

**SULFUR DIIMIDES AND THEIR TIN(IV) COMPLEXES, AND
CONTRIBUTIONS TO IMPROVED MODELS FOR X-RAY CRYSTAL
STRUCTURES**

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Dedication

*To Tian; it's dangerous to go alone! Take this. *opens hand with a cool rock, a pretty flower I didn't know was poisonous, and two billion kisses**

To Callisto, Persephone, and Daphne, biiiiiig stretch

Abstract

Modernization of X-ray crystallographic structure model refinement using NoSpherA2 and an extensive investigation of the chemical and electrochemical properties of sulfur diimides (SDIs) and their tin(IV) chloride complexes are described.

NoSpherA2, an X-ray model refinement tool recently integrated into the free-to-use Olex2 program, is shown by thorough comparative analysis to significantly outperform conventional Independent Atom Model (IAM) methods. Consistent improvements in hydrogen atom placement and non-H bond precisions demonstrate the benefits of incorporating NoSpherA2 into routine processing of crystallographic data.

The synthesis of a systematic series of SDIs is presented alongside a comprehensive study of their fundamental properties, both on their own and as ligands in tin(IV) complexes. Their voltammetric behaviour is meticulously documented and suggests the SDIs are acting as redox-active ligands. This foundational work positions SDIs as promising candidates in this very active field of research, and provides warrant and clear direction for future endeavours therein.

Contribution of Authors and Preface

Chapters 2–5 of this thesis are reproduced from the following publications with permission from the corresponding publishers and all co-authors:

- Chapter 2** – Hill, N.D.D.; Boéré, R.T., Small Molecule X-ray Crystal Structures at a Crossroads. *Chemistry-Methods*, **2025**, e202400052.
- Chapter 3** – Hill, N.D.D.; Lilienthal, E.; Bender, C.O.; Boéré, R.T., Accurate Crystal Structures of $C_{12}H_9CN$, $C_{12}H_8(CN)_2$, and $C_{16}H_{11}CN$ Valence Isomers Using Nonspherical Atomic Scattering Factors. *Journal of Organic Chemistry*, **2022**, 87, 16213–16229.
- Chapter 4** – Hill, N.D.D.; Boéré, R.T., N,N' -Diaryl-Sulfurdiimides are Strongly Redox-Tuned. *Chemistry – A European Journal*, **2024**, e202400563.
- Chapter 5** – Hill, N.D.D.; Boéré, R.T., N,N' -Diaryl-Sulfurdiimide and N,N' -*Tert*-Butyl-Sulfurdiimide Complexes of Tin(IV) Chloride. Submitted to *Chemistry – A European Journal*, **2025**.

In Chapter 3, all compounds were synthesized by Dr Christopher Bender, and preliminary inventory and organization of the samples was done by Elaura Lilienthal. Elemental analyses reported in Chapters 4 and 5 were performed by either Jackson Knott or Dr Dylan Webb. Raman spectroscopic data in Chapter 5 was collected by Dr Douglas Turnbull. Otherwise, I am responsible for conducting all synthetic, experimental, and computational work and all writing and composition contained in this thesis, with the help of Dr René Boéré in the role of my Thesis Advisor throughout. The publications listed above are reproduced in the indicated chapters, with formatting changes made to satisfy the manuscript requirements set by the University of Lethbridge School of Graduate Studies. All compound, table, figure, and scheme numbers are retained in the individual chapters, preceded by the chapter number or appendix letter. The *Angewandte Chemie* citation style is used throughout this thesis, which necessitated reformatting the References sections of some chapters that used different styles per the journal's requirements. All compound numbers, references, and reference numbers reset at the start of each chapter.

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List of Abbreviations

ADP.....	Anisotropic Displacement Parameter
BCOT	Benzocyclooctatetraene
Bipy.....	2,2'-bipyridine
CE	Crystal Explorer
CIF.....	Crystallographic Information File
CN	Coordination Number
CNDO	Complete Neglect of Differential Overlap
COT	Cyclooctatetraene
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
CSD	Cambridge Structural Database
CV	Cyclic Voltammetry (or Voltammogram)
DABCO	Diazabicyclooctane
DCBN	Dihydrocyclobuta[<i>a</i>]naphthalenes
DFT	Density Functional Theory
DTA	Dithiazole
DTDA.....	1,2,3,5-Dithiadiazole
ED.....	Electron Density
EPR.....	Electron Paramagnetic Resonance
FMO	Frontier Molecular Orbital
FTIR	Fourier-Transform Infrared
FWHM.....	Full Width at Half Maximum
GUI.....	Graphical User Interface
HAR	Hirshfeld Atom Refinement
HDDA	Hexadehydro-Diels-Alder (reaction)
HFC	Hyperfine Coupling
HOMO.....	Highest Occupied Molecular Orbital
HMDS.....	Hexamethyldisilazane

HSQC Heteronuclear Single Quantum Coherence
 ICSD Inorganic Crystal Structure Database
 IAM Independent Atom Model
 IR.....Infrared (spectroscopy)
 IRC Intrinsic Reaction Coordinate
 LUMO.....Lowest Unoccupied Molecular Orbital
 MO.....Molecular Orbital
 MP Melting Point
 NBO.....Natural Bond Orbitals
 NCOT Naphthocyclooctatetraenes
 NMR Nuclear Magnetic Resonance
 NoSpherA2 Non-Spherical Atoms in Olex2
 NSA NoSpherA2
 P.....Perpendicular
 PCM.....Polarizable Continuum Model
 PLNM Principle of Least Nuclear Motion
 RA Redox-active
 RNI.....Redox Non-Innocent
 RT.....Room Temperature
 SAP.....Sheared Antiparallel
 SEEPR.....Simultaneous Electrochemical Electron Paramagnetic Resonance
 SCF.....Self-Consistent Field
 SC-XRD Single Crystal X-ray Diffraction
 SDI.....Sulfur Diimide
 SOMO.....Singly Occupied Molecular Orbital
 SP Sheared Parallel
 s.u. Standard Uncertainty
 SW Square-Wave
 SWV.....Square-Wave Voltammetry (or Voltammogram)
 TAAM Transferable Aspherical Atom Model

TDA	Thiadiazole
TCBN	Tetrahydrocyclobuta[<i>a</i>]naphthalene
TD-DFT.....	Time-Dependent Density Functional Theory
THF	Tetrahydrofuran
TMS.....	Trimethylsilyl
UV-PES.....	Ultraviolet-Photoelectron Spectroscopy
UV-Vis	Ultraviolet-Visible (Spectroscopy)
XRD.....	X-ray Diffraction

Chapter 1. Introduction

1.1. Origins of Thiazyl Chemistry

Sulfur-nitrogen chemistry, interchangeably called thiazyl chemistry, is an expansive area of inquiry with considerable pedigree. The first thiazyl compound was reported by Gregory in 1835, detailing the detection of tetrasulfur tetranitride, S_4N_4 .^[1] The precise molecular composition was determined decades later in 1896,^[2-4] and its distinctive cage structure was elucidated in 1944 by Lu and Donohue using gas-phase electron diffraction,^[5] later confirmed in solid-state by X-ray diffraction in 1952.^[6] These compounds caught the interest of many researchers, and an extensive catalogue of binary thiazyl compounds (i.e. containing only S and N atoms) and their derivatives was developed which has been repeatedly reviewed and added to, a few of which are shown in Figure 1.1 below.^[7-13]

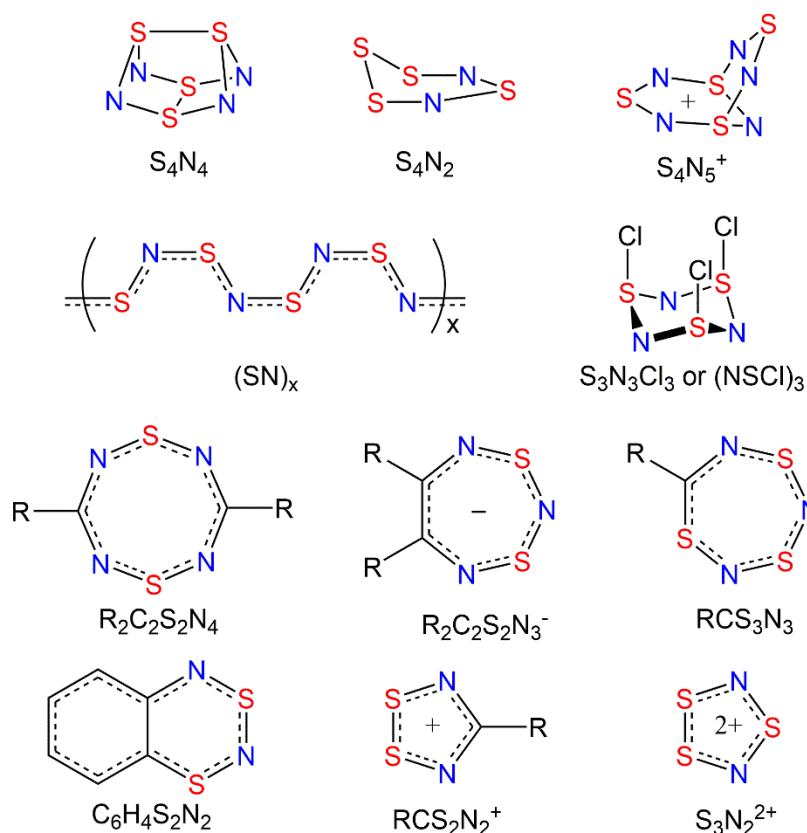
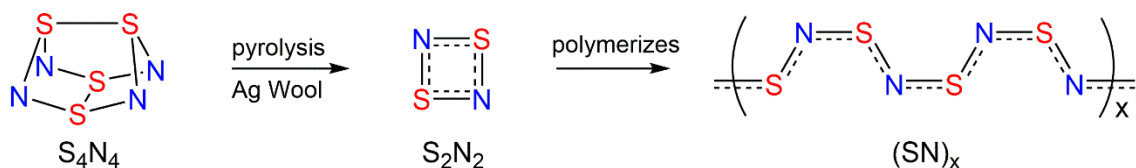


Figure 1.1. Binary thiazyl compounds and some examples of their derivatives. Adapted from several figures and schemes from Oakley.^[10]

Thiazyl compounds find close analogs in the very common and well-known nitrogen oxides, such as NO, NO₂, N₂O, NO₃[•], etc., which are typically sufficiently stable for routine use. But with a heavier chalcogen analog like sulfur, small binary S,N molecules tend to be highly reactive and often polymerize to form larger units or, rather dramatically, explosively decompose to their constituent elements.^[7, 11, 14-16] Compounds with N,E moieties (moiety: a contiguous portion of a molecule with a distinct composition. E = chalcogen. Here, principally O, S, and Se) have extensive libraries of stable radical species, exceeded in number only by carbon-based radicals.^[17-18] There are several factors that contribute to the stability of these N,E-based radicals: 1) many such compounds have a neutral charge arising from an odd number of N atoms, which carry five valence electrons. 2) They strongly tend towards forming π -radicals, which are less reactive due to delocalization, and are less susceptible to dimerization or coupling reactions than a σ -radical.^[10, 19-20] 3) In the case of N,S (or N,Se) radicals, the high electronegativity of nitrogen coupled with the polarizability of sulfur further stabilize these ‘extra’ electrons. Such factors are also key to the nature of N-S bonds and the redox behaviour of thiazyl moieties.



Scheme 1.1. Pyrolysis of S₄N₄ over Ag wool produces S₂N₂, which polymerizes over time to (SN)_x. Figure adapted from Rawson.^[21]

The neutral nitrogen monoxide monomer (NO[•]) radical can be isolated at room temperature.^[17-19] By contrast, the analogous sulfur nitride monomer (NS[•]) is so extraordinarily prone to polymerization that it cannot be isolated as a monomer in liquid-state or solid-state, but only transiently generated in gaseous phase.^[16] Fairly recently, NS[•] was photolytically released from [Cr(NS)(CH₃CN)₅]²⁺ and spin-trapped by [Fe(S₂CNEt₂)₂], which allowed an unprecedented characterization of its solution-state reactivity.^[22] Gas-

phase $\text{NS}\cdot$ can be generated by pyrolysis over silver or quartz wool, which produces a variety of binary S,N compounds.^[7, 11, 15, 23-24] One such product is S_2N_2 , shown in Scheme 1.1. As with other small binary thiazyls, S_2N_2 is highly shock-sensitive and will enthusiastically revert to its elements with little provocation, but if it remains undisturbed it will slowly polymerize to form crystals of polysulfur nitride, $(\text{SN})_x$, a unique inorganic polymer which has become one of the most, if not the most, impactful and best studied thiazyl compounds.

1.2. $(\text{SN})_x$: The First Polymeric Metal

First described in 1910,^[25] polysulfur nitride (or polythiazyl, $(\text{SN})_x$) forms fibrous bronze-coloured crystals with a metallic sheen and is insoluble in organic solvents, relatively stable (when it is highly pure and fully polymerized),^[11, 21, 24, 26-28] and exhibits far less of the propensity of its thiazyl congeners to explode under normal conditions.^[7, 14-16, 23] The peculiarly metallic properties of $(\text{SN})_x$ generated keen interest, most of all due to its remarkable conductivity which results from its half-filled conduction band,^[15-16, 26] shown in Figure 1.2. It was initially reported as a semi-conductor,^[7, 29-30] but more exacting experiments demonstrated that the highly pure $(\text{SN})_x$ is a conductor on par with liquid mercury, and is a true metallic polymer.^[11, 14, 24, 31] The metallic conductivity of $(\text{SN})_x$ has been attributed to the suppression of Peierl's distortions (periodic deformations in the crystal lattice which widen the band gap and are deleterious to one-dimensional conductors) by structural features of its unit cell symmetry (principally, the 2-fold screw axis along the chains) and strong inter-chain interactions, illustrated in Figure 1.2.^[32-35] The lack of Peierl's distortions is evident in the highly uniform S-N bond lengths.^[21, 24, 36-37]

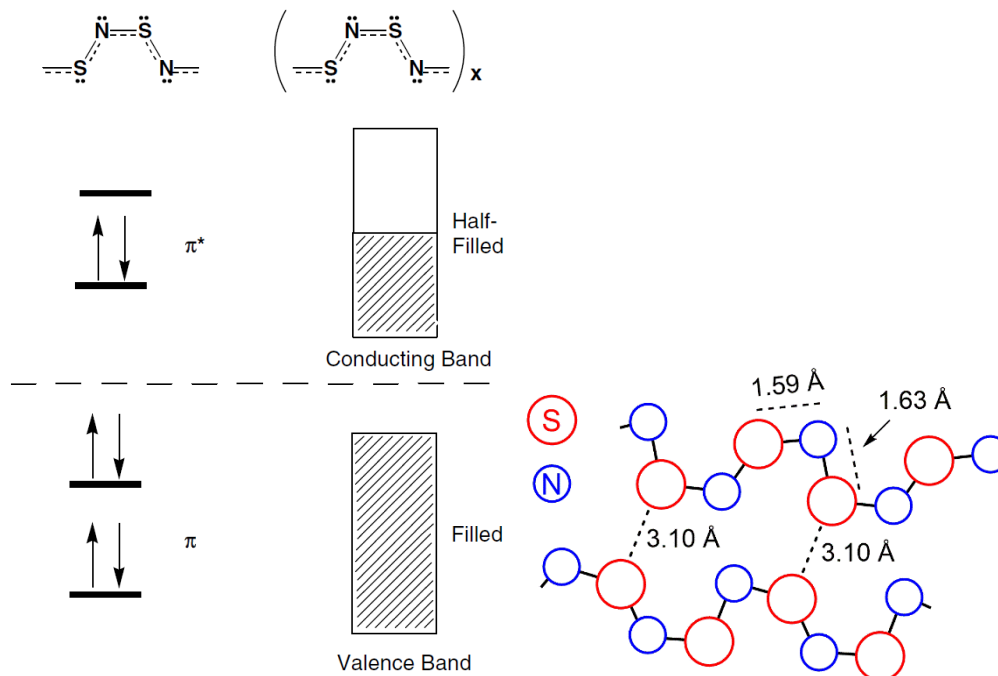


Figure 1.2. Molecular orbital and band occupancy diagrams of an $(\text{SN})_x$ fragment (left), adapted from Chivers.^[15] Structural diagram of $(\text{SN})_x$ fragment showing S-N bond lengths and S---S interchain contacts (right), adapted from Labes.^[11]

The interest in $(\text{SN})_x$ greatly multiplied in 1975 with the discovery that it becomes superconducting at 0.26 K,^[38] the first example of superconductivity in a polymeric compound. Understandably, this was closely followed by intense investigation into the physical and electronic properties of $(\text{SN})_x$.^[24, 39-44] In 1972, somewhat preceding this revelatory discovery, Banister described the electronic properties of binary S,N heterocycles as ‘electron-rich aromatics’, wherein S atoms provide two π -electrons and N atoms provide one, and correlated their π -electron counts to their molecular structures, see Figure 1.3.^[45] This electron-richness is also operative in acyclic thiazyl chains and has spurred a great deal of research directed towards harnessing the conductivity of S,N systems in so-called ‘molecular wires’.^[21, 34] Industrial-scale use of $(\text{SN})_x$ has not been realized, primarily due to the time and energy costs of pyrolyzing S_4N_4 to S_2N_2 followed by slow (days to weeks) polymerization of $\text{S}_2\text{N}_2 \rightarrow (\text{SN})_x$, as well as the aforementioned predilection of both of these materials towards expedited self-disassembly.^[14, 21] While

progress has been made in finding safer syntheses of (SN)_x crystals or films^[14], work in this area has largely focused on creating compounds or chains with smaller S,N oligomers to function as small ‘fragments’ or models of (SN)_x.^[21, 34-35, 46] A theoretical study from Whangbo *et al.*^[47] predicted that, because a unit of R-C is isolobal (i.e. frontier orbitals are similar in number, symmetry, energy, shape, and number of electrons) with S⁺ as a substituent in an S,N system, a polymer with (RCNSN) monomeric units will have greater chemical stability than (SN)_x, and similar conductivity.

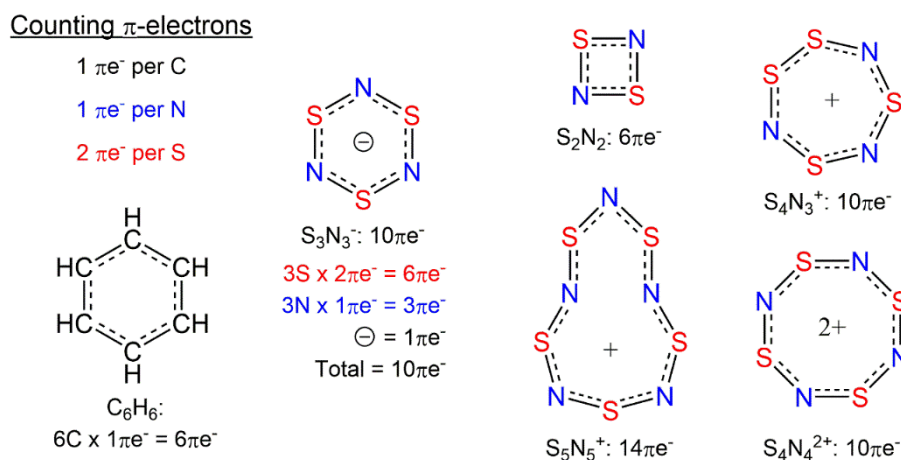


Figure 1.3. Examples of stable S,N heterocycles with π -electron counts conforming to the $(4n+2)$ Hückel rule for aromaticity. Figure adapted from Chivers.^[15]

1.3. (SN)_x Model Compounds

A key feature revealed by the investigations into the electronic properties of (SN)_x is the extensive π -electron delocalization along S,N chains.^[26, 48-50] This property is largely retained in smaller thiazyl units, demonstrated by e.g. ‘electron-rich aromatic’ properties in binary S,N cycles (Figure 1.3),^[16, 45] and strong substituent effects in benzo-fused dithiazoles^[51-53] (Figure 1.4a) and acyclic thiazyl-bridged organic compounds (Figure 1.4d).^[54-55] Figure 1.4 presents a non-exhaustive depiction of categories of thiazyl compounds that have been investigated as models of (SN)_x. Each category boasts an impressive collection of research articles and reviews, which by regrettable necessity shall receive only cursory summaries.

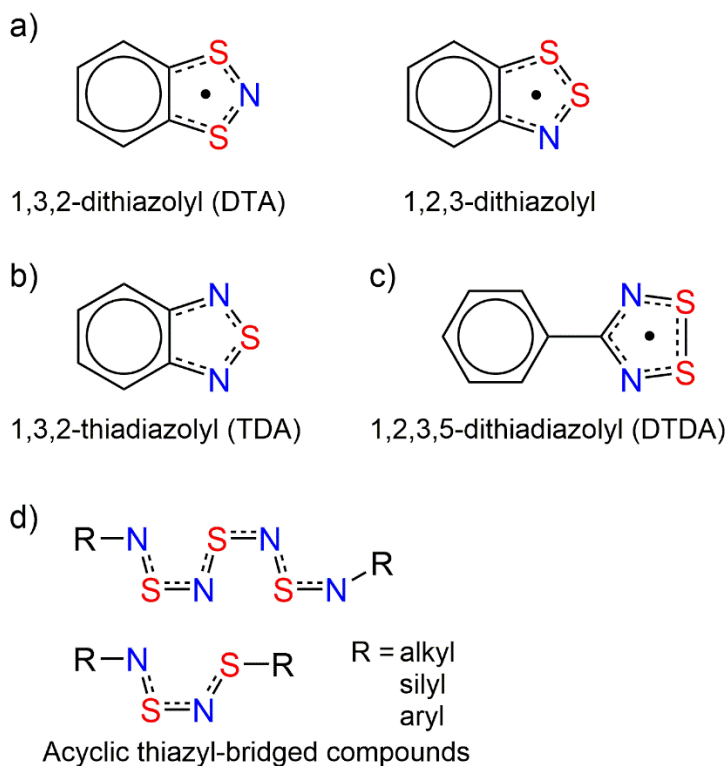


Figure 1.4. Examples of (SN)_x model compounds

1.3.1. Fused and Pendant S,N Heterocycles

The most prolifically studied model (SN)_x compounds are the 5-membered C,N,S-type heterocycles, which can be benzo-fused as in the case of dithiazoles (DTA, Figure 1.4a) and thiadiazoles (TDA, Figure 1.4b), or part of a pendant ring like 1,2,3,5-dithiadiazoles (DTDA, Figure 1.4c). Selenium analogues of these compounds have also been well-studied, but will not be prominently featured in this work. Benzo-fused DTAs and TDAs are excellent electron acceptors due to the high electronegativity and polarizability of the N,S cycles, and have been incorporated into aromatic compounds to modulate their electronic structures.^[51, 54, 56-61] Both can form conductive charge-transfer salts wherein DTAs act as an electron donor,^[62-66] and TDAs can act as either acceptor^[58, 60-61] or donor.^[61, 67]

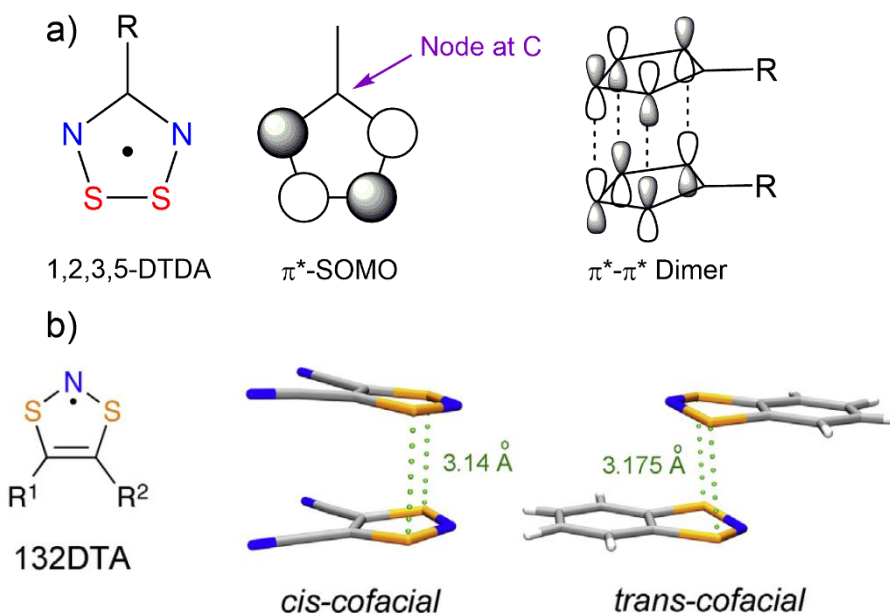


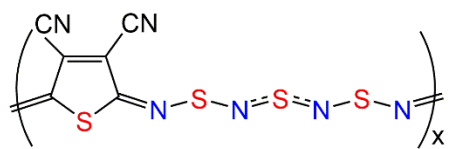
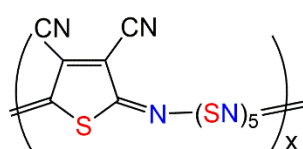
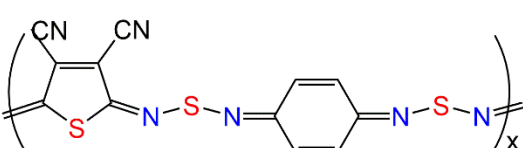
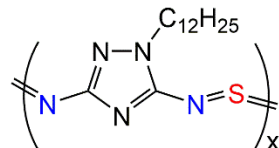
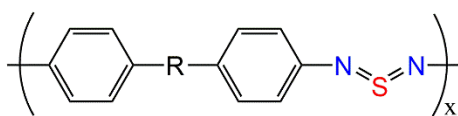
Figure 1.5. a) Structure and orbital diagram of a 1,2,3,5-DTDA, and illustration of *cis-cofacial* dimerization. b) Structural diagram of a 1,3,2-DTA and illustrations of *cis-cofacial* and *trans-cofacial* dimerization, adapted from Preuss.^[68]

Neutral DTAs and DTDAs possess an unpaired electron, which has led to significant interest in their electronic and magnetic properties. Their neutral radicals are remarkably stable in solution, and have been proposed as spin probes for electron paramagnetic resonance (EPR) spectroscopy.^[10, 69] DTAs and DTDAs have garnered particularly strong interest in materials research as candidate compounds for neutral radical conductors,^[52-53, 70-76] a concept proposed by Haddon in 1975,^[77] and for molecular magnetic materials, as they have been shown to exhibit long-range magnetic ordering through strong magnetic exchange interactions.^[19, 62-64, 70-71, 75, 78-80] Progress towards applications in both areas, especially with regard to their magnetic properties, has been hindered by their strong tendency to dimerize, resulting in spin-pairing of the unpaired electrons. Figure 1.5 illustrates examples of this dimerization where the π^* singly occupied molecular orbitals (SOMO) of two units of DTDA or DTA overlap to form a ‘pancake bond,’ which is a category of the well-known π -stacking interactions where delocalized π -based radicals of organic and light atoms associate with ‘covalent-like’ electron sharing.^[68, 81-82] Such dimerization

inhibits their conductivity and quenches their bulk magnetic properties. Retaining these characteristics is in principle a problem that can be mitigated through controlling the arrangement of molecules in the solid state to reduce overlap of the unpaired electron SOMOs, and thus has been a subject of considerable interest in the field of crystal engineering.^[71, 76, 79, 83-86] Unlike DTAs, the pendant heterocycle of DTDAs is electronically insulated from the rest of the molecule by an orbital node at C, shown in Figure 1.5a, and experiences only weak effects from the substituents,^[51, 87] which allows for broad derivatization of the DTDA without greatly affecting the electronic properties of the heterocycle. There is continued strong interest in these systems and their magnetic and conductive properties. Considerable effort has been directed to exploring the feasibility of the exemplars discussed here in applications such as molecular conductors, magnets, and switches,^[17, 19, 52, 62, 64, 66, 70-71, 75, 78, 83, 88-102] and photovoltaic materials,^[57, 103-108] among others.^[71, 78, 109-111]

1.3.2. Acyclic Thiazyl-Bridged Mono-, Oligo-, and Polymers

In line with the suggestion of Whangbo^[47] that C,N,S polymers may have conductive properties analogous to (SN)_x, numerous groups have investigated oligomers and polymers of aromatic organic groups connected by S,N chains, or monomers of two organic (not necessarily aromatic) groups bridged by an S,N chain. These thiazyl-bridged compounds have most often been investigated as candidates for creating molecular wires for nano-scale electronic devices.^[21, 34-35, 112-113] Some examples of C,N,S polymers are depicted in Figure 1.6,^[56-57, 114-120] the most conductive of which was several orders of magnitude lower than (SN)_x.^[118] The reduced conductivity in C,N,S polymers is generally thought to be caused by the disruption of the interchain contacts (which prevent Peierl's distortions in (SN)_x, as discussed above) by the incorporation of organic units.^[14, 24, 32-37, 54, 116-117]

	Conductivity σ ($\Omega^{-1}\cdot\text{cm}^{-1}$) [ref]	
	$\sim 10^3$	[14]
	$\sim 10^{-4}$ $\sim 10^{-6}$	[116] [117]
	$\sim 10^{-6}$	[117]
	$\sim 10^{-6}$ $\sim 10^{-7}$	[116] [117]
	No Data	[119]
	No Data	[114]

R = e.g. C_2H_2 , N=N, S

Figure 1.6. Examples of C,N,S polymers and their conductivities (if available) compared against $(\text{SN})_x$

Other work towards molecular wires has focused on monomers of R groups (most often R is aryl, alkyl, or trimethylsilyl) bridged by S,N chains of varying lengths, the most prolific variety of which have been reported by the Zibarev group.^[34-35, 46, 112, 121-124] They repeatedly note the extensive delocalization of the π -system, which encompass the S,N chain and any conjugated R groups, analogous to the delocalization seen in $(\text{SN})_x$, which grants substantial modulation of the electronic properties of the compounds by substituent effects of the R groups. Zibarev concludes that acyclic thiazyl compounds of this type are in principle capable of acting as molecular wires.^[35]

1.4. Sulfur Diimides

Among the acyclic thiazyl compounds are sulfur diimides (SDIs), R-NSN-R, which are a principal focus of this thesis. The first known SDI was reported in 1956 by Göhring and Weis,^[125] the *n*-butyl derivative S(N^{*n*}Bu)₂. This was closely followed by several aryl SDI compounds,^[126-127] and the ubiquitous *t*-butyl^[128-130] and trimethylsilyl^[131] SDIs. Today, sulfur diimides have an extensive library of derivatives including the parent hydrogen SDI (H-NSN-H),^[132-135] a diverse range of alkyl and aryl substituents,^[34, 121, 128-129, 136-140] and heteroatom derivatives (e.g. boryl, silyl, germanyl, phosphinyl, stannyl, arsiny).^[141-149] Recently, a series of hypersilyl SDIs (e.g. S(NSi(SiMe₃)₃)₂) was reported by the Stalke group,^[150] which are exceptionally electron rich.

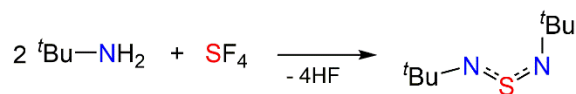
1.4.1. Synthesis of Sulfur Diimides

There are many unique syntheses for sulfur diimides which typically fall into a few broad categories, detailed below. Sulfur diimides are susceptible to hydrolysis, vastly more so in acidic conditions, breaking down into their constituent amines and sulfur dioxide.^[54, 125, 128-129, 151] Procedures in the synthesis of sulfur diimides are generally carried out under inert atmosphere using anhydrous solvents. Figure 1.8 details several methods for synthesizing SDIs. The products are depicted in *EZ* conformation w.r.t. the N-S bonds, shown in Figure 1.7. Depending on the *N*-substituents, the lowest energy conformation is either *EZ* or *ZZ*, whereas the *EE* conformation is the globally highest energy conformation.

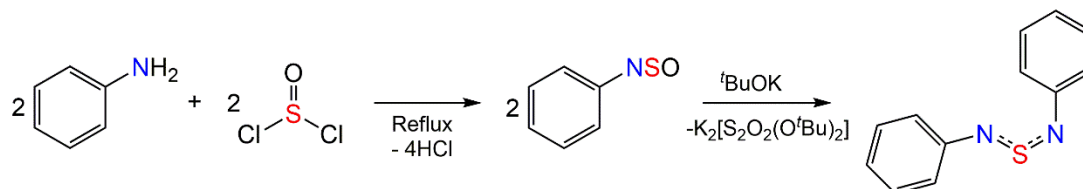


Figure 1.7. Possible conformations of sulfur diimides

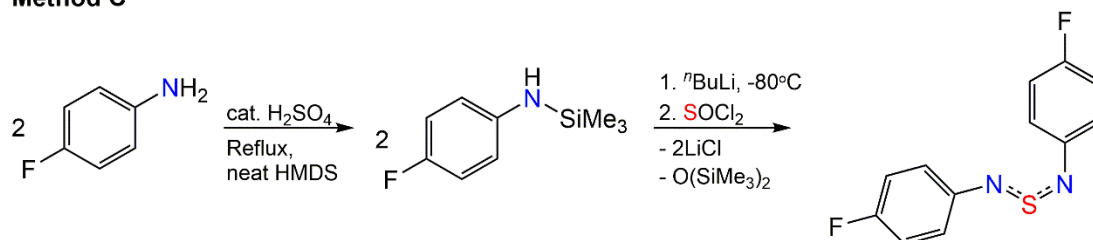
Method A



Method B



Method C



Other Methods

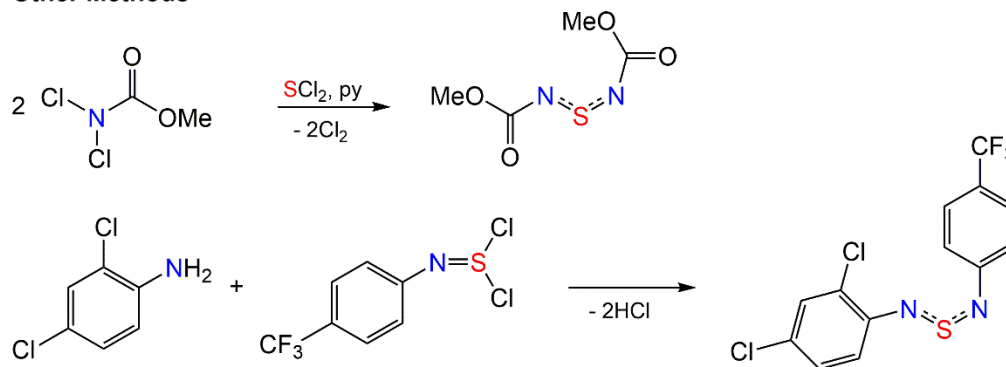


Figure 1.8. Most common syntheses of SDIs (Methods A, B, and C), and selected examples of less common methods.

The chronologically first and most direct method (Method A in Figure 1.8) used to synthesize sulfur diimides is the reaction of a primary amine (R-NH₂) with a sulfur halide, either S(I), S(II) or S(IV), e.g. S₂Cl₂, SCl₂, SF₄, RNHSCl₂.^[125, 127-128, 152-155] The original synthesis from Göhring combined *n*-butylamine with sulfur tetrachloride to form *bis*(*N,N'*-*n*-butyl)sulfurdiimide. A sacrificial excess of amine is used to react with the HCl that is also produced, forming *n*-BuNH₃Cl and preventing hydrolysis of the SDI.

Method B converts a primary amine to *N*-sulfinylamine by reflux (boiling) with thionyl chloride, SOCl_2 .^[156-157] In the second step, potassium *tert*-butoxide (others have used metallic sodium or pyridine) is added to the sulfinylamine, which couples two units of NSO together, producing the sulfur diimide and disulfite^[137-138] $[\text{S}_2\text{O}_5]^{2-}$ or dithionite^[127, 158] $[\text{S}_2\text{O}_4]^{2-}$ salt. Some groups report evolution of SO_2 gas rather than formation of salt.^[126, 137, 159-160]

Method C refluxes the starting amine with neat hexamethyldisilazane (HMDS) and catalytic acid (e.g. H_2SO_4) to make the monosilylated amine $\text{R-NH}(\text{SiMe}_3)$, which must be distilled prior to the next step. The silylated amine is dissolved and cooled to -80°C . A strong base is added to deprotonate the amine (e.g. *n*-butyllithium), followed by addition of thionyl chloride to couple two amines together, producing the sulfur diimide and hexamethyldisiloxane ($\text{O}(\text{SiMe}_3)_2$). This method is not as well represented in literature as methods A and B, but as seen in Chapter 4, it is viable and sometimes superior to other methods.^[161]

There is extensive variation of methods within each of the general synthetic pathways above, and several syntheses which do not fit into any of them, briefly listed here. Methyl *N,N*-dichlorocarbamate can be reacted with SCl_2 to form *bis*(methoxycarbonyl)sulfur diimide.^[154, 162-164] Some diaryl-SDIs were made by a reaction between the corresponding aniline, elemental sulfur (S_8), and mercury acetamide.^[165] A unique SDI with trimethylstannyl substituents, $(\text{Me}_3\text{Sn-N})_2\text{S}$, can be synthesized by reacting *tris*-trimethylstannylamine with either S_4N_4 or the cyclic trimer $(\text{SNCl})_3$.^[149] The simplest sulfur diimide, H-NSN-H , is highly reactive and short-lived, but can be transiently produced by pyrolysis of S_4N_4 ,^[132] a microwave-induced reaction between H_2S and N_2 ,^[134] or by reaction of strong acid (HX) with M-NSN-M .^[133, 135]

These syntheses exclusively produce symmetric sulfur diimides in which the *N*-substituents are identical. There are also several methods to make asymmetric variants, which greatly adds to the number of accessible derivatives. Asymmetric SDIs can be synthesized by reacting anionic amines with either *N*-sulfinylamines^[34, 123, 161] or imidosulfur dichlorides,^[166] by condensation of an aniline with an *N*-arylimidosulfur dichloride,^[154, 167] or by using metallic sodium to scramble the substituents of two different SDIs, shown in Figure 1.9.^[158] There is one report of an (*N*-*tert*-butyl-*N'*-trimethylsilyl)sulfur diimide made by reacting trimethylsilyl azide (Me_3SiN_3) with an *N*-sulphenylchloroamine ($\text{Me}_3\text{SiN}(\text{tBu})\text{SCl}$),^[166] but no experimental details are provided.

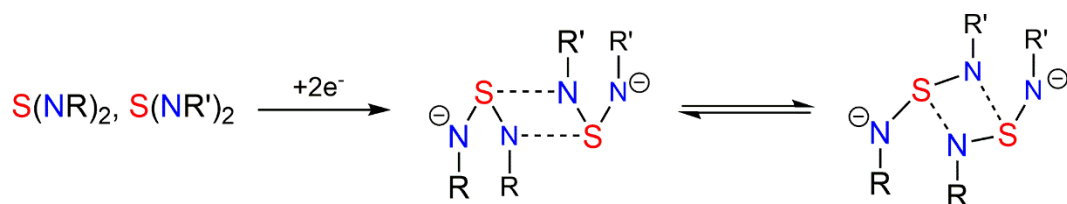


Figure 1.9. Skeletal scrambling mechanism of SDIs proposed by Bestari, adapted from Bestari.^[158]

1.4.2. SDI Coordination Chemistry

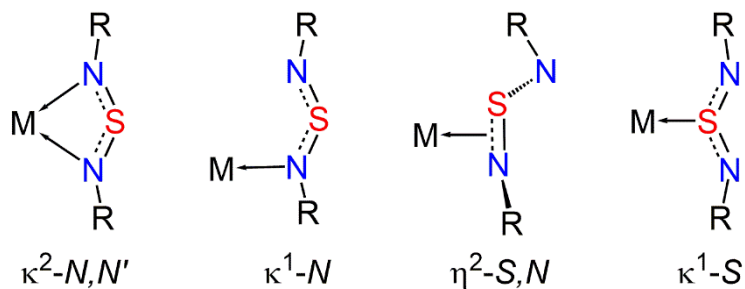


Figure 1.10. Possible coordination modes of SDI metal complexes.

Since the first reported coordination complex incorporating a sulfur diimide as a ligand in 1972,^[168] an extensive coordination chemistry of SDIs has developed which covers many of the transition and post-transition metals, as well as several lanthanides.^[151, 169-192] The majority of reported SDI ligands have R groups that are alkyl (mostly *tert*-butyl) or trimethylsilyl, while most of the remainder have aryl R groups. Multiple coordination

modes have been reported, depicted in Figure 1.10, most commonly κ^1 -N through one nitrogen atom of the -NSN- moiety or κ^2 -N,N' through both nitrogens, and much less frequently η^2 -S,N. There are credible claims of κ^1 -S coordination based on NMR evidence, but the assignment remains tentative, as the proposed complex, $[\kappa^1$ -S-(MeN)₂S]W(CO)₅, could not be structurally characterized.^[175, 180]

1.5. Non-Innocent and Redox-Active Ligands

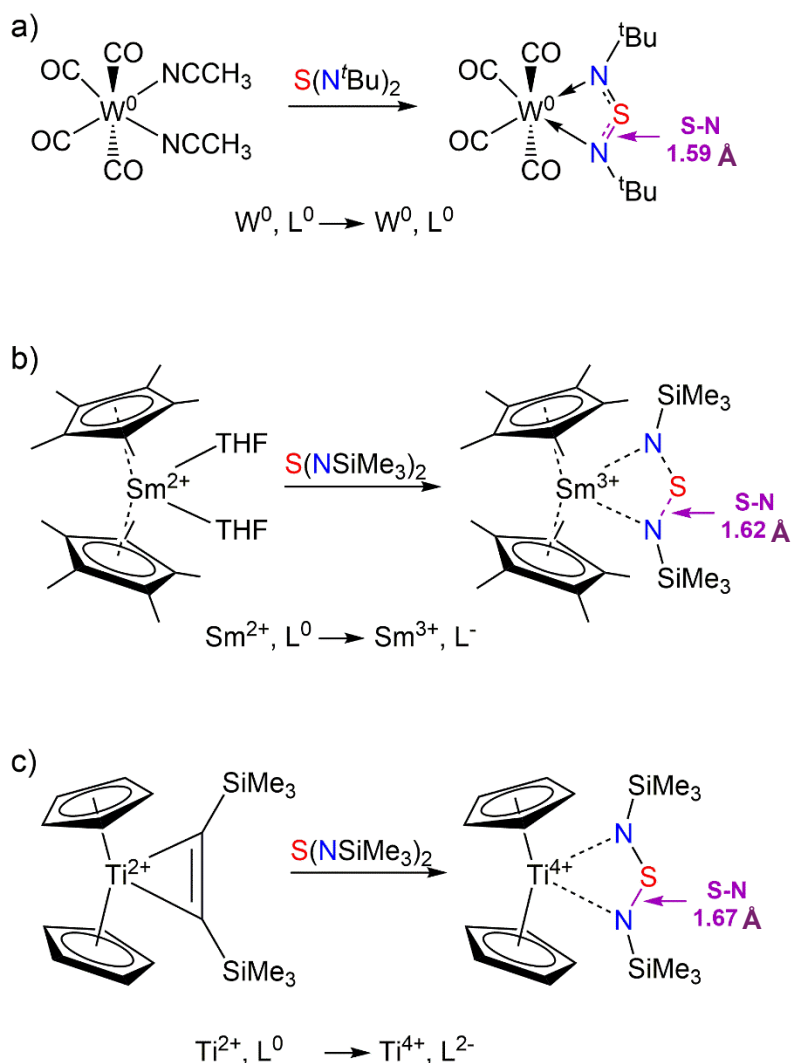


Figure 1.11. Illustrations of redox non-innocence exhibited in different complexes with SDI ligands from a) Meij,^[174] b) Klementyeva,^[188] and c) Kaleta.^[189]

The properties of SDI ligands are greatly impacted by their coordination mode. SDIs which are coordinated in $\kappa^2\text{-N,N'}$ fashion have been demonstrated to function as non-innocent^[171-172, 174, 178, 188-189] and redox-active ligands,^[170, 172] illustrated in Figures 1.11 and 1.12, respectively. These properties are not operative when the SDI ligands employ other coordination modes.^[173-174] A commonly used definition of an innocent ligand is one which allows the unambiguous assignment of oxidation states of the central atoms.^[193] Put another way, when experimental measurements (e.g. chemical behaviour, voltammetry, or spectroscopy) of a complex agree with the assigned formal oxidation states (as determined by accepted rules of electron counting), the ligands are acting innocently.^[194] For example, *formally*, a chloride ligand will always be in the -1 oxidation state, so that the oxidation state of Fe in a neutral complex of FeCl_3 is assigned as Fe(III), or Fe^{3+} . This formal assignment agrees with all experimental determinations, thus the chloride ligands in FeCl_3 are acting innocently [Note: the term ‘acting innocently’ is used because innocent and non-innocent behaviour is a collective property that depends on both the ligands and the metal.^[195-196] Common parlance puts the onus of innocence on the ligands, and this will be used interchangeably throughout this thesis with the acknowledgment that the issue is nuanced]. By contrast, the oxidation states of a complex containing a non-innocent ligand are obfuscated and require further investigation to make an assignment. Examples of this behaviour are shown in Figure 1.11. The term ‘non-innocent ligand’ has recently been applied to systems where the observed non-innocence is due to structural or chemical changes to the ligand,^[196-199] but this work uses it exclusively to refer to redox non-innocence, describing spontaneous (generally metal-to-ligand) charge transfer. For interested readers, effective introductions to and discussions of non-innocent and redox-active ligands have been published by Chirik, Wieghardt, Kaim, and Ganguly.^[196, 200-202]

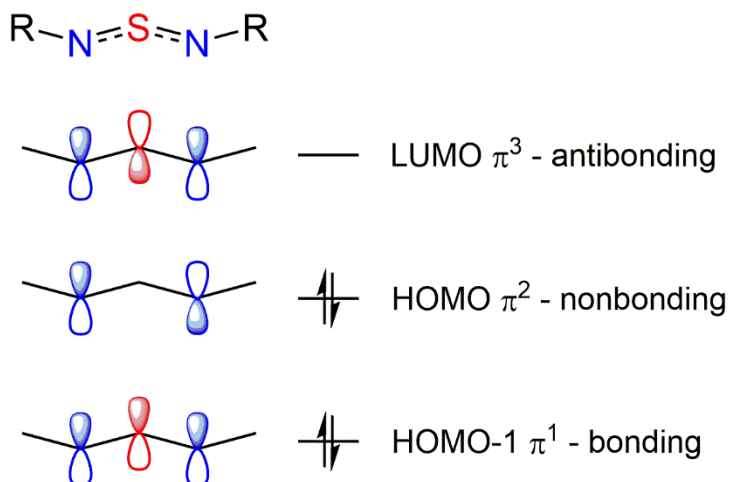


Figure 1.12. Diagram of π -molecular orbitals (MOs) of a generic sulfur diimide (arbitrarily drawn in *EE* conformation, *EZ* and *ZZ* π -MOs are highly similar)

In the case of SDI complexes, crystallographic analysis of the S-N bond length can reliably determine the extent of metal-to-ligand electron transfer. Figure 1.12 is a simplified π -MO diagram of a generic SDI. The lowest unoccupied molecular orbital (LUMO) of SDIs is π -antibonding with respect to -NSN- such that partial or full occupation of the LUMO will elongate the N-S bonds, noted in Figure 1.11.^[189] This method, supported by computational and spectroscopic evidence, has been used to determine cases in which a κ^2 -*N,N'*-SDI ligand is neutral,^[171-172, 174, 178] monoanionic,^[188] and dianionic.^[189] Non-innocent ligands can also be redox-active, meaning that reduction or oxidation of the complex involves, and often is principally localized on, the ligand.^[200-201] There are two instances from literature where complexes with a κ^2 -*N,N'*-SDI ligand were chemically or electrochemically reduced and subsequently examined by Electron Paramagnetic Resonance (EPR) spectroscopy, which showed that the radical anions were primarily localized on the SDI.^[170, 172]

Redox-active (RA) ligands have frontier orbitals which are similar in energy to those of the associated metal, and can participate in or even dominate redox reactions involving the complex. This can allow novel reactivity in a complex, or protect the metal centre from

deleterious changes in oxidation state during redox reactions. RA ligands have been an extremely active area of inquiry in recent years due to their wide-ranging and impactful applications. Chirik and Wieghardt articulated the ability of RA ligands to confer ‘nobility’ to base metals such as iron and copper, such that they can perform catalytic functions which have previously been the near-exclusive domain of precious (and expensive) metals.^[200] Among many examples of this type of reactivity, Small and Brookhart made an iron complex with RA ligands that catalyzed the oligomerization of ethylene to α -olefins with activity and selectivity similar to precious metal catalysts,^[203] and a 2020 article from Mashima details a series of early transition metal and lanthanide complexes with RA ligands that display a variety of catalytic activities such as hydrodehalogenation of alkyl halides and polymerization of 2-vinylpyridine.^[204] Other applications of RA ligands include bistable molecular switches,^[205] C-X bond activations (X = H, C, S, Cl, Br, I) and C-Y bond formations (Y = C, N, S),^[206-207] small molecule activation enabling e.g. photochemical H₂ production, CO₂ fixation, and water oxidation,^[206-208] and charge-transfer materials in metal-organic frameworks (MOFs) that have the potential to substantially impact materials design for renewable energy and photovoltaic technology.^[209] In a 2019 Concepts article, van der Vlugt discusses modes of activity of RA ligands and their importance to *inter alia* catalysis, renewable energy, and fuel cell research, emphasizing their capacity to act as electron reservoirs that can reversibly store and release electrons.^[210] They note that RA ligands can promote radical-type reactivity while suppressing the formation of free radicals which can severely limit chemoselectivity and substrate scope. For the sake of brevity, the above examples were chosen as a summary of the breadth of the development and applications of RA ligands, which are the subject of numerous reviews as well as a forum in *Inorganic Chemistry*.^[196, 207-209, 211-213]

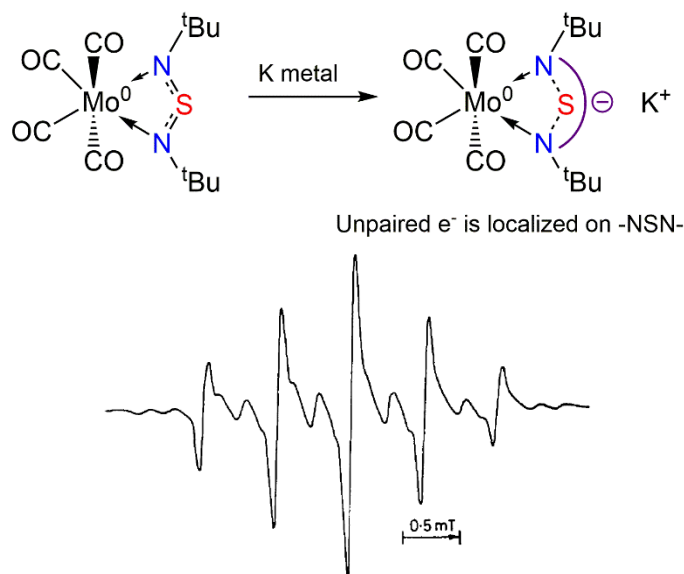


Figure 1.13. SDI acting as a redox-active ligand. Chemical reduction by potassium metal results in a radical anion that is primarily localized on the SDI ligand, demonstrated by the dominant 1:2:3:2:1 coupling pattern (characteristic of coupling to two equivalent ¹⁴N atoms) observed by electron paramagnetic resonance (EPR) spectroscopy.

The implementation of RA ligands extends the range of metals that can perform a given function. The redox properties of such complexes can be fine-tuned through intentional design of their RA ligands, maximizing their efficacy and achieving greater control over a process.^[205, 214] Given the evidence that sulfur diimides can act as RA ligands,^[170, 172] described above and illustrated in Figure 1.13, and their synthetic versatility that effectively limits the list of possible derivatives to the chemist's imagination, SDIs are a very attractive target to investigate as a potentially powerful class of RA ligand.

