forming 1-aza-2,3,4-triphospholenium heterocycles (Figure 3.2a).¹⁵ It was also found that cationic $[P_3'Bu_3R]^+$ ($R = Me, F$) heterocycles, which bear an activated $P-P^+$ dipole, are capable of inserting isonitriles and nitriles in a [3+1] and [3+2] fashion, respectively (Figure 3.2b).¹⁶ These examples of $P_3'Bu_3$ cycloadditions provide a major advance in the synthesis of phosphorus-rich heterocycles which have generally only been accessed through condensation reactions,¹⁷⁻²⁰ while insertion methods into P–P bonds have also been reported but are rare and share no common patterns of reactivity.^{21,22} As such, we sought to determine the scope of activity of the $P_3'Bu_3$ cycloaddition towards other unsaturated substrates, in an effort to establish if the $P_3'Bu_3$ cycloaddition was a modular method to access new phosphorus-rich heterocycles with a variety of substrates (Figure 3.2c).

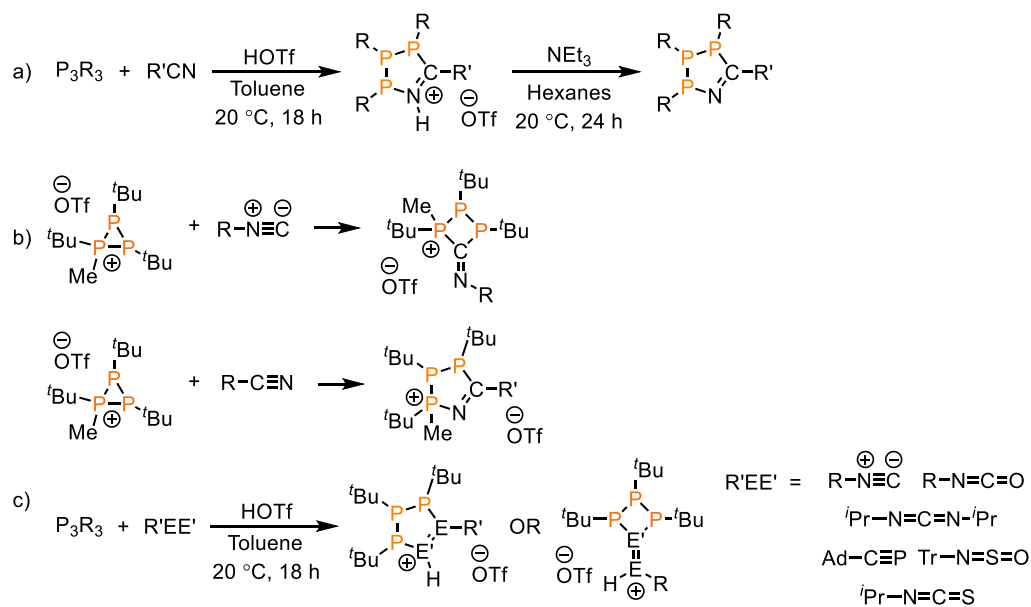


Figure 3.2 (a) Our group's previous report on the acid-mediated cycloaddition of $\text{P}_3\text{}^t\text{Bu}_3$; (b) our group's previous report on the cycloaddition of isonitriles and nitriles into $[\text{P}_3\text{}^t\text{Bu}_3\text{Me}][\text{OTf}]$; and c) the focus of the work herein developing the substrate scope of $\text{P}_3\text{}^t\text{Bu}_3$ cycloadditions.

3.3 Results

Given the ability of nitriles to insert into $\text{P}_3\text{}^t\text{Bu}_3$ in the presence of acid, we investigated the acid-mediated insertion of other C/N based unsaturated substrates into $\text{P}_3\text{}^t\text{Bu}_3$ to determine patterns of reactivity for this rather large class of molecules and to characterize the rings formed in this manner.

3.4 Insertion of isonitriles ($R-N\equiv C$) into $P_3^tBu_3$

We have previously demonstrated the insertion of isonitriles to $[P_3^tBu_3Me]^+$ cation,¹⁶ however it was unclear if isonitriles could likewise be inserted into $P_3^tBu_3$ in an acid-mediated fashion. We began our study with the reaction between $P_3^tBu_3$ and 2,6-dimethylphenylisonitrile (XylNC) in the presence of HOTf at 0 °C, which resulted in the formation of an orange solution. After removing volatiles *in vacuo* and triturating the oily solid with diethyl ether, a spectroscopically pure yellow solid **[1-H][OTf]** was obtained (Figure 3.3). The $^{31}P\{^1H\}$ NMR spectrum of **[1-H][OTf]** in $CDCl_3$ demonstrates an AMX spin system ($\delta^{31}P\{^1H\} = 43.6, 32.3,$ and -91.9 , $^1J_{AM} = 147$ Hz, $^2J_{AX} = 91$ Hz, $^1J_{MX} = 144$ Hz), (**Figure B.3**) suggestive of insertion of the isonitrile into the cyclic phosphane (Figure 3.3).

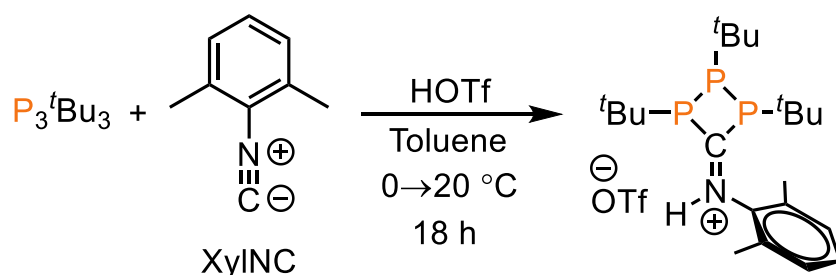


Figure 3.3 The reaction of $P_3^tBu_3$ with XylNC in the presence of triflic acid to form **[1-H][OTf]**.

The $^{31}P\{^1H\}$ NMR spectrum is inconclusive as to whether the isonitrile added in a [3+1] fashion, as seen in the reaction of XylNC with $[P_3^tBu_3Me]^+$,¹⁶ or [3+2] fashion as is the case for nitriles.¹⁵ As such, single crystals of **[1-H][OTf]** suitable for X-ray diffraction were grown from a fluorobenzene solution layered with *n*-hexane, revealing a [3+1] insertion of the isonitrile carbon atom to form a P_3C four membered ring with a protonated imino substituent (Figure 3.4). The iminium $C1=N1$ bond of **[1-H][OTf]** measures 1.306(2) Å, demonstrating an expected lengthening from the 1.161(2) Å $C\equiv N$ bond length observed in crystalline XylNC.²³ Likewise, the $C14-N1$ Xyl-N bond of **[1-H][OTf]** demonstrates an increase in bond length from 1.403(1) Å to

1.45(1) Å, resulting from the cationic iminium withdrawing electron density from the Xyl-N bond. P–P bond lengths in **[1-H][OTf]** [2.2194(5) and 2.2043(5) Å] are largely unchanged from $P_3^tBu_3$,²⁴ while XylNC–P bond lengths measuring 1.831(1) and 1.836(1) Å are nearly identical to the C–P bond lengths of 1.828(1) and 1.881(1) Å observed in the P_3C ring formed from the reaction of $[P_3^tBu_3Me][OTf]$ and tPrNC .¹⁶ The planes formed by H–N1–C14 and C1–P1–P3 are nearly coplanar, meeting at an angle of 4.21°, while torsion angles between P1–C1–N1–H and P1–C1–N1–C14 lie nearly planar at 0(1)° and 173.1(1)°, respectively.

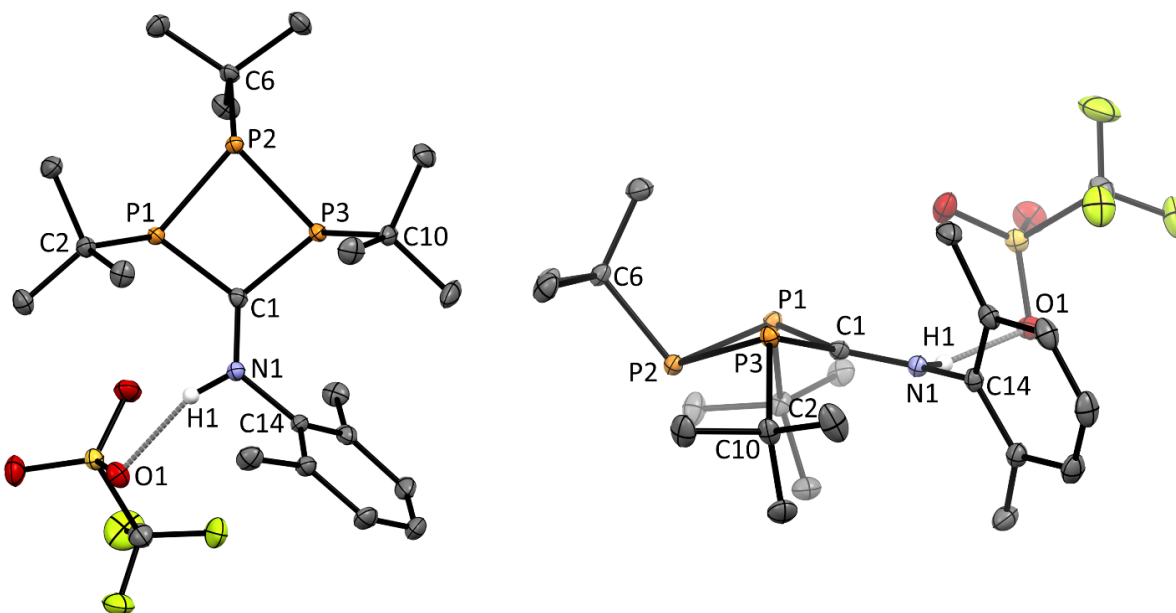


Figure 3.4 Single crystal X-ray structure of **[1-H][OTf]**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°): C1–N1 1.306(2); N1–C14 1.45(1); N1–H1 0.90(2); C1–P1 1.831(1); C1–P3 1.836(1); P1–P2 2.2043(5); P2–P3 2.2194(5); N1–C1–P1 126.0(1); N1–C1–P3 131.7(1); P1–C1–P3 101.92(6); C1–P1–P2 83.80(4); P1–P2–P3 80.16(2); C1–N1–C14 127.7(1); C1–N1–H1 120(1); H1–N1–C14 112(1).

[1-H][OTf] could be deprotonated with NEt_3 in *n*-hexane to form neutral **1**, which displays a $^{31}P\{^1H\}$ NMR spectrum with an AMX spin pattern in which all peaks are shifted downfield relative to **[1-H][OTf]** ($\delta^{31}P\{^1H\}$ = 73.5, 39.2, and –79.3, $^1J_{AM}$ = 153 Hz, $^2J_{AX}$ = 81 Hz, $^1J_{MX}$ =

141 Hz) (**Figure B.6**). Single crystal X-ray diffraction of crystals grown through slow evaporation of a saturated solution of the resulting material in *n*-hexane reveal the P₃C framework remains intact upon deprotonation of the nitrogen atom (Figure 3.5). Deprotonation of [**1-H**][OTf] results in a shortening of the C=N bond of **1** from 1.306(2) Å to 1.279(2) Å, indicative of a more electron-rich imine moiety. The shortening of the C=N bond is contrasted by a slight lengthening of the C–P bonds [1.872(1) and 1.927(5) Å], and little change in the length of P–P bonds [2.2198(5) and 2.280(6) Å] of the P₃C framework. Computations were conducted on this neutral parent framework to glean insight into the electronic structure of **1**. Natural bond order populations calculated at the PBE1PBE D3 def2-TZVP level of theory (**Table B.5**) reveal delocalization of P1 and P3 lone pairs (as viewed in the HOMO, **Figure B.28**) into the π^* of the C=N bond (as viewed in the LUMO, **Figure B.29**), each contributing 8 kcal/mol of stabilization to **1**. There is also a donation of the nitrogen lone pair, contributing 8 kcal/mol of stabilization, into the P1-C1 σ^* anti-bonding orbital observed in the LUMO+1 (see **Figure B.30**). Free base **1** still has a relatively planar imine RN=CP₂ core, with the intersection of the C2–N1=C1 and P1–C1–P3 planes meeting at 10.20° and torsion angles of P1–C1–N1–C2 and P3–C1–N1–C2 being -0.3(2)° and -168.1(2)°, respectively. Notably, the deprotonation of [**1-H**][OTf] to form **1** results in broadening of the ¹H NMR signals (measured 34 Hz full width half height) corresponding to the ^tBu moieties at P1 and P3, potentially due to restricted rotation due to steric clash with the freely rotating xylyl substituent (**Figure B.4**).

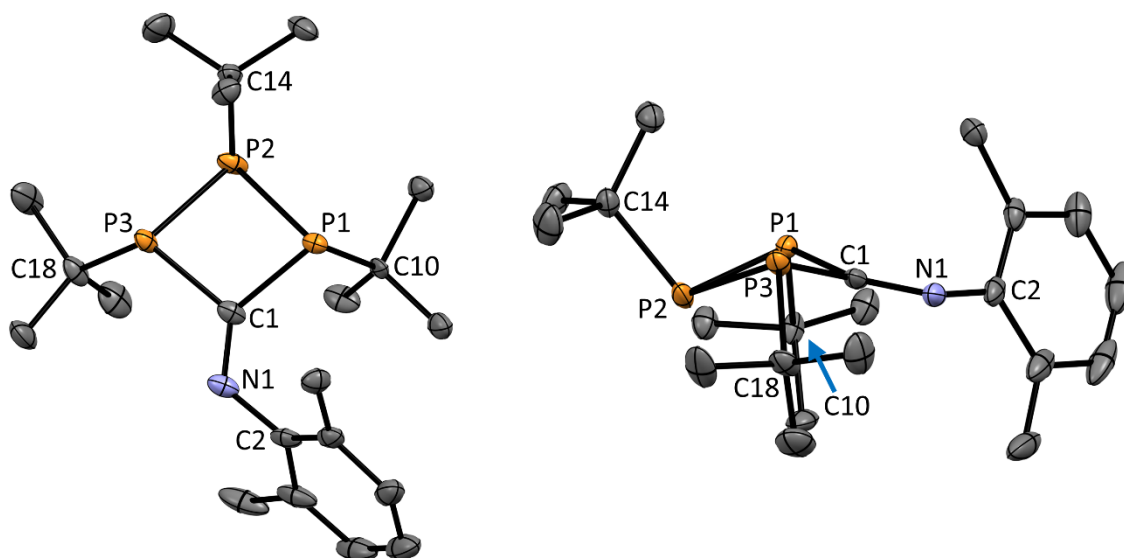


Figure 3.5 Single crystal X-ray structure of **1**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°): C1-N1 1.279(2); N1-C2 1.418(2); C1-P1 1.872(1); C1-P3 1.927(5); P1-P2 2.2198(5); P2-P3 2.280(6); N1-C1-P1 135.7(1); N1-C1-P3 123.0(2); P1-C1-P3 100.5(2); C1-P1-P2 84.01(4); C1-P3-P2 81.2(2); P1-P2-P3 80.9(2); C1-N1-C2 123.4 (1).

The successful addition of XylNC to $P_3^tBu_3$ encouraged us to explore the reaction of $P_3^tBu_3$ with *tert*-butylisocyanide ($tBuNC$) to determine if a more electron donating substituent afforded the same reactivity. To a toluene solution of $tBuNC$ and $P_3^tBu_3$ at 0 °C, HOTf was added, resulting in the formation of a dark orange solution. The solution was allowed to stir at 22 °C for 18 h, and a $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture revealed a complex mixture of products which were difficult to assign identities to. Two discrete species could be identified through shared J coupling values: one with an AMX spin system akin to that seen in **[1-H][OTf]** but spanning a much shorter range of chemical shift [$\delta^{31}P\{^1H\}$ = -19.91 (dd, J = 332.0, 8.5 Hz), -29.78 (dd, J = 234.5, 8.5 Hz), -45.82 (dd, J = 332.0, 234.5 Hz), and another species displaying two multiplets associated with an AA'XX' spin pattern at $\delta^{31}P\{^1H\}$ = 78.86 and -14.88 (Figure 3.6). These suggest that $tBuNC$ inserts into both $P_3^tBu_3$ and $P_4^tBu_4$ (known to form upon reaction of $P_3^tBu_3$ with HOTf)¹⁵ to form both a 4- and 5-membered heterocycle. The reaction mixture was diluted in

MeCN and analysed by ESI-MS to determine if any proposed species could be observed. While there was no observation of the 4- membered insertion product, a species with $m/z = 348.21334$ was observed which corresponds to a molecular formula of $[(^t\text{BuP})_4(\text{NC})]^+\text{H}$, consistent with the loss of isobutene from an addition product of $^t\text{BuNC}$ and P_4^tBu_4 . Given the complexity of the mixture as evidenced by NMR spectroscopy and the inability to detect proposed product peaks by the acid-mediated addition of $^t\text{BuNC}$ and P_3^tBu_3 to be unselective.

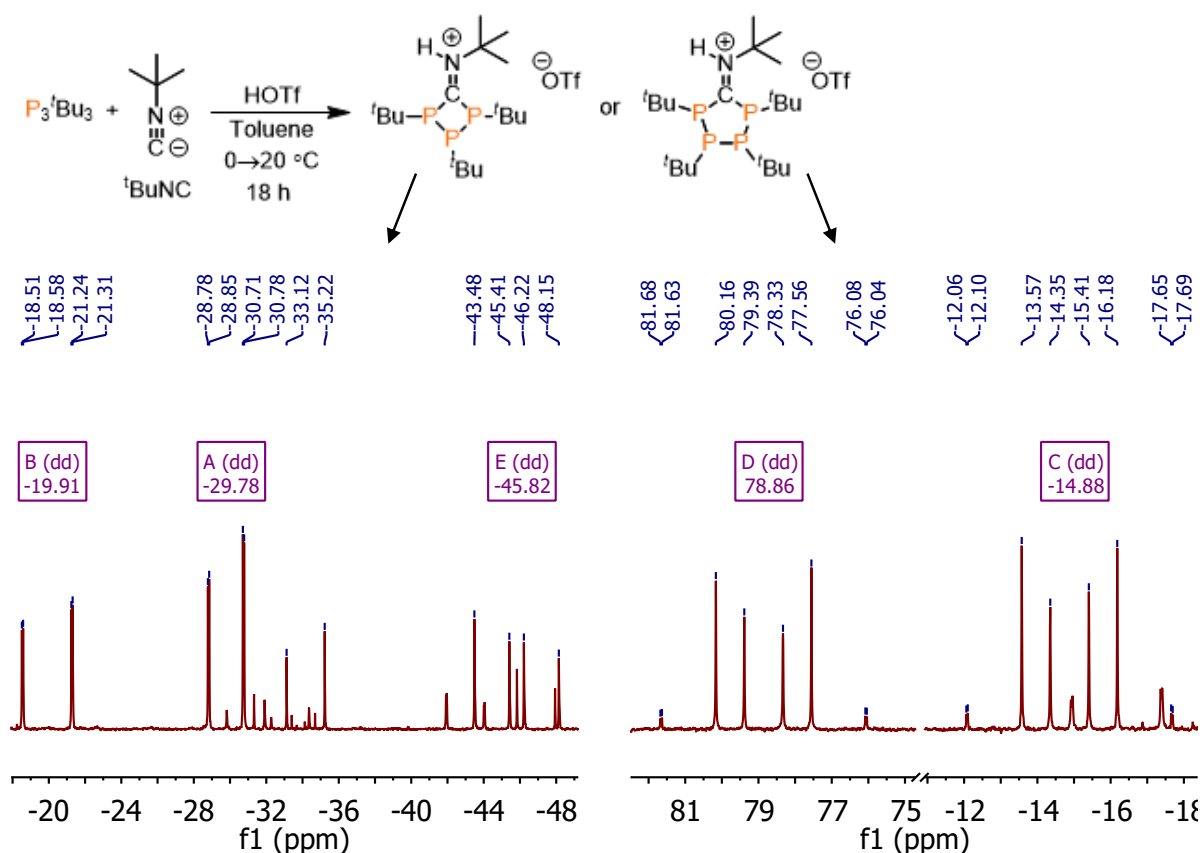


Figure 3.6 The reaction of P_3^tBu_3 and $^t\text{BuNC}$ in the presence of triflic acid, and selected regions of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500MHz, C_6D_6) consistent with possible P_3C and P_4C heterocycles formed in situ as shown in the synthetic scheme.

3.4.1 Insertions of Carbodiimides $\text{R}-\text{C}=\text{N}=\text{C}-\text{R}$ to P_3^tBu_3

We hypothesized that carbodiimides would prove amenable to insertion into P_3^tBu_3 due to the availability of one $\text{C}=\text{N}$ bond to insert into the cyclic phosphane whilst also bearing an imino

moiety which could act as an exocyclic base akin to that observed in the insertion chemistry of XylNC. Diisopropylcarbodiimide (DIC) was reacted with $P_3^tBu_3$ and HOTf in C_6D_6 , producing a $^{31}P\{^1H\}$ NMR spectrum with an AMX spin system where $\delta^{31}P\{^1H\} = -79.26$ (dd, $J = 254.6, 209.1$ Hz), -113.37 (dd, $J = 209.0, 187.3$ Hz), -137.11 (dd, $J = 254.7, 187.3$ Hz). This is indicative of insertion of the substrate into $P_3^tBu_3$, albeit in less than 20% yield (Figure 3.7). Attempts to isolate the species by recrystallization were unsuccessful, resulting in the formation of oils. This initially came as a surprise, however, it has been reported that carbodiimides react with triflic acid to form ureas.²⁵ It is likely that the small amount of product observed by $^{31}P\{^1H\}$ NMR is merely the result of insertions formed before triflic acid degrades the majority of DIC. Though the reaction was not suitable for the high-yielding formation of insertion product, the oil formed was analyzed by ESI-MS to support the formation of the proposed insertion product. The $[M+H]$ mass spectrum for the 1:1 insertion product between $P_3^tBu_3$ and DIC at $m/z = 391.25557$ was clearly visible, complimenting the ^{31}P NMR data and suggesting that carbodiimides undergo insertion in acidic conditions (Figure 3.12).

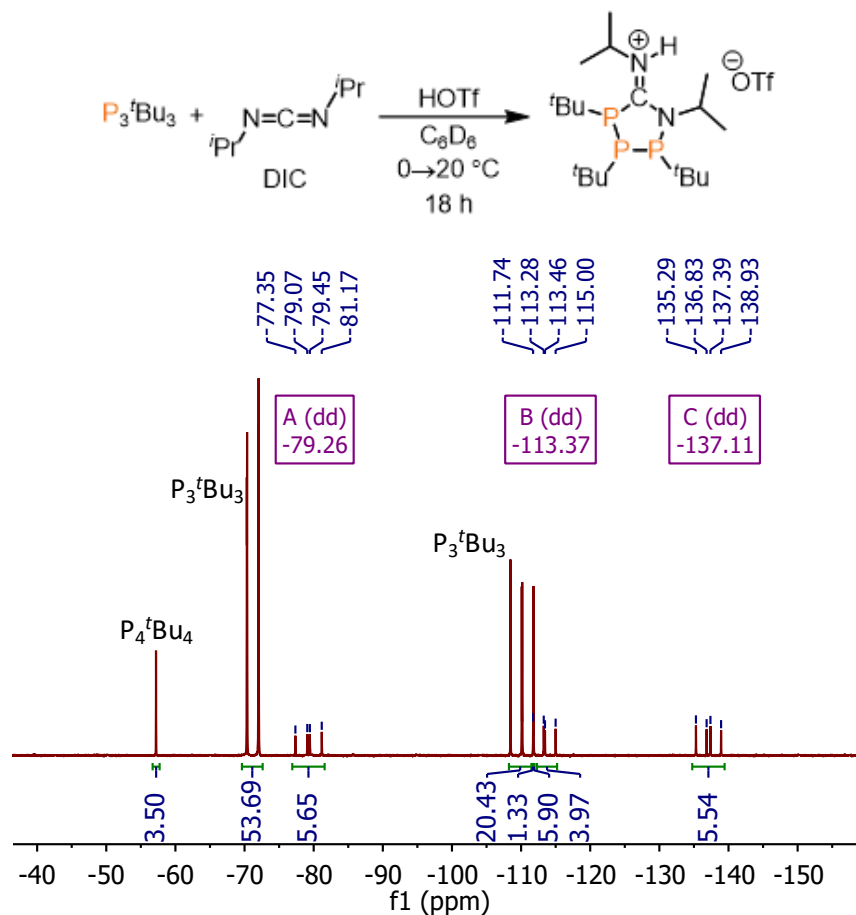


Figure 3.7 The reaction of $P_3^tBu_3$ and DIC in the presence of triflic acid and the $^{31}P\{^1H\}$ NMR spectrum (500MHz, C_6D_6) of the reaction mixture, demonstrating the formation of an AMX likely corresponding to the product displayed in the reaction scheme (top).

3.4.2 Insertions of Isocyanates $R-N=C=O$ to $P_3^tBu_3$

Isocyanates were tested as a potential substrate for insertion given that two potential insertion motifs are accessible, either via insertion across the $C=N$ bond or the $C=O$ bonds. $P_3^tBu_3$ and *tert*-butylisocyanate ($tBuNCO$) were stirred in toluene and reacted with $HOTf$, resulting in a yellow solution. After allowing the reaction to stir for 18 h, an aliquot of the solution was analyzed by $^{31}P\{^1H\}$ NMR, displaying a single AMX spin system [$\delta^{31}P\{^1H\}$ = 234.1, 39.6, and -17.4 , $^1J_{AM}$

= 265 Hz, $^2J_{AX} = 2$ Hz, $^1J_{MX} = 265$ Hz] consistent with selective substrate insertion into $P_3^tBu_3$ (Figure B.9).

To determine the connectivity of the insertion product, the volatiles of the reaction mixture were removed *in vacuo* and the remaining residue washed with Et_2O to afford a yellow solid which was recrystallized by layering a solution of the solid in fluorobenzene with *n*-hexane at -30 °C. Single crystals isolated from the recrystallization were analyzed by single crystal X-ray diffraction, verifying the insertion of isocyanate into $P_3^tBu_3$ to form **[2-H][OTf]** (Figure 3.8). In a similar motif to isonitriles and carbodiimides, the nitrogen atom of isocyanate serves as an exocyclic proton reservoir, while the C=O bond inserts into $P_3^tBu_3$, forming a novel P_3CO heterocyclic framework. Here the C1–O1 bond length measures 1.318(2) Å, significantly longer than the 1.172(4) Å C=O bond length of crystalline isocyanate {2,6-[2,4,6-(*i*Pr) $_3$ C $_6$ H $_2$] $_2$ C $_6$ H $_3$ }-NCO 26 and supporting a change in bond order. The C1=N1 bond length of **[2-H][OTf]** measures 1.299(2) Å, slightly shorter but similar to that of **[1-H][OTf]**. The P1–O1 bond distance measures 1.716(1) Å, longer than most trivalent phospholane P–O bonds in the CCDC but similar to strongly electron-withdrawn P–O bonds in a phosphorus oxalate reported by Cowley and coworkers measuring 1.699(2) Å. 27 The endocyclic C1 carbon atom is formally trigonal planar (Σ angles = 359°), while the P1 fragment lies 6.35° below this plane. The ring is also minimally bent, with the planes of P1–O1–C1–P3 and P1–P2–P3 lying at 23.43° to one another.

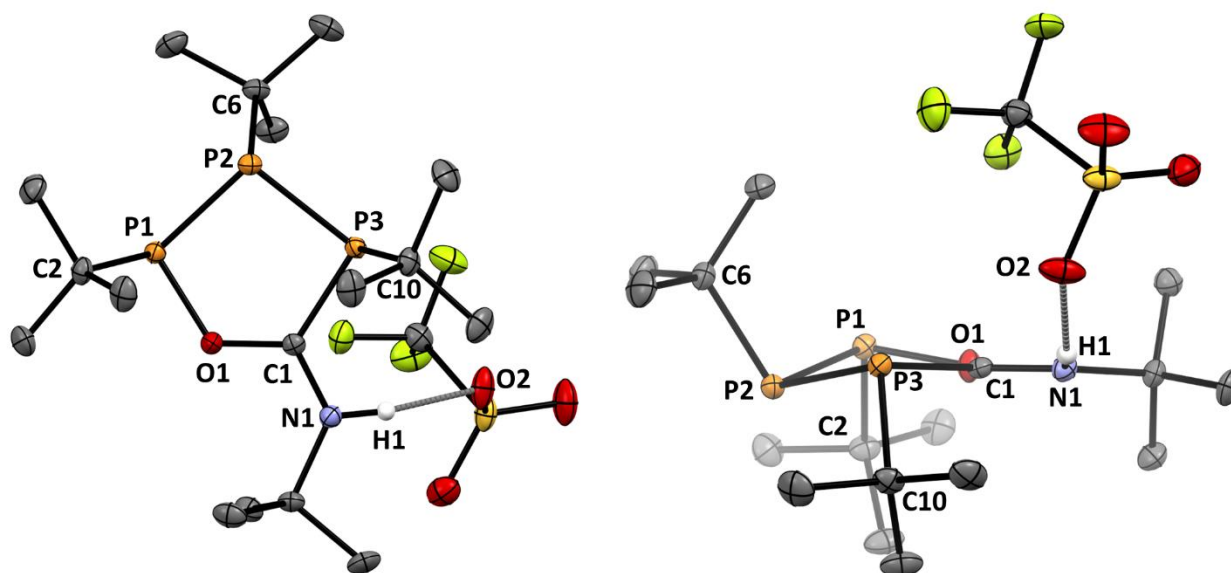


Figure 3.8 Single crystal X-ray structure of **[2-H][OTf]**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°): H1-N1 0.91(2); N1-C14 1.507(2); N1-C1 1.299(2); C1-P3 1.851(1); C1-O1 1.318(2); P1-O1 1.716(1); P1-P2 2.2204(6); P2-P3 2.1995(6); H1-N1-C14 119(1); H1-N1-C1 112(1); C1-N1-C14 128.4(1); O1-C1-N1 117.6(1); P3-C1-N1 120.7(1); P3-C1-O1 121.6(1); C1-O1-P1 123.07(9); O1-P1-P3 98.63(4); P1-P2-P3 94.10(2); P2-P3-C1 96.60(5).

The salt of **[2-H][OTf]** is readily deprotonated by NEt_3 in *n*-hexane to form colourless base **2**, which bears an AMX $^3\text{P}\{^1\text{H}\}$ NMR spectrum shifted upfield from **[2-H][OTf]** ($\delta^{31}\text{P} = 173.1$, 14.9, and -31.8 , $^1J_{\text{AM}} = 267$ Hz, $^2J_{\text{AX}} = 4$ Hz, $^1J_{\text{MX}} = 248$ Hz). Crystals of **2** suitable for single-crystal X-ray diffraction are grown from *n*-hexane, revealing the fidelity of the P_3CO framework upon deprotonation. Here, the C1–O1 bond lengthens to 1.377(3) Å from the 1.318(2) Å bond length observed in **[2-H][OTf]**, while the P1–O1 bond shortens to 1.676(2) Å from the 1.716(1) Å observed in **[2-H][OTf]**. The C1=N1 bond also shortens to 1.269(3) Å from 1.299(2) Å upon deprotonation, akin to the shortening observed in **1**, while the C1–P3 bond slightly lengthens from 1.851(1) to 1.870(3) Å. Calculations were again run on this neutral parent P_3CO framework to gain insight into the bonding of this new heterocycle. NBO calculations run at the PBE1PBE D3 def2-TZVP level of theory determined the donation of an oxygen lone pair in a *p*-orbital (as determined

by NBO analysis in **Table B.9**, viewed in the HOMO-1 in **Figure B.36**) into the co-planar C=N π^* p -type orbital (**Table B.10**, viewed in **Figure B.37**), providing a stabilizing interaction of 33 kcal/mol. Likewise, NBO calculations reveal a donation of the nitrogen lone pair into the C–O σ^* orbital, providing a stabilization of 26 kcal/mol to the structure of **2** (**Table B.10**). The ring **2** remains very similar to **[2-H][OTf]** in regards to planarity (Σ angles = 359°), with the trigonal plane based at C1 bent 7.1° out of plane with P1, and the P1–O1–C1–P3 and P1–P2–P3 planes lying at 23.56° to one another.

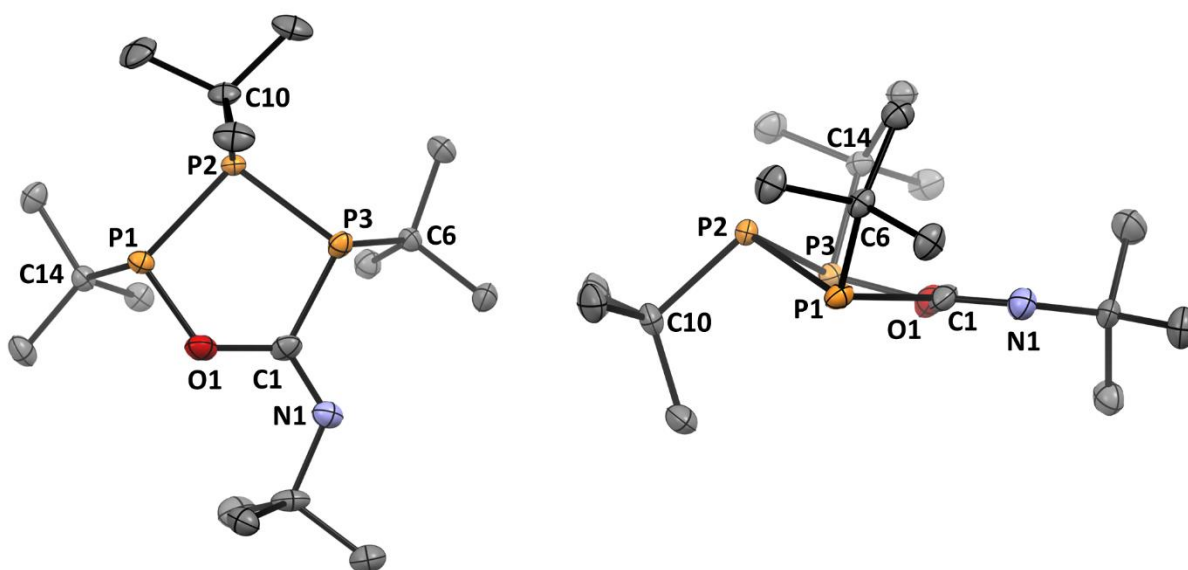


Figure 3.9 Single crystal X-ray structure of **2**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°): N1–C2 1.495(3); N1–C1 1.269(3); C1–P1 1.870(3); C1–O1 1.377(3); P3–O1 1.676(2); P1–P2 2.2034(9); P2–P3 2.216(1); C1–N1–C2 124.7(2); O1–C1–N1 122.4(2); P1–C1–N1 120.9(2); P1–C1–O1 116.3(2); C1–O1–P3 124.5(2); O1–P3–P2 101.32(7); P1–P2–P3 92.89(3); P2–P1–C1 97.57(8).

The P_3CO framework accessed through the reaction of $tBuNCO$ with P_3tBu_3 in the presence of triflic acid represented a novel framework. However, the difference in the insertion chemistry of XylNC and $tBuNC$ prompted us to try an isocyanate insertion with differing electronic parameters to $tBuNCO$. We attempted the acid-mediated insertion of phenylisocyanate ($PhNCO$) into P_3tBu_3 , whereby triflic acid was added at 0 °C to a solution of $PhNCO$ and P_3tBu_3 in toluene.

This immediately formed a dark brown solution, which was allowed to stir at 20 °C for 18 h. An aliquot of this solution was obtained for analysis by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, and revealed the formation of a number of products which could not be easily assigned. We were able to assign two main species in solution: one with an AMX spin system spanning a very narrow chemical shift range compared to most P_3^tBu_3 insertions (Figure 3.10 left), and one with AMX spin system which also displayed large amounts of broadening (33 Hz FWHH) (Figure 3.10 left). ESI-MS analysis confirmed that the expected P_3CO insertion product of PhNCO into P_3^tBu_3 in the presence of acid was formed in some capacity, with a peak at $m/z = 384.17708$ corresponding to the $\text{M}+\text{H}$ species (Figure 3.13).

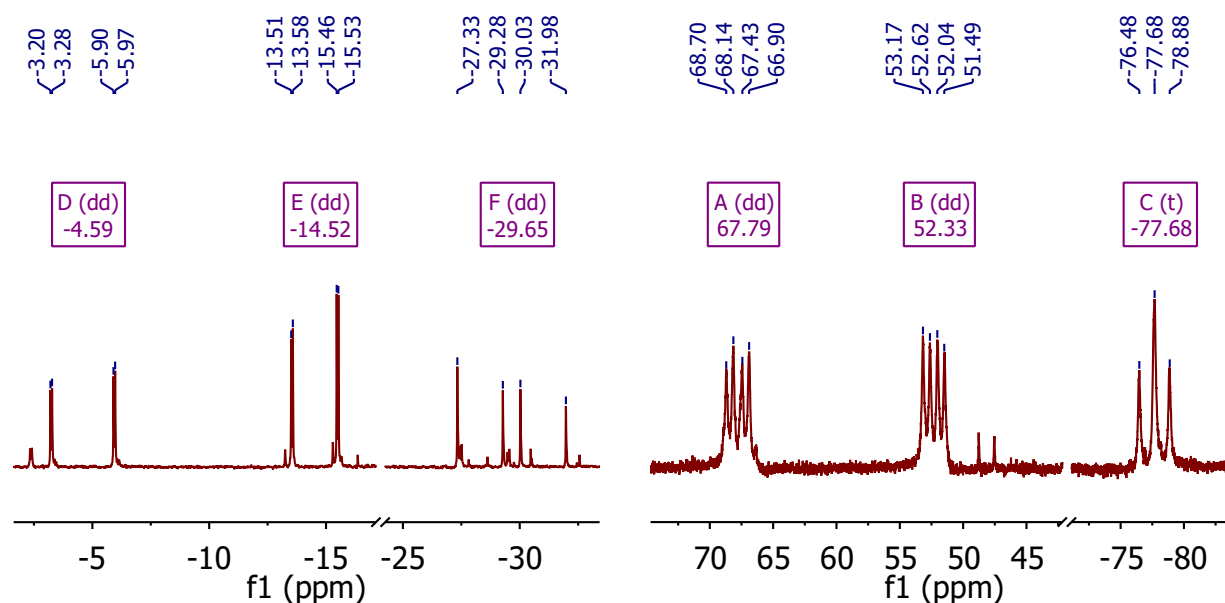


Figure 3.10 Selected regions of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of PhNCO with P_3^tBu_3 and HOTf, demonstrating chemical shifts and splitting patterns of unidentified species formed in situ.

3.4.3 Miscellaneous substrates

Isonitriles, carbodiimides, and isocyanates have a rich history of cycloaddition chemistry and were obvious choices to conduct experiments with based on their cost and availability, however the insertion of unsaturated substrates with heavier main group elements afforded a

possibility of accessing a diverse array of unexplored heterocycles with multiple row 3 elements. Commercially available 1-adamantylphosphaethyne (AdCP) was tested as a heavier congener to nitriles, however the addition of HOTf to a stirring mixture of AdCP and $P_3^tBu_3$ only resulted in the formation of $P_4^tBu_4$ with unknown impurities stemming from the phosphaehtyne substrate. We also attempted the addition of (triphenylmethyl)thionyl imide ($TrN=S=O$) to $P_3^tBu_3$ in the presence of one equivalent of HOTf, however we yet again saw no reaction occur as the substrate appeared to degrade in the acidic conditions. Isopropyl isothiocyanate ($iPrNCS$), a heavy chalcogen congener to $tBuNCO$, was reacted with $P_3^tBu_3$ and HOTf at 0 °C and warmed to 22 °C where it was allowed to stir for 18 h. However the reaction yielded no observable insertion products, with $^{31}P\{^1H\}$ NMR displaying only broad peaks which could not be assigned to any one product (**Figure B.16**).

3.4.4 Returning to the $[P_3^tBu_3Me][OTf]$ framework

The methylated $P_3^tBu_3$ cation, $[P_3^tBu_3Me][OTf]$, is known to undergo insertions of isonitriles,¹⁶ offers a clear comparison to $P_3^tBu_3$ cycloadditions in the presence of acid. As such, the reactivity of $[P_3^tBu_3Me][OTf]$ with DIC, $tBuNCO$, and $PhNCO$ was tested. The reaction of $[P_3^tBu_3Me][OTf]$ with DIC in toluene for 24 h at 22 °C resulted in no reaction, with ^{31}P NMR spectra only showing the AMX spin pattern associated with the $P_3^tBu_3Me^+$ cation. Upon heating the reaction at 60 °C for 72 h in a sealed J Young tube, $^{31}P\{^1H\}$ NMR spectra revealed the formation of an AMX spin system ($\delta^{31}P = 56.9, 45.2, \text{ and } -22.9$, $^1J_{AM} = 264$ Hz, $^1J_{MX} = 420$ Hz, $^2J_{AX} = \text{not observed}$) alongside a host of doublets (**Figure B.17**), suggesting that DIC inserts into $[P_3^tBu_3Me][OTf]$ unselectively. The reaction of $[P_3^tBu_3Me][OTf]$ with $tBuNCO$ in toluene at 0 °C resulted in the formation of a red solution over 30 minutes, with a $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture revealing unselective reactivity but clear formation of an AMX spin system ($\delta^{31}P$

= -18.0, -34.7, and -49.5, $^1J_{AM} = 325$ Hz, $^1J_{MX} = 412$ Hz, $^2J_{AX}$ = not observed) buried in an amongst peaks corresponding to unidentified species (**Figure B.18**). The reaction of $[P_3^tBu_3Me][OTf]$ with PhNCO in a toluene warmed from 0 °C to 22 °C and stirred for 24 h resulted in no reaction, while prolonged heating at 60 °C for 7 days yielded a series of products by $^{31}P\{^1H\}$ NMR which could not be identified (**Figure B.19**).

3.5 Discussion

The insertion reactions discussed herein can be broken into three main parts: the reaction of $P_3^tBu_3$ with RNC substrates in the presence of HOTf; the reaction of $P_3^tBu_3$ with RNCO substrates in the presence of HOTf; and the reaction of $[P_3^tBu_3Me][OTf]$ with DIC and RNCO substrates. In discussing these reactions, two paths of selective reactivity are likely to occur: one in which the substrate is protonated and then reacts with $P_3^tBu_3$, and another in which $P_3^tBu_3$ is protonated and immediately reacts with the substrate *in situ*.

The reaction of $P_3^tBu_3$ with $RN\equiv C$ substrates proceeds well for isonitriles with aryl substituents compared with alkyl substituents. Alkyl substituents would render the isonitrile N atom more basic than aryl substituents, likely resulting in faster protonation of the substrate, and also makes a more nucleophilic $RN\equiv C$ fragment as a result of the greater electron donation of alkyl substituents. As a result of this, alkyl isonitriles appear to engage in unselective insertions with $P_3^tBu_3$ and likely with $P_4^tBu_4$, which is known to form upon exposure of $P_3^tBu_3$ to HOTf.¹⁶ It is possible that in the case of the less basic aryl isonitrile, the reactivity for other phosphane oligomers is minimized on account of the less nucleophilic isonitrile, and selective reactivity with $P_3^tBu_3$ is observed.

The reaction of $P_3^tBu_3$ with RNCO substrates in the presence of HOTf proceeds selectively for electron donating alkyl isocyanates, while aryl isocyanates react to form a variety of

unidentified products. In this scenario, a simple mechanism can be proposed in which the isocyanate is first protonated, forming an iminium, which exhibits a resonance form bearing a $^+C=O$ dipole which can then undergo cycloaddition (Figure 3.11). It appears that the basicity of the nitrogen atom is more consequential in this case, as alkyl substituents increase the basicity of the isocyanate more than aryl substituents and allow for the selective addition of $C=O$ to $P_3^tBu_3$ through polarization of the $C=O$ bond. The aryl isocyanates react unselectively, potentially due to the rapid formation of neutral and protonated $P_4^tBu_4$ and other phosphane oligomers which then react with the arylisocyanate.

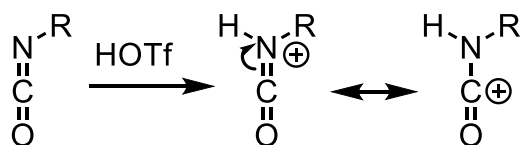


Figure 3.11 The protonation of isocyanates and resonance forms of the protonated substrate.

The inability of 1-adamantylphosphethyne, a heavy congener to an alkyl nitrile, to undergo acid-mediated cycloaddition with $P_3^tBu_3$ likely results from the flipped polarity of the substrate. It is proposed that nitriles undergo cycloaddition through a pathway involving nucleophilic attack at the cyclic phosphane by the nitrile nitrogen atom, followed by intramolecular ring-closure,¹⁶ however the greater electronegativity of carbon compared to phosphorus makes the pnictogen atom in this case less nucleophilic, and may result in lessened reactivity. The unsuccessful reaction with (triphenylmethyl)thionyl imide seems to stem from the acid-induced degradation of the substrate, while the lack of reactivity observed with isopropyl isothiocyanate may stem from a small difference in electronegativity between carbon and sulfur, making the dipole weaker and less amenable to nucleophilic attack.

In the case of $[P_3^tBu_3Me][OTf]$, it is evident that while the ring reacts cleanly with isonitriles, the reactivity observed with other unsaturated substrates is highly unselective or not feasible at all. This difference in reactivity may be due to $[P_3^tBu_3Me][OTf]$ being a weaker electrophile than $[P_3^tBu_3H][OTf]$, thereby preventing reactivity except in situations where particularly strong nucleophiles, such as isonitriles or nitriles, are used.

3.6 Conclusions

We report the insertion chemistry of $P_3^tBu_3$ with isonitriles, carbodiimides, and isocyanates in the presence of HOTf, as well as investigations into the insertion of such substrates into $[P_3^tBu_3Me][OTf]$. It was found that xylyl isonitrile inserts cleanly into $P_3^tBu_3$ when reacted in the presence of one equivalent of HOTf, while *tert*-butylisonitrile demonstrates unselective reactivity. The protonated insertion product of xylyl isonitrile and $P_3^tBu_3$ is deprotonated to form the stable free base of the P_3C heterocyclic framework. The reaction between $P_3^tBu_3$ and diisopropylcarbodiimide in the presence of acid appears to form an expected P_3CN insertion product, however this reaction is hampered by the side-reaction of carbodiimide with acids to form ureas *in situ*. The reaction of $P_3^tBu_3$ with *tert*-butylisocyanate in the presence of HOTf proceeded cleanly with addition of the C=O fragment into the cyclic phosphane, generating the first P_3CO heterocycle reported in the literature. This species, protonated on the exocyclic nitrogen, can likewise be deprotonated to form the neutral molecule. Comparatively, reactions of $[P_3^tBu_3Me][OTf]$ with isocyanates and DIC yielded no evidence of clean cycloaddition reactivity. It should also be noted that 1-adamantylphosphethyne, (triphenylmethyl)thionyl imide, and isopropyl isothiocyanate did not exhibit selective addition reactions with $P_3^tBu_3$.

This study determines that the scope of the acid-mediated $P_3^tBu_3$ ring expansion is limited to nitriles, aryl isonitriles, and alkyl isocyanates within the substrates assessed herein, highlighting

the necessity of nitrogenous bases within the unsaturated substrate to act as a substrate dipole activator in acid-mediated ring-expansions, and also the requirement of acid-mediated mechanisms for adding isocyanates and carbodiimides to $P_3^tBu_3$ which do not selectively insert into $[P_3^tBu_3Me][OTf]$. However, despite the limited scope, this study highlights the potential for this inorganic ring expansion reaction to generate new phosphorus rich heterocyclic frameworks – for which very few robust methods exist – in a modular fashion, and may yet afford a host of new heterocycles with further investigations into an expanded scope of substrates.

3.7 References

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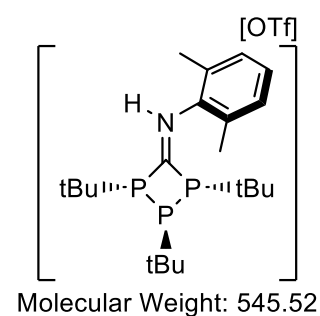
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3.8 Experimental

3.8.1 General Considerations

Storage and manipulation of all compounds were performed under an inert atmosphere either in an argon-filled MBraun Labmaster Pro or a dinitrogen-filled MBraun 200B glovebox equipped with a cold-well; or using an argon Schlenk line using standard techniques. *n*-Hexane, toluene, diethyl ether, and THF were dried and purified using an MBraun Grubbs/Dow solvent purification system²⁸ and stored over activated 4Å molecular sieves. CDCl₃ was dried over CaH₂, de-gassed and vacuum distilled prior to use. (P^{*i*}Bu)₃ was prepared per literature procedures.²⁹ (Triphenylmethyl)thionyl imide was synthesized according to literature procedures.³⁰ All other reagents were purchased from Sigma-Aldrich or Fisher Scientific and used as received. ¹H and ¹³C NMR spectrometry chemical shifts were referenced to residual proteo-solvent resonances and naturally abundant ¹³C resonances for all deuterated solvents. All heteronuclear NMR spectrum were referenced externally to IUPAC standards. Chemical shift assignments are based on NMR experiments performed on Bruker Avance NEO 500 MHz or AV III 300 MHz spectrometers.

3.8.2 Synthesis of [1-H][OTf]



A 25 mL ampoule equipped with a J. Young needle valve was charged with 264 mg (1 mmol, 1.0 eq.) of (P^{*i*}Bu)₃, 34.6 mg (1.05 mmol, 1.05 eq.) of xylyl isonitrile, 2 mL of toluene, and a magnetic stir bar. The ampoule was sealed, interfaced with a Schlenk line, and the solution was cooled in an ice-water bath. The needle-valve was removed and 93 μL (1.05 mmol, 1.05 eq., 158 mg) of neat HOTf acid was added against a counter-flow of inert gas using a glass 100 μL microsyringe, resulting in an immediate color change from colorless to orange. The ampoule was sealed and the solution stirred for 18 h, resulting in an orange-yellow

suspension (note: occasionally a brown color was noted, this did not affect the reaction outcome). All volatiles were removed under dynamic fine vacuum, first at 22 °C, then at 60 °C for 1h. To the resulting tacky solid, ca. 10 mL of Et₂O was added via cannula, and the ampoule was placed in an ultrasonic bath to effect trituration, leading to a bright yellow solid over an orange-to-brown solution. The solid was isolated by filtration over a medium porosity glass frit, washed with ca. 2 mL of Et₂O, and dried to a constant mass *in vacuo*, yielding the title compound as a bright yellow spectroscopically pure solid. Crystals suitable for single crystal X-ray diffraction studies were grown by layering 1 mL of a 15 mg/mL fluorobenzene solution of [1-H][OTf] with 3 mL of *n*-hexane and allowing for slow diffusion to occur over 2 days (451 mg, 82.7%).

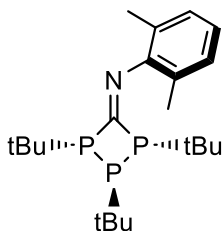
¹H NMR (500 MHz, CDCl₃) δ 13.14 (s, 1H, N-H), 7.29 (dd, observed triplet, *J* = 7.7 Hz, 1H, *p*-C_{Ar}-H), 7.18 (overlapping doublets, apparent triplet, *J* = 8.2 Hz, 2H, *m*-C_{Ar}-H), 2.48 (s, 3H, *o*-CH₃), 2.47 (s, 3H, *o*-CH₃), 1.59 (d, *J* = 16.1 Hz, 9H, P-C(CH₃)₃), 1.35 (dt, *J* = 13.6, 1.2 Hz, 9H, P-PC(CH₃)₃-P), 0.88 (d, *J* = 16.2 Hz, 9H, P-C(CH₃)₃).

¹³C NMR (126 MHz, CDCl₃) δ 214.5 (C=N), 138.2 (*o*-C_{Ar}), 134.7 (d, *J* = 3.3 Hz, ipso-C_{Ar}), 133.7 (*o*-C_{Ar}), 130.9 (*m*-C_{Ar}), 130.7(*p*-C_{Ar}), 129.5 (*m*-C_{Ar}), 43.0 (P-C(CH₃)₃), 41.5 (P-C(CH₃)₃), 30.1 (dd, *J* = 13.6, 4.2 Hz, P-C(CH₃)₃), 29.7 (dd, *J* = 13.4, 4.2 Hz, P-C(CH₃)₃), 29.2 (dt, *J* = 13.8, 5.4 Hz, P-PC(CH₃)₃-P), 28.9 (m, P-PC(CH₃)₃-P), 19.3 (*o*-CH₃), 19.1 (d, *J* = 12.2 Hz, *o*-CH₃).

³¹P NMR (203 MHz, CDCl₃) δ 43.6 (dd, *J* = 147, 91 Hz, P-P-P), 32.3 (dd, *J* = 144, 91 Hz, P-P-P), -91.9 (dd, apparent triplet, observed *J* = 145 Hz, P-P-P).

HRMS (ESI+) *m/z*: [M + H] calcd for C₂₁H₃₆NP₃H⁺ 396.2133. Found 396.2135.

3.8.3 Synthesis of **1**



Molecular Weight: 395.45

A 1 dr. vial was charged with 100 mg of [**1-H**][**OTf**] (0.183 mmol, 1 eq.), 3 mL of *n*-hexane and a small stir bar. To the resultant suspension was added 39 μ L of neat NEt₃ (28 mg, 0.278 mmol, 1.5 eq.). The vial was capped and the suspension was erratically stirred until the solid [**1-H**][**OTf**] was consumed (ca. 20 min), resulting in a yellow solution over a colorless semi-solid. All volatiles were removed *in vacuo*, the resulting solid was triturated with 1 mL *n*-hexane, and all volatiles were removed again to ensure complete removal of excess NEt₃. The solid residue was extracted with 2 $\times$ 3.5 mL *n*-hexane and solids were removed by passage through a 0.2 μ m syringe filter. All volatiles were removed *in vacuo* to yield the title compound as a pale yellow solid. Crystals suitable for single crystal X-ray diffraction studies were grown slow evaporation of a ca. 10 mg/mL *n*-hexane solution of **1** over ca. 2 weeks (57 mg, 78.6%).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.03 – 6.97 (overlapping dd, apparent triplet, 2H, *m*-C_{Ar}-H), 6.90 (dd, observed triplet, *J* = 7.5 Hz, 1H, *p*-C_{Ar}-H), 2.33 (s, 3H, *o*-CH₃), 2.26 (s, 3H, *o*-CH₃), 1.40 (br s, 9H, $\nu_{1/2}$ = 32Hz, P-C(CH₃)₃), 1.33 (dt, *J* = 12.9, 0.9 Hz, 9H, P-PC(CH₃)₃-P), 0.79 (s, 9H, $\nu_{1/2}$ = 32Hz, P-C(CH₃)₃).

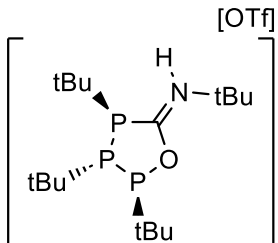
¹³C NMR (126 MHz, Chloroform-*d*) δ 150.61 (t, *J* = 9.0 Hz, ipso-C_{Ar}), 129.39 (*m*-C_{Ar}), 128.85 (*o*-C_{Ar}), 128.05 (*m*-C_{Ar}), 124.52(*o*-C_{Ar}), 124.02 (*p*-C_{Ar}), 29.74 (dt, *J* = 14.0, 5.4 Hz, P-PC(CH₃)₃-P), 29.23 (d, *J* = 4.7 Hz, P-C(CH₃)₃), 29.13 (d, *J* = 4.7 Hz, P-C(CH₃)₃), 28.36 – 27.62 (m, P-PC(CH₃)₃-P), 19.77 (*o*-CH₃), 19.60 – 19.12 (m *o*-CH₃).

³¹P NMR (203 MHz, Chloroform-*d*) δ 73.5 (dd, *J* = 153, 81 Hz, **P-P-P**), 39.2 (dd, *J* = 141, 81 Hz, **P-P-P**), -79.3 (t, 81 Hz, **P-P-P**).

HRMS (ESI+) m/z : $[M + H]^+$ calcd for $C_{21}H_{36}NP_3H^+$ 396.2133. Found 396.2135.

Remaining P-C(CH₃)₃ and C=N resonances could not be unambiguously assigned, the former were not observed by direct detection or ¹H-¹³C HMBC NMR spectrometry, while an ill-defined multiplet at ca. 179.5 ppm may be observed, however, due to poor signal-to-noise at even long acquisition times, and lack of correlation in 2D NMR experiments, unambiguous assignment cannot be made.

3.8.4 Synthesis of [2-H][OTf]


Molecular Weight: 513.47

A 25 mL ampoule equipped with a J. Young needle valve was charged with 264 mg (1 mmol, 1.0 eq.) of (P^tBu)₃, 1 mL (8.75 mmol, 8.75 eq. 0.868 mg) of *tert*-butylisocyanate, 1 mL of toluene, and a magnetic stir bar. The ampoule was sealed, interfaced with a Schlenk line, and the solution was cooled in an ice-water bath. The needle-valve was removed and 93 μ L (1.05 mmol, 1.05 eq., 158 mg) of neat HOTf acid was added against a counter-flow of inert gas using a glass 100 μ L microsyringe, resulting in an immediate color change from colorless to bright yellow. The ampoule was sealed and the solution stirred for 18 h, resulting in a yellow suspension. All volatiles were removed under dynamic fine vacuum, first at 22 °C, then at 60 °C for 1h. To the resulting tacky solid, ca. 4 mL of Et₂O was added via cannula, and the ampoule was placed in an ultrasonic bath to effect trituration, leading to a pale yellow solid over a highlighter yellow solution. The solid was isolated by filtration over a medium porosity glass frit, washed with ca. 1 mL of Et₂O, and dried to a constant mass *in vacuo*, yielding the title compound as an off-white solid of > 98% spectroscopic purity. Crystals suitable for single crystal X-ray diffraction studies were grown by layering 4 mL of a 40 mg/mL fluorobenzene solution of [2-H][OTf] with 12 mL of *n*-hexane and allowing for slow diffusion to occur over 2 days at – 40 °C (307 mg, 59.7%).

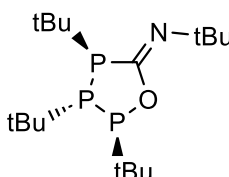
^1H NMR (500 MHz, Chloroform-*d*) δ 11.14 (s, 1H, N-**H**), 1.57 (s, 9H, N-C(CH₃)₃), 1.36 (d, J = 15.6 Hz, 9H, P-C(CH₃)₃), 1.33 (d, J = 8.2 Hz, 9H, P-C(CH₃)₃), 1.30 (d, J = 8.3 Hz, 9H, P-C(CH₃)₃).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.7 – 188.1 (m, C=N), 61.5 (N-C(CH₃)₃), 36.7 (dd, J = 24.3, 12.5 Hz, P-C(CH₃)₃), 35.5 (dd, J = 32.8, 9.2 Hz, P-C(CH₃)₃), 30.5 (apparent dt, J = 13.8, 7.0 Hz, P-PC(CH₃)₃-P), 30.2 (dd, J = 14.9, 5.5 Hz, P-C(CH₃)₃, overlapping P-PC(CH₃)₃-P), 28.6 (N-C(CH₃)₃), 26.1 (dd, J = 17.2, 5.3 Hz, P-C(CH₃)₃).

^{31}P NMR (203 MHz, Chloroform-*d*) δ 234.1 (dd, J = 265.3, 1.7 Hz, O-P), 39.6 (d, J = 286 Hz, C-P), -17.4 (dd, J = 286, 265 Hz, P-P-P). ^{31}P NMR (203 MHz, Chloroform-*d*) δ 234.10 (dd, J = 265.3, 1.7 Hz), 39.62 (d, J = 286.1 Hz), -17.35 (dd, J = 286.1, 265.3 Hz).

HRMS (ESI+) m/z : [M + H] calcd for C₁₇H₃₆NOP₃H⁺ 364.2082. Found 364.2082.

3.8.5 Synthesis of **2**


Molecular Weight: 363.40

A 1 dr. vial was charged with 100 mg of [**2-H**][OTf] (0.195 mmol, 1 eq.), 3 mL of *n*-hexane and a small stir bar. To the resultant suspension was added 41 μL of neat NEt₃ (29 mg, 0.292 mmol). The vial was capped and the suspension was erratically stirred until the solid [**2-H**][OTf] was consumed (ca. 20 min), resulting in a colorless solution over a colorless semi-solid. All volatiles were removed *in vacuo*, the resulting solid was triturated with 1 mL *n*-hexane, and all volatiles were removed again to ensure complete removal of excess NEt₃. The solid residue was extracted with 2 $\times$ 3.5 mL *n*-hexane and solids were removed by passage through a 0.2 μm syringe filter. All volatiles were removed *in vacuo* to yield the title compound as a pale yellow solid. Crystals suitable for single crystal X-ray diffraction studies were grown slow evaporation of a ca. 10mg/mL *n*-hexane solution of **2** over ca. 4 days (54 mg, 76.2%).

^1H NMR (500 MHz, Chloroform-*d*) δ 1.33 (s, 9H, N-C(CH₃)₃), 1.29 (dd, J = 13.2, 0.8 Hz, 9H, P-C(CH₃)₃), 1.28 (d, J = 13.4 Hz, 9H, P-C(CH₃)₃), 1.20 (dd, J = 13.2, 0.8 Hz, 9H, P-C(CH₃)₃).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.5 – 163.7 (m, C=N), 56.8 (d, J = 7.8 Hz, N-C(CH₃)₃), 34.4 (dd, J = 30.5, 9.9 Hz, P-C(CH₃)₃), 32.33 (dd, J = 20.3, 13.2 Hz, P-C(CH₃)₃), 30.96 – 30.26 (m, overlapping P-PC(CH₃)₃-P and N-C(CH₃)₃), 29.49 (dd, J = 13.0, 5.0 Hz, P-C(CH₃)₃), 29.11 – 28.43 (m, P-PC(CH₃)₃-P), 26.27 (dd, J = 16.8, 6.4 Hz, P-C(CH₃)₃).

^{31}P NMR (203 MHz, Chloroform-*d*) δ 173.1 (dd, J = 248, 4 Hz, O-P), 14.9 (dd, J = 267, 4 Hz, C-P), -31.8 (dd, J = 267, 248 Hz, P-P-P).

HRMS (ESI+) m/z : [M + H] calcd for C₁₇H₃₆NOP₃H⁺ 364.2082. Found 364.2082

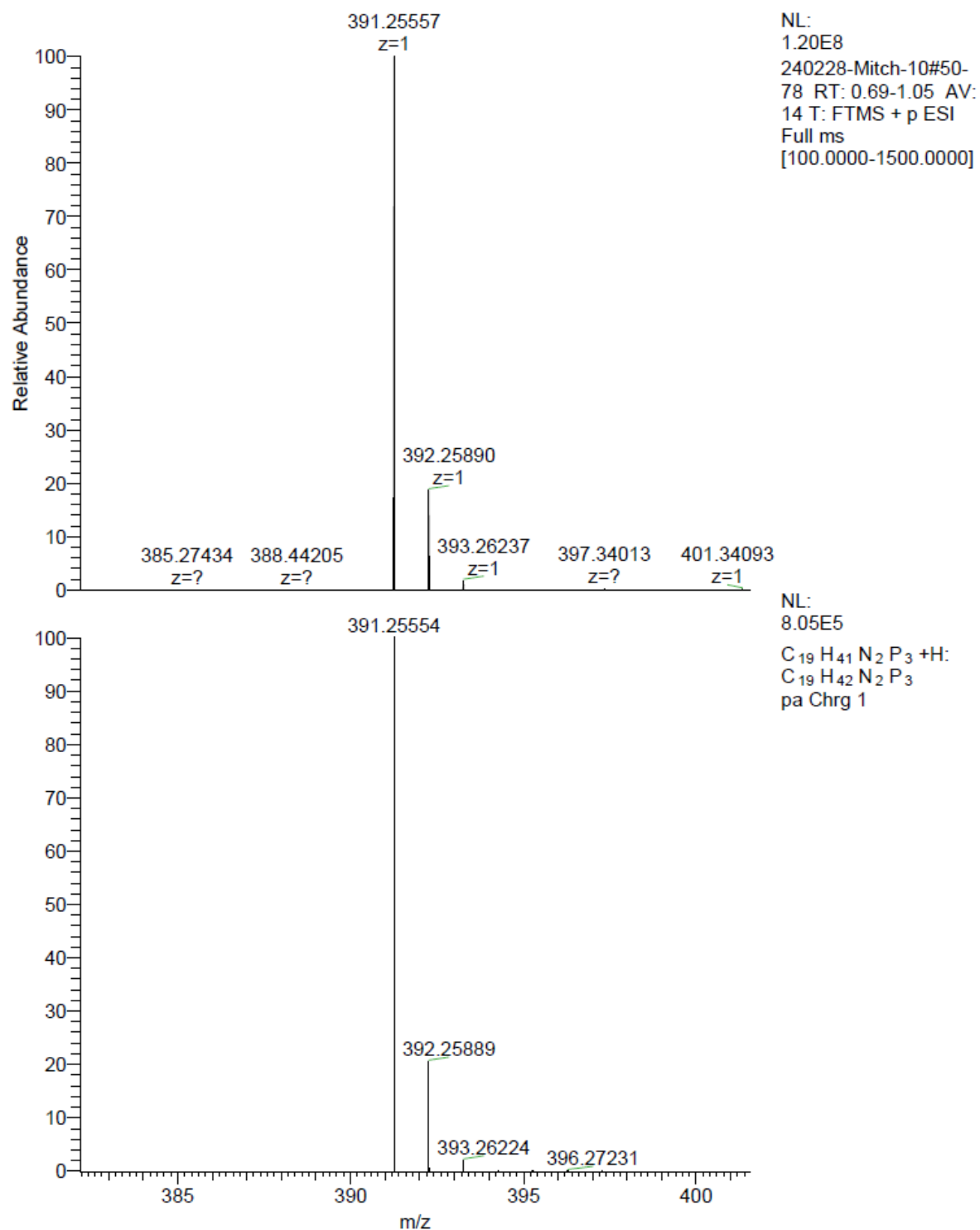


Figure 3.12 ESI-MS mass spectrum (positive mode) of the addition product of DIC and $P_3^tBu_3$ in the presence of HOTf.

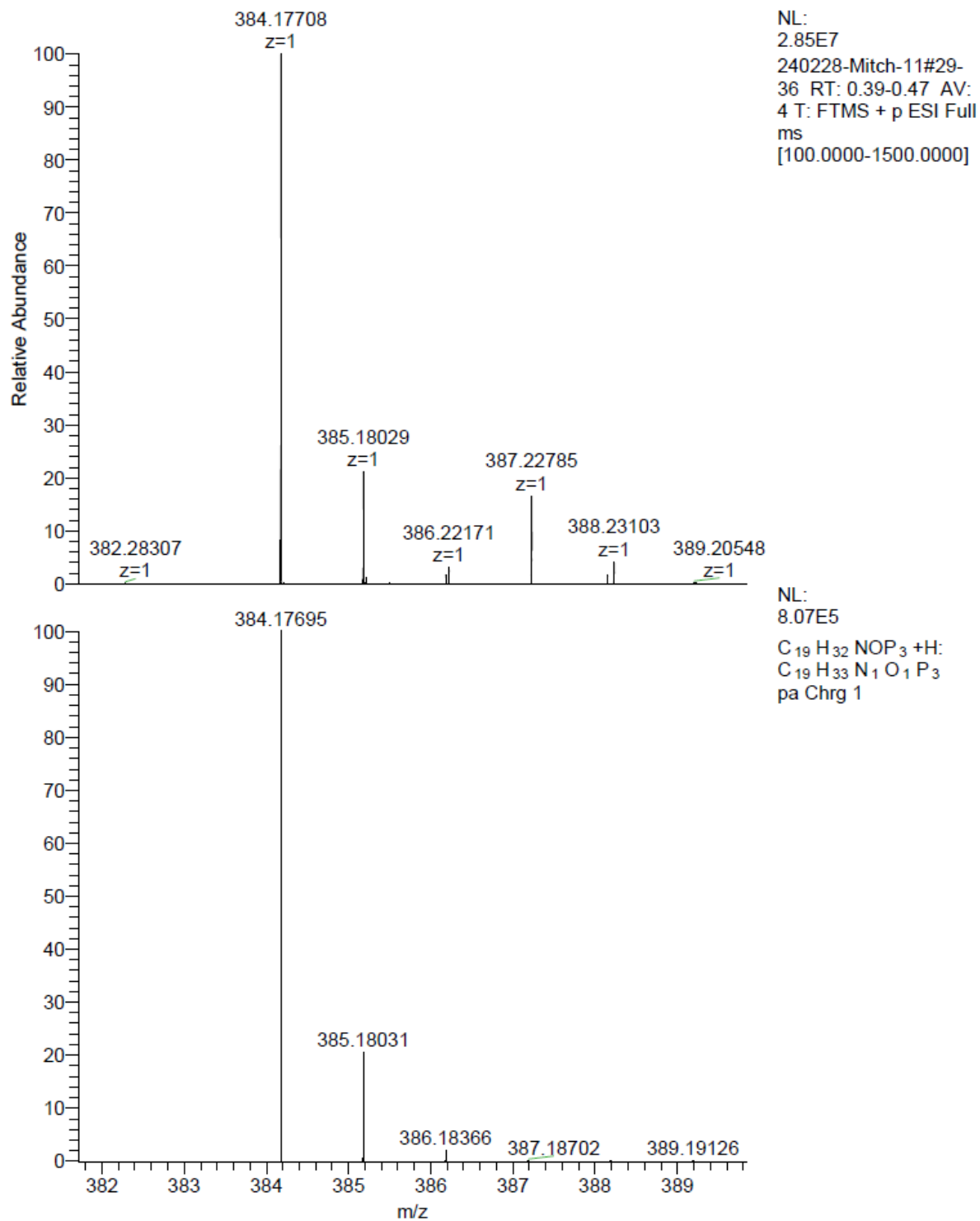


Figure 3.13 ESI-MS mass spectrum (positive mode) of the addition product of PhNCO and P₃^tBu₃ in the presence of HOTf.

Chapter 4. Investigations into the equilibration and ring-opening polymerization of cyclic P(V)-O-Si-O heterocycles, and development towards stabilizing RPO₂ polymers and monomers

Chapter 4 describes investigations into the synthesis of P-O-Si-O heterocycles, their dynamic solution behaviour, and potential to undergo thermal ROP. Further work on the stabilization of P-O materials to prevent such dynamic behaviour through sterics and electronics is outlined.

Collaborators: Jade Watson and Martin Trapero assisted in the synthesis of phosphonate starting materials and heterocycles. Jade Watson assisted in the synthesis of M^SFluid^{tBu}-Br. Dr. Peter Williams assisted in ESI-MS studies of heterocycles. Dr. Brian Patrick collected single crystal diffraction data. Christopher Barr collected DOSY NMR data.

4.1 Abstract

Ring-opening polymerization has long been used as strategy to discover new families of main group element-containing polymers. The discovery of polyphosphonates, made of monomers with formula RPO₂ that are isolobal to siloxanes R₂SiO, presented an opportunity to develop hybrid phosphonate-siloxane polymers with P-O-Si-O backbones. Herein we describe detailed studies into the synthesis of P-O-Si-O heterocycles, which are candidates for polymer precursors for ROP studies. We synthesized a series of [RP(O)-O-SiR'-O]₂ (R = Ph, R' = Me, Ph, Mes; R = R' = Mes) eight-membered rings with varying steric demands. Multinuclear NMR studies and DOSY NMR measurements reveal that species with Me and Ph substituents at silicon equilibrate in solution, while species with Mes substituents at silicon are solution-stable. Electrospray ionization mass spectrometric studies reveal that i) trace moisture selectively abstracts RPO₂ from the

P–O–Si–O backbone, forming phosphonic acids and oligo-siloxane linkages; ii) that eight membered rings undergo rapid equilibration into 12-membered $[\text{RP}(\text{O})\text{--O--R}_2\text{Si--O}]_3$ rings and 6-membered $[\text{RP--O--R}_2\text{Si--O--R}_2\text{Si--O}]$ rings; and iii) that increasing steric hindrance at silicon prevents solution equilibration. Polymerization studies on low-melting rings reveal that the least sterically hindered ring, $[\text{PhP}(\text{O})\text{--O--Me}_2\text{Si--O}]_2$, undergoes ROP to form a mixture of polymer and small oligomers, while $[\text{PhP}(\text{O})\text{--O--Ph}_2\text{Si--O}]_2$ likely only forms a glassy phase of small oligomers upon heating based on NMR and GPC evidence. Attempts to stabilize the phosphonates electronically for the design of more robust P–O and P–O–Si–O heterocycles resulted in insoluble materials for electron-withdrawing substituents and highly reactive materials for electron-donating substituents. Progress towards isolating a monomeric RPO_2 unit was made through the synthesis of an RPCl_2 precursor, in which R is sterically demanding difluorenyl hydrindacene $\text{M}^{\text{S}}\text{Fluid}^{\text{tBu}}$.

4.2 Introduction

Ring-opening polymerization (ROP) is a valuable tool to access a host of polymeric materials,^{1, 2} and has been especially instrumental to the synthesis of main group and metallo-polymers.³⁻⁶ Isoelectronic or isolobal design of established ROP monomers can allow for the strategic design of new polymer classes. Polysiloxanes $[\text{RR}'\text{Si--O}]_n$, in particular, present a promising scaffold for the design of new main group polymers, as their combination of high thermal stability, chemical inertness, biocompatibility, and simple preparation via ROP of cyclic siloxanes has made these polymers ubiquitous across all facets of modern society.⁷ Recently, a new class of main group polymers, the polyphosphonates $[\text{RP}(=\text{O})\text{--O}]_n$, were developed as isolobal analogues to polysiloxanes (Figure 4.1a).⁸ It was hypothesized that 6-membered cyclic phosphonates would possess an appropriate amount of ring strain to undergo ROP akin to cyclic siloxanes, and this was borne out by formation of high molecular weight polymers by heating the monomers in a melt. Polyphosphonates were found to have molar masses on the upper-bound of

13-17 kDa as established through MALDI-ToF MS, behaving as brittle thermoplastics in the solid state akin to polydiphenylsiloxane. However, oligo- and poly-phosphonates were found to be dynamic in solution, and, without sufficient kinetic stabilization, depolymerized back to their cyclic phosphonate precursors upon dissolution (Figure 4.1a) – a behaviour only seen in polysiloxanes in the presence of acid or base activators.⁹⁻¹¹

While this isolobal analogy provided access to silicon-free polymers, another strategy to build upon siloxanes for new classes of main group polymer is to form hybrids of the type $[\text{SiR}_2\text{--O--ER}_x\text{--O}]_n$ (E = main group element). Incorporation of one or more elements into the siloxane chain has the potential to unlock new polymer classes with modified or tunable physical properties imparted by the hybrid $[\text{E--O--Si--O}]_n$ system. This strategy was previously attempted through the synthesis of a series of strained cyclic borasiloxanes of the formula $[\text{PhB--O--(SiR}_2\text{--O)}_x]_y$ which were postulated to undergo ROP to form B--O--Si--O polymers.¹² However, it was found that these rings undergo ring expansion and rearrangements when they are heated through the melt with or without an activator like $\text{K}[\text{OSiMe}_3]$ (Figure 4.1b).

The discovery of polyphosphonates and previous investigations into siloxane hybrids prompted us to look into whether a hybrid of polyphosphonates and polysiloxanes could be synthesized. The high phosphorus content of these polymers, in combination with known synergistic mechanisms in phosphorus and silicon materials to quench flames,^{13, 14} makes phosphonate-siloxane main-chain polymers excellent candidates for flame retardant materials akin to other main group polymers.¹⁵⁻¹⁸ A survey of the literature found that the synthesis of polyphosphonosiloxanes has been attempted only once by a polycondensation route between dimethyl H-phosphonate and dichlorodimethylsilane,¹⁹ yielding low-molecular weight polymers with degrees of polymerization of $n = 28$ (molar mass $\approx 4000 \text{ g mol}^{-1}$ defined by ^1H NMR

spectroscopy) and with their material properties left unexplored (Figure 4.1c). We hypothesized that if a skeletal silicon atom in a cyclic siloxane was replaced by a phosphorus atom, these rings would be able to undergo ROP given that the small difference in the covalent radii of silicon (1.11 Å) and phosphorus (1.07 Å)²⁰ would afford similar structural parameters as a fully siloxane ring, and that the established thermal ROP methods of cyclic tri- and tetra-siloxanes could be applied to generate polysiloxanes.⁷ However, we found that cyclic phosphonosiloxanes have been reported sparsely in the literature. Most examples are missing robust structural characterization,²¹⁻²⁴ one example was crystallized with no further characterization as a side-product of a xerogel reaction,²⁵ and one example was synthesized purposefully and structurally characterized, though lacked thorough spectroscopic analysis.²⁶ Herein we report a systematic study into the synthesis of [RP(O)–O–SiR'₂–O]₂ heterocycles, simplified as **P^RSi^{R'}**, and our investigation of their ROP behaviour.

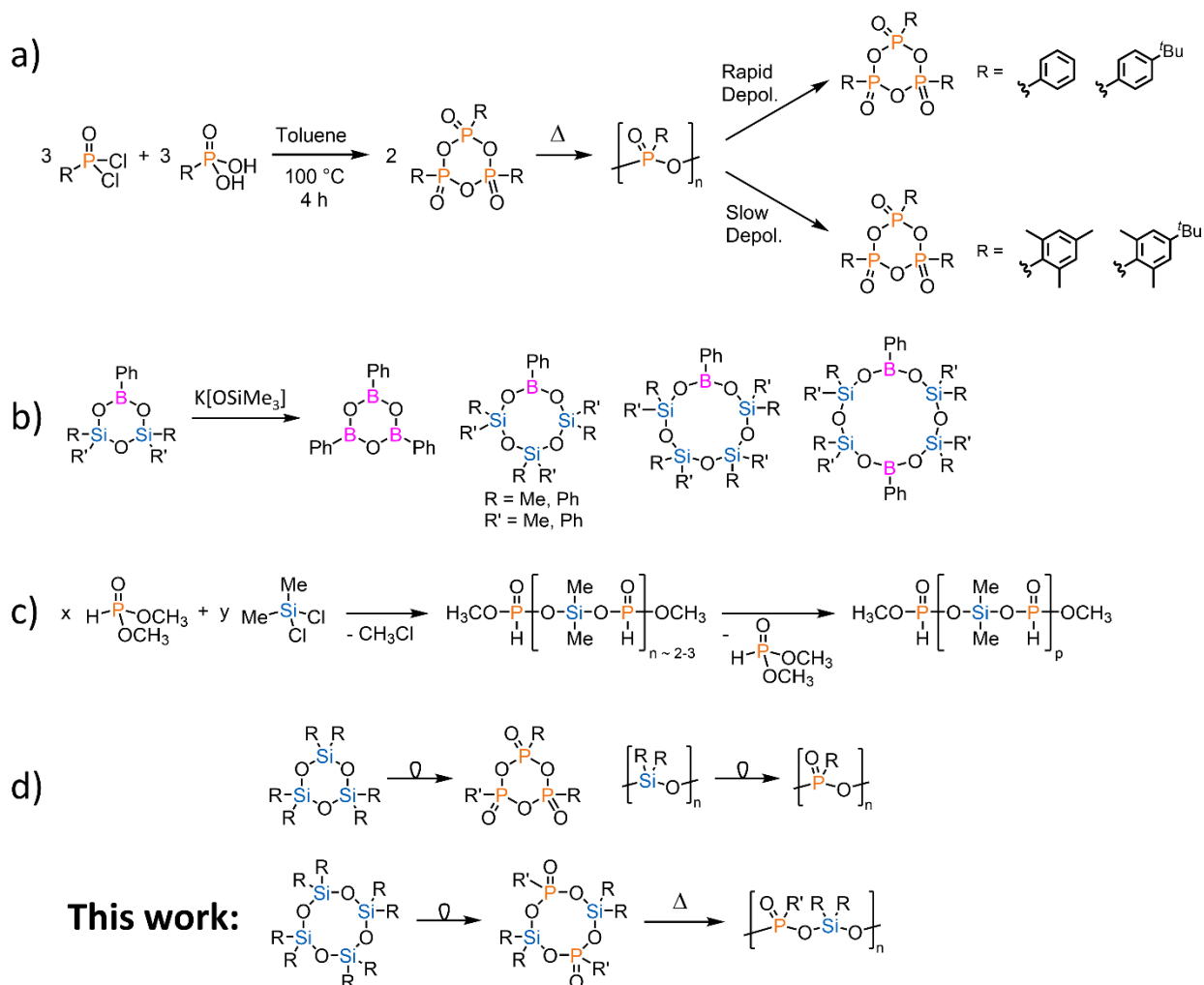
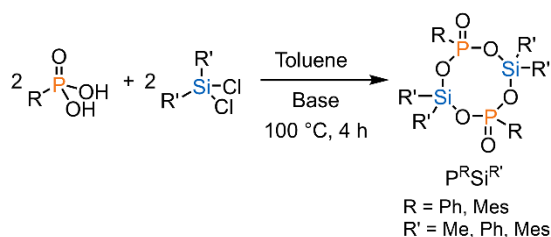


Figure 4.1 a) Reported synthesis of cyclic phosphonates and polyphosphonates, and solution behaviour of polyphosphonates (see ref. 3); b) Visualization of the steric-related depolymerization dynamics of polyphosphonates; c) previous attempt at hybrid borasiloxanes using cyclic boradisiloxanes, yielding various ring disproportionation products (see ref 12); c) previous attempts at a mixed phosphonate-siloxane polymer (see ref 19); and d) proposed cyclic phosphonosiloxanes and their polymers described in this work.

4.3 Results and Discussion

4.3.1 Synthesis and characterization of cyclic phosphonosiloxanes $\text{P}^{\text{R}}\text{Si}^{\text{R}'}$ ($\text{R} = \text{Ph}, \text{R}' = \text{Me}, \text{Ph}, \text{Mes}; \text{R} = \text{Mes}, \text{R}' = \text{Mes}$)

We synthesized 8-membered cyclic $\text{P}^{\text{R}}\text{Si}^{\text{R}'}$ heterocycles by heating equimolar amounts of phosphonic acid and dichlorosilane in toluene for 4 hours at 100 °C, under a nitrogen atmosphere, in the presence of two molar equivalents of Proton-sponge® base (Scheme 4.1). This resulted in the precipitation of Proton-sponge® hydrochloride salt from a clear toluene solution. Subsequent filtration of the salt followed by washing with toluene and evaporating volatiles *in vacuo* yielded white amorphous powders. These were recrystallized by layering CH_2Cl_2 or PhF solution with hexanes or pentane. $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ is found to be semi-soluble in hexanes and pentane, especially in the presence of trace amounts of CH_2Cl_2 , and as such crystallization is preferably performed by dropping a solution of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ in a minimal amount of CH_2Cl_2 into an excess of pentane, and allowing the semi-soluble suspension to stand at -30 °C for 24 h, leading to the formation of tacky, low-melting single crystals.



Scheme 4.1 Synthetic scheme for the synthesis of $\text{P}^{\text{R}}\text{Si}^{\text{R}'}$ heterocycles

Single-crystal XRD studies of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$, $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$, $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$, and $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$ confirmed the eight-membered ring structure of each species (Figure 4.2). $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ and $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ form “long chair” conformations,²⁷ in which $\text{P}=\text{O}$ moieties sit *trans* to one another (referred to *vide infra* as “all-*trans*”). This has also been observed for previously reported crystal structures of $\text{P}^{\text{Ph}}\text{Si}^{\text{tBu}}$ and $\text{P}^{\text{OSiMe}_3}\text{Si}^{\text{Ph}}$.^{25, 26} Single crystals of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$ revealed a structure with a “boat” conformation also

seen in $[\text{SiPh}_2\text{-O}]_4$ (D_4^{Ph}), in which P=O moieties sit *cis* to one another (referred to *vide infra* as “all-*cis*”), likely as a result of the increased steric demands at silicon. Further increasing steric bulk at phosphorus and silicon in $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$ results in a distorted S_4^m conformation,²⁷ pushing the ring

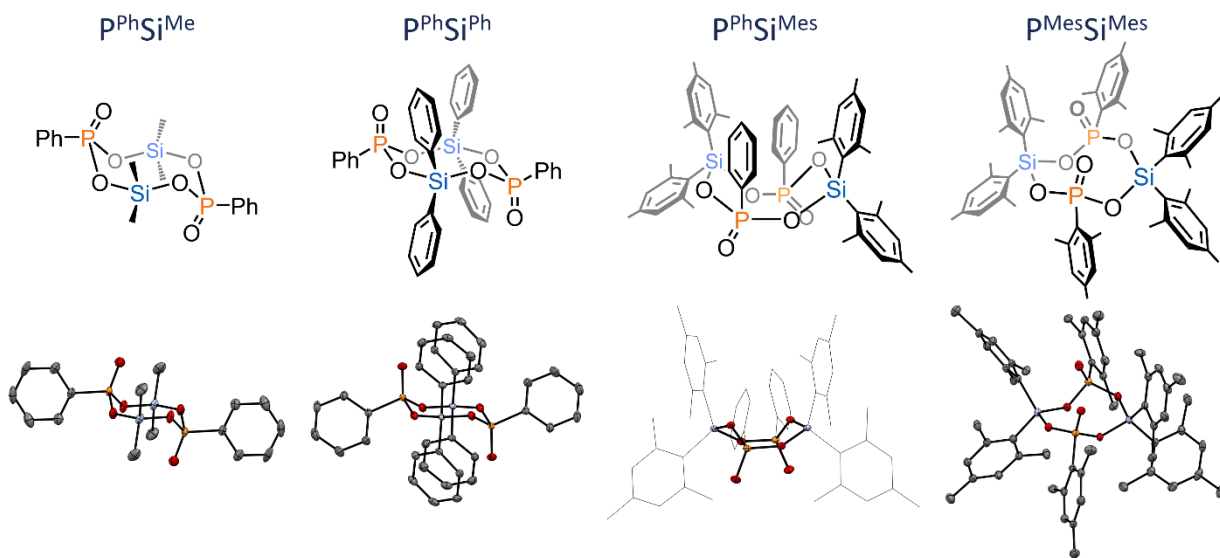


Figure 4.2 Single crystal X-ray structures of $\text{P}^{\text{R}}\text{Si}^{\text{R}'}$ species with chemical structures and compound labels shown above for clarity. H atoms have been omitted for clarity, and aryl rings on $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$ have been shown in wireframe to better display the “boat” structure. to the limits of conformational flexibility.

Multinuclear NMR spectroscopy complements the solid state structures observed (Figure 4.3). ^{31}P NMR spectra display singlets in the range of -0.2 to -2.8 ppm with ^{29}Si satellites ($^2J_{\text{PSi}} = 10\text{-}12$ Hz), which were previously unmentioned in the other reports of P-O-Si-O rings,^{25, 26} but are valuable in verifying the P-O-Si connectivity of the ring species. ^{29}Si NMR spectra display signals in ranges typical of $\text{O-SiMe}_2\text{-O}$ and $\text{O-SiAr}_2\text{-O}$ moieties and also confirmed the P-O-Si framework through clear coupling to phosphorus, with $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ appearing as a triplet at -4.6 ppm ($^2J_{\text{SiP}} = 10$ Hz), and $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$, $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$, and $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$ appearing as triplets between -36 and -39 ppm ($^2J_{\text{PSi}} = 11\text{-}12$ Hz). Notably, a series of minor signals were also observed in the NMR spectra of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ and $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ (Figure 4.3), which may be attributed to larger oligomeric $[\text{P}^{\text{R}}\text{Si}^{\text{R}'}]_n$ species.

Contrary to **P^{Ph}Si^{Me}** and **P^{Ph}Si^{Ph}**, evidence of higher oligomeric species were not observed in initial ³¹P NMR studies on single crystals of **P^{Ph}Si^{Mes}** grown at -30 °C in CH₂Cl₂/hexanes for 7 days, with only a single peak observed at -2.75 ppm in the ³¹P{¹H} NMR spectrum (Figure 4.3). However, bulk recrystallization of a second batch left to stand for 21 days revealed a 50:50 mixture of two individual species by ³¹P{¹H} NMR spectroscopy, with peaks at -2.75 ppm and -3.88 ppm (Figure C.14). ¹H NMR spectroscopy of this sample reveals an aromatic region in which two sets of peaks between 8.0 and 7.0 ppm represent two different molecules with equivalent phenyl environments, while two sets of aromatic peaks associated with *m*-H peaks of Mes₂Si moieties are present, one molecule in which both *m*-H environments are symmetric and another which bears two different *m*-H environments (Figure C.13). This sample over 7 days slowly shifted ³¹P{¹H} signal ratios between peaks at -2.75 ppm and -3.88 ppm from 50:50 to 70:30 with no other species present (Figure C.15), while ¹H signals corresponding to inequivalent *m*-H Mes₂Si environments decreased concurrently. ¹H DOSY studies on the 70:30 mixture revealed that both species have virtually identical diffusion coefficients (Figure 4.24), which leads us to conclude that the upfield species present both in **P^{Ph}Si^{Mes}** and **P^{Ph}Si^{*t*Bu}** derivatives are the kinetically stable all-*cis* isomers, which in the case of **P^{Ph}Si^{Mes}** also appears to be, empirically, the most favoured crystallizable species at -30 °C. **P^{Mes}Si^{Mes}**, the most sterically encumbered of the species herein, displays only one species in both ³¹P and ²⁹Si NMR spectra, suggesting that the addition of mesityl groups provides kinetic stability to the P–O–Si–O linkages and prevents equilibration.

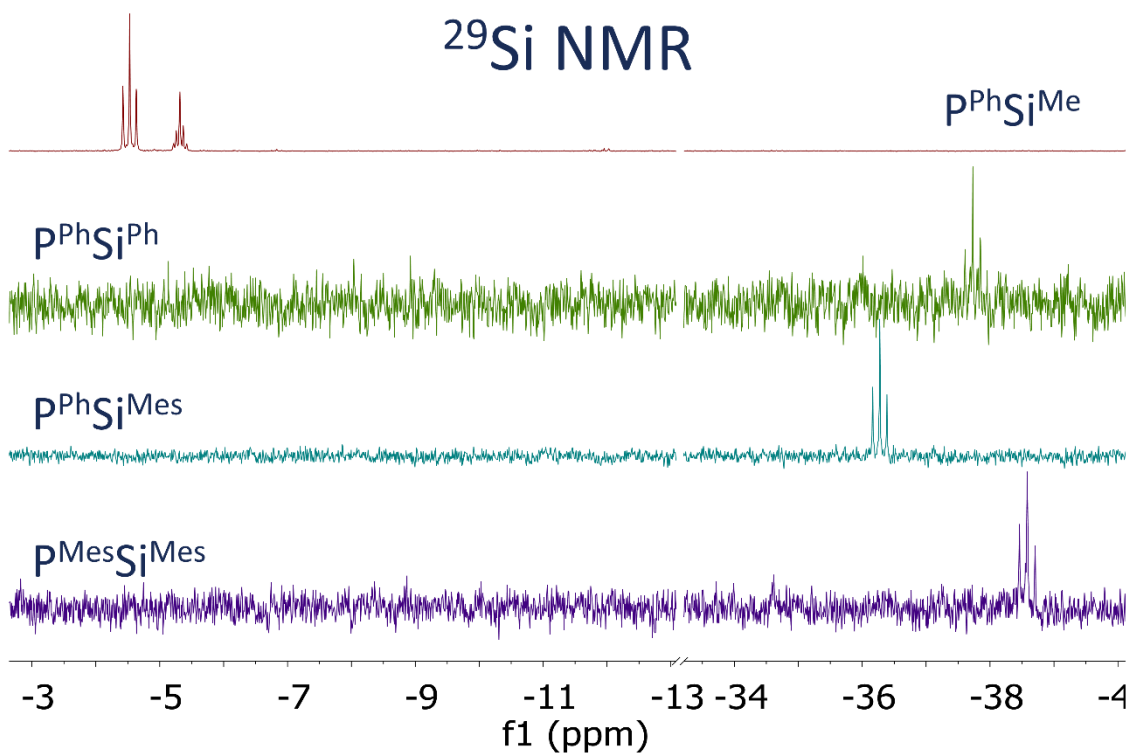
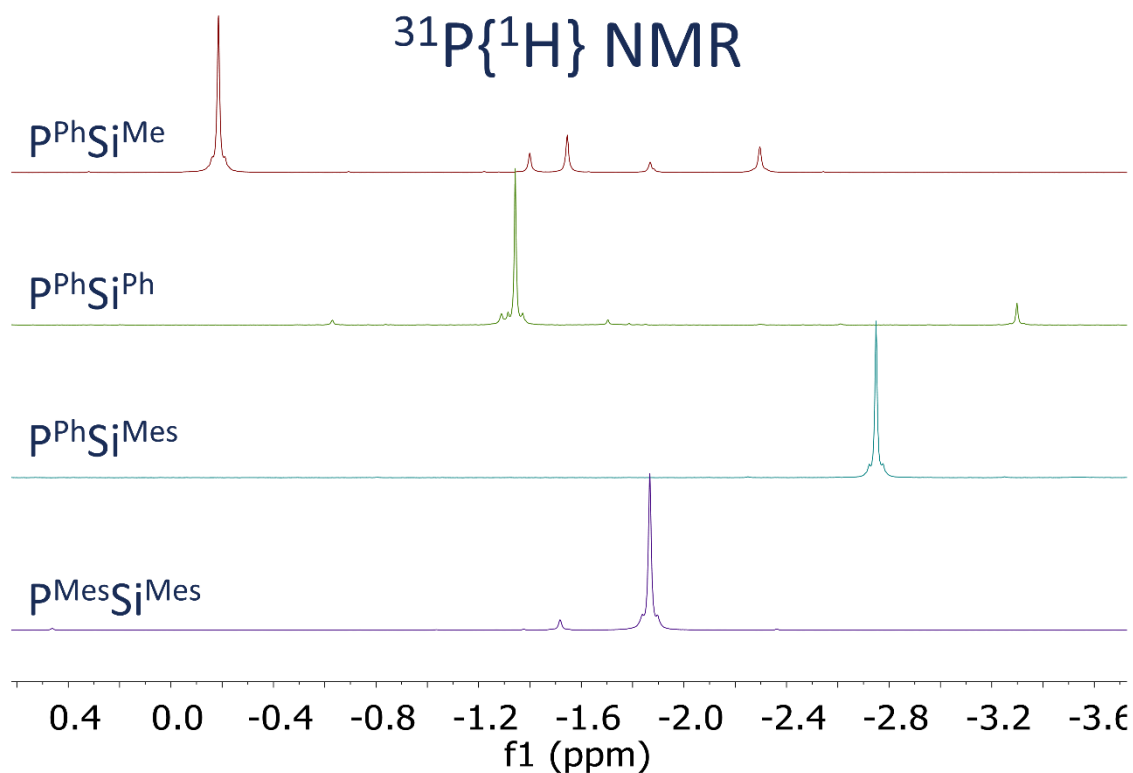


Figure 4.3 Stacked $^{31}\text{P}\{^1\text{H}\}$ (top) and ^{29}Si (bottom) NMR spectra of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$, $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$, $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$, and $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$. All spectra were obtained in CDCl_3 .

To support our hypothesis that **P^RSi^R** rings with inadequate kinetic stabilization were undergoing solution equilibration to higher oligomers, we conducted ¹H DOSY NMR on freshly prepared solutions of **P^RSi^R** single crystals dissolved in CDCl₃ (Figure 4.4). In the case of PPhSiMe, the peaks with the largest integrations which we attribute to our main product had *D* coefficients of approximately 1.55x10⁻¹⁰ m² s⁻¹, while the host of minor products in the ¹H NMR had smaller diffusion coefficients ranging from 1.5 – 1.3x10⁻¹⁰ m² s⁻¹, indicating that **P^{Ph}Si^{Me}** equilibrates into larger ring species upon dissolution. Likewise, the major product of the **P^{Ph}Si^{Ph}** ¹H NMR sample had *D* coefficients of approximately 7x10⁻¹⁰ m² s⁻¹ while the host of other peaks in the aromatic region had smaller *D* coefficients ranging from 6.8-6.3 x10⁻¹⁰ m² s⁻¹, corresponding to higher molecular weight species. These observations give evidence that **P^RSi^R** species are dynamic in solution, though this was never commented on in the most well-characterized example of these species in the literature, **P^{Ph}SiⁱBu**.²⁶

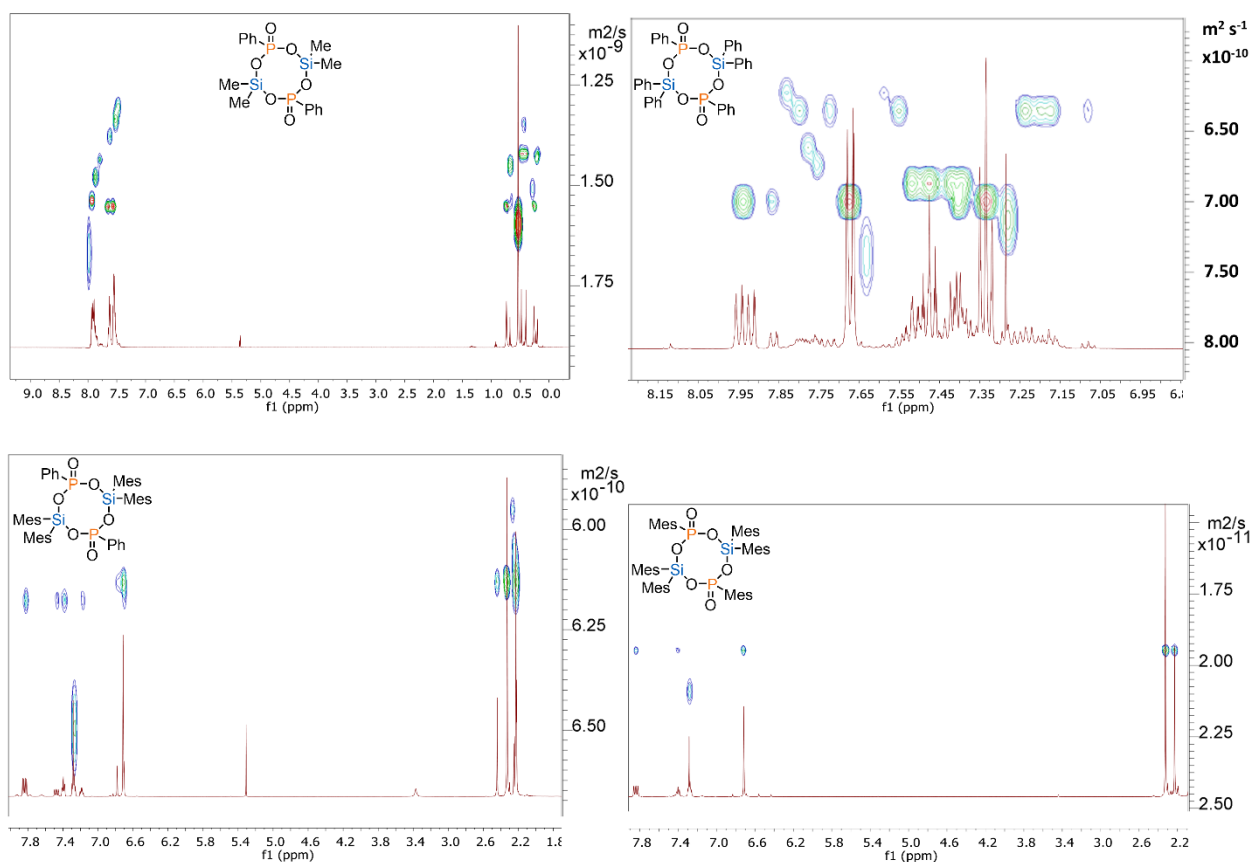


Figure 4.4 DOSY spectra of **P^{Ph}Si^{Me}** (top left), **P^{Ph}Si^{Ph}** (top right), **P^{Ph}Si^{Mes}** (bottom left), and **P^{Mes}Si^{Mes}** (bottom right).

Given that dynamic behaviour of P–O–Si–O rings was not previously commented on in the literature, previously reported **P^{Ph}Si^{tBu}** was resynthesized to determine the extent of its equilibration with higher order rings or oligomers.²⁶ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the compound displayed a major species at -4.6 ppm with ^{29}Si satellites ($^2J_{\text{PSi}} = 17.6$ Hz) as well as a minor species at -6.4 ppm ($^2J_{\text{PSi}} = 18.3$ Hz) (Figure C.21), while the ^{29}Si spectrum displayed two triplets at 13.8 ppm ($^2J_{\text{SiP}} = 17.8$ Hz) and 14.6 ppm ($^2J_{\text{SiP}} = 18.2$ Hz) (Figure C.23). The presence of a single species in solution, as evidenced by $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, in combination with similar J couplings between the two observed species, suggests that **P^{Ph}Si^{tBu}** forms all-*cis* and all-*trans* isomers akin to **P^{Ph}Si^{Mes}**. Ergo, when R' is small for **P^RSi^{R'}** species such as **P^{Ph}Si^{Me}** and **P^{Ph}Si^{Ph}**, P–O–Si–O heterocycles equilibrate into multiple species with varying *cis* or *trans* configurations, while when

R' is larger (e.g. **P^{Ph}Si^{tBu}**, **P^{Ph}Si^{Mes}**) the rings tend to only form a mixture of all-*cis* and all-*trans* isomers.

The temperature dependence of the oligomer distribution in solution was investigated by means of $^{31}\text{P}\{^1\text{H}\}$ VT-NMR studies on prototypical heterocycle **P^{Ph}Si^{Ph}** (Figure 4.5). Samples were equilibrated at each temperature for 20 minutes, and were locked and shimmed prior to spectrum collection after the temperature equilibration was complete. The first study looked to the change in speciation in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum upon heating from -50 °C up to 10 °C in CDCl₃. It was immediately observed that all peaks in the -50 °C spectrum, both corresponding to **P^{Ph}Si^{Ph}** and oligomers, were extremely broad, such that ^{29}Si satellites were no longer visible. Upon warming, it was observed that relative peak ratios did not change significantly, but rather all peaks underwent an upfield drift in their chemical shift with oligomeric peaks undergoing a $\Delta\delta = 1.00\text{-}1.55$ ppm while the main **P^{Ph}Si^{Ph}** peak shifted upfield by $\Delta\delta = 0.69$ ppm. The second VT-NMR study looked at the change in speciation upon heating a sample of **P^{Ph}Si^{Ph}** from 0 °C to 100 °C in Tol-d⁸. A similar trend was observed as in the first study, in which ratios of **P^{Ph}Si^{Ph}** to oligomers remained virtually identical, while species underwent an upfield change in their chemical shift. The temperature independence of relative populations may be due to an isentropic oligomerization process, in which the equilibrium populations are dictated solely by the enthalpic contribution given a similarity of entropy between the **P^{Ph}Si^{Ph}** ring and higher oligomers (indeed, eight-membered siloxane rings bear more entropy as polymers than as rings)⁷; alternatively, the temperature independence of relative populations may be due to activation barriers that are too high to permit equilibration amongst them within the time-frame of these experiments. The temperature dependence of peak-widths and chemical shifts may be a result of conformational dynamics within each species made possible by the presence of long and flexible P–O and Si–O

bonds.⁷ Temperature dependent shifts have been previously observed in P^{III} species²⁸ and P^V species,²⁹ as ^{31}P serves as a sensitive nucleus for NMR thermometry.

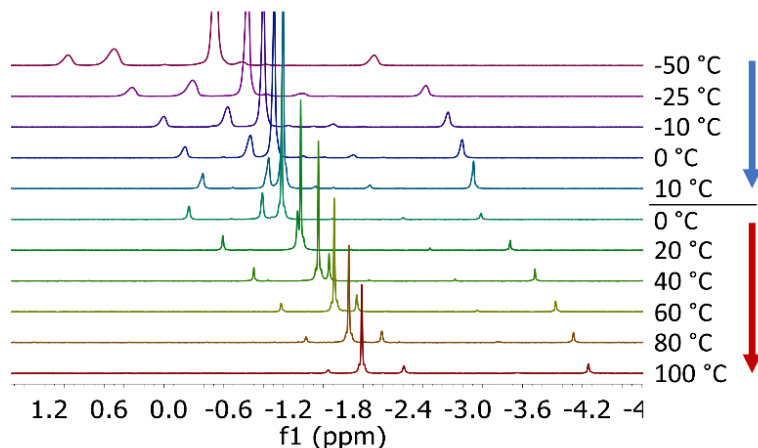


Figure 4.5 Variable temperature $^{31}P\{^1H\}$ NMR studies (203 MHz) of $P^{Ph}Si^{Ph}$, in which temperatures -50 to 10 °C were obtained in $CDCl_3$ and temperatures 0 to 100 °C were obtained in $Tol-d^8$.

While the dynamic nature of the rings is evident in solution, suggesting they may be able to undergo ring-opening in the solid state with sufficient heating, differential scanning calorimetry (DSC) was conducted to determine whether $P^R Si^R$ heterocycles displayed any potential for undergoing thermally-induced ROP to form $[P^R Si^R]_n$ polymers (Figure 4.6). For $P^{Ph}Si^{Me}$ and $P^{Ph}Si^{Ph}$, the first heating cycle is characterized by an endotherm characteristic of the material undergoing a melt at temperature T_m , where $T_m = 127$ °C for $P^{Ph}Si^{Me}$ and 148 °C for $P^{Ph}Si^{Ph}$. No ROP exotherms were discernible, however this was expected given the lack of strain in eight-membered rings and their propensity to polymerize slowly upon prolonged heating. In subsequent cooling and heating cycles, calorigrams displayed clear deflections in the baseline indicative of a glass transition (T_g), where $T_g = -15$ °C for $P^{Ph}Si^{Me}$ and 40 °C for $P^{Ph}Si^{Ph}$. Contrary to $P^{Ph}Si^{Me}$ and $P^{Ph}Si^{Ph}$, $P^{Ph}Si^{Mes}$ displayed no clear melt transitions, instead displaying multiple endo- and exothermic phenomena in the first heating run, followed by successive cooling and heating runs with

no indication of a T_g . This may be due to decomposition of $\mathbf{P}^{\text{Ph}}\mathbf{Si}^{\text{Mes}}$ in the heating process, or due to the formation of amorphous glassy material with no visible transitions within the temperature window. $\mathbf{P}^{\text{Mes}}\mathbf{Si}^{\text{Mes}}$ did undergo a melt in the first heating at $T_m = 130\text{ }^{\circ}\text{C}$ and displayed no other endothermic features consistent with a melt in subsequent heating cycles until $275\text{ }^{\circ}\text{C}$. Cooling runs revealed an exotherm at $223\text{ }^{\circ}\text{C}$ in successive cooling runs consistent with recrystallization of the material. The difference in behaviour between $\mathbf{P}^{\text{Ph}}\mathbf{Si}^{\text{Me}}/\mathbf{P}^{\text{Ph}}\mathbf{Si}^{\text{Ph}}$ and $\mathbf{P}^{\text{Ph}}\mathbf{Si}^{\text{Mes}}/\mathbf{P}^{\text{Mes}}\mathbf{Si}^{\text{Mes}}$ likely results from the steric bulk of the dimesitylsiloxane unit, which provides a significant amount of kinetic stabilization to the rings and likely precludes ring-opening or the formation of glassy states.

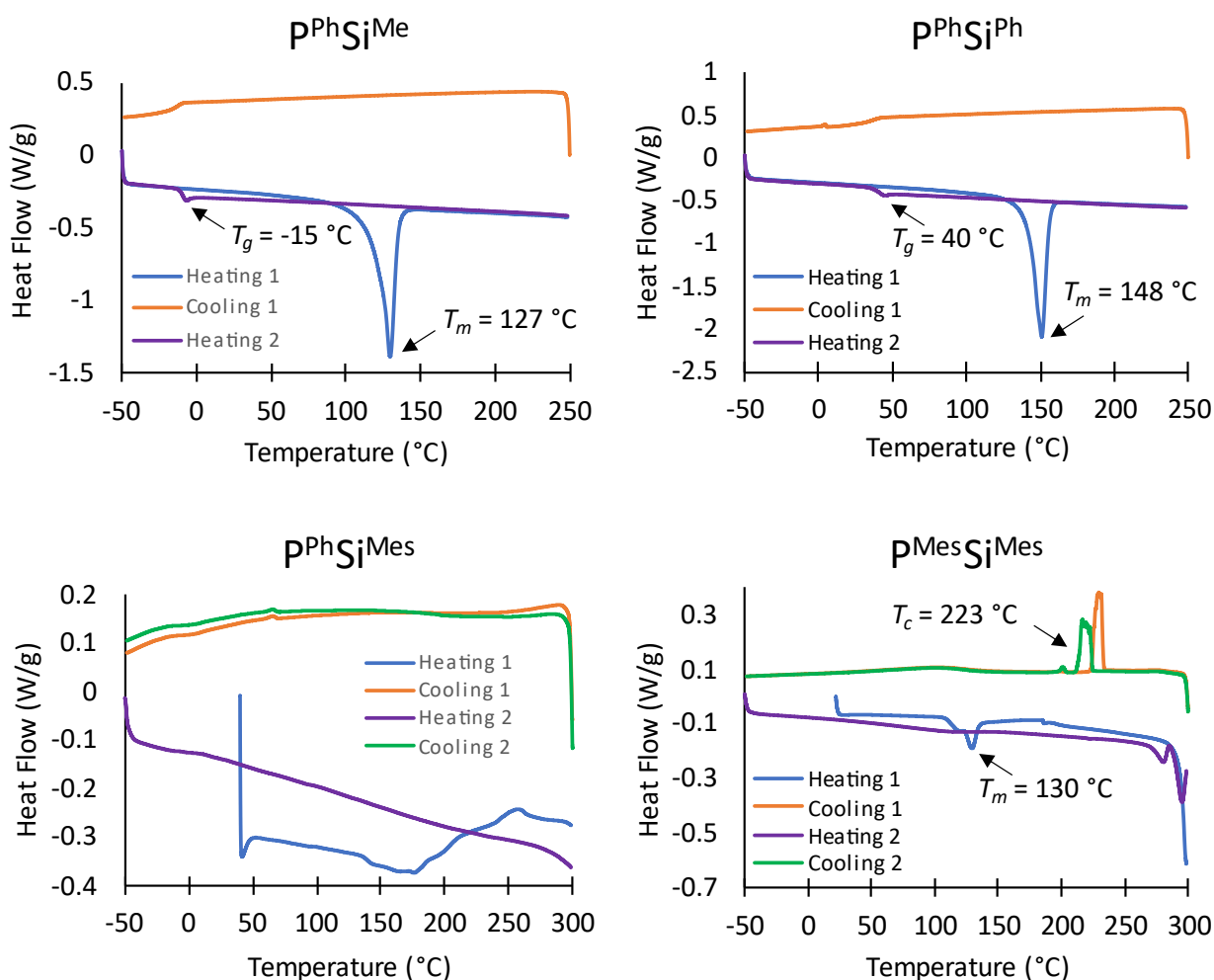


Figure 4.6 DSC calorigrams of $\mathbf{P}^{\text{R}}\mathbf{Si}^{\text{R'}}$ rings, where exotherms are deflected upwards.

4.3.2 Unraveling the dynamic nature of $\text{P}^{\text{R}}\text{Si}^{\text{R}'}$ heterocycles with ESI-MS

The solution NMR spectra of pristine $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ and $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ reveal complex dynamic behaviour and display multiple species other than the major eight-membered ring product, making conclusive characterization of these materials a challenge. As such, we examined $\text{P}^{\text{R}}\text{Si}^{\text{R}'}$ rings by ESI-MS to determine the species favourably formed in the equilibration process and gain insight into why these rings display dynamic phenomena.

We first analyzed $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ in undried MeCN in positive mode, which revealed a complex mass spectrum that bore no peaks corresponding to the major product. No conditions could be found that allowed for observation of the M^+ peak, so it was concluded that in undried MeCN $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ is effectively reacted with any moisture in the solution, forming a host of products which are outlined in Figure 4.7. One species present throughout the collection at $m/z = 311$ is six-membered heterocycle $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_2$ (shown in orange in Figure 4.7), a stable product in which one phosphonate unit is extruded from $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$. Other species present in the mass spectrum represent further extrusions of RPO_2 and recombinations of rings to form polysiloxane rings with inserted RPO_2 units. This reactivity in wet solvent makes thermodynamic sense: Si-O bonds are thermodynamically favourable compared to P-O bonds (452 vs 335 kJ mol^{-1} , respectively), lend more flexibility and entropy to rings, and extrusion of RPO_2 through reaction with water is thermodynamically favourable.

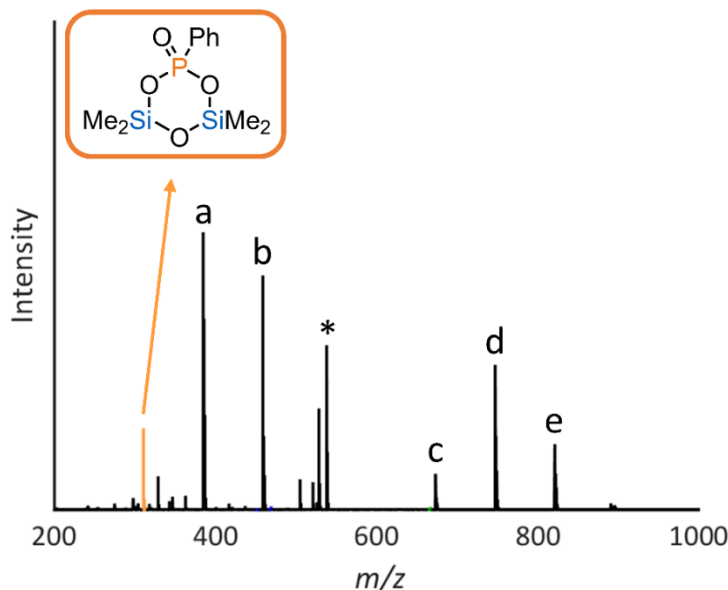


Figure 4.7 Positive mode ESI-MS of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ as a $10 \mu\text{g mL}^{-1}$ solution in wet MeCN after 2 hours. Species labelled in the mass spectrum correspond to species $(\text{PhPO}_2)_x(\text{SiMe}_2\text{O})_y(\text{H/Na/K})$ as follows: a) $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_3(\text{Na})$; b) $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_4(\text{Na})$; c) $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_5(\text{Na})$; d) $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_6(\text{Na})$; e) $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_7(\text{Na})$. Species labelled with “*” are unidentifiable based on $(\text{PhPO}_2)_x(\text{SiMe}_2\text{O})_y(\text{H/Na/K})$ speciation.

$\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ was then analyzed by positive mode ESI-MS in freshly dried MeCN, which saw peaks corresponding to the ring as $\text{M}+\text{Na}$ and $\text{M}+\text{K}$ adducts to be the most intense, verifying their formation and recrystallization. Other peaks of small intensity were also present in the $t = 0$ h mass spectrum; at $m/z = 311$, the six-membered $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_2$ ring – previously observed in the mass spectrum of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ in wet MeCN – was detected, alongside the trimeric $[\text{PhP}(\text{O})-\text{O}-\text{SiMe}_2-\text{O}]_3$ at $m/z = 665$ and tetrameric $[\text{PhP}(\text{O})-\text{O}-\text{SiMe}_2-\text{O}]_4$ (though this may also be a contact dimer of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$) (Figure 4.8, top). While the result was certainly more positive than that seen in wet MeCN, online monitoring of the solution over five hours revealed that the $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ still degrades over time, reaching to 25% of the original intensity (Figure 4.8, bottom). Major species in this degradation after 5 h still demonstrate the phosphonate extrusion pathways seen in the experiments using wet MeCN, with six-membered ring $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_2$ representing the main species in the

equilibration mixture, and other species including ten-membered ring $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_3$, $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_3$, $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_4$, and others making up the equilibration mixture.

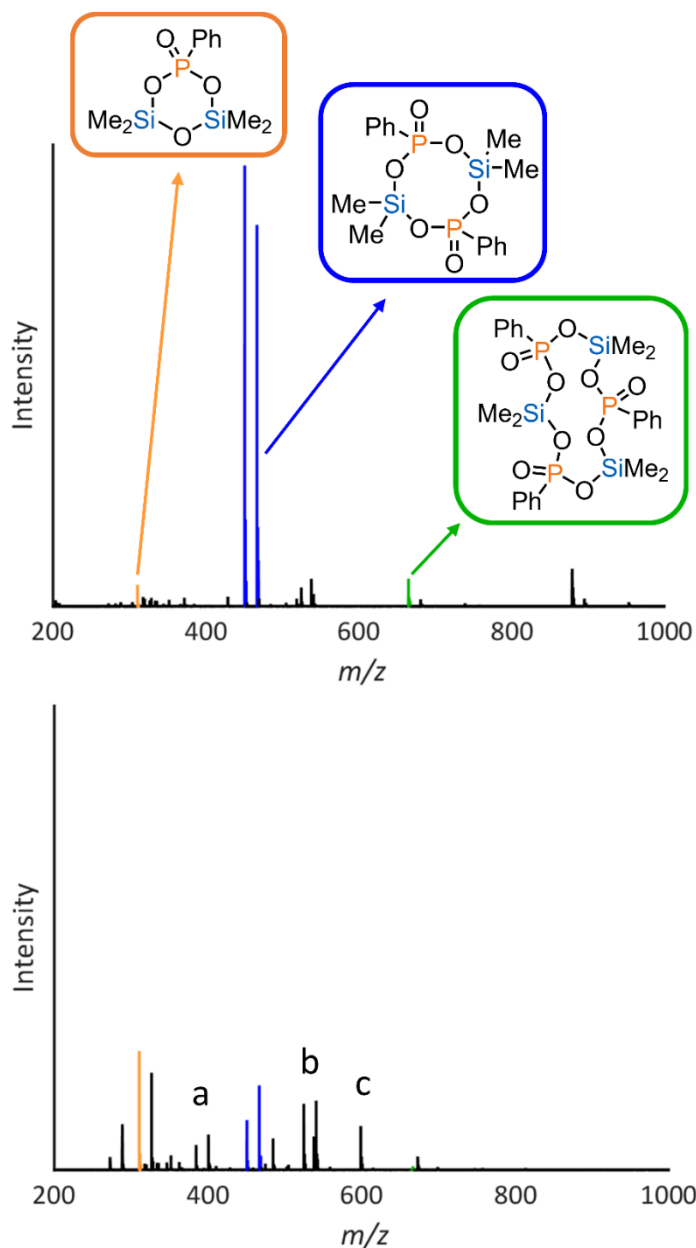


Figure 4.8 Positive mode ESI-MS of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ as a $10 \mu\text{g mL}^{-1}$ solution in dry MeCN at $t = 0$ h (top) and after 5 h (bottom). Species labelled in the mass spectrum after 5 h correspond to species as follows: a) $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_3(\text{Na/K})$; b) $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_3(\text{Na/K})$; c) $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_4(\text{Na})$.

Given that $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ appeared to still be degrading by phosphorus extrusion despite using dry MeCN, we hypothesized that plasticizers in the plastic syringe used to inject the sample, which

typically are composed of terephthalic acids, were likely reacting with phosphonate moieties in a similar fashion to water. As such, we conducted a final ESI-MS measurement of **P^{Ph}Si^{Me}** with dry MeCN and a glass syringe to avoid the presence of any potential reactive contaminants and to give a sense of how the rings equilibrate in conditions we used for NMR spectroscopy (Figure 4.9). The $t = 0$ mass spectrum in these conditions showed **P^{Ph}Si^{Me}** overwhelmingly as the major species, with $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_2$ ring, $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_3$, $[\text{PhP}(\text{O})\text{--O--SiMe}_2\text{--O}]_3$, and $[\text{PhP}(\text{O})\text{--O--SiMe}_2\text{--O}]_4$ composing the minor species at $t = 0$. The peak corresponding to **P^{Ph}Si^{Me}** decreases to 25% of the original intensity, now after 13 h instead of 5 h as when using a plastic syringe. The equilibration, however, is virtually identical to that seen in the plastic syringe, suggesting that any small amounts of trace water may facilitate the extrusion of one phosphonate moiety out of $[\text{PhP}(\text{O})\text{--O--SiMe}_2\text{--O}]_2$ and $[\text{PhP}(\text{O})\text{--O--SiMe}_2\text{--O}]_3$ to form $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_2$ and $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_3$, respectively.

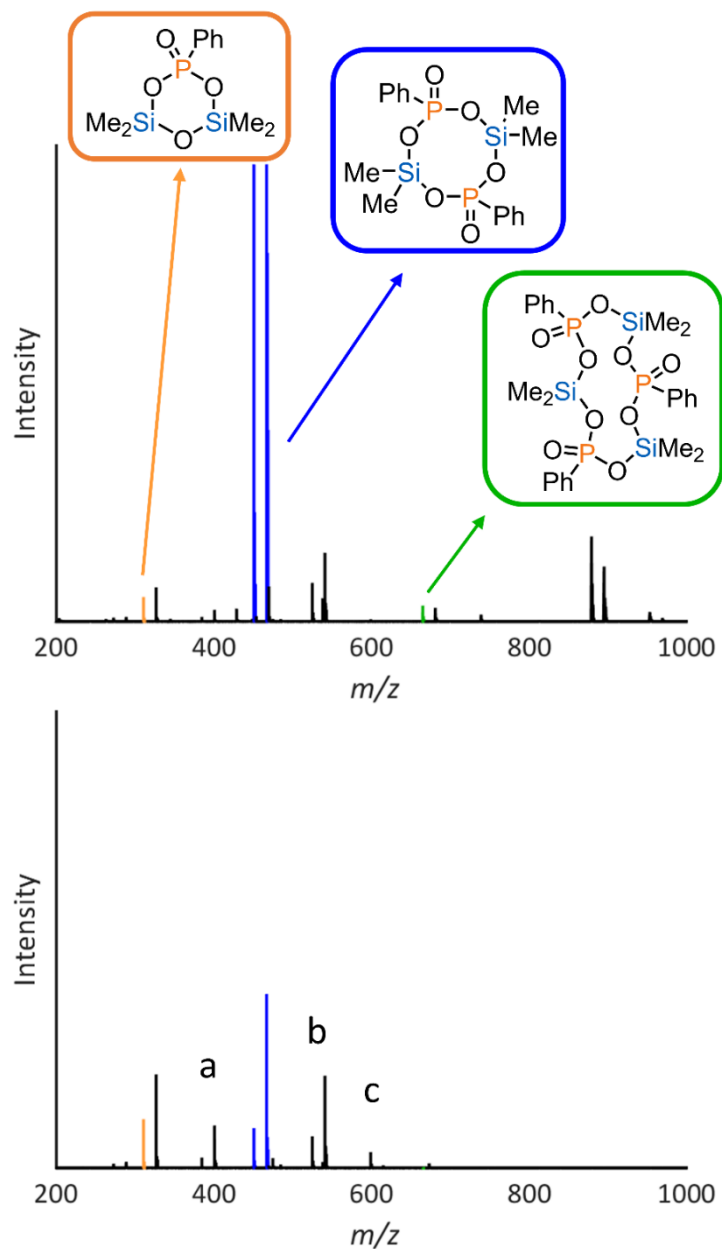


Figure 4.9 Positive mode ESI-MS of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ as a $10 \mu\text{g mL}^{-1}$ solution in dry MeCN in a glass syringe at $t = 0$ h (top) and after 13 h (bottom). Species labelled in the mass spectrum after 13 h are as follows: a) $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_3(\text{Na/K})$; b) $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_3(\text{Na/K})$; c) $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_4(\text{Na})$.

The common equilibration pattern of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ into i) $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_2$ and its dimerization product or contact dimer $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_4$, and ii) a trimer of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$, begged the question as to whether the chromatograms obtained through onboard monitoring could reveal qualitative information on the mechanistic pathway of the degradation (Figure 4.10). When

observing the chromatograms obtained from online monitoring of $\mathbf{P^{Ph}Si^{Me}}$ in dry MeCN in a glass syringe, the kinetics at $t = 0$ are defined by the slow decrease of $\mathbf{P^{Ph}Si^{Me}+Na}$, the immediate decrease and then stabilization of $\mathbf{P^{Ph}Si^{Me}+K}$, the immediate increase in $[\text{PhP(O)-O-SiMe}_2\text{-O}]_3\text{+Na}$, and a steady increase in $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_2\text{+Na}$. The $[\mathbf{P^{Ph}Si^{Me}}]\text{+Na}$ evidently decomposes or scrambles to act as the initial source for $[\text{PhP(O)-O-SiMe}_2\text{-O}]_3\text{+Na}$ and $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_2\text{+Na}$. The apparent stability of $\mathbf{P^{Ph}Si^{Me}+K}$ is curious, but is likely due to a preferential interactions between potassium in a binding pocket composed either of bidentate P=O bonds or the POSiO framework with flanking Ph interactions. As time passes, the trimer $[\text{PhP(O)-O-SiMe}_2\text{-O}]_3\text{+Na}$ completely converts to products such as $(\text{PhPO}_2)_2(\text{SiMe}_2\text{O})_3(\text{Na/K})$ over the 13 h of monitoring, while $(\text{PhPO}_2)(\text{SiMe}_2\text{O})_2\text{+Na}$ grows in steadily. Conversely, $\mathbf{P^{Ph}Si^{Me}+Na}$ is consumed at a rapid rate compared to $\mathbf{P^{Ph}Si^{Me}+K}$, which persists as the main $\mathbf{P^{Ph}Si^{Me}}$ source throughout the solution equilibration process. The process of these equilibrations is summarized in Figure 4.10.

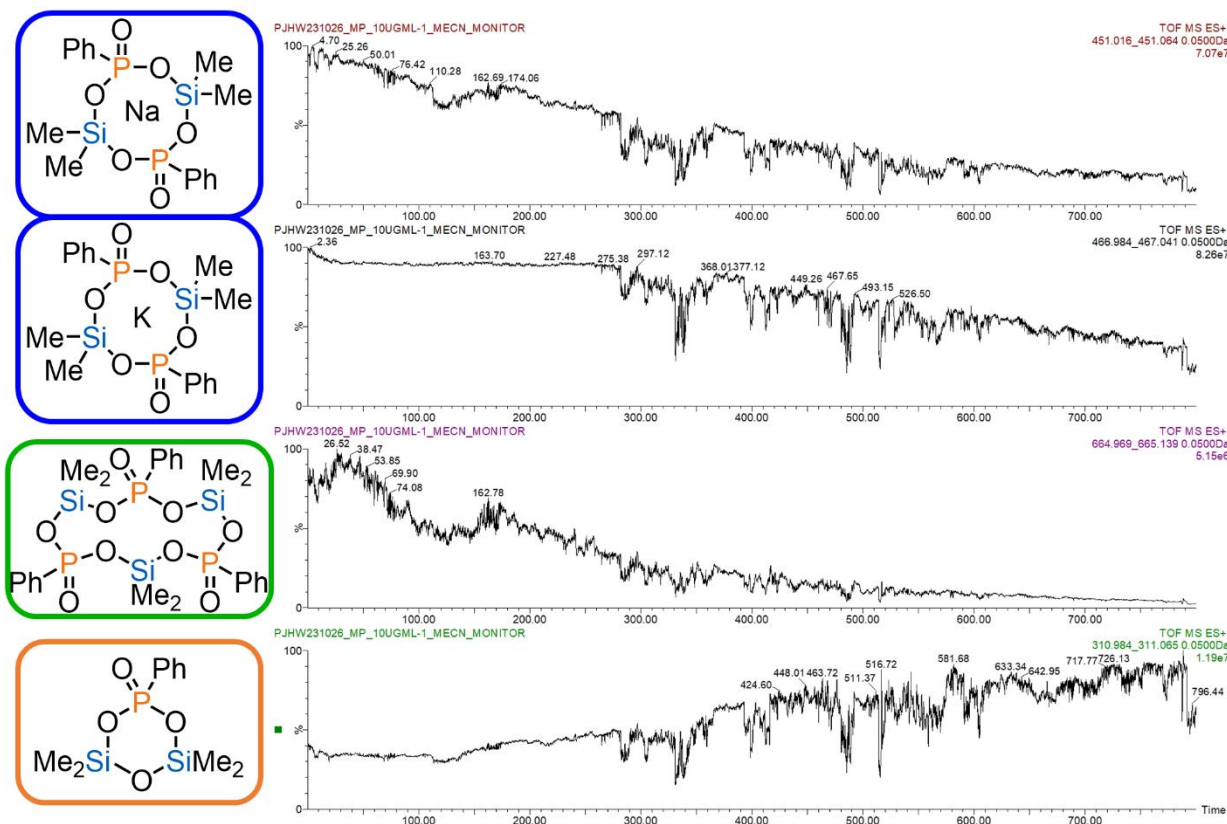
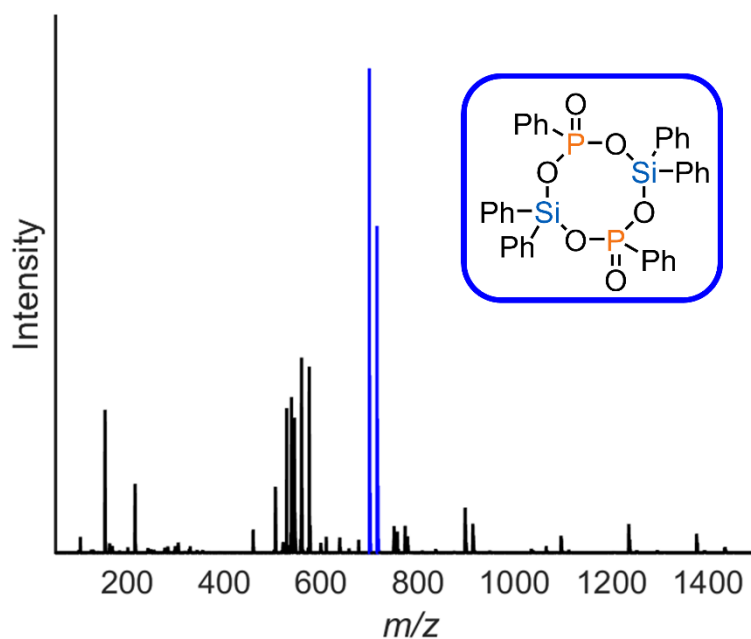


Figure 4.10 Positive mode ESI-MS online monitoring chromatograms detailing relative proportions of key species present in mass spectra of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ over a period of 800 minutes (top), and a qualitative equilibration pathway for the formation of common products of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ equilibration in solution (bottom).

With parameters and dry conditions optimized for $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$, positive mode ESI-MS measurements were undertaken on $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$, $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$, and $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$. The mass spectra of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$

displayed the ring as the most intense peaks, though far more degradation at $t = 0$ was observed than was observed for **P^{Ph}Si^{Me}** (Figure 4.11), suggesting that the greater electron donation from methyl substituents provide more stability to P–O–Si–O rings in MeCN than phenyl substituents. The mass spectrum bears a host of species at higher and lower m/z values than the **P^{Ph}Si^{Ph}** ring (outlined in Figure 4.11), suggesting that a substantial amount of ring fragmentation and recombination phenomena take place immediately upon dissolution. As previously observed in the mass spectrum of **P^{Ph}Si^{Me}**, the mass spectrum of **P^{Ph}Si^{Ph}** bore the common species of (PhPO₂)(SiMe₂O)₂ ring, (PhPO₂)₂(SiMe₂O)₃, (PhPO₂)(SiMe₂O)₃, and [PhP(O)–O–SiMe₂–O]₄. Given the increased complexity of the mass spectrum in positive mode, especially regarding species with smaller m/z values, we observed the mass spectrum of **P^{Ph}Si^{Ph}** in negative mode to determine if any information could be gleaned on the equilibrium or degradation pattern of the sample. The negative mode generally displayed species with higher phosphorus content, but more distinctly bore almost exclusively species reacted with water (Figure 4.11, bottom right), which verifies that trace amounts of moisture in even freshly dried solvents can facilitate dynamic or degradative behaviour in phosphonate-siloxane hybrids. For example, phenyl phosphonic acid was the fourth most observed species, providing a clear degradation pathway for RPO₂ extrusion from **P^{Ph}Si^{Me}** and **P^{Ph}Si^{Ph}**. It should also be noted that in negative mode, m/z values are smaller than those obtained in positive mode, suggesting that the formation of acids results in either small chains or more unstable ring species than the more silicone-rich rings observed in positive mode.



Most intense species in ESI+ mode			
SiPh_2O	PhPO_2	H_2O	Relative intensity (%)
2	2	0	170.2393
2	1	0	83.0148
3	2	0	15.8478
3	1	0	10.198
4	3	0	6.6322
4	4	0	4.5668
4	2	0	4.3448
5	3	0	1.3492
1	2	1	0.89512
5	2	0	0.83315

Most intense species in ESI- mode			
SiPh_2O	PhPO_2	H_2O	Relative intensity (%)
1	2	1	100
2	1	1	13.2931
1	1	1	2.85801
0	1	1	0.963746
2	2	1	0.734139
1	2	0	0.134441
0	2	0	0.114804
2	3	1	0.112689
1	0	1	0.067674
3	2	1	0.030212

Figure 4.11 Positive mode ESI-MS of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ in dry MeCN (top), and relative product distributions in mass spectra of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ obtained in positive mode (bottom left) and negative mode (bottom right).