1.6. NoSpherA2 – Modernizing How We Process SC-XRD Experimental Data

It would be difficult to overstate the importance of single-crystal X-ray diffraction (SC-XRD) to modern chemistry; it is one of the most powerful methods for precise and unambiguous structural characterizations. While processing the SC-XRD data collected in this work, a new tool for refining the crystal structure models came to our attention, and it quickly became apparent that it represented an important and substantial advance in the field. This tool, named NoSpherA2,^[215] is described in detail in Chapter 2. In brief,

structure model refinement methods commonly used today employ the Independent Atom Model (IAM), which has been standard practice in structure determinations since the inception of the field of chemical crystallography. The IAM simplifies the necessary mathematical operations by treating atoms in the structure model as non-interacting spheres of homogeneous electron density, which they very much are not. X-rays are diffracted by electrons, so different shapes of electron distribution around atoms (caused by interactions with proximal atoms in the crystal lattice) must lead to subtly different diffraction patterns. Thus, the assumption of IAM that electrons are spherically distributed around atoms necessarily leads to structure models which contain intrinsic inaccuracies. Using modern Hirshfeld Atom Refinement methods and density functional theory (DFT) computations, NoSpherA2 takes atomic interactions into account when simulating the shape of electron distributions around atoms in the model, enabling a considerably closer match of the refined model to the collected data. Having become keenly interested in the application of NoSpherA2, I undertook a project that would test its capabilities and practicality, which produced a publication that comprises Chapter 3 of this thesis. The results from that work and several other high-quality studies confirmed that NoSpherA2 proffers dramatic improvements to the quality of the refined models, while requiring no specialized equipment and relatively modest effort to implement.

1.7. Scope of the Thesis

Chapters 2–5 of this thesis are assembled from published or submitted papers from two related but distinct projects. As such, each chapter contains detailed introductory remarks specific to the topics and chemistry it describes.

Chapter 2 gives an effective introduction to the methods and theory of structure model refinements and provides historical context to a discussion of contemporary shortcomings with common standard practice in the field. Structure refinement using the

NoSpherA2 software is described in detail, emphasizing the improvements it offers over current methods, and an evidence-based case is made that refining structures with NoSpherA2 (or similar software, as it becomes available) should be adopted as standard practice by the chemistry community.

Chapter 3 is a thorough analysis of high-quality crystal structures of a series of rare and interesting polycyclic nitriles, which are part of a legacy collection from Dr Christopher Bender's library of photochemically produced compounds. The crystal structures are fully refined using both standard IAM methods and NoSpherA2. Alongside in-depth commentary on the crystal structures obtained, which represent a substantial increase in the number of published structures of their archetypes, the structure refinements using IAM and NoSpherA2 are carefully compared to each other and to neutron diffraction data, an alternative crystallographic technique which excels in some key areas where X-ray diffraction performs poorly.

Chapter 4 details the synthesis and characterization of a series of diaryl sulfur diimides with systematic variations of their aryl substituents. The well-known *tert*-butyl and trimethylsilyl SDIs are characterized alongside the aryl series. Their electrochemical properties are carefully investigated, particularly regarding the effects of different substituents on the reduction potentials and the nature and stability of their radical anions. This chapter also investigates and definitively answers an enduring question regarding the solution-state conformations of SDIs, and corrects some historical errors in the assignment of IR vibrational modes of SDIs.

Chapter 5 is a direct continuation of the work in Chapter 4. Having thoroughly documented the properties and electrochemical profiles of the free SDIs, this work uses them as ligands in tin(IV) tetrachloride (SnCl_4) complexes. The complexes are characterized them for their own sake and to assess the potential of SDIs to act as redox-

active ligands. An intensive multi-nuclear NMR investigation reveals that these complexes undergo a ligand exchange equilibrium when dissolved in acetonitrile. This chapter presents the first crystallographically confirmed examples of $\kappa^1\text{-O}$ coordination of an *N*-sulfinylamine (PhNSO) and $\kappa^2\text{-N,N'}$ coordination of diaryl-SDIs, as well as a voltammetric study which indicates that SDIs suppress the reduction of Sn(IV), leading to the tentative suggestion that the SDIs may act as RA ligands.

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Chapter 2. Small Molecule X-ray Crystal Structures at a Crossroads

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2.1. Introduction

The standing of small-molecule chemical crystallography has never been higher as witnessed by over 1.3 million curated entries in the Cambridge Structural Database (CSD), with about 60,000 additions each year.^[1] Few synthetic chemistry papers today lack identity verification via the ubiquitous ‘crystal structure’. Significantly, there is currently an extraordinary ferment on the experimental side of this science.^[2] Ever more powerful home X-ray sources and detectors are complemented by synchrotron sources of immense intensity.^[3,4] Neutron diffraction has re-emerged with powerful new sources suitable for the typical sizes of synthetic crystals,^[5-7] and for micro- and nanocrystals, solids electron diffraction has emerged spectacularly from its origins in electron microscopy.^[8,9]

It is equally important to recognize that improvements in crystal structure refinement models for single-crystal X-ray diffraction (SC-XRD) are now urgently needed.^[10] Besides synchrotrons, even routine data obtained on modern home lab instruments are often of a quality that outpaces the assumptions of the traditional “independent atom method” (IAM) employed as the default in structure determinations for the first 110 years of chemical crystallography.^[11-13] A characteristic feature has been the use of neutral atom scattering factors, which are often not chemically appropriate due to subtle and continuous variations in atomic partial charges.^[10] Another deficiency of the standard approach is that hydrogen nuclei must be placed artificially close to the atoms they are bonded to (and hence diffraction by neutrons, which interact with nuclei rather than electrons, must be used to get accurate H-atom positions).^[10]

Several alternative methods have emerged out of quantum crystallography^[11,12] that now make it possible to compute custom atomic scattering (form) factors which reflect

the actual electron densities of each atom in the asymmetric units of crystals.^[13-19] These include several ‘database’ methods: the Invariom of Dittrich,^[16] or the TAAM method of Dominiak and co-workers.^[17] Hirshfeld Atom Refinement (HAR) is also recognized as a reliable methodology to improve on the IAM.^[12,13] An early example was the HART method of Jayatilaka based on TONTO DFT software.^[19] These all remain fully experimental structure determinations, but make use of various types of quantum calculations to improve on the isolated-atom gas-phase self-consistent field calculations that IAM scattering factors have been based on.^[20] Yet, despite the provocative claim, made in 2016, that “hydrogen atoms can be located accurately and precisely by X-ray crystallography” with HAR,^[14,15] the uptake by chemical crystallographers since has been minimal. In this Concepts article, we report on our experience implementing HAR with the recently introduced *Non-Spherical Atomic scattering in Olex2* (NoSpherA2) method.^[10,21] By systematic application to datasets with a typical range of quality from a synthetic chemistry research program, we confirm that H-atoms are placed at near-neutron accuracies. Moreover, we have detected a systematic increase in average bond precisions (for *other than* bonds to H) that trend closely with crystal/data quality, over about 65 published structures.^[22-31] Significantly, we found smooth transitions from marginal to large improvements with increasing data quality. Herein we argue in favour of wide adoption of the NoSpherA2 method in ‘routine’ chemical crystallography.

2.2. Brief Theoretical Background

Small-molecule SC-XRD does not intuit structures directly from the experimental data, the “diffraction spots”. Instead, the data are formulated in terms of a set of geometrically indexed *observed structure factor magnitudes*, $|F_{\text{obs}}|$. A structure model is then created – the details, including *inter alia* correct assignment of phases for each datum, are available from standard textbooks and not discussed further^[32] – from which a

theoretical set of values are computed that are comparable to the data, the *calculated structure factors* F_{calc} .

An accurate structure model is achieved by sequential adjustments of both atom positions and thermally-induced positional deviations via a least-squares procedure first introduced by Hughes in 1941,^[33] until the best possible agreement of $|F_{\text{calc}}|$ to $|F_{\text{obs}}|$ is obtained – the ‘final model’ – which is characterized by various residuals, i.e. the *R*-factors, of which R_1 is the best known (equation 1).

$$R_1 = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|} \quad (1)$$

In over a century of X-ray diffraction experiments by crystals, experimental data quality has been dramatically improved, to the point where data quality (F_{obs}) today either matches or exceeds that of the model (F_{calc}). The core parameters in computing F_{calc} are the strengths of incident X-ray scattering by the electrons associated with each atom in the crystal lattice – the form factors. The almost universal approach has been to define form factors within the IAM approximation, which assumes that the electrons with which the X-rays interact are localized spherically around the constituent atoms, keyed to their atomic numbers alone for the numbers of electrons involved and thus treating all atoms of a given element identically.^[11,12]

This approximation has obvious shortcomings, namely that atoms in a crystal lattice are not non-interacting spheres and that their charges vary subtly with chemical structure.^[10] While most electron density (ED) is expected to congregate closely around the nuclei, there is also ED to be found along covalent bonds between atoms so that the electrons around atoms in a molecule have non-spherical distribution.^[10] Nowhere is this truer than in the case of hydrogen, with its single electron most often found in a covalent bond to a more electronegative atom, and thus polarized towards the non-hydrogen atom

in the bond, leaving the hydrogen nucleus significantly offset from the centre of its ED. Since the diffraction data only give the distribution of the ED, the IAM model requires misplacement of hydrogen nuclei with E-H distances foreshortened by 12-15%. Another consequence of the approximation that is familiar to all who work with SC-XRD is that “ R_i ” never goes to zero – to such an extent that a residual of 5% is considered a mark of an excellent structure.

Many improvements and corrections to the IAM have been proposed over the years, but most have required exceptional data quality (e.g. for ‘multipole refinements’) and specialist theory and software. In this work, we report on our results using a practical and user-friendly implementation of Hirshfeld atom partitioning in conjunction with ‘static’ quantum mechanical calculations on models obtained during the refinement of small molecule crystal structures. Readers are urged to consult the original publication by Kleemiß et al.^[10] for a full description of the NoSpherA2 method, which has been fully implemented as an optional method of structure refinement in the widely used Olex2 suite of crystallographic software.^[21] This software is free to academic users and can be downloaded from <https://www.olexsys.org/> and paired with a range of supported quantum computational programs as explained at <https://www.olexsys.org/olex2/docs/nosphera2/nosphera2/>.

2.3. Selected Examples from Implementation of HAR with NoSpherA2

Our first experience with aspherical atomic form factors in model refinement resulted in the publication of 17 structures of related phenolic triarylphosphines and -phosphine chalcogenides.^[22] The structure shown in Figure 2.1A is typical. All the models could be refined with the ‘correct’ placement of the H atoms (that is, E-H bond lengths as from neutron diffraction).^[34] Refinement of anisotropic displacement parameters (ADP) was possible for all atoms in many but not all cases, with the exceptions treated by

isotropic displacements for the H atoms attached to C. A second study treated a series of 14 organonitrile ring and cage valence isomers, for which Figure 2.1B is a typical example.^[23] For this study, a range of crystal/dataset quality was again (intentionally) included. Except for some minor components of disorders, all the H atoms were refined positionally as well as their ADPs. Refinements led to significant reductions in R_1 , as well the other common indicators of better agreement of model to data.^[10,32]

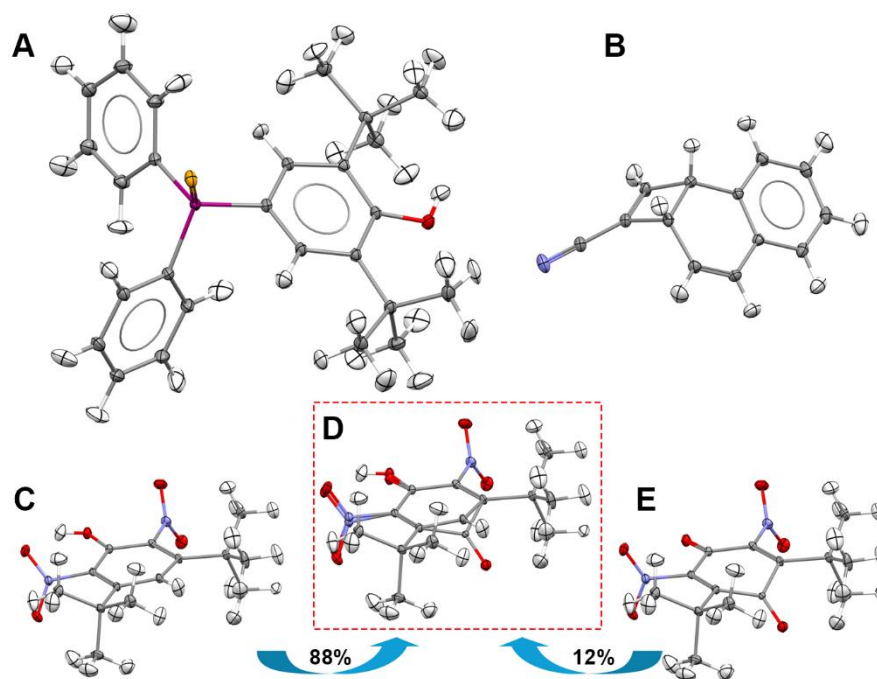


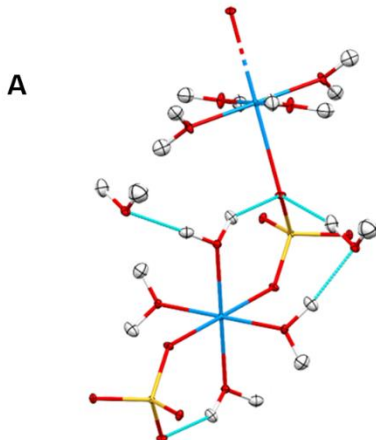
Figure 2.1. Displacement ellipsoids plots (30% probability) from final HAR with NoSpherA2 refinements of (A) a phenolic phosphine selenide^[22] and (B) a polycyclic organic nitrile^[23] in Olex2 with accurate H-atom placement. (C) – (E) Depictions of the solid solution disorder in a crystal (D) found to contain 88% of nitro-phenol (C) and 12% nitro-quinone (E).^[29]

Additional structures from more disparate compound types were also treated by HAR with NoSpherA2.^[24-29] Significantly, where H-bonding exists in the crystals, the refinements also result in very low standard uncertainties (s.u.) in the E-H and H ··· D distances, and with good agreement to neutron diffraction values.^[34] A consideration in Figure 2.1 are the seemingly large ADPs for the H-atoms. While this may be surprising, the reader is asked to recall that in the typical constrained refinement employed with IAM models, the ‘riding’

H atoms are defined to have isotropic displacements of between 1.2× to 1.5× those of the attaching atoms E. It is for this reason that typically ‘H-atoms are omitted for clarity’ from displacement ellipsoids plots, or if included, the H atoms are assigned arbitrary small spherical radii. By drawing at 30% probability, the structure models in Figure 2.1 may instead be said to ‘include H-atoms for accuracy’, visually emphasising the relative rigidity of **1B** versus the much greater flexibility of the substituents (Bu groups and whole phenyl rings) subtending from the central heavy atoms in **1A**. The ADP depiction of the hydrogen atoms communicates a rich tapestry of structural detail.

The three structures depicted in Figure 2.1C-E are from a recent publication that reports excellent refinement models for the chemically related nitro-phenol **1C** and nitro-quinone **1E**, from HAR with NoSpherA2.^[29] The middle structure **1D** emerged from a disordered alternate crystal sample of **3C**, which was recognized to be from a molecular solid solution containing 12% **1E** in the **1C** lattice (which is 88% of the total occupancy). In the IAM disorder model, a fully satisfactory refinement was achieved with a standard two-part disorder between the ring C-H of the phenol and the out of plane C=O moiety of the quinone. But, to implement HAR, it was necessary to also include in the disorder model the O-H and the =O at the left side of the ring – a difference of only 0.12 e; but quantum mechanics cannot treat ‘fractional electrons’. Thus HAR with NoSpherA2 helped us to develop a superior disorder model, which refined very well despite the low occupancy of the minor component.^[29]

XRD (Mo K α) using NoSpherA2 on CuSO₄·5H₂O
 $R_1 = 2.59\%$; Max pk 0.6; min pk -0.6 (100 K)



Combined neutron diffraction on CuSO₄·5H₂O
and CuSO₄·5D₂O at RT: $R_1 = 3.7\% - 0.1$ (RT)

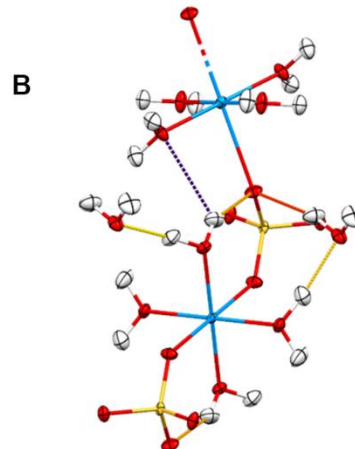


Figure 2.2. Comparison of (A) 100 K SC-XRD structure of CuSO₄·5H₂O refined using HAR with NoSpherA2 (left)^[30] with (B) the results of a RT combined neutron diffraction study from large crystals of CuSO₄·5H₂O and CuSO₄·5D₂O.^[35]

To expand the range of compound types amenable to HAR with NoSpherA2, we reported the redetermination by modern SC-XRD of CuSO₄ and its mono-, tri-, and pentahydrates,^[30] and hydrated Cu and Ni chlorides.^[31] For the well-known deep-blue pentahydrate, i.e. [Cu(OH₂)₄]SO₄·H₂O, a direct comparison is possible between the 100 K X-ray structure (Figure 2.2A) and a RT combined neutron diffraction structure on CuSO₄·5H₂O and CuSO₄·5D₂O (Figure 2.2B).^[35] Comparing the two, the smaller ADP of the heavy atoms in the 100 K XRD structure is evident. Even more striking is how well the NoSpherA2 hydrogen ADPs agree with those of the superb neutron structure model. A detailed comparison of the H-bonding parameters between the two models was undertaken, showing excellent numerical consistency.^[30] In view of the extreme sparsity of neutron data for metal hydrate structures, HAR with NoSpherA2 is of obvious value.

2.4. Improvement in overall structure precision

In many of our results, we were excited to discover that significant improvements in average bond distances (as computed by PLATON on the most prevalent bond types, usually C–C) occur with aspherical form factors, since we kept track of similarly refined

models in the IAM and NoSpherA2 (Figure 2.3). We find it extremely significant to detect markers of structure improvement in the s.u. of the derived parameters of the non-hydrogen atoms.^[36] Figure 2.3 collects four scatter plots showing the improvements in average C-C (usually) bond precision in Å, expressed as a %-lowering from the IAM value, versus the R_{int} (i.e. the residual for the agreement between repeatedly measured experimental observations, a marker of raw data quality)^[36] and R_1 (as a marker of the final model quality with the aspherical form factors). Each graph is the result of studies on sets of from 6 to 17 chemically closely-related crystal structures treated in the cited articles. (Note: no specific mathematical relationships are implied although the data fit best to logarithmic functions; the purpose is to show graphically trends we encountered repeatedly from crystals that are a typical cross-section of our synthetic program, albeit with a standing policy to always obtain best data possible.)

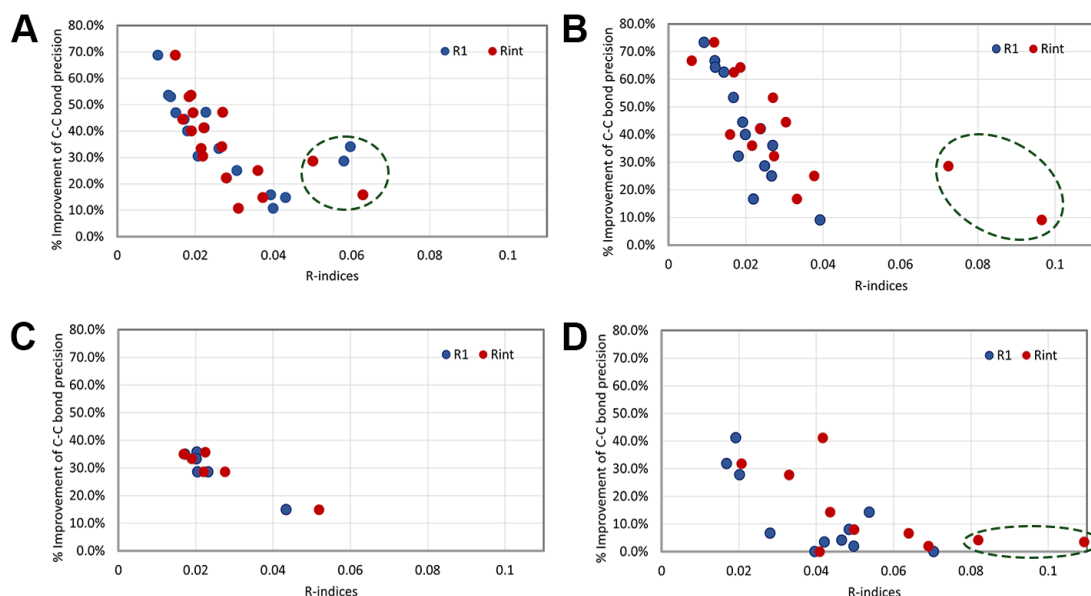


Figure 2.3. Scatter plots of structure precision improvement from HAR with NoSpherA2 compared to IAM with quality of the raw data (R_{int}) and of the final model (R_1) for (A) 17 triarylphosphine and -phosphinechalcogenides,^[22] (B) 14 organonitrile valence isomers,^[23] (C) 6 arylchlorothiatiazines,^[24] and (D) 11 diarylsulfurdiimides.^[28] (In set D, for two molecules the C-Br precisions are employed). Points within the green ovals seem to provide greater than deserved improvements.

Whilst the highs and lows in bond precision improvement vary from set to set, the graphs present a uniform picture. First, there is a generally similar relationship of improvement with R_1 (blue) and R_{int} (red), though sometimes a better improvement is given by one or the other indicator (see the cited articles for details). Second, in no case did implementing HAR with NoSpherA2 lower the bond precisions. (A perceptive reader might object that we have excluded similar structures that cannot be refined successfully with aspherical form factors. We agree! Indeed, the protocols we follow – see ‘Workflow’ in Section 2.5 – are designed to leave inferior datasets in the IAM. But with the four extended sets presented in Figure 2.3, none failed to qualify for HAR with NoSpherA2.) Third, the correlations show no deleterious discontinuities; indeed several points circled in green render more improvement than expected from the given index value. Finally, and perhaps most significantly, there is a consistent pattern that the best data and model quality delivered the greatest improvements in structure precision. We consider this at once very satisfying and also of practical significance. After all, if even poor crystals give acceptable structures (i.e. no CheckCIF “A” or “B” alerts and a passing R_1 – the very definition of a *publishable structure* today), the perception may be that efforts invested in growing the best quality crystals, changing solvents to eliminate lattice solvent inclusions and the other hard work of optimizing synthetic results are poor investments of time.^[37] If, however, HAR with NoSpherA2 returns significantly improved structural data – we have seen beyond 70% improvement in some cases – then there is a big payoff for the work of improving crystal and data quality.^[2,37] Selected comparisons of bond distance s.u. between the IAM and HAR are provided for three representative compounds (Figure 2.4) in Table 2.1: organic (1), main group (2) and organometallic (3) (see the table footnotes for data and refinement characteristics). These will provide further depth to the average improvements shown in the scatter plots (Figure 2.3). In 1, the refined C–H distances are compared to the standard ‘riding model’ constrained values commonly used with the IAM.

In **2**, the O-H involved in H-bonding was refined without constraints in both the IAM and HAR, with about half the s.u. in the latter. The raw data quality and final R_1 in the case of **3** are lower than in either **1** or **2**; correspondingly, the improvements in the s.u. are smaller.

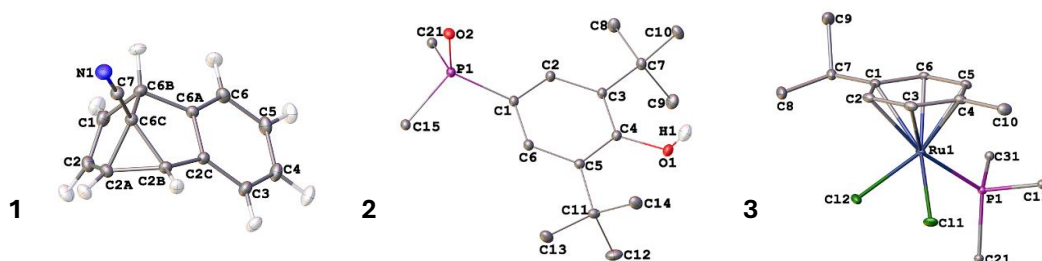


Figure 2.4. Structure models of example compounds used in Table 2.1

Table 2.1. Selected bond distance (Å) precision improvements in the three compound classes listed in Figure 2.4.

1 ^a	HAR/NSA ^b	IAM ^c	Δprecis. ^d	2 ^e	HAR/NSA	IAM	Δprecis.	3 ^f	HAR/NSA	IAM	Δprecis.
N1–C7	1.1453(4)	1.1460(15)	73.3%	P1–O2	1.4955(2)	1.4970(8)	75.0%	Ru1–Cl1	2.4141(3)	2.4144(3)	0.0%
C6C–C7	1.4215(4)	1.4352(14)	71.4%	P1–C1	1.7946(4)	1.7951(11)	63.6%	Ru1–Cl2	2.4115(3)	2.4118(3)	0.0%
C1–H1	1.065(4)	0.95	—	P1–C15	1.8073(4)	1.8083(11)	63.6%	Ru1–P1	2.3804(3)	2.3805(3)	0.0%
C1–C2	1.3311(5)	1.3279(17)	70.6%	P1–C21	1.8082(4)	1.8090(11)	63.6%	Ru1–C1	2.2400(10)	2.2414(13)	23.1%
C1–C6B	1.5171(5)	1.5273(15)	66.7%	O1–H1	0.946(7)	0.841(16)	56.3%	Ru1–C2	2.2472(10)	2.2445(13)	23.1%
C2–H2	1.059(4)	0.95	—	O1–C4	1.3745(4)	1.3808(13)	69.2%	Ru1–C3	2.2059(10)	2.2042(13)	23.1%
C2–C2A	1.4706(4)	1.4851(15)	73.3%	C1–C2	1.3959(5)	1.3939(15)	66.7%	Ru1–C4	2.2084(10)	2.2081(13)	23.1%
C2A–H2A	1.069(4)	1.00	—	C1–C6	1.3970(5)	1.3961(15)	66.7%	Ru1–C5	2.1804(10)	2.1798(12)	16.7%
C2A–C2B	1.5452(4)	1.5526(14)	71.4%	C2–C3	1.3979(5)	1.3941(15)	66.7%	Ru1–C6	2.2121(10)	2.2118(12)	16.7%
C2B–H2B	1.063(4)	1.00	—	C3–C4	1.4167(5)	1.4159(14)	64.3%	P1–C11	1.8352(11)	1.8367(14)	21.4%
C2B–C2C	1.4727(4)	1.4846(13)	69.2%	C3–C7	1.5383(5)	1.5406(14)	64.3%	P1–C21	1.8642(10)	1.8643(12)	16.7%
C2C–C3	1.3820(4)	1.3887(15)	73.3%	C4–C5	1.4188(5)	1.4154(15)	66.7%	P1–C31	1.8480(10)	1.8474(12)	16.7%
C2C–C6A	1.3939(4)	1.3999(14)	71.4%	C5–C6	1.3971(5)	1.3946(15)	66.7%	C1–C2	1.4308(14)	1.4334(19)	26.3%
C3–H3	1.072(4)	0.95	—	C5–C11	1.5396(5)	1.5448(14)	64.3%	C1–C6	1.4178(14)	1.4171(18)	22.2%
C3–C4	1.3881(5)	1.3953(16)	68.8%	C7–C8	1.5381(5)	1.5374(15)	66.7%	C1–C7	1.5155(16)	1.513(2)	20.0%
C4–H4	1.064(4)	0.95	—	C7–C9	1.5431(5)	1.5430(15)	66.7%	C2–C3	1.4077(17)	1.401(2)	15.0%
C4–C5	1.3862(5)	1.3934(18)	72.2%	C7–C10	1.5398(5)	1.5391(15)	66.7%	C3–C4	1.4295(15)	1.429(2)	25.0%
C5–H5	1.077(4)	0.95	—	C11–C12	1.5387(5)	1.5390(15)	66.7%	C4–C5	1.4186(14)	1.4184(18)	22.2%
C5–C6	1.3893(5)	1.3953(17)	70.6%	C11–C13	1.5374(5)	1.5361(16)	68.8%	C4–C10	1.5017(17)	1.502(2)	15.0%
C6–H6	1.064(4)	0.95	—	C11–C14	1.5380(5)	1.5385(15)	66.7%	C5–C6	1.4220(15)	1.419(2)	25.0%
C6–C6A	1.3814(4)	1.3890(14)	71.4%					C7–C8	1.5229(16)	1.526(2)	20.0%
C6B–H6B	1.073(4)	1.00	—					C7–C9	1.5362(16)	1.538(2)	20.0%

^a Full structure of 2*a*,2*b*,6*b*,6*c*-tetrahydrobenzo(*a*)cyclopropano(*ca*)pentalene-6C-carbonitrile (**1**): $R_{\text{int}} = 1.59\%$; R_1 reduces from 2.93% to 0.92%.^[23] ^b Bond distances (Å) refined using HAR with NoSpherA2. ^c Bond distances (Å) refined using IAM using olex2.refine. IAM bond distances for E-H are defined and have no s.u. values. ^d Change in precision as a percentage of the IAM s.u. value; positive values are improvements. Example (**1**, N1–C7): $((15-4)/15)*100\% = 73.3\%$. ^e Structure of diphenyl-(3,5-di*tert*butyl-4-hydroxyphenyl)-phosphine oxide (**2**), truncated at the first C of the two Ph rings at P: $R_{\text{int}} = 1.44\%$; R_1 reduces from 2.98% to 1.04%.^[22] ^f Structure of [Ru(η^6 -*p*-cymene)(P(Cy)₂Ph)Cl₂] (**3**), truncated at the first C of the Ph and Cy rings at P: $R_{\text{int}} = 3.93\%$; R_1 reduces from 3.36% to 2.97%.^[25]

It will be most interesting to monitor improvements in structure precision from refinements with aspherical scattering factors as results accumulate in the literature. We hypothesize that the greatest effects will be for lighter element structures because they have the largest ratios of valence to core electrons. Some indication of this can be found for the first three entries in Table 2.1 for compound 3, which involve only heavy elements and show no changes in precision. On the other hand, a distinct benefit of HAR with NoSpherA2 for transition metals is that the largely non-bonding *d* and *f* electrons are correctly treated, as well as the correct spin states, which will vary from compound to compound.^[10] Finally, we note that even in the cases where the structure precision has not, or has only marginally, improved, we still gain well-behaved refinement models with the H nuclei at their true positions.

2.5. Prospects for NoSpherA2

The prospects for NoSpherA2 are very encouraging as it is such excellent software and genuinely easy to use. A detailed description of the work flow we typically employ for HAR with NoSpherA2 is presented below for the convenience of readers wishing to implement the method. For each supported software package, the program suggests functionals and wavefunctions suitable to the structure/elements being modelled. Readers who desire further insight into these choices may consult a helpful recent ‘best-practices’ guideline to DFT methods.^[38]

1. Complete the best possible structure model in the IAM, including disorder, solvent masking, etc. *IAM is 90-98% accurate, compact, reliable, familiar – always the best starting point.*
2. Refine using olex2.refine (Gauss-Newton on F^2) with spherical form factors; validate and save the file! *Ensure atoms are all named correctly (atom labels are used in DFT to define the .tscb, so it does not rely only on the SFAC code to identify atom types, as the IAM does!)*
3. Implement NoSpherA2 in a copy of the original folder. *Easily done in Olex2, with ability to rapidly move between IAM and HAR models.*
4. Relax the constrained E-H distances within AFIX (> NeutronHDist, followed by 1 cycle of L.S.; where "> function" indicates typing at the command line.)
5. Select NoSpherA2 and choose the computational software and level of theory (see step 7).
6. Obey the laws of quantum mechanics: no half bonds(!); correct spin multiplicity(!) *The quantum calculation always works on what's on the screen, so use GROW to define a computationally compatible molecule. It is even possible to calculate on aggregates, e.g. H-bonded dimers.*
Computational options include: Relativistic, DISP (for anomalous scattering) and Solvation (water is recommended); see <https://www.olexsys.org/categories/nosphera2/> for explanations.
7. Step through the three Levels in NoSpherA2 refinement: Test – Work – Final.
 - a. **Test:** purpose is to check for glitches (naming errors, correct spin state, etc).
 - b. **Work:** here the HAR model is fully developed.
 - i. After successful .tscb calculation, refine model to XRD convergence again in olex2.refine.
 - ii. Relax desired AFIX by atom selection, followed by > AFIX 0 at command line, and refine again (usually all E-H; but consider retaining the constraints for minor disorder components, poorly-defined terminal alkyl groups, etc.).
 - iii. Relax selected H atoms to anisotropic displacement ellipsoids (select, then > ANIS -h) and refine.
 - iv. Examine model carefully (badly behaved H atoms benefit from RIGU on E-H and/or ISOR restraints).
 - c. **Final:** iterative (usually 10x) for polishing the form factor calculations, followed by final L.S. refinement.
8. Validate model by careful examination of final parameters, comparison to expected E-H distances from neutron diffraction, submitting to IUCr CheckCIF, etc. *Models that fail validation must remain in the IAM (which has been retained in Step 2!)*
9. Publish! (Be sure to cite the recommended articles; open the CIF file to obtain a record of the NoSpherA2 calculations, restraints applied, etc. for a full reporting of the model).

Encouragingly, more than 100 papers have thus far acknowledged publishing SC-XRD structures using HAR with the aid of NoSpherA2 in about three years since release (out of ~170 total citations). Since not all adopters will cite the original paper as requested, these estimates could be on the low side, but the total is likely still well below 1% of the structures deposited to the CSD in that period. Why is the adoption of refinement using custom aspherical form factors so low? Possibly the prevailing habit of ‘omitting H-atoms for clarity’ reflects a sense that, somehow, the H-atoms are structurally unimportant, a view that Thompson and White argue strongly against.^[39] Many synthetic chemists seem to be unaware that quantitative work on hydrogen bonding has always required artificial ‘normalization’ of the E-H bond distances to their neutron diffraction values.^[40] It can be hoped that greater appreciation for the *general* improvement in structure precision as outlined above will help to convince synthetic/structural chemists to adopt custom aspherical form factors to achieve both benefits: true H-atom positions, often with ADPs, and better bond distances and angles from more accurate placement of *all* the atoms in the structure.

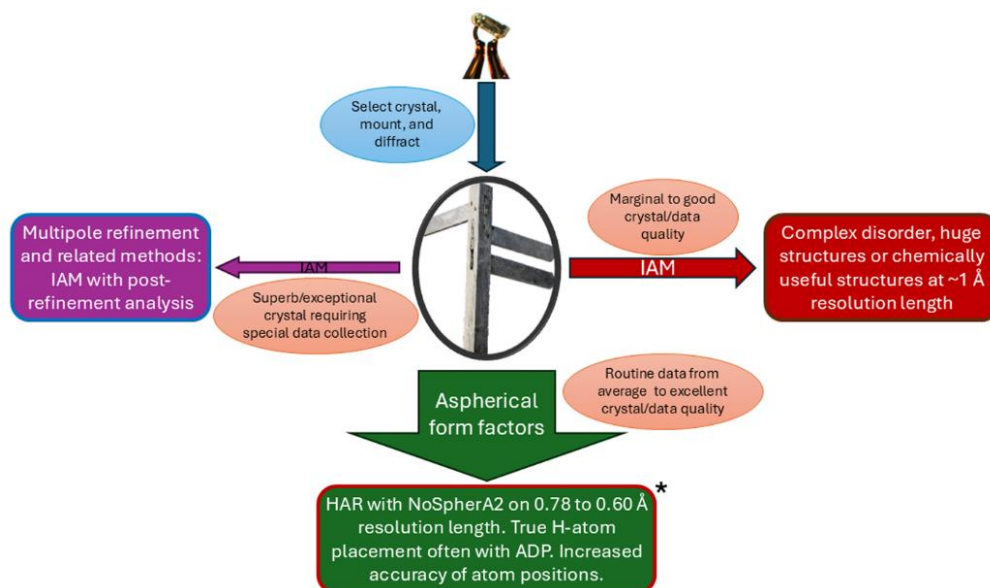


Figure 2.5. The “crossroads” in small molecule X-ray crystallography. *Similar benefits are possible with database methods (Invariom, TAAM) but have not been tested in this work.

Scientists who determine structures by SC-XRD now face a ‘crossroads’ in their approach to structure model refinement (Figure 2.5). First, it is important to recognize that the IAM is not displaced by the new methods. It will remain as a robust, compact, reasonably accurate method that forms the core of structure modelling. The IAM is essential to automation in structure determination, which is of tremendous value in making sense of weak data from poor crystals and in solving other crystallographic puzzles. For the many datasets obtained on marginal crystals, but from which modern methods can somehow pull out a ~ 1 Å resolution length structure,^[37] the IAM is an effective – and sufficient – method. At the opposite pole are the superb crystals that diffract out to the maximum resolution lengths of Mo or even Ag radiation. Here, multipole techniques and other traditional post-IAM-refinement methods will continue to function, alongside some of the leading-edge quantum crystallographic strategies.^[11,12]

However, for the vast majority of ‘routine’ datasets on average-to-excellent crystals, from Cu or Mo radiation and, increasingly, from synchrotron sources, the standard choice today should be some implementation of refinement with aspherical form factors. The authors only have experience with NoSpherA2 and are quite comfortable with modern computational software.^[41] We perceive an advantage with HAR, insofar as it is an *ab initio* approach that requires no prior knowledge of a particular structure. The database approaches, by contrast, are empirical methods that require some prior knowledge of the structure type – or the generation of new database components. Interestingly, efforts to combine TAAM with HAR have been reported, in an attempt to combine novel local structure elements (more computationally intensive) with large-scale but repetitive global components (less computationally demanding and hence calculating much faster).^[42] No doubt, these methodologies will continue to evolve, but from our experience there is every reason for commencing large scale, ‘routine’, adoption of NoSpherA2 in chemical crystallography.

We further anticipate that, as a consequence of and corollary to wide adoption of custom aspherical form factor-based methods, there will need to be a community-wide engagement. The development of ‘standard protocols for the use of aspherical form factors in chemical crystallography’ will consolidate best practices and provide guidance to users. The eventual full incorporation of these methods into automated validation software will be eagerly anticipated. Efforts to co-deposit custom scattering factor sets along with the reflection and model data into repositories such as the CSD or the ICSD will greatly increase the global availability of these improved structure models. Notably, the journal *Zeitschrift für Kristallographie – New Crystal Structures* now accepts HAR re-determinations with NoSpherA2 of already published crystal structures.^[43]

2.6. Conclusions

The developments in SC-XRD highlighted in this article have brought us to a crossroads. Do we stay in the well-worn path of the IAM? Or do we embrace refinement with custom aspherical scattering factors tuned to the actual electronic environment of each atom in the structure? Do we continue in deliberately misplacing each hydrogen atom in our models, when accurate placement is attainable by reliable and quite feasible methodologies applicable to routine X-ray diffraction experiments? HAR with NoSpherA2 is publicly available, verified to be reliable, and supported by a major software developer. Moreover, the method provides significant improvements in overall structure precision by more accurate placement of all the atoms in the unit cell. These improvements accrue especially to the best data sets from the best crystals available. At this crossroads, a turn towards such globally better models is warranted.

2.7. References and Notes

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Chapter 3. Accurate crystal structures of $C_{12}H_9CN$, $C_{12}H_8(CN)_2$, and $C_{16}H_{11}CN$ valence isomers using non-spherical atomic scattering factors

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3.1. Introduction

There is continuing strong interest in the preparation and applications of benzobarrelenes (1,4-dihydro-1,4-ethenonaphthalenes, **I** in Chart 3.1),^[1–6] which are derivatives of the parent barrelene (*bicyclo*[2,2,2]-2,5,7-octatriene) first reported by Zimmerman in 1960.^[7] Benzobarrelenes are particularly suited as chelating bis- η^2 -ethene ligands for low-valent transition metals, such that more than 70% of the 117 reported crystal structures in the Cambridge Structure Database (CSD, version 2021.2)^[8] are of such complexes. Schlesinger et al. devised synthetic strategies for an impressive range of partially halogenated benzobarrelene derivatives which can then be further functionalized.^[3] Rhodium complexes of such benzobarrelenes are highly efficient catalysts for 1,4-addition of phenylboronic acid to 2-cyclohexen-1-one. Marder et al. have developed a hexadehydro-Diels-Alder (HDDA) reaction in which substituted benzobarrelenes and barrelene-like compounds with extended ring systems can be synthesized from a benzyne-trapping reaction with an aromatic reagent (benzene, toluene, anthracene).^[1] Fluorinated benzobarrelenes have also recently been reported.^[2] In all, about 20 structures of type **I** (Chart 3.1) have been reported, excluding metal coordination complexes and those embedded into additional rings. We have provided one of these entries in a previous report on a fully saturated tetrabromobenzobarrelene and 2,3-dibromo-1,4-ethenonaphthalene which is derived from the former by double dehydrobromination.^[9]

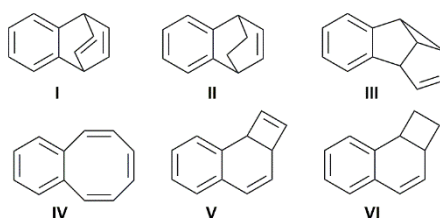


Chart 3.1.

Selective saturation of the alkene ‘staves’ of benzobarrelenes is possible.^[10] Dihydrobenzobarrelenes (1,4-dihydro-1,4-ethanonaphthalenes, **II** in Chart 3.1) are of interest as spacers between antipodal redox sites^[11] or as a vector to benzannulation via the Alder-Rickert reaction involving thermolytic removal of the saturated stave of the barrelene.^[12-14] About 20 crystal structures of type **II**, excluding metal coordination complexes and embedded rings, are reported in the CSD. However, all but four of these are affected by positional disorders between the ‘saturated’ and ‘unsaturated’ barrelene staves, frustrating explorations of a structure correlation principle for the Alder-Rickert reaction.⁶ Additional ordered crystal structures of type **II** are therefore highly desirable.

Benzosemibullvalenes, **III** in Chart 3.1, known exhaustively as 2*a*,2*b*,6*b*,6*c*-tetrahydro-1,2*b*,3,6-tetramethylbenzo(*a*)cyclopropa(*c,d*)pentalenes, are benzofused derivatives of tricyclo[3.3.0.0^{2,8}]octa-3,6-dienes. They represent a polycyclic system with dramatic ring strain that has attracted modern structural research interest and are most often the product of the photolytic rearrangement of benzobarrelenes.^[15-19] Sajimon et al. demonstrated that there is a degree of regioselective control in this rearrangement based on the steric bulk of substituents on the benzobarrelene.^[20] There have also been successful attempts to synthesize benzosemibullvalenes by conventional means, by either dehydrobromination^[21] or by thermolytic isomerization of perphenylbutenyne which proceeds through formation of an intermediate carbene compound via a reverse Skattebøl rearrangement.^[22] Despite the intrinsic interest in such strained structures, fewer than ten

exemplars of type **III**, excluding metal complexes and embedded rings, could be retrieved from the CSD.

Cyclooctatetraenes (COTs) are anti-aromatic [8]-annulenes with a distinctly non-planar geometry which see a great deal of use in coordination chemistry as sterically demanding ligands.^[23-24] There has been strong directed research in recent years towards geometric modifications of polycyclic arenes to modulate electronic and optical properties that arise from three-dimensional nanocarbon structures.^[25-31] COTs are an essential component to introducing stable and rational curvature into polycyclic sheets due to their tub-shaped geometry, and to this end there has been significant inquiry as to how to incorporate COTs into these systems. In pursuit of this goal, Bello-Garcia et al. have contributed a large number of easily accessible functionalized benzocyclooctatetraenes, BCOTs (benzo[8]annulenes, **IV** in Chart 3.1), via Ru-catalyzed [2+2+2] cycloaddition of arylenyne to dihydrobiphenylenes followed by a straightforward ring opening reaction.^[32] Even with this significant contribution, structures of simple BCOTs remain rare, with only 11 structures currently reported in the CSD.

Although there has been an overall decline in the prevalence of photochemistry since the 1990s, there has been continued interest in the production of highly strained polycyclic systems which have well established photosynthetic methods but are difficult to access through conventional chemical means. *2a,8b*-dihydrocyclobuta[*a*]naphthalenes, DCBNs, (**V** in Chart 3.1), are benzannulated derivatives of bicyclo[4.2.0]octa-2,4,7-triene and belong to this category. Much of the recent research in this area is directed towards DCBN systems containing embedded rings,^[33-39] but for accuracy the geometry comparisons in this work will focus on just three DCBN crystal structures without embedded rings deposited in the CSD to date.

Partly saturated derivatives of **V** are the TCBNs, (**VI** in Chart 3.1), 1,2,2*a*,8*b*-tetrahydrocyclobuta[*a*]naphthalenes, benzannulated derivatives of bicyclo[4.2.0]octa-2,4-dienes. These have been explored in recent literature by several groups investigating the fundamental reactivity and modification of synthetic stereo- and regioselectivity of the archetypical photoreaction of naphthalenes with substituted alkenes to form TCBNs.^[40-45] There are 12 TCBN crystal structures without embedded rings deposited in the CSD to date.

One of us produced a rich set of related compounds from a lengthy research programme in mechanistic photochemistry, composed of unusual valence isomers that are the products of excited-state reactions.^[10, 46-50] A treasure trove of crystals are now available, mostly of suitable quality for single crystal X-ray diffraction, and their crystal and molecular structures are reported herein. In all, 14 high-quality structures of types **I** – **VI** (Chart 3.1) are reported (including two naphtho-fused analogs), mostly mono- or dinitriles, and of which only one of type **VI** was previously reported but with a different space group and no record of fractional atom coordinates.^[51] These structures significantly expand the number of accurately characterized 3D geometries for such hydrocarbon cage compounds, for example in the case of **III**, our work constitutes a 30% increase in reported SC-XRD geometries, and for **V** an increase of 67%.

All these structures have been refined with a recently reported state-of-the-art Hirshfeld atom refinement (HAR) approach^[52] that results in an average improvement in the C-C bond precision of over 49% based on standard uncertainties calculated by the refinement software compared to standard refinements using spherical form factors, i.e. the independent atom model (IAM). This HAR approach in the software program NoSpherA2, uses custom form factors that are fully polarized to the actual atom positions in the molecules, which permits accurate placement of hydrogen atoms with a precision

that approaches that of neutron diffraction, the acknowledged ‘gold standard’ for light atom structures.^[53] Our group has previous experience in the application of the NoSpherA2 method in the context of organophosphines^[54] and copper(II) sulfates.^[55] The data quality of our 14 structures is sufficient to compute well-behaved anisotropic displacement parameters, accurately representing the vibrational displacements of the H nuclei. In this, the NoSpherA2 HAR approach also mimics one of the most appealing attributes of neutron diffraction, but at much lower experimental cost. These capabilities are especially welcome with the recognition of the importance of London dispersion interactions (the attractive component of the van der Waals potential) on many aspects of chemical interaction and structure. These are overwhelmingly hydrocarbon interactions, ranging from small molecules,^[54, 56-61] crystal structure directors,^[62] chemical reaction mechanisms,^[63] and biological macromolecular interaction mechanisms.^[64] A dispersion energy donor scale has recently been proposed.^[65] There is now even direct evidence for CH $\cdots$ HC ‘bonding’ with the shortest approach of 1.566(5) Å in crystals of tri(3,5-*tert*butylphenyl)methane at 20 K.^[66]

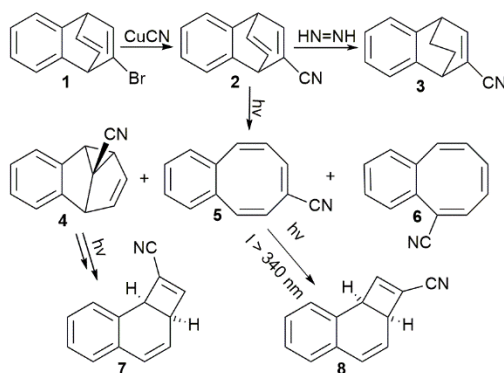
The ongoing interest in weak intermolecular interactions in the ever-growing field of ‘crystal engineering’ also requires accurate treatment of C–H bonds.^[67-68] In this paper, the interest is C–H $\cdots$ N $\equiv$ C– non-classical hydrogen bonding. Clear evidence for this interaction as a ‘building block’ in crystal engineering has been obtained from a large, statistical, survey of the CSD.^[69] Accurate placement of C–H atoms in hydrocarbons will remove the E–H bond “normalizations” that are now routinely applied to compare experiment with computation in the analysis of H-bonding.^[70] Meanwhile, Wood *et al.* have analyzed the CSD for dipolar C $\equiv$ N $\cdots$ C $\equiv$ N interactions in structures of organic nitriles, in view of the high polarity of these functional groups.^[71] They found that some 37% of structures containing nitriles met their rigorous search criteria for such interactions. We end this paper with a brief consideration of such nitrile-nitrile interactions, in conjunction

with CH to nitrile H-bonding, as they have been encountered in the structures reported here.

3.2. Results and Discussion

3.2.1. Chemical Background

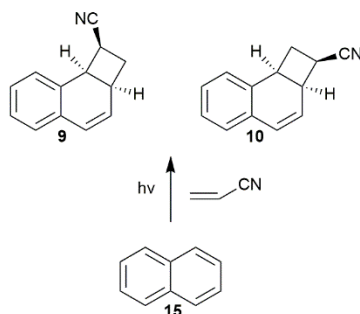
C₁₂H₉CN valence isomers and related species. Bromobenzobarrelene **1** (Scheme 3.1) is prepared by the reaction of benzyne with bromobenzene. This then undergoes nucleophilic substitution by CuCN, converting to the cyanobenzobarrelene, **2**.^[46] Treatment with diazene (generated by acidification of potassium azodicarboxylate) selectively hydrogenates the unsubstituted stave of the barrelene, resulting in **3**.^[10] Photolysis of **2** is carried out in a Pyrex vessel with a medium pressure mercury lamp, producing a mixture of valence isomers, **4**, **5**, and **6**.^[46] Irradiation of **4** at 276 nm leads to 6-cyanobenzocyclooctatetraene (for which a crystal structure has not been determined), whose subsequent isolation followed by further irradiation through a Pyrex filter (>310 nm) leads to **7**.^[47, 50] Irradiation of 7-cyanobenzocyclooctatetraene **5** at wavelengths $\geq$ 340nm, produces **8**.^[48]



Scheme 3.1. Chemical and photochemical interconversion of C₁₂H₉CN valence isomers and related species

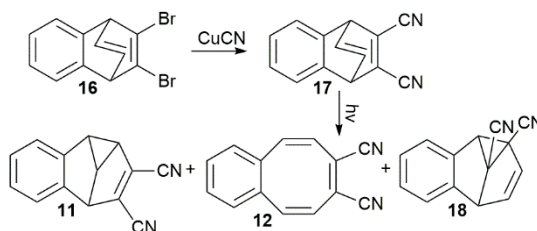
C₁₂H₁₁CN valence isomers. Compounds **9** and **10** are saturated analogs of **7** and **8**, and are produced in a 13:1 ratio by 313 nm irradiation of naphthalene in the presence of

acrylonitrile (Scheme 3.2).^[72] Numerous solvents were assessed in this synthesis, of which 2-propanol exhibited best overall quantum yield and lowest fraction of substituted naphthalene side products.



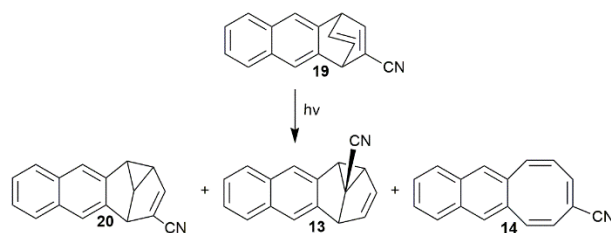
Scheme 3.2. Photochemical synthesis of $C_{12}H_{11}CN$ valence isomers

$C_{12}H_8(CN)_2$ valence isomers. Analogously to Scheme 1, dibromobenzobarrelene **16**, made from the dehydrobromination of higher brominated barrelenes such as tetrabromo-1,4-ethanonaphthalene,^[9] reacts with CuCN to form the dinitrile **17**, which is then photolyzed with 254 nm radiation to produce a mixture of **11**, **12**, and **18** (82%, 6%, and 12%, respectively),^[9, 73] which were separated by column chromatography (Scheme 3.3).



Scheme 3.3. Synthesis and photochemical interconversion of $C_{12}H_8(CN)_2$ valence isomers

Like the reactions described above, the cyanonaphthobarrelene **19** is obtained from the treatment of the corresponding bromonaphthobarrelene with CuCN; the latter barrelene is prepared as usual from the reaction of 2,3-naphthyne with bromobenzene.^[46] Direct irradiation of **19** with 313 nm light produces a mixture of compounds **13**, **14**, and **20** in much the same way as the benzo-fused analogs **4** and **5** (Scheme 3.4).^[49]



Scheme 3.4. Photochemical interconversion of $C_{16}H_{11}CN$ valence isomers

3.2.2. Crystallography

The new single-crystal X-ray diffraction structures obtained in this work belong to four major structural categories: benzobarrelenes (**1**, **2**) and a partially hydrogenated analog **3**, benzo- and naphthosubstituted bicyclics (**4**, **11**, **13**), benzocyclooctatetraenes (**5**, **6**, **12**, **14**), and di/tetra-hydrocyclobuta[*a*]naphthalenes (DCBN, TCBN) (**7**, **8**, **9**, **10**). Because of the proclivity of photochemistry to produce many isomers via excited-state reactions, spread across all four categories are valence isomers with the formula $C_{13}H_9N$ (**2**, **4**, **5**, **6**, **7**, **8**); two (**11**, **12**) are valence isomers of $C_{14}H_8N_2$ and two (**13**, **14**) are naphtho- rather than benzofused analogues of formula $C_{17}H_{11}N$.

Barrelenes and a barrelene derivative. The barrelenes in this series are typified by a benzo-fused bicyclic ring system with apical sp^3 carbons connected through two ethene staves. Our work includes the structure (Figure 3.1) of 2-bromo-1,4-dihydro-1,4-ethanonaphthalene, **1**, and 2-cyano-1,4-dihydro-1,4-ethanonaphthalene, **2**, both in Sohncke space groups ($Pca2_1$ and $P2_1$) and a derivative of **2** with one saturated and one unsaturated stave, 2-cyano-1,4-dihydro-1,4-ethanonaphthalene, **3**. Compounds **1** and **2** (Figure 3.1) have highly similar structures, excepting of course the substitution of Br (**1**) versus the nitrile (**2**). In structure **3** in $P2_1/c$, there are two independent molecules in the asymmetric unit ($Z' = 2$). One of these molecules is disordered (0.63/0.37) over the barrelene cage and nitrile substitution sites. A satisfactory disorder model was implemented, but the geometry reported for **3** is that of the ordered molecule since the disorder model accentuates a structural distortion that is not fully resolved. The geometry

of **3** is distinct from **1** and **2**, owing to the hydrogenation of the unsubstituted ethene arm. When compared to the benzobarrelenes, as expected the C9-C10 bond is elongated to 1.5460(8) Å from 1.325(3) in **2**. This also shortens the bonds to the apical sp^3 carbons from the substituted stave (C1-C2, C3-C4), and lengthens the bonds from the apical carbons to the unsubstituted stave (C1-C10, C4-C9) – see Table 3.1.

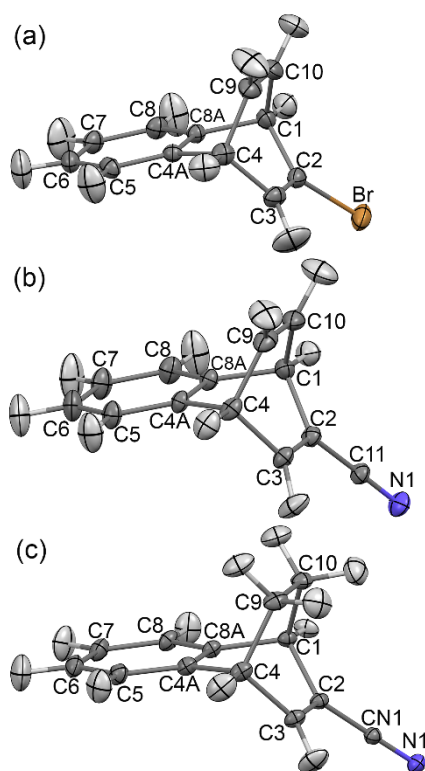


Figure 3.1. Displacement ellipsoid plots (50% probability) for structures at 173 K: (a) **1**, (b) **2**, and at 100 K: (c) **3**. The second (disordered) molecule in the asymmetric unit of **3** is omitted.

The geometries of **1** and **2** were compared to analogous barrelenes previously deposited to the CSD (Table 3.1), restricted to structures which are not part of a coordination complex and where the bicyclic barrelene moiety is not embedded in other rings (since additional ring strain could influence the geometry). Similar search criteria were used for compound **3**, save only that the search was for barrelenes with one saturated and one unsaturated stave. Individual bond lengths and angles were compared between

our acquired structures and CSD analogs using the 99% confidence rule (only deviations of more than s.u.*2.58 to the mean comparator values are taken as significant).^[8] By this method, compound **2** had one bond length (C3-C4) outside of the range of the analogs. However, when comparing the global average of bonds to the apical sp^3 carbons, the C3-C4 bond of **2** falls within the range and is not considered an outlier. Compound **1** has overall more short bonds than long (67%) and slightly more wide angles than narrow (58%) when compared to the average values for the analogous set of compounds, while compound **2** has overall more short bonds than long (78%), and an equal number of angles wider and narrower than the mean. In view of the paucity of extant structures, wherever values from our new structures fit at the 99% confidence level, the means have been recomputed to include the results from this work (as indicated in footnotes to Table 3.1 – 3.4).

Comparing **3** to analogous structures from the CSD is not such a straightforward task, as the set of 18 unique comparators (some of which have up to 6 independent barrelene moieties, for a total of 39 comparative geometries) are deeply affected by disorder, with only 4 unique comparators encompassing 8 total entries judged by us as free of disorder. Goh et al.^[6] analyze this issue in detail, and suggests that the disorder in these mixed ene/ane barrelene cages is due to a high similarity in crystal-packing requirements of the H_2C-CH_2 and the $HC=CH$ staves. Uno^[74] and Mithani^[14] specifically mention this disorder, but do not address it at any length, while Aotake,^[12] Tanaka,^[13] and Kaya^[5] do not mention any ene/ane disorder in the barrelene cages. Unsurprisingly, the C-C bonds of these staves, C2-C3 and C9-C10, experience the greatest distortion of the disorder. From the CSD comparators without disorder, the average length of C9-C10 (H_2C-CH_2) is 1.53(2) Å, and C2-C3 ($HC=CH$) is 1.316(10) Å, which is within the normal range for single and double C-C bonds, and is the motif that we must necessarily expect for these ordered structures. In the disordered structures, the average bond lengths of C9-C10 and

C2-C3 are 1.40(2) Å and 1.46(2) Å respectively, intermediate between single and double bonds. These data can be found in full in Table A.20.

The structure of compound **3** conforms closely to the *reliable* comparator structures in the CSD, with all but one bond length and all but one bond angle fitting within the range of the analog values at the 99% confidence level, and with deviations from the mean tending towards more longer bonds than shorter (67%), and slightly more narrow angles than wide (58%). The Cremer-Pople puckering parameters,^[82-84] hereafter referred to as puckering parameters, for the barrelene moieties of **1** - **3** (Table A.1) all closely conform to boat geometry ($Q = 0.7528 - 0.8482$, $\theta \approx \pi/2$, $\varphi \approx \pi$), consistent with the absence of steric effects in this substitution pattern (contrast a tetrabromobarrelene previously reported^[9]).

Table 3.1. Selected bond distances and angles in structures of the barrelenes and barrelene derivatives.^a

Bonds (Å)	1	2	Average ^b	3 ^c	Average ^d
C1-C2	1.5242(19)	1.5240(15)	1.534(8)	1.5178(6)	1.513(12)
C1-C8A	1.5256(16)	1.5188(15)	1.530(14)	1.5132(7)	1.516(16)
C1-C10	1.533(2)	1.5181(16)	1.529(7)	1.5630(7)	1.558(9)
C2-C3	1.3336(19)	1.3306(16)	1.324(7)	1.3480(7) ^e	1.316(10)
C3-C4	1.528(2)	1.5131(15)	1.531(10)	1.5064(7)	1.513(9)
C4-C4A	1.5269(18)	1.5196(15)	1.537(14)	1.5115(7)	1.512(5)
C4-C9	1.531(2)	1.5190(17)	1.531(9)	1.5652(7)	1.558(12)
C4A-C8A	1.3965(17)	1.3879(13)	1.405(13)	1.4009(6)	1.394(5)
C9-C10	1.327(2)	1.3250(19)	1.322(10)	1.5447(7)	1.54(2)
Angles (°)					
C1-C2-C3	115.13(13)	114.45(9)	113.6(15)	114.77(4)	114.5(5)
C1-C8A-C4A	112.05(11)	112.73(9)	112.5(8)	112.97(4)	113.0(6)
C1-C10-C9	113.30(13)	113.98(12)	113.7(12)	109.32(4)	109.3(8)
C2-C1-C10	105.56(11)	105.44(9)	106.5(11)	105.43(4)	105.5(5)
C2-C1-C8A	105.43(11)	104.28(9)	104.8(9)	107.52(4)	108.1(6)
C2-C3-C4	111.88(13)	113.01(11)	114.0(15)	113.66(4) ^e	114.7(5)
C3-C4-C9	106.63(12)	106.41(10)	106.5(8)	105.43(4)	105.8(9)
C3-C4-C4A	105.76(11)	104.59(9)	104.7(6)	108.12(4)	108.2(7)
C4A-C4-C9	105.14(11)	105.72(10)	104.8(12)	106.35(4)	105.1(7)
C4-C4A-C8A	112.38(11)	112.35(10)	111.8(10)	113.26(4)	113.0(6)
C4-C9-C10	113.78(13)	113.70(10)	114.1(13)	109.53(4)	109.6(8)
C8A-C1-C10	105.21(11)	105.33(9)	105.0(8)	106.13(4)	105.7(7)

^a Atom labels are taken from the first exemplar (see Figure 3.1a) and applied to all structures for ease of comparison. The atom numbering schemes should be consulted for identifying specific entries. ^b Average of specified bond length/angle of structural analogs collected from the CSD. Values from structures introduced in this paper are included in this average unless otherwise specified. Comparators used in this category: FIBDAX,^[3] FIBDEB,^[3] FIBDOL,^[3] FIXLIJ,^[4] GEGGEE,^[75] LEKLAO,^[18] LEZLOR,^[17] LICGIP,^[3] LICGOV,^[3] LICGUB,^[3] LICHAI,^[3] LICHEM,^[3] MEYHOP,^[9] SATPUY,^[76] TUGHAH,^[2] TUGHEL,^[2] WEJBOC,^[77] XAHFAR,^[1] XAHFEV.^[11] ^c Geometry of the disordered molecule in the asymmetric unit is omitted. ^d Average of specified bond length/angle of structural analogs collected from the CSD. Values from structures introduced in this paper are included in this average unless otherwise specified. Comparators used in this category: NAHZAX,^[11] TIVFUZ,^[78] VAKBAK,^[79] ZIZZOX.^[80] Comparators which were obtained from the CSD, but excluded due to disorder: FALHIK,^[81] MICBUW,^[6] MICCAD,^[6] MICCEH,^[6] OCOHUL,^[74] PIBCIO,^[13] PIBCOU,^[13] PIBCUA,^[13] PIBDAH,^[13] PIBDEL,^[13] PIBDUB,^[13] RAKPUQ,^[5] WEXRIA,^[14] YOSFAP,^[12] ^e Statistical outlier omitted from the averaged values.

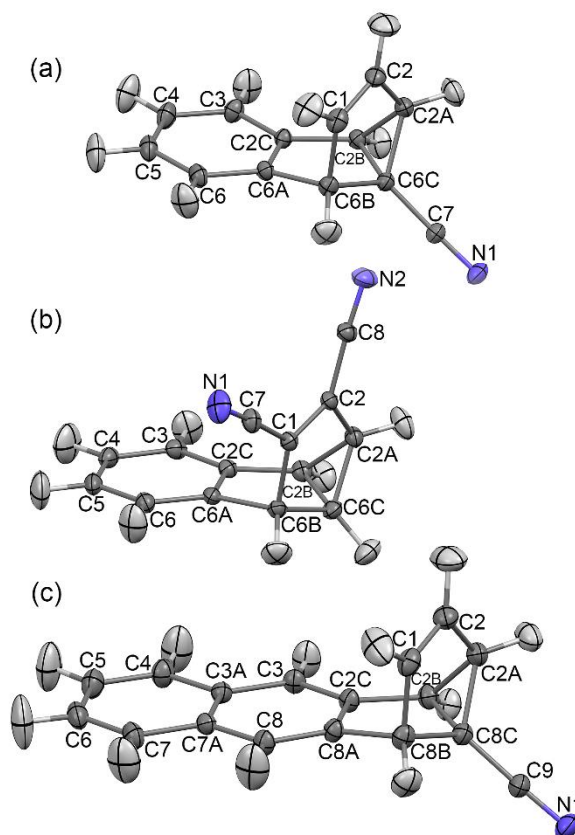


Figure 3.2. Displacement ellipsoid plots (50% probability) for structures at 173 K: (a) 4, (b) 11 (a second molecule in the asymmetric unit is highly similar and is omitted), and (c) 13 (the geometry shown has been inverted to harmonize with those of 4 and 11).

Benzo- and naphthoselibullvalenes. Semibullvalenes have a characteristic three-ring system consisting of two fused 5-membered rings which are bridged (at C2A/C2B) to form a 3-membered ring (Figure 3.2). In our compounds **4**, **11**, and **13**, one of the 5-membered rings is also fused to a benzene ring along the C2C-C6A position, and the other 5-membered ring contains a double bond along C1-C2. *2a,2b,6b,6c*-tetrahydrobenzo(*a*)cyclopropana(*ca*)pentalene-6C-carbonitrile, **4**, crystallizes in $P2_12_12_1$ with $Z' = 1$ and bears the nitrile substituent at the central apical sp^3 site C6C. In dinitrile variant *2a,2b,6b,6c*-tetrahydrobenzo(*a*)cyclopropana(*ca*)pentalene-1,2-dicarbonitrile, **11** ($Pbca$, $Z' = 2$), the cyano groups are located on sp^2 C atoms of the cage edge rather than the apical sp^3 . It crystallizes with two ordered molecules in the asymmetric unit which have very similar geometries, dimensions of which are presented comparatively in Table 3.2 (as **11**¹ and

11²); only one is shown in Figure 3.2b. The C1-C2 type bond lengths of **11**, at 1.3530(12) and 1.3515(12) Å, are anomalously long due to the two nitrile substituents at these C atoms on either side of a formal double bond, for which these data are excluded from the average comparator distances from the CSD. The lengthening of the C1-C2 type bonds also widens the C2A-C6C-C6B type angles, which for one of the two unique molecules of **11** (Column **11**¹ of Table 3.2 below) is sufficient to make this angle an outlier, and it has therefore been excluded from the combined average. 2a,2b,8b,8c-tetrahydro-cyclopropa[3,4]pentaleno[1,2-b]naphthalene-8C-carbonitrile, **13** (P2₁2₁2₁ with *Z'* = 1, Fig. 2c) is a direct naphtho-fused analog to **4** and one of two exemplars in this study with the extended annulene. It is the first structure of its kind to be reported.

Table 3.2. Selected bond distances and angles in structures of the benzo- and naphthosemibullvalenes

Bonds (Å)	4	11¹	11²	13^a	Average^b
C1-C2	1.3311(5)	1.3520(12) ^c	1.3506(12) ^c	1.326(3)	1.327(7)
C1-C6B	1.5171(5)	1.5286(13)	1.5214(13)	1.524(3)	1.522(15)
C2-C2A	1.4706(4)	1.4754(13)	1.4732(13)	1.470(3)	1.478(7)
C2A-C2B	1.5452(4)	1.5757(14)	1.5743(14)	1.538(3)	1.566(25)
C2A-C6C	1.5102(4)	1.5020(14)	1.5050(15)	1.515(3)	1.510(12)
C2B-C2C	1.4727(4)	1.4792(13)	1.4735(13)	1.474(3)	1.481(6)
C2B-C6C	1.5107(4)	1.5021(14)	1.5003(15)	1.511(3)	1.508(14)
C2C-C6A	1.3939(4)	1.4050(13)	1.4017(12)	1.416(3)	1.408(13)
C6A-C6B	1.5129(4) ^c	1.5191(13)	1.5221(14)	1.517(3)	1.526(6)
C6B-C6C	1.5424(4)	1.5473(14)	1.5513(15)	1.542(3)	1.553(15)
Angles (°)					
C1-C2-C2A	111.72(3)	111.18(9)	111.15(9)	111.15(9)	111.5(9)
C1-C6B-C6A	101.31(2)	101.90(7)	101.93(7)	101.93(7)	102.0(12)
C1-C6B-C6C	102.72(2)	102.85(8)	102.77(9)	102.77(9)	103.2(6)
C2-C2A-C2B	120.72(3)	120.01(9)	120.70(9)	120.70(9)	120.5(9)
C2-C1-C6B	110.82(3)	110.54(9)	110.42(9)	110.42(9)	110.7(9)
C2-C2A-C6C	105.81(3)	106.56(9)	106.56(9)	106.56(9)	106.6(10)
C2A-C2B-C2C	119.96(3)	122.26(9)	121.17(9)	121.17(9)	120.7(14)
C2A-C2B-C6C	59.22(2)	58.39(6)	58.55(7)	58.55(7)	58.8(10)
C2A-C6C-C2B	61.53(2)	63.27(7)	63.18(7)	63.18(7)	62.5(15)
C2A-C6C-C6B	104.92(2)	105.38(9)	104.77(9)	104.77(9)	104.2(8)
C2B-C2A-C6C	59.253(19)	58.37(7)	58.26(7)	58.26(7)	58.7(9)
C2B-C2C-C6A	110.84(3)	110.05(9)	110.35(9)	110.35(9)	110.3(7)
C2B-C6C-C6B	105.74(2)	104.96(9)	104.86(9)	104.86(9)	105.2(7)
C2C-C2B-C6C	106.05(2)	107.23(9)	107.59(9)	107.59(9)	106.9(8)
C2C-C6A-C6B	109.59(2)	109.16(8)	109.15(9)	109.15(9)	109.2(6)
C6A-C6B-C6C	103.19(2)	103.84(8)	104.05(9)	104.05(9)	103.3(4)

^a Atom labels are taken from the first exemplar (see Figure 3.2a) and applied to all structures for ease of comparison. The atom numbering schemes should be consulted for identifying specific entries. ^b Average of specified bond length/angle of structural analogs collected from the CSD. Values from structures introduced in this paper are included in this average unless otherwise specified. Comparators used in this category: CEFPOU,^[16] FOYGEF,^[20] FOYGUV,^[20] FOYHAC,^[20] LEKLES,^[18] LEKLIW,^[19] LEZLUX,^[17] RUNZIK,^[21] SAGSEZ,^[22] SUFTIY.^[15] ^c Statistical outlier omitted from the averaged values.

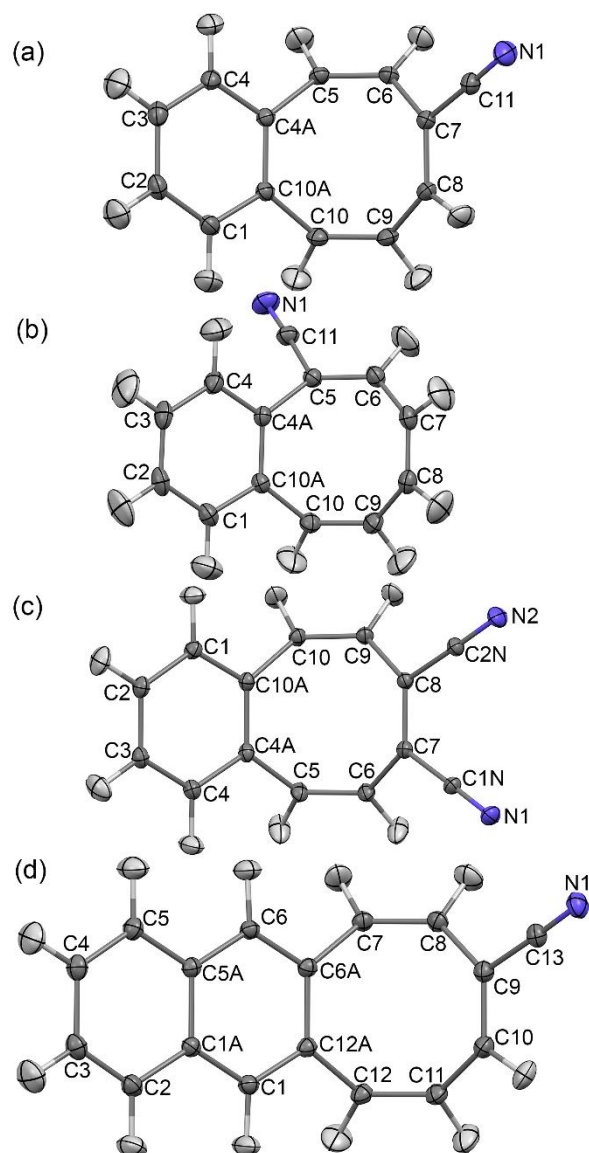


Figure 3.3. Displacement ellipsoid plots (50% probability) for structures at 173 K: (a) 5, (b) 6, and at 100 K: (c) 12 (a second molecule in the asymmetric unit is highly similar and is omitted) and (d) 14 (only the major component of the two-part disorder model involving C9,10,13 and N1 is shown).

A search for analogs in the CSD was restricted to benzosemibullvalenes which are not coordinated to a metal and excluded substructures in which the semibullvalene skeleton atoms are embedded in other rings. There are no naphtho-fused semibullvalenes in the CSD, so the geometry of **13** is compared to the same benzo-fused structures as compounds **4** and **11**. The benzo-fused analogue bond lengths and angles in compound **4**

are all within the range of values from the CSD structures found, with no preference for longer or shorter bonds (50%), and slightly more wide angles than narrow (56%). The geometry of **11**¹ and **11**² are highly similar, with more short than long bonds (70% and 80%, respectively), and more narrow angles than wide (69% and 56%). Bond lengths and angles for naphtho-fused **13** all fall within the range of the CSD comparators at the 99% confidence level and are thus included in the combined average values presented below. There are slightly more short bonds than long (60%), and equal numbers of narrow and wide angles (50%). The puckering parameters^[82-84] of the 5-membered rings in compounds **4**, **11**, and **13** (Table A.2) are all consistent with twist ring conformations ($q_2 = 0.195 - 0.225$, $\varphi_2 \approx \pi/5 + 18^\circ$). The 7-membered rings of these compounds (C1-C2-C2A-C2B-C2C-C6A-C6B in compounds **4** and **11**, for example) are all in a twist-boat conformation ($q_2 = 1.1559 - 1.1707$, $\varphi_2 \approx \pi/14$, $q_3 = 0.193 - 0.1999$, $\varphi_3 \approx \pi/14$).

Benzo- and naphthocyclooctatetraenes. Benzo-fused 7-benzocyclooctenecarbonitrile **5** crystallizes in a Sohncke space group ($P2_12_12_1$ with $Z' = 1$), whereas the remaining three exemplars crystallize centrosymmetrically. Structure **6** is isomeric 5-benzocyclooctenecarbonitrile ($P\bar{1}$, $Z' = 1$); **12**, is 8-benzocyclooctenedicarbonitrile ($P2_1/c$, $Z' = 2$; only the first exemplar of these highly similar structures is shown in Figure 3.3c) while **14** is naphtho-fused 9-cycloocta[1,2-*b*]naphthalenecarbonitrile ($P2_1/c$, $Z' = 1$). The placement of the nitrile substituent in **14** was found to be disordered (0.80/0.20) between attachment to C9 and C10, respectively. An excellent two-part disorder model was refined and the reported geometry of **14** is from the major component only. As with other searches in this work for comparators in the CSD, those coordinated to metals or embedded in other rings were excluded. There are no naphtho-fused COTs in the CSD, so the geometry of **14** is compared to the same benzo-fused COT structures as compounds **5**, **6**, and **12**.

Table 3.3. Selected bond distances and angles in structures of the benzo- and naphthocyclooctatetraenes.^a

Bonds (Å)	5	6	12 ¹	12 ²	14 ^b	Average ^c
C4A-C5	1.4736(9)	1.4821(4)	1.4760(10)	1.4826(11)	1.4803(8)	1.480(6)
C4A-C10A	1.3970(9)	1.3916(4)	1.4002(10)	1.4018(10)	1.4266(8) ^d	1.400(11)
C5-C6	1.3298(9)	1.3383(4)	1.3387(11)	1.3377(11)	1.3408(9)	1.331(7)
C6-C7	1.4686(9)	1.4536(4)	1.4717(10)	1.4721(10)	1.4681(9)	1.467(10)
C7-C8	1.3421(9)	1.3334(4)	1.3570(10) ^d	1.3546(10) ^d	1.3496(9)	1.33(2)
C8-C9	1.4551(9)	1.4549(4)	1.4696(10)	1.4739(11)	1.4604(9)	1.466(10)
C9-C10	1.3334(10)	1.3334(4)	1.3391(11)	1.3401(11)	1.3408(9)	1.333(9)
C10-C10A	1.4733(9)	1.4678(4) ^d	1.4820(10)	1.4791(10)	1.4809(8)	1.483(8)
Angles (°)						
C10-C10A-C4A	123.90(6)	124.02(2)	124.05(7)	123.15(7)	124.33(5) ^d	123.0(10)
C4A-C5-C6	126.62(6)	126.95(3)	127.90(7)	127.44(7)	128.60(6)	127.1(18)
C10A-C4A-C5	123.94(6)	122.33(2)	124.08(7)	123.86(7)	124.11(5)	123.0(15)
C5-C6-C7	125.54(6)	125.05(3)	127.82(7)	126.27(8)	127.32(6)	125.8(17)
C6-C7-C8	126.25(6)	124.83(3)	126.35(7)	125.21(7)	126.69(6)	126(2)
C7-C8-C9	125.59(6)	126.99(3)	126.07(7)	125.60(7)	126.33(7)	125.6(15)
C8-C9-C10	126.48(6)	127.61(3)	127.16(7)	126.08(7)	127.75(6)	126.3(19)
C9-C10-C10A	126.72(6)	126.58(3)	128.25(7)	127.49(8)	128.84(6) ^d	126.9(18)

^a Atom labels are taken from the first exemplar (see Figure 3.3a) and applied to all structures for ease of comparison. The atoms numbering schemes should be consulted for identifying specific entries. ^b Disorder in the nitrile position; the major component of the two-part disorder model is reported here. ^c Average of specified bond length/angle of structural analogs collected from the CSD. Values from structures introduced in this paper are included in this average unless otherwise specified. Comparators used in this category: BUYUYUP,^[85] CUDYUV,^[86] FIVHIB,^[87] LEZMAE,^[17] LIPVAJ,^[88] QOGYER,^[89] QOGZAO,^[74] OWUVUA,^[32] OWUWAH,^[32] OWUWEL.^[32] ^d Statistical outlier omitted from the averaged values.

As in the similar situation in compound **11**, the C7-C8 double bond of **12** is significantly lengthened compared to the other double bonds due to the substituent effects of the nitriles at either end of the double bond. In a search of the CSD, 32 structures were located with *cis*-1,2-dicyanoethenes that are also attached to two *sp*³ carbon atoms, yielding a mean C=C bond length of 1.341 (6) Å. In 1,996 cases of analogous *cis*-1,2-ethenes with hydrogen substituents in place of the cyano groups, the average was found to be 1.31 (5) Å, indicative of significant lengthening caused by the two flanking nitriles. Naturally, the C7-C8 bond lengths of **12**¹ and **12**² are excluded from the combined average for BCOT

and NCOT double bonds presented in Table 3.3. This elongated C7-C8 bond widens several angles around the COT ring, resulting in the exclusion of the C5-C6-C7 angle of **12**¹ from the combined average.

The ring fusion C6A-C12A bond in compound **14** (i.e. C4A-C10A entry in Table 3.3) is anomalously long compared to other collected structures. This is thought to be due to the polycyclic system sacrificing the aromaticity of the ring to which the COT is fused in order to enhance the aromaticity of the remote ring in accordance with Clar's rule (i.e. favouring the Kekulé resonance structure with the greatest number of aromatic π -sextets).^[90] This effect also influences the bond angles in the COT ring which results in the exclusion of the C10-C10A-C4A and C9-C10-C10A angles from the combined average. The bond lengths and angles of compound **5** all fit into the range of the analogous structures collected from the CSD, with slightly more long bonds than short (63%), and predominantly wider angles than narrow (75%). Compound **6** has a long C5-C6 bond which is excluded from the combined average, but otherwise its bond lengths and angles fit within the range of analogs with longer than shorter bonds (63%) and equal numbers of narrower and wider angles (50%) when compared to means. The two independent molecules of compound **12**, the dinitrile, have highly similar structures where the bond lengths tend to be longer than the average (75% and 88% for **12**¹ and **12**², respectively), and bond angles are mostly wider than narrower (100% and 88%). Compound **14** has more longer than shorter bonds compared to the average (75%), and all bond angles examined are wider than the average (100%). The puckering parameters^[82-84] for the 8-membered rings in **5**, **6**, **12**, and **14** (Table A.3) are found to be consistent with tub geometry ($q_2 = 1.1263 - 1.1804$, $\varphi_2 \approx \pi/4$, $q_3 = 0.0142 - 0.0483$, $q_4 = -0.0106 - 0.0099$), which is strongly conserved with some minor twisting, which, however, does not seem to fit a clear pattern for number and locations of the substituents. We can presume that the rigid benzo-fusing at one of the two edges should be effective at sustaining the tub shape.

DCBN and TCBN derivatives. Compounds **7** – **10** are polycyclic systems in which a (ring-fused) 1,3-dicyclohexene ring is fused to a cyclobutane or cyclobutene ring at the saturated carbons. In 1-2*a*,8*b*-dihydrocyclobuta[*a*]naphthalenecarbonitrile, **7**, ($P2_1/n$, $Z' = 1$) and in 2-2*a*,8*b*-dihydrocyclobuta[*a*] naphthalenecarbonitrile, **8** ($P2_1/c$, $Z' = 1$), it is a cyclobutene ring (Figure 3.4a,b). The benzene ring fusion is at C4A-C8A, and cyclobutene ring is at C2A-C8B. Since the two nitrile substituents occur at the ethene bridge atoms (C1,2) steric congestion that might perturb the basic structure is not expected and, consequently, the base six-membered ring in **7** is found to be close to planarity (standard deviation from the L.S. plane is 0.021 Å) and the cyclobutene is quite planar (deviation of only 0.003 Å). The ‘envelope fold angle’ between these L.S. planes is 65.56(3)°. In **8**, the two rings have deviations of 0.033 and 0.040 Å and the ‘envelope’ dihedral is 65.29(2)°.

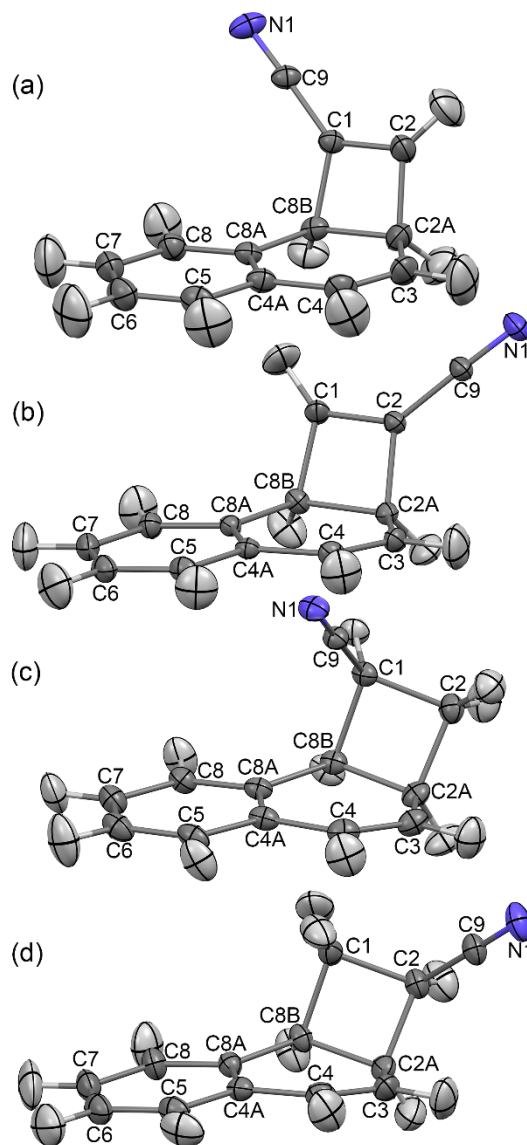


Figure 3.4. Displacement ellipsoid plots (50% probability) for structures at 173 K: (a) 7, (b) 8, and (d) 10, and at 100 K: (c) 9 (the geometry shown has been inverted to harmonize with those of 7, 8, and 10).

In *endo*-1-1,2,2*a*,8*b*-tetrahydrocyclobuta[*a*]naphthalenecarbonitrile, **9** ($P2_12_12_1$, $Z' = 1$) and *endo*-2-1,2,2*a*,8*b*-tetrahydrocyclobuta[*a*]naphthalenecarbonitrile, **10** ($P2_12_12_1$, $Z' = 1$), both of the nitrile substituents are oriented in towards the fold created by the ring fusions (Figure 3.4c,d). In these structures, the saturation of the C1–C2 bond induces considerable conformational changes. Thus, in **9** the standard deviations from L.S. planes for the 4- and 6-membered rings (fused benzo-rings are omitted from this analysis) are 0.209 and 0.107

Å, respectively. In **10**, these values are 0.268 and 0.131 Å. Interestingly, despite the considerable ring twisting, the 'envelope' dihedral angles between these L.S. average planes remain quite similar to the unsaturated analogs. The angles for **9** and **10** are 66.34(6) and 67.85(6), respectively, and thus slightly less acute than in **7** and **8**.

Separate comparator groups were sought from a search of the CSD for the DCBN and TCBN structure types (Table 3.4). It is notable that there are only 3 unique comparators in the CSD for DCBNs with the search filters adopted in this work, namely those entries which are coordinated to a metal or in which the skeleton of the DCBN are embedded in other rings have been excluded. The C2A-C8B-C8A angle in both **7** and **8** is significantly wider than the mean by 1.2 degrees and 1.7 degrees, respectively. Angles C1-C8B-C8A and C3-C2A-C8B in structure **8** also do not fit the average, and the C2-C2A bond length in **7** is anomalously short. Structures **7** and **8** have more short bonds than long compared to means (78% and 56%, respectively). Structure **7** has more wide than narrow angles (58%), and structure **8** has more narrow angles than wide (58%). Structures **9** and **10** have slightly more short bonds than long compared to means (56% for both). There are equal numbers of wide and narrow angles in structure **9** (50%), and more narrow angles than wide in structure **10** (67%). Puckering parameters^[82-84] for **9** indicate the 4-membered ring has puckered geometry ($q_2 = -0.2092$), and the 6-membered cyclohexyl ring adopts a conformation between envelope and half-chair, favouring envelope ($Q = 0.1862$, $\theta = 61.0^\circ$, $\varphi = 310.7^\circ$). For **10**, the 4-membered ring is puckered ($q_2 = -0.2686$), and the 6-membered cyclohexyl ring is intermediate between envelope and twist-boat, slightly favouring envelope ($Q = 0.2303$, $\theta = 115.3^\circ$, $\varphi = 134.3^\circ$). Puckering parameters cannot be assigned for **7** and **8** due to τ values less than 5° , as expected for these highly planar rings. Puckering parameter data for **9** - **10** can be found in Table A.4. Structure **9** was reported previously in 1968,^[51] but as being in $P2_1/c$ ($Z' = 1$) and only a room-temperature unit cell was

determined. It contains neither atom coordinates nor R-factor statistics, and as such no comparisons can be made.

Table 3.4. Selected bond distances and angles in structures of the DCBN and TCBN derivatives.

Bonds (Å)	7	8	DCBN Avg ^a	9	10	TCBN Avg ^b
C1-C2	1.3393(5)	1.3438(4)	1.340(4)	1.5571(13)	1.5422(14)	1.542(18)
C1-C8B	1.5239(5)	1.5178(4)	1.522(12)	1.5773(12)	1.5414(14)	1.57(3)
C2-C2A	1.5216(6) ^c	1.5283(4)	1.527(4)	1.5547(15)	1.5528(14)	1.562(15)
C2A-C3	1.4942(6)	1.4935(4)	1.492(12)	1.4954(16)	1.4805(14)	1.48(2)
C2A-C8B	1.5742(6)	1.5753(4)	1.579(6)	1.5571(13)	1.5399(13)	1.56(2)
C3-C4	1.3373(6)	1.3397(4) ^c	1.334(6)	1.3456(16)	1.3315(14)	1.324(17)
C4-C4A	1.4623(6)	1.4642(4)	1.462(8)	1.4678(14)	1.4557(13)	1.467(18)
C4A-C8A	1.4042(5)	1.4029(4)	1.405(6)	1.4048(14)	1.3928(12)	1.41(3)
C8A-C8B	1.5011(5)	1.5019(4)	1.507(7)	1.4993(13)	1.4865(13)	1.51(3)
Angles (°)						
C1-C2-C2A	93.64(3)	94.68(2)	94.4(8)	89.48(7)	88.07(8)	88.8(12)
C1-C8B-C2A	84.83(3)	86.30(2)	85.6(8)	88.66(7)	88.56(7)	87.7(14)
C1-C8B-C8A	114.49(3)	116.67(3) ^c	113.9(15)	117.87(8)	117.58(9)	116.2(18)
C2-C1-C8B	95.21(3)	93.97(3)	94.5(8)	88.46(7)	88.40(8)	89.1(12)
C2-C2A-C3	115.07(4)	114.18(3)	115.4(13)	113.25(10)	113.17(9)	117(3)
C2-C2A-C8B	86.32(3)	84.93(2)	85.3(9)	89.28(7)	88.07(7)	88.8(8)
C2A-C3-C4	122.27(4)	122.78(3)	121.6(17)	122.97(10)	122.71(10)	123.2(16)
C2A-C8B-C8A	117.10(3)	117.61(2) ^c	115.5(10)	118.39(8)	117.45(9)	116(3)
C3-C2A-C8B	115.97(3)	115.18(3) ^c	117.0(12)	113.23(9)	113.19(9)	114(2)
C3-C4-C4A	123.39(4)	123.20(3)	123.6(5)	122.94(10)	122.81(10)	123.0(16)
C4-C4A-C8A	120.50(3)	120.47(3)	120.6(7)	119.96(9)	119.62(9)	119.4(14)
C4A-C8A-C8B	120.65(3)	120.30(3)	120.4(4)	118.95(8)	119.05(8)	120.0(10)

^a Average of specified bond length/angle of structural analogs collected from the CSD. Values from structures introduced in this paper are included in this average unless otherwise specified. Comparators used in this category: DIWVUD,^[91] MONPHC,^[92] MONPHD.^[92] ^b Average of specified bond length/angle of structural analogs collected from the CSD. Values from structures introduced in this paper are included in this average unless otherwise specified. Comparators used in this category: AXOQIO,^[41] EWIXUF02,^[40] FMPCBN,^[93] HZOBUR,^[94] JUYOR,^[44] PHBNPH,^[45] QETHAY,^[43] QETHEC,^[43] RECGAH,^[95] YEQFIJ,^[42] YICXOX^[96]. ^c Statistical outlier omitted from the averaged values.

3.2.3. Structure Refinement with Aspherical Atomic Scattering Factors.

Hirshfeld Atom Refinement (HAR) was undertaken for all 14 structures using the recently reported NoSpherA2 software.^[52] This program is included with current releases

of the Olex2 crystallographic software suite^[97] and harmonizes with the olex2.refine engine. It seamlessly integrates with several popular density-functional theory (DFT) computational packages, and here we have used it with the freely downloadable ORCA computational software suite.^[98-99] Fast and accurate DFT functionals such as B3LYP or PBE enable the computation of accurate custom atom scattering factors that directly reflect the electron densities of all the atoms within their structural environment, and thus polarized correctly to their precise locations in the structures. Although this is correctly described as *quantum crystallography*, it remains a fully experimental structure determination because DFT is used only to calculate atomic scattering factors, which are then used to construct the F_{calc} values for the model and minimized against F_{obs} in the conventional manner. The benefit comes, however, from the customization of the atom scattering factors, rather than using one set of standard compiled factors from very old self-consistent field (SCF) calculations on a set of spherical, neutral atoms.^[100] For the fourteen structures reported in this work, comparison of the NoSpherA2 refinements with well-performed conventional models refined in the IAM, the structure accuracy as indicated by the average precision of the C-C bonds (as calculated by PLATON, and prominently displayed near the tops of all CheckCIF reports) improved, on average, from 0.0022 to 0.0012 Å, a 49% improvement, detailed in Table 3.5. Notably, *all* the structures gained in this precision indicator, ranging from 26 to 73% improvement; that is to say, none of the refinements deteriorated from the use of this HAR method.

Table 3.5. Summary of Results and Quality Analysis for NoSpherA2 Refinement of Structures.^{a,b}

Structure	C-C bond precision (Å) ^c	Impr. %	R ₁	R _{int}	Data/par. ratio
1	0.0019–0.0028	32.1	0.0181	0.0273	12.0
2	0.0016–0.0025	36.0	0.0270	0.0216	11.3
3	0.0007–0.0015	53.3	0.0168	0.0270	8.4
4	0.0004–0.0015	73.3	0.0092	0.0118	11.0
5	0.0009–0.0015	60.0	0.0199	0.0159	11.6
6	0.0005–0.0015	66.7	0.0120	0.0060	11.3
7	0.0006–0.0016	62.5	0.0143	0.0169	10.5
8	0.0005–0.0014	64.3	0.0121	0.0186	10.2
9	0.0015–0.0018	16.7	0.0220	0.0332	8.7
10	0.0015–0.0020	25.0	0.0267	0.0377	7.5
11	0.0015–0.0021	28.6	0.0249	0.0724	8.3
12	0.0011–0.0019	42.1	0.0238	0.0237	9.2
13	0.0030–0.0033	9.1	0.0392	0.0965	7.8
14	0.0010–0.0018	44.4	0.0192	0.0304	8.3
Average	0.0012–0.0019	42.4			

^a All DFT calculations employed ORCA 4.2 using the PBE/def2-TZVP computational method. ^b All atoms were refined anisotropically, with the exception of **3** and **13**, which implement disorder models. In structure **3**, all H atoms of the disordered molecule (the second molecule of the asymmetric unit) are refined isotropically in both components of the disorder model. In structure **13**, only the H atom involved in the minor component of the disorder model (H9) is refined isotropically. ^c C-C bond precision taken from the CheckCIF Report. First value given is C-C bond precision in Å from structures refined using NoSpherA2, second value is from structures refined to IAM.

Here we report successful HAR refinement of all 14 structures, each of which also has a sufficiently high data-to-parameter ratio to enable good quality anisotropic displacement parameters of all the atoms in each structure, except for the H atoms in the minor component of the two-part disorder model of **13**, as well as all H atoms in the disordered and distorted molecule of **3**. The quality of these displacement models is evident from Figures 3.1 - 3.4. Regarding the accuracy of the C-H bond distances, we have undertaken a statistical analysis with comparison to a 2010 survey of available neutron diffraction data in the CSD over various measurement temperature ranges.^[101] The C-H bond distances of **1** - **14** as calculated using NoSpherA2 are in very good agreement with the neutron diffraction data (Table 3.6). Of the 150 C-H bonds in our structures, 140 are

statistically similar at a 99% confidence level to the categorical average C-H bond length from neutron data (Table A.5–A.19).

Table 3.6. Comparison of C-H bond lengths from this work with values from neutron diffraction.

C–H type	IAM C-H ^a (Å)	% dev ^b	1 – 14 ^c C-H (Å)	n	% dev ^b	Neutron C-H ^d	n
Z ₃ -Csp ³ -H	1.00	9.0	1.077(14)	28	2.0	1.099(7)	66
Z ₂ -Csp ³ -H ₂	0.99	8.9	1.090(18)	10	0.6	1.097(6)	136
Csp ² or C(ar)-H	0.95	8.3	1.075(16)	112	0.9	1.085(9)	184

^a IAM standard values (AFIX @ 100 K) ^b % deviation vs. neutron diffraction data. ^c This work. Errors are std. dev. of the sets of values. ^d Neutron diffraction data at 60 ≤ T ≤ 140 K. From Allen, F. H., Bruno, I. J.; *Acta Crystallogr B*, **2010**, 66 (Pt 3), 380-6.

Figure 3.5 details the distribution of C-H bond lengths found in **1** – **14**, which are most commonly in the 1.08 – 1.10 Å range, with a steady rise in frequency from 1.04 – 1.07 Å and a steep drop in frequency above 1.10 Å. This is indicative of the C-H bond lengths calculated by NoSpherA2 being close to C-H bond lengths determined by neutron diffraction experiments, and of a possible trend to shorter values. Defining a ‘short’ C-H bond length as being more than 2.58 standard deviations shorter than that of the ‘Csp² or C(ar)-H’ category of neutron data returns the 1.04 – 1.06 Å C-H bond lengths from this work (Figure 3.5). There are 23 such C-H bonds in this range from 6 structures. Analysis of these data show that the short bonds occur with no preference between structure types (two type **I** (**1** and **2**), two type **III** (**4** and **13**), one type **IV** (**5**), one type **VI** (**10**)). Structure **5** has a particularly large number of short bonds, occurring in eight out of nine C-H bonds. Close analysis of the structures, with special attention paid to **5**, has turned up no obvious indication as to the cause of these bonds being so anomalously short, especially the absence of any correlation with the structure quality indicators listed in Table 3.5. The exo-hydrogen bound to C2 in **9** is the outlying long C-H bond modelled at 1.132 Å. In future applications of the NoSpherA2 method, anomalous outliers could easily be constrained during refinement; herein we have chosen to employ unconstrained values as part of an overall evaluation of the method.^{54,55}

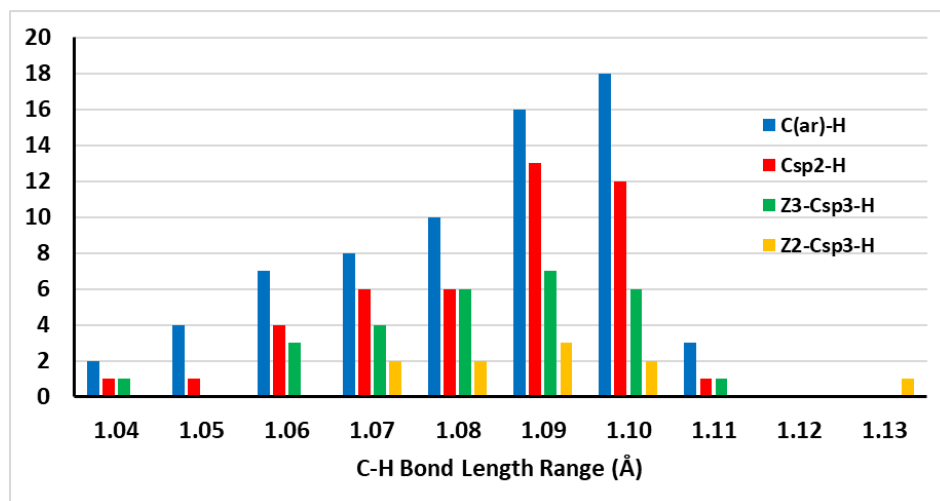


Figure 3.5. Histogram of C-H bond lengths for the different types of carbons in compounds 1 – 14

3.2.4. Analysis of C-H $\cdots$ N $\equiv$ C Non-Classical H-Bonding and Dipolar C $\equiv$ N $\cdots$ C $\equiv$ N Interactions in 2 – 14

Dunitz's skepticism about the significance of any interactions weaker than classical H-bonding^[102] has been resolutely countered by Lecomte *et al.*,^[103] by a consideration of the electron density distribution, and the Laplacian thereof, which affects *all* interatomic interactions, within and between molecules and ions. In other words, the strengths of intermolecular interactions are on a smooth gradient from the smallest to the largest interaction energies; consequently frequency matters. Many small interactions in composite can merge to overcome a single 'obviously' stronger interaction of a different kind. Evidence for C-H $\cdots$ N $\equiv$ C H-bonding has been obtained from vibrational spectroscopy.^[104] A fine-tuned consideration of C-H $\cdots$ N $\equiv$ C short contacts, interpreted by a thorough computational analysis, has been undertaken by Lushtinetz *et al.*^[105] on a set of nitrile-functionalized thiophene oligomers. The interaction energy of non-classical C-H $\cdots$ N $\equiv$ C H-bonds was computed to be -21.7 kJ/mol and the interaction angle $\angle$ C-H $\cdots$ N $\equiv$ C was found to be close to 150° and the H $\cdots$ N distance to be 2.43 Å (at the MP2/cc-pvdz level of theory).^[105] This places the interaction in the low-end of 'moderate H-bonds' by energy on the scale of Jeffrey, but in the (expected) 'weak H-bond' range according to distance (see Table A.21). A retrospective analysis recognizes that weak H-

bonds of this type cannot compete with stronger structure-directing factors (including strong dispersion forces), but that in the absence of other mechanisms, we may expect C-H $\cdots$ N $\equiv$ C H-bonding to contribute to structure direction.^[106]

A survey of the CSD was undertaken on all organic nitrile to C-H short contacts out to ($\Sigma r_{vdW} + 0.1\text{\AA}$) found several thousand hits, but no evidence of a maximum in the distance distribution indicative of a definitive supramolecular contact. The interaction angle $\angle\text{C-H}\cdots\text{N}\equiv\text{C}$ did show a broad distribution with a maximum at $\sim 136(20)^\circ$, also fitting the moderate interaction pattern of Jeffrey (Table A.21). Wood *et al.* have analyzed the CSD for dipolar $\text{C}\equiv\text{N}\cdots\text{C}\equiv\text{N}$ interactions in structures of organic nitriles, in view of the high polarity of these functional groups.^[71] They found that some 37% of structures containing nitriles met their rigorous search criteria. Three distinct interaction geometries were identified, namely the sheared antiparallel (most common; with simultaneous contacts of each $\text{N}^{\delta-}$ to $\text{C}^{\delta+}$), perpendicular, and sheared parallel (each with contacts from a single $\text{N}^{\delta-}$ to $\text{C}^{\delta+}$ - see Figure A.1). A search for such contacts in our structures indicates that they are often found cooperatively with the H-bonding.

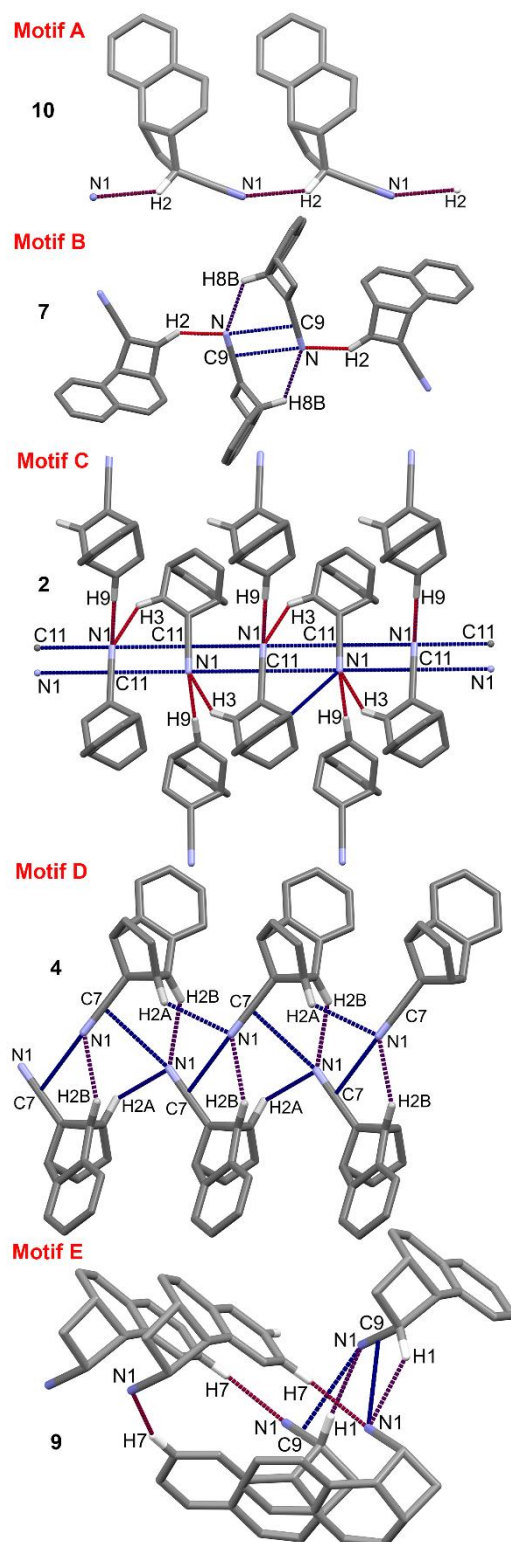


Figure 3.6. Five motifs encountered from combinations of $\text{-C}\equiv\text{N}\cdots\text{H-C}$ bonds and dipolar $\text{C}\equiv\text{N}\cdots\text{C}\equiv\text{N}$ interactions.