The mass spectra obtained of $\mathbf{P^{Ph}Si^{Mes}}$ ($m/z = 883.2604$) and $\mathbf{P^{Mes}Si^{Mes}}$ ($m/z = 883.2604$) were demonstrative of the kinetic stability that steric bulk imparts on the P–O–Si–O framework, demonstrating very little degradation or equilibration compared to $\mathbf{P^{Ph}Si^{Me}}$ and $\mathbf{P^{Ph}Si^{Ph}}$ (Figure 4.12).

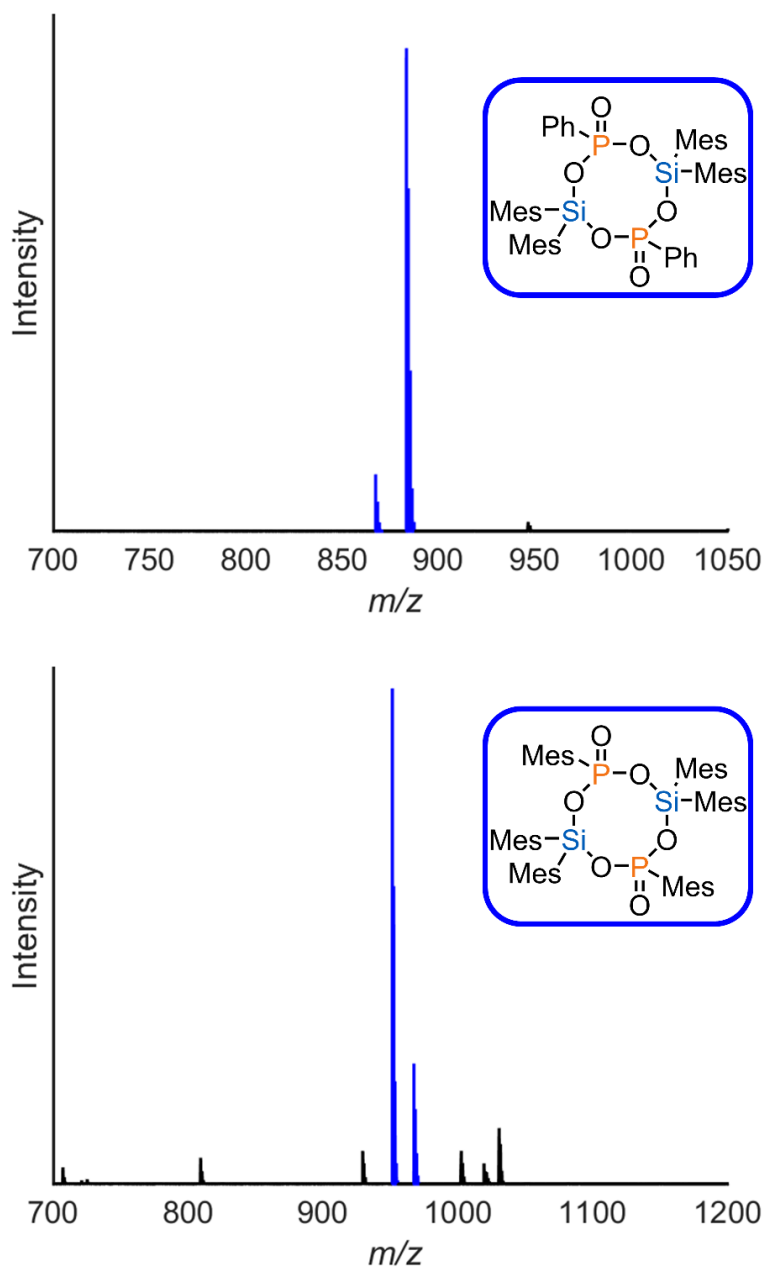


Figure 4.12 ESI+ mass spectrum of $\mathbf{P^{Ph}Si^{Mes}}$ in dry MeCN (top), and ESI+ mass spectrum of $\mathbf{P^{Mes}Si^{Mes}}$ in dry MeCN (bottom).

4.3.3 Polymerization tests of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ and $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$

Given that they had the least amount of steric bulk and were most likely to undergo ring-opening, polymerizations of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ and $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ were attempted by flame sealing freshly recrystallized samples in a thick-walled glass tube and heating the cyclic precursors 10 °C above their respective melting points as determined by DSC.

$\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ was heated at 150 °C for 4 h, transforming from a free-flowing melt to a viscous, transparent “goop” with molasses-like flow. The material was left to cool to ambient temperature and was left in the sealed tube for 3 days, where it slowly transformed into globular crystallites in situ (Figure 4.13a). The tube was then cracked open in a glovebox and 20 mg of the material was analyzed by NMR spectroscopy. The ^1H NMR spectrum was surprisingly broad, displaying three well-defined peaks in the aryl region at 7.87, 7.55, and 7.46 ppm which correspond exactly to the *m*, *o*, and *p* protons of the phenyl groups of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$, while the alkyl region displays a large broad singlet at 0.49 ppm (corresponding well to the SiMe_2 environments of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$) flanked by two broad peaks at 0.68 and 0.16 ppm, with two peaks overlapping the main peak at 0.39 and 0.23 ppm (Figure 4.13b). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a broad peak at 12.02 ppm, a major peak at -0.18 ppm, followed by two other broad peaks at -1.49 and -2.52 ppm, and a final sharp peak at -1.89 ppm (Figure 4.13). ^{29}Si DEPT NMR spectra were successfully obtained for all $\text{P}^{\text{R}}\text{Si}^{\text{R'}}$ rings, however, the rapid relaxation of the material generated in ROP conditions resulted in inadequate polarization transfer to obtain adequate signal. As a result of this, an inverse-gated ^{29}Si spectrum was obtained with a 200 second delay to allow for complete relaxation of silicon nuclei, which yielded two broad singlets at -4.46 and -5.25 ppm (compared to the signals observed at -4.53 and -5.31 ppm in the ^{29}Si DEPT NMR spectrum of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$) (Figure 4.13d). Through superimposing the post-ROP material $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with that of pristine $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ (Figure 4.13e), we note that the peaks of each spectrum nearly perfectly overlap. This may be due to one of two

reasons: either the (P–O–Si–O–Si–O)-like environments of larger cyclic oligomers formed by dissolution of **P^{Ph}Si^{Me}** also form in ROP conditions, or the local tacticity of **P^{Ph}Si^{Me}** rings manifest in the polymers (as shown in Figure 4.13e). For example, the all-trans environment of **P^{Ph}Si^{Me}** – when extended from a ring to a linear polymer – represent a syndiotactic rr tacticity, while an all-cis ring would represent an isotactic mm tacticity. If the peaks do indeed manifest due to tacticity, the polymer is stereoirregular atactic, which is expected for an uncontrolled thermal ROP.

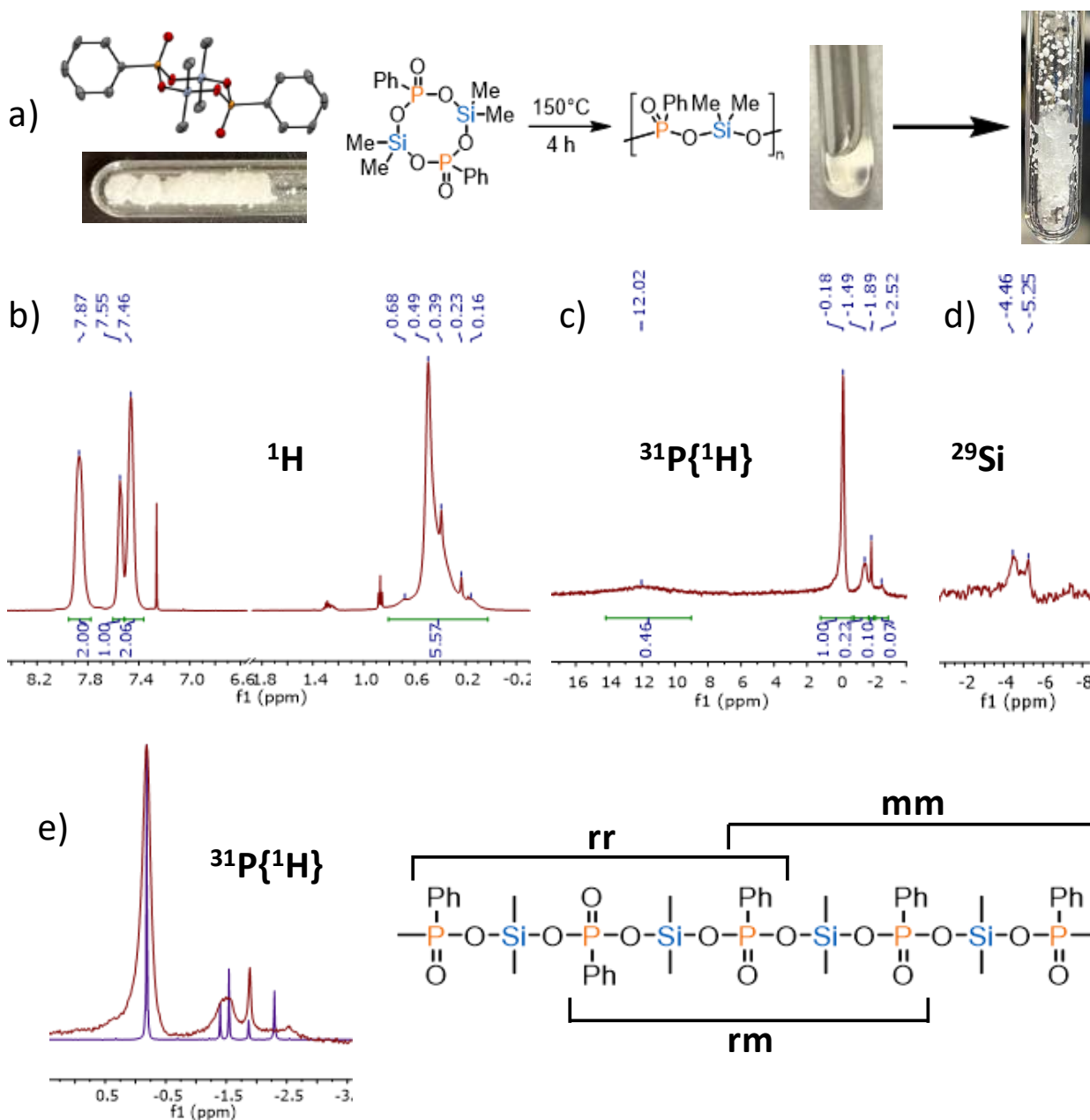


Figure 4.13 (a) Synthetic scheme for the ROP of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ and in-situ crystallization of the post-ROP material; (b) ^1H NMR spectrum (CDCl_3 , 500 MHz), (c) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 203 MHz), and (d) ^{29}Si INEPT NMR spectrum (CDCl_3 , 99 MHz) of the post-ROP material; and (e) stacked $^{31}\text{P}\{^1\text{H}\}$ spectra of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ ring (purple) and post-ROP material (red) with potential tacticity triads.

Given that the NMR spectra were suggestive of polymer formation, DSC studies were taken to assess if the thermodynamic properties of the material differed from $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$. The first

heating cycle saw a large melt endotherm at 112 °C, slightly lower than the T_m of **P^{Ph}Si^{Me}** at 127 °C, and likely corresponds to the melt of unpolymerized ring species and/or the melt of bulk crystalline domains in a formed polymer. The first cooling cycle displays a T_g at -9 °C and an exotherm at -66 °C. The second heating cycle only displayed the T_g at 3 °C, which is greater than that observed for the **P^{Ph}Si^{Me}** ring at -15 °C, and the second cooling cycle and third heating cycle then demonstrated the same exotherms and T_g values as previously observed earlier heating/cooling runs. While the DSC measurement is not definitive in assessing whether there is polymer formation, the difference of the T_g and T_m of the post-ROP material from the **P^{Ph}Si^{Me}** rings support that a transformation of the **P^{Ph}Si^{Me}** occurs in ROP conditions.

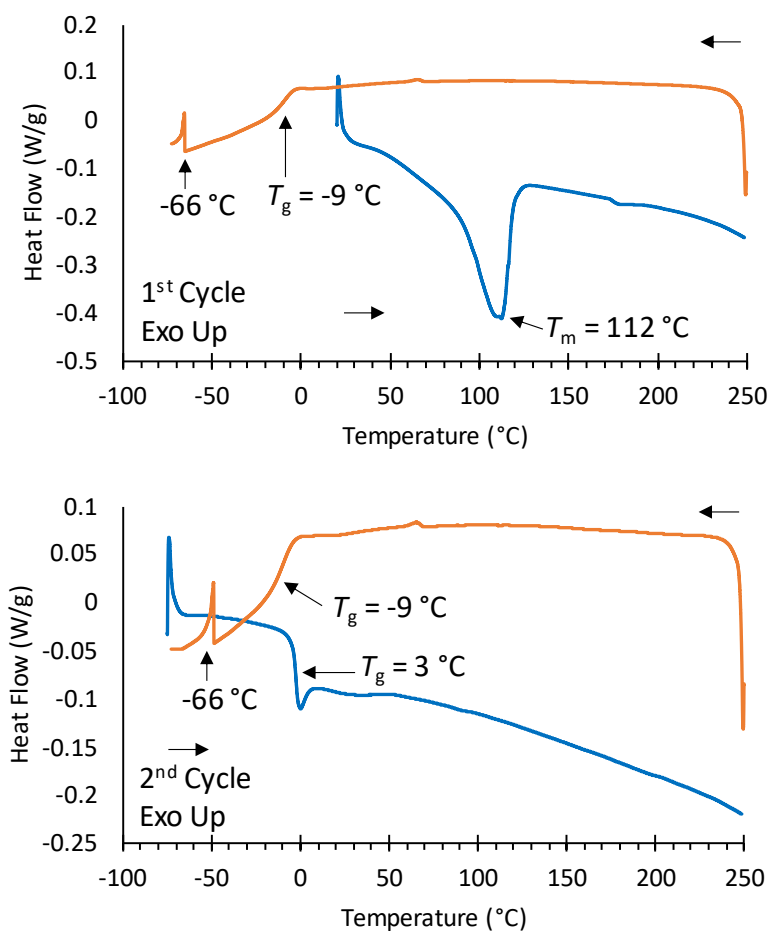


Figure 4.14 DSC calorigrams of the post-ROP material of **P^{Ph}Si^{Me}**, with heating shown in blue and cooling shown in orange. Cycles begin with heating, and key features are labelled.

To assess if the material formed had a high molar mass consistent with polymer formation, matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-ToF MS) were collected. However, no peaks above 1243 Da were observed (Figure 4.25), and those peaks that were observable did not correspond to any easy-to-assign fragments of $[\text{PhP}(\text{O})\text{-O-SiMe}_2\text{-O}]$. The material was then analyzed by gel permeation chromatography (GPC) to determine the molar mass of the material using polystyrene standards. The GPC chromatogram of absorbance at 246 nm (the absorbance of the PhPO_2 moiety) vs retention time displayed two distinct populations: one corresponding to small heterocycles and mobile phase appearing at retention times between 20-30 min, and a broad population spanning from 14 to 20 min corresponding to polymeric material with $M_n = 31,113$ Da, $M_w = 48,111$ Da, $D = 1.546$ (Figure 4.26). Taking into account all of the characterization, we conclude that the material formed from the thermal ROP of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ is likely to be a mixture of $[\text{PhP}(\text{O})\text{-O-SiMe}_2\text{-O}]_n$ polymer with other oligomers of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$, and dissolution of the polymer in dilute solutions of THF likely results in depolymerization as evidenced by GPC and the lack of observable high molecular weight peaks in MALDI-ToF MS.

$\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ was heated at 185 °C for 4 h, transforming from a free-flowing melt to an immobile translucent material, which was left to cool to ambient temperature to form a hard transparent plastic (Figure 4.15a). During this process, no change in the material was observed, and so the tube was cracked open in a glovebox and 18 mg of the material slowly dissolved into CDCl_3 and was analyzed by NMR spectroscopy. The ^1H NMR spectrum of the post-ROP material was taken approximately 30 minutes after preparation, and was identical to that of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ (Figure 4.15b). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum also displayed identical spectral features to pristine $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ (Figure 4.15c), and the ^{29}Si inverse-gated spectrum of the sample displays a sharp triplet at the same chemical shift as $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ (Figure C.22). MALDI-ToF MS spectra of the material displays no major peaks above 2000 Da (Figure 4.29), and the only fragmentations visible correspond to the

fragmentation of $\text{Ph}_2\text{Si}[\text{PhP}(\text{O})\text{--O--SiPh}_2\text{--O}]_5\text{--PO+K}$. GPC analysis of the material displays a chromatogram with peaks at retention times correlating to small heterocycles of **P^{Ph}Si^{Ph}** and mobile phase, with no evidence of polymer (Figure 4.28). DSC analysis of the ROP material displayed a glass transition at 44 °C, similar to that previously observed in DSC analyses of **P^{Ph}Si^{Ph}** (Figure 4.27). The similarity between the NMR spectra for the **P^{Ph}Si^{Ph}** ring and post-ROP material, in combination with the lack of peaks in GPC analysis and MALDI-TOF MS which correlate to high molar mass suggests that **P^{Ph}Si^{Ph}** does not undergo thermal ROP. It is likely that the addition of phenyl rings at silicon provides less flexibility in the P–O–Si–O chain and provides more kinetic stabilization of the eight-membered ring. Indeed, the increased rigidity of the diphenylsiloxane unit (which has been reported in the literature as forming highly crystalline, inflexible polymers only through the ROP of six-membered rings^{30, 31}) may only allow for the formation of small oligomers of **P^{Ph}Si^{Ph}** instead of the formation of long chain polymers.

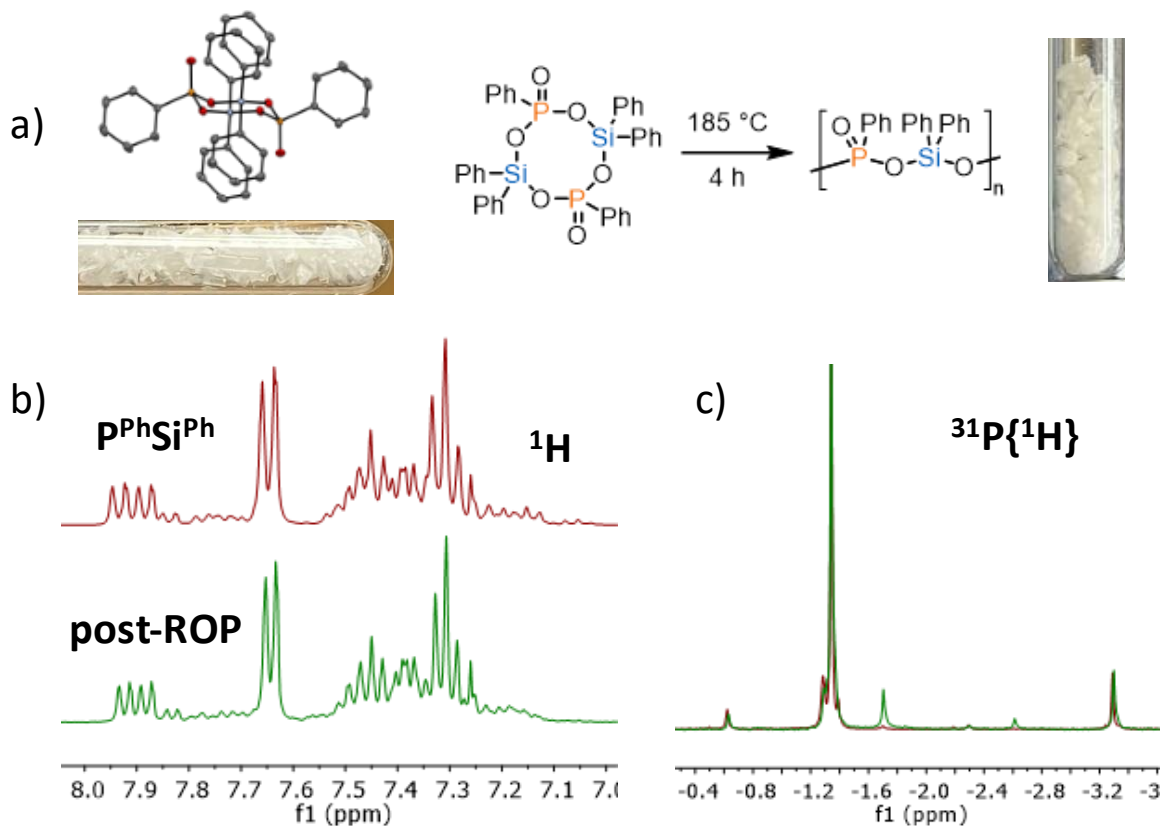


Figure 4.15 a) Scheme for the proposed ROP of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$; b) stacked ^1H NMR spectra of pristine $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ and the post-ROP material; c) superimposed $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of pristine $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ and post-ROP material.

4.3.4 Balancing emerging P–O dynamics with electronics and sterics

Given that the addition of phosphonates into the D_4 backbone imparts a significant amount of equilibria not experienced by eight-membered silicones alone, we sought to conduct a small study into the effect of electronics and sterics on RPO_2 moieties to determine i) if electronic modifications showed evidence of stabilizing phosphonate heterocycles, and ii) if significant steric contributions could allow access to the monomeric unit of polyphosphonates, RPO_2 , to glean insight into the fundamental nature of the P–O bonds and why they exhibit such dynamic behaviour (Figure 4.16).

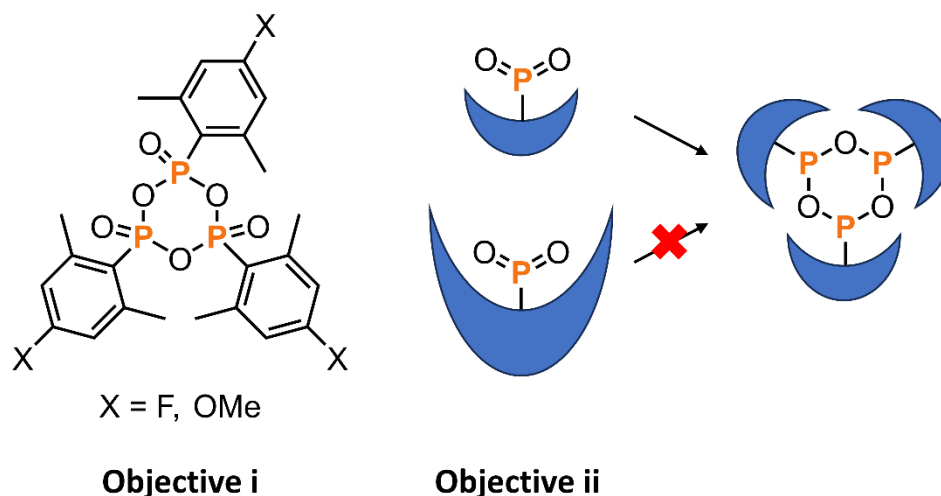
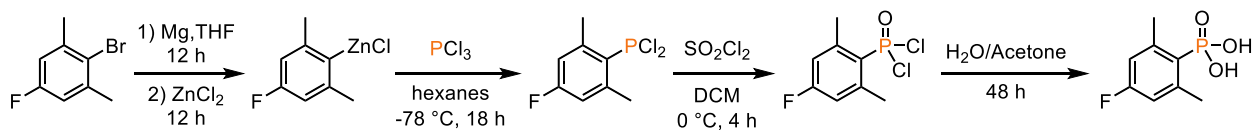


Figure 4.16 Outline of objectives for electronically (left) and sterically (right) stabilizing phosphonates for the design of less dynamic PO and POSiO materials

4.3.4.1 Phosphonate stabilization with electronic modification

Our strategy for studying electronic modifications was to investigate the synthesis of cyclic phosphonates of the formula $[X\text{MesP}(\text{O})-\text{O}]_3$, in which the 4-methyl of mesityl is substituted for either an electron-withdrawing fluorine atom or electron donating methoxy (OMe). Given that our group previously established the stabilizing effect of ortho-methyl phenyls, studying new cyclic phosphonates with this kinetic stabilization would allow for the formation of solution stable materials which we hypothesized would be easier to glean insight from, as opposed to unstabilized 4-substituted phenyl substituents which may still exhibit significant dynamic behaviour. We first synthesized the phosphonic dichloride and phosphonic acid starting materials bearing 4-fluoro-2,6-dimethylphenyl and 4-methoxy-2,6-dimethylphenyl substituents, referred to as “*p*-FAr” and “*p*-MeOAr” for the remainder of the text.



Scheme 4.2 Synthesis of *p*-FArPOCl₂ and *p*-FArPO(OH)₂ starting materials

We began with the synthesis of *p*-FAr starting materials by applying literature methods our group previously established (Scheme 4.2).⁸ *p*-FArPOCl₂ was readily synthesized in a three-step process from 1-bromo-4-fluoro-2,6-dimethylbenzene, displaying a ³¹P{¹H} NMR spectrum with a doublet at 30.9 ppm (⁵*J*_{PF} = 4.0 Hz) and a ¹⁹F NMR spectrum with a doublet at -104.4 ppm (⁵*J*_{PF} = 4.0 Hz). Phosphonic acid *p*-FArPO(OH)₂ was subsequently synthesized through the reaction of *p*-FArPOCl₂ in a 1:1 v/v solution of water and acetone, in which the acid precipitates from the aqueous reaction mixture over 48 h on account of its low solubility. Filtration of the solid yields crude *p*-FArPO(OH)₂, which displays a ³¹P{¹H} NMR spectrum with a doublet at 16.4 ppm (⁵*J*_{PF} = 2.7 Hz) and a ¹⁹F NMR spectrum with a doublet at -113.1 ppm (⁵*J*_{PF} = 2.7 Hz). Careful heating of a saturated 1:1 v/v methanol/water solution of *p*-FArPO(OH)₂ affords block-like crystals suitable for single crystal X-ray crystallography, verifying its structure (Figure 4.17). The acid forms flat planes of molecules along the *ac* plane while forming infinite hydrogen bond chains along the *b* axis, while also demonstrating infinite $\pi^{\delta+}$ - $\sigma^{\delta-}$ offset pi-stacking interactions between the fluoroaryl moieties along the whole structure. These $\pi^{\delta+}$ - $\sigma^{\delta-}$ pi-stacking may only lend <5 kcal/mol of stabilization energy per pair of acids – on the order of van der Waals interactions – but this motif extended along the length of the lattice provides far more stabilization than one would expect,³² and these interactions will be important to consider *vide infra*.

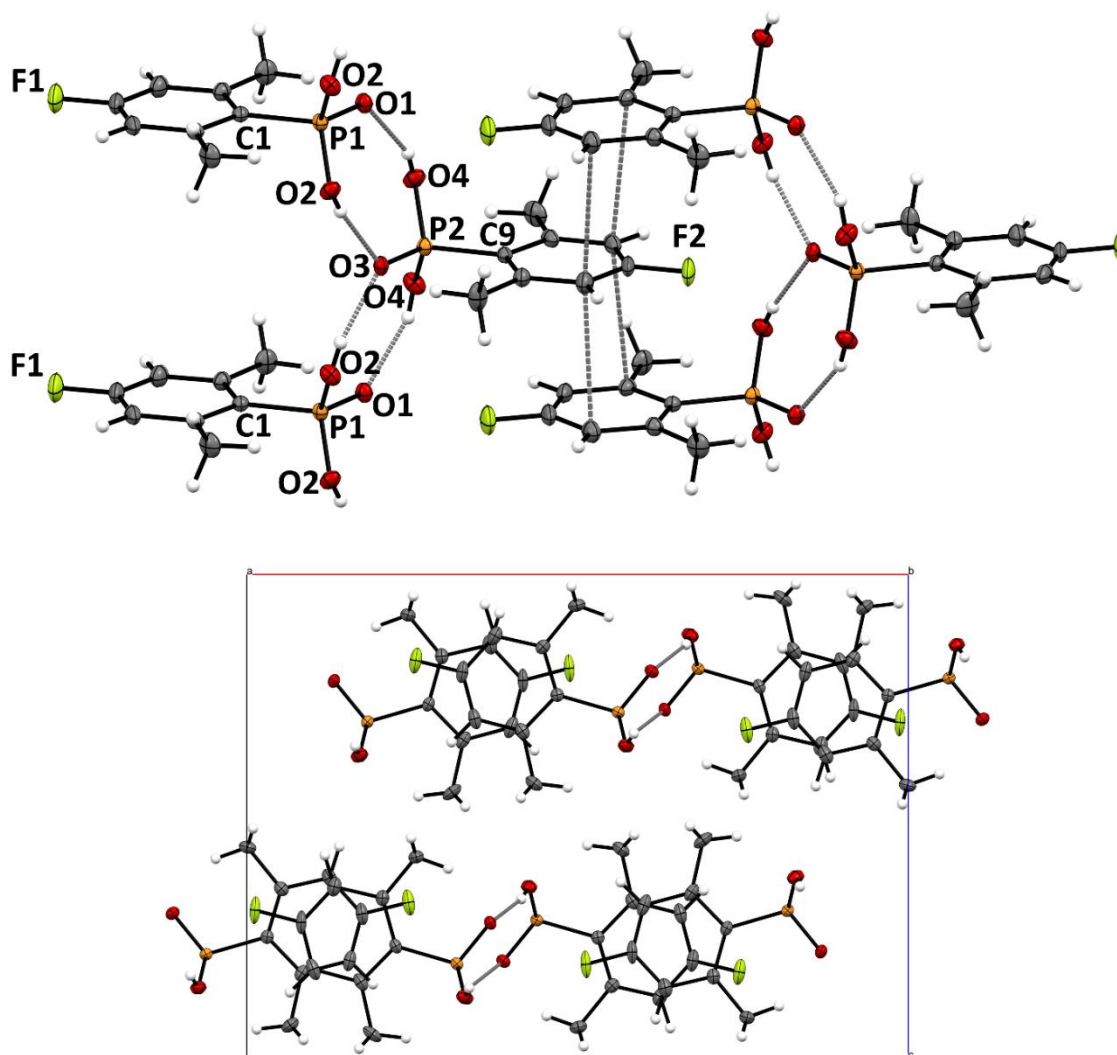
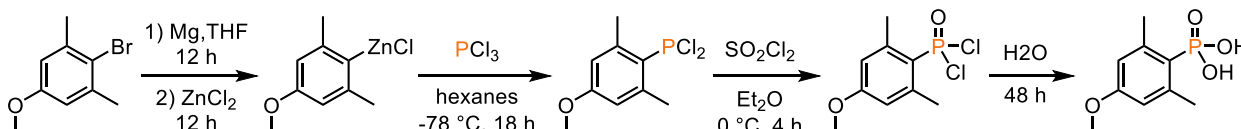


Figure 4.17 Single-crystal X-ray structure of *p*-FArPO(OH)₂ demonstrating intermolecular hydrogen bonding and π - π stacking interactions (top) and as viewed down the crystallographic *b*-axis (bottom). Ellipsoids are drawn at 50% probability. Select bond lengths (Å) and angles (°) for *p*-FArPO(OH)₂: P1-O1 1.500(2); P1-O2 1.5563(15); P1-C1 1.797(3); P2-O3 1.4974(19); P2-O4 1.5580(16); P2-C9 1.799(3); O1-P1-O2 112.35(7); O2-P-O2 102.96(12); O1-P1-C1 113.31(12); O2-P1-C1 107.61(8); O3-P2-O4 112.28(7); O4-P2-O4 102.65(13); O3-P2-C9 113.05(11); O4-P2-C9 107.98(8).

Contrary to the relatively straightforward synthesis of *p*-FAr starting materials, the synthesis of *p*-MeOAr starting materials were plagued by a host of challenges. The synthesis of *p*-MeOArPCl₂ proceeded according to literature methods, however the subsequent synthesis of *p*-

MeOArPOCl₂ using SO₂Cl₂ in CH₂Cl₂ resulted in complete decomposition of the *p*-MeOAr substrate into an intractable viscous liquid. The donation of electron density into the aryl substituent clearly makes the substrate prone to reactions with halogenated solvents. To avoid this unwanted reactivity, small changes to the reaction pathway were made to accommodate the sensitivity of the donating phosphines in halogenated solvents (Scheme 4.3).



Scheme 4.3 Synthesis of *p*-MeOArPOCl₂ and *p*-MeOArPO(OH)₂ starting materials.

The preparation of *p*-MeOArPOCl₂ from *p*-MeOArPCl₂ and SO₂Cl₂ was instead conducted in Et₂O, yielding colourless crystals of the phosphonic dichloride upon removal of volatiles which displays a ³¹P{¹H} NMR spectrum with a singlet at 32.8 ppm. Recrystallization of the solid from a concentrated solution of Et₂O afforded single crystals of *p*-MeOArPOCl₂ suitable for single crystal X-ray diffraction, as shown in Figure C.45 Single crystal X-ray structure of *p*-MeOArPOCl₂. The reaction of *p*-MeOArPOCl₂ with water over 24 hours affords the phosphonic acid *p*-MeOArPO(OH)₂, which displays a ³¹P{¹H} NMR spectrum with a singlet at 18.3 ppm. After removal of all volatiles in vacuo, crude *p*-MeOArPO(OH)₂ can be recrystallized from MeOH to yield single crystals suitable for X-ray diffraction (Figure 4.18). The three crystallographically-identical molecules in the lattice of *p*-MeOArPO(OH)₂ shares very similar metrical parameters to *p*-FArPO(OH)₂, especially in P-O and P=O bond lengths. The main difference is the shortening of the P-C bond length from 1.797(3) and 1.799(3) Å in molecules of *p*-FArPO(OH)₂ to 1.784(2), 1.781(2), and 1.780(2) Å in *p*-MeOArPO(OH)₂. In terms of the crystal lattice, *p*-MeOArPO(OH)₂ also crystallizes in a hydrogen bonded lattice down the *b*-axis in a very similar fashion to *p*-FArPO(OH)₂. However, the lattice of *p*-MeOArPO(OH)₂ is absent of any non-covalent interactions

in the *p*-MeOAr side chain (Fig 4.18, bottom), likely as a result of repulsion between electron-rich aryl moieties and the added steric contribution of the MeO moiety, suggesting that *p*-MeOAr species bear much weaker intermolecular interactions than *p*-FAr species and may have greater solubility as a consequence.

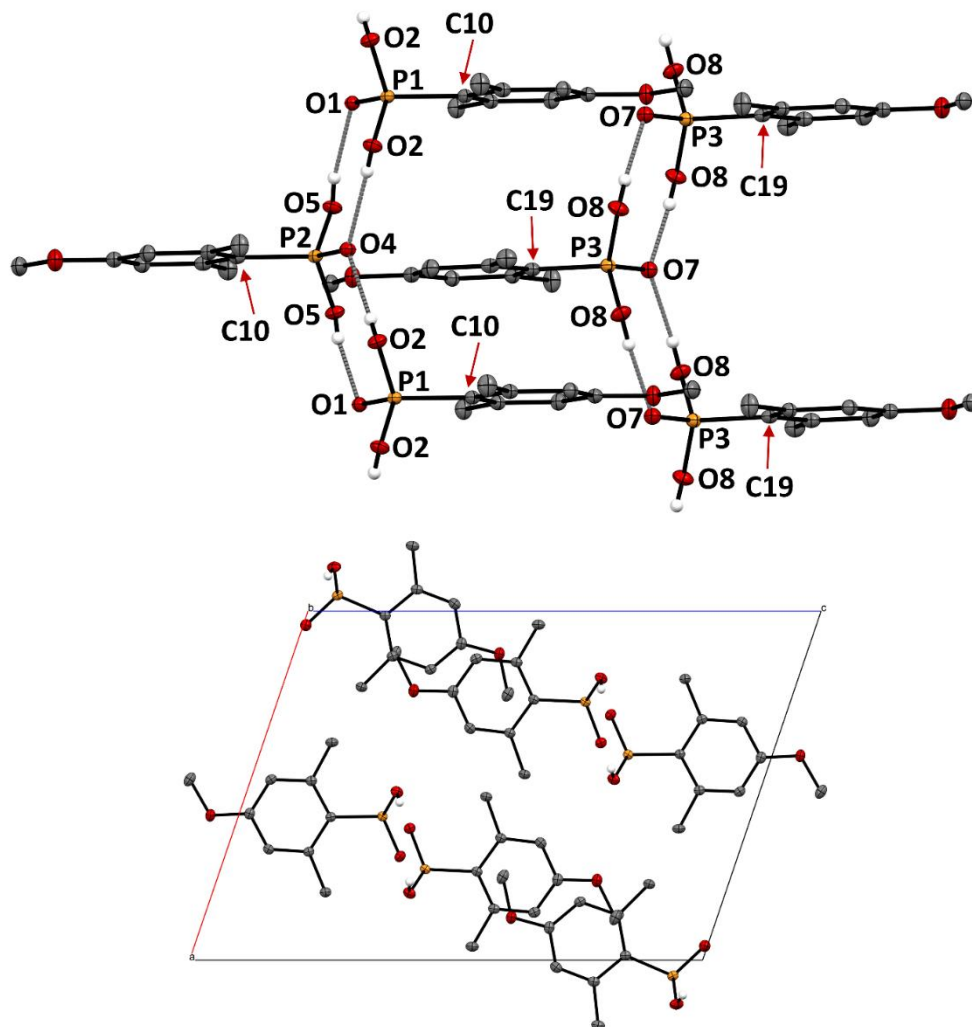
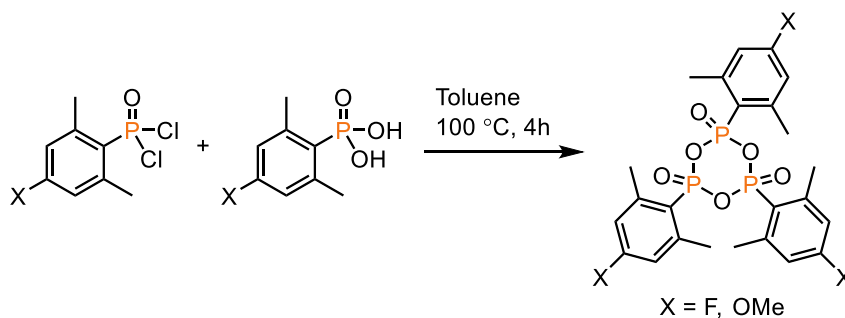


Figure 4.18 Single-crystal X-ray structure of *p*-MeOArPO(OH)₂ demonstrating intermolecular hydrogen bonding interactions (top) and as viewed down the crystallographic *b*-axis (bottom). Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity, except those involved in hydrogen bonding interactions. Select bond lengths (Å) and angles (°) for *p*-MeOArPO(OH)₂: P1-O1 1.5037(15); P1-O2 1.5524(11); P1-C1 1.783(2); P2-O4 1.5040(16); P2-O5 1.5524(11); P2-C10 1.781(2); P3-O7 1.5026(16); P3-O8 1.5536(12); P3-C19 1.781(2); O1-P1-O2 111.69(6); O2-P-O2 101.85(9); O1-P1-C1 113.05(9); O2-P1-C1 108.98(6); O4-P2-O5 111.77(6); O5-P2-O5 101.37(9); O4-P2-C10 113.42(9); O5-P2-C10 108.90(6); O7-P3-O8 111.83(6); O8-P3-O8 101.43(9); O7-P3-C19 113.51(9); O8-P3-C19 108.76(6).

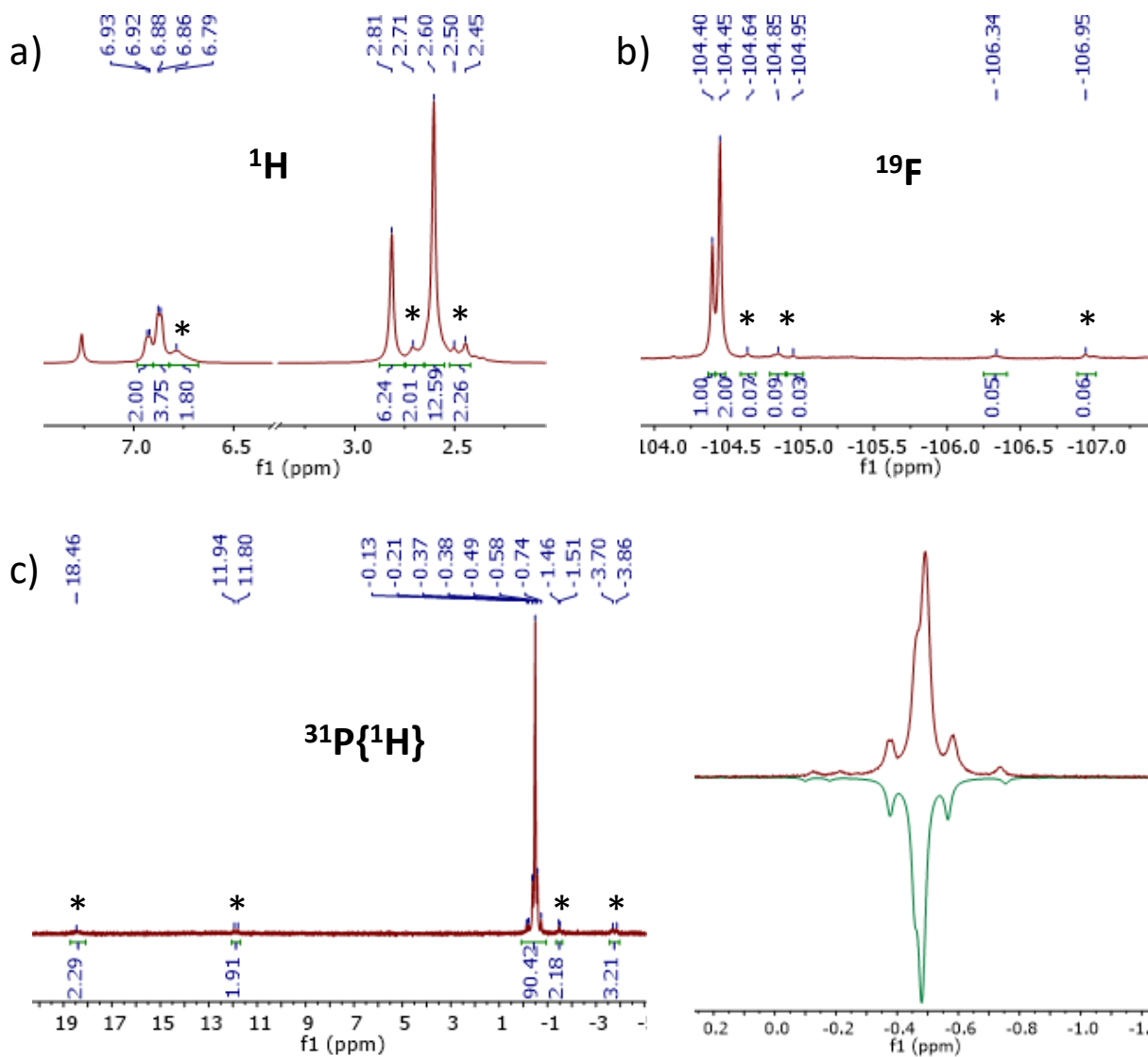
With starting materials in hand, we conducted the synthesis of cyclic phosphonates as previously described in the literature⁸ to determine if the electronically modified rings displayed greater solution stability than the prototypical solution-stable [MesP(O)–O]₃ (Scheme 4.4).



Scheme 4.4 Synthesis of electronically-modified cyclic phosphonates.

Equimolar amounts of *p*-FArPOCl₂ and *p*-FArPO(OH)₂ were combined in a schlenk flask with 10 mL of toluene and stirred at 100 °C for 4 h, yielding a clear solution. Upon ceasing stirring and allowing the solution to cool to ambient temperature, a colourless powder precipitated from solution. The supernatant was removed from solution and the powder was dried in vacuo to yield crude [*p*-FArP(O)–O]₃. However, after drying, [*p*-FArP(O)–O]₃ proved to be extremely insoluble in virtually all common organic solvents, though displayed a small amount of solubility in CDCl₃ such that NMR spectra of a heterogeneous suspension could be obtained (Figure 4.19). The ¹H NMR aryl region displays peaks at two doublets at 6.93 and 6.87 ppm which integrate 2:4 and demonstrate the same coupling to fluorine of ⁵J_{HF} = 6.5 Hz, indicative of an AB₂ spin system akin to that seen in [MesP(O)–O]₃. Likewise, two singlets at 2.81 and 2.60 ppm integrating 6:12 correspond well to an AB₂ spin system. However a broad singlet at 6.79 ppm and the presence of methyl peaks at 2.71, 2.50, and 2.45 ppm suggest that other products – such as an all-*cis* [*p*-FArP(O)–O]₃ ring or an eight-membered all-*trans* [*p*-FArP(O)–O]₄ ring – may be concomitantly synthesized alongside [*p*-FArP(O)–O]₃. This hypothesis of concomitant by-product

formation is supported by the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum, which displays two large singlets at 104.4 ppm integrating 1:2, while a series of other small singlets between 104.6 and 107.0 ppm are present. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[p\text{-FArP}(\text{O})\text{-O}]_3$ displays a major series of peaks between -0.13 to -0.74 ppm, which belong to a complex AB_2 splitting pattern as further supported by simulation of the spin pattern with the following parameters: $^{31}\text{P}\{^1\text{H}\}$ AB_2 , $\delta\text{A} = -0.377$, $\delta\text{B} = -0.522$, $J_{\text{AB}} = 42.36$, $\text{LW} = 5.0$ Hz (Figure 4.19c). While NMR studies give ample evidence for the formation of the fluorinated cyclic phosphonate, $[p\text{-FArP}(\text{O})\text{-O}]_3$ could not be recrystallized after many attempts, which always yielded amorphous powders which tended to be more insoluble than the amorphous product initially used for recrystallization. It is likely that preferential interactions between $p\text{-FAr}$ moieties as seen in the single crystal X-ray structure of $p\text{-FPO}(\text{OH})_2$, in combination with the relative rigidity of the formed cyclic phosphonates, induce aggregation of formed $[p\text{-FArP}(\text{O})\text{-O}]_x$ heterocycles and preclude structure elucidation of $[p\text{-FArP}(\text{O})\text{-O}]_3$ and assessment of its solution stability.



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Given the difficult processability of $[p\text{-FArP}(\text{O})\text{-O}]_3$, we sought to determine if the $[p\text{-MeOArP}(\text{O})\text{-O}]_3$ would be more feasible to synthesize and characterize, or if it suffered from the same processability issues as the $p\text{-FAr}$ derivative. Equimolar amounts of $p\text{-MeOArPOCl}_2$ and $p\text{-MeOArPO}(\text{OH})_2$ were combined in a Schlenk flask, suspended in toluene, and heated for 4 h at 100 °C. However, an intractable, viscous material was isolated after the 4 hours passed, which likely formed from decomposition of the donating phosphonate materials. As such, an alkali salt of $p\text{-MeOArPO}(\text{OH})_2$ was synthesized, which would provide us with a substantial driving force for ring formation through MCl ($\text{M} = \text{Na}, \text{K}$) precipitation. Stirring a suspension of 2 equivalents of NaH with 1 equivalent of $p\text{-MeOArPO}(\text{OH})_2$ in MeCN at ambient temperature for 24 hours yielded an insoluble white solid after gas evolution ceased, which was completely insoluble in all common organic solvents, and even boiling water. When trying to dissolve the solid in DMSO-d_6 while sonicating the heterogeneous mixture, a viscous hydrogel-like material was obtained, suggesting that the sodium-phosphonate salt bears high lattice enthalpy and not amenable to dissolution (Figure 4.30). As a result of this, $p\text{-MeOArPO}(\text{ONa})_2$ was used without further purification for the synthesis of $[p\text{-MeOArP}(\text{O})\text{-O}]_3$. Equimolar amounts of $p\text{-MeOArPO}(\text{ONa})_2$ and $p\text{-MeOArPOCl}_2$ were heated to reflux in THF for 4 hours, followed by stirring at ambient temperature for 16 hours. The volatiles were subsequently removed *in vacuo*, after which the crude material was extracted with THF which was subsequently evaporated. The resulting material displayed a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with a distorted triplet at 9.6 ppm, similar in nature to the AB_2 spin pattern of $[\text{MesP}(\text{O})\text{-O}]_3$,⁸ as well as a singlet at 22.6 ppm and a broad singlet at -2.2 ppm (Figure 4.20). The ^1H NMR spectrum displayed a complex mixture of peaks which made assignment unfeasible. Given the majority of the crude material was made of the species at 9.6 ppm by $^{31}\text{P}\{^1\text{H}\}$ NMR and the material appeared much more soluble than $[p\text{-FArP}(\text{O})\text{-O}]_3$, recrystallization of the material was attempted with several conditions; however, recrystallizations

continuously yielded insoluble powders which were unable to be dissolved by common organic solvents. We hypothesize that the added donation of electron density into the ring yet again resulted in the spontaneous decomposition of the product, or caused spontaneous ring-opening of a $[p\text{-MeOArP}(\text{O})\text{-O}]_3$ ring *in situ*.

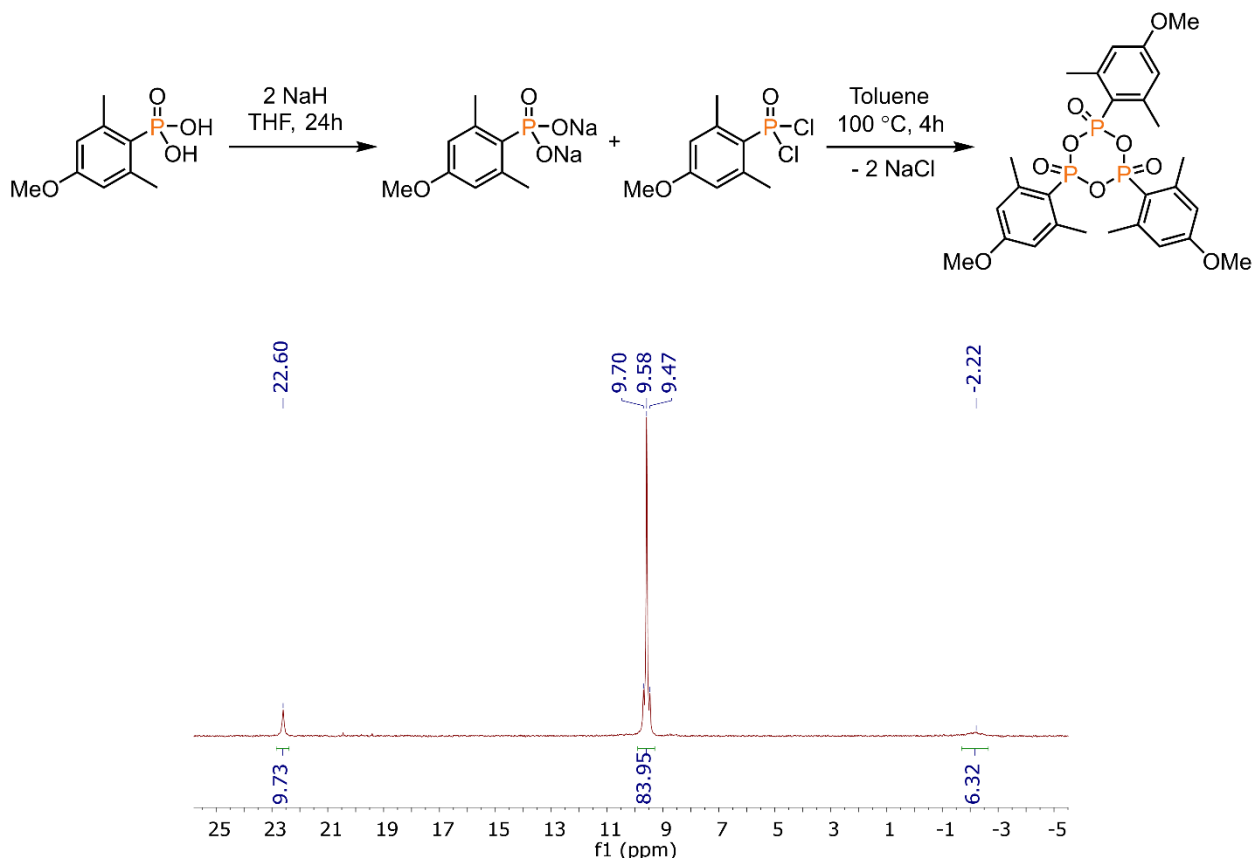


Figure 4.20 Synthetic scheme outlining the formation of $p\text{-MeOArPO}(\text{ONa})_2$, and its subsequent reaction with $p\text{-MeOArPOCl}_2$ to form a cyclic $[p\text{-MeOArP}(\text{O})\text{-O}]_3$ species (top), and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 203 MHz) of the crude material from the synthesis of $[p\text{-MeOArP}(\text{O})\text{-O}]_3$.

Based on this small study into the formation of electron-withdrawing and electron-donating cyclic phosphonates, with the goal of stabilizing RPO_2 moieties and preventing dynamic exchange in both phosphonate and hybrid P-O-Si-O rings, we conclude that the electronic modification of ArPO_2 units appears to destabilize the ring compared to standard aryl substituents, such that pristine material cannot be isolated. It would therefore appear, as demonstrated in our group's

seminal study on the synthesis of polyphosphonates,⁸ that kinetic stabilization of RPO₂ units through steric protection is the most simple and effective way to prevent dynamics in phosphonate-based materials.

4.3.4.2 Phosphonate stabilization with extreme steric modification

Understanding the fundamental nature of the aryl-substituted RPO₂ monomeric unit may provide valuable insight into its fundamental structure and bonding, and may better inform the design of more stable phosphonate materials. We are not the first to pursue this goal; Schreiner and coworkers have conducted meticulous studies on the *in situ* formation of phenyl phosphinidene in solid argon matrices at 10 K through irradiation of PhP(C₂H₄) at 254 nm, and its subsequent reaction with O₂ upon continued irradiation to form PhPO₂ (Figure 4.21).³³ However, the physical properties and metrical parameters of RPO₂ are difficult to obtain in these experimental conditions, for which achieving IR characterization in an argon matrix at 10 K is already an achievement. Moreover, RPO₂ species have been isolated as adducts with Lewis bases, though the donation of the base into the phosphorus centre has a large effect on the electronic character of the phosphonate unit and does not give an accurate picture of the bonding scheme in pristine RPO₂ (Figure 4.21).^{8, 34, 35} We predict that the use of sterically encumbering ligands will allow for the first formation of free monomeric RPO₂ at ambient temperature, providing a route for the measurement of its metrical parameters through single crystal X-ray experiments and assessing ambient temperature IR parameters and reactivity.

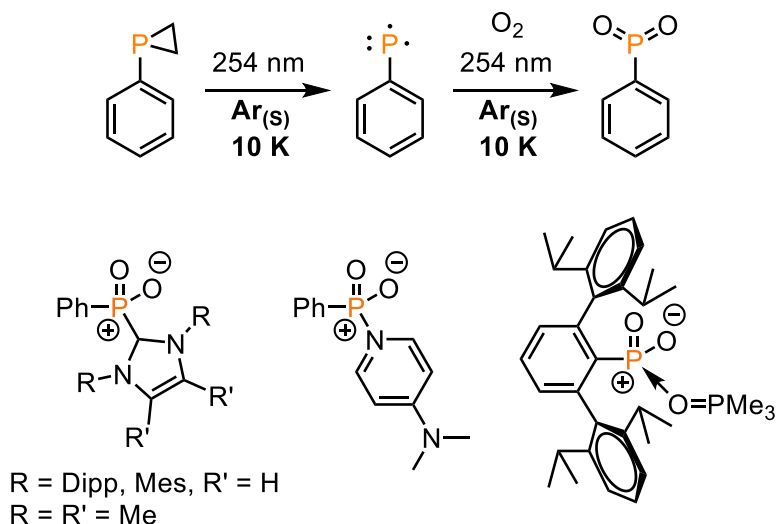


Figure 4.21 The formation of PhPO₂ in argon matrices as reported by Schreiner (top), and examples of Lewis base-stabilized RPO₂ (bottom).

Extreme steric protection can be provided by a newly developed class of substituent based on the sterically-hindered difluorenyl hydrindacene M^sFluid (Figure 4.22a) scaffold developed by Matsuo and coworkers,³⁶ which was recently made more sterically bulky in reports by Tan and coworkers to form M^sFluid^{*t*Bu} and M^sFluid* (Figure 4.22a).^{37, 38} These rigid and sterically demanding substituents have allowed for the isolation of dicoordinate germanium species,³⁷ and monocoordinate germylyne radicals,³⁸ triplet stibinidenes³⁹ and triplet bismuthinidenes.⁴⁰ The latter of these species, which are heavy analogues of phosphinidenes, inspired us to use the ligand scaffold to mimic the strategy of Schneider, generating a sterically protected phosphinidene that we could react with oxygen gas under UV radiation to form a monomeric RPO₂ molecule that would not oligomerize at ambient temperature. For our study, we initially pursued the synthesis of M^sFluid^{*t*Bu}-Li(THF)₂ as per literature procedure.³⁷ The lithioarene could then be reacted with PCl₃

to yield $M^s\text{Fluid}^{t\text{Bu}}\text{-PCl}_2$, which could subsequently be reduced to form a free phosphinidene which we could expose to O_2 while irradiating at 254 nm (Figure 4.22b).

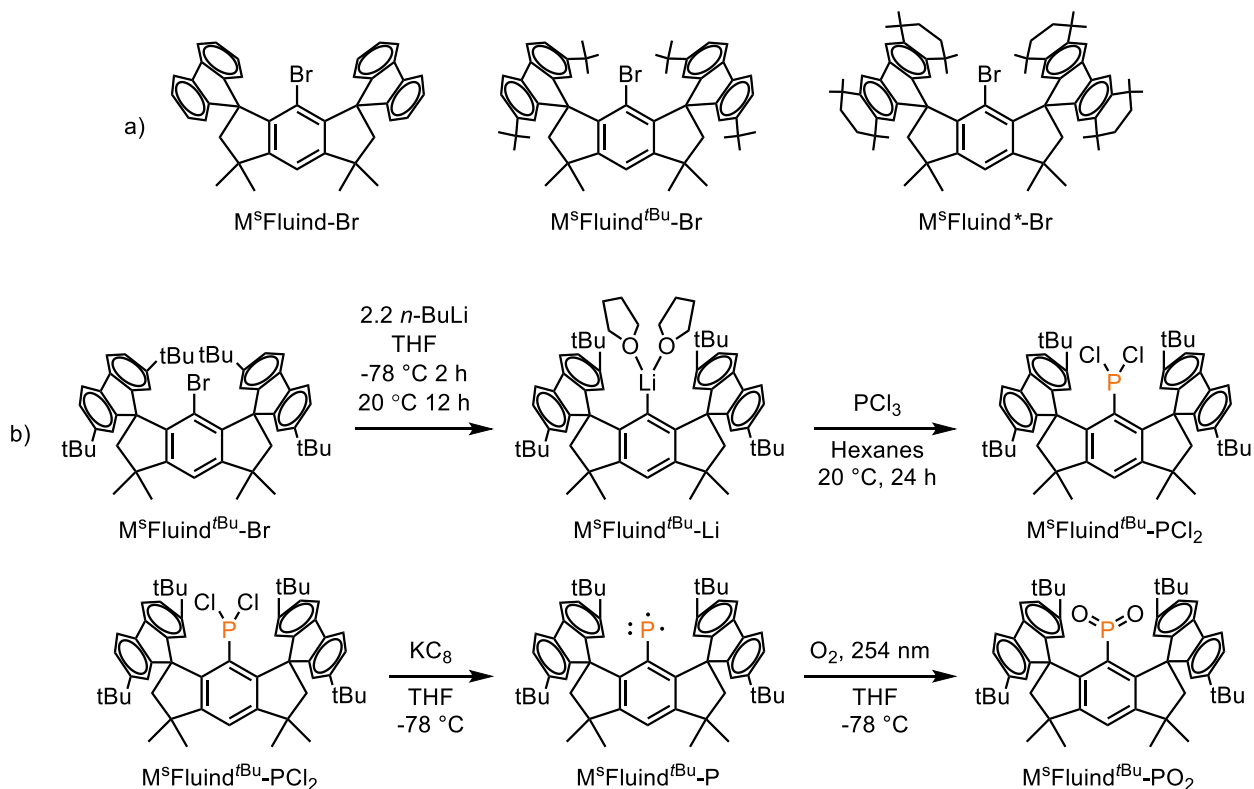


Figure 4.22 (a) Structural representations of $M^s\text{Fluid-Br}$, $M^s\text{Fluid}^{t\text{Bu}}\text{-Br}$, $M^s\text{Fluid}^*\text{-Br}$; (b) proposed synthetic scheme of $M^s\text{Fluid}^{t\text{Bu}}\text{-PO}_2$.

$M^s\text{Fluid}^{t\text{Bu}}\text{-Br}$ was initially difficult to reproduce according to the reported procedure, with yields suffering due to poor solubility of $M^s\text{Fluid}^{t\text{Bu}}\text{-Br}$ combined with difficulties in separating the product from upstream starting materials. However we were able to isolate $M^s\text{Fluid}^{t\text{Bu}}\text{-Br}$ in adequate purity and yields similar to that reported in the literature. Lithiation of $M^s\text{Fluid}^{t\text{Bu}}\text{-Br}$ proved troublesome even when done exactly as per literature: $t\text{BuLi}$ was added to $M^s\text{Fluid}^{t\text{Bu}}\text{-Br}$ suspended in THF at $-78\text{ }^\circ\text{C}$, and this mixture was left to stir at $-78\text{ }^\circ\text{C}$ for 2 h, and then stirred at $-10\text{ }^\circ\text{C}$ for 12 h. However, we found that lithiation was either incomplete (as evidenced by the unique fingerprint ^{13}C NMR spectra of $M^s\text{Fluid}^{t\text{Bu}}\text{-Br}$ and $M^s\text{Fluid}^{t\text{Bu}}\text{-Li}$) or showed little evidence for occurring at all. After re-trying the synthesis several more times with no

evidence of forming the lithioarene as a major product, we ultimately attempted to selectively recrystallize $\text{M}^{\text{s}}\text{Fluid}^{t\text{Bu}}\text{-Li(THF)}_2$ from a reaction mixture demonstrating incomplete lithiation. Recrystallizing a reaction mixture from a saturated toluene solution which was left to stand at $-30\text{ }^{\circ}\text{C}$ for 3 weeks afforded 372 mg of single crystals of $\text{M}^{\text{s}}\text{Fluid}^{t\text{Bu}}\text{-Li(THF)}_2$ (3% yield compared to the 72% yield reported in literature). The identity of $\text{M}^{\text{s}}\text{Fluid}^{t\text{Bu}}\text{-Li(THF)}_2$ is confirmed by diagnostic peaks at $\delta = 25.5, 67.5, 68.2, 157.9,$ and 160.5 ppm in ^{13}C NMR spectra.³⁷

With a small amount of pure $\text{M}^{\text{s}}\text{Fluid}^{t\text{Bu}}\text{-Li(THF)}_2$ in hand, we dissolved all of the material in hexanes and added 30 equivalents of PCl_3 to the reaction in one shot at $20\text{ }^{\circ}\text{C}$. The reaction was stirred for 24 hours, during which LiCl was precipitated from a colourless supernatant. Once the mixture was filtered and the volatiles removed, a colourless solid was isolated which demonstrated a crude ^1H NMR spectrum with peaks corresponding to multiple species, while the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displayed a singlet at 159.7 ppm in the expected region for a monosubstituted dichlorophosphine. This impure solid was recrystallized *via* slow diffusion of pentane into a THF solution, and yielded 101 mg of colourless blocks which were adequate for single crystal X-ray diffraction and sent for crystallographic studies. Single crystal X-ray diffraction verified the unambiguous structure of $\text{M}^{\text{s}}\text{Fluid}^{t\text{Bu}}\text{-PCl}_2$ (Figure 4.23).

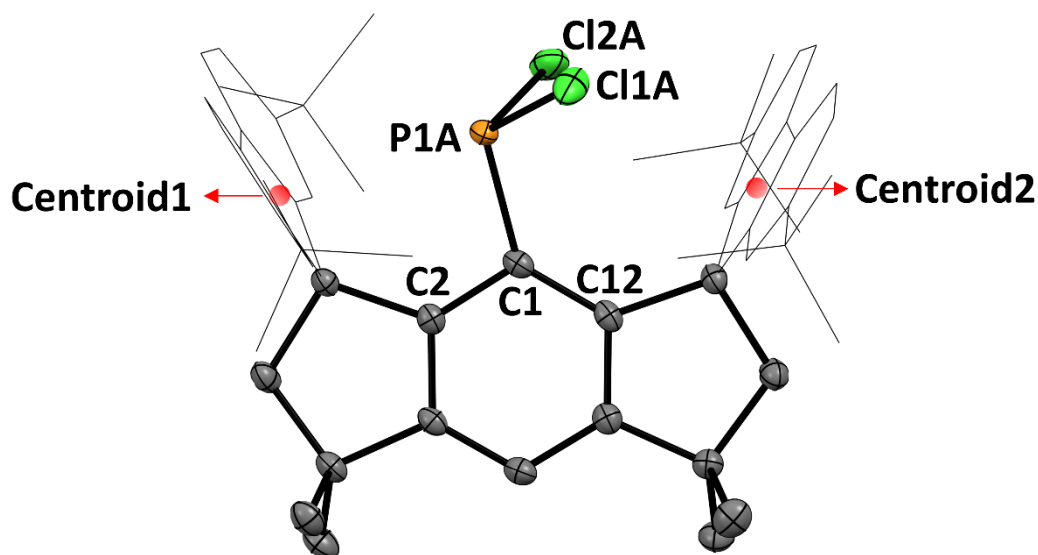


Figure 4.23 Single-crystal X-ray structure of $M^s\text{Fluid-PCl}_2$. Ellipsoids are drawn at 50% probability. Hydrogen atoms, positionally disordered P1B-Cl1B-Cl2B, and a rotationally disordered tert-butyl group are omitted for clarity. Select bond lengths (Å) and angles (°) for $M^s\text{Fluid-PCl}_2$: P1-O1 1.5037(15); P1A-C1 1.868(3); P1B-C1 1.869(2); P1A-Cl1A 2.059(4); P1A-Cl2A 2.047(4); P1B-Cl1B 2.058(1); P1B-Cl2B 2.0540(8); P1A-centroid1 2.847; P1B-centroid 2.955; P1A-C1-C12 103.1(1); P1A-C1-C2 139.1(1); P1B-C1-C2 107.5(1); P1B-C1-C12 134.7(1); C1-P1A-Cl1A 101.2(2); C1-P1A-Cl2A 102.6(2); C1-P1B-Cl1B 104.03(6); C1-P1B-Cl2B 103.21(6).

$M^s\text{Fluid}^{t\text{Bu}}\text{-PCl}_2$ crystallizes with one molecule in the unit cell, and with the PCl_2 moiety crystallizing with positional disorder over two sites in between the fluorene arms as identified using the difference map (for simplification, we will discuss only P1A/Cl1A/Cl2A in the discussion of the structure, as both disordered phosphorus centres have similar metrical parameters). The metrical parameters of $M^s\text{Fluid}^{t\text{Bu}}\text{-PCl}_2$ emphasize the relative steric strain the rigid fluorenyl arms impart on the phosphorus centre, as the phosphorus atom lies off-centre with angles between P1A-C1-C2 and P1A-C1-C12 diverging from 120° to $139.1(1)$ and $103.1(1)^\circ$, respectively. This phenomenon was similarly observed in the structure of $M^s\text{Fluid-PCl}_2$ ($M^s\text{Fluid}^{t\text{Bu}}$ lacking tert-butyl groups on fluorene arms) reported by Beckmann and coworkers.⁴¹

The P-C bond length of $\text{M}^{\text{s}}\text{Fluid}^{\text{tBu}}\text{-PCl}_2$ measures 1.868(3) Å, which is also similar to that of $\text{M}^{\text{s}}\text{Fluid-PCl}_2$.⁴¹

Shortly after we determined the solid state structure of $\text{M}^{\text{s}}\text{Fluid}^{\text{tBu}}\text{-PCl}_2$, Tan and coworkers reported the synthesis of $\text{M}^{\text{s}}\text{Fluid}^{\text{tBu}}\text{-PCl}_2$ as a starting material en route to synthesizing diarylphosphinyl radicals.⁴² However, our attempts for isolating RPO_2 at ambient temperature remain on-going as we continue with the re-synthesis of $\text{M}^{\text{s}}\text{Fluid}^{\text{tBu}}\text{-PCl}_2$ to explore its reactivity to reducing agents and oxygen sources.

4.3.5 Conclusions

We report the synthesis and characterization of novel hybrid phosphonate-siloxane heterocycles, $\text{P}^{\text{R}}\text{Si}^{\text{R'}}$, through the condensation of phosphonic acids and dichlorosilanes. These molecules are dynamic in the absence of sufficient steric protection, forming multiple species in solution with evidence for the formation of higher oligomers. VT-NMR of a prototypical dynamic species demonstrated that equilibration is not driven by ΔS , suggesting that these processes are likely isentropic. ESI-MS studies revealed that heterocycles without steric protection are highly sensitive to trace moisture, and verified potential equilibration pathways for $\text{P}^{\text{R}}\text{Si}^{\text{R'}}$ equilibration such as through oligomerization or phosphonate extrusion. Rings lacking sufficient steric protection also under melts and form glassy materials, as evidenced by DSC. Rings with greater steric contributions do not display such dynamic behaviour, nor do they undergo well-defined melts to form glassy phases. The ring with the least amount of steric hindrance, $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$, displayed evidence for forming polymeric P-O-Si-O materials through thermal ROP, as evidenced by NMR spectroscopy and GPC. This provides promise for the design of new main group polymers through the development of siloxane hybrids, however, methods for stabilizing these polymers are necessary given that distributions of polymer and cyclic species are present and likely due to

depolymerization phenomena. Finally, we attempted to redesign phosphonate units to prevent dynamic behavior in P–O containing heterocycles, however it was found that electronic modifications of mesityl phosphonates resulted in either high insolubility when electron withdrawing moieties were employed, while electron donating moieties resulted in instability of the phosphonate molecules. This work suggests that electronic modifications may not be compatible with sterically protected phosphonate rings, and testing electronic effects on stability of polyphosphonates may require a different approach. Furthermore, we have begun to synthesize the RPO₂ monomeric unit to further shed light on its dynamic behaviour, and have isolated the RPCl₂ precursor for this synthetic goal.

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4.5 Experimental

4.5.1 General procedures, reagents, and instrumentation

Storage and manipulation of all compounds were performed under an inert atmosphere either in a nitrogen-filled MBraun Labmaster Pro glovebox or using a nitrogen Schlenk line employing standard techniques. Hexanes, toluene, CH_2Cl_2 , and THF were dried and purified using an MBraun Grubbs/Dow solvent purification system, and stored over activated 4Å molecular sieves. Tol-d^8 were dried over sodium/benzophenone ketyl, degassed and vacuum distilled prior to use; Fluorobenzene (PhF), pentane, and CDCl_3 was dried over calcium hydride and thermally distilled and degassed prior to use. All other reagents were purchased from Sigma-Aldrich and used as received. MesPO(OH)_2 was prepared according to literature procedures (Arz *et al.* *J. Am. Chem. Soc.*, 2019, **141**, 2894-2899). Ring-opening polymerizations were conducted by sealing approximately 300 mg of heterocycle and heating the tube at 15 °C over the T_m as found by DSC until the material became immobile or highly viscous.

ESI mass spectra^{1,2,3} of $\text{P}^{\text{R}}\text{Si}^{\text{R'}}$ samples were collected on a Waters (Milford, USA) Synapt G2-Si mass spectrometer and analyzed using Waters MassLynx V4.2. Samples were dissolved in MeCN to form 10 $\mu\text{g mL}^{-1}$ solutions, which were prepared in a dinitrogen atmosphere glovebox and loaded into a syringe with PEEK tubing attached. The samples were then brought out of the glovebox and were infused into a Synapt G2-Si mass spectrometer, in either positive ion mode or negative ion mode. The conditions for each sample are as follows. $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$: resolution mode; flow rate = 10 $\mu\text{L min}^{-1}$; m/z range = 50-1200; scan time = 1 s; source temperature = 100 °C; desolvation temperature = 250 °C; cone gas = 50 L h⁻¹; desolvation gas = 400 L h⁻¹; capillary = 3.1 kV; sampling cone = 0 V; source offset = 0 V; nebuliser = 2.5 bar; trap collision energy = 8.0 V; transfer collision energy = 0.0 V. $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$: resolution mode; flow rate = 10 $\mu\text{L min}^{-1}$; m/z range = 50-1500; scan time = 1 s; source temperature = 100 °C; desolvation temperature = 250 °C; cone gas = 50 L

h-1; desolvation gas = 400 L h⁻¹; capillary = 3.1 kV; sampling cone = 0 V; source offset = 0 V; nebuliser = 2.5 bar; trap collision energy = 8.0 V; transfer collision energy = 0.0 V. **P^{Mes}Si^{Mes}**: resolution mode; flow rate = 10 µL min⁻¹; *m/z* range = 50-1800; scan time = 1 s; source temperature = 100 °C; desolvation temperature = 250 °C; cone gas = 50 L h⁻¹; desolvation gas = 400 L h⁻¹; sampling cone = 0 V; source offset = 0 V; nebuliser = 2.5 bar; trap collision energy = 8.0 V; transfer collision energy = 0.0 V. positive ion mode: capillary = 3.1 kV; negative ion mode: capillary = 2.0 kV. **P^{Mes}Si^{Mes}**: resolution mode; flow rate = 10 µL min⁻¹; *m/z* range = 50-2000; scan time = 1 s; source temperature = 100 °C; desolvation temperature = 250 °C; cone gas = 50 L h⁻¹; desolvation gas = 400 L h⁻¹; sampling cone = 0 V; source offset = 0 V; nebuliser = 2.5 bar; trap collision energy = 8.0 V; transfer collision energy = 0.0 V. positive ion mode: capillary = 3.1 kV; negative ion mode: capillary = 2.0 kV.

Routine mass spectra for phosphonate materials were obtained on a an Ultimate HPLC system (Thermo, MA) connected to an Exactive™ Plus Orbitrap electrospray ionization mass spectrometry system (Thermo, MA). The samples were dissolved in MeOH, MeCN, or CH₂Cl₂, and manually injected into the MS system bypassing the HPLC system. The Orbitrap mass spectrometer nebulization parameters were set to generate a stable ion flux. The mass range scanned was from 100 to 1500 *m/z* in positive and negative mode. Positive mode was calibrated using Pierce™ LTQ Velos ESI Positive Ion Calibration Solution (Thermo, MA) while negative mode was calibrated using Pierce™ ESI Negative Ion Calibration Solution (Thermo, MA) resulting in mass accuracy within ± 5 ppm of the ions theoretical exact mass.

IR spectra were obtained either on a Bruker Alpha FT-IR spectrometer equipped with a platinum single-reflection diamond ATR module, or with KBr pellets on a Perkin Elmer Spectrum Two FTIR spectrometer.

^1H and ^{13}C NMR spectrometry chemical shifts were referenced to residual proteo-solvent resonances and naturally abundant ^{13}C resonances for all deuterated solvents. All heteronuclear NMR spectrum were referenced externally to IUPAC standards. Chemical shift assignments are based on NMR experiments performed on Bruker Avance NEO 500 MHz or AV III 300 MHz spectrometers.

The single crystal X-ray diffraction experiments were carried out on a Bruker APEX II diffractometer using either Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) or Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$) and collected at 90 (2) or 100(2) K. The data collection was performed using a CCD area detector from a single crystal mounted on a glass fibre. The total number of runs and images was based on the strategy calculation from the program APEX3. Data reduction, scaling and absorption corrections were performed using SAINT. The structures were solved and the space group determined by the SHELXT5 structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of SHELXL6 in Olex2.7 All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atom positions were calculated geometrically and refined using the riding model (except where carbon atoms lay on special positions, in which case added constraints were added to hydrogen atoms), whereas all oxygen-bound hydrogen atoms were located in the Fourier difference map and freely refined.

Differential scanning calorimetry samples were run on a TA instruments DSC25 using TZero aluminum DSC pans with hermetic lids. A TZero aluminum DSC pan with a TZero aluminum hermetic lid was used as a reference. Samples were measured for two complete heating and cooling cycles at 10°C per minute.

Gel permeation chromatography (GPC) was performed on a Malvern RI max Gel Permeation Chromatograph, equipped with an automatic sampler, pump, injector, and inline

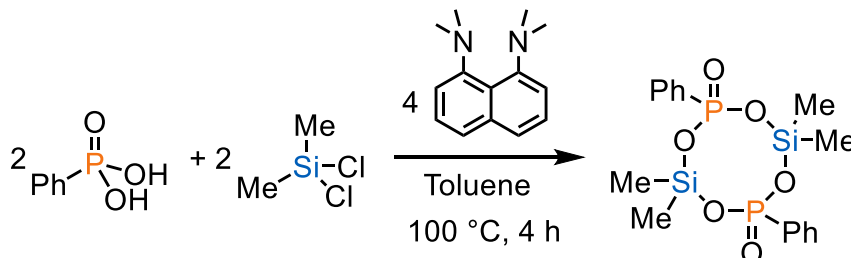
degasser. The columns ($2 \times \text{T5000}$) were contained within an oven ($35\text{ }^{\circ}\text{C}$) and consisted of styrene/divinyl benzene gels. Sample elution was detected by means of a differential refractometer. THF (Fisher) containing 0.1 %w/w $[\text{nBu}_4\text{N}][\text{Br}]$ was used as the eluent at a flow rate of 1 mL min^{-1} . Samples were dissolved in THF (2 mg mL^{-1}) and filtered with a Ministart SRP15 filter (poly(tetrafluoroethylene) membrane of $0.45\text{ }\mu\text{m}$ pore size) before analysis. The calibration was conducted using monodisperse polystyrene standards obtained from Aldrich. The lowest and highest molecular weight standards used were 2,300 Da and 994,000 Da respectively.

MALDI-TOF MS measurements were performed on a Bruker Ultraflextreme operating in positive mode. Samples were prepared by mixing a 1 mg/mL solution of sample in a 1:10 ratio with a 20 mg/mL THF solution of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile matrix. $1\text{ }\mu\text{L}$ was transferred to a stainless-steel sample plate and allowed to dry in air.

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4.5.2 Synthesis of $\mathbf{P^{Ph}Si^{Me}}$



A 20 mL J Young tube was charged with 6.53 mmol of $\text{PhPO}(\text{OH})_2$ (1.03 g, 1 eq), 8.49 mmol of Me_2SiCl_2 (1.03 mL, 1.3 eq), 13.07 mmol of Proton-sponge® (2.80 g, 2 eq), and 10 mL of toluene. The solution was allowed to stir for 4 h at 100 °C, during which a white precipitate formed and settled at the bottom. The solution was allowed to cool to room temperature, and was then filtered through a filter frit under a nitrogen atmosphere. The volatiles of the supernatant were then removed *in vacuo* at 30 °C to yield a tacky solid, which was suspended in cold hexanes, re-filtered cold, and had the volatiles removed *in vacuo* to yield crude $\mathbf{P^{Ph}Si^{Me}}$. The solid was then dissolved in 4 mL of CH_2Cl_2 and layered with 15 mL of hexanes, which was left to stand at -30 °C for 72 h to single crystals of $\mathbf{P^{Ph}Si^{Me}}$ (600 mg, 42.9%).

^1H NMR (500 MHz, CDCl_3): δ 7.93 – 7.78 (m, 4H, 2 x $\text{C}^{3,5}\text{-H}$), 7.59 – 7.50 (m, 2H, 2 x $\text{C}^4\text{-H}$), 7.48 (dq, $J = 7.1, 3.5, 2.5$ Hz, 4H, 2 x $\text{C}^{2,6}\text{-H}$), 0.49 (s, 12H, 2 x Me_2Si).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 132.44 (d, $J = 3.1$ Hz, 2C, 2 x $\text{C}^4\text{-H}$), 131.05 (d, $J = 10.9$ Hz, 4C, 2 x $\text{C}^{3,5}\text{-H}$), 128.45 (d, $J = 16.3$ Hz, 4C, 2 x $\text{C}^{2,6}\text{-H}$), -0.30 (d, $J = 2.7$ Hz, 4C, 2 x Me_2Si).

$^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, CDCl_3) δ -0.21 (major product, all-*trans*), -1.42, -1.57, -1.89, -1.91, -2.32 (minor product, all-*cis*).

^{29}Si NMR (99 MHz, CDCl_3) δ -4.56 (t, $J = 10.4$ Hz, major product, all-*trans*), -5.27 (d, $J = 4.8$ Hz), -5.34 (t, $J = 5.4$ Hz, minor product, all-*cis*), -5.43 (d, $J = 5.1$ Hz), -6.86 (t, $J = 8.0$ Hz), -11.79 (d, $J = 7.2$ Hz), -12.02 (d, $J = 7.3$ Hz).

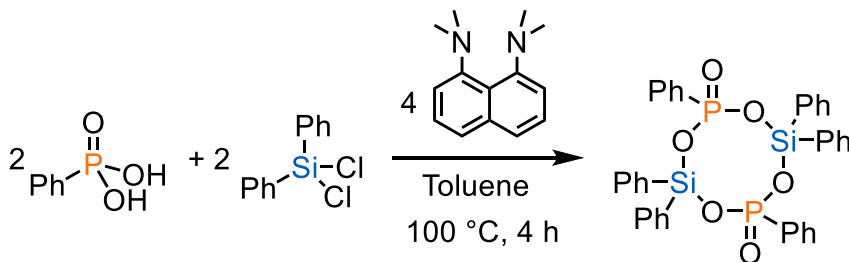
ATR-IR (cm⁻¹): 3062 (w), 2968 (w), 1592 (w), 1487 (w), 1440 (m), 1402 (w), 1254 (s), 1137 (m), 1033 (bs), 1012 (bs), 980 (bs), 837 (s), 814 (bs), 759 (s), 729 (s), 693 (s).

HRMS (ESI+) *m/z*: [M + Na] calcd for C₁₆H₂₂O₆P₂Si₂Na⁺ 451.0327. Found 451.0389.

Note: The compound is highly soluble in CH₂Cl₂, CHCl₃, PhF, Toluene, and THF, and is sparingly soluble in aliphatic hydrocarbons.

Note: Various minor signals were detected in the ³¹P{¹H} NMR spectrum of **P^{Ph}Si^{Me}** at δ = -1.42, -1.57, -1.89, -1.91, and -2.32 ppm (Figure C.3), and in the ²⁹Si NMR spectrum of **P^{Ph}Si^{Me}** at -5.27, -5.34, -5.43, -6.86, -11.79, and -12.02 ppm (Figure C.4). These signals manifest as a host of peaks in the ¹H and ¹³C{¹H} NMR spectra (Figure C.1 and Figure C.2), and all originate from unidentified oligomeric species, as evidenced by DOSY and ESI-MS studies (*vide supra*).

4.5.3 Synthesis of **P^{Ph}Si^{Ph}**



A 20 mL J Young tube was charged with 4.00 mmol of PhPO(OH)₂ (632 mg, 1 eq), 4.00 mmol of Ph₂SiCl₂ (1.01 mL, 1 eq), 8.00 mmol of Proton-sponge® (1.68 g, 2 eq), and 10 mL of toluene. The solution was allowed to stir for 4 h at 100 °C, during which a white precipitate formed and settled at the bottom. The solution was allowed to cool to room temperature, and was then filtered through a filter frit under a nitrogen atmosphere. The volatiles of the supernatant were then removed *in vacuo* at 30 °C to yield a colourless semi-solid. This was triturated with hexanes, which was subsequently removed and the remaining solid was dried *in vacuo* to yield crude **P^{Ph}Si^{Ph}**. The solid

was then dissolved in 4 mL of CH₂Cl₂ and layered with 15 mL of hexanes, which was left to stand at -30 °C for 72 h to yield single crystals of **P^{Ph}Si^{Ph}** (629 mg, 46.6%).

¹H NMR (500 MHz, CDCl₃): δ 7.89 (dd, *J* = 15.1, 7.2 Hz, 4H, 2 x *PC*^{3,5}-*H*), 7.63 (d, *J* = 7.0 Hz, 8H, 4 x *SiC*^{3,5}-*H*), 7.45 (t, *J* = 7.5 Hz, 4H, 2 x *PC*^{2,6}-*H*), 7.44 – 7.40 (m, 6H, 6 x *C*⁴-*H*), 7.35 (t, *J* = 7.6 Hz, 8H, 4 x *SiC*^{2,6}-*H*).

¹³C{¹H} NMR (126 MHz, CDCl₃): δ 134.69 (s, ²*J*_{CSi} = 4.4 Hz, 8C, 4 x *SiC*^{3,5}-*H*), 132.59 (d, *J* = 3.2 Hz, 4C, 2 x *PC*⁴-*H*), 131.76, 131.66 (d, *J* = 9.1 Hz), 131.47 (d, *J* = 11.2 Hz, 4C, 2 x *PC*^{3,5}-*H*), 131.44 (d, *J* = 9.7 Hz), 129.72, 128.80 (d, *J* = 2.3 Hz), 128.51 (d, *J* = 16.6 Hz, 4C, 2 x *C*^{2,6}-*H*), 128.24, 128.22 (d, *J* = 10.8 Hz).

³¹P{¹H} NMR (203 MHz, CDCl₃) δ -0.65, -1.31, -1.37 (²*J*_{PSi} = 11.5 Hz, major product, all-*trans*), -1.73, -1.81, -2.63, -3.32 (²*J*_{PSi} = 11.4 Hz, minor product, all-*cis*).

²⁹Si NMR (99 MHz, CDCl₃) δ -37.69 (t, ²*J*_{PSi} = 11.6 Hz, major product, all-*trans*), -37.83 (d, *J* = 5.6 Hz), -37.90 (d, *J* = 5.8 Hz), -38.16 (t, *J* = 5.6 Hz), -38.38 (t, ²*J*_{PSi} = 11.5 Hz, minor product, all-*cis*).

ATR-IR (cm⁻¹): 3073 (w), 3051 (w), 3006 (w), 2322 (w), 2113 (w), 1593 (m), 1429 (m), 1224 (bm), 1128 (bs), 1008 (bs), 973 (s), 718 (s), 691 (s)

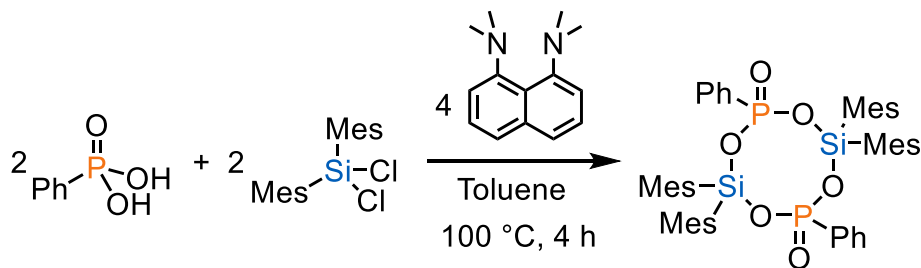
HRMS (ESI+) *m/z*: [M + Na] calcd for C₃₆H₃₀O₆P₂Si₂Na⁺ 699.0954. Found 699.1087.

Note: The compound is highly soluble in CH₂Cl₂, CHCl₃, PhF, Toluene, and THF, and is insoluble in aliphatic hydrocarbons.

Note: Various minor signals were detected in the ³¹P{¹H} NMR spectrum of **P^{Ph}Si^{Ph}** at δ = -0.57, -1.24, -1.64, -2.24, -2.55, and -3.21 ppm (Figure C.7), and in the ²⁹Si NMR spectrum of **P^{Ph}Si^{Ph}** at -37.80 (d, *J* = 5.6 Hz), -37.87 (d, *J* = 5.8 Hz), -38.13 (t, *J* = 5.6 Hz), -38.35 (t, *J* = 11.5 Hz) (Figure

C.8). These signals manifest as a host of peaks in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Figure C.5 and Figure C.6), and originate from unidentified oligomeric species, as evidenced by DOSY and ESI-MS studies (*vide supra*). In this particular case, given the small range of chemical shifts for the phenyl rings in $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ oligomer mixture and the continual oligomerization of the $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ ring over the course of NMR spectral acquisition, the assigning of carbons (especially quaternary carbons) was extremely difficult and could not reliably be done even with the assistance of HSQC and HMBC NMR. As such only carbons which compared similarly to $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ were assigned.

4.5.4 Synthesis of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$



A 20 mL J Young tube was charged with 4.00 mmol of $\text{PhPO}(\text{OH})_2$ (632 mg, 1 eq), 4.00 mmol of $\text{Mes}_2\text{SiCl}_2$ (1.348 g, 1 eq), 8.00 mmol of Proton-sponge® (1.68 g, 2 eq), and 15 mL of toluene. The solution was allowed to stir for 4 h at 100 °C, during which a white precipitate formed and settled at the bottom. The solution was allowed to cool to room temperature, and was then filtered through a filter frit under a nitrogen atmosphere. The volatiles of the supernatant were then removed *in vacuo* at 30 °C to yield a colourless solid. The solid was then dissolved in 4 mL of CH_2Cl_2 and layered with 15 mL of pentane, and was left to stand at -30 °C for 7 days to yield small amounts of single crystals of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$. The recrystallization can also be kept at -30 °C for 21 days, yielding larger amounts of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$ (906 mg, 53.6%).

^1H NMR (500 MHz, CDCl_3): δ 7.81 (dd, $J = 15.1, 7.7$ Hz, 4H, 2 x $\text{PC}^{3,5}\text{-H}$), 7.38 (t, $J = 7.6$ Hz, 2H, 2 x $\text{PC}^4\text{-H}$), 7.25 (t, $J = 9.8$ Hz, 4H, 2 x $\text{PC}^{2,6}\text{-H}$), 6.69 (s, 8H, 4 x $\text{SiC}^{2,6}\text{-H}$), 2.30 (s, 24H, 8 x $\text{SiMes-Me}^{2,6}$), 2.20 (s, 12H, 4 x SiMes-Me^4).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 144.55 (s, 8C, 4 x $\text{SiC}^{2,6}$), 140.74 (s, 4C, 4 x SiC^4), 131.92 (d, $J = 3.2$ Hz, 2C, 2 x PC^4), 131.14 (d, $J = 11.4$ Hz, 4C, 2 x $\text{PC}^{3,5}\text{-H}$), 129.54 (s, 8C, 4 x $\text{SiC}^{3,5}\text{-H}$), 129.33 (d, $J = 188.2$ Hz, 2C, 2 x PC^1), 128.03 (d, $J = 16.4$ Hz, 2 x $\text{PC}^{2,6}\text{-H}$), 126.43 (s, 4C, 4 x SiC^1), 23.26 (s, 8C, 8 x $\text{SiMes-Me}^{2,6}$), 21.10 (s, 4C, 4 x SiMes-Me^4).

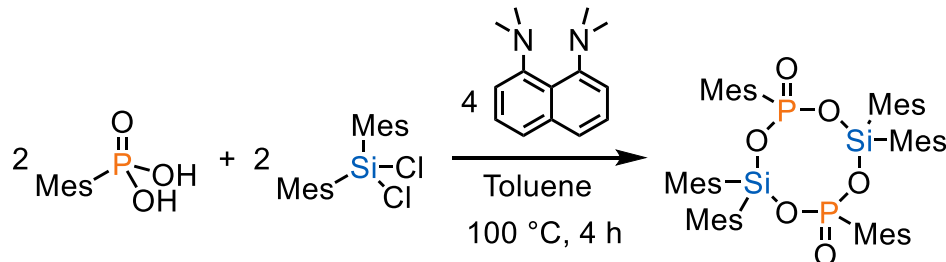
$^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, CDCl_3) δ -2.75 (s, $^2J_{\text{PSi}} = 11.0$ Hz, all-*trans*).

^{29}Si NMR (99 MHz, CDCl_3) δ -36.28 (t, $^2J_{\text{PSi}} = 11.1$ Hz, all-*trans*).

HRMS (ESI+) m/z : $[\text{M} + \text{K}]$ calcd for $\text{C}_{48}\text{H}_{54}\text{O}_6\text{P}_2\text{Si}_2\text{Na}^+$ 883.2571. Found 883.2604.

4.5.5 Synthesis of $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$

A 20 mL J Young tube was charged with 4.00 mmol of $\text{MesPO}(\text{OH})_2$ (800 mg, 1 eq), 4.00 mmol



of $\text{Mes}_2\text{SiCl}_2$ (1.348 g, 1 eq), 8.00 mmol of Proton-sponge® (1.68 g, 2 eq), and 15 mL of toluene.

The solution was allowed to stir for 4 h at 100 °C, during which a white precipitate formed and settled at the bottom. The solution was allowed to cool to room temperature, and was then filtered through a filter frit under a nitrogen atmosphere. The volatiles of the supernatant were then removed *in vacuo* at 30 °C to yield a colourless solid. The solid was then dissolved in 4 mL of CH_2Cl_2 and layered with 15 mL of pentane, and was left to stand at -30 °C for 3 days to yield single crystals of $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$ (979 mg, 52.7%).

^1H NMR (500 MHz, CDCl_3): δ 6.76 (d, $J = 4.7$ Hz, 4H, 2 x $\text{PC}^{3,5}\text{-H}$), 6.68 (s, 8H, 4 x $\text{SiC}^{3,5}\text{-H}$), 2.33 (s, 24H, 8 x $\text{SiMes-Me}^{2,6}$), 2.30 (s, 12H, 4 x $\text{PMes-Me}^{2,6}$), 2.25 (s, 6H, PMes-Me^4), 2.20 (s, 12H, PMes-Me^4).

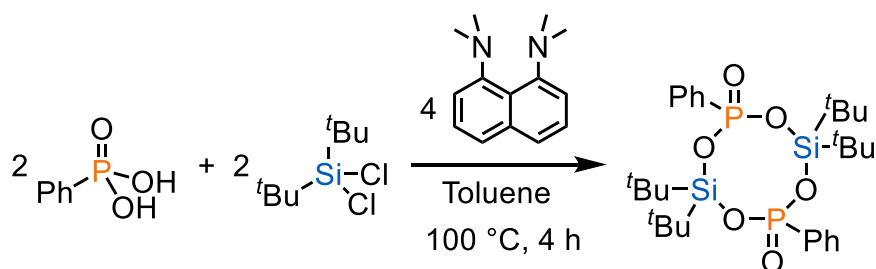
$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 144.19 (s, 8C, 4 x $\text{SiC}^{2,6}$), 143.65 (d, $J = 13.2$ Hz, 4C, 2 x $\text{PC}^{2,6}$), 141.38 (d, $J = 3.2$ Hz, 2C, 2 x PC^4), 140.07 (s, 4C, 4 x SiC^4), 130.12 (d, $J = 16.8$ Hz, 4C, 2 x $\text{PC}^{3,5}\text{-H}$), 129.32, (s, 8C, 4 x $\text{SiC}^{3,5}\text{-H}$), 128.43 (d, $J = 2.7$ Hz, 4C, 4 x SiC^1), 123.36 (d, $J = 199.6$ Hz, 2C, 2 x PC^1), 23.51 (d, $J = 3.8$ Hz, 4C, 4 x $\text{PMes-Me}^{2,6}$), 23.43 (s, 8C, 8 x $\text{SiMes-Me}^{2,6}$), 21.06 (s, 4C, 4 x SiMes-Me^4), 21.04 (d, $J = 1.6$ Hz, 2 x PMes-Me^4).

$^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, CDCl_3) δ -1.89 (s, $^2J_{\text{PSi}} = 12.0$ Hz).

^{29}Si NMR (99 MHz, CDCl_3) δ -38.61 (t, $^2J_{\text{PSi}} = 12.2$ Hz).

HRMS (ESI+) m/z : $[\text{M} + \text{Na}]$ calcd for $\text{C}_{54}\text{H}_{66}\text{O}_6\text{P}_2\text{Si}_2\text{Na}^+$ 951.3771. Found 951.3831.

4.5.6 Synthesis of $\text{P}^{\text{Ph}}\text{Si}^t\text{Bu}$



A 20 mL J Young tube was charged with 4.00 mmol of $\text{PhPO}(\text{OH})_2$ (632 mg, 1 eq), 4.00 mmol of $t\text{Bu}_2\text{SiCl}_2$ (0.845 mL, 1 eq), 8.00 mmol of Proton-sponge® (1.68 g, 2 eq), and 15 mL of toluene. The solution was allowed to stir for 4 h at 100 °C, during which a white precipitate formed and settled at the bottom. The solution was allowed to cool to room temperature, and was then filtered through a filter frit under a nitrogen atmosphere. The volatiles of the supernatant were then removed *in vacuo* at 30 °C to yield a colourless solid. The solid was then dissolved in 5 mL of CH_2Cl_2 and precipitated into 15 mL of hexanes, after which the supernatant was removed and the solid was dried *in vacuo* to yield $\text{P}^{\text{Ph}}\text{Si}^t\text{Bu}$ (783 mg, 65.6%).

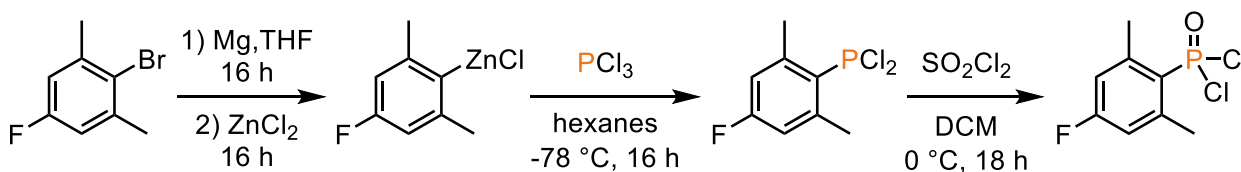
^1H NMR (360 MHz, CDCl_3): δ 8.32 – 8.23 (m, 4H, 2 x $\text{PC}^{3,5}\text{-H}$), 7.23 – 7.15 (m, 6H, 2 x $\text{PC}^{3,5}\text{-H}$ and 2 x PC^4), 1.35 (s, 18H, 4 x Si^tBu).

$^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, CDCl_3) δ -4.58 (s, $^2J_{\text{PSi}} = 17.6$ Hz, major product, all-*trans*), -6.44 (s, $^2J_{\text{PSi}} = 18.3$ Hz, minor product, all-*cis*).

^{29}Si NMR (99 MHz, CDCl_3) δ -13.81 (t, $J = 17.8$ Hz, major product, all-*trans*), -14.63 (t, $J = 18.2$ Hz, minor product, all-*cis*).

Note: Phenyl peaks for both isomers directly overlap, resulting in an artificially low integration of the *tert*-butyl peak at 1.16 ppm.

4.5.7 Synthesis of 4-fluoro-2,6-dimethylphenylphosphonic dichloride (*p*-FArPOCl₂)



The procedure was adapted from a reported synthesis of MesPOCl₂ (Arz *et al.* *J. Am. Chem. Soc.*, 2019, **141**, 2894-2899). In a 500 mL Schlenk flask, magnesium turnings (3.83 g, 150 mmol) were suspended in THF (150 mL). 1,2-dibromoethane (0.02 mL, 0.230 mmol) was then added to activate the magnesium metal surface. The mixture was stirred at ambient temperature for 1 h. 2-bromo-5-fluoro-1,3-dimethylbenzene (25.25g, 124 mmol) was then added slowly and allowed to stir for 16 h. The light brown solution was transferred via cannula into a 500 mL Schlenk flask with additional THF (250 mL) and cooled to 0 °C. ZnCl₂ was added in small portions to avoid exotherms and the colourless suspension was warmed to ambient temperature and stirred for 16 h. The suspension was intermittently transferred via cannula into a solution of POCl₃ (50 mL, 78.15 g, 569 mmol) in hexanes (250 mL) at -78 °C. The reaction mixture was warmed to ambient temperature and stirred for 16 h. The volatiles were removed *in vacuo* and the colourless solid was dried under vacuum for ca. 2 h. The solid was transferred into a frit and extracted with 2 x 250 mL of hot hexanes. The volatiles of the filtrate were removed under vacuum to yield 18.19 g (65%

yield from 2-bromo-5-fluoro-1,3-dimethylbenzene) of ***p*-FArPCL₂** as a colourless oil with a single ³¹P{¹H} resonance at δ = 163.6 ppm, which was used immediately without further purification. In a 250 mL Schlenk flask, ***p*-FArPCL₂** was dissolved in CH₂Cl₂ (125 mL) and neat sulfuryl chloride (10.91 g, 81 mmol) was added dropwise at 0 °C, whereby the solution was warmed to ambient temperature and stirred for 18 h. The volatiles were removed *in vacuo* to give crude ***p*-FArPOCl₂** as colourless microcrystalline material, which was found to be of sufficient purity for further synthesis (16.90 g, 56.5%).

¹H NMR (500 MHz, 298 K, CDCl₃) δ 2.78 (d, ²J_{HP} = 1.5 Hz, 6H, C^{2,6}-Me), 6.90 (dd, *J* = 9.1, 5.7 Hz, 2H, C^{3,5}-H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 165.15 (dd, *J* = 257.4, 4.8 Hz, 1C, PC), 147.04 (dd, *J* = 18.4, 9.6 Hz, 2C, C^{2,6}), 127.24 (dd, *J* = 150.3, 2.9 Hz, 1C, FC), 117.94 (t, *J* = 20.7 Hz, 2C, C^{3,5}), 23.97 (dd, *J* = 3.8, 1.4 Hz, 2C, C^{2,6}-Me).

³¹P{¹H} NMR (203 MHz, CDCl₃) δ 30.81 (d, *J* = 4.0 Hz).

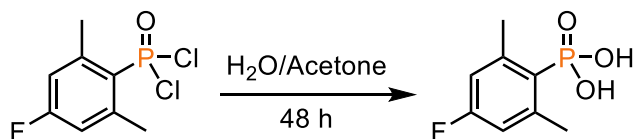
¹⁹F{¹H} NMR (471 MHz, CDCl₃) δ -104.45 (d, *J* = 3.9 Hz).

HRMS (ESI+) *m/z*: [M + H] calcd for C₈H₈Cl₂FOPH⁺ 240.97467. Found 240.97470.

IR (cm⁻¹) 3062 (w), 2980 (w), 2943 (w), 2860 (w), 1582 (s), 1459 (m), 1420 (m), 1388 (m), 1295 (s), 1264 (s), 1152 (s), 1073 (s), 1034 (s), 980 (s), 881 (s), 855 (s)

4.5.8 Synthesis of 4-fluoro-2,6-dimethylphenylphosphonic acid (***p*-FArPO(OH)₂**)

The procedure was adapted from a reported synthesis of MesPO(OH)₂ (Arz *et al. J. Am. Chem.*



Soc., 2019, **141**, 2894-2899). In a 250 mL round bottom flask, ***p*-FArPOCl₂** (6.99 g, 29.00 mmol)

was suspended in a mixture of H₂O (75 mL) and acetone (75 mL) and were allowed to stir at ambient temperature for 24 h. The solution was filtered and the volatiles were removed under vacuum at 25 °C to give crude **pFArPO(OH)₂** as a colourless solid which was subsequently dried for 72 h at ambient temperature (5.74 g, 96%).

¹H NMR (300 MHz, Methanol-d⁴) δ 6.85 (ddt, *J* = 9.7, 3.5, 0.6 Hz, 2H, *C*^{3,5}-*H*), 2.64 (dt, *J* = 1.7, 0.5 Hz, 6H, *C*^{2,6}-CH₃).

¹³C NMR (126 MHz, Methanol-d⁴) δ 164.94 (dd, *J* = 249.6, 3.9 Hz, 1C, *C*⁴-F), 147.22 (dd, *J* = 13.1, 8.7 Hz, 2C, *C*^{2,6}), 126.52 (dd, *J* = 184.2, 3.1 Hz, 1C, *PC*), 116.79 (dd, *J* = 20.5, 16.2 Hz, 2C, *C*^{3,5}-*H*), 23.89 (dd, *J* = 3.3, 1.4 Hz, *C*^{2,6}-CH₃).

³¹P{¹H} NMR (122 MHz, Methanol-d⁴) δ 16.38 (d, *J* = 2.6 Hz).

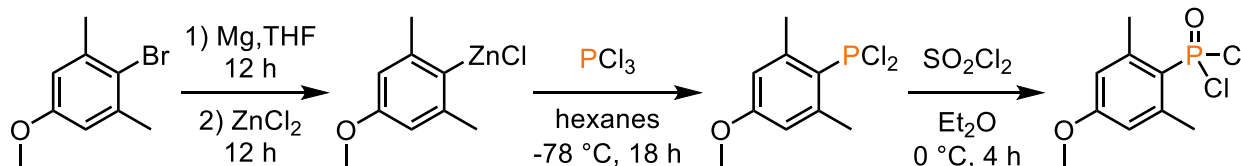
¹⁹F{¹H} NMR (282 MHz, Methanol-d⁴) δ -113.07.

HRMS (ESI+) *m/z*: [M + H] calcd for C₈H₁₀FO₃PH⁺ 205.04244. Found 205.04262.

IR (cm⁻¹) 2750 (bw), 2292 (bw), 2109 (bw), 1586 (m), 1474 (m), 1414 (m), 1388 (m), 1293 (m), 1224 (m), 1194 (m), 1142 (m), 1094 (s), 1032 (w), 980 (s), 911 (s), 859 (s), 758 (m)

4.5.9 Synthesis of 4-methoxy-2,6-dimethylphenylphosphonic dichloride (**p-MeOArPOCl₂**)

The procedure was adapted from a reported synthesis of MesPOCl₂ (Arz *et al.* *J. Am. Chem. Soc.*,



2019, **141**, 2894-2899). In a 500 mL Schlenk flask, magnesium turnings (3.83 g, 158 mmol) were suspended in THF (150 mL). 1,2-dibromoethane (0.02 mL, 0.230 mmol) was then added to activate the magnesium metal surface. The mixture was stirred at ambient temperature for 1 h. 2-

bromo-5-methoxy-1,3-dimethylbenzene (18 mL, 24.48g, 114 mmol) was then added slowly and allowed to stir for 16 h. The dark grey solution was transferred via cannula into a 500 mL Schlenk flask with additional THF (250 mL) and cooled to 0 °C. ZnCl₂ was added in small portions and the colourless suspension was warmed to ambient temperature and stirred for 16 h. The suspension was intermittently transferred via cannula into a solution of PCl₃ (50 mL, 78.15 g, 569 mmol) in hexanes (250 mL) at -78 °C. The reaction mixture was warmed to ambient temperature and stirred for 16 h. The volatiles were removed under vacuum and the colourless solid was dried under vacuum for ca. 2 h. The solid was transferred into a frit and extracted with 2 x 250 mL of hot hexanes. The volatiles of the filtrate were removed under vacuum to yield ***p*-MeOArPCl₂** as a colourless crystalline solid with a ³¹P{¹H} resonance at δ = 167.1 ppm, which was used immediately without further purification. In a 250 mL Schlenk flask, ***p*-MeOArPCl₂** was dissolved in diethyl ether (125 mL) and neat sulfuryl chloride (9.85 mL, 16.28 g, 121 mmol) was added dropwise at 0 °C, whereby the solution was warmed to ambient temperature and stirred for 18 h. The volatiles were removed under vacuum to give crude ***p*-MeOArPOCl₂** as colourless crystals. The material was purified in concentrated solution of diethyl ether (ca. 100 mL) at ambient temperature to yield colourless crystals (16.57 g, 57.0%).

¹H NMR (500 MHz, CDCl₃) δ 6.68 (d, *J* = 6.1 Hz, 2H, *C*^{3,5}-*H*), 3.85 (s, 3H, *OCH*₃), 2.75 (d, *J* = 1.6 Hz, 6H, *C*^{2,6}-*CH*₃).

¹³C NMR (126 MHz, CDCl₃) δ 163.24 (d, *J* = 4.0 Hz, 1C, *C*⁴-*OMe*), 145.84 (d, *J* = 18.2 Hz, 1C, *PC*), 116.20 (d, *J* = 20.0 Hz, *C*^{3,5}-*H*), 55.50 (s, 1C, *OCH*₃), 24.08 (d, *J* = 3.8 Hz, 2C, *C*^{2,6}-*CH*₃).

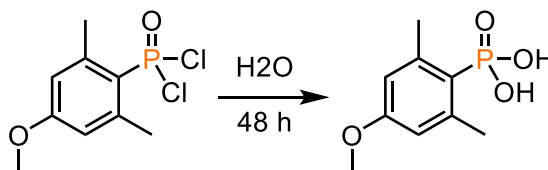
³¹P{¹H} NMR (203 MHz, CDCl₃) δ 32.68.

HRMS (ESI+) *m/z*: [M + H] calcd for C₉H₁₁Cl₂O₂PH⁺ 252.99465. Found 252.99480.

IR (cm⁻¹) 3077 (w), 2999 (w), 2946 (w), 2837 (w), 1592 (m), 1554 (m), 1466 (bm), 1379 (w), 1310 (m), 1267 (bs), 1198 (m), 1176 (m), 1097 (s), 1041 (m), 1004 (m), 956 (m), 937 (m), 885 (m), 846 (m)

4.5.10 Synthesis of 4-methoxy-2,6-dimethylphenylphosphonic acid (*p*-MeOArPO(OH)₂)

The procedure was adapted from a reported synthesis of MesPOCl₂ (Arz *et al.* *J. Am. Chem. Soc.*,



2019, **141**, 2894-2899). In a 250 mL RBF, *p*-MeOArPOCl₂ (981 mg, 3.88 mmol) was suspended in H₂O (125 mL) and allowed to stir at ambient temperature for 24 h. The solution was filtered and the volatiles were removed under vacuum at 25 °C to give crude *p*-MeOArPO(OH)₂ as a colourless solid which was subsequently dried for 72 h at ambient temperature.

¹H NMR (500 MHz, THF-d⁸) δ 10.29 (s, 2H, OH), 6.57 (d, *J* = 3.7 Hz, 2H, C^{3,5}-H), 3.74 (s, 3H, OCH₃), 2.57 (d, *J* = 1.6 Hz, 6H, C^{2,6}-CH₃).

¹³C{¹H} NMR (126 MHz, THF-d⁸) δ 161.81 (d, *J* = 3.3 Hz, 1C, C⁴), 145.20 (d, *J* = 12.9 Hz, 2C, C^{2,6}), 121.52 (d, *J* = 191.1 Hz, PC), 114.95 (d, *J* = 16.0 Hz, 2C, C^{3,5}-H), 54.97 (s, 1C, OCH₃), 23.75 (d, *J* = 3.1 Hz, C^{2,6}-CH₃).

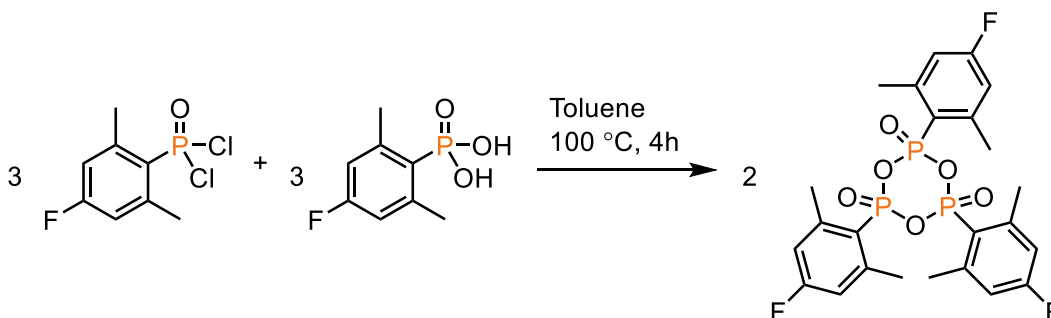
³¹P{¹H} NMR (203 MHz, THF-d⁸) δ 21.55.

HRMS (ESI+) *m/z*: [M + H] calcd for C₉H₁₃O₄PH⁺ 217.06243. Found 217.06322.

IR (cm⁻¹) 2752 (bw), 2288 (bw), 2098 (bw), 1593 (s), 1561 (m), 1468 (m), 1444 (m), 1313 (m), 1239 (w), 1183 (bm), 1131 (bs), 1107 (s), 1054 (m), 1036 (m), 982 (s), 960 (m), 939 (m), 913 (s), 855 (m), 836 (m), 777 (bm)

4.5.11 Synthesis of tris[4-fluoro-2,6-dimethylphenylphosphonic anhydride] [*p*-FArP(O)-O]₃

In a 100 mL Schlenk flask equipped with a reflux condenser, *p*-FArPOCl₂ (590 mg, 2.45 mmol)



and *p*-FArPO(OH)₂ (500 mg, 2.45 mmol) were dissolved in toluene (ca. 10 mL) and the mixture was refluxed for 4 h. The reaction mixture was cooled to ambient temperature without stirring, whereupon a colourless solid formed. The supernatant was removed via cannula and the solid was dried under vacuum at ambient temperature to yield crude [*p*-FArP(O)-O]₃ as a colourless solid with AB₂ symmetry in NMR spectra (663 mg, 73%).

¹H NMR (500 MHz, CDCl₃) δ 6.93 (d, *J* = 6.7 Hz, 2H, *C*^{3,5}-*H*_A), 6.87 (d, *J* = 7.3 Hz, 4H, *C*^{3,5}-*H*_B), 2.81 (s, 6H, *C*^{2,6}-*Me*_A), 2.60 (s, 12H, *C*^{2,6}-*Me*_B).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 165.50 (d, *J* = 255.9 Hz, 1C, *FC*⁴_A), 165.28 (d, *J* = 257.5 Hz, 2C, *FC*⁴_B), 147.67 (d, *J* = 11.0 Hz, 1C, *C*^{2,6}_A), 147.00 (d, *J* = 6.5 Hz, 2C, *C*^{2,6}_B), 117.78 – 117.55 (m, 1C, *C*^{3,5}_A), 117.40 (dd, *J* = 11.8, 7.7 Hz, 2C, *C*^{3,5}_B), 24.03 (s, 2C, *C*^{2,6}-*Me*_A), 23.59 (s, 4C, *C*^{2,6}-*Me*_B).

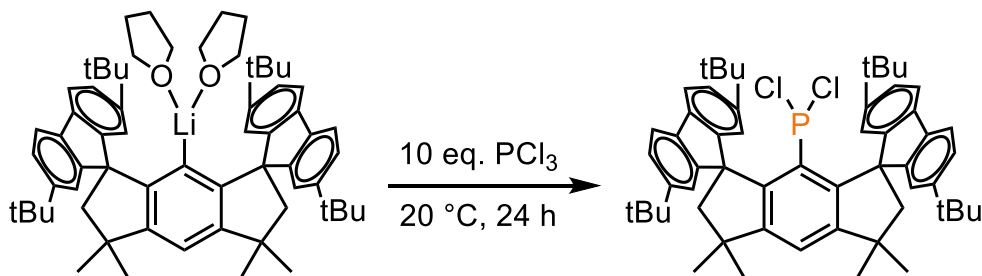
¹⁹F{¹H} NMR (471 MHz, CDCl₃) δ -104.40 (*p*-FAr_A), -104.45 (*p*-FAr_B).

³¹P{¹H} NMR (203 MHz, CDCl₃) highly coupled AB₂ spin pattern, peaks as assigned by simulation: *P*_A = -0.377 ppm, *P*_B = -0.522 ppm, *J*_{AB} = 42.36 Hz, Line width 5.0 Hz.

HRMS (ESI⁺) *m/z*: [*M* + *H*] calcd for C₂₄H₂₄F₃O₆P₃H⁺ 559.08106. Found 559.07899.

IR (cm⁻¹) 3076 (w), 2976 (w), 1582 (s), 1467 (bm), 1418 (w), 1385 (w), 1290 (s), 1241 (m), 1149 (w), 1090 (s), 1034 (m), 967 (s), 939 (s), 900 (s), 872 (s), 762 (m), 747 (s), 708 (w)

4.5.12 Synthesis of M^sFluind^tBu-PCl₂



In a 20 mL scintillating vial, M^sFluid^tBu-Li(THF)₂ (0.372 g, 0.418 mmol) was dissolved in 10 mL of hexanes. 30 equivalents of PCl₃ (171 mg, 109 μL) was added in one shot to the stirring solution, and the mixture was allowed to stir for 24 h. White precipitate was immediately produced, and after filtration of the solids and evaporation of all volatiles the formation of crude M^sFluid^tBu-PCl₂ as yielded a white powder. The material was purified through recrystallization by slow diffusion of pentane into a THF solution at ambient temperature to yield colourless crystals adequate for single-crystal X-ray diffraction (0.101 g, 0.120 mmol, 29%).

¹H NMR (500 MHz, C₆D₆) δ 7.52 (d, J = 7.9 Hz, 3H), 7.39 (s, 3H), 7.30 (s, 1H), 7.25 (d, J = 7.8 Hz, 4H), 7.13 (d, J = 8.4 Hz, 2H), 1.50 (s, 12H), 1.29 (s, 36H).

 $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, C_6D_6) δ 159.70.

4.5.13 Supporting Figures

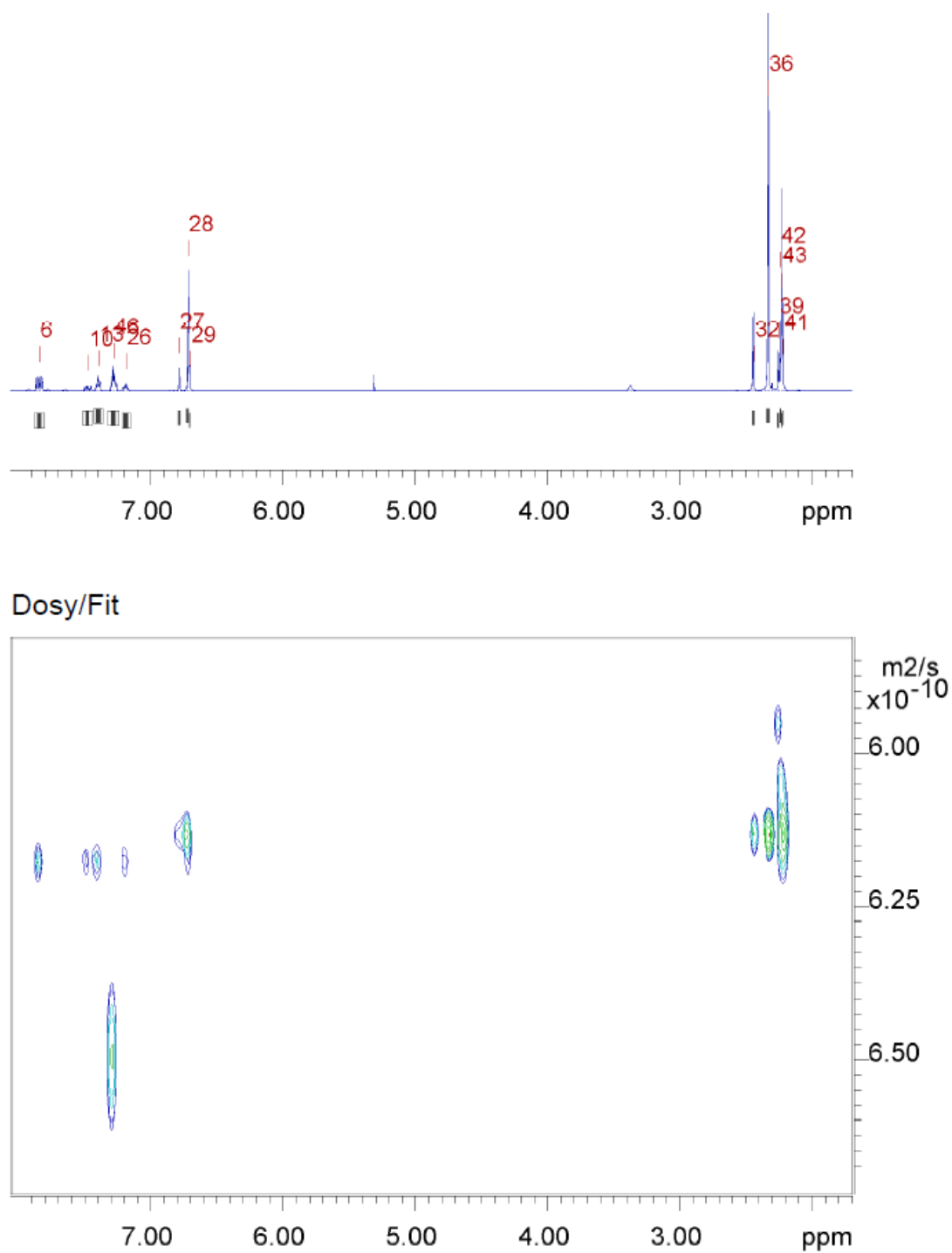


Figure 4.24 1H DOSY of *cis/trans* mixture of $P^{Ph}Si^{Mes}$

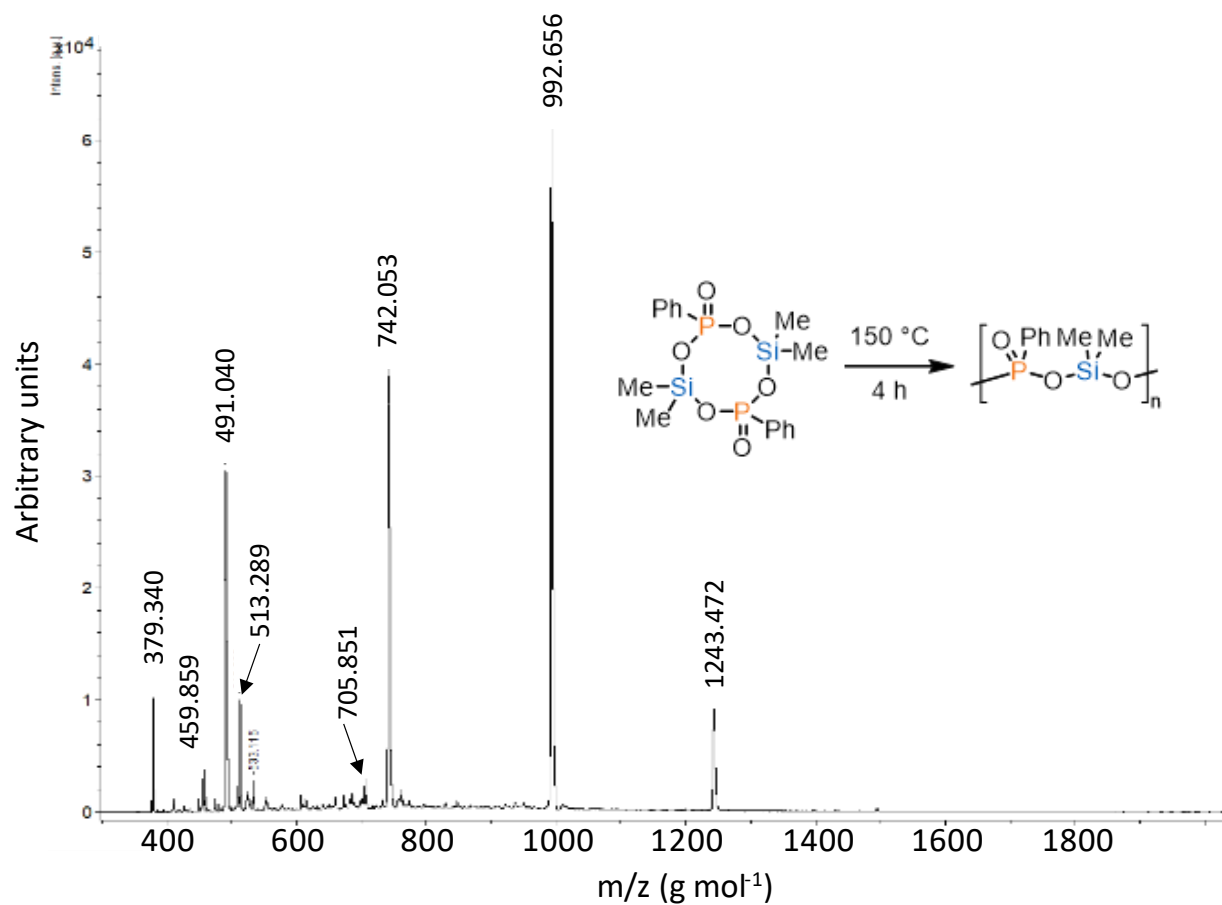


Figure 4.25 MALDI-ToF MS spectrum of **P^{Ph}Si^{Me}** post-ROP material.

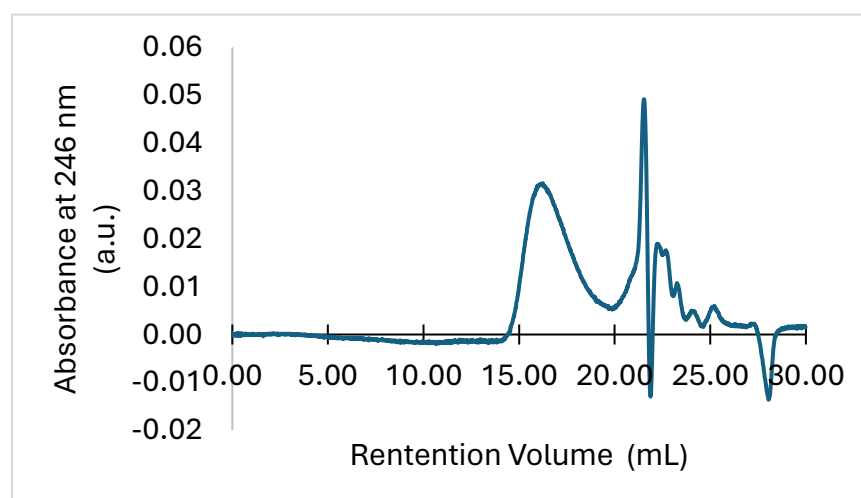


Figure 4.26 GPC chromatogram of post-ROP material of **P^{Ph}Si^{Me}**.

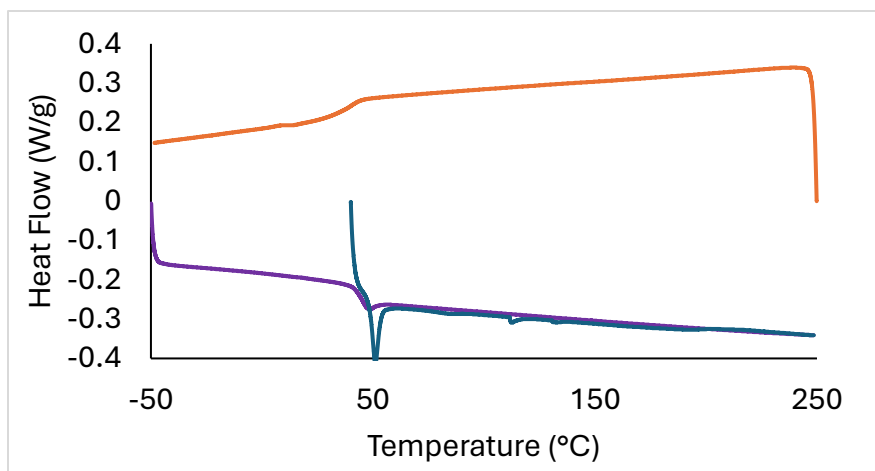


Figure 4.27 DSC calorigram of the post-ROP material of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$.

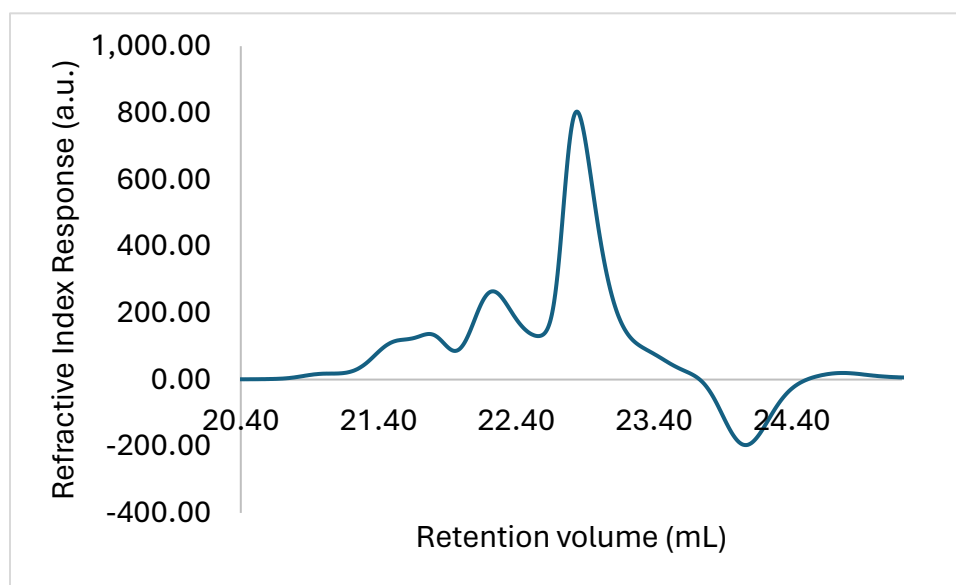


Figure 4.28 GPC chromatogram of post-ROP material of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$.

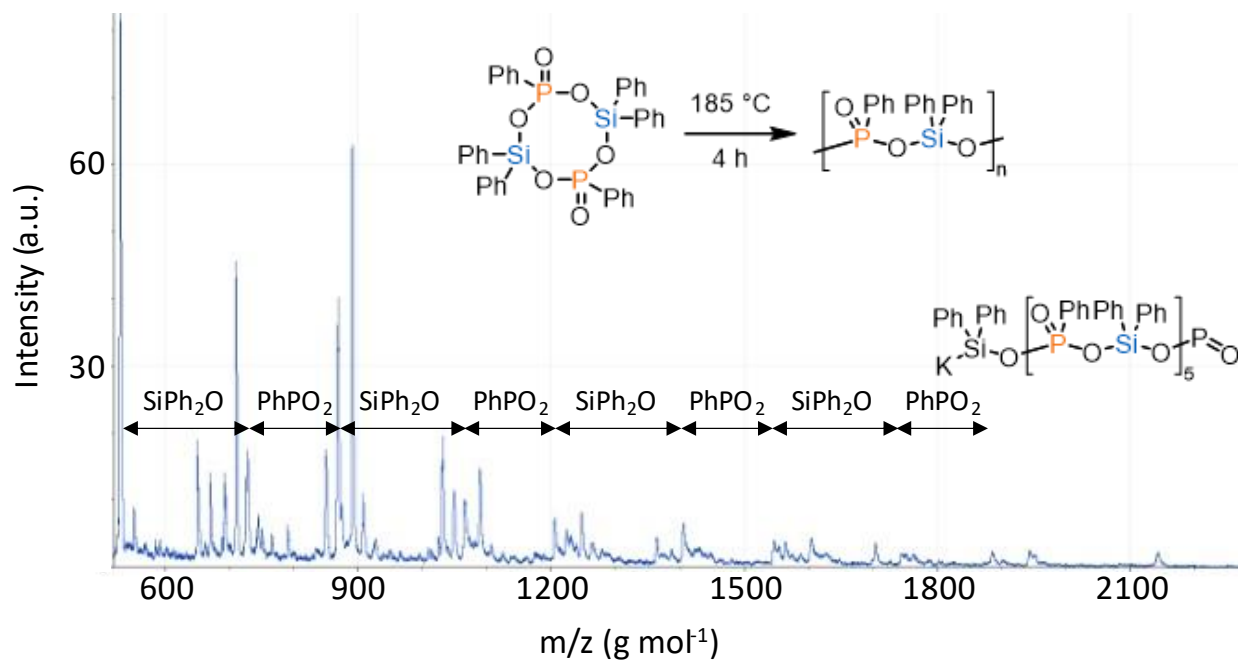


Figure 4.29 MALDI-ToF MS spectrum of **P^{Ph}Si^{Ph}** post-ROP material.



Figure 4.30 Viscous gel formed from the attempted dissolution of *p*-MeOArPO(OH)₂ in DMSO-d₆.

Chapter 5. Outlook and Future Work

The work presented in this thesis focuses on the development of synthetic routes to phosphorus-rich heterocyclic frameworks and their photophysical properties, as well as the development of novel main group element-containing polymers. The triflic acid-mediated insertion of nitriles into sterically encumbered (RP)₃ rings has resulted in the formation of P₃CN rings with structure-colour relationships and acid-base colour sensing behaviour. Investigations into the insertion of other unsaturated CN-based small molecules into (tBuP)₃ has furthered our understanding of the scope of the (tBuP)₃ cycloaddition reaction, as well as the discovery of new P₃CO 5-membered heterocycles. The synthesis and comprehensive characterization of P–O–Si–O heterocycles revealed complex dynamic behaviour in solution and thermal properties suggestive of potential ring-opening polymerization behaviour, culminating in the discovery of a high molar mass P–O–Si–O polymer. Investigations into the stabilization of RPO₂ moieties through modification of electronics and sterics are not straightforward, revealing distinct challenges in reactivity, processability, and synthetic design.

This outlook chapter serves to outline future directions based on the results obtained during the course of the studies described in this thesis.

5.1 1,3-Dipolar Cycloadditions of Nitriles with Sterically Encumbered Cyclic Triphosphanes

Chapter 2 describes the insertion of nitriles into increasingly sterically encumbered cyclic phosphanes P₃Mes₃, P₃Dipp₃, P₃Tripp₃, and uncovers emergent colouration in sterically encumbered derivatives which correlates to a structural bending of the P₃CN ring. This phenomenon is rare for phosphorus-rich heterocycles and opens an avenue for the discovery of new charge-transfer phenomena in other main group species. Sterically encumbered cyclic

pnictogens of the formula (RAs)₃ (R = Dipp, Tripp),¹ (RSb)₃ [R = (Me₃Si)₂CH],² and (RBi)₃ [R = (Me₃Si)₂CH,³ (Me₃Si)CH₂,⁴ and 2-(Me₂NCH₂)C₆H₄⁵] are known, and we hypothesize that they may demonstrate similar reactivity with nitriles in the presence of HOTf. This could provide an avenue for the discovery of strategic colouration in heavier pnictogen systems, which may also provide interesting structural correlations as bonding orbitals become more *p*-based while lone pairs become more *s*-based (Figure 5.1).