Table 3.7. Table of C-H...N≡C non-classical H-bonding and dipolar C≡N...C≡N interactions

Cmpd	Contact ^a	d(D-H)/Å	d(H-A)/Å	d(H-A)-r _{vdW} ^b	d(D-A)/Å	D-H...A/ ^{oc}	Description
2	C3-H3...N1 ¹	1.08(3)	2.37(3)	-0.38	3.296(3)	142(2)	Terminal bifurcated
	C11...N1 ¹	—	—	+0.08	3.326(3)	97.1(1)	Sheared antiparallel
	N1...C11 ¹	—	—	+0.12	3.369(3)	94.9(1)	Sheared antiparallel
	C9-H9...N1 ²	1.08(2)	2.38(2)	-0.37	3.452(2)	174(2)	Terminal bifurcated
3	C3-H3...N1 ³	1.083(6)	2.530(6)	-0.22	3.2332(7)	121.7(4)	Terminal net forming
	C23-H23...N2 ⁴	1.07(1)	2.41(1)	-0.13	3.383(2)	150.8(9)	Dimer forming
	N1...C2N ⁴	—	—	0.00	3.248(1)	94.19(4)	Sheared antiparallel
	C1N...N2 ⁴	—	—	+0.02	3.2663(8)	93.27(6)	Sheared antiparallel
	N2...C2N ⁴	—	—	+0.31	3.555(1)	91.97(6)	Sheared antiparallel
4	C2A-H2A...N1 ²	1.070(4)	2.715(5)	+0.04	3.4014(4)	121.7(3)	Terminal bifurcated
	C2B-H2B...N1 ⁵	1.063(4)	2.575(4)	-0.08	3.4651(4)	140.9(3)	Terminal bifurcated
	N1...C7 ⁵	—	—	+0.13	3.3874(4)	—	Perpendicular nitrile
6	C8-H8...N1 ⁶	1.075(4)	2.618(4)	-0.13	3.4846(4)	137.3(3)	Chain forming
7	C2-H2...N ⁷	1.063(5)	2.350(5)	-0.40	3.2195(6)	138.1(4)	Links between dimers
	C8B-H8B...N ⁸	1.082(4)	2.628(5)	-0.12	3.3771(6)	125.3(3)	Dimer forming
	N...C9 ⁸	—	—	-0.01	3.2406(6)	94.11(3)	Sheared antiparallel
8	C3-H3...N ⁹	1.077(3)	2.762(3)	+0.12	3.4989(5)	125.5(2)	Dimer forming
	N...C9 ⁹	—	—	+0.12	3.3740(5)	85.17(2)	Sheared antiparallel
9	C7-H7...N1 ¹⁰	1.083(12)	2.470(13)	-0.18	3.4784(14)	154(11)	Terminal net forming
	C1-H1...N1 ²	1.091(11)	2.578(11)	-0.07	3.4498(11)	136.2(8)	Simple chain forming
	N1...C9 ⁵	—	—	+0.31	3.561(1)	105.81(7)	Sheared parallel
10	C2-H2...N1 ¹¹	1.066(10)	2.516(10)	-0.23	3.3827(12)	137.7(8)	Simple chain forming

Table 3.7. Cont'd

Cmpd	Contact ^a	d(D-H)/Å	d(H-A)/Å	d(H-A)-r _{vdW} ^b	d(D-A)/Å	D-H...A/ ^{°c}	Description
11	C6C-H6C...N11 ¹⁵	1.09(1)	2.51(1)	-0.24	3.562(1)	163.2(7)	Terminal net forming
	C3-H3...N12 ¹²	1.08(1)	2.60(1)	-0.14	3.393(1)	130.2(7)	Terminal net forming
	C16C-H16C...N1 ¹³	1.07(1)	2.61(1)	-0.14	3.673(2)	169.7(7)	Terminal net forming
	C12A-H12A...N11 ¹⁴	1.09(1)	2.63(1)	-0.12	3.529(1)	139.3(7)	Terminal net forming
	N2...C18 ¹⁰	—	—	+0.06	3.312(1)	96.17(7)	Perpendicular nitrile
	N11...C18 ¹⁴	—	—	+0.24	3.488(1)	86.48(7)	Perpendicular nitrile
12	C9-H9...N4 ¹⁵	1.083(9)	2.426(9)	-0.34	3.2905(9)	135.8(7)	Terminal bifurcated
	C13-H13...N1 ¹⁷	1.09(1)	2.46(1)	-0.29	3.468(1)	152.8(8)	Terminal bifurcated
	C11-H11...N3 ¹⁶	1.09(1)	2.46(1)	-0.29	3.496(1)	157.8(8)	Terminal bifurcated
	C20-H20...N3 ²⁰	1.09(1)	2.55(1)	-0.20	3.347(1)	121.7(7)	Terminal bifurcated
	C16-H16...N1 ¹⁸	1.073(9)	2.550(9)	-0.20	3.3067(9)	126.8(8)	Terminal bifurcated
	C12-H12...N2 ¹⁷	1.08(1)	2.57(1)	-0.19	3.569(1)	154.6(8)	Terminal bifurcated
	C15-H15...N1 ¹⁸	1.098(9)	2.635(9)	-0.12	3.3616(9)	123.1(7)	Terminal bifurcated
	C15-H15...N4 ¹⁹	1.098(9)	2.68(1)	+0.07	3.468(1)	128.1(7)	Terminal bifurcated
	N3...C1N-N1 ⁴	—	—	+0.16	3.413(1)	104.15(6)	Perpendicular nitrile
13	C2A-H2A...N1 ¹⁰	1.09(2)	2.69(2)	-0.06	3.413(3)	123(1)	Chain forming
	N1...C9-N1 ¹⁰	—	—	+0.09	3.336(3)	84.8(1)	Perpendicular nitrile
14	C10-H10...N1 ²¹	1.08(2)	2.45(2)	-0.30	3.517(1)	168(1)	Dimer forming

^a Symmetry codes: ¹ 1-X, -1/2+Y, 2-Z; ² -1+X, +Y, +Z; ³ 3/2-X, -1/2+Y, 1/2-Z; ⁴ 1-X, 1-Y, 1-Z; ⁵ -1/2+X, 3/2-Y, 1-Z; ⁶ -1+X, -1+Y, +Z; ⁷ -1/2+X, 1/2-Y, -1/2+Z; ⁸ -X, -Y, 1-Z; ⁹ -X, 2-Y, 1-Z; ¹⁰ -1/2+X, 1/2-Y, 1-Z; ¹¹ +X, -1+Y, +Z; ¹² 1/2+X, 1/2-Y, 1-Z; ¹³ 1/2-X, -Y, -1/2+Z; ¹⁴ 1/2-X, -1/2+Y, +Z; ¹⁵ +X, +Y, +Z; ¹⁶ +X, 1/2-Y, -1/2+Z; ¹⁷ 1-X, -Y, 1-Z; ¹⁸ 1+X, +Y, 1+Z; ¹⁹ -X, -1/2+Y, 1/2-Z; ²⁰ 1+X, 1/2-Y, 1/2+Z; ²¹ 2-X, 1-Y, 1-Z. ^b d(D-A)-r_{vdW} in the case of dipolar C≡N...C≡N interactions. ^c N...C-N/[°] in the case of dipolar C≡N...C≡N interactions.

The most important non-classical C-H $\cdots$ N $\equiv$ C H-bonds in the lattices of **2** – **14**, based on $d(\text{H}\cdots\text{A}) - r_{\text{vdW}}$ and largest $\angle\text{H}\cdots\text{N}\equiv\text{C}$, are listed in Table 3.7, with a description of their chief features. Five motifs have been determined from the combination of these interactions with dipolar C $\equiv$ N $\cdots$ C $\equiv$ N interactions, for which the optimal $d(\text{C}\cdots\text{N}) = 3.30$ Å, being primarily electrostatic, is effectively the Σr_{vdW} , as determined by Wood et al.¹⁰⁵ In all, nine of the thirteen nitrile structures show one of the three types of dipolar nitrile-nitrile contacts, which is a much higher fraction than the global average of 21% reported by these authors.^[71] Since **8** has such a dipolar nitrile contact, the weak H-bond that correlates with it is included in Table 3.7, whereas **5** has been excluded for a total absence of contacts shorter than $\Sigma r_{\text{vdW}} - 0.1$ Å.

Motif A (Figure 3.6) consists of a single chain-forming series of C-H $\cdots$ N $\equiv$ C H-bonds, as illustrated in the lattice structure of **10**. There are no dipolar nitrile contacts. This motif is also found in the lattice of **6** (Figure A.2).

Motif B, illustrated best by the lattice structure of **7**, is a discrete dimer of sheared antiparallel (SAP) nitriles, supported further by a matching pair of C8BH8B $\cdots$ N $\equiv$ C H-bonds. Extension of the motif occurs via the considerably stronger C2H2 $\cdots$ N $\equiv$ C H-bonds linking the dimers into chains. This motif is also present in the lattice structure of **8** (without the second, external link) and **3** (where there are quads from two sets of SAP nitriles) and, geometrically, also in **13** where the dimer is supported on the H-bonds because here the nitriles are too far apart to interact strongly (Table 3.7 and Figure A.2).

Motif C, found in the lattice of **2**, is a further variant on **B**, wherein strong SAP nitrile contacts form an infinite ribbon with equal contact distances, supported again by bridging C3H3 $\cdots$ N $\equiv$ C H-bonds; contacts between ribbons are maintained by C9H9 $\cdots$ N $\equiv$ C H-bonds of comparable strength.

Motif D exemplifies perpendicular (P) nitrile contacts, which in the lattice of **4** produces another continuous ribbon structure analogous to that of **2**, supported by double bridging H-bonds. Other exemplars of this motif can be found in the lattices of **11**, **12** and **14**, also with a simple continuous ribbon in **14**. As may be expected, the dinitriles **11** and **12** have, in addition to these P chain-forming nitrile interactions, many additional H-bonds leading to complex 3D networks (Table 3.7 and Figure A.2).

Motif E contains the only sheared parallel nitrile (SP) interaction, found in the lattice of **9**, where it is also ribbon forming and supported by a bridging H-bond. A second terminal H-bond provides links to adjacent ribbons. While similar to the most common **motif C**, it differs by the angle of interaction between the nitrile moieties.

3.3. Conclusions

In this paper, we have shown that HAR can be applied to a set of average to good-quality, “standard resolution” crystallographic datasets. In all cases, it was possible to refine atom positions and to model ADPs for H-atoms with limited restraints, and in the best cases, fully unrestrained refinements were possible. The most important outcomes of our study are the trends derived from Table 3.5, indicating improvement in overall structure precision in all 14 structure models compared to employing an equivalent IAM refinement. Moreover, this data shows that the greatest improvement in accuracy comes with the highest quality datasets, but also that no discontinuities occur. In other words, there does not seem to be a downside to routinely employing the HAR/NoSpherA2 approach, with the expectation that the best standard- or higher-resolution datasets will afford the greatest improvement in accuracy versus equivalent IAM refinement. Many of the structures of the valence isomers reported in this work significantly increase the number of exemplars in rare organic structure classes.

Table 3.8. Crystallographic collection and refinement parameters for crystal structures of 1 - 14

Parameter	1	2	3	4	5	6	7
Chemical Formula	C ₁₂ H ₉ Br	C ₁₃ H ₉ N	C ₁₃ H ₁₁ N	C ₁₃ H ₉ N	C ₁₃ H ₉ N	C ₁₃ H ₉ N	C ₁₃ H ₉ N
Formula Weight (g/mol)	233.109	179.223	181.239	179.223	179.223	179.223	179.223
Temperature (K)	173	173	100	173	173	173	173
Crystal System	orthorhombic	monoclinic	monoclinic	orthorhombic	orthorhombic	triclinic	monoclinic
Space Group	<i>Pca</i> 2 ₁	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
a (Å)	18.8566(13)	8.1796(5)	10.9643(2)	5.5108(1)	7.0407(2)	6.5819(2)	8.4209(7)
b (Å)	7.8568(6)	6.4120(4)	8.3710(2)	9.1248(2)	9.4027(2)	7.5472(2)	13.0840(11)
c (Å)	6.3785(5)	9.1633(6)	21.4696(4)	17.5736(4)	14.1692(3)	10.2062(3)	9.3215(8)
α (°)	90	90	90	90	90	106.310(2)	90
β (°)	90	100.496(6)	101.356(2)	90	90	97.187(2)	112.354(1)
γ (°)	90	90	90	90	90	101.294(2)	90
Volume (Å ³)	944.99(12)	472.55(5)	1931.95(7)	883.69(3)	938.02(4)	468.35(3)	949.85(14)
Z	4	2	8	4	4	2	4
Z'	1	1	2	1	1	1	1
R ₁ ^a [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0181	0.0270	0.0168	0.0092	0.0199	0.0120	0.0143
wR ₂ [all data]	0.0323	0.0496	0.0337	0.0211	0.0426	0.0307	0.0311
Twin; ^a major fraction	0.921(6)	0.618 ^b					
CCDC	2112984	2112985	2112987	2112986	2112990	2112992	2112993

Table 3.8. Cont'd

Parameter	8	9	10	11	12	13	14
Chemical Formula	C ₁₃ H ₉ N	C ₁₃ H ₁₁ N	C ₁₃ H ₁₁ N	C ₁₄ H ₈ N ₂	C ₁₄ H ₈ N ₂	C ₁₇ H ₁₁ N	C ₁₇ H ₁₁ N
Formula Weight (g/mol)	179.223	181.239	181.239	204.233	204.233	229.283	229.283
Temperature (K)	173	100	173	173	100	173	100
Crystal System	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
a (Å)	8.8036(7)	5.7696(1)	9.3073(6)	11.7370(9)	12.3616(4)	5.5530(11)	13.7748(6)
b (Å)	10.3463(8)	8.2484(1)	5.6081(3)	13.8928(10)	13.2693(4)	8.9395(18)	8.1983(3)
c (Å)	10.8587(8)	20.6639(3)	18.3728(11)	24.4482(18)	13.5889(4)	22.594(5)	11.4516(5)
α (°)	90	90	90	90	90	90	90
β (°)	110.844(1)	90	101.384(6)	90	111.485(4)	90	114.501(5)
γ (°)	90	90	90	90	90	90	90
Volume (Å ³)	924.33(12)	983.39(3)	940.12(10)	3986.5(5)	2074.10(12)	1121.6(4)	1176.78(10)
Z	4	4	4	16	8	4	4
Z'	1	1	1	2	2	1	1
R ₁ ^a [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0121	0.0220	0.0267	0.0249	0.0238	0.0392	0.0192
wR ₂ [all data]	0.0241	0.0566	0.0440	0.0350	0.0531	0.0643	0.0369
Twin; major fraction		0.602					
CCDC	2112988	2112989	2112991	2112994	2112996	2112995	2112997

^a Racemic twin refinement except 2. ^b Twin integration in CrysAlisPro, twofold rotation around [0.98, -0.00, -0.20] in reciprocal space

3.4. Experimental

3.4.1. General Methods

The sources of all the compounds used in this study have been outlined under Chemical Background. Isolated samples were available as crystalline solids suitable for single-crystal X-ray diffraction.

3.4.2. Crystallography

Crystals were selected under a polarizing microscope and checked for optical extinction. Colorless or pale-yellow crystals were mounted in Paratone™ oil either on the ends of thin capillaries or on a 100 μm MiTeGen loop and cooled to 173 (2) or 100 (1) K using the diffractometer cooling devices. Data were collected either on Bruker ApexII CCD (Mo $K\alpha$) or Rigaku-Oxford Diffraction SuperNova HPC (Cu $K\alpha$) diffractometers. Data collection and reduction was controlled, respectively, with *SAINT-Plus* or *CrysAlisPro* 1.171.38.43 (Rigaku Oxford Diffraction, 2021). The data were processed and corrected for Lorentz and polarization effects by standard methods and corrected for absorption by semi-empirical methods from equivalents. Structures were solved with *shelXT*^[107] and refined using Levenberg–Marquardt minimization with *olex2.refine* within the Olex2 suite of programs.^[97] The refinements employed NoSpherA2, (Non-SPHERical Atom-form-factors in Olex2)^[52] an implementation of HAR that makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED). The ED is calculated from a Gaussian basis set single determinant SCF wavefunction in DFT at the PBE/def2-TZVP level of theory using ORCA 4.5. The CIF files of the finalized structures of **1** – **14** and of the structures of the comparators collected from the CSD were run through the PLATON crystallographic software suite^[108-109] to extract the Cremer puckering parameters and least-squares planes values. Crystal data and structure refinement parameters are summarized in Table 3.8, and full archival data is available in CIF format.

3.5. References

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Chapter 4. *N,N'*-Diaryl-Sulfurdiimides Are Strongly Redox Tuned

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4.1. Introduction

Sulfur diimides (SDIs, R-NSN-R) are imines of sulfur dioxide^[1] (Figure 4.1) and were entirely unknown until the first report of the isolation of *n*-Bu-NSN-*n*-Bu in an historic paper by Becke-Göhring and Weis in 1956,^[2] soon followed by similar compounds with (CH₃)₃Si-NSN-Si(CH₃)₃,^[3-4] *t*-Bu-NSN-*t*-Bu,^[5-8] and the first aromatic derivative (Ph-NSN-Ph).^[9] An ongoing interest in inorganic chemistry is their anionic derivatization in the syntheses of diimidodisulfates, [(R'N)₂SR]⁻, and triimidodisulfates, [(R'N)₃S]⁻.^[10-12] The latter have recently been developed as ligands for single-molecule magnets.^[12] Bis-trimethylsilyl SDI is important enough to be commercially available and serves as a major synthon for unsaturated sulfur-nitrogen chains and heterocycles.^[1, 13-15] The organic chemistry of SDIs has been reviewed repeatedly,^[16-17] and has recently been revived intensively due to significant advances in pharmaceutical applications.^[18] A reliable thermodynamic scale has been developed for the replacement of the SO bonds in SO₂ with SNR groups.^[19] The nature of the NS bonds in SDIs has been discussed in great depth^[20-22] but is now definitively confirmed to be of the heteroallylic nature shown at the bottom of Figure 4.1;^[21] in graphical schemes the shorthand partially dashed double line notation has been adopted, but in text, whether written NSN or -NSN-, this heteroallylic character will always be intended.

Sulfur diimides are capable of incorporating an extensive range of substituents. A great number and variety of SDIs have been (separately or in collaboration) synthesized by Herberhold, Hörhold, and Wrackmeyer, including organic alkyl, perfluoroalkyl, aryl or perfluoroaryl R-groups, and heteroatom groups such as silyl, phosphinyl, germanyl, etc.^[4, 23] A wide variety of mostly aryl SDIs was developed by the Russian school led by Zibarev.^[24-27] A key driving force for much of this work was the exploration of -{NSN-}_∞ chains to

mimic or model the behaviour of $(\text{SN})_x$.^[28] Recently, $-(\text{Ar-NSN-Ar})_\infty$ chain polymers have been reported, after a long unsuccessful search for such species.^[29-30] Closely related to these achievements is the report of an unusual SDI that appears to be dominated by $\text{C}_{\text{aryl}}=\text{N}$ bonds and consequently possesses very long N-S bonds.^[31]

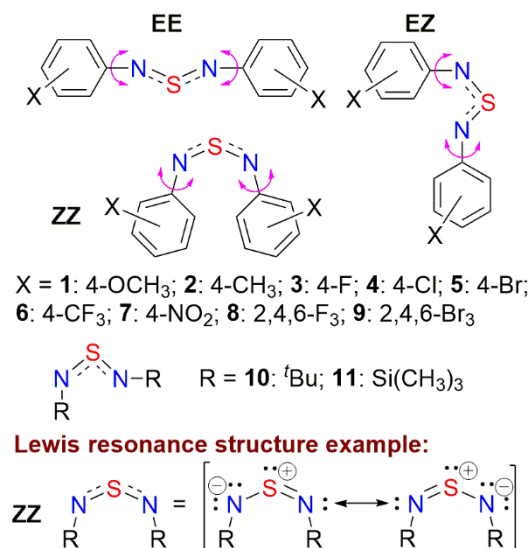


Figure 4.1. Isomers and conformations in aryl sulfur diimides and compound identification codes. The resonance structures corresponding to the simplified bonding notation is shown for Z/Z as an example (see text). Double-headed arrows around the N-C bonds indicate the C-C-N-S torsions.

Cyclic diimides are known for all chalcogens,^[1] and fused-ring aryl-1,2,5-chalcogenadiazoles, **12** (Figure 4.2), are undoubtedly the largest of this very important and heavily studied class of SDIs. However, the electronic structures and resultant properties (especially luminescence) of such cyclic systems is dominantly a function of their modified aryl rings rather than the chalcogen atom and as such will not be further discussed in this article;^[32-34] for the role of the chalcogen in **12** see ref. 35.^[35]

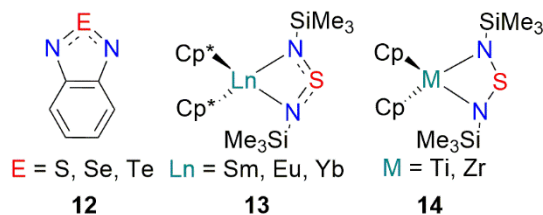


Figure 4.2. Line structures of some important compounds.

As shown in Figure 4.1, three conformations must be considered for SDIs, E/E, E/Z, and Z/Z, making them much more complex than SO₂, although the bonding in the two systems is now recognized to be analogous.^[36] Whereas the majority of coordination complexes of SDIs, with the exception of late transition metals, are chelated structures that mandate the E/E conformation, E/Z and Z/Z are common for the free molecules. Some early results already hinted that chelated SDIs can sometimes function as redox non-innocent ligands in coordination complexes. Hunter et al. (1980) and Klein et al. (1996) showed by electron paramagnetic resonance (EPR) spectroscopy that several chemically or electrochemically reduced complexes localize the electron density of the added electron primarily on the SDI ligand, thereby leaving the oxidation state of the metal formally unchanged.^[37-38] Redox-active ligands have had a profound impact on coordination chemistry, and made possible reactivities that were previously inaccessible, or prohibitively expensive. They have many uses, including, though certainly not limited to: efficient electrode materials for lithium ion batteries,^[39] strong dyes and pigments,^[40] and semiconducting nanosheets.^[41] Perhaps most notable is the transformative potential of complexes with redox-active ligands in the field of catalysis. Brookhart et al. tested the activity of an iron-based catalyst with a redox-active ligand system for synthesizing α -olefins, and found the activity to be comparable to that of precious metal catalysts, with excellent selectivity.^[42]

Recently, we demonstrated approximately one electron reduction of coordinated **11** at several lanthanocene derivatives [LnCp*₂(Me₃SiNSNSiMe₃)],^[43] **13** (Figure 4.2), which are the first structurally characterized complexes of SDI radical anions,^[1,44] supported by a preliminary voltammetric study of **11**. Similarly, Kaleta et al.^[45] used DFT calculations and crystallographic assessment of the N-S bond lengths to establish approximately 2e⁻ transfer to the SDI from the metal centres in titanocene and zirconocene complexes, **14**,^[45] whilst a reductive insertion reaction of a zirconium nitride to an SDI has also been

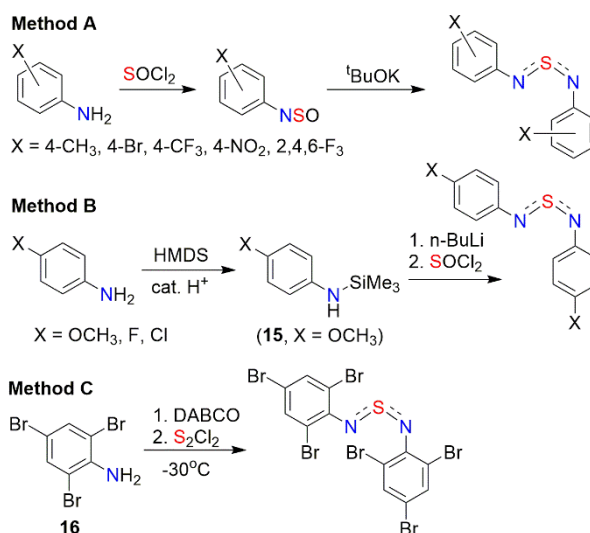
reported.^[46] These discoveries of dramatic redox non-innocence accompanying such SDI complexes induced us to consider the degree of redox tuning that may be possible with variations in SDI substituents; however, there is an extreme paucity of reliable voltammetric data on SDIs in the literature.^[47] We therefore set out to undertake a systematic study employing voltammetry, and here report a thorough comparative structural, spectroscopic, electrochemical, and EPR-spectroelectrochemical study on a deliberately selected series of 4- and 2,4,6- substituted diaryl SDIs (**1** – **9**, Figure 4.1). Their voltammetry is contrasted with that of the most studied SDIs in coordination chemistry, *t*-Bu-NSN-*t*-Bu, **10**, and Me₃Si-NSN-SiMe₃, **11**.

4.2. Results and Discussion

4.2.1. Synthesis

A series of nine aryl sulfur diimides (compounds **1** – **9**, Figure 4.1), with push- and pull ring substituents,^[48-53] was synthesized, and the well-known *bis*-*t*-Bu, **10**, and *bis*-trimethylsilyl, **11**, analogues were also prepared by literature methods.^[5,54] Three synthetic routes were used for **1** – **9**, all beginning from the corresponding substituted aniline (Scheme 4.1). Method A proceeds by sulfinylation of the respective aniline by refluxing with thionyl chloride. Except for the case of *bis*(4-nitrophenyl)sulfur diimide (**7**), the sulfinylaniline is used in the next step without purification and reacted with potassium *tert*-butoxide to yield the sulfur diimide. Method A works for compounds **1** – **8** (compound **9** was not attempted by this method), but compounds **1**, **3**, and **4** were made in better yield by method B. Method B involves refluxing the substituted aniline with neat hexamethyldisilazane (HMDS) and an acid catalyst to produce a monosilylated aniline, which must be distilled before continuing. This is then reacted at -65 °C with an equimolar amount of butyllithium, followed by addition of thionyl chloride to yield the sulfur diimide. Compound **9** was synthesized using a one-step method adapted from

Konstantinova et al.^[55] in which the substituted aniline is reacted with sulfur monochloride in the presence of diazabicyclooctane (DABCO). Compounds **1** – **5**, **7**, and **9** are previously reported in the literature,^[23-24] while compounds **6** and **8** are not, save for a failed attempt to synthesize **6**.^[56] All have been fully characterized including with new single-crystal X-ray diffraction (SC-XRD) structures; the structures of reagents **15** and **16** were also determined (full details are in the Experimental and Section B.1).



Scheme 4.1. Synthetic methods employed for the aryl SDIs (SDI compound labels identified in Figure 4.1).

4.2.2. Solid-State Structures from X-ray Diffraction

Compounds **1** – **7** and **9** are all found to crystallize E/Z, and only **8** crystallizes as Z/Z (Figures 4.3 and 4.4, as well as Section B.2). In most cases, the Z-oriented phenyl ring is nearly coplanar to the NSN moiety, while the E-oriented ring is twisted out of plane to varying degrees. This is consistent with the other *para*-substituted aryl sulfur diimides in the CSD, namely refcodes BAZLOD,^[57] NEMHIW,^[56] and NEMHUI^[56]. There is no clear correlation of the substituent's electron donating/withdrawing properties to the N-S-N-*C*_{ipso} torsion angles. This is well illustrated by the Z' = 2 structure of **6** (see Figure 4.3), in which the E-oriented ring on N2 is almost co-planar to NSN (torsion angle 3.8(6)°), whereas

that on N4 is strongly twisted ($-48.3(5)^\circ$). While **9** crystallizes as E/Z, both phenyl rings are almost orthogonal, torsions of $85.9(3)^\circ$ and $85.4(3)^\circ$, relative to the NSN moiety, presumably due to steric pressure from the large *ortho*-bromine substituents. This is a rare conformation, only otherwise observed in *bis*(2,4,6-*tri-tert*-butylphenyl)sulfurdiimide (CSD refcode: BEQHEK),^[58] which also contains very bulky *ortho* substituents. Aside from these two cases, every example from the CSD of aryl SDIs with at least one *ortho* substituent crystallize as Z/Z, as does **8**.^[25,56,58-61] Interestingly, the SC-XRD of **10**^[62] (CSD refcode: HOVYAS01) and **11**^[63] (YEFJUO) are found as E/Z.

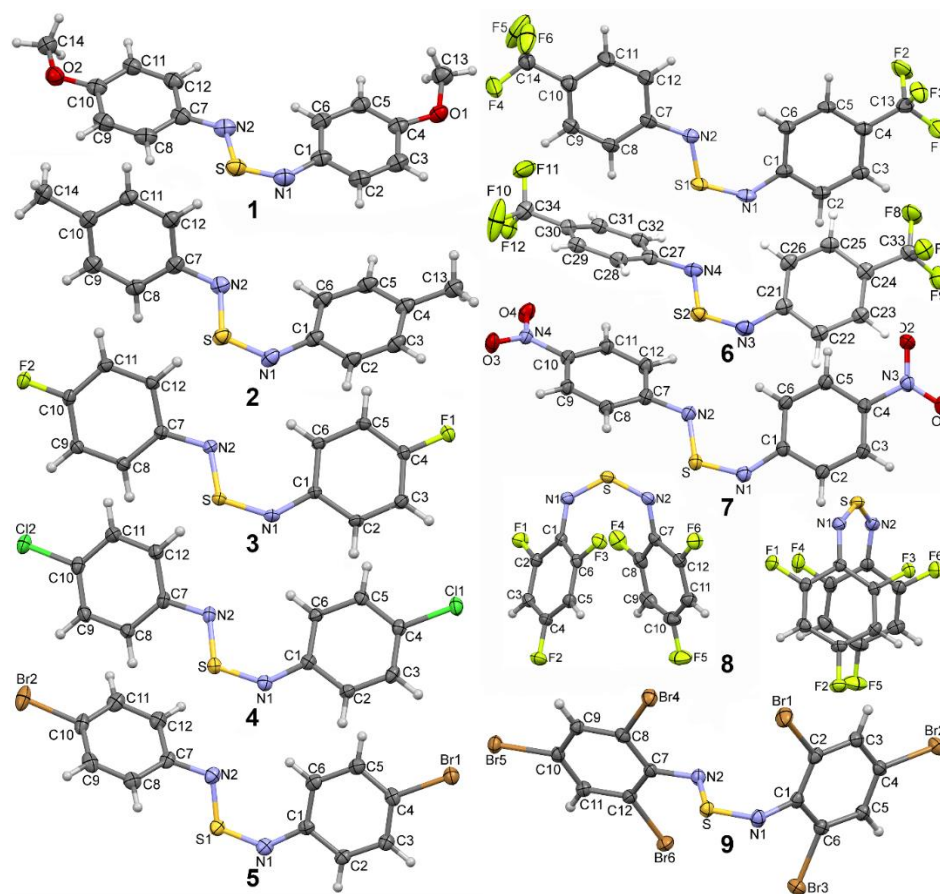


Figure 4.3. Displacement ellipsoids plots (40% probability) of **1** – **9** as found in the crystals. H atoms are rendered as spheres with 0.10 Å radii; full anisotropic rendering of H atoms via HAR for **1** – **9**, **15**, and **16** are provided in Appendix B (Figures B.1-B.11), as is the second molecule of the $Z' = 2$ structure **5**; only the main component of CF_3 disorder in the structure of **6** is shown (see Figure B.6).

Crystal structures of **2**, **3**, and **9** have been previously published with CSD refcodes: TOLIMS,^[64] NEMHUI,^[56] and HEPZIL^[25] (the Cambridge Structure Database (CSD),^[65] release 2023.2.0). Our redeterminations improve upon previous depositions, providing a full structure for TOLIMS, which only had unit cell information previously, and lower acquisition temperatures and R-factors for NEMHUI and HEPZIL. Further, all structure models presented in this work have been refined by a Hirshfeld atom refinement (HAR) approach using the recently released NoSpherA2,^[66] included with the current version of the Olex2 crystallographic software suite.^[67] NoSpherA2 enables the use of custom atom scattering factors polarized to actual atom positions, enabling precise H-atom placement with near to neutron diffraction accuracy, and calculation of anisotropic displacement parameters for hydrogen atoms. Our group has previous experience applying NoSpherA2, demonstrating the remarkable improvement in bond precision over Independent Atom Model (IAM) refinement with relatively modest computational effort.^[68-70] Accurate H-atom geometries are particularly important to this work because of the impact of dispersion interactions between the two R groups on each SDI on the geometries adopted. Further details on the refinement models adopted, along with a statistical analysis of structure precision improvements are provided in Section B.3 and Table B.27 for interested readers.

Full interatomic distances and angles are provided in Appendix B (Tables B.2 – B.25). In view of the large number of structures, it was fortunate to discover that these data are generally very consistent. In Figure 4.4, geometric values that are averageable at the 99% confidence level are displayed. All the indicated parameters could be included in the averages for structures of **1** – **7**, which all crystallize as E/Z. Moreover, for **9**, though E/Z differs by the orthogonal displacement of the two aryl rings unlike the other seven cases, all the parameters *except* the S-N-C angle in the Z branch fit within the averages. The compilation of geometric data displayed in Figure 4.4A is the most systematic and reliable available for diaryl SDIs.

4.2.3. DFT Calculations

For each of the compounds **1** – **9**, density functional theory (DFT) calculations were performed on the neutral species. Geometry optimizations and frequency calculations were undertaken with multiple approaches, leading to the adoption of a triple- ζ Pople basis set with polarization functions to account for the electron rich NSN moiety; the well-attested B3LYP functional performed well. All three conformational isomers, E/E, E/Z, and Z/Z, were examined. The E/Z calculations compute with excellent geometric agreement with the solid-state structures obtained by SC-XRD for compounds **1** – **7**. For the computed neutral structures that are compiled in Figure 4.4(B), over both conformations, the average deviation magnitude is less than 1%. By contrast, the conformation computed with standard DFT methods for both **8** and **9** differ substantially from the XRD structures. **8** crystallizes in the Z/Z conformation, unlike all of the other sulfur diimides in this series, while **9** crystallizes E/Z, but in the optimized E/Z geometry, the *E*-oriented aryl ring approaches co-planarity with the NSN bridge, whereas in the experimental structure both aryl rings are nearly orthogonal to the NSN moiety. By making use of Grimme's post-SCF dispersion correction D3 (with Becke-Johnson damping),^[71] the agreement between computational and experimental geometries became very close for all of **1** to **8** whilst the ring orientation in **9** remains different, possibly because co-planar or orthogonal C₆H₂Br₃ rings have a small energetic difference. Therefore, a relaxed scan DFT calculation was undertaken, showing that the barrier to rotation for the *E*-branch aryl ring is only 4 kJ/mol (see Section B.4). Fascinatingly, the computed Z/Z geometry is lower in energy than E/Z, with or without invoking the dispersion correction in the case of **8** and **9** (see Table 4.1 below). Experimentally, the dominant solution state conformations of the *para*-substituted sulfur diimides (**1** – **7**) are proposed to be E/Z, while the dominant tri-substituted sulfur diimide conformations (**8**, **9**) are proposed to be Z/Z, based on the NMR and UV-vis evidence obtained in this work (see below) and by Zibarev and co-workers.^[25]

This is a contrast to the solid-state conformation of **9**, known to be E/Z by crystallographic characterization. The calculated energies without empirical dispersion corrections conform to the proposed conformations, namely E/Z being the lowest energy conformation for **1** – **7**, and Z/Z the lowest energy conformation for **8** and **9** (Table 4.1).

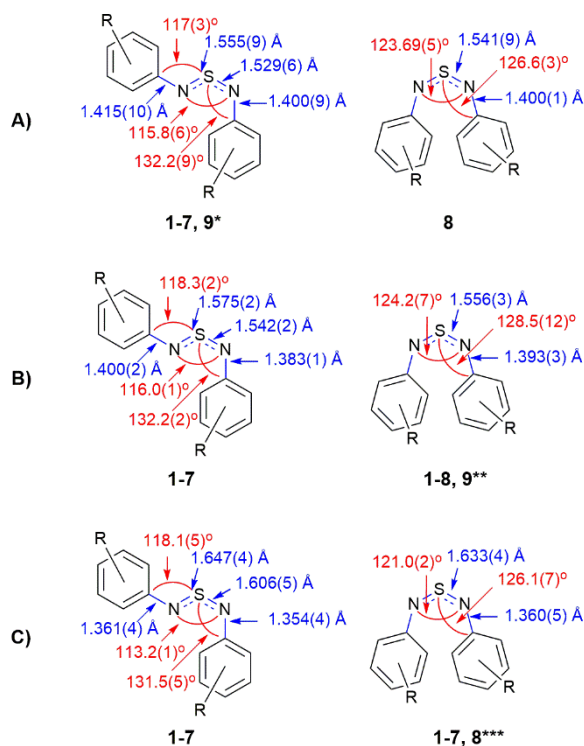


Figure 4.4. Averaged (A) experimental and (B) computed bond angles and bond lengths for neutral SDIs from SC-XRD structures in the E/Z and Z/Z conformations (at the RB3LYP-D3BJ/6-311++G(2d,p) level of theory). (C) Averaged computed geometries for the monoanions using UB3LYP-D3BJ/6-311++G(2d,p). Restrictions: * in (A), **1** – **7** and **9** are E/Z, but $\angle\text{SNC}$ of the Z branch of **9** is an excluded outlier; ** in (B), both **8** and **9** are general outliers and excluded from E/Z, while in Z/Z the $d(\text{NS})$ of **9** are excluded outliers; *** in (C) likewise **8** and **9** are excluded from E/Z, whilst **9** is fully excluded from Z/Z, and the $\angle\text{NSN}$ of **8** is excluded from Z/Z.

When dispersion correction is added, the lowest energy conformation for all of the sulfur diimides becomes Z/Z, reflecting a known tendency of D3BJ to overestimate (intramolecular) π -stacking interactions between pendant aryl rings attached to thiazyls^[71-72]. As there is convincing UV-vis and NMR evidence for compounds **1** – **7** being predominantly E/Z in solution, it seems likely that similar overestimation of π -stacking stabilization is operative for D3BJ correction in aryl SDIs.

Table 4.1. Computed relative energies (kJ/mol) of **1** – **11** in neutral and monoanionic minimized geometries with and without empirical dispersion corrections applied.

		1	2	3	4	5	6	7	8	9	10	11
Substituent		4-OCH ₃	4-CH ₃	4-F	4-Cl	4-Br	4-CF ₃	4-NO ₂	2,4,6-F ₃	2,4,6-Br ₃	^t Bu	SiMe ₃
Neutral	E/E	35.8	33.9	34.3	34.9	35.6	36.4	31.6	35.4	54.1	27.1	16.3
D3BJ^a	E/Z	7.3	6.9	5.9	7.3	8.2	10.8	6.8	17.5	25.3	0	0
	Z/Z	0	0	0	0	0	0	0	0	0	30.3	11.9
Neutral	E/E	25.1	23.8	25.2	24.3	24.1	22.4	21.6	13.3	20.5	22.1	10.3
No Disp^b	E/Z	0	0	0	0	0	0	0	0.3	4.7	0	0
	Z/Z	7.2	7.2	7.9	7.8	7.9	7.4	8.9	0	0	32.3	16.6
Anion	E/E	13.2	9.5	11.2	9.3	9.6	7.4	7.2	3.3	21.7	11.7	17.4
D3BJ^c	E/Z	6.8	4.9	5	3.3	3.4	1.9	0	2	6.9	0	0
	Z/Z	0	0	0	0	0	0	4.7	0	0	^e	^e
Anion	E/E	3.1	1.3	2.9	2.6	2.8	2.2	3.8	0	0	7.4	10
No Disp^d	E/Z	0	0	0	0	0	0	0	3.8	0.3	0	0
	Z/Z	5.4	7	6.6	8.1	8.6	10	16.3	15.8	15.4	^e	^e

^a Employing the RB3LYP-D3BJ/6-311++G(2d,p) level of theory. ^b Employing the RB3LYP/6-311++G(2d,p) level of theory. ^c Employing the UB3LYP-D3BJ/6-311++G(2d,p) level of theory. ^d Employing the UB3LYP/6-311++G(2d,p) level of theory. ^e For both **10** and **11**, when the Z/Z structures are given a charge of -1, they spontaneously minimize to E/Z.

4.2.4. Solution Structures from NMR Spectroscopy

^1H , ^{13}C , and ^{19}F NMR data for **1** – **9** are presented in Table 4.2 and full archival spectra are provided in Appendix B (Figure B.140 – B.182). The *para*-substituted aryl sulfur diimides, **1** – **7**, show fluxionality between the E/Z and Z/E conformations at ambient temperature, a phenomenon that was previously noted by a number of researchers in their analyses of the structure of sulfur diimides.^[25,63,73-77] This is independently evident both in the ^1H NMR spectrum from a significant broadening of the signals of the *ortho*-protons, and in ^{13}C NMR spectrum for the *ortho*-carbons. For example, the two doublets in the ^1H spectrum of **6** (Figure B.160) have highly disparate linewidths, with full widths at half maximum (FWHM) of 4.5 Hz and 22.0 Hz for the *meta* and *ortho* protons, respectively. Similarly, in the ^{13}C NMR spectrum of **3**, the *ortho* carbon signal is significantly broadened compared to the others, with FWHM = 91.6 Hz, compared to 13.1 Hz, 11.5 Hz, and 9.0 Hz for the *ipso*, *meta*, and *para* signals (Figure B.150). For compounds **1** – **7**, the order of the broadening effect in the ^{13}C NMR spectra is $o > i > m > p$. Upon cooling to ~233 K, we observe splitting of some peaks into the distinct signals from the E and Z branches as the exchange is inhibited. The magnitude of this splitting follows the same order as above, $o > i > m > p$. Figure 4.5 is an overlay of $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compounds (a) **3** and (b) **9**, each taken at room temperature (RT) and -40 °C (295 K and 233 K) and truncated to highlight the aromatic regions (~100 ppm to ~170 ppm). Compound **3** was chosen as an exemplar of **1** – **7**, showing the fluxionality of the E/Z oriented SDIs by the splitting of *ipso*, *ortho*, and *meta* signals into separate peaks, one each for the E and Z branches of the SDI as the E/Z $\leftrightarrow$ Z/E exchange is slowed by the reduced temperature. The spectrum of **9** was chosen to represent **8** and **9**, which are symmetrical, showing no splitting of peaks at reduced temperatures seen in **1** – **7**.

Table 4.2. ^1H , ^{13}C , and ^{19}F NMR data for **1** – **9** at ambient temperatures^f.

Cmpd	H ₂ (X) ^g	H ₃	X ₄ (^1H , ^{19}F)	C ₁	C ₂	C ₃	C ₄	X ₄ (^{13}C)
1	6.75, d (8.3)	7.49, s	3.84, s	140.2, s	125.0, s	114.3, s	158.5, s	55.7, s
2	7.15, d (8.1)	7.37, d (7.2)	2.36, s	143.7, s	123.4, s	129.6, s	136.9, s	21.4, s
3	7.03, s	7.44, s	-113	142.1, d (1.9)	125.1, s	116.0, d (22.6)	161.3, d (248)	–
4	7.32, d (8.7)	7.41, d (7.8)	–	144.1, s	124.7, s	129.3, s	132.7, s	–
5	7.34, d (7.9)	7.47, d (8.6)	–	144.5, s	125.0, s	132.3, s	120.7, s	–
6	7.43, s	7.57, d (8.2)	-61.9	147.7, q (1.4)	123.2, s	126.4, q (3.7)	128.9, q (32.8)	124.1, q (272)
7	7.60, d (8.7)	8.27, d (9.0)	–	149.8, s	124.0, s	125.2, s	146.2, s	–
8	-113 (^{19}F)	6.52, m (abb'xx')	-109	117.9, td (17.7, 5.1)	153.6, ddd (252, 14.7, 7.0)	99.9, ddd (26.6, 23.6, 4.8)	160.3, dt (251, 14.4)	–
9	–	7.56, s	–	141.0, s	117.1, s	133.8, s	118.7, s	–

^aIn CDCl₃; format: δ (ppm), multiplicity, (J (Hz)). ^bNumbering scheme as in Figure 0.5, with H and X labelled as per the attached C atoms. ^c $\delta(^1\text{H})$, relative to residual CHCl₃ at 7.27 ppm. ^d $\delta(^{13}\text{C}\{^1\text{H}\})$, relative to residual CHCl₃ at 77.23 ppm. ^e $\delta(^{19}\text{F}\{^1\text{H}\})$ (**3,6**) or ^{19}F (**8**)), relative to external CFCl₃ at 0.00 ppm. ^fNMR data for **1** – **9** at low temperature is available in Table B.30. ^gAll ^1H NMR signals for the *ortho*-H (H₁) of SDIs **1** – **7** are broad even at RT due to fluxionality.

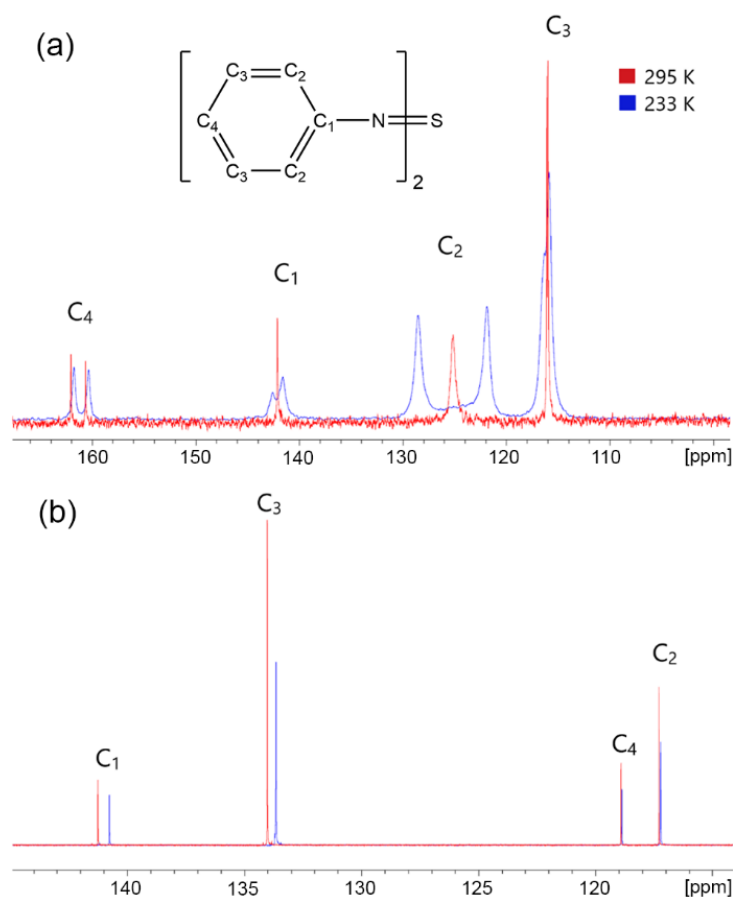


Figure 4.5. Overlay of $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (aryl-C signals from ~110 to 165 ppm) at 295 and 233K of (a) **3** and (b) **9**.

Zibarev et al. studied a series of aryl SDIs with bulky *ortho*-substituents, which included **9**, over a wide temperature range from 293 K to 163 K.^[25] They found that **9** contains exclusively one symmetrical conformer, while other SDIs with methyl groups in one or both *ortho* positions contained a mixture of 12% – 16% unsymmetrical (E/Z) conformer. From NOE measurements of one of these compounds they were able to determine that the symmetrical geometry present was Z/Z, and not E/E. Independently, and around the same time, Herberhold et al. investigated a series of various alkyl SDIs, as well as phenyl SDI, and determined the conformation using ^{15}N NMR spectroscopy.^[78] They used SDIs which are dominantly E/Z in geometry in solution, but contain a minor component of symmetrical conformer, and compared their ^{15}N NMR data of acyclic SDIs to that of several cyclic SDIs, which enforce a Z/Z geometry and provide an expected resonance for nitrogen. They found that the chemical shift of their symmetrical conformer was consistent with the cyclic SDIs, i.e.

their symmetrical conformer was confirmed to be Z/Z. This issue is of particular importance for our study, since we wished to know what the dominant species were on which we perform the solution state voltammetry; fortunately we were able to use CH₂Cl₂ as the electrochemistry solvent, with expected isomer distributions similar to the CDCl₃ employed in the NMR studies.

A most helpful resource in assigning the ¹³C NMR signals for all of the sulfur diimides was the table of aryl substituent effects on chemical shifts in Silverstein and Webster.^[79] We used the established chemical shifts of diphenylsulfur diimide^[80] to introduce new substituent parameters for R = NSN-Ar, enabling calculation of expected shifts for aryl SDIs (see Table B.31). Adding the modifiers from the table for the other substituents in each of our compounds resulted in excellent agreement with observed ¹³C data for **1** – **7** (within 0.4 ppm), and good agreement with the more highly substituted **8** and **9** (within 2.5 ppm).

4.2.5. Electronic Structure and Bonding of SDIs

The previous section counters a persistent myth of SDIs – namely, that E/E should logically be the lowest energy conformation^[81] – and we now turn to a second wrong idea, that the (genuinely very short) S–N bonds are simultaneous ‘double bonds’ to hypervalent sulfur. Previous work, particularly of Stalke and co-workers, has provided irrefutable experimental and computational evidence against this idea,^[20-22] brilliantly confirming that the Lewis resonance formulation (Figure 4.1) is fully valid, whilst also elucidating the real differences in structures and reactivity that result from an allylic resonance with a third-period central atom. This situation is notably different from other heteroallylic systems, such as phospho(III)amidines and diphospho(III)amidines, wherein the central atom remains C.^[82] Hence, there is not only sulfur diimide, but also an extensive triimide chemistry.^[10-11,83] Although Pauling is strongly associated with the now-deprecated notion of valence expansion by hybridization (i.e. *dsp*³ models for S^{IV}),^[84-85] it seems to be forgotten that his even more fundamental concept of element electronegativity was directly based on the concept of enhanced strengths of bonds

with partial ionic character.^[86] This recognition leads directly to the idea of bond shortening from an ionic contribution to a covalent bond, which Leusser *et al.* conclude causes the foreshortened bonds in SDIs.^[21] It is a fundamental property of thiazyl chemistry that SN π -bonds are highly polarized.^[87] Despite intensive computational investigations over two decades,^[81,88-101] the literature is remarkably devoid of a thorough discussion of the electronic structures of SDIs, which not only display allylic-type resonance but are exceedingly electron rich from the four formally non-bonded electron pairs.

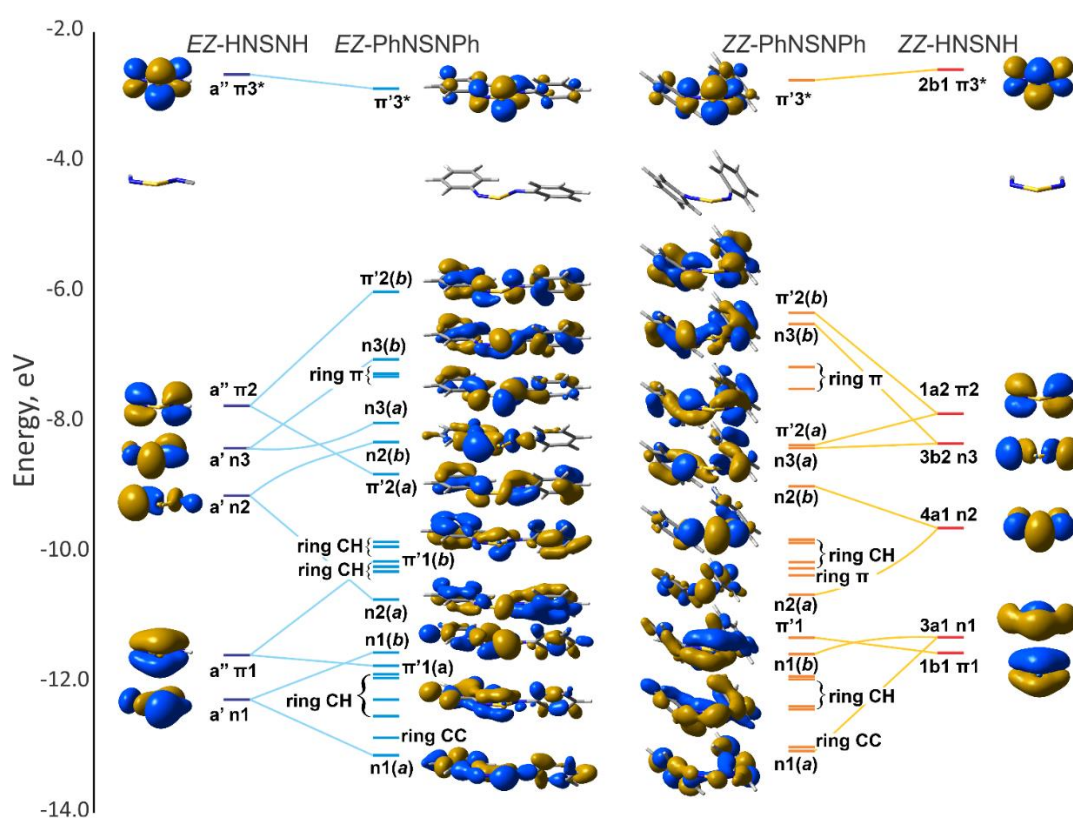


Figure 4.6. Molecular orbital correlation diagram comparing the valence π and lone pair (LP) energy levels, with Kohn-Sham orbital surfaces (isovalues = 0.04), of the parent HNSNH and the diphenyl SDI, as computed at the B3LYP-D3BJ/6-311G++(2d,p) level of theory. The E/Z and Z/Z isomers in their gas-phase lowest energy conformations are shown. The molecular orientations of the MO surfaces as well as the first virtual levels are shown at top. Energy levels for the parent SDIs are doubly labelled by symmetry and type.

In our analysis (Figure 4.6), we restrict the discussion to just the E/Z and Z/Z isomers that can be ground state geometries (though the situation in E/E will be very similar), and we commence by formally treating the parent HNSNH molecules before considering the influences of aryl substituents. Importantly, the parent SDI also serves

as model system for **10** and **11**. Figure 4.6 presents the computed energy levels and Kohn-Sham MO surfaces, omitting the four lowest levels that correspond to the σ -bonds (i.e. primarily constituted from the N and S atomic s orbitals). This leaves the filled and virtual orbitals that have formal π -symmetry as well as $n(S)$ and $n(N)$, i.e. the MOs associated with “lone pair” character. The scenarios for the two isomers are very similar, though at this level of theory, the sequence of the $n1$ and $\pi1$ MOs is reversed (due to a 0.72 eV stabilization of the former in E/Z). There is considerable mixing of the $n(S)$ and $n(N)$ levels in E/Z, enabled by the symmetry lowering from C_{2v} to C_s . The net NS bond order is easily rationalized as 1.5 from the four σ bonds, non-bonding $n1$ – $n3$, plus double occupancy of $\pi1$ (bonding) and $\pi2$ (non-bonding) in both isomers (compare computed natural bonding orbitals theory, NBO, estimates of 1.33 for the Z branch and 1.40 for E in the E/Z isomer,^[21] or Wiberg bond index, reported as a single value of 1.54, without clarifying if this is an average or taken from a symmetric isomer).^[100] There are just two experimental reports on this parent SDI. Carlsen et al. prepared HNSNH in the gas phase by pyrolysis of tetrasulfur tetraimide, $S_4(NH)_4$ ^[102] and identified it from mass spectrometry and ultra-violet photoelectron spectroscopy (UV-PES), but the PE spectrum has unfortunately not been reported.^[102] Haas prepared and then isolated HNSNH in a frozen Ar matrix, where it was identified as a mixture of E/Z and Z/Z by infrared spectroscopy (see below). Previous computational studies on HNSNH have been reported by Zahedi,^[81] Shahbazian,^[98] and Tuononen,^[94] but only structure and isomer preferences were discussed and no details on molecular orbitals or bonding have been published.

For each isomer, approximate correlations are provided to corresponding energy levels in the PhNSNPh cases, which are used here as simplified models for **1** – **9**. Recognize first the complete loss of symmetry, in both instances, due to out of plane aryl rotation; hence there is no longer a formal σ/π distinction, though the orbitals designated as π' are those with the greatest π character over the planar NSN region; moreover, rapid N- C_{ipso} rotation in solution may render the SDIs effectively planar. The

influence of the aryl groups is extremely strong and in almost all cases the parent levels are recognized in one significantly stabilized and one strongly destabilized aryl-interacting MO (respectively designated by the *a* and *b* distinctions in the labels of Figure 4.6).^[88] The frontier molecular orbitals (FMOs) are still recognizable in π^*2 and π^*3 , for both isomers, but especially for the former, the aryl contributions are very significant, resulting in a strong destabilization of the HOMO. This results in a much smaller HOMO-LUMO gap for the aryl systems (with significant impacts on colour and hence UV-vis spectroscopy, see below). The correlation lines drawn in Figure 4.6 are only approximate due to the evident σ/π mixing; MO surfaces and lines are drawn only for those of the PhNSNPh energy levels with significant NSN contributions, whereas those that are not drawn are strongly localized on the aromatic rings. This is especially so for the HOMO-1 and -2 'ring π ' MOs, which have negligible impact on bonding but are very much in play for electronic excitation transitions (see below). In summary, aryl SDIs have complex electronic structures with many highly polarizable $p(\pi)$ contributions as well as six (formally) σ non-bonding electrons. Additionally, the obvious flexibility of the chain structures and NMR evidence for fluxionality in solution are expected to greatly complicate their real-world electronic structures. And yet, despite all the additional complexity, the FMOs will still have the expected sequence of $(n3)^2(\pi2)^2(\pi3)^0$ levels across the substituent classes being considered in this work, consistent with the line drawings of e.g. Figure 4.1. Reactivity towards either nucleophiles^[10-12,103] or free electrons^[91] is expected at the $\pi3/\pi^*3$ LUMOs, for which the highest coefficients are always at sulfur. At the same time, significant delocalization of both the HOMO and LUMO into the aryl π -system will influence the redox tuning that is the topic of this work. Excellent agreement is found between the energy levels for the E/Z isomer of PhNSNPh in our calculations (via Koopman's theorem) with an experimental investigation by UV-PES.^[28]

4.2.6. Infrared Spectroscopy

The original literature assignments, dating from their first syntheses, were based on analogies to organo-nitrogen analogues including PhNSO.^[9,23,55,104-108] Several independent groups assigned the various NSN vibrational modes to different bands.^[23,55,104] The application of vibrational energy calculations from modern, dispersion corrected, DFT methods paints a picture with significant differences. There is to our knowledge only a single published study presenting the vibrational spectra of the parent HNSNH (Table 4.3).^[109] The data are reported in a frozen Ar matrix and these compounds were produced as mixtures from trapping reactions, present as E/Z and Z/Z isomer mixtures as expected from miniscule differences in their energies.^[98,109]

Excellent agreement of an average of $\pm 10\text{ cm}^{-1}$ is achieved between these experimental values and our B3LYP-D3BJ/6-311++G(2d,p) DFT calculations, and with good agreement on intensities, leading to a very high confidence in the assignments of the spectral bands. The relevant NSN vibrations (3 for E/Z and 2 for Z/Z, reflecting C_s and C_{2v} point group symmetries, respectively) are included in Table 4.3 and a full assignment is presented in Table B.44. To further calibrate our DFT computed spectra, we also undertook a full geometry minimization with frequency assignments for Z-PhNSO since it has been most often used to predict the bands in aryl SDIs. Our approach substantiates the original assignments of Meij *et al.* for the natural and ^{15}N enriched compounds in IR and Raman^[106] and the agreement of computed with experimental values averages to $\pm 12\text{ cm}^{-1}$ (Table B.45).

Table 4.3. Experimental and computed IR data for HNSNH and aryl SDIs^a

Cmpd	Subst. H (E/Z) ^b	$\nu(\text{ringNS})$ n/a	$\nu(\text{rNSNr})$ n/a	$\nu(\text{ringNS})$ n/a	$\nu_{\text{as}}(\text{NSN})$ 1181 s 1166, 13%	$\nu_{\text{s}}(\text{NSN})$ 934 m 935, 11%	$\delta(\text{NSN})$ 410 w 416, 17%	$\delta(\text{NSN})$ n/a	$\rho(\text{NSN})$ n/a
	H (Z/Z) ^b	n/a	n/a	n/a	1157 m 1121, 65%	unobs. 907, 9%	410 w 412, 17%	n/a	n/a
	Ph ^c	1298 s ^d 1293, 46%	1265 s 1258, 98%	1218 s ^e 1216, 100%	1070 s 1050, 83%	957 m 943, 24%	803 m 790, 21%	634 s 631, 21%	337 w 333, 5%
1	4-OCH ₃	1268 m 1272, 5%	1239 m 1230, 100%	Unobs. ^g 1214, 27%	1027vs 1044, 41%	952 vs 936, 4%	743 s 740, 1%	585 s 584, 9%	417, w 411, 1%
2	4-CH ₃	1293 m ^d 1294, 30%	1263 m 1256, 95%	1223 m ^e 1218, 97%	1062 s 1043, 81%	961 m 942, 27%	750 m 739, 21%	585 w 580, 13%	386 m 383, 10%
3	4-F	1306 w 1297, 5%	1270 m 1258, 10%	1206 vs 1200, 92% ^h	1061 s 1043, 28%	958 943, 12%	759 m 747, 4%	581 s 577, 14%	410 s 411, 1%
4	4-Cl	1294 m ^d 1293, 26%	1268 s 1252, 33%	1219 m ^e 1219, 50%	1061 s 1041, 62%	967 m 943, 13%	815 vs 790, 11%	683 m 676 5%	389 vs 386, 41%
5	4-Br	1293 w ^d 1292, 8%	1267 m 1252, 36%	1221 m ^e 1220, 31%	1058 s 1039, 41%	957 m 929, 5%	799 s 787, 24%	666 m 657, 5%	382 s 376, 5%
6	4-CF ₃	1318 vs ^d 1307, 18%	1273 s 1260, 61%	1236 m ^e 1224, 33%	1049vs 1033, 55%	967 m 949, 5%	717 w 725, 3%	654 m 651, 1%	436 w 429, <1%
7	4-NO ₂	1252 vs ^d 1264, 71%	1314 vs ^f 1318, 100%	1232 sh ^e 1225, 44%	1059 m 1045, 16%	967 w 945, 4%	787 m 784, 8%	676 m 666, 2%	389 m 363, 1%
8	2,4,6-F ₃	1443 vs ^j 1447, 68%	1250 sh ^j 1252, 66%	1240 sh ^j 1243, 4%	1038, vs 1047, 42%	985 vs 972, 23%	748 m 754, 4%	689 s 682, 18%	438 s 423. 5%
9	2,4,6-Br ₃	1248 s ^d 1234, 97%	1422 vs ^j 1396, 52%	1240 s ^e 1228, 16%	1093,m 1069, 44%	987 w 978, 16%	820 m 799, 25%	675 m 654, 15%	560 s 560, 6%

^a Data from this work unless noted, from crystalline solid using ATR/KBr; the second line of each entry are the computed values, at the B3LYP-D3BJ/6-311++G(2d,p) level of theory in Gaussian W16. ^b Data from Haas et al.,^[60] frozen Ar matrix. ^c Data from Cramer,^[5] or Meij et al.^[59c] Liquid thin films. ^d Z branch only. ^e E branch only. ^f $\nu(\text{rNSNr})$ contribution; there are six ring breathing bands that strongly couple to the NO₂ groups and weakly to NSN. Very weak. ^g Obscured by very large $\nu(\text{ring})$ band, 1239 cm⁻¹. ^h strongly coupled to C-F vibration, splits E and Z. ⁱ The 1287 s band (computed 1266, 58%) found at the more normal energy does not have NSN character; this is instead merged into one of three high energy bands that merge with $\nu(\text{ring-Br})$. ^j In Z/Z there is C₂ symmetry; two of these bands have $\nu(\text{rNSNr})$ character, as and s, and overlay a strong $\nu(\text{C-F})$ at 1265 cm⁻¹.

The same approach, when applied to PhNSNPh, for which complete IR data is available in the literature,^[9] along with $^{14}\text{N}/^{15}\text{N}$ comparisons for both IR and Raman for some of the principal bands,^[106] achieved similar agreement levels ($\pm 10\text{ cm}^{-1}$), but with a considerably more complex interpretation (see Table B.46). In short, the assumption that frequency assignments from the terminal PhNSO molecule could be directly applied to the disubstituted PhNSNPh was, in retrospect, incorrect. This, along with the very strong mixing of vibrational modes of the phenyl ring atoms and those of the bridging -NSN- moiety, casts doubt on the assignment of the 1268 cm^{-1} band to $\nu_{\text{as}}(\text{NSN})$.^[9, 106] There are in fact three very close, strong bands (1298 , 1265 and 1218 cm^{-1}), whose assignment is now identified to (very similar) vibrations with mixed character, namely: the *Z*-branch $\nu_{\text{as}}(\text{ringNS})$, $\nu_{\text{as}}(\text{ringNSNring})$, and the *E*-branch $\nu_{\text{as}}(\text{ringNS})$. The $\nu_{\text{as}}(\text{NSN})$ vibrational mode therefore appears to be distributed amongst these three bands and that at 1070 cm^{-1} , of which the latter is more concentrated on the NSN atoms and should be considered as the primary $\nu_{\text{as}}(\text{NSN})$ band in diaryl SDIs. Interestingly, the energies of these four bands bracket those of the fundamental in HNSNH at 1181 cm^{-1} . By contrast, the symmetric stretch, $\nu_{\text{s}}(\text{NSN})$, in PhNSNPh at 957 cm^{-1} is much closer to the fundamental at 934 cm^{-1} in HNSNH, suggesting that this mode is far less susceptible to mixing with the aryl ring vibrations. Fascinatingly, the symmetric bend, $\delta_{\text{s}}(\text{NSN})$, at 803 cm^{-1} in PhNSNPh is double the energy of the fundamental at 410 cm^{-1} in HNSNH. We do not have an explanation for this phenomenon.

The exceptional opportunity afforded in this work, that of having nine further aryl SDIs for which the solid-state geometries have been unambiguously determined by crystallographic analysis, has now enabled us to confidently assign the key vibrational frequencies of these crystalline solids, as presented in Table 4.3, each based on computed spectra from DFT calculations. Despite this, we have not utilized FTIR further in our investigation of SDI conformations, since the computed signals for the *E/E*, *E/Z*, and *Z/Z* conformations, typically differing by a few tens of wavenumbers (see

Figure B.104 – B.139), are probably too similar to reliably identify specific isomers or mixtures in solution.

4.2.7. Mechanisms of SDI Isomer Interconversion

In a 1983-era computational study employing rigid scan methods, Raghavachari et al. proposed an isomerism mechanism for the parent SDI, HNSNH, that is intermediate between N-S bond rotation and in-plane inversion.^[110] Later, Zahedi et al. applied QST2 and QST3 methods to search for transition states for dimethyl sulfur diimide.^[95] They concluded that the interconversion paths only exist between E/Z ↔ E/E and E/Z ↔ Z/Z, reporting transition state energies ranging from +47 to +88 kJ/mol relative to the isomer energies. However, little information was provided on the mechanism(s) of interconversion. We applied modern relaxed scan DFT calculations, using our standard B3LYP-D3BJ/6-311++G(2d,p) level of theory, for interconverting HNSNH along the paths proposed by Zahedi. Indeed, for this compound, the lowest computed path between isomers is effectively N-S bond rotation with only minor departures from planarity at the N atoms (see Section B.4). The transition states (TS) are confirmed to be saddle points (one imaginary frequency) and the paths have been confirmed by intrinsic reaction coordinate (IRC) calculations, conducted forward and backwards from the TS.^[111] Also in agreement is that the energies are in the order Z/Z < E/Z (+0.7) < E/E (+13.9 kJ/mol). The computed barriers between Z/Z to E/Z (+68), and E/Z to E/E (+77 kJ/mol) along the relaxed scans are quite similar to what Raghavachari reported.

However, while similar transition states could be found for interconversions of PhNSNPh, employed as a model system for **1** – **9**, it was found that the S-N-C_{ipso} angles open up considerably (to ~150°). Moreover, IRC scans detect very different paths over the barriers (Figure 4.7). After opening these angles, a subtle re-organization involving inversion at one or both N atoms occurs that requires little further changes in the aryl ring orientations, consistent with the principle of least nuclear motion (PLNM).^[112-114] Figure 4.7 shows a few key geometries through the Z/Z ↔ E/Z IRC path. The key point

is that the aryl SDIs, possibly as a result of resonance delocalization into the aromatic rings, have access to surprisingly low energy paths between isomers. The computed barrier energies are +54 kJ/mol for E/Z $\leftrightarrow$ Z/Z and +78 kJ/mol for E/Z $\leftrightarrow$ E/E. These barrier energies are consistent with the E/Z $\leftrightarrow$ Z/E fluxionality established by solution NMR for **1** – **7** at RT. Moreover, the slightly higher barriers to, and considerably higher energies computed for E/E, are consistent with a very low population but easy access to this conformer when required (as in chelation to metals).

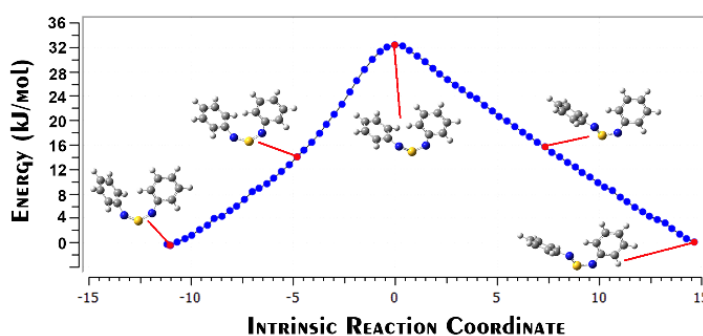


Figure 4.7. B3LYP-D3BJ/6-311++G(2d,p) calculation of IRC path for conversion of PhNSNPh from Z/Z (left) to Z/E (right); as is common for this type of calculation, the barrier shown is not the full height because the start and end points are not fully optimized in the IRC calculations.

4.2.8. UV-vis and TD-DFT

The UV-vis absorption spectra of the intensely coloured aryl SDIs **1** – **9** were measured as solutions in CH₂Cl₂ (Figure 4.8).^[115] These are strong chromophores, with absorption coefficients ranging from 3600 (**9**) to almost 15000 L · mol⁻¹ · cm⁻¹ (**1**). Of particular interest to this study was the observation of distinct variations in the principal absorption maxima, λ_1 and λ_2 , in the visible region. The *para*-substituted aryl SDIs **1** – **7** band maxima are more intense ($\epsilon_{\text{max}} > 5000$) and the order of intensities is $\lambda_1 > \lambda_2$, whereas the bands for **8**, **9** feature $\lambda_1 < \lambda_2$ and the maximum intensities are lower ($\epsilon_{\text{max}} < 5000$). There are significant variations in the positions of the band maxima, which generally follow the electron withdrawing propensities of the substituents, but not fully. The band envelope differences suggested that potentially the major components in solution may be different for these two sets of compounds (as already

suspected from the NMR evidence). Hence, we studied predicted absorption spectra using TD-DFT calculations with the optimized isomer structures.

Single point TD-DFT calculations were performed on compounds **1** – **9** using CAMB3LYP-D3BJ/6-311++G(2d,p) and a PCM model of solvation for CH₂Cl₂. N = 6 singlet states were solved for **1** – **8**, and N = 12 singlet states were solved for **9**. Calculations were run for all conformations (E/E, E/Z, Z/Z), which showed that the closest agreement between simulation and experiment was achieved with the proposed solution-state conformations, namely E/Z for the *para*-substituted compounds **1** – **7**, and Z/Z for the tri-substituted compounds **8** and **9** (Table 4.4 and Figures B.95 – B.103), in accord with our DFT and NMR results (Table 4.1 and Figure 4.5). While this method will be insensitive to minor isomers, it has great and heretofore untapped utility in assigning the principal conformation of SDIs in solution.

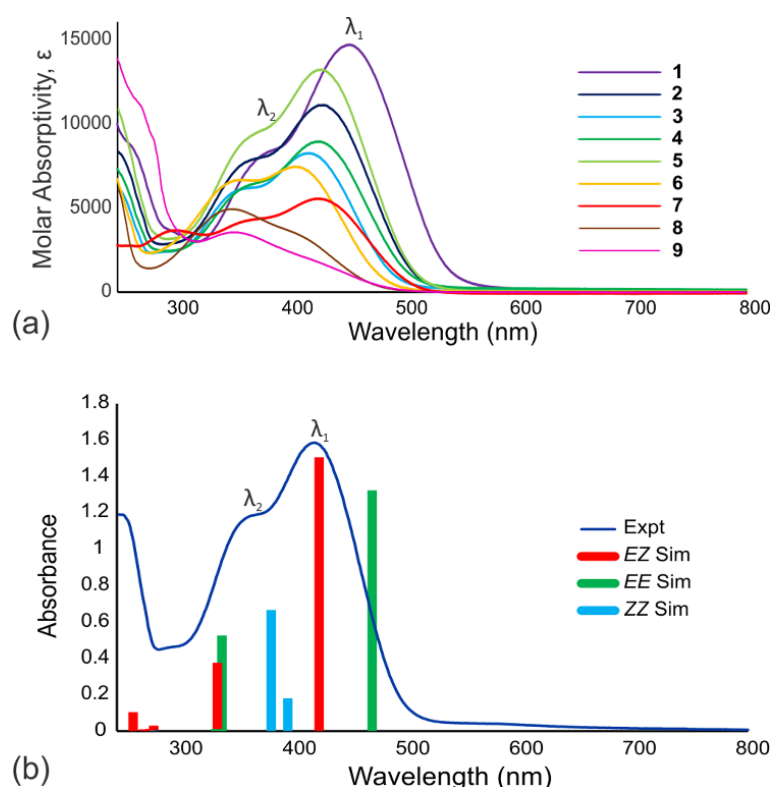


Figure 4.8. (a) Overlaid spectral traces in the visible and near-UV region for **1** – **9** as measured in dilute CH₂Cl₂ solutions (10 mm pathlength quartz cells). (b) UV-vis spectrum of **3** (blue trace) with calculated oscillators from TD-DFT frequency calculations of the possible conformers (E/E = Green, E/Z = Red, Z/Z = Light Blue).

The computed oscillators for each of the three possible conformations are sufficiently distinct to enable confident assignment of the experimental spectra as containing predominantly E/Z or Z/Z conformers of the SDI. The calculated values for **8** closely conform to experimental values, while the calculated values for **9** see a higher deviation from experimental, most likely because of the known over-estimation of stabilization due to intramolecular π -stacking introduced by the D3BJ dispersion correction. Notwithstanding, even the largest deviations of the simulated UV-vis oscillators fit sufficiently well to the experimental spectra, and this simulated set of data is strongly supportive of our proposed compositions of the sulfur diimides in solution. It may be noted that Sicinska et al. previously assigned the two bands in these spectra to individual isomers, an assumption that can now be shown to have been correct in some cases, for example by the identifications shown in Figure 4.8(b).^[75]

Table 4.4. Experimental vs. TD-DFT principal peaks from UV-vis measurements and calculations.

Comp.	Subst.	Experimental (nm)		TD-DFT (nm) ^a		Difference (nm)	
		λ_1	λ_2	λ_1	λ_2	λ_1	λ_2
1^b	4-OCH ₃	453.1	382.9	456.5	339.8	3.4	43.1
2^b	4-CH ₃	431.0	370.8	433.1	336.5	2.1	34.3
3^b	4-F	418.3	360.9	421.7	331.9	3.4	29.0
4^b	4-Cl	427.0	367.3	429.6	336.7	2.6	30.6
5^b	4-Br	427.9	372.1	430.6	337.6	2.7	34.5
6^b	4-CF ₃	406.2	355.9	409.9	334.9	3.7	21.0
7^b	4-NO ₂	425.9	372.1	432.2	345.4	6.3	26.7
8^{c,d}	2,4,6-F ₃	407	350.1	401.1	353.2	6	3.1
9^{c,d}	2,4,6-Br ₃	428	353.4	412.8	333.8	15	19.6
Average						5.0	26.9
Std. Dev.						3.9	10.8

^a TD-DFT calculations used CAMB3LYP-D3BJ/6-311++G(2d,p), with CH₂Cl₂ PCM solvation model. ^b TD-DFT values given are calculated oscillators for the E/Z conformation of the SDI. ^c TD-DFT values given are calculated oscillators for the Z/Z conformation of the SDI. ^d λ_1 values for **8** and **9** are estimated due to poorly defined peaks.

4.2.9. Voltammetry

The electrochemical properties of the sulfur diimides were assessed by square wave (SWV) and cyclic voltammetry (CV) using the $\text{CH}_2\text{Cl}_2/0.4 \text{ M } [\text{tBu}_4][\text{PF}_6]$ solvent-electrolyte combination uniformly. The electrochemical processes by CV for each sulfur diimide were shown to be under diffusion control by a linear plot of peak currents versus the square root of scan rates (Figures B.64 – B.72). All samples were referenced internally to the ferrocene/ferrocenium redox process (designated in this work by $\text{Fc}^{+/0}$) at 0.0 V.^[116] Key voltammetric data for **1** – **11** are reported in Table 4.5 in CH_2Cl_2 at a scan rate of $0.2 \text{ V} \cdot \text{s}^{-1}$ and more detailed data are provided in Appendix B (Tables B.32A – B.33) along with exhaustive SWV and CV plots (Figures B.18 – B.63). The voltammetric responses for the nine aryl SDIs are broadly comparable but shift significantly over the accessible solvent/electrolyte window (Table 4.5 and Section B.8), whereas **10** and **11** each show only one irreversible reduction process at very negative potentials.^[43]

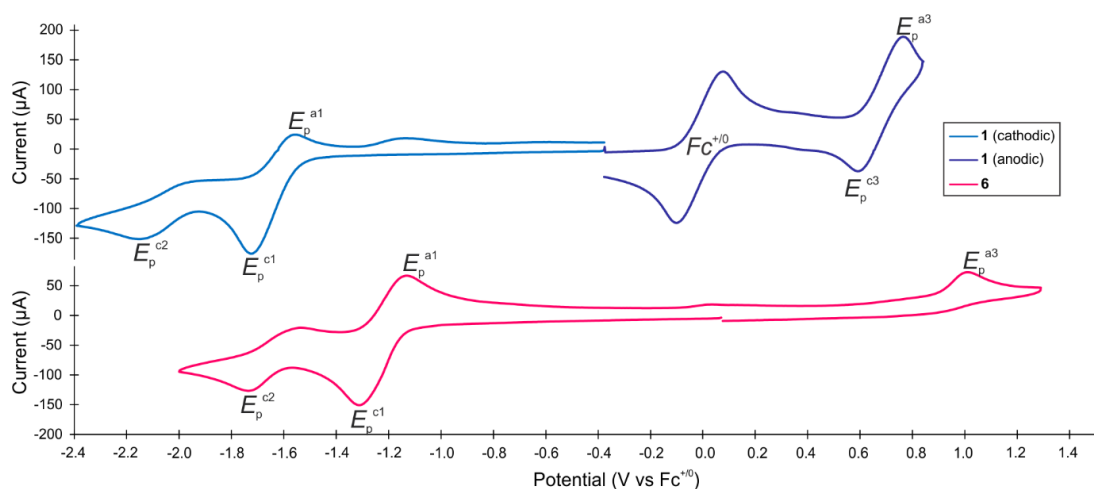


Figure 4.9. Comparative CV scans illustrating the most accessible redox processes in the anodic and cathodic regimes for representative examples of electron donating (top, **1**) contrasted with electron withdrawing (bottom, **6**) aryl SDIs. The top anodic trace also shows the signal from the ferrocene internal standard that is added to the analyte/electrolyte solutions in final scans. Initial scan directions are cathodic for **1** (cathodic) and **6**; anodic for **1** (anodic).

Typically, the aryl SDIs **1** to **9** show three processes (Figure 4.9), namely a first (labelled E^1) and second (E^2) reduction and an oxidation (E^3 , not reported for **8** because ill defined). Importantly, E^1 has been shown to be a one-electron process, in all cases,

by simultaneous electrochemical electron paramagnetic resonance (SEEP) spectroscopy (see below for details) through the generation of radical anions *in situ* at the specified potentials. By comparison of the peak currents, E^3 is readily confirmed to also be a $1e$ transfer in the oxidation of **1**, for which the oxidation is well behaved with a strong return wave. A wide range of potentials is displayed with differing substituents (Figure 4.10), affecting both the cathodic and anodic processes, with a variation in E_m^1 from -0.92 to -1.65 V. As shown, E^1 is much more negative for **1** than for **6**. Similarly, E^3 is found much more positive in **6** than in **1**, and the difference may be even larger than indicated as there is some uncertainty in the correct oxidation peak assignments of **6** – **9**. However, as all attempts to confirm the identity for E^3 by SEEP have thus far failed, detailed analysis will be restricted to E^1 .

The redox stability window $\Delta E_p^{a(3-1)}$ for all the aryl SDIs is large (average of 2.41 V), fairly constant, and not apparently correlating with any other feature of the data (see below). The redox window $\Delta E_p^{c(1-2)}$, ranging from 0.32 to 0.89 V is small for all but the most electron withdrawing substituents (NO_2 in **7** and 2,4,6-trifluorophenyl in **8**). Significantly, in **7** the E^2 process shows a strong return wave and peak currents very comparable to those of E^1 , thus consistent with a second $1e$ reduction. The E^2 peak currents for all the other aryl SDIs are anomalously small, which also needs further discussion (to follow). Formal potentials, measured as E_m^1 , could only be obtained for the first reduction; remaining processes and determinations of averages and ranges employ the relevant cathodic or anodic peak potentials.

A clear pattern (as illustrated in Figure 4.10) emerges from the voltammograms that the more electron withdrawing substituents correspond to less negative E^1 potentials, and the more electron donating substituents correspond to more negative E^1 . Since the LUMO topologies identified in DFT calculations in aryl SDIs of both E/Z and Z/Z conformations have significant coefficients at aromatic ring C atoms (Figure 4.6 and Figure B.73), these trends fit with the determined electronic structures. Indeed, the magnitude of the substituent effect in **1** – **9** on E^1 processes is remarkably large,

with a 0.73 V difference between the most electron donating and electron withdrawing substituents. The magnitude of the substituent effects in aryl sulfur diimides is even greater than one of the most important ligands in redox non-innocent ligand research, 2,2'-bipyridine (bipy), which shows a range of only 0.59 V with the same substituents as this sulfur diimide series, in a 4,4'-X₂-2,2'-bipy configuration.^[117-118]

A contrasting class of comparators are aryl-1,2,3,5-dithiadiazoles (DTDA), which share with SDIs the characteristic of redox MOs centred on delocalized SN bonds. The reductions of these neutral radical species are much less sensitive to remote effects, showing a range of just 0.12 V between 4-methoxy and 4-trifluoromethyl aryl substituents, compared to 0.41 V for sulfur diimides.^[50] This has been attributed to a node in the SOMO of DTDA between the phenyl ring and the heterocycle, which effectively insulates the electronic environment of the heterocycle from the resonance effects of the aryl substituents.

Table 4.5. Summary of cyclic and square wave voltammetric data for redox processes of **1-11**.^a

Process: Cmpd.	-1/-2			0/-1						+1/0	
	E_p^{c2} (V)	E_{SW}^2 (V)	$\Delta E_p^{c(1-2)}$ (V)	E_p^{c1} (V)	E_p^{a1} (V)	E_m^1 (V)	ΔE_{pp} (V)	I_a/I_c ^b	E_{SW}^1 (V)	E_p^{a3} (V)	$\Delta E_p^{a(3-1)}$ (V)
1	-2.131	-2.034	0.414	-1.717	-1.589	-1.653	0.128	0.52	-1.642	0.749	2.338
2	-2.036	-1.966	0.391	-1.645	-1.527	-1.586	0.118	0.64	-1.566	1.081	2.608
3	-1.987	-2.047	0.391	-1.596	-1.453	-1.525	0.143	0.65	-1.547	1.209	2.662
4	-1.871	-1.765	0.404	-1.467	-1.335	-1.401	0.132	0.67	-1.394	1.229	2.564
5	-1.889	-1.917	0.430	-1.459	-1.330	-1.395	0.129	0.73	-1.408	1.247	2.577
6	-1.720	-1.653	0.407	-1.313	-1.175	-1.244	0.138	0.70	-1.254	0.969	2.144
7	-1.871	-1.793	0.886	-0.985	-0.863	-0.924	0.122	0.83	-0.912	1.109	1.972
8	-2.157	-2.064	0.678	-1.479	-1.279	-1.379	0.200	1	-1.404	—	—
9	-1.721	-1.706	0.319	-1.402	-1.255	-1.328	0.147	0.64	-1.334	1.143	2.398
10	—	—	—	-2.571	—	—	—	—	-2.627	—	—
11	—	—	—	-2.717	—	—	—	—	-2.347	—	—

^aGC electrode, A = 7.1 mm², ν = 0.2 V s⁻¹, T = 22 °C, with 0.4 M [ⁿBu₄N][PF₆] supporting electrolyte in CH₂Cl₂. All potentials are Volts vs E⁰ Fc⁺⁰. ^b I_a/I_c ratios are estimated except for **3**, **7**, and **8**, due to unsatisfactory baseline for anodic component (-/2- process disrupted baseline for all other compounds). ^c A second and more intense oxidation peak at 1.55 V is observed, with a better fitting $\Delta E_p^{a(3-1)}$ of 2.72 V. ^d A second and more intense oxidation peak at 1.74 V is observed, with a better fitting $\Delta E_p^{a(3-1)}$ of 2.60 V.

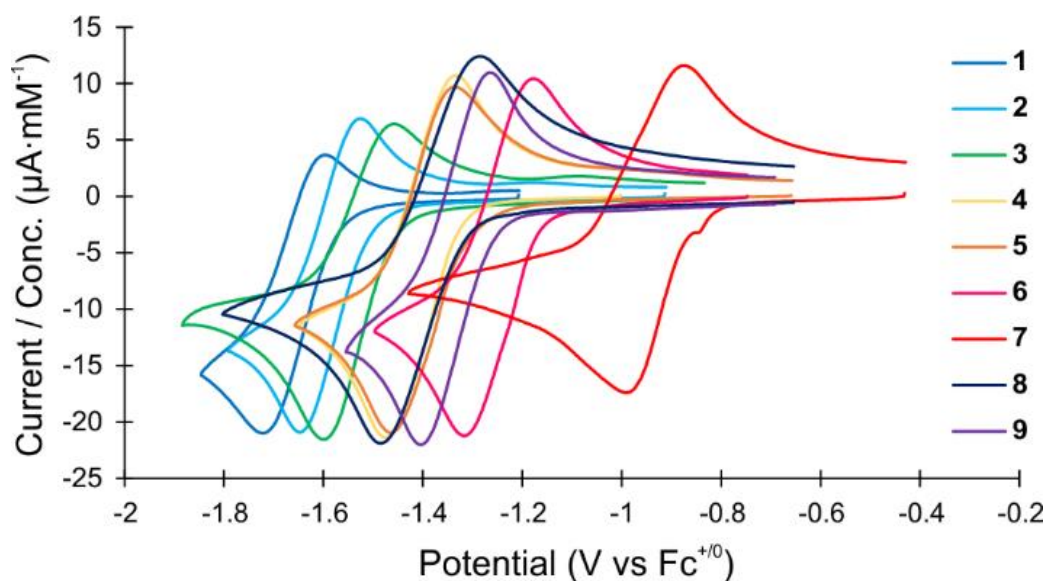


Figure 4.10. Overlays of cyclic voltammograms of the 0/- process for compounds **1** – **9**, referenced to $Fc^{+/0}$ at 0.0 V; initial scan directions are cathodic. The y-axis values are scaled to the experimental concentration of each species to present a relatively uniform set of overlaid cyclic voltammograms. A similar overlay of CVs without adjustment for concentration is found in Figure B.18.

An additional issue highlighted in the series of overlapping E^1 CV traces shown in Figure 4.10 is the significance of the marked differences in I_a/I_c ratios, from 1:1 for **8** down to 0.52:1 for **1**, which could be attributable to chemical (so-called EC mechanism) or electrochemical (the rate of heterogeneous electron transfer) irreversibility, or a combination of the two. Analysis of the anodic and cathodic current ratios for **1** to **9** was difficult in most cases due to the proximity of the E^2 process. Therefore, we employed the Tomeš criterion to assess electrochemical reversibility (Table B.33), measuring the difference at the one-quarter and three-quarter cathodic wave potentials.^[119-120] In an aqueous solution, the potential difference for a reversible process would be 56.5 mV. Our electrochemistry was done in a low dielectric solvent, and as such it is expected that the potential differences measured will be intrinsically larger, despite the use of 0.4 M supporting electrolyte to mitigate this effect. Hence, the average $\Delta E(\frac{1}{4} - \frac{3}{4}) = 68$ mV led us to conclude that the first reductions of these aryl SDIs appear to be either Nernstian or close-to-Nernstian in their responses, consistent with sufficiently fast rates of electron transfer relative to the standard CV scan rates employed. Thus, the cases with lower I_a/I_c ratios are attributed to EC processes with follow-on chemical reactions, which consume the produced SDI radical anions at

varying rates for different species. This has been correlated to the varying radical anion lifetimes as deduced from the SEEPR experiments (next section).

The above conclusions relating to anion radical stability also bears on the anomalously low currents observed for most E^2 processes, as clearly evident for **1** and **6** in Figure 4.9. Broadly, two possibilities should be considered. Firstly, for those with shorter lifetimes the time delay to traverse $\Delta E_p^{c(1-2)}$ leads to such a loss of redox-active material that the apparent currents for this second reduction are greatly diminished. Evidence for this was the observation of significant deposits on the working electrodes during cathodic voltammetry experiments. Secondly, if the initial products somehow aggregate to larger species, expected to have smaller diffusion coefficients, this could result in lower fluxes and hence lower peak currents. In this scenario, E^2 (except possibly in the case of **7**) would be measuring a second reduction of *different species*. Support for this potentiality is provided by the reported high reactivity of SDI radical anions.^[121-122] In the original report, scrambling of mixtures of aryl SDIs occurred with a catalytic amount of alkali metal reducing agents. Although originally proposed as *radical couplings* via their $\pi 3^*$ SOMOs, a similar process may operate (Figure 4.11) between one radical and a neutral SDI. While there are no reports that higher aggregated ring- or (branch)chained radicals can be formed by such a process, there are many known examples of rapid changes in molecularity of thiazyl compounds under redox conditions.^[1] This could serve as an alternative explanation for the highly unusual appearances of the redox waves we observed for the E^2 processes in **1** – **6**, **8**, and **9**. A similar concept has been proposed before.^[47]

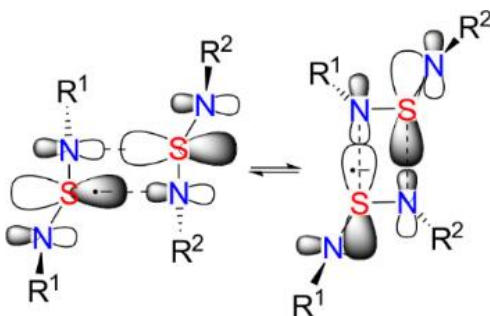


Figure 4.11. Sulfur diimide radical anion scrambling reaction following Bestari et al.^[122]

The correlation of E_p^{c1} to the energy of the LUMOs as calculated by DFT is excellent ($R^2 > 0.97$, Figure 4.12). This evidence therefore indicates that the reductions of aryl SDIs are strongly redox tunable by suitable variations in substituents. Moreover, the linear fits in Figure 4.12 will allow reasonable predictions of the reduction potentials of unknown sulfur diimides from relatively straightforward DFT computations. An excellent correlation also exists between E_p^{a3} for oxidation of **1** – **5**, consistent with the orbital topologies calculated for the HOMOs, but fails for the other exemplars for undetermined reasons.

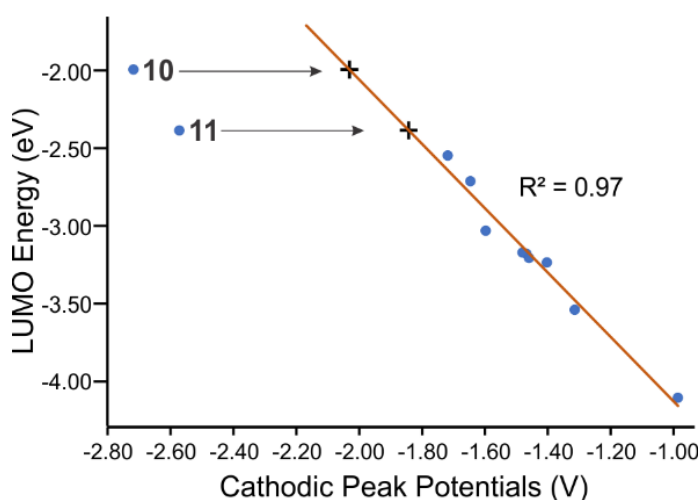


Figure 4.12. Plot of E_p^{c1} of **1** – **11** vs DFT LUMO Energies calculated using B3LYP-D3BJ/6-311++G(2d,p), with linear fit through **1** – **9** and extrapolated points (+) for **10** and **11** to this line.

An interesting question is whether these predictions are also valid for non-aryl SDIs. For the alkyl and silyl compounds **10** and **11** (Table 4.5), the only process observed is an irreversible reduction ($I_a/I_c = 0$), with strong dependency of E_p^{c1} on scan rate. This is indicative of significantly slowed rates of electron transfer (electrochemical irreversibility) in addition to rapid EC decomposition processes. Importantly, the SEEP signals were determined under steady-state conditions.^[43] A difficulty with irreversible redox processes in voltammetry is that the apparent potentials become functions of the rates of the follow-up reactions in the EC process and become, even more dramatically, dependent on the rates of heterogeneous electron transfer – this is the so-called *overpotential* that readily exceeds many tenths

of volts.^[123-125] Clearly, the measured E_p^{c1} of **10** and **11** do not fit to the correlation line for reductions of **1** – **9** in Figure 4.12. Do they then belong to a different correlation, of similar slope, at much more negative potentials? Or should we extrapolate E_p^{c1} via their computed LUMO energies (+ marks on the linear fit)? The latter, yielding apparent Nernstian potentials of –2.06 V for **10** and –1.87 V for **11**, at the very least establish a lower limit for these two potentials.

4.2.10. EPR Spectroscopic Results

Electron Paramagnetic Resonance (EPR) spectra were obtained for reduction of the SDIs in this series. The lifetime of SDI radical anions is quite short when electrochemically reduced, requiring the use of simultaneous electrochemical electron paramagnetic resonance (SEEP). Samples were prepared in quartz flat cells in CH_2Cl_2 with $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte. Electrodes (working = Pt, reference = Ag, auxiliary = Pt) were placed in the cell and a voltage corresponding to the 0/–1 redox process (as determined by *in situ* SWVs) was applied.^[126] For each of **1** to **9**, this resulted in production of an EPR signal (Figure 4.13 and Figures B.74 – B.82) which, along with comparable current densities in each CV of **1** to **9**, provides confirmation that all sulfur diimides in this series undergo a one-electron reduction in the first cathodic process.

The lifetimes of the radical species are strongly dependent on the electron-withdrawing abilities of the substituents, with the most electron-donating (methoxy, **1**^{•–}) having the shortest lifetime, some tens of seconds, and the most electron-withdrawing (nitro, **7**^{•–}) having a lifetime of minutes. In fact, the strongest signal from **7**^{•–} was obtained when electrolysis preceded the EPR scan by ~30 seconds to build up a higher radical concentration. This trend extends to **11**^{•–}, which under near-identical conditions has a lifetime of < 5 seconds due to its highly electron-donating SiMe_3 groups, combined with the lack of electron delocalization lent by the aryl rings in **1** to **9**.^[43] Hyperfine couplings (HFCs) on the NSN nitrogen atoms decrease from **1**^{•–} to **7**^{•–} with more electron-withdrawing substituents (Table 4.6). They increase for the trihaloaryl groups and **9**^{•–} has the largest nitrogen HFC in the series, consistent with a

higher population of the Z/Z conformation, which tends towards a radical anion more localized on the NSN moiety due to diminished π -delocalization to the aryl rings. The aryl *ortho*-hydrogens of compounds **1**^{•-} – **7**^{•-} have significantly large HFCs, on the order of 3 – 5.5 MHz (2 – 4 mT). The *meta*-hydrogens have significantly smaller couplings, except in **2** and **3** where they are 0.8 – 3.8 MHz (0.6 – 2.8 mT). This is in full accordance with the expected β coupling due to the $p(\pi)$ spin densities of the attached C atoms (see Figure B.84).

Radicals **8**^{•-} and **9**^{•-} only contain *meta*-hydrogens, and these have small couplings. The EPR spectra of **1**^{•-}, **4**^{•-}, **5**^{•-}, **7**^{•-}, and **9**^{•-} are dominated by the 1:2:3:2:1 quintet, which is consistent with the large spin density localized on the two nitrogen atoms (Figure B.84) and the absence of high-abundance isotopes with large gyromagnetic ratios on the aryl groups. Excellent simulated fits for all experimental data were obtained while treating the nitrogen HFCs as identical, implying that the conformation of the sulfur diimide radical anions are symmetrical. When running the simulations, the parameters for the nitrogen atoms were initially varied independently, but were found to refine similarly, such that the agreement of the simulation to the experimental data did not worsen when the nitrogen HFC were restricted to identical values. Radicals **2**^{•-}, **3**^{•-}, **6**^{•-} and **8**^{•-} show more complex multiplets that display the influence of strong coupling to aryl-hydrogens and/or aryl- or trifluoromethyl ¹⁹F nuclei. The *g*-values do not greatly vary over most of the series (2.0062 to 2.0065) with **5**^{•-} and **9**^{•-} at 2.0070 and 2.0090 significant outliers, attributable to spin-orbit coupling from the heavy Br nuclei, with an effect that increases in lock step from two to six Br substituents.

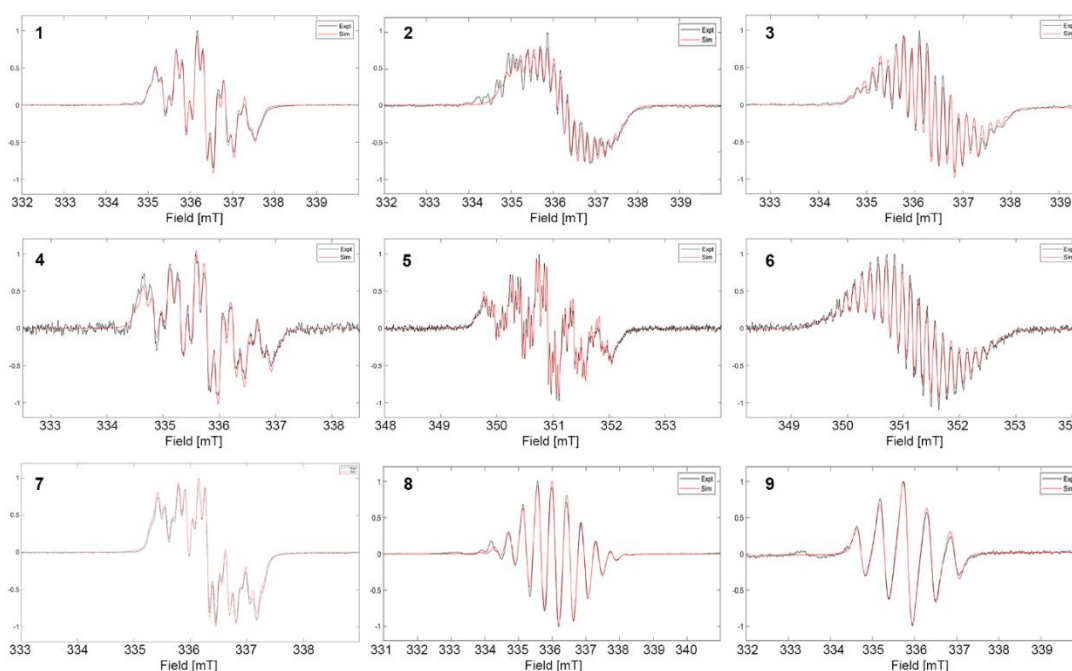


Figure 4.13. EPR spectral data for 1^- to 9^- . Black lines are experimental spectra and red are line-fitted simulations undertaken with EasySpin-5.2.31. The intensities (y-axes) are in arbitrary units.

For each of the anions 1^- – 9^- , density functional theory (DFT) calculations were performed at the UB3LYP/6-311++G(2d,p) level of theory with and without the D3BJ post-SCF dispersion correction in the three nominal conformations E/Z, Z/Z and E/E. Some averaged geometrical data is provided in Figure 4.4(C) for the first two conformations, and the energetics of the isomeric structures are included in Table 4.1, while fuller details are provided in Section B.4. In the E/Z conformation, the Z-branch SN bond length is computed to increase by 4.2% on reduction to the anion and the E-branch by 4.6% in the monoanion, whilst the corresponding C_{ipso} -N bonds decrease by 2.6 and 2.8%. In the symmetric Z/Z conformer, the SN bonds increase by 4.9% and CN decrease by 2.4%, and $\angle(NSN)$ decrease by a few degrees for each conformer. All these changes are consistent with partial occupancy of the $3\pi^*$ LUMO of the neutral SDIs (see Figure 4.6). Interestingly, in the anions 1^- – 7^- , using the full dispersion corrected calculations, the structures minimize to fully planar in E/Z and E/E but the Z/Z conformations maintain essentially the same folded conformation of the neutral species (structures are provided in Appendix B, see Tables B.47 and B.48). Only in the di-*ortho* substituted anions, 8^- and 9^- , do the Z/Z conformations adopt the close face-

to-face aryl ring spacing. Also, in their E/Z isomers, the Z-branch aryl rings are twisted by dihedrals of 39 and 56°, respectively, whereas the E/E isomers adopt the fully coplanar conformation common for aryl SDI anion radicals.

Most interestingly, the computed energies of the conformers in the gas phase (Table 4.1) provide ambiguous predictions about the ‘most stable conformation’. Indeed, the trends from the calculations with and without the D3BJ post-SCF dispersion corrections are effectively mirror images. Ignoring dispersion, the E/Z conformer is almost always the lowest except **8** and **9**, for which E/E is lowest, but the energy differences are negligible, and a mixture of isomers would ensue. Including dispersion, which we consider more accurate despite some expected over-correction, Z/Z and E/Z are within 5 kJ/mol for all except **9**, while E/E is in most cases less favoured by more significant margins (≥ 10 kJ/mol). Importantly, the energetic differences are very small, and with the reduced π -bond orders, the anions could reasonably be expected to exist as freely exchanging conformers in solution.