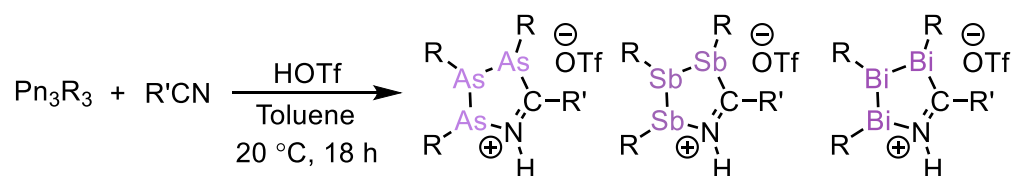


Figure 5.1 Proposed reaction of cyclic pnictogens, Pn₃R₃ (Pn = as, Sb, Bi) with nitriles in the presence of triflic acid.

The rings formed through the P₃R₃ cycloadditions with nitriles are also extremely electron rich, and may be capable of undergoing reversible redox chemistry. Preliminary results of cyclic voltammetry (1.0 M [NBu₄][PF₆] in THF doped with ferrocene, with platinum working and counter electrode with a Ag pseudo-reference) of [P₃Tripp₃PhCN-H][OTf] demonstrate that the species undergoes a first one-electron reduction to release ½ H₂ and generate the P₃Tripp₃PhCN free base (confirmed by the reaction of [P₃Tripp₃PhCN-H][OTf] with CoCp₂), while a second one-electron reduction results in unspecified decomposition (Figure 5.2, top). Methylated ring [P₃Tripp₃PhCN-Me][OTf] also undergoes a one electron reduction in THF to decompose the ring to form Tripp-P=P-Tripp, also confirmed by the reaction of [P₃Tripp₃PhCN-Me][OTf] with CoCp₂ (Figure 5.2, bottom). Oxidation of these rings are not visible given that THF decomposes before any electron transfers are visible, however future work will look to the oxidation of these electron-rich species with experimental oxidation reagents.

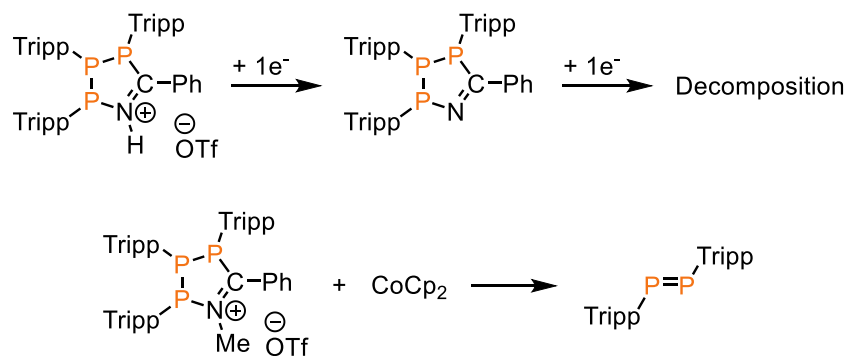


Figure 5.2 Redox phenomena in sterically-encumbered, cationic 1-aza-2,3,4-triphospholene rings

5.2 Exploring the scope of the P₃^tBu₃ cycloaddition

Chapter 3 describes the reaction of P₃^tBu₃ and [P₃^tBu₃Me][OTf] with unsaturated substrates in an effort to expand upon the preliminary reaction scope reported by our group.^{6, 7} While the scope of the P₃^tBu₃ cycloaddition in the presence of HOTf is proven to be limited to XylNC and ^tBuNCO, both of which bear an exocyclic amine, there is still unexplored chemical space in which this reaction may be applicable. Carbodiimide showed selective insertion which was hampered by degradation by HOTf, however the use of non-coordinating acids such as H{Al[OC(CF₃)₃]₄} may allow for insertion without degrading the carbodiimide. Other substrates that add with specificity to the cyclic phosphane scaffold are formed of unsaturated bonds between C/N/O. As such, we hypothesize that other substrates in this vein, such as gases N₂O, CO, and CO₂ and molecules like diazonium salts, may undergo addition with P₃^tBu₃ in the presence of HOTf or with [P₃^tBu₃Me][OTf] (see proposed examples in Figure 5.3, left). Preliminary results show that the reaction of diazonium salt [*p*-MeOC₆H₄-N₂][OTf] with neutral P₃^tBu₃ in CH₂Cl₂ undergoes a selective cycloaddition to form a new AMX spin system which we hypothesize corresponds to the [3+1] cycloaddition product akin to the addition of isonitriles substrates (Figure 5.3, right).

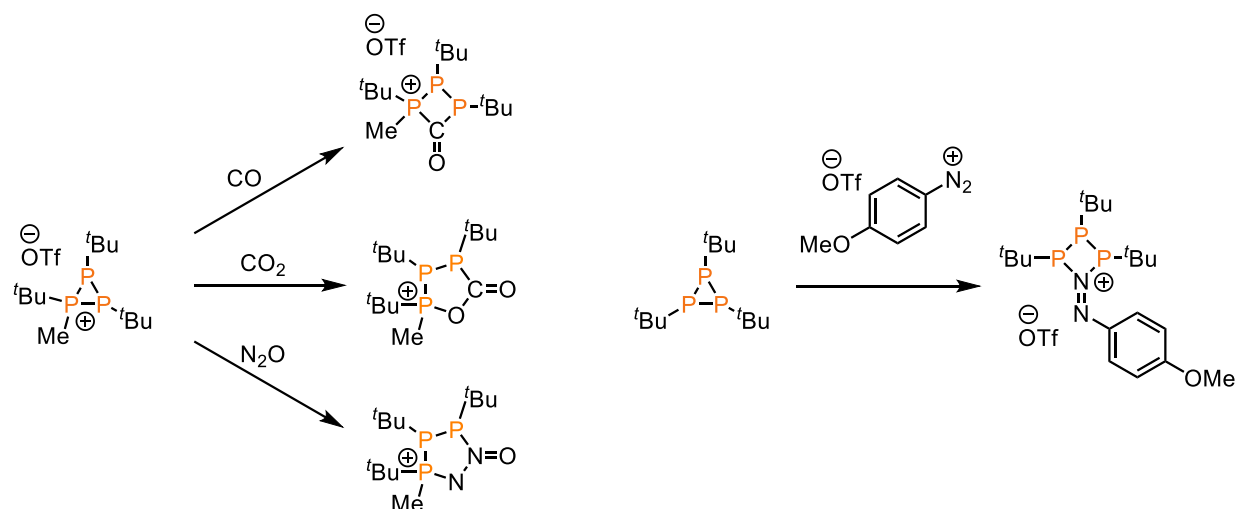


Figure 5.3 Possible reactions of P_3tBu_3 scaffolds with C/N/O gases (left) and diazonium salt (right)

Our attempts at forming ring systems by adding unsaturated substrates with third row main group elements, such as $R-C\equiv P$ and $R-N=S=O$, were unsuccessful. However, we hypothesize that P_3tBu_3 cycloadditions with unsaturated bonds with elements other than C/N/O may be accessible through the use of inherently charged substrates. For example, recently discovered cyaphide anions of the form $^-C\equiv P$ have been shown to undergo cycloaddition with azides to form CPN_3 heterocycles,⁸ and we are currently investigating the reactivity of this substrate with P_3tBu_3 .

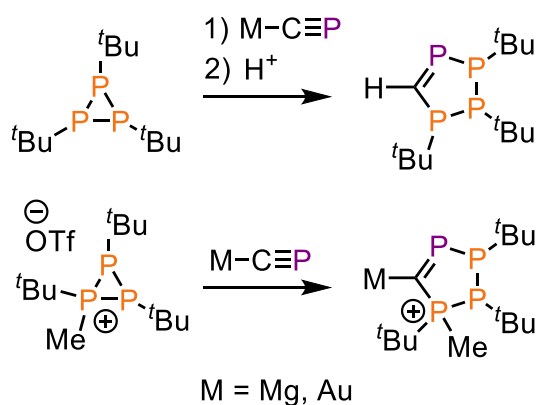


Figure 5.4 Potential cycloaddition products of cyaphide anion with cyclic phosphane

5.3 Investigations into the equilibration and ROP of cyclic P(V)–O–Si–O heterocycles, and methods for stabilizing RPO₂

The first part of chapter 4 describes the formation of hybrid phosphonate-siloxane heterocycles, and attempts are forming polymers with a P–O–Si–O main chain. These studies reveal that there is great potential for forming polymeric species for sterically unhindered derivatives if added stabilization can be provided, either in the form of crosslinking or through preventing back-biting phenomena. Consequently, we are exploring the synthesis of [PhP(O)–O–SiMeH–O]₂ and [PhP(O)–O–Si(Me)(HC=CH₂)–O]₂ rings, which are able to undergo Pt-catalyzed hydrosilylation when blended in a single ROP (Figure 5.5), or vulcanization with elemental sulfur to form crosslinks between vinyl chains in the latter example.⁹ We hypothesize that experimenting with a recent back-biting prevention strategy may also stabilize the polymers at high molar masses by limiting depolymerization phenomena due to any active polymer ends that may form in the driving conditions of thermal ROP.¹⁰ Furthermore, we will look to determine if polymeric phosphonate-siloxanes exhibit any flame retardancy, as synergistic effects between silicone and phosphorus flame retarding mechanism have resulted in such materials being proposed as excellent flame retardants.^{11, 12}

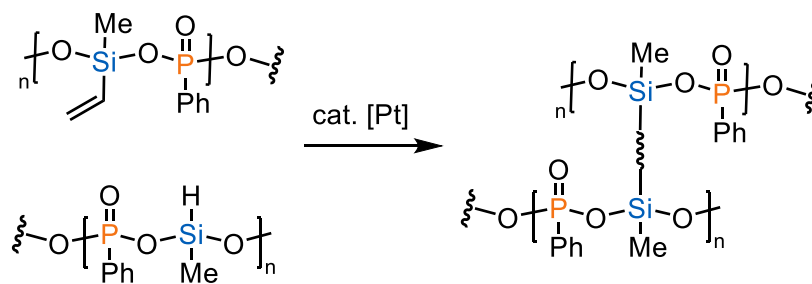


Figure 5.5 Possible route to P–O–Si–O polymer cross-linking.

The second part of chapter 4 looks to the stabilization of phosphonate materials. In the case of polyphosphonates, it appears the combination of *ortho*-methyl groups and *para*-substituted electronic modifications result in poor solubility and reactivity. Future work will involve the synthesis of unsubstituted aryl substituents to observe the effect of electronics alone. We also look to expand upon the phosphonate polymer family to determine the effect of replacing the aryl substituent with oxygen-based –OR substituents (to form “polyphosphates” of the form $[(RO)P(O)-O]_n$) and nitrogen-based –NR₂ substituents (to form “polyphosphoramidates” of the form $[(R_2N)P(O)-O]_n$), which may have unique recyclability or moisture stability compared to aryl phosphonates. In the case of stabilizing RPO₂ with M^SFluid^{tBu}, studies are ongoing, though we hypothesize that M^SFluid* will give the greatest chance of successfully isolating RPO₂.

5.4 References

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Appendix A.

Supplementary Information on Chapter 2

A.1 NMR Spectra

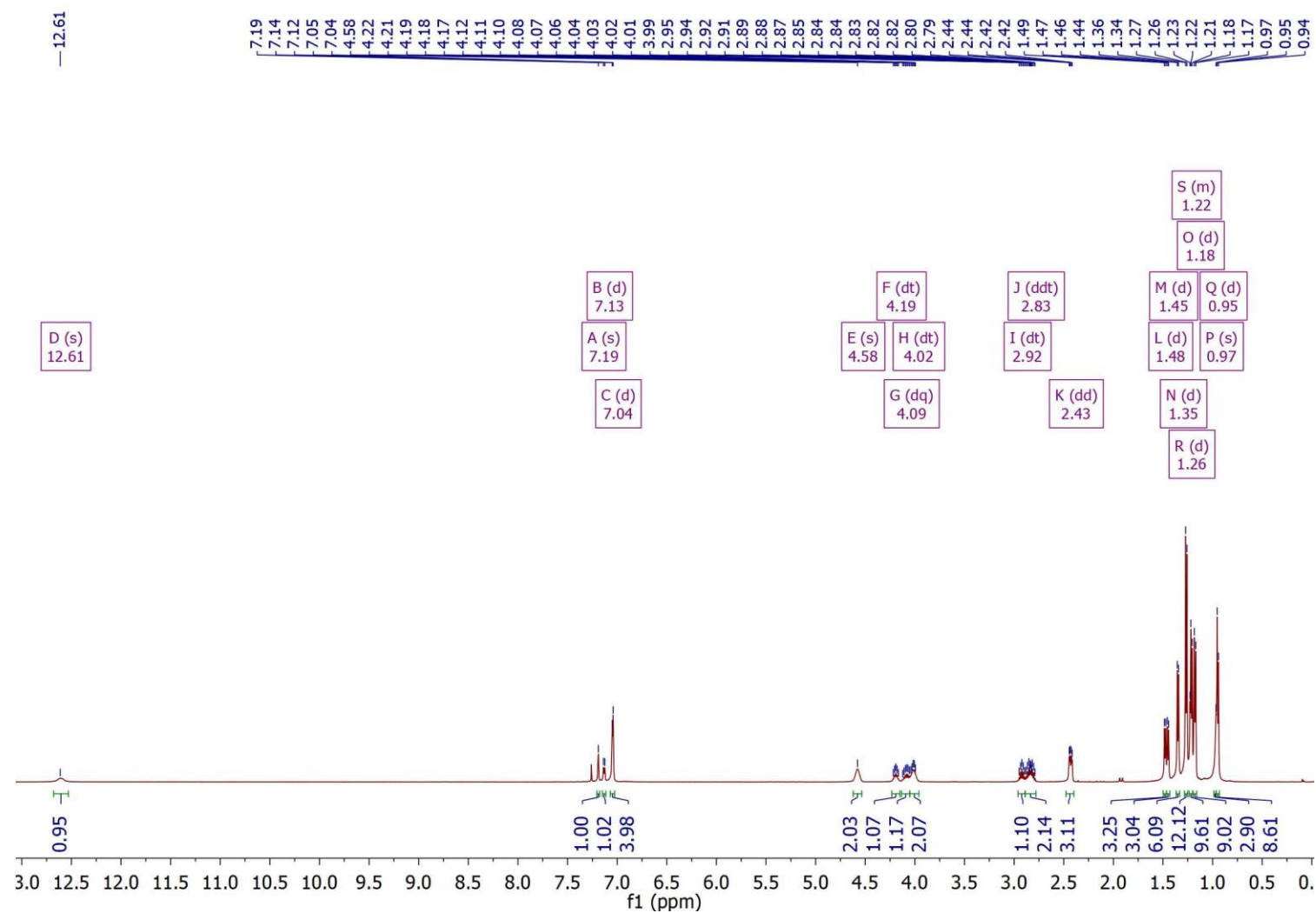


Figure A.1 ^1H NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Me}$)

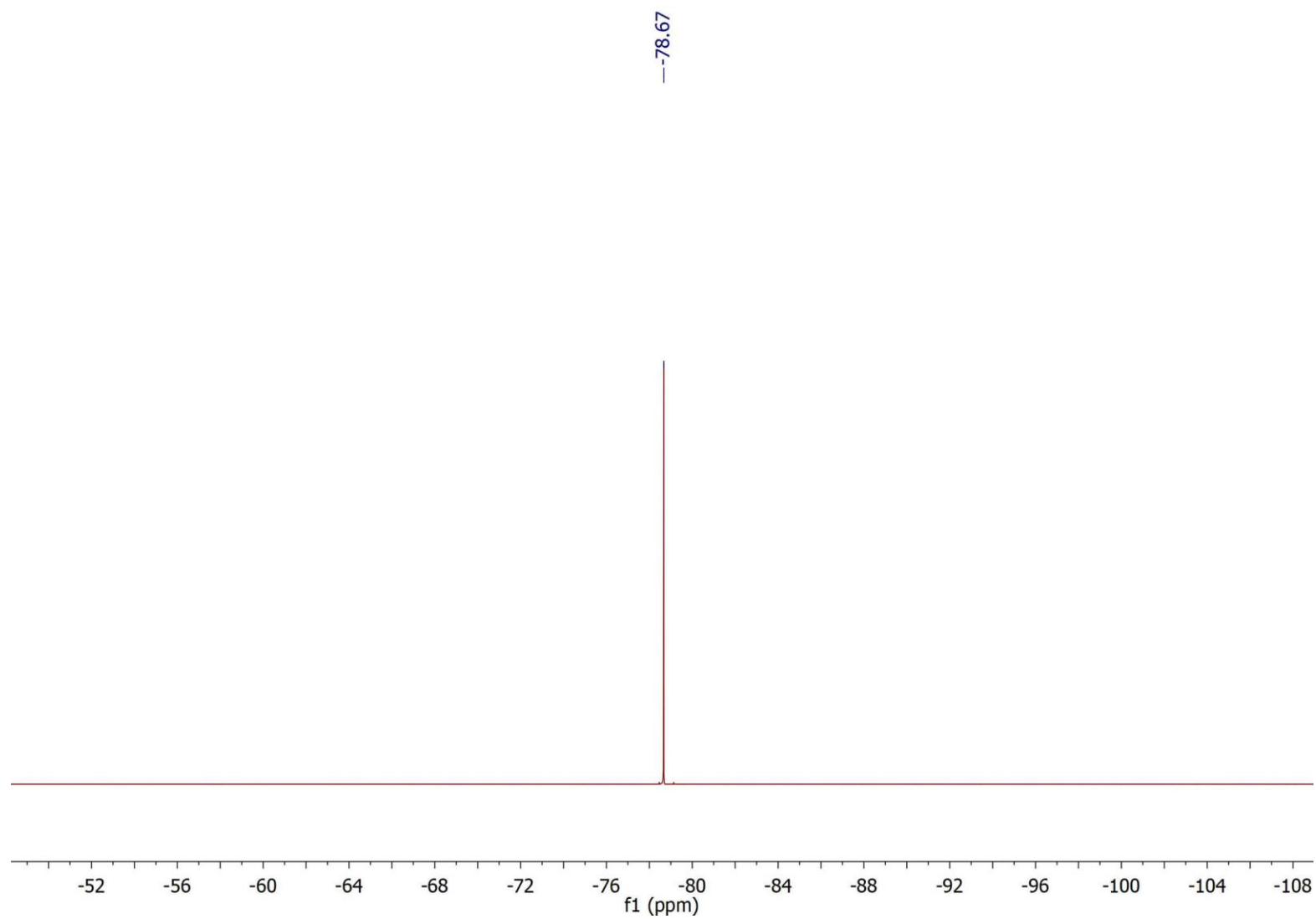


Figure A.2 ^{19}F NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Me}$)

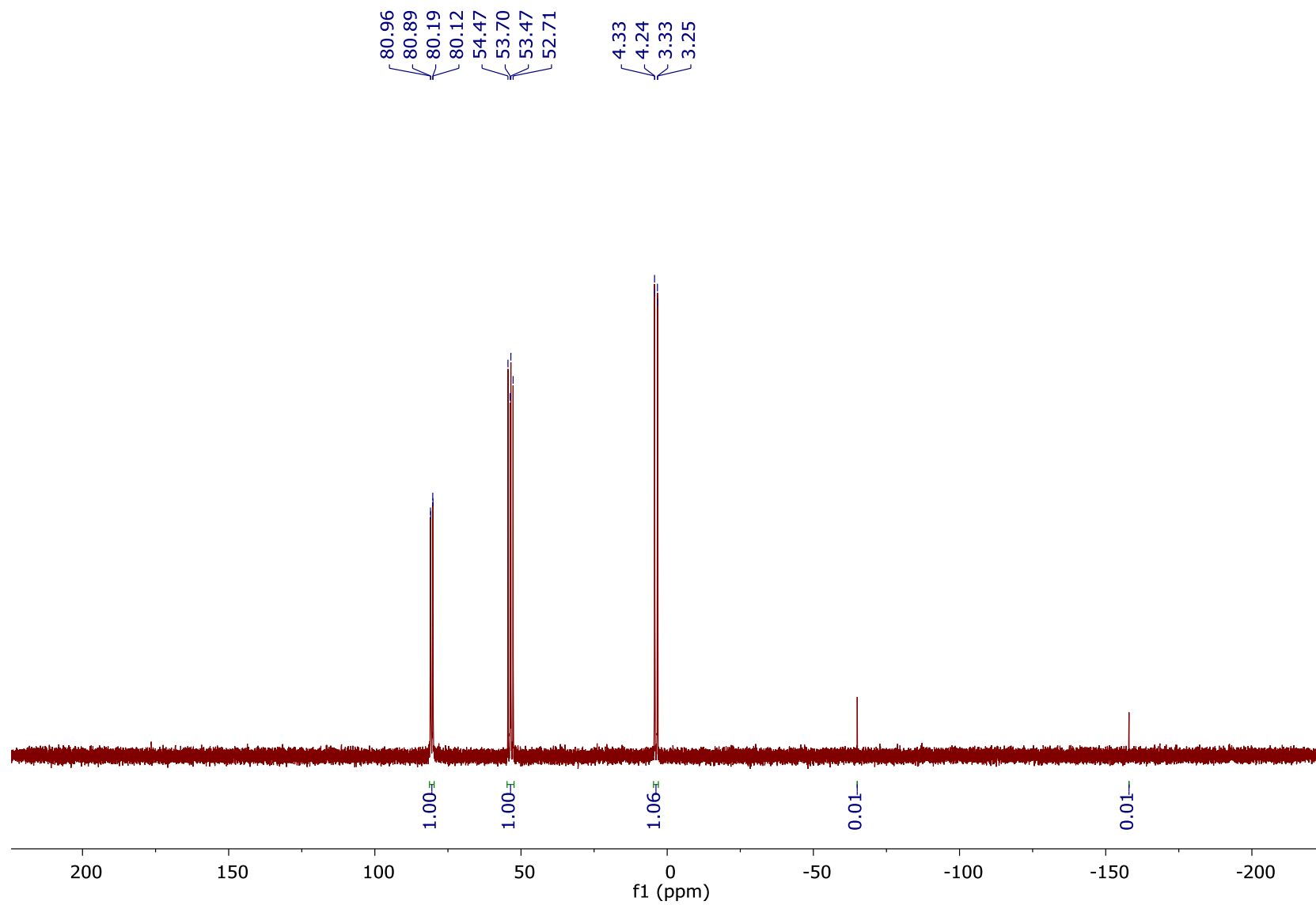


Figure A.3 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Me}$)

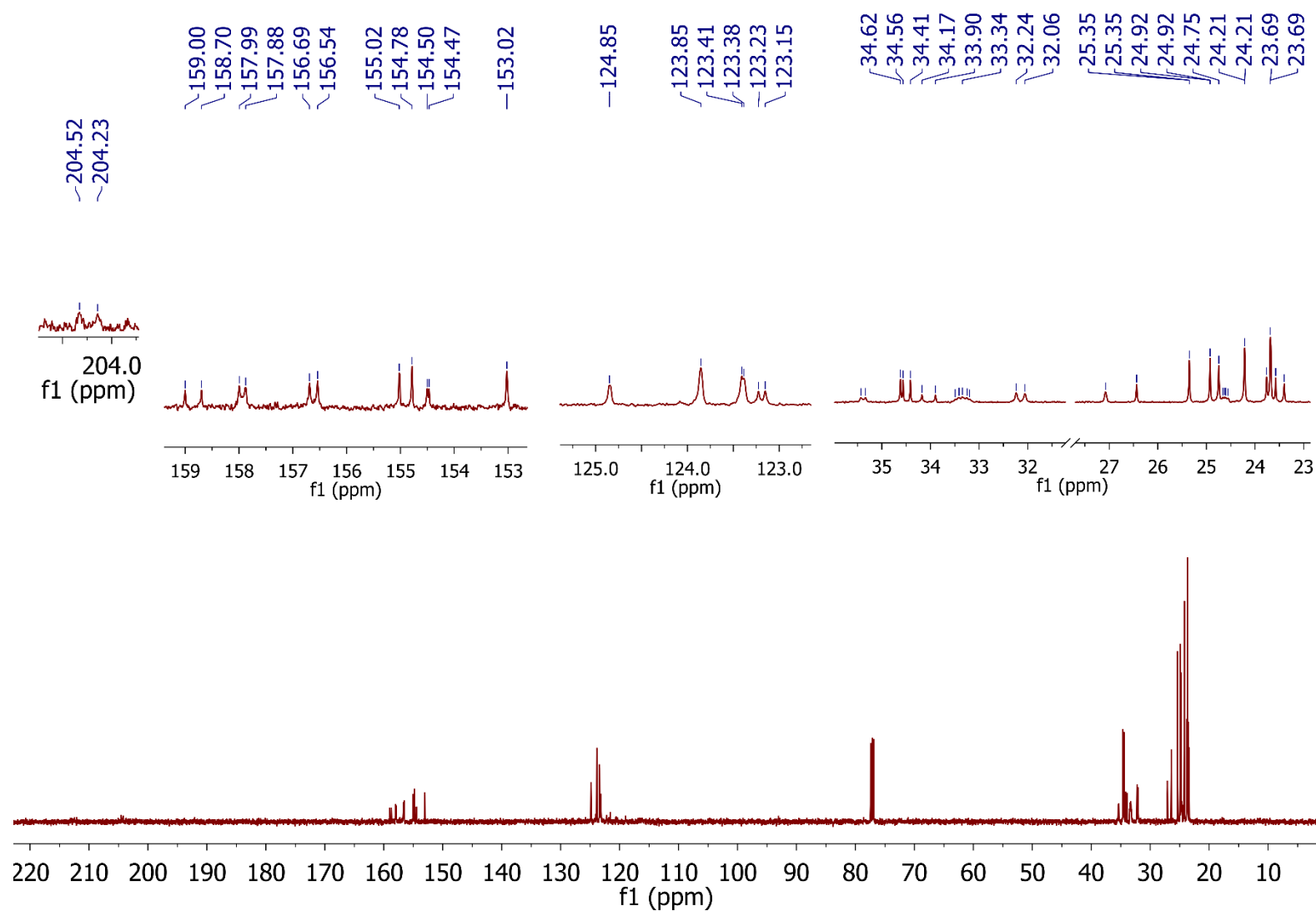


Figure A.4 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Me}$). Inset figures are magnifications of all peaks associated with $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Me}$) for added clarity, boxes denote multiplicity and chemical shifts for added clarity.

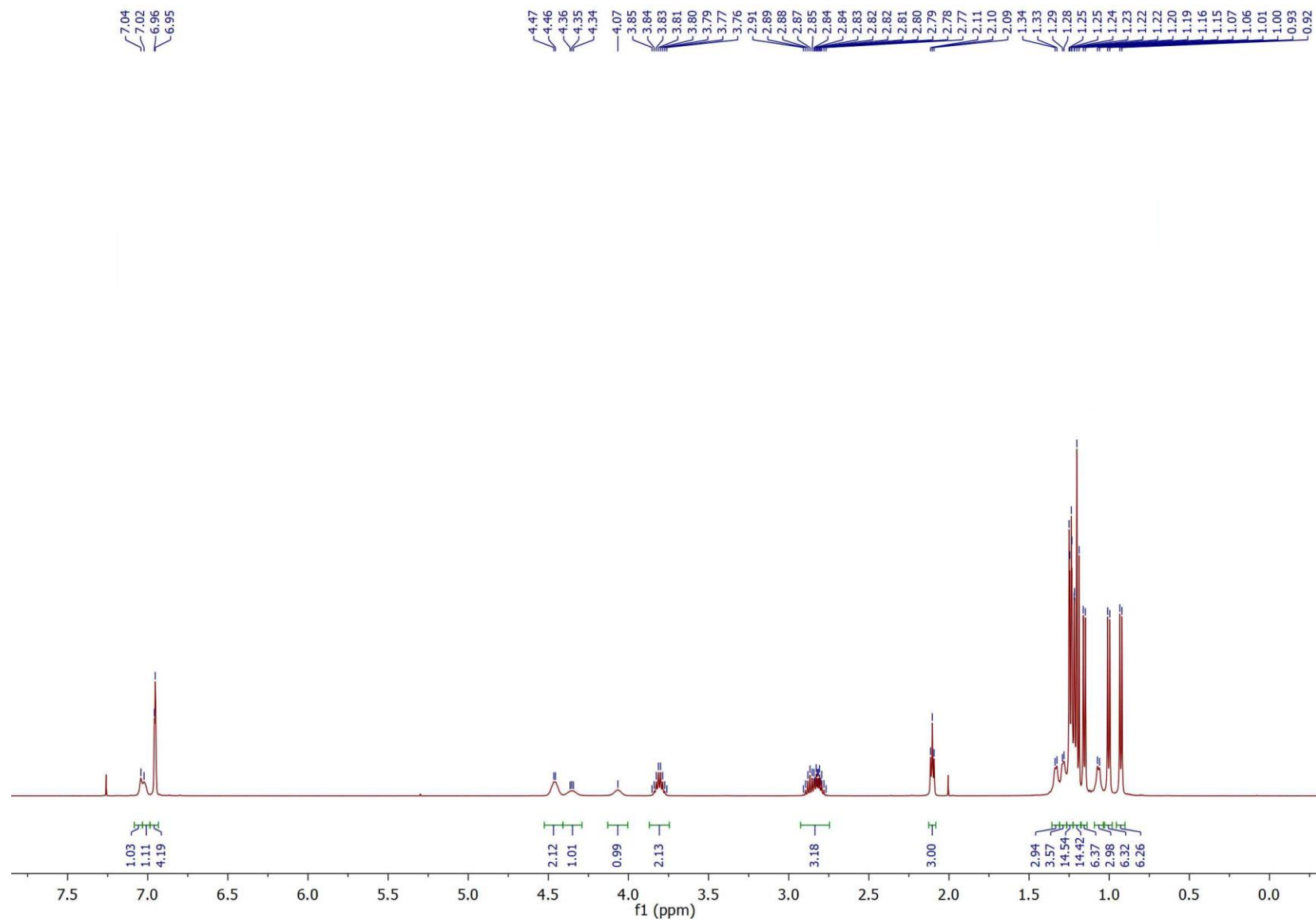


Figure A.5 ^1H NMR spectrum (CDCl_3) of compound 2_{Tripp} ($\text{R}' = \text{Me}$)

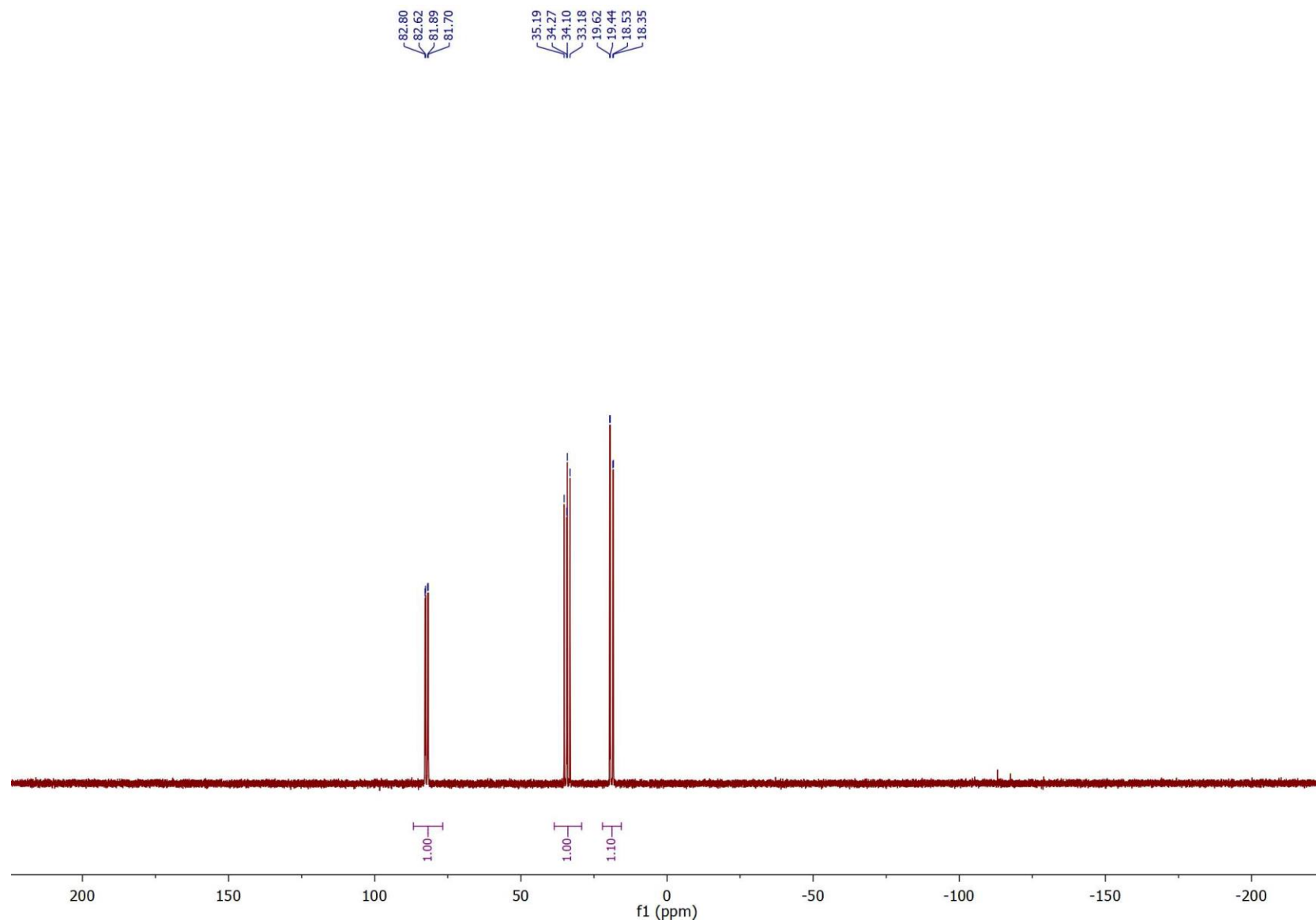


Figure A.6 ³¹P{¹H} NMR spectrum (CDCl₃) of compound **2_{Tripp}** (**R'** = **Me**)

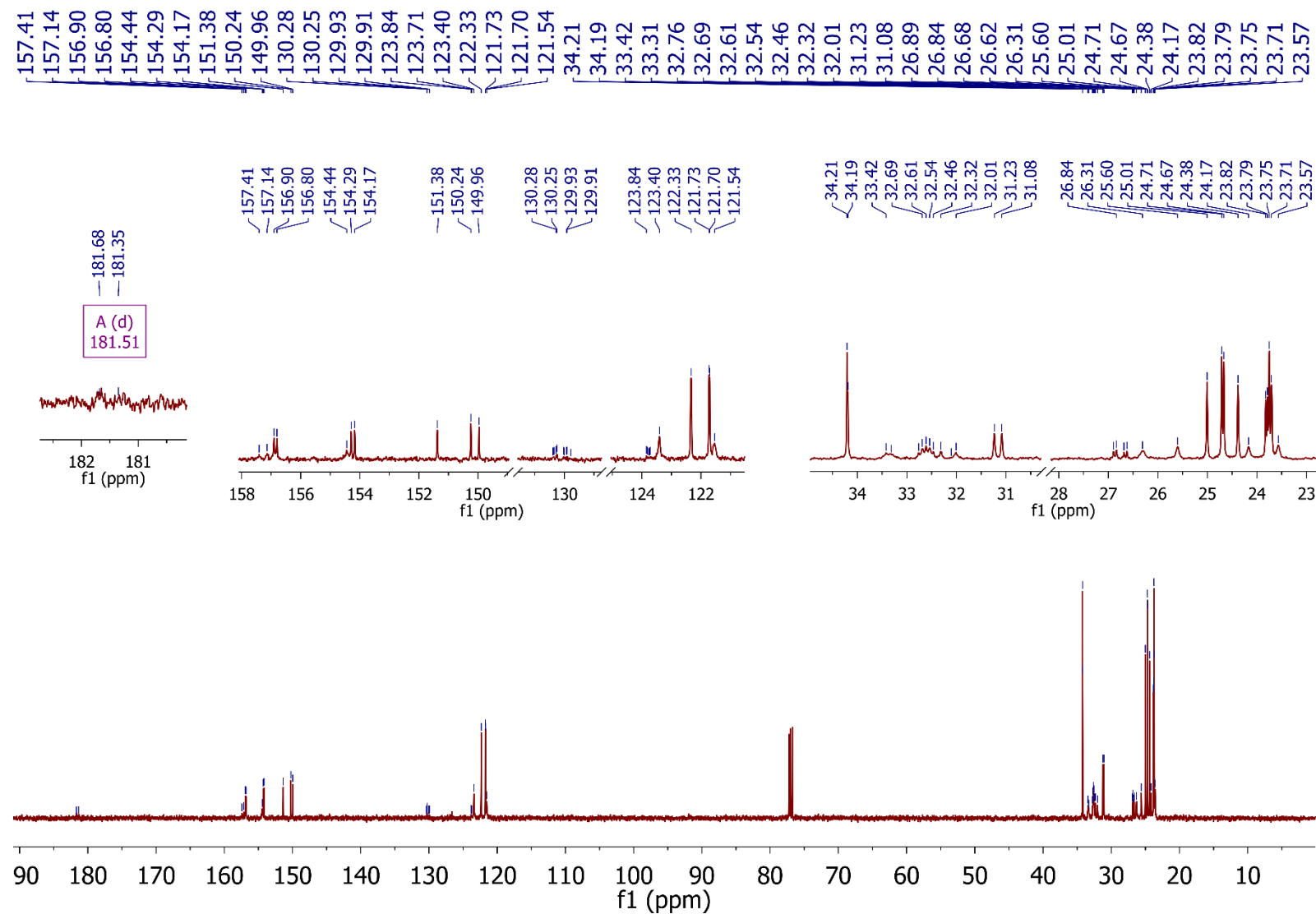


Figure A.7 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound **2_{Tripp}** (**R'** = **Me**). Inset figures are magnifications of all peaks associated with **2_{Tripp}** (**R'** = **Me**) for added clarity.

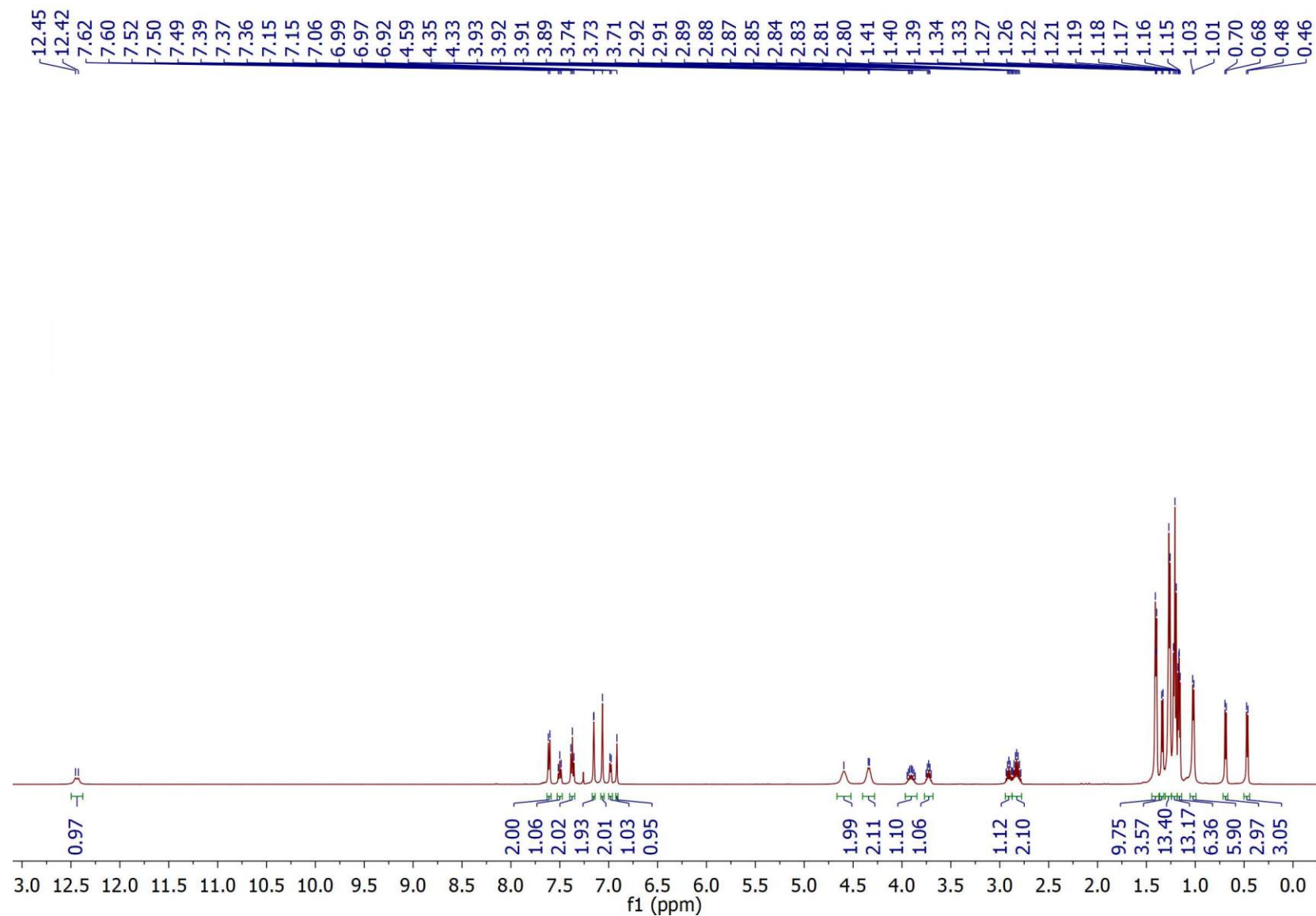


Figure A.8 ^1H NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$)

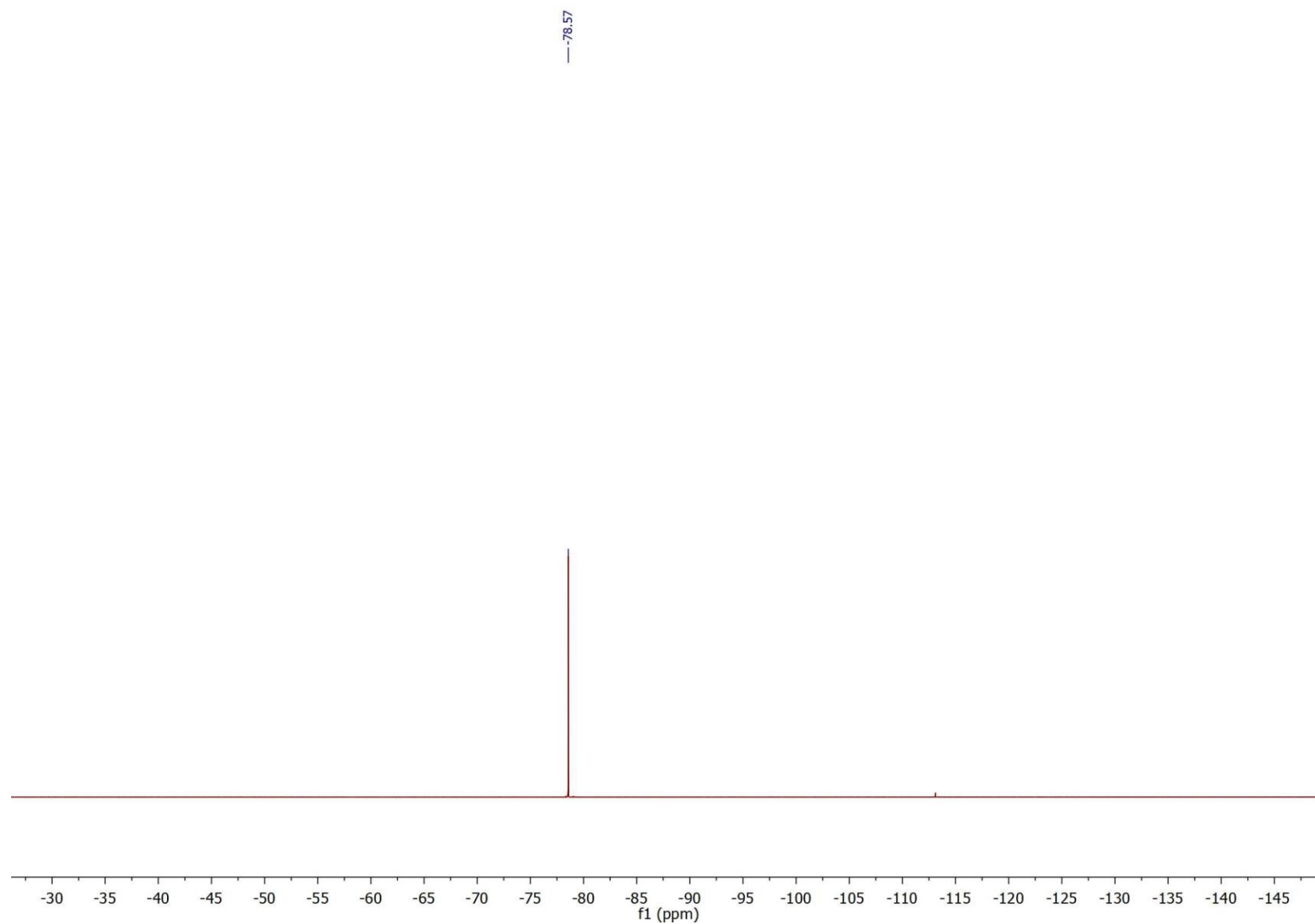


Figure A.9 ^{19}F NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$)

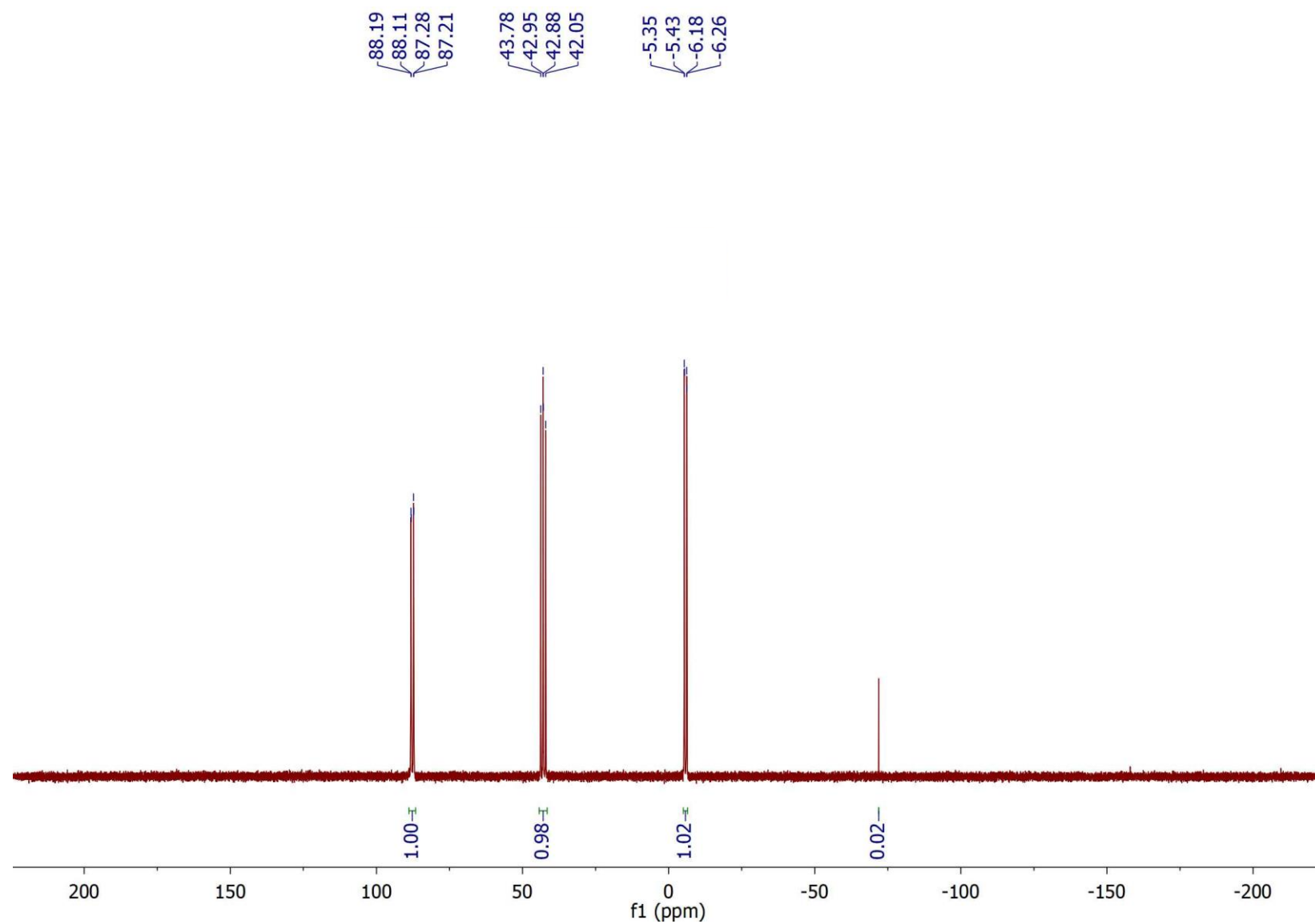


Figure A.10 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$)

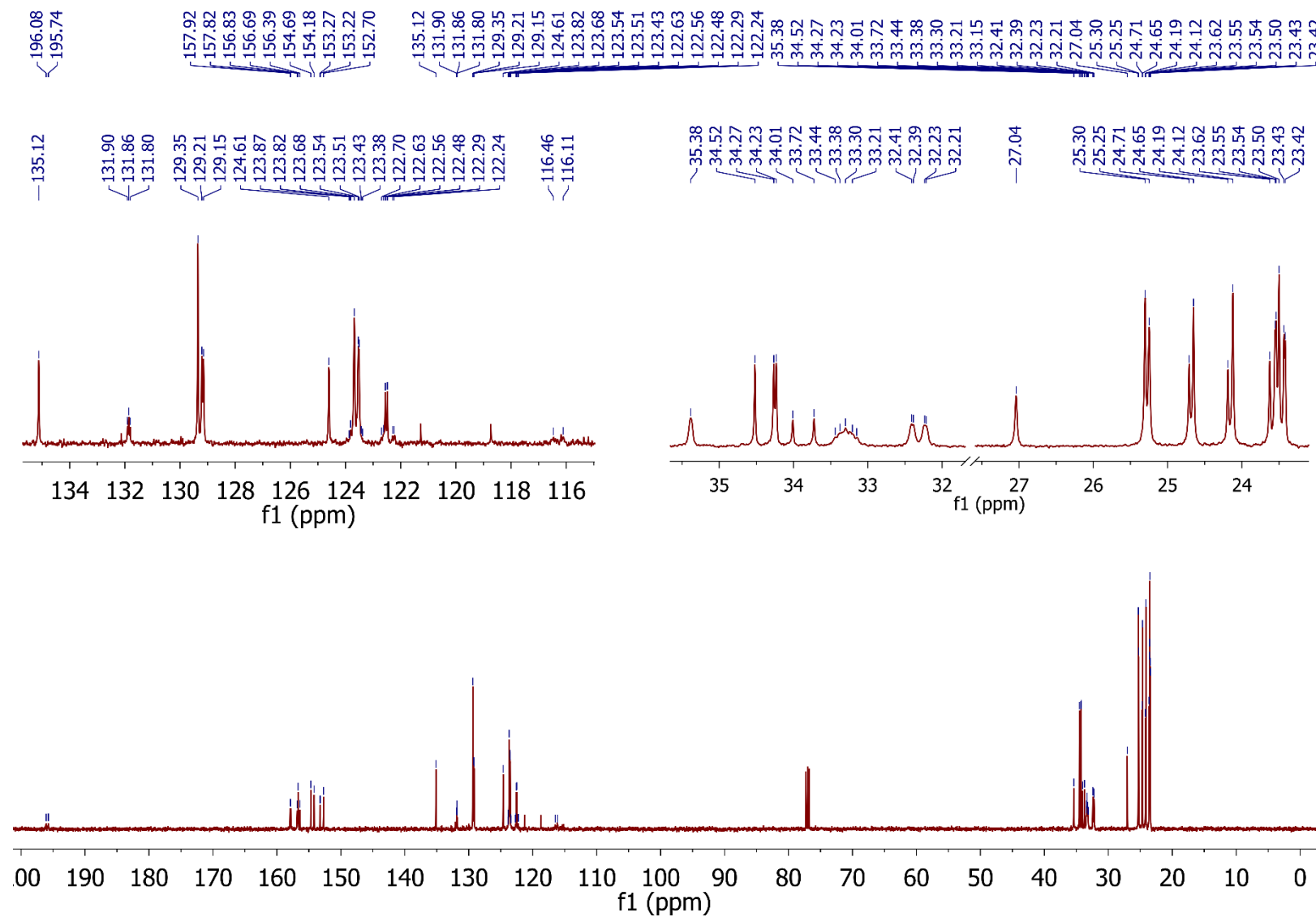


Figure A.11 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$). Inset figures are magnifications of some peaks associated with $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$) for added clarity.

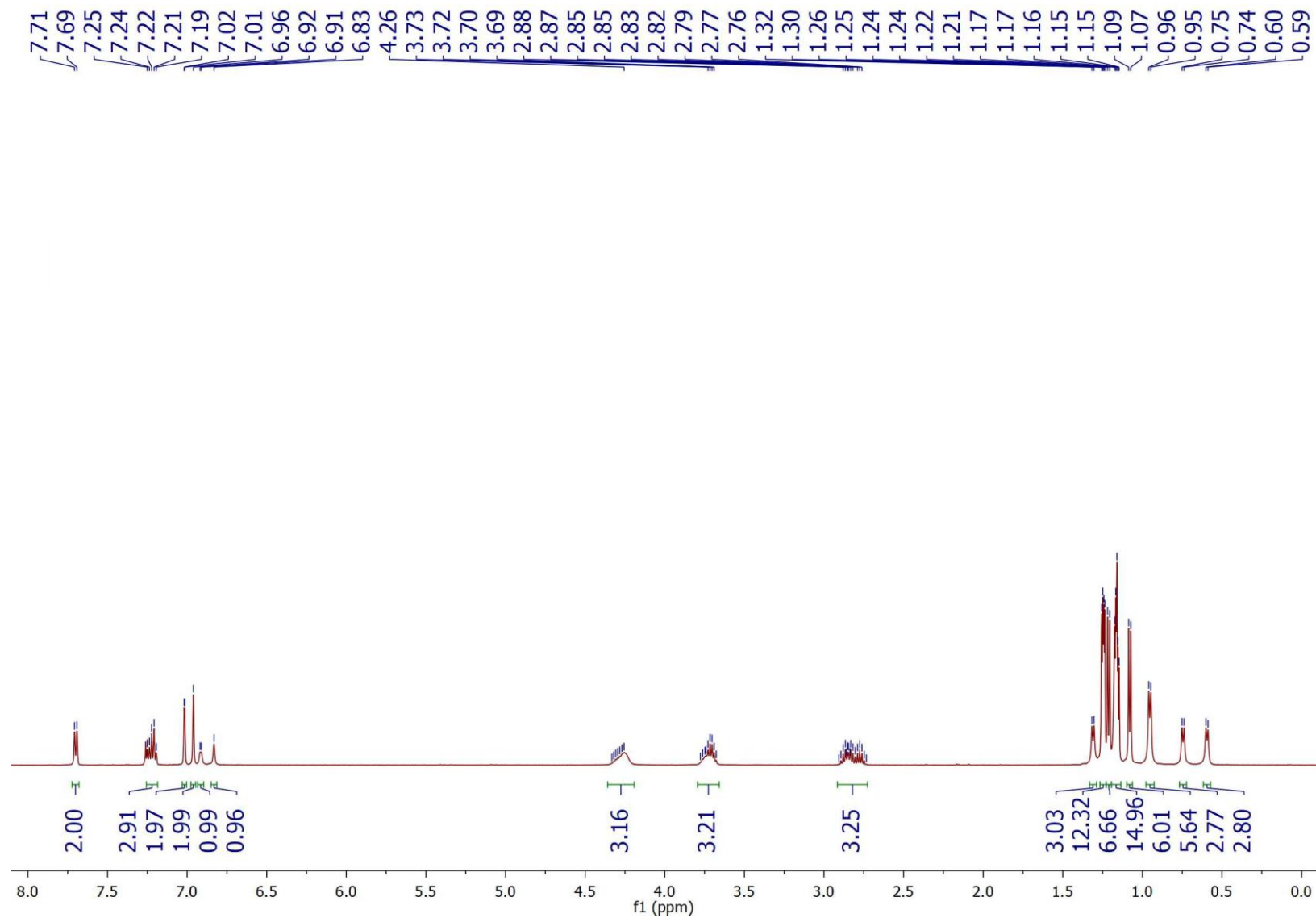


Figure A.12 ^1H NMR spectrum (CDCl_3) of compound 2_{Tripp} ($\text{R}' = \text{Ph}$)

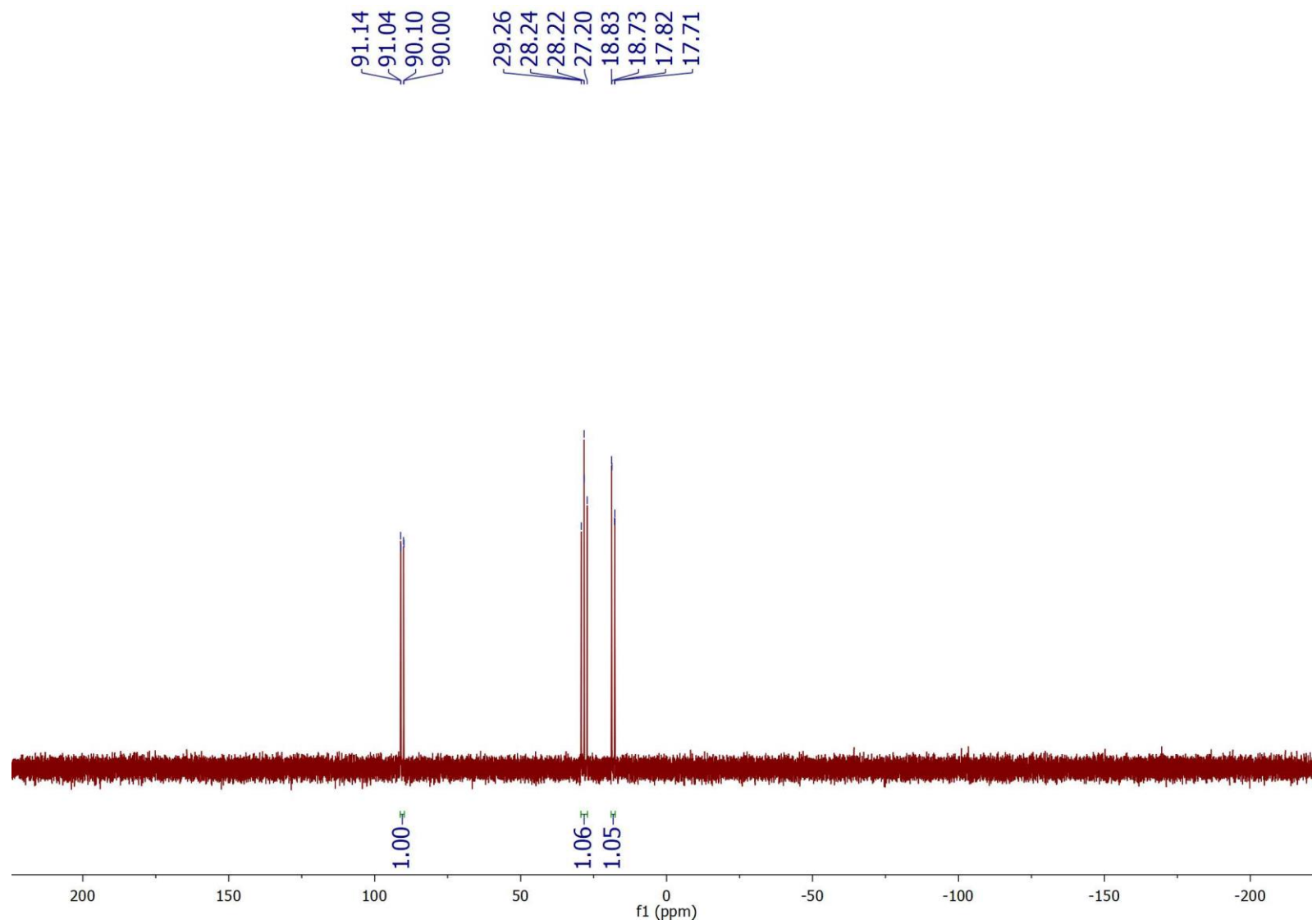


Figure A.13 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound **2_{Tripp}** (**R' = Ph**)

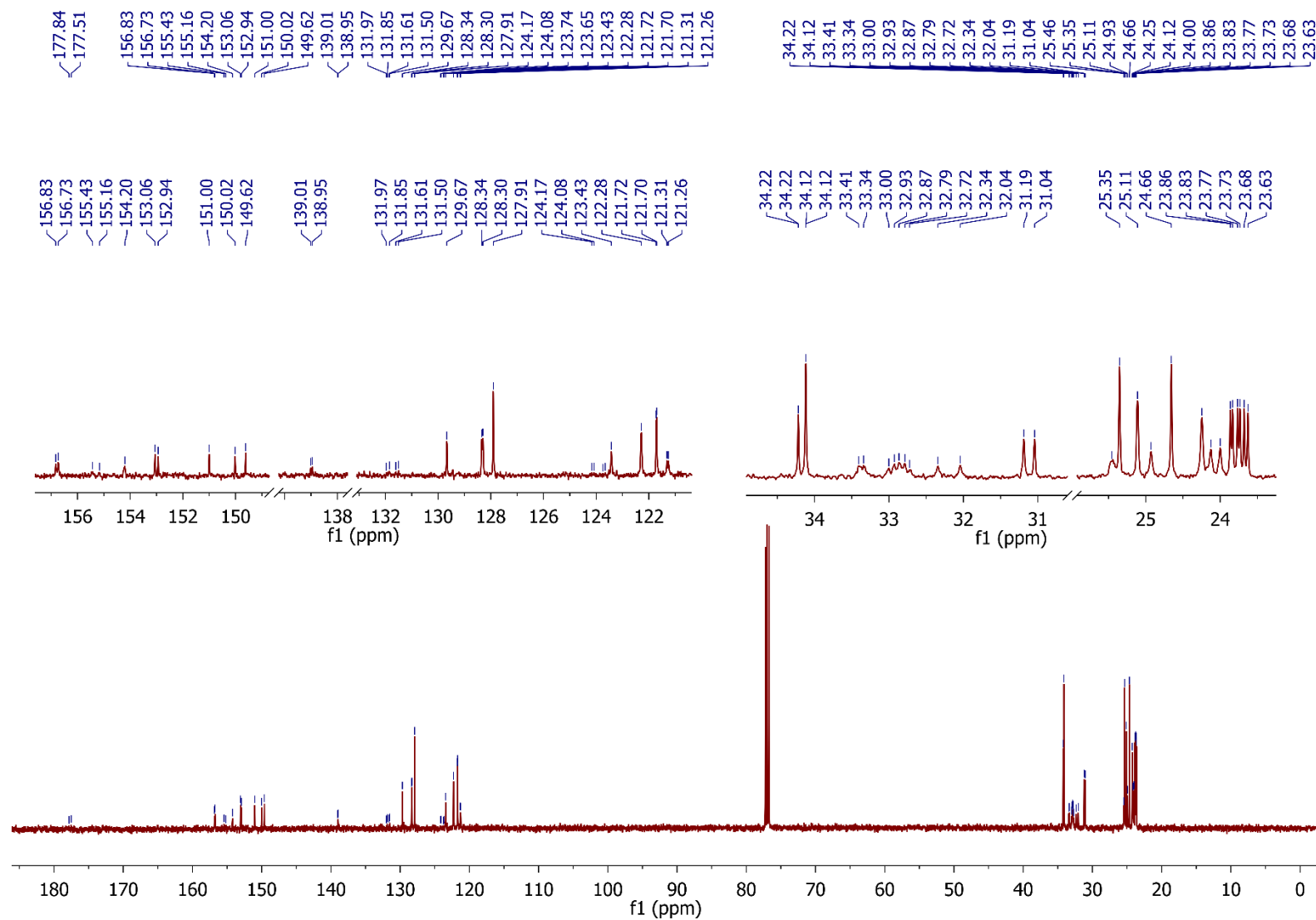


Figure A.14 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound 2_{Tripp} ($\text{R}' = \text{Ph}$). Inset figures are magnifications of some peaks associated with 2_{Tripp} ($\text{R}' = \text{Ph}$) for added clarity.

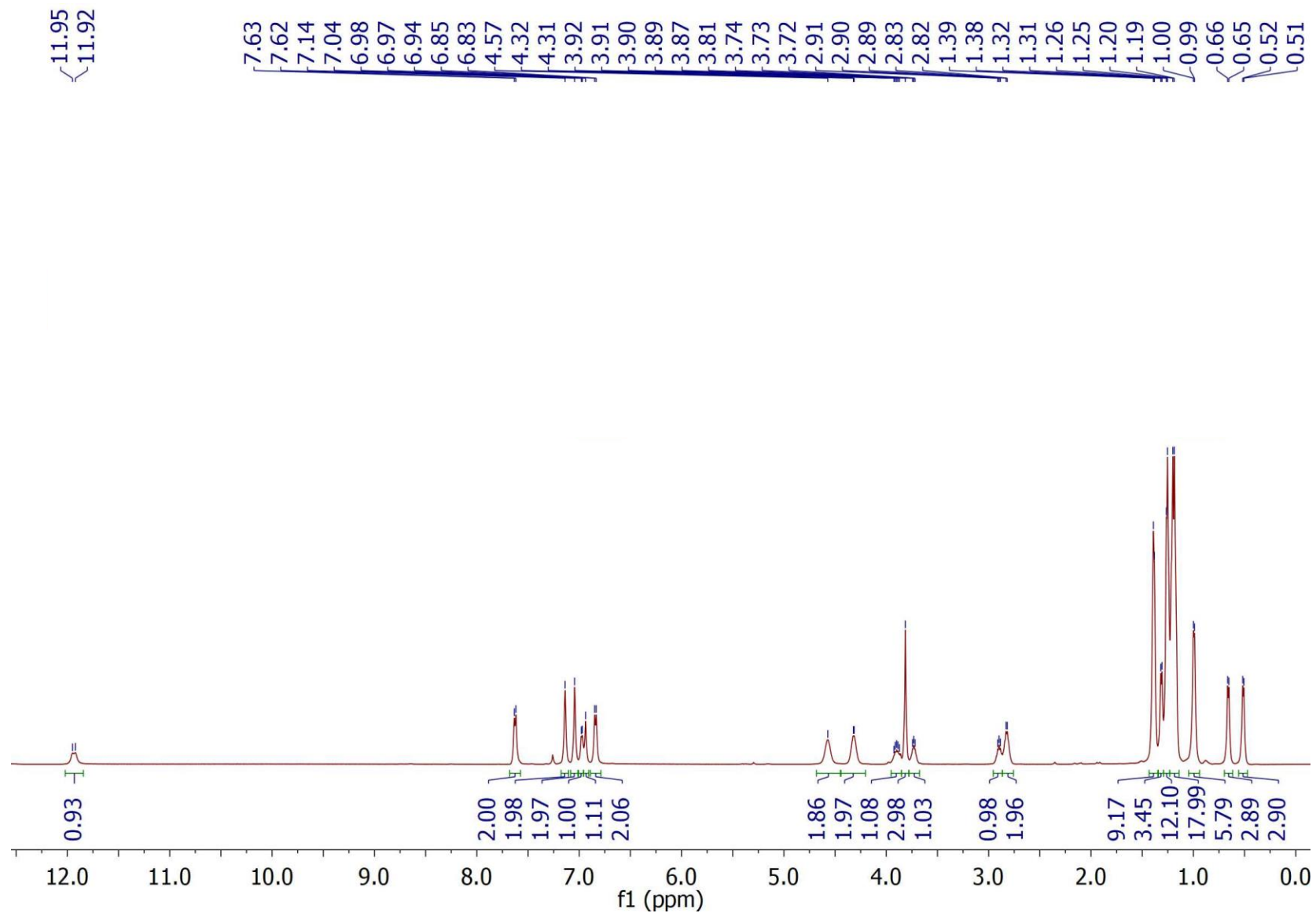


Figure A.15 ^1H NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-MeOC}_6\text{H}_4$)

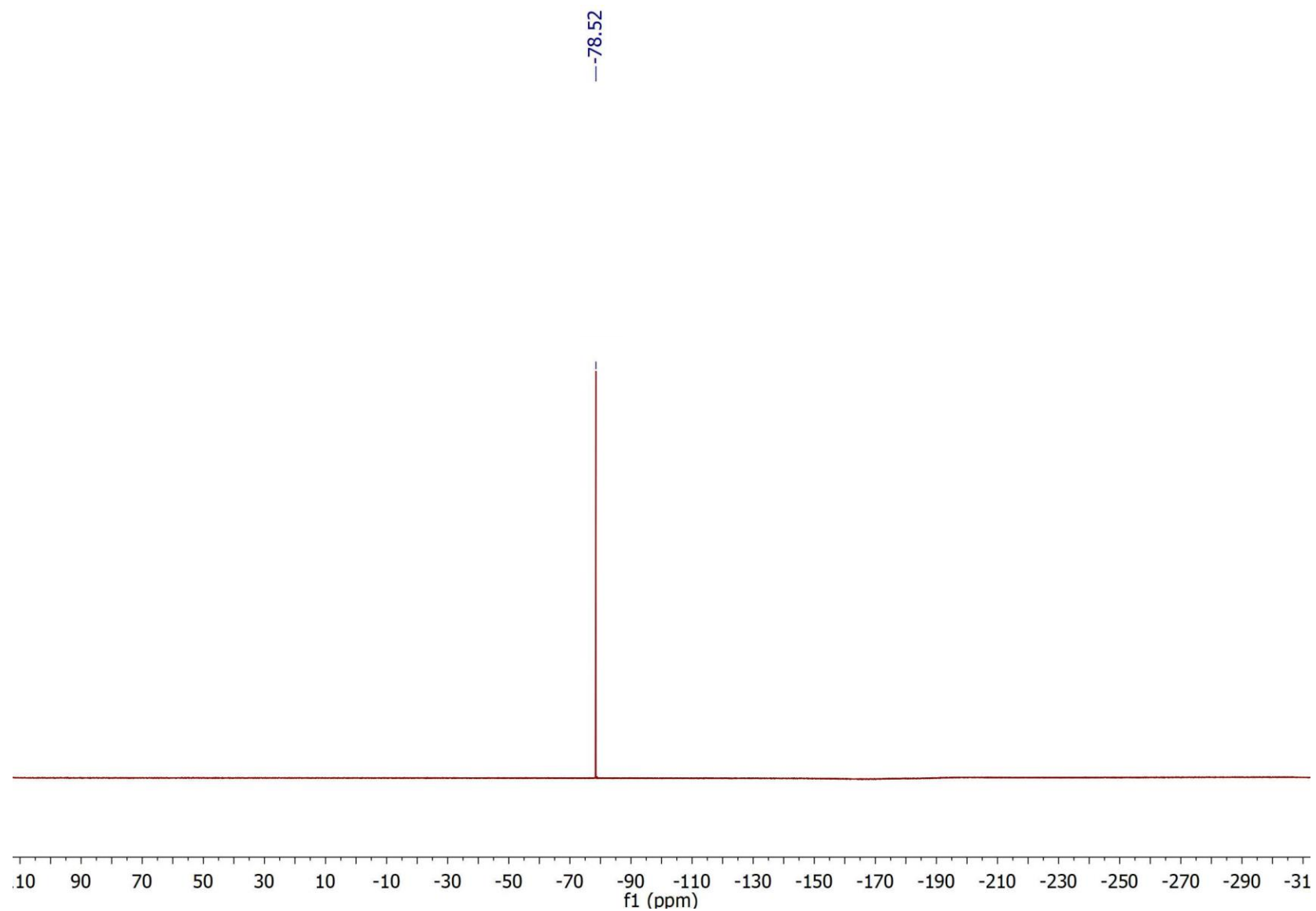


Figure A.16 ^{19}F NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-MeOC}_6\text{H}_4$)

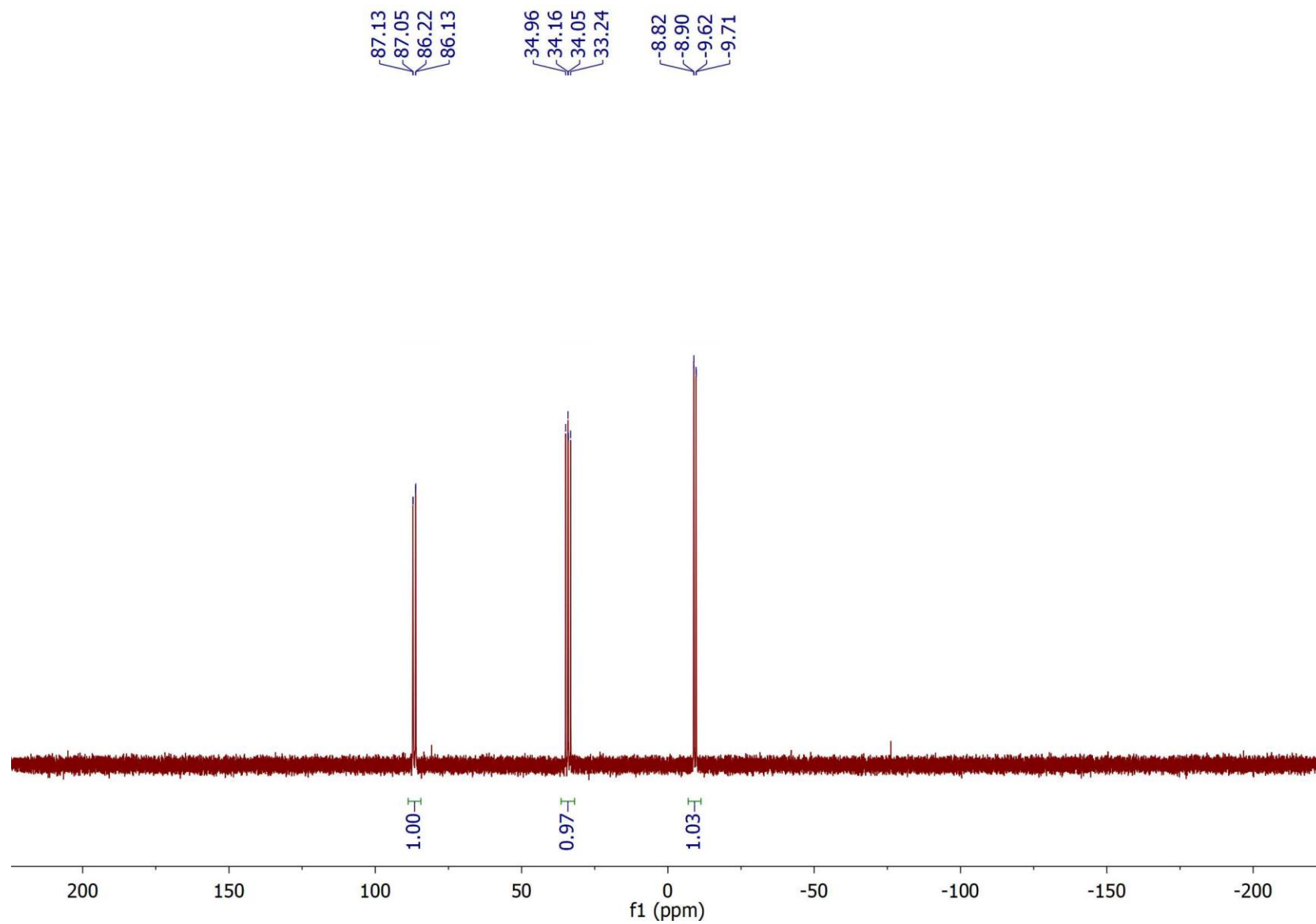


Figure A.17 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-MeOC}_6\text{H}_4$)

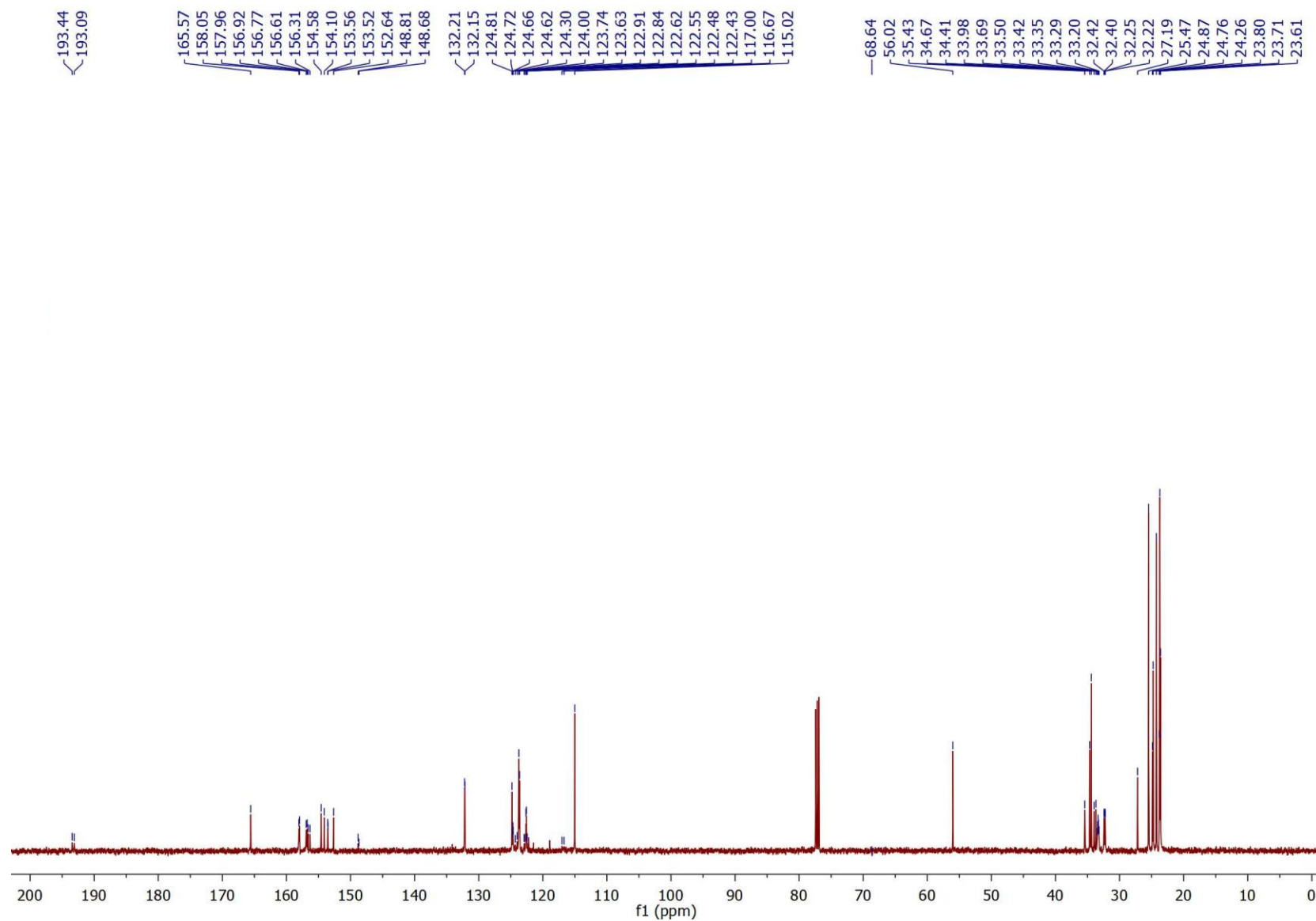


Figure A.18 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound $[1_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-MeOC}_6\text{H}_4$)

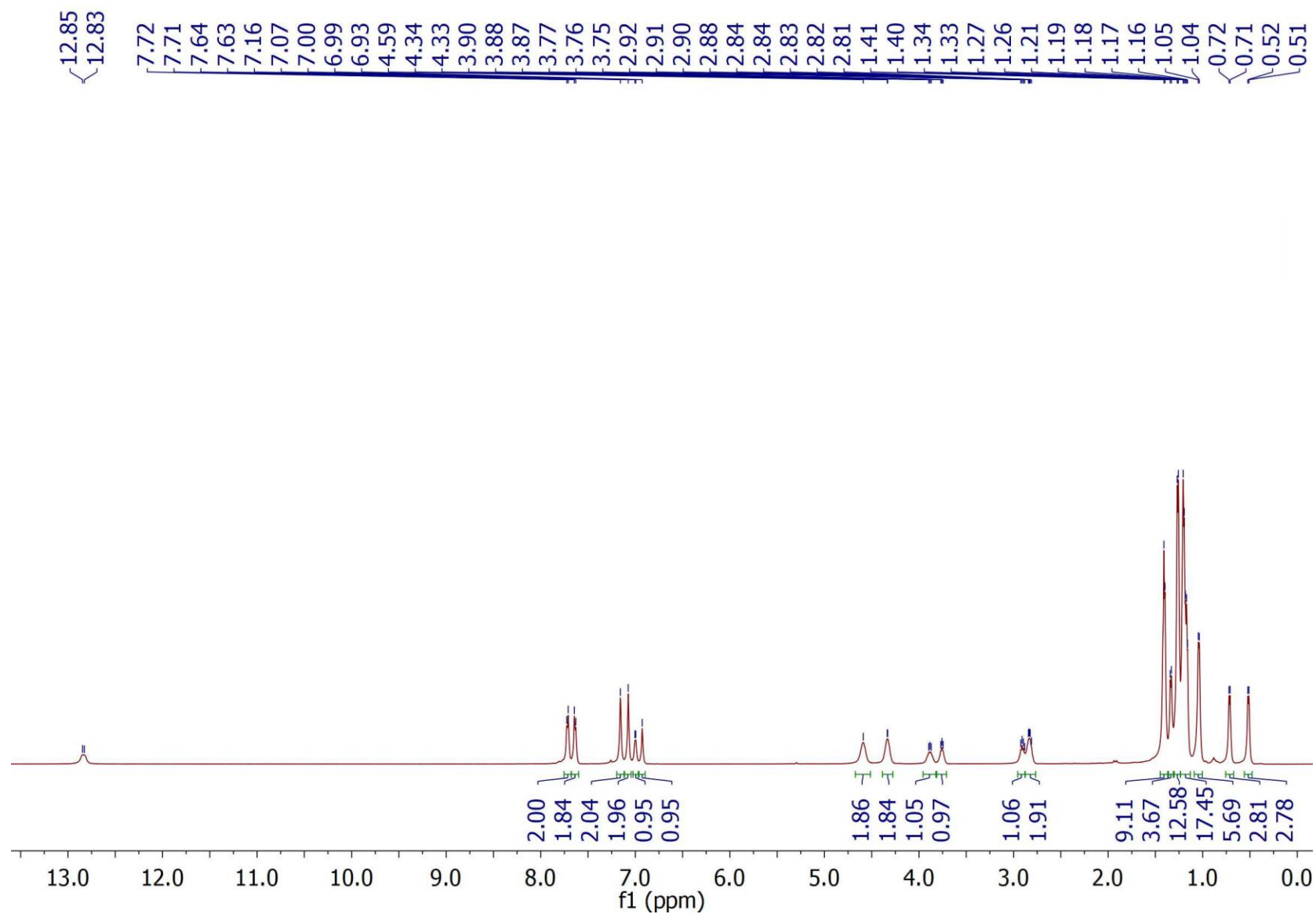


Figure A.19 ^1H NMR spectrum (CDCl_3) of compound $[1_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-CF}_3\text{C}_6\text{H}_4$)

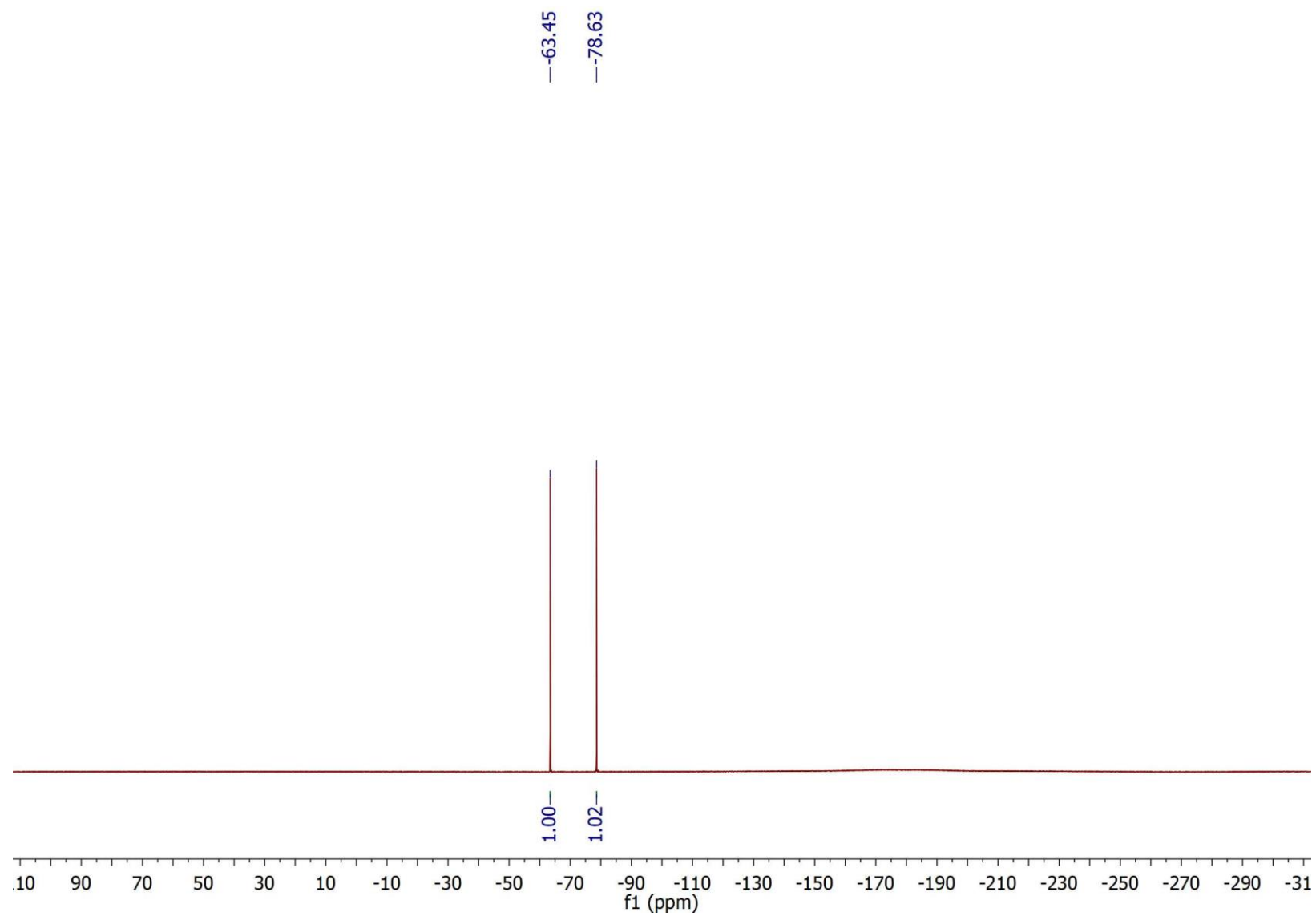


Figure A.20 ^{19}F NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-CF}_3\text{C}_6\text{H}_4$)

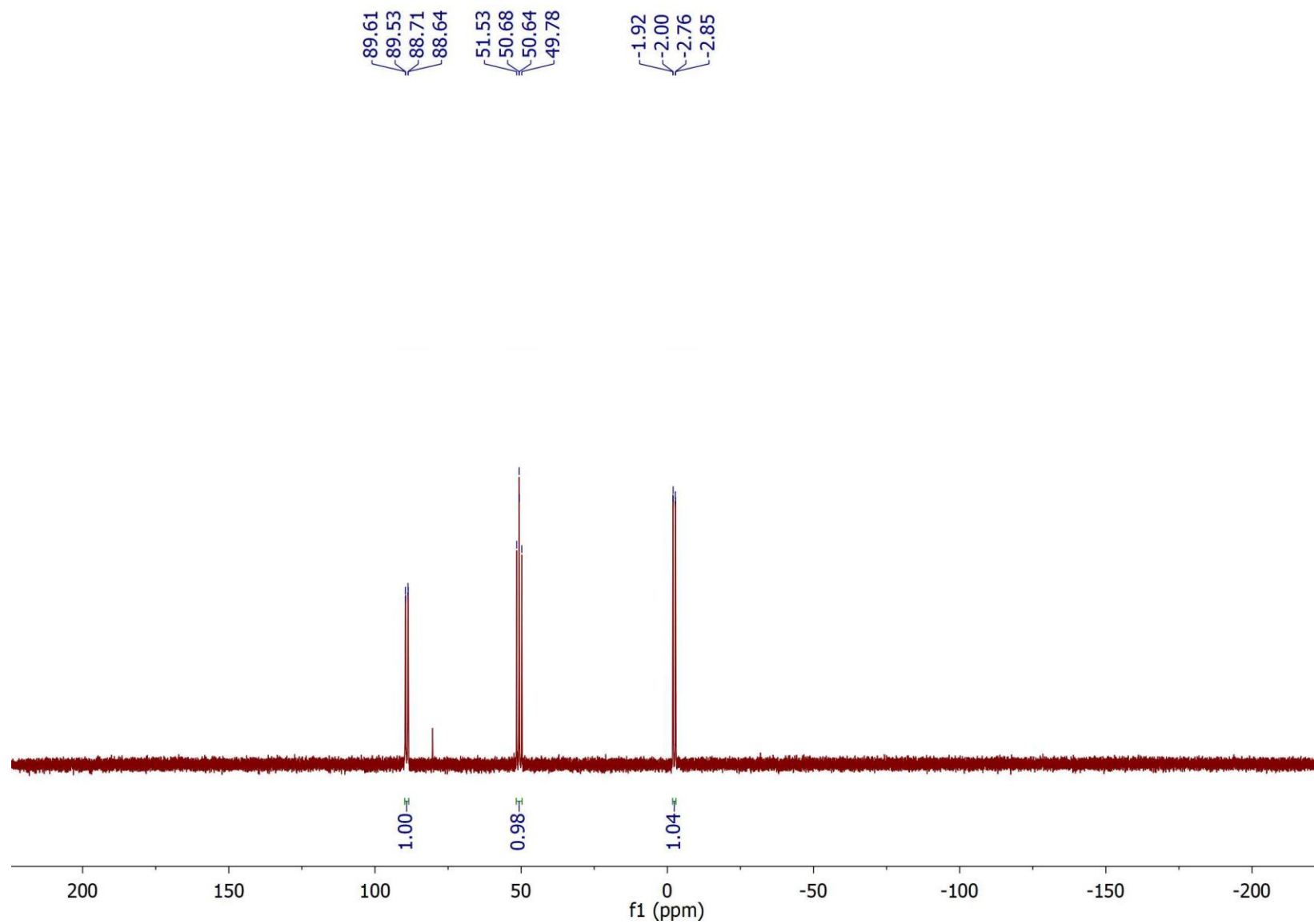


Figure A.21 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-CF}_3\text{C}_6\text{H}_4$)

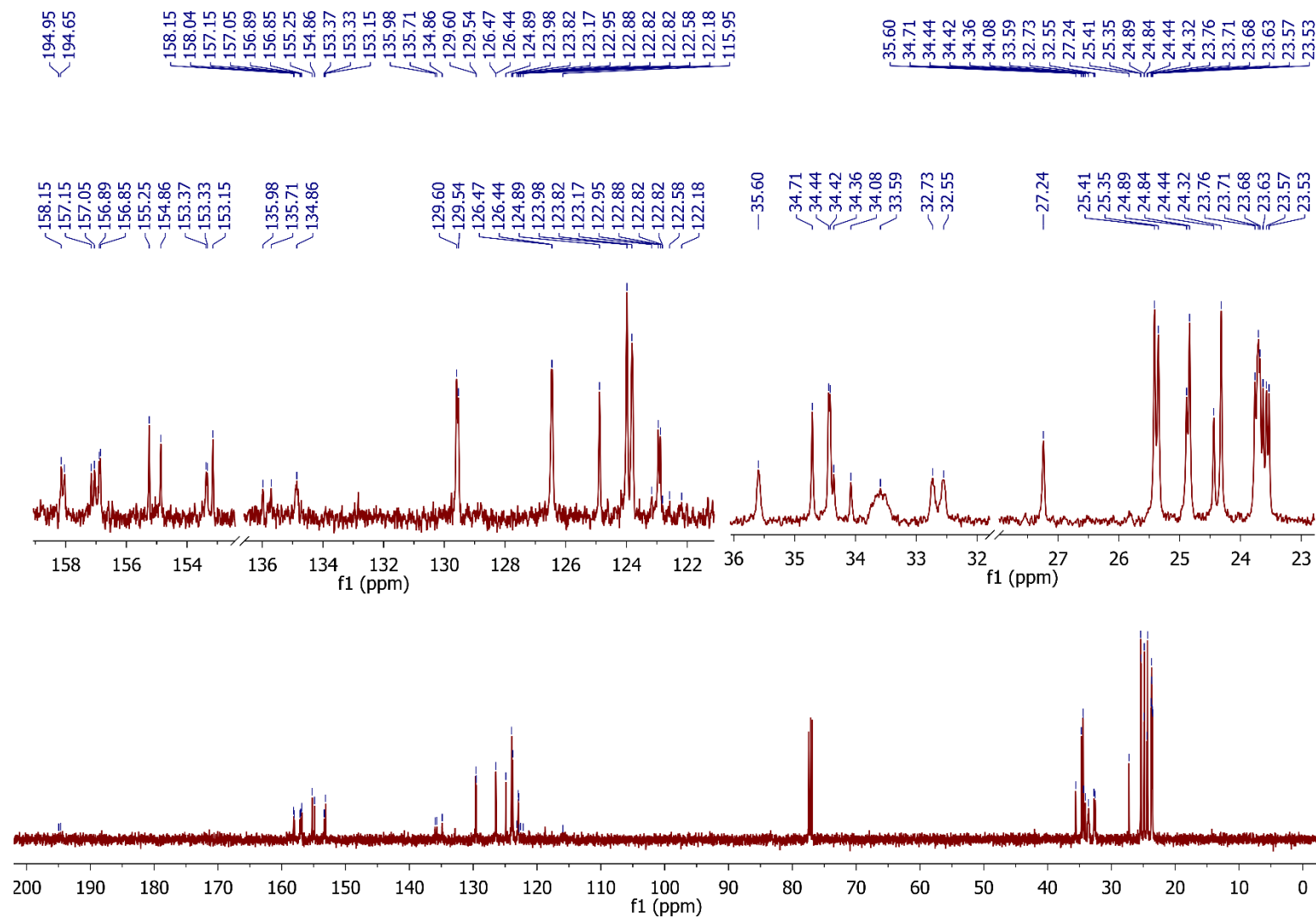


Figure A.22 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-CF}_3\text{C}_6\text{H}_4$). Inset figures are magnifications of some peaks associated with $[\mathbf{1}_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-CF}_3\text{C}_6\text{H}_4$) for added clarity.

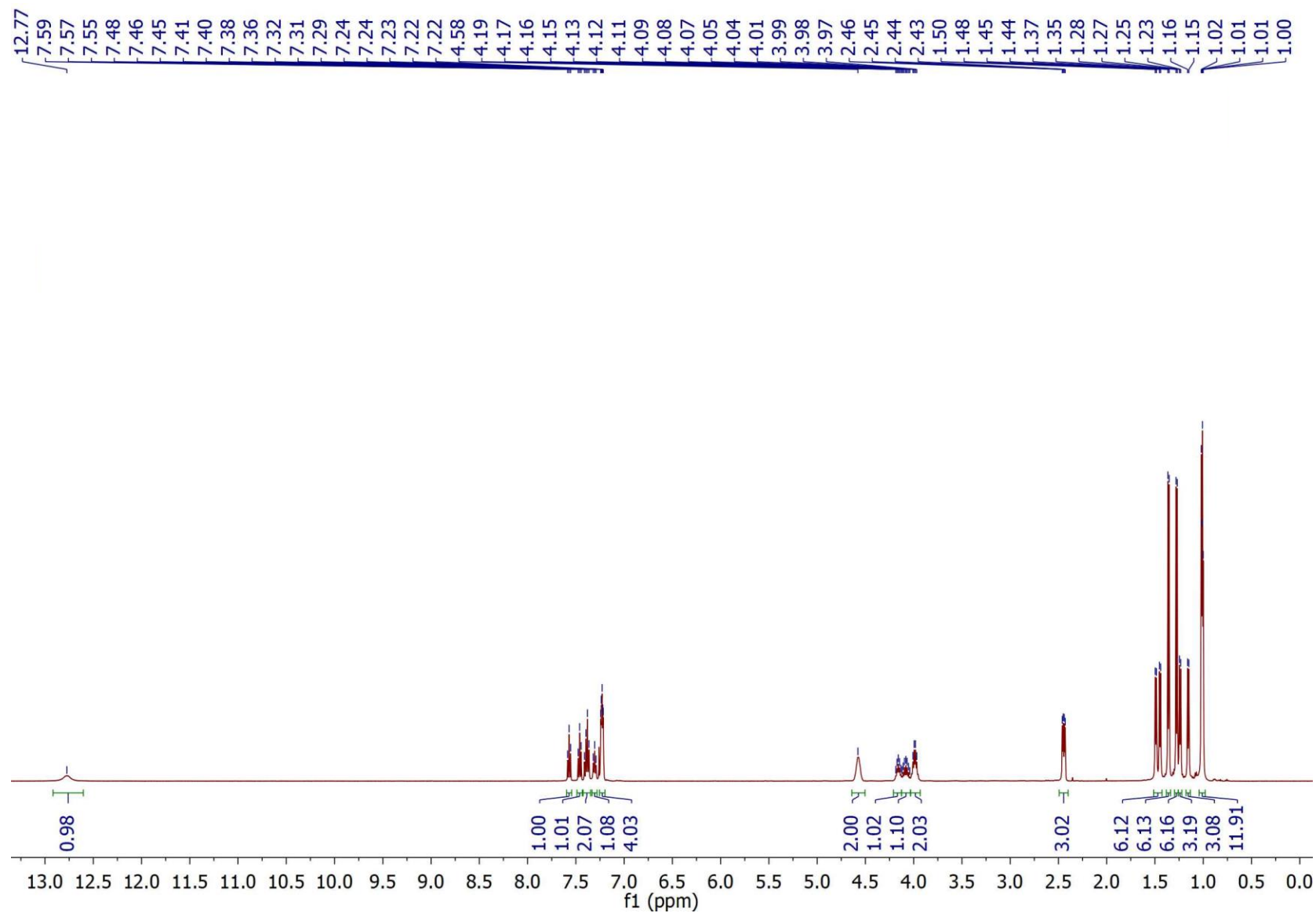


Figure A.23 ^1H NMR spectrum (CDCl_3) of compound $[1_{\text{Dipp}}]^+$ ($\text{R}' = \text{Me}$)

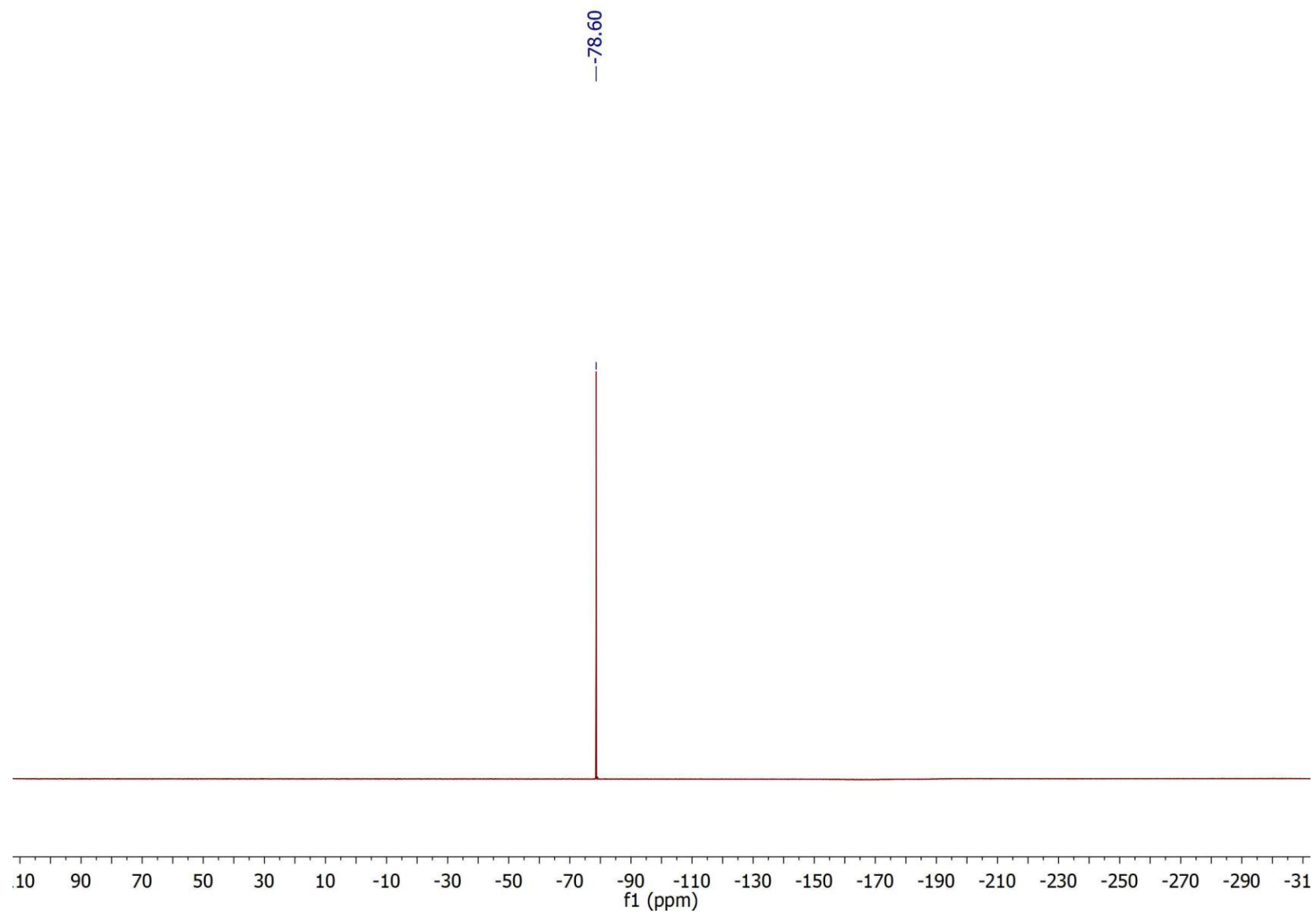


Figure A.24 ^{19}F NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Me}$)

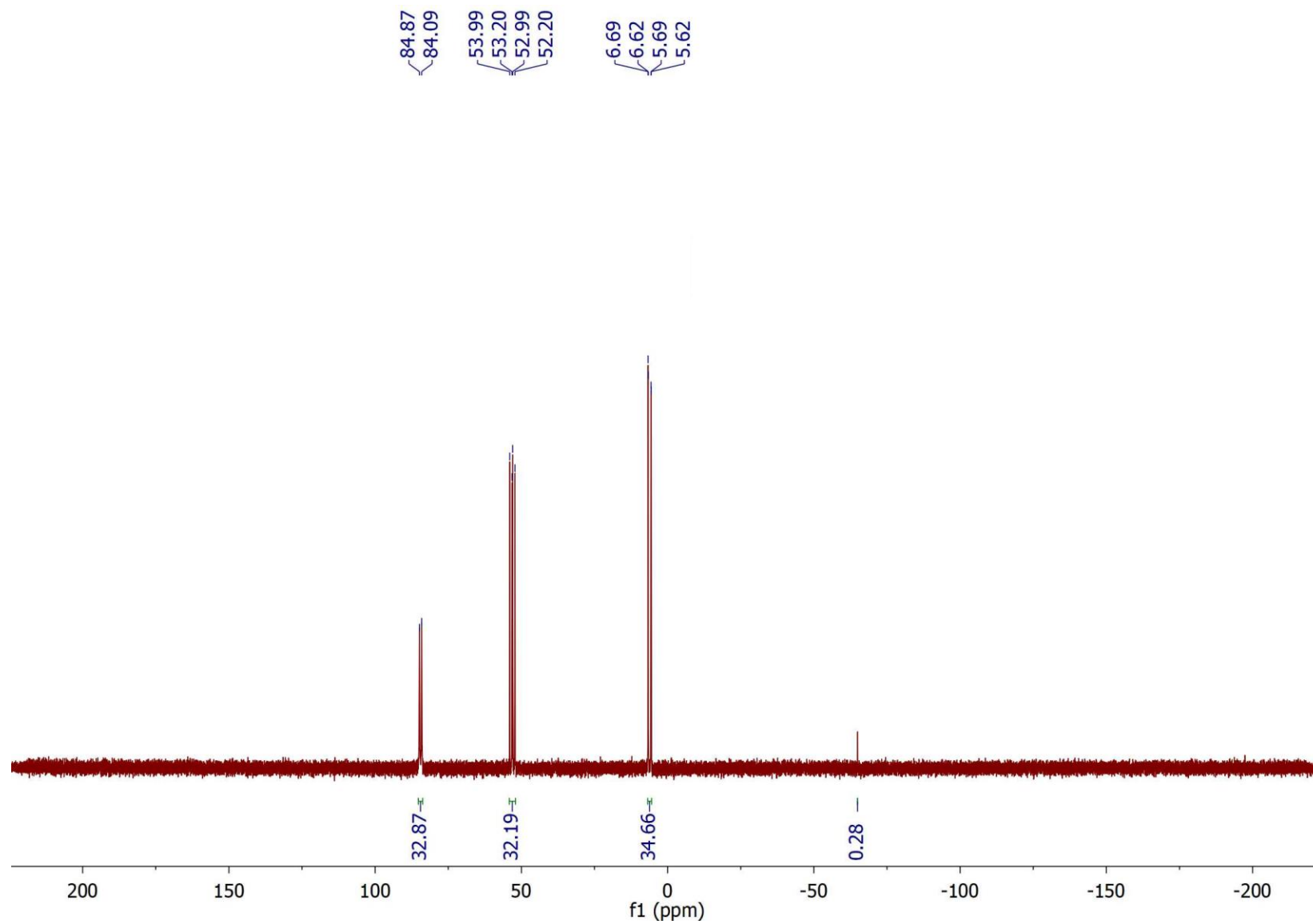


Figure A.25 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Me}$)

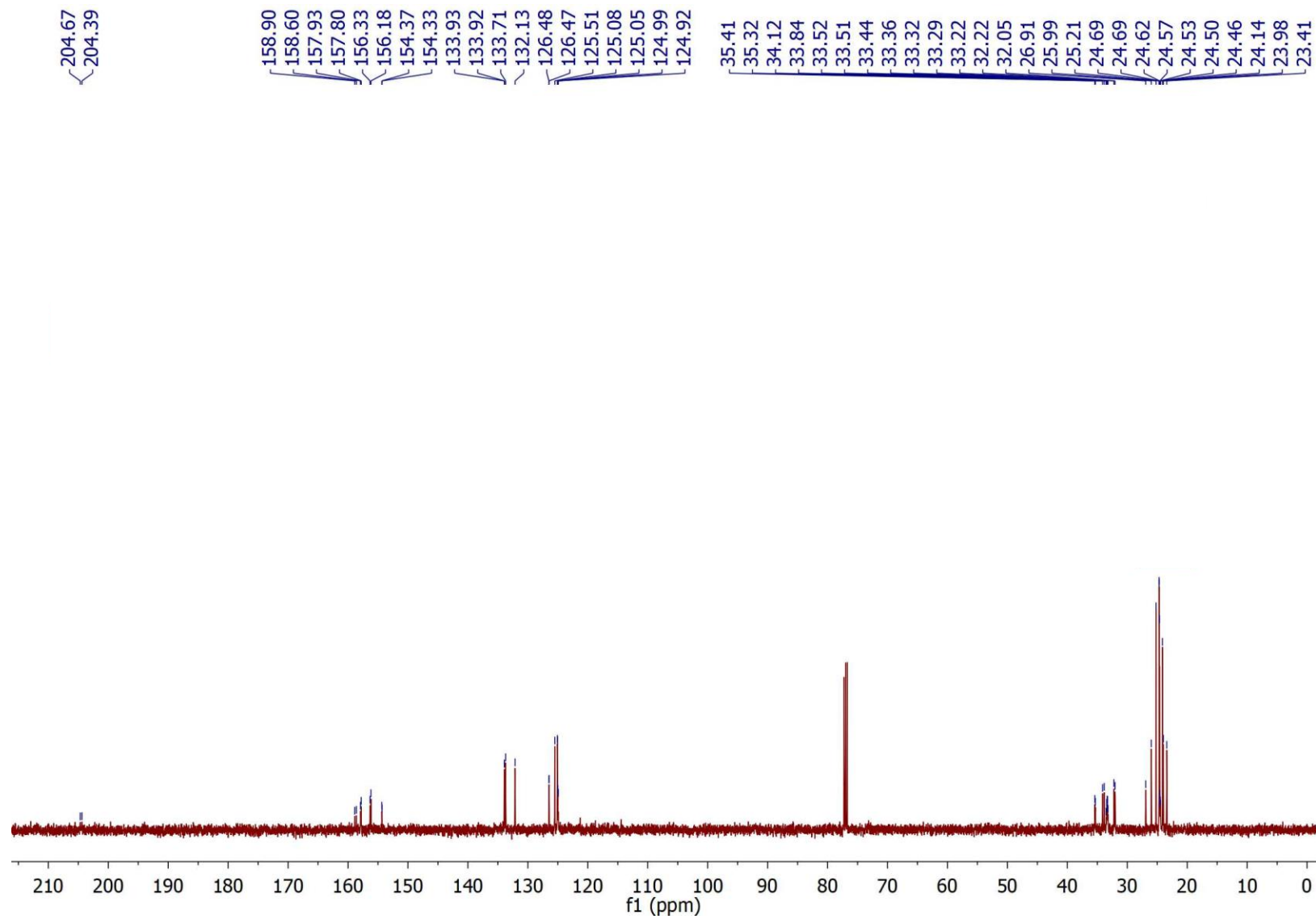


Figure A.26 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Me}$)

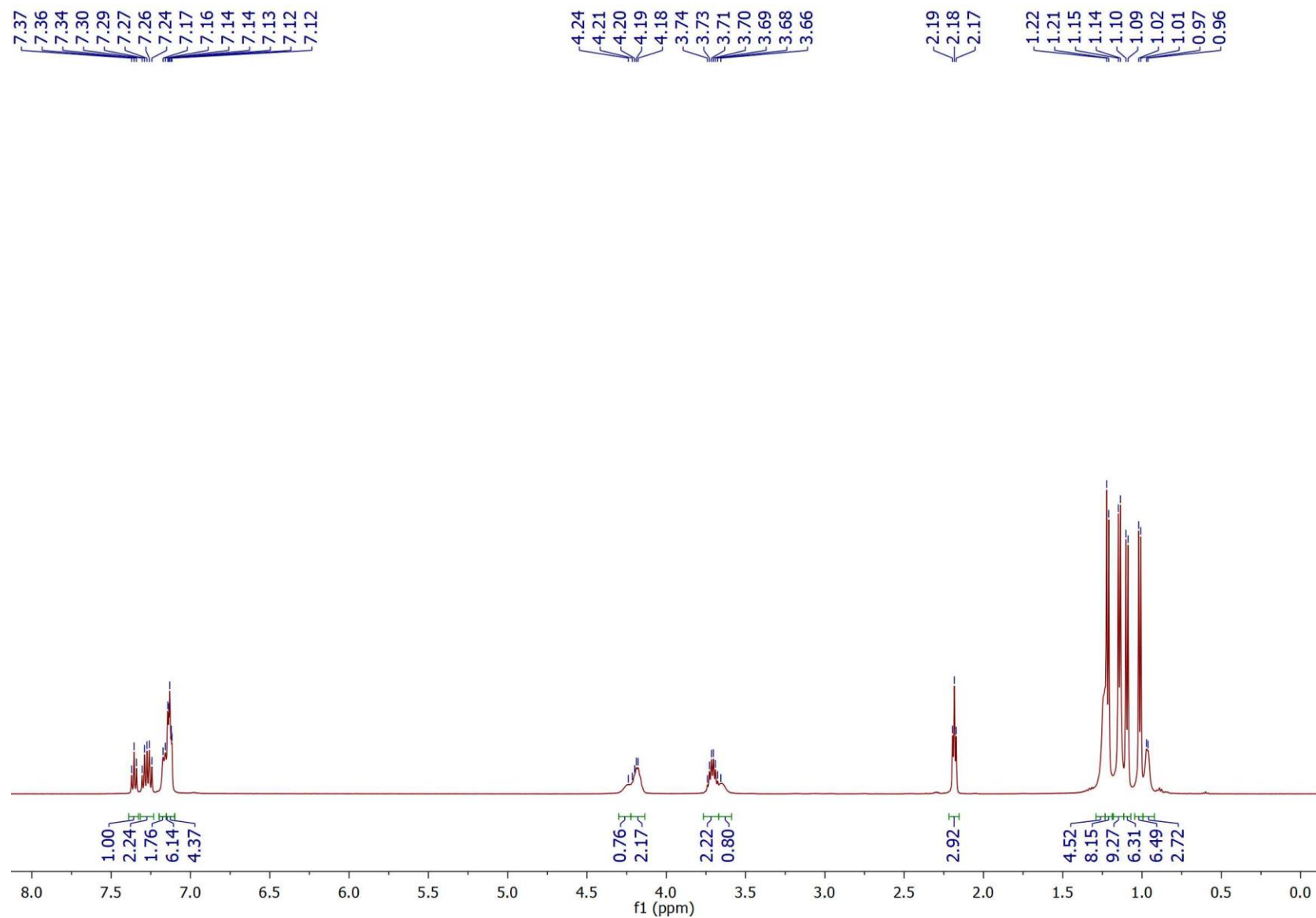


Figure A.27 ¹H NMR spectrum (CDCl₃) of compound **2**_{Dipp} (R' = Me)

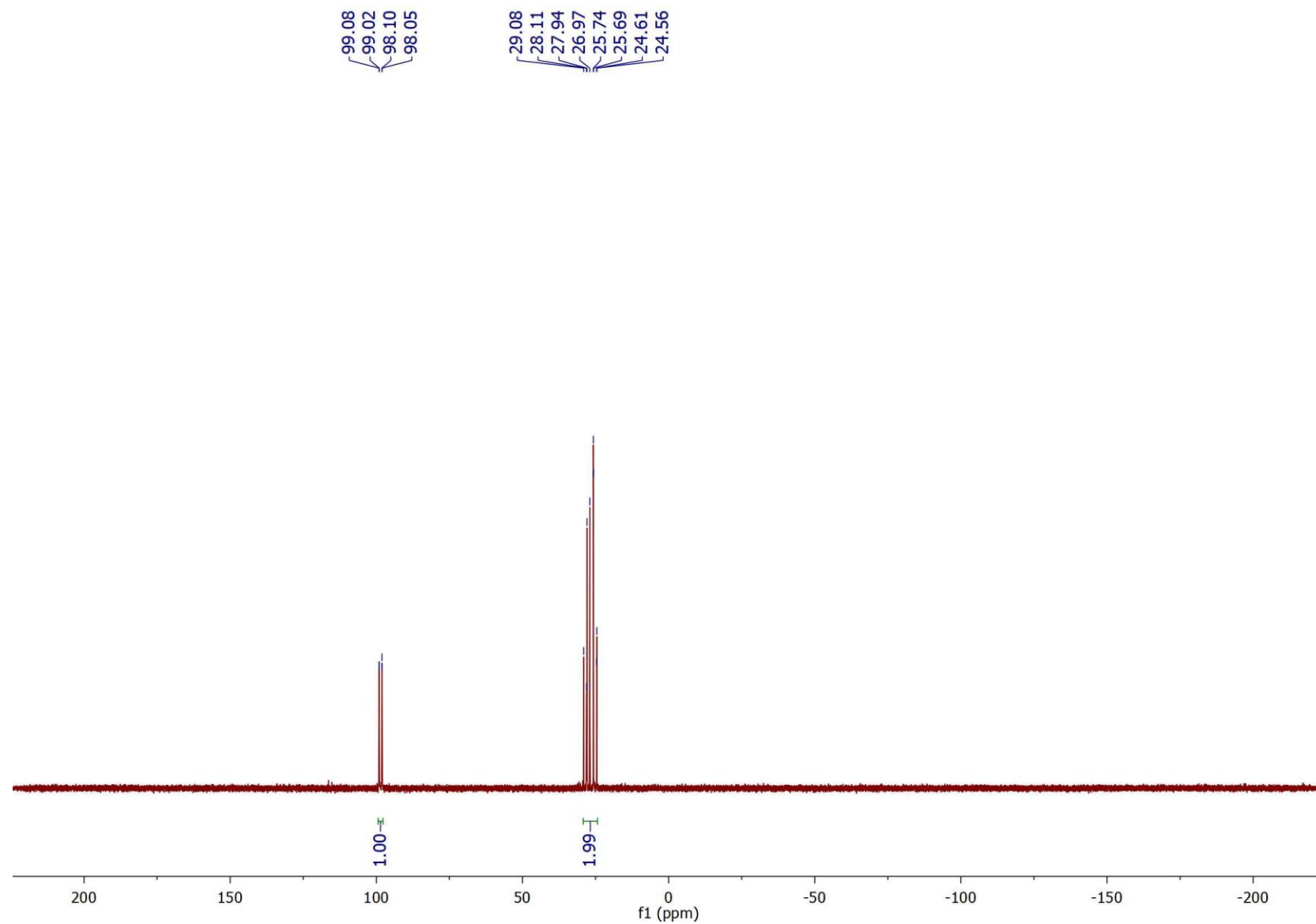


Figure A.28 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound **2_{Dipp}** ($\text{R}' = \text{Me}$)

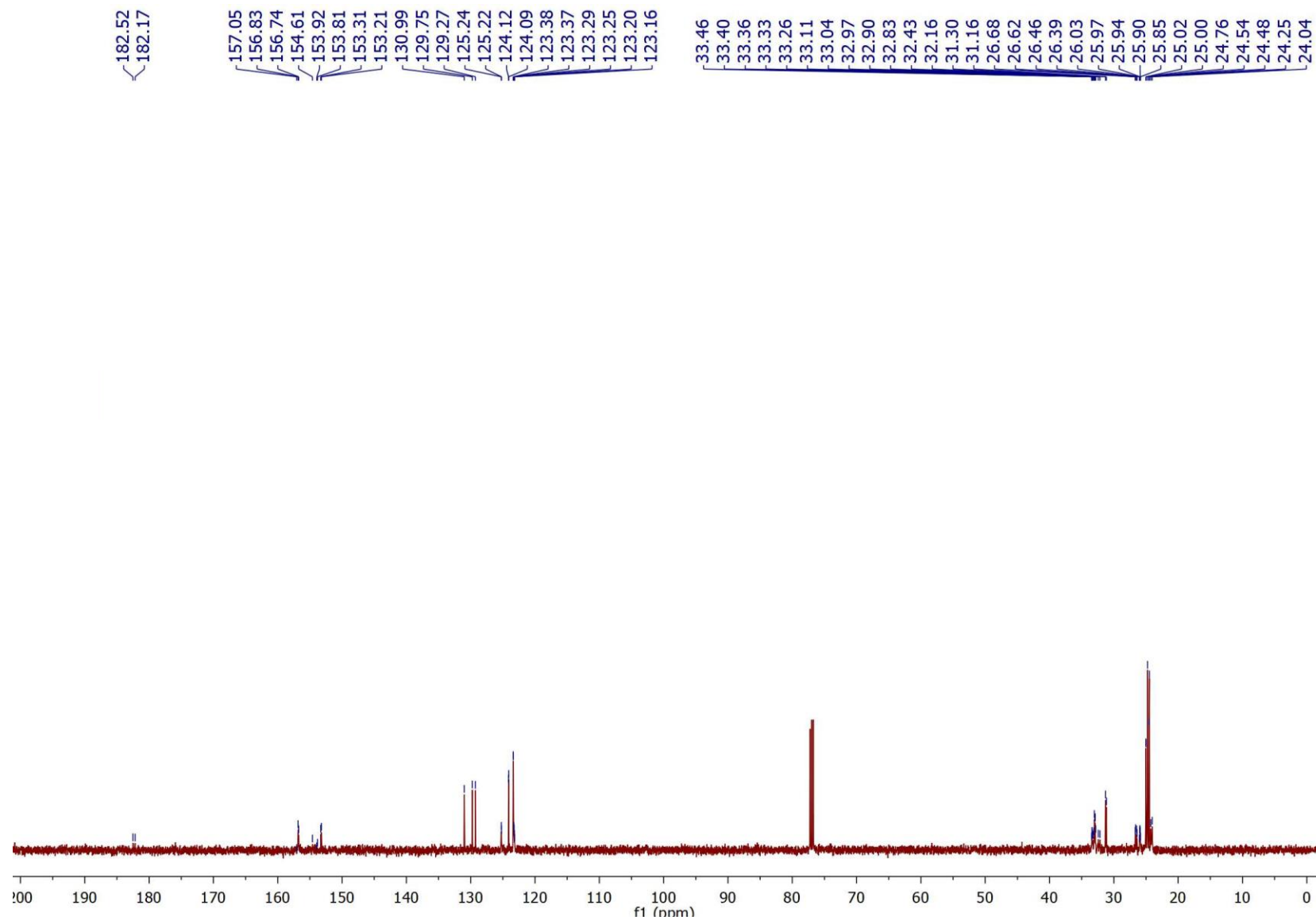


Figure A.29 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound **2_{Dipp}** (**R'** = **Me**)

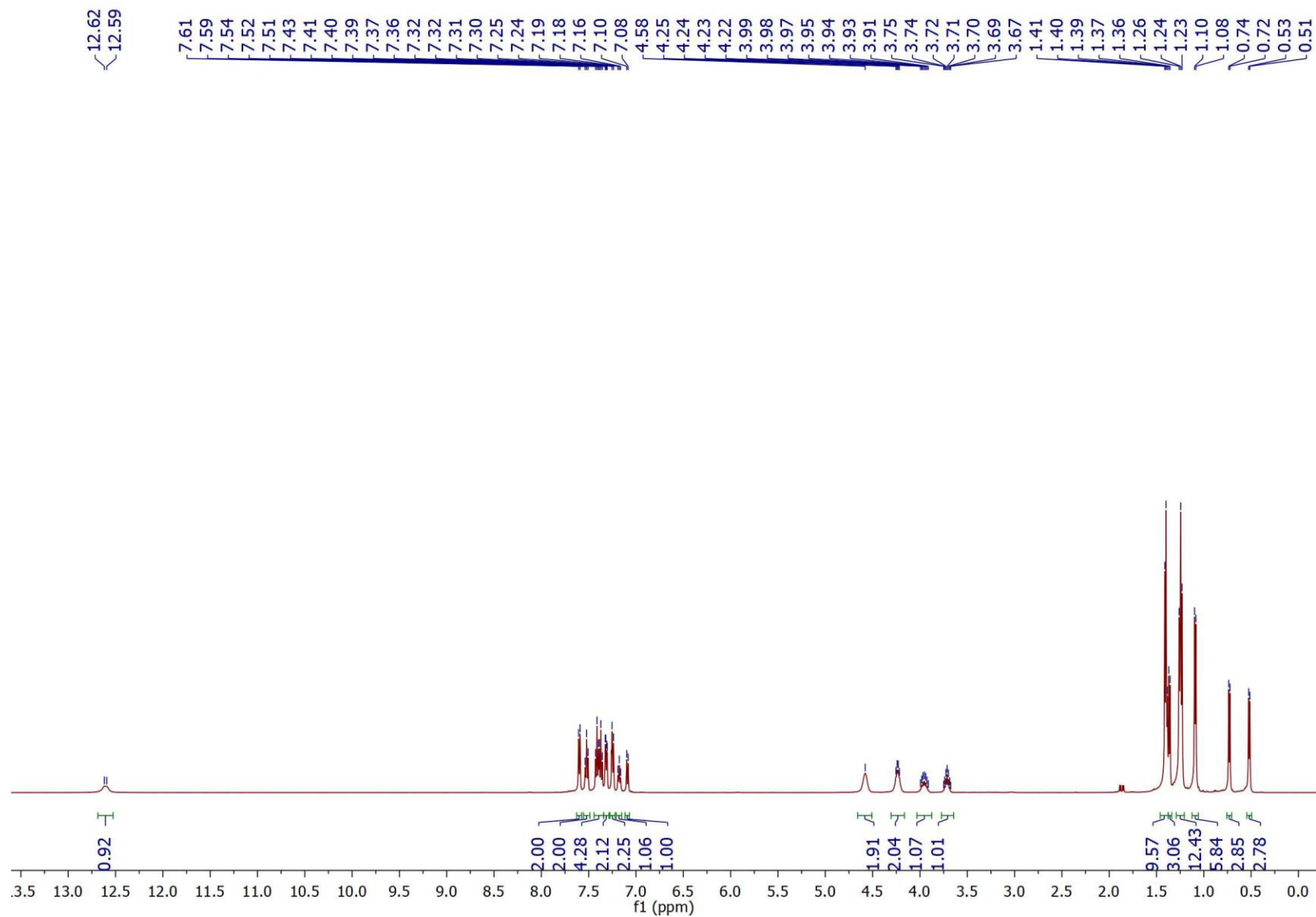


Figure A.30 ^1H NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Ph}$) (* = consistent impurity)

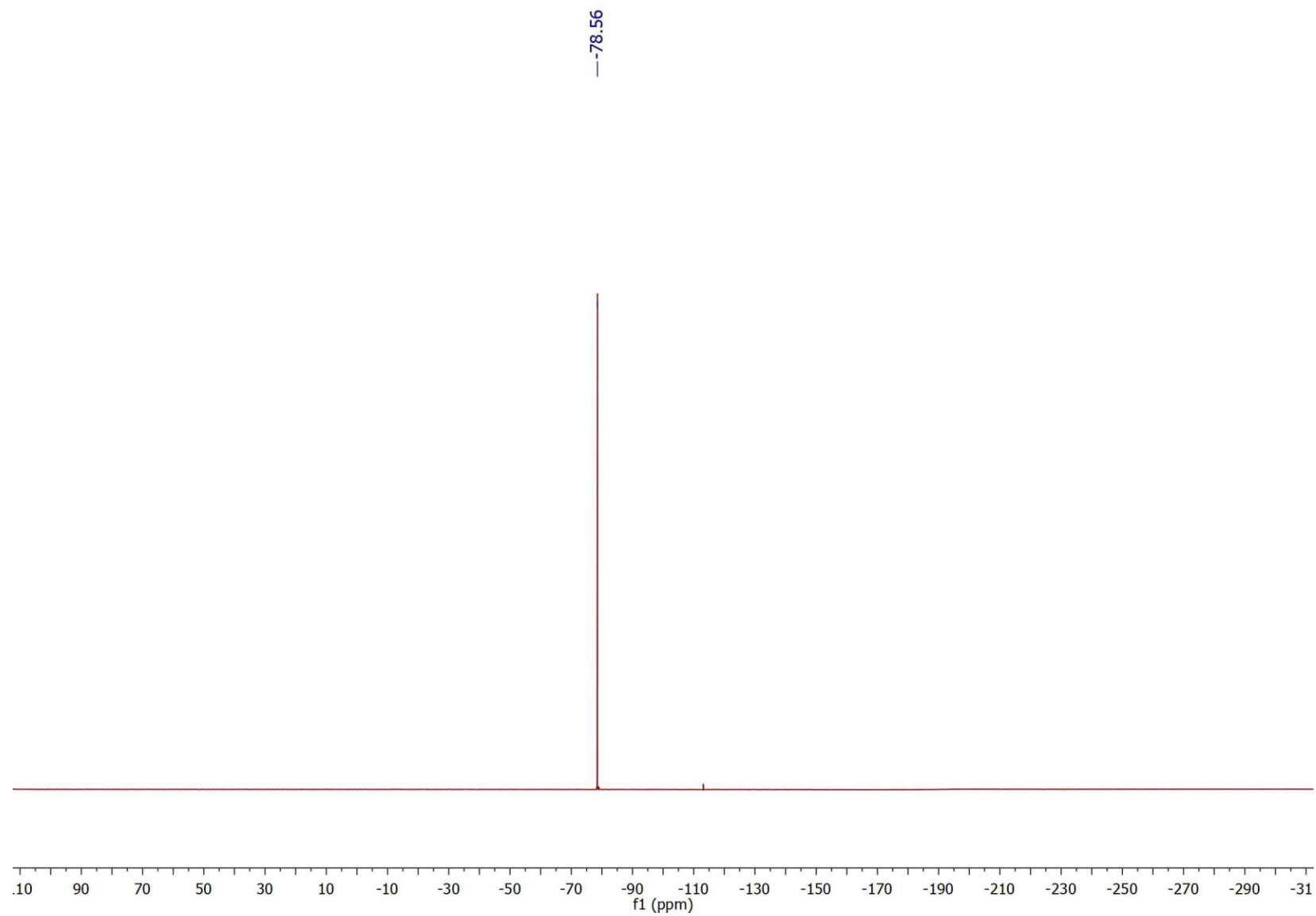


Figure A.31 ^{19}F NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Dipp}}]^+$ ($\mathbf{R}' = \mathbf{Ph}$) (* = consistent impurity)

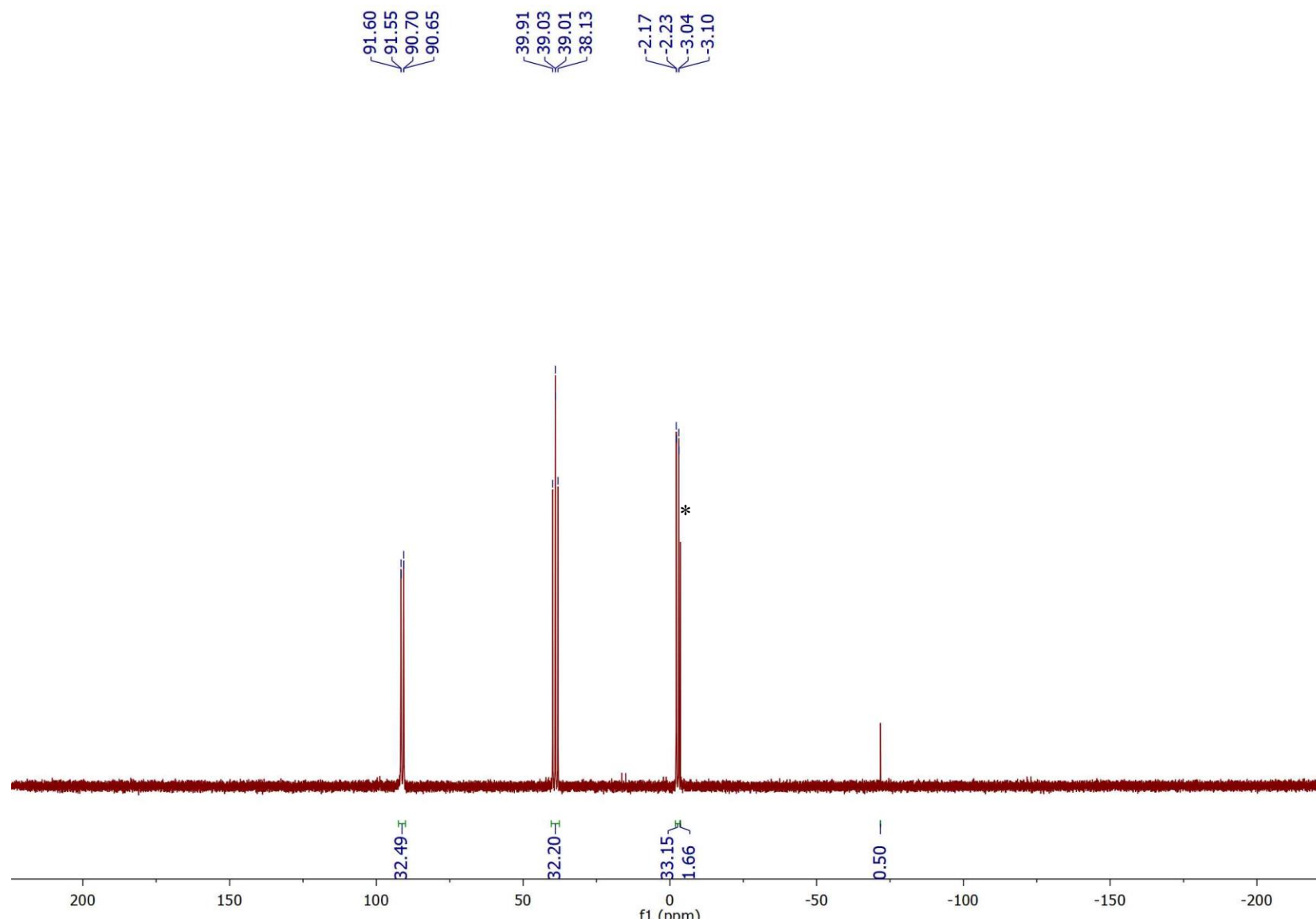


Figure A.32 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Ph}$) (* = consistent impurity)