This is further borne out by the EPR spectroscopic results. In all cases, the (dominant) ^{14}N HFC is found to be the same for both nuclei, thus equal nitrogen environments at ambient temperature, whether static or dynamic. The DFT computed HFC constants (Table 4.6) provide a most interesting outcome: the *general agreement* of all the predicted values with experiment is utterly convincing regarding the identity of these radical anions. But the specific values, radical by radical, vary from nucleus to nucleus over the three limiting conformations used in the computations. Since the ^{14}N HFC are the most prominent in all the spectra and usually the largest in magnitude, we draw attention to the larger than observed prediction of the ^{14}N HFC values for Z/Z and smaller than observed for the other two conformers. Moreover, a simple average of the computed values for this HFC between E/Z and Z/Z (“E/Z-Z/Z” in Table 4.6) provide a superb fit to experiment, with deviations (per MHz) of less than 3% for **1** – **7**. Only for **8** and **9** do the HFC agreements fit closer to a pure Z/Z conformation, consistent with the expected greater dispersion interactions between substituents in

these radical anions. Interpretation of these values necessarily must leave a considerable margin: computationally from the inability to accurately predict very flexible radicals; experimentally from the significantly under-parameterized spectral data. Nevertheless, considering the detailed comparison of the HFC computational predictions, the evidence points to radical anions that are present as mixtures of E/Z and Z/Z conformations. Interestingly, a relaxed scan calculation for SN bond rotation, conducted on $3^{\cdot-}$, provides a smooth isomerization path with a computed barrier of < 13 kJ/mol, consistent with a population weighted dynamic average of conformations in solution. Moreover, the timescales of the EPR experiments evidently allow for identification of intact radical anions in solution and do not show the decay of magnetization that might be expected from rapid radical-radical substituent exchange according to the synthetic study of Bestari et al.^[122]

Table 4.6. Experimental EPR Spectroscopic Data Compared with DFT Computed Values^a

	1-OCH₃	2 - CH₃	3 - F	4 - Cl	5 - Br	6 - CF₃	7 - NO₂	8 - F₃	9 - Br₃
g-value	2.0062	2.0063	2.0064	2.0065	2.0070	2.0063	2.0063	2.0065	2.0090
HFC (MHz)									
2 ¹⁴N^b	13.83	13.26	13.70	13.19	13.11	12.28	10.00	12.79	15.65
E/Z	8.16	7.79	8.00	7.53	7.47	7.47	7.47	11.29	10.80
Z/Z	19.24	18.94	19.36	18.66	18.69	18.69	18.69	18.40	17.37
E/E	7.62	7.24	7.38	7.05	6.99	6.99	6.99	6.87	5.53
E/Z-Z/Z	13.84	13.37	13.68	13.09	13.08	12.38	9.72	14.85	14.09
2 ¹H^c	4.32	5.64	4.12	4.19	4.01	4.13	3.73		
E/Z	7.01	6.51	6.87	6.63	6.57	6.57	6.57		
Z/Z	5.65	5.52	5.71	5.56	5.46	5.46	5.46		
E/E	5.72	5.95	6.25	5.93	5.88	5.88	5.88		
2 ¹H^c	3.77	4.90	4.12	3.74	3.91	2.90	3.01		
E/Z	4.45	4.33	4.58	4.39	4.35	4.35	4.35		
Z/Z	4.64	4.36	4.64	4.51	4.39	4.39	4.39		
E/E	3.54	3.06	3.22	3.28	3.26	3.26	3.26		
2 ¹H^d	1.16	3.73	3.67	1.34	1.60	1.06	0.42	1.42	1.89
E/Z	2.57	2.73	2.87	2.83	2.80	2.80	2.80	2.32	1.43
Z/Z	2.11	2.11	2.11	2.20	2.15	2.15	2.15	2.67	1.29
E/E	1.49	1.67	1.61	1.85	1.87	1.87	1.87	2.18	2.60
2 ¹H^d	1.16	1.59	0.78	1.18	1.18	0.89	0.19	1.41	1.63
E/Z	1.21	1.29	1.36	1.36	1.34	1.34	1.34	1.60	1.43
Z/Z	1.96	1.92	2.01	1.98	5.00	1.90	1.90	1.57	1.29
E/E	1.46	1.16	1.32	1.15	5.00	1.11	1.11	1.88	2.11
nX		4.24 ^e	9.57 ^f			7.92 ^g	0.64 ^h	11.38 ^g	
E/Z		6.89 ^e	11.17 ^f			15.51 ^g	0.98 ^h	6.96 ^g	
Z/Z		5.78 ^e	9.41 ^f			12.26 ^g	0.91 ^h	4.66 ^g	
E/E		5.33 ^e	8.54 ^f			10.42 ^g	0.97 ^h	8.16 ^g	

^a An alternate table reports HFS in mT, Table B.34. Experimental values are from full line-fitting of the experimental data in EasySpin. Computed HFC values are from UB3LYP-D3BJ/6-311++G(2d,p) calculations based on the conviction that the dispersion correction gives more accurate geometries, even if not always indicating the most stable conformations in solution. HFC have been symmetry averaged to match the experimental signals; full original data are in Table B.36. ^b Assigned to the ¹⁴N nuclei of NSN bridge. ^c Assigned to *ortho*-H of aryl rings, unable to assign E or Z branch. ^d Assigned to *meta*-H of aryl rings, unable to assign E or Z branch. ^e Assigned to ¹H nuclei of the two CH₃ groups. ^f Assigned to *para*-¹⁹F nuclei. ^g Assigned to ¹⁹F nuclei of the two CF₃ groups for **6**, and the 2,4,6-F atoms for **8**. ^h Assigned to ¹⁴N nuclei of the two NO₂ groups.

4.3. Conclusions

Acyclic sulfur diimides are an important class of delocalized molecules with allylic character that are noteworthy for having a third-period element, sulfur, as the central atom. They have been known for a considerable period but have not been as well studied as closely related organic heterocumulenes. The application of a systematic approach, with full attention to the rich isomeric diversity encountered in solution, the solid state, and amongst different redox states, affords important insights into the redox properties of this class which is of great significance *inter alia* to the behaviour of SDIs as chelating ligands to metals. As shown by systematic voltammetric investigation, supported by SEEP spectroscopy, this work has characterized the strong redox tunability of aryl SDIs. The linear correlation for the E^1 process provides a reliable index for the redox tuning of any conceivable diaryl SDI. It also provides an absolute lower limit for the thermodynamic redox first reduction potentials of the important SDI ligands **10** and **11**. Whether the alkyl or heteroatom-substituted SDIs are truly more difficult to reduce by as much as one volt remains an open question that can only be resolved by a systematic study by voltammetry of more exemplars of such SDIs.

4.4. Experimental Section

4.4.1. Chemical Synthesis

Reagents and general procedures are reported in Section B.1, along with a detailed synthetic report for the reliable preparation of all the SDIs discussed in this report. Synthesis of previously unreported **6** and **8** are described here.

Synthesis of bis(4-trifluoromethylphenyl)sulfurdiimide (6). 4-trifluoromethylaniline (8.0 mL, 64 mmol) was dissolved in ~50 mL of dry benzene and stirred under N_2 flow. To this was added $SOCl_2$ (10 mL, 138 mmol) diluted in 30 mL of benzene. Solid anilinium chloride salt formed on addition of $SOCl_2$ but dissolved with heating. The reaction mixture

was refluxed for ~3 hours, until the evolution of HCl vapors ceased. The solvent was removed, leaving a bright yellow oil, which was 4-trifluoromethyl-N-sulfinylaniline. Yield: 11.4 g, 86%. ^1H NMR (300 MHz, CDCl_3): δ = 7.68 ppm (d; $^3\text{J}(\text{H,H})$ = 8.7 Hz, 2ArH), 7.91 ppm (d; $^3\text{J}(\text{H,H})$ = 8.4 Hz, 2ArH). $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, CDCl_3): δ = -62 ppm (s, CF_3).

Dissolved 4-trifluoromethyl-N-sulfinylaniline (9.07 g, 43.8 mmol) in dry toluene, and stirred under N_2 flow. On addition of potassium *tert*-butoxide (3.68 g, 33 mmol), the solution immediately turned dark red. The mixture was refluxed for 4 hours, after which the toluene was removed. The remainder was dissolved in pentane, and then filtered under N_2 . The pentane was then removed, leaving a dark red oil. This was distilled under vacuum (115 °C). The distillate contains the impurities of the crude product, leaving sulfur diimide behind in the boiling flask. Yield: 4.29 g, 56%. ^1H NMR (700 MHz, CDCl_3): δ = 7.42 ppm (d; $^3\text{J}(\text{H,H})$ = 8.1 Hz, 4H, *o*-ArH), 7.57 ppm (d; $^3\text{J}(\text{H,H})$ = 8.4 Hz, 4H, *m*-ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3): δ = 123.2 ppm (s, 4C, *o*-ArC), 124.1 ppm (q, $^1\text{J}(\text{C,F})$ = 272 Hz, 2C, CF_3), 126.4 ppm (q, $^3\text{J}(\text{C,F})$ = 3.7 Hz, 4C, *m*-ArC), 128.9 ppm (q, $^2\text{J}(\text{C,F})$ = 32.8 Hz, 2C, *p*-ArC), 147.7 ppm (q, $^5\text{J}(\text{C,F})$ = 1.4 Hz, 2C, *i*-ArC). ^{19}F NMR (282 MHz, CDCl_3): δ = -62 ppm (s, 6F, CF_3). FTIR (cm^{-1}): 3221, 2934, 1911, 1670, 1608, 1575, 1504, 1413, 1388, 1318, 1273, 1236, 1161, 1103, 1066, 1049, 1012, 967, 904, 874, 841, 755, 736, 717, 654, 636, 595, 570, 513, 436. MP: 37.2-39.5 °C. Anal. Calcd for $\text{C}_{14}\text{H}_8\text{F}_6\text{N}_2\text{S}$: C, 48.00; H, 2.30; N, 8.00; S, 9.15%. Found: C, 48.18; H, 2.09; N, 8.36; S, 8.90%.

Synthesis of bis(2,4,6-trifluorophenyl)sulfurdiimide (8). In a round-bottomed side-arm flask, 2,4,6-trifluoroaniline (2.04 g, 13.9 mmol) was dissolved in ~80 mL dry benzene and stirred under N_2 flow. Over ~10 minutes, SOCl_2 (2.2 mL, 30 mmol) diluted in ~20 mL of benzene was added. The reaction mixture was refluxed for ~2.5 hours, until the evolution of HCl vapors ceased. Removed solvent to yield a dark yellow oil, 2,4,6-trifluorophenyl-N-

sulfinylaniline. Yield: 2.12 g, 79%. ^1H NMR (300 MHz, CDCl_3): δ = 6.83 ppm (m; 2ArH); ^{19}F NMR (282 MHz, CDCl_3): δ = -105 ppm (m; 1F; *p*-ArF), -107 ppm (m; 2F; *o*-ArF).

In a round-bottomed side-arm flask, 2,4,6-trifluorophenyl-N-sulfinylaniline (2.12 g, 11.0 mmol) was dissolved in ~100 mL dry benzene, and potassium *tert*-butoxide (0.7 g, 6.2 mmol) was added. This was stirred at RT, changing colour from pale yellow to a medium orange solution. Upon reflux, the solution turned dark yellow. Refluxed for 2.5 hours, then cooled to RT, leaving a dark gel-like substance. This was washed three times with dH_2O , the organic phase was separated, dried over MgSO_4 , and solvent was removed. Yield: 1.49 g, 84%. ^1H NMR (700 MHz, CDCl_3): δ = 6.52 ppm (4H; t; *m*-ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3): δ = 99.9 ppm (ddd, $^2\text{J}(\text{C},\text{F})$ = 26.6 Hz, $^2\text{J}(\text{C},\text{F})$ = 23.6 Hz, $^4\text{J}(\text{C},\text{F})$ = 4.8 Hz, 4C, *m*-ArC), 117.9 ppm (td, $^2\text{J}(\text{C},\text{F})$ = 17.7 Hz, $^4\text{J}(\text{C},\text{F})$ = 5.1 Hz, 2C, *i*-ArC), 153.6 ppm (ddd, $^1\text{J}(\text{C},\text{F})$ = 252.3 Hz, $^3\text{J}(\text{C},\text{F})$ = 14.7 Hz, $^3\text{J}(\text{C},\text{F})$ = 7.0 Hz, 4C, *o*-ArC), 160.3 ppm (dt, $^1\text{J}(\text{C},\text{F})$ = 250.6 Hz, $^3\text{J}(\text{C},\text{F})$ = 14.4 Hz, 2C, *p*-ArC). ^{19}F NMR (282 MHz, CDCl_3): δ = -109 ppm (m; 2F; *p*-ArF), -113 ppm (m; 4F; *o*-ArF). FTIR (cm^{-1}): 510, 835, 985, 1038, 1123, 1267, 1443, 1486, 1605, 3105. MP: 95.9-96.5 °C. Anal. Calcd for $\text{C}_{12}\text{H}_4\text{F}_6\text{N}_2\text{S}$: C, 44.73; H, 1.25; N, 8.69; S, 9.95%. Found: C, 44.72; H, 1.11; N, 8.99; S, 11.61%.

4.4.2. Crystallography

Crystals were selected under a polarizing microscope and checked for optical extinction. Colourless or pale-yellow crystals were mounted in Fomblin™ oil on a 100 μm MiTeGen loop and cooled to 173(2) or 100(1) K using the diffractometer cooling devices. Data were collected either on Bruker ApexII CCD (Mo $\text{K}\alpha$) or Rigaku-Oxford Diffraction SuperNova HPC (Cu $\text{K}\alpha$) diffractometers. Data collection and reduction was controlled, respectively, with *SAINT-Plus* or *CrysAlisPro* 1.171.38.43 (Rigaku Oxford Diffraction, 2021). The data were processed and corrected for Lorentz and polarization effects by standard methods and corrected for absorption by semi-empirical methods from

equivalents. Structures were solved with ShelXT^[127] and refined using Levenberg–Marquardt minimization with olex2.refine within the Olex2 suite of programs.^[67] The refinements employed NoSpherA2, (Non-SPHERical Atom-form-factors in Olex2)^[66] an implementation of HAR that makes use of tailor-made aspherical atomic form factors calculated on-the-fly from a Hirshfeld-partitioned electron density (ED). The ED is calculated from a Gaussian basis set single determinant SCF wavefunction in DFT at the PBE/def2-TZVP level of theory using ORCA 4.5. Crystal data and structure refinement parameters are summarized in Table B.1 in Appendix B, and full archival data is available in CIF format.

4.4.3. Voltammetry

Cyclic (CV) and square-wave (SWV) voltammetry experiments were performed with a Princeton Applied Research PARSTAT 2273 potentiostat using the PowerSuite software version 2.58, and the embedded PowerCV software version 2.46. Experiments were done in a nitrogen-filled MBraun glovebox with oxygen and moisture rigorously excluded. The working electrode used was a glassy-carbon inlaid-disk electrode with a surface area of 7.1 mm², the reference electrode was silver wire, and the counter electrode was a coiled platinum wire. Dichloromethane was initially dried by distillation from CaH₂ under nitrogen and subsequently freeze-thaw degassed before transfer to the glovebox.

4.4.4. Simultaneous Electrochemical EPR (SEEPR)

SEEPR experiments were conducted in CH₂Cl₂/[ⁿBu₄N][PF₆] by using a miniature Wilmad WG-808 quartz electrolytic flat cell with platinum foil working electrode, Teflon-coated silver reference electrodes, and a platinum wire auxiliary electrode. The Bruker EMX Plus EPR spectrometer was operating at X-band frequencies (9.8 GHz) and during electrolysis the spectra were monitored in intensity-versus-field mode. The spectra were simulated using EasySpin 5.2.31 software within the MatLab software suite.

4.4.5. Computation

Computations were carried out by Gaussian 16W V1.1 using the GaussView 6.0.16 GUI. The functional used was B3LYP, with a 6-311++G(2d,p) basis set. D3BJ dispersion correction was used when indicated. PCM CH₂Cl₂ solvent model was used when indicated. For UV-vis simulations (e.g. Figure 4.8), a single-point calculation CAMB3LYP-D3BJ/6-311++G(2d,p) was applied to the geometry-optimized structures calculated by B3LYP-D3BJ/6-311++G(2d,p) method. Vibrational spectra (IR and Raman) were computed using the frequency calculation in Gaussian 16W, including ¹⁵N isotope substitution. Gaussian relaxed scan techniques as well as IRC calculations were undertaken, using the standard method including dispersion correction, to assess the mechanisms of isomer interconversion.

4.5. References

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Chapter 5. *N,N'*-Diaryl-Sulfurdiimide and *N,N'*-*Tert*-Butyl-Sulfurdiimide Complexes of Tin(IV) Chloride

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5.1. Introduction

Sulfur diimides (SDIs), R-NSN-R, are diimines of sulfur dioxide, while sulfinylamines are the corresponding monoimines, R-NSO.^[1] Both are known to coordinate to metals by varying modes (Figures 5.1c and 5.2c).^[2-3] The first SDI coordination chemistry was reported in 1972,^[4] detailing the κ^1 -*N* coordination of di-*tert*-butyl sulfur diimide to Pt(II) and Rh(I). Since then, a considerable breadth of SDI coordination complexes have been developed, covering many of the transition metals, as well as several post-transition metals and lanthanides.^[5-29] Importantly, SDIs have proven redox non-innocent (RNI) ligand character^{[30][31-42]} in a number of complexes,^[7-8, 12, 16, 25-26] and have been shown to act as redox-active ligands.^[6, 8] Despite that many aryl SDIs are known, metal-SDI complexes reported in literature are predominantly alkyl or heteroelement alkyl analogues, while there are only a few structurally-verified aryl-SDI complexes.^[18-20, 22] By far the most extensive coordination chemistry has instead involved just two non-aryl moieties, namely *tert*-butyl (*t*Bu) and trimethylsilyl (TMS), which were included for comparison in our ligand study, and shown to be stronger donors to the unsaturated -NSN- moiety. In our recent comprehensive investigation of the voltammetry of diarylsulfurdiimides, we demonstrated a very high degree of redox tuning of their one-electron reductions and oxidations with aryl-ring substituents.^[43] If the observed tunability is retained when they are ligands in a coordination complex, it would mark SDIs as highly desirable RNI ligands.

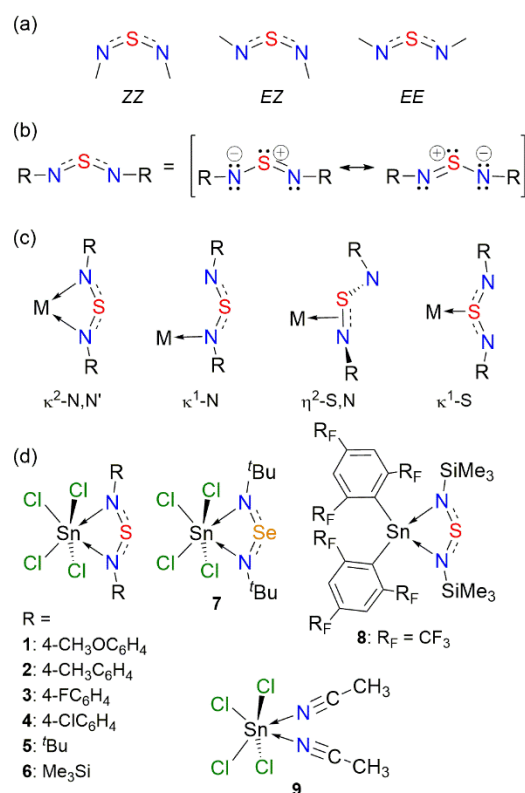


Figure 5.1. (a) Known isomers of SDIs. (b) Bonding notation employed. (c) Coordination modes of SDI metal complexes. (d) Compounds studied or referenced.

Three isomers are possible for uncoordinated SDI ligands (Figure 5.1a); *EZ* or *ZZ* are lowest energy, depending on substituent, while *EE* is an accessible higher-energy conformer.^[43] The bonding in SDIs is delocalized and heteroallylic (Figure 5.1b).^[44] A significant contributor to the number and variety of metal-SDI complexes is the multiple possible modes of coordination of the -NSN- moiety (Figure 5.1c); they are known to coordinate κ^1 through N, η^2 to an NS bond, or κ^2 through both N.^[23] The only claimed κ^1 -S coordination was based on NMR observations at -60°C; the proposed S-coordinated SDI was not isolated, and the assignment remains tentative.^[10-11] Despite the long history of SDI coordination chemistry, there is a dearth of structural evidence from single-crystal X-ray diffraction (SC-XRD). Three structures have been reported with confirmed κ^1 -N coordination (with CSD – the Cambridge Structure Database^[45] – refcodes): [BuNS(*t*Bu)N]Pt(η^2 -C₂H₄)Cl₂, ETPSIM,^[24] [Me₃SiNS(Me₃Si)N]GaCl₃, JIQVOV,^[5] [BuNS(*t*Bu)N]Li,

OXUKIC.^[29] The most commonly reported coordination mode is $\kappa^2\text{-}N,N'$, with a diverse range of metal and co-ligands. First, there are $[\text{S}(\text{N}^t\text{Bu})_2]\text{W}(\text{OC})_4$, WCBSDI,^[12] and $[\text{S}(\text{NSiMe}_3)_2]\text{SnCl}_4$, BUFLAP.^[16] Secondly, four metallocene complexes: $[\text{S}(\text{NSiMe}_3)_2]\text{TiCp}_2$, QASVIR,^[26] $[\text{S}(\text{NSiMe}_3)_2]\text{MCp}^*_2$: M = Eu, VAPXIW; M = Yb, VAPXOC; M = Sm, VAQGIC.^[25] In two closely related derivatives: $[\text{S}(\text{N}^t\text{Bu})_2]\text{Mn}(\text{CO})_3\text{-Mn}(\text{CO})_5$, WEDMEX, is $\kappa^2\text{-}N,N'$ coordinated, whereas in $\kappa^2\text{-}N,N'$ - $[\text{S}(\text{N}^t\text{Bu})_2]\text{Mn}(\text{CO})_3\text{-}\eta^3\text{-NNS-[Mn}(\text{CO})_3]$, WEDMIB, with the photon-induced displacement of two CO ligands, the SDI adds an additional π coordination to the second Mn centre.^[7]

Roesky reported an early example of an SnCl_4 complex of the related $\text{Se}(\text{N}^t\text{Bu})_2$ selenodiimide **7**, which has been structurally characterized as a THF solvate (CSD refcode: LADZOF).^[46] Despite the well-known instability of selenodiimide ligands, there are nine reported crystal structures of metal coordination complexes of this type.^[47-51] We note in passing that tellurium(IV) diimides form dimers that are versatile bridging or chelating ligands, but of a quite different type.^[1] The report of an SDI complex of Sn(II), **8** (Figure 5.1d), is of significant interest to this project. This claim is based on spectroscopic evidence and the notion that the bulky 2,4,6-*tris*-trifluoromethylphenyl substituent suppresses the tendency of Ar_2Sn moieties to polymerize.^[28] The relevance of this Sn(II) complex to the voltammetric investigation for the reduction of the Sn(IV) complexes **1** – **5** in this study is without doubt, as it might be expected that Sn(II) will resist the facile transfers observed for d^2 or f^n electron configurations. A notable recent addition to the library of SDI compounds are hypersilyl SDIs, e.g. $\text{S}(\text{NSi}(\text{SiMe}_3)_3)_2$, reported by the Stalke group.^[52] Experimental and computational data show a considerably larger accumulation of negative charge on the nitrogen atoms compared to the ubiquitous *tert*-butyl SDI. Hypersilyl SDIs should thus be excellent $\sigma\text{-N}$ donors and chelating ligands (making allowance for their steric bulk), marking them as exciting targets for further investigation into the properties of SDI ligands.

In an attempted preparation of the unsubstituted phenyl analog of **1–5**, crystalline κ^1 -O-[(PhNSO)₂]₂SnCl₄ **10** was instead obtained and identified by SC-XRD, and is the first crystallographically confirmed exemplar of this coordination mode.^[2] The free RNSO ligand is known exclusively in the *Z*-isomeric geometry (Figure 5.2a) and has heteroallylic bonding analogous to that of SDIs but weighted towards the resonance isomer with the negative charge at O (Figure 5.2b). Several very old reports claiming the synthesis of early transition metal halide and oxohalide complexes of RNSO likely involve κ^1 -O coordination.^[53-54] However, all structurally characterized complexes of this ligand type to date have involved the other modes: η^2 -NS, κ^1 -S, or κ^1 -N (Figure 5.2c).^[2] An internally chelated κ^1 -O coordination as a pendant group has been structurally confirmed in the Te(IV) compound **11** (CSD refcode: GEWLIG), albeit with a very long Te...O distance.^[55] There is a long-standing claim in the literature for a *bis*(triphenylphosphino)platinum complex dicoordinated by κ^1 -O-OSNH ligands **12a**.^[56-57] However, the reported SC-XRD structure failed to detect the supposed N-bound H atoms. Moreover, the geometry at platinum is strongly indicative of Pt(II) rather than Pt(0) as would be required for coordination by neutral HNSO. In accord with earlier concerns,^[58] we conclude that this purported HNSO complex is instead a complex of the well-known κ^1 -N bound [NSO]⁻ anions **12b**.^[1] For further analysis of the **12a/b** structure dichotomy, see the discussion in Section C.2.

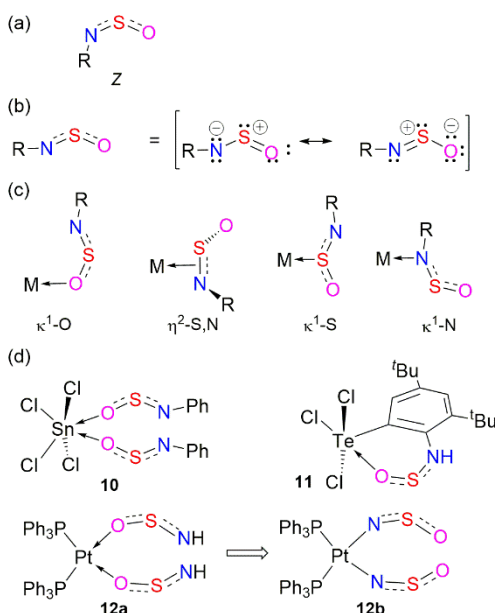


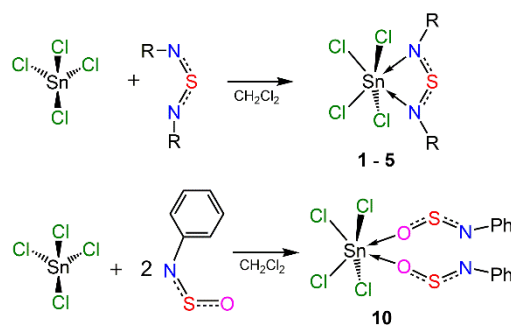
Figure 5.2. (a) Geometry of RNSO. (b) Bonding notation employed. (c) Coordination modes of RNSO metal complexes. (d) Compounds studied or referenced.

In our investigation of the potential redox activity of diaryl-SDI ligands, we selected SnCl_4 as a starting point where spontaneous charge transfer from Sn(IV) was not expected. The sole known exemplar before this work was $\kappa^2\text{-}N,N'\text{-[S(NSiMe}_3)_2]\text{SnCl}_4$, **6** (CSD refcode: BUFLAP), which was obtained by the 1:1 reaction of SnCl_4 with $\text{S(NSiMe}_3)_2$ or, alternatively, by using an excess of the sulfinylamine $\text{Me}_3\text{Si-NSO}$.^[16] The former method led to the synthesis and characterization of five additional SDI complexes of SnCl_4 **1–5**, which include the first structurally confirmed coordination complexes with $\kappa^2\text{-}N,N'$ -diaryl-SDIs, while the latter method unexpectedly produced the *cis*-disulfinylaniline complex **10**. Here, we present a detailed analysis of their solid-state and solution characterizations, supported throughout by employing density functional theory (DFT) computational tools. A complex ligand exchange equilibrium in CH_3CN solution was discovered using ^{119}Sn NMR, spontaneously forming the *cis*-diacetonitrile adduct of SnCl_4 , **9**, which has given insight into the otherwise cryptic voltammetric behaviour of these complexes. The characterization of $\kappa^1\text{-O-}[(\text{PhNSO})_2]\text{SnCl}_4$, **10**, is thoroughly described and analyzed.

5.2. Results and Discussion

5.2.1. Synthesis

The sulfur diimides, dissolved in either CH_2Cl_2 or CHCl_3 , were reacted with SnCl_4 to form the respective $\kappa^2\text{-}N,N'[\text{S}(\text{NR})_2]\text{SnCl}_4$ complexes **1-5** (Scheme 5.1). Addition of the SnCl_4 resulted in immediate precipitation of the complexes. These products are highly insoluble in most organic solvents (except acetonitrile, see below) and could not be purified by recrystallization. Considerable effort was expended to obtain crystalline product suitable for SC-XRD, with best results when both reagents were in dilute solutions, and dropwise addition of the SnCl_4 component was slow. An array of reaction conditions was attempted – varying temperatures, solvents, reaction times, and concentrations – to which the quantity and quality of the final products seemed to be insensitive. For the *tert*-butyl SDI complex **5**, only microcrystalline product was obtained which was unsuitable for SC-XRD structure determination.



Scheme 5.1. Synthesis of complexes **1-5** and **10**

In an attempt to synthesize the phenyl analog of **1-5**, *N*-sulfinylaniline, PhNSO , was made by a well-established method^[59] and reacted with SnCl_4 at low temperature, followed by a lengthy reflux in an attempt to drive the ligand coupling reaction.^[16] However, the only product that could be isolated from the reaction mixture was the unexpected coordination complex of SnCl_4 with two units of PhNSO (Scheme 5.1). This complex is soluble in chloroform allowing characterization by solution NMR, and crystallized whereby it was identified as **10** by SC-XRD.

A full suite of NMR experiments was conducted, despite challenges presented by the insolubility of **1–5** in most solvents, and voltammetric characterizations were undertaken. Solid-state techniques employed were SC-XRD, infrared (IR) and Raman spectroscopy, and elemental analysis (EA). We attempted to ascertain melting points for these complexes, but found that they slowly thermally decompose above ca. 130°C. The remnants are a dark solid in the tube which did not melt up to 400°C, and a yellow band above the heating aperture which is consistent with sublimation of either displaced SDIs or S₈ from ligand decomposition.

5.2.2. X-ray Crystallography of the SDI Complexes

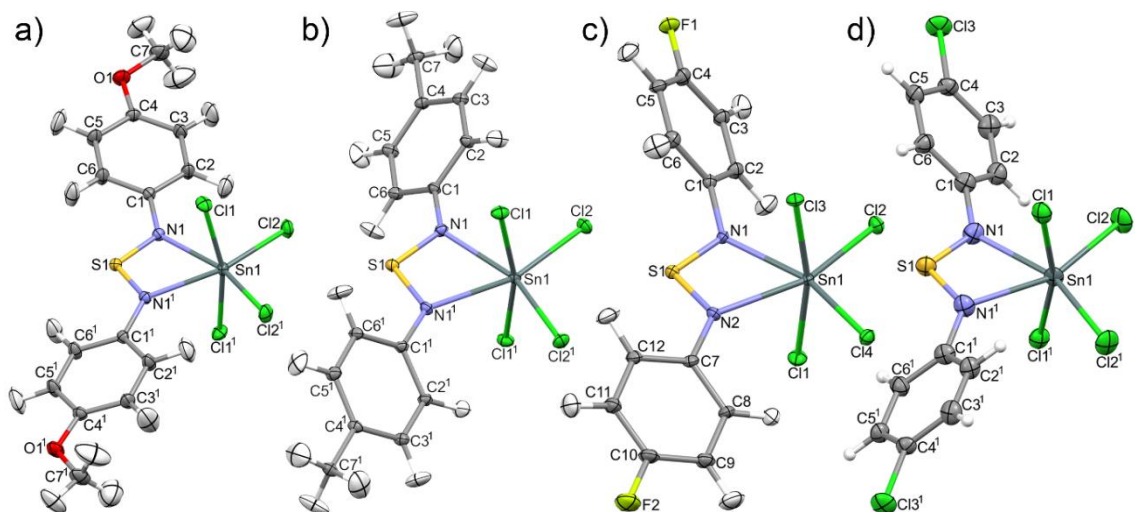


Figure 5.3. Displacement ellipsoids plots (40% probability) of the molecular structures of complexes: (a) **1** (*Pbcn*, $Z' = 0.5$, ¹ 1-x,y,1.5-z); (b) **2** (*Pbcn*, $Z' = 0.5$, ¹ 1-x,y,1.5-z); (c) **3** (*P*₂₁/*c*, $Z' = 1$); (d) **4** (*Pbcn*, $Z' = 0.5$, ¹ 1-x,y,0.5-z). Hydrogen atoms in **4** are refined isotropically.

1, **2**, and **4** are isostructural in space group *Pbcn* (in which the complexes crystallize with 2-fold rotational site-symmetry through S1 and Sn1), while **3** crystallizes in *P*₂₁/*c* at a general position. The molecular structures of **1–4** are highly similar, with the SDI unit coordinating to SnCl₄ in a κ^2 -N,N' bidentate fashion, forming a 4-membered chelate ring (Figure 5.3). The average S-N bond length in **1–3** is 1.578(3) Å, which is intermediate between the length of a single bond and double bond^[60] and slightly lengthened compared to the free SDIs, for which the *E* branch has an average length of 1.555(9) Å (1% longer,

Figure 5.4a). The S-N bond length of **4** is considerably shorter at 1.51(2) Å. The average N-S-N angle in **1-4** is 98.5(8)°, compared to 115.8(6)° for the unbound SDIs, suggesting that significant strain is introduced by chelate formation. There is only one other example in the CSD of a Cl₄Sn-SDI complex, the aforementioned *bis*-trimethylsilyl analog (CSD refcode: BUFLAP^[16]) which crystallizes with mirror site-symmetry in *P*2₁/*m*. This has a more relaxed N-S-N angle compared to **1-4** at 103.7°, and slightly shorter N-S bond lengths at 1.537(4) Å. The experimental geometries are in good agreement with computation at the B3PW91-D3BJ/def2-TZVP level of theory (Figure 5.4b).

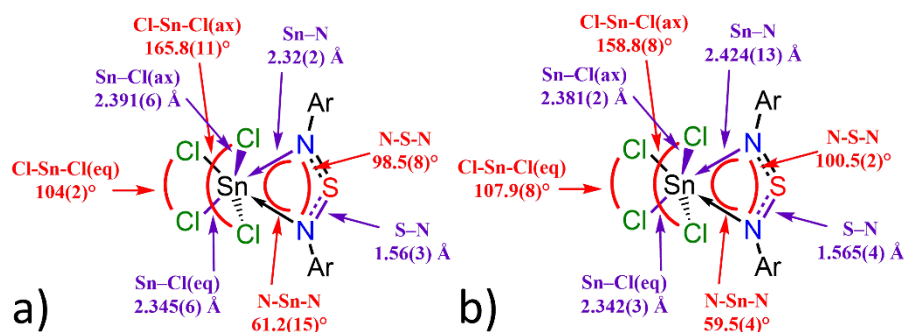


Figure 5.4. (a) Averaged experimental bond lengths and angles of **1-4** from SC-XRD structures. (b) Averaged computed bond lengths and angles of **1-4** at the B3PW91-D3BJ/def2-TZVP level of theory. Errors quoted in parentheses here are standard deviations of the averaged bond lengths/angles.

There are 11 previously characterized structures in the CSD in which a sulfur- (SDI, *n* = 7) or selenodiimide (SeDI, *n* = 4) has coordinated to a metal in *N,N'*-bidentate fashion. In all these SDI and SeDI entries, the N-substituents are either *tert*-butyl or trimethylsilyl, but the aryl N-substituents in **1-4** fit well into trends, as described here. For the M-SDI complexes, each comparator from the CSD has a different metal centre, and the M-N bond length correlates well to the single bond covalent radii (r_{SBCR}) of the metals calculated by Hu *et al.*,^[61] based on parameters determined by Allinger (Table 5.1 and Figure 5.5).^[62] The N-S-N bond angles follow this trend equally well, with larger-radius metals having a larger N-S-N angle. There is no clear trend in the N-M-N bond angles. When M-SeDI complexes are included in this analysis, the correlation of r_{SBCR} to M-N bond length is retained, but the

correlation to N-E-N bond angles becomes significantly weaker, with the linear R^2 value dropping from 0.91 to 0.69. One of the selenodiimide compounds, TUTPII, was excluded from this analysis due to its Co(I) metal centre, which does not have a valid r_{SBCR} value. The lengthening of S-N bonds as a result of metal-to-ligand charge transfer populating the SDI π^* LUMO^[25-26] is shown for cases where the approximate charge transfer is $0e$ (e.g. *Sn(IV)*, WCBSDI), $1e$ (e.g. VAQGIG), and $2e$ (QASVIR). The average S-N bond length over the five structurally characterized $[\text{S}(\text{NR})_2]\text{SnCl}_4$ complexes is only slightly longer than the average over the *E*-branch of free SDIs that crystallize *EZ* (see discussion above), as expected for *Sn(IV)* wherein spontaneous charge transfer to the SDI is impossible.

Intermolecular contacts in **1-4** are dominated by Cl atoms in close contact ($d \leq (r_{\text{vdw}} - 0.1 \text{ \AA})$) with S (all), H (all), and $\text{SnCl} \cdots \text{ClPh}$ (**4** only). These interactions comprise 11 of the 17 unique contacts at this radius, others being $\text{O} \cdots \text{H}$ in **1**, $\text{C} \cdots \text{H}$ contacts in **1** and **2**, and $\text{F} \cdots \text{H}$ in **3**. The strongest contacts ($d \leq (r_{\text{vdw}} - 0.2 \text{ \AA})$) are $\text{Cl} \cdots \text{S}$ (**1**, **3**, and **4**) and $\text{Cl} \cdots \text{H}$ (**1**, **2**, and **3**), $\text{O} \cdots \text{H}$ (**1**), and $\text{F} \cdots \text{H}$ (**3**) – see Table C.15 and Figure C.8 in Appendix C. It is presumed that these short contacts are responsible for the instant precipitation and subsequent insolubility of the formed complexes. However, a more nuanced interpretation of these properties is undertaken by DFT computational studies detailed below.

Table 5.1. Metal single bond covalent radii (r_{SBCR}),^a average $d(\text{M-N})$ and $d(\text{S-N})$ (Å); N-E-N bond angles (°) for $\kappa^2\text{-N,N'}$ SDI or SeDI chelate complexes.^c

CSD Code	M, E	r_{SBCR} (Å)	$d(\text{M-N})^b$	$\angle(\text{N-E-N})$	$d(\text{S-N})^b$
WEDMEX ^c	Mn, S	1.93	2.030±0.010	94.1±0.1	1.596±0.004
WUHFOV	Pd, Se	2.04	2.050	89.7	–
SAPROT	Pt, Se	2.05	2.026	87.2	–
WCBSDI	W, S	2.06	2.173	93.4	1.584±0.003
QASVIR ^c	Ti, S	2.08	2.057±0.005	97.1±1.4	1.668±0.020
<i>Sn(IV)</i> ^d	Sn, S	2.16	2.32±0.02	100±2	1.56±0.03
LADZOF	Sn, Se	2.16	2.258	92.8	–
VAPXOC	Yb, S	2.32	2.356	104.2	1.636±0.015
VAPXIW	Eu, S	2.38	2.444	104.0	1.609±0.002
VAQGIG	Sm, S	2.39	2.457	103.9	1.620±0.003

^a Calculated by Hu *et al.*^[61] ^b M-N bond lengths are an average of M-N1 and M-N2; similarly for S-N1/S-N2 ^c Bond lengths and angles reported are the average of two unique molecules in the asymmetric unit ($Z' = 2$) ^d Bond lengths and angles here are the averages of BUFLAP and **1-4**, which share a common metal (Sn) and chalcogen (S). ^e Errors are standard deviations of the averaged bond lengths/angles.

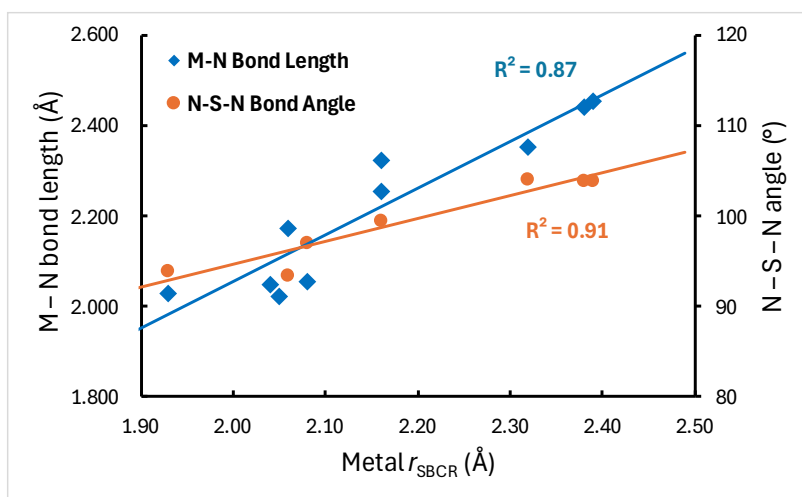


Figure 5.5. Graph of metal single bond covalent radii from Hu^[61] (x-axis) vs M-N bond lengths (left-hand y-axis) and N-S-N bond angles (right-hand y-axis) of 4-membered M-N-S-N chelate rings.

5.2.3. X-ray Crystallography of the PhNSO Complex

Complex **10**, which crystallizes in $P\bar{1}$ without site symmetry, is the first structural characterization of an aryl-*N*-sulfinylamine (Ar-NSO) σ -coordinated to a metal through oxygen. Two units of *N*-sulfinylaniline (Ph-NSO) coordinate to the SnCl_4 centre in *cis* fashion, forming a distorted octahedral geometry (Figure 5.6). The Sn-Cl bond lengths in **10** range from 2.3568(4)–2.3700(4) Å, unlike **1-4** in which axial Sn-Cl are elongated by

0.02–0.05 Å compared to equatorial. This is also seen in other examples of hexacoordinate Cl_4SnL_2 retrieved from the CSD. When the 'L' ligands are *cis*-monodentate (O or N, $n = 20$), as with **10**, the axial and equatorial Sn–Cl bonds differ by less than standard error calculated on the averaged series. By contrast, when 'L' is an *O,O'*- or *N,N'* bidentate ligand (forming 4- or 5-membered chelate rings, $n = 26$), the average Sn–Cl_{ax} bond length is about 0.04 Å longer than Sn–Cl_{eq}. An explanation for this may be that the steric demand of the bidentate ligands enforces a wider L–Sn–Cl(eq) angle ($\angle\text{N–Sn–Cl}_{\text{eq}}$ 96.2° – 98.8° in **1–4** compared to **10** where $\angle\text{O–Sn–Cl}_{\text{eq}}$ are 89.5° and 90.9°), pushing the axial Cl away from Sn. The Sn–O bond lengths of **10** were compared to all instances in the CSD of $\text{Cl}_4\text{Sn–O,O'}$ where O ligands are monodentate ($n = 18$ after 1 removed due to disorder and high (18%) R_1),^[63–77] which average 2.12 ± 0.04 Å. Of these, the average Sn–O length of **10** is on the long end, exceeded only slightly in QOPBAZ by 0.08 Å.^[72]

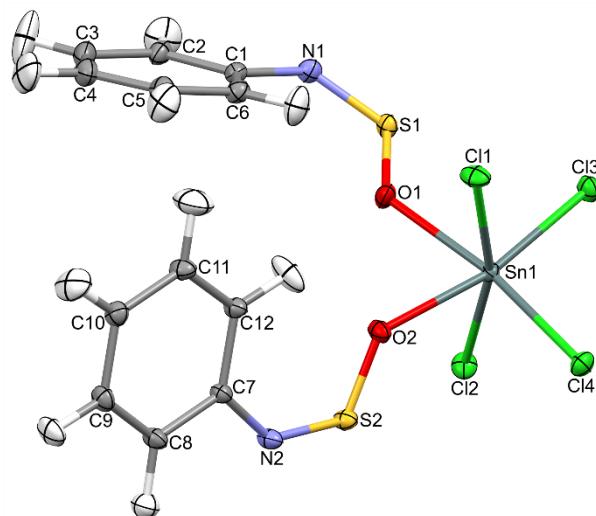


Figure 5.6. Displacement ellipsoids plot (40% probability) of the molecular structure of **10** ($P1$, $Z' = 1$) as found in its crystal structure.

The structure of the ligand in **10** may be directly compared with that of PhNSO (CSD refcode: BEMFUU).^[78] The two S–O lengths of 1.4922(12) and 1.5029(12) Å average to about 3% longer (at the 99% confidence level) than 1.458(1) Å in the free ligand, and the S–N lengths of 1.5034(14) and 1.5039(14) Å average to <1% shorter (and still significant at the

99% level) than 1.516(1) Å in PhNSO. There is no variation in C-N lengths within the s.u., while the two O-S-N angles of 115.48(7) and 115.57(7)° are more than 4% smaller than 120.61(6)° in PhNSO. These changes are consistent with charge transfer from O to Sn upon coordination, by considering the formal resonance structures (Figure 5.2b). The SC-XRD geometry of the metal complex **10** is in excellent overall agreement with the DFT calculated values with the exception of the Sn-O distance, which is elongated by 7% in the computation (Table C.14).

There are only a few instances of metal-coordinated sulfinylamines that are confirmed by SC-XRD (CSD refcodes given). In the Te(IV) ring compound **11**, GEWLIG, formal κ^1 -O coordination occurs where the pendant RNSO oxygen adopts a dative bond, with considerably longer $d(\text{O-Te})$ of 2.461(2) Å than the 2.2031(11) and 2.2213(11) Å to Sn(IV) in **10**.^[55] There are three η^2 -NS coordinated exemplars (Figure 5.2c) which result from oxidative addition to zero-valent metal complex reagents at Pt(II), MSLAPT,^[18] η^2 -NS-[2,4,6-Me₃PhNSO]Pt(PPh₃)₂; at Os(II), VIHKEC (disordered at a special position),^[79] η^2 -NS-[4-MePhNSO]Os(PPh₃)₂; and at Ni(II), YEVTUO, η^2 -NS-[4-MePhNSO]Ni(PPh₃)(CN^tBu).^[80] There are two κ^1 -S modalities at Rh(I), PRPMSA,^[81] κ^1 -S-[4-MePhNSO]RhCl(PPh₃) and Mn(I), XEDQOM,^[82] κ^1 -S-[Me₃SiNSO]Mn(η^5 -C₅H₅)(CO)₂. And there is a single report of κ^1 -N mode coordinated to GaCl₃, ITAPIE,^[83] κ^1 -N-[Me₃SiNSO]GaCl₃, which is very comparable to κ^1 -N-[S(NSiMe₃)₂]GaCl₃, JIQVOV.^[5]

5.2.4. Computational Results

The molecular geometries of **1-6**, **9**, and **10** were optimized in Gaussian 16W at the B3PW91-D3BJ/def2TZVP level of theory, starting from SC-XRD structures. The geometric agreement between experimental and computed structures is excellent, as shown in Figure 5.4b. Comparing the Cl₄Sn-(NSN) fragments (i.e. excluding aryl rings and substituents) of **1-4**, the largest difference in Sn-N bond lengths is 5%, while the average difference in N-S

and Sn-Cl bond lengths is < 1.5% (Table C.13). The average difference in bond angles is about 3%. Frequency calculations confirm these optimized geometries as stable minima and provide simulations of IR and Raman spectra.

Natural Bond Orbitals (NBO) charge distributions of **1-6** and **9** were computed to provide insight into their complexation behaviour (Figure 5.7, Table C.16). The magnitude of the negative charge on coordinating N atoms is by far the smallest for **9**, essentially identical for **1-4**, gets larger for **5**, and much larger in **6**. The larger negative charges on N have no apparent relationship to charges on Sn atoms, and only a small, loosely correlated effect on the net values on the SnCl_4 fragments ($\Delta N = 0.8\ e$; $\Delta \text{SnCl}_4 = 0.07\ e$). There was, however, a sharp increase of positive charge on S concurrent with the increase of negative charge on N. This seems to indicate that higher negative charge at N from the R-substituents is not primarily transferred to the SnCl_4 moiety, as might be reasonably expected, but instead induces internal charge transfer of the SDI ligand, consistent with the polarizable π character of the chelating ligand backbones.

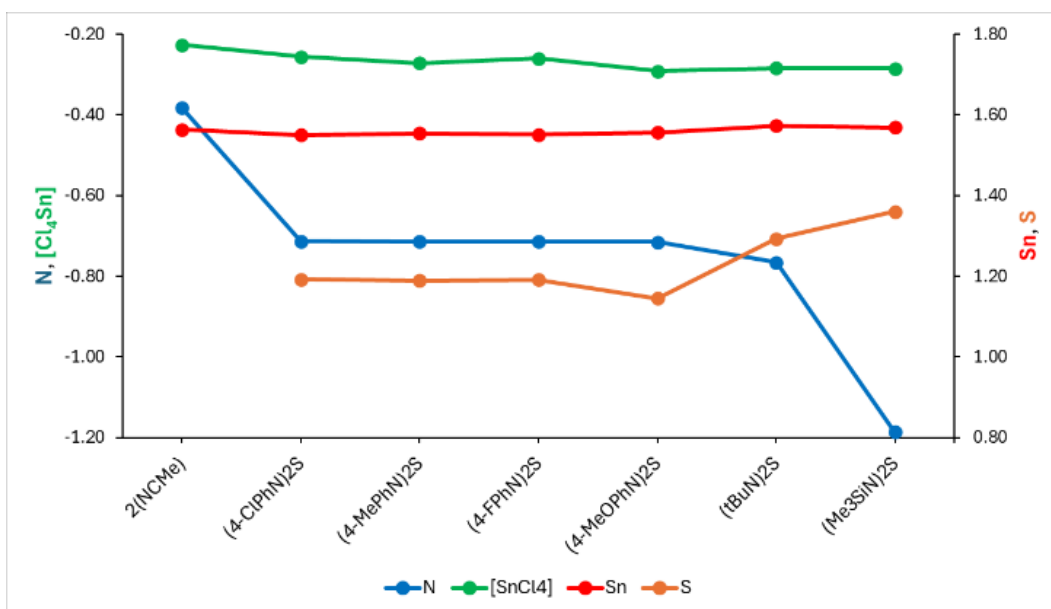


Figure 5.7. NBO charges on selected atoms/groups within $\text{Cl}_4\text{Sn-L}$, where L are identified as entries on the x-axis. Charges at N and Cl_4Sn fragments are plotted on the left-hand y-axis. Charges at Sn and S atoms are plotted on the right-hand y-axis.

To calculate complexation energies, DFT-optimized structures were divided into SnCl_4 and ligand fragments, and a single-point calculation was done at the same level of theory using counterpoise correction. Values obtained (Table C.17) were plotted against NBO charges to investigate whether there is a correlation. Complexation energies do not correlate well to NBO charges on either N or Sn, possibly due to polarization of N-S and Sn-Cl compensating for charge accumulation. However, there is a convincing correlation between complexation energy and the net charge of the SnCl_4 fragment shown in Figure 5.8, which only somewhat deviates for the aliphatic 'Bu SDI. Of significance here is the awareness raised by Davydova *et al.*^[84-86] on the difference between the (high) strength of the bonding in $[(\text{ligand-N})_2]\text{SnCl}_4$ complexes and their overall gas-phase stabilities, noting that while there are numerous Lewis acid-base complexes of SnCl_4 that are stable in the solid state, many are unstable or marginally stable in the gas phase compared to their SnCl_4 and ligand components. This instability is greatly affected by the reorganizational energies of the components that must be paid in the adduct formations, and of these the greatest components are usually the energy cost of the changes in SnCl_4 conformation from the native T_d geometry to the (distorted) O_h required in the complexes. We have already noted the variations in Sn-Cl bond lengths and angles in the SDI complexes (**1-4**, **6**) compared to the more regular geometry in the non-chelating PhNSO complex **10**. Reorganizational energies may be especially relevant for chelating SDI complexes since these must adopt the *EE* conformation, which we have previously shown to be 30-40 kJ/mol higher in energy than their preferred *EZ* conformations.^[43] The cumulative effect of SnCl_4 and SDI ligand reorganizational energies may well render such complexes intrinsically unstable in the gas phase, in line with the observed liberation of free SDIs during thermal decomposition as described above.

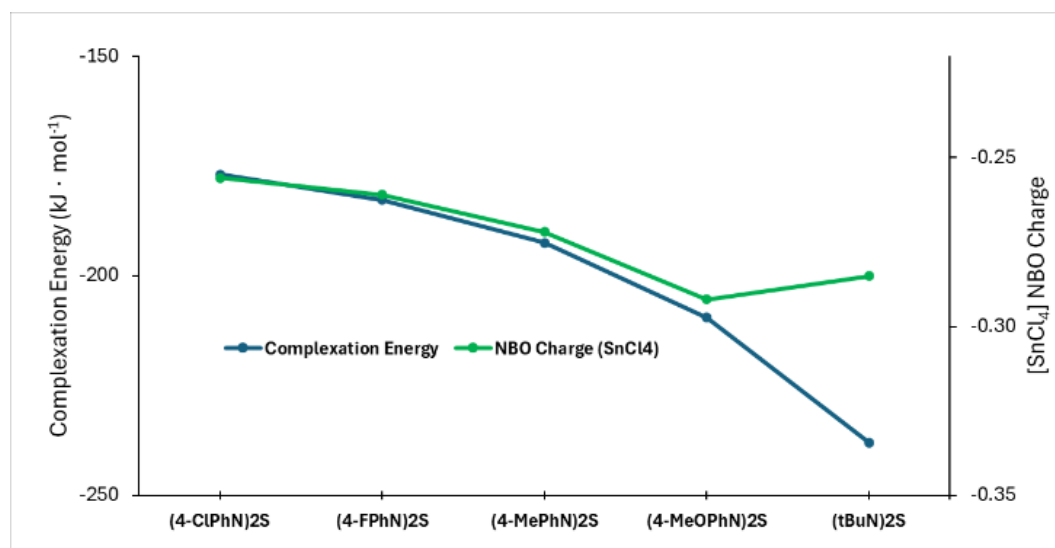


Figure 5.8. Calculated complexation energies (left-hand y-axis) of $\text{Cl}_4\text{Sn-L}$, where L are identified as entries on the x-axis, plotted against NBO charges on Cl_4Sn fragments (right-hand y-axis). NBO charges and complexation energies were calculated at the B3PW91-D3BJ/def2-TZVP level of theory.

Molecular lattice energies in the complexes of **1–4** were calculated with CrystalExplorer21 (CE), which has been shown to compare favourably to experimental estimates from sublimation enthalpies with accuracy comparable or superior to more computationally expensive methods.^[87] CE uses atom coordinates and symmetry data from CIF files to calculate *inter alia* interaction energies between discrete molecules in a crystal structure using counterpoise calculations. Lattice energies are obtained by running the counterpoise calculations on a cluster of molecules within a specified range of the originating molecule. As discussed in the XRD section above, we hypothesized that the insolubility of **1–5** in most common organic solvents might be explained by large lattice energies due to the short $\text{S} \cdots \text{Cl}$ contacts. Indeed, the molecular lattice energies in these complexes are high, ranging from -154 to -212 kJ/mol, consistent with the similar short contacts present in the solid-state lattice of these complexes as mentioned above.