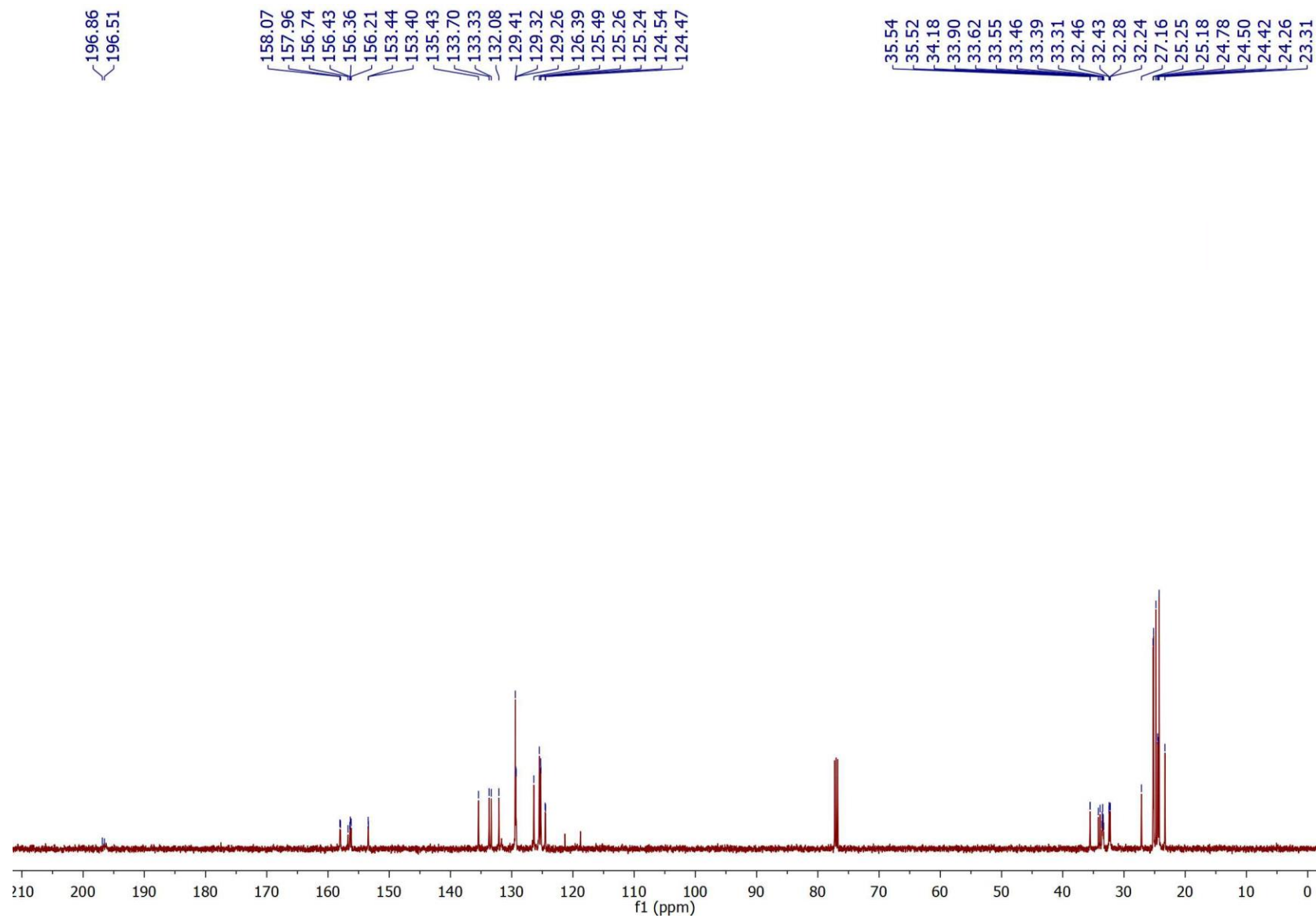


Figure A.33 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Dipp}}]^+$ ($\text{R}' = \text{Ph}$) (* = consistent impurity)

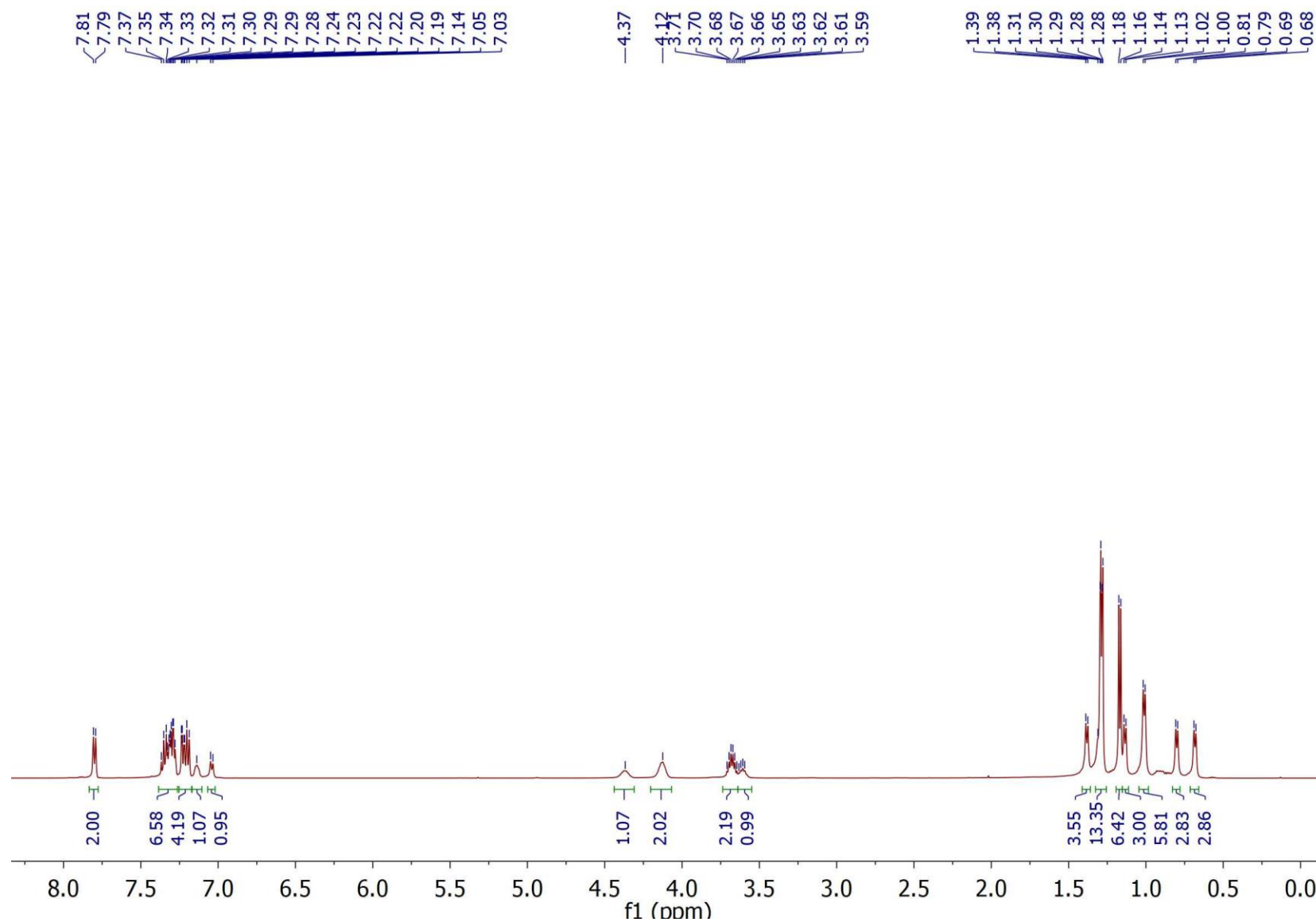


Figure A.34 ^1H NMR spectrum (CDCl_3) of compound **2_{Dipp}** ($\text{R}' = \text{Ph}$)

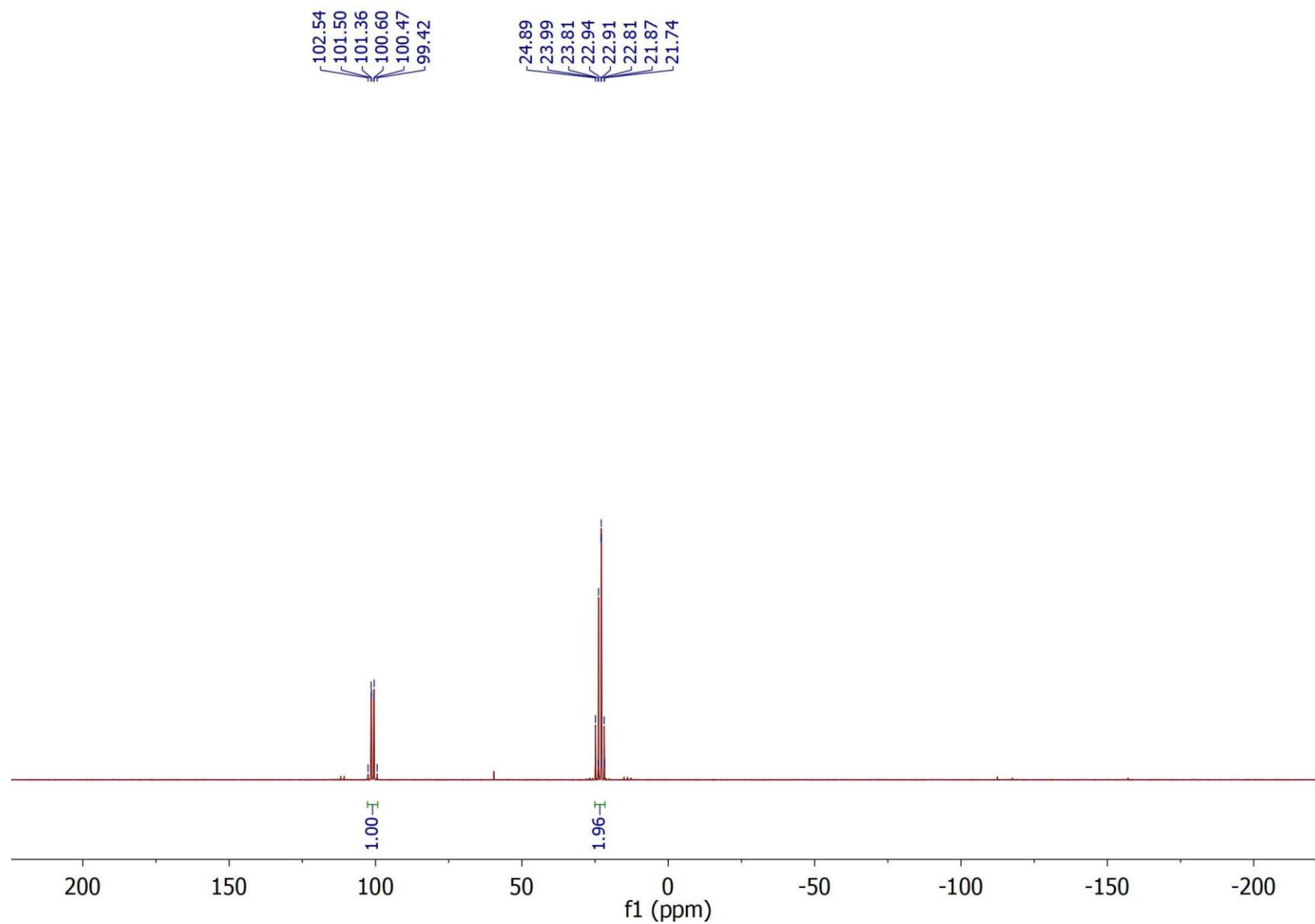


Figure A.35 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound **2_{Dipp}** ($\text{R}' = \text{Ph}$)

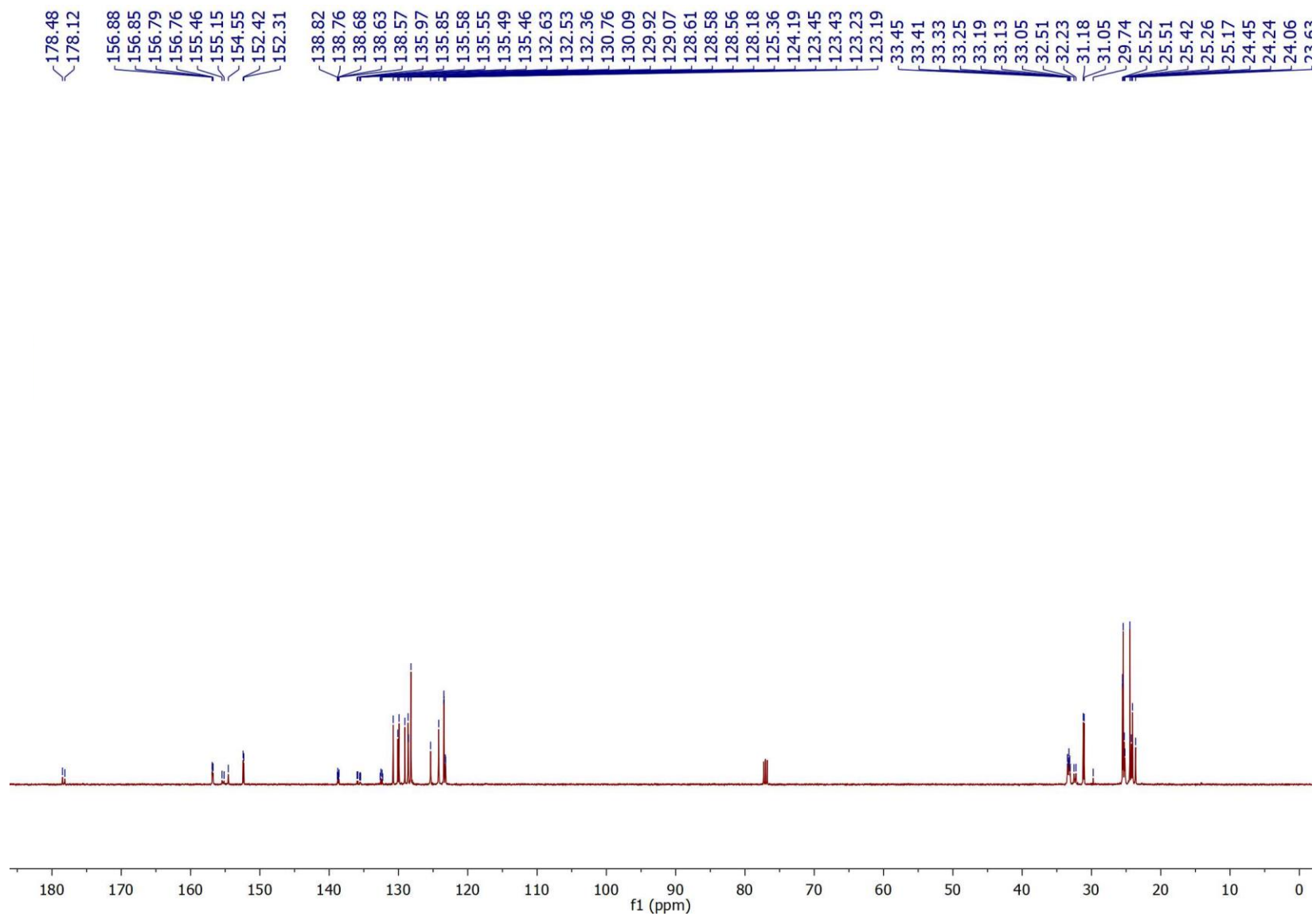


Figure A.36 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound **2Dipp** (**R'** = **Ph**)

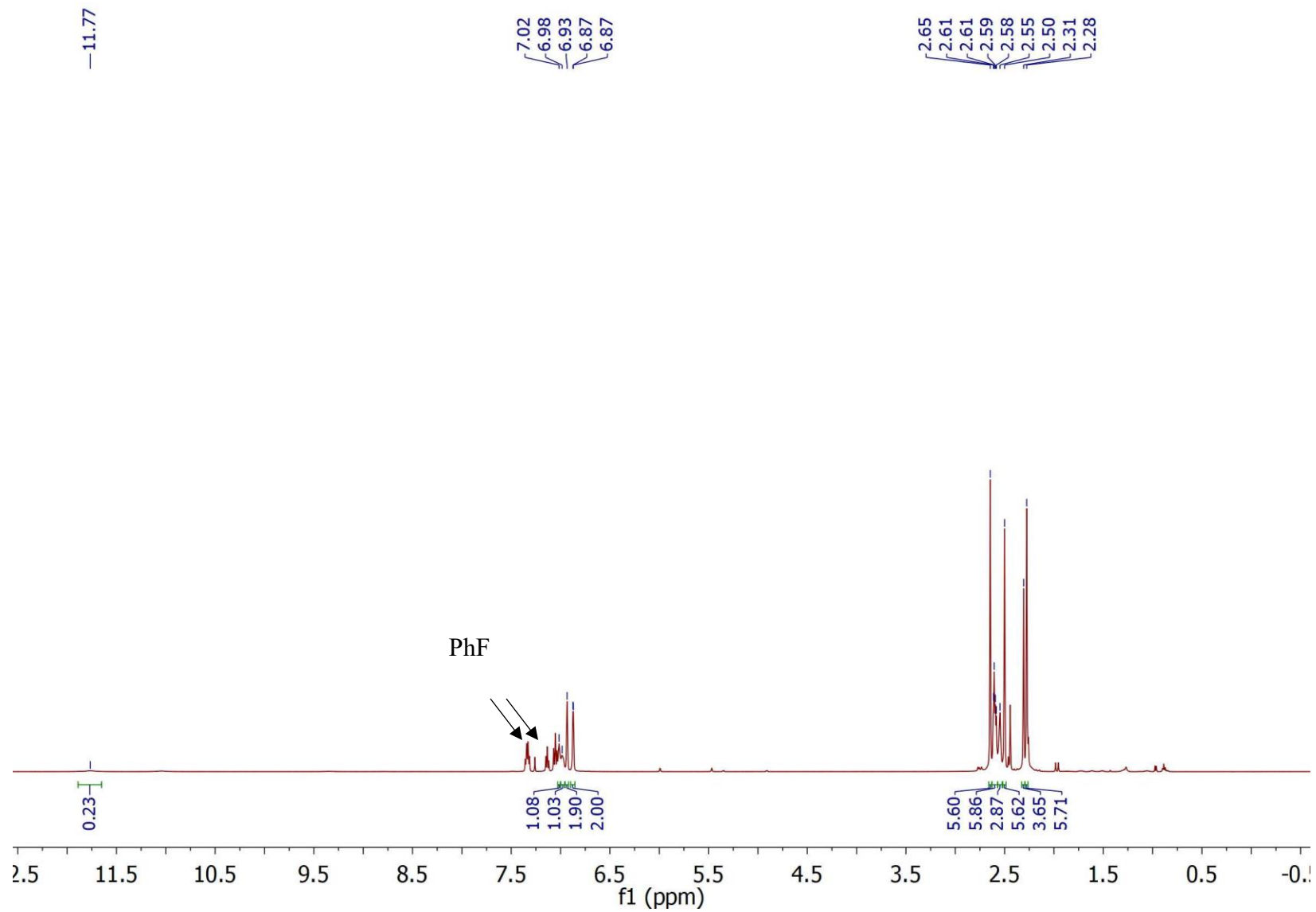


Figure A.37 ^1H NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Me}$)

--78.51

--113.12

pH

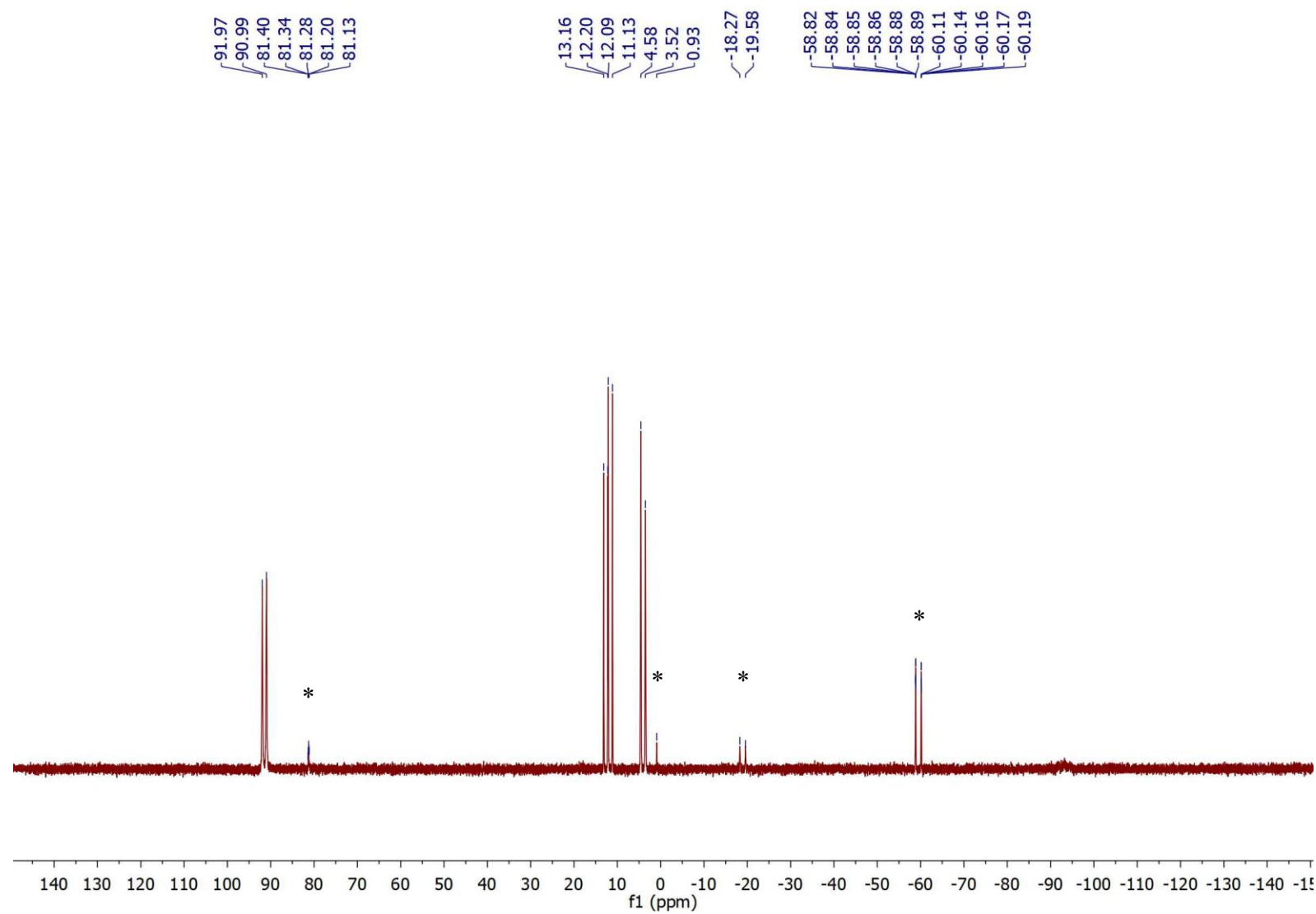


Figure A.39 ^{31}P NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Me}$) (* = unknown degradative impurities)

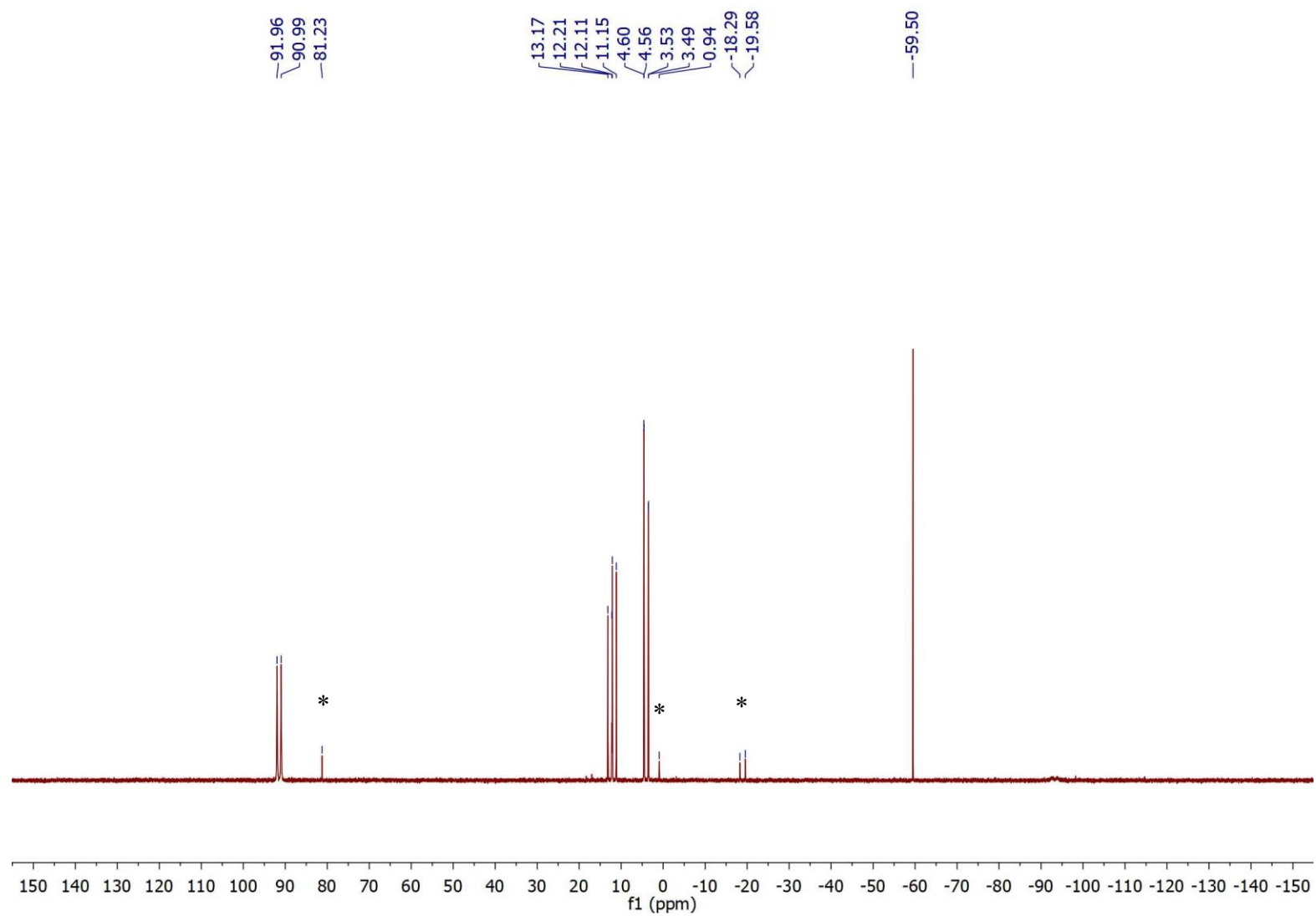
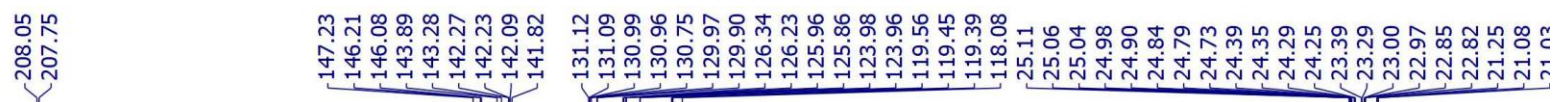


Figure A.40 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Me}$) (* = unknown degradative impurities)



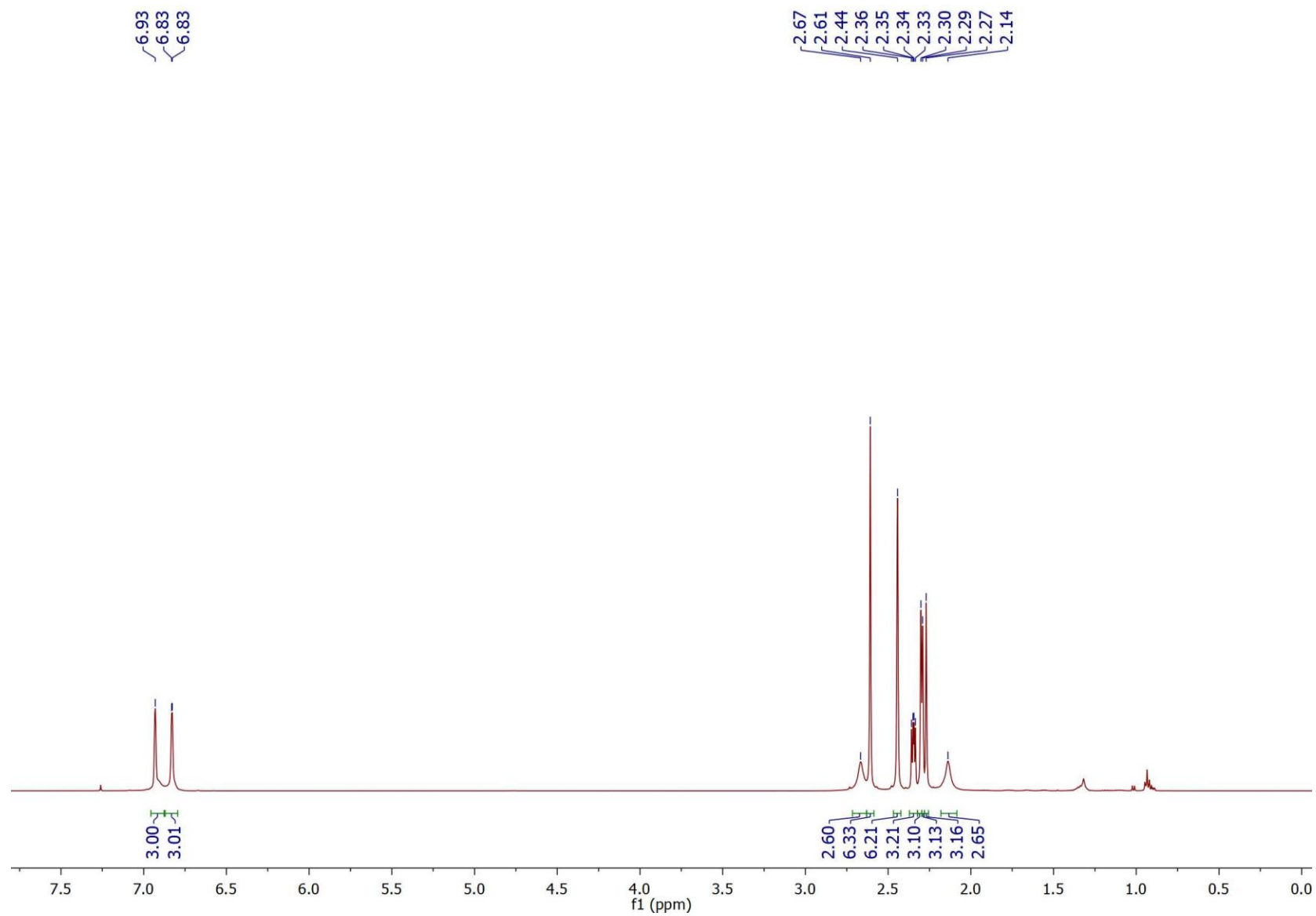


Figure A.42 ^1H NMR spectrum (CDCl_3) of compound **2_{Mes}** ($\text{R}' = \text{Me}$)

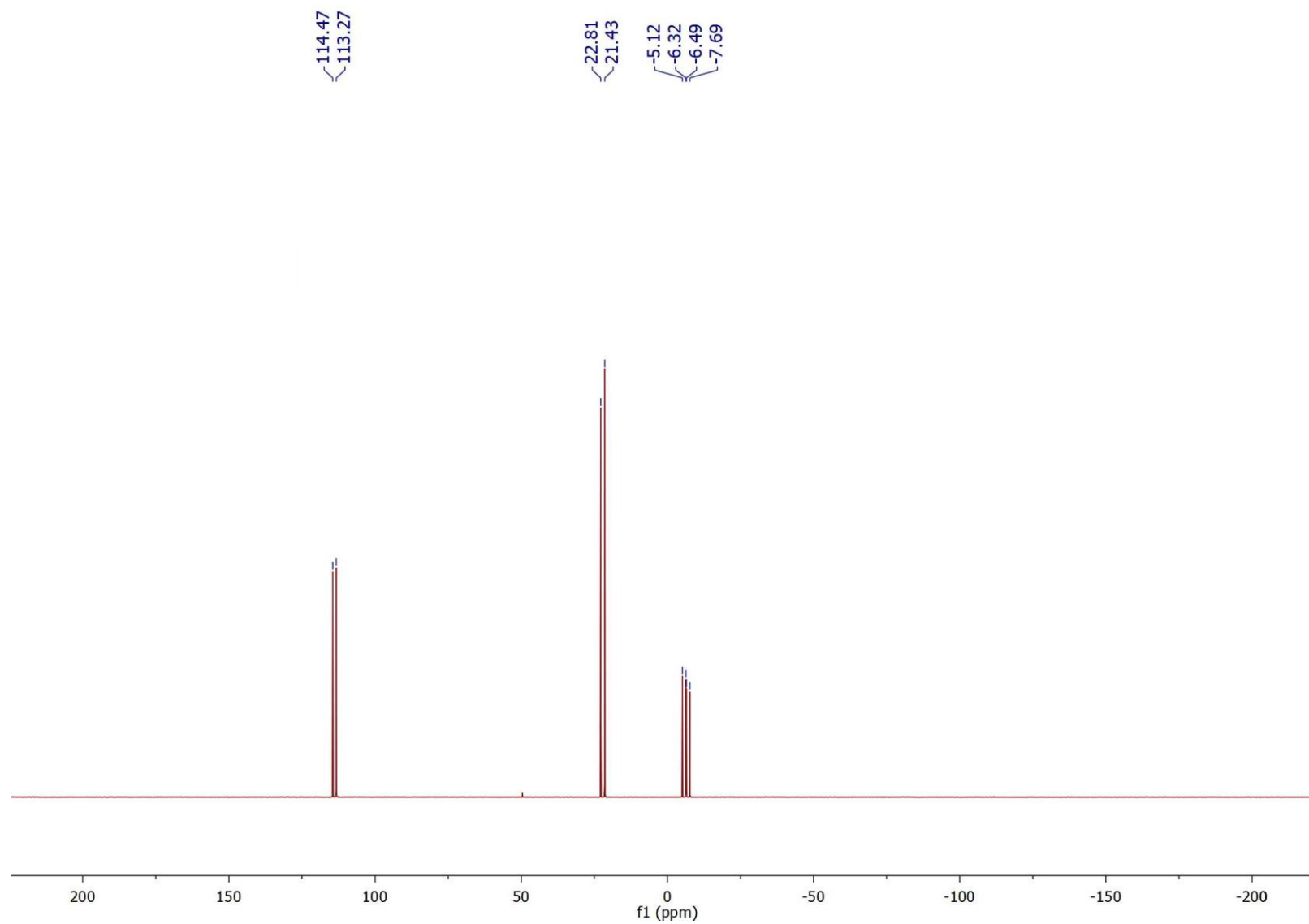
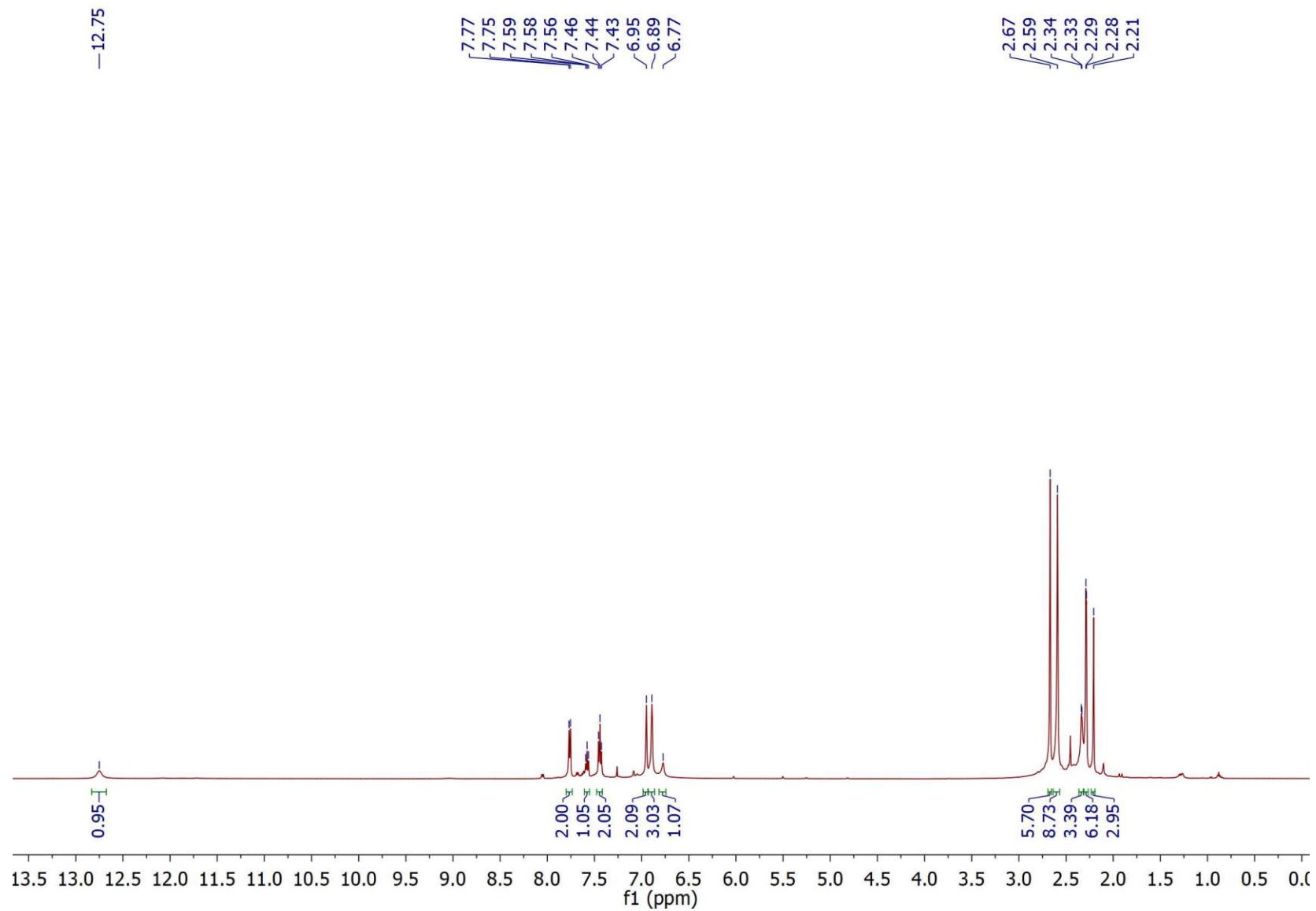


Figure A.43 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound **2_{Mes}** ($\text{R}' = \text{Me}$)

185.68
185.66
185.61
185.59
185.30
185.28
185.23
185.21
145.50
145.47
145.38
145.35
140.21
140.16
140.14
140.05
140.02
138.96
137.53
137.52
133.37
133.27
133.05
132.95
130.24
130.02
129.99
129.69
129.27
128.45
128.33
128.22
128.15
128.10
128.01
127.98
127.89
127.84
127.75
127.72
127.58

25.55
25.47
25.26
25.18
24.65
24.39
23.97
23.89
23.84
23.80
23.76
23.68
23.43
23.40
23.31
23.29
23.22
21.09
21.02
20.84

Figure A.44 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound 2_{Mes} ($\text{R}' = \text{Me}$)



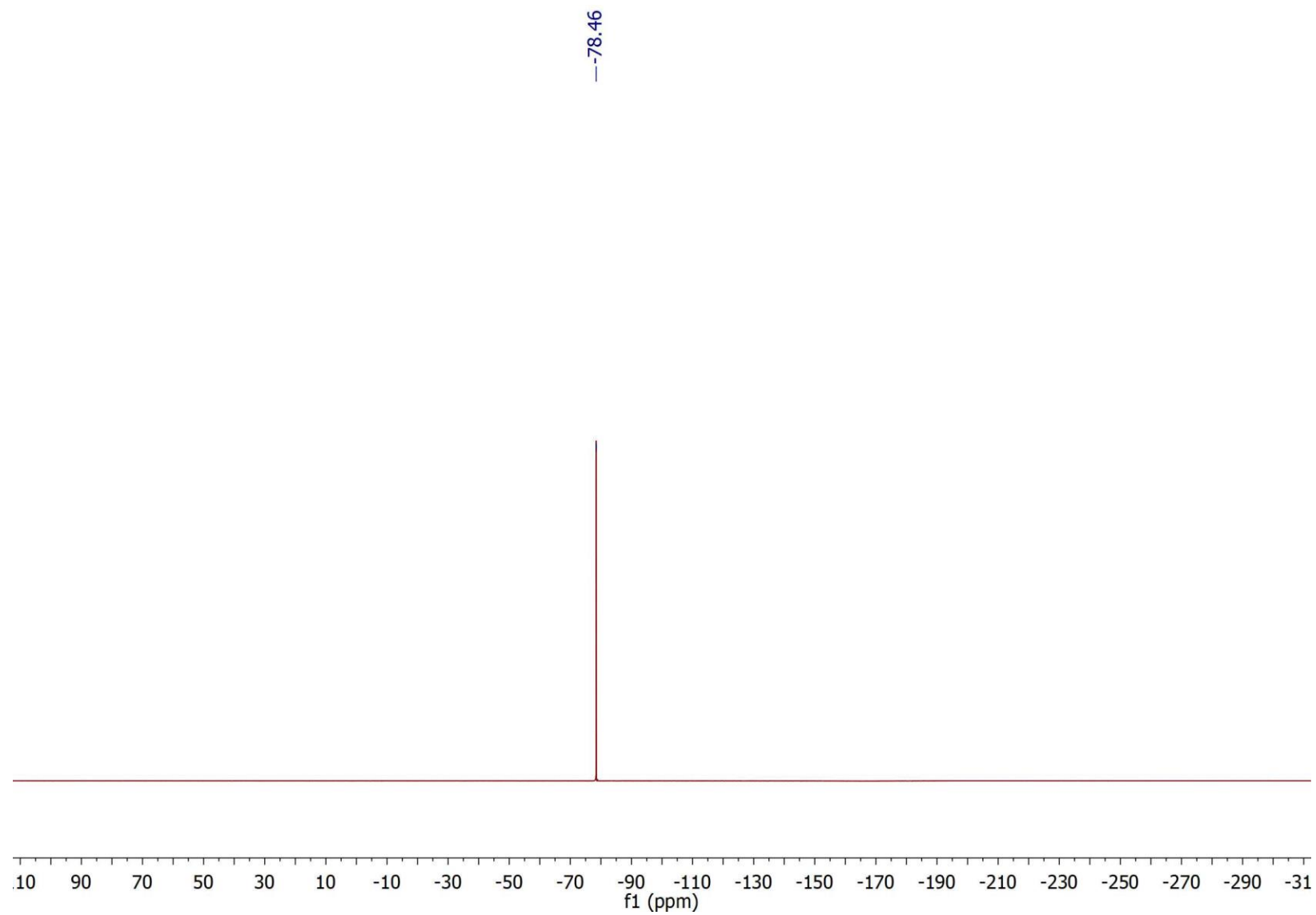


Figure A.46 ^{19}F NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Ph}$)

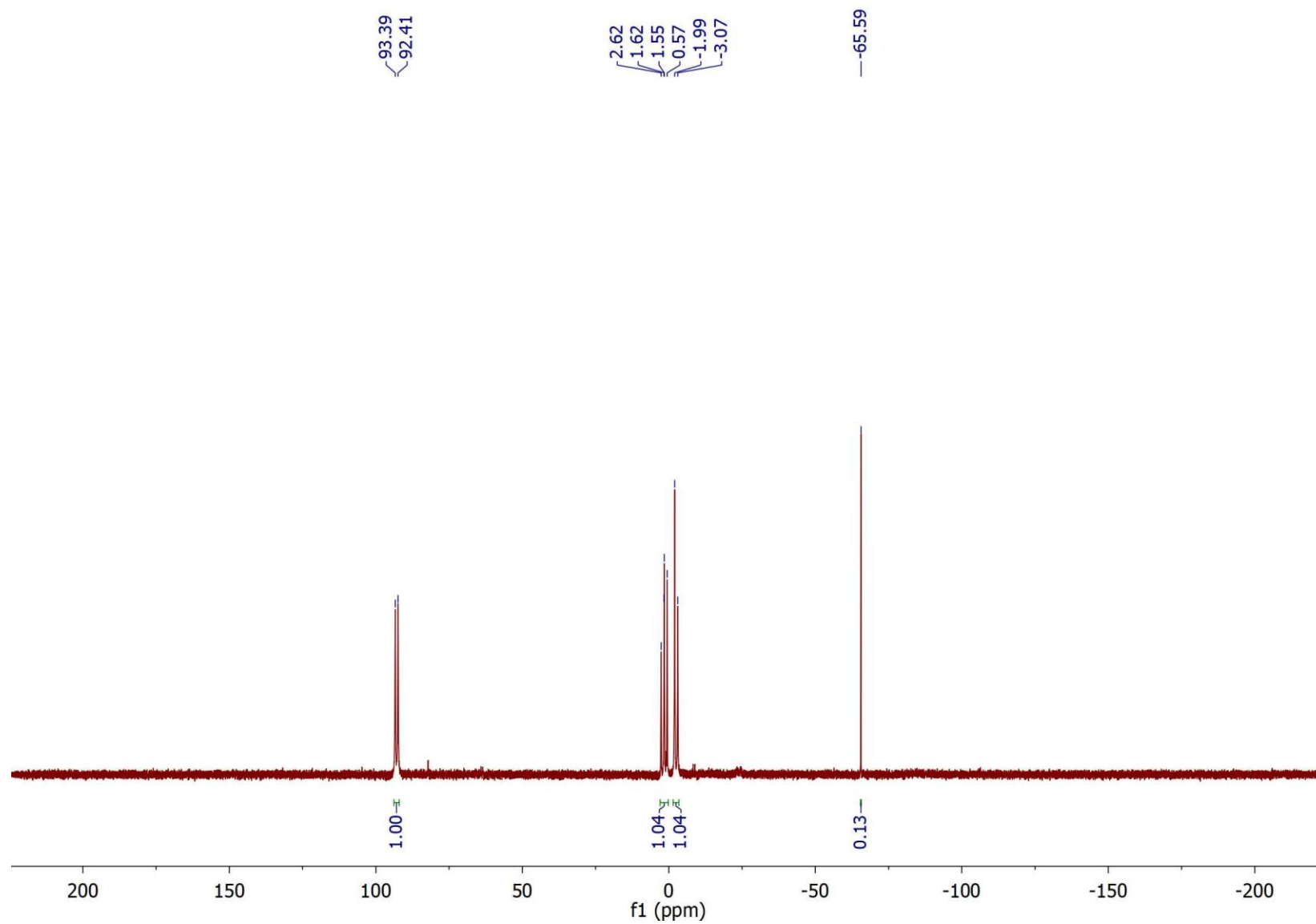


Figure A.47 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Ph}$)

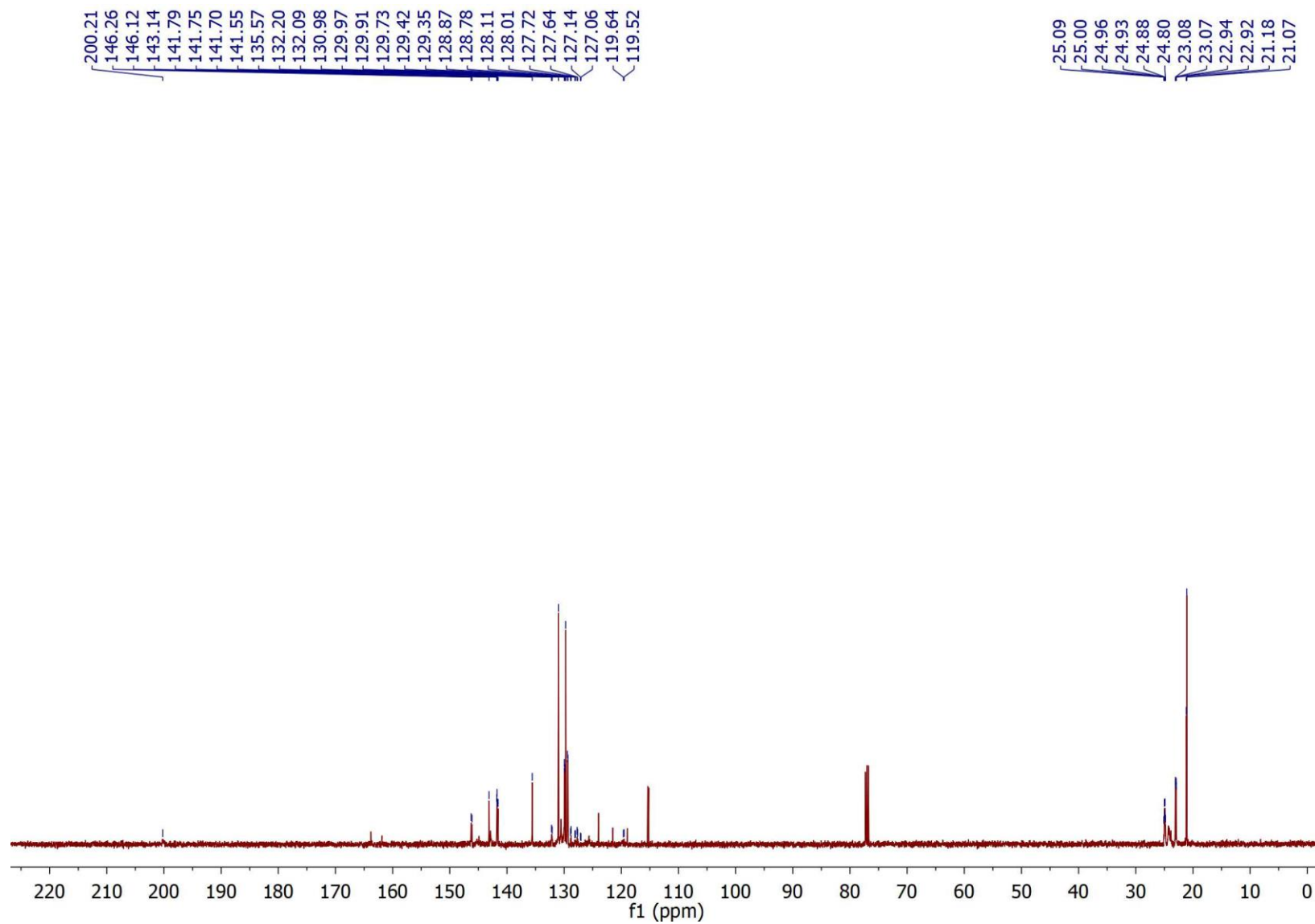


Figure A.48 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{Mes}}]^+$ ($\text{R}' = \text{Ph}$)

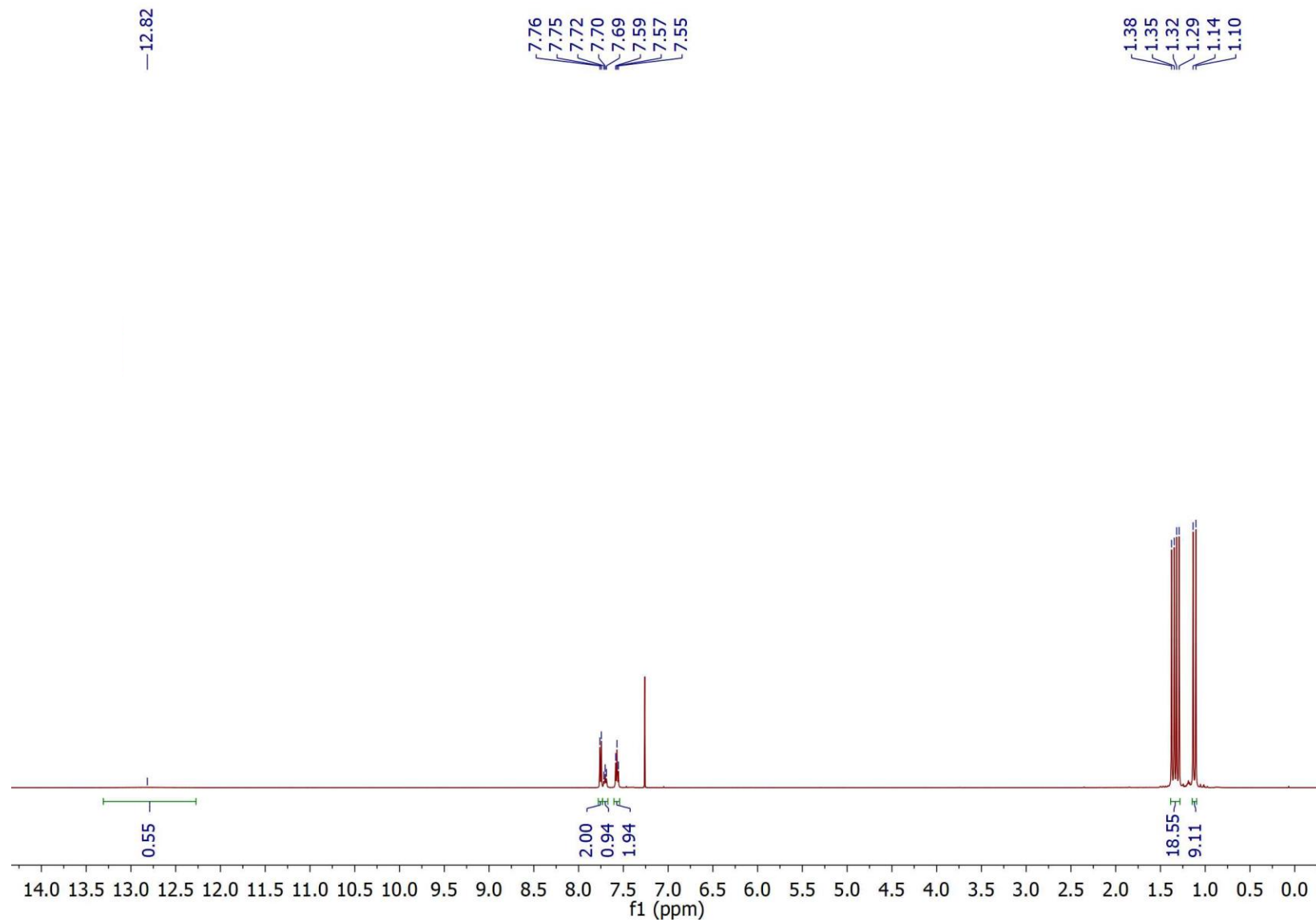


Figure A.49 ¹H NMR spectrum (CDCl₃) of compound [1_{tBu}]⁺ (R' = Ph)

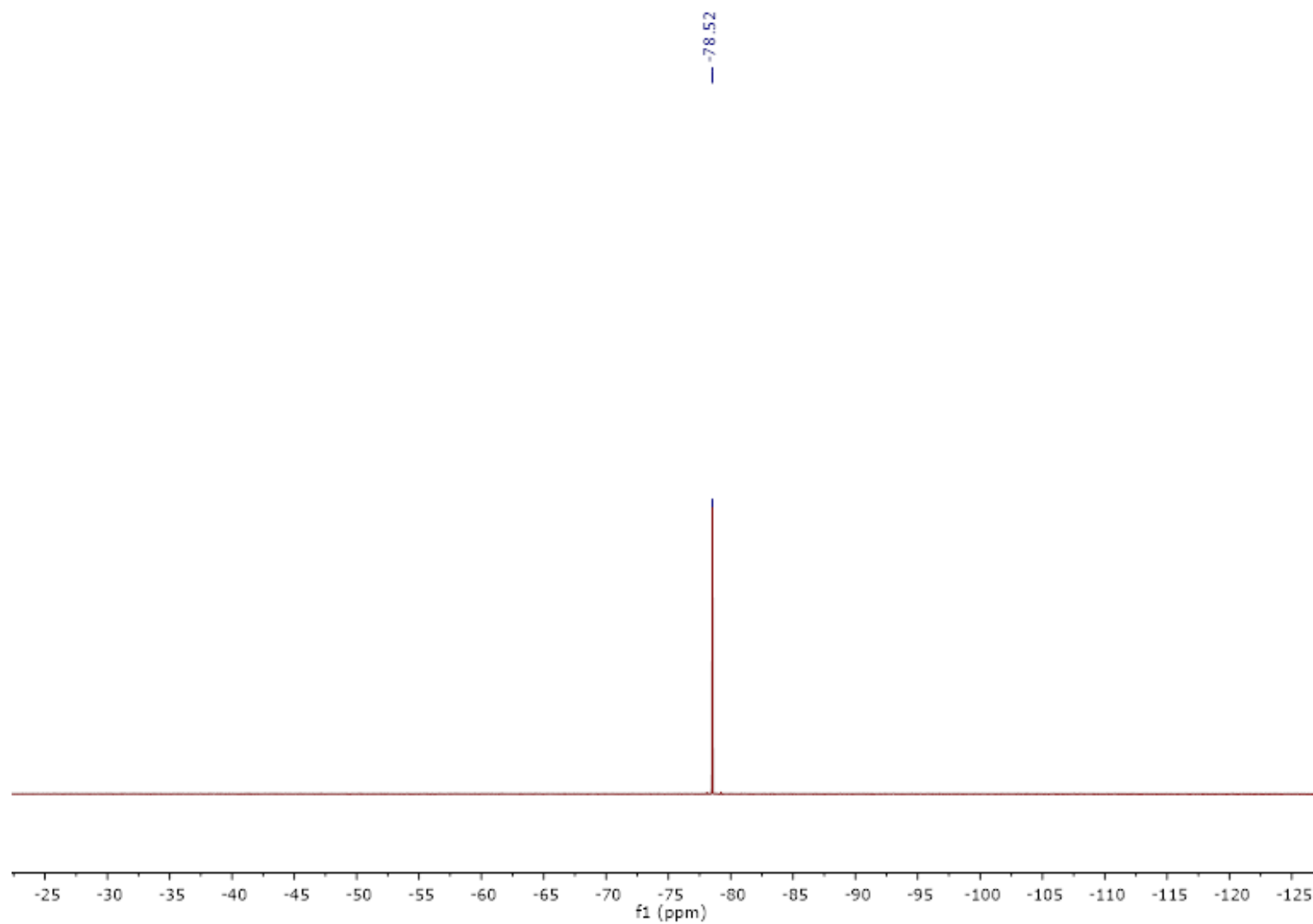


Figure A.50 ^{19}F NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{tBu}}]^+$ ($\text{R}' = \text{Ph}$)

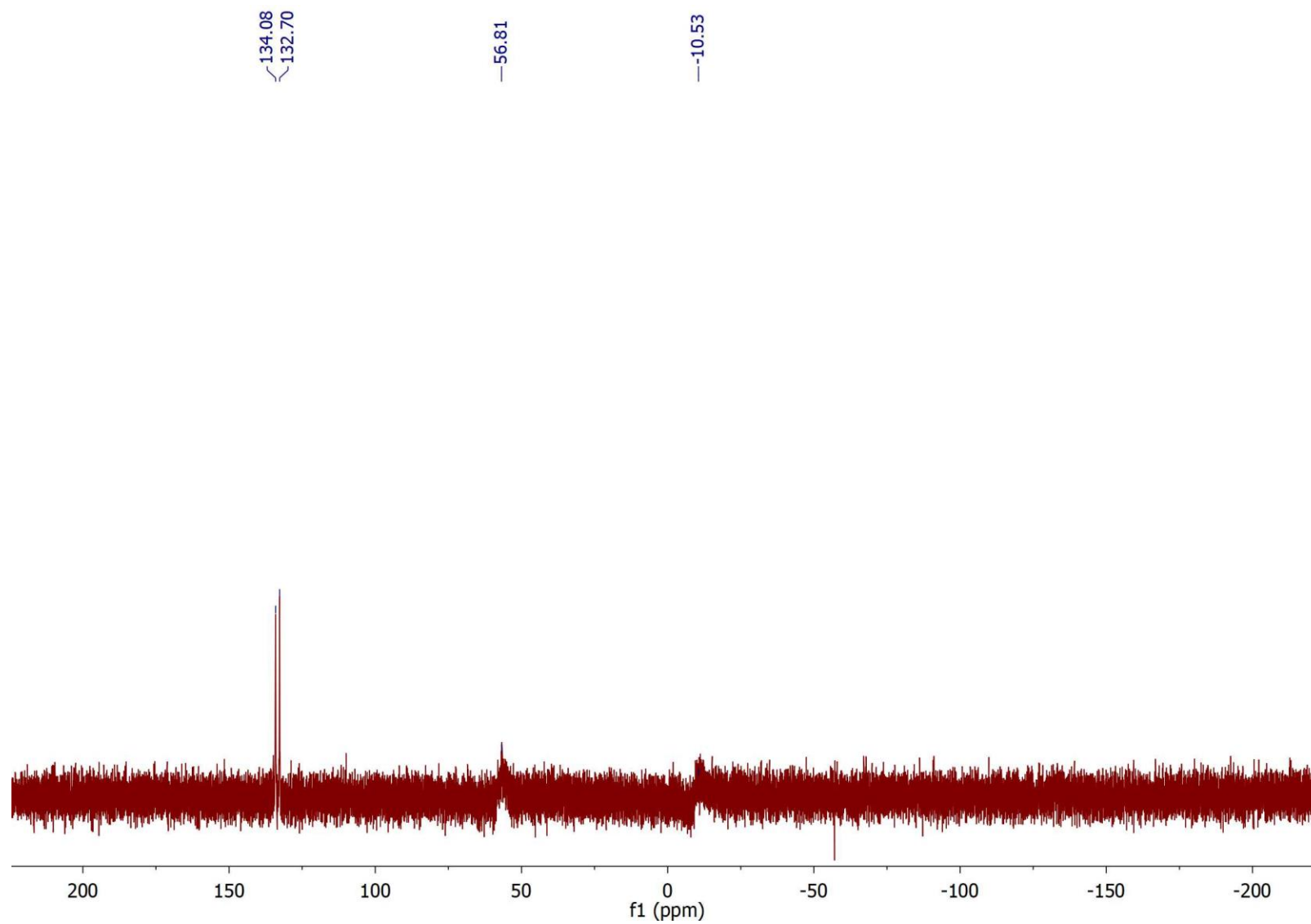


Figure A.51 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{tBu}}]^+$ ($\text{R}' = \text{Ph}$)

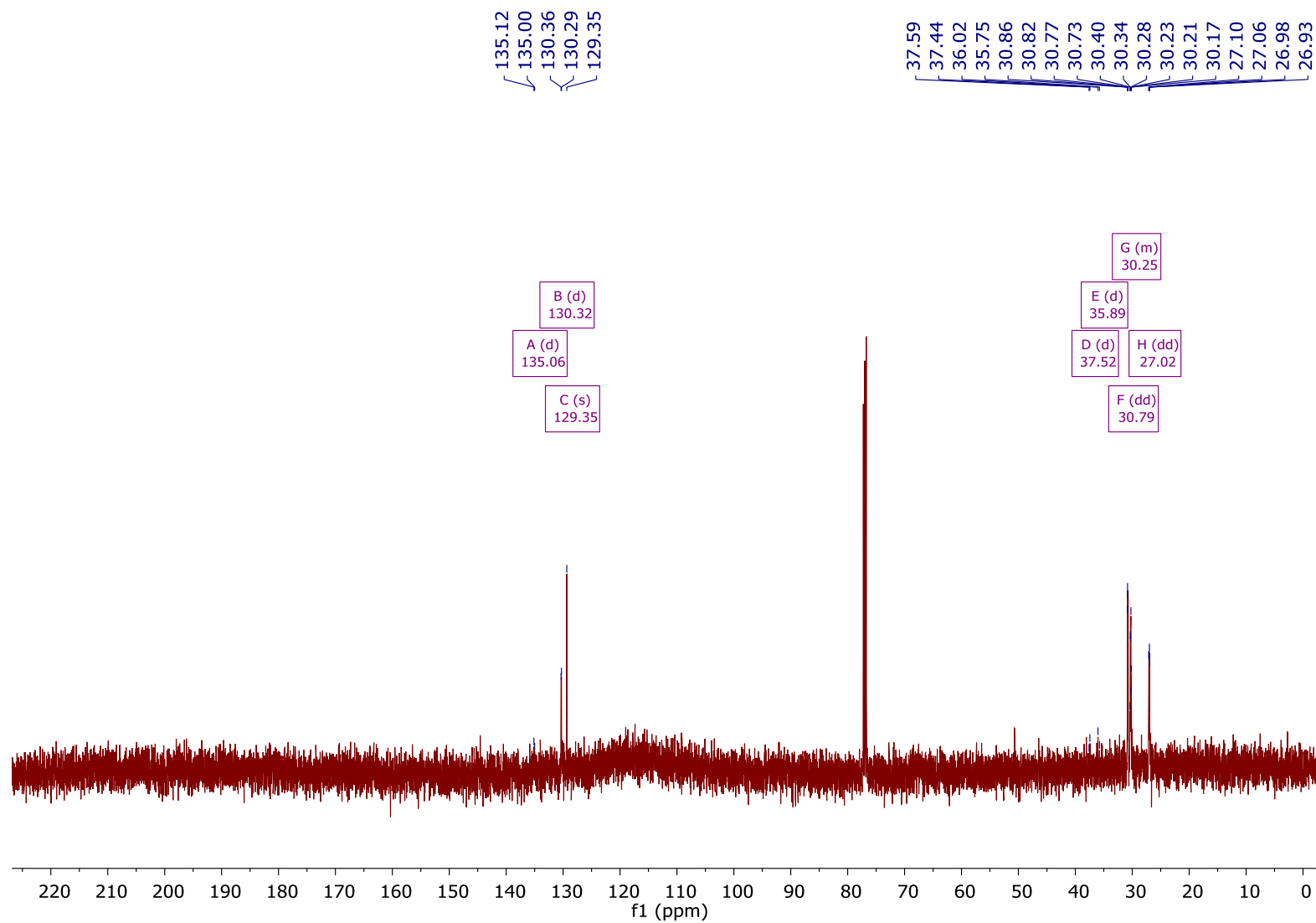


Figure A.52 $^{13}\text{C}\{^1\text{H}\}$ UDEFT NMR spectrum (CDCl_3) of compound $[\mathbf{1}_{\text{tBu}}]^+$ ($\text{R}' = \text{Ph}$)

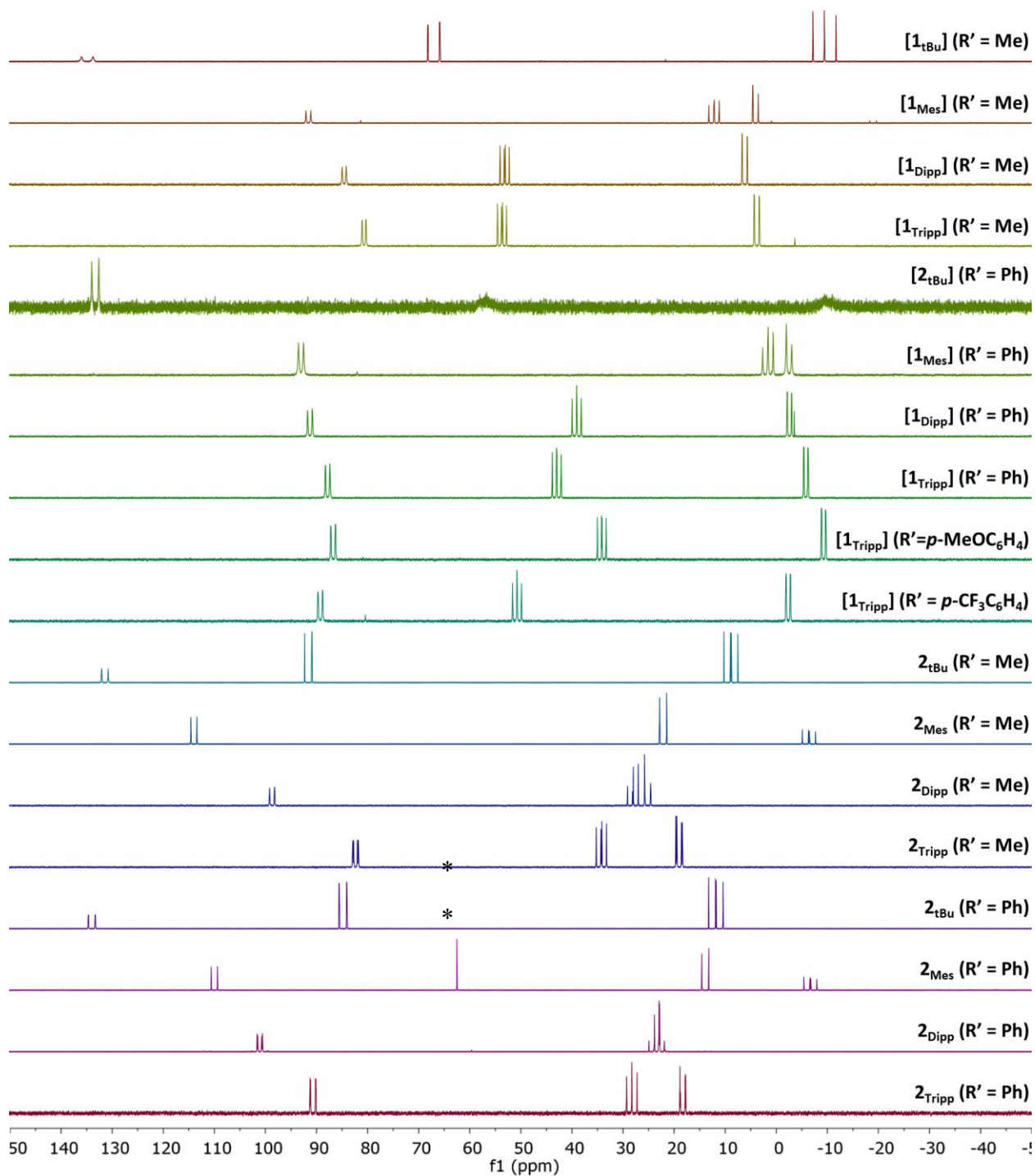


Figure A.53 Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in CDCl_3 of 1-aza-2,3,4-triphosphenes synthesized herein (* denotes unknown impurities)

A.2 UV-Visible spectroscopy

A.2.1 General Remarks Triflate salts used for UV-Visible spectroscopy were washed with copious amounts of hexanes, and recrystallized prior to use. Free bases were recrystallized prior to use and separation from [NEt₃H][OTf] was verified by ¹H NMR. All UV-Vis spectra were obtained in CH₂Cl₂ in Spectrosil® Far UV Quartz window cuvettes sealed with GL14 caps (both from Starna Cells, Inc.). Samples were prepared in volumetric flasks in a dinitrogen-filled MBraun 200B glovebox equipped with a cold-well, which was maintained at 20 °C. Spectra were obtained either on an Agilent Technologies Cary 60 UV-Vis spectrometer at the medium speed setting from which a CH₂Cl₂ background was obtained separately and manually subtracted, or on an Agilent Technologies Cary 60 UV-Vis spectrometer from 300-800 nm coupled to a Cary Single Cell Peltier thermocouple at 20 °C at the medium speed setting from which a CH₂Cl₂ background was obtained and automatically subtracted. All compounds in the study were found to follow Beer-Lambert law, and plots were not taken for **2_{tBu}** (**R'** = **Me**) and **2_{Dipp}** (**R'** = **Me**) which exhibited no clear absorbance bands beyond 350 nm.

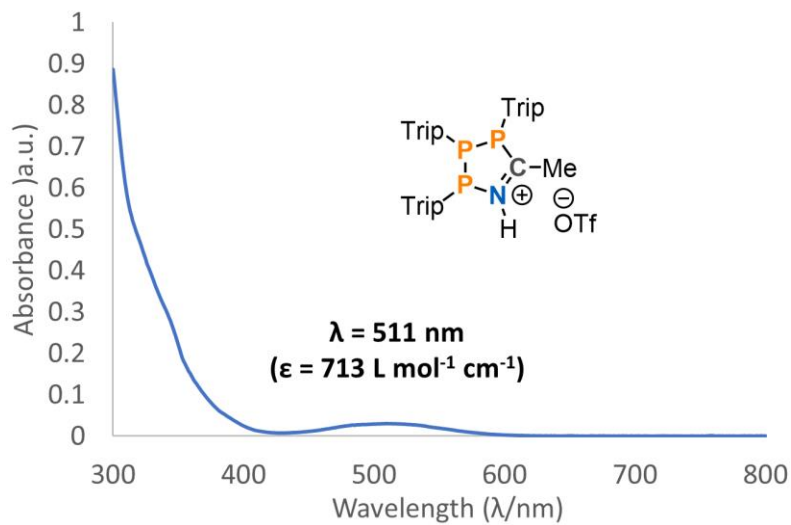


Figure A.54 UV-Visible spectrum of $[1_{\text{Tripp}}]^+$ ($R' = \text{Me}$), $4.660 \times 10^{-5} \text{ M}$ CH_2Cl_2 solution.

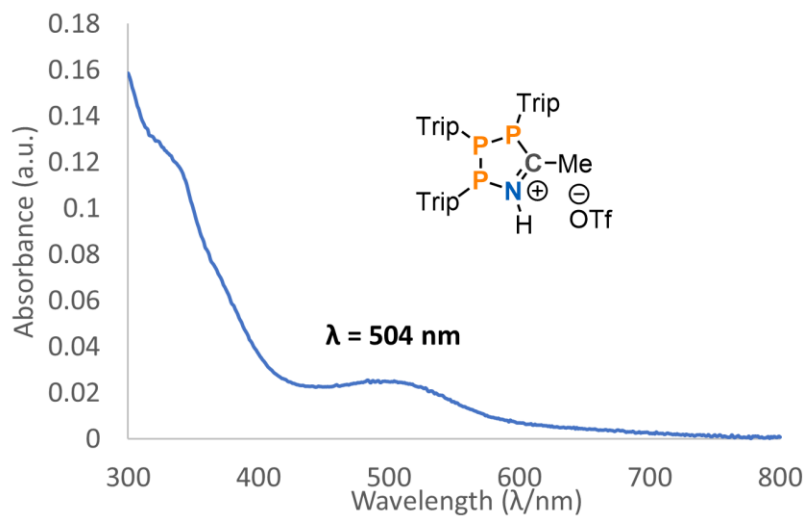


Figure A.55 UV-Visible spectrum of $[1_{\text{Tripp}}]^+$ ($R' = \text{Me}$), solid state dropcast thin film.

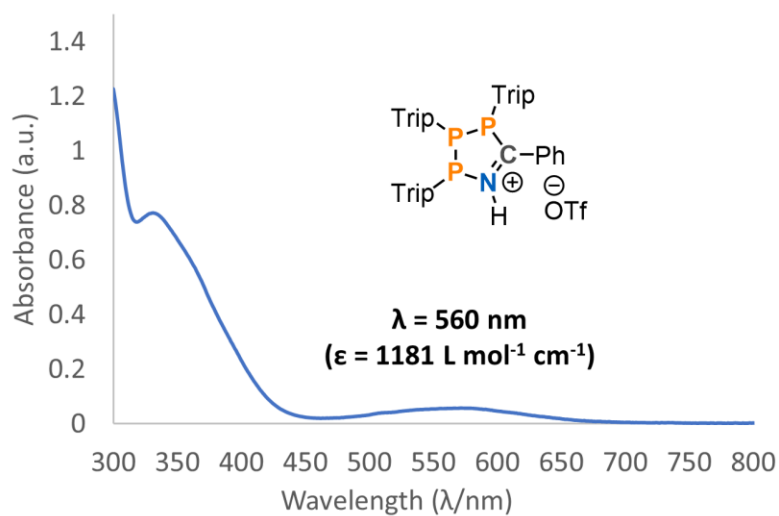


Figure A.56 UV-Visible spectrum of $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$), $5.229 \times 10^{-5} \text{ M}$ CH_2Cl_2 solution

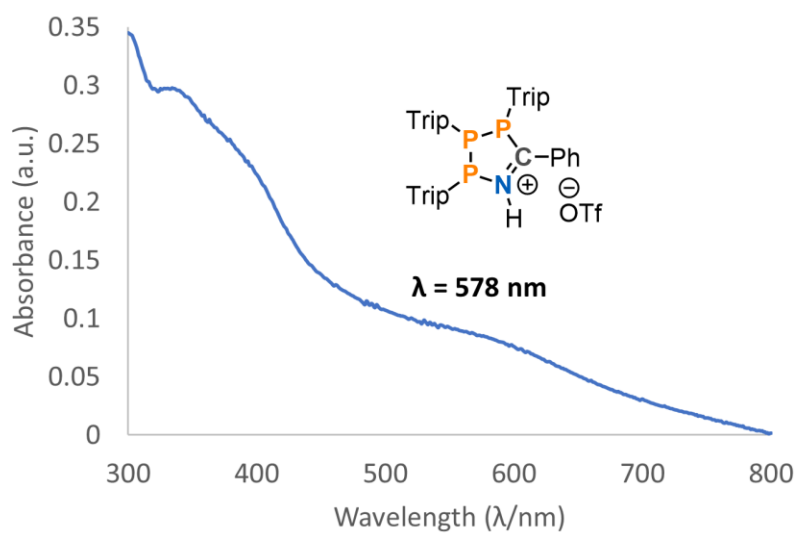


Figure A.57 UV-Visible spectrum of $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$), solid state dropcast thin film

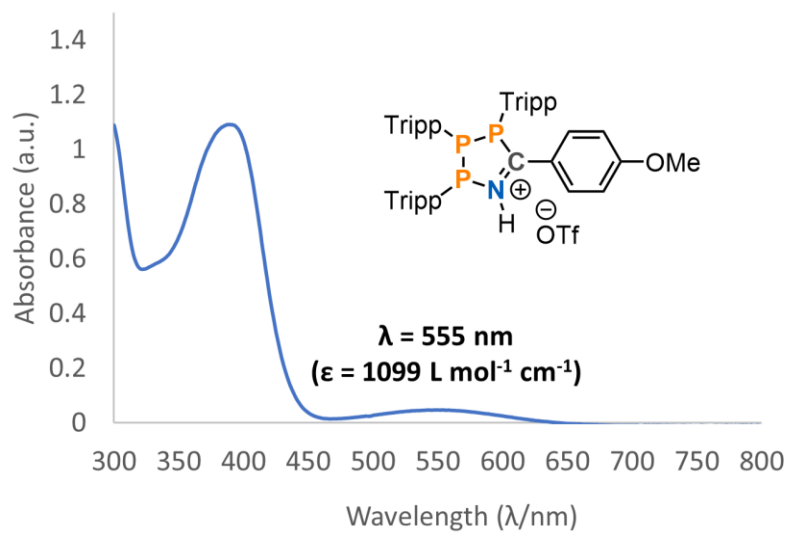


Figure A.58 UV-Visible spectrum of $[1_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-MeOC}_6\text{H}_4$), $5.070 \times 10^{-5} \text{ M}$ CH_2Cl_2 solution

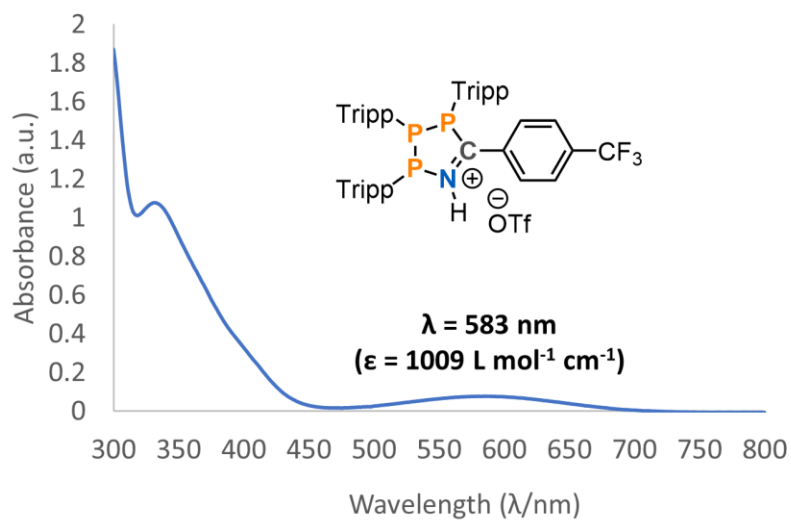


Figure A.59 UV-Visible spectrum of $[1_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-CF}_3\text{C}_6\text{H}_4$), $8.202 \times 10^{-6} \text{ M}$ CH_2Cl_2 solution

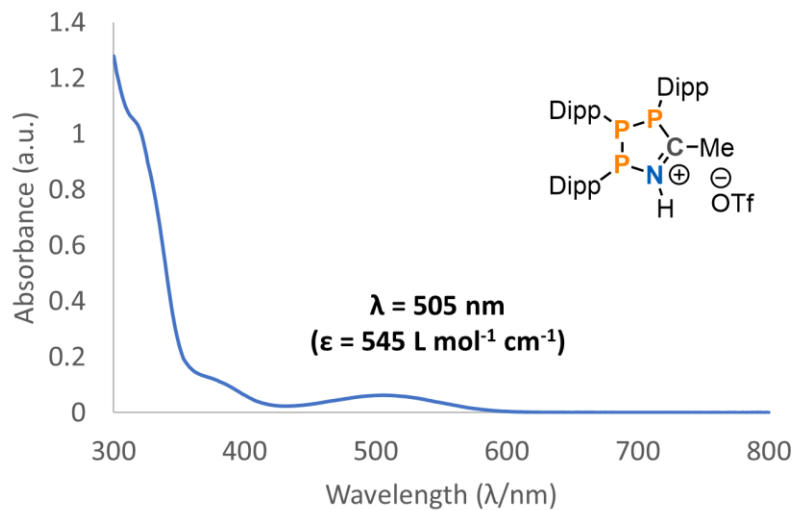


Figure A.60 UV-Visible spectrum of $[1_{\text{Dipp}}]^+$ ($R' = \text{Me}$), $1.085 \times 10^{-4} \text{ M}$ CH_2Cl_2 solution

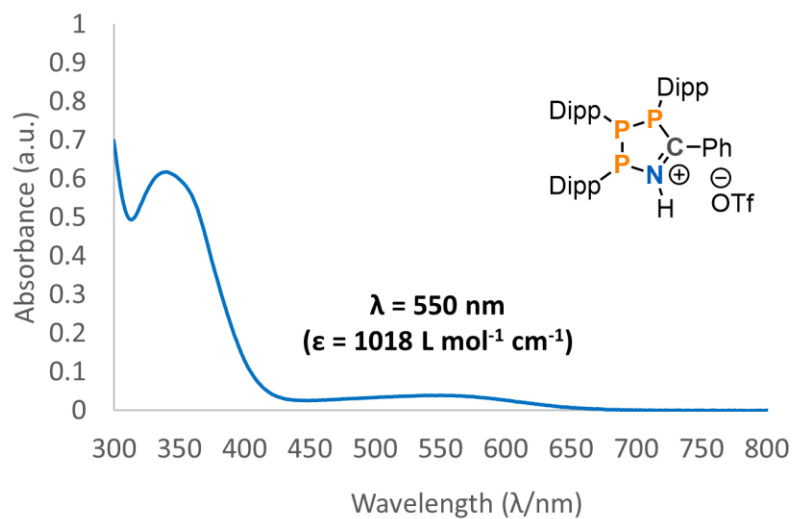


Figure A.61 UV-Visible spectrum of $[1_{\text{Dipp}}]^+$ ($R' = \text{Ph}$), $6.025 \times 10^{-5} \text{ M}$ CH_2Cl_2 solution

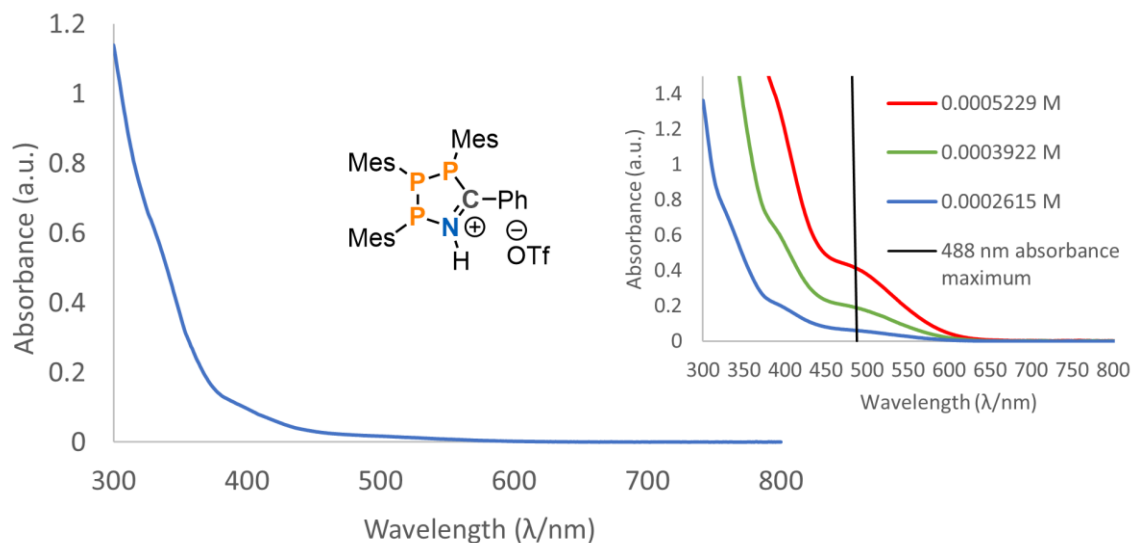


Figure A.62 UV-Visible spectrum of $[1_{\text{Mes}}]^+$ ($R' = \text{Ph}$), 1.112×10^{-4} M CH_2Cl_2 solution; inset: higher concentration solutions of $[1_{\text{Mes}}]^+$ ($R' = \text{Ph}$) demonstrating the appearance of a low absorptivity absorbance band attributed to a charge transfer phenomenon in this system.

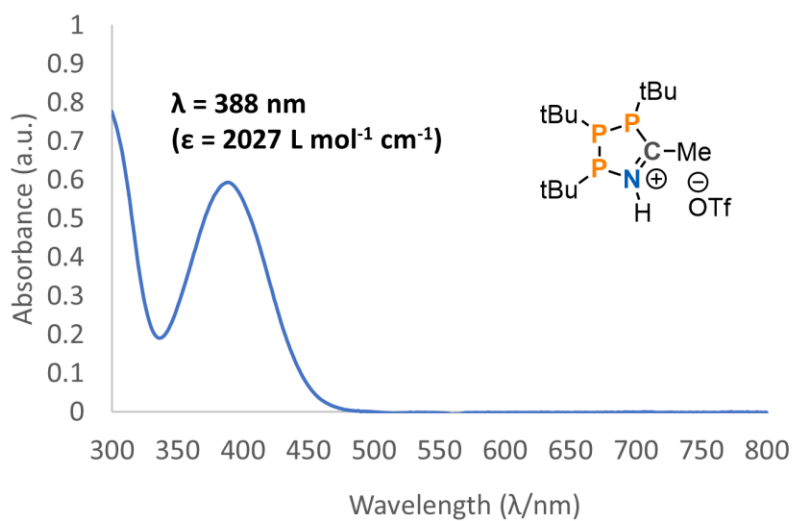


Figure A.63 UV-Visible spectrum of $[1_{\text{tBu}}]^+$ ($R' = \text{Me}$), 2.855×10^{-4} M CH_2Cl_2 solution

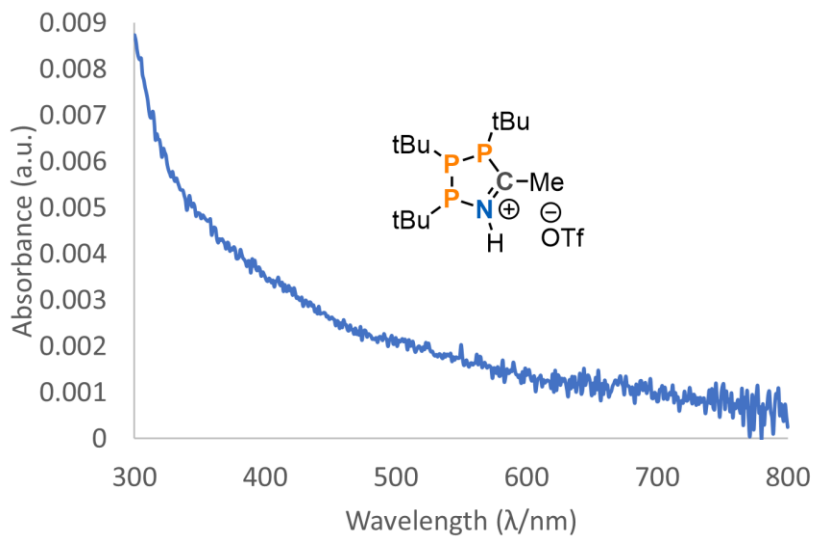


Figure A.64 UV-Visible spectrum of $[1_{tBu}]^+$ ($R' = \text{Me}$), solid state dropcast thin film

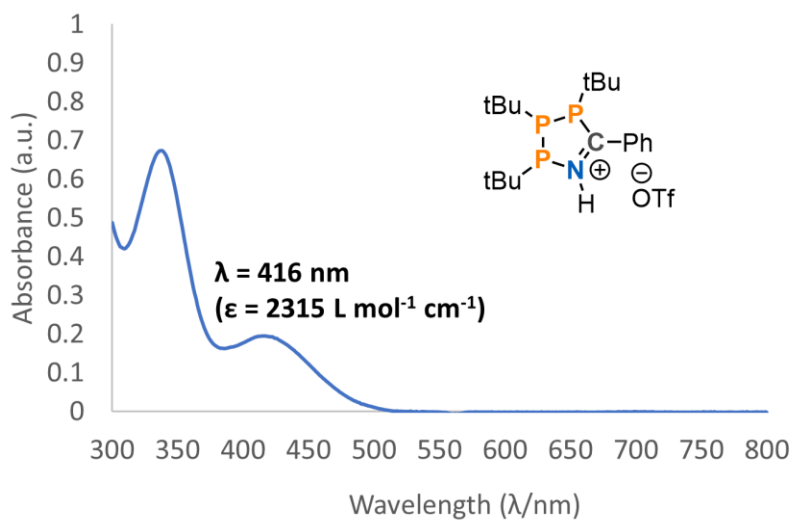


Figure A.65 UV-Visible spectrum of $[1_{tBu}]^+$ ($R' = \text{Ph}$), $8.827 \times 10^{-5} \text{ M}$ CH_2Cl_2 solution

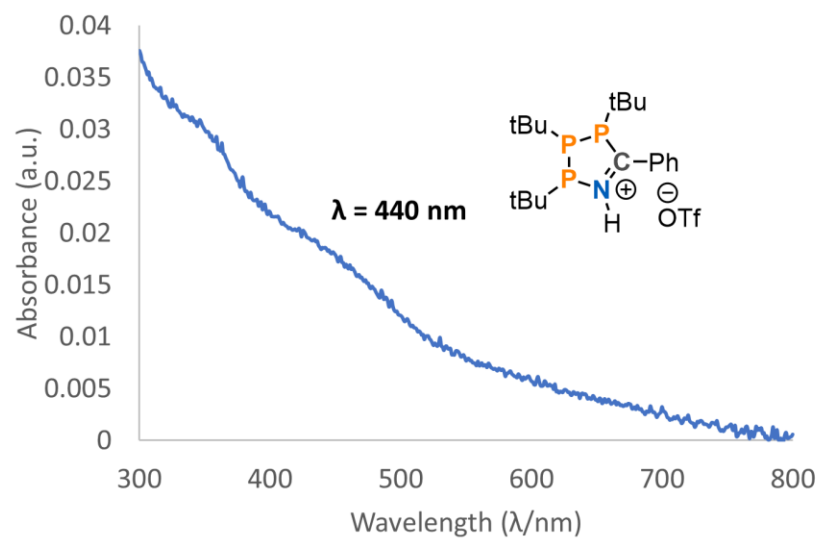


Figure A.66 UV-Visible spectrum of $[1_{tBu}]^+$ ($R' = Ph$), solid state dropcast thin film

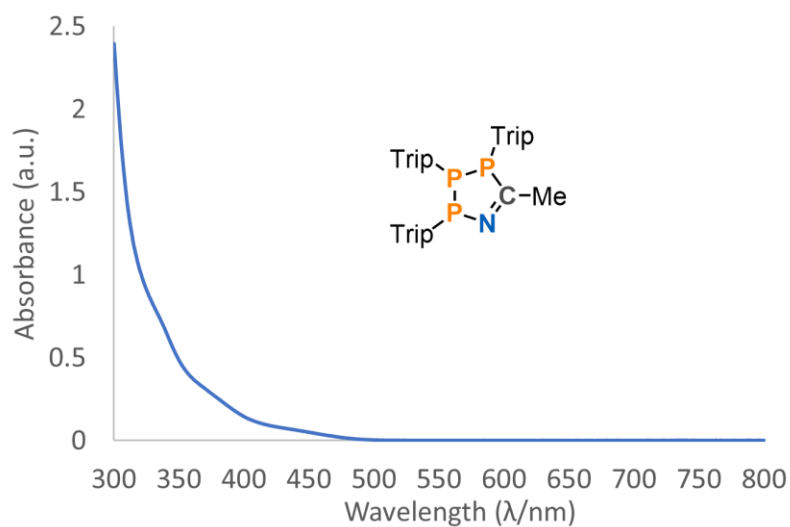


Figure A.67 UV-Visible spectrum of 2_{Tripp} ($R' = Me$), 6.720×10^{-5} M CH_2Cl_2 solution

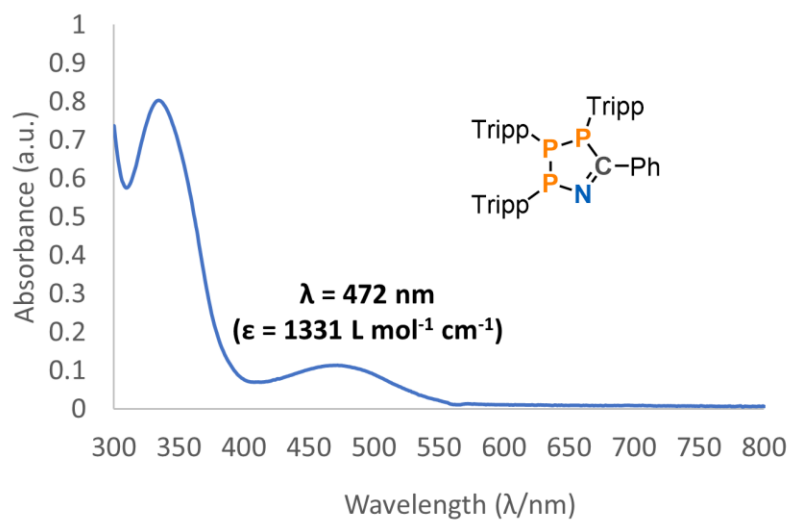


Figure A.68 UV-Visible spectrum of **2_{Tripp} (R' = Ph)**, $6.947 \times 10^{-5} \text{ M}$ CH_2Cl_2 solution

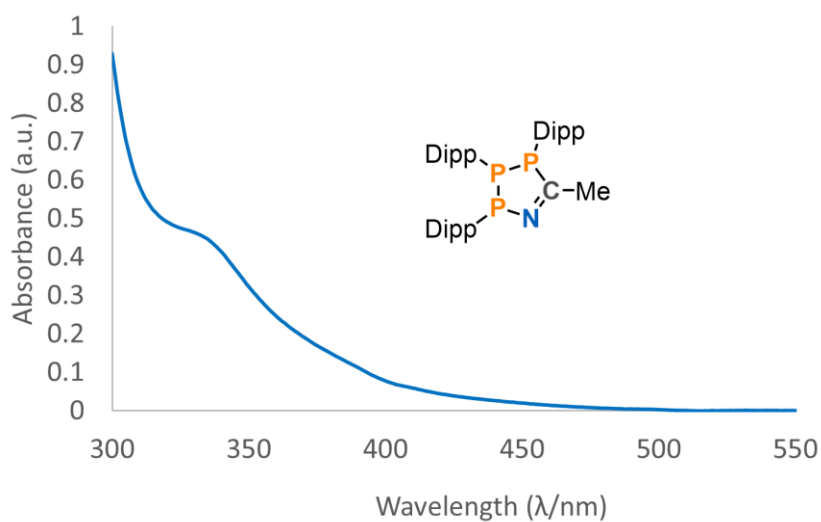


Figure A.69 UV-Visible spectrum of **2_{Dipp} (R' = Me)**, $9.719 \times 10^{-5} \text{ M}$ CH_2Cl_2 solution

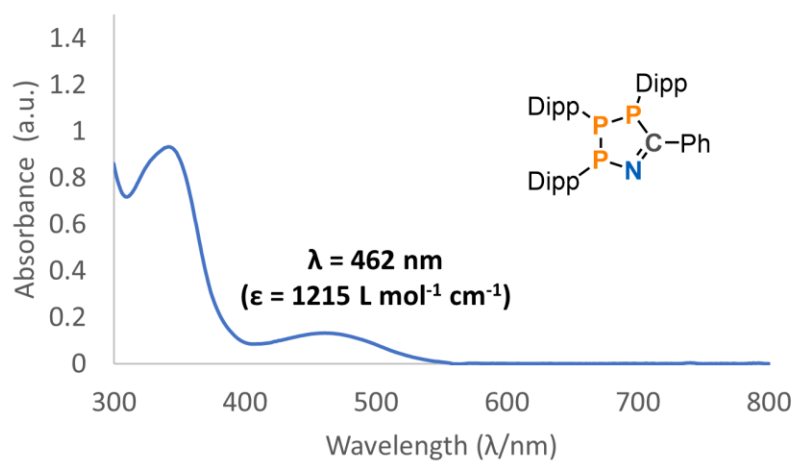


Figure A.70 UV-Visible spectrum of **2_{Dipp}** (**R'** = **Ph**), 1.108x10⁻⁴ M CH₂Cl₂ solution

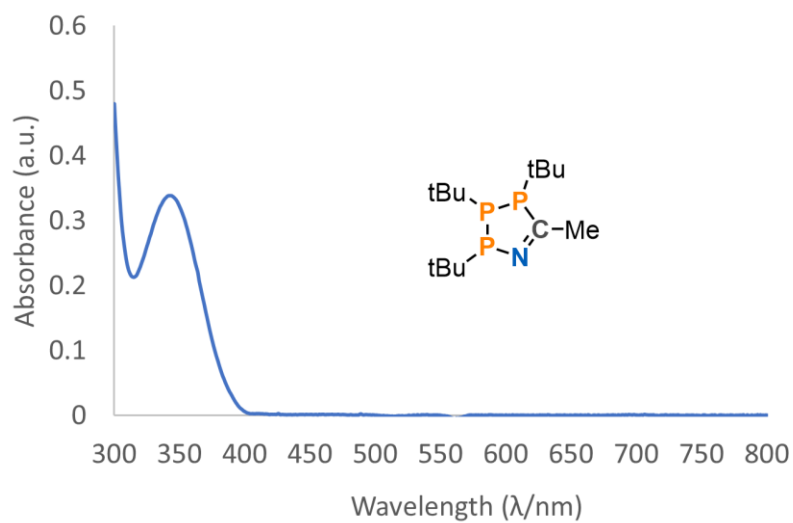


Figure A.71 UV-Visible spectrum of **2_{tBu}** (**R'** = **Me**), 1.283x10⁻⁴ M CH₂Cl₂ solution

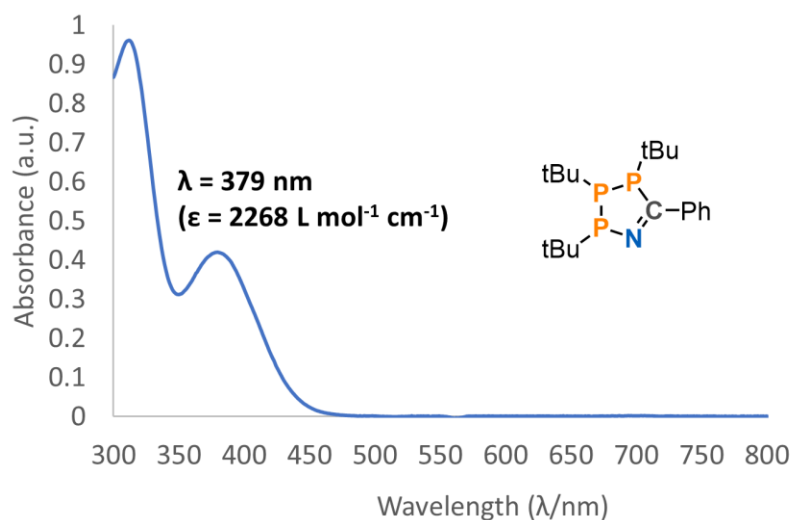
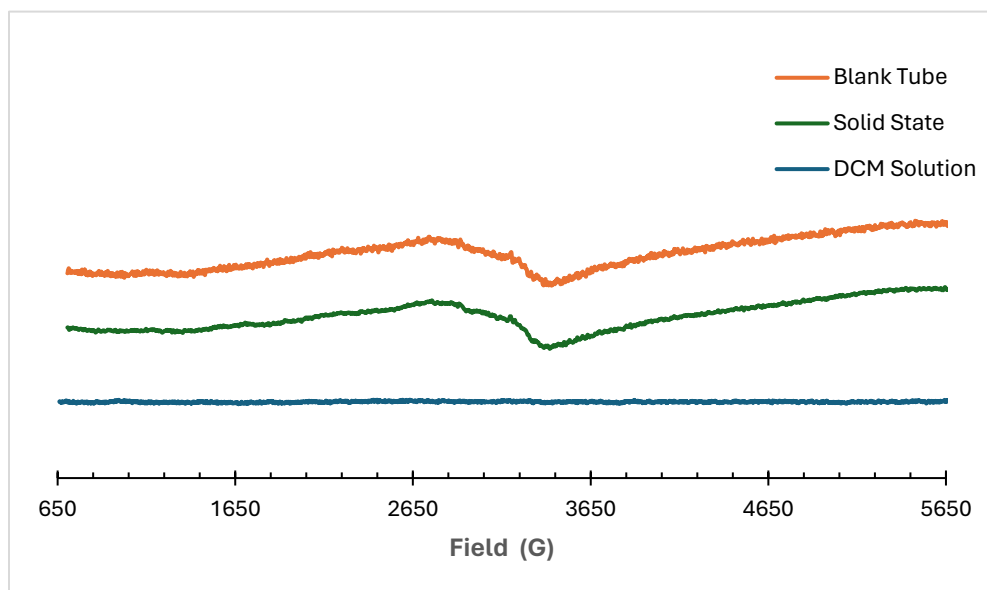


Figure A.72 UV-Visible spectrum of **2_{tBu}** (**R'** = **Ph**), 1.851x10⁻⁴ M CH₂Cl₂ solution

A.3 EPR spectroscopy

EPR spectra in both solid state and solution are shown for [**1_{Tripp}**]⁺ (**R'** = **Ph**), as a prototypical example to demonstrate the diamagnetic nature of the species reported herein.



A.4 Crystallographic Details

A.4.1 General Remarks

Red blocks of $[1_{\text{Tripp}}]^+$ ($R' = \text{Me}$) were grown from layering hexanes over a fluorobenzene solution at $-30\text{ }^{\circ}\text{C}$. Dark blue blocks of $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$) were grown from layering hexanes over a fluorobenzene solution at $-30\text{ }^{\circ}\text{C}$. Red blocks of $\{[1_{\text{Dipp}}]^+ (R' = \text{Me})\} \cdot \text{PhF}$ were grown from layering hexanes over a fluorobenzene solution at $-30\text{ }^{\circ}\text{C}$. Dark blue blocks of $[1_{\text{Dipp}}]^+$ ($R' = \text{Ph}$) were grown from layering hexanes over a fluorobenzene solution at $-30\text{ }^{\circ}\text{C}$. Yellow blocks of $[1_{\text{Mes}}]^+$ ($R' = \text{Me}$) were grown via the slow diffusion of a hexanes/pentane mixture into a fluorobenzene solution doped with a small amount of toluene at $-30\text{ }^{\circ}\text{C}$. Orange blocks of $[1_{\text{Mes}}]^+$ ($R' = \text{Ph}$) were grown from layering a fluorobenzene solution with hexanes at $-30\text{ }^{\circ}\text{C}$. Orange blocks of $\{[1_{\text{tBu}}]^+ (R' = \text{Ph})\} \cdot \text{CH}_2\text{Cl}_2$ were grown by layering a CH_2Cl_2 solution with hexanes at $-30\text{ }^{\circ}\text{C}$. Black-blue rectangular prisms of $[1_{\text{Tripp}}]^+$ ($R' = p\text{-CF}_3\text{C}_6\text{H}_4$) were grown by layering a fluorobenzene solution with hexanes at $-30\text{ }^{\circ}\text{C}$. Burgundy prisms of $[1_{\text{Tripp}}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4$) were grown by layering a fluorobenzene solution with hexanes at $-30\text{ }^{\circ}\text{C}$. Pale yellow prisms of 2_{Tripp} ($R' = \text{Me}$) were grown from a saturated pentane solution at $-30\text{ }^{\circ}\text{C}$. Orange needles of 2_{Tripp} ($R' = \text{Ph}$) were grown from a saturated acetonitrile solution at $-30\text{ }^{\circ}\text{C}$. Yellow blocks of 2_{Dipp} ($R' = \text{Me}$) were grown from a saturated hexanes solution at $-30\text{ }^{\circ}\text{C}$. Orange prisms of 2_{Dipp} ($R' = \text{Ph}$) were grown from a saturated pentane solution at $-30\text{ }^{\circ}\text{C}$. Colourless blocks of 2_{Mes} ($R' = \text{Me}$) were grown from a saturated hexanes solutions at $-30\text{ }^{\circ}\text{C}$. Yellow blocks of 2_{Mes} ($R' = \text{Ph}$) were grown from a saturated hexanes solutions at $-30\text{ }^{\circ}\text{C}$. Yellow needles of 2_{tBu} ($R' = \text{Ph}$) were grown from a saturated hexanes solution at $-30\text{ }^{\circ}\text{C}$.

The single crystal X-ray diffraction experiments were carried out on a Bruker APEX II diffractometer using either Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$) or Cu-K α radiation ($\lambda = 1.54178\text{ \AA}$) and collected at 90 (2) or 100(2) K. The data collection was performed using a CCD area detector from a single crystal mounted on a glass fibre. The total number of runs and images was based on the strategy calculation from the program APEX3. Data reduction, scaling and absorption corrections were performed using SAINT. The structures were solved and the space group determined by the SHELXT⁵ structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of SHELXL⁶ in Olex2.⁷ All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atom positions were calculated geometrically and refined using the riding model, whereas all nitrogen-bound hydrogen atoms were located in the Fourier difference map and freely refined. In the case of $[1_{\text{tBu}}]^+$ ($R' = \text{Ph}$) the PLATON SQUEEZE solvent mask was used due to the presence of severely disordered CH_2Cl_2 molecule in the lattice.⁸ A disordered CF_3 group in $[1_{\text{Tripp}}]^+$ ($R' = p\text{-CF}_3\text{C}_6\text{H}_4$) was successfully modelled over two positions and refined with the sum of the occupancies set to 1. A fluorobenzene molecule in the $\{[1_{\text{Dipp}}]^+ (R' = \text{Me})\} \cdot \text{PhF}$ solvate demonstrated positional disorder and was successfully modelled over 3 positions with the sum of the occupancies set to 1. 2_{Mes} ($R' = \text{Me}$) crystallized with two crystallographically unique molecules in the asymmetric unit ($Z = 8$, $Z' = 2$), related to each other by two-fold symmetry along the c-axis. 2_{Mes} ($R' = \text{Ph}$) also crystallized with two

crystallographically unique molecules in the asymmetric unit ($Z = 4$, $Z' = 2$), related to each other by inversion symmetry.

Below we briefly discuss some trends in core P_3CN bond lengths of the synthesized 1-aza-2,3,4-triphospholenes. For the purpose of this discussion, we will refer to the phosphorus atoms of the central P_3CN framework as P_C (phosphorus bound to the nitrile carbon atom), P_N (phosphorus bound to the nitrile nitrogen atom), and P_P for the phosphorus atom bound between P_C and P_N .

C=N: When comparing the $[1R]^+$ ($R' = Me$) series, the length of C=N bonds were invariant within experimental error for both, with values of 1.299(2) Å in $[1Dipp]^+$ to 1.309(9) Å in $[1Mes]^+$ and the $2R$ ($R' = Me$) series was similarly invariant with bond lengths of 1.278(6) Å in $2tBu$ to 1.289(6) Å in $2Tripp$. Similarly, the C=N bonds for the $[1R]^+$ ($R' = Ph$) series were invariant within experimental error, with values of 1.309(4) Å in $[1Mes]^+$ to 1.312(4) Å in $[1Dipp]^+$, while deprotonation to $2R$ ($R' = Ph$) lowered the bond lengths to a narrow range of 1.280(3) Å in $2Mes$ to 1.294(5) Å in $2Tripp$. Overall a shortening in C=N bond length is observed upon deprotonation, This makes sense chemically, as protonation of the imino moiety naturally results in partial donation of electron density compared to the neutral state.

P_C-P : $[1Tripp]^+$ ($R' = Me$) and $[1Dipp]^+$ ($R' = Me$) have slightly longer bonds (2.226(1) Å and 2.2360(5) Å, respectively) than than $[1Mes]^+$ ($R' = Me$) and $[1tBu]^+$ ($R' = Me$) (2.192(3) Å and 2.192(1) Å, respectively). Deprotonation results in $2Tripp$ ($R' = Me$) and $2Dipp$ ($R' = Me$) having bonds shortened to 2.185(1) Å and 2.1947(5) Å, while both molecules in $2Mes$ ($R' = Me$) (2.193(1) Å, 2.192(1) Å) and $2tBu$ ($R' = Me$) (2.191(2) Å) are invariant within experimental error to their protonated forms. Similar trends were seen in $[1R]^+$ ($R' = Ph$) species. P_C-P distances incrementally increased from 2.1958(4) Å in $[1tBu]^+$ ($R' = Ph$) to 2.2262(4) Å in $[1Tripp]^+$ ($R' = Ph$). For $2R$ ($R' = Ph$) species, similar trends to $2R$ ($R' = Me$) species are seen in P_C-P bonds, with $2tBu$ ($R' = Ph$) showing virtually no change in length (2.1935(3) Å) from $[1tBu]^+$ ($R' = Ph$), and slight but steady shortening in the lengths of $2Mes$ ($R' = Ph$) (2.1861(9)/2.1907(8) Å), $2Dipp$ ($R' = Ph$) (2.1972(5) Å), and $2Tripp$ ($R' = Ph$) (2.201(1) Å) compared to their protonated states.

P_N-P : In the case of P_N-P bonds, all $[1R]^+$ ($R' = Me$) species are very similar to each other within error (2.233(1) Å, 2.2387(6) Å, 2.237(3) Å and 2.212(1) Å for $R = Tripp$, $Dipp$, Mes , tBu respectively), but upon deprotonation P_N-P bonds in $2R$ ($R = Tripp, Dipp, Mes; R' = Me$) are lengthened to similar values of 2.265(2), 2.2682(5), and 2.271(2)/2.266(2) Å in $R = Tripp$, $Dipp$, and Mes respectively, while $2tBu$ ($R' = Me$) slightly lengthens to 2.227(1) Å. Similar trends were seen in $[1R]^+$ ($R' = Ph$) species. P_N-P distances ranged from 2.2086(6) Å for $[1tBu]^+$ ($R' = Ph$) to 2.2458(6) Å for $[1Tripp]^+$ ($R' = Ph$), while bond lengths increase steadily from $2tBu$ ($R' = Ph$) (2.2322(3) Å) to $2Mes$ ($R' = Ph$) (2.2497(9)/2.256(1) Å) to $2Dipp$ ($R' = Ph$) (2.2725(9) Å), while $2Tripp$ ($R' = Ph$) increases only slightly to 2.256(1) Å.

P_N-N and P_C-C : We noted consistent differences in the distances of P_N-N and P_C-C bond distances between protonated and deprotonated states across all the species in our study regardless of substituent at phosphorus. This is illustrated by $[1Tripp]^+$ ($R' = Ph$)/ $2Tripp$ ($R' = Ph$) as a

comparative example. When considering the P_N–N bond, [1_{Tripp}]⁺ (**R'** = **Ph**) measures 1.775(1) Å similar to those of other [1_R]⁺ (**R'** = **Ph**) species, while deprotonation lowers the P_N–N bond length to 1.708(3) Å. In the case of the P_C–C bond, [1_{Tripp}]⁺ (**R'** = **Ph**) measures 1.820(1) Å similarly to the other [1_R]⁺ (**R'** = **Ph**) species, while deprotonation increases the bond length to 1.853(4) Å. In comparing bond distances in the P₃CN core across the series of [1_R]⁺ (**R'** = **Ph**, *p*-MeOC₆H₄, *p*-CF₃C₆H₄), no substantial differences were found, and as such their structural differences manifest solely in a change in deplanarization.

Table A.1 Summary of crystallographic data, Part 1

	[1Tripp] ⁺ (R' = Me)	[1Tripp] ⁺ (R' = Ph)	{[1Dipp] ⁺ (R' = Me)}·PhF	[1Dipp] ⁺ (R' = Ph)	[1Mes] ⁺ (R' = Me)	[1Mes] ⁺ (R' = Ph)
Empirical formula	C ₄₈ H ₇₃ F ₃ NO ₃ P ₃ S	C ₅₃ H ₇₅ NO ₃ F ₃ P ₃ S	C ₄₅ H ₆₀ F ₄ NO ₃ P ₃ S	C ₄₄ H ₅₇ NO ₃ F ₃ P ₃ S	C ₃₀ H ₃₇ F ₃ NO ₃ P ₃ S	C ₃₅ H ₃₉ F ₃ NO ₃ P ₃ S
Formula weight	894.04	956.11	863.91	829.87	641.57	703.64
Temperature/ K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>a</i> /Å	13.0397(5)	13.2057(6)	10.6808(4)	10.8554(10)	11.5917(10)	11.005(2)
<i>b</i> /Å	21.2666(8)	14.4979(7)	20.4088(8)	11.7203(11)	22.103(2)	12.506(2)
<i>c</i> /Å	18.7063(7)	16.1649(8)	20.8267(8)	18.4078(16)	13.3286(12)	15.198(3)
α /°	90	65.0680(10)	90	106.573(2)	90	113.278(6)
β /°	101.2170(10)	79.1030(10)	96.752(2)	104.787(2)	115.243(3)	98.207(7)
γ /°	90	64.9930(10)	90	94.530(3)	90	93.456(7)
Volume/Å ³	5088.4(3)	2543.1(2)	4508.4(3)	2141.1(3)	3088.8(5)	1886.1(6)
<i>Z</i>	4	2	4	2	4	2
ρ_{calc} /cm ³	1.167	1.249	1.273	1.287	1.380	1.239
μ /mm ⁻¹	0.207	0.212	0.234	0.241	0.311	0.261
<i>F</i> (000)	1920	1024	1832	880	1344	736
Crystal size/mm ³	0.13 × 0.1 × 0.05	0.14 × 0.12 × 0.06	0.35 × 0.22 × 0.2	0.2 × 0.17 × 0.12	0.15 × 0.09 × 0.05	0.11 × 0.09 × 0.04
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	Mo K α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.184 to 50.862	2.778 to 61.258	2.804 to 61.174	3.676 to 52.918	3.686 to 44.992	3.574 to 55.912
Index ranges	-13 ≤ <i>h</i> ≤ 15, -25 ≤ <i>k</i> ≤ 25, -22 ≤ <i>l</i> ≤ 22	-18 ≤ <i>h</i> ≤ 18, -20 ≤ <i>k</i> ≤ 20, -23 ≤ <i>l</i> ≤ 23	-15 ≤ <i>h</i> ≤ 15, -29 ≤ <i>k</i> ≤ 23, -29 ≤ <i>l</i> ≤ 29	-13 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 14, -22 ≤ <i>l</i> ≤ 23	-12 ≤ <i>h</i> ≤ 11, 0 ≤ <i>k</i> ≤ 23, 0 ≤ <i>l</i> ≤ 14	-14 ≤ <i>h</i> ≤ 14, -16 ≤ <i>k</i> ≤ 16, -20 ≤ <i>l</i> ≤ 18
Reflections collected	50698	63351	60974	34614	4016	20519
Independent reflections	9359 [<i>R</i> _{int} = 0.0762, <i>R</i> _{sigma} = 0.0706]	15654 [<i>R</i> _{int} = 0.0503, <i>R</i> _{sigma} = 0.0480]	13812 [<i>R</i> _{int} = 0.0373, <i>R</i> _{sigma} = 0.0341]	8818 [<i>R</i> _{int} = 0.0502, <i>R</i> _{sigma} = 0.0553]	4016 [<i>R</i> _{int} = 0.222, <i>R</i> _{sigma} = 0.1394]	9011 [<i>R</i> _{int} = 0.0667, <i>R</i> _{sigma} = 0.1052]
Data/restraint s/parameters	9359/36/582	15654/0/599	13812/0/534	8818/0/512	4016/0/381	9011/0/428
Goodness-of-fit on <i>F</i> ²	1.1	1.012	1.026	1.018	1.064	0.967
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0674, <i>wR</i> ₂ = 0.1632	<i>R</i> ₁ = 0.0400, <i>wR</i> ₂ = 0.0880	<i>R</i> ₁ = 0.0408, <i>wR</i> ₂ = 0.1005	<i>R</i> ₁ = 0.0515, <i>wR</i> ₂ = 0.1183	<i>R</i> ₁ = 0.0852, <i>wR</i> ₂ = 0.1812	<i>R</i> ₁ = 0.0526, <i>wR</i> ₂ = 0.1084
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1110, <i>wR</i> ₂ = 0.1816	<i>R</i> ₁ = 0.0613, <i>wR</i> ₂ = 0.0979	<i>R</i> ₁ = 0.0575, <i>wR</i> ₂ = 0.1094	<i>R</i> ₁ = 0.0823, <i>wR</i> ₂ = 0.1376	<i>R</i> ₁ = 0.1575, <i>wR</i> ₂ = 0.2095	<i>R</i> ₁ = 0.0928, <i>wR</i> ₂ = 0.1261
Largest diff. peak/hole / e Å ⁻³	1.61/-0.62	0.61/-0.41	0.66/-0.47	0.56/-0.47	0.38/-0.44	0.40/-0.40

Table A.2 Summary of crystallographic data, Part 2

	[18Bu]⁺ (R' = Ph)	2Tripp (R' = Me)	2Tripp (R' = Ph)	2Dipp (R' = Me)	2Dipp (R' = Ph)	2Mes (R' = Me)
Empirical formula	C ₂₀ H ₃₃ F ₃ NO ₃ P ₃ S	C ₄₇ H ₇₂ NP ₃	C ₅₂ H ₇₄ NP ₃	C ₃₈ H ₅₄ NP ₃	C ₄₃ H ₅₆ NP ₃	C ₂₉ H ₃₆ NP ₃
Formula weight	517.44	743.96	806.03	617.73	679.79	491.5
Temperature/ K	100(2)	90(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	orthorhombic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P-1	P-1	Pca2 ₁
a/Å	9.5059(5)	16.9451(7)	12.9840(4)	11.3450(8)	8.7516(4)	15.6132(9)
b/Å	14.4773(8)	13.2118(6)	8.7134(3)	11.9683(8)	11.3824(5)	12.7998(7)
c/Å	21.4699(12)	20.9116(10)	42.5367(14)	15.3035(10)	20.2888(11)	26.6995(16)
α/°	90	90	90	80.276(2)	86.071(2)	90
β/°	91.586(2)	104.798(4)	98.699(3)	79.095(2)	89.119(3)	90
γ/°	90	90	90	63.100(2)	79.852(2)	90
Volume/Å ³	2953.6(3)	4526.3(4)	4757.0(3)	1811.4(2)	1984.75(17)	5335.8(5)
Z	4	4	4	2	2	8
ρ _{calc} /cm ³	1.164	1.092	1.125	1.133	1.138	1.224
μ/mm ⁻¹	0.309	1.422	1.39	0.19	0.179	0.241
F(000)	1088	1624	1752	668	732	2096
Crystal size/mm ³	0.41 × 0.37 × 0.35	0.18 × 0.12 × 0.07	0.1 × 0.01 × 0.01	0.26 × 0.14 × 0.09	0.24 × 0.12 × 0.07	0.26 × 0.16 × 0.05
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.31 to 61.024	5.394 to 112.118	4.202 to 112.108	2.722 to 61.234	2.012 to 52.862	3.05 to 55.85
Index ranges	-13 ≤ h ≤ 13, 0 ≤ k ≤ 20, 0 ≤ l ≤ 30	-18 ≤ h ≤ 17, 0 ≤ k ≤ 14, 0 ≤ l ≤ 22	-13 ≤ h ≤ 12, -9 ≤ k ≤ 9, -44 ≤ l ≤ 45	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21	-10 ≤ h ≤ 10, -14 ≤ k ≤ 13, -25 ≤ l ≤ 25	-20 ≤ h ≤ 20, -16 ≤ k ≤ 16, -35 ≤ l ≤ 35
Reflections collected	48692	52653	39675	53484	28331	75209
Independent reflections	8885 [R _{int} = 0.045, R _{sigma} = 0.0331]	5896 [R _{int} = 0.199, R _{sigma} = 0.1066]	6153 [R _{int} = 0.1149, R _{sigma} = 0.0775]	11113 [R _{int} = 0.0357, R _{sigma} = 0.0328]	8107 [R _{int} = 0.0308, R _{sigma} = 0.0355]	12747 [R _{int} = 0.0594, R _{sigma} = 0.0461]
Data/restraint s/parameters	8885/0/293	5896/0/479	6153/390/561	11113/0/392	8107/0/436	12747/1/615
Goodness-of-fit on F ²	1.081	1.066	1.042	0.93	1.037	1.036
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0410, wR ₂ = 0.1112	R ₁ = 0.0669, wR ₂ = 0.1526	R ₁ = 0.0596, wR ₂ = 0.1308	R ₁ = 0.0363, wR ₂ = 0.1134	R ₁ = 0.0373, wR ₂ = 0.0860	R ₁ = 0.0405, wR ₂ = 0.0832
Final R indexes [all data]	R ₁ = 0.0507, wR ₂ = 0.1148	R ₁ = 0.1001, wR ₂ = 0.1677	R ₁ = 0.0867, wR ₂ = 0.1455	R ₁ = 0.0523, wR ₂ = 0.1289	R ₁ = 0.0507, wR ₂ = 0.0925	R ₁ = 0.0601, wR ₂ = 0.0907
Largest diff. peak/hole / e Å ⁻³	0.49/-0.62	0.43/-0.26	0.66/-0.35	0.43/-0.19	0.33/-0.21	0.34/-0.22

Table A.3 Summary of crystallographic data, Part 3

	2^{Mes} (R' = Ph)	2^{tBu} (R' = Ph)	[1^{Tripp}]⁺ (R' = <i>p</i>- MeOC₆H₄)	[1^{Tripp}]⁺ (R' = <i>p</i>- CF₃C₆H₄)	P₆Mes₆·Et₂O
Empirical formula	C ₃₄ H ₃₈ NP ₃	C ₁₉ H ₃₂ NP ₃	C ₅₄ H ₇₇ F ₃ NO ₄ P ₃ S	C ₅₄ H ₇₃ F ₆ NO ₃ P ₃ S	C ₅₈ H ₇₆ OP ₆
Formula weight	553.56	367.36	986.13	1024.11	975.00
Temperature/ K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2/ <i>c</i>
<i>a</i> /Å	13.3026(7)	7.3017(5)	13.7735(12)	14.4906(6)	13.273(4)
<i>b</i> /Å	15.2580(8)	9.9102(7)	14.3310(12)	15.0696(7)	8.550(3)
<i>c</i> /Å	16.3831(8)	15.2826(11)	16.4614(14)	17.5125(9)	24.630(8)
α /°	103.595(2)	91.383(2)	67.221(2)	69.989(2)	90
β /°	90.873(2)	101.010(2)	80.664(3)	82.093(2)	97.626(4)
γ /°	109.755(2)	104.534(2)	64.226(2)	72.732(2)	90
Volume/Å ³	3025.6(3)	1047.75(13)	2697.7(4)	3428.6(3)	2770.3(15)
<i>Z</i>	4	2	2	2	2
ρ_{calc} /cm ³	1.215	1.164	1.214	0.992	1.169
μ /mm ⁻¹	0.22	0.284	0.203	0.167	0.232
<i>F</i> (000)	1176	396	1056	1088	1044
Crystal size/mm ³	0.2 × 0.096 × 0.064	0.27 × 0.22 × 0.18	0.27 × 0.1 × 0.03	0.46 × 0.3 × 0.19	0.25 × 0.20 × 0. 10
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 Θ range for data collection/°	2.934 to 55.928	2.722 to 61.014	2.684 to 56.782	3.216 to 52.826	1.668 to 25.332
Index ranges	-17 ≤ <i>h</i> ≤ 17, -20 ≤ <i>k</i> ≤ 19, -21 ≤ <i>l</i> ≤ 21	-10 ≤ <i>h</i> ≤ 10, -14 ≤ <i>k</i> ≤ 14, -21 ≤ <i>l</i> ≤ 21	-18 ≤ <i>h</i> ≤ 17, -19 ≤ <i>k</i> ≤ 18, -21 ≤ <i>l</i> ≤ 21	-17 ≤ <i>h</i> ≤ 18, -18 ≤ <i>k</i> ≤ 18, -21 ≤ <i>l</i> ≤ 21	-15 ≤ <i>h</i> ≤ 15, -10 ≤ <i>k</i> ≤ 10, -29 ≤ <i>l</i> ≤ 19
Reflections collected	52172	24581	50897	71096	21991
Independent reflections	13662 [<i>R</i> _{int} = 0.0682, <i>R</i> _{sigma} = 0.0675]	6401 [<i>R</i> _{int} = 0.0354, <i>R</i> _{sigma} = 0.0301]	13452 [<i>R</i> _{int} = 0.0643, <i>R</i> _{sigma} = 0.0742]	14047 [<i>R</i> _{int} = 0.0320, <i>R</i> _{sigma} = 0.0258]	5012 [<i>R</i> _{int} = 0.1005, <i>R</i> _{sigma} = 0.0912]
Data/restraint s/parameters	13662/0/703	6401/0/217	13452/311/67 7	14047/87/658	5012/147/365
Goodness-of- fit on <i>F</i> ²	1.042	1.032	1.013	1.045	0.998
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0519, <i>wR</i> ₂ = 0.1250	<i>R</i> ₁ = 0.0268, <i>wR</i> ₂ = 0.0704	<i>R</i> ₁ = 0.0517, <i>wR</i> ₂ = 0.1099	<i>R</i> ₁ = 0.0539, <i>wR</i> ₂ = 0.1478	<i>R</i> ₁ = 0.0694, <i>wR</i> ₂ = 0.1921
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0755, <i>wR</i> ₂ = 0.1369	<i>R</i> ₁ = 0.0301, <i>wR</i> ₂ = 0.0723	<i>R</i> ₁ = 0.0972, <i>wR</i> ₂ = 0.1284	<i>R</i> ₁ = 0.0647, <i>wR</i> ₂ = 0.1567	<i>R</i> ₁ = 0.1136, <i>wR</i> ₂ = 0.2279
Largest diff. peak/hole / e Å ⁻³	0.40/-0.32	0.44/-0.23	0.45/-0.47	0.70/-0.50	0.902/-0.508

A.4.2 Crystal Structures of $[1_R]^+$ (R')

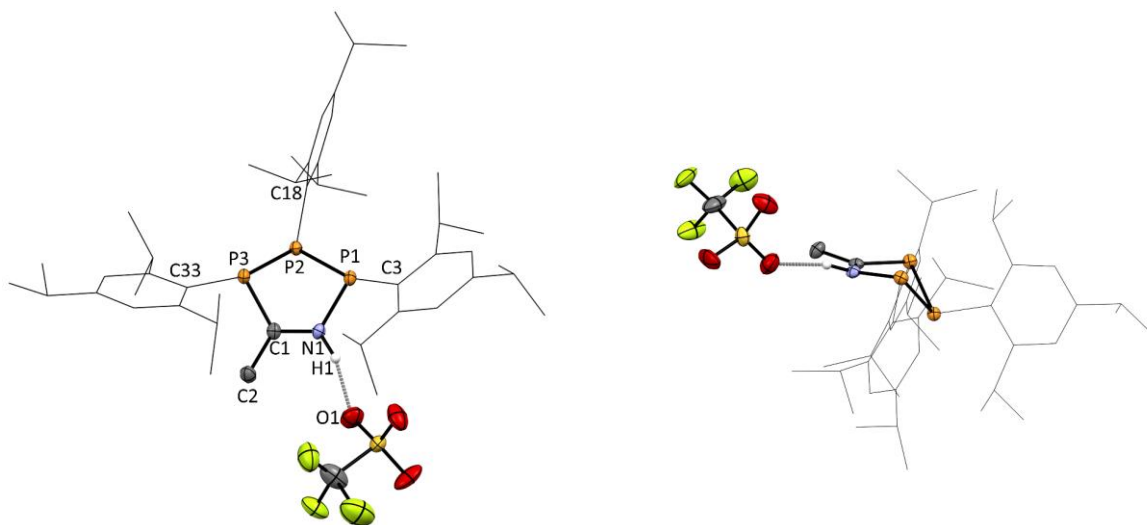


Figure A.73 Solid state molecular structure of $[1_{\text{Tripp}}]^+$ ($R' = \text{Me}$). Thermal ellipsoids are drawn at the 50% probability level. Tripp substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: P1-P2 2.233(1), P3-P2 2.226(1), P1-N1 1.787(3), P3-C1 1.810(4), C1-N1 1.300(5), C1-C2 1.496(5), N1-H1 0.95(5), O1-H1 1.79(5), P1-C3 1.835(4), P2-C18 1.844(4), P3-C33 1.79(5); P1-N1-C1 120.3(3), P3-C1-N1 118.5(3), P1-P2-P3 86.90(5), P2-P1-N1 90.7(1), P2-P3-C1 91.4(1), P2-P3-C33 113.3(1), C1-P3-C33 107.0(2), P2-P1-C3 100.3(1), N1-P1-C3 109.3(2), P1-P2-C18 99.6(1), P3-P2-C18 112.2(1).

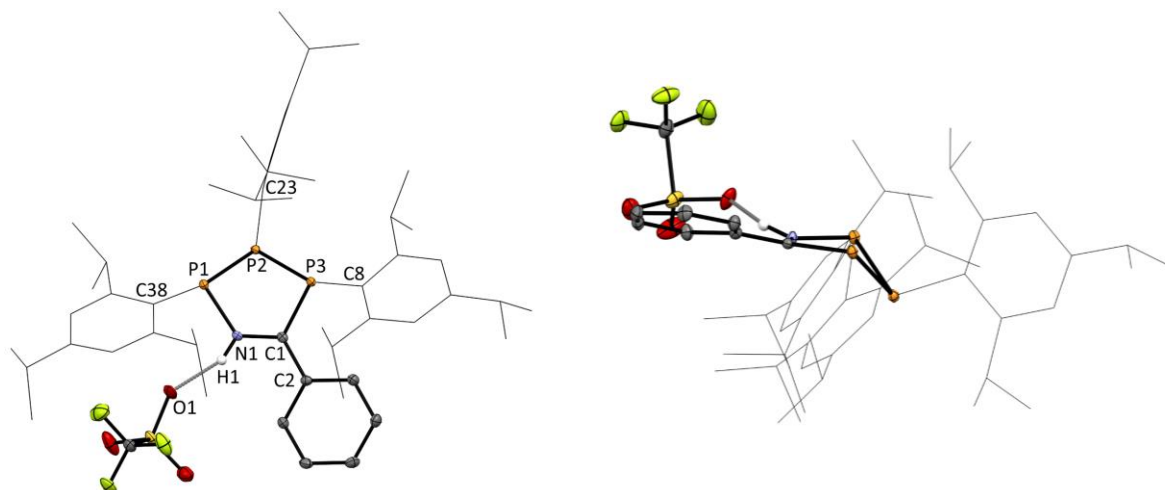


Figure A.74 Solid state molecular structure of $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$). Thermal ellipsoids are drawn at the 50% probability level. Tripp substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: P1-P2 2.2458(6), P3-P2 2.2262(4), P1-N1 1.775(1), P3-C1 1.820(1), C1-N1 1.312(2), C1-C2 1.471(2), N1-H1 0.89(2), O1-H1 1.84(2), P1-C38 1.830(2), P2-C23 1.855(1), P3-C8 1.826(2); P1-N1-C1 125.0(1), P3-C1-N1 115.3(1), P1-P2-P3 88.30(2), P2-P1-N1 92.00(4), P2-P3-C1 95.01(5), P2-P3-C8 107.37(5), C1-P3-C8 111.19(7), P2-P1-C38 111.68(5), N1-P1-C38 101.43(6), P1-P2-C23 109.34(5), P3-P2-C23 98.82(5).

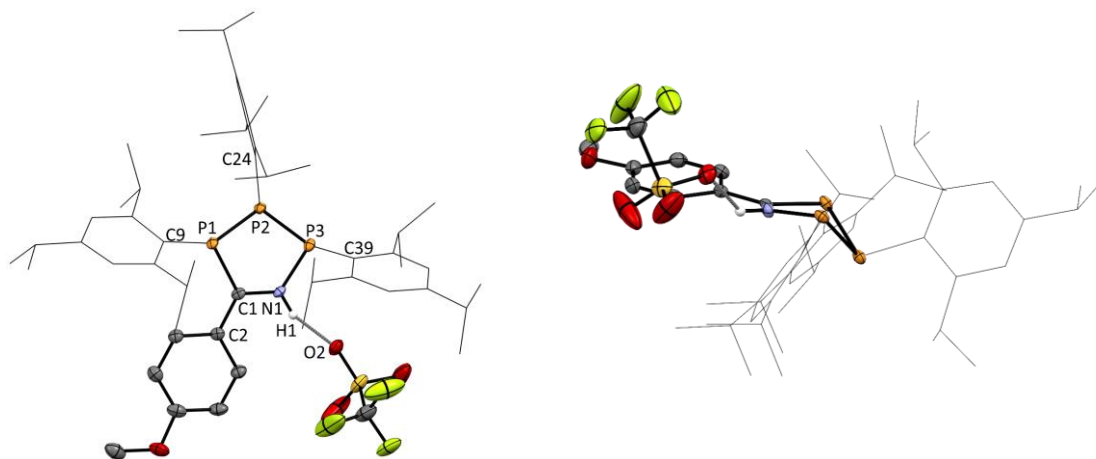


Figure A.75 Solid state molecular structure of $[1_{\text{Tripp}}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4$). Thermal ellipsoids are drawn at the 50% probability level. Tripp substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: P3-P2 2.2435(8), P1-P2 2.226(1), P3-N1 1.773(2), P1-C1 1.824(2), C1-N1 1.319(4), C1-C2 1.451(3), N1-H1 0.86, P3-C39 1.836(3), P2-C24 1.853(2), P1-C9 1.830(3), H1-O2 1.978; P3-N1-C1 125.2(2), P1-C1-N 114.5(2), P2-P3-N1 91.42(7), P2-P1-C1 94.28(8), P1-P2-P3 87.97(3), P2-P3-C39 112.51(8), N1-P3-C39 100.4(1), P2-P1-C9 106.70(8), C1-P1-C9 111.0(1), P3-P2-C24 109.02(8), P1-P2-C24 100.04(8).

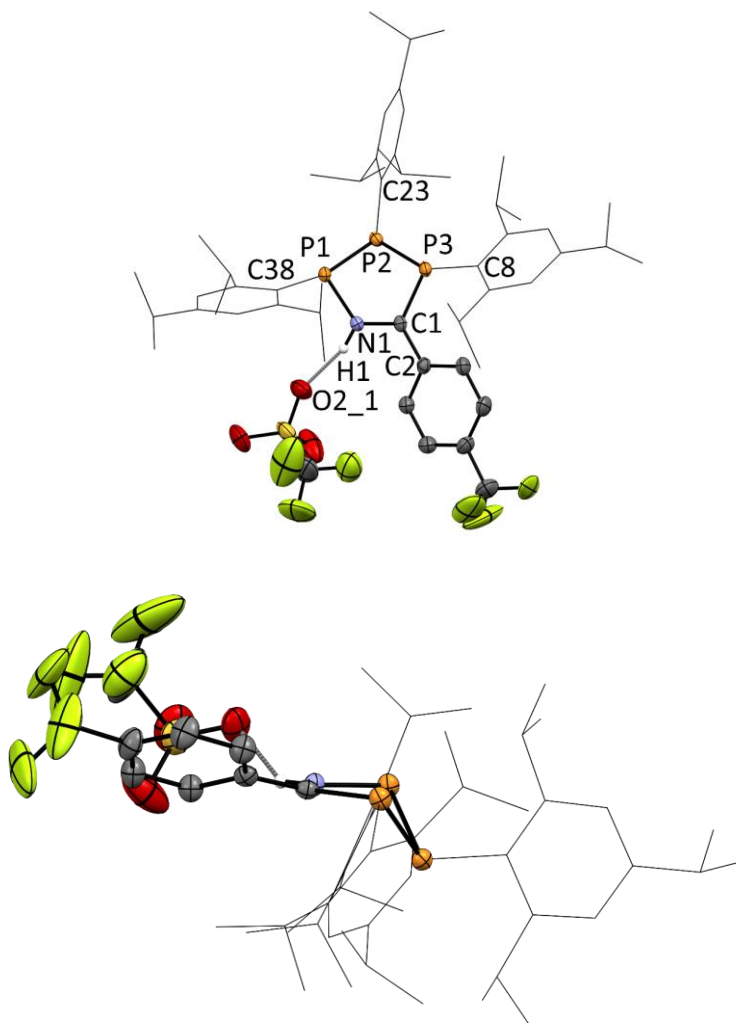


Figure A.76 Solid state molecular structure of $[1_{\text{Tripp}}]^+$ ($R' = p\text{-CF}_3\text{C}_6\text{H}_4$). Thermal ellipsoids are drawn at the 50% probability level. Tripp substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: P1-P2 2.2557(7), P2-P3 2.2247(7), P1-N1 1.7767(16), P3-C1 1.8190(19), N1-C1 1.311(2), C1-C2 1.468(3), N1-H1 0.860, O2_1-H1 1.984, P1-C38 1.8295(19), P2-C23 1.8410(19), P3-C8 1.8318(19); P1-N1-C1 123.15(13), P3-C1-N1 114.76(14), P1-P2-P3 85.76(2), P2-P1-N1 89.70(5), P2-P3-C1 92.35(6), P2-P3-C8 104.12(7), C1-P3-C8 111.56(9), P2-P1-C38 110.61(7), N1-P1-C38 101.40(8), P3-P2-C23 102.11(6), P1-P2-C23 114.04(6).

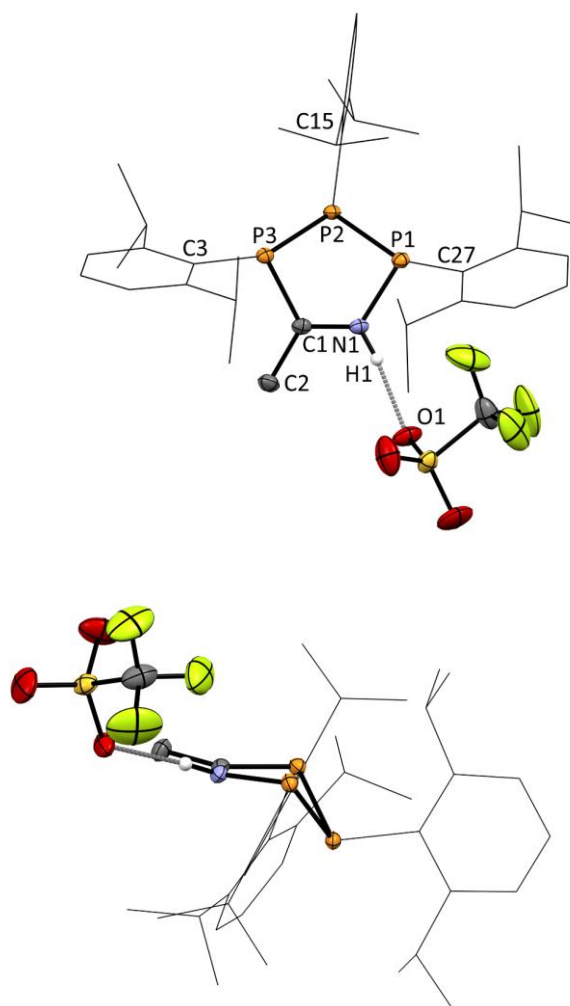


Figure A.77 Solid state molecular structure of $[1_{\text{Dipp}}]^+$ ($R' = \text{Me}$). Thermal ellipsoids are drawn at the 50% probability level. Dipp substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.2387(6), P2-P3 2.2360(5), P1-N1 1.781(1), P3-C1 1.816(1), C1-N1 1.299(2), C1-C2 1.491(2), N1-H1 0.85(2), O1-H1 1.89(2), P1-C27 1.831(1), P2-C15 1.848(1), P3-C3 1.836(1); P1-N1-C1 121.58(9), P3-C1-N1 117.8(1), P1-P2-P3 86.98(2), P2-P1-N1 90.53(4), P2-P3-C1 91.13(4), N1-P1-C27 104.52(6), P2-P1-C27 105.82(4), C1-P3-C3 105.57(6), P2-P3-C3 111.54(4), P1-P2-C15 103.96(5), P3-P2-C15 110.46(5).

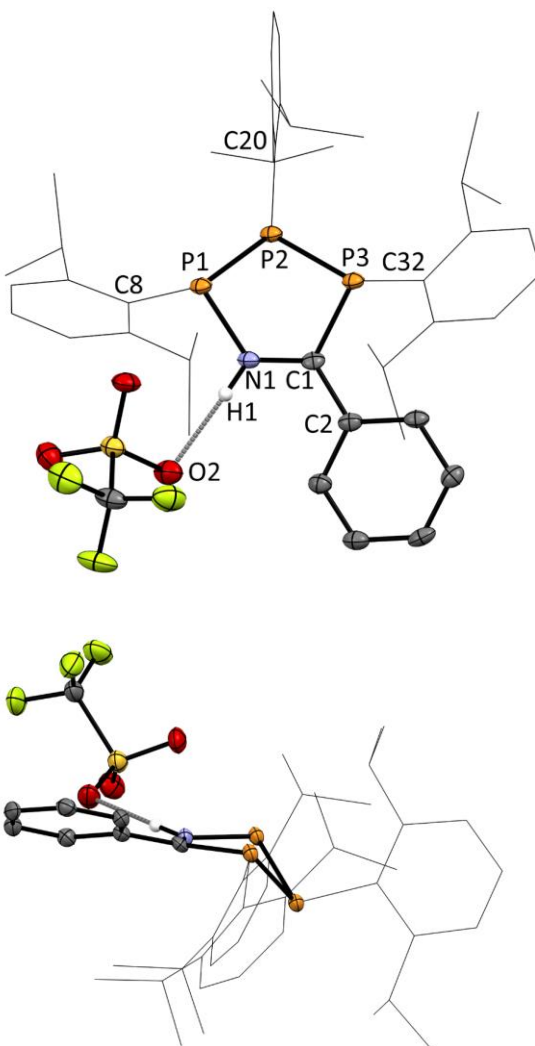


Figure A.78 Solid state molecular structure of $[1_{\text{Dipp}}]^+$ ($R' = \text{Ph}$). Thermal ellipsoids are drawn at the 50% probability level. Dipp substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.243(1), P3-P2 2.212(1), P1-N1 1.790(2), P3-C1 1.822(3), C1-N1 1.312(4), C1-C2 1.473(3), N1-H1 0.87(4), P1-C8 1.838(3), P2-C20 1.854(3), P3-C32 1.842(4), O2-H1 2.04(4); P1-N1-C1 124.0(2), P3-C1-N1 115.8(2), P2-P1-N1 91.23(8), P2-P3-C1 93.98(9), P3-P2-P1 88.53(4), P2-P1-C8 104.6(1), N1-P1-C8 104.7(1), P2-P3-C32 105.80(9), C1-P3-C32 112.4(1), P1-P2-C20 107.61(9), P3-P2-C20 103.55(9).

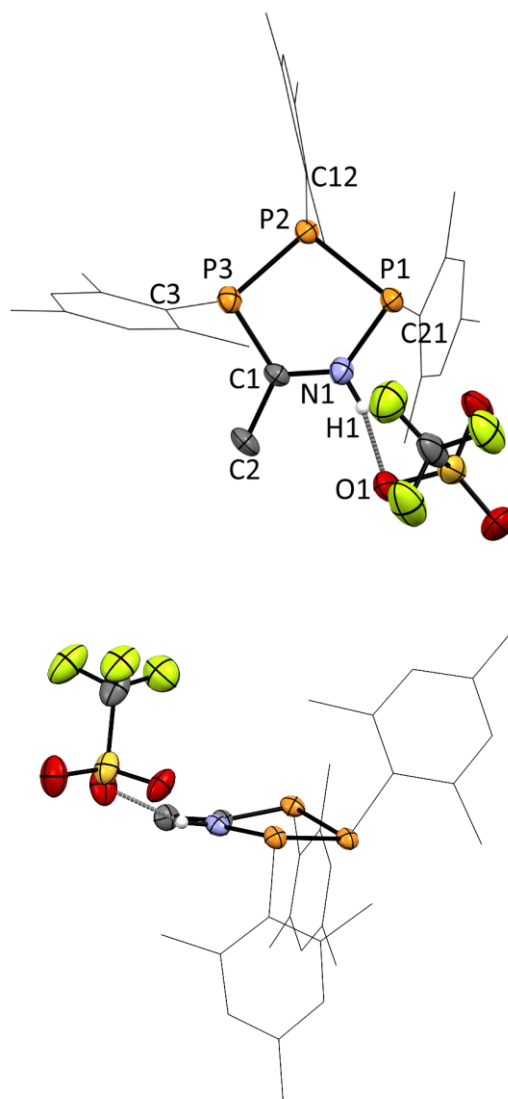


Figure A.79 Solid state molecular structure of $[1_{\text{Mes}}]^+$ ($R' = \text{Me}$). Thermal ellipsoids are drawn at the 50% probability level. Mes substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: P1-P2 2.237(3), P2-P3 2.192(3), P1-N1 1.778(8), P3-C1 1.782(8), C1-N1 1.309(9), C1-C2 1.50(1), N1-H1 0.88, O1-H1 1.993, P1-C21 1.835(7), P2-C12 1.849(7), P3-C3 1.825(6); P1-N1-C1 127.4(6), P3-C1-N1 118.8(6), P1-P2-P3 95.5(1), P2-P1-N1 95.4(2), P2-P3-C1 98.6(3), N1-P1-C21 102.0(3), P2-P1-C21 99.0(3), C1-P3-C3 106.3(4), P2-P3-C3 109.7(3), P1-P2-C12 106.3(3), P3-P2-C12 100.5(3).

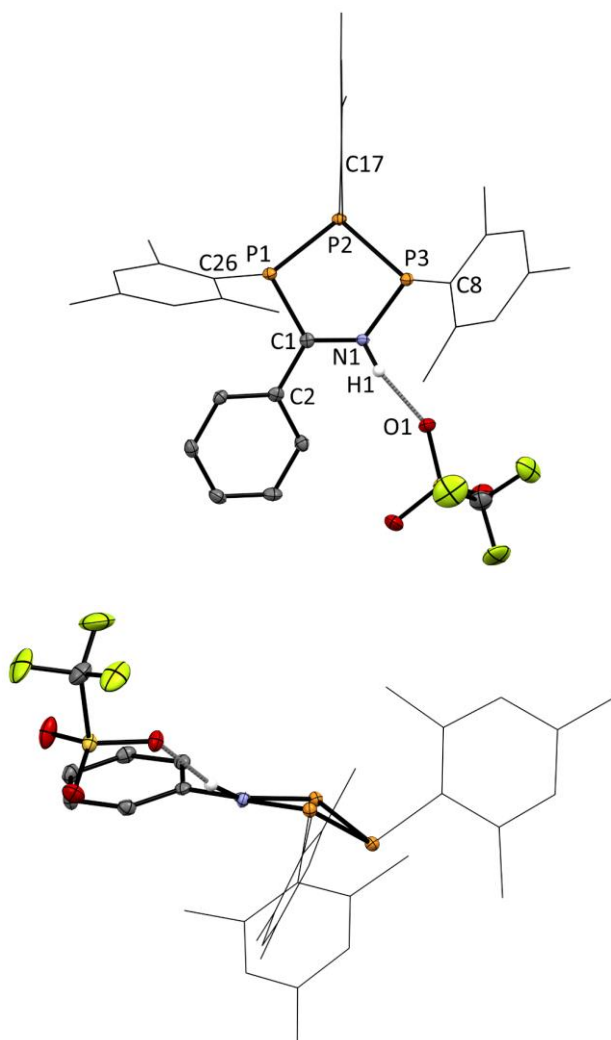


Figure A.80 Solid state molecular structure of $[1_{\text{Mes}}]^+$ ($R' = \text{Ph}$). Thermal ellipsoids are drawn at the 50% probability level. Mes substituents shown in wireframe for clarity, and all protons except H1 have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: P3-P2 2.238(1), P1-P2 2.206(1), P3-N1 1.772(2), P1-C1 1.804(2), C1-N1 1.309(4), C1-C2 1.475(3), N1-H1 0.87(3), P3-C8 1.830(3), P2-C17 1.844(2), P1-C26 1.823(3), H1-O1 1.92(3); P3-N1-C1 126.3(2), P1-C1-N1 118.8(2), P2-P3-N1 95.34(8), P2-P1-C1 97.42(9), P1-P2-P3 93.42(4), P2-P3-C8 100.68(8), N1-P3-C8 106.6(1), P2-P1-C26 110.44(9), C1-P1-C26 105.1(1), P3-P2-C17 104.64(8), P1-P2-C17 103.39(8).

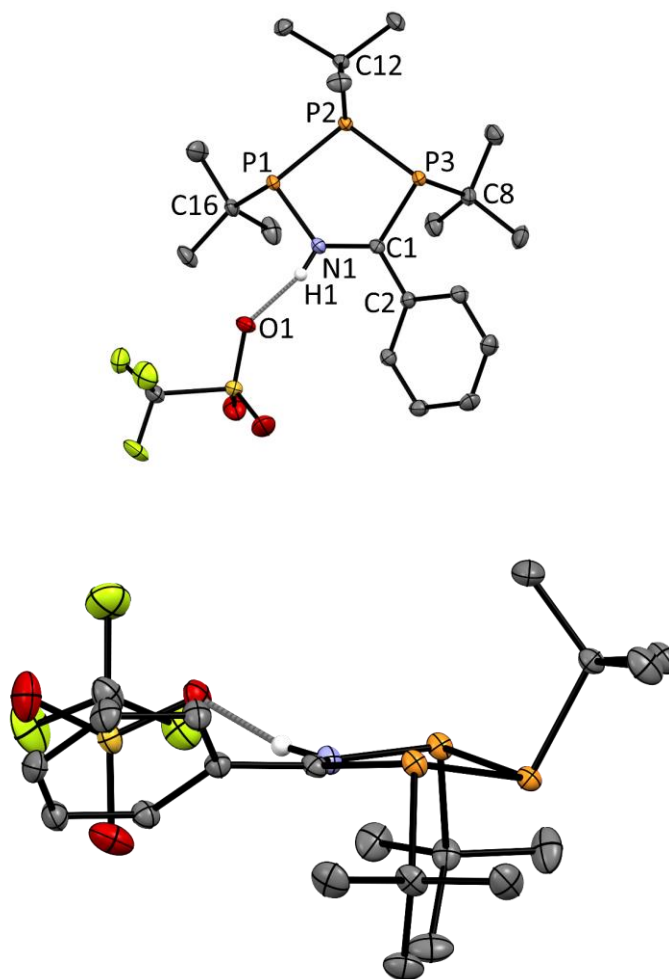


Figure A.81 Solid state molecular structure of **[1_{tBu}]** (**R' = Ph**). Thermal ellipsoids are drawn at the 50% probability level, and all protons except H1 and CH₂Cl₂ protons have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P2-P3 2.2086(6), P1-P3 2.1958(6), P2-N1 1.768(2), P1-C1 1.817(2), C1-N1 1.311(2), C1-C4 1.469(2), N1-H1 0.87(3), P2-C5 1.870(2), P3-C2 1.891(2), P1-C6 1.893(2), H1-O1 1.88(3); P2-N1-C1 125.8(1), P1-C1-N1 120.0(1), P3-P2-N1 97.35(5), P3-P1-C1 98.65(6), P1-P3-P2 95.30(2), P3-P2-C5 105.31(6), N1-P2-C5 102.37(8), P3-P1-C6 105.24(6), C1-P1-C6 106.27(8), P2-P3-C2 99.62(6), P1-P3-C2 101.07(6).

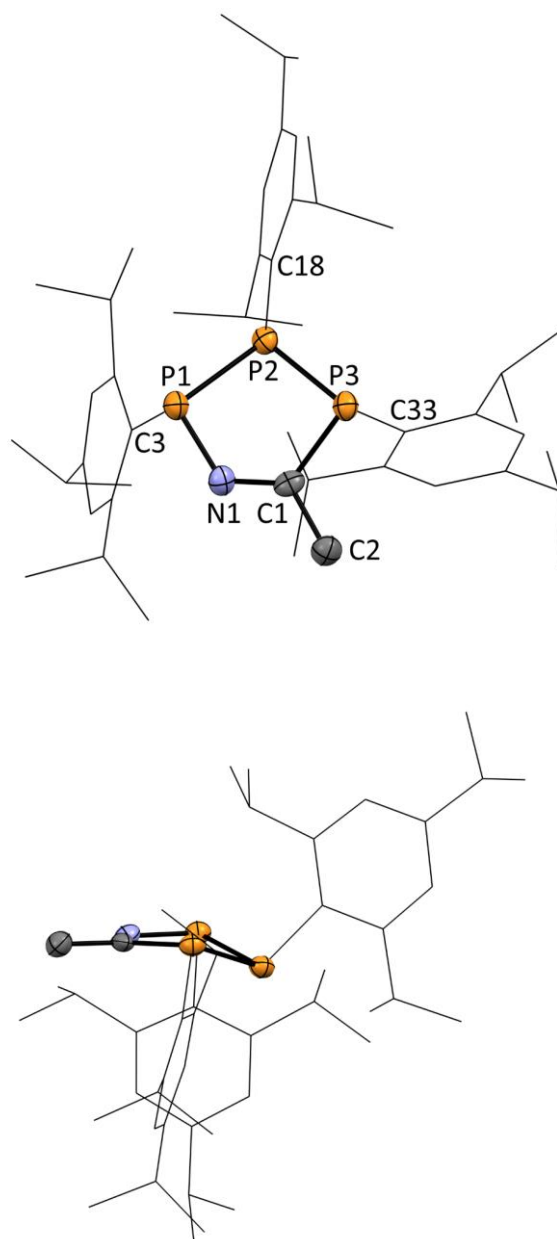


Figure A.82 Solid state molecular structure of **2_{Tripp} (R' = Me)**. Thermal ellipsoids are drawn at the 50% probability level. Tripp substituents shown in wireframe for clarity, and protons have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.265(2), P2-P3 2.185(1), P1-N1 1.715(4), P3-C1 1.850(4), C1-N1 1.289(6), C1-C2 1.502(6), P1-C3 1.866(4), P2-C18 1.849(5), P3-C33 1.848(4); P1-N1-C1 123.3(3), P3-C1-N1 123.2(3), P1-P2-P3 93.62(6), P2-P1-N1 98.4(1), P2-P3-C1 96.2(1), N1-P1-C3 100.9(2), P2-P1-C3 99.5(1), C1-P3-C33 104.6(2), P2-P3-C33 106.0(1), P1-P2-C18 107.7(1), P3-P2-C18 101.4(1).

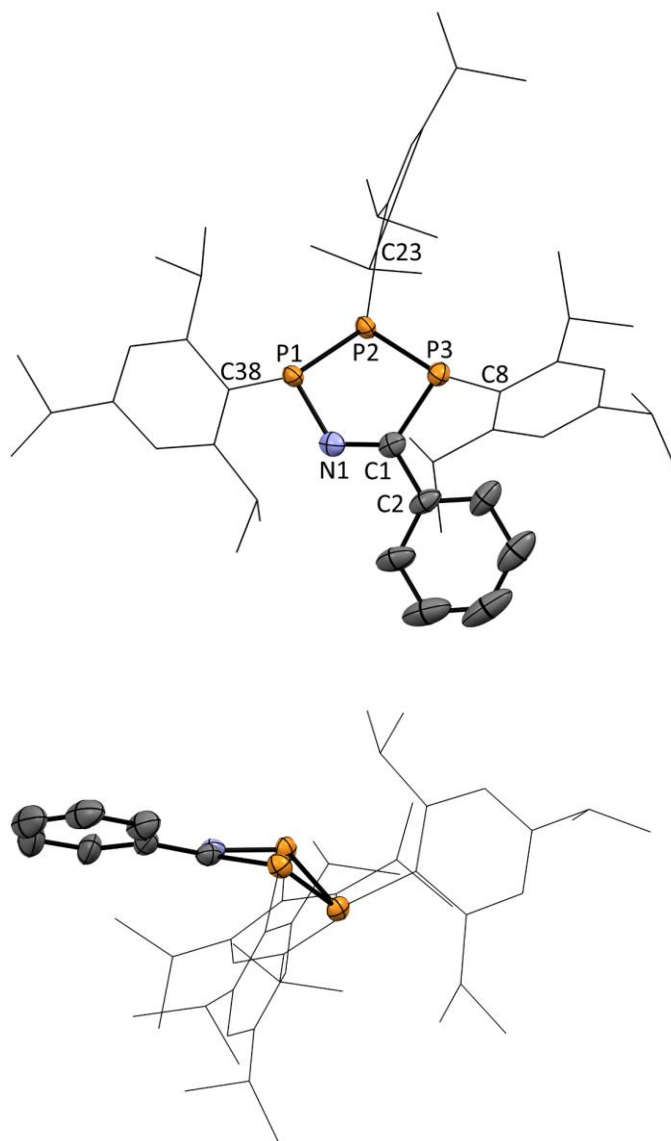


Figure A.83 Solid state molecular structure of **2_{Tripp}** (**R' = Ph**). Thermal ellipsoids are drawn at the 50% probability level. Tripp substituents shown in wireframe for clarity, and protons have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.256(1), P3-P2 2.201(1), P1-N1 1.708(3), P3-C1 1.853(4), C1-N1 1.294(5), C1-C2 1.489(5), P1-C38 1.842(4), P2-C23 1.859(4), P3-C8 1.857(4); P1-N1-C1 120.7(3), P3-C1-N1 121.9(3), P2-P1-N1 97.1(1), P2-P3-C1 94.4(1), P3-P2-P1 89.90(5), P2-P1-C38 104.3(1), N1-P1-C38 108.7(2), P2-P3-C8 104.8(1), C1-P3-C8 109.4(2), P1-P2-C23 110.1(1), P3-P2-C23 98.7(1).a

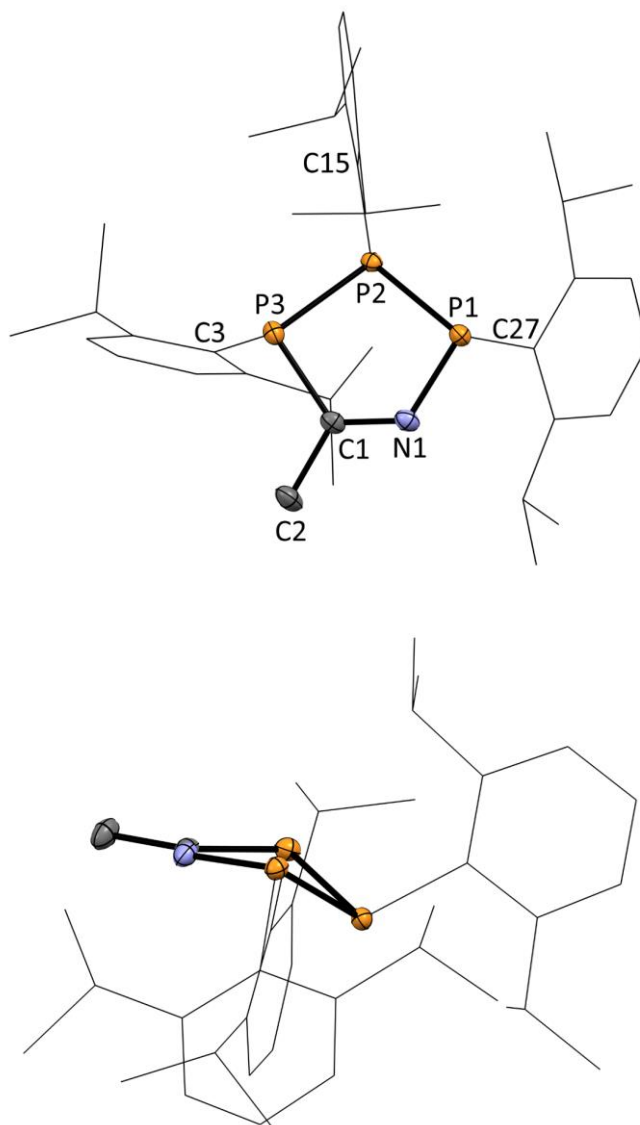


Figure A.84 Solid state molecular structure of **2_{Dipp}** (**R'** = **Me**). Thermal ellipsoids are drawn at the 50% probability level. Dipp substituents shown in wireframe for clarity, and protons have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.2682(5), P2-P3 2.1947(5), P1-N1 1.714(1), P3-C1 1.846(1), C1-N1 1.280(2), C1-C2 1.500(2), P1-C27 1.858(1), P2-C15 1.852(1), P3-C3 1.852(2); P1-N1-C1 122.73(9), P3-C1-N1 122.7(1), P1-P2-P3 91.87(2), P2-P1-N1 97.10(4), P2-P3-C1 94.69(4), N1-P1-C27 105.39(5), P2-P1-C27 98.78(4), C1-P3-C3 105.02(6), P2-P3-C3 103.55(4), P1-P2-C15 110.36(4), P3-P2-C15 103.73(4).

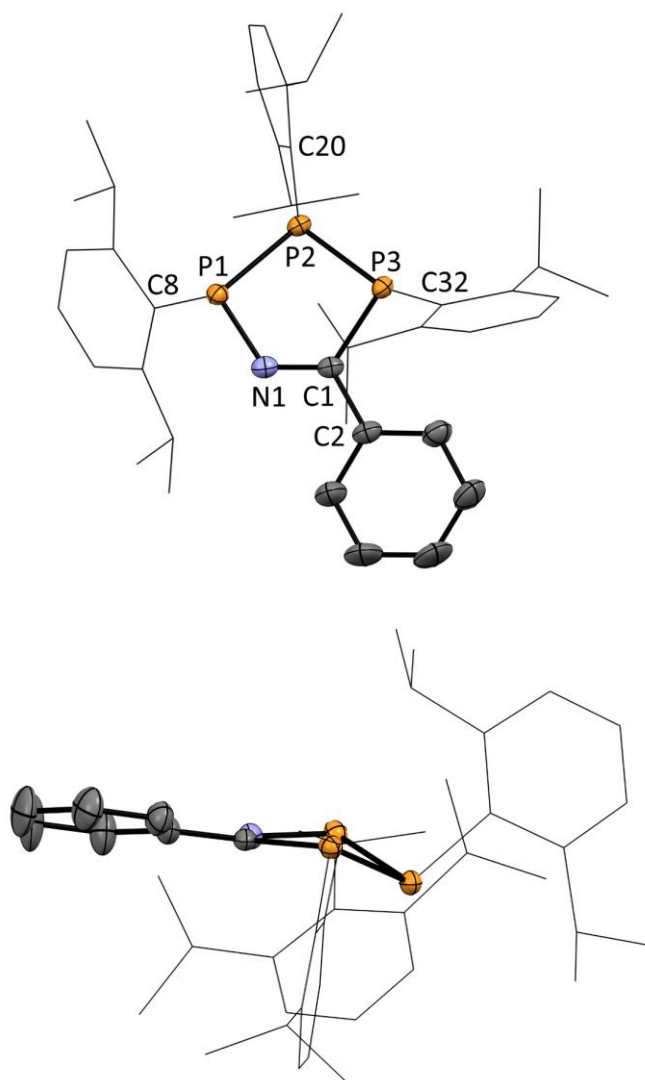


Figure A.85 Solid state molecular structure of **2_{Dipp}** (**R'** = **Ph**). Thermal ellipsoids are drawn at the 50% probability level. Dipp substituents shown in wireframe for clarity, and protons have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.2725(6), P3-P2 2.1972(5), P1-N1 1.697(1), P3-C1 1.870(2), C1-N1 1.282(2), C1-C2 1.498(2), P1-C8 1.864(2), P2-C20 1.858(1), P3-C32 1.859(2); P1-N1-C1 123.0(1), P3-C1-N1 122.5(1), P2-P3-C1 96.14(5), P2-P1-N1 98.79(5), P1-P2-P3 91.91(2), P2-P1-C8 103.97(5), N1-P1-C8 107.82(7), P2-P3-C32 104.97(5), C1-P3-C32 106.23(7), P1-P2-C20 100.97(5), P3-P2-C20 106.94(5).

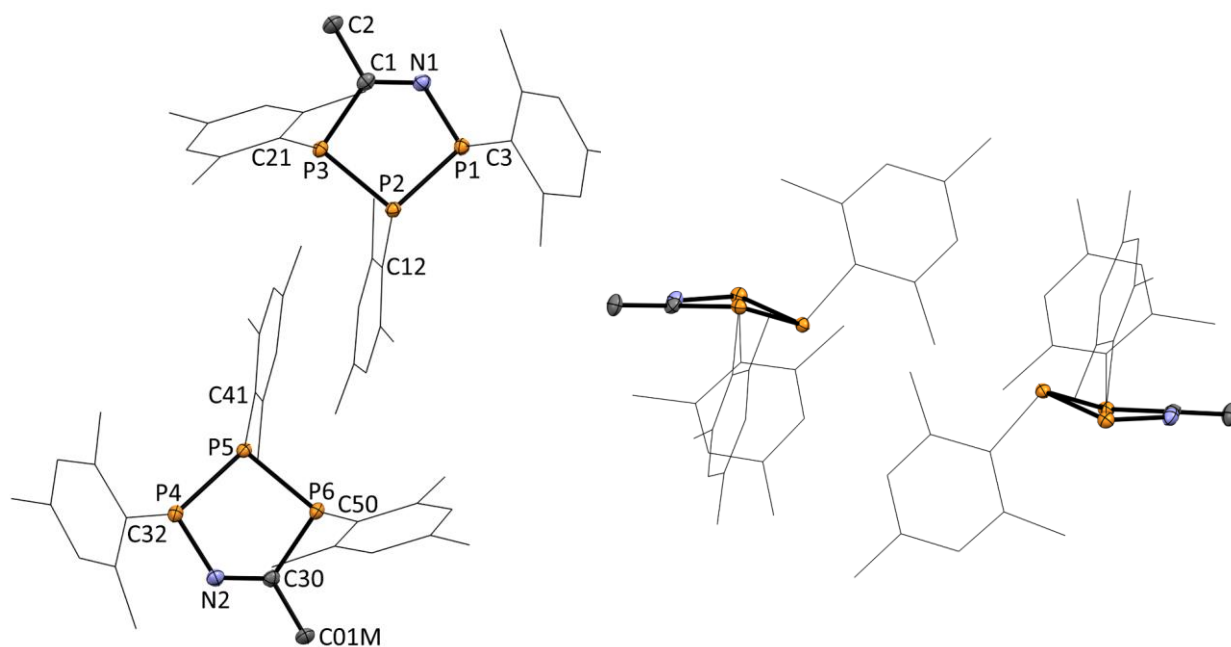


Figure A.86 Solid state molecular structure of **2_{Mes}** (**R'** = **Me**). Thermal ellipsoids are drawn at the 50% probability level. Mes substituents shown in wireframe for clarity, and protons have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.266(2), P3-P2 2.193(1), P1-N1 1.705(3), P3-C1 1.855(4), C1-N1 1.279(5), C1-C2 1.506(5), P1-C3 1.849(3), P2-C12 1.850(3), P3-C21 1.843(4), P4-P5 2.271(2), P6-P5 2.192(1), P4-N2 1.706(4), P6-C30 1.853(4), C30-N2 1.280(5), C30-C01M 1.512(5), P4-C32 1.842(5), P5-C41 1.853(3), P6-C50 1.841(4); P1-N1-C1 122.7(3), P3-C1-N1 123.6(3), P2-P1-N1 99.8(1), P2-P3-C1 96.7(1), P3-P2-P1 92.78(5), P2-P1-C3 100.0(1), N1-P1-C3 105.0(2), P2-P3-C21 106.6(1), C1-P3-C21 105.2(2), P1-P2-C12 106.5(1), P3-P2-C12 101.4(1), P4-N2-C30 122.9(3), P6-C30-N2 123.4(3), P5-P4-N2 99.5(1), P5-P6-C30 96.8(1), P6-P5-P4 92.62(5), P5-P4-C32 99.0(1), N2-P4-C32 105.3(2), P5-P6-C50 106.5(1), C30-P6-C50 104.6(2), P4-P5-C41 107.0(1), P6-P5-C41 101.5(1).

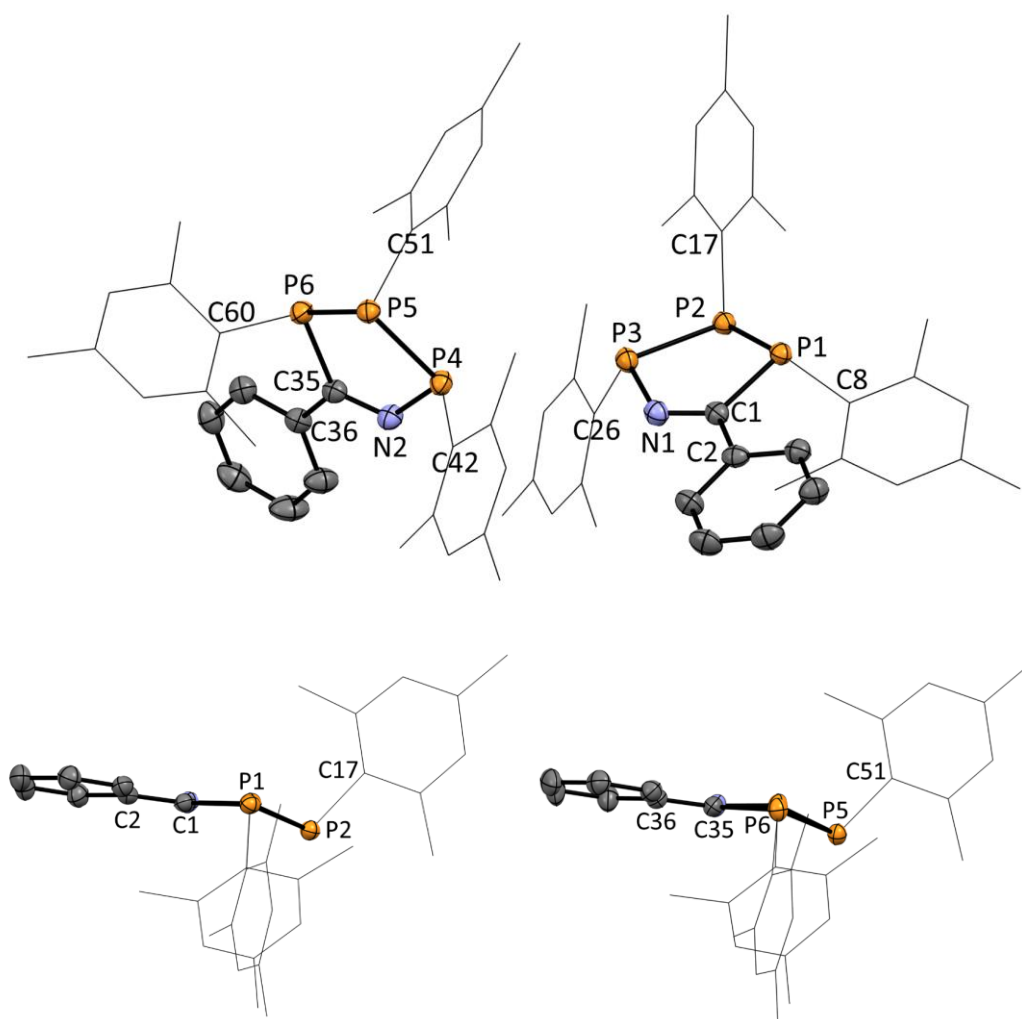


Figure A.87 Solid state molecular structure of **2_{Mes}** (**R' = Ph**). Thermal ellipsoids are drawn at the 50% probability level. Mes substituents shown in wireframe for clarity, and protons have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.1862(8), P2-P3 2.2496(8), P4-P5 2.256(1), P5-P6 2.1907(8), P3-N1 1.693(2), P4-N2 1.693(2), P1-C1 1.869(2), P6-C35 1.869(3), C1-N1 1.280(2), C35-N2 1.281(3), C1-C2 1.487(3), C35-C36 1.489(3), P1-C8 1.844(3), P2-C17 1.846(2), P3-C26 1.836(2), P4-C42 1.837(2), P5-C51 1.848(2), P6-C60 1.842(3); P1-C1-N1 121.9(2), P3-N1-C1 123.9(2), P1-P2-P3 92.98(3), P2-P1-C1 96.62(7), P2-P3-N1 99.50(7), P4-N2-C35 123.8(2), P6-C35-N2 122.0(2), P4-P5-P6 92.69(3), P5-P4-N2 99.43(7), P5-P6-C35 96.71(7), C1-P1-C8 108.3(1), P2-P1-C8 102.58(7), N1-P3-C26 105.4(1), P2-P3-C26 102.99(8), P1-P2-C17 101.69(8), P3-P2-C17 105.24(8), N2-P4-C42 106.4(1), P5-P4-C42 102.70(8), C35-P6-C60 106.9(1), P5-P6-C60 103.01(8), P4-P5-C51 103.15(8), P6-P5-C51 104.26(8).

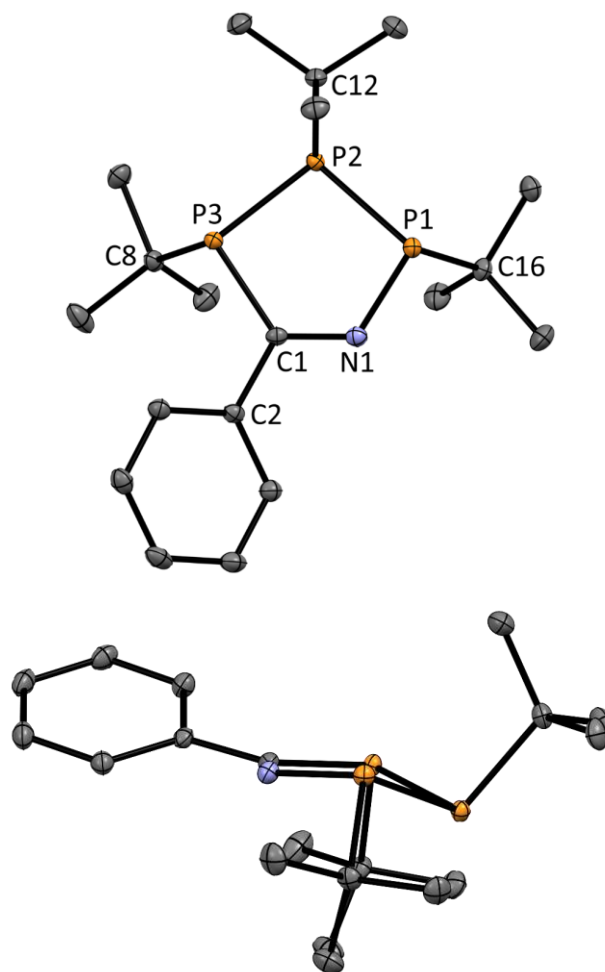


Figure A.88 Solid state molecular structure of **2_{tBu}** (**R' = Ph**). Thermal ellipsoids are drawn at the 50% probability level, and all protons have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.2322(3), P3-P2 2.1935(3), P1-N1 1.7043(8), P3-C1 1.8732(8), C1-N1 1.288(1), C1-C2 1.495(1), P1-C16 1.873(1), P2-C12 1.897(1), P3-C8 1.896(1); P1-N1-C1 121.68(7), P3-C1-N1 122.90(7), P2-P1-N1 100.37(3), P2-P3-C1 96.65(3), P3-P2-P1 93.01(1), P2-P1-C16 105.65(3), N1-P1-C16 102.19(4), P2-P3-C8 102.52(3), C1-P3-C8 104.48(4), P1-P2-C12 101.49(3), P3-P2-C12 101.57(3).

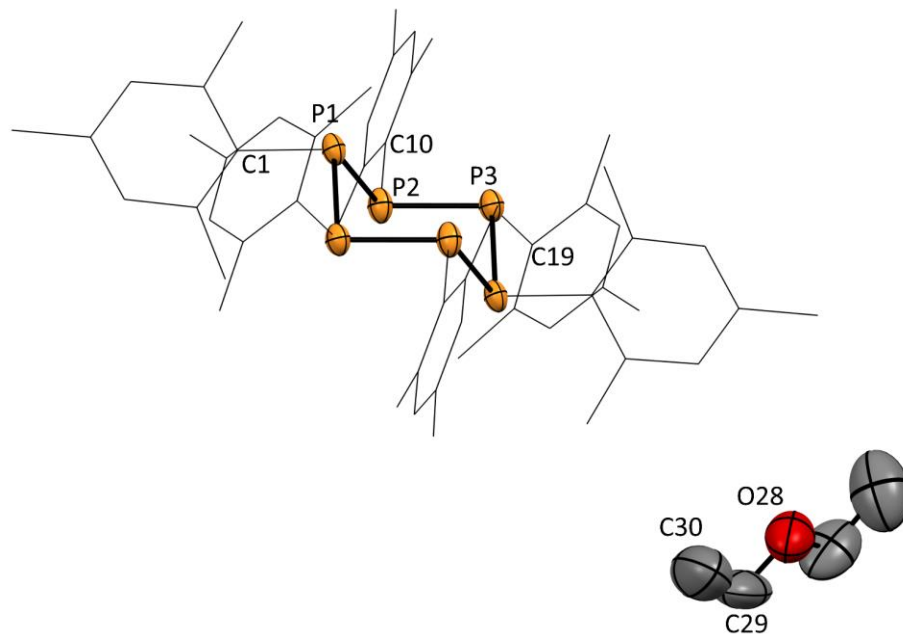
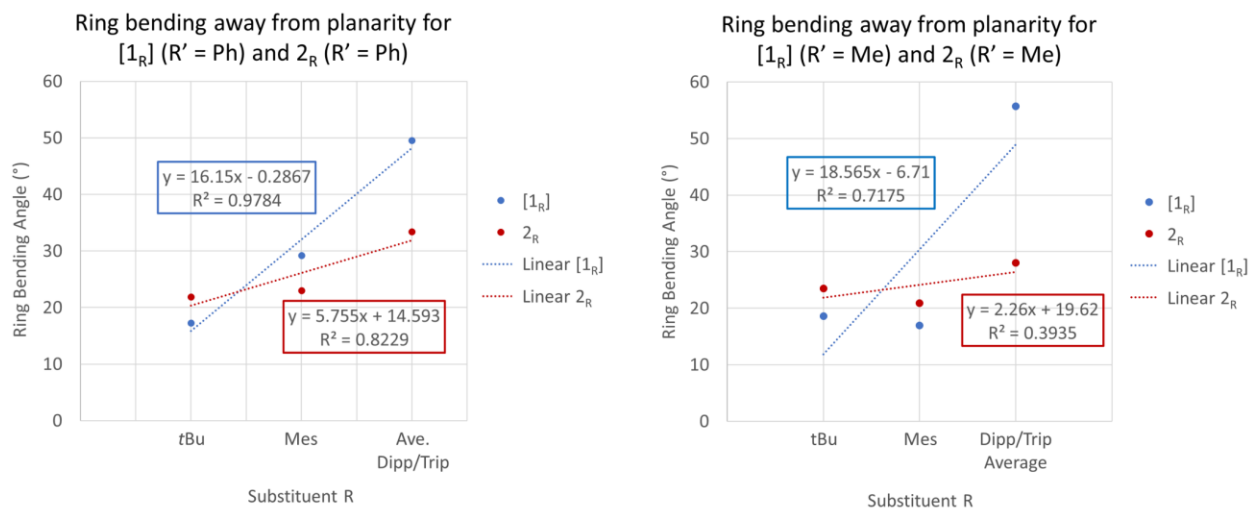


Figure A.89 Solid state molecular structure of $\text{P}_6\text{Mes}_6 \cdot \text{Et}_2\text{O}$. Thermal ellipsoids are drawn at the 50% probability level, and all protons have been omitted for clarity. Selected bond lengths [Å] and angles [°]: $\text{P1-P2} = 2.239(2)$, $\text{P2-P3} = 2.237(1)$, $\text{P3-P1} = 2.241(2)$, $\text{P1-C1} = 1.867(4)$, $\text{P2-C10} = 1.82(2)$, $\text{P3-C19} = 1.858(4)$, $\text{C30-C29} = 1.50(2)$, $\text{C29-O28} = 1.40$; $\text{P3-P1-P2} = 96.76(5)$, $\text{P1-P2-P3} = 97.71(5)$, $\text{P2-P3-P1} = 103.50(6)$, $\text{plane(P1-P2-P3)-plane(P1-P3-P1-P3)} = 74.48$.

Table A.4 Comparison of P_N and P_C bond distances

	[1 _{tBu}] ⁺ (R' = Me)	[1 _{Mes}] ⁺ (R' = Me)		[1 _{Dipp}] ⁺ (R' = Me)	[1 _{Tripp}] ⁺ (R' = Me)		
P _N -P _C Distance (Å)	3.237(1)	3.278(3)		3.0797(5)	3.067(1)		
% change	NA	1.27		-5.11	-5.54		
	2 _{tBu} (R' = Me)	2 _{Mes} (R' = Me) A	2 _{Mes} (R' = Me) B	2 _{Dipp} (R' = Me)	2 _{Tripp} (R' = Me)		
P _N -P _C Distance (Å)	3.190(1)	3.227(1)	3.228(1)	3.2072(5)	3.245(2)		
% change	NA	1.16	1.19	0.54	1.72		
	[1 _{tBu}] ⁺ (R' = Ph)	[1 _{Mes}] ⁺ (R' = Ph)		[1 _{Dipp}] ⁺ (R' = Ph)	[1 _{Tripp}] ⁺ (R' = Ph)	[1 _{Tripp}] ⁺ (R' = <i>p</i> -MeOC ₆ H ₄)	[1 _{Tripp}] ⁺ (R' = <i>p</i> -CF ₃ C ₆ H ₄)
P _N -P _C Distance (Å)	3.2549(6)	3.235(1)		3.110(1)	3.1149(7)	3.104(1)	3.0489(6)
% change	NA	0.06		-4.66	-4.49	-4.86	-6.76
	2 _{tBu} (R' = Ph)	2 _{Mes} (R' = Ph) A	2 _{Mes} (R' = Ph) B	2 _{Dipp} (R' = Ph)	2 _{Tripp} (R' = Ph)		
P _N -P _C Distance (Å)	3.2107(4)	3.2171(7)	3.2178(9)	3.2131(5)	3.149(1)		
% change	NA	0.11	0.22	0.07	-1.96		

**Figure A.90** Comparison of Rate of Change in Crystallographically-Measured Ring Bending

A.5 Computational Details

A.5.1 General Remarks

Computations were carried out using Gaussian09ⁱ or Gaussian16ⁱⁱ and the standalone version of NBO 6.0.ⁱⁱⁱ

Structure optimizations employed the GGA DFT functional BP86^{iv} in conjunction with Grimme's dispersion correction D3(BJ)^v and the def2-SVP basis set^{vi} (notation BP86-D3/def2-SVP). All structures were fully optimized and confirmed as minima by frequency analyses. The vertical excitation energies of the first ten singlet and triplet states have been predicted by TD-DFT computations using the B3LYP^{vii} functional as well as the cc-pVTZ^{viii} basis set using the respective BP86-D3/def2-SVP optimized gas-phase S^0 geometry. For the visualization of the charge density difference between the ground state and selected excited states we used MultiWfn 3.6 employing Gaussian16 formatted checkpoint files.^{ix} For the visualization of 3D-quantum chemical results we used GaussView6.1.1.^x In addition to the electronic supporting information we provide a multi-structure xyz-file including all calculated molecules. For a better understanding and a more intuitive view of the calculated 3D structures, we strongly recommend using this file e.g. with the free program MERCURY.^{xi}

Please note that all computations were carried out for single, isolated molecules in the gas phase (ideal gas approximation). There may well be significant differences between gas phase and condensed phase.

Computational references:

(i) Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

(ii) Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.;

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(x) GaussView, Version 6.1, Roy Dennington, Todd A. Keith and John M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

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A.5.2 Summary of calculated data

Table A.5 Summary of thermodynamic. All calculations were carried out on the BP86-D3/Def2-SVP level of theory.

Compound	NIMAG	HF	ZPE	H_{tot} [a.u.]	G°_{tot} [a.u.]
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[1_{Tripp}]⁺ (R' = Me)	0	-3873.49838	683.66705	-3872.33616	-3872.51881
[1_{Tripp}]⁺ (R' = Ph)	0	-4065.12643	716.30174	-4063.90892	-4064.09967
[1_{Tripp}]⁺ (R' = p-MeOC₆H₄)	0	-4179.57680	736.16803	-4178.32498	-4178.52147
[1_{Tripp}]⁺ (R' = p-CF₃C₆H₄)	0	-4401.92343	718.91313	-4400.69792	-4400.89935
2_{Tripp} (R' = Me)	0	-2911.91540	658.96099	-2910.80152	-2910.96518
2_{Tripp} (R' = Ph)	0	-3103.54735	691.84108	-3102.37813	-3102.54813
[1_{Dipp}]⁺ (R' = Ph)	0	-3711.51196	563.18492	-3710.55224	-3710.71122
2_{Dipp} (R' = Ph)	0	-2749.93707	538.81388	-2749.02565	-2749.16254
[1_{Mes}]⁺ (R' = Ph)		-3357.92383	405.81360	-3357.22576	-3357.36557
[1_{tBu}]⁺ (R' = Me)	0	-2591.41525	278.26302	-2590.93615	-2591.03779
[1_{tBu}]⁺ (R' = Ph)	0	-2783.04469	311.20849	-2782.50999	-2782.61844
2_{tBu} (R' = Me)	0	-1629.84352	254.30348	-1629.41175	-1629.49031
2_{tBu} (R' = Ph)	0	-1821.46914	287.12662	-1820.98198	-1821.06857

A.5.3 Calculated UV-Vis spectra

Table A.6 Calculated electronic excitations of $[1_{\text{Tripp}}]^+$ ($R' = \text{Me}$)

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	1A	500.4	0.0025	HOMO $\rightarrow$ LUMO
S2	1A	388.4	0.0148	HOMO $\rightarrow$ LUMO+1
S3	1A	369.1	0.0017	HOMO-1 $\rightarrow$ LUMO

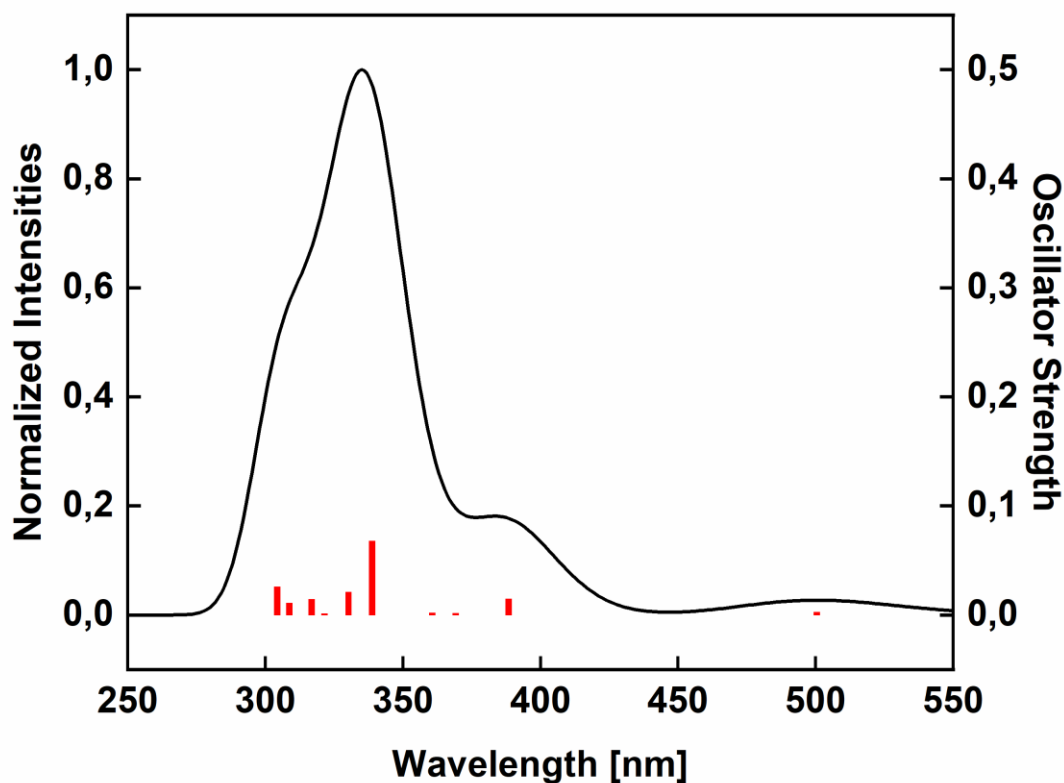


Figure A.91 Predicted UV-vis absorption spectra of $[1_{\text{Tripp}}]^+$ ($R' = \text{Me}$) including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV

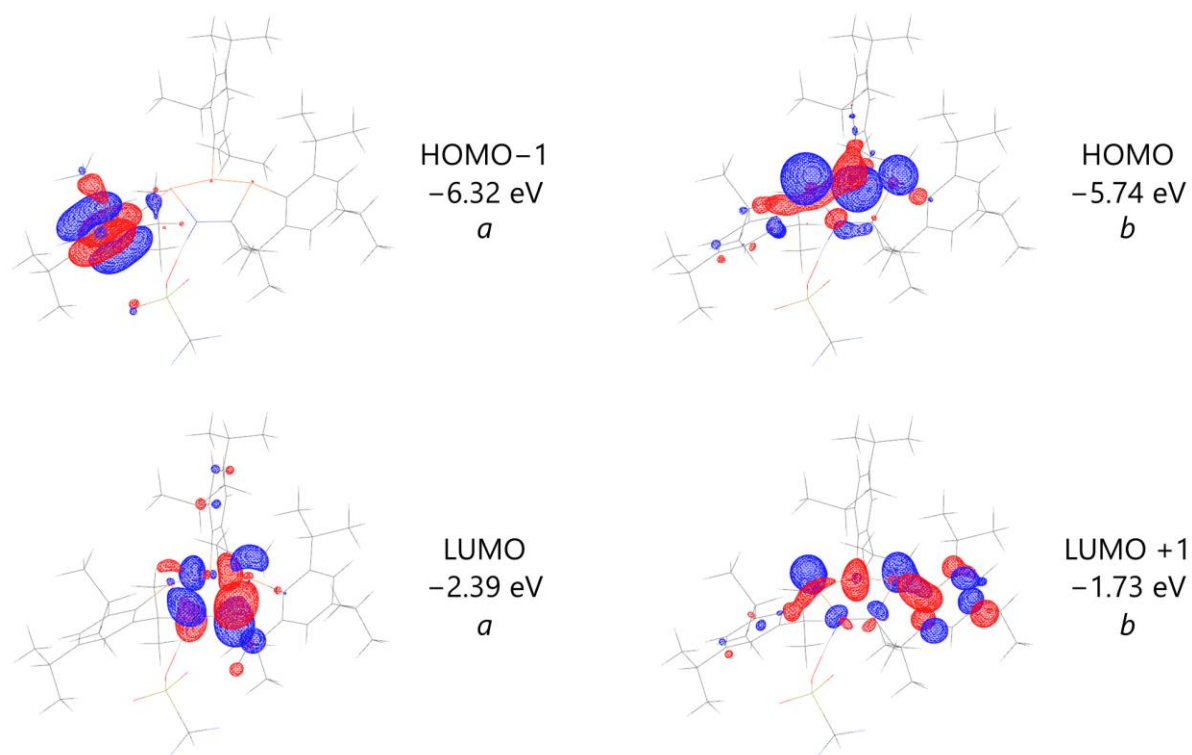


Figure A.92 Relevant Kohn-Sham orbitals of $[1_{\text{Tripp}}]^+$ ($R' = \text{Me}$) (B3LYP-D3/cc-PVTZ)

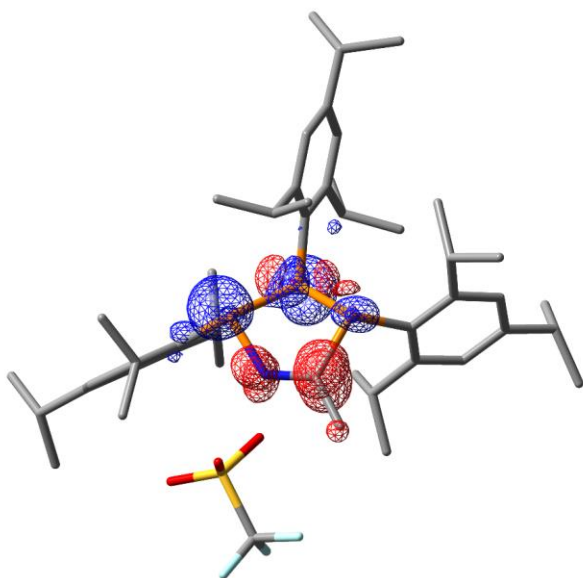


Figure A.93 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex $[1_{\text{Tripp}}]^+$ ($R' = \text{Me}$). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 1.260)

Table A.7 Calculated electronic excitations of $[1_{tBu}]^+$ ($R' = Me$)

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	1A	380.6	0.0368	HOMO→LUMO
S2	1A	304.1	0.0311	HOMO-1→LUMO
S3	1A	291.0	0.0057	HOMO-2→LUMO

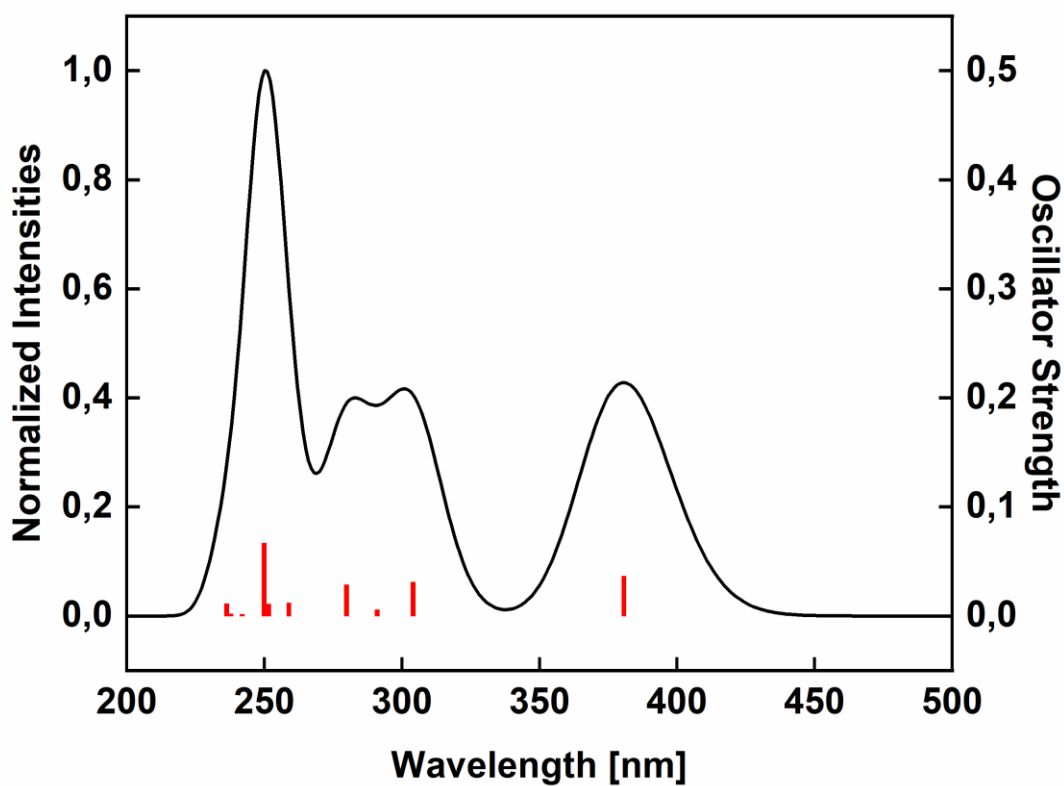


Figure A.94 Predicted UV-vis absorption spectra of $[1_{tBu}]^+$ ($R' = Me$) including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV

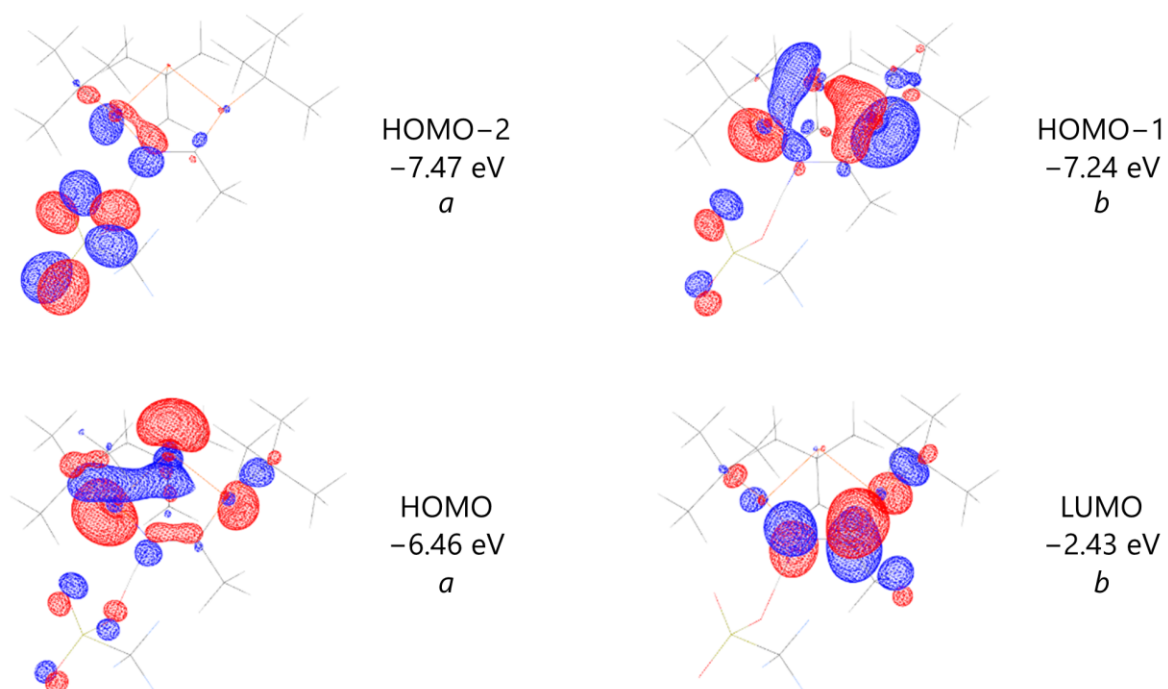


Figure A.96 Relevant Kohn-Sham orbitals of $[1_{tBu}]^+$ ($R' = \text{Me}$) (B3LYP-D3/cc-PVTZ)

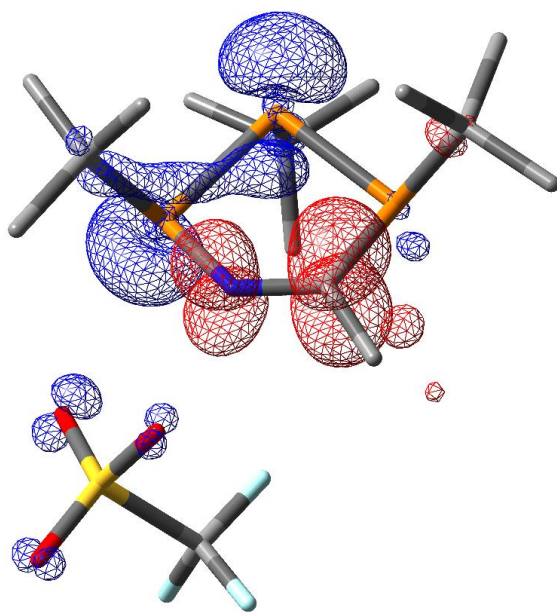


Figure A.95 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex $[1_{tBu}]^+$ ($R' = \text{Me}$). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 1.863)

Table A.8 Calculated electronic excitations of $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$)

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	1A	567.2	0.0156	HOMO $\rightarrow$ LUMO
S2	1A	425.3	0.0021	HOMO-1 $\rightarrow$ LUMO
S3	1A	412.7	0.0272	HOMO-2 $\rightarrow$ LUMO

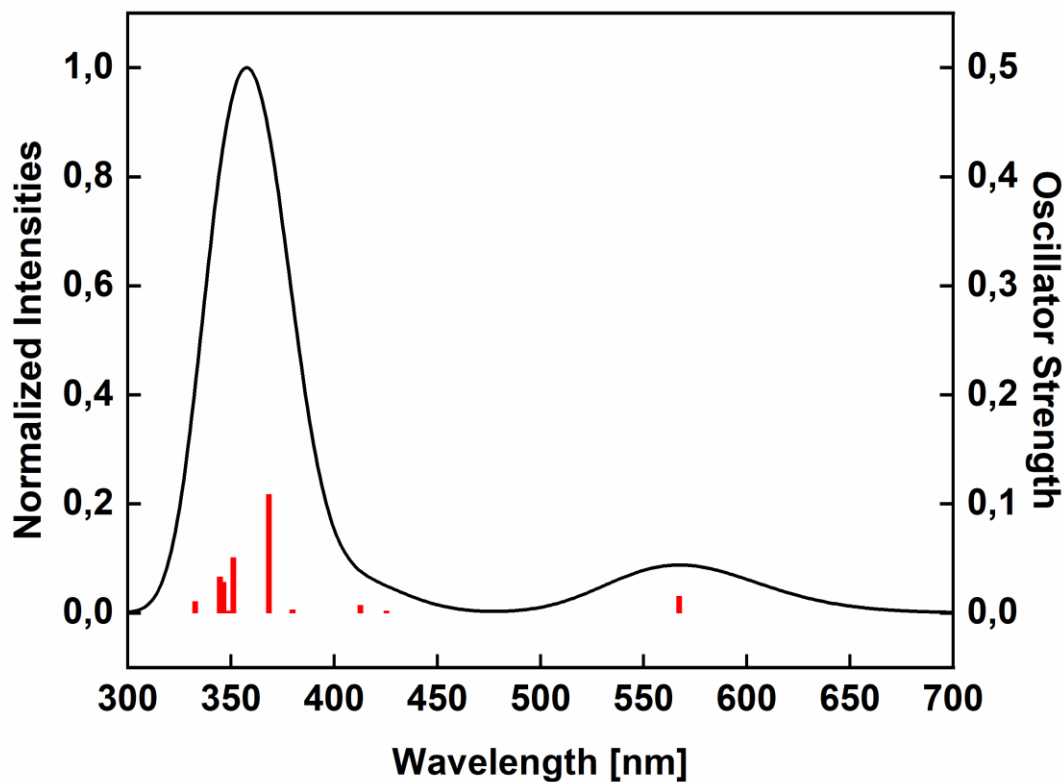


Figure A.97 Predicted UV-vis absorption spectra of $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$) including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV

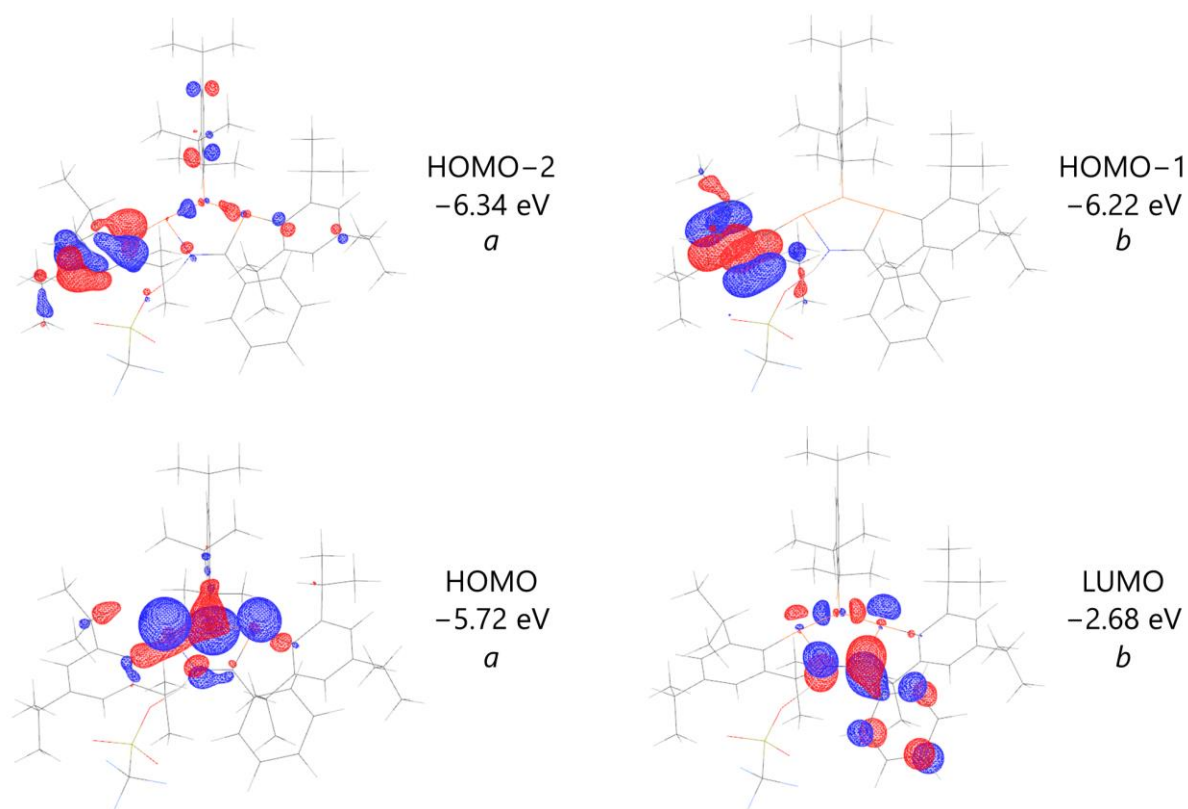


Figure A.98 Relevant Kohn-Sham orbitals of $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$) (B3LYP-D3/cc-PVTZ)

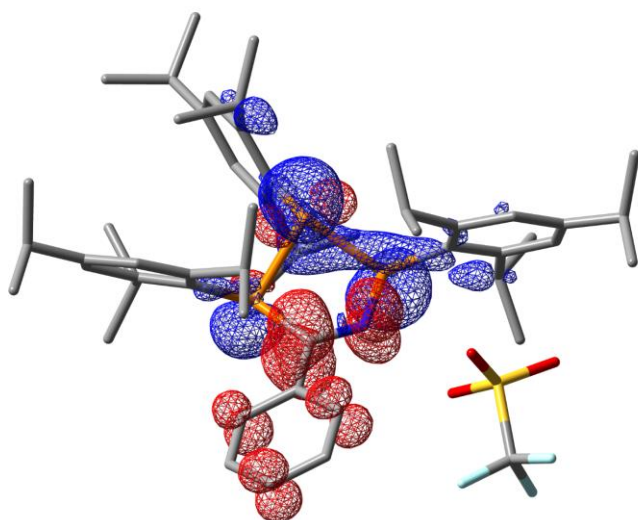


Figure A.99 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 2.377).

Table A.9 Calculated electronic excitations of $[1_{\text{Tripp}}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4$)

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	1A	543.8	0.0182	HOMO $\rightarrow$ LUMO
S2	1A	411.8	0.0042	HOMO-1 $\rightarrow$ LUMO
S3	1A	402.5	0.0670	HOMO-2 $\rightarrow$ LUMO

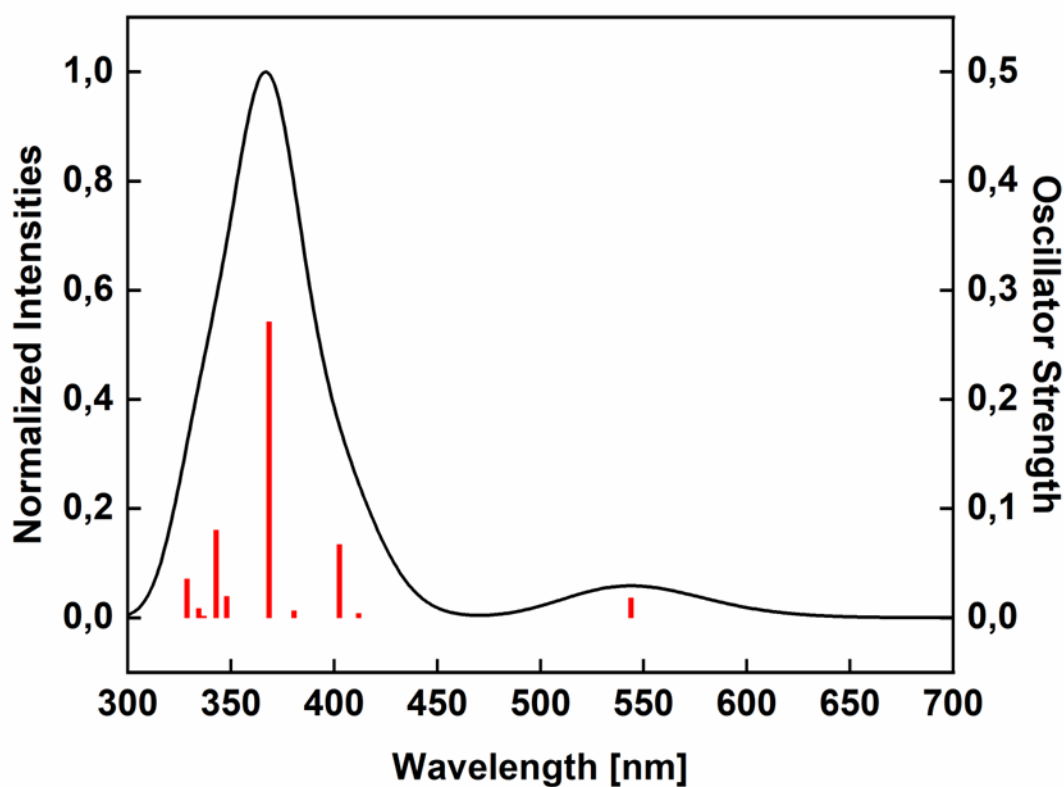


Figure A.100 Predicted UV-vis absorption spectra of $[1_{\text{Tripp}}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4$) including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV.

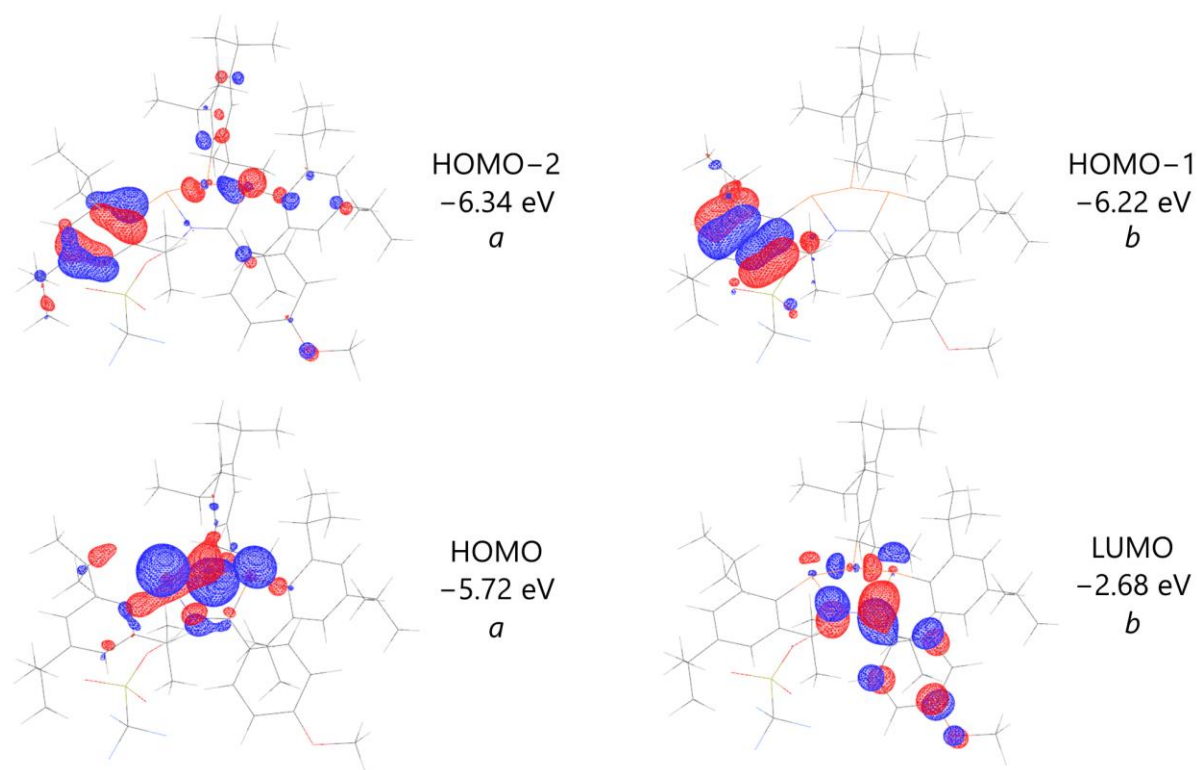


Figure A.101 Relevant Kohn-Sham orbitals of $[1_{\text{Tripp}}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4$) (B3LYP-D3/cc-PVTZ)

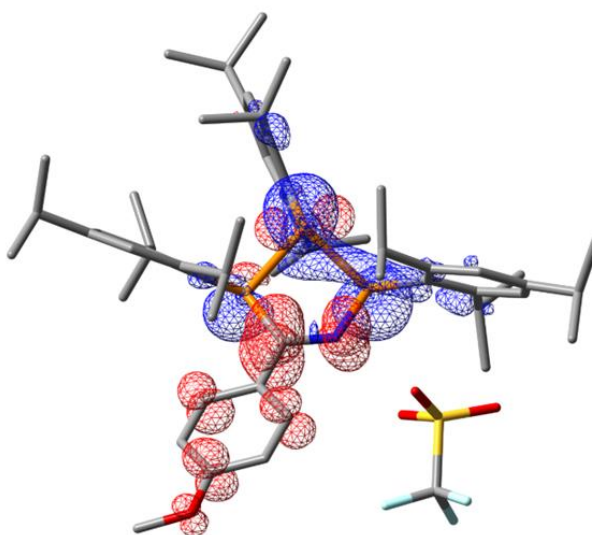


Figure A.102 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex $[1_{\text{Tripp}}]^+$ ($R' = p\text{-MeOC}_6\text{H}_4$). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 2.074).

Table A.10 Calculated electronic excitations of $[1_{\text{Tripp}}]^+$ ($R' = p\text{-CF}_3\text{C}_6\text{H}_4$)

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	1A	598.8	0.0181	HOMO $\rightarrow$ LUMO
S2	1A	448.3	0.0019	HOMO-1 $\rightarrow$ LUMO
S3	1A	433.3	0.0242	HOMO-2 $\rightarrow$ LUMO

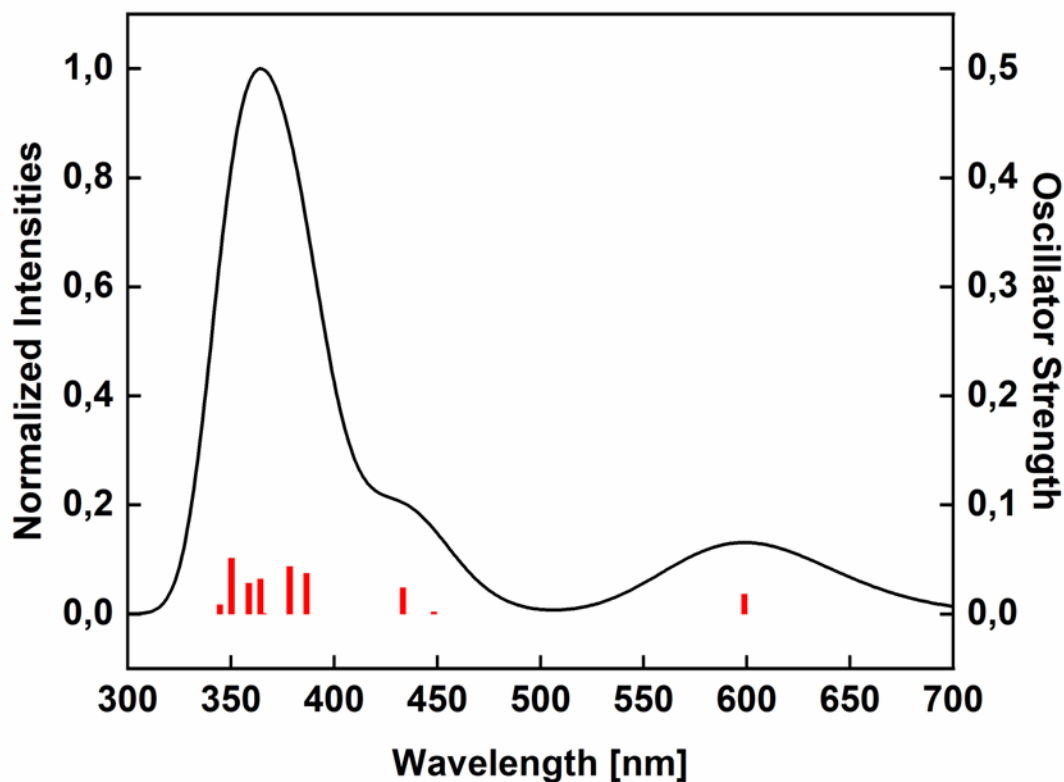


Figure A.103 Predicted UV-vis absorption spectra of $[1_{\text{Tripp}}]^+$ ($R' = p\text{-CF}_3\text{C}_6\text{H}_4$) including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV.

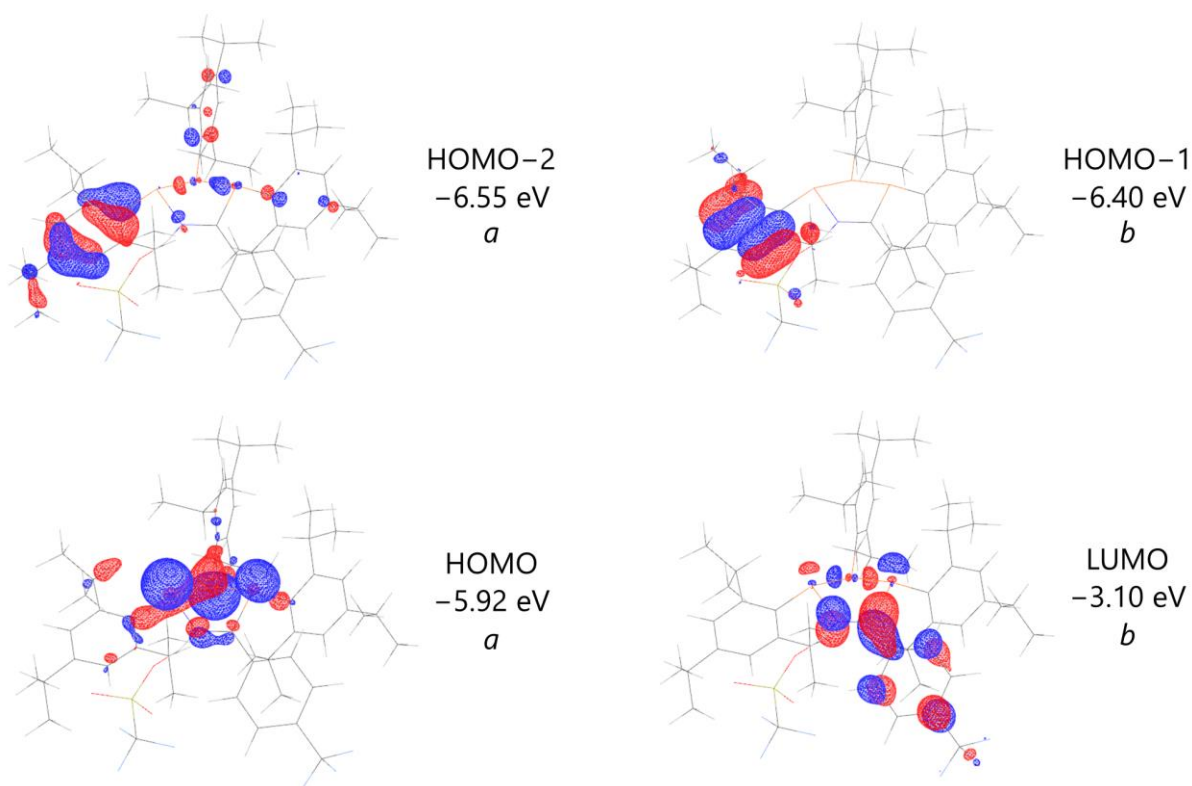


Figure A.104 Relevant Kohn-Sham orbitals of $[1_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-CF}_3\text{C}_6\text{H}_4$) (B3LYP-D3/cc-PVTZ)

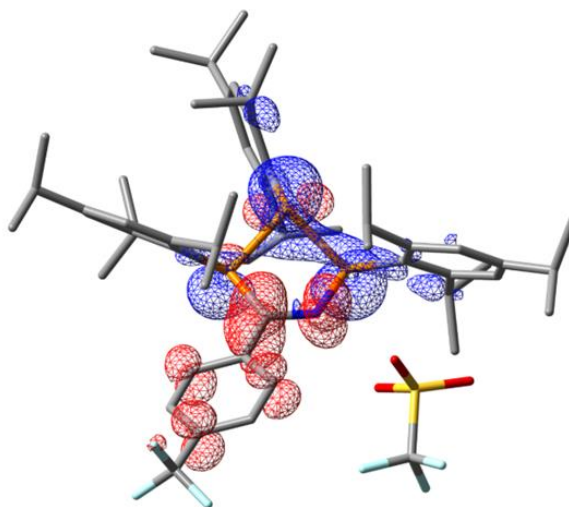


Figure A.105 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex $[1_{\text{Tripp}}]^+$ ($\text{R}' = p\text{-CF}_3\text{C}_6\text{H}_4$). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 2.266).

Table A.11 Calculated electronic excitations of $[1_{\text{Dipp}}]^+$ ($R' = \text{Ph}$)

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	1A	583.7	0.0215	HOMO $\rightarrow$ LUMO
S2	1A	425.9	0.0026	HOMO-1 $\rightarrow$ LUMO
S3	1A	406.1	0.0392	HOMO-2 $\rightarrow$ LUMO

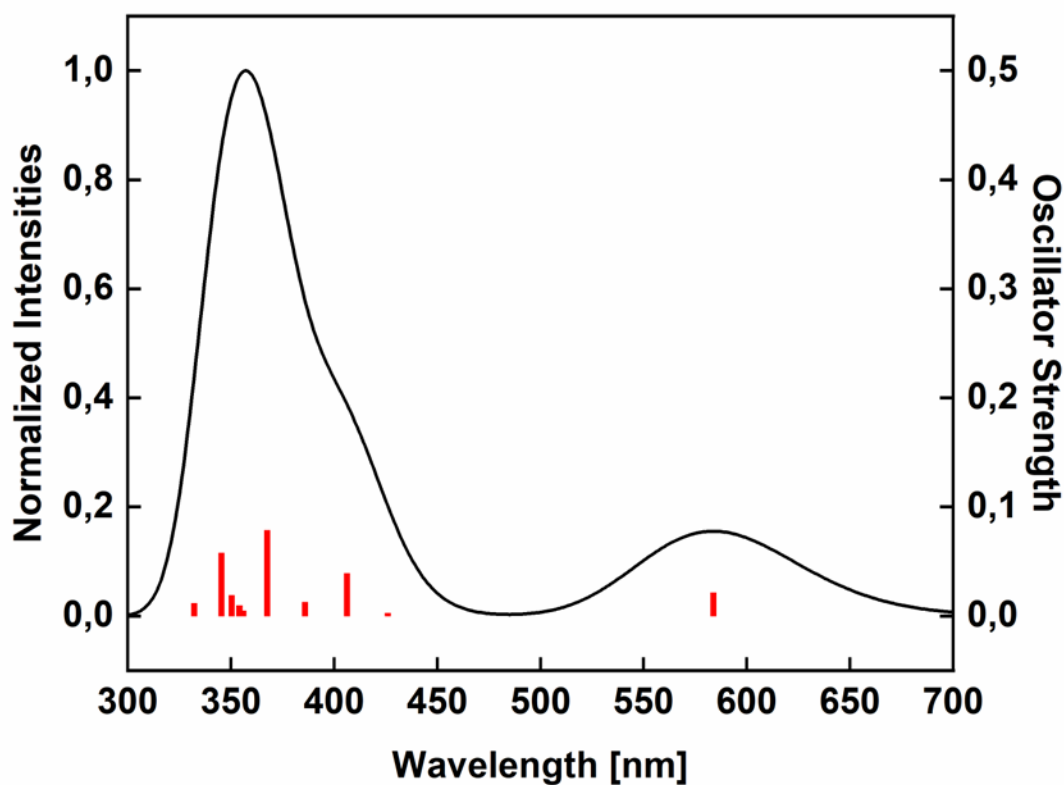


Figure A.106 Predicted UV-vis absorption spectra of $[1_{\text{Dipp}}]^+$ ($R' = \text{Ph}$) including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV.

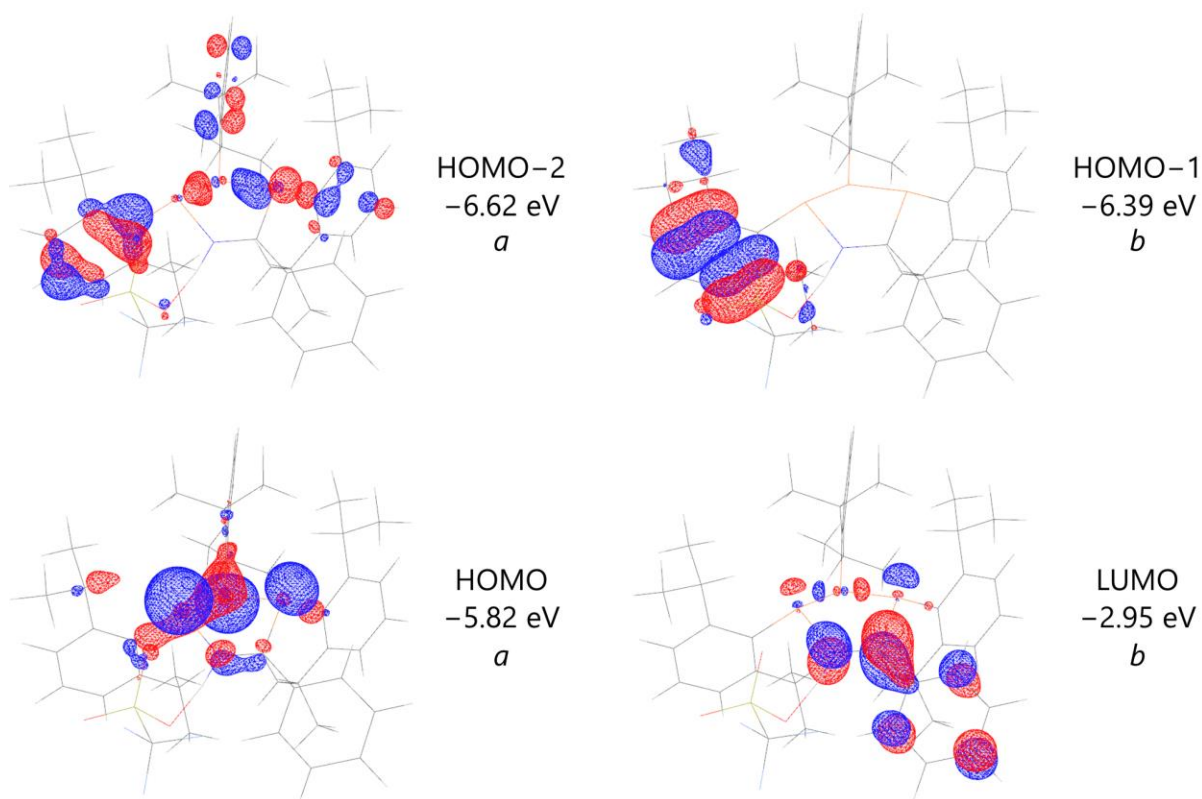


Figure A.107 Relevant Kohn-Sham orbitals of $[1_{\text{Dipp}}]^+$ ($\text{R}' = \text{Ph}$) (B3LYP-D3/cc-PVTZ)

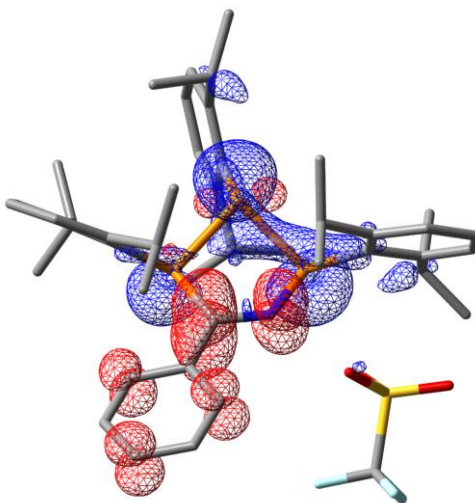


Figure A.108 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex $[1_{\text{Dipp}}]^+$ ($\text{R}' = \text{Ph}$). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 2.304).

Table A.12 Calculated electronic excitations of $[1_{\text{Mes}}]^+$ ($R' = \text{Ph}$)

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	1A	467.8	0.0413	HOMO $\rightarrow$ LUMO
S2	1A	428.9	0.0622	HOMO-1 $\rightarrow$ LUMO HOMO-2 $\rightarrow$ LUMO
S3	1A	425.0	0.0076	HOMO-1 $\rightarrow$ LUMO HOMO-2 $\rightarrow$ LUMO

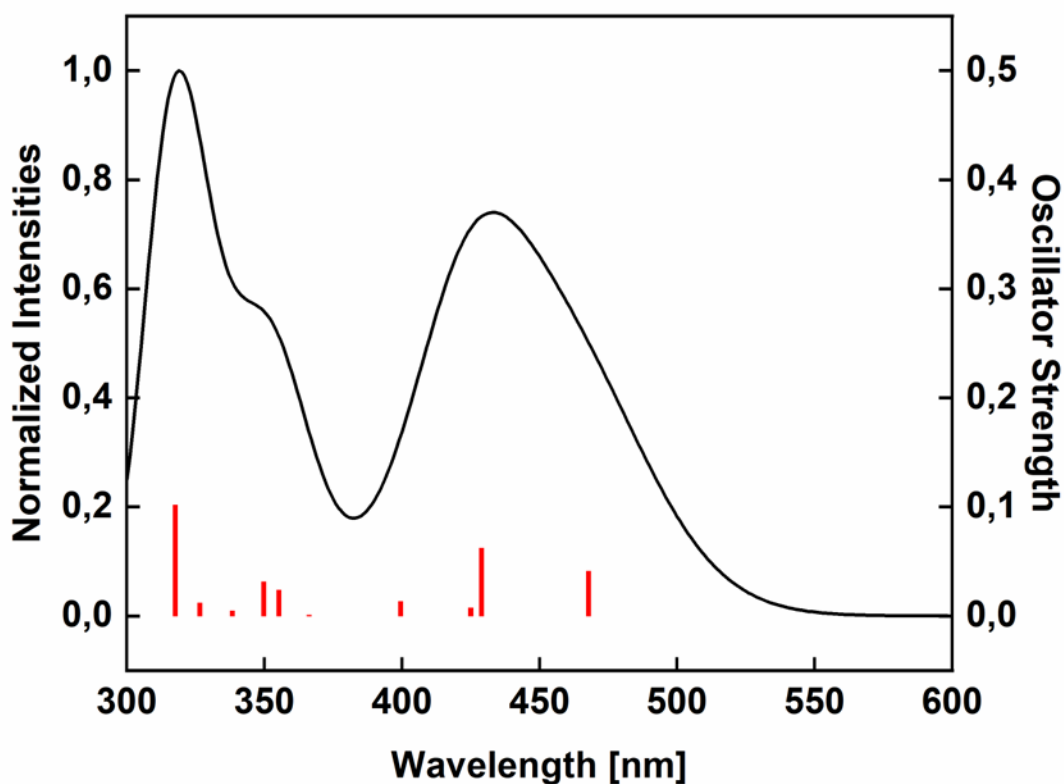


Figure A.109 Predicted UV-vis absorption spectra of $[1_{\text{Mes}}]^+$ ($R' = \text{Ph}$) including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV

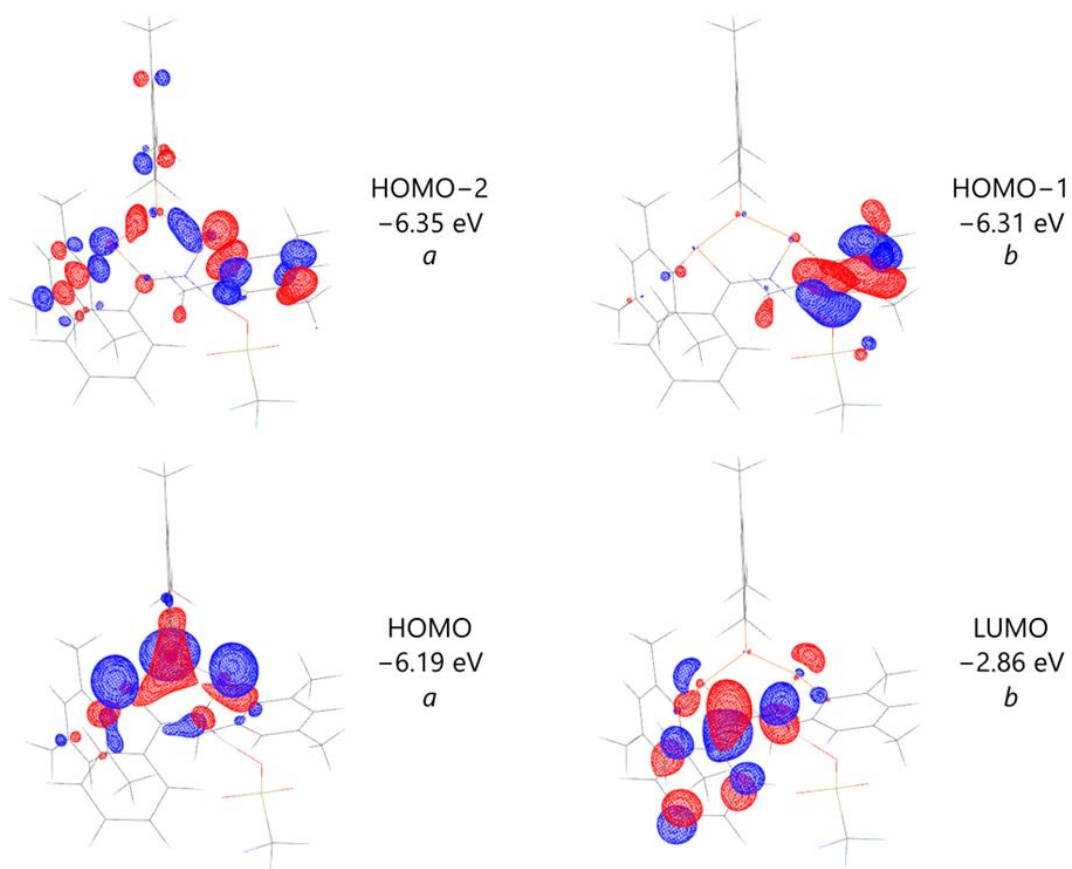


Figure A.110 Relevant Kohn-Sham orbitals of $[1_{\text{Mes}}]^+$ ($R' = \text{Ph}$) (B3LYP-D3/cc-PVTZ)

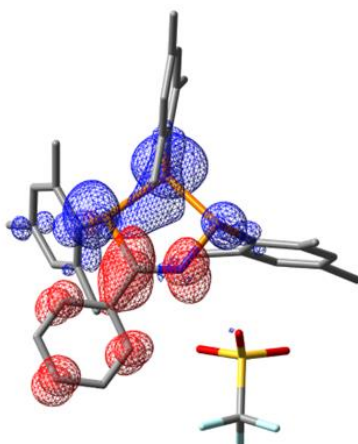


Figure A.111 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex $[1_{\text{Mes}}]^+$ ($R' = \text{Ph}$). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 2.637)

Table A.13 Calculated electronic excitations of $[1_{tBu}]^+$ ($R' = Ph$)

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	1A	400.5	0.0512	HOMO $\rightarrow$ LUMO
S2	1A	334.1	0.0865	HOMO-1 $\rightarrow$ LUMO
S3	1A	325.8	0.0537	HOMO-2 $\rightarrow$ LUMO

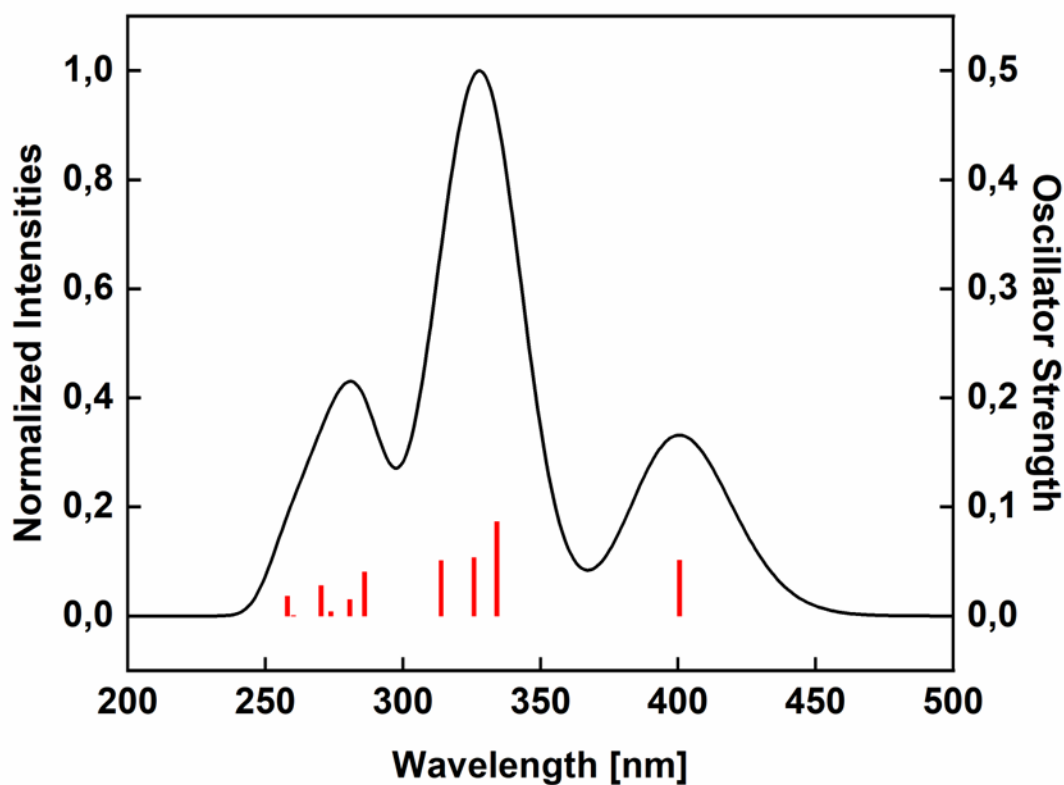


Figure A.112 Predicted UV-vis absorption spectra of $[1_{tBu}]^+$ ($R' = Ph$) including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV.

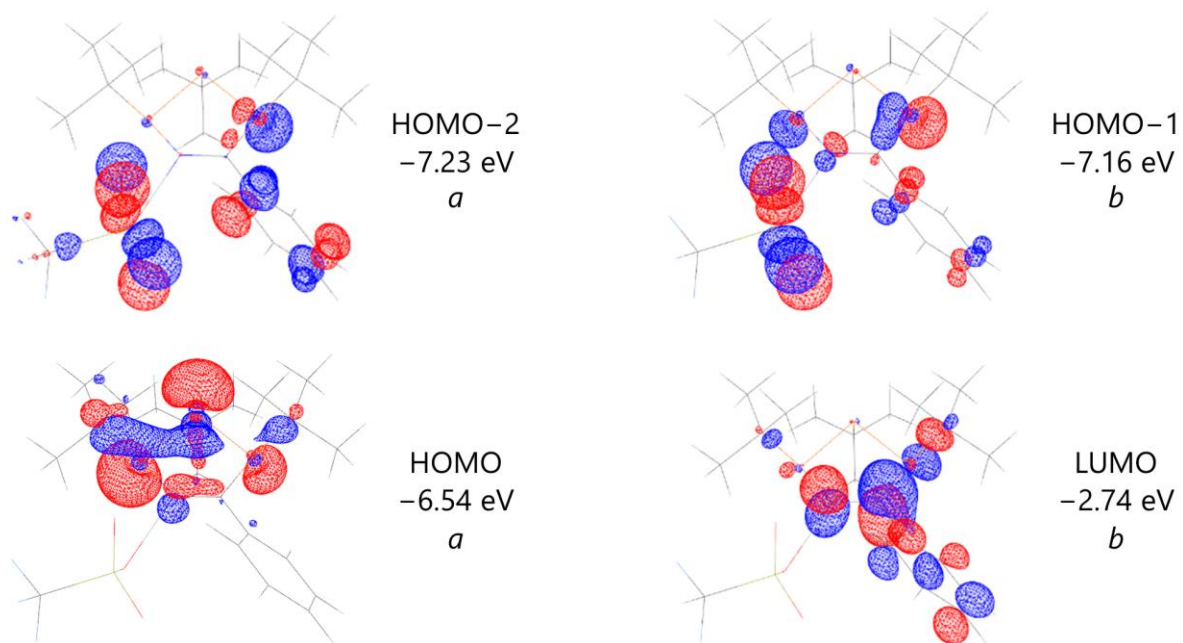


Figure A.113 Relevant Kohn-Sham orbitals of $[1_{tBu}]^+$ ($R' = Ph$) (B3LYP-D3/cc-PVTZ)

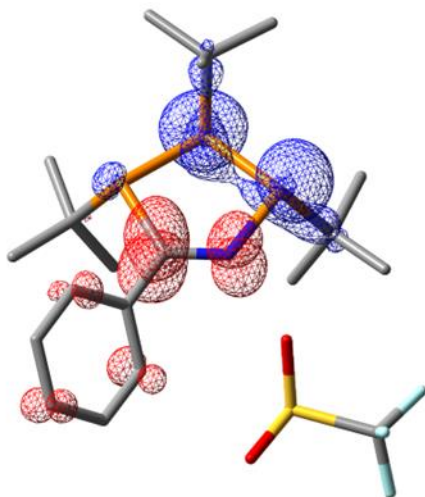


Figure A.114 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex $[1_{tBu}]^+$ ($R' = Ph$). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 2.404)

Table A.14 Calculated electronic excitations of **2_{tBu}** (**R'** = **Me**)

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	¹ A	332.8	0.0232	HOMO→LUMO
S2	¹ A	284.3	0.0276	HOMO-1→LUMO
S3	¹ A	279.5	0.0239	HOMO→LUMO+1

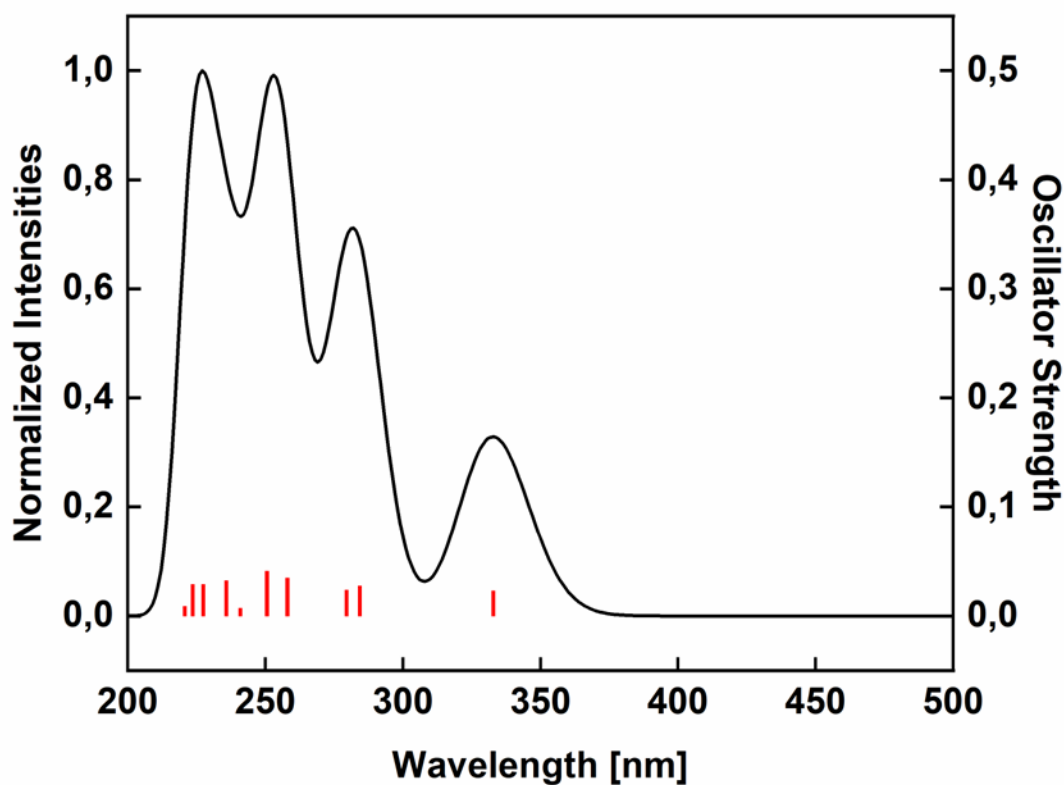


Figure A.115 Predicted UV-vis absorption spectra of **2_{tBu}** (**R'** = **Me**) including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV.

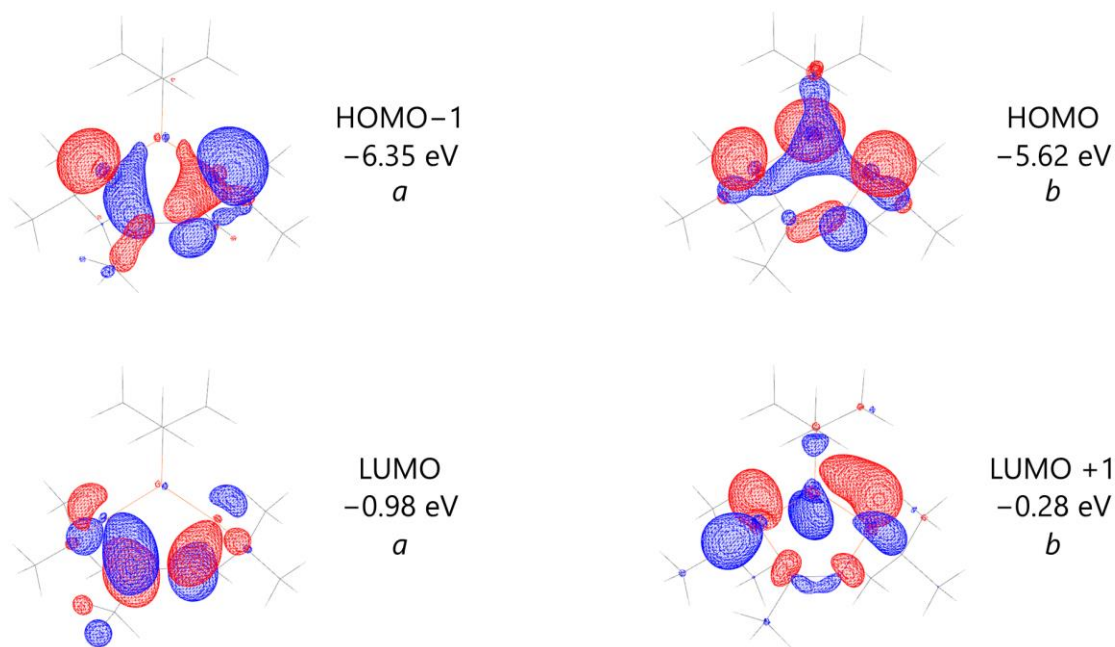


Figure A.116 Relevant Kohn-Sham orbitals 2_{tBu} ($R' = Me$) (B3LYP-D3/cc-PVTZ)

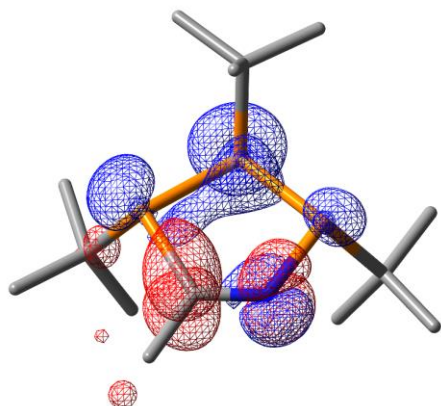


Figure A.117 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex 2_{tBu} ($R' = Me$). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 1.396).

Table A.15 Calculated electronic excitations of **2_{tBu} (R' = Ph)**

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	¹ A	393.4	0.0495	HOMO→LUMO
S2	¹ A	327.2	0.1179	HOMO-1→LUMO
S3	¹ A	291.8	0.0025	HOMO→LUMO+1

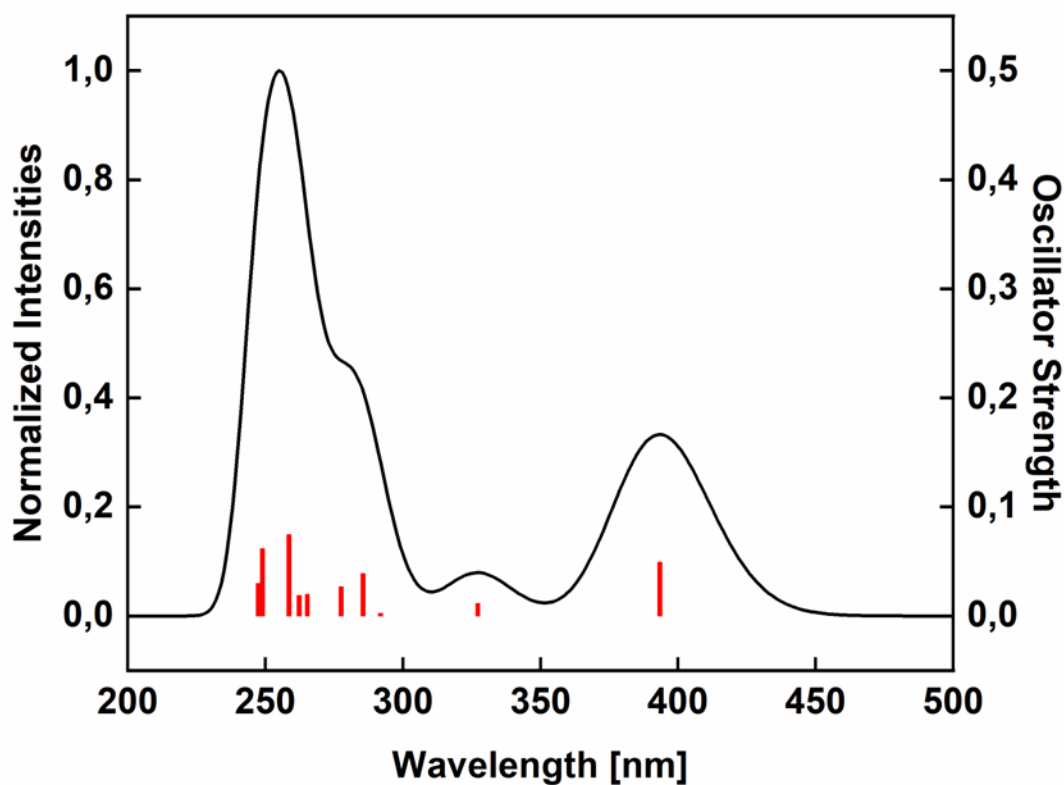


Figure A.118 Predicted UV-vis absorption spectra of **2_{tBu} (R' = Ph)** including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV.

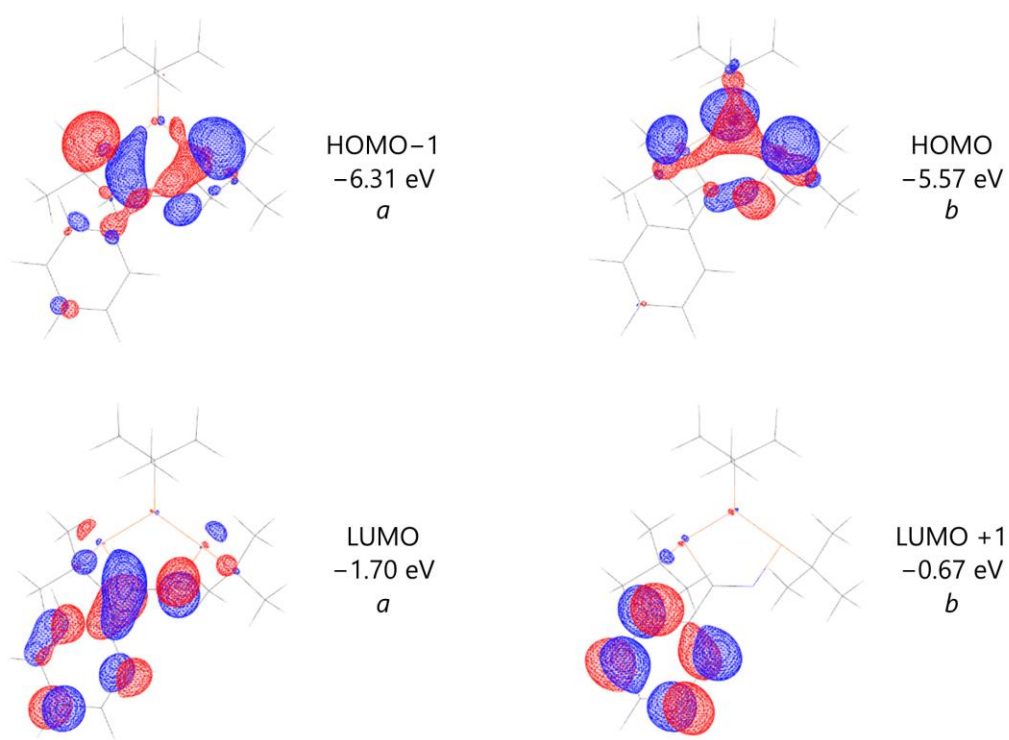


Figure A.119 Relevant Kohn-Sham orbitals of **2_{tBu}** (**R'** = **Ph**) (B3LYP-D3/cc-PVTZ)

Figure A.120 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex **2_{tBu}** (**R'** = **Ph**). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 2.701).

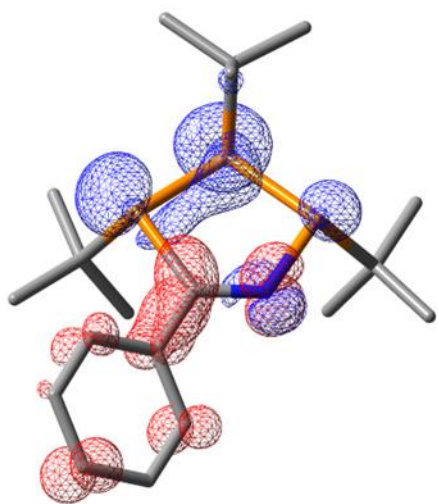


Table A.16 Calculated electronic excitations of **2_{Tripp} (R' = Me)**

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	¹ A	364.8	0.0042	HOMO→LUMO
S2	¹ A	346.3	0.0044	HOMO→LUMO+1
S3	¹ A	332.9	0.0696	HOMO→LUMO+2

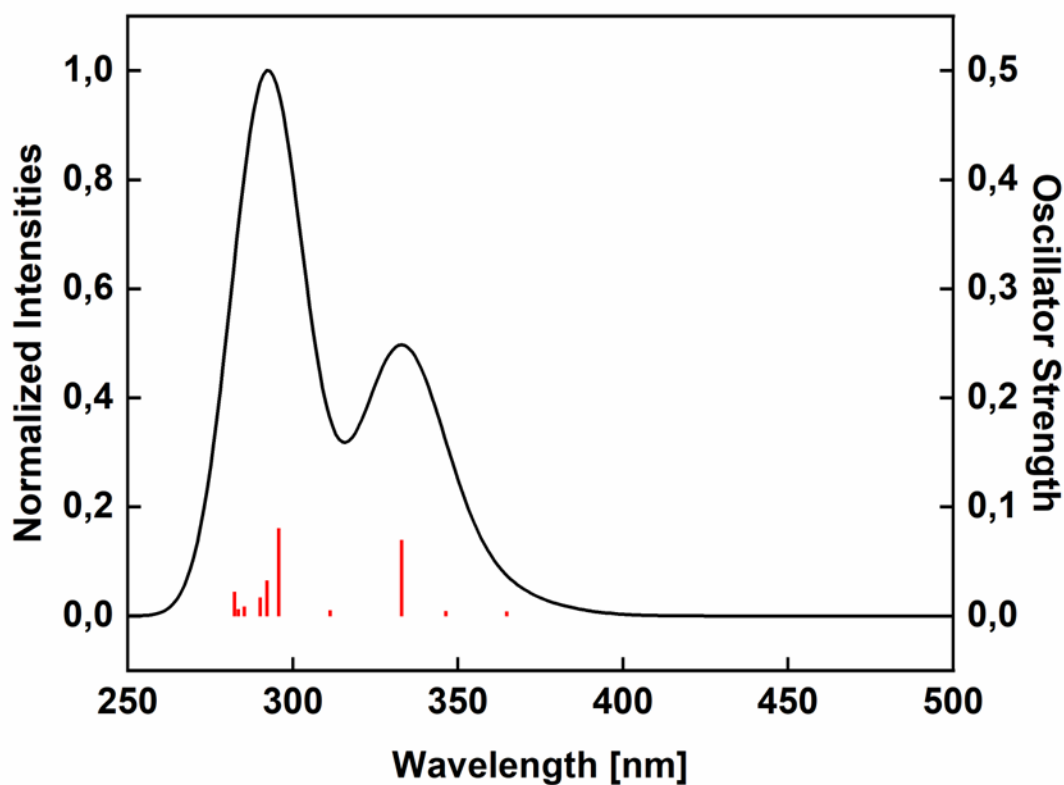


Figure A.121 Predicted UV-vis absorption spectra of **2_{Tripp} (R' = Me)** including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV.

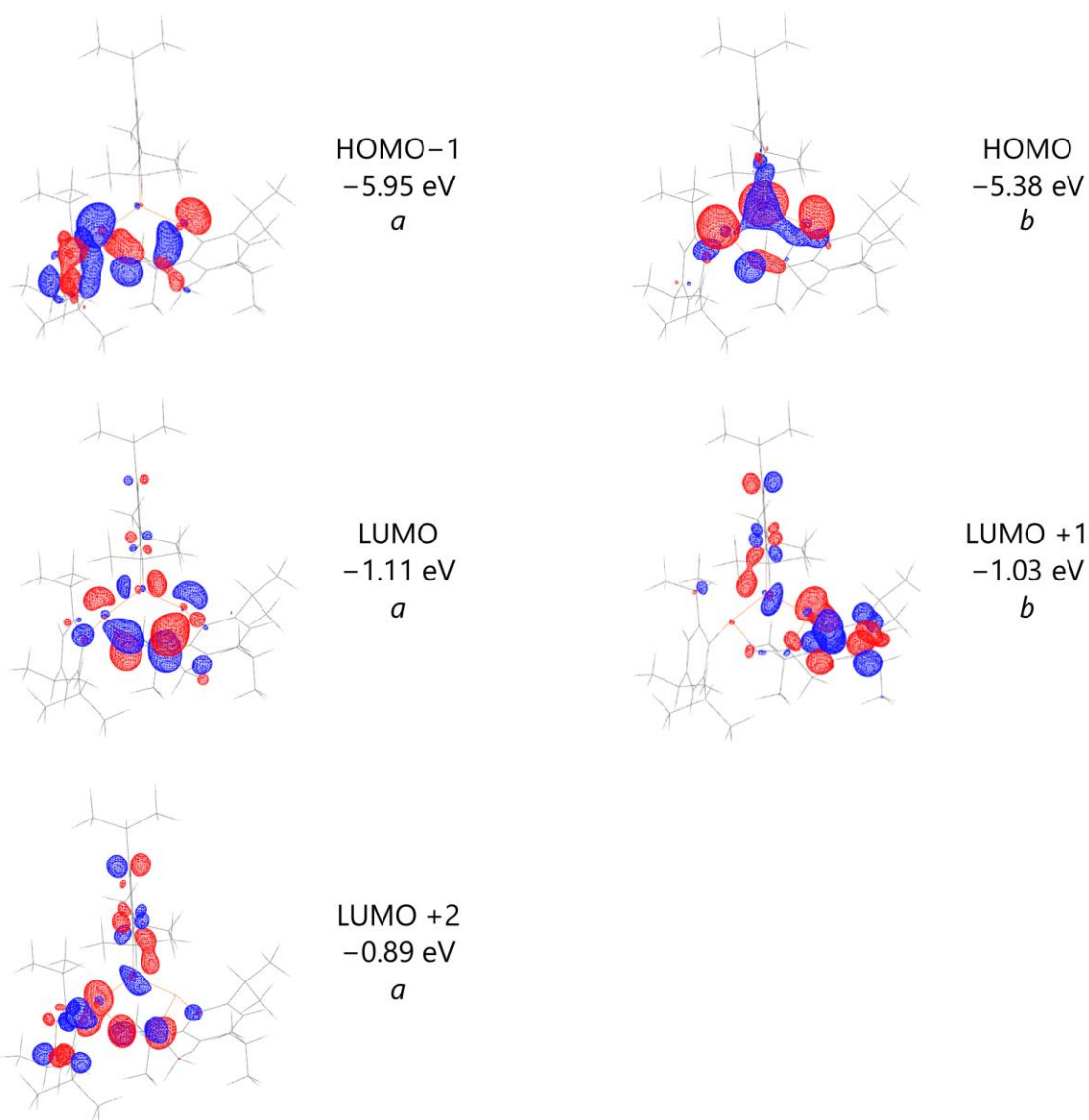


Figure A.122 Relevant Kohn-Sham orbitals of **2_{Tripp}** (**R'** = **Me**) (B3LYP-D3/cc-PVTZ)

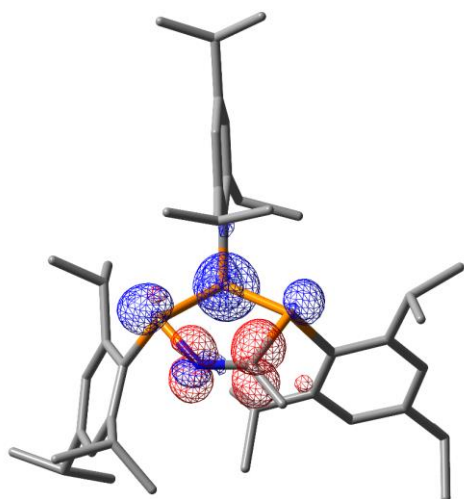


Figure A.123 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex **2_{Tripp}** (**R'** = **Me**). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 1.241).

Table A.17 Calculated electronic excitations of **2_{Tripp} (R' = Ph)**

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	1A	474.1	0.0216	HOMO→LUMO
S2	1A	374.5	0.0821	HOMO-1→LUMO
S3	1A	362.2	0.0207	HOMO→LUMO+1

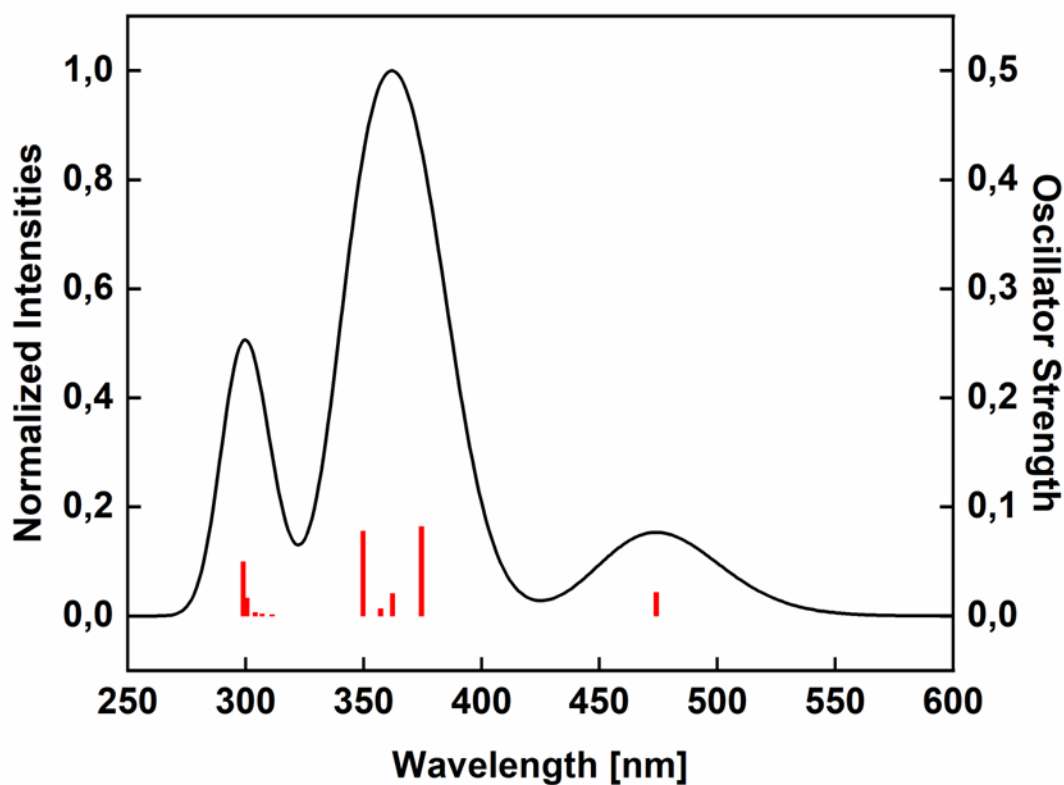


Figure A.124 Predicted UV-vis absorption spectra of **2_{Tripp} (R' = Ph)** including oscillator strengths (given as red bars) at the B3LYP/cc-pVTZ level of theory. The phenomenological broadening (Gaussian) used to generate the illustrated spectra is $\sigma = 0.2$ eV.