5.2.5. Vibrational Spectroscopy

Exceptional average agreement of ± 10 to ± 21 cm^{-1} was found between experimental and DFT-computed (scaled) IR and Raman peak values, leading to a high degree of confidence in peak assignments. There are only a few strong calculated peaks that are experimentally unobserved, all of which are from Raman and are likely due to lattice selection rules, indicating that bulk samples have the same composition as the crystals picked for SC-XRD. Significant differences are observed in the stretching modes (ν) between complexes with aryl (**1–4**) and alkyl (**5**, or silyl, **6**) SDIs. The $\nu_s(\text{SN-R})$ mode in **5** and **6** is around 80–100 cm^{-1} lower in frequency than in **1** and **3** (not observed in **2** and **4**), and both symmetric and asymmetric $\nu(\text{NSN})$ modes of **5** are ~ 100 cm^{-1} higher in frequency than **1–4**. The bending (δ) and wagging (ρ) modes were found at similar wavenumbers across the series. No clear trend in the remote *para*-substituent effects was found in **1–4**. Comprehensive data tables, experimental and simulated spectra, and additional discussion can be found in Section C.6 and Tables C.20–C.24. The characteristic Sn–Cl bands were readily assigned from the DFT vibrational calculations. The two most intense bands are $\nu_s(\text{Sn-Cl}_{\text{eq}})$, which is found at 331, 335 and 341 cm^{-1} in **2**, **3** and **4**, respectively; and $\nu_s(\text{Sn-Cl}_{\text{ax}})$, which is found at 292 and 300 cm^{-1} in **2** and **3** (too weak to pick in **4**). These frequencies are in good agreement with 304 and 293 cm^{-1} in $[\text{SnCl}_4\text{Br}_2]^{2-}$ or 293 and 278 cm^{-1} in $[\text{SnCl}_4\text{I}_2]^{2-}$,^[116] as well as 322 and 279 cm^{-1} in $[\text{SnCl}_4\text{bipy}]$ or 319 and 271 cm^{-1} in $[\text{SnCl}_4\text{phen}]$.^[117] Neither of the papers by Clark *et al.* were able to assign the bands as we have done here.

Table 5.2. Infrared (IR) and Raman (R) data for important vibrational bands of **1-6**.^{a,b}

Vib. Mode	1 - IR ^c	2 - IR	2 - R	3 - IR	3 - R	4 - IR	4 - R	5 - IR	5 - R	6 - IR ^d
$\nu_{as}(\text{SN-R})^e$	1254	–	–	1262	–	–	–	1176	–	–
$\nu_s(\text{SN-R})^f$	–	1250	1250	–	1249	–	1249	–	–	1155
$\nu_{as}(\text{NSN})^g$	1000	1034	–	1013	–	1014	–	1116	–	–
$\nu_s(\text{NSN})^h$	972	982	984	984	984	958	987	–	1109	–
$\delta_1(\text{NSN})^i$	826	849	851	856	858	830	851	872	–	852
$\delta_2(\text{NSN})$	726	776	777	733	793	695	696	760	789	–
$\rho(\text{NSN})$	553	504	–	498	–	482	–	499	–	–
$\nu_s(\text{Sn-Cl}_{eq})$	–	–	331	–	335	–	341	–	–	–
$\nu_s(\text{Sn-Cl}_{ax})$	–	–	292	–	300	–	–	–	–	–
$\delta_s(\text{Sn-Cl}_{ax})$	–	–	–	–	145	–	146	–	–	–

^a All values are given in cm^{-1} . ^b Assignments were made by visual assessment of vibration animations in the GaussView 6.0.16 GUI. ^c The Raman spectrum of **1** had very poor signal-to-noise due to extreme fluorescence; no useable results were obtained. ^d Reported IR data from Roesky.^[16] ^e Calculated IR intensities for **2** and **4** are <1%, no experimental peaks observed. Calculated Raman intensities for **2**, **3**, and **4** are 1–2%, and there are nearby large observed bands that might be obscuring them. Calculated Raman intensity for **5** is <1%, no experimental peak observed. ^f Calculated IR intensities for **1**, **3**, and **4** are <1%, no experimental peaks observed. Calculated IR intensity for **5** is 1%, may be obscured by band at 1176 cm^{-1} . Calculated Raman intensity for **5** is <1%, no experimental peak observed. ^g Calculated Raman intensities for **2**, **3**, and **4** are <1%, no experimental peaks observed. ^h Calculated IR intensity for **5** is 2%, likely a shoulder of 1116 cm^{-1} band. ⁱ Calculated Raman intensity for **5** is <1%, no experimental peak observed.

5.2.6. NMR Spectroscopy and Solution Speciation

Complexes **1-5** were only found to be appreciably soluble in acetonitrile, out of the many solvents that were tested. Therefore, NMR characterization was undertaken in CD_3CN solutions, and it immediately became apparent that dissolution in this solvent was accompanied by a significant degree of dissociation of complexes **1-5**. In view of the complexity of the observed ^1H , ^{13}C , and ^{19}F NMR spectra, we resorted first to ^{119}Sn NMR spectroscopy to probe the solution speciation in CD_3CN . The chemical shift range of this nucleus is very large, well over 4000 ppm, and shifts are sensitive indicators of ligand-type and coordination number (CN).^[88] Neat SnCl_4 was measured by us at -149.5 ppm w.r.t. external SnMe_4 , concurring with previous reports.^[89-91] In CH_2Cl_2 solution, the ^{119}Sn shift of SnCl_4 is -160 ppm at -78°C , indicating that the geometry at tin in this environment is close to that of the free molecules.^[92] Importantly to the issue of solution-state speciation of SnCl_4 , neat mixtures of different SnX_4 halides have been shown to undergo rapid

interhalogen exchange.^[89-90, 93] It has been reported that the shielding at ^{119}Sn nuclei increases incrementally by about 150 ppm with increasing coordination number (CN) from four to six,^[88, 94-96] but this is low compared to other reports on phosphine and halo complexes where up to 300 ppm per increase in CN have been reported.^[89] This fits well with our measurement of a CD_3CN solution made from crystalline $\text{Cl}_4\text{Sn}(\text{NCCH}_3)_2$, **9** (Figure 5.1), which had a ^{119}Sn shift of -683 ppm. This is a difference of about 530 ppm between four- and six-coordinate tin(IV) (~ 265 ppm per CN increment).^[97]

^{119}Sn NMR spectra collected on solutions of **1-5** were found to contain signals from two tin-containing species. The higher frequency signal (**1-4**: ~ -620 ppm; **5**: -563 ppm) is the coordinated Sn-SDI complex, and the lower frequency signal (**1-4**: ~ -681 ppm; **5**: -674 ppm) is assigned to **9**. Why is there this variation in the shifts assigned to **9**? This question spurred us to an intensive investigation on the solution NMR behaviour of all the SDI complexes, as detailed in Section C.7. In summary, this showed that there is a strong concentration, as well as temperature, dependence of the solution speciation of **1-5** (Figure 5.9 and Table 5.3), clearly indicating dynamic equilibrium behaviour of the type depicted in Scheme 5.2, which is probably a highly simplified picture of the true solution-state behaviour.

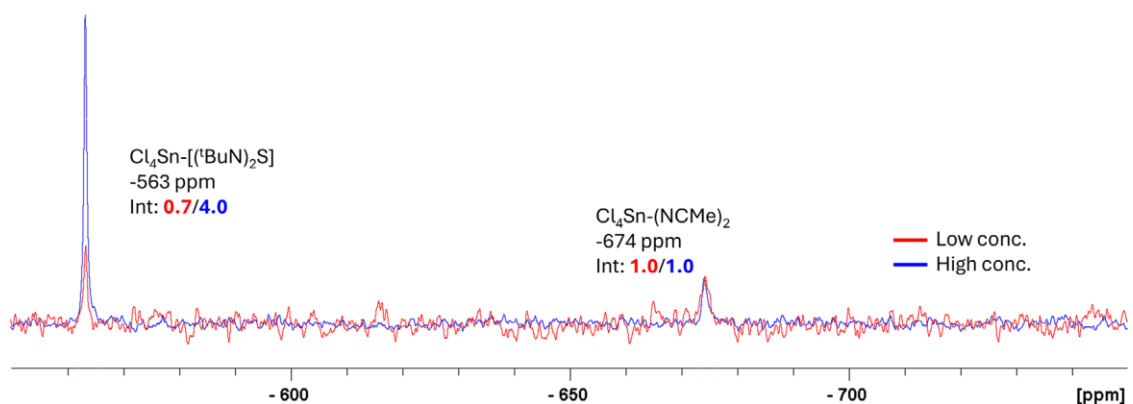


Figure 5.9. ^{119}Sn NMR spectrum of **5**, with overlay of low conc. (red trace) and high conc. (blue trace), showing difference in ratio between Sn-SDI complex (left, -563 ppm) and Sn-(NCCD₃)₂ complex (right, -674 ppm)

As seen in Table 5.3, the ^{119}Sn NMR spectrum shows that a dilute CD₃CN solution of **5** featured the highest proportion of SDI-complex to Cl₄Sn-(NCCD₃)₂, consistent with the stronger donor characteristics of this ligand vs. the aryl-SDIs. Moreover, it shows a dramatic increase in the relative proportion of **5** vs. **9** in saturated solution, such that the concentration of **5** exceeds that of **9** considerably (Figure 5.9 and Table 5.3). Thus, we attributed the variations in the measured chemical shifts of **9** to the well-known phenomenon of a ‘population weighted average shift’ for two interchanging species in solution.^[98] Hence, the ^{119}Sn shifts reported for the SDI complexes are also expected to be population-weighted rather than absolute shift values, albeit with a relatively small variation in shift. As discussed in Section C.7, complex **4** unexpectedly displays extremely high solubility in CD₃CN solution, and unlike all the other exemplars, could not seem to be made fully saturated. In view of this high solubility, solutions of this complex were selected for additional low-temperature NMR experiments. These variable temperature experiments (233–295 K) have defied full interpretation but among other insights, they provide evidence for a significant temperature dependence on the shift of **9**, with concomitant splitting of the signal into two sharp peaks at low temperature that we tentatively ascribe to the *cis* and *trans* isomers of this complex, supported by a related

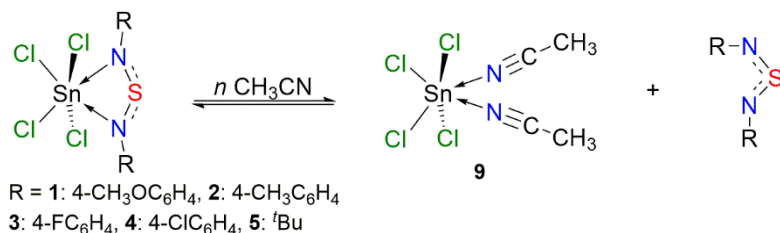
study from Knight and Merbach.^[99] In the solid state, the isolated crystals of **9** were determined to be the *cis*-isomer as depicted in Figure 5.1 and Scheme 5.2 (CSD Refcode: EKEHAD, EKEHAD10).^[100] Section C.8 discusses in brief some of the possibilities of $\text{SnCl}_4 + n\text{CH}_3\text{CN}$ speciation, and previous work in the area. As shown in Scheme 5.2, the equilibria between (possibly several) $\text{Cl}_4\text{Sn}(\text{NCCH}_3)_n$ and SDI complexes may be influenced by the previously discussed reorganizational energies.^[84-86]

Table 5.3. ^{119}Sn NMR^a chemical shifts and integration ratios of **1-5**, **9**, and neat SnCl_4 .

Cmpd	δ (ppm)	Ratio (low conc/sat'd.) ^b
1	-615	1:3 / 1:2
2	-617	1:4 / 1:3.5
3	-616	1:8 / 1:6
4	-618	1:3 / 8:1
5	-563	1:1.5 / 4:1
9	-683	
SnCl_4 (neat)	-150	

^a In CD_3CN ; ^{119}Sn spectra are referenced to external SnMe_4 (90% in C_6D_6) at 0.0 ppm.

^b Approximate integration ratio of high frequency peak (Sn-coordinated SDI) to low frequency peak ($\text{Cl}_4\text{Sn}(\text{NCCD}_3)_2$) in low concentration versus saturated samples.

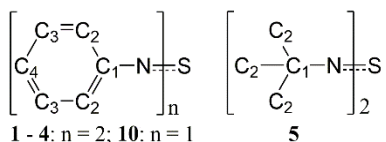


Scheme 5.2. Solution equilibria of the SDI complexes in acetonitrile solutions

Table 5.4. ^1H , ^{13}C , and ^{19}F NMR data for Sn-complexes **C1**–**C5** and **C10**^e and the corresponding unbound ligands, **L1**–**L5** and **L10**.^h

Cmpd	H ₂ ^f	H ₃	X ₄ (^1H , ^{19}F)	C ₁	C ₂ ^f	C ₃	C ₄	X ₄ (^{13}C)
C1	7.24, d (8.6)	6.96, d (8.7)	3.80, s	138.0, s	130.2, s	115.4, s	162.0, s	56.2, s
L1	7.45, s	6.89, d (8.9)	3.79, s	140.7, s	125.6, s	115.1, s	159.4, s	56.2, q (14.6)
C2	7.24, d (7.7)	7.21, d (8.4)	2.34, s	142.5, s	127.8, s	130.8, s	141.5, s	20.9, s
L2	7.34, s	7.17, d (8.1)	2.33, s	144.0, s	123.5, s	130.1, d (11.7)	137.6, s	20.8, q (6.0)
C3	7.33, s	7.17, t (7.7)	-116.2, s	140.2, d (3.3)	130.2, d (9.0)	117.2, d (23.0)	163.5, d (251)	–
L3	7.42, s	7.08, t (8.8)	-115.5, s	142.8, d (2.6)	125.8, s	116.6, d (23.0)	161.8, d (245)	–
C4	7.44, d (8.5)	7.31, d (8.6)	–	142.0, s	125.7, s	130.1, s	133.2, s	–
L4	7.35, s	7.32, d (8.4)	–	144.9, s	125.4, s	129.9, s	132.6, s	–
C5	1.72, s	–	–	68.8, s	30.9, s	–	–	–
L5 ^g	1.42, s	–	–	61.0, s	30.7, s	–	–	–
C10 ^g	7.87, d (7.0)	7.43, m (H ₃ +H ₄)	–	–	–	–	–	–
L10 ^g	7.87, m	7.40, m (H ₃ +H ₄)	–	–	–	–	–	–

^aIn CD₃CN; format: δ (ppm), multiplicity, (J (Hz)). ^b $\delta(^1\text{H})$, relative to residual solvent at 1.94 ppm. ^c $\delta(^{13}\text{C}\{^1\text{H}\})$, relative to residual solvent at 1.32 ppm. ^d $\delta(^{19}\text{F}\{^1\text{H}\})$ relative to external CFCl₃ at 0.00 ppm. ^eNMR samples of **1**–**5** are a mixture containing other species. ^f*Ortho*-H and *ortho*-C of all unbound SDIs are broad at room temperature due to conformational fluxionality, detailed in our previous work.^[43] Both *ortho*-H and *meta*-H of **C3** are broad. ^g**L5**, **C10**, and **L10** data are only available in CDCl₃, referenced to residual solvent at 7.26 ppm (^1H) and 77.23 ppm (^{13}C). ^hNumbering scheme as follows, with H and X labelled as per the attached C atoms:



Recognizing the speciation and concentration dependences from the ^{119}Sn NMR spectra, it was possible to identify all of the ^1H , ^{13}C , and ^{19}F NMR signals pertaining to **1**–**5**. Assignments for the complexes and the unbound SDI ligands (designated e.g. **C1** and **L1**, respectively) are reported in Table 5.4. Unlike the others, PhNSO complex **10** was soluble in the non-coordinating solvent CDCl₃, and no decomplexation of this species was observed. In **1**–**5**, ^1H and ^{13}C NMR spectra showed the presence of additional signals, which

are thoroughly described in Section C.7. Despite working under exacting conditions of solvent and complex dryness, using Schlenk techniques and a nitrogen-filled glove box for all sample handling, it is possible that some decomposition via hydrolysis was operative in these experiments.

5.2.7. Solution Electrochemistry

Since the original purpose of this study was to explore the redox properties of SDI ligands in Sn(IV) complexes, considerable effort was made to characterize the products using voltammetry. It was expected that non-innocent behaviour (i.e. spontaneous e transfer) would be inoperative in the case of Sn(IV), which was substantiated by the SC-XRD results that show none of the bond lengthening of the N-S-N backbone that have been reported for group 4 or lanthanide Cp₂M-SDI complexes.^[25-26] Drawing from studies of Sn complexes with RA ligands^[101-104] and the demonstrated ability of SDIs to act as RA ligands,^[6, 8] the critical question became whether redox activity at the ligand might protect the Sn(IV) from reduction to Sn(II/0) by the ligand accepting the additional electron or electrons.

The speciation issues elucidated by NMR spectroscopy are certainly present in solution voltammetry experiments, which necessarily used acetonitrile as solvent, and will affect our attempts to investigate the electrochemical behaviour of 1-5. Square wave (SWV) and cyclic voltammograms (CV) of the Sn-SDI complexes were collected in distilled and degassed CH₃CN with [nBu₄N][PF₆] supporting electrolyte (0.1-0.2 mol·L⁻¹). The electrochemical processes in the CV of each compound were shown to be under diffusion control by a linear plot of peak currents versus the square root of scan rates (Figures C.92-C.97). Samples were internally referenced to the ferrocene/ferrocenium redox process (referred to hereafter as Fc^{+/0}) at 0.0 V.^[105] A full listing of CV and SWV scans are reported in Appendix C (Figure C.75-C.91). The 3-5 mM concentrations (using standard

voltammetry conditions) are expected to reflect the *lower* Sn-SDI:Sn-(NCCD₃)₂ ratios among the NMR studies (Table 5.3). As such, there are presumed to be *at minimum* three distinct electrochemically active species in solution; predominantly **9** and an equimolar amount of the free SDI ligands, and a smaller amount of Cl₄Sn-SDI complexes. It is possible that other minor species are also present, either produced by the exchange equilibrium or by EC (electrochemical→chemical) processes during voltammetric experiments, see Section C.8 and Figure C.25 in Appendix C.

Our approach to understanding the electrochemical behaviour of these dynamic mixtures, similar to our NMR investigation, was to first examine the solution voltammetry of **9** to serve as a reference against the Cl₄Sn-SDI system. A CV from this study is depicted in Figure 5.10a. Attempts to implement internal referencing with ferrocene were confounded by adverse reactivity, thus the voltammograms of **9** presented here and in Section C.11 have made use of external referencing to equivalent concentrations of ferrocene versus the solid Ag wire *quasi*-reference electrode.

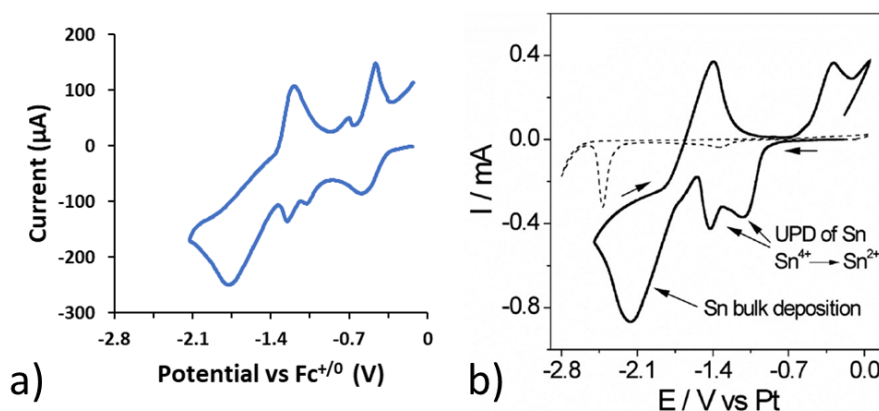
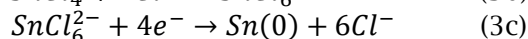
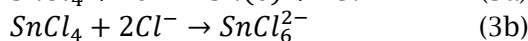
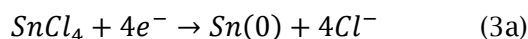


Figure 5.10. (a) CV of 0.005 M SnCl₄/acetonitrile, 0.07 cm² Pt working electrode, 200 mV · s⁻¹ (from this work); (b) CV of 0.1 M SnCl₄/BMP-TFSI, 0.5 cm² Cu working electrode, 10 mV · s⁻¹ (Adapted with permission from R. Al-Salman et al. *Chem. Mater.* **2015**, 27, 3830-3837. Copyright 2015 American Chemical Society)

Extensive work has been reported previously on the polarography and voltammetry of Sn(IV) halides (see Section C.10). From that body of work, Young *et al.* proposed a

mechanism (Scheme 5.3) for the reduction of SnCl_4 wherein the overall four-electron reduction process (3a) is limited by a concurrent chemical process to form SnCl_6^{2-} (3b), which is reduced at larger negative potentials (3c).^[107]



Scheme 5.3. Redox processes operative in the reduction of SnCl_4 in solutions according to Young.^[107]

Our voltammetry of $\text{Cl}_4\text{Sn}(\text{NCCH}_3)_2$ in CH_3CN strongly resembles that of a 2015 study by Al-Salman *et al.* which reported CV of SnCl_4 in an ionic liquid (Figure 5.10b).^[106] Three cathodic processes are observed in Al-Salman's CV, of which the first two are assigned to underpotential $\text{Sn}(\text{IV} \rightarrow \text{II})$ and $\text{Sn}(\text{II} \rightarrow 0)$ reductions. The third cathodic peak at about -2.2 V is assigned by Al-Salman to bulk deposition, i.e. $\text{Sn}(\text{IV}) \rightarrow \text{Sn}(0)$, with a typical offset anodic 'stripping' peak at about -1.4 V (their potentials are only to the Pt *pseudo*-reference electrode and hence not on the $\text{Fc}^{+/0}$ scale). A second anodic peak could then be from a solution-phase $\text{Sn}(\text{II} \rightarrow \text{IV})$ process. Our results strongly resemble this overall behaviour in CV, notwithstanding small differences that can be reasonably attributed to differences in solvents (ionic liquid vs. CH_3CN) and analytes (SnCl_4 vs. $\text{Cl}_4\text{Sn}(\text{NCCH}_3)_2$ in equilibrium), and are less comparable to polarographic studies in which $\text{Sn}(0)$ is expected to become amalgamated. Nevertheless, the $\text{Sn}(\text{IV})$ chloride redox mechanisms painstakingly elucidated by Young and others via polarography should not be discounted, especially regarding the possible role of $[\text{SnCl}_5\text{X}]^{n-}$ and $[\text{SnCl}_6]^{2-}$ species in the equilibria.

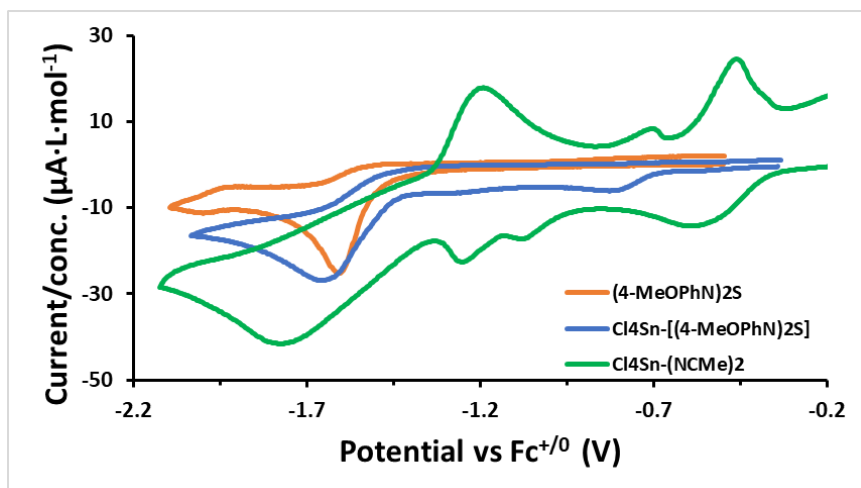


Figure 5.11. Overlay of cyclic voltammograms taken in $\text{CH}_3\text{CN}/n\text{Bu}_4\text{PF}_6(0.2 \text{ M})$ from $(4\text{-MeOPhN})_2\text{S}$ (orange trace), **1** (blue trace), and **9** (green trace), all scan rates are 0.200 V/s . Dividing the current by analyte concentrations provides more accurate comparisons of the different peak heights.

The results for the voltammetry of **1**–**5** are presented in detail in Section C.11, and may be summarized by the overlays presented in Figure 5.11, which reports on the cathodic region of **1** compared to that of the free SDI. In our previous investigation of the voltammetry of the SDIs used in this work, CH_2Cl_2 was used as the generally more suitable solvent for these molecules. To ensure that the comparisons made here for **1**–**5** are valid, two of the free SDIs, $(4\text{-MeOPhN})_2\text{S}$ and $(4\text{-MePhN})_2\text{S}$, were re-investigated in $\text{CH}_3\text{CN}/n\text{Bu}_4\text{PF}_6(0.2 \text{ M})$, of which the former is shown in Figure 5.11. A representative CV of **9** is also included for purposes of discussion. Up to the cutoff around -2.2 V , the CV traces of **1** and the free SDI are almost identical, indicating that the SDI ligand somehow dominates the voltammetric response of this mixture, which we understand to consist of about 14% complex **1** and 43% each of unbound SDI and **9** (Table 5.3). Under these conditions, complex **1** has a small cathodic peak at about -0.8 V , and almost continual cathodic current flow from this point until the trace merges with the main cathodic peak for the mixture at -1.66 V , slightly further negative than -1.61 V for the SDI in the same solvent/electrolyte.

Even more telling is the complete absence of anodic processes in the whole range up to -0.25 V, whereas solutions of **9** show several strong anodic peaks. In summary, there is evidence for the presence of some cathodic activity from either **1** or **9**, but the dominant processes seem to be those of the SDI ligands. The only reasonable interpretation that we can put forward for these results is that the SDI massively suppresses the reduction processes of Sn(IV) in this solvent/electrolyte system, even when the mixture is in dynamic equilibrium. The SDI ligands, therefore, do seem to be redox-active. Presumably, this means that the short-lived SDI anions formed in reduction are stronger ligands than the neutral molecules, coordinate upon reduction, and suppress all or most of the cathodic processes that otherwise operate on **9**. Regrettably, the complexity of these solution equilibria does not afford suitable conditions to be able to systematically compare the SDI substituent effects on the redox behaviours of their SDI complexes. Summary voltammetric data from this study that compare the ligands and complexes are presented in Table 5.5, but the reader should recognize that a small positive adjustment is required for potentials of the SDIs that were only measured in CH_2Cl_2 /electrolyte solutions (**L3-L5**) for valid comparisons.

Table 5.5. Principal cathodic peak potentials of solutions containing Sn-complexes in CH_3CN , **C1-C5** (E_c^2), compared to solutions of only their corresponding unbound ligands in CH_2Cl_2 or CH_3CN as indicated, **L1-L5** (E_c^1). All values are internally referenced to $\text{Fc}^{+/0}$.

n	Scan rate ($\text{V}\cdot\text{s}^{-1}$)	Ln E_c^1 (V)	Cn E_c^2 (V)^d	ΔE (V)
1	0.200	-1.717 ^a / -1.608 ^b	-1.659	0.058 / -0.051
2	0.200	-1.645 ^a / -1.576 ^b	-1.618	0.027 / -0.042
3	0.200	-1.596 ^a	-1.718	-0.122
4	0.200	-1.467 ^a	-1.360	0.107
5	0.500	-2.770 ^c	-2.620	0.150

^a 0.004 – 0.005 M analyte, 0.4 M [$^n\text{Bu}_2\text{N}$][PF_6] in CH_2Cl_2 ; working electrode: glassy carbon (GC) (7.1 mm^2), reference electrode: Ag wire, counter electrode: coiled Pt wire. ^b 0.004 M analyte, 0.2 M [$^n\text{Bu}_2\text{N}$][PF_6] in CH_3CN ; working electrode: Pt (7.1 mm^2), reference electrode: Ag wire, counter electrode: coiled Pt wire. ^c 0.007 M analyte, 0.4 M [$^n\text{Bu}_2\text{N}$][PF_6] in CH_2Cl_2 ; working electrode: Pt (7.1 mm^2), reference electrode: Ag wire, counter electrode: coiled Pt wire. ^d 0.003 – 0.006 M analyte, 0.2 M [$^n\text{Bu}_2\text{N}$][PF_6] in CH_3CN ; working electrode: Pt (7.1 mm^2), reference electrode: Ag wire, counter electrode: coiled Pt wire.

5.3. Conclusions

A series of sulfur diimides (SDIs) were combined with SnCl_4 to form the corresponding $\text{Cl}_4\text{Sn}[\kappa^2\text{-}N,N'\text{-SDI}]$ complexes **1–5**. In the course of synthetic work, a novel sulfinylaniline (PhNSO) complex of SnCl_4 was made, $\text{Cl}_4\text{Sn}(\kappa^1\text{-O-PhNSO})_2$, **10**. All of these compounds are previously unreported, and represent the first structurally characterized complexes where a diaryl-SDI is bidentate to the metal centre (**1–4**), and the first example of acyclic $\kappa^1\text{-O}$ coordination of a sulfinylamine (RNSO) to a metal (**10**). Solution-state characterizations of **1–5** were complicated by extremely low solubility in non-coordinating organic solvents, necessitating dissolution in acetonitrile which displaces the SDI ligands in a concentration-dependent equilibrium that favours formation of the *bis*-acetonitrile adduct of SnCl_4 (**9**) in dilute solutions. Building on our previous systematic investigation of SDIs and their electrochemical properties,^[43] our aim was to assess their redox behaviour in complexes as prospective redox-active ligands. While this work indicates that the SDIs may indeed be operating as redox-active ligands, the complex mixtures produced by the ligand exchange equilibrium in acetonitrile were not conducive to a systematic evaluation of their electrochemical behaviour, and thus our goals were not fully realized. However, the valuable data and insights gleaned from this undertaking provide a clear direction and incentive for further research in this promising area, since confirmation and quantification of the electrochemical properties of **1–5** were impeded only by the lack of a suitable non-coordinating solvent. An alternative route forward would be employing SDIs that are stronger donors, such as Stalke's hypersilyl SDIs,^[52] so that displacement of the SDI ligands is mitigated or precluded. In order to retain the redox-tunability seen in the free diaryl SDIs,^[43] it may even be possible to create an asymmetric SDI with one aryl-N and one hypersilyl-N substituent using the rearrangement method reported by Bestari and Oakley,^[108] or alternative synthetic routes to asymmetric SDIs described in literature.^[109–111]

5.4. Experimental Section

5.4.1. Reagents and General Procedures.

Tin tetrachloride, either neat or 1 M in CH₂Cl₂, was purchased from Sigma-Aldrich and used as received. Aryl sulfur diimides, Ar-NSN-Ar, were synthesized using methods from our previous work.^[43] *Bis(tert-butyl)sulfurdiimide* was synthesized by the literature method,^[112] and redistilled under vacuum before use. Unless otherwise stated, all reactions were performed under N₂ using modified Schlenk and vacuum line techniques. NMR were obtained on a 300 MHz Bruker Avance II or 700 MHz Bruker Avance III HD spectrometer. Low-temperature NMR spectroscopy utilized the Bruker SmartCooler BCU II on the 700 MHz spectrometer. Sealed ampoules of acetonitrile-*d*₃ were purchased from Sigma-Aldrich and used as received for NMR samples. ¹H NMR spectra were referenced to residual acetonitrile (CD₂HCN) at 1.94 ppm and ¹³C NMR spectra were referenced to CD₃CN at 1.32 ppm. ¹⁹F spectra were referenced to external CFCl₃ at 0.0 ppm. ¹¹⁹Sn NMR spectra were referenced to external tetramethyl tin (90% in *d*⁶-benzene) at 0.0 ppm.

5.4.2. Chemical Synthesis

Synthesis of [N,N'-bis(4-methoxyphenyl)sulfurdiimide-κ²-N,N']tetrachlorotin (1)

In a dry Schlenk tube, *bis(4-methoxyphenyl)sulfurdiimide* (0.58 g, 2.1 mmol) was dissolved in 15 mL of CH₂Cl₂ that was distilled over CaH₂. SnCl₄ (0.53 g, 2.0 mmol) was dissolved in 10 mL dry CH₂Cl₂ and syringe-transferred under nitrogen to be added dropwise to the stirring solution. On contact with SnCl₄, the solution (very dark red from the sulfur diimide) immediately turned very dark blue. Stirring continued for an hour, then filtered on a filter-stick, leaving dark blue crystals, confirmed by SC-XRD to be the titular coordination complex. Yield: 0.70 g, 65%. ¹H NMR (700 MHz, CD₃CN, ppm): δ = 3.80 (s, 6H, CH₃), 6.96 (d, 8.7 Hz, 4H, *m*-ArH), 7.24 (d, 8.6 Hz, 4H, *o*-ArH). ¹³C{¹H} NMR (176 MHz, CD₃CN, ppm): δ = 56.2 (s, CH₃), 115.4 (s, *m*-ArC), 130.2 (s, *o*-ArC), 138.0 (s, *i*-ArC), 162.0 (s,

p-ArC). ^{119}Sn NMR (261 MHz, CD_3CN , ppm): $\delta = -615$ (s, Sn). FTIR (cm^{-1}): 1254, 1000, 972, 826, 726, 553. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{Cl}_4\text{N}_2\text{O}_2\text{SSn}$: C, 31.44; H, 2.64; N, 5.24; S, 6.00%. Found: C, 31.28; H, 2.37; N, 5.22; S, 6.33%.

Synthesis of [N,N'-bis(4-methylphenyl)sulfurdiimide- κ^2 -N,N']tetrachlorotin (2)

In a side-arm round-bottom flask, *bis*(4-tolyl)sulfurdiimide (1.80 g, 6.4 mmol) was dissolved in CHCl_3 and heated to 50°C in a water bath. Dissolved SnCl_4 (0.8 mL, 6.8 mmol) in CHCl_3 and added dropwise by addition funnel. The red SDI solution changed instantaneously to a dark blue/green. Let stir at 50°C for 30 minutes, then cooled to room temperature (RT). Filtered on a filter-stick under nitrogen and dried, leaving green crystals. Yield: 2.94 g, 86%. ^1H NMR (700 MHz, CD_3CN , ppm): $\delta = 2.34$ (s, 6H, CH_3), 7.21 (d, 8.4 Hz, 4H, *m*-ArH), 7.24 (d, 7.7 Hz, 4H, *o*-ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CD_3CN , ppm): $\delta = 20.9$ (s, CH_3), 127.8 (s, *o*-ArC), 130.8 (s, *m*-ArC), 141.5 (s, *p*-ArC), 142.5 (s, *i*-ArC). ^{119}Sn NMR (261 MHz, CD_3CN , ppm): $\delta = -617$ (s, Sn). FTIR (cm^{-1}): 1250, 1034, 982, 849, 776, 504. Raman (100 mW, cm^{-1}): 1250, 984, 851, 777, 331, 292. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{Cl}_4\text{N}_2\text{SSn}$: C, 33.44; H, 2.81; N, 5.57; S, 6.38%. Found: C, 33.67; H, 2.24; N, 5.69; S, 6.24%.

Synthesis of [N,N'-bis(4-fluorophenyl)sulfurdiimide- κ^2 -N,N']tetrachlorotin (3)

Following the procedure for **2**, dissolved *bis*(4-fluorophenyl)sulfurdiimide (0.3 g, 1.2 mmol) in ~ 10 mL CHCl_3 , added SnCl_4 (0.4 mL, 3.4 mmol), and harvested the crystals. Yield: 0.35 g, 57%. ^1H NMR (700 MHz, CD_3CN , ppm): $\delta = 7.17$ (t, 7.7 Hz, 4H, *m*-ArH), 7.33 (s, 4H, *o*-ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CD_3CN , ppm): $\delta = 117.2$ (d, 23.0 Hz, *m*-ArC), 130.2 (d, 9.0 Hz, *o*-ArC), 140.2 (d, 3.3 Hz, *i*-ArC), 163.5 (d, 251 Hz, *p*-ArC). ^{19}F (282 MHz, CD_3CN , ppm): $\delta = -116.2$ (s, *p*-ArF). ^{119}Sn NMR (261 MHz, CD_3CN , ppm): $\delta = -616$ (s, Sn). FTIR (cm^{-1}): 1262, 1013, 984, 856, 733, 498. Raman (75 mW, cm^{-1}): 1249, 984, 858, 793, 335, 300, 145. Anal. Calcd for $\text{C}_{12}\text{H}_8\text{Cl}_4\text{F}_2\text{N}_2\text{SSn}$: C, 28.22; H, 1.58; N, 5.48; S, 6.28%. Found: C, 28.18; H, 1.48; N, 5.34; S, 6.95%.

Synthesis of [N,N'-bis(4-chlorophenyl)sulfurdiimide- κ^2 -N,N']tetrachlorotin (4)

Bis(4-chlorophenyl)sulfurdiimide (0.48 g, 1.7 mmol) was dissolved in ~10 mL CHCl₃, and cooled to -47°C in *m*-xylenes slush bath. SnCl₄ (1 M in CH₂Cl₂, 1.8 mL, 1.8 mmol) was diluted in ~10 mL CHCl₃ in an addition funnel and added dropwise over 40 minutes. The colour turned very dark immediately, so much so that the colour was indeterminate. The solution was stirred overnight, and the crystals were harvested after washing with CHCl₃. Yield: 0.51 g, 70%. ¹H NMR (700 MHz, CD₃CN, ppm): δ = 7.31 (d, 8.6 Hz, 4H, *m*-ArH), 7.44 (d, 8.5 Hz, 4H, *o*-ArH). ¹³C{¹H} NMR (176 MHz, CD₃CN, ppm): δ = 125.7 (s, *o*-ArC), 130.1 (s, *m*-ArC), 133.2 (s, *p*-ArC), 142.0 (s, *i*-ArC). ¹¹⁹Sn NMR (261 MHz, CD₃CN, ppm): δ = -618 (s, Sn). FTIR (cm⁻¹): 1014, 958, 830, 695, 482. Raman (75 mW, cm⁻¹): 987, 851, 696, 341, 146. Anal. Calcd for C₁₂H₈Cl₆N₂SSn: C, 26.51; H, 1.48; N, 5.15; S, 5.90%. Found: C, 26.79; H, 1.80; N, 5.20; S, 5.70%.

Synthesis of [N,N'-bis(tert-butyl)sulfurdiimide- κ^2 -N,N']tetrachlorotin (5)

Following the procedure for 2, *bis*(*tert*-butyl)sulfurdiimide (0.18 g, 1.0 mmol) was reacted with SnCl₄ (0.1 mL, 1.2 mmol). SDI solution turned from very light yellow to light pink on addition of SnCl₄, and very small white crystals of the complex were collected. Yield: 0.22 g, 73%. ¹H NMR (700 MHz, CD₃CN, ppm): δ = 1.72 (s, CH₃). ¹³C{¹H} NMR (176 MHz, CD₃CN, ppm): δ = 30.9 (s, CH₃), 68.8 (s, CCH₃). ¹¹⁹Sn NMR (261 MHz, CD₃CN, ppm): δ = -563 (s, Sn). FTIR (cm⁻¹): 1176, 1116, 872, 760, 499. Raman (50 mW, cm⁻¹): 1109, 789. Anal. Calcd for C₈H₁₈Cl₄N₂SSn: C, 22.10; H, 4.17; N, 6.44; S, 7.37%. Found: C, 21.70; H, 4.47; N, 6.88; S, 7.21%.

- κ^1 -NFollowing the method of Koutsantonis *et al.*,^[100] dissolved SnCl₄ (4.95 g, 19 mmol) in 8 mL dry CHCl₃, and added CH₃CN (2 mL, 38 mmol). Clear and colourless crystals began to form in ~30 minutes, and the solution was left undisturbed for 72 hours. Solvent was decanted and the product dried by vacuum, whereupon the crystals turned an opaque

white. Yield: 4.49 g, 69%. ^1H NMR (700 MHz, CD_3CN , ppm): δ = 1.97 (s, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CD_3CN , ppm): δ = 1.77 (s, CH_3), 117.8 (s, CCH_3). ^{119}Sn NMR (261 MHz, CD_3CN , ppm): δ = -683 (s, Sn).

Synthesis of di[N-sulfinylaniline- κ^1 -O]tetrachlorotin (10)

Following a modified method from Roesky,^[16] dissolved *N*-sulfinylaniline (14.78 g, 106 mmol) in ~50 mL CHCl_3 in a side-arm RBF. Tin tetrachloride (4.9 mL, 42 mmol) was diluted in ~50 mL CHCl_3 in an addition funnel and attached to the RBF. The dissolved PhNSO was cooled to -40°C in a CO_2 /acetone bath, then SnCl_4 was added dropwise over several minutes. When addition was complete, warmed to RT and stirred for 20 hours, then refluxed for 44 hours during which the colour turned very dark red. Cooled to RT and stored at -30°C for several days with no visible formation of solid. Removed solvent by vacuum, leaving yellow/brown crystals suitable for SC-XRD. Yield: 18.56 g, 82%. ^1H NMR (300 MHz, CDCl_3 , ppm): δ = 7.43 (m, 3H: *m*-ArH and *p*-ArH), 7.87 (d, 3 Hz; 2H: *o*-ArH).

5.4.3. Crystallography

A summary crystal data and refinement table, full reports on each structure and analyses of the intra- and intermolecular distances and angles of all SC-XRD experiments are provided in Sections C.1 – C.4 of Appendix C.

5.4.4. Voltammetry

Cyclic (CV) and square-wave (SWV) voltammetry experiments were performed with a Princeton Applied Research PARSTAT 2273 potentiostat using the PowerSuite software version 2.58, and the embedded PowerCV software version 2.46. Experiments were done in a nitrogen-filled MBraun glovebox with oxygen and moisture rigorously excluded. The working electrode used was a platinum inlaid-disk electrode with a surface area of 7.1 mm^2 , the (quasi-)reference electrode was silver wire, and the counter electrode was coiled

platinum wire. Tetrabutylammonium hexafluorophosphate ($[\text{tBu}_4\text{N}][\text{PF}_6]$) was recrystallized from 99% ethanol and used as supporting electrolyte. Acetonitrile was initially distilled from P_2O_5 , subsequently distilled from CaH_2 , and freeze-thaw degassed before being transferred to the glovebox and stored over molecular sieves.

5.4.5. Computation

Geometry optimization and frequency computations were carried out by Gaussian 16w v1.1 using the GaussView 6.0.16 GUI. The functional used was B3PW91, with D3BJ dispersion correction and a def2-TZVP basis set. Vibrational spectra (IR and Raman) were computed using the frequency calculation in Gaussian 16w. Complexation energies were calculated by dividing DFT-optimized structures into SnCl_4 and Ligand fragments, and a single-point calculation was done at the same level of theory with counterpoise active (NBO calculations must be disabled to run counterpoise calculations). Lattice energy calculations were run in CrystalExplorer v21.5 (CE),^[113-114] which uses the embedded Tonto computational software,^[115] at the B3LYP-DGDZVP level of theory with D2 dispersion correction applied. CE outputs interaction energies between the originating molecule and each unique symmetry-related molecule in the lattice within a specified radius (3.8 Å by default). These interaction energies are tallied along with the multiplicity of each interaction, the sum of which is divided by 2 to obtain the lattice energy.

5.5. References and Notes

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Chapter 6. Conclusions and Future Directions

6.1. Conclusions

In the course of this work, we became aware of NoSpherA2, a recently developed tool with the potential to advance our methods of refining structure models from SC-XRD experiments. Chapter 2 gives a brief primer on contemporary refinement methods and their limitations with particular focus on the Independent Atom Model (IAM) which assumes perfectly spherical and neutral atomic scattering factors. The Hirshfeld Atom Refinement (HAR) method that NoSpherA2 uses is described along with the consistent improvements NoSpherA2 offers by generating more realistic custom atomic scattering factors. A critical review of recent studies that utilized NoSpherA2, including my published work which comprises Chapter 3 of this thesis, is then presented, detailing the exceptional improvements in structural precision attained using NoSpherA2. Emphasis is placed on the accessibility of NoSpherA2, which is embedded in the ubiquitous and free Olex2 program and runs on a typical personal computer. In light of the superb quality of model structures made possible by NoSpherA2 and the minimal resources it requires to implement, a call-to-action is made to the chemical crystallography community to adopt NoSpherA2 (and similar software that may follow) as routine procedure in the refinement of crystal structure models.

Chapter 3 reports an in-depth comparative analysis of 14 crystal structures refined using both NoSpherA2 and IAM, and shows the greatly increased accuracy in hydrogen atom placements and non-hydrogen structural features such as bond precision that were achieved using NoSpherA2. The crystal structures themselves are significant contributions to rare structure classes and are thoroughly evaluated, with particular attention given to non-classical hydrogen bonds and dipolar nitrile-nitrile interactions and their relevance to the supramolecular structures.

The synthesis and characterization of a coherent series of N,N' -sulfur diimides (SDIs) is presented in Chapter 4. Comprehensive voltammetry experiments demonstrate the very strong influence of the N -substituents on their redox potentials and radical anion lifetimes. A remarkable finding of this study is that the reduction potentials of the diaryl-SDIs are *predictable*, correlating linearly with the calculated LUMO energy of the neutral SDI. Combined with the vast range of possible substituent combinations, this outstanding result establishes SDIs as a highly flexible template for designing compounds and, potentially, coordination complexes with bespoke redox properties.

Chapter 5 presents five novel complexes of tin(IV) tetrachloride (SnCl_4) with SDI ligands, adding to the one previously known exemplar from Roesky.^[1] X-ray crystallography confirms that the diaryl-SDIs coordinate in $\kappa^2\text{-}N,N'$ fashion, which was already known for Roesky's *bis*-trimethylsilyl SDI complex but never previously confirmed for diaryl-SDIs, as well as the first $\kappa^1\text{-}O$ coordination of an N -sulfinylamine (RNSO). Voltammetric experiments on the complexes provide evidence that the SDIs suppress $\text{Sn(IV} \rightarrow \text{0)}$ reduction, despite the activity of a ligand-exchange equilibrium which favours displacement of SDIs at the low concentrations used for voltammetry ($\sim 0.005 \text{ mol} \cdot \text{L}^{-1}$). While tentative due to obfuscating conditions, this result suggests that SDIs are acting as RA ligands in this system.

In summary, this thesis describes significant advancements in two important areas: sulfur diimides and their potential utility as redox-active ligands and X-ray crystallography. Chapters 2 and 3 demonstrate the ability of NoSpherA2 to dramatically improve the accuracy of crystallographic models over contemporary methods, and make an evidence-based case for modernizing standard procedures of SC-XRD experiments via the implementation of Hirshfeld Atom Refinement with custom aspherical atomic scattering factors. X-ray crystallography is one of the most important tools used for

structural characterizations, and the exceptional model quality and accessibility that NoSpherA2 offers to the field represents a significant and exciting step forward. Chapters 4 and 5 are the most comprehensive repository of information extant in literature specifically focused on SDIs, and report on the preliminary steps taken into a systematic investigation of SDIs as redox-active ligands. The extensive collection of new data (with copious reference and appreciation to preceding relevant work) and in-depth discussion of the fundamental properties of SDIs, both on their own and as ligands, provides a valuable resource for any subsequent research in the area.

6.2. Future Directions

The indication from Chapter 5 that SDIs are acting as redox-active ligands is an exciting finding, and is the most important avenue of research to follow up on. The first and most urgent task should be to definitively establish whether the SDIs are acting as redox-active ligands in this system, and quantify that behaviour if it is affirmed. The key issues that prevented this work from doing so were 1) the insolubility of the SnCl_4 complexes in non-coordinating solvents, and 2) the tendency of the SDI ligands to be displaced by acetonitrile. The solubility issue may have a very simple solution. Roesky made the first SnCl_4 complex with *bis*-TMS SDI^[1] and was able to recrystallize the complex and obtain ^1H NMR data in liquid SO_2 . It is plausible that the complexes from Chapter 5 would also be soluble in SO_2 . This approach could allow purification by recrystallization as well as solution-state characterizations of the complexes free from the interference brought on by the ligand exchange equilibrium, including voltammetric and EPR experiments which would conclusively answer the crucial question of whether SDIs are truly acting as redox-active ligands.

The voltammetric data from Chapter 4 demonstrate that the electronic and redox properties of SDIs are strongly influenced by the *N*-substituents, and Chapter 5 shows

that the SDIs with the most electron-donating substituents (R-NSN-R, R = 4-methoxyphenyl and *tert*-butyl) were less susceptible to being displaced by acetonitrile. It follows that SDIs with more and/or stronger electron-donating substituents would be stronger ligands. That would particularly benefit diaryl-SDIs, which have a very limited coordination chemistry due in part to their being poor σ -donors,^[2] and could be realized by using aryl substituents with e.g. 4-*N,N*-dimethylamino or 3,5-*N,N*-diethylamino, as in Figure 6.1a, which are considerably more electron-donating than methoxy.^[3] Although alkyl- and silyl-SDIs are already substantially better σ -donors than their aryl congeners, enhancing their electron-donating properties could also be very useful, especially considering that even *bis(tert-butyl)*SDI was subject to displacement from SnCl₄ by acetonitrile. The recently reported hypersilyl-SDIs (see Figure 6.1b) exhibit exceptionally high negative charge density at the nitrogen atoms, and are expected to be excellent donors for metal chelation, provided the steric bulk of the substituents does not preclude coordination.^[4]

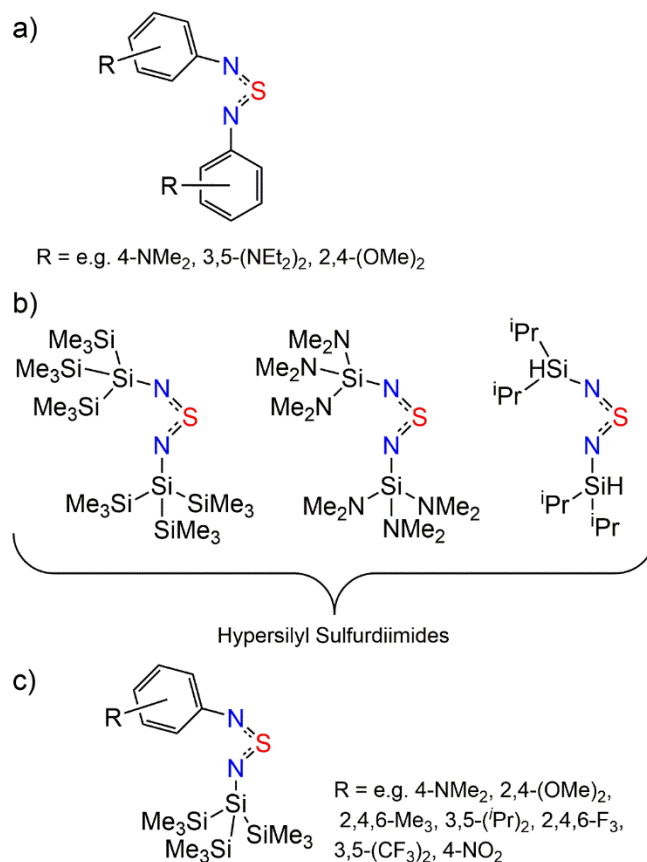


Figure 6.1. a) Examples of proposed synthetic targets for future SDI coordination chemistry. b) Hypersilyl SDIs reported by Stark et al.^[4]

Using the synthetic or scrambling methods described in Section 1.4.1.,^[5-10] It might be possible to create an asymmetric sulfur diimide where one *N*-substituent is aryl and the other is e.g. hypersilyl, as in Figure 6.1c. It would be fascinating to investigate whether such an SDI could be the ‘best of both worlds’, taking advantage of the strong σ -donating properties of hypersilyl-SDIs to make them stronger ligands while retaining the extended π -system and easily tuned redox properties of the diaryl-SDIs.

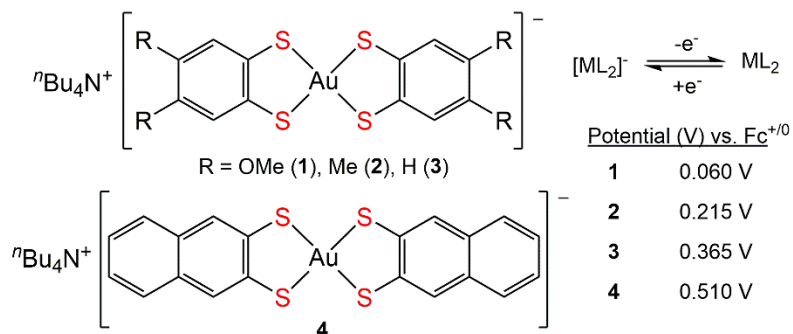


Figure 6.2. Dithiolenes complexes and their oxidation potentials vs $\text{Fc}^{+/0}$. Cyclic voltammetry was conducted in DMF with $\sim 0.10 \text{ mol} \cdot \text{L}^{-1}$ $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte with a Pt working electrode.