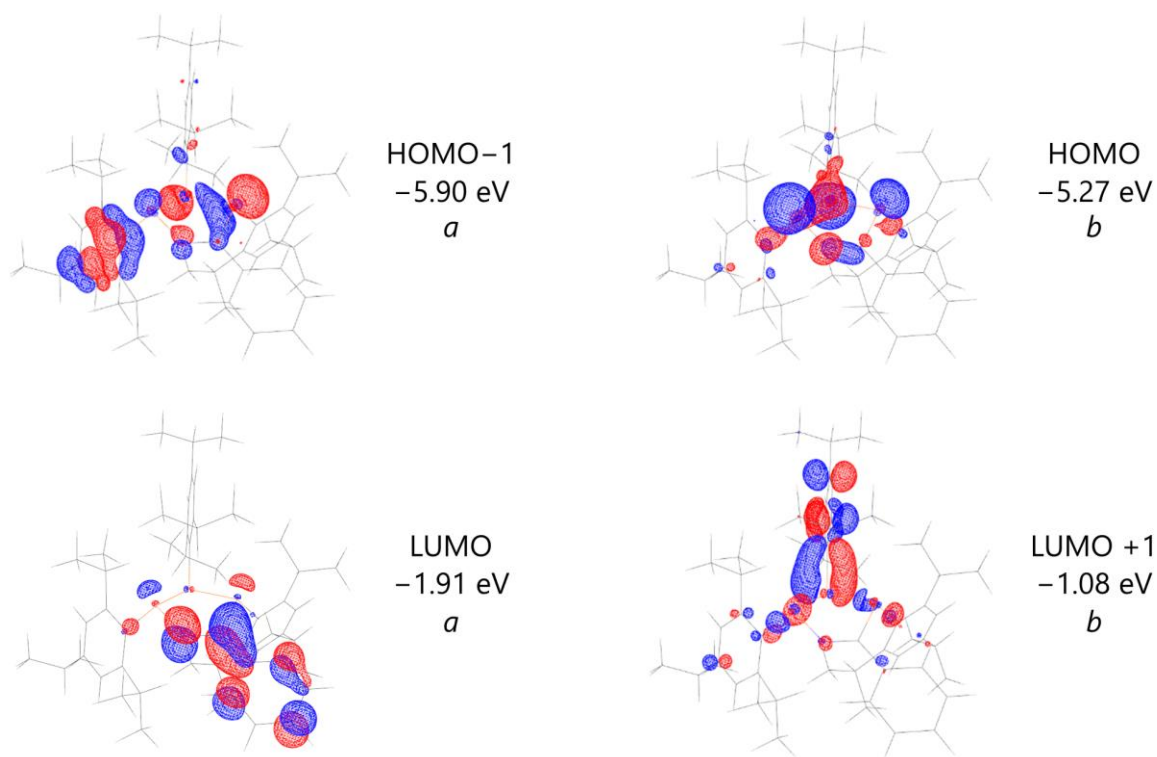


Figure A.125 Relevant Kohn-Sham orbitals of **2_{Tripp}** (**R'** = **Ph**) (B3LYP-D3/cc-PVTZ).

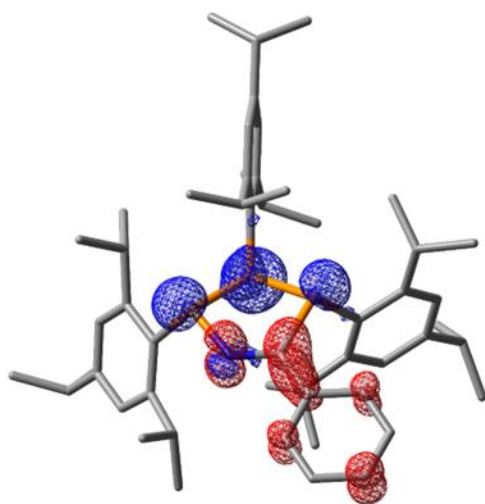


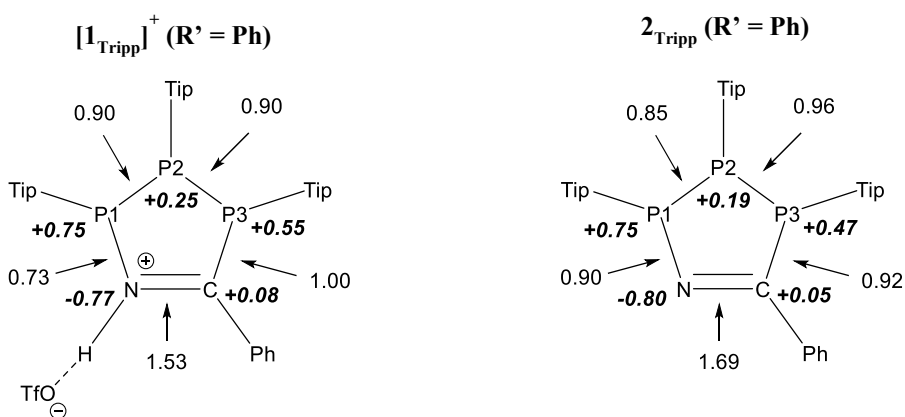
Figure A.126 Charge density difference diagram of the first excited state (HOMO-LUMO) illustrating charge transfers during excitation of complex **2_{Tripp}** (**R'** = **Ph**). The blue regions correspond to the electron donor regions and the red regions to corresponding acceptor regions (D index = 2.777).

A.5.4 NBO Analysis

To gain further insight into the electronic structure of $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$) and its neutral deprotonated congener 2_{Tripp} , NBO analyses were performed on the BP86-D3/def2-SVP//b3lyp/cc-pVTZ level of theory, revealing a charge transfer of 0.14 e from the OTf-counteranion in $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$). Two distinct σ - and π -type NBOs between the C and N atom (Figure S37) show the corresponding Natural Localized Molecular Orbital, NLMO, and the % of the individual atoms to this NLMO, indicating a double bond (WBI = 1.53) and a s-type lone pair of electrons (LP) on each of the P atoms. Both the σ - and π -component are significantly polarized towards the N-atom, with both N and C being nearly sp^2 -hybridized. The LP on P3 interacts weakly with the π^* -orbital of the C–N π -bond, resulting in a resonance stabilization of ca. 9 kcal/mol. The atomic charges on P1 (+0.75) and P3 (+0.55) indicate charge flow to the nitrile unit, while P2 (+0.25) shows no excess positive charge. The bonding between P1–P2 and P2–P3 is best described as minimally polarized single bonds with mainly p-character at the P atoms. The P1–N bond is significantly polarized towards the N-atom (76.08%), which is further underlined by a rather low WBI of 0.73. Para-substitution of the benzonitrile does not significantly influence the charge transfer from the triflate to the $P_3\text{CN}$ -ring.

The main difference between $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$) and 2_{Tripp} ($R' = \text{Ph}$) is that the π -component of the C–N bond is less polarized towards N and that the WBI is higher compared to the triflate species (1.69 vs. 1.53). In addition, the N atom now possesses a sp^2 -type LP of electrons, which is delocalized into the σ^* -orbital of the P3–C bond, resulting in a stabilization energy of 16.20 kcal·mol^{−1}. The NPA charges at the atoms of the $P_3\text{CN}$ ring change only marginally.

In the following the NPA Charges (shown in bold) and Wiberg Bond indexes (shown on the end of arrows) in $[1_{\text{Tripp}}]^+$ ($R' = \text{Ph}$) (left) and 2_{Tripp} ($R' = \text{Ph}$) (right) are summarized:



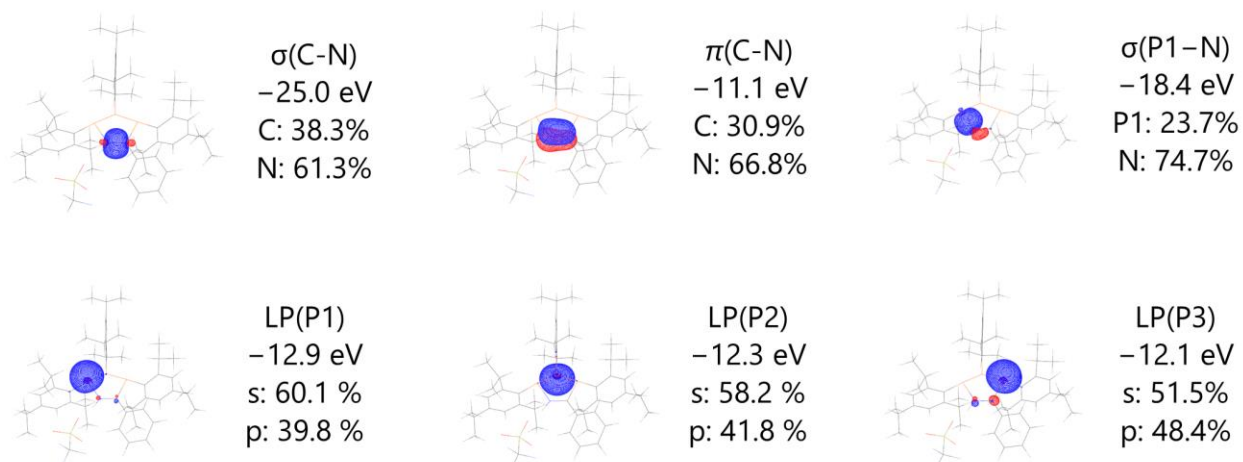


Figure A.127 Selected NLMOs of $[1_{\text{Tripp}}]^+$ ($\text{R}' = \text{Ph}$) (BP86-D3/def2-SVP//b3lyp/cc-pVTZ)

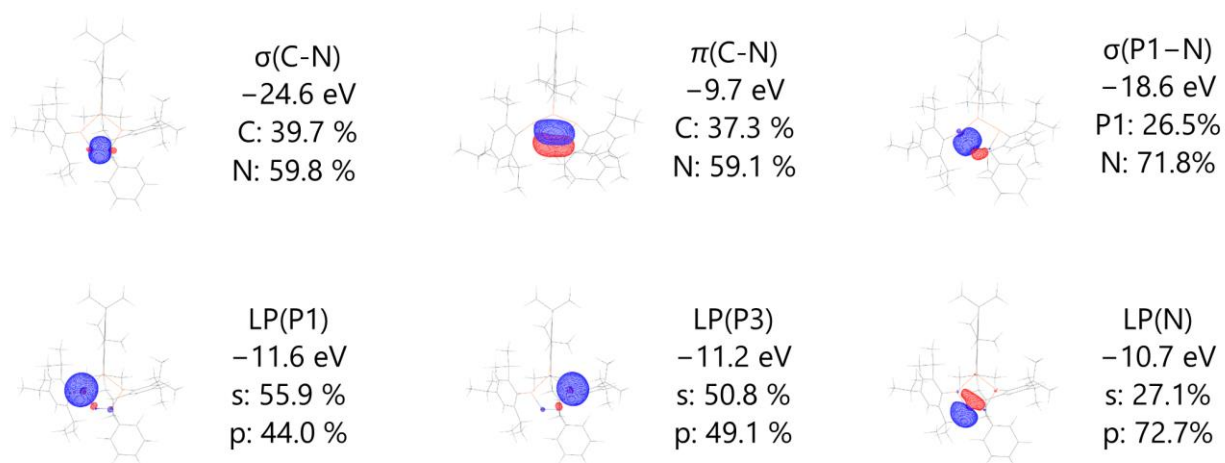


Figure A.128 Selected NLMOs of 2_{Tripp} ($\text{R}' = \text{Ph}$) (BP86-D3/def2-SVP//b3lyp/cc-pVTZ)

A.5.5 Optimized Structures (.xyz files)

A.1.1.1 $[I_{tBu}]^+$ ($R' = Me$)

```

57
[P3tBu3MeCNH]OTf @BP86-D3/def2SVP
S      3.62049      0.11972     -0.29870
O      2.93826      1.31228      0.28018
O      5.04213      0.19728     -0.67169
O      2.74302     -0.56834     -1.37540
F      4.22188     -0.75902      2.16271
F      3.98408     -2.35518      0.68928
F      2.22297     -1.32489      1.47469
C      3.51930     -1.15980      1.09450
N      0.33133     -0.21822     -0.65862
H      1.41678     -0.33464     -1.01910
P     -0.12629      1.39056     -0.07596
P     -2.28997      0.90355      0.34397
P     -1.96589     -1.30194      0.36548
C     -0.17789      2.32899     -1.73490
C     -1.03728      1.63374     -2.79613
H     -2.09359      1.54554     -2.46756
H     -0.65539      0.61995     -3.03150
H     -1.02412      2.22455     -3.73797
C      1.27866      2.48120     -2.21794
H      1.72981      1.50537     -2.48751
H      1.92822      2.92945     -1.44080
H      1.29442      3.13050     -3.11994
C     -0.77471      3.70081     -1.36297
H     -0.79983      4.35082     -2.26362
H     -0.16628      4.21677     -0.59108
H     -1.81644      3.60849     -0.98695
C     -2.24310      1.22592      2.24592
C     -2.14324      2.75617      2.39101
H     -2.19725      3.03767      3.46494
H     -2.96764      3.27638      1.85921
H     -1.17731      3.13742      1.99661
C     -1.07227      0.53937      2.96554
H     -0.08942      0.86328      2.56302
H     -1.13420     -0.56545      2.87917
H     -1.09402      0.79481      4.04759
C     -3.58701      0.71481      2.79491
H     -3.66391      0.94171      3.88053
H     -3.67751     -0.38610      2.67727
H     -4.44988      1.19057      2.28338
C     -3.22967     -2.00599     -0.89812
C     -3.04326     -1.43879     -2.31039
H     -3.81744     -1.85392     -2.99235
H     -2.05080     -1.69147     -2.73588
H     -3.14545     -0.33573     -2.31396
C     -3.10232     -3.54167     -0.88445
H     -3.91403     -3.98405     -1.50167
H     -3.19452     -3.95036      0.14286
H     -2.14067     -3.89084     -1.30849
C     -4.60530     -1.59675     -0.33509
H     -4.72253     -0.49325     -0.30817

```


H	-4.76409	-1.98884	0.69113
H	-5.40638	-2.00903	-0.98553
C	-0.34954	-1.32579	-0.51298
C	0.28689	-2.62282	-0.93314
H	-0.21957	-3.01334	-1.84162
H	0.17557	-3.38789	-0.13992
H	1.35953	-2.47324	-1.16457

A.1.1.2 $[I_{tBu}]^+$ ($R' = Ph$)

64			
[P3tBu3PhCNH]OTf @BP86-D3/def2SVP			
P	-2.53032	1.01451	-0.26702
P	-0.83256	-1.79547	-0.47113
P	-2.86896	-1.13317	0.22197
N	-0.05386	-0.19884	-0.42983
C	-0.69796	0.94863	-0.38485
C	-3.89034	-1.65308	-1.32697
C	1.18555	2.45844	0.27868
H	1.55080	1.68590	0.97185
C	0.02537	2.22727	-0.49491
C	-0.07985	-2.65737	1.05027
C	-2.84401	1.91841	1.40526
C	1.86071	3.68180	0.17642
H	2.78102	3.83089	0.75894
C	-5.29189	-1.05050	-1.11953
H	-5.74096	-1.37201	-0.15653
H	-5.96902	-1.37615	-1.93883
H	-5.25969	0.05968	-1.13376
C	-3.94886	-3.19150	-1.27971
H	-2.94267	-3.63883	-1.42569
H	-4.60287	-3.57010	-2.09486
H	-4.35615	-3.56028	-0.31503
C	-0.45973	3.24322	-1.35666
H	-1.36020	3.05542	-1.96175
C	1.38304	4.68261	-0.68596
H	1.92134	5.63963	-0.76876
C	-4.33433	1.65217	1.69692
H	-4.98914	2.04405	0.89080
H	-4.61791	2.15951	2.64385
H	-4.54102	0.56823	1.82082
C	1.30354	-3.16405	0.60142
H	1.23019	-3.83905	-0.27617
H	1.77664	-3.72834	1.43327
H	1.97821	-2.32801	0.34804
C	0.22285	4.46182	-1.45286
H	-0.14579	5.24198	-2.13650
C	-1.96753	1.37205	2.53785
H	-2.15708	0.29306	2.70638
H	-2.19988	1.90678	3.48463
H	-0.88711	1.50737	2.32989
C	-3.29262	-1.17865	-2.65872
H	-3.24084	-0.07098	-2.70928
H	-3.92730	-1.52626	-3.50316

H	-2.27103	-1.58429	-2.81453
C	-2.61037	3.42747	1.20900
H	-1.53986	3.67058	1.07077
H	-2.96394	3.96459	2.11569
H	-3.17174	3.82444	0.33836
C	0.04171	-1.74095	2.27110
H	0.75313	-0.91258	2.08177
H	0.43816	-2.32439	3.13032
H	-0.94403	-1.33151	2.57000
C	-1.02815	-3.84009	1.32681
H	-2.02872	-3.49837	1.66683
H	-0.59367	-4.47127	2.13113
H	-1.16224	-4.48655	0.43299
H	1.05553	-0.19041	-0.68102
S	3.44001	0.14090	0.00440
F	4.33836	-2.39349	-0.18187
F	5.31757	-0.98163	-1.53056
O	2.42705	-0.22940	-1.09117
F	5.78553	-0.95874	0.60417
O	2.91730	-0.16034	1.37472
O	4.11441	1.44281	-0.19897
C	4.80605	-1.13322	-0.29883

A.1.1.3 $2_{tBu} (R' = Me)$

48			
P3tBu3MeCN @BP86-D3/def2SVP			
P	1.66185	-0.22879	0.71914
P	0.17019	0.92708	-0.55231
P	-1.55945	0.15011	0.61162
N	0.61803	-1.43114	1.38680
C	-0.66823	-1.33181	1.37316
C	-1.50468	-2.36182	2.09887
H	-2.05309	-3.00161	1.37462
H	-2.26486	-1.88061	2.74806
H	-0.84604	-3.00869	2.70938
C	2.60972	-1.28267	-0.55797
C	3.50862	-2.22934	0.26172
H	2.89892	-2.90638	0.89344
H	4.19488	-1.66449	0.92687
H	4.12809	-2.85082	-0.42174
C	1.67661	-2.08029	-1.47552
H	2.26947	-2.70822	-2.17704
H	1.04122	-1.40231	-2.08167
H	1.01313	-2.74939	-0.89166
C	3.45782	-0.29138	-1.37386
H	4.09110	-0.84286	-2.10241
H	4.13040	0.30662	-0.72316
H	2.81687	0.41117	-1.94819
C	0.37425	2.66531	0.25703
C	0.32139	2.65200	1.79142
H	0.44878	3.68487	2.18538
H	1.12939	2.02180	2.21829
H	-0.65284	2.26528	2.15683

C	-0.76229	3.53700	-0.30733
H	-1.75387	3.16419	0.02562
H	-0.75533	3.55272	-1.41753
H	-0.65571	4.58433	0.05246
C	1.74159	3.18259	-0.22805
H	1.90330	4.22436	0.12616
H	1.81035	3.18381	-1.33650
H	2.57116	2.56001	0.16944
C	-2.69513	-0.60574	-0.74682
C	-2.00991	-1.70905	-1.56241
H	-2.70353	-2.10170	-2.33900
H	-1.69324	-2.56272	-0.92936
H	-1.11048	-1.31800	-2.07814
C	-3.96846	-1.13085	-0.05431
H	-4.70597	-1.45162	-0.82247
H	-4.44465	-0.34497	0.56802
H	-3.76781	-2.00550	0.59480
C	-3.07077	0.57327	-1.66610
H	-2.17677	0.98925	-2.17566
H	-3.55912	1.39452	-1.10075
H	-3.78179	0.22560	-2.44738

A.1.1.4 $2_{tBu}(R' = Ph)$

55			
P3tBu3PhCN @BP86-D3/def2SVP			
P	1.44607	1.30130	-0.70826
P	1.76416	-0.71069	0.30169
P	-0.32365	-1.36979	-0.09767
N	-0.26674	1.38903	-0.65792
C	-2.48714	0.46527	-0.68037
C	-3.25698	-0.60269	-1.19533
H	-2.75177	-1.53998	-1.47768
C	-3.13495	1.67792	-0.34547
H	-2.52294	2.50745	0.03940
C	-1.01717	0.34428	-0.50099
C	2.68054	-1.61555	-1.13321
C	3.45269	2.47964	0.76608
H	3.81976	3.25463	1.47353
H	3.98259	2.62237	-0.19934
H	3.73920	1.48720	1.17485
C	-4.52141	1.80701	-0.49852
H	-5.01724	2.75062	-0.22097
C	-0.99596	-1.71363	1.67952
C	-5.28116	0.73595	-1.00734
H	-6.37064	0.84059	-1.12992
C	-0.10464	-2.84557	2.22757
H	0.95448	-2.52486	2.31361
H	-0.14119	-3.74562	1.57845
H	-0.45813	-3.13920	3.24021
C	-4.64377	-0.46531	-1.36220
H	-5.23008	-1.30196	-1.77327
C	-0.91953	-0.48399	2.59120
H	-1.52926	0.35530	2.19900

H	0.12508	-0.13211	2.69897
H	-1.29996	-0.73559	3.60619
C	1.92708	2.59839	0.60189
C	2.76467	-3.09564	-0.71774
H	1.75353	-3.55070	-0.65819
H	3.25543	-3.21705	0.27077
H	3.35279	-3.67017	-1.46722
C	4.08614	-0.98845	-1.18438
H	4.71304	-1.51808	-1.93492
H	4.60082	-1.05302	-0.20241
H	4.03904	0.08088	-1.48139
C	1.22012	2.38197	1.94388
H	1.50093	3.18509	2.66093
H	1.51019	1.41033	2.39336
H	0.11812	2.39513	1.82579
C	1.54490	3.96445	-0.00155
H	0.45154	4.03136	-0.17268
H	2.05455	4.13835	-0.97221
H	1.84119	4.78112	0.69288
C	-2.44847	-2.21529	1.57341
H	-2.78358	-2.57559	2.57086
H	-2.54083	-3.06023	0.85976
H	-3.14459	-1.41616	1.25422
C	1.98617	-1.48379	-2.49635
H	1.89876	-0.42082	-2.80463
H	0.96815	-1.92574	-2.47334
H	2.57267	-2.01877	-3.27611

A.1.1.5 $[I_{Mes}]^+ (R' = Ph)$

85			
P3Mes3PhCN @ BP86/def2SVP			
P	-2.14000	-0.62795	0.45177
P	-0.32817	-1.60838	-0.43203
P	-1.79090	1.34613	-0.54027
N	0.46273	-0.13642	-1.02897
C	-3.54640	-1.43060	-2.01143
C	0.77167	-2.19737	0.90650
C	0.56187	2.10204	-1.99041
C	-0.55599	3.10217	1.49797
C	-3.47182	-1.40894	-0.58614
C	-0.08254	1.05293	-1.18477
C	-4.49931	-2.03363	0.18277
C	1.01122	-1.52728	2.14106
C	-5.58046	-2.64458	-0.48303
H	-6.36930	-3.12477	0.11948
C	-2.99947	2.71700	1.48003
C	-0.17545	3.25407	-2.36502
H	-1.24340	3.32350	-2.10126
C	-4.64831	-2.05551	-2.62358
H	-4.69858	-2.06768	-3.72541
C	-2.49478	-0.81387	-2.90052
H	-2.46905	0.29126	-2.79331
H	-2.69166	-1.04419	-3.96525
H	-1.48206	-1.19946	-2.65767

C	1.37726	-3.46718	0.64529
C	-1.70113	2.48187	0.91885
C	-5.67934	-2.66544	-1.88395
C	1.79850	4.19880	-3.42185
H	2.28386	5.01747	-3.97594
C	1.92678	2.01017	-2.35972
H	2.52251	1.13651	-2.06851
C	-3.11897	3.52607	2.62110
H	-4.12297	3.69084	3.04685
C	0.43912	4.29440	-3.07260
H	-0.14634	5.18222	-3.35665
C	-2.00119	4.12673	3.22976
C	2.15985	-4.05876	1.64722
H	2.64142	-5.02784	1.43830
C	-0.74499	3.90414	2.64520
H	0.14421	4.37540	3.09550
C	-4.25263	2.09676	0.90130
H	-4.30244	2.20375	-0.20322
H	-5.15872	2.55940	1.33917
H	-4.30439	1.00471	1.10536
C	2.53567	3.05456	-3.06387
H	3.60129	2.97207	-3.32440
C	1.30008	-4.13525	-0.70806
H	0.26609	-4.20191	-1.10350
H	1.72639	-5.15655	-0.66654
H	1.89604	-3.54168	-1.43498
C	0.56277	-0.12130	2.42022
H	1.33215	0.55917	2.00135
H	0.48186	0.07164	3.50746
H	-0.41172	0.13615	1.96236
C	1.80299	-2.17207	3.10733
H	1.99512	-1.65086	4.05971
C	-4.46832	-2.08081	1.69797
H	-3.55829	-2.58942	2.07845
H	-5.35164	-2.62462	2.08681
H	-4.46560	-1.06653	2.14975
C	2.38768	-3.42963	2.88390
C	0.84814	3.00827	0.95891
H	1.14024	1.99565	0.62655
H	1.57885	3.31171	1.73284
H	0.99000	3.68259	0.08860
C	-6.84194	-3.32734	-2.58382
H	-6.49771	-4.16656	-3.22537
H	-7.37090	-2.61215	-3.24894
H	-7.57856	-3.73169	-1.86208
C	3.30409	-4.05104	3.90665
H	3.07112	-3.70727	4.93433
H	4.35574	-3.76184	3.68911
H	3.25653	-5.15856	3.88437
C	-2.15428	4.96625	4.47500
H	-2.99864	5.68051	4.38179
H	-1.23501	5.54405	4.69492
H	-2.36845	4.32821	5.36006
H	1.48063	-0.38850	-1.35837
S	3.64891	-0.65170	-0.20212
O	2.85530	-1.05282	-1.45759

F	6.05173	0.49541	-0.01794
F	5.88743	-0.95267	-1.64568
F	4.97285	1.02280	-1.84396
O	4.10219	-1.78208	0.63417
O	3.04818	0.54133	0.47240
C	5.24167	0.01591	-0.97671

A.1.1.6 $[I_{Dipp}]^+ (R' = Ph)$

112			
[P3Dip3PhCN]OTf @ BP86/def2SVP			
C	-0.13546	1.50460	-0.42923
C	-0.44068	2.92810	-0.63473
C	-1.67161	3.48971	-0.20938
H	-2.44434	2.85844	0.25481
C	-1.91939	4.85436	-0.39981
H	-2.87759	5.27903	-0.06396
C	-0.96075	5.67562	-1.02165
H	-1.16395	6.74807	-1.16724
C	0.25417	5.12284	-1.46492
H	1.00431	5.75570	-1.96294
C	0.51472	3.76116	-1.26987
H	1.46770	3.33567	-1.61770
C	-1.96415	-1.75136	1.10026
C	-2.05125	-1.18597	2.40568
C	-3.06605	-1.64168	3.26850
H	-3.15555	-1.19542	4.27097
C	-3.96421	-2.63999	2.87883
H	-4.76016	-2.96645	3.56627
C	-3.84974	-3.21840	1.61192
H	-4.55720	-4.00235	1.30566
C	-2.86501	-2.79249	0.70324
C	-1.09528	-0.13592	2.95985
H	-0.38289	0.14894	2.16157
C	-0.26087	-0.75516	4.09799
H	-0.91104	-1.13718	4.91206
H	0.43248	-0.01282	4.53849
H	0.34199	-1.60746	3.72106
C	-1.83871	1.14223	3.38973
H	-2.49693	1.50032	2.57400
H	-1.11920	1.94386	3.65667
H	-2.47805	0.96353	4.27944
C	-2.78113	-3.49264	-0.64962
H	-2.20364	-2.82905	-1.32775
C	-2.00357	-4.81592	-0.50026
H	-0.98916	-4.64713	-0.08058
H	-1.89258	-5.32428	-1.48094
H	-2.53265	-5.51082	0.18620
C	-4.15377	-3.70198	-1.30950
H	-4.76328	-4.46156	-0.77536
H	-4.02059	-4.06342	-2.35027
H	-4.71730	-2.75053	-1.33504
C	2.37953	-2.17198	-0.29166
C	3.40575	-2.68560	0.56953

C	4.39405	-3.53084	0.02819
H	5.18602	-3.92338	0.68252
C	4.38873	-3.87340	-1.32851
H	5.17044	-4.53376	-1.73595
C	3.38363	-3.37480	-2.16396
H	3.37800	-3.65534	-3.22860
C	2.36680	-2.52770	-1.67700
C	3.51075	-2.28370	2.04344
H	2.48137	-2.05176	2.39354
C	4.33305	-0.98573	2.17851
H	5.37072	-1.13692	1.81271
H	4.38576	-0.65690	3.23728
H	3.88858	-0.15971	1.58610
C	4.05975	-3.39248	2.95498
H	3.50624	-4.34406	2.81967
H	3.96528	-3.08831	4.01764
H	5.13649	-3.59391	2.77265
C	1.28342	-2.10318	-2.66474
H	0.67406	-1.31240	-2.18977
C	0.33397	-3.28273	-2.94352
H	0.85967	-4.10672	-3.47115
H	-0.52175	-2.95642	-3.56985
H	-0.07221	-3.69536	-2.00048
C	1.83810	-1.50222	-3.96655
H	2.47982	-0.62265	-3.76337
H	1.00137	-1.16575	-4.61249
H	2.43271	-2.23470	-4.55165
C	2.87045	1.76078	-0.06913
C	2.76446	2.58931	1.08644
C	3.88690	3.35792	1.45874
H	3.81287	4.01683	2.33792
C	5.09638	3.28288	0.75823
H	5.95580	3.89560	1.07279
C	5.21735	2.40083	-0.32216
H	6.18122	2.30640	-0.84572
C	4.12214	1.62684	-0.74927
C	1.55765	2.62267	2.01665
H	0.75413	2.00737	1.56574
C	0.99642	4.03830	2.23745
H	1.71227	4.67508	2.79889
H	0.06017	3.99052	2.83013
H	0.76946	4.54496	1.28010
C	1.93426	1.95610	3.35373
H	2.22876	0.89965	3.19897
H	1.07587	1.98096	4.05444
H	2.78192	2.48253	3.83949
C	4.32004	0.66453	-1.91931
H	3.42280	0.01020	-1.96832
C	5.51571	-0.27895	-1.71023
H	6.48466	0.26342	-1.70896
H	5.55153	-1.03042	-2.52499
H	5.42289	-0.82941	-0.75305
C	4.39574	1.42579	-3.25412
H	3.46983	2.01219	-3.42929
H	4.52280	0.72312	-4.10381
H	5.25210	2.13279	-3.26534

N	-1.07245	0.62638	-0.13197
P	-0.86694	-1.15756	-0.26147
P	1.25959	-0.94550	0.56509
P	1.51003	0.78184	-0.86084
H	-2.11415	0.91432	0.05227
C	-5.24909	1.46315	-1.49634
F	-4.35292	2.31981	-2.03481
F	-5.92721	0.87168	-2.49387
F	-6.11200	2.16968	-0.74465
O	-3.44115	-0.50001	-1.43282
O	-3.56474	1.06450	0.51566
O	-5.41964	-0.63514	0.18174
S	-4.35416	0.16924	-0.45053

A.1.1.7 $2_{Dipp} (R' = Ph)$

103			
P3Dip3PhCN @ BP86/def2SVP			
C	1.64790	0.69790	-1.29046
C	3.07721	0.96979	-1.56833
C	3.49165	2.30157	-1.81455
H	2.72045	3.08413	-1.85405
C	4.84699	2.60213	-1.99186
H	5.15762	3.64308	-2.17353
C	5.81268	1.57830	-1.93598
H	6.87957	1.81653	-2.07013
C	5.40999	0.25029	-1.71140
H	6.15850	-0.55622	-1.67319
C	4.05265	-0.05295	-1.52941
H	3.74791	-1.09411	-1.34578
C	-1.56904	2.59490	-0.01015
C	-0.84291	3.60740	0.68232
C	-1.50291	4.30989	1.71351
H	-0.95657	5.08282	2.27216
C	-2.83855	4.05028	2.04432
H	-3.32081	4.60358	2.86557
C	-3.56380	3.10232	1.31196
H	-4.62338	2.92435	1.54773
C	-2.95474	2.37579	0.27239
C	0.57219	4.01650	0.28109
H	1.14517	3.08529	0.09108
C	1.33027	4.82828	1.34058
H	0.89328	5.83918	1.48486
H	2.38188	4.97400	1.01904
H	1.34501	4.31968	2.32599
C	0.52538	4.79229	-1.05219
H	0.08911	4.17512	-1.86131
H	1.54704	5.09185	-1.36892
H	-0.08403	5.71472	-0.94625
C	-3.80672	1.43793	-0.59065
H	-3.15549	0.62023	-0.96607
C	-4.95596	0.74142	0.15071
H	-4.59709	0.22982	1.06366
H	-5.41256	-0.02656	-0.50604

H	-5.75928	1.45144	0.44053
C	-4.31794	2.20567	-1.82685
H	-4.96497	3.05421	-1.51999
H	-4.91032	1.53840	-2.48728
H	-3.47299	2.61644	-2.41655
C	-2.01545	-1.59279	-0.24740
C	-2.68380	-2.17286	0.87902
C	-3.81826	-2.97663	0.65746
H	-4.34947	-3.41436	1.51582
C	-4.27489	-3.23633	-0.64153
H	-5.17036	-3.85847	-0.79820
C	-3.56851	-2.73250	-1.74078
H	-3.90358	-2.98227	-2.76010
C	-2.42726	-1.92163	-1.57260
C	-2.17853	-1.95156	2.30894
H	-1.08556	-1.75555	2.22854
C	-2.80592	-0.70079	2.95230
H	-2.59151	0.20813	2.35269
H	-2.39952	-0.53746	3.97245
H	-3.90834	-0.80829	3.03562
C	-2.34457	-3.18890	3.20645
H	-3.40898	-3.39414	3.44828
H	-1.81814	-3.03069	4.17018
H	-1.92192	-4.09622	2.72846
C	-1.65614	-1.50609	-2.82193
H	-0.84514	-0.82005	-2.50858
C	-0.96839	-2.73126	-3.45431
H	-0.30111	-3.22571	-2.72024
H	-0.35186	-2.42383	-4.32474
H	-1.71008	-3.47962	-3.80546
C	-2.52394	-0.73860	-3.83215
H	-3.35724	-1.36104	-4.22114
H	-1.91221	-0.41667	-4.70024
H	-2.95709	0.17080	-3.37058
C	2.13483	-1.54782	0.69472
C	2.50215	-0.67469	1.76058
C	3.22254	-1.20722	2.85025
H	3.51491	-0.53815	3.67504
C	3.56819	-2.56125	2.90756
H	4.13224	-2.95288	3.76900
C	3.18677	-3.41979	1.86818
H	3.44799	-4.48662	1.92541
C	2.46946	-2.93931	0.75569
C	1.99605	-3.92549	-0.31467
H	1.97661	-3.37248	-1.27998
C	2.91406	-5.14308	-0.50023
H	3.96987	-4.84104	-0.65817
H	2.58959	-5.73106	-1.38331
H	2.88284	-5.82959	0.37231
C	0.54467	-4.36157	-0.02017
H	0.48036	-4.86730	0.96647
H	0.17430	-5.06431	-0.79563
H	-0.14738	-3.49498	0.00148
C	2.15264	0.80882	1.81135
H	1.60377	1.06036	0.88620
C	1.20047	1.12327	2.98073

H	0.28201	0.50709	2.91063
H	0.88887	2.18783	2.95065
H	1.68005	0.93363	3.96433
C	3.42021	1.68369	1.84371
H	3.98767	1.54088	2.78763
H	3.15342	2.75696	1.77417
H	4.09669	1.44349	0.99982
N	0.76501	1.63701	-1.45892
P	-0.92594	1.37493	-1.27030
P	-0.71646	-0.35173	0.22678
P	1.13246	-1.05289	-0.80016

A.1.1.8 $[I_{Tripp}]^+$ ($R' = Me$)

132			
[P3Tip3MeCNH]OTf @BP86-D3/def2SVP			
P	0.77530	-0.62589	0.17981
P	-1.02512	-1.43434	-0.99366
P	1.37145	0.51935	-1.67379
N	-1.29801	0.20662	-1.70301
C	-0.35088	1.06631	-1.97612
C	2.11028	-1.92121	0.18481
C	-2.82364	-1.31810	1.35372
C	-2.60202	-1.58745	-0.02868
C	-0.67312	2.33962	-2.69589
C	3.67598	1.98856	-1.25552
C	4.38373	-3.63142	0.42246
C	1.74856	2.83488	0.05456
C	2.92812	-1.88410	1.36378
C	1.68325	-2.90965	-2.18873
H	0.97875	-2.05717	-2.23237
C	2.28592	1.93499	-0.91953
C	5.61643	-4.51805	0.52508
H	5.61295	-5.18093	-0.36878
C	-5.15095	-2.09625	1.12772
C	2.61898	3.76635	0.64891
H	2.20453	4.45696	1.40029
C	3.57253	-3.65150	-0.72236
H	3.83467	-4.34355	-1.53925
C	-1.74520	-0.75638	2.26689
H	-1.11692	-0.09146	1.64207
C	2.45449	-2.81051	-0.87781
C	3.98963	3.82937	0.34571
C	4.33135	0.99976	-2.22097
H	3.52038	0.56370	-2.84481
C	-4.91931	-2.33220	-0.23327
H	-5.75232	-2.69301	-0.85726
C	-4.08696	-1.59849	1.89699
H	-4.26074	-1.37635	2.95923
C	0.30403	2.83593	0.53928
H	-0.27298	2.06753	-0.01136
C	-3.67156	-2.09318	-0.83292
C	4.49406	2.93374	-0.61019
H	5.56847	2.96776	-0.85057

C	-6.53102	-2.29630	1.73350
H	-7.17528	-2.72232	0.93197
C	5.58094	-5.41528	1.77624
H	5.60856	-4.81134	2.70773
H	6.45629	-6.09747	1.79655
H	4.66021	-6.03292	1.80331
C	2.59271	-2.77684	-3.42211
H	3.18170	-1.83828	-3.37762
H	1.98018	-2.75319	-4.34722
H	3.30459	-3.62319	-3.51797
C	-0.40054	4.18272	0.29419
H	0.04311	4.99198	0.91209
H	-1.46992	4.08756	0.56258
H	-0.33812	4.50011	-0.76564
C	4.04336	-2.73547	1.44969
H	4.67458	-2.68632	2.34993
C	4.90810	4.80836	1.06276
H	5.91429	4.70752	0.59824
C	6.90264	-3.66868	0.47291
H	6.93343	-3.04335	-0.44264
H	7.80597	-4.31399	0.48401
H	6.96418	-2.98612	1.34690
C	5.33487	1.66051	-3.18072
H	4.88136	2.52004	-3.71539
H	5.67869	0.92564	-3.93763
H	6.23961	2.02787	-2.65216
C	2.70119	-0.88072	2.49672
H	1.63713	-0.56799	2.44774
C	4.97421	-0.16207	-1.43601
H	5.77250	0.21145	-0.76055
H	5.42515	-0.90502	-2.12640
H	4.22860	-0.69245	-0.81149
C	5.04038	4.43540	2.55340
H	4.06314	4.52218	3.07376
H	5.75802	5.10773	3.06855
H	5.39310	3.39103	2.67573
C	-3.53568	-2.37785	-2.33140
H	-2.58197	-1.92773	-2.68541
C	0.82954	-4.18932	-2.22462
H	1.46467	-5.09960	-2.18495
H	0.22008	-4.23001	-3.15128
H	0.13315	-4.22338	-1.36152
C	0.21275	2.44771	2.02674
H	0.68317	1.46105	2.20627
H	-0.85195	2.38558	2.32230
H	0.71755	3.19584	2.67402
C	-2.29557	0.12126	3.39995
H	-2.96919	0.89761	2.98709
H	-1.45824	0.62509	3.92487
H	-2.84868	-0.46544	4.16354
C	-7.13672	-0.94160	2.15390
H	-6.56366	-0.49667	2.99457
H	-8.18826	-1.06760	2.48805
H	-7.10076	-0.21338	1.32051
C	-0.86064	-1.89359	2.81267
H	-1.47119	-2.62545	3.38266

H	-0.07587	-1.50018	3.49104
H	-0.35467	-2.45573	1.99776
C	-6.50941	-3.29932	2.90192
H	-6.09599	-4.28002	2.58820
H	-7.53351	-3.46571	3.29727
H	-5.88666	-2.92404	3.74160
C	4.45042	6.26779	0.88232
H	4.36996	6.53551	-0.19093
H	5.16772	6.96686	1.36057
H	3.45722	6.44047	1.34786
C	2.93598	-1.46983	3.89657
H	2.36528	-2.40956	4.04283
H	2.61137	-0.74528	4.67163
H	4.00769	-1.68876	4.08865
C	3.54890	0.38553	2.26061
H	4.63182	0.13985	2.24354
H	3.37391	1.13400	3.06089
H	3.29902	0.86469	1.29324
C	-3.42302	-3.89237	-2.58590
H	-2.55156	-4.32157	-2.04974
H	-3.30359	-4.10565	-3.66914
H	-4.33207	-4.42190	-2.23052
C	-4.65960	-1.72195	-3.15472
H	-5.64201	-2.20181	-2.96225
H	-4.45130	-1.82656	-4.24018
H	-4.74363	-0.64596	-2.90366
H	-2.34786	0.53532	-1.81311
S	-3.91675	1.63944	-0.28434
F	-4.45645	4.12292	0.53485
O	-2.62796	1.74510	0.46720
C	-4.38883	3.43983	-0.62288
F	-3.45608	4.03959	-1.40589
F	-5.57406	3.51965	-1.24474
O	-3.71208	1.12298	-1.71531
O	-5.08937	1.07825	0.41808
H	-0.72160	2.13876	-3.78814
H	-1.66211	2.71774	-2.37220
H	0.10791	3.10293	-2.52212

A.1.1.9 $[I_{Tripp}]^+ (R' = Ph)$

139			
[P3Tip3PhCNH]OTf @BP86-D3/def2SVP			
P	0.95414	-0.86013	0.38940
P	-0.99112	-1.28820	-0.74893
P	1.33858	0.70627	-1.18281
N	-1.29912	0.48036	-0.84795
C	-0.36153	1.39292	-1.00982
C	2.31556	-2.04737	-0.06293
C	-2.63293	-1.17154	1.66249
C	-2.35807	-1.75972	0.38825
C	-0.70052	2.79876	-1.24587
C	3.89619	1.65562	-0.87449
C	4.62649	-3.67358	-0.48436

C	2.34886	2.59885	0.80826
C	3.27242	-2.23777	0.98808
C	1.56113	-2.56356	-2.49501
H	0.91054	-1.68686	-2.31322
C	2.58118	1.76490	-0.32599
C	5.86217	-4.53070	-0.71938
H	5.78514	-4.93124	-1.75475
C	-4.76280	-2.40348	1.75921
C	-1.94721	3.31780	-0.81402
H	-2.67659	2.67759	-0.29247
C	3.41664	3.37682	1.29080
H	3.23507	4.02796	2.16070
C	3.68333	-3.46644	-1.50400
H	3.85131	-3.95054	-2.47936
C	-1.31610	5.51423	-1.65959
H	-1.55755	6.57678	-1.81953
C	-0.07453	5.00506	-2.08519
H	0.65489	5.66341	-2.58121
C	-1.66347	-0.25073	2.39424
H	-0.99040	0.21031	1.64315
C	2.53743	-2.66863	-1.33029
C	4.70708	3.32777	0.73425
C	4.23552	0.69119	-2.01107
H	3.35302	0.03144	-2.16186
C	-4.45118	-3.00755	0.53501
H	-5.18267	-3.69683	0.08478
C	-3.82969	-1.50790	2.30949
H	-4.05812	-1.02721	3.27168
C	1.04952	2.62884	1.60578
H	0.30862	1.98842	1.08877
C	-3.27618	-2.70394	-0.17362
C	-2.24573	4.66934	-1.02652
H	-3.21712	5.06116	-0.69088
C	4.92743	2.44585	-0.33540
H	5.94298	2.36402	-0.75575
C	-6.09863	-2.64925	2.44087
H	-6.66079	-3.36317	1.79876
C	5.91208	-5.73031	0.24608
H	6.00645	-5.39440	1.30037
H	6.78401	-6.38011	0.02325
H	4.99298	-6.34634	0.17100
C	2.24034	-2.32234	-3.85298
H	2.90645	-1.43623	-3.81732
H	1.47250	-2.13772	-4.63203
H	2.84462	-3.19109	-4.18835
C	0.44606	4.03934	1.72165
H	1.08920	4.70623	2.33421
H	-0.54782	3.99128	2.21125
H	0.31618	4.51088	0.72861
C	0.23590	3.65638	-1.87509
H	1.20653	3.25658	-2.20671
C	4.40007	-3.04520	0.75022
H	5.13247	-3.17546	1.56234
C	5.84485	4.15461	1.31588
H	6.72919	3.99375	0.65985
C	7.14971	-3.68665	-0.63861

H	7.12372	-2.84215	-1.35659
H	8.04318	-4.30571	-0.86393
H	7.28479	-3.25904	0.37743
C	4.46029	1.44442	-3.33358
H	3.56257	2.03431	-3.61225
H	4.67498	0.73562	-4.16069
H	5.31657	2.14757	-3.25603
C	3.17954	-1.54199	2.34776
H	2.15720	-1.11659	2.43292
C	5.40685	-0.23834	-1.65338
H	6.36352	0.31491	-1.54512
H	5.54684	-0.99729	-2.45032
H	5.20918	-0.77913	-0.70658
C	6.21354	3.65747	2.72847
H	5.36713	3.79761	3.43371
H	7.08410	4.21627	3.13128
H	6.46711	2.57781	2.72016
C	-3.10408	-3.32331	-1.55971
H	-2.07183	-3.10066	-1.90179
C	0.64994	-3.80555	-2.52394
H	1.23971	-4.72555	-2.72248
H	-0.12564	-3.71002	-3.31159
H	0.13332	-3.94511	-1.55194
C	1.28797	2.00208	2.99321
H	1.63248	0.95459	2.89526
H	0.35290	2.00401	3.58788
H	2.05519	2.56491	3.56429
C	-2.36262	0.90125	3.13606
H	-3.08047	1.41209	2.46606
H	-1.61356	1.63557	3.49591
H	-2.91315	0.54425	4.03158
C	-6.91023	-1.33896	2.51238
H	-6.43248	-0.61507	3.20650
H	-7.93830	-1.53394	2.88385
H	-6.96050	-0.85594	1.51685
C	-0.78951	-1.09752	3.34091
H	-1.42011	-1.59725	4.10612
H	-0.03915	-0.46964	3.86310
H	-0.24623	-1.89067	2.78585
C	-5.92626	-3.29576	3.82841
H	-5.36744	-4.25237	3.76538
H	-6.91389	-3.50174	4.29204
H	-5.36943	-2.62461	4.51655
C	5.52306	5.66068	1.31128
H	5.27274	6.01657	0.29111
H	6.38868	6.24918	1.68039
H	4.65917	5.89158	1.96971
C	3.36202	-2.50930	3.52919
H	2.65364	-3.36040	3.46576
H	3.17855	-1.98062	4.48743
H	4.39025	-2.92628	3.57720
C	4.16763	-0.35981	2.40824
H	5.21576	-0.70913	2.29299
H	4.08918	0.17198	3.37909
H	3.96749	0.37319	1.60122
C	-3.24696	-4.85482	-1.54373

H	-2.54685	-5.32082	-0.81950
H	-3.03043	-5.27125	-2.54974
H	-4.27518	-5.17326	-1.27165
C	-4.06418	-2.65392	-2.56297
H	-5.12228	-2.84222	-2.28567
H	-3.89659	-3.04962	-3.58721
H	-3.92822	-1.55409	-2.56960
H	-2.35813	0.68111	-1.10110
S	-4.82987	0.82835	-0.59767
F	-6.93063	2.46905	-0.60102
O	-4.31604	1.47943	0.64612
C	-5.89106	2.16927	-1.40005
F	-5.16622	3.29476	-1.59434
F	-6.36330	1.75930	-2.58842
O	-3.73391	0.64871	-1.65209
O	-5.74331	-0.32985	-0.46412

A.1.1.10 $[I_{Tripp}]^+ (R' = p\text{-MeOC}_6\text{H}_4)$

143			
[P3Tip3(p-OMePhCN)H]Otf @BP86-D3/def2SVP			
P	1.03321	-1.09156	0.37250
P	-0.90541	-1.50117	-0.78387
P	1.34439	0.61002	-1.07019
N	-1.27956	0.25685	-0.73815
C	-0.38020	1.22007	-0.83533
C	2.44520	-2.16882	-0.19187
C	-2.52826	-1.61104	1.64026
C	-2.23853	-2.10715	0.33108
C	-0.76961	2.61833	-0.95511
C	3.86887	1.61860	-0.68680
C	4.84044	-3.61078	-0.78217
C	2.29632	2.38035	1.06213
C	3.42859	-2.39349	0.82675
C	1.67823	-2.51930	-2.64888
H	0.98702	-1.69553	-2.38690
C	2.55283	1.64014	-0.12964
C	6.11277	-4.38271	-1.10231
H	6.06940	-4.64212	-2.18363
C	-4.61367	-2.91982	1.66363
C	-2.05264	3.05941	-0.52349
H	-2.77473	2.35362	-0.08315
C	3.33490	3.16769	1.59248
H	3.13389	3.74719	2.50766
C	3.86929	-3.37287	-1.76849
H	4.04844	-3.75967	-2.78446
C	-1.48911	5.34571	-1.15552
C	-0.20839	4.92032	-1.58536
H	0.51774	5.63090	-2.00189
C	-1.58970	-0.70337	2.42649
H	-0.92393	-0.18707	1.70601
C	2.68103	-2.66455	-1.51123
C	4.62144	3.21099	1.02742
C	4.22982	0.74830	-1.89129

H	3.41382	0.00402	-2.01773
C	-4.28474	-3.43679	0.40439
H	-4.99340	-4.12229	-0.08630
C	-3.70984	-2.02909	2.26758
H	-3.95093	-1.61786	3.25860
C	1.00721	2.28982	1.87181
H	0.28930	1.65756	1.31435
C	-3.12340	-3.04887	-0.28532
C	-2.40227	4.40098	-0.62401
H	-3.38985	4.75043	-0.29164
C	4.87109	2.41124	-0.09951
H	5.88692	2.39769	-0.52624
C	-5.93978	-3.25018	2.32853
H	-6.47765	-3.94494	1.64583
C	6.18151	-5.70053	-0.30589
H	6.23590	-5.50580	0.78614
H	7.08114	-6.28670	-0.58779
H	5.28661	-6.32911	-0.49009
C	2.31538	-2.13495	-3.99394
H	2.93311	-1.21885	-3.89849
H	1.52245	-1.93179	-4.74267
H	2.95775	-2.94010	-4.40811
C	0.34081	3.65671	2.10524
H	0.96169	4.30461	2.75988
H	-0.64199	3.52387	2.60145
H	0.17256	4.19581	1.15323
C	0.13975	3.57107	-1.47465
H	1.13821	3.24849	-1.80736
C	4.59746	-3.10866	0.50567
H	5.34851	-3.26772	1.29548
C	5.72927	4.04242	1.65858
H	6.61245	3.96801	0.98566
C	7.37060	-3.52137	-0.87726
H	7.33111	-2.58659	-1.47214
H	8.28670	-4.07749	-1.16653
H	7.47638	-3.23573	0.19072
C	4.27780	1.58429	-3.18194
H	3.29900	2.07153	-3.37324
H	4.51972	0.94749	-4.05869
H	5.04777	2.38191	-3.11415
C	3.31671	-1.83289	2.24644
H	2.27913	-1.45790	2.37492
C	5.51234	-0.06865	-1.66804
H	6.41786	0.57167	-1.61280
H	5.65748	-0.77983	-2.50689
H	5.44552	-0.66148	-0.73404
C	6.13470	3.46112	3.02838
H	5.29017	3.51115	3.74789
H	6.98404	4.02741	3.46478
H	6.43551	2.39740	2.93904
C	-2.93110	-3.57479	-1.70692
H	-1.90236	-3.30825	-2.02732
C	0.83174	-3.80154	-2.76271
H	1.46385	-4.67022	-3.04487
H	0.03587	-3.68432	-3.52684
H	0.34346	-4.04517	-1.79666

C	1.29634	1.56981	3.20334
H	1.68844	0.55111	3.01907
H	0.37162	1.48025	3.80735
H	2.04509	2.12285	3.80756
C	-2.32658	0.39062	3.21797
H	-3.05288	0.91448	2.56728
H	-1.60149	1.12594	3.62227
H	-2.87614	-0.02569	4.08815
C	-6.79526	-1.97419	2.47315
H	-6.34063	-1.27441	3.20639
H	-7.81561	-2.22415	2.83300
H	-6.86325	-1.43834	1.50611
C	-0.69885	-1.57418	3.33477
H	-1.31986	-2.13331	4.06599
H	0.02855	-0.95437	3.89729
H	-0.12801	-2.31905	2.74190
C	-5.74539	-3.96845	3.67725
H	-5.15411	-4.90026	3.56102
H	-6.72540	-4.23411	4.12654
H	-5.21193	-3.31899	4.40367
C	5.34395	5.52955	1.76636
H	5.06769	5.94716	0.77664
H	6.18763	6.12684	2.17059
H	4.47827	5.67447	2.44665
C	3.54352	-2.90245	3.32816
H	2.86354	-3.76735	3.18745
H	3.35208	-2.47545	4.33440
H	4.58558	-3.28673	3.32771
C	4.25924	-0.62502	2.41910
H	5.31966	-0.92097	2.27091
H	4.16476	-0.19223	3.43662
H	4.02800	0.17355	1.68606
C	-3.03976	-5.10676	-1.79146
H	-2.33613	-5.60342	-1.09141
H	-2.80438	-5.45189	-2.82000
H	-4.06307	-5.46494	-1.55238
C	-3.90153	-2.86320	-2.67031
H	-4.95615	-3.08965	-2.40891
H	-3.72283	-3.18941	-3.71697
H	-3.78964	-1.76240	-2.60645
H	-2.33998	0.43423	-0.97585
S	-4.83020	0.43710	-0.49591
F	-7.01154	1.96747	-0.39452
O	-4.35399	1.02162	0.79526
C	-5.95355	1.78058	-1.20411
F	-5.28531	2.95237	-1.30661
F	-6.39912	1.43965	-2.42468
O	-3.72440	0.38804	-1.55226
O	-5.68802	-0.77006	-0.45082
O	-1.92408	6.62684	-1.20758
C	-1.05316	7.62639	-1.72236
H	-1.61093	8.57950	-1.66932
H	-0.12451	7.71238	-1.11516
H	-0.77752	7.42369	-2.78115

A.1.1.11 $[I_{Tripp}]^+ (R' = p\text{-CF}_3\text{C}_6\text{H}_4)$

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[P3Tip3(p-CF₃PhCN)H]OTf @BP86-D3/def2SVP

P	1.24347	-1.19381	0.36854
P	-0.64450	-1.79353	-0.79170
P	1.36891	0.55343	-1.04892
N	-1.20496	-0.08794	-0.74068
C	-0.40979	0.95951	-0.81611
C	2.74770	-2.12590	-0.21005
C	-2.25181	-2.11010	1.62343
C	-1.91562	-2.54601	0.30341
C	-0.95201	2.31980	-0.91013
C	3.75289	1.85766	-0.67128
C	5.26002	-3.34495	-0.81187
C	2.10456	2.41443	1.08701
C	3.74324	-2.28157	0.81065
C	2.02433	-2.49897	-2.67825
H	1.25566	-1.75197	-2.40255
C	2.44632	1.71626	-0.10972
C	6.60082	-3.98541	-1.14139
H	6.56656	-4.27131	-2.21629
C	-4.19148	-3.62719	1.61696
C	-2.24243	2.61158	-0.40429
H	-2.86666	1.82527	0.05044
C	3.04477	3.31264	1.62285
H	2.77794	3.85957	2.54104
C	4.27569	-3.17533	-1.79892
H	4.49159	-3.52766	-2.82024
C	-1.93182	4.95353	-0.98587
C	-0.65154	4.66902	-1.50050
H	-0.04101	5.47552	-1.93114
C	-1.40774	-1.12964	2.42938
H	-0.81642	-0.51623	1.71919
C	3.02990	-2.57631	-1.53638
C	4.31754	3.51020	1.05823
C	4.21877	1.04843	-1.88149
H	3.44281	0.27777	-2.08440
C	-3.81558	-4.07785	0.34554
H	-4.45067	-4.82174	-0.16049
C	-3.38285	-2.66117	2.24058
H	-3.66250	-2.29960	3.24060
C	0.83461	2.17157	1.89536
H	0.18320	1.48201	1.32352
C	-2.70207	-3.55748	-0.33577
C	-2.72599	3.92327	-0.44882
H	-3.72959	4.14430	-0.05973
C	4.65627	2.75699	-0.07699
H	5.66480	2.86880	-0.50722
C	-5.47072	-4.11288	2.27793
H	-5.94037	-4.83719	1.57598
C	6.83065	-5.26910	-0.32072
H	6.88953	-5.04629	0.76563
H	7.78243	-5.75947	-0.61357
H	6.00644	-5.99586	-0.47025
C	2.63156	-2.02162	-4.00754

H	3.16117	-1.05511	-3.88334
H	1.82856	-1.87387	-4.75848
H	3.34934	-2.75225	-4.43554
C	0.03254	3.45633	2.16652
H	0.58167	4.14240	2.84539
H	-0.93245	3.20914	2.65368
H	-0.18702	4.01082	1.23396
C	-0.16308	3.36051	-1.45791
H	0.83838	3.13842	-1.85623
C	4.97038	-2.88718	0.48319
H	5.73065	-2.99232	1.27280
C	5.31854	4.46372	1.69457
H	6.20946	4.48858	1.02834
C	7.75856	-2.98391	-0.95980
H	7.60435	-2.07364	-1.57384
H	8.72616	-3.44094	-1.25480
H	7.84827	-2.66294	0.09959
C	4.31282	1.92910	-3.13940
H	3.33426	2.39916	-3.36970
H	4.62013	1.32801	-4.02070
H	5.05607	2.74361	-3.00642
C	3.58047	-1.74376	2.23419
H	2.50430	-1.51270	2.38183
C	5.51956	0.27845	-1.59994
H	6.38280	0.95819	-1.43968
H	5.76502	-0.37905	-2.45904
H	5.41354	-0.36590	-0.70469
C	5.77693	3.93694	3.06967
H	4.92810	3.89689	3.78472
H	6.55496	4.59668	3.50744
H	6.19525	2.91300	2.98819
C	-2.46258	-4.02889	-1.76910
H	-1.47231	-3.64236	-2.08923
C	1.30516	-3.85286	-2.83150
H	2.01951	-4.64974	-3.12855
H	0.50779	-3.79289	-3.60067
H	0.83529	-4.16688	-1.87663
C	1.20189	1.45056	3.20723
H	1.68877	0.47915	2.99591
H	0.29517	1.25840	3.81451
H	1.89908	2.05949	3.81926
C	-2.24793	-0.15447	3.27166
H	-3.04055	0.30733	2.65233
H	-1.60241	0.64321	3.69184
H	-2.72910	-0.66048	4.13461
C	-6.45218	-2.93812	2.47074
H	-6.06704	-2.22020	3.22590
H	-7.43777	-3.30498	2.82681
H	-6.58469	-2.38008	1.52317
C	-0.41097	-1.92508	3.29598
H	-0.95530	-2.56976	4.01772
H	0.25441	-1.24642	3.86745
H	0.22680	-2.58637	2.67289
C	-5.18917	-4.85067	3.60064
H	-4.50538	-5.71137	3.44925
H	-6.13171	-5.23170	4.04684

H	-4.71898	-4.17312	4.34486
C	4.76359	5.89707	1.79307
H	4.45021	6.27784	0.79971
H	5.52961	6.58803	2.20235
H	3.88079	5.94365	2.46509
C	3.97134	-2.76685	3.31357
H	3.42733	-3.72386	3.17814
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H	-1.63898	-5.98998	-1.19993
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H	-3.30486	-3.69167	-3.76700
H	-3.52649	-2.30632	-2.62504
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F	-5.41354	2.23372	-1.22034
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A.1.1.12 $2_{Tripp} (R' = Me)$

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C	-0.15629	1.06994	2.42155
C	-0.44173	2.10248	3.48962
H	-0.75363	3.06668	3.03673
H	0.45284	2.25685	4.12379
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C	5.37843	-0.46148	-0.67389
C	4.42115	-1.40777	-1.07690

H	4.63862	-2.05827	-1.93841
C	3.19456	-1.56838	-0.40440
C	3.76766	0.92522	2.53430
H	2.73518	1.32024	2.60573
C	3.93245	-0.07515	3.70211
H	3.17511	-0.88394	3.65763
H	3.81239	0.43946	4.67918
H	4.93911	-0.54557	3.68173
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H	-2.48155	0.17695	-2.21103
C	-1.61282	2.52133	0.27434
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H	-3.88531	3.37892	2.86221
H	-5.54057	2.75439	2.55974
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H	-0.35186	7.38249	-1.00815
C	0.90863	2.67192	-0.40436
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C	1.35154	2.40109	-1.85751
H	0.65190	1.70544	-2.36310
H	2.36054	1.93871	-1.87177
H	1.39798	3.33802	-2.45309
C	1.90857	3.59710	0.31892
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A.1.1.13 $2_{Tripp} (R' = Ph)$

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H	-3.77351	-0.73027	-2.00447
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H	-5.41140	-1.96058	-3.41467
C	-3.90406	-3.21554	-4.36171
H	-4.63066	-3.75960	-4.98606
C	-2.53122	-3.51936	-4.44245
H	-2.17952	-4.30108	-5.13481
C	-1.60650	-2.82625	-3.65104
H	-0.53007	-3.04287	-3.71480
C	-2.78542	-0.20323	0.44149
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H	4.47576	2.21106	1.33717
H	5.46087	0.78431	1.75397
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H	-5.78236	0.89453	1.74783
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H	-3.58221	1.80058	-1.13468
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H	-5.87494	2.57436	-1.60031
C	-5.69107	-1.11149	3.60664
C	-5.06956	-0.97449	5.01255
H	-5.83503	-1.14029	5.80005
H	-4.63220	0.03349	5.16551
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H	-6.82096	-2.58403	2.41582
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H	1.15260	4.94653	-2.54199
C	0.79064	3.10622	-1.45303
C	0.93224	2.73189	2.42954
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H	1.84553	2.86098	4.40705
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C	-0.53123	2.75801	2.92247
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H	-0.61112	2.33920	3.94819
H	-1.19017	2.15680	2.26223
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H	1.72667	6.97242	-1.66800
C	3.18178	7.05757	-0.07894
H	3.27944	6.86900	1.01149
H	3.44154	8.12268	-0.25721
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H	0.94773	8.73201	-0.07160
C	0.48472	2.39332	-2.77406
H	0.23859	1.33735	-2.54227
C	1.70574	2.37088	-3.71684
H	2.00419	3.39514	-4.02653
H	1.47207	1.79722	-4.63854
H	2.57778	1.88953	-3.23009
C	-0.75208	2.99520	-3.47458
H	-1.64013	2.96544	-2.81144
H	-0.99272	2.42085	-4.39406
H	-0.58086	4.05090	-3.77479
C	2.61284	-1.71196	-0.41084
C	2.55346	-3.14322	-0.41627
C	3.47869	-3.85506	0.37895
H	3.42726	-4.95461	0.39359
C	4.47515	-3.23311	1.14826
C	4.56514	-1.83238	1.07390
H	5.36369	-1.31541	1.62850
C	3.67643	-1.06326	0.30037
C	1.61987	-3.94994	-1.32476
H	0.65287	-3.40964	-1.37326
C	2.18831	-3.97288	-2.76276
H	2.29315	-2.94917	-3.17459
H	1.51955	-4.54460	-3.44135
H	3.18814	-4.45743	-2.78413
C	1.33357	-5.38512	-0.84736
H	2.21763	-6.05040	-0.94901
H	0.52511	-5.83066	-1.46324
H	1.00751	-5.41787	0.21280

C	5.43386	-4.05551	2.00590
H	5.14773	-5.12282	1.86927
C	6.89787	-3.90746	1.54030
H	7.01153	-4.17701	0.47013
H	7.56948	-4.56389	2.13341
H	7.25932	-2.86426	1.66380
C	5.28687	-3.72591	3.50644
H	5.56877	-2.67241	3.71825
H	5.94433	-4.37711	4.12086
H	4.24233	-3.86873	3.85180
C	3.95657	0.44084	0.16907
H	3.01199	0.95660	-0.10973
C	4.95526	0.68928	-0.98432
H	5.93273	0.20773	-0.76814
H	5.13024	1.77655	-1.12730
H	4.57660	0.27323	-1.94034
N	0.23179	-1.41558	-2.03269
P	1.53313	-0.51837	-1.38011
P	0.34439	0.68968	0.21959
P	-1.58401	0.38610	-0.87434
H	1.23455	1.66308	2.38126
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Appendix B.

Supplementary Information on Chapter 3

B.1 NMR spectra

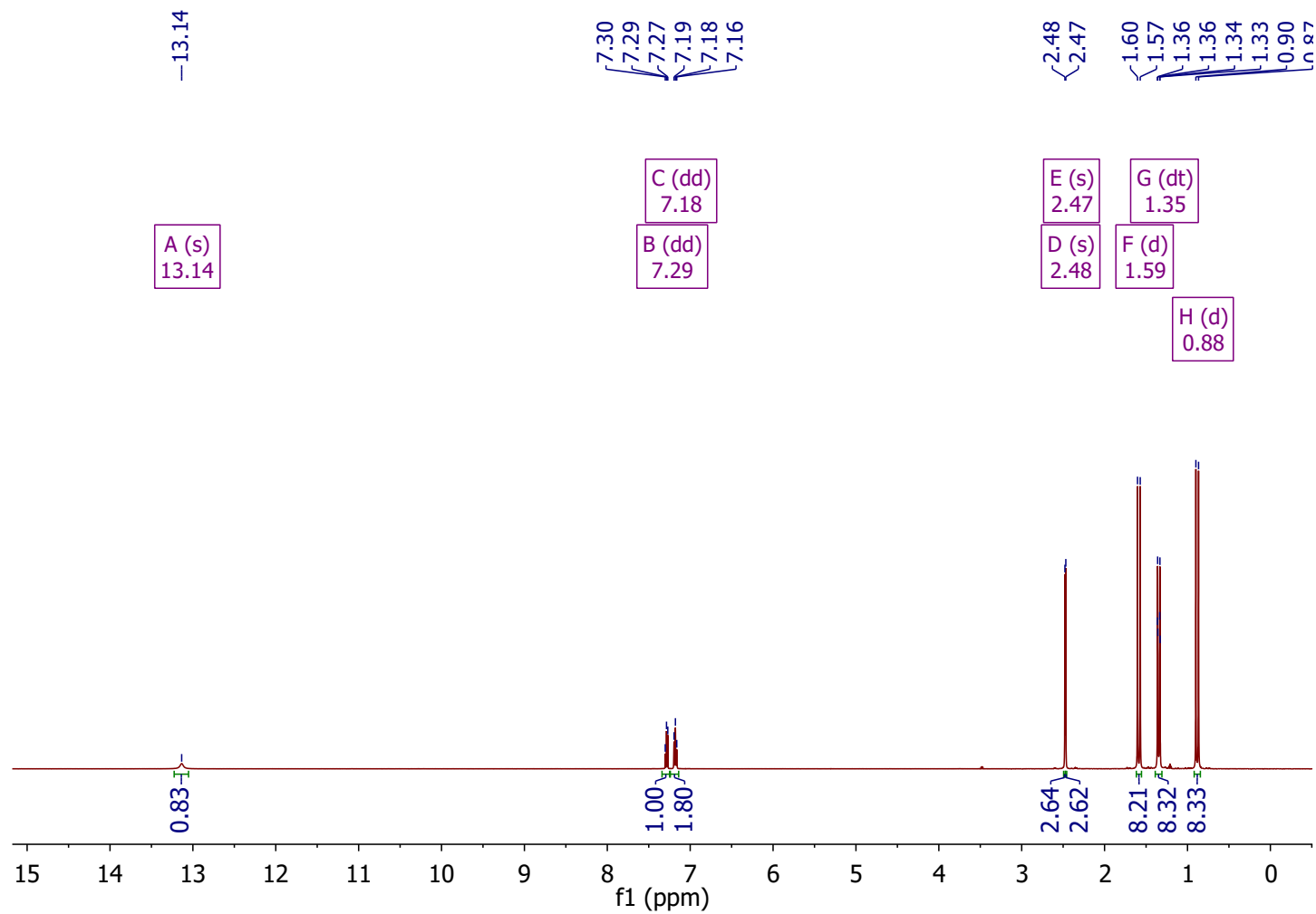


Figure B.1 ^1H NMR spectrum (500 MHz, CDCl_3) of **[1-H][OTf]**

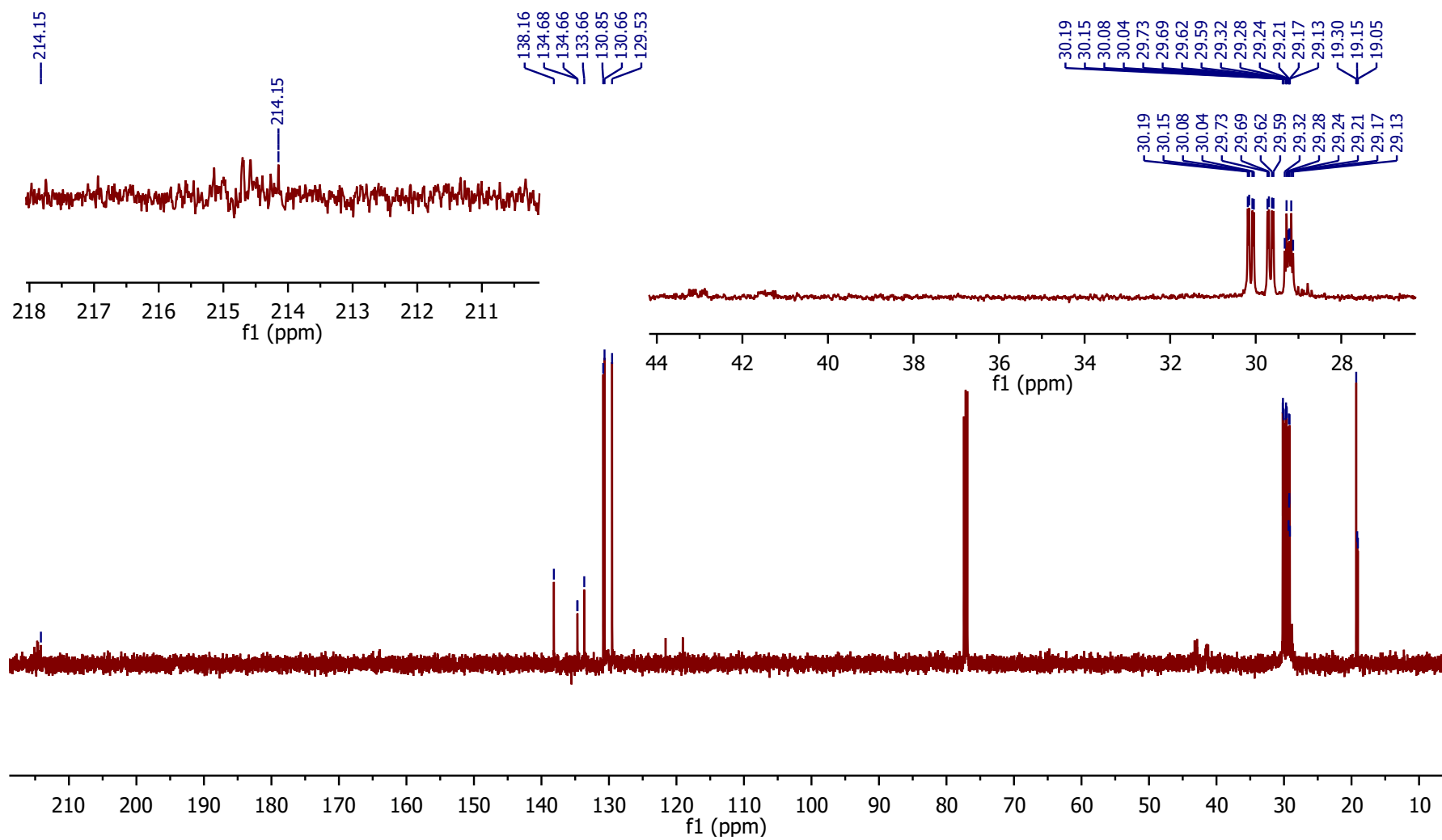


Figure B.2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (500 MHz, CDCl_3) of [1-H][OTf]

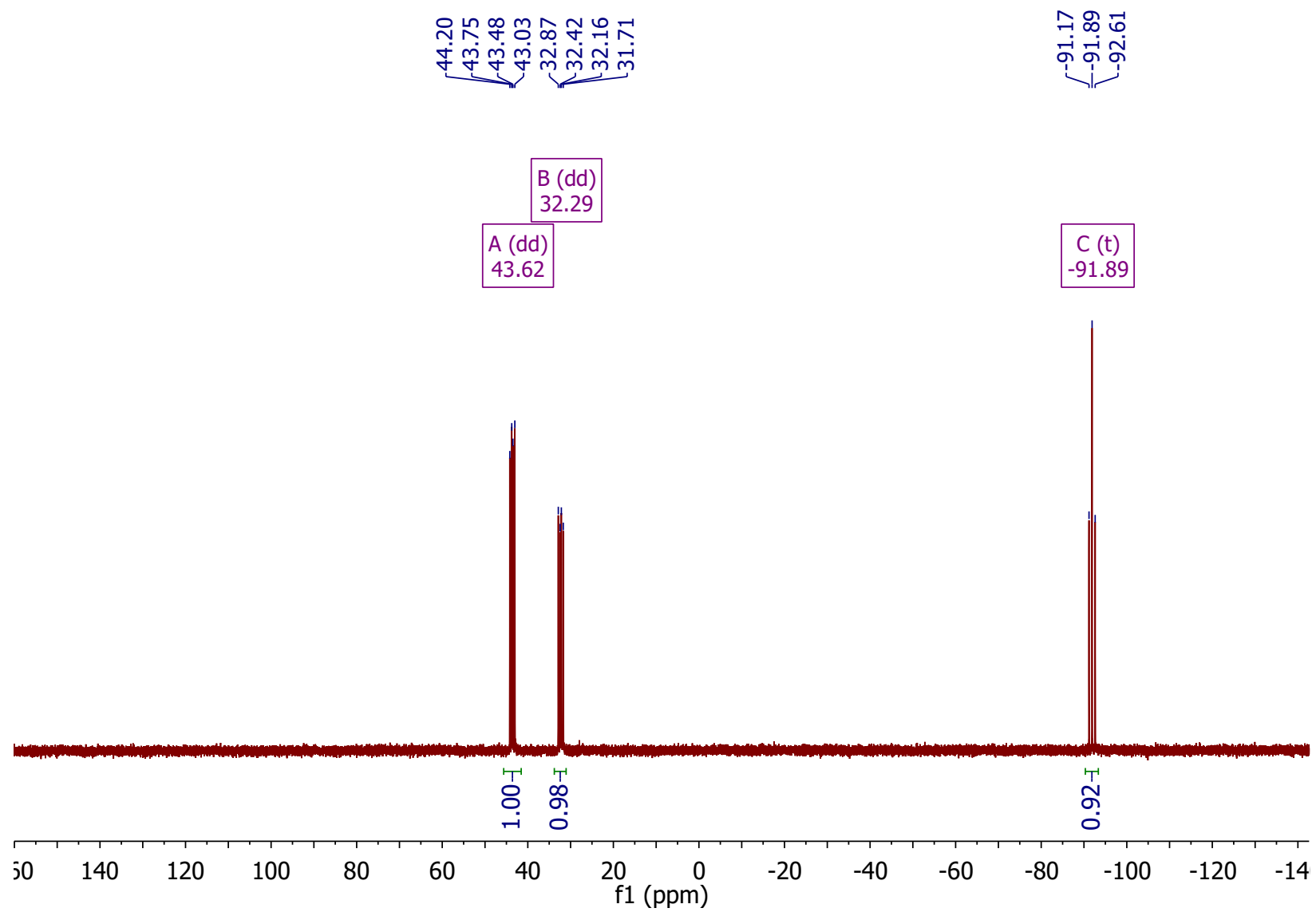


Figure B.3 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500 MHz, CDCl_3) of $[\mathbf{1-H}][\text{OTf}]$

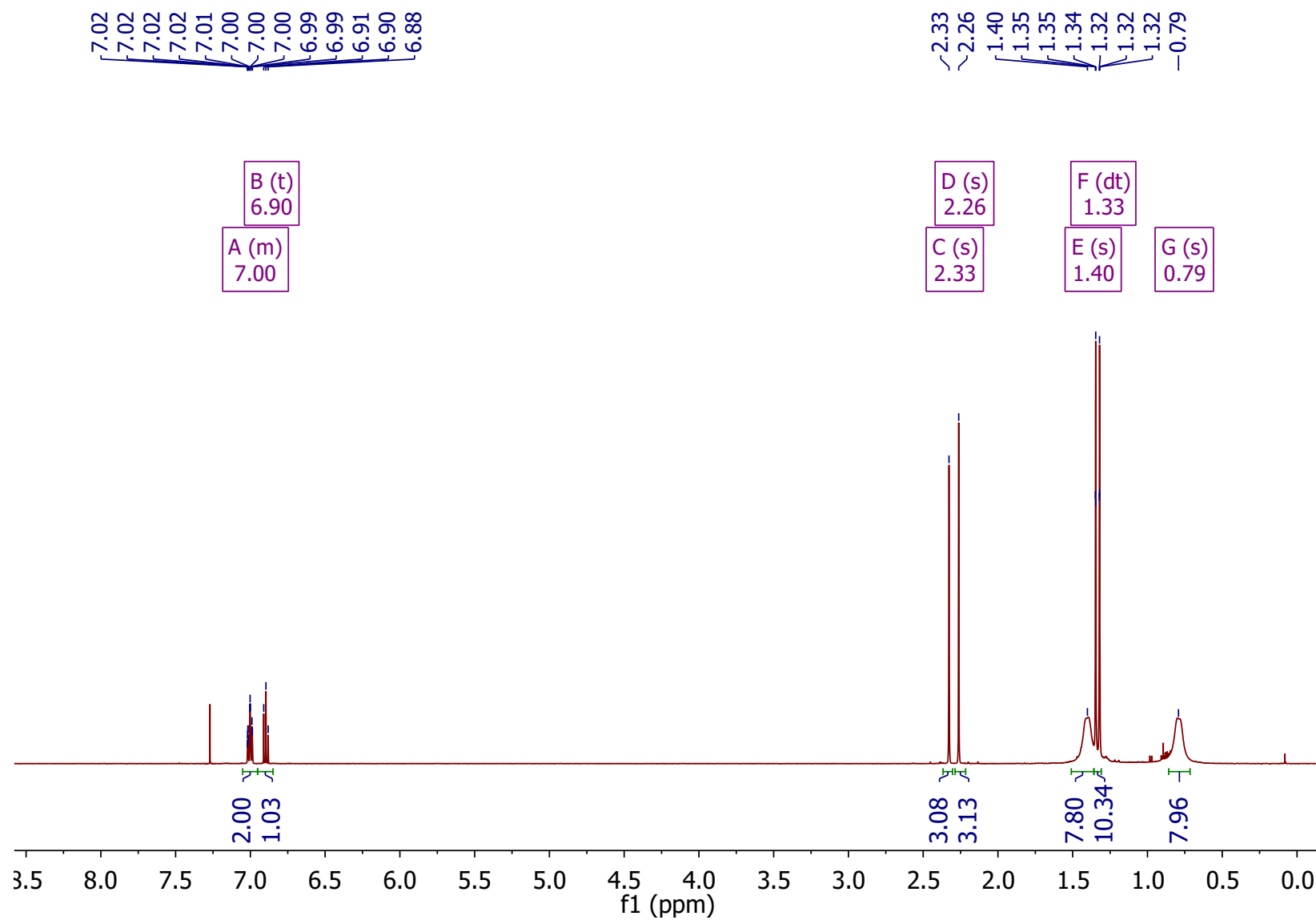


Figure B.4 ^1H NMR spectrum (500 MHz, CDCl_3) of **1**

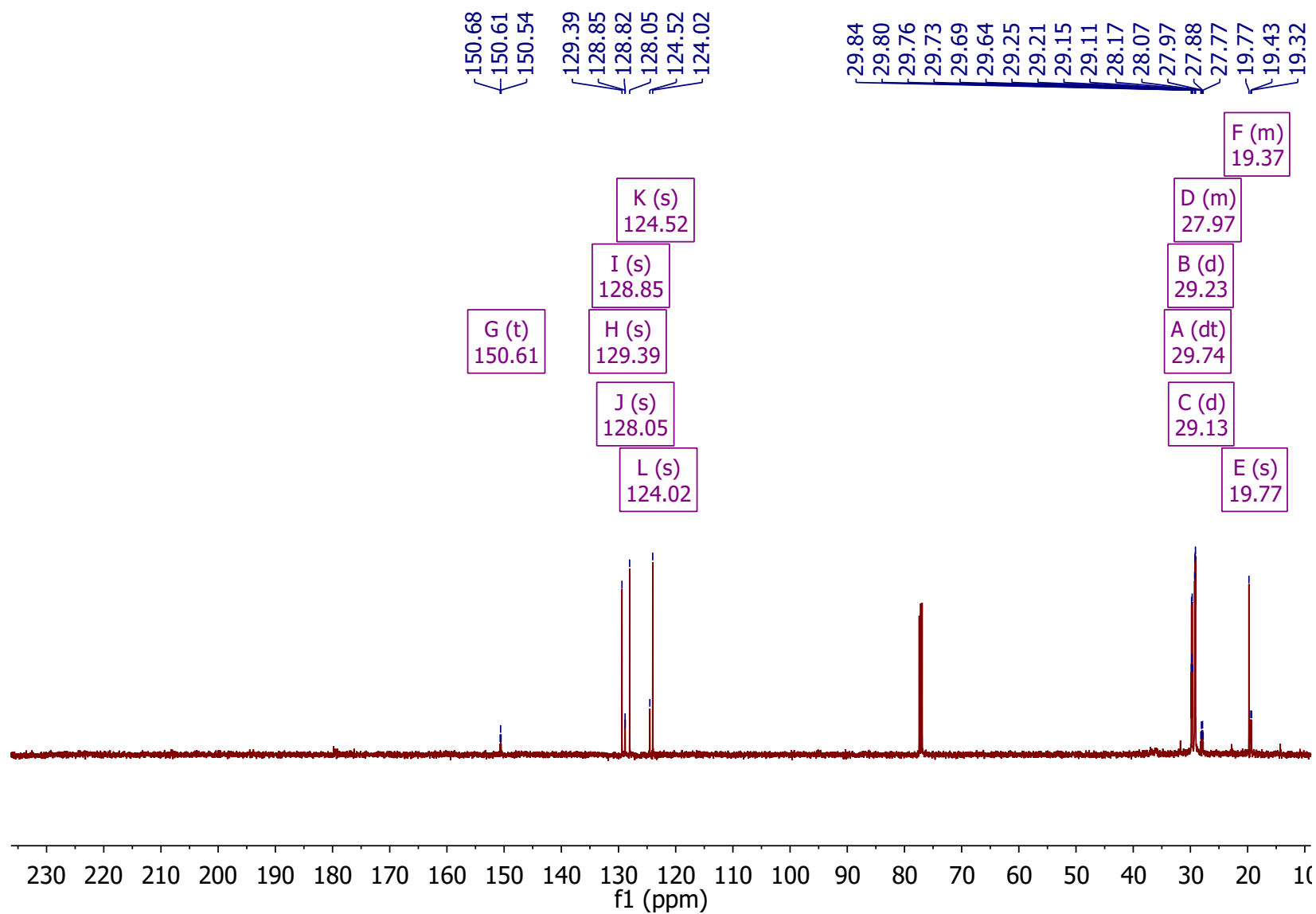


Figure B.5 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (500 MHz, CDCl_3) of **1**

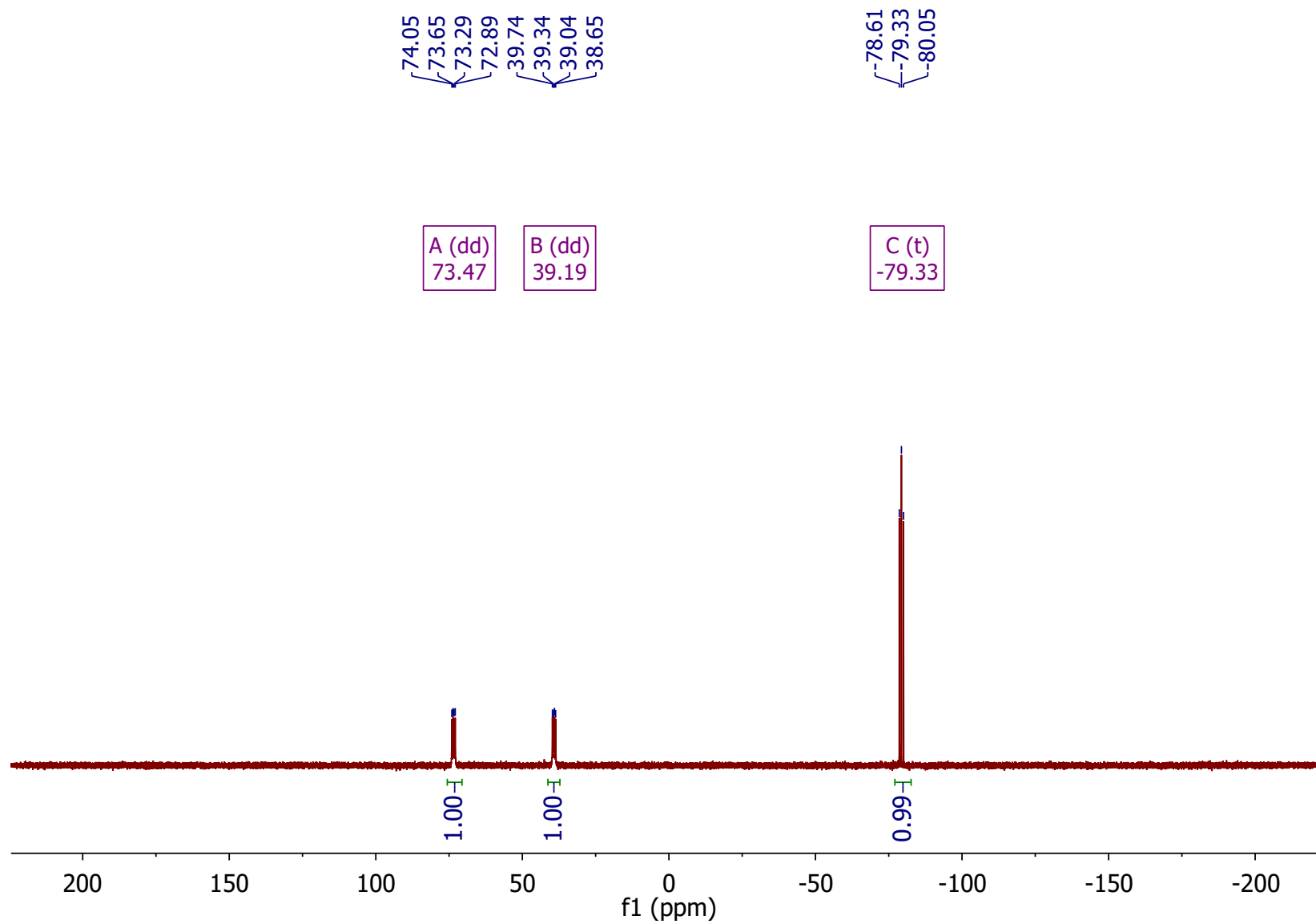


Figure B.6 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500 MHz, CDCl_3) of **1**

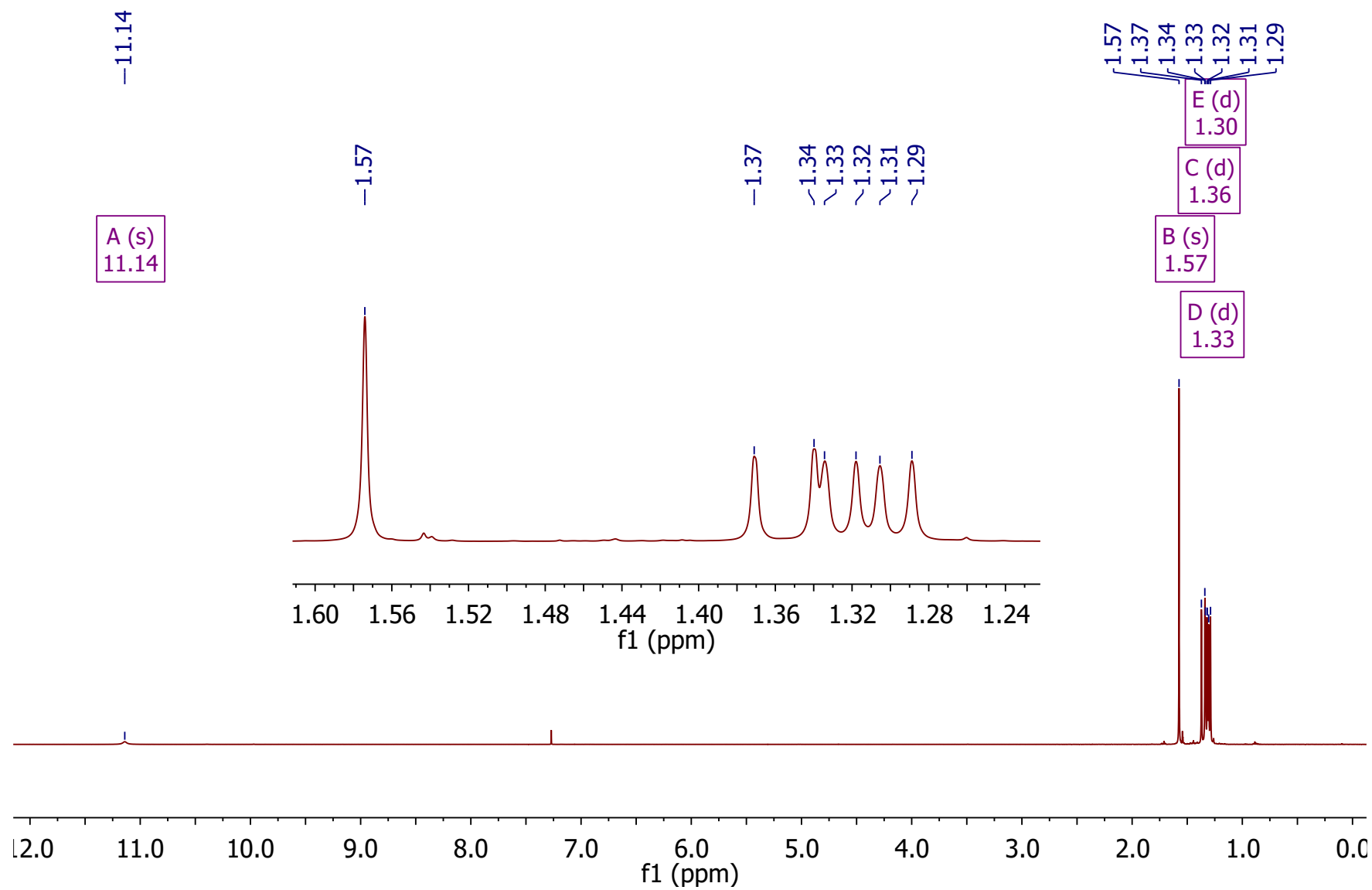


Figure B.7 ¹H NMR spectrum (500 MHz, CDCl₃) of [2-H][OTf]

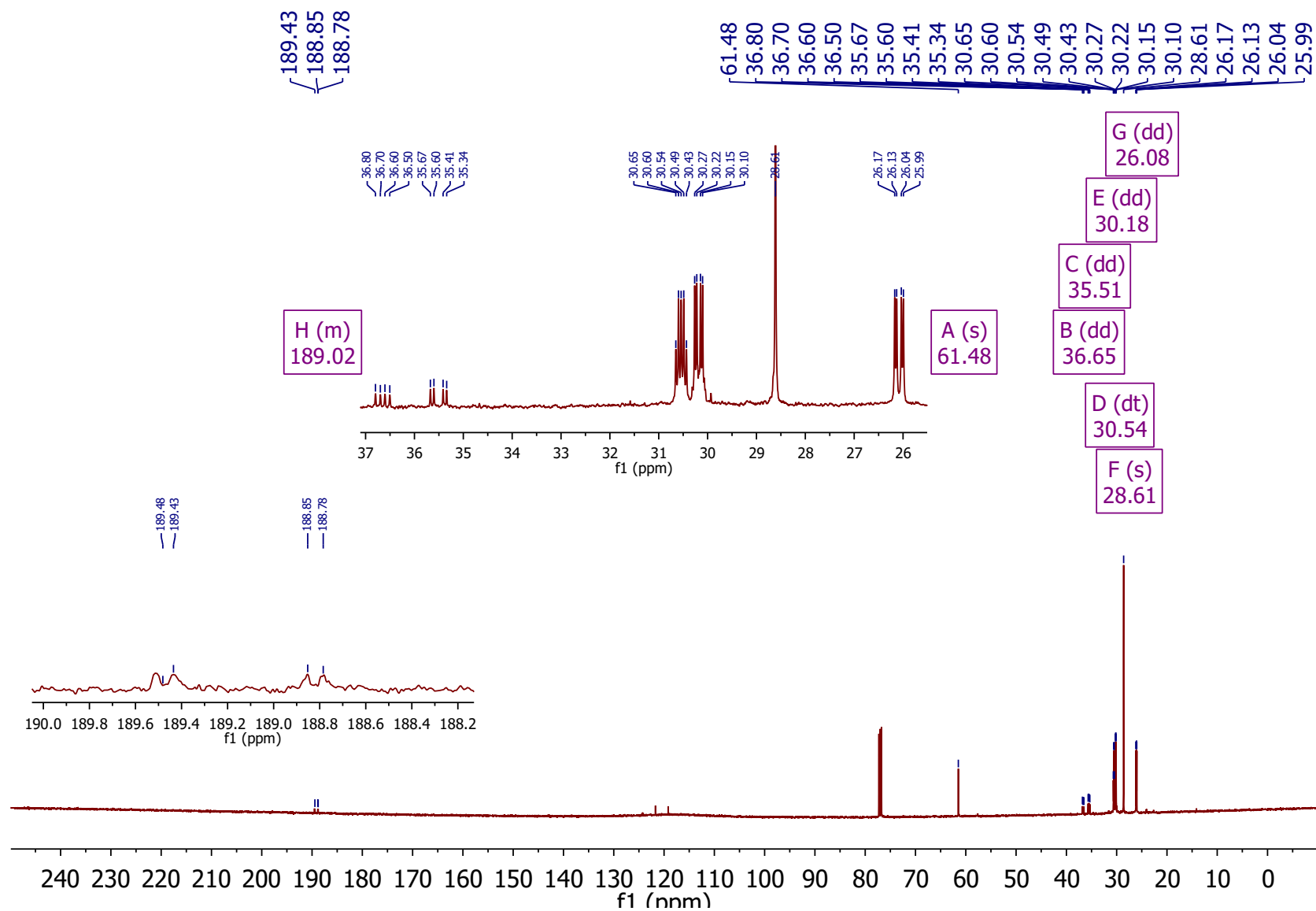


Figure B.8 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (500 MHz, CDCl_3) of **[2-H][OTf]**

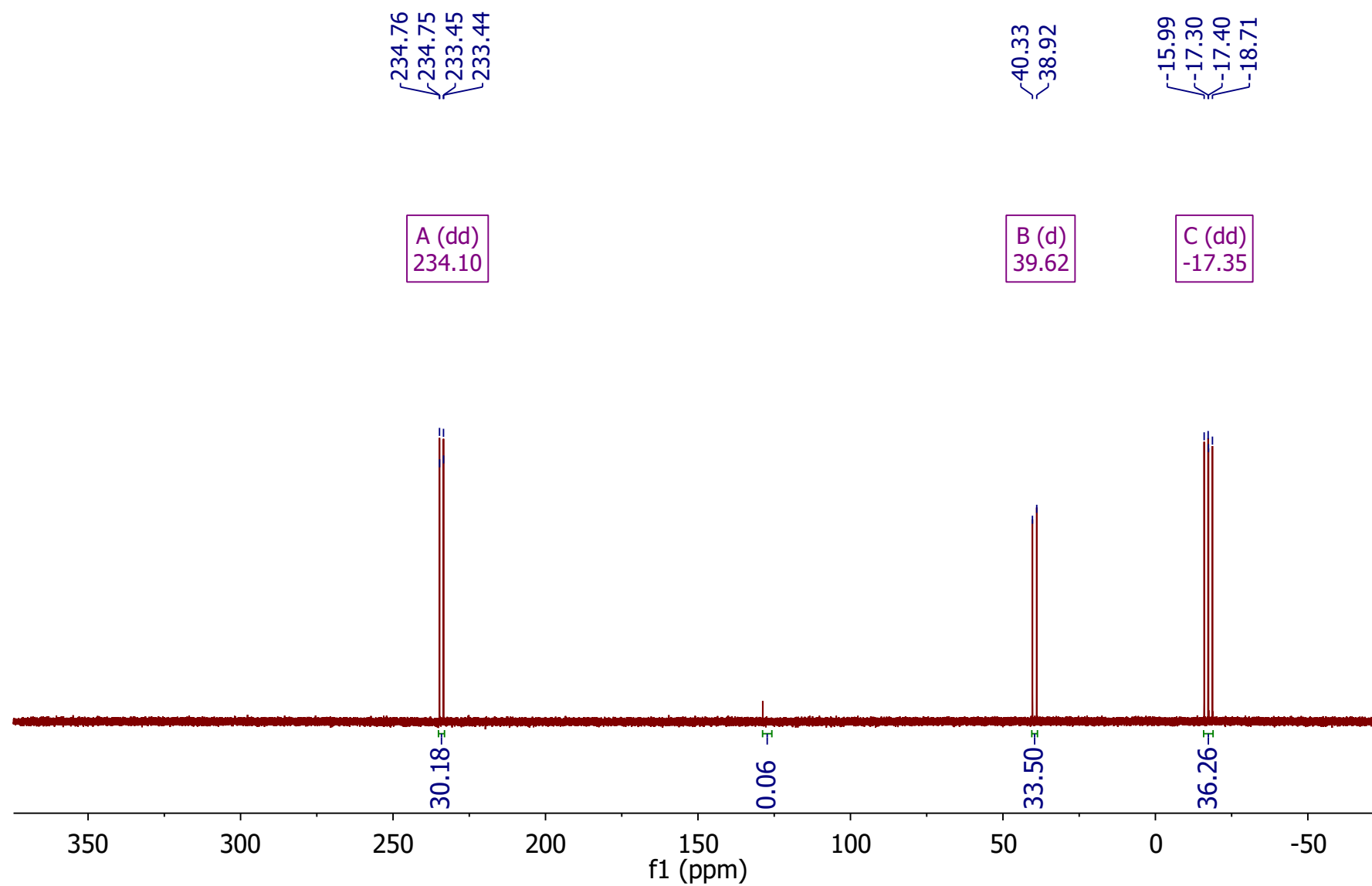


Figure B.9 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500 MHz, CDCl_3) of $[2\text{-H}][\text{OTf}]$

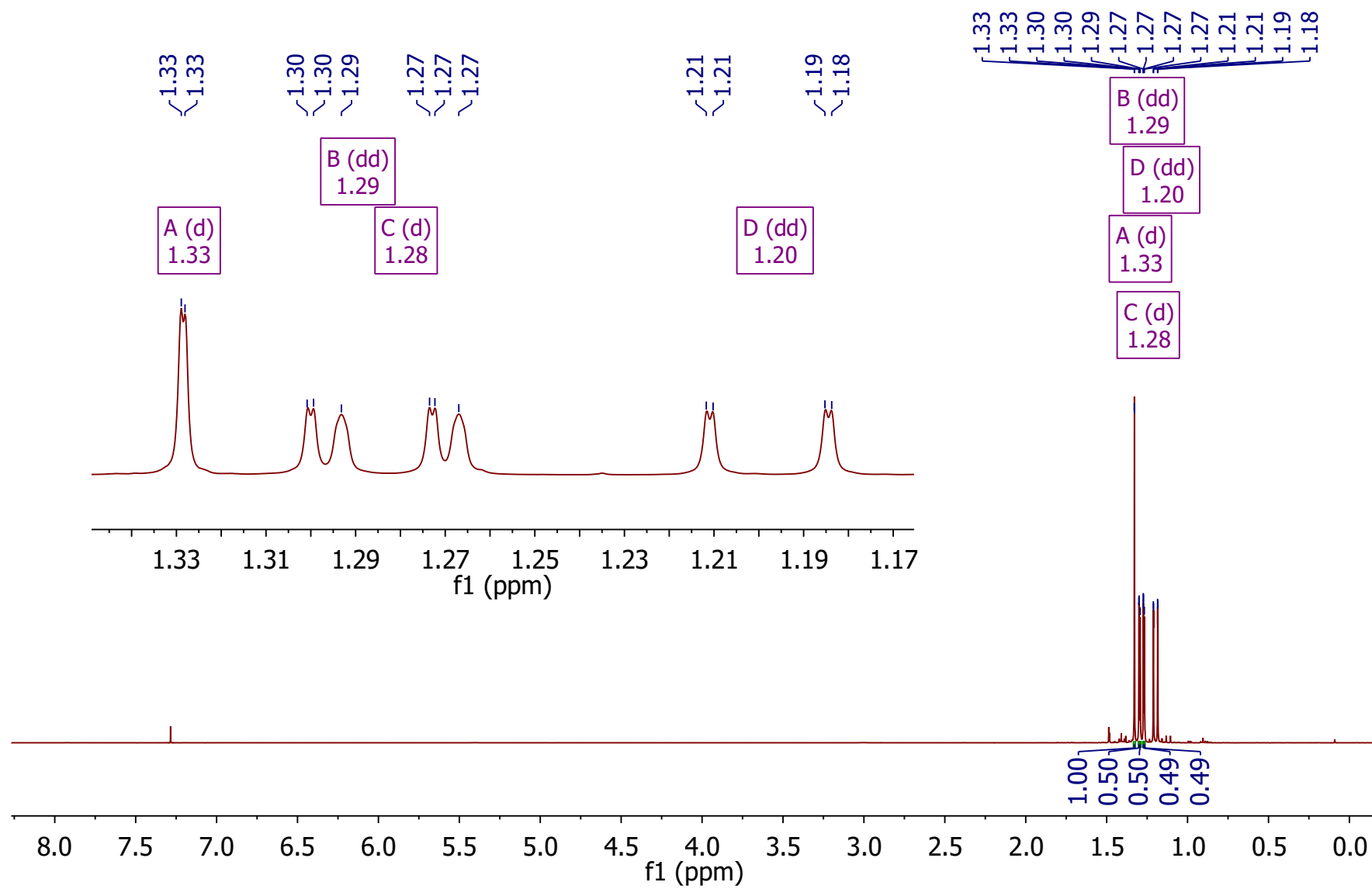


Figure B.10 ^1H NMR spectrum (500 MHz, CDCl_3) of **2**

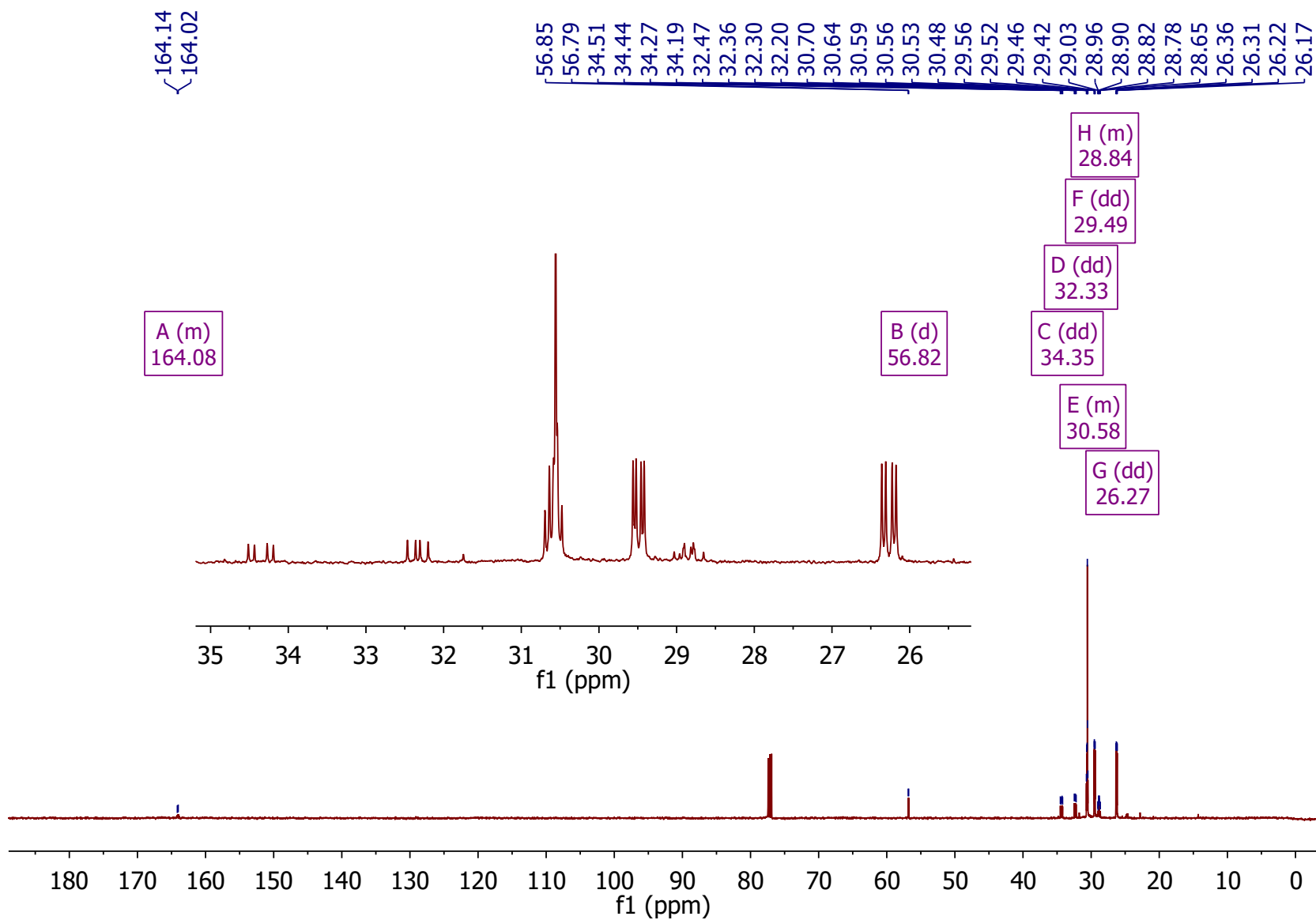


Figure B.11 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (500 MHz, CDCl_3) of **2**

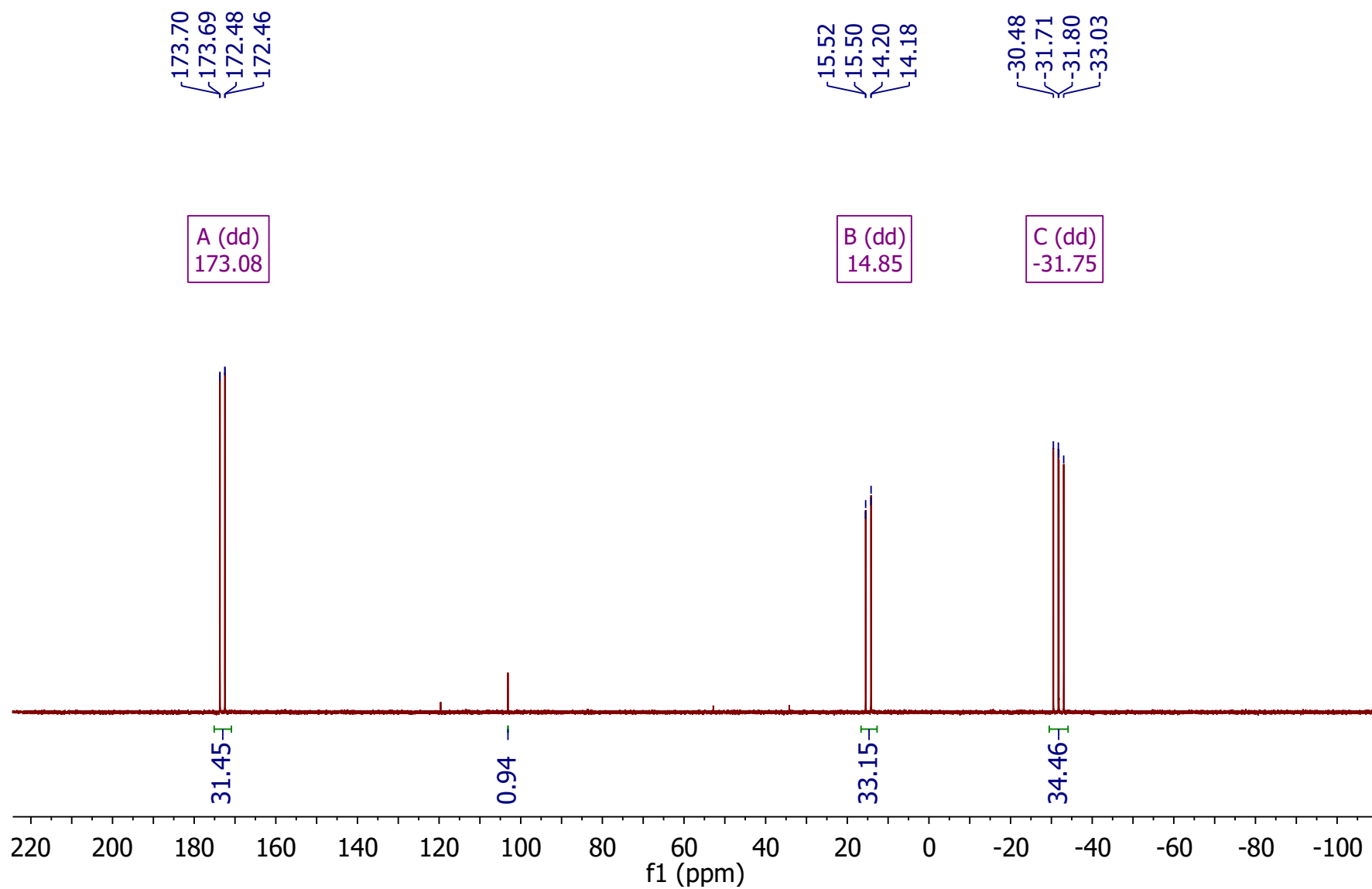


Figure B.12 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500 MHz, CDCl_3) of **2**

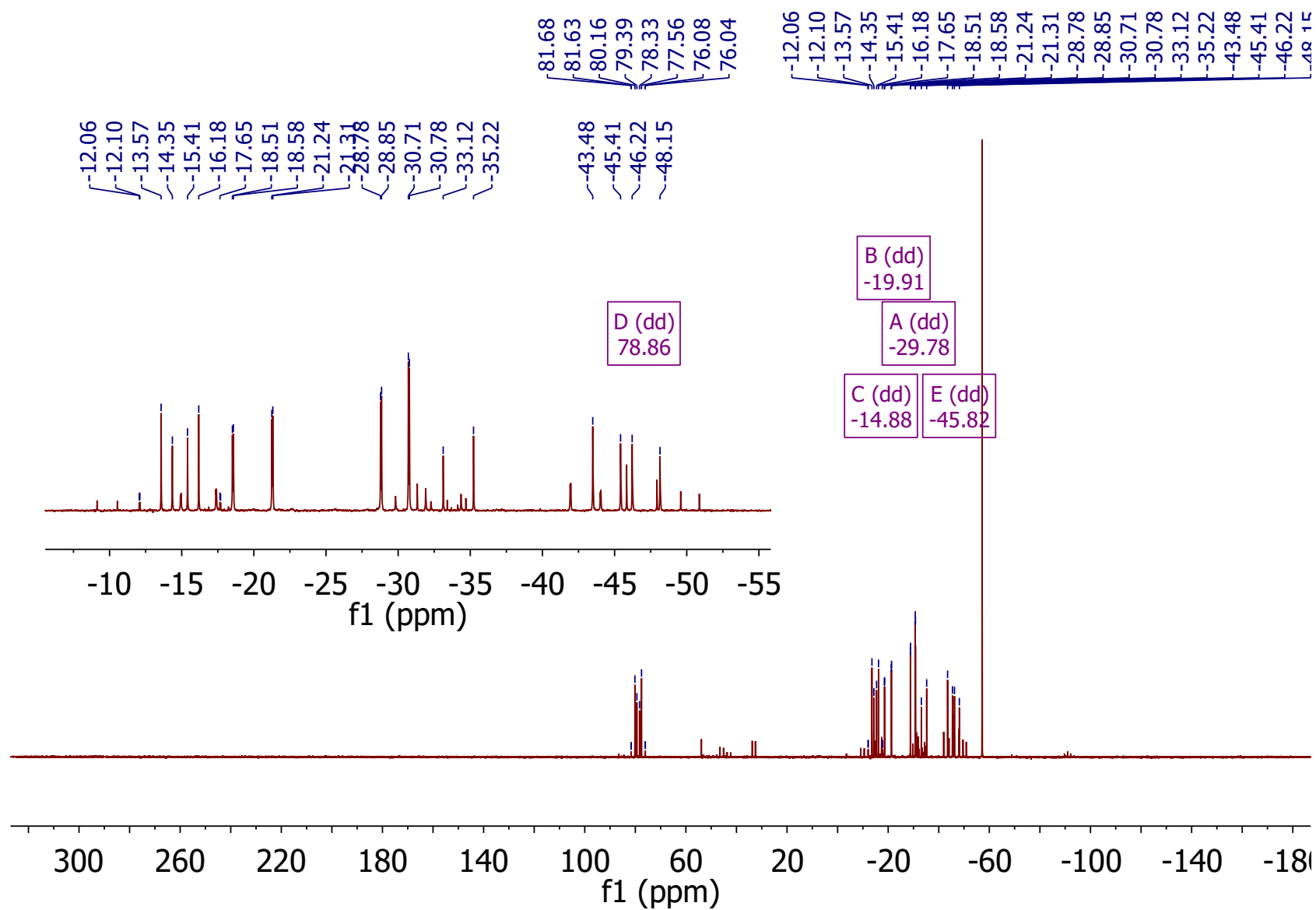


Figure B.13 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500 MHz, C_6D_6) of the reaction mixture of P_3^tBu_3 , $^t\text{BuNC}$, and HOTf in toluene

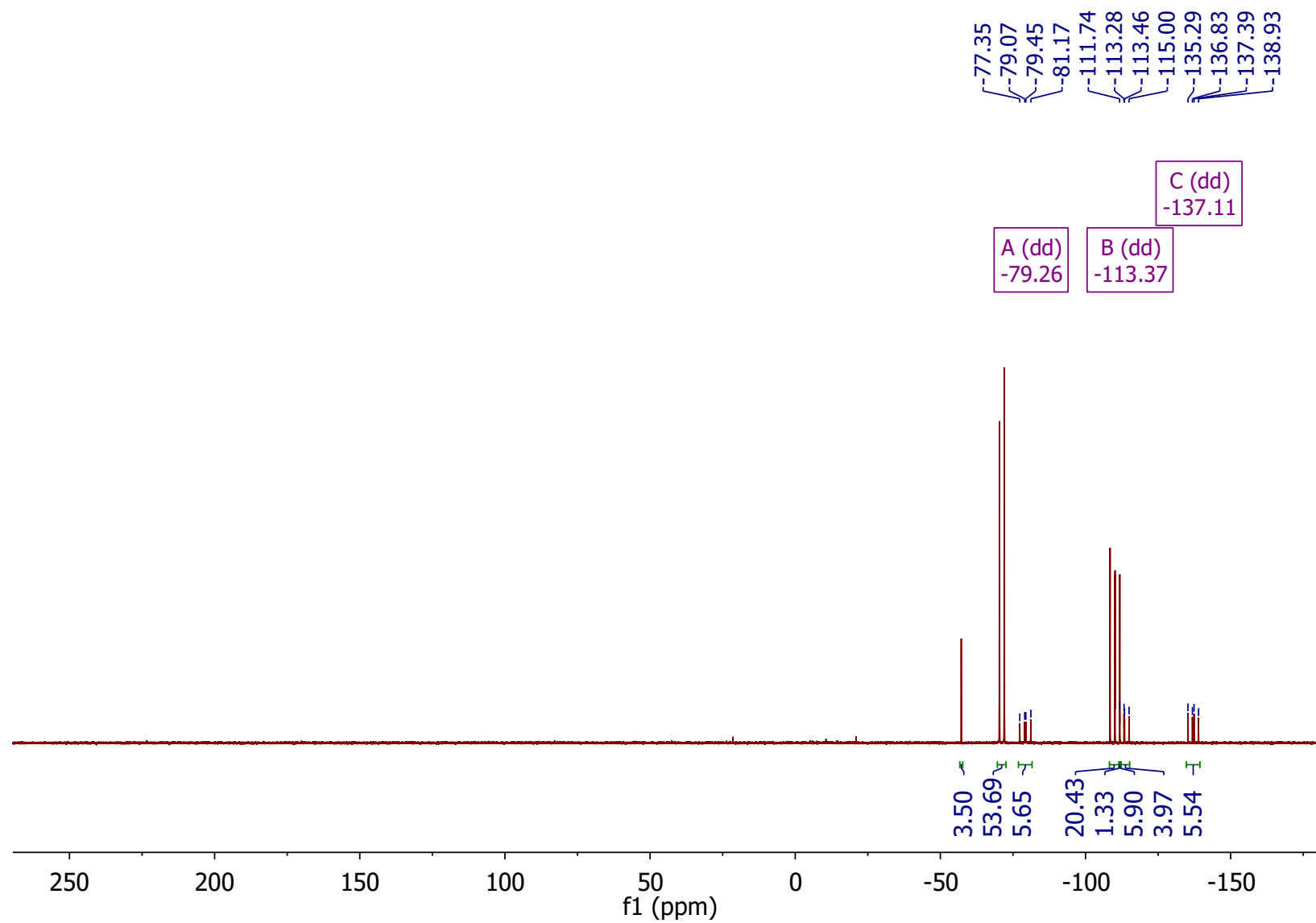


Figure B.14 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500 MHz, C_6D_6) of the reaction mixture of P_3Bu_3 , DIC, and HOTf in C_6D_6

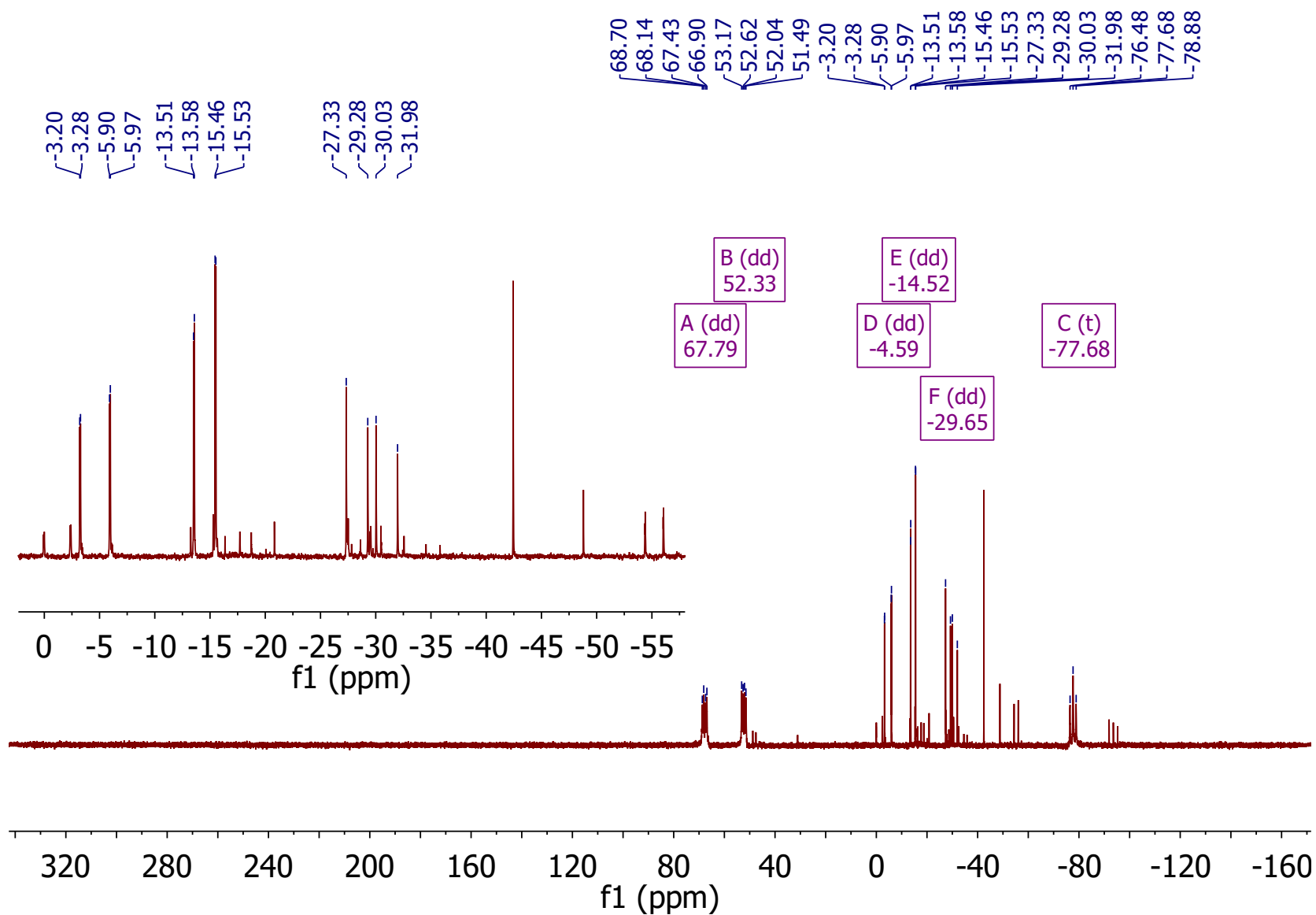


Figure B.15 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500 MHz, C_6D_6) of the reaction mixture of P_3^tBu_3 , PhNCO , and HOTf in toluene

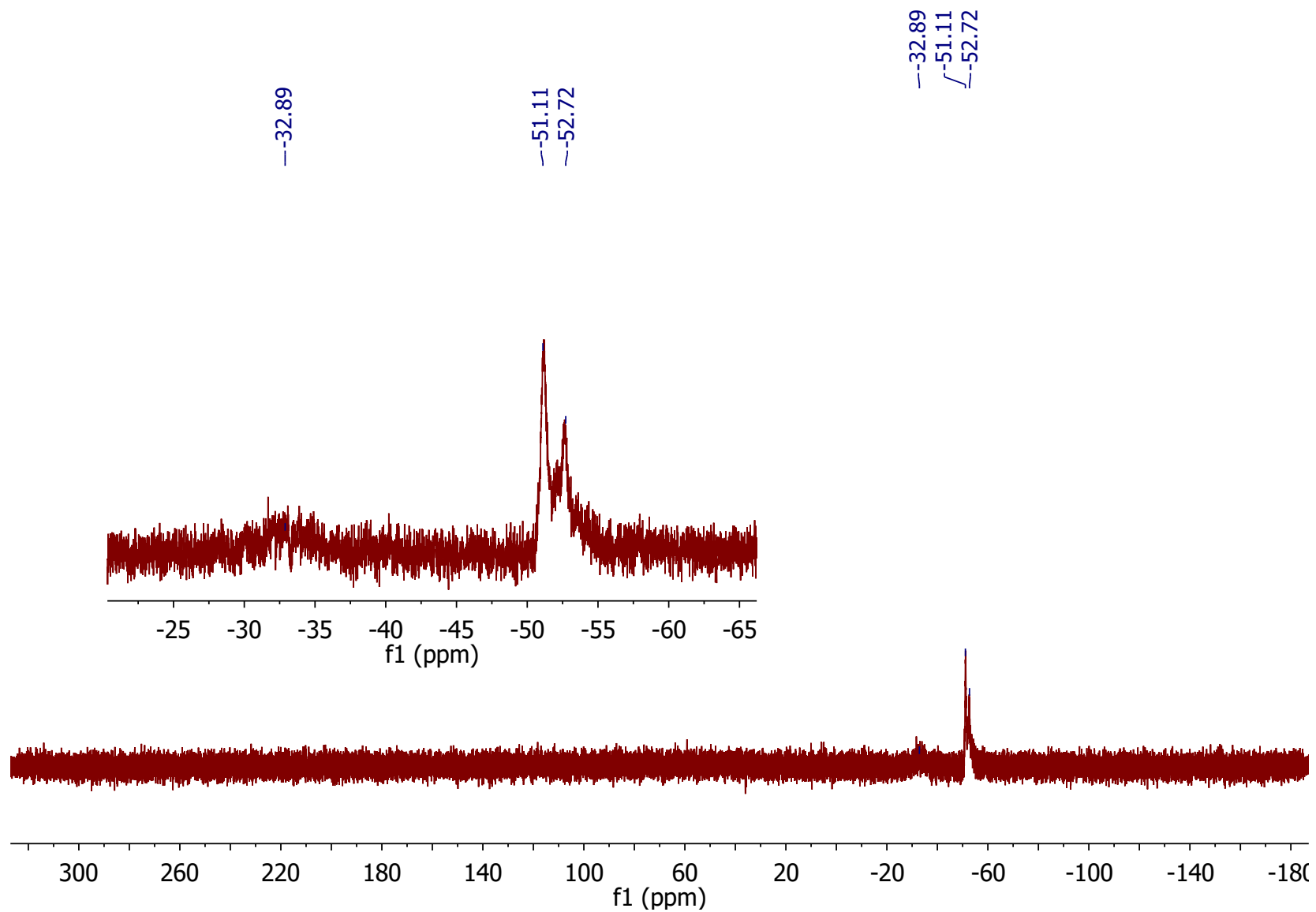


Figure B.16 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500 MHz, C_6D_6) of the reaction mixture of P_3^tBu_3 , $i\text{PrNCS}$, and HOTf in toluene after 24 h

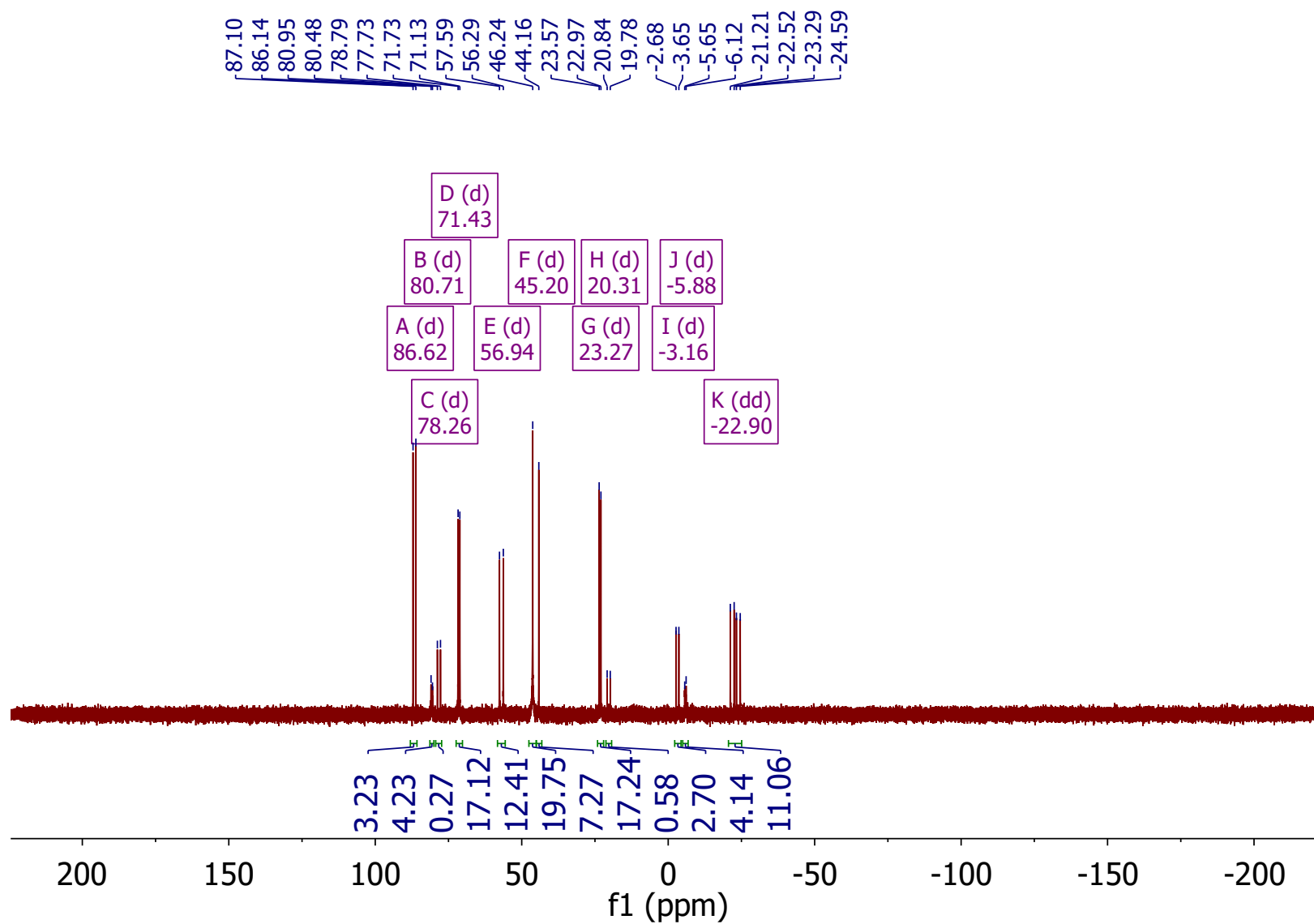


Figure B.17 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500 MHz, CDCl_3) of the reaction mixture of $[\text{P}_3^t\text{Bu}_3\text{Me}][\text{OTf}]$ and DIC heated at 60 °C for 72 h in toluene.

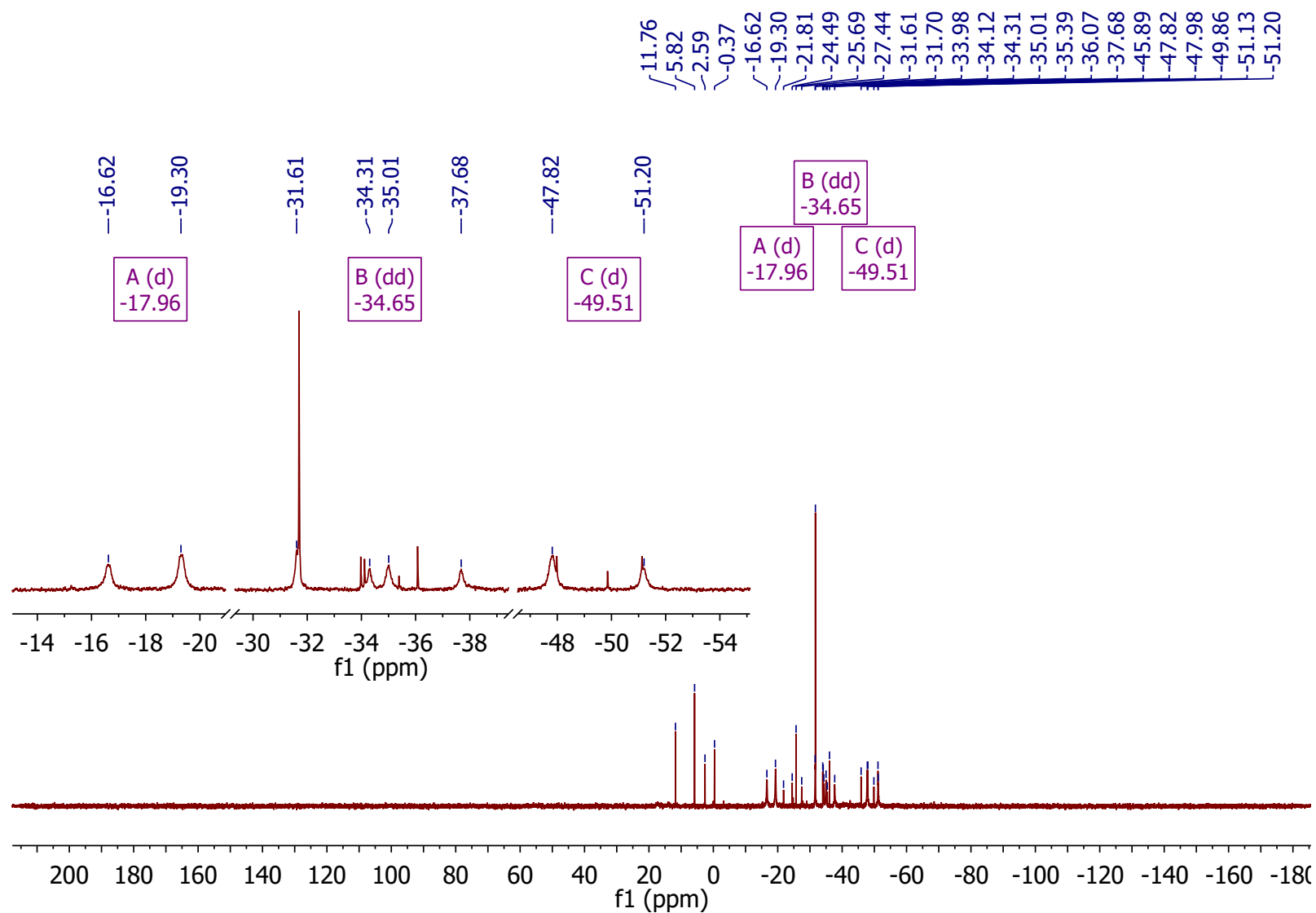


Figure B.18 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (300 MHz, CDCl_3) of the reaction mixture of $[\text{P}_3^t\text{Bu}_3\text{Me}][\text{OTf}]$ and $^t\text{BuNCO}$ at 22 °C in toluene after 30 minutes.

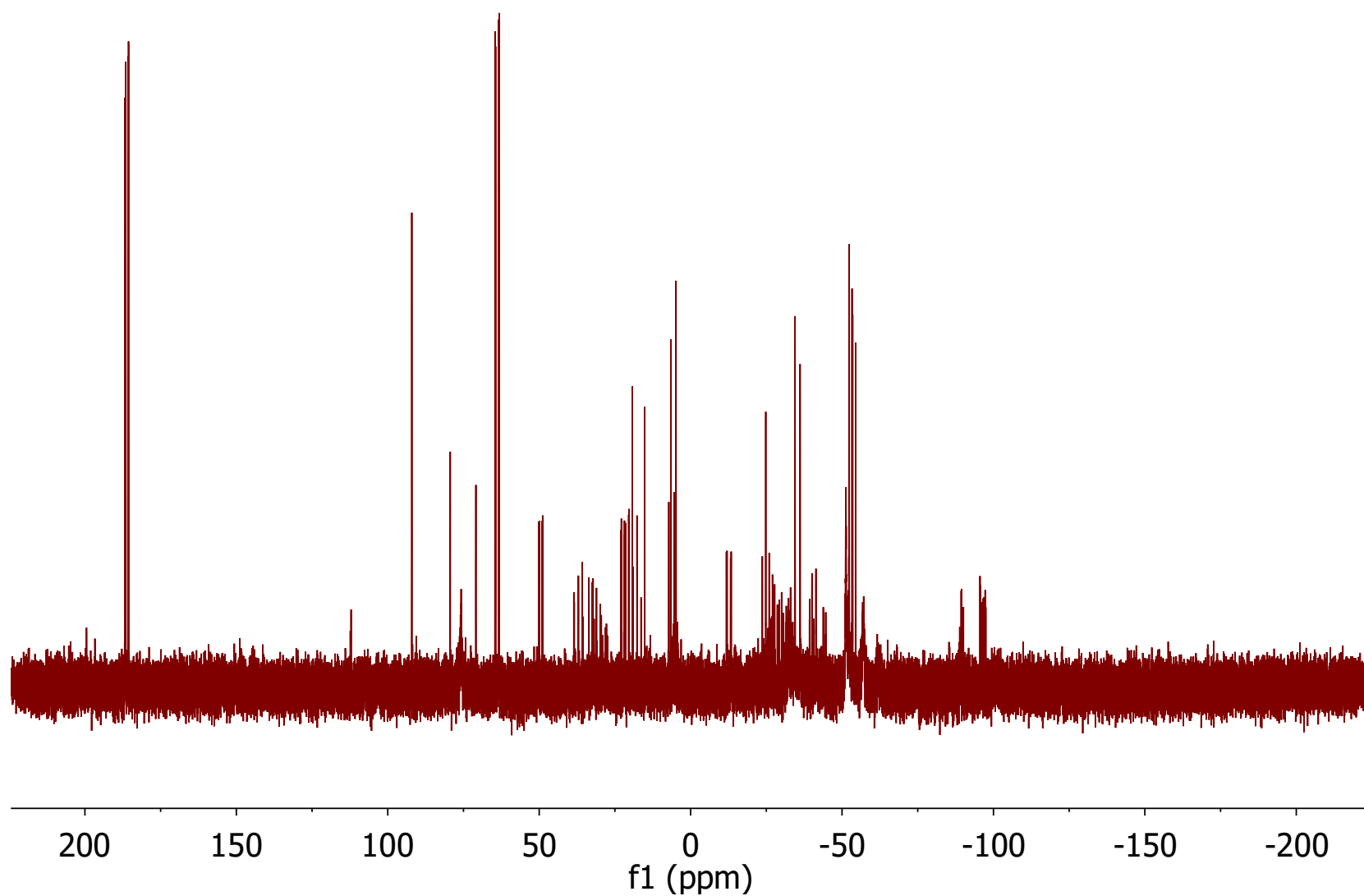


Figure B.19 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (500 MHz, CDCl_3) of the reaction mixture of $[\text{P}_3^t\text{Bu}_3\text{Me}][\text{OTf}]$ and PhNCO heated at 60 °C for 7 days in toluene

B.2 Crystallographic details

Data were collected using a Bruker APEX II area detector diffractometer equipped with a Kryoflex low-temperature device operating at $T = 100(2)$ K. Data were measured using MoK_α radiation (microfocus sealed X-ray tube, 50 kV, 0.99 mA). The total number of runs and images was based on the strategy calculation from the program APEX3. Data reduction, scaling and absorption corrections were performed using SAINT. The structures were solved and the space group determined by the SHELXT¹ structure solution program using Intrinsic Phasing and refined by Least Squares using version 2019/3 of SHELXL.² All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the N-H protons in [1-H][OTf] and [2-H][OTf] which were located in the difference map and refined freely.

	[1-H][OTf]	1	[2-H][OTf]	2
chemical formula	C21H37NP3,CF3O3S	C21H36NP3	C17H37NOP3,C1F3O3S	C34H72N1O1P3
crystal colour	Yellow	Yellow	Yellow	Colourless
Fw; F(000)	545.49; 1152	395.42; 1712	513.45; 1088	363.38; 1584
T (K)	100(2)	100(2)	100(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
space group	P21/n	Pbca	P21/c	Pbca
a (Å)	12.3415(10)	8.7766(10)	8.5712(9)	10.2857(19)
b (Å)	12.6497(9)	16.8443(19)	12.1897(14)	11.313(2)
c (Å)	18.2805(14)	31.211(4)	24.812(3)	36.933(7)
α (deg)	90	90	90	90
β (deg)	107.999(2)	90	90.143(7)	90
γ (deg)	90	90	90	90
Z	4	8	4	8
V (Å³)	2714.2(4)	4614.1(9)	2592.4(5)	4297.6(14)
ρ_{calcd} (g cm⁻³)	1.335	1.138	1.316	1.123
μ (mm⁻¹)	0.340	0.262	0.354	0.279
θ range (deg);	1.768 – 30.564	1.305 – 30.528	0.821 – 30.622	1.103 – 30.525
completeness	1.000	1.000	0.997	1.000
collected reflections; R_c	44075; 0.0295	31102; 0.0400	34037; 0.0601	43702; 0.0226
unique reflections; R _{int}	44075; 0.0378	31102; 0.0449	34037; 0.0678	43702; 0.0341
R ₁ ^a ; wR ₂ ^b [I > 2σ(I)]	0.0340; 0.0820	0.0368; 0.0782	0.0320; 0.0794	0.0649; 0.1521
R ₁ ; wR ₂ [all data]	0.0449; 0.0877	0.0558; 0.0856	0.0354; 0.0813	0.0714; 0.1558
GOF	1.035	1.029	1.030	1.141
largest diff peak and hole	1.678 and -0.398	0.343 and -0.224	0.362 and -0.269	1.988 and -0.626

Error! Not a valid link. $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$

$$^b wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

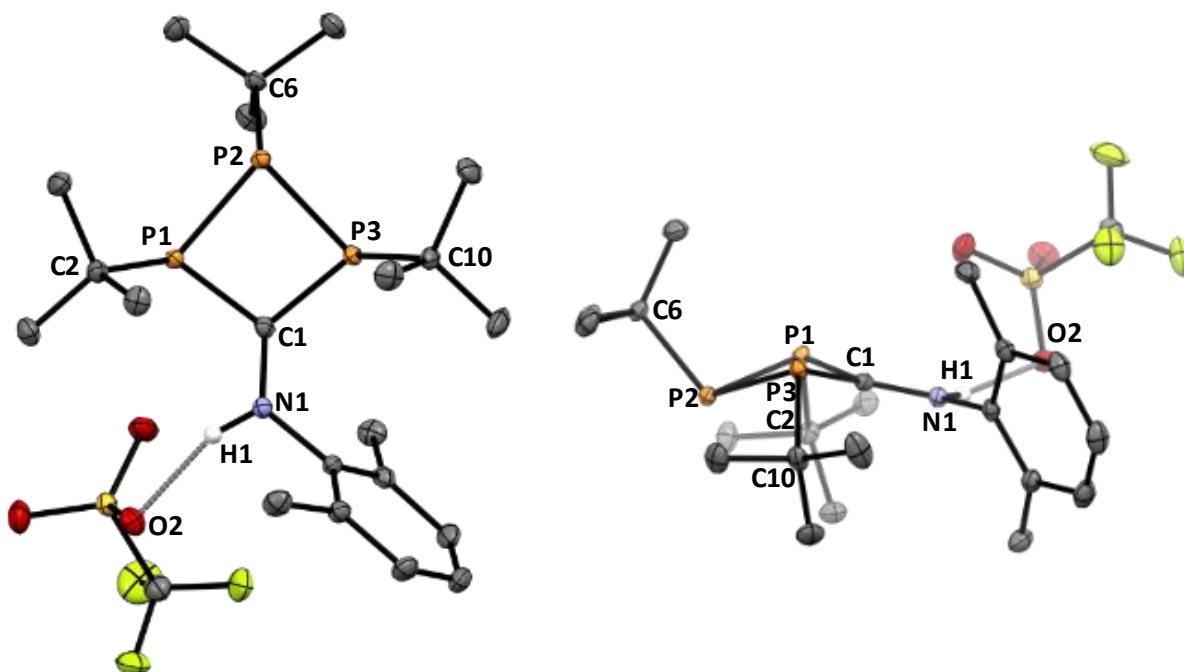


Figure B.20. Molecular structure of **[1-H][OTf]**.

Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°) for **[1-H][OTf]** [calculated values in square brackets]: C1-N1 1.306(2) [1.308]; N1-C14 1.45(1) [1.427]; N1-H1 0.90(2) [1.014]; C1-P1 1.831(1) [1.8020]; C1-P3 1.836(1) [1.8036]; P1-P2 2.2043(5) [2.2064]; P2-P3 2.2194(5) [2.2174]; N1-C1-P1 126.0(1) [125.996]; N1-C1-P3 131.7(1) [132.335]; P1-C1-P3 101.92(6) [101.599]; C1-P1-P2 83.80(4) [83.787]; P1-P2-P3 80.16(2) [78.337]; C1-N1-C14 127.7(1) [128.402];. C1-N1-H1 120(1) [116.3]; H1-N1-C14 112(1) [115.167].

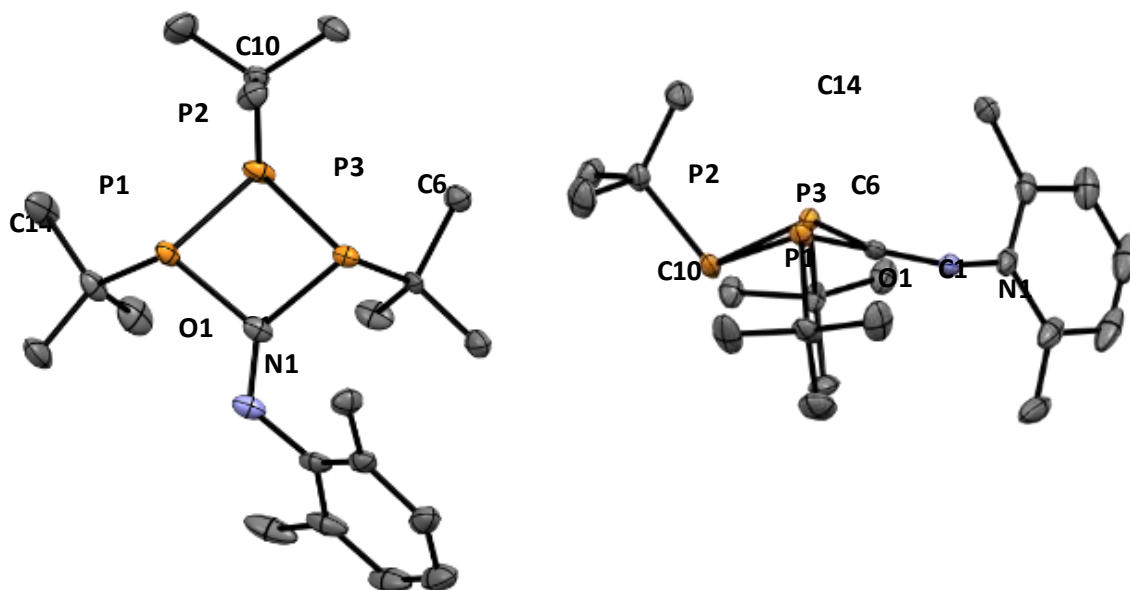


Figure B.21. Molecular structure of **1**.

Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Only one disordered component shown. Select bond lengths (Å) and angles (°) for **1** [calculated values in square brackets]: C1-N1 1.279(2) [1.2660]; N1-C2 1.418(2)[1.39615]; C1-P1 1.872(1) [1.8601]; C1-P3 1.927(5) [1.8356]; P1-P2 2.2198(5) [2.2106]; P2-P3 2.280(6) [2.20621]; N1-C1-P1 135.7(1) [135.257]; N1-C1-P3 123.0(2) [123.976]; P1-C1-P3 100.5(2) [100.656]; C1-P1-P2 84.01(4) [83.754]; C1-P3-P2 81.2(2) [84.439]; P1-P2-P3 80.9(2) [80.191]; C1-N1-C2 123.4 (1) [124.693].

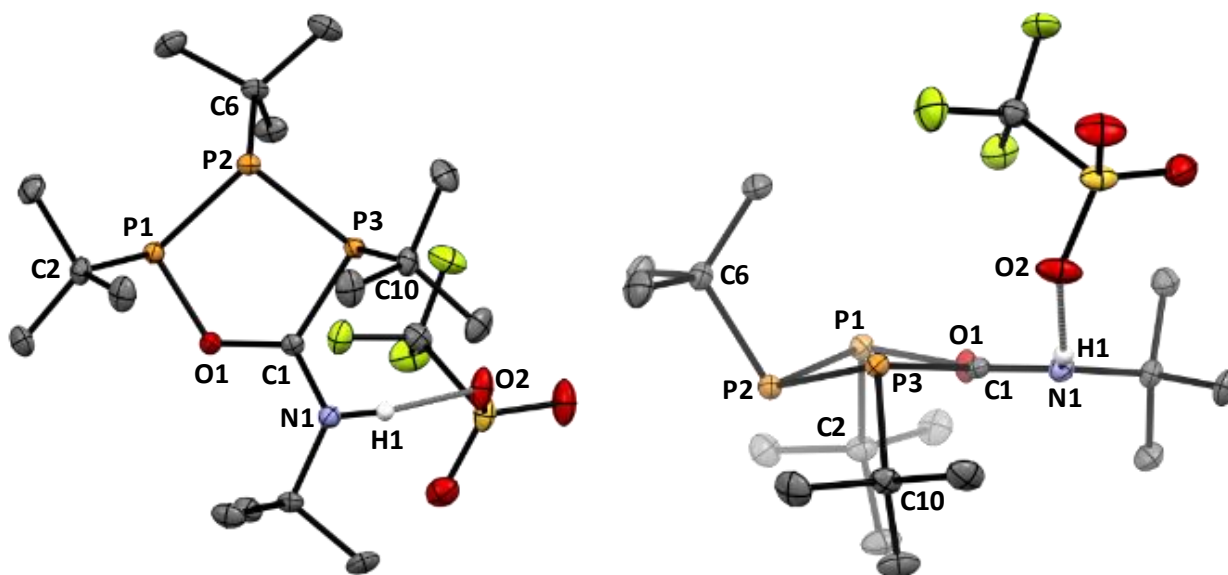


Figure B.22. Molecular structure of [2-H][OTf].

Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°) for [2-H][OTf] [calculated values in square brackets]: H1-N1 0.91(2) [1.00933]; N1-C14 1.507(2) [1.49027]; N1-C1 1.299(2) [1.30693]; C1-P3 1.851(1) [1.83804]; C1-O1 1.318(2) [1.29191]; P1-O1 1.716(1) [1.73425]; P1-P2 2.2204(6) [2.21509]; P2-P3 2.1995(6) [2.18835]; H1-N1-C14 119(1) [115.479]; H1-N1-C1 112(1) [115.212]; C1-N1-C14 128.4(1) [129.305]; O1-C1-N1 117.6(1) [117.998]; P3-C1-N1 120.7(1) [120.577]; P3-C1-O1 121.6(1) [121.203]; C1-O1-P1 123.07(9) [124.230]; O1-P1-P3 98.63(4) [98.435]; P1-P2-P3 94.10(2) [94.084]; P2-P3-C1 96.60(5) [97.283]; P3-C1-O1 121.6(1) [121.203].

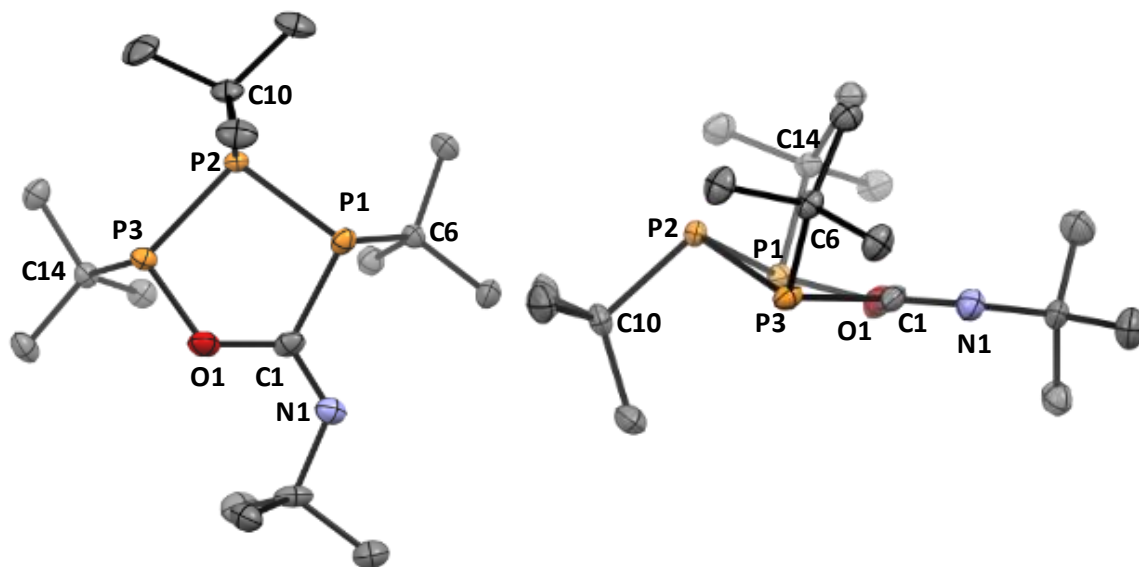


Figure B.23. Molecular structure of **2**.

Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (°) for **1** [calculated values in square brackets]: N1-C2 1.495(3) [1.46274]; N1-C1 1.269(3) [1.25423]; C1-P1 1.870(3) [1.84893]; C1-O1 1.377(3) [1.36695]; P3-O1 1.676(2) [1.67577]; P1-P2 2.2034(9) [2.18534]; P2-P3 2.216(1) [2.21530]; C1-N1-C2 124.7(2) [125.680]; O1-C1-N1 122.4(2) [124.447]; P1-C1-N1 120.9(2) [118.960]; P1-C1-O1 116.3(2) [116.197]; C1-O1-P3 124.5(2) [125.087]; O1-P3-P2 101.32(7) [100.447]; P1-P2-P3 92.89(3) [93.079]; P2-P1-C1 97.57(8) [98.041].

B.3 Computational details

All the calculations were conducted using the Gaussian16.C01 program suite.³ For all calculations the PBE0 hybrid (PBE1PBE)⁴ functional was used in combination with the Ahlrichs⁵ def2-TZVP basis set. Grimme's empirical dispersion with Becke-Johnson dampening (D3) was used for all calculations.⁶ The stationary points were confirmed as energy minima by the lack of imaginary frequencies. NBO calculations were performed with NBO 7 included in the Gaussian 16 program suite.⁷

B.3.1 DFT of [1-H][OTf]

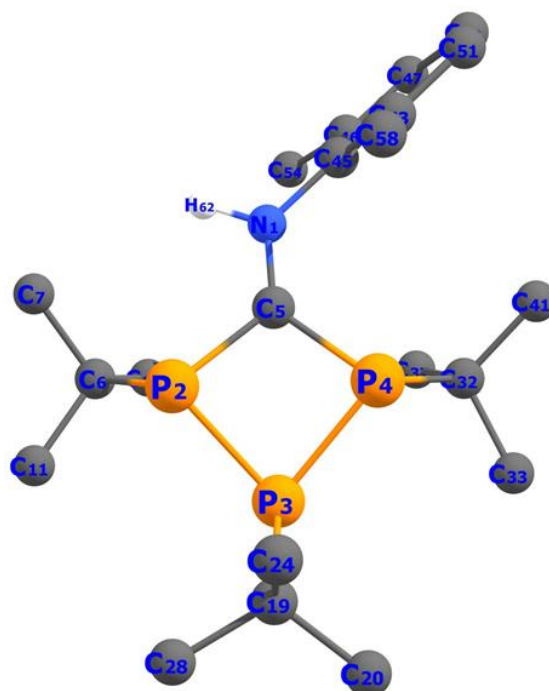
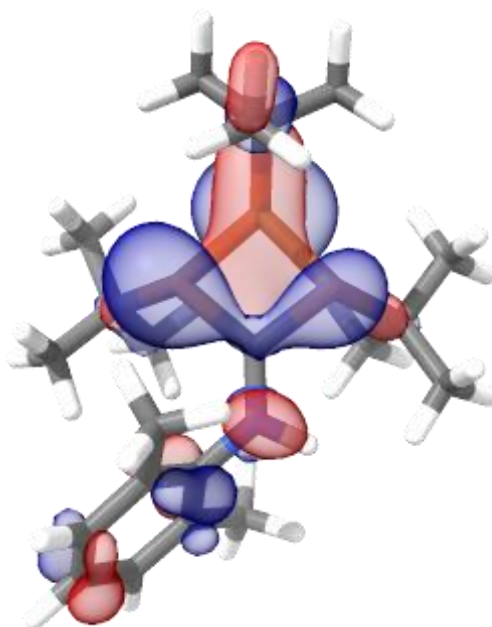


Figure B.24 DFT optimized gas-phase structure of [1-H][OTf] (PBE0-D3/def2-TZVP)

Figure B.25 Calculated HOMO of [1-H][OTf]



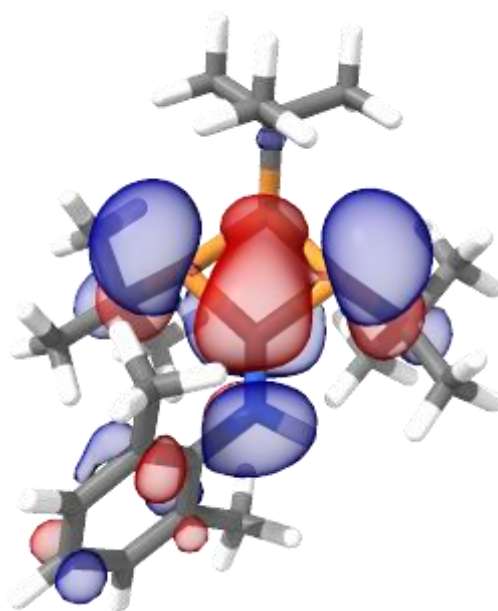


Figure B.26 Calculated HOMO of [1-H][OTf]

Table B.1 XYZ coordinates of computed structure of [1-H][OTf]

Freq	RPBE1PBE	def2TZVP	
Charge	1		
Multiplicity	1		
Total Energy	-1.900124031867651E+03		
Dipole Moment	2.27413439E+00	8.90232144E+00	2.24591654E+01
N	0.393534	5.685488	11.241145
P	2.499655	5.850936	13.048447
P	3.087342	3.747266	13.360292
P	2.471126	3.729527	11.230354
C	1.498288	5.168931	11.714601
C	1.347123	6.355631	14.447493
C	0.780347	7.735484	14.120514
H	0.062301	7.719453	13.295006
H	1.56494	8.453038	13.87304
H	0.238636	8.114701	14.991667
C	2.265287	6.456992	15.664091
H	1.681007	6.801921	6.52153
H	3.077947	7.169698	15.50508
H	2.69477	5.487467	15.925857
C	0.23886	5.349151	14.711399
H	-0.354672	5.681707	15.568243
H	0.644655	4.363362	14.94508
H	-0.440503	5.248499	13.863399
C	4.964806	3.790911	3.346218
C	5.407621	2.332665	13.243469
H	5.147039	1.899929	12.274688
H	4.965626	1.713888	14.028497
H	6.494774	2.275445	13.345951
C	5.588561	4.611029	12.230253
H	6.677776	4.588906	12.330433
H	5.274522	5.656249	12.269115

H	5.338933	4.212298	11.245385
C	5.356262	4.363906	14.706938
H	6.442041	4.309853	14.824559
H	4.905073	3.807012	15.532372
H	5.070346	5.415101	14.798863
C	1.398788	2.193283	11.008834
C	2.364144	1.053949	11.336568
H	2.68336	1.072464	12.380587
H	3.248368	1.067583	10.694372
H	1.846952	0.106006	11.165771
C	0.206522	2.161632	11.949143
H	-0.509368	2.946764	11.707785
H	0.511571	2.263389	12.992448
H	-0.310123	1.203109	11.841236
C	0.957732	2.077216	9.554181
H	0.497532	1.095762	9.408647
H	1.802608	2.152421	8.866383
H	0.220096	2.831066	9.284462
C	-0.318999	5.323094	10.059067
C	-1.675161	5.005588	10.196892
C	-2.373037	4.650019	9.052894
H	-3.419797	4.381838	9.135157
C	-1.749478	4.647268	7.814443
H	-2.309159	4.369627	6.929446
C	-0.426017	5.028818	7.700789
H	0.044582	5.066737	6.725103
C	0.322693	5.386412	8.818699
C	-2.361965	5.071181	11.525456
H	-3.393102	4.731612	11.439702
H	-2.392433	6.096304	11.910871
H	-1.868978	4.455276	12.280929
C	1.737911	5.83765	8.645279

H	2.440693	5.001609	8.71699
H	2.036813	6.572867	9.393656
H	1.865091	6.286796	7.660463
H	0.016621	6.480673	11.745187

B.3.2 DFT of **1**

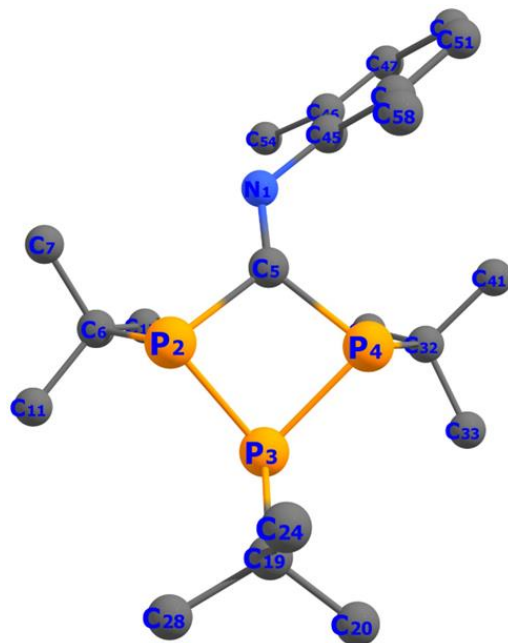


Figure B.27 DFT optimized gas-phase structure of **1** (PBE0-D3/def2-TZVP)

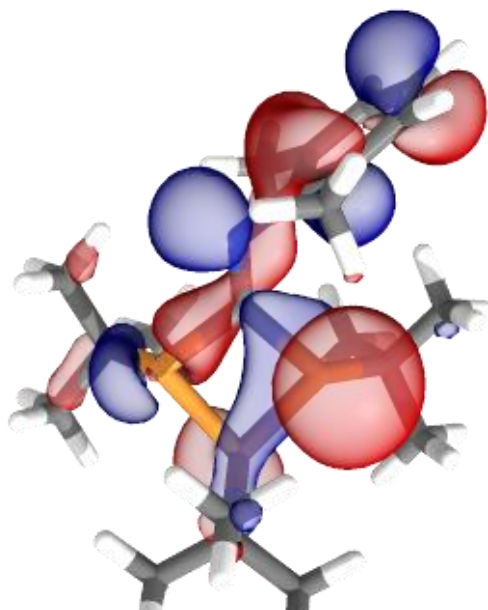


Figure B.28 Calculated HOMO of **1**

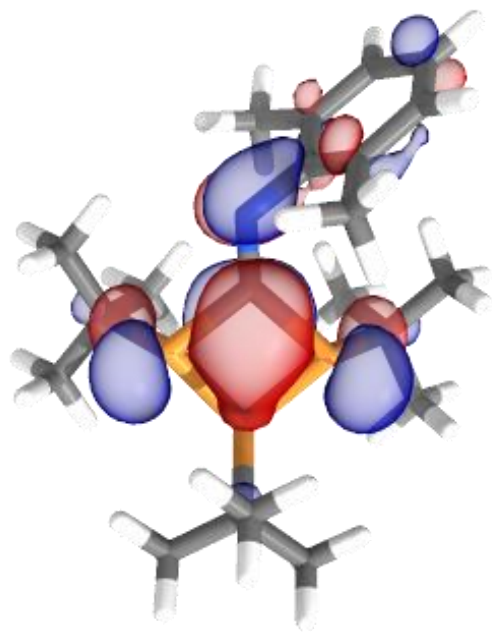


Figure B.29 Calculated LUMO of **1**

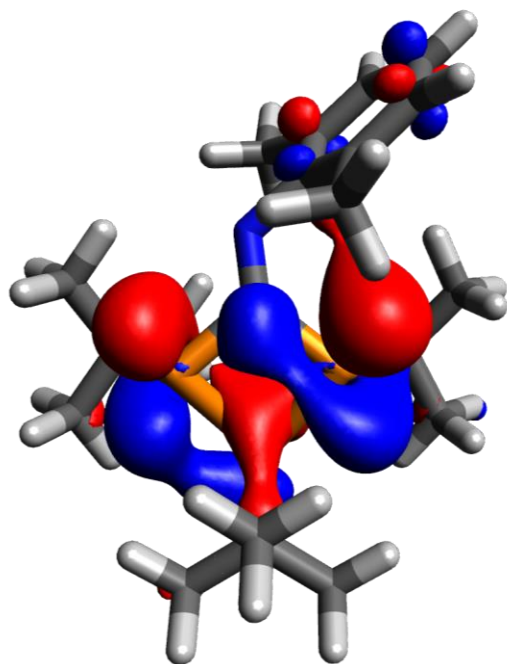


Figure B.30 Calculated LUMO+1 of **1**

Table B.2 XYZ coordinates of computed structure of **1**

Freq	RPBE1PBE	def2TZVP	
Charge	0		
Multiplicity	1		
Total Energy	-1.899728699420599E+03		
Dipole Moment	1.54935334E-01	-5.39628313E-01	3.82258635E-01
N	0.467808	5.782509	11.202912
P	2.507964	5.878895	13.046291
P	3.105125	3.775995	13.343908
P	2.478471	3.693353	11.225583
C	1.496689	5.210054	11.668051
C	1.304176	6.273013	14.431968
C	0.67411	7.618234	14.078559
H	0.102989	7.550378	13.150859
H	1.433502	8.394782	13.957494
H	-0.002888	7.926653	14.882422
C	2.149416	6.397162	15.694845
H	1.512724	6.700585	16.532155
H	2.937227	7.146529	15.581708
H	2.614279	5.443297	15.95858
C	0.227925	5.217564	14.625291
H	-0.430813	5.512093	15.449648
H	0.664745	4.247384	14.871643
H	-0.382928	5.107359	13.729588
C	4.988829	3.826865	13.299324
C	5.44974	2.381233	13.140837
H	5.156694	1.976741	12.168677
H	5.032589	1.736357	13.91887
H	6.541352	2.329517	13.207184
C	5.584718	4.684172	12.194857
H	6.678053	4.657484	12.259095
H	5.266651	5.725036	12.281026

H	5.295165	4.320978	11.206976
C	5.413551	4.365682	14.662506
H	6.504569	4.338807	14.74941
H	4.994926	3.772384	15.479978
H	5.095447	5.403382	14.794571
C	1.359742	2.180452	11.132534
C	2.2726	1.001081	1.459441
H	2.649024	1.053586	12.483763
H	3.125085	0.9483	10.776895
H	1.704154	0.071211	1.358158
C	0.200905	2.228517	12.112631
H	-0.459877	3.066687	11.895309
H	0.553412	2.319905	13.141953
H	-0.387979	1.308122	12.033639
C	0.847383	2.036691	9.702453
H	0.31894	1.082471	9.60666
H	1.668661	2.04052	8.981724
H	0.152993	2.831952	9.432661
C	-0.222302	5.371624	10.060911
C	-1.587711	5.067734	10.187066
C	-2.291023	4.672233	9.058493
H	-3.339839	4.413164	9.158559
C	-1.681495	4.629429	7.814622
H	-2.24523	4.326342	6.940231
C	-0.359319	5.017822	7.691471
H	0.110592	5.034237	6.713545
C	0.392725	5.398399	8.797361
C	-2.272824	5.189311	11.511647
H	-3.356112	5.178471	11.384882
H	-1.983349	6.118444	12.008142
H	-2.012618	4.375767	12.194544
C	1.804992	5.860038	8.61248

H	2.528479	5.067282	8.827192
H	2.042594	6.691906	9.278424
H	1.961973	6.184476	7.582852

Table B.3 Abridged calculated Wiberg bond indices of **1**

Atom		1	2	3	4	5	6	7	8	9
1	N	0	0.0728	0.03	0.1274	1.7628	0.014	0.0021	0.0023	0.0001
2	P	0.0728	0	0.9472	0.0409	0.9745	0.8799	0.0114	0.0007	0.0011
3	P	0.03	0.9472	0	0.9493	0.0475	0.0164	0.0127	0.0006	0.0009
4	P	0.1274	0.0409	0.9493	0	0.9475	0.0089	0.001	0.0009	0.0001
5	C (ring)	1.7628	0.9745	0.0475	0.9475	0	0.0127	0.0017	0.0005	0.0001
6	C	0.014	0.8799	0.0164	0.0089	0.0127	0	1.0058	0.0015	0.0017
19	C	0.0013	0.0166	0.8829	0.0167	0.0062	0.0052	0.0005	0	0.0001
32	C	0.0136	0.0089	0.0169	0.8784	0.0132	0.0045	0.0002	0	0
45	C (Xyl)	1.0704	0.0264	0.0017	0.0039	0.018	0.0003	0.0002	0.0003	0

Table B.4 Abridged natural bond orbital analysis of **1**

LP = Lone pair

BD = Bonding

38. (1.81878) LP (1) N 1 s(25.26%)p 2.95(74.54%)d 0.01(0.20%)

f 0.00(0.00%)

0.0000 0.5023 -0.0164 -0.0026 0.0000

-0.0320 0.0037 -0.0013 0.8526 0.0326

0.0043 -0.1278 -0.0034 -0.0011 0.0056

-0.0003 0.0003 0.0003 0.0126 -0.0005

0.0368 -0.0021 0.0210 -0.0002 0.0017

0.0004 -0.0041 0.0000 0.0006 0.0028

0.0041

39. (1.89829) LP (1) P 2 s(54.32%)p 0.84(45.60%)d 0.00(0.08%)

f 0.00(0.00%)

0.0000 0.0000 0.7370 -0.0057 -0.0003

0.0000 0.2711 -0.0125 0.0004 0.0000

0.0000 0.0334 0.0014 0.0028 -0.0002

0.0000 -0.6171 0.0185 -0.0021 0.0002

-0.0068 0.0013 0.0169 -0.0068 0.0029

-0.0029 -0.0028 0.0032 -0.0162 0.0120

0.0008 -0.0015 0.0022 -0.0010 -0.0030

-0.0012 -0.0019

40. (1.95463) LP (1) P 3 s(59.12%)p 0.69(40.72%)d 0.00(0.15%)

f 0.00(0.00%)

0.0000 0.0000 0.7689 0.0002 -0.0005

0.0000 0.0830 0.0028 0.0015 -0.0003

0.0000 0.1090 -0.0040 0.0002 0.0001

0.0000 0.6230 -0.0151 0.0037 0.0000

0.0061 0.0020 -0.0111 0.0062 -0.0106

0.0023 -0.0075 -0.0006 -0.0311 0.0127

-0.0003 0.0025 -0.0013 0.0018 0.0009

0.0010 -0.0030

41. (1.89327) LP (1) P 4 s(53.84%)p 0.86(46.07%)d 0.00(0.09%)

f 0.00(0.00%)

0.0000 0.0000 0.7338 -0.0035 -0.0004

0.0000 0.0417 -0.0040 -0.0012 0.0000

0.0000 -0.4354 0.0119 -0.0029 0.0001

0.0000 -0.5186 0.0130 -0.0002 0.0000

0.0008 -0.0013 0.0032 0.0007 -0.0191

0.0126 0.0159 -0.0061 -0.0073 0.0053

0.0013 -0.0032 0.0019 0.0011 -0.0002

0.0024 0.0006

42. (1.99092) BD (1) N 1- C 5

(60.66%) 0.7788* N 1 s(42.71%)p 1.33(56.78%)d 0.01(0.47%)

f 0.00(0.03%)

0.0000 0.6532 0.0222 0.0001 0.0001

0.6607 -0.0212 0.0019 -0.3612 0.0056

0.0049 -0.0149 -0.0040 -0.0007 -0.0559

-0.0013 0.0099 -0.0007 -0.0034 0.0001

0.0152 0.0005 -0.0355 0.0006 -0.0013

-0.0096 0.0058 0.0010 -0.0015 0.0038

-0.0142

(39.34%) 0.6272* C 5 s(37.15%)p 1.69(62.71%)d 0.00(0.08%)

f 0.00(0.05%)

0.0000 0.6055 0.0696 -0.0115 -0.0005

-0.6870 0.0350 -0.0329 0.3618 -0.0387

0.0143 -0.1420 0.0055 -0.0056 -0.0025

-0.0215 0.0017 0.0053 -0.0003 -0.0031

0.0067 0.0092 -0.0039 -0.0117 0.0044

0.0122 -0.0061 -0.0016 0.0026 -0.0020

0.0175

43. (1.95372) BD (2) N 1- C 5

(58.61%) 0.7655* N 1 s(0.17%)p99.99(99.55%)d 1.51(0.25%)

f 0.18(0.03%)

0.0000 0.0405 -0.0046 -0.0015 -0.0001

0.0510 0.0000 -0.0005 0.1260 0.0009
 -0.0003 0.9881 -0.0247 0.0000 -0.0013
 0.0012 0.0158 0.0056 -0.0452 -0.0010
 0.0075 0.0004 0.0113 0.0003 -0.0129
 0.0011 -0.0020 0.0094 -0.0055 0.0018
 0.0006
 (41.39%) 0.6434* C 5 s(0.36%)p99.99(99.54%)d 0.18(0.07%)
 f 0.09(0.03%)
 0.0000 0.0592 -0.0087 -0.0063 0.0000
 -0.0275 0.0062 -0.0025 0.2300 -0.0023
 0.0027 0.9701 -0.0246 0.0033 0.0008
 -0.0045 -0.0052 -0.0208 0.0026 0.0121
 -0.0004 -0.0014 -0.0038 -0.0043 -0.0154
 0.0003 -0.0078 0.0031 -0.0044 0.0009
 0.0026
 44. (1.97471) BD (1) N 1- C 45
 (58.78%) 0.7667* N 1 s(31.68%)p 2.15(67.95%)d 0.01(0.34%)
 f 0.00(0.03%)
 0.0000 0.5628 -0.0014 0.0030 -0.0002
 -0.7437 0.0099 0.0023 -0.3501 -0.0079
 0.0081 0.0602 0.0039 -0.0021 0.0483
 0.0021 -0.0067 -0.0001 -0.0060 0.0002
 0.0100 0.0018 -0.0292 -0.0003 -0.0014
 0.0096 0.0048 -0.0003 0.0000 -0.0102
 -0.0090
 (41.22%) 0.6420* C 45 s(29.24%)p 2.42(70.67%)d 0.00(0.06%)
 f 0.00(0.03%)
 0.0000 0.5404 0.0208 0.0022 -0.0003
 0.7727 0.0001 0.0013 0.3294 -0.0216
 0.0042 -0.0247 0.0024 -0.0017 0.0048
 0.0157 0.0002 -0.0016 0.0044 -0.0053
 0.0111 0.0056 -0.0051 -0.0092 0.0001

-0.0079 -0.0034 -0.0028 0.0014 0.0048

0.0120

45. (1.93413) BD (1) P 2- P 3

(48.87%) 0.6991* P 2 s(11.67%)p 7.49(87.39%)d 0.08(0.91%)

f 0.00(0.03%)

0.0000 0.0000 0.3415 -0.0067 -0.0006

0.0000 0.4284 0.0263 -0.0026 0.0000

0.0000 -0.6102 -0.0019 0.0113 0.0004

0.0000 0.5631 -0.0070 -0.0103 -0.0005

-0.0295 -0.0093 0.0295 -0.0028 -0.0749

0.0182 -0.0333 0.0093 0.0109 -0.0014

-0.0111 0.0057 -0.0020 -0.0078 -0.0062

-0.0040 0.0012

(51.13%) 0.7150* P 3 s(11.62%)p 7.50(87.22%)d 0.10(1.13%)

f 0.00(0.03%)

0.0000 0.0000 0.3409 -0.0032 0.0003

0.0000 -0.1713 0.0020 0.0018 0.0000

0.0000 0.7506 0.0147 -0.0019 -0.0001

0.0000 -0.5284 0.0029 0.0075 0.0002

-0.0409 0.0025 0.0441 -0.0060 -0.0800

0.0027 -0.0235 -0.0120 0.0219 -0.0073

0.0103 -0.0027 0.0048 0.0055 0.0085

0.0037 -0.0012

46. (1.95806) BD (1) P 2- C 5

(38.01%) 0.6165* P 2 s(16.86%)p 4.89(82.39%)d 0.04(0.74%)

f 0.00(0.01%)

0.0000 0.0000 0.4095 0.0300 0.0006

0.0000 -0.8543 -0.0277 -0.0088 -0.0006

0.0000 -0.2883 -0.0053 -0.0074 -0.0010

0.0000 0.0966 -0.0259 -0.0032 0.0003

0.0486 0.0113 -0.0345 0.0043 -0.0103

-0.0010 0.0461 0.0197 -0.0318 -0.0061

-0.0038 0.0054 0.0021 -0.0034 0.0013
 -0.0024 -0.0061
 (61.99%) 0.7873* C 5 s(29.59%)p 2.37(70.10%)d 0.01(0.26%)
 f 0.00(0.05%)
 0.0000 0.5438 -0.0115 0.0073 0.0002
 0.7196 0.0393 -0.0023 0.4111 -0.0036
 -0.0069 -0.1103 0.0156 0.0085 0.0253
 0.0038 -0.0102 -0.0007 -0.0088 0.0021
 0.0275 -0.0027 -0.0309 0.0048 0.0061
 -0.0143 -0.0062 -0.0023 -0.0044 0.0089
 0.0112
 47. (1.93237) BD (1) P 2- C 6
 (40.18%) 0.6339* P 2 s(17.18%)p 4.79(82.23%)d 0.03(0.58%)
 f 0.00(0.01%)
 0.0000 0.0000 0.4144 0.0100 0.0009
 0.0000 0.0101 0.0169 0.0049 0.0005
 0.0000 0.7296 0.0203 0.0055 0.0006
 0.0000 0.5375 -0.0126 0.0058 -0.0001
 -0.0012 -0.0012 -0.0081 0.0030 0.0638
 0.0094 -0.0284 -0.0177 0.0196 -0.0077
 -0.0047 0.0019 -0.0008 -0.0044 0.0028
 -0.0014 -0.0069
 (59.82%) 0.7734* C 6 s(20.40%)p 3.89(79.41%)d 0.01(0.17%)
 f 0.00(0.02%)
 0.0000 0.4506 -0.0294 0.0071 0.0000
 -0.0498 -0.0020 0.0001 -0.7664 -0.0231
 0.0145 -0.4510 -0.0035 0.0114 0.0006
 0.0005 0.0018 -0.0001 0.0333 -0.0052
 -0.0234 0.0027 -0.0029 0.0000 0.0060
 -0.0048 -0.0041 0.0084 0.0029 0.0030
 0.0053
 48. (1.93245) BD (1) P 3- P 4

(50.61%) 0.7114* P 3 s(12.07%)p 7.19(86.74%)d 0.10(1.17%)

f 0.00(0.03%)

0.0000 0.0000 0.3473 -0.0025 0.0003

0.0000 -0.7510 -0.0104 0.0041 0.0002

0.0000 -0.4949 -0.0098 0.0020 0.0002

0.0000 -0.2410 0.0076 0.0067 0.0001

0.0532 0.0077 0.0697 -0.0125 0.0282

-0.0028 0.0502 -0.0028 -0.0214 -0.0038

0.0085 0.0044 0.0051 -0.0075 -0.0035

-0.0026 -0.0080

(49.39%) 0.7028* P 4 s(12.17%)p 7.14(86.93%)d 0.07(0.88%)

f 0.00(0.03%)

0.0000 0.0000 0.3488 -0.0040 -0.0004

0.0000 0.8269 0.0135 -0.0105 -0.0002

0.0000 0.2568 -0.0149 -0.0074 -0.0001

0.0000 0.3449 -0.0046 -0.0078 -0.0002

0.0584 -0.0171 0.0490 -0.0099 0.0248

0.0002 0.0329 0.0089 -0.0278 0.0058

-0.0049 -0.0045 -0.0084 0.0082 0.0044

0.0016 0.0076

49. (1.94784) BD (1) P 3- C 19

(39.53%) 0.6287* P 3 s(17.14%)p 4.79(82.05%)d 0.05(0.81%)

f 0.00(0.01%)

0.0000 0.0000 0.4137 0.0149 0.0014

0.0000 0.6197 0.0199 0.0095 0.0009

0.0000 -0.4066 -0.0026 -0.0065 -0.0003

0.0000 -0.5198 0.0195 -0.0074 -0.0001

-0.0342 -0.0152 -0.0590 -0.0152 0.0448

0.0078 0.0090 0.0085 0.0258 -0.0080

0.0040 -0.0006 0.0002 -0.0036 0.0053

-0.0002 -0.0047

(60.47%) 0.7777* C 19 s(21.37%)p 3.67(78.44%)d 0.01(0.16%)

f 0.00(0.02%)

0.0000 0.4616 -0.0246 0.0055 0.0001
-0.6745 -0.0191 0.0122 0.3909 0.0108
-0.0086 0.4193 0.0048 -0.0125 -0.0207
0.0023 -0.0282 0.0044 0.0166 -0.0027
0.0090 -0.0004 -0.0033 -0.0004 -0.0077
-0.0059 -0.0003 0.0010 -0.0072 -0.0009
0.0069

50. (1.96711) BD (1) P 4- C 5

(38.77%) 0.6227* P 4 s(16.38%)p 5.06(82.92%)d 0.04(0.68%)

f 0.00(0.01%)

0.0000 0.0000 0.4042 0.0206 0.0007
0.0000 -0.3595 -0.0138 0.0009 0.0004
0.0000 0.8226 0.0121 0.0099 0.0010
0.0000 -0.1492 -0.0254 -0.0049 -0.0004
-0.0406 -0.0140 0.0025 0.0085 -0.0054
-0.0090 -0.0571 -0.0104 -0.0376 -0.0049
0.0029 -0.0011 -0.0064 0.0037 0.0049
0.0031 -0.0011

(61.23%) 0.7825* C 5 s(32.80%)p 2.04(66.94%)d 0.01(0.20%)

f 0.00(0.05%)

0.0000 0.5723 -0.0208 0.0046 -0.0001
0.0491 0.0071 -0.0019 -0.8013 -0.0116
0.0153 0.1562 0.0047 -0.0024 -0.0195
0.0031 0.0054 -0.0008 -0.0140 0.0005
-0.0273 -0.0028 -0.0253 0.0049 -0.0070
-0.0035 0.0142 -0.0068 -0.0039 -0.0126
0.0080

51. (1.93381) BD (1) P 4- C 32

(40.10%) 0.6333* P 4 s(17.59%)p 4.65(81.81%)d 0.03(0.59%)

f 0.00(0.01%)

0.0000 0.0000 0.4193 0.0095 0.0009

0.0000 -0.4153 -0.0058 -0.0026 0.0002
 0.0000 -0.2455 -0.0279 -0.0059 -0.0009
 0.0000 0.7645 0.0024 0.0083 0.0001
 0.0052 0.0121 -0.0476 -0.0112 -0.0142
 -0.0121 0.0030 0.0058 0.0542 0.0019
 -0.0010 -0.0027 -0.0068 0.0008 0.0061
 0.0022 -0.0043
 (59.90%) 0.7739* C 32 s(20.75%)p 3.81(79.06%)d 0.01(0.17%)
 f 0.00(0.02%)
 0.0000 0.4547 0.0272 0.0065 0.0000
 0.3685 0.0172 -0.0077 0.3565 0.0137
 -0.0056 -0.7257 -0.0111 0.0158 0.0091
 -0.0006 -0.0260 0.0044 -0.0215 0.0027
 0.0035 -0.0010 0.0212 -0.0036 -0.0030
 0.0063 0.0072 -0.0048 -0.0071 -0.0020
 -0.0030

Table B.5 Abridged second order perturbation theory analysis of fock matrix in NBO basis of **1**

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u
38. LP (1) N 1	112. BD*(1) P 4- C 5	21.97	0.49	0.093
38. LP (1) N 1	156. BD*(2) C 45- C 53	16.1	0.35	0.0067
39. LP (1) P 2	109. BD*(2) N 1- C 5	8.01	0.36	0.048
41. LP (1) P 4	109. BD*(2) N 1- C 5	8.16	0.36	0.048
45. BD (1) P 2- P 3	108. BD*(1) N 1- C 5	6.86	1.02	0.075
46. BD (1) P 2- C 5	110. BD*(1) N 1- C 45	8.54	0.96	0.081
48. BD (1) P 3- P 4	108. BD*(1) N 1- C 5	7.87	1.02	0.08

B.3.3 DFT of [2-H][OTf]

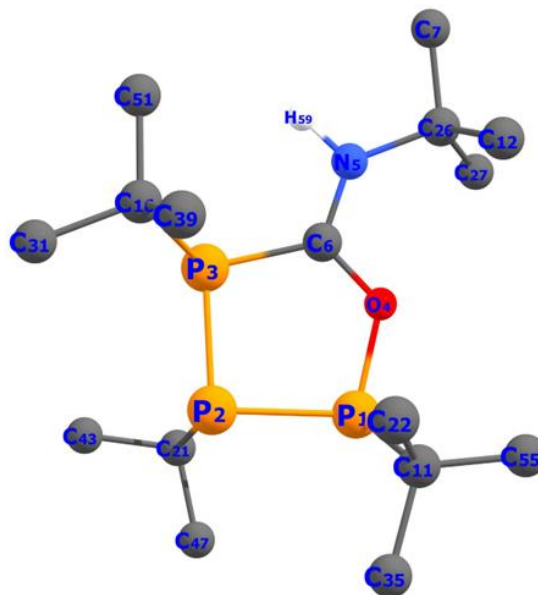


Figure B.31 DFT optimized gas-phase structure of [2-H][OTf] (PBE0-D3/def2-TZVP)

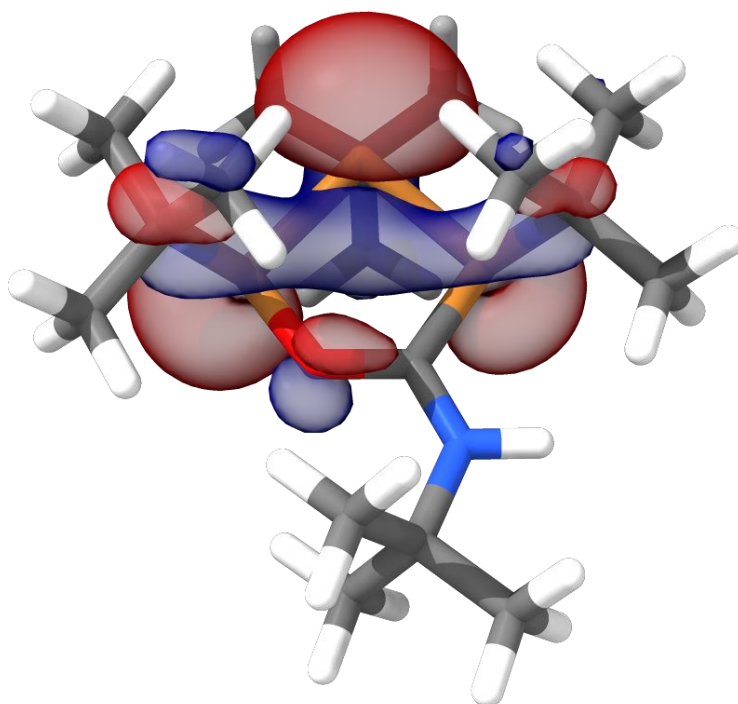


Figure B.32 Calculated HOMO of [2-H][OTf]

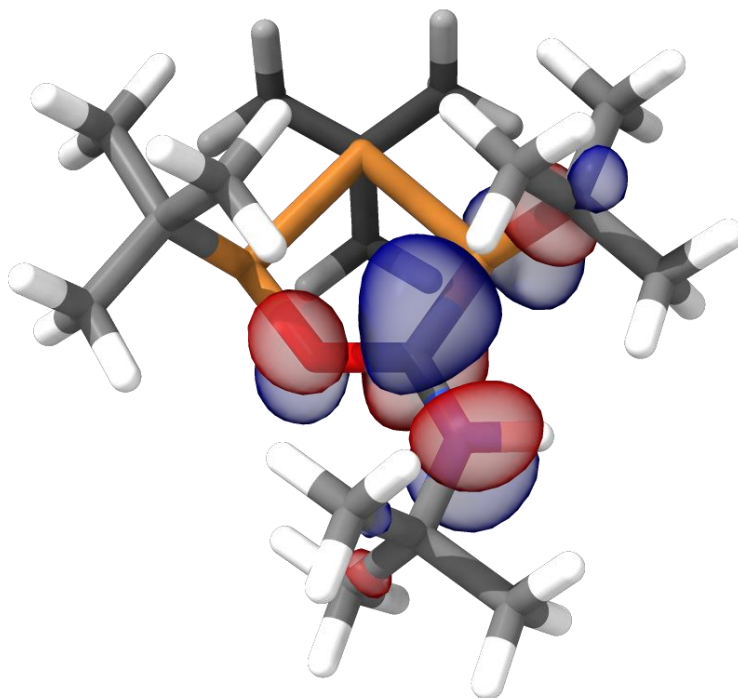


Figure B.33 Calculated LUMO of [2-H][OTf]

Table B.6 XYZ coordinates of computed structure of [2-H][OTf]

Freq	RPBE1PBE	def2TZVP	
Charge	1		
Multiplicity	1		
Total Energy	-1.823023477459202E+03		
Dipole Moment	1.02440407E+01	5.41230625E+00	6.46438943E+00
P	7.015515	1.719077	1.98701
P	5.190258	2.399333	0.932343
P	4.738328	3.962618	2.395484
O	6.682903	2.409965	3.542537
N	5.721085	3.839356	4.954664
C	5.787896	3.316153	3.758894
C	5.959484	4.422013	7.261574
H	6.114098	5.472074	7.00018
H	6.484163	4.23321	8.197738
H	4.894211	4.250453	7.437337
C	6.671427	-0.056456	2.384341
C	6.246303	2.043913	6.555165
H	5.181127	1.857908	6.707058
H	6.763949	1.822837	7.489565
H	6.620572	1.359026	5.795632
C	2.973446	3.637558	2.976826
C	7.020805	4.419534	-0.014899
H	6.606672	5.171744	0.660187
H	7.40823	4.944491	-0.893121
H	7.866547	3.933409	0.476469
C	5.967285	3.416484	-0.455294
C	5.318154	-0.334086	3.013113
H	5.190993	0.194573	3.960004
H	5.226222	-1.403787	3.221671
H	4.503324	-0.056723	2.342622

C	6.498727	3.497952	6.17925
C	7.978597	3.770122	5.940969
H	8.394683	3.114604	5.177331
H	8.523969	3.595742	6.86971
H	8.141495	4.807489	5.642961
C	2.134858	3.930074	1.732408
H	2.277018	4.952884	1.375395
H	1.077846	3.805153	1.981699
H	2.366812	3.240333	0.917661
C	6.786876	-0.750825	1.025485
H	5.978233	-0.459901	0.350304
H	6.722789	-1.831959	1.172891
H	7.74302	-0.543064	0.536801
C	2.724345	2.219576	3.45859
H	2.921538	1.492564	2.670193
H	1.675818	2.114273	3.752637
H	3.337072	1.967406	4.327309
C	4.807266	4.133792	-1.139118
H	4.031026	3.4367	-1.464121
H	5.176628	4.661164	-2.023027
H	4.351046	4.878304	-0.480933
C	6.578557	2.384345	-1.400381
H	7.419356	1.860338	-0.936816
H	6.96136	2.889809	-2.291195
H	5.844366	1.642863	-1.725431
C	2.623929	4.648658	4.067068
H	3.063535	4.386665	5.032857
H	1.541069	4.644959	4.218335
H	2.914728	5.667465	3.799078
C	7.803707	-0.519628	3.302104
H	8.785527	-0.331501	2.861729
H	7.712602	-1.595679	3.472673

H	7.765603	-0.026466	4.27583
H	5.053614	4.589228	5.059182

B.3.4 DFT of 2

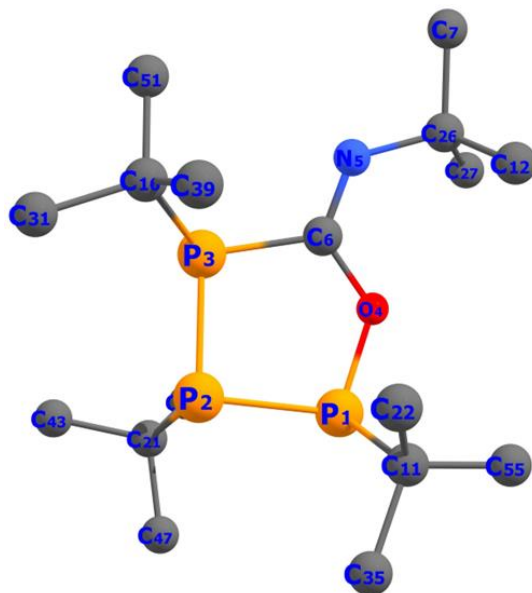


Figure B.34 DFT optimized gas-phase structure of **2** (PBE0-D3/def2-TZVP)

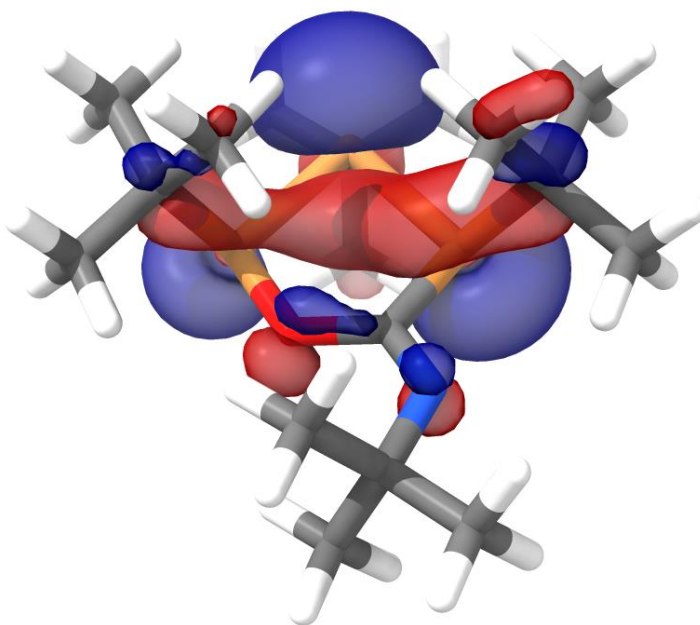


Figure B.35 Calculated HOMO of **2**

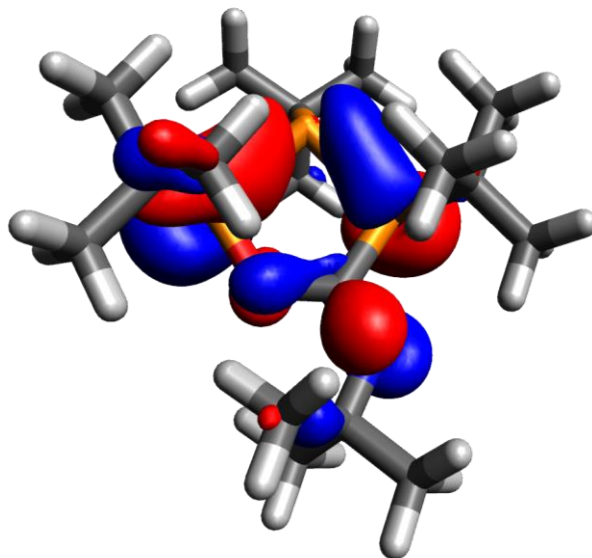


Figure B.36 Calculated HOMO-1 of 2

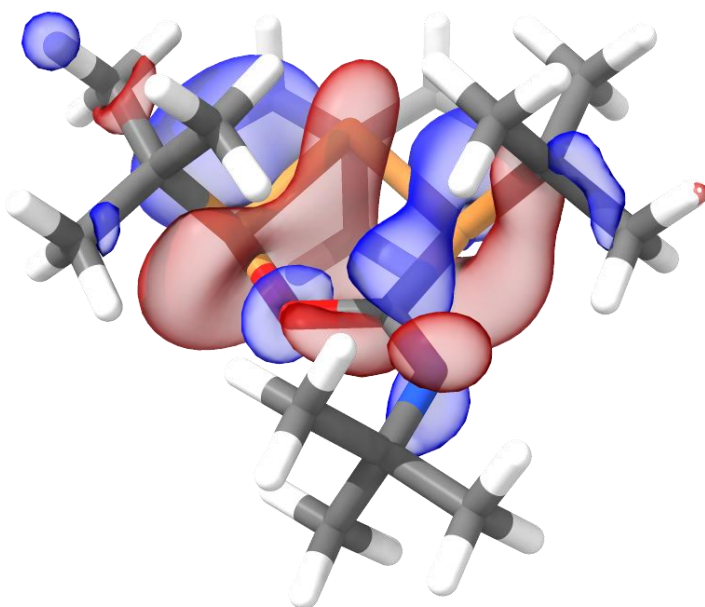


Figure B.37 Calculated LUMO of 2

Table B.7 XYZ coordinates of computed structure of **2**

Freq	RPBE1PBE	def2TZVP	
Charge	0		
Multiplicity	1		
Total Energy	-1.822619403623957E+03		
Dipole Moment	-1.30089495E-01	-5.98931289E-01	-3.25255709E-01
P	7.086864	1.775128	1.974669
P	5.217902	2.403003	0.964577
P	4.82739	3.989518	2.415849
O	6.894214	2.522514	3.462116
N	5.606574	3.718348	4.976439
C	5.839433	3.319169	3.810455
C	5.719232	4.10801	7.327781
H	5.722959	5.184378	7.14488
H	6.244579	3.910102	8.26519
H	4.680692	3.787427	7.436065
C	6.707869	0.000699	2.411808
C	6.336383	1.871128	6.436225
H	5.301226	1.52605	6.495849
H	6.823317	1.646407	7.388291
H	6.845508	1.313182	5.651852
C	3.047937	3.723777	2.963808
C	7.00925	4.389747	-0.115957
H	6.621562	5.142257	0.573783
H	7.356156	4.905226	-1.018227
H	7.873116	3.907401	0.346795
C	5.938944	3.376275	-0.488901
C	5.385868	-0.209075	3.128411
H	5.321889	0.38359	4.042243
H	5.276418	-1.262637	3.407174
H	4.5455	0.055795	2.484874
C	6.382654	3.373201	6.167311

C	7.826788	3.851611	6.027751
H	8.347793	3.318407	5.233123
H	8.363901	3.690482	6.965835
H	7.849436	4.919978	5.801657
C	2.193352	3.919176	1.715061
H	2.377666	4.890573	1.248536
H	1.135428	3.87613	1.992252
H	2.380237	3.139039	0.972947
C	6.719033	-0.747338	1.08135
H	5.885103	-0.442404	0.444221
H	6.626531	-1.821897	1.265867
H	7.651157	-0.583694	0.532406
C	2.776285	2.358312	3.570452
H	2.959591	1.562111	2.847023
H	1.72692	2.295819	3.87834
H	3.395979	2.185459	4.45141
C	4.760903	4.085759	-1.147726
H	3.968527	3.384221	-1.421769
H	5.096658	4.592365	-2.058383
H	4.33454	4.841894	-0.483545
C	6.516059	2.33141	-1.439082
H	7.364694	1.81004	-0.987579
H	6.873453	2.818361	-2.352108
H	5.766992	1.587196	-1.722512
C	2.734203	4.828086	3.972182
H	3.358246	4.735076	4.861058
H	1.681822	4.756529	4.266552
H	2.898593	5.817709	3.538286
C	7.869865	-0.481093	3.279455
H	8.828435	-0.34977	2.771045
H	7.746827	-1.545486	3.503315
H	7.914626	0.056989	4.228179

Table B.8 Abridged calculated Wiberg bond indices of **2**

	Atom	1	2	3	4	5	6	7	8	9
1	P	0	0.9466	0.0278	0.6824	0.0285	0.0314	0.0007	0	0.0001
2	P	0.9466	0	0.9845	0.0322	0.0195	0.0202	0.0001	0	0
3	P	0.0278	0.9845	0	0.0446	0.0564	0.93	0.0005	0	0.0005
4	O	0.6824	0.0322	0.0446	0	0.1399	0.9561	0.0008	0	0.0001
5	N	0.0285	0.0195	0.0564	0.1399	0	1.8276	0.0162	0.0011	0.0133
6	C	0.0314	0.0202	0.93	0.9561	1.8276	0	0.0077	0.0003	0.0004
11	C	0.8647	0.0172	0.0028	0.0243	0.0052	0.0043	0	0	0
16	C	0.0057	0.0166	0.8865	0.0068	0.0108	0.0132	0.0001	0	0
21	C	0.0155	0.8864	0.0194	0.0019	0.0014	0.0039	0	0	0
26	C	0.0012	0.0024	0.0241	0.0035	0.9651	0.0131	0.9977	0.001	0.0015

Table B.9 Abridged natural bond orbital analysis of **2**

LP = Lone pair

BD = Bonding

35. (1.95150) LP (1) P 1 s(58.35%)p 0.71(41.61%)d 0.00(0.04%)

f 0.00(0.00%)

0.0000 0.0000 0.7638 -0.0080 -0.0001

0.0000 -0.2801 0.0176 -0.0007 -0.0002

0.0000 -0.2749 0.0122 -0.0036 0.0004

0.0000 -0.5112 0.0148 -0.0031 0.0001

-0.0139 0.0066 -0.0019 0.0023 -0.0030

0.0069 -0.0007 0.0001 -0.0087 0.0055

-0.0003 0.0041 -0.0007 -0.0008 0.0015

0.0010 0.0008

36. (1.94229) LP (1) P 2 s(56.54%)p 0.77(43.28%)d 0.00(0.17%)

f 0.00(0.00%)

0.0000 0.0000 0.7520 0.0010 -0.0006

0.0000 -0.1677 0.0007 -0.0012 0.0002

0.0000 0.0005 0.0012 0.0000 0.0000

0.0000 0.6360 -0.0149 0.0038 0.0001

0.0053 -0.0008 0.0157 -0.0087 -0.0009

0.0010 -0.0162 0.0015 -0.0315 0.0112

-0.0017 -0.0019 0.0007 0.0001 0.0001

-0.0031 0.0022

37. (1.90085) LP (1) P 3 s(52.75%)p 0.89(47.15%)d 0.00(0.09%)

f 0.00(0.00%)

0.0000 0.0000 0.7263 -0.0042 -0.0002

0.0000 -0.1730 0.0147 0.0013 -0.0002

0.0000 0.3408 -0.0104 0.0022 -0.0003

0.0000 -0.5700 0.0152 -0.0008 0.0002

0.0078 -0.0044 -0.0089 0.0020 0.0168

-0.0119 0.0117 -0.0040 -0.0110 0.0073

0.0016 0.0038 -0.0006 -0.0001 0.0012

-0.0009 -0.0031

38. (1.93932) LP (1) O 4 s(35.34%)p 1.83(64.55%)d 0.00(0.12%)

f 0.00(0.00%)

0.0000 0.5944 0.0068 -0.0015 0.0001

0.5463 0.0012 0.0037 -0.5517 -0.0053

-0.0038 -0.2063 -0.0030 -0.0021 0.0284

-0.0003 0.0115 -0.0002 -0.0117 0.0000

-0.0022 0.0005 0.0087 0.0000 0.0014

-0.0012 0.0013 0.0002 0.0005 0.0016

0.0021

39. (1.83753) LP (2) O 4 s(0.18%)p99.99(99.64%)d 0.88(0.16%)

f 0.04(0.01%)

0.0000 0.0426 0.0061 0.0008 0.0000

-0.1997 0.0002 -0.0015 0.2057 0.0016

0.0003 -0.9562 0.0026 -0.0038 -0.0109

0.0002 0.0247 -0.0014 -0.0207 -0.0007

0.0004 -0.0002 -0.0216 0.0002 0.0060

0.0018 -0.0024 0.0007 -0.0051 -0.0012

-0.0016

40. (1.85310) LP (1) N 5 s(27.40%)p 2.64(72.38%)d 0.01(0.21%)

f 0.00(0.00%)

0.0000 0.5234 -0.0082 -0.0023 -0.0001

0.2152 -0.0057 0.0013 0.8155 0.0275

0.0039 0.1082 0.0053 -0.0001 -0.0272

0.0012 -0.0039 0.0004 -0.0075 0.0002

0.0302 -0.0025 0.0193 0.0002 -0.0012

-0.0010 -0.0037 -0.0001 -0.0002 -0.0015

0.0054

41. (1.94510) BD (1) P 1- P 2

(47.70%) 0.6907* P 1 s(13.36%)p 6.41(85.65%)d 0.07(0.97%)

f 0.00(0.02%)

0.0000 0.0000 0.3655 -0.0030 -0.0010

0.0000 -0.3859 -0.0297 0.0054 0.0001

0.0000 0.7660 -0.0055 -0.0111 -0.0007
 0.0000 0.3460 -0.0046 -0.0058 -0.0002
 -0.0529 0.0039 -0.0272 0.0097 0.0562
 -0.0133 -0.0475 0.0104 -0.0174 0.0026
 -0.0062 -0.0008 -0.0053 -0.0033 -0.0096
 0.0085 -0.0014
 (52.30%) 0.7232* P 2 s(12.26%)p 7.07(86.67%)d 0.09(1.05%)
 f 0.00(0.02%)
 0.0000 0.0000 0.3501 -0.0037 0.0003
 0.0000 0.3956 0.0031 -0.0019 0.0000
 0.0000 -0.7842 -0.0146 0.0041 0.0002
 0.0000 -0.3081 0.0073 0.0062 0.0001
 -0.0657 -0.0016 -0.0432 0.0045 0.0608
 -0.0060 -0.0182 -0.0067 -0.0128 -0.0061
 0.0090 -0.0024 0.0048 0.0026 0.0074
 -0.0072 0.0009
 42. (1.97456) BD (1) P 1- O 4
 (19.78%) 0.4448* P 1 s(11.50%)p 7.54(86.73%)d 0.15(1.77%)
 f 0.00(0.01%)
 0.0000 0.0000 0.3338 0.0592 0.0005
 0.0000 0.8460 0.0683 0.0127 0.0022
 0.0000 0.3478 0.0077 0.0083 0.0008
 0.0000 -0.1533 -0.0457 -0.0073 -0.0006
 0.0934 0.0163 -0.0032 -0.0252 -0.0136
 -0.0019 0.0527 0.0402 -0.0564 -0.0165
 0.0025 -0.0060 -0.0062 -0.0027 -0.0028
 -0.0010 0.0060
 (80.22%) 0.8956* O 4 s(30.27%)p 2.29(69.43%)d 0.01(0.29%)
 f 0.00(0.01%)
 0.0000 0.5502 -0.0036 0.0018 -0.0002
 -0.7863 -0.0116 0.0063 -0.2381 0.0114
 0.0006 0.1375 0.0084 -0.0013 0.0079

-0.0012 -0.0216 0.0003 -0.0019 -0.0004

0.0417 -0.0003 -0.0246 0.0018 -0.0021

0.0050 0.0022 0.0013 0.0008 -0.0001

-0.0063

43. (1.94747) BD (1) P 1- C 11

(37.59%) 0.6131* P 1 s(17.04%)p 4.82(82.13%)d 0.05(0.83%)

f 0.00(0.01%)

0.0000 0.0000 0.4125 0.0131 0.0008

0.0000 0.1694 -0.0137 -0.0015 -0.0003

0.0000 -0.4534 -0.0301 0.0013 -0.0001

0.0000 0.7654 0.0017 0.0094 0.0000

-0.0137 -0.0035 0.0191 0.0067 -0.0533

-0.0093 -0.0113 -0.0102 0.0671 -0.0019

0.0013 -0.0004 -0.0063 -0.0052 -0.0039

-0.0012 0.0007

(62.41%) 0.7900* C 11 s(21.15%)p 3.72(78.65%)d 0.01(0.18%)

f 0.00(0.02%)

0.0000 0.4589 -0.0292 0.0062 0.0001

-0.0930 -0.0123 0.0030 0.5403 0.0182

-0.0092 -0.6965 -0.0097 0.0155 -0.0078

0.0013 0.0080 -0.0012 -0.0343 0.0023

-0.0092 0.0000 0.0209 -0.0022 -0.0022

0.0003 0.0097 0.0044 0.0069 -0.0032

-0.0027

44. (1.93999) BD (1) P 2- P 3

(51.64%) 0.7186* P 2 s(13.63%)p 6.26(85.31%)d 0.08(1.04%)

f 0.00(0.03%)

0.0000 0.0000 0.3692 -0.0005 0.0003

0.0000 0.6564 0.0066 -0.0034 0.0000

0.0000 0.5938 0.0158 -0.0025 -0.0001

0.0000 -0.2631 0.0083 0.0053 0.0001

0.0623 0.0069 -0.0572 0.0075 -0.0390

0.0039 0.0322 -0.0048 -0.0218 -0.0046
 0.0087 -0.0059 -0.0051 -0.0029 -0.0070
 -0.0047 0.0067
 (48.36%) 0.6954* P 3 s(13.39%)p 6.40(85.74%)d 0.06(0.83%)
 f 0.00(0.03%)
 0.0000 0.0000 0.3660 -0.0022 -0.0009
 0.0000 -0.6607 -0.0252 0.0064 0.0001
 0.0000 -0.5550 0.0057 0.0101 0.0004
 0.0000 0.3348 -0.0047 -0.0060 -0.0004
 0.0650 -0.0025 -0.0386 0.0088 -0.0408
 0.0068 -0.0063 0.0090 -0.0263 0.0043
 -0.0067 0.0023 0.0085 0.0032 0.0082
 0.0037 -0.0077
 45. (1.94789) BD (1) P 2- C 21
 (40.46%) 0.6361* P 2 s(17.52%)p 4.66(81.68%)d 0.05(0.79%)
 f 0.00(0.01%)
 0.0000 0.0000 0.4185 0.0107 0.0014
 0.0000 -0.6096 -0.0187 -0.0102 -0.0006
 0.0000 0.1309 0.0012 0.0021 0.0001
 0.0000 -0.6536 0.0163 -0.0088 -0.0003
 -0.0058 -0.0058 0.0654 0.0183 -0.0139
 -0.0034 0.0157 0.0131 0.0510 -0.0015
 0.0040 -0.0038 0.0004 -0.0051 0.0017
 -0.0022 0.0016
 (59.54%) 0.7716* C 21 s(21.10%)p 3.73(78.73%)d 0.01(0.15%)
 f 0.00(0.02%)
 0.0000 0.4586 -0.0257 0.0061 0.0001
 0.6752 0.0232 -0.0114 -0.1260 -0.0059
 0.0023 0.5608 0.0057 -0.0155 -0.0063
 0.0007 0.0341 -0.0047 -0.0067 0.0011
 0.0141 -0.0010 0.0078 -0.0018 -0.0046
 0.0100 -0.0015 0.0039 -0.0021 0.0052

-0.0030

46. (1.95324) BD (1) P 3- C 6

(38.62%) 0.6215* P 3 s(15.60%)p 5.36(83.58%)d 0.05(0.81%)

f 0.00(0.01%)

0.0000 0.0000 0.3945 0.0193 0.0005

0.0000 0.6840 0.0190 0.0053 0.0006

0.0000 -0.6020 -0.0097 -0.0079 -0.0009

0.0000 -0.0660 -0.0232 -0.0065 -0.0002

-0.0769 -0.0180 0.0094 -0.0105 -0.0054

0.0037 -0.0112 0.0070 -0.0375 -0.0084

0.0013 -0.0027 0.0064 -0.0019 0.0040

-0.0038 -0.0039

(61.38%) 0.7834* C 6 s(33.26%)p 2.00(66.48%)d 0.01(0.22%)

f 0.00(0.05%)

0.0000 0.5750 -0.0426 0.0101 0.0005

-0.6177 -0.0480 0.0057 0.5183 0.0207

-0.0120 0.1068 0.0154 0.0022 -0.0368

0.0117 -0.0063 0.0022 0.0031 -0.0024

0.0039 -0.0019 -0.0212 0.0123 -0.0033

0.0115 -0.0102 0.0005 -0.0035 0.0048

0.0134

47. (1.93831) BD (1) P 3- C 16

(40.61%) 0.6373* P 3 s(18.23%)p 4.45(81.18%)d 0.03(0.57%)

f 0.00(0.01%)

0.0000 0.0000 0.4269 0.0089 0.0010

0.0000 0.2283 -0.0018 -0.0027 -0.0003

0.0000 0.4529 0.0246 0.0061 0.0005

0.0000 0.7442 -0.0053 0.0080 0.0000

0.0087 0.0104 0.0301 0.0064 0.0399

0.0139 -0.0022 -0.0080 0.0525 0.0015

-0.0021 -0.0015 0.0067 -0.0028 0.0040

-0.0033 -0.0024

(59.39%) 0.7706* C 16 s(20.70%)p 3.82(79.11%)d 0.01(0.17%)

f 0.00(0.02%)

0.0000 0.4541 -0.0275 0.0066 0.0000

-0.2057 -0.0093 0.0048 -0.5414 -0.0189

0.0092 -0.6744 -0.0105 0.0157 0.0100

-0.0013 0.0139 -0.0022 0.0322 -0.0042

-0.0070 0.0001 0.0172 -0.0029 -0.0010

-0.0016 -0.0102 0.0019 -0.0082 -0.0002

0.0041

48. (1.99136) BD (1) O 4- C 6

(68.36%) 0.8268* O 4 s(34.08%)p 1.93(65.64%)d 0.01(0.27%)

f 0.00(0.01%)

0.0000 0.5838 0.0011 -0.0004 0.0001

0.1996 0.0006 -0.0001 0.7705 -0.0164

-0.0056 0.1500 -0.0056 -0.0020 0.0079

0.0010 0.0012 0.0005 0.0211 0.0007

-0.0411 -0.0022 -0.0225 -0.0009 -0.0023

-0.0019 -0.0051 -0.0017 0.0012 -0.0069

-0.0022

(31.64%) 0.5625* C 6 s(27.92%)p 2.58(71.97%)d 0.00(0.10%)

f 0.00(0.01%)

0.0000 0.5270 0.0372 -0.0066 -0.0007

-0.2135 0.0070 -0.0087 -0.8100 0.0396

-0.0061 -0.1275 0.0055 -0.0042 0.0134

0.0069 0.0018 0.0019 0.0001 0.0092

-0.0034 -0.0227 -0.0067 -0.0089 0.0032

0.0030 0.0078 0.0015 -0.0018 0.0077

0.0007

49. (1.98855) BD (1) N 5- C 6

(59.21%) 0.7695* N 5 s(40.88%)p 1.43(58.59%)d 0.01(0.50%)

f 0.00(0.03%)

0.0000 0.6392 0.0170 0.0005 0.0005

-0.7114 0.0206 0.0004 -0.2406 0.0057
 0.0052 0.1463 -0.0032 0.0005 0.0471
 0.0015 -0.0033 -0.0004 -0.0034 -0.0006
 0.0360 0.0011 -0.0385 0.0012 -0.0016
 0.0089 0.0035 0.0023 0.0007 -0.0094
 -0.0086
 (40.79%) 0.6387* C 6 s(38.32%)p 1.61(61.56%)d 0.00(0.08%)
 f 0.00(0.04%)
 0.0000 0.6177 0.0410 -0.0046 -0.0006
 0.7511 -0.0379 0.0176 0.1849 -0.0176
 0.0053 0.1229 -0.0014 -0.0024 0.0034
 0.0142 0.0025 0.0017 0.0020 -0.0007
 0.0104 0.0176 -0.0077 -0.0104 -0.0014
 -0.0116 -0.0030 0.0006 0.0002 0.0103
 0.0118
 50. (1.96774) BD (2) N 5- C 6
 (60.32%) 0.7767* N 5 s(0.80%)p99.99(98.91%)d 0.33(0.26%)
 f 0.04(0.03%)
 0.0000 0.0887 0.0097 0.0009 0.0001
 -0.1586 0.0086 -0.0006 0.1146 -0.0047
 0.0017 -0.9748 0.0224 -0.0017 0.0043
 -0.0005 0.0305 0.0055 0.0380 -0.0001
 0.0133 0.0003 0.0004 -0.0002 0.0121
 0.0038 -0.0016 -0.0109 -0.0025 -0.0027
 0.0008
 (39.68%) 0.6299* C 6 s(0.55%)p99.99(99.31%)d 0.21(0.12%)
 f 0.05(0.03%)
 0.0000 0.0716 0.0175 0.0056 0.0000
 0.0537 -0.0049 0.0032 0.1868 -0.0040
 0.0039 -0.9773 0.0074 -0.0015 0.0040
 0.0039 -0.0248 -0.0137 -0.0173 0.0031
 -0.0021 0.0018 -0.0026 0.0008 0.0158

-0.0006 -0.0052 -0.0026 -0.0011 0.0009
 0.0020
 51. (1.96647) BD (1) N 5- C 26
 (58.74%) 0.7664* N 5 s(30.71%)p 2.25(68.97%)d 0.01(0.29%)
 f 0.00(0.04%)
 0.0000 0.5541 -0.0055 0.0024 -0.0005
 0.6448 -0.0001 -0.0011 -0.5105 -0.0074
 0.0094 -0.1147 -0.0034 0.0011 -0.0425
 -0.0021 -0.0088 -0.0005 0.0118 0.0001
 -0.0125 0.0007 -0.0264 0.0000 0.0040
 -0.0082 0.0065 -0.0021 0.0036 0.0031
 -0.0142
 (41.26%) 0.6423* C 26 s(23.06%)p 3.33(76.89%)d 0.00(0.05%)
 f 0.00(0.01%)
 0.0000 0.4801 0.0083 0.0016 0.0002
 -0.7258 -0.0048 -0.0017 0.4749 -0.0183
 0.0055 0.1272 -0.0023 0.0008 0.0160
 -0.0055 0.0040 0.0002 -0.0030 -0.0013
 -0.0045 0.0063 0.0093 0.0007 -0.0023
 -0.0011 -0.0060 -0.0009 -0.0007 -0.0009
 0.0039

Table B.10 Abridged second order perturbation theory analysis of fock matrix in NBO basis of 2

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u
39. LP(2) O4	109. BD*(2) N5-C6	33.33	0.4	0.103
40. LP(1) N5	107. BD*(1) O4-C6	26.33	0.64	0.115
46. BD(1) P3-C6	110. BD*(1) N5-C26	8.62	0.87	0.077
37. LP(1) P3	109. BD*(2) N5-C6	5.88	0.38	0.042
38. LP(1) O4	105. BD*(1) P3-C6	7.56	0.7	0.065

Supplementary references

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Appendix C.

Supplementary Information on Chapter 4

C.1 NMR spectra

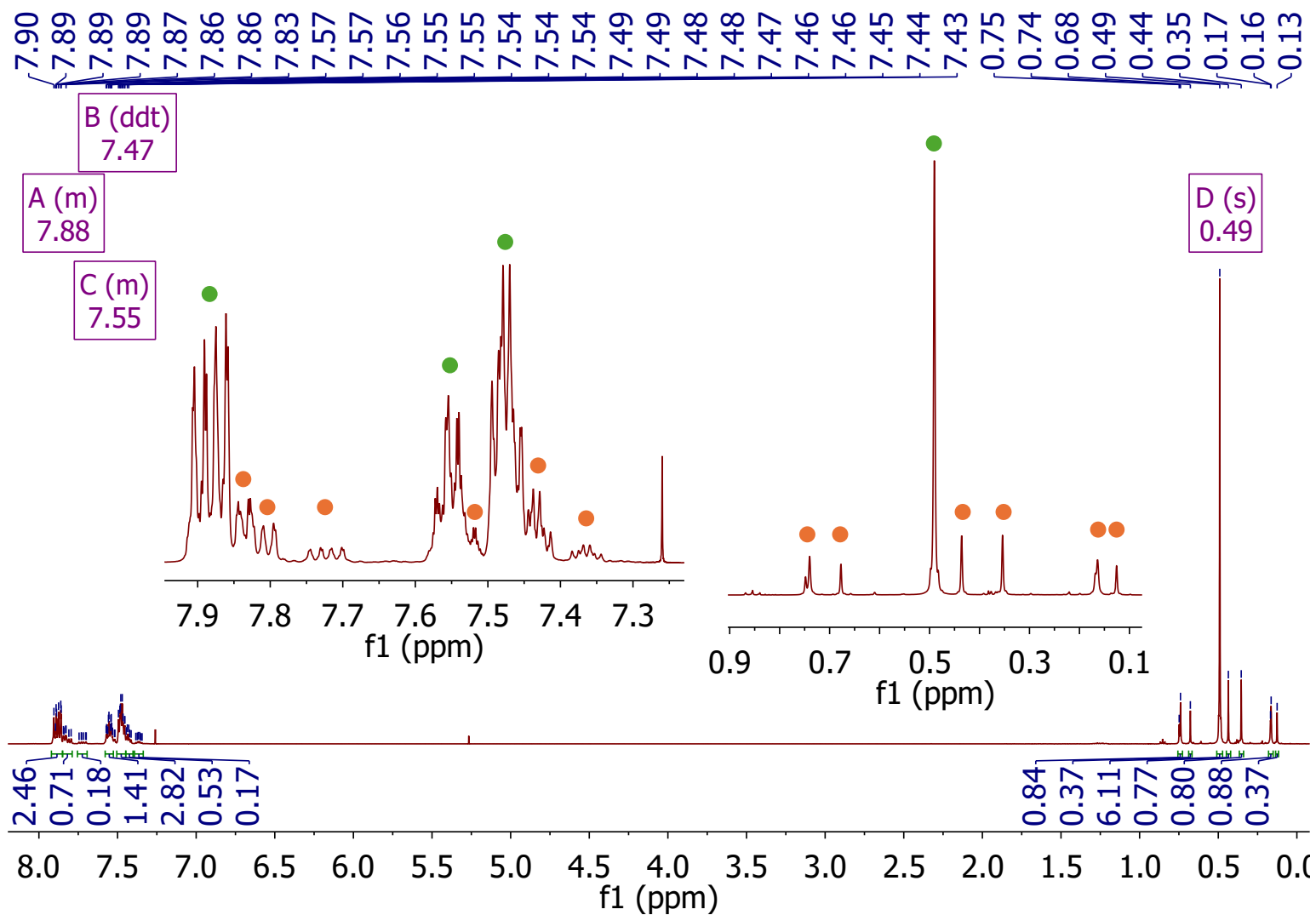


Figure C.1 ^1H NMR spectrum (500 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ (green = main product, orange = equilibration products).

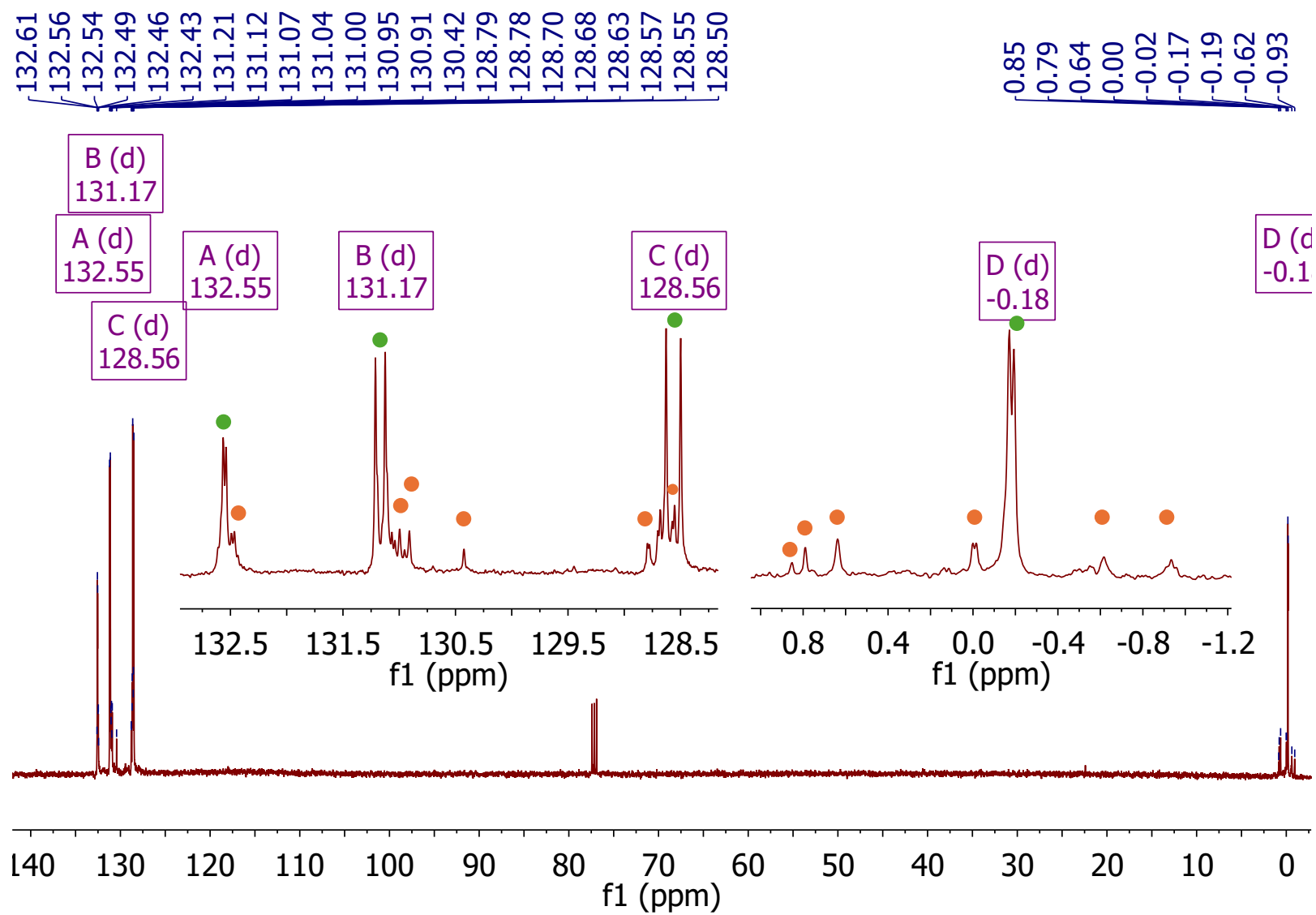


Figure C.2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ (green = main product, orange = equilibration products).

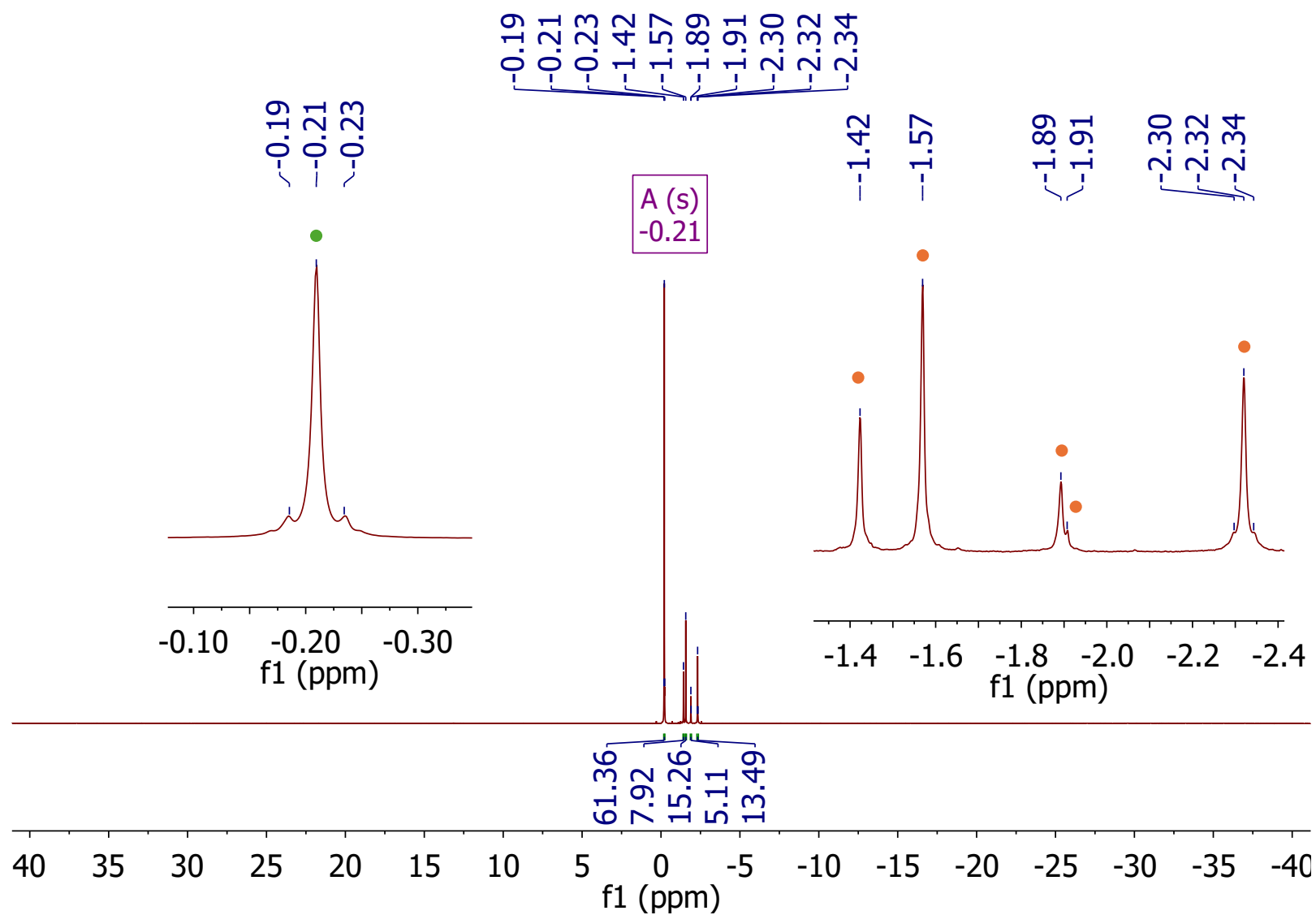


Figure C.3 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ (green = main product, orange = equilibration products).

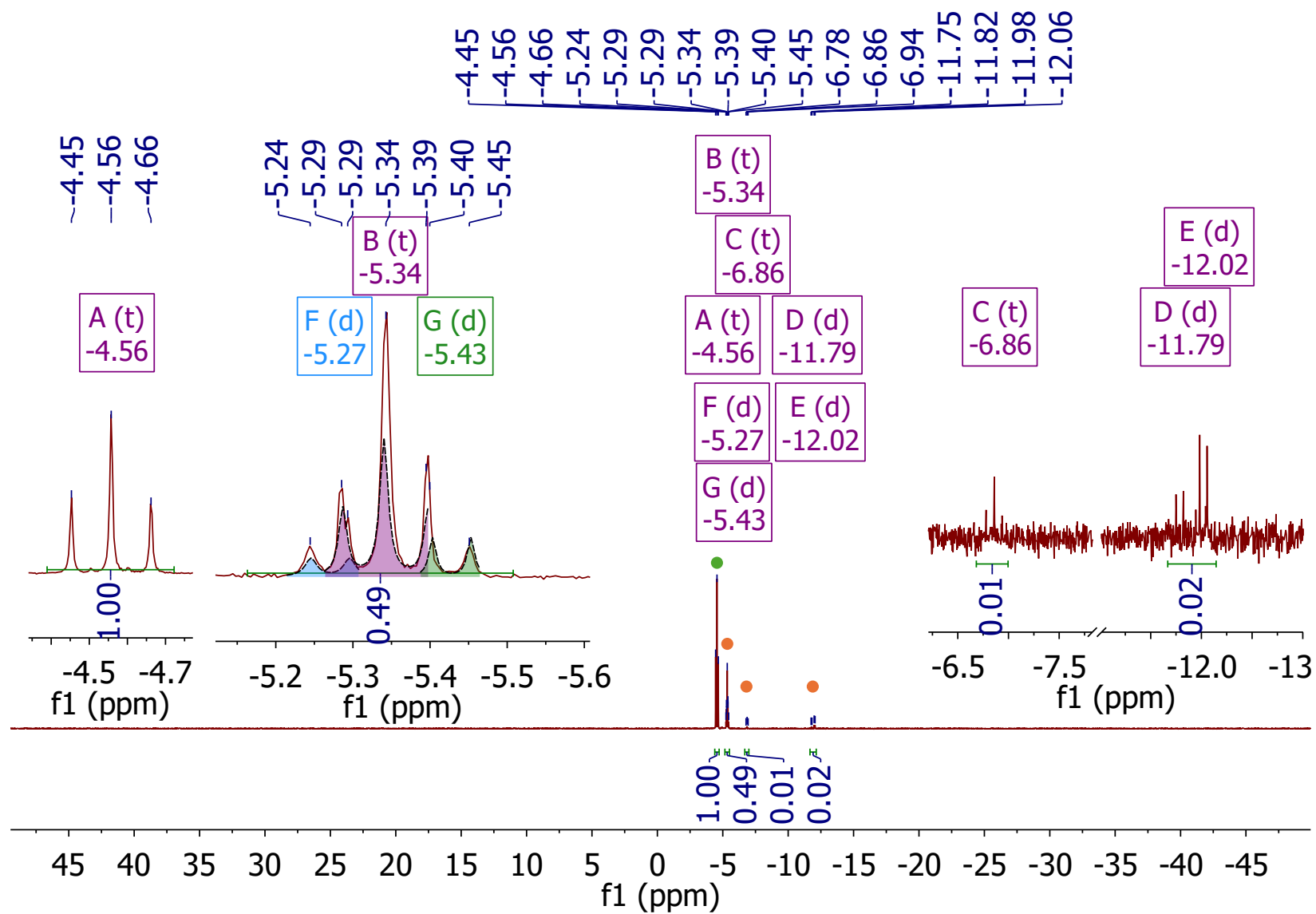


Figure C.4 ^{29}Si DEPT NMR spectrum (99 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}$ (green = main product, orange = equilibration products).

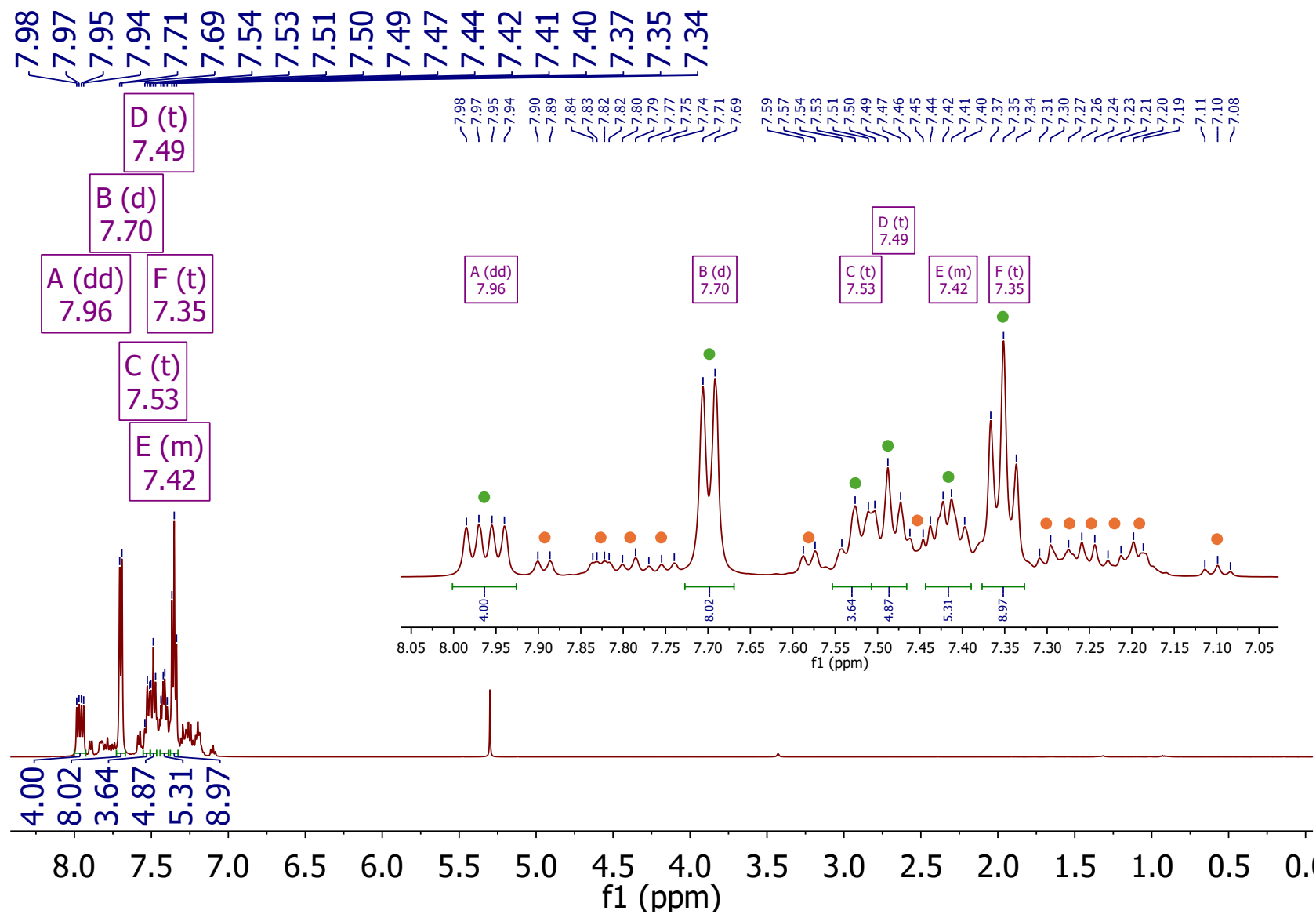


Figure C.5 ^1H NMR spectrum (500 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ (green = main product, orange = equilibration products).

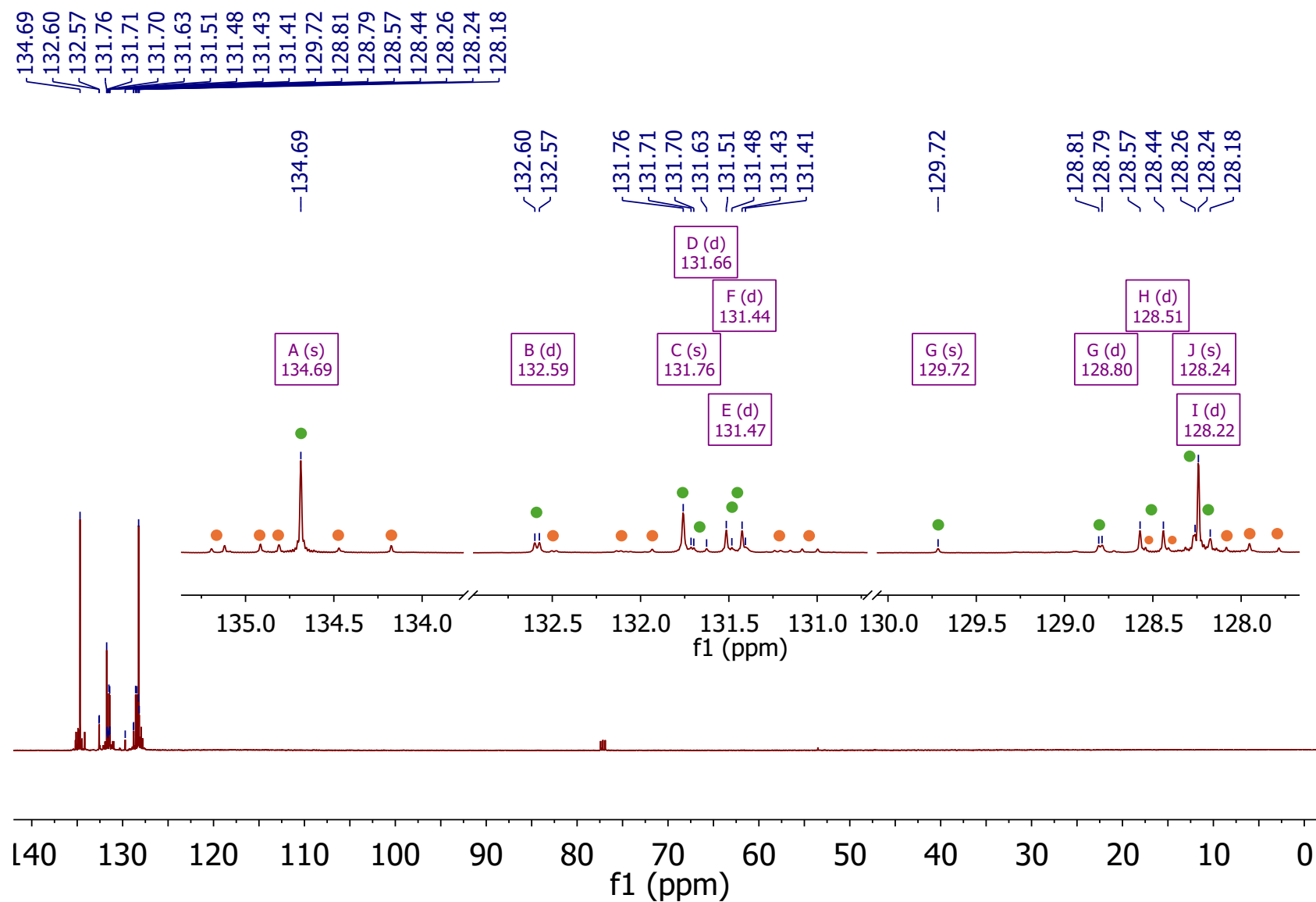


Figure C.6 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ (green = main product, orange = equilibration products).

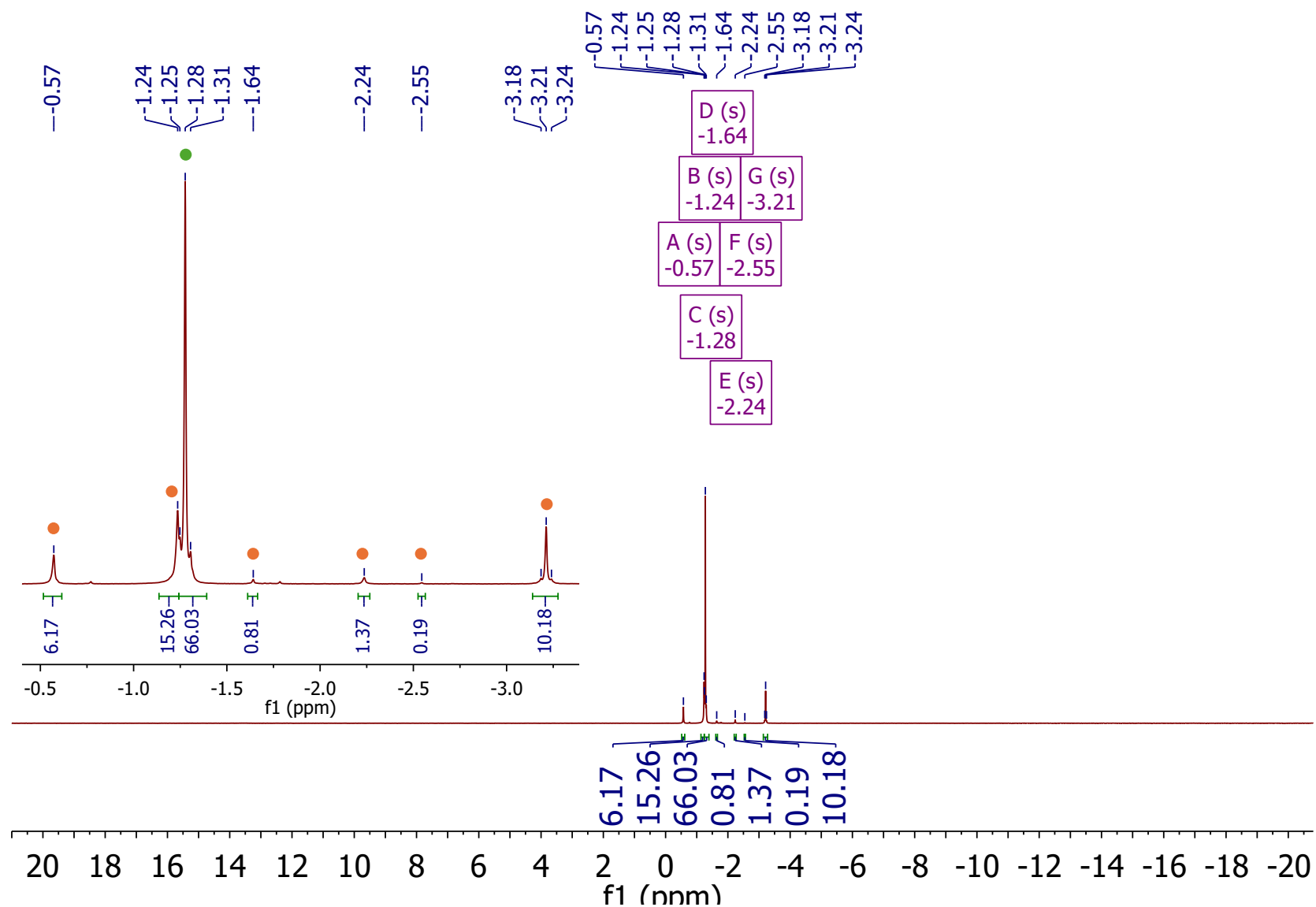


Figure C.7 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ (green = main product, orange = equilibration products).

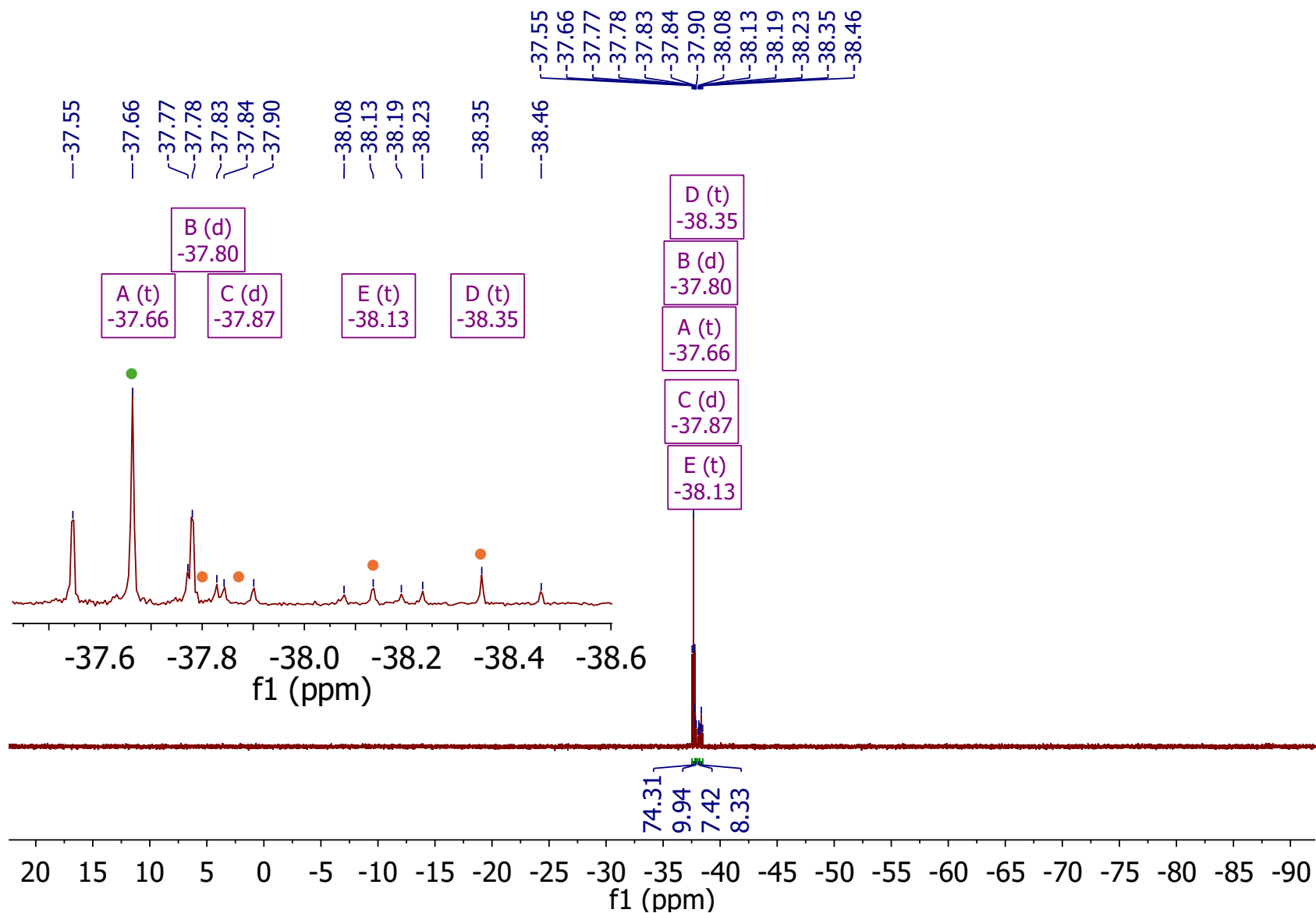


Figure C.8 ^{29}Si DEPT NMR spectrum (99 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$ (green = main product, orange = equilibration products).

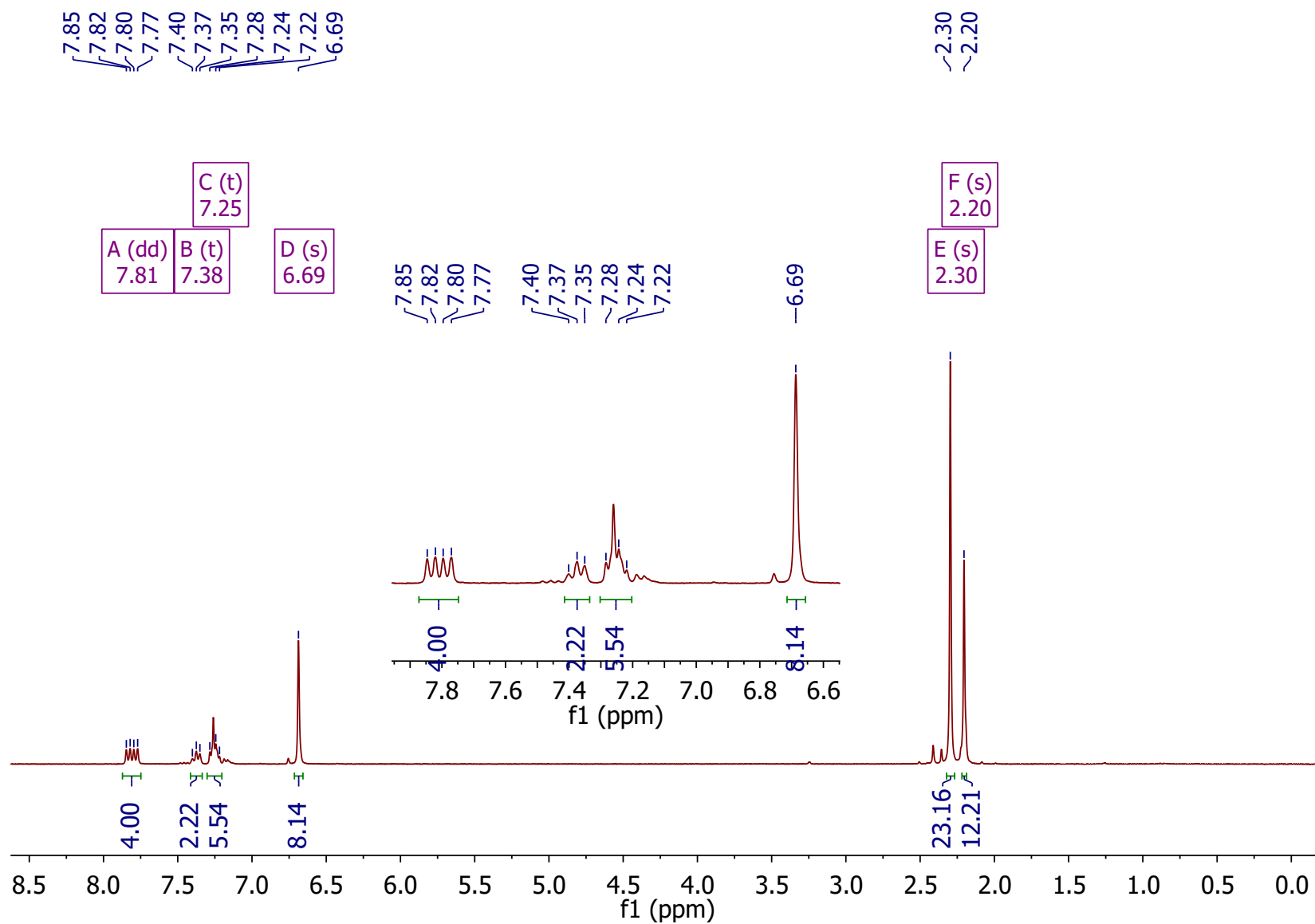


Figure C.9 ^1H NMR spectrum (500 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Me}}_3$.

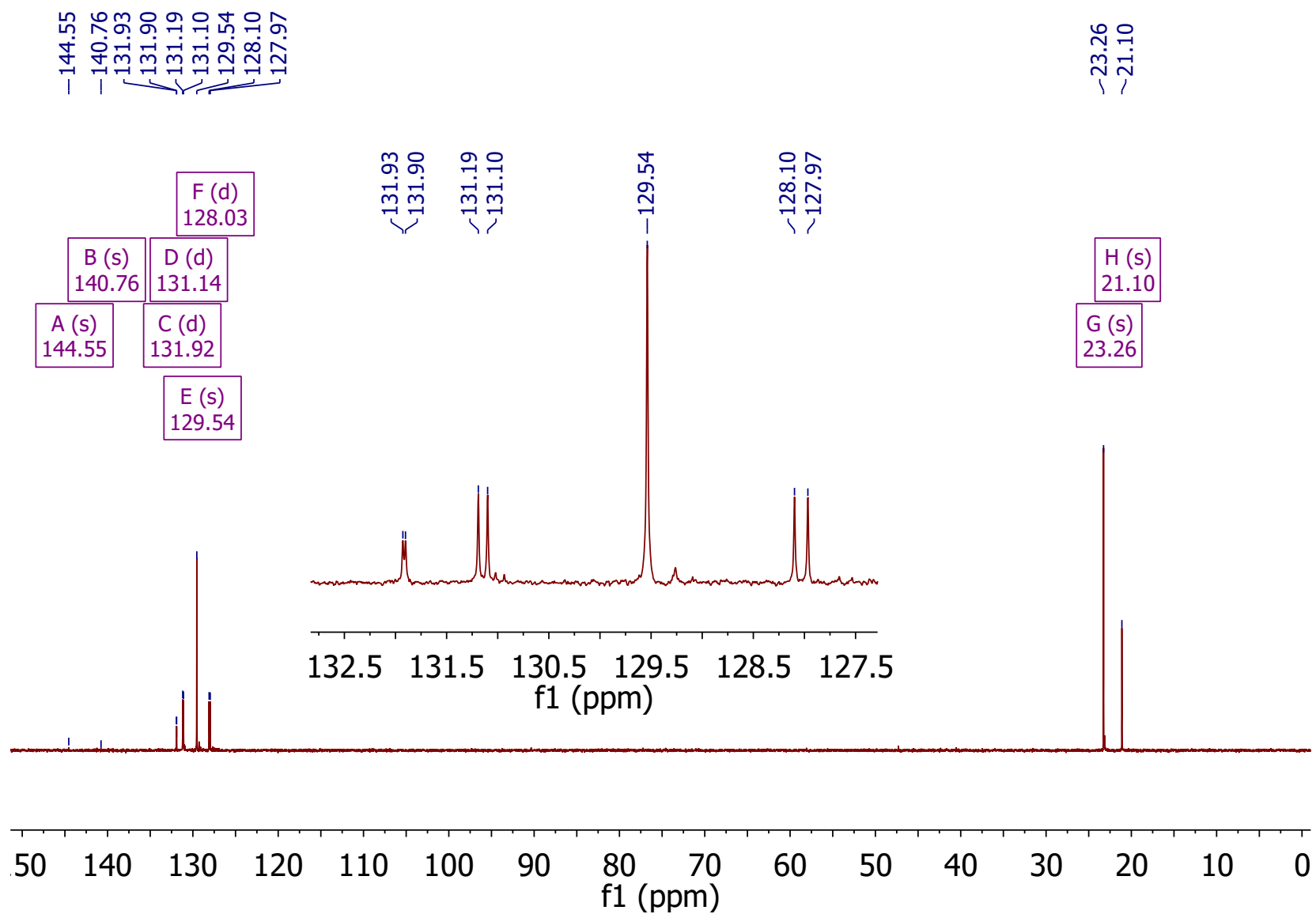


Figure C.10 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$.

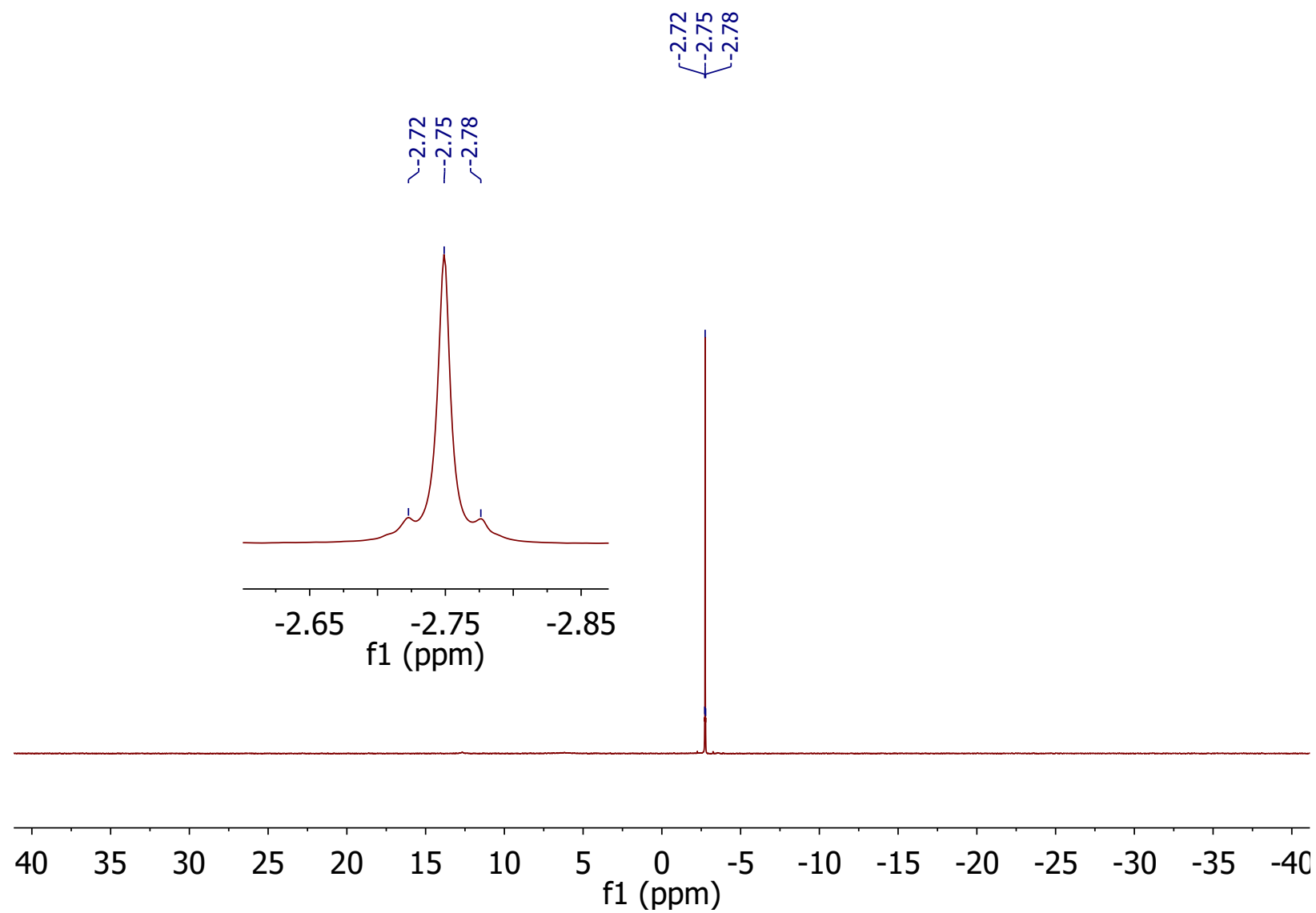


Figure C.11 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$

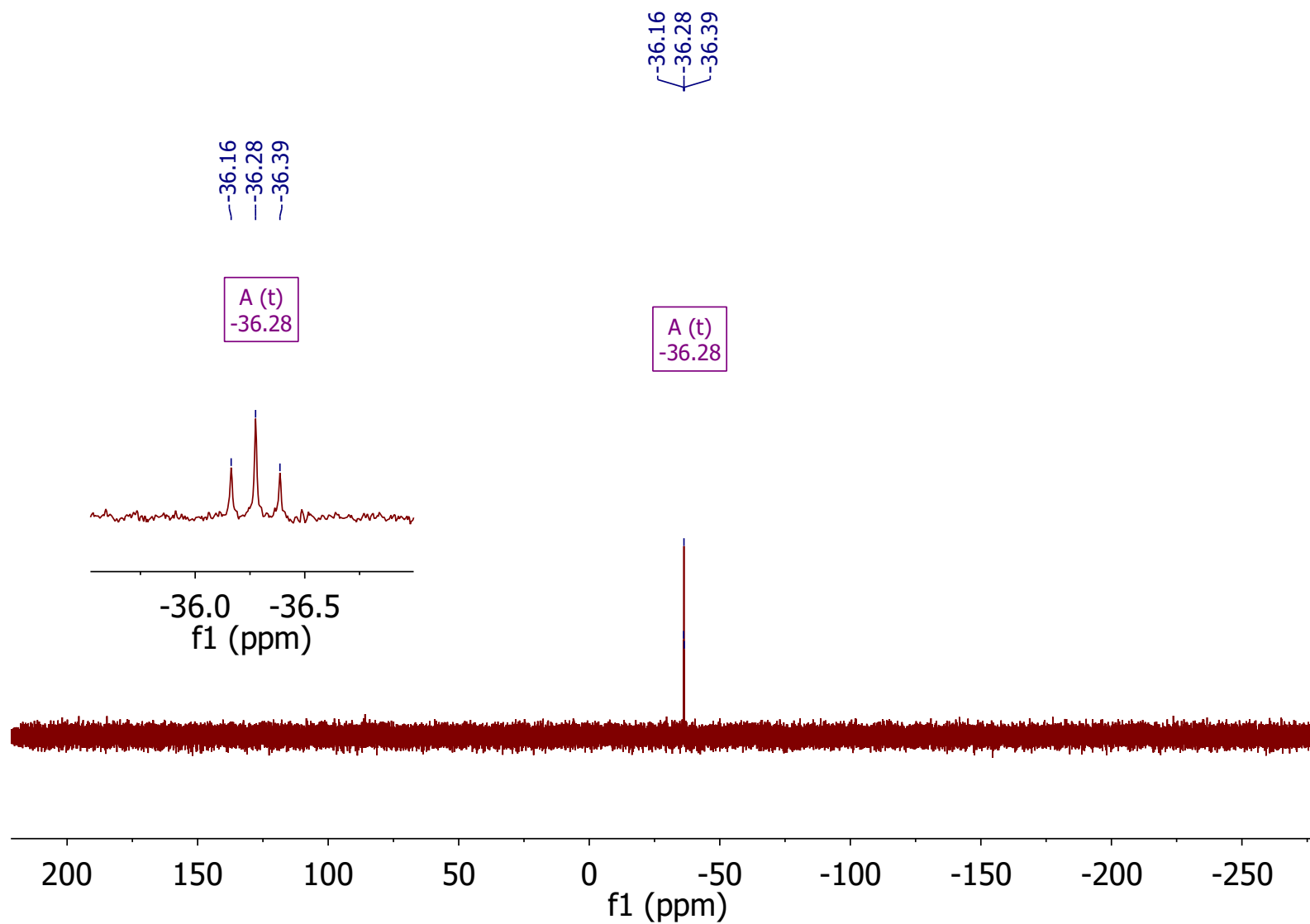


Figure C.12 ^{29}Si DEPT NMR spectrum (99 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$ grown at -30 °C in CH_2Cl_2 /hexanes for 7 days

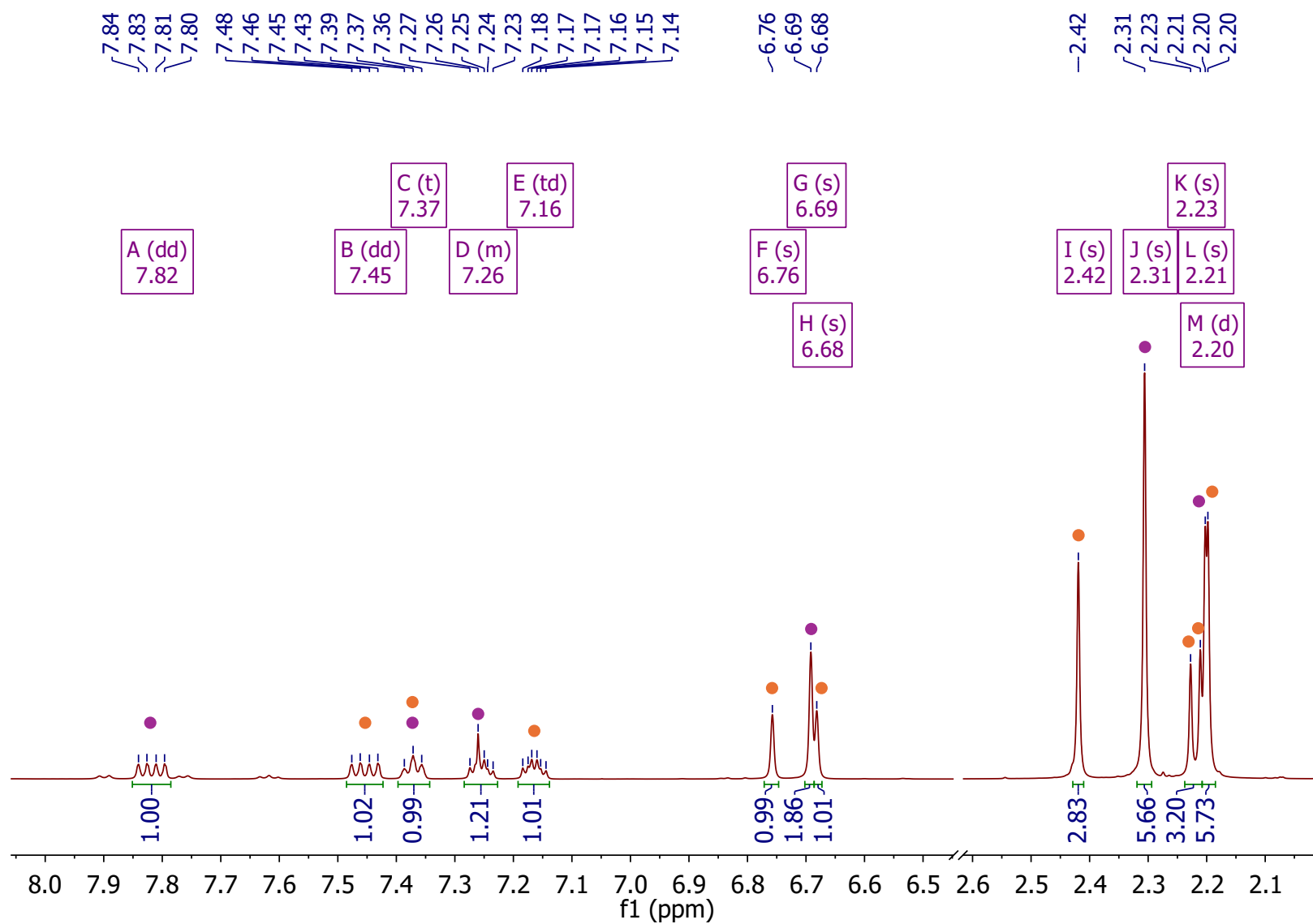


Figure C.13 ^1H NMR spectrum (500 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$ grown at -30°C over 21 days (blue = all-*trans*, orange = all-*cis*)

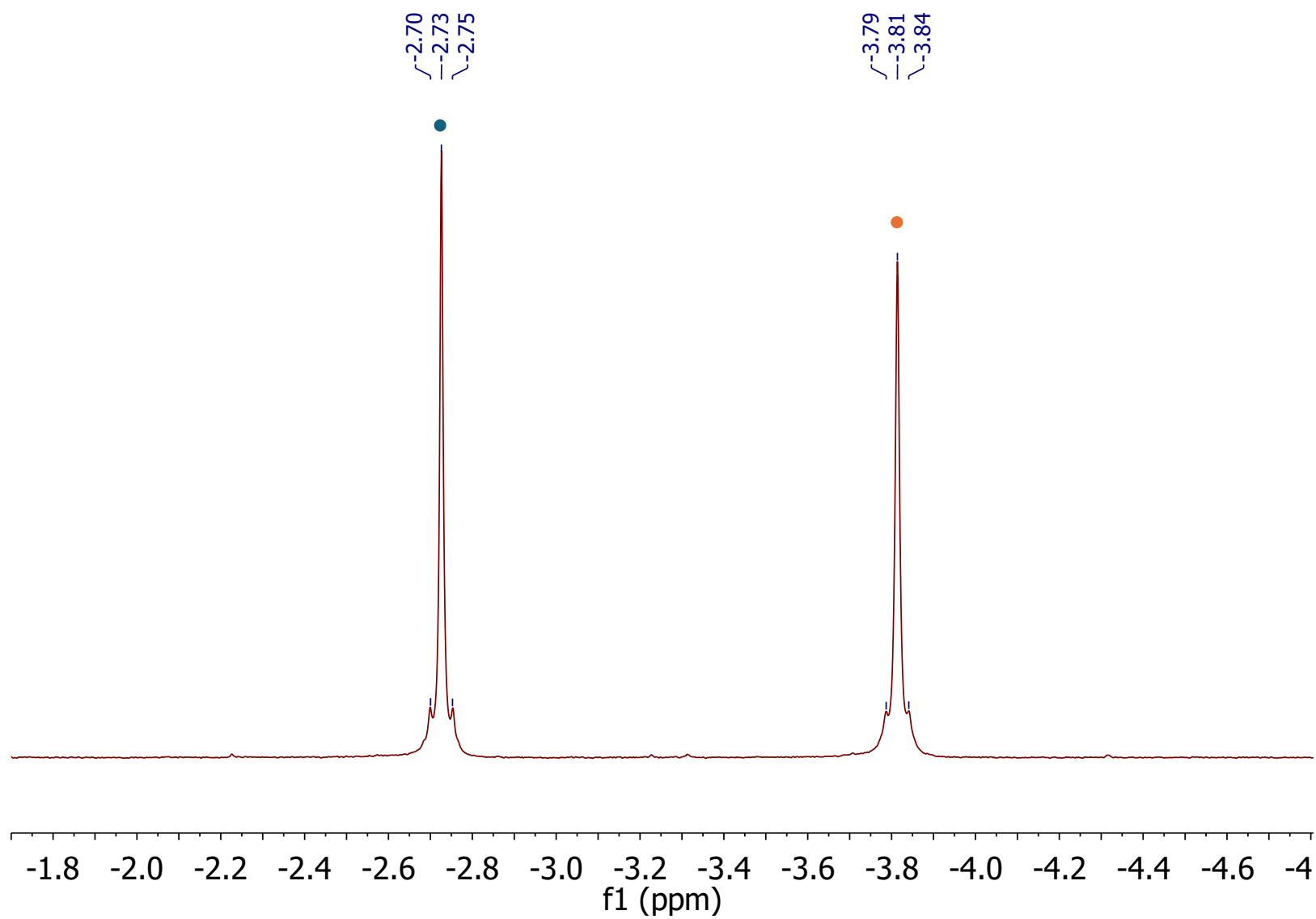


Figure C.14 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$ grown at $-30\text{ }^\circ\text{C}$ over 21 days (blue = all-*trans*, orange = all-*cis*)

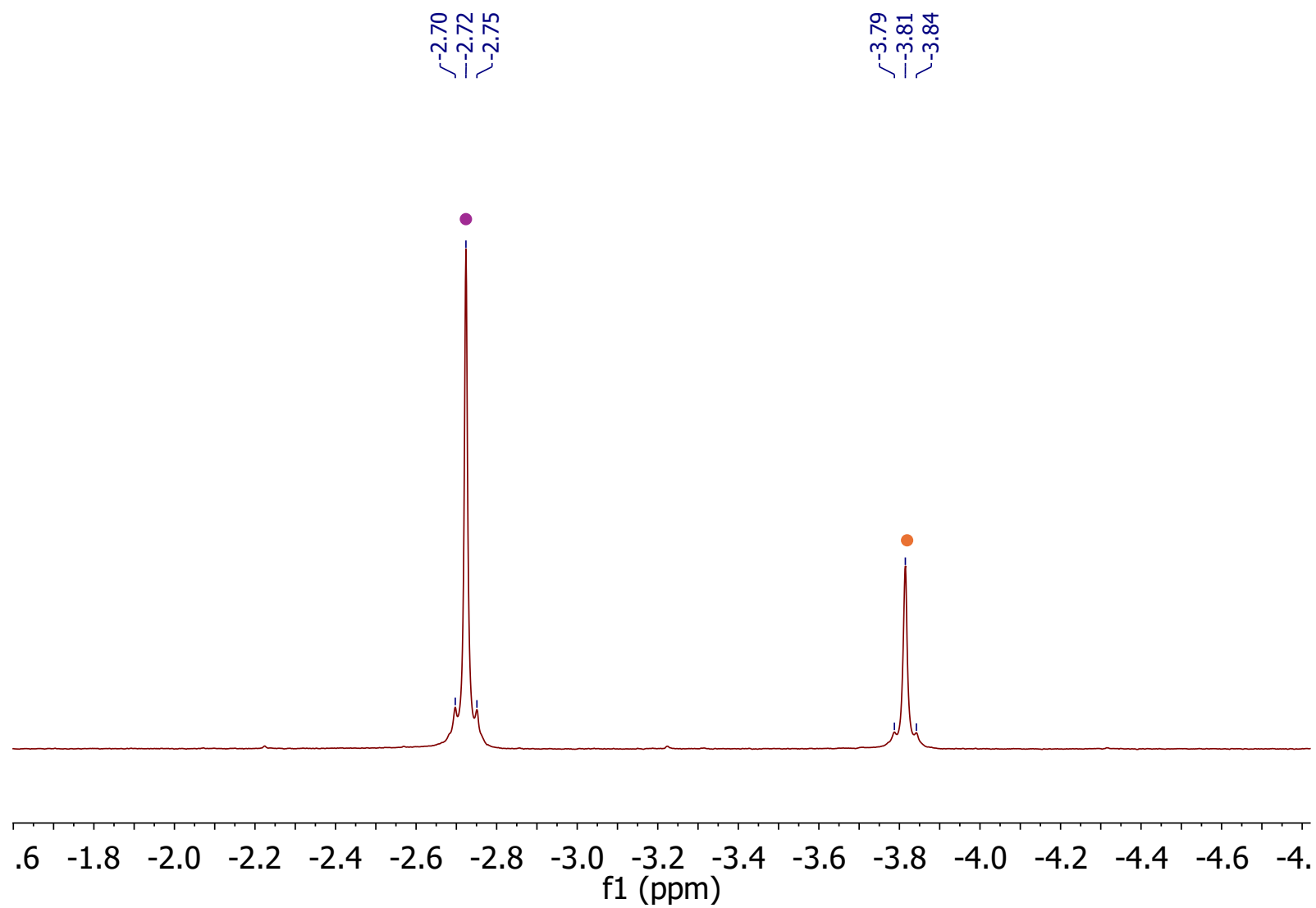


Figure C.15 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$ grown at $-30\text{ }^\circ\text{C}$ over 21 days, 7 days post-dissolution (blue = all-*trans*, orange = all-*cis*)

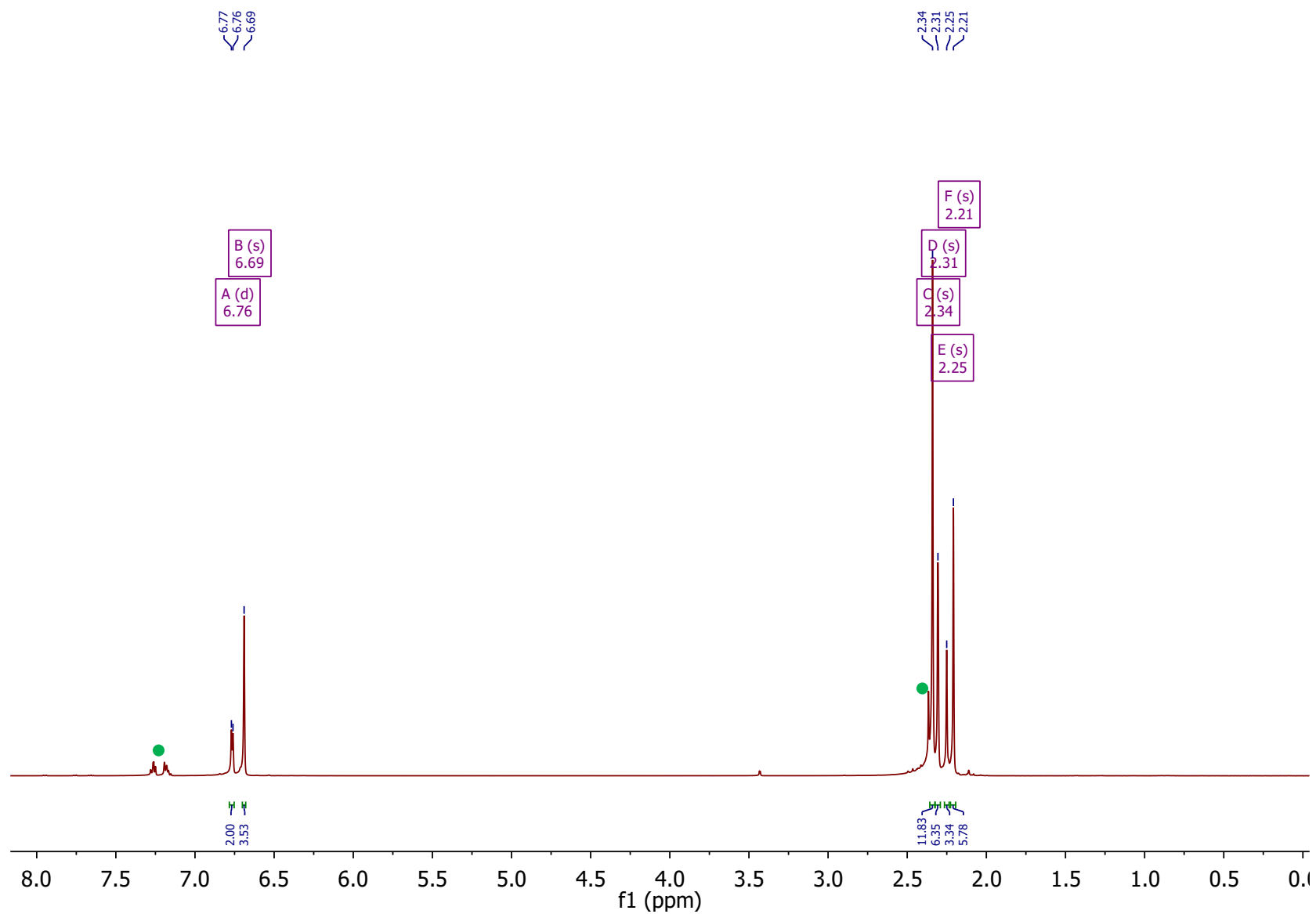


Figure C.16 ^1H NMR spectrum (500 MHz, CDCl_3) of $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$ (green = toluene in lattice)

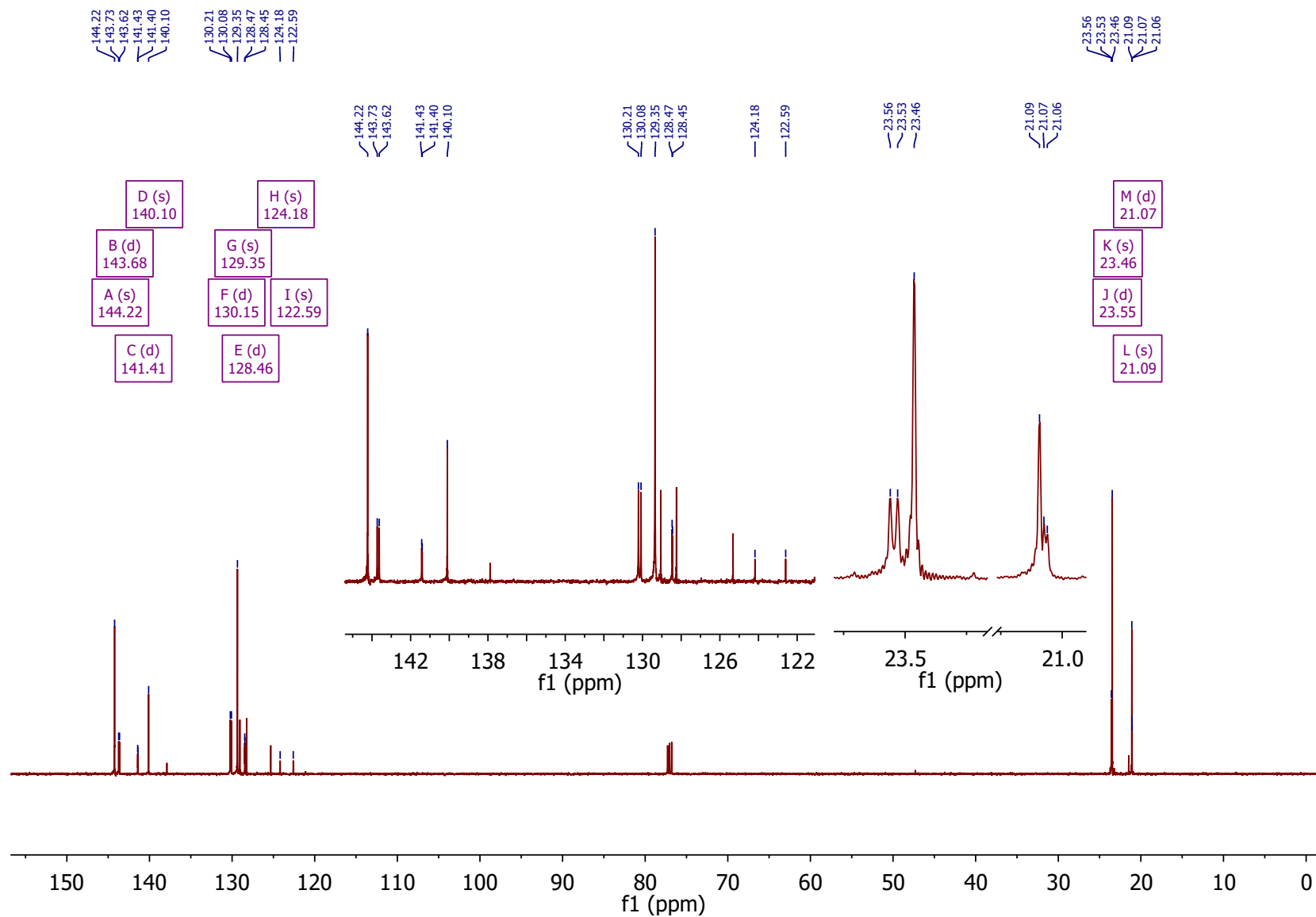


Figure C.17 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$.

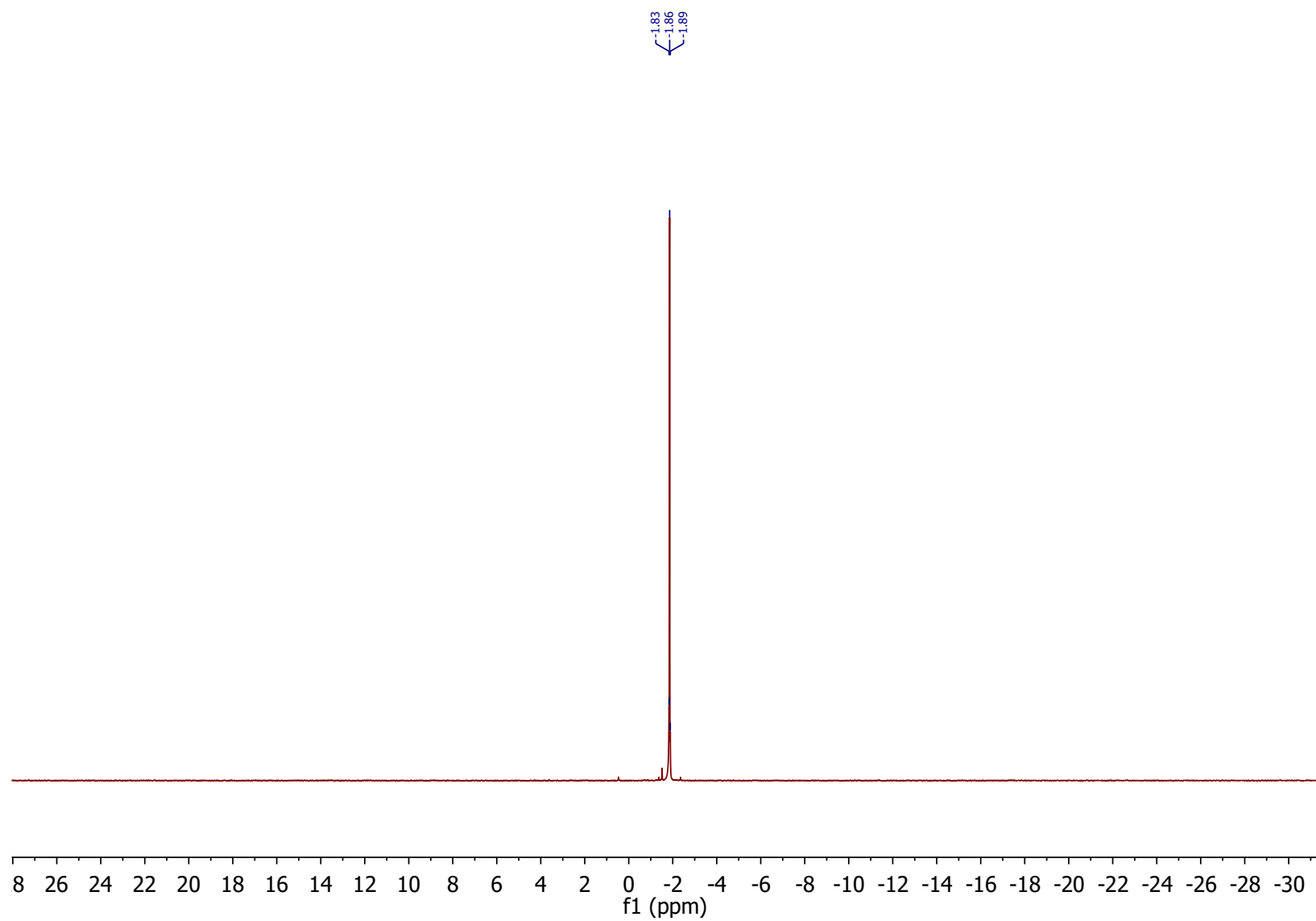


Figure C.18 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$.

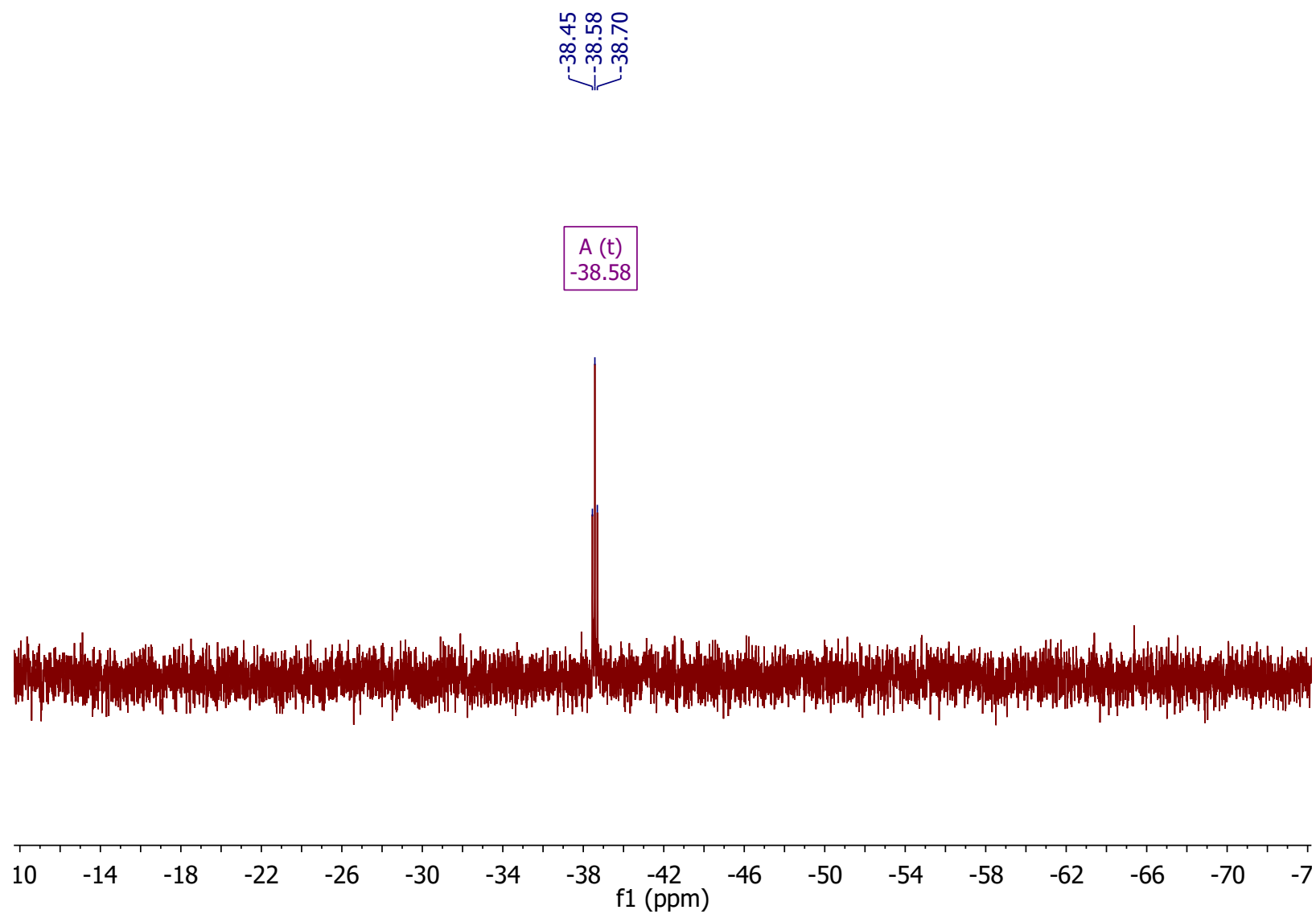


Figure C.19 ^{29}Si DEPT NMR spectrum (99 MHz, CDCl_3) of $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$.

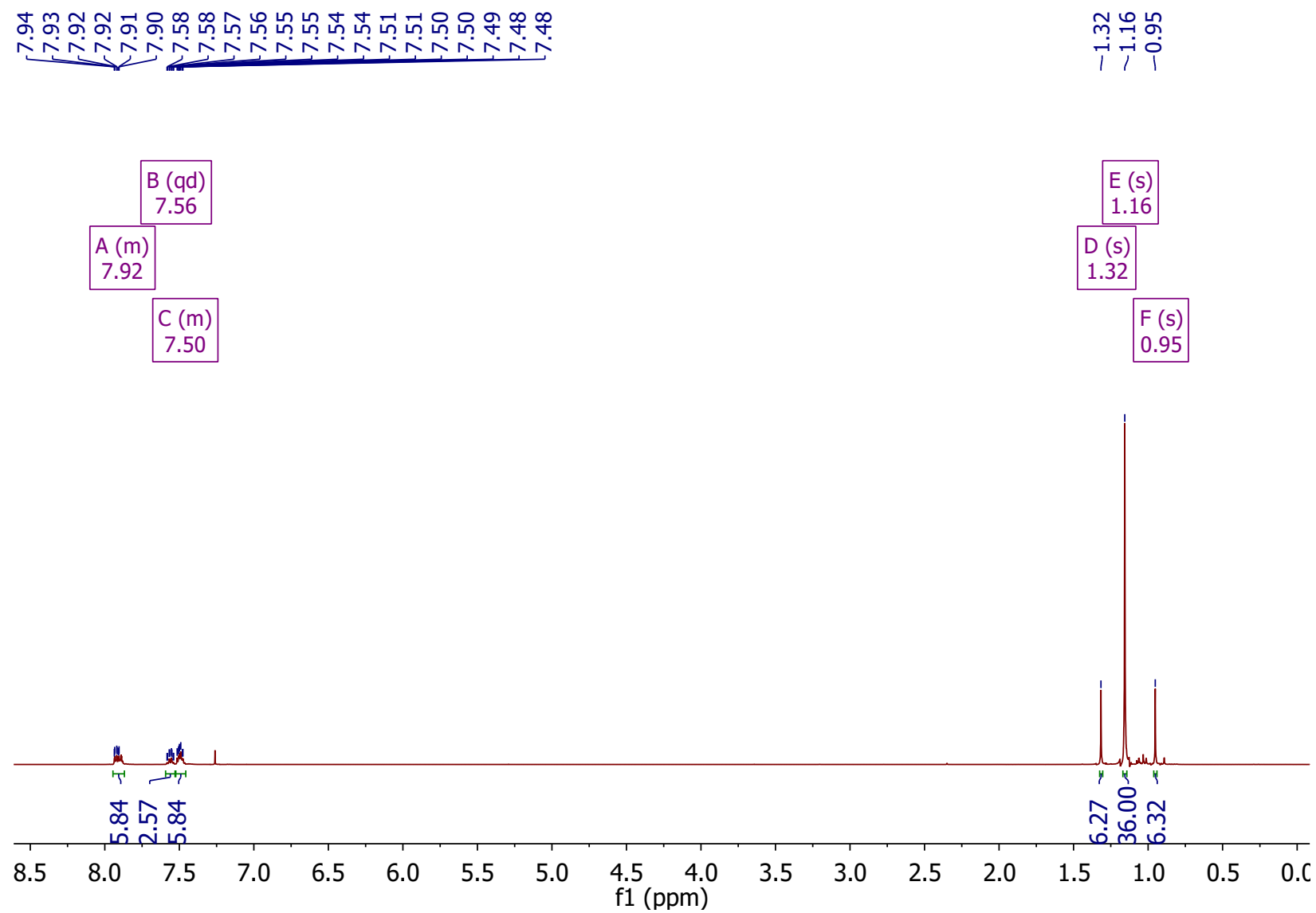


Figure C.20 ^1H NMR spectrum (500 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^t\text{Bu}$.

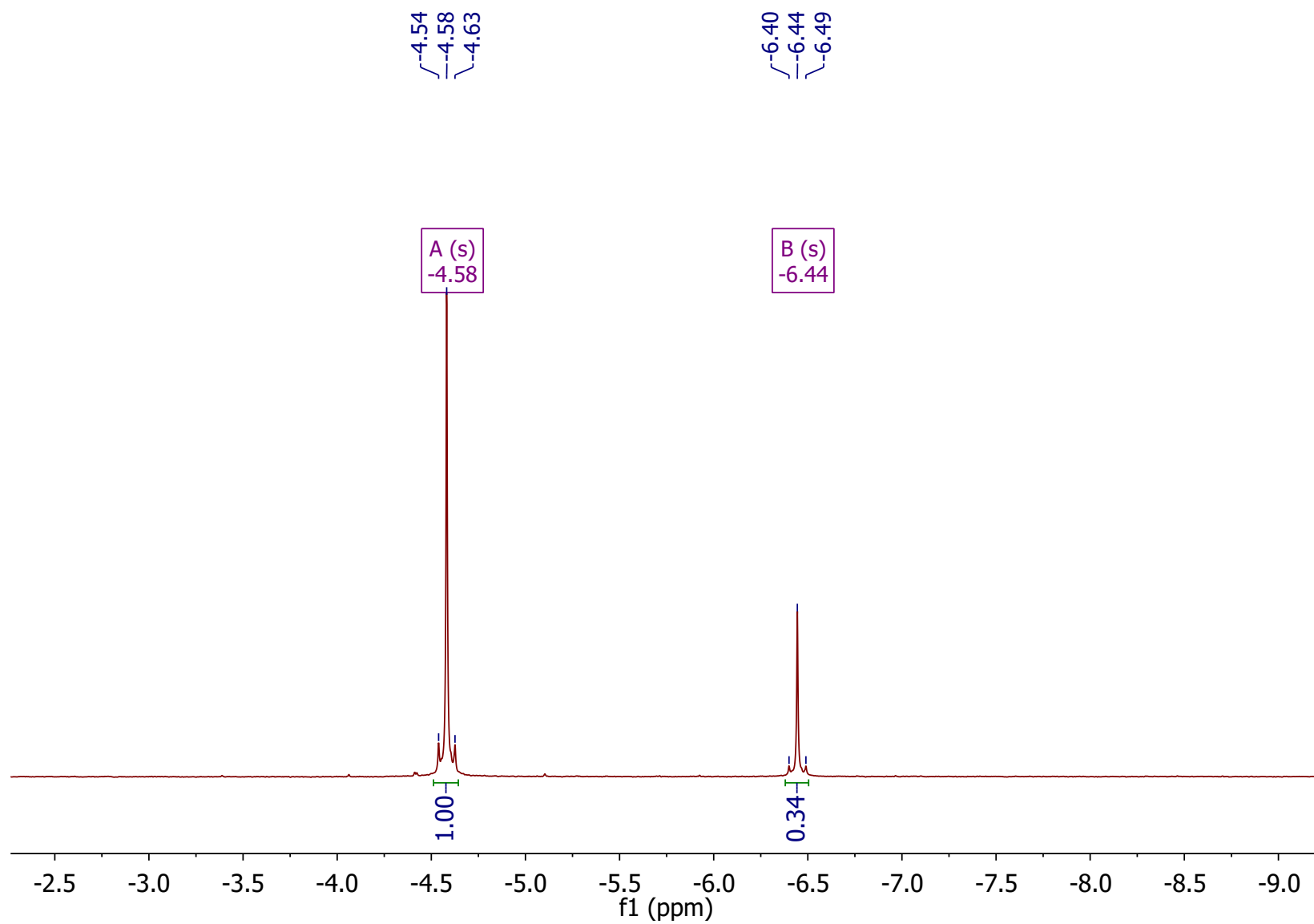


Figure C.21 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^t\text{Bu}$.

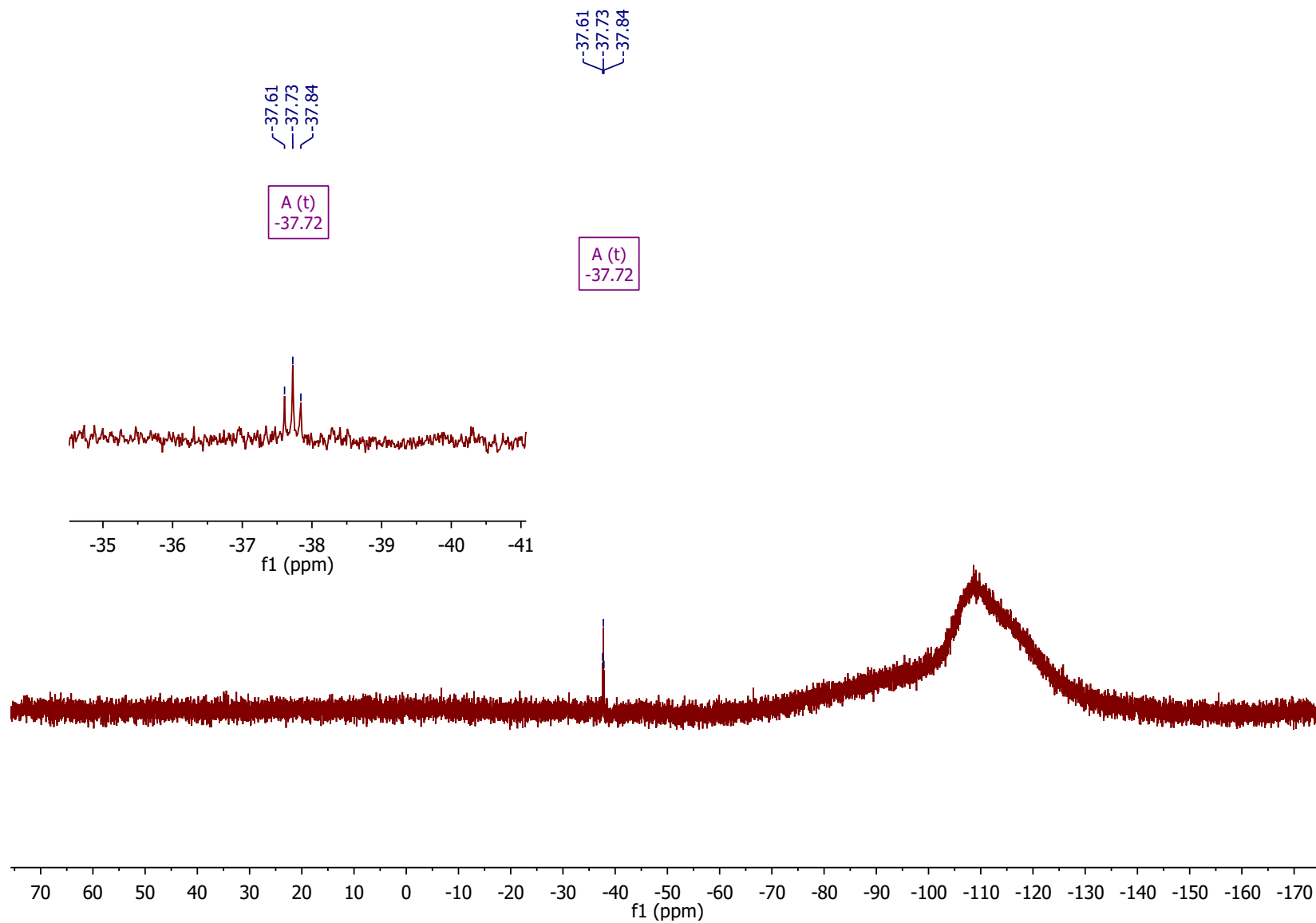


Figure C.22 Inverse gated ^{29}Si NMR spectrum (99 MHz, CDCl_3) of the post-ROP material of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$

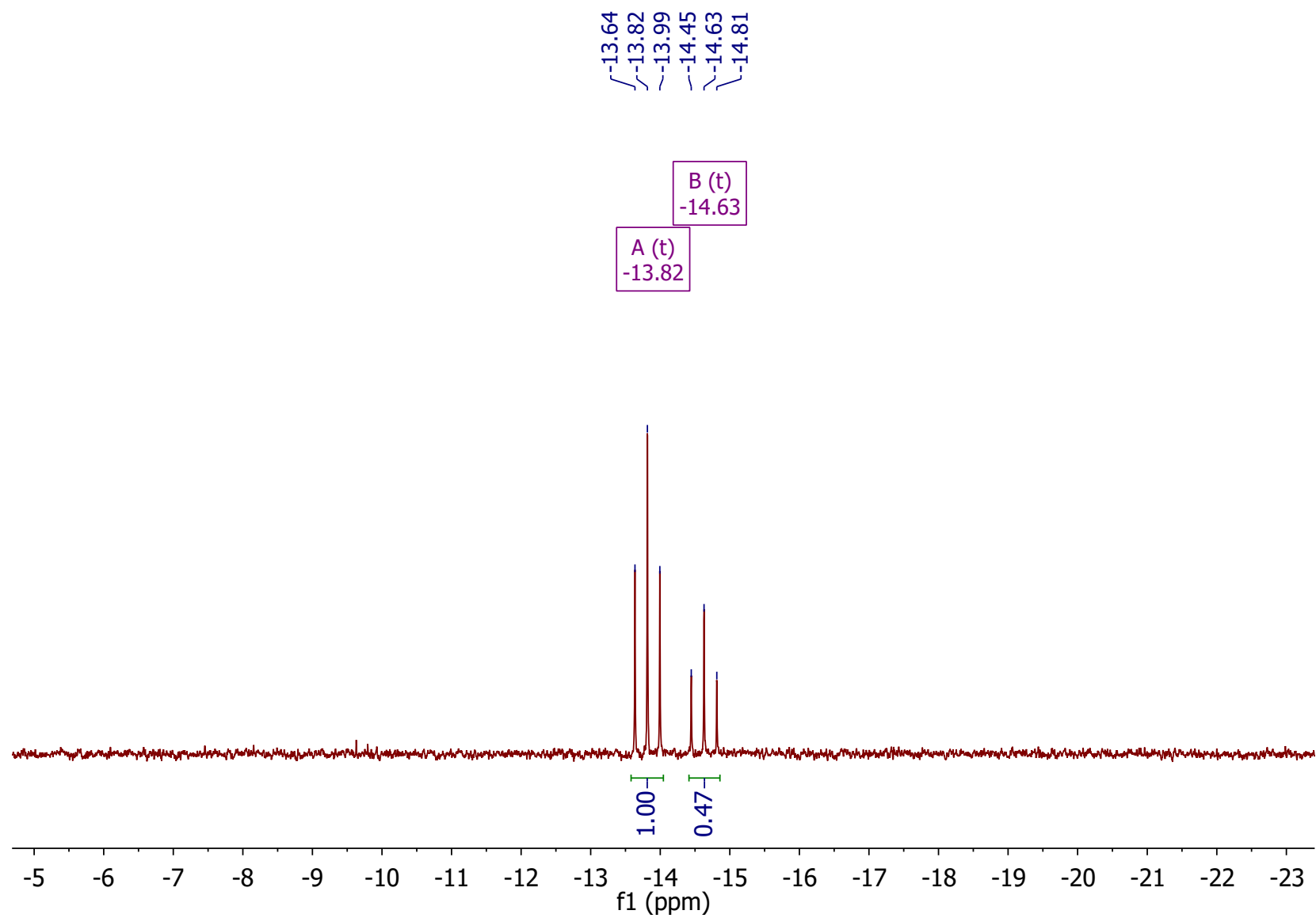


Figure C.23 ^{29}Si DEPT NMR spectrum (99 MHz, CDCl_3) of $\text{P}^{\text{Ph}}\text{Si}^{\text{tBu}}$.

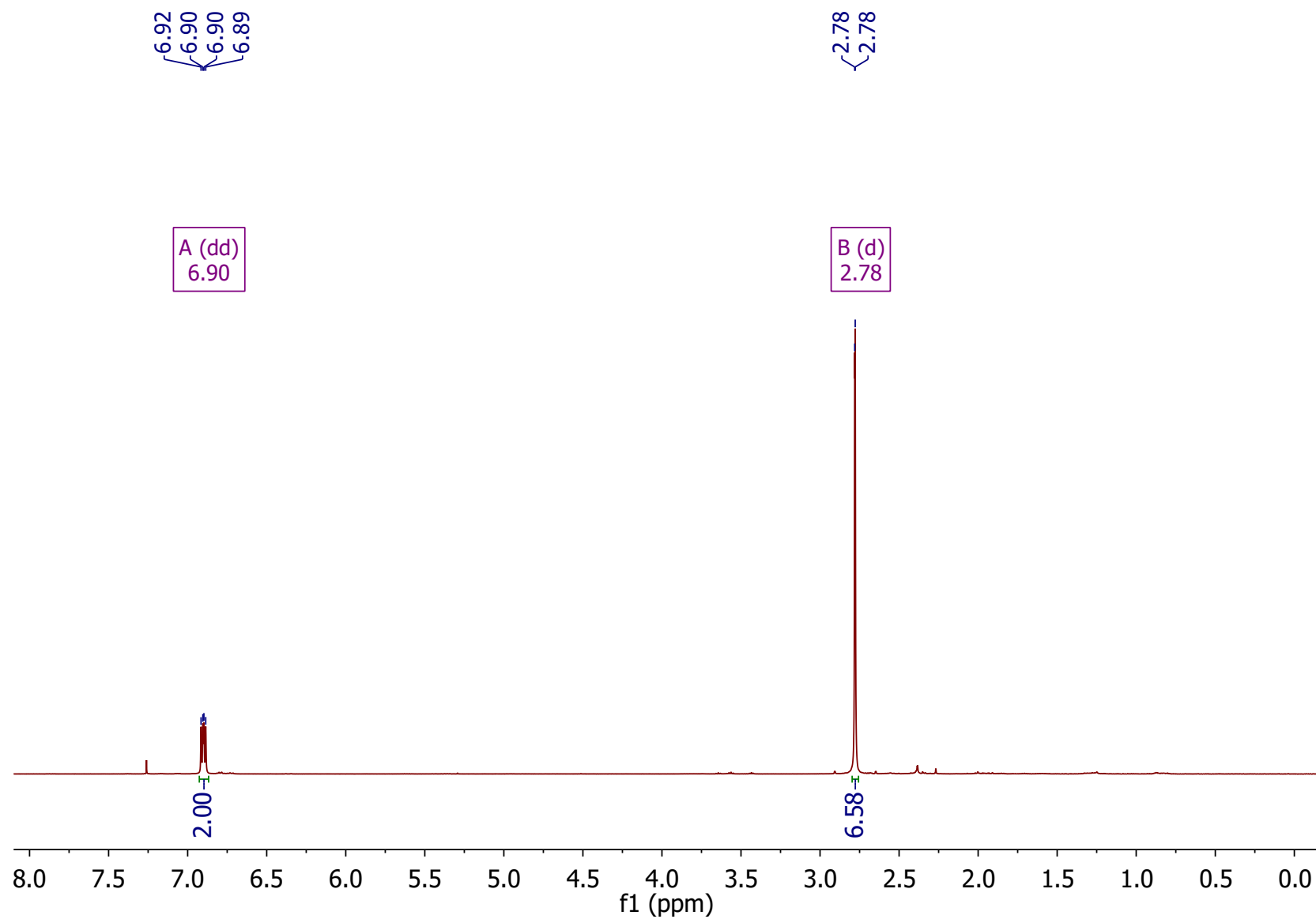


Figure C.24 ^1H NMR spectrum (500 MHz, CDCl_3) of $p\text{-FArPOCl}_2$.

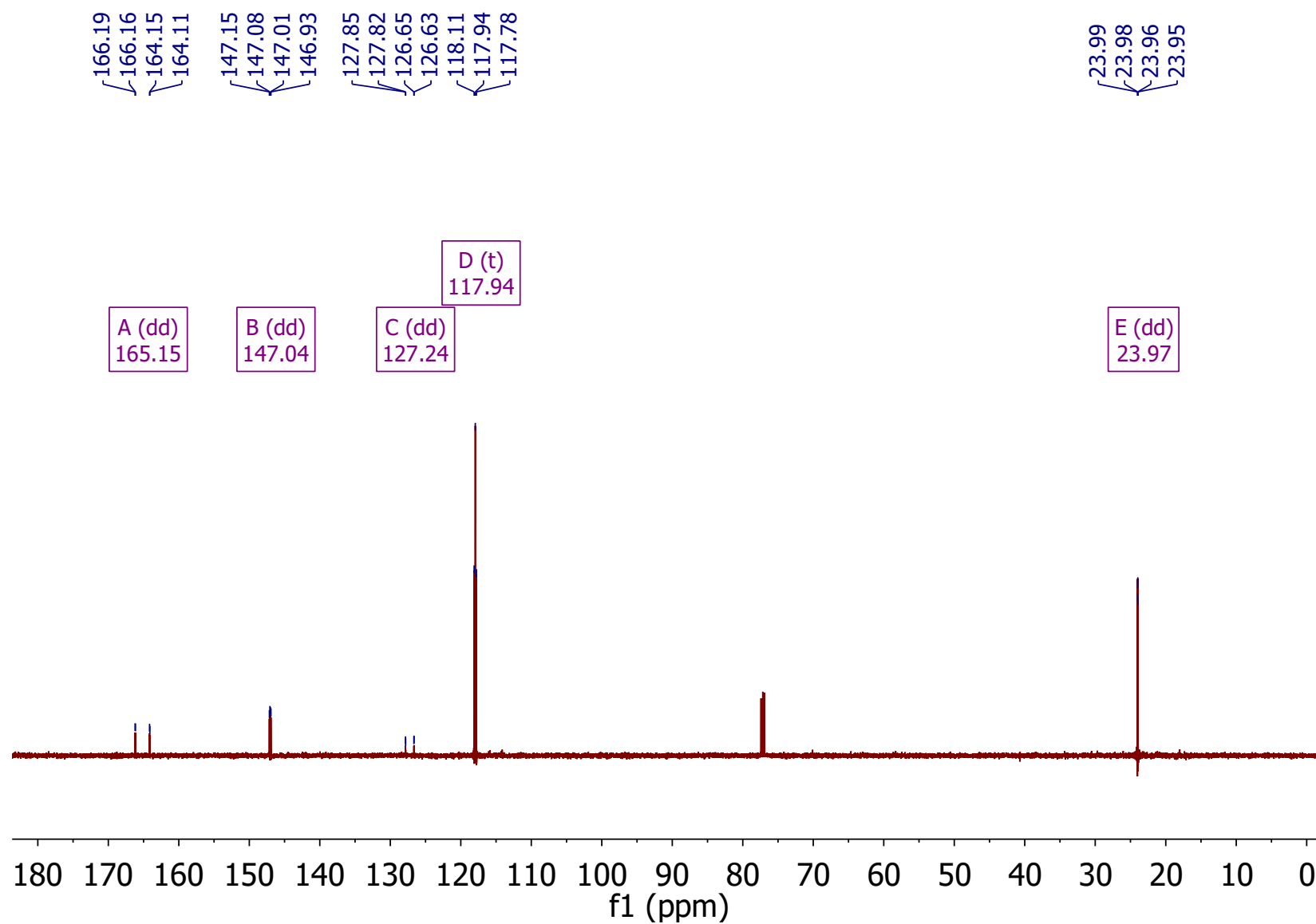


Figure C.25 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of $p\text{-FArPOCl}_2$.

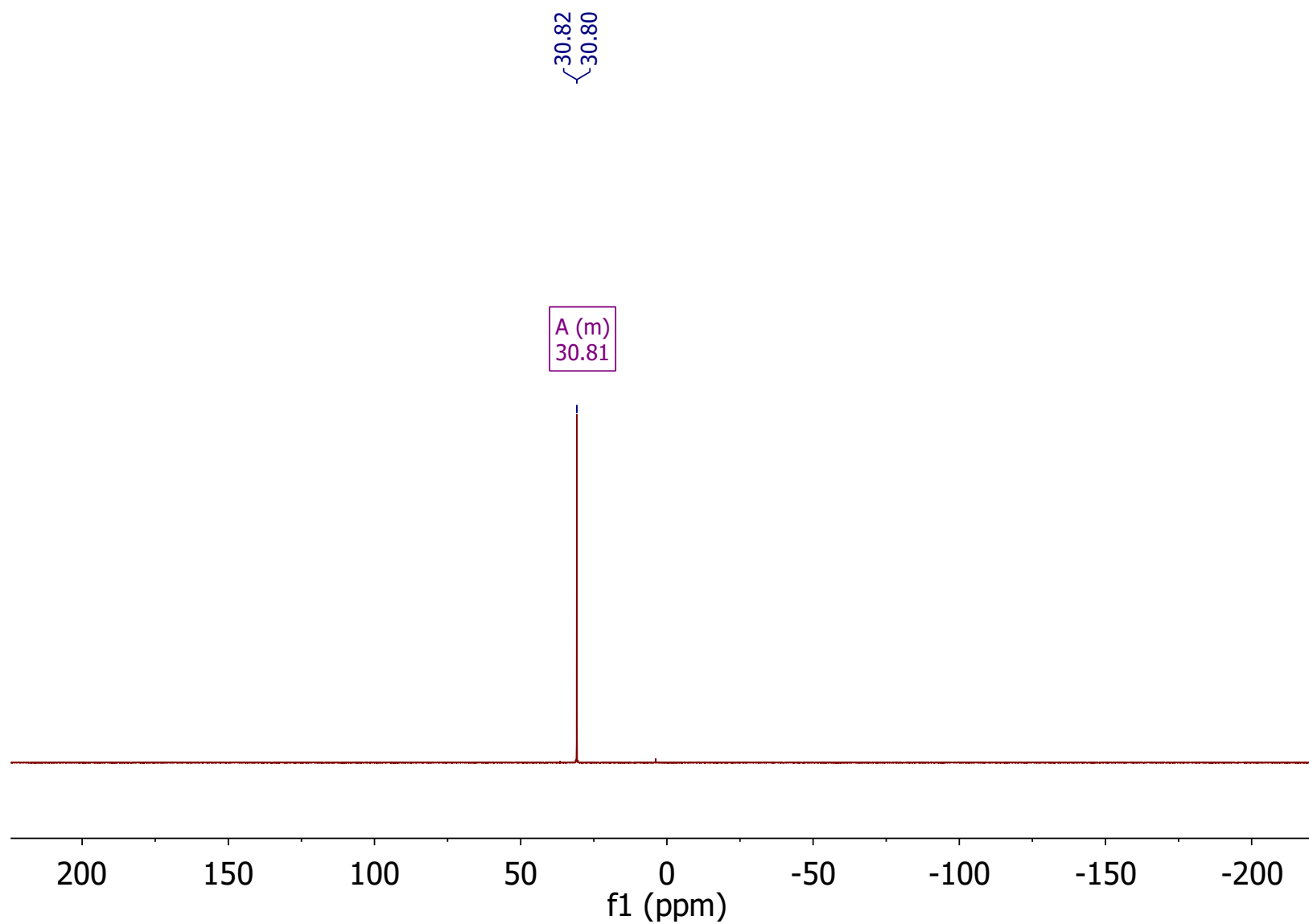


Figure C.26 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of $p\text{-FArPOCl}_2$.

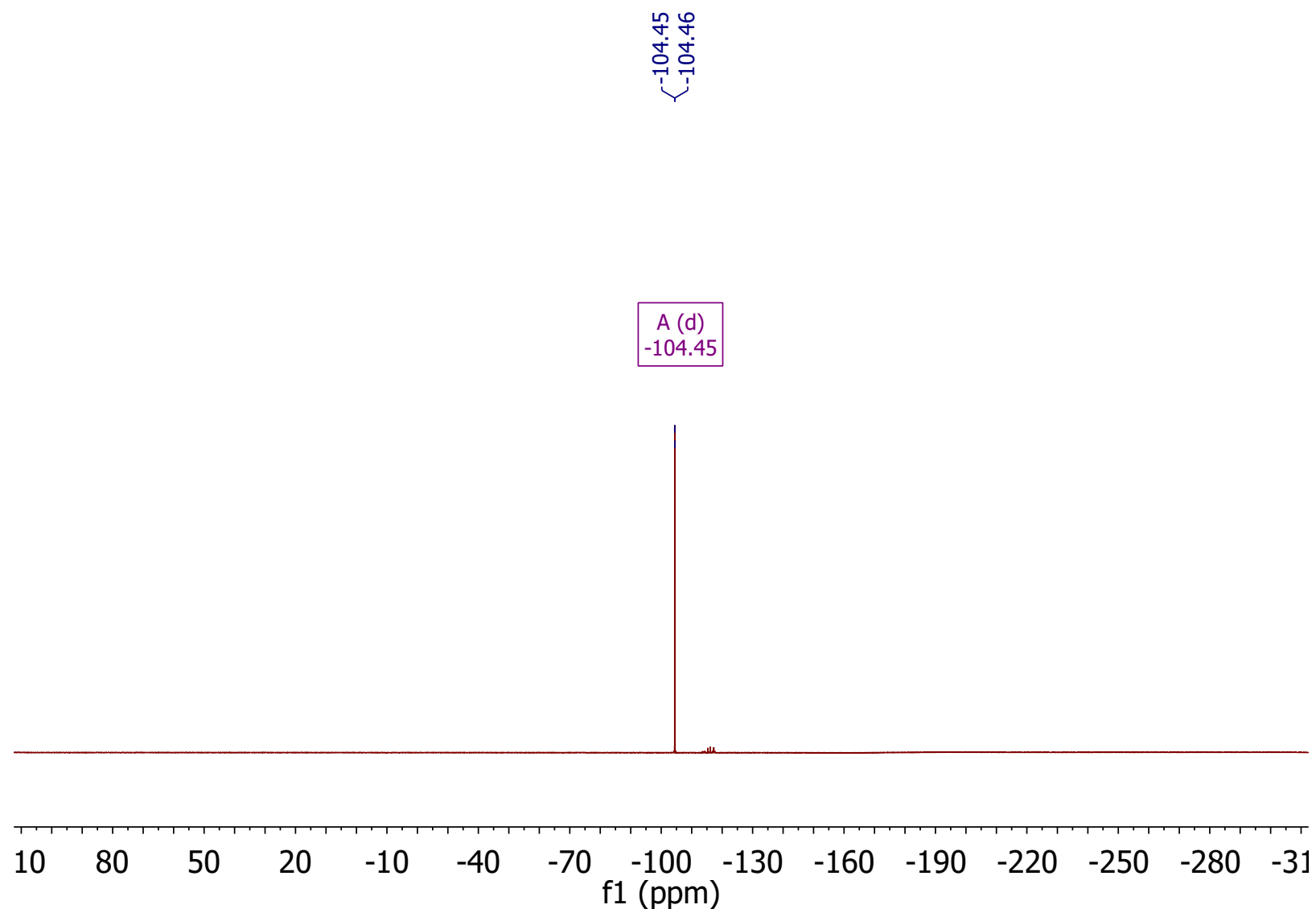


Figure C.27 $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (471 MHz, CDCl_3) of $p\text{-FArPOCl}_2$.

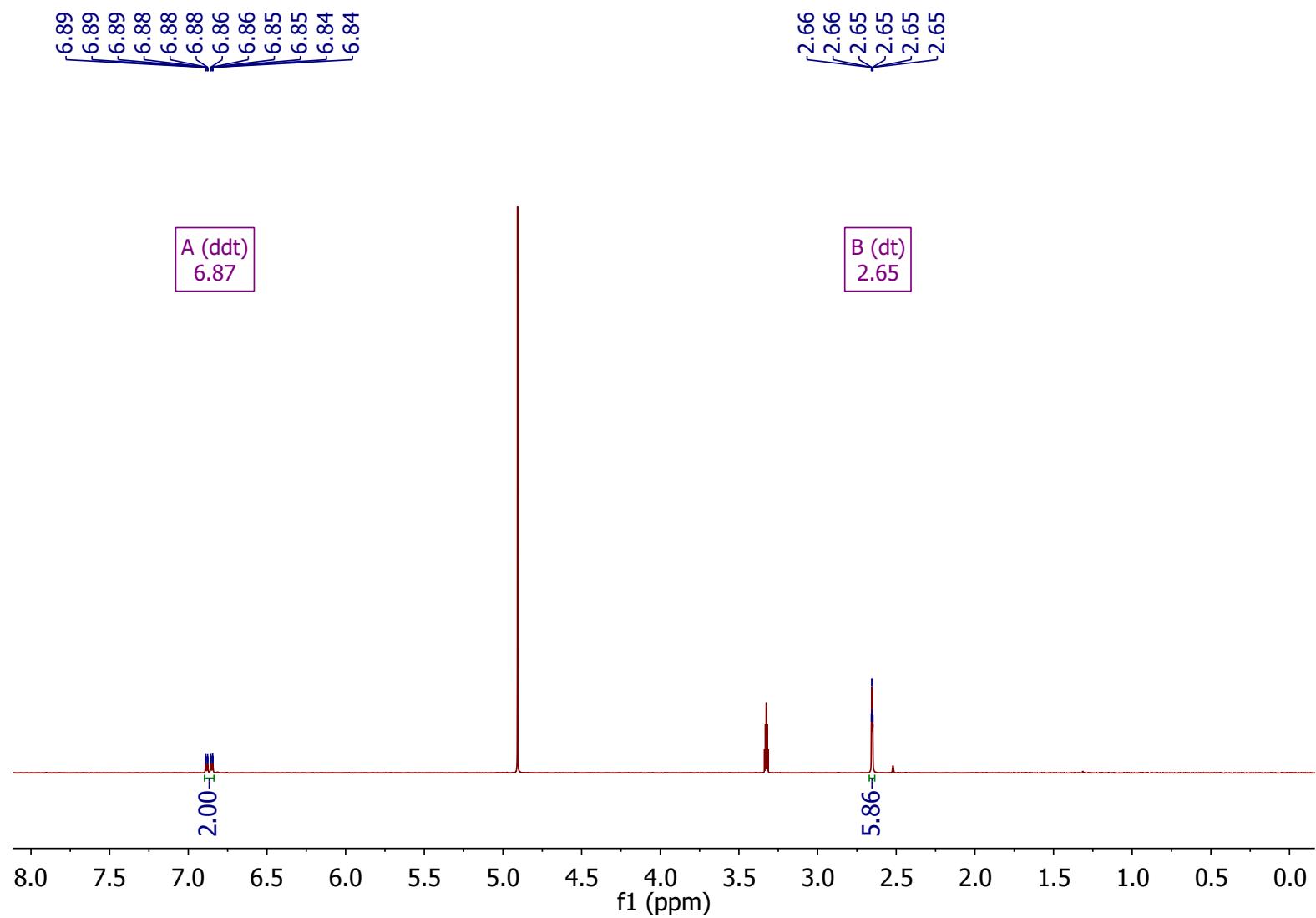


Figure C.28 ¹H NMR spectrum (300 MHz, MeOD) of *p*-FArPO(OH)₂.

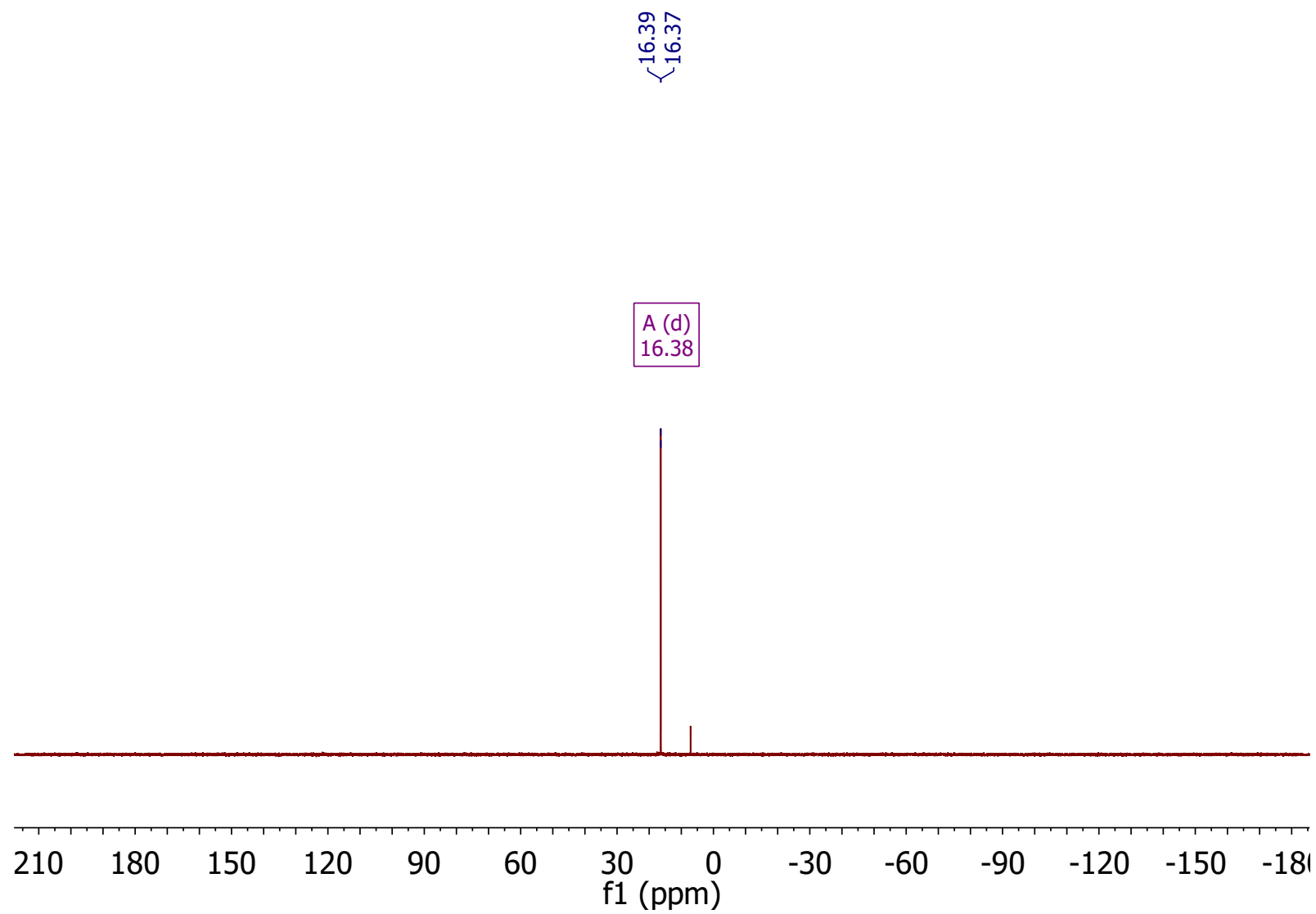


Figure C.29 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (122 MHz, MeOD) of $p\text{-FArPO}(\text{OH})_2$.

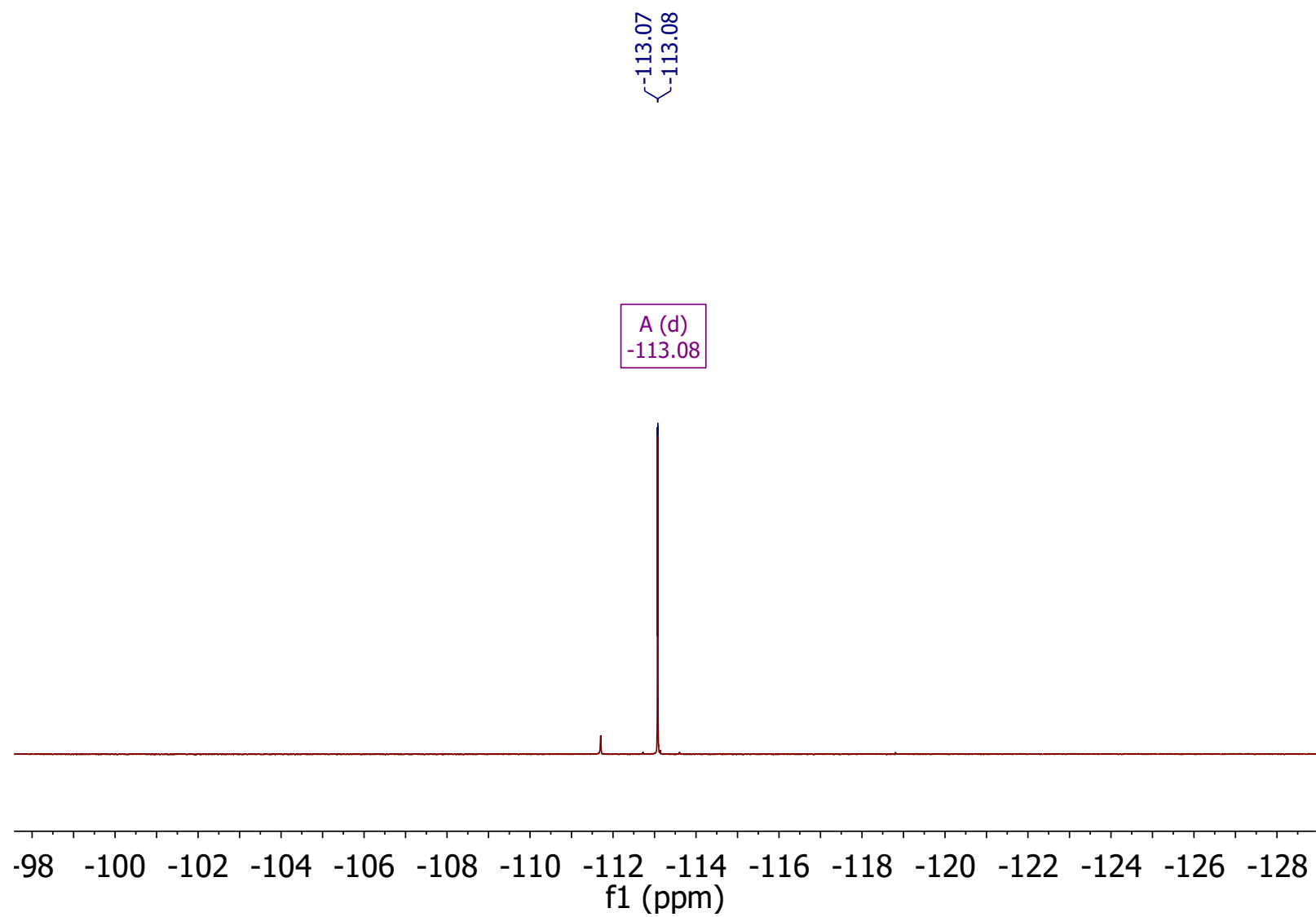


Figure C.30 $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (282 MHz, MeOD) of $p\text{-FArPO(OH)}_2$.

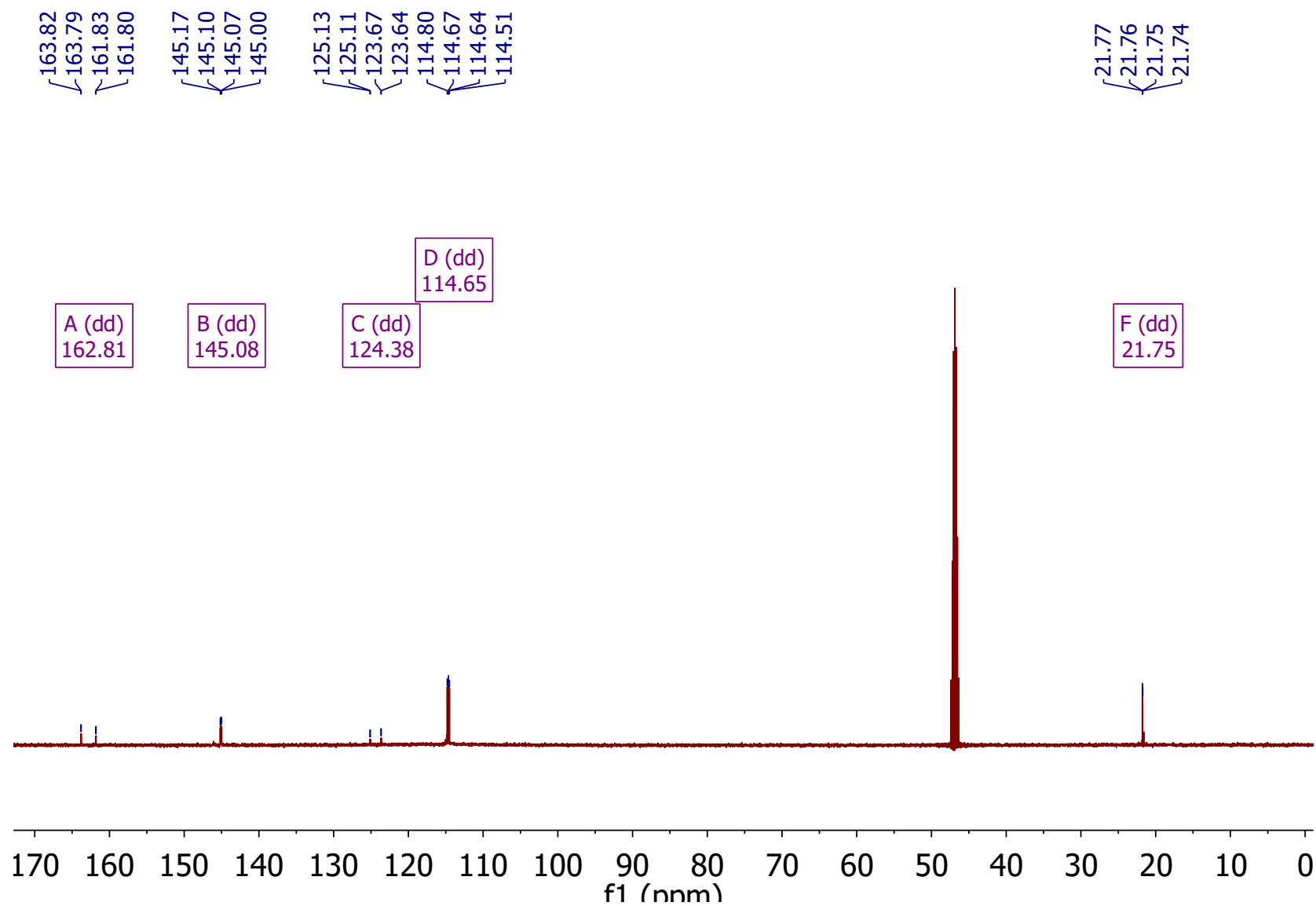


Figure C.31 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, MeOD) of *p*-FArPO(OH)₂.

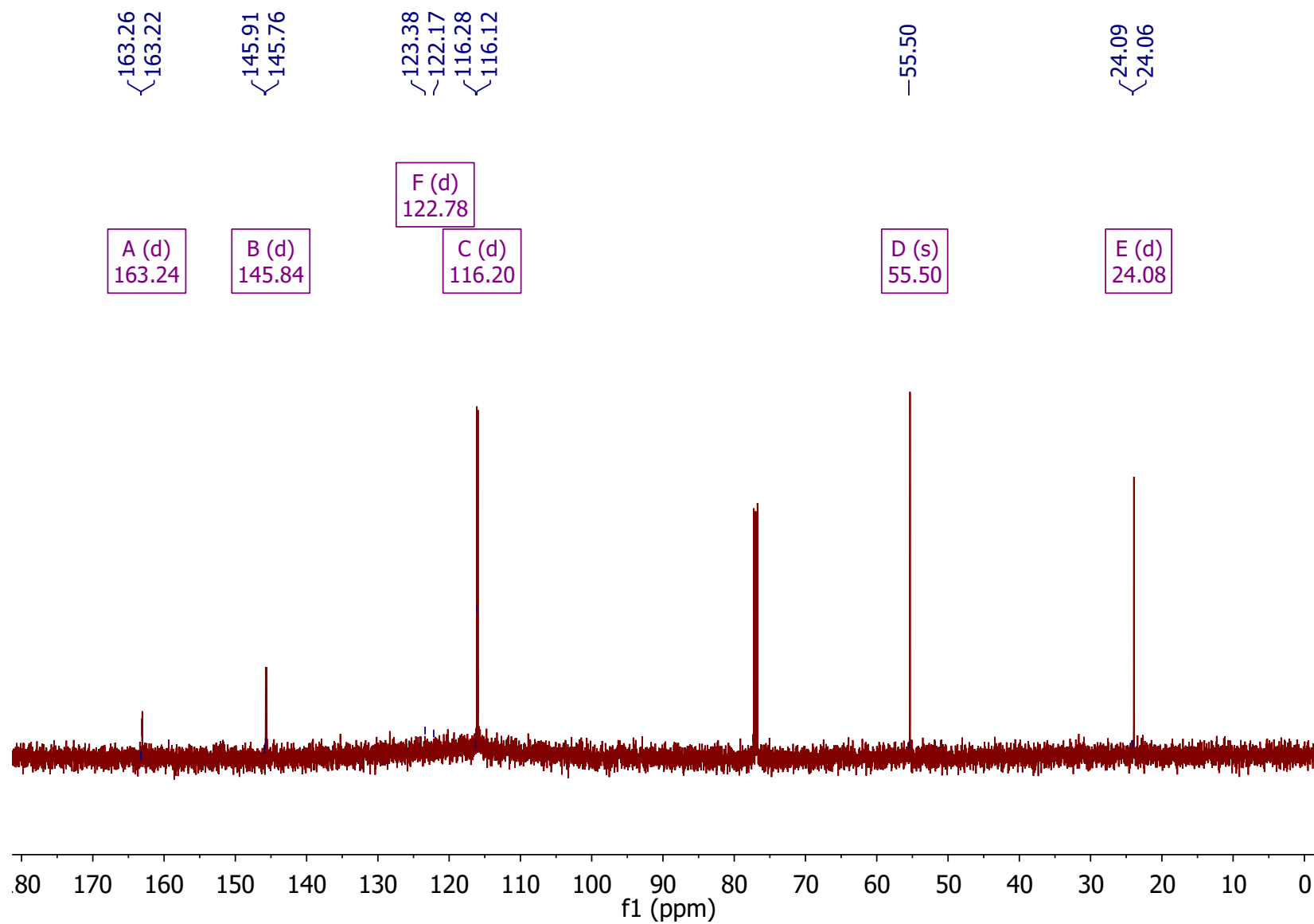


Figure C.32 ^1H NMR spectrum (500 MHz, CDCl_3) of $p\text{-MeOArPOCl}_2$.

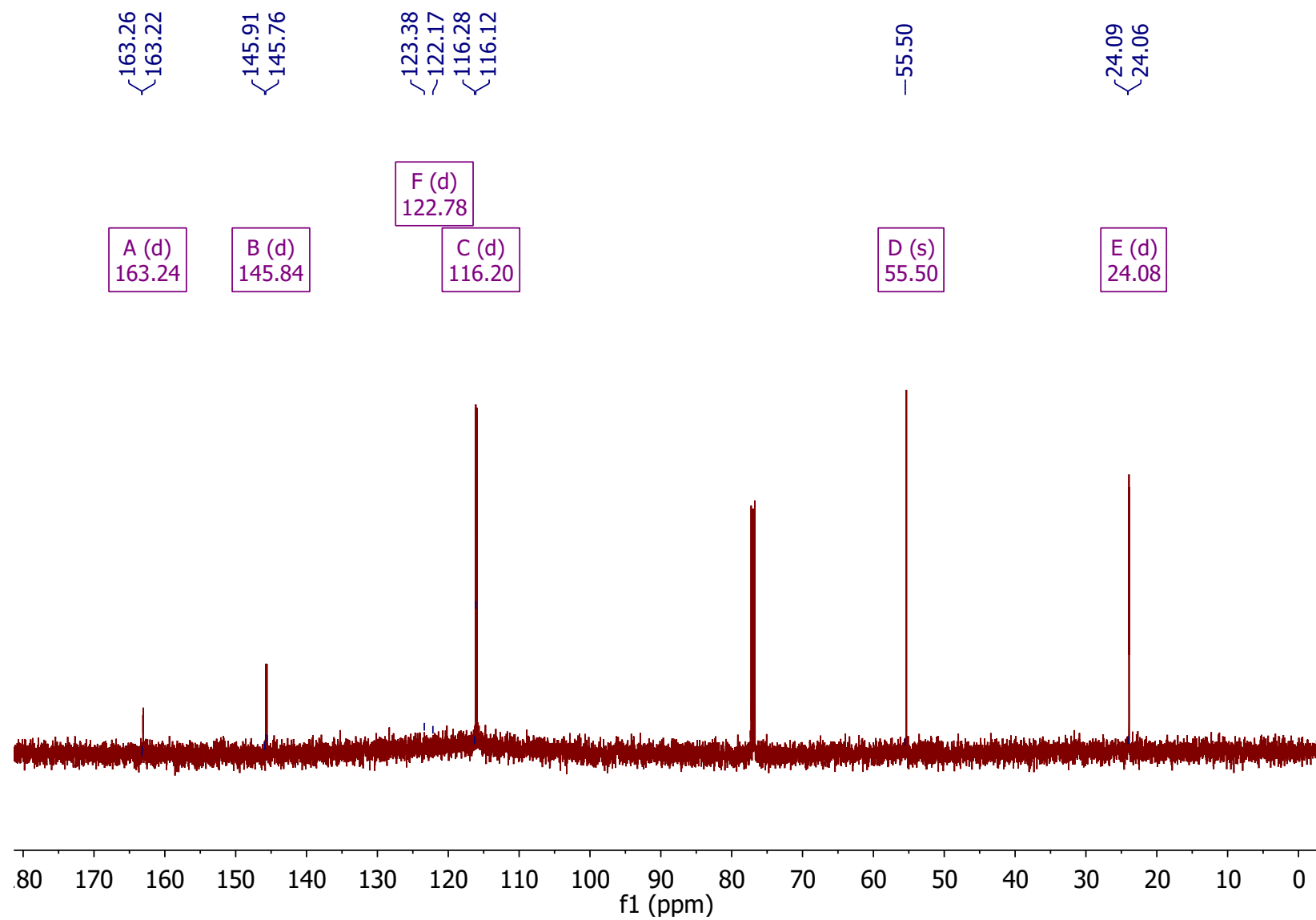


Figure C.33 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of $p\text{-MeOArPOCl}_2$.

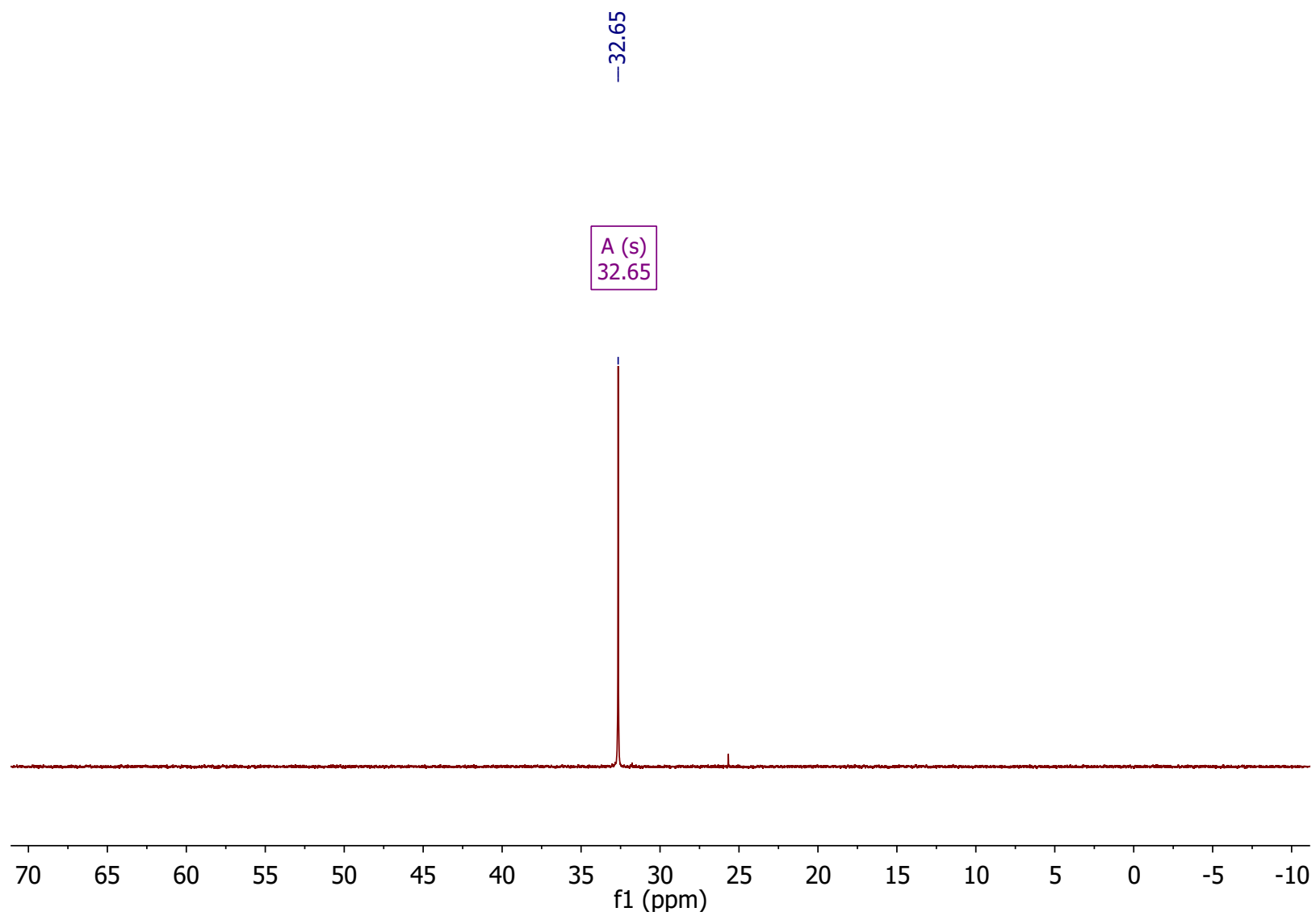


Figure C.34 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of *p*-MeOArPOCl₂.

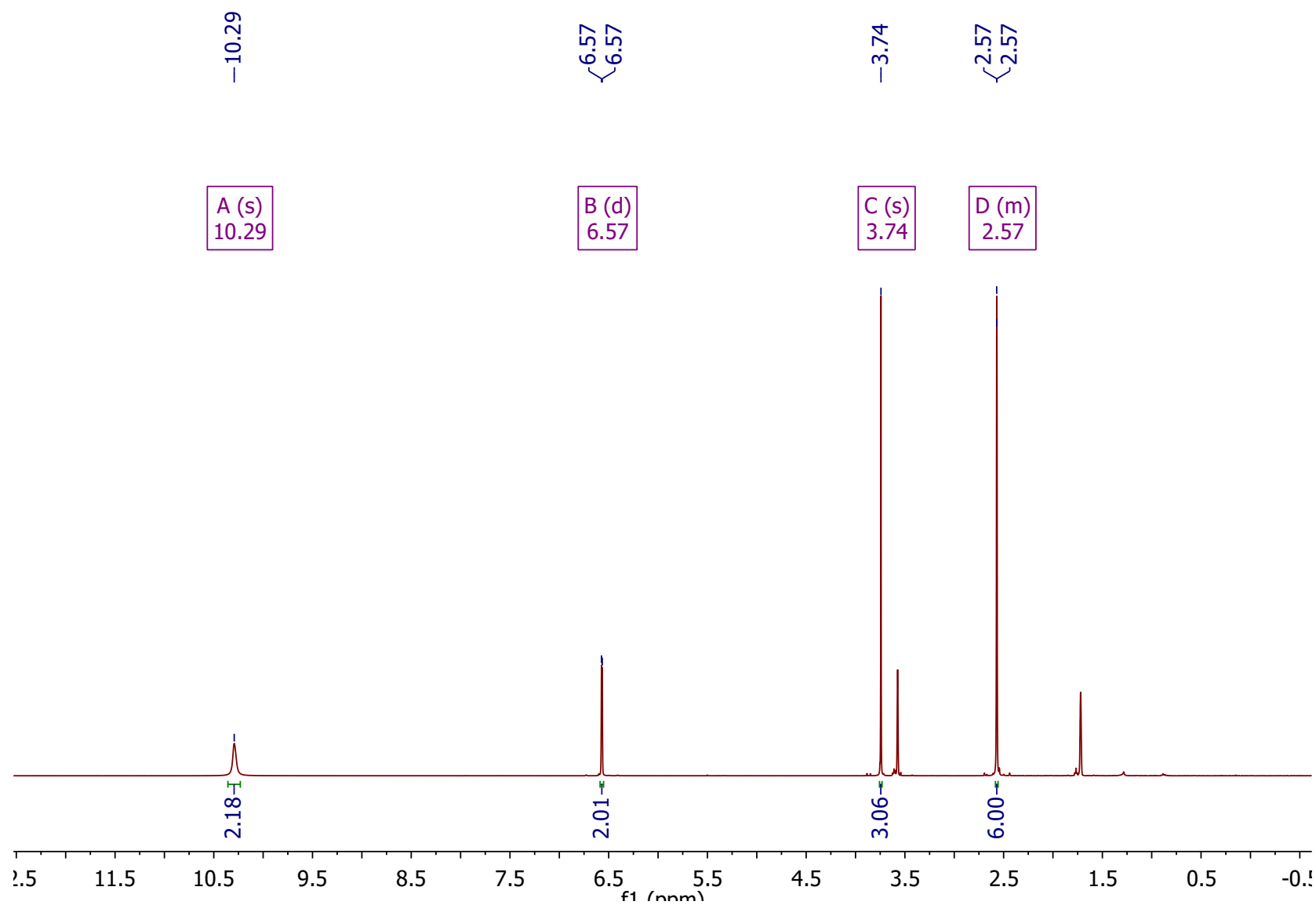


Figure C.35 ^1H NMR spectrum (500 MHz, THF-d^8) of $p\text{-MeOArPO(OH)}_2$.

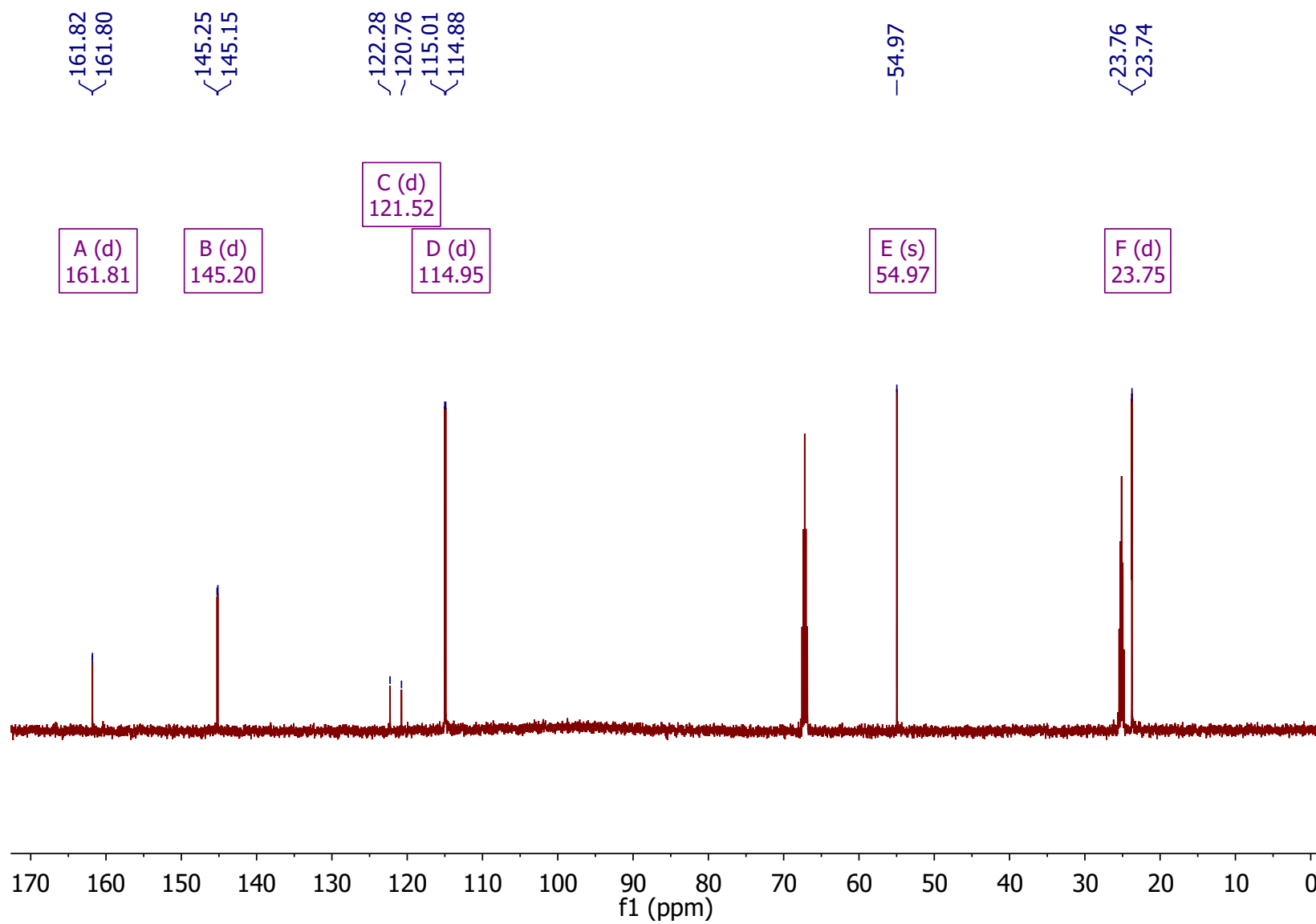


Figure C.36 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, THF-d_8) of $p\text{-MeOArPO(OH)}_2$.

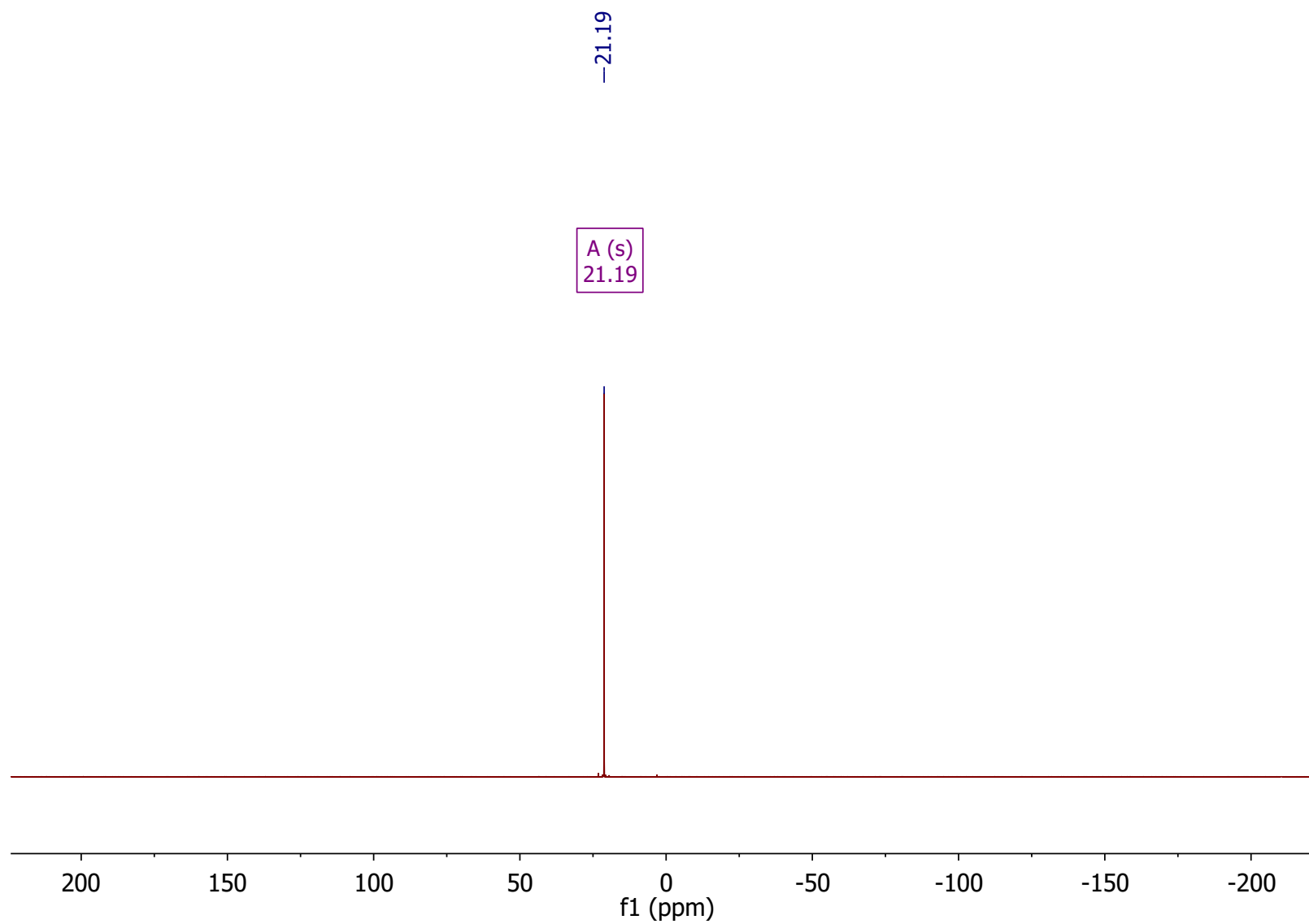


Figure C.37 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, THF-d^8) of $p\text{-MeOArPO(OH)}_2$.

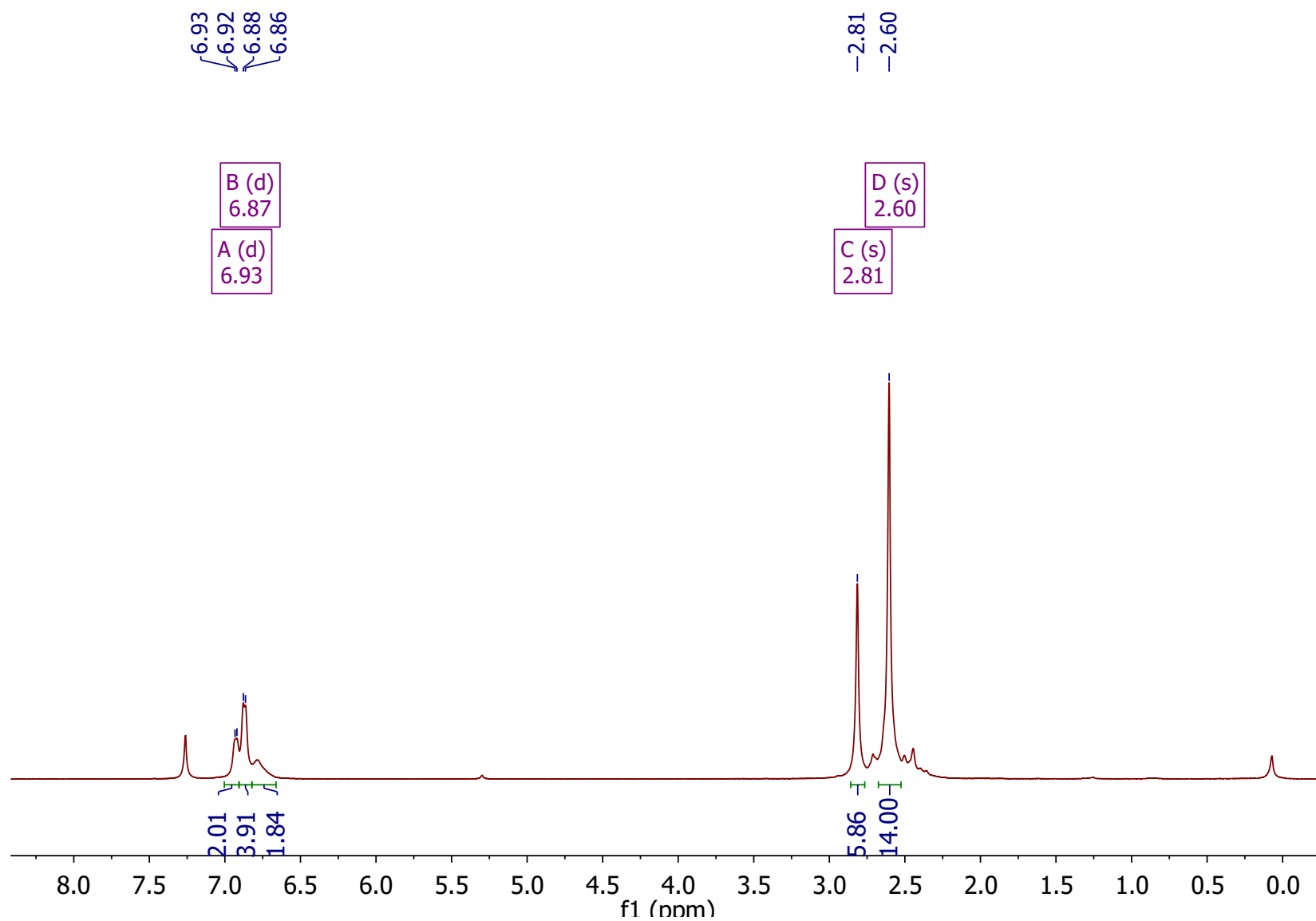


Figure C.38 ¹H NMR spectrum (500 MHz, CDCl₃) of [p-FArP(O)-O]₃.

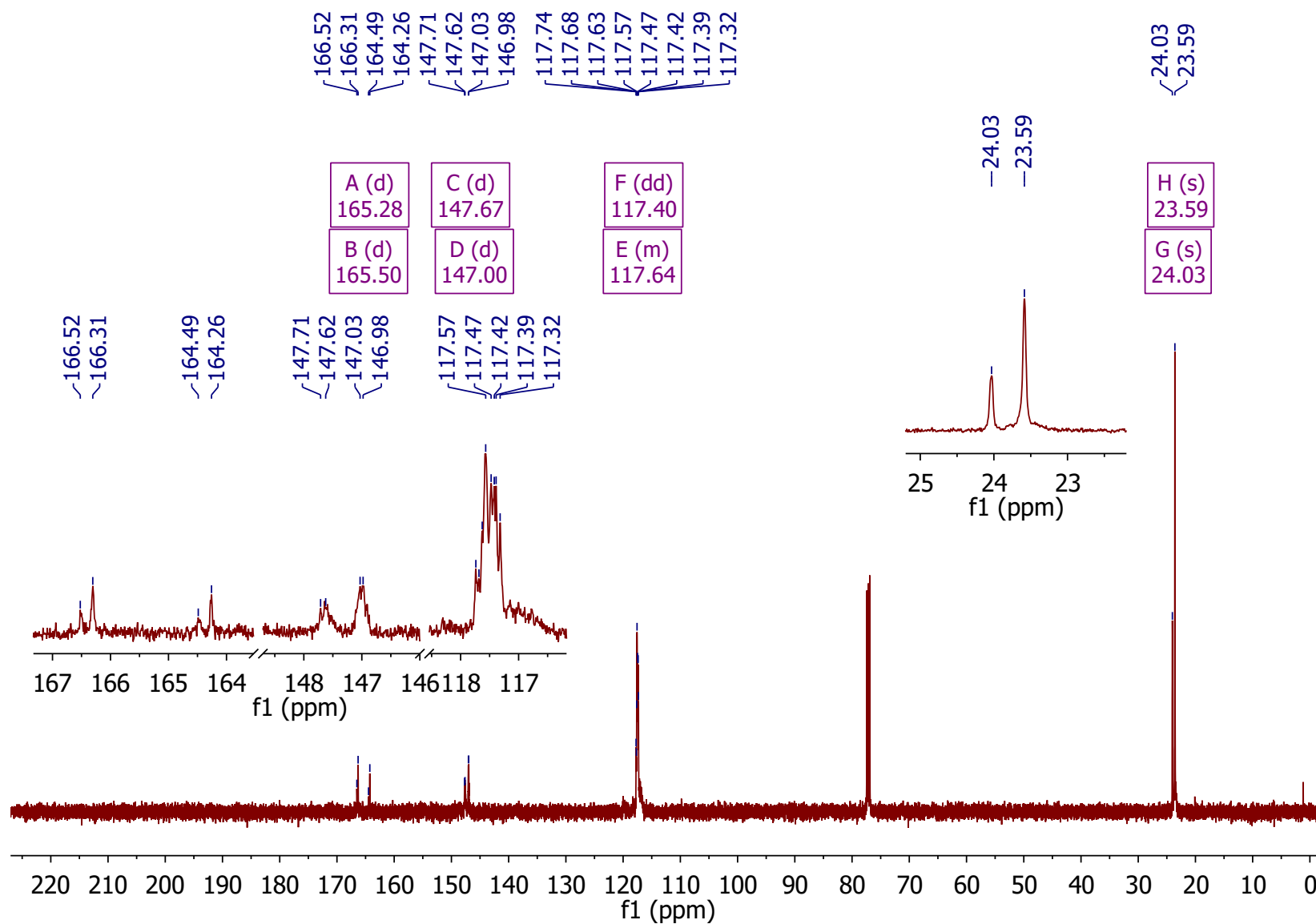


Figure C.39 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of $[p\text{-FArP}(\text{O})\text{-O}]_3$.

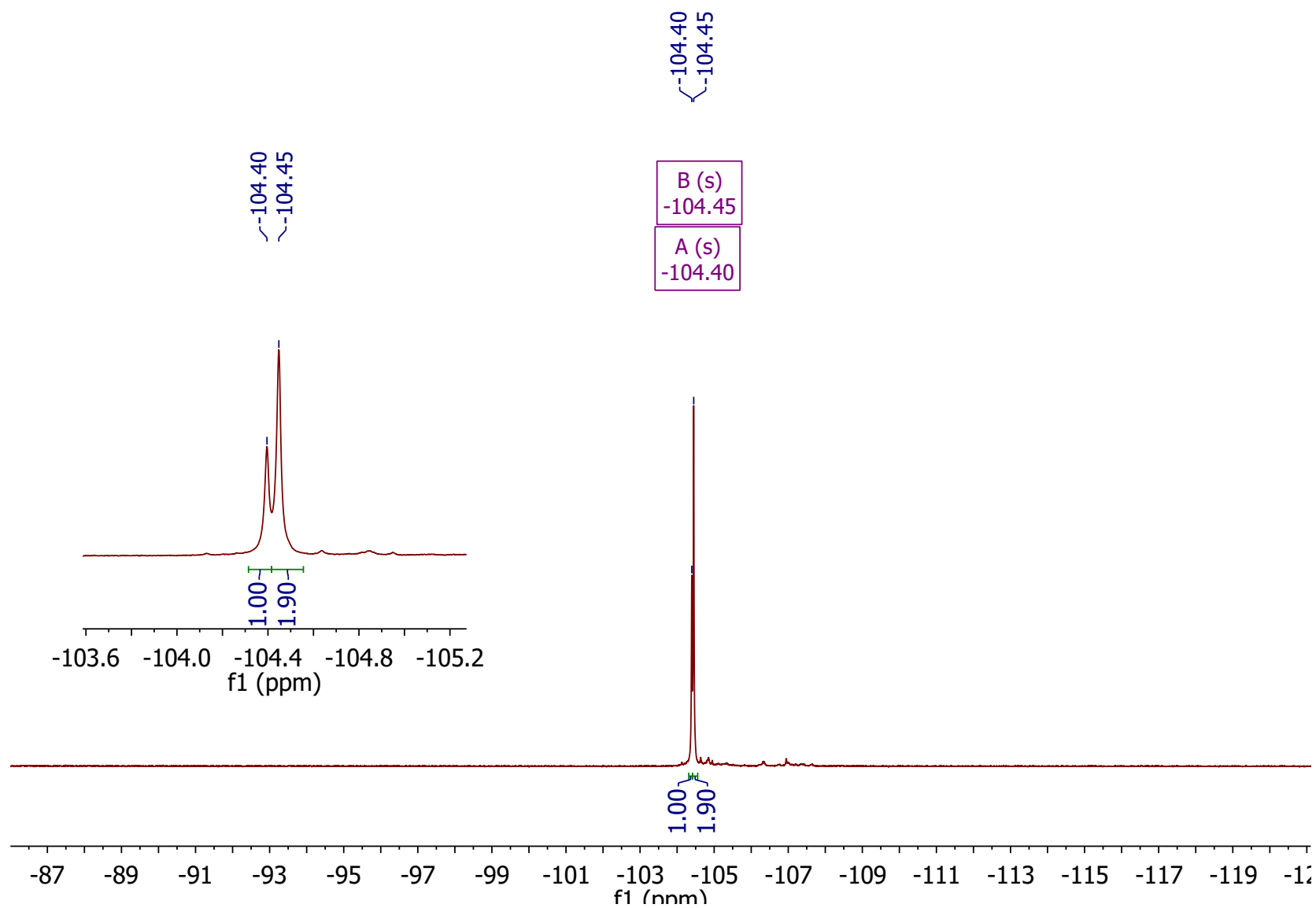


Figure C.40 $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (471 MHz, CDCl_3) of $[p\text{-FArP}(\text{O})\text{-O}]_3$.

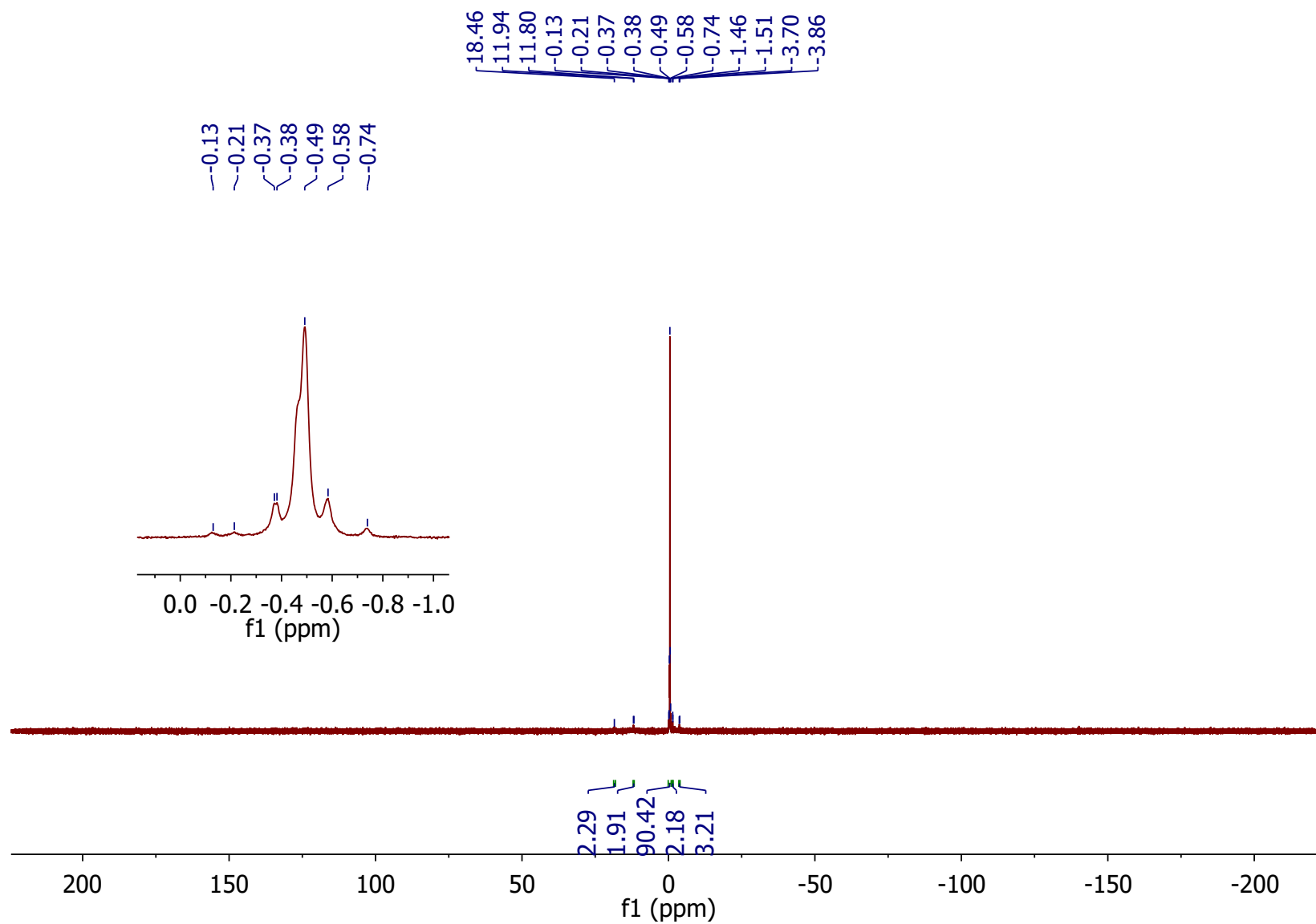


Figure C.41 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of $[p\text{-FArP}(\text{O})\text{-O}]_3$.

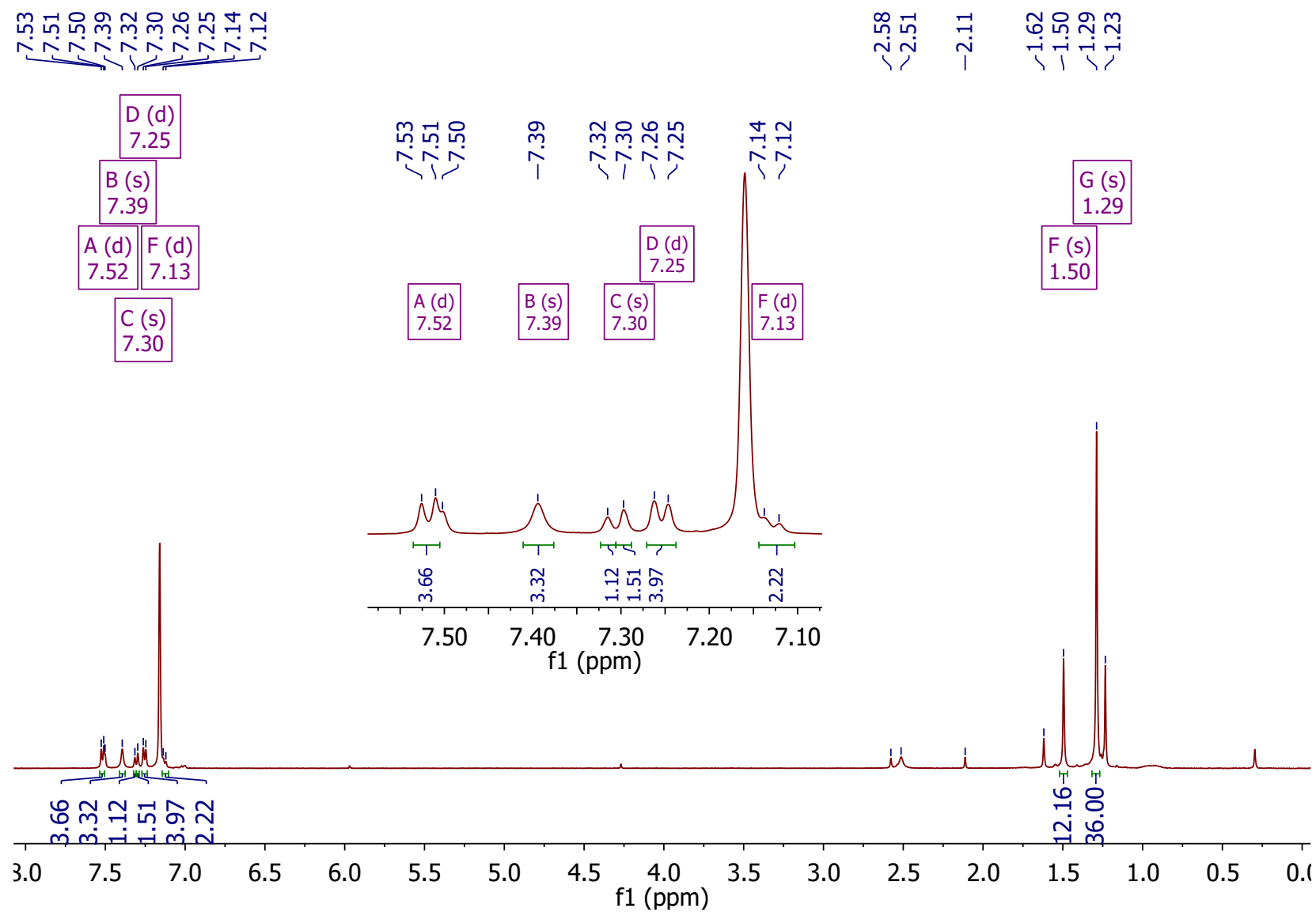


Figure C.42 ^1H NMR spectrum (500 MHz, CDCl_3) of $\text{M}^s\text{Fluid}^{t\text{Bu}}\text{-PCl}_2$.

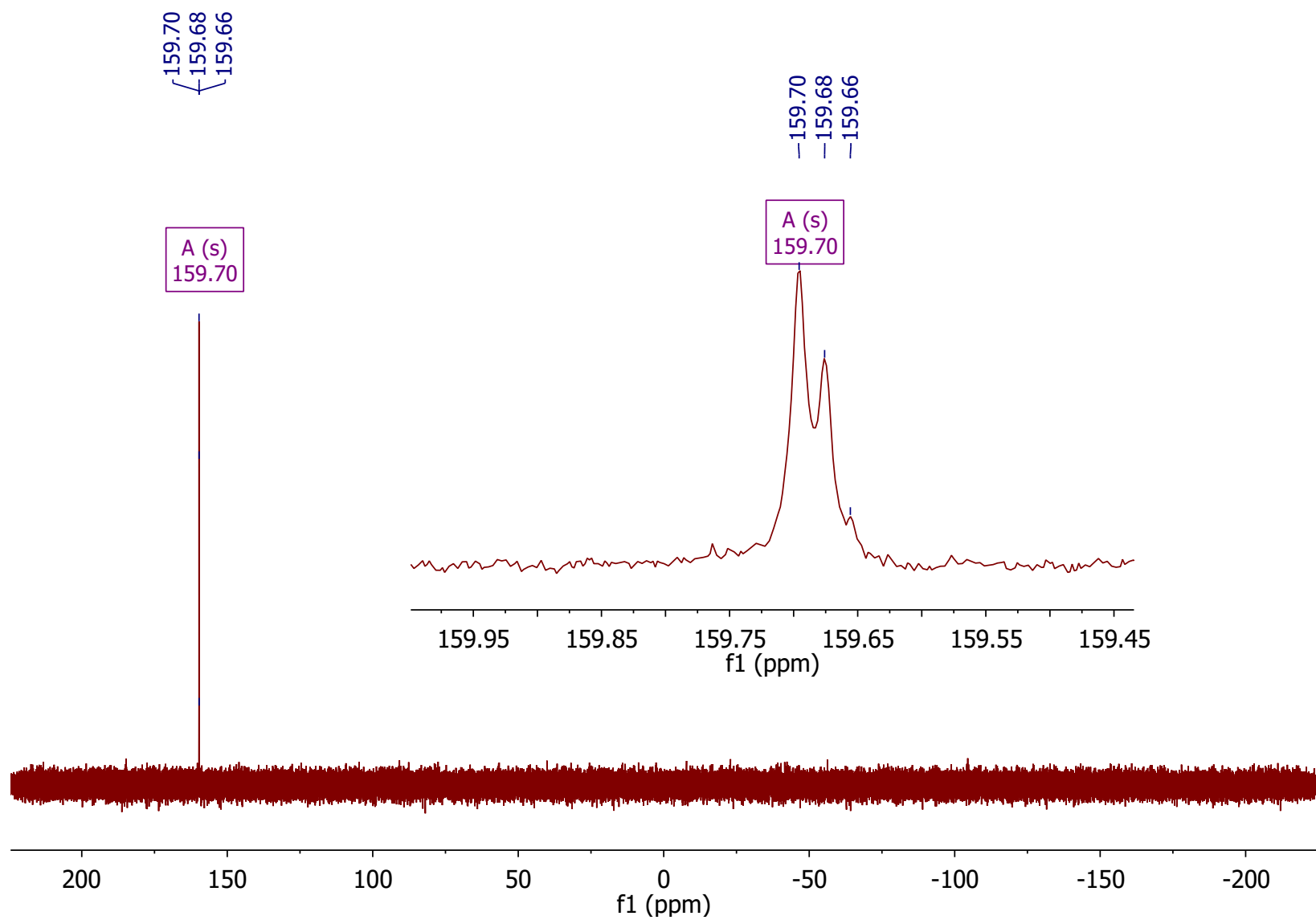


Figure C.43 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (203 MHz, CDCl_3) of $\text{M}^{\text{sFluid}}\text{tBu-PCl}_2$.

C.2 Crystallographic Details

Table C.1 Summary of crystallographic details, Part 1

	P^{Ph}SiⁱMe	P^{Ph}SiⁱPh	P^{Ph}SiⁱMes	P^{Mes}SiⁱMes
Empirical formula	C ₁₆ H ₂₂ O ₆ P ₂ Si ₂	C ₇₂ H ₆₀ O ₁₂ P ₄ Si ₄	C ₄₈ H ₅₆ O ₆ P ₂ Si ₂ · CH ₂ Cl ₂	C ₅₄ H ₆₆ O ₆ P ₂ Si ₂
Formula weight	428.45	1353.44	929.95	929.18
Temperature/K	99.86	100	100	100
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic
Space group	P2 ₁ /n	P-1	C2/c	Pna2 ₁
a/Å	6.3411(13)	9.9664(6)	22.5521(19)	17.4972(5)
b/Å	8.2544(17)	10.7120(7)	18.3084(14)	17.2803(5)
c/Å	20.000(4)	16.2899(11)	24.1525(19)	16.3045(5)
α/°	90	96.4875(19)	90	90
β/°	95.465(3)	90.131(2)	107.669(2)	90
γ/°	90	109.5746(18)	90	90
Volume/Å ³	1042.1(4)	1626.61(18)	9502.0(13)	4929.8(3)
Z	2	1	8	4
ρ _{calc} /g/cm ³	1.365	1.382	1.300	1.252
μ/mm ⁻¹	0.352	0.254	0.302	0.186
F(000)	448.0	704.0	3920.0	1984.0
Crystal size/mm ³	0.27 × 0.22 × 0.18	0.36 × 0.27 × 0.17	0.33 × 0.11 × 0.03	0.13 × 0.09 × 0.07
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.092 to 55.012	2.518 to 61.366	2.922 to 51.436	3.312 to 55.92
Index ranges	-8 ≤ h ≤ 8, -10 ≤ k ≤ 10, -23 ≤ l ≤ 26	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -23 ≤ l ≤ 23	-22 ≤ h ≤ 27, -22 ≤ k ≤ 19, -29 ≤ l ≤ 29	-23 ≤ h ≤ 23, -20 ≤ k ≤ 22, -20 ≤ l ≤ 21
Reflections collected	9272	94484	36115	54894
Independent reflections	2388 [R _{int} = 0.0310, R _{sigma} = 0.0314]	10055 [R _{int} = 0.0285, R _{sigma} = 0.0145]	9010 [R _{int} = 0.0635, R _{sigma} = 0.0607]	11739 [R _{int} = 0.0743, R _{sigma} = 0.0593]
Data/restraints/parameters	2388/0/120	10055/0/415	9010/0/562	11739/1/595
Goodness-of-fit on F ²	1.229	1.103	1.084	0.848
Final R indexes [I > 2σ (I)]	R ₁ = 0.0755, wR ₂ = 0.1945	R ₁ = 0.0289, wR ₂ = 0.1206	R ₁ = 0.0827, wR ₂ = 0.2223	R ₁ = 0.0424, wR ₂ = 0.1081
Final R indexes [all data]	R ₁ = 0.0803, wR ₂ = 0.1967	R ₁ = 0.0320, wR ₂ = 0.1268	R ₁ = 0.1137, wR ₂ = 0.2412	R ₁ = 0.0655, wR ₂ = 0.1259
Largest diff. peak/hole / e Å ⁻³	1.09/-0.59	0.48/-0.29	1.59/-0.49	0.37/-0.30

Table C.2 Summary of crystallographic details, Part 2

	<i>p</i> -MeOArPOCl ₂	<i>p</i> -MeOArPO(OH) ₂	<i>p</i> -FArPO(OH) ₂	M ^s Fluid ^{tBu} -PCl ₂
Empirical formula	C ₉ H ₁₁ Cl ₂ O ₂ P	C ₉ H ₁₃ O ₄ P	C ₈ H ₁₀ FO ₃ P	C ₅₆ H ₆₅ Cl ₂ P
Formula weight	253.05	216.16	204.13	839.95
Temperature/K	100	100	100	100
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	P2 ₁ /m	P2 ₁ /m	Pnma	P2 ₁ /c
<i>a</i> /Å	7.932(3)	12.700(3)	18.7302(19)	12.2159(10)
<i>b</i> /Å	6.863(3)	6.8782(13)	6.7143(7)	21.5121(18)
<i>c</i> /Å	10.592(4)	17.669(4)	13.6828(14)	18.0035(15)
α /°	90	90	90	90
β /°	109.272(8)	108.745(4)	90	91.567(2)
γ /°	90	90	90	90
Volume/Å ³	544.3(4)	1461.6(5)	1720.8(3)	4729.4(7)
<i>Z</i>	2	6	8	4
ρ_{calc} /g/cm ³	1.544	1.474	1.576	1.180
μ /mm ⁻¹	0.713	0.267	0.306	0.207
<i>F</i> (000)	260.0	684.0	848.0	1800.0
Crystal size/mm ³	0.22 × 0.21 × 0.2	0.44 × 0.26 × 0.23	0.22 × 0.18 × 0.15	0.16 × 0.14 × 0.08
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.44 to 61.092	2.434 to 61.216	3.686 to 61.152	2.95 to 61.164
Index ranges	-11 ≤ <i>h</i> ≤ 11, -9 ≤ <i>k</i> ≤ 9, -15 ≤ <i>l</i> ≤ 14	-18 ≤ <i>h</i> ≤ 13, -9 ≤ <i>k</i> ≤ 9, -22 ≤ <i>l</i> ≤ 25	-26 ≤ <i>h</i> ≤ 24, -9 ≤ <i>k</i> ≤ 9, -19 ≤ <i>l</i> ≤ 19	-17 ≤ <i>h</i> ≤ 17, -30 ≤ <i>k</i> ≤ 30, -25 ≤ <i>l</i> ≤ 25
Reflections collected	8624	21424	29041	143255
Independent reflections	1778 [<i>R</i> _{int} = 0.0177, <i>R</i> _{sigma} = 0.0125]	4830 [<i>R</i> _{int} = 0.0178, <i>R</i> _{sigma} = 0.0151]	2849 [<i>R</i> _{int} = 0.0335, <i>R</i> _{sigma} = 0.0166]	14502 [<i>R</i> _{int} = 0.0624, <i>R</i> _{sigma} = 0.0372]
Data/restraints/parameters	1778/0/82	4830/0/265	2849/0/159	14502/0/605
Goodness-of-fit on <i>F</i> ²	1.103	1.054	1.116	1.023
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0376, <i>wR</i> ₂ = 0.1202	<i>R</i> ₁ = 0.0447, <i>wR</i> ₂ = 0.1326	<i>R</i> ₁ = 0.0501, <i>wR</i> ₂ = 0.1717	<i>R</i> ₁ = 0.0572, <i>wR</i> ₂ = 0.1521
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0389, <i>wR</i> ₂ = 0.1213	<i>R</i> ₁ = 0.0476, <i>wR</i> ₂ = 0.1354	<i>R</i> ₁ = 0.0560, <i>wR</i> ₂ = 0.1780	<i>R</i> ₁ = 0.0865, <i>wR</i> ₂ = 0.1709
Largest diff. peak/hole / e Å ⁻³	0.93/-0.93	1.16/-0.78	0.67/-0.67	1.05/-0.54

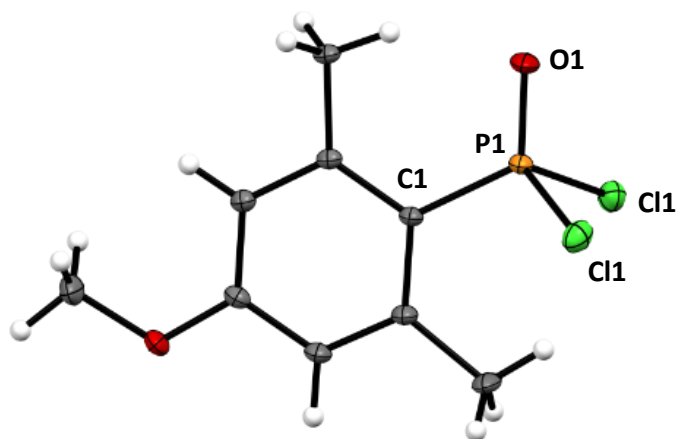


Figure C.45 Single crystal X-ray structure of *p*-MeOArPOCl₂

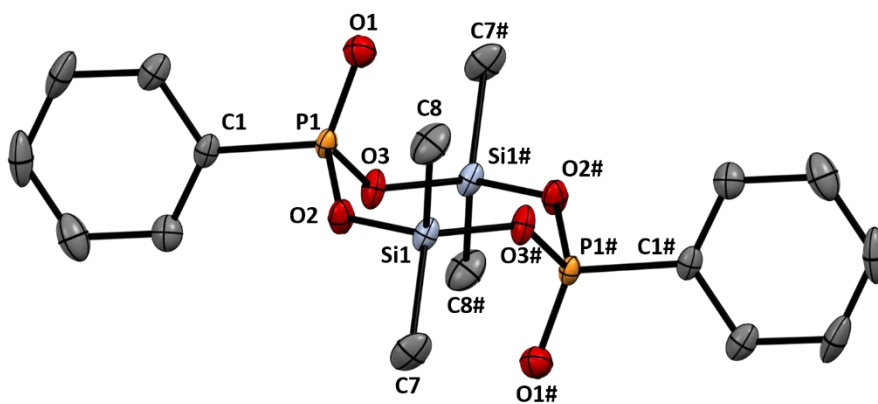


Figure C.44 Single crystal X-ray structure of **P^{Ph}Si^{Me}**

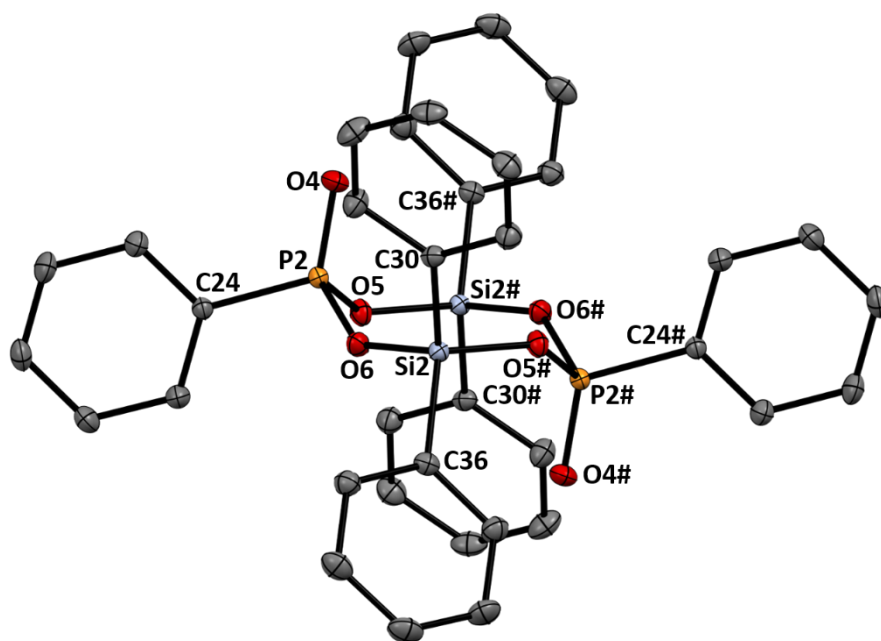


Figure C.46 Single crystal X-ray structure of $\text{P}^{\text{Ph}}\text{Si}^{\text{Ph}}$

Figure C.47 Single crystal X-ray structure of $\text{P}^{\text{Ph}}\text{Si}^{\text{Mes}}$

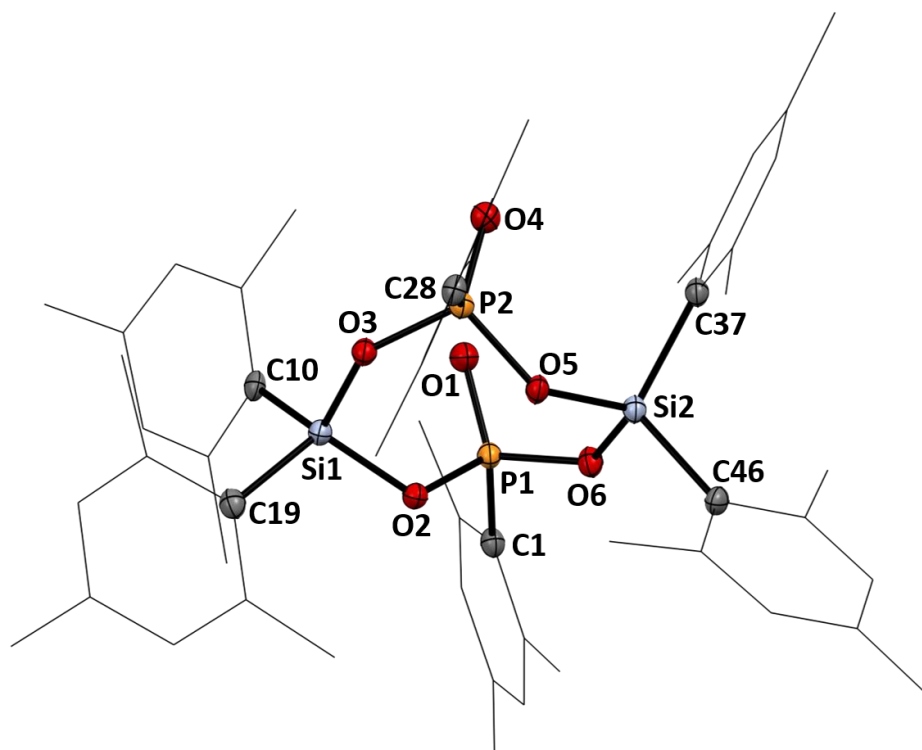
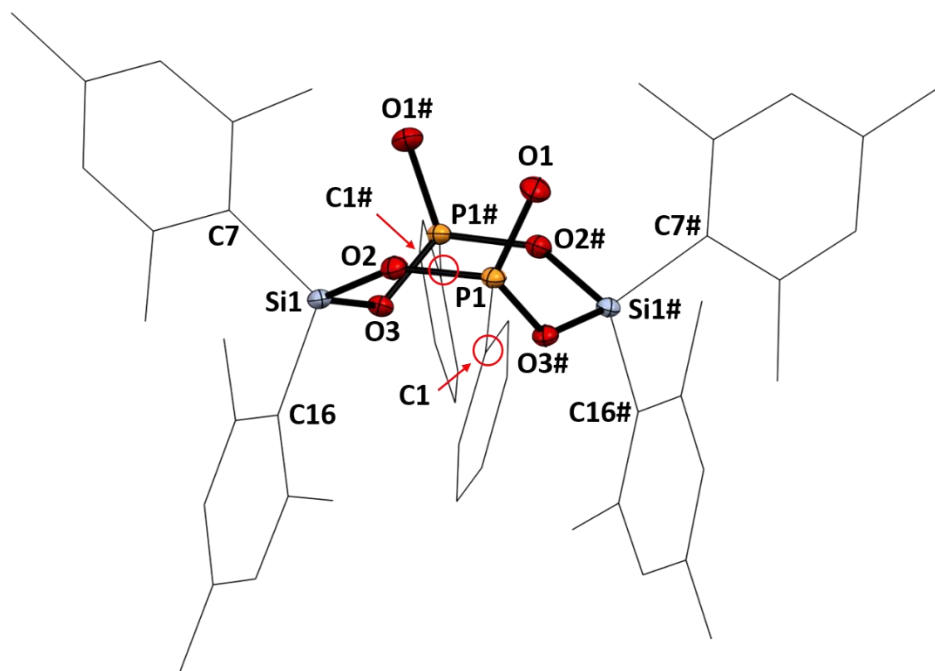


Figure C.48 Single crystal X-ray structure of $\text{P}^{\text{Mes}}\text{Si}^{\text{Mes}}$