It would be worthwhile to explore variations in not just the aryl substituents, but in the aryl systems as a whole. Examples of naphthyl^[11-12] and biphenyl^[13] SDIs have been reported and minimally characterized, but have otherwise been essentially ignored up to this point. Dithiolenes are a well-established category of redox-active ligands of the type shown in Figure 6.2. The redox properties of their coordination complexes respond to substituent effects in a fashion qualitatively similar to SDIs,^[14-17] and voltammetry of the Au(III) complexes in Figure 6.2 demonstrates a difference in the redox potentials between phenyl and naphthyl systems, wherein the naphthyl derivative (4) has a significantly higher oxidation potential vs $\text{Fc}^{+/0}$ than the phenyl (1). It is reasonable to expect that SDIs employing naphthyl-based substituents would have a similar modulation to their redox properties. These systems would offer a vast range of possible derivatives, and may be most sensibly approached by a survey of α - and β -naphthyl SDIs using a selection of the same substituents from Chapter 4 whose voltammetry has been thoroughly characterized at various positions relative to the *N*-attachment, illustrated in Figure 6.3 below.

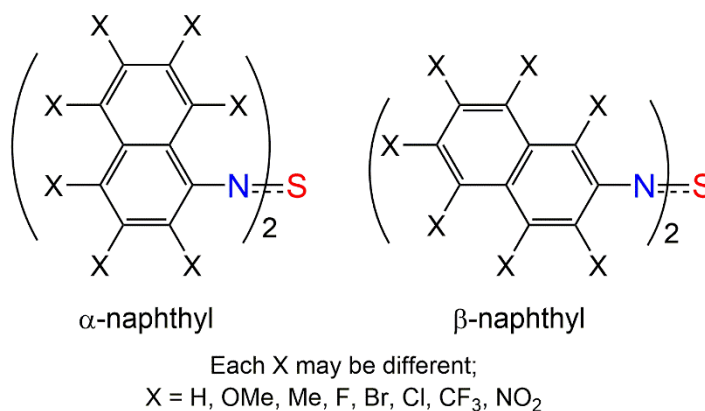


Figure 6.3. Proposed naphthyl-SDI derivatives

In this work, tin tetrachloride was chosen because the strongly Lewis acidic Sn centre was anticipated to compensate somewhat for the poor σ -donating power of diaryl-sulfurdiimides, and because the redox non-innocence observed in SDI ligands^[11, 18-22] was expected to be inoperative for Sn(IV), thus limiting the range of expected behaviours. It is possible, however, that a more electron-rich metal centre would be a conducive substrate for diaryl-SDI ligands, since κ^2 - N,N' -SDIs in general are known to be strong π -acceptors^[23-25] and Chapter 4 demonstrated that aryl-SDIs far surpass alkyl and TMS analogues in this respect. A reasonable place to start could be the Ti(II) $\text{Cp}_2\text{Ti}(\text{C}_2(\text{SiMe}_3)_2)$ complex prepared by Kaleta^[17] (Figure 6.4) which spontaneously transfers two electrons to $(\text{TMS-N})_2\text{S}$ upon complexation, resulting in a Ti(IV) complex with a 2- charge on the SDI. An aryl SDI in such a system might be a stronger ligand than would be indicated by their σ -donating ability.

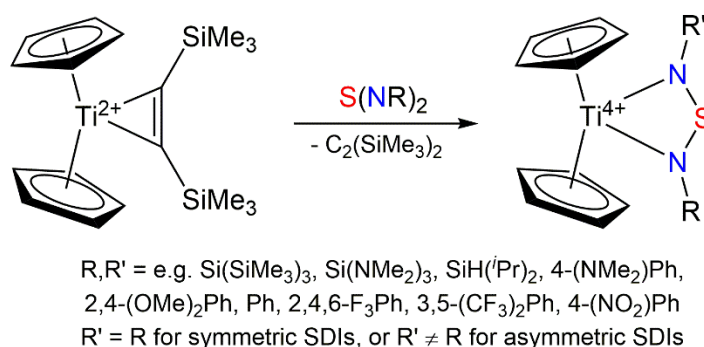


Figure 6.4. Titanocene-SDI complex synthesis from Kaleta et al.,^[21] noting two-electron transfer from Ti(II) to the redox non-innocent SDI ligand.

Finally, it would be interesting to investigate the viability of inducing a change in a metal's oxidation state by varying the substituents of an SDI ligand. For example, Meij and Hunter reported complexes of Group 6 metal carbonyls with *tert*-butyl SDI ligands^[18, 20] in which the metals (Cr, Mo, W) are in the M(0) oxidation state, with no electron transfer to the SDI ligands observed. If a more electron-withdrawing SDI could be used in such a complex, perhaps even one of the more electron-rich diaryl-SDIs, it might be reasonable to expect redox non-innocent behaviour to be operative, similar to the lanthanocene complexes with *bis*-TMS SDI made by Klementyeva which underwent one-electron transfer to the SDI ligand (See Figure 6.5b).^[22] Those complexes exhibited interesting paramagnetic behaviour as a result, and expanding this behaviour to transition or main group metals by tuning the redox properties of SDI ligands would offer a novel avenue of research into, to cite just one example, thiazyl-based molecular magnets.^[26-29]

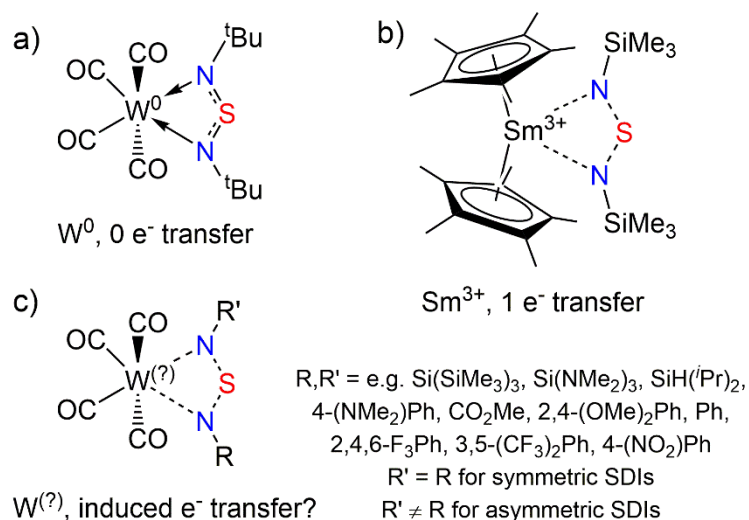


Figure 6.5. Known complexes from a) Hunter^[18] and b) Klementyeva,^[22] which measure zero- and one-electron transfer to the SDI ligand, respectively. c) Proposed target complex with possible SDI ligands that might induce $M \rightarrow \text{SDI}$ electron transfer.

The only SDI ligands that have been confirmed and thoroughly investigated in the suggested target complexes (i.e. lanthanocene complexes from Klementyeva^[22] in Figure 6.5b, group 6 carbonyl complexes from Meij^[20] and Hunter^[18] in Figure 6.5a, and titanocene complexes from Kaleta^[21] in Figure 6.4), are $S(\text{N}^t\text{Bu})_2$ and $S(\text{NSiMe}_3)_2$. As such, there is an opportunity to greatly expand the variety of SDIs used in these and similar complexes to explore the range of responses that might be evoked.

6.3. References

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Appendix A. Supporting Information for Chapter 3

Reproduced from the Supporting Information document accompanying “Hill, N.D.D.; Boéré, R.T., ‘*Small Molecule X-ray Crystal Structures at a Crossroads*’. *Chem.-Methods*. 2025, e202400052.”

A.1. Geometric Analyses of the Crystal Structures’ Derived Parameters

Table A.1. Puckering parameters for barrelenes, **1** – **3**.

Compound	Ring size	Atom list	q(2) / Å	Phi(2) / deg	q(3) / Å	(Q) / Å	Theta / deg	Phi / deg	Assignment
1	6	C1-C2-C3-C4-C4A-C8A	0.8168(14)	179.65(9)	0.0079(13)	0.8167(14)	89.44(9)	179.65(9)	Boat
	6	C1-C2-C3-C4-C9-C10	0.7917(14)	359.80(10)	0.0013(14)	0.7917(14)	89.91(10)	359.80(10)	Boat
	6	C1-C8A-C4A-C4-C9-C10	0.8251(14)	180.17(9)	-0.0020(14)	0.8250(14)	90.14(10)	180.17(9)	Boat
2	6	C1-C2-C3-C4-C4A-C8A	0.8218(19)	0.15(13)	-0.0067(19)	0.8218(19)	90.47(13)	0.15(13)	Boat
	6	C1-C2-C3-C4-C9-C10	0.7847(19)	180.06(14)	-0.0023(19)	0.7847(19)	90.17(14)	180.06(14)	Boat
	6	C1-C8A-C4A-C4-C9-C10	0.8063(19)	0.49(13)	0.0017(19)	0.8063(19)	89.88(14)	0.49(13)	Boat
3	6	C1-C2-C3-C4-C4A-C8A	0.7528(6)	358.95(4)	0.0011(6)	0.7528(6)	89.92(5)	358.95(4)	Boat
	6	C1-C2-C3-C4-C9-C10	0.8481(6)	181.26(4)	0.0046(6)	0.8482(6)	89.69(4)	181.26(4)	Boat
	6	C1-C8A-C4A-C4-C9-C10	0.8479(6)	358.76(4)	0.0049(6)	0.8479(6)	89.67(4)	358.76(4)	Boat

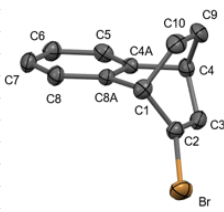
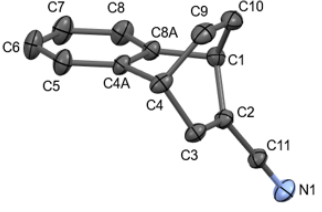
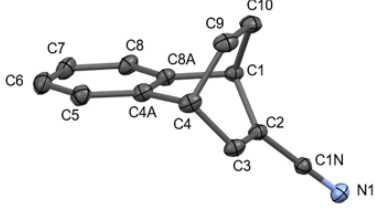




Table A.2. Puckering parameters for semibullvalenes, **4**, **11**, and **13**.

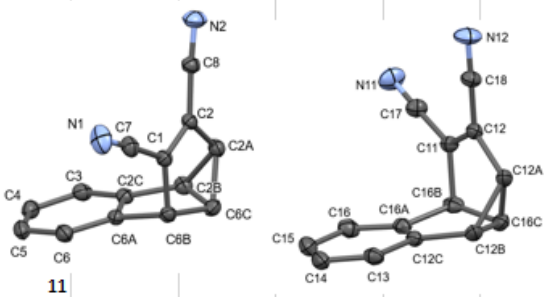
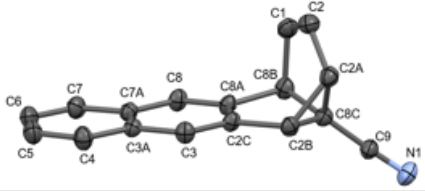
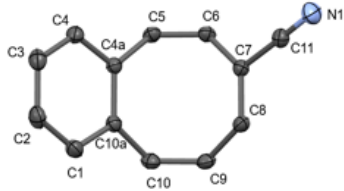
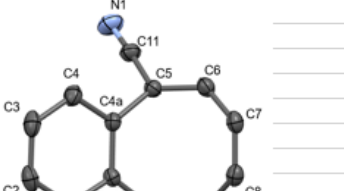
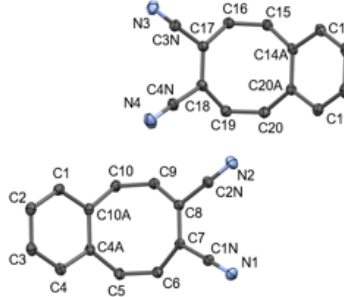
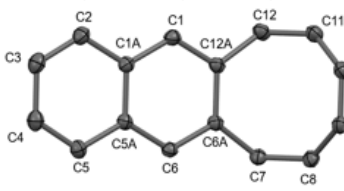
Compound	Ring size	Atom list	q(2) / Å	Phi(2) / deg	q(3) / Å	Phi(3) / deg	(Q) / Å	Assignment
4	5	C1-C2-C2A-C6C-C6B	0.1988(3)	304.64(9)				Twist
	5	C2B-C2C-C6A-C6B-C6C	0.2121(3)	123.23(8)				Twist
	7	C1-C2-C2A-C2B-C2C-C6A-C6B	1.1707(3)	103.345(15)	0.1979(3)	157.52(9)	1.1873(3)	Twist-Boat
11	5	C1-C2-C2A-C6C-C6B	0.1851(10)	302.0(3)				Twist
	5	C2B-C2C-C6A-C6B-C6C	0.2152(10)	125.2(3)				Twist
	7	C1-C2-C2A-C2B-C2C-C6A-C6B	1.1559(10)	104.51(5)	0.1999(10)	155.7(3)	1.1731(10)	Twist-Boat
	5	C11-C12-C12A-C16C-C16B	0.2054(11)	127.0(3)				Twist
	5	C12B-C12C-C16A-C16B-C16C	0.1984(11)	308.0(3)				Twist
	7	C11-C12-C12A-C12B-C12C-C16A-C16B	1.1568(10)	282.37(5)	0.1980(10)	334.4(3)	1.1735(10)	Twist-Boat
13	5	C1-C2-C2A-C8C-C8B	0.195(2)	125.9(6)				Twist
	5	C2B-C2C-C8A-C8B-C8C	0.225(2)	302.4(5)				Twist
	7	C1-C2-C2A-C2B-C2C-C8A-C8B	1.164(2)	284.12(10)	0.193(2)	337.5(6)	1.180(2)	Twist-Boat
 								
4								
								
13								

Table A.3. Puckering parameters for COTs, **5**, **6**, **12**, and **14**.

Compound	Ring size	Atom list	q(2) / Å	Phi(2) / deg	q(3) / Å	Phi(3) / deg	q(4) / Å	(Q) / Å	Assignment
5	8	C4A-C5-C6-C7-C8-C9-C10-C10A	1.1786(4)	226.14(2)	0.0203(4)	226.7(12)	0.0033(4)	1.1788(4)	Tub
6	8	C4A-C5-C6-C7-C8-C9-C10-C10A	1.1797(3)	44.342(16)	0.0483(3)	19.7(4)	0.0099(3)	1.1807(3)	Tub
12	8	C4A-C5-C6-C7-C8-C9-C10-C10A	1.1263(13)	47.49(6)	0.0243(13)	79(3)	-0.0106(13)	1.1266(13)	Tub
	8	C14A-C15-C16-C17-C18-C19-C20-C20A	1.1804(13)	45.64(6)	0.0142(13)	81(5)	0.0018(13)	1.1804(13)	Tub
14	8	C6A-C7-C8-C9-C10-C11-C12-C12A							

*PLATON was unable to calculate puckering parameters for **14**, as there is disorder on the 8-membered ring in the placement of the nitrile substituent between carbons C9 and C10. The major component of the disorder model is shown here.

Table A.4. Puckering parameters for cyclobutenes, **9** – **10**.

Compound	Ring size	Atom list	q(2) / Å	Phi(2) / deg	q(3) / Å	(Q) / Å	Theta / deg	Phi / deg	Assignment
9	4	C1-C2-C2A-C8B	-0.2092(11)						Puckered
	6	C2A-C3-C4-C4A-C8A-C8B	0.1629(10)	310.7(4)	0.0903(10)	0.1862(10)	61.0(3)	310.7(4)	Between Envelope and Half-Chair, closest to Envelope conformation
10	4	C1-C2-C2A-C8B	0.2686(9)						Puckered
	6	C2A-C3-C4-C4A-C8A-C8B	0.2082(8)	134.3(2)	-0.0986(8)	0.2303(8)	115.3(2)	134.3(2)	Between Envelope and Twist-boat, slightly closer to envelope

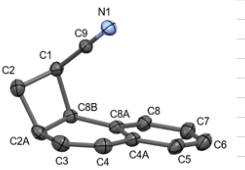
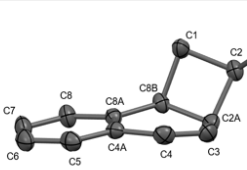



Table A.5. Statistical comparison of C-H bond lengths in 1 to neutron diffraction data.

C-H bond type	AtomA	AtomB	dist	su	Single s.u. criterion			Fit with neutron data?
					-s.u.*2.58	+s.u.*2.58	Neutron mean	
Z ₃ -Csp ³ -H	C1	H1	1.072	0.014	1.03588	1.10812	1.099	fit
Z ₃ -Csp ³ -H	C4	H4	1.087	0.014	1.05088	1.12312	1.099	fit
C(ar)-H	C5	H5	1.079	0.014	1.04288	1.11512	1.085	fit
C(ar)-H	C6	H6	1.062	0.012	1.03104	1.09296	1.085	fit
C(ar)-H	C7	H7	1.104	0.014	1.06788	1.14012	1.085	fit
C(ar)-H	C8	H8	1.056	0.013	1.02246	1.08954	1.085	fit
Csp ² -H	C9	H9	1.038	0.014	1.00188	1.07412	1.085	nofit
Csp ² -H	C10	H10	1.067	0.018	1.02056	1.11344	1.085	fit
Csp ² -H	C3	H3	1.09	0.017	1.04614	1.13386	1.085	fit

Table A.6. Statistical comparison of C-H bond lengths in 2 to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	su	Single s.u. criterion			Fit with neutron data?
					-s.u.*2.58	+s.u.*2.58	Neutron mean	
Z ₃ -Csp ³ -H	C1	H1	1.07	0.02	1.0184	1.1216	1.099	fit
Z ₃ -Csp ³ -H	C4	H4	1.09	0.02	1.0384	1.1416	1.099	fit
C(ar)-H	C5	H5	1.05	0.02	0.9984	1.1016	1.085	fit
C(ar)-H	C6	H6	1.06	0.02	1.0084	1.1116	1.085	fit
C(ar)-H	C7	H7	1.05	0.02	0.9984	1.1016	1.085	fit
C(ar)-H	C8	H8	1.08	0.02	1.0284	1.1316	1.085	fit
Csp ² -H	C9	H9	1.07	0.02	1.0184	1.1216	1.085	fit
Csp ² -H	C10	H10	1.10	0.02	1.0484	1.1516	1.085	fit
Csp ² -H	C3	H3	1.090	0.017	1.04614	1.13386	1.085	fit

Table A.7. Statistical comparison of C-H bond lengths in 3 to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion			Fit with neutron data?
					-s.u.*2.58	+s.u.*2.58	Neutron mean	
Z ₃ -Csp ³ -H	C1	H1	1.084	0.005	1.0711	1.0969	1.099	fit
Z ₃ -Csp ³ -H	C4	H4	1.093	0.006	1.07752	1.10848	1.099	fit
Z ₂ -Csp ³ -H	C9	H9a	1.095	0.006	1.07952	1.11048	1.097	fit
Z ₂ -Csp ³ -H	C9	H9b	1.093	0.006	1.07752	1.10848	1.097	fit
Z ₂ -Csp ³ -H	C10	H10a	1.088	0.007	1.06994	1.10606	1.097	fit
Z ₂ -Csp ³ -H	C10	H10b	1.074	0.006	1.05852	1.08948	1.097	fit
C(ar)-H	C5	H5	1.084	0.006	1.06852	1.09948	1.085	fit
C(ar)-H	C6	H6	1.076	0.007	1.05794	1.09406	1.085	fit
C(ar)-H	C7	H7	1.097	0.006	1.08152	1.11248	1.085	fit
C(ar)-H	C8	H8	1.091	0.006	1.07552	1.10648	1.085	fit
Csp ² -H	C3	H3	1.083	0.006	1.06752	1.09848	1.085	fit

Table A.8. Statistical comparison of C-H bond lengths in 4 to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion			Fit with neutron data?
					-s.u.*2.58	+s.u.*2.58	Neutron mean	
Csp ² -H	C1	H1	1.067	0.004	1.05668	1.07732	1.085	fit
Csp ² -H	C2	H2	1.061	0.005	1.0481	1.0739	1.085	nofit
C(ar)-H	C3	H3	1.074	0.005	1.0611	1.0869	1.085	fit
C(ar)-H	C4	H4	1.066	0.005	1.0531	1.0789	1.085	fit
C(ar)-H	C5	H5	1.078	0.004	1.06768	1.08832	1.085	fit
C(ar)-H	C6	H6	1.066	0.005	1.0531	1.0789	1.085	fit
Z ₃ -Csp ³ -H	C6B	H6B	1.074	0.004	1.06368	1.08432	1.099	nofit
Z ₃ -Csp ³ -H	C2A	H2A	1.070	0.004	1.05968	1.08032	1.099	nofit
Z ₃ -Csp ³ -H	C2B	H2B	1.064	0.004	1.05368	1.07432	1.099	nofit

Table A.9. Statistical comparison of C-H bond lengths in 5 to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion			Fit with neutron data?
					-s.u.*2.58	+s.u.*2.58	Neutron mean	
C(ar)-H	C1	H1	1.054	0.008	1.03336	1.07464	1.085	nofit
C(ar)-H	C2	H2	1.055	0.008	1.03436	1.07564	1.085	nofit
C(ar)-H	C3	H3	1.058	0.009	1.03478	1.08122	1.085	fit
C(ar)-H	C4	H4	1.048	0.008	1.02736	1.06864	1.085	nofit
Csp ² -H	C5	H5	1.052	0.008	1.03136	1.07264	1.085	nofit
Csp ² -H	C6	H6	1.058	0.008	1.03736	1.07864	1.085	fit
Csp ² -H	C8	H8	1.057	0.008	1.03636	1.07764	1.085	fit
Csp ² -H	C9	H9	1.059	0.008	1.03836	1.07964	1.085	fit
Csp ² -H	C10	H10	1.073	0.008	1.05236	1.09364	1.085	fit

Table A.10. Statistical comparison of C-H bond lengths in 6 to neutron diffraction data.

C-H bond	AtomA	AtomB	Dist	s.u.	Single s.u. criterion			Fit with neutron data?
					-s.u.*2.58	+s.u.*2.58	Neutron mean	
C(ar)-H	C1	H1	1.096	0.004	1.08568	1.10632	1.085	fit
C(ar)-H	C2	H2	1.085	0.004	1.07468	1.09532	1.085	fit
C(ar)-H	C3	H3	1.092	0.004	1.08168	1.10232	1.085	fit
C(ar)-H	C4	H4	1.103	0.004	1.09268	1.11332	1.085	fit
Csp ² -H	C6	H6	1.092	0.003	1.08426	1.09974	1.085	fit
Csp ² -H	C7	H7	1.085	0.004	1.07468	1.09532	1.085	fit
Csp ² -H	C8	H8	1.094	0.003	1.08626	1.10174	1.085	fit
Csp ² -H	C9	H9	1.088	0.003	1.08026	1.09574	1.085	fit
Csp ² -H	C10	H10	1.079	0.003	1.07126	1.08674	1.085	fit

Table A.11. Statistical comparison of C-H bond lengths in 7 to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion		Neutron mean	Fit with neutron data?
					-s.u.*2.58	+s.u.*2.58		
Z ₃ -Csp ³ -H	C8B	H8B	1.090	0.004	1.07968	1.10032	1.099	fit
Z ₃ -Csp ³ -H	C2A	H2A	1.096	0.005	1.0831	1.1089	1.099	fit
Csp ² -H	C2	H2	1.073	0.005	1.0601	1.0859	1.085	fit
Csp ² -H	C3	H3	1.100	0.005	1.0871	1.1129	1.085	fit
Csp ² -H	C4	H4	1.084	0.005	1.0711	1.0969	1.085	fit
C(ar)-H	C5	H5	1.095	0.005	1.0821	1.1079	1.085	fit
C(ar)-H	C6	H6	1.097	0.005	1.0841	1.1099	1.085	fit
C(ar)-H	C7	H7	1.099	0.005	1.0861	1.1119	1.085	fit
C(ar)-H	C8	H8	1.088	0.005	1.0751	1.1009	1.085	fit

Table A.12. Statistical comparison of C-H bond lengths in 8 to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion		Neutron mean	Fit with neutron data?
					-s.u.*2.58	+s.u.*2.58		
Csp ² -H	C1	H1	1.098	0.004	1.08768	1.10832	1.085	fit
Csp ² -H	C3	H3	1.089	0.004	1.07868	1.09932	1.085	fit
Csp ² -H	C4	H4	1.088	0.004	1.07768	1.09832	1.085	fit
C(ar)-H	C5	H5	1.091	0.004	1.08068	1.10132	1.085	fit
C(ar)-H	C6	H6	1.096	0.004	1.08568	1.10632	1.085	fit
C(ar)-H	C7	H7	1.094	0.004	1.08368	1.10432	1.085	fit
C(ar)-H	C8	H8	1.095	0.004	1.08468	1.10532	1.085	fit
Z ₃ -Csp ³ -H	C8B	H8B	1.101	0.004	1.09068	1.11132	1.099	fit
Z ₃ -Csp ³ -H	C2A	H2A	1.102	0.004	1.09168	1.11232	1.099	fit

Table A.13. Statistical comparison of C-H bond lengths in 9 to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion		Neutron mean	Fit with neutron data?
					-s.u.*2.58	+s.u.*2.58		
Z ₂ -Csp ³ -H	C1	H1	1.091	0.011	1.06262	1.11938	1.097	fit
Z ₂ -Csp ³ -H	C2	H2b	1.132	0.014	1.09588	1.16812	1.097	fit
Z ₂ -Csp ³ -H	C2	H2a	1.103	0.013	1.06946	1.13654	1.097	fit
Z ₃ -Csp ³ -H	C2A	H2Aa	1.079	0.012	1.04804	1.10996	1.099	fit
Z ₃ -Csp ³ -H	C8B	H8B	1.091	0.012	1.06004	1.12196	1.099	fit
Csp ² -H	C3	H3	1.092	0.012	1.06104	1.12296	1.085	fit
Csp ² -H	C4	H4	1.108	0.012	1.07704	1.13896	1.085	fit
C(ar)-H	C5	H5	1.113	0.013	1.07946	1.14654	1.085	fit
C(ar)-H	C6	H6	1.097	0.013	1.06346	1.13054	1.085	fit
C(ar)-H	C7	H7	1.083	0.012	1.05204	1.11396	1.085	fit
C(ar)-H	C8	H8	1.085	0.012	1.05404	1.11596	1.085	fit

Table A.14. Statistical comparison of C-H bond lengths in **10** to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion			Fit with neutron data?		
					-s.u.*2.58	+s.u.*2.58	Neutron mean			
Z ₂ -Csp ³ -H	C1	H1B	1.078	0.010	1.0522	1.1038	1.097	fit		
Z ₂ -Csp ³ -H	C1	H1A	1.080	0.011	1.05162	1.10838	1.097	fit		
Z ₂ -Csp ³ -H	C2	H2	1.066	0.010	1.0402	1.0918	1.097	fit		
Z ₃ -Csp ³ -H	C2A	H2A	1.058	0.010	1.0322	1.0838	1.099	nofit		
Z ₃ -Csp ³ -H	C8B	H8B	1.076	0.009	1.05278	1.09922	1.099	fit		
Csp ² -H	C3	H3	1.075	0.009	1.05178	1.09822	1.085	fit		
Csp ² -H	C4	H4	1.065	0.010	1.0392	1.0908	1.085	fit		
C(ar)-H	C5	H5	1.060	0.010	1.0342	1.0858	1.085	fit		
C(ar)-H	C6	H6	1.070	0.010	1.0442	1.0958	1.085	fit		
C(ar)-H	C7	H7	1.069	0.011	1.04062	1.09738	1.085	fit		
C(ar)-H	C8	H8	1.070	0.010	1.0442	1.0958	1.085	fit		

Table A.15. Statistical comparison of C-H bond lengths in **11** to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion			Fit with neutron data?		
					-s.u.*2.58	+s.u.*2.58	Neutron mean			
C(ar)-H	C3	H3	1.095	0.010	1.0692	1.1208	1.085	fit		
C(ar)-H	C4	H4	1.109	0.010	1.0832	1.1348	1.085	fit		
C(ar)-H	C5	H5	1.093	0.009	1.06978	1.11622	1.085	fit		
C(ar)-H	C6	H6	1.088	0.010	1.0622	1.1138	1.085	fit		
C(ar)-H	C13	H13	1.105	0.009	1.08178	1.12822	1.085	fit		
C(ar)-H	C14	H14	1.085	0.010	1.0592	1.1108	1.085	fit		
C(ar)-H	C15	H15	1.101	0.010	1.0752	1.1268	1.085	fit		
C(ar)-H	C16	H16	1.092	0.010	1.0662	1.1178	1.085	fit		
Z ₃ -Csp ³ -H	C6B	H6B	1.101	0.009	1.07778	1.12422	1.099	fit		
Z ₃ -Csp ³ -H	C6C	H6C	1.088	0.009	1.06478	1.11122	1.099	fit		
Z ₃ -Csp ³ -H	C12A	H12A	1.095	0.010	1.0692	1.1208	1.099	fit		
Z ₃ -Csp ³ -H	C12B	H12B	1.089	0.009	1.06578	1.11222	1.099	fit		
Z ₃ -Csp ³ -H	C16B	H16B	1.103	0.009	1.07978	1.12622	1.099	fit		
Z ₃ -Csp ³ -H	C16C	H16C	1.077	0.010	1.0512	1.1028	1.099	fit		
Z ₃ -Csp ³ -H	C2A	H2A	1.081	0.009	1.05778	1.10422	1.099	fit		
Z ₃ -Csp ³ -H	C2B	H2B	1.075	0.009	1.05178	1.09822	1.099	fit		

Table A.16. Statistical comparison of C-H bond lengths in **12** to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion		Neutron mean	Fit with neutron data?	
					-s.u.*2.58	+s.u.*2.58			
Csp ² -H	C5	H5	1.089	0.009	1.06578	1.11222	1.085	fit	
Csp ² -H	C6	H6	1.096	0.010	1.0702	1.1218	1.085	fit	
Csp ² -H	C9	H9	1.085	0.009	1.06178	1.10822	1.085	fit	
Csp ² -H	C10	H10	1.097	0.009	1.07378	1.12022	1.085	fit	
Csp ² -H	C15	H15	1.099	0.010	1.0732	1.1248	1.085	fit	
Csp ² -H	C16	H16	1.076	0.010	1.0502	1.1018	1.085	fit	
Csp ² -H	C19	H19	1.100	0.010	1.0742	1.1258	1.085	fit	
Csp ² -H	C20	H20	1.089	0.010	1.0632	1.1148	1.085	fit	
C(ar)-H	C1	H1	1.077	0.009	1.05378	1.10022	1.085	fit	
C(ar)-H	C2	H2	1.086	0.010	1.0602	1.1118	1.085	fit	
C(ar)-H	C3	H3	1.097	0.010	1.0712	1.1228	1.085	fit	
C(ar)-H	C4	H4	1.096	0.009	1.07278	1.11922	1.085	fit	
C(ar)-H	C11	H11	1.088	0.009	1.06478	1.11122	1.085	fit	
C(ar)-H	C12	H12	1.080	0.010	1.0542	1.1058	1.085	fit	
C(ar)-H	C13	H13	1.095	0.010	1.0692	1.1208	1.085	fit	
C(ar)-H	C14	H14	1.070	0.009	1.04678	1.09322	1.085	fit	

Table A.17. Statistical comparison of C-H bond lengths in **13** to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion		Neutron mean	Fit with neutron data?	
					-s.u.*2.58	+s.u.*2.58			
C(ar)-H	C1	H1	1.091	0.007	1.07294	1.10906	1.085	fit	
C(ar)-H	C2	H2	1.092	0.008	1.07136	1.11264	1.085	fit	
C(ar)-H	C3	H3	1.080	0.008	1.05936	1.10064	1.085	fit	
C(ar)-H	C4	H4	1.091	0.008	1.07036	1.11164	1.085	fit	
C(ar)-H	C5	H5	1.083	0.008	1.06236	1.10364	1.085	fit	
C(ar)-H	C6	H6	1.071	0.007	1.05294	1.08906	1.085	fit	
Csp ² -H	C7	H7	1.081	0.007	1.06294	1.09906	1.085	fit	
Csp ² -H	C8	H8	1.087	0.007	1.06894	1.10506	1.085	fit	
Csp ² -H	C10	H10	1.101	0.012	1.07004	1.13196	1.085	fit	
Csp ² -H	C11	H11	1.095	0.007	1.07694	1.11306	1.085	fit	
Csp ² -H	C12	H12	1.096	0.008	1.07536	1.11664	1.085	fit	

Table A.18. Statistical comparison of C-H bond lengths in **14** to neutron diffraction data.

C-H bond type	AtomA	AtomB	Dist	s.u.	Single s.u. criterion			Fit with neutron data?
					-s.u.*2.58	+s.u.*2.58	Neutron mean	
Z ₃ -Csp ³ -H	C2A	H2A	1.114	0.018	1.06756	1.16044	1.099	fit
Z ₃ -Csp ³ -H	C2B	H2B	1.040	0.018	0.99356	1.08644	1.099	nofit
Z ₃ -Csp ³ -H	C8B	H8B	1.056	0.019	1.00698	1.10502	1.099	fit
Csp ² -H	C1	H1	1.098	0.018	1.05156	1.14444	1.085	fit
Csp ² -H	C2	H2	1.10	0.02	1.0484	1.1516	1.085	fit
C(ar)-H	C3	H3	1.096	0.018	1.04956	1.14244	1.085	fit
C(ar)-H	C4	H4	1.04	0.02	0.9884	1.0916	1.085	fit
C(ar)-H	C5	H5	1.099	0.019	1.04998	1.14802	1.085	fit
C(ar)-H	C6	H6	1.061	0.018	1.01456	1.10744	1.085	fit
C(ar)-H	C7	H7	1.04	0.02	0.9884	1.0916	1.085	fit
C(ar)-H	C8	H8	1.10	0.02	1.0484	1.1516	1.085	fit

Table A.19. Analysis of ‘short’ C-H bond lengths (1.04 – 1.06 Å) in **1** – **14**.

Short bonds	1.04	1.05	1.06	
C(ar)-H	13 (2)	2 (2), 5 (2)	1 (2), 2 (1), 5 (2), 10 (1), 13 (1)	
Csp ² -H	1 (1)	5 (1)	4 (1), 5 (3)	
Z ₃ -Csp ³ -H	13 (1)		4 (1), 10 (1), 13 (1)	
Total n				
C(ar)-H	2	4	7	
Csp ² -H	1	1	4	
Z ₃ -Csp ³ -H	1	0	3	
# Short bonds by structure				
1	3			
2	3			
4	2			
5	8			
10	2			
14	5			

Table A.20. Bond length and angle data for Type II structures^a

Bond Lengths										Angles											
NAME	C1-C2	C1-C8A	C1-C10	C2-C3	C3-C4	C4-C4A	C4-C9	C4A-C8A	C9-C10	C1-C2-C3	C1-C8A-C4A	C1-C10-C9	C2-C3-C4	C2-C1-C8A	C2-C1-C10	C3-C4-C4A	C3-C4-C9	C4-C4A-C8A	C4-C9-C10	C4A-C4-C9	C8A-C1-C10
FALHX	1.509	1.518	1.557	1.384	1.515	1.515	1.56	1.421	1.504	112.178	112.979	111.388	114.68	108.106	105.657	108.161	105.612	112.211	109.248	106.241	106.227
MICBUW	1.545	1.516	1.539	1.442	1.545	1.516	1.539	1.409	1.447	111.769	112.896	111.772	111.769	106.778	106.227	106.778	106.227	112.896	111.772	106.992	106.992
MICGAD	1.516	1.515	1.54	1.376	1.524	1.528	1.541	1.402	1.486	112.941	113.602	110.565	113.534	107.753	106.449	107.199	107.058	111.825	110.861	105.146	105.769
MICGZH	1.521	1.515	1.538	1.383	1.515	1.52	1.526	1.388	1.469	113.184	113.822	111.907	112.775	107.188	105.489	107.698	106.301	111.96	110.13	106.986	105.257
NAHZAX	1.494	1.522	1.571	1.298	1.525	1.52	1.561	1.388	1.525	115.197	113.106	109.175	114.926	108.755	105.548	108.336	104.611	112.915	110.087	104.802	104.633
NAHZAX	1.516	1.534	1.554	1.306	1.517	1.514	1.555	1.387	1.523	114.61	112.88	110.308	115.293	108.174	104.885	108.767	104.886	113.423	109.647	104.519	104.643
NAHZAX	1.515	1.525	1.553	1.32	1.51	1.504	1.55	1.396	1.516	114.265	112.538	109.792	114.448	107.547	105.876	108.004	106.226	112.958	109.823	105.555	105.457
NAHZAX	1.535	1.551	1.552	1.33	1.496	1.513	1.546	1.394	1.516	113.507	112.264	109.817	114.853	107.842	104.947	108.502	106.367	113.248	109.999	105.111	105.996
ODCHUL	1.529	1.531	1.536	1.415	1.531	1.514	1.538	1.424	1.463	112.348	112.599	111.297	112.588	106.972	106.37	106.898	106.296	112.505	111.486	106.404	106.918
PBICBO	1.507	1.533	1.574	1.368	1.552	1.516	1.522	1.43	1.499	113.093	111.603	108.714	113.56	107.541	108.151	106.347	107.458	112.705	112.185	105.624	105.792
PBICBO	1.507	1.524	1.555	1.411	1.57	1.513	1.494	1.426	1.416	114.838	112.803	112.907	110.901	106.065	103.654	105.215	105.63	112.919	113.021	107.954	106.45
PBICBO	1.559	1.501	1.49	1.385	1.521	1.524	1.472	1.422	1.443	112.819	113.088	112.001	112.755	106.323	104.163	106.937	106.292	111.836	113.045	106.101	107.722
PBICBO	1.545	1.499	1.546	1.415	1.532	1.525	1.501	1.439	1.426	110.765	113.129	111.741	113.778	106.533	105.092	105.878	106.989	111.267	112.712	106.903	107.88
PBICBO	1.536	1.53	1.527	1.406	1.565	1.509	1.508	1.455	1.437	112.505	111.433	111.928	111.971	106.815	107.666	106.793	106.629	112.002	112.285	107.088	105.834
PBICBO	1.508	1.523	1.511	1.397	1.536	1.493	1.566	1.434	1.449	114.03	111.577	112.893	111.745	105.32	106.387	106.893	105.994	113.148	110.506	106.437	108.128
PBICOU	1.534	1.516	1.518	1.444	1.535	1.515	1.521	1.433	1.443	111.917	112.281	112.569	111.908	106.488	105.977	106.201	106.206	112.578	111.759	107.59	107.38
PBICOU	1.518	1.556	1.552	1.402	1.515	1.512	1.548	1.437	1.476	112.549	112.231	110.469	113.289	107.731	106.292	107.646	106.319	112.249	111.366	106.327	106.6
PBICOU	1.533	1.512	1.546	1.413	1.527	1.511	1.546	1.434	1.461	112.555	112.052	112.087	112.598	107.227	105.84	107.536	106.541	112.821	110.664	106.308	106.618
PBICOU	1.537	1.514	1.532	1.408	1.536	1.512	1.525	1.435	1.463	112.95	112.188	111.484	112.063	107.441	106.182	107.641	106.392	112.486	111.549	106.439	106.07
PBICUA	1.557	1.514	1.525	1.424	1.551	1.515	1.54	1.42	1.451	112.165	113.07	111.655	112.105	107.338	106.44	106.021	106.249	111.941	111.559	106.29	106.283
PBICUA	1.537	1.5	1.547	1.414	1.531	1.509	1.535	1.436	1.475	112.685	112.464	111.084	112.208	107.922	105.672	107.653	106.513	112.417	111.116	106.66	106.491
PBIDAH	1.527	1.508	1.542	1.414	1.55	1.518	1.546	1.444	1.443	112.439	112.642	111.981	112.378	108.012	106.056	106.367	111.741	111.594	106.134	106.379	106.1
PBIDAH	1.527	1.509	1.533	1.417	1.53	1.509	1.536	1.437	1.456	112.335	112.325	111.501	112.263	107.263	106.776	107.288	106.498	112.051	111.37	106.786	106.509
PBIDAH	1.533	1.512	1.53	1.421	1.525	1.501	1.549	1.436	1.41	112.277	112.595	113.118	112.352	107.063	105.847	107.259	106.133	112.13	111.471	106.43	105.865
PBIDAH	1.518	1.509	1.534	1.422	1.527	1.515	1.53	1.44	1.46	112.632	113.383	113.239	112.36	107.762	106.075	106.274	113.017	111.078	113.763	107.639	106.838
PBIDEL	1.514	1.514	1.539	1.384	1.533	1.511	1.539	1.402	1.484	112.906	113.103	110.967	113.545	106.927	106.269	106.454	105.442	112.866	110.987	106.484	106.618
PBIDEL	1.53	1.498	1.563	1.353	1.525	1.519	1.567	1.411	1.494	113.731	113.118	110.814	113.784	108.475	106.212	108.943	105.14	112.615	109.905	105.07	104.584
PBIDUB	1.534	1.512	1.545	1.392	1.521	1.513	1.539	1.395	1.467	112.964	112.928	111.437	112.889	106.765	105.369	107.268	105.715	113.289	110.937	106.596	106.516
PBIDUB	1.531	1.508	1.546	1.393	1.538	1.511	1.541	1.403	1.455	112.5	113.012	111.649	113.083	106.893	108.121	106.905	105.451	112.983	111.228	106.606	106.245
RAKPUJ	1.508	1.558	1.548	1.394	1.52	1.517	1.538	1.464	1.489	115.452	113.763	113.167	114.093	105.788	107.109	106.303	107.224	112.87	110.352	105.512	102.429
TIVPLZ	1.5	1.505	1.566	1.312	1.524	1.519	1.545	1.386	1.568	114.903	113.421	107.267	115.193	107.776	106.147	106.454	105.212	115.633	111.21	104.85	106.168
VARBAK	1.525	1.533	1.569	1.312	1.513	1.511	1.587	1.397	1.574	114.759	112.646	109.315	114.927	107.365	106.227	106.464	105.216	113.456	108.189	106.261	105.558
WEKRIA	1.525	1.522	1.531	1.418	1.524	1.513	1.528	1.41	1.453	111.526	112.213	110.857	112.521	107.841	106.495	107.348	107.028	112.392	111.62	106.264	106.888
YOSFAP	1.531	1.51	1.517	1.406	1.539	1.508	1.532	1.416	1.456	111.87	113.475	111.11	112.594	106.655	107.085	107.175	105.956	111.395	111.65	107.077	106.903
YOSFAP	1.519	1.51	1.546	1.379	1.52	1.512	1.552	1.426	1.484	113.586	112.533	110.524	113.091	106.539	106.402	106.969	106.317	112.526	111.052	106.213	107.047
YOSFAP	1.525	1.525	1.532	1.426	1.527	1.503	1.536	1.419	1.443	113.075	112.092	112.123	111.966	105.963	106.684	105.644	107.749	111.636	111.746	105.905	106.783
YOSFAP	1.523	1.52	1.533	1.417	1.522	1.519	1.54	1.429	1.45	113.302	113.449	111.701	111.494	107.58	106.165	107.434	106.502	112.975	111.339	106.461	106.505
ZIZXOX	1.503	1.497	1.541	1.329	1.515	1.504	1.549	1.401	1.546	114.014	112.639	108.85	113.862	109.027	105.278	108.165	107.492	112.503	109.023	104.459	107.044
ZIZXOX	1.511	1.485	1.555	1.318	1.51	1.511	1.561	1.392	1.529	114.093	114.229	109.652	114.316	108.85	105.053	109.021	106.913	111.555	108.792	104.176	105.634
Min	1.494	1.485	1.490	1.298	1.496	1.493	1.472	1.386	1.410	110.765	111.423	107.267	110.901	105.063	103.654	105.215	104.611	111.078	108.189	104.176	102.429
Max	1.559	1.538	1.574	1.444	1.570	1.528	1.587	1.464	1.574	115.452	114.229	113.167	115.293	109.027	108.151	109.021	107.749	113.636	113.045	107.954	108.128
Mean	1.524	1.535	1.542	1.385	1.528	1.513	1.539	1.418	1.476	113.1	112.7	111.1	113.1	107.3	106.2	112.5	111.0	110.2	106.2	106.2	106.2
Std Dev.	0.014	0.013	0.017	0.040	0.015	0.006	0.021	0.020	0.040	1.1	0.6	1.3	1.1	0.9	0.8	0.9	0.7	0.6	1.1	0.9	1.0
Av Pres	1.523 (14)	1.515(12)	1.542(17)	1.38(4)	1.527(15)	1.513(6)	1.54(2)	1.418(20)	1.48(4)	113.1(11)	112.7(6)	111.0(13)	113.1(11)	107.3(9)	106.0(8)	107.3(9)	106.2(7)	112.5(6)	111.0(11)	106.2(9)	106.2(10)
Av Pres	1.517(5)	1.512(7)	1.561(5)	1.347(7)	1.505(8)	1.511(7)	1.563(5)	1.401(7)	1.546(8)	113.1(11)	112.7(6)	111.0(13)	113.1(11)	107.3(9)	106.0(8)	107.3(9)	106.2(7)	112.5(6)	111.0(11)	106.2(9)	106.2(10)
Stats incl Cmpd 3																					
Min	1.494	1.485	1.49	1.298	1.496	1.493	1.472	1.386	1.41	110.765	111.423	107.267	110.901	105.063	103.654	105.215	104.611	111.078	108.189	104.176	102.429
Max	1.559	1.538	1.574	1.444	1.570	1.528	1.587	1.464	1.574	115.452	114.229	113.167	115.293	109.027	108.151	109.021	107.749	113.636	113.045	107.954	108.128
Mean	1.523	1.535	1.542	1.385	1.528	1.513	1.539	1.418	1.477	113.2	112.7	111.0	113.1	107.3	106.0	112.5	111.0	110.2	106.2	106.2	106.2
Std Dev.	0.014																				

A.2. Intermolecular Short Contacts and Non-classical Hydrogen Bonding

Table A.21. Ranking of Hydrogen Bond Strengths Following Jeffrey^a

	Strong	Moderate	Weak
Interaction type:	Mostly covalent	Mostly electrostatic	Electrost./disp.
$d(\text{H}\cdots\text{A})$ (Å)	1.2 – 1.5	1.5 – 2.2	> 2.2
$d(\text{D}\cdots\text{A})$, 2nd period (Å)	2.2 – 2.5	2.5 – 3.2	> 3.2
<i>lengthening</i> of D–H	0.08 – 0.25	0.02 – 0.08	< 0.2
D–H versus H$\cdots$A	D–H $\approx$ H $\cdots$ A	D–H < H $\cdots$ A	D–H $\ll$ H $\cdots$ A
Directionality:	strong	moderate	weak
$\angle\text{D–H}\cdots\text{A}$ (°)	170 – 180	> 130	> 90
Bond energy (kJ·mol^{–1})	60 – 160	16 – 60	< 16
IR shift $\Delta\bar{\nu}_{\text{DH}}$ (cm^{–1})	25%	10 – 25 %	< 10 %
¹H shift (ppm)	14 – 22	< 14	

^a Jeffrey, G. A. *An introduction to hydrogen bonding*. Oxford university press: New York, 1997, Vol.12, pp 330.

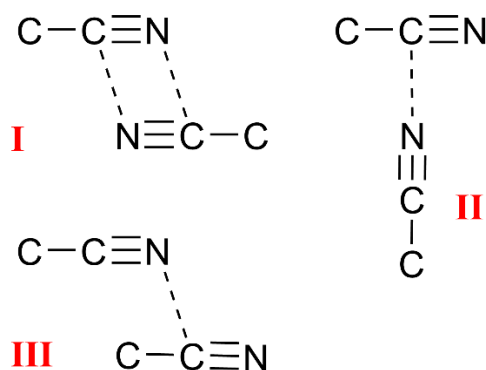


Figure A.1. The three commonly observed $\text{C}\equiv\text{N}\cdots\text{C}\equiv\text{N}$ interaction motifs: (I) sheared antiparallel, (II) perpendicular, and (III) sheared parallel. (Wood, P. A.; Borwick, S. J.; Watkin, D. J.; Motherwell, W. D.; Allen, F. H., Dipolar $\text{C}\equiv\text{N}\cdots\text{C}\equiv\text{N}$ interactions in organic crystal structures: database analysis and calculation of interaction energies. *Acta Crystallogr B* 2008, 64 (Pt 3), 393-6.)

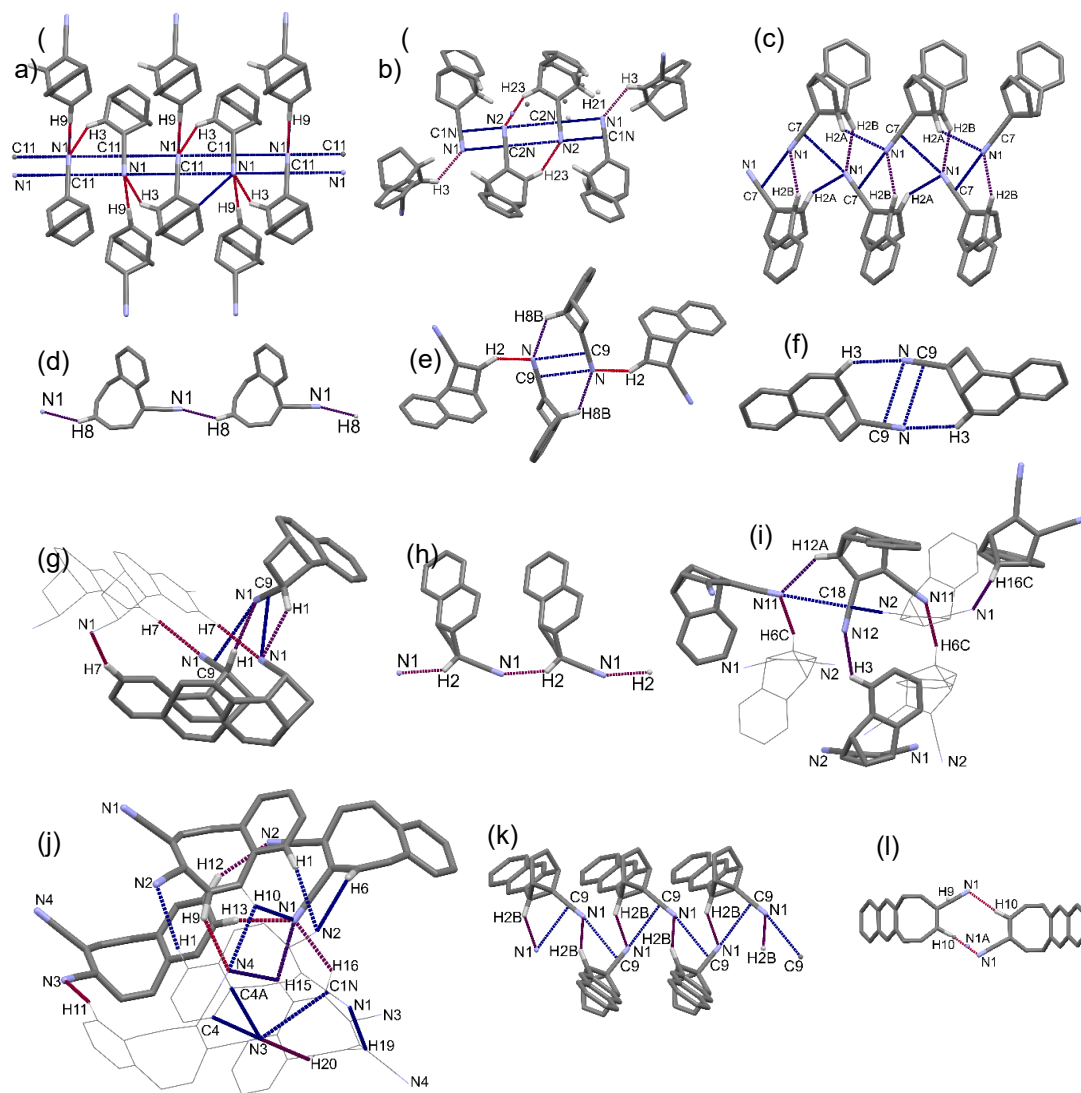


Figure A.2. Combined nitrile dipolar contacts and non-classical $\text{C}\equiv\text{N}\cdots\text{H}-\text{C}$ bonds. (a) 2, (b) 3, (c) 4, (d) 6, (e) 7, (f) 8, (g) 9, (h) 10, (i) 11, (j) 12, (k) 13, (l) 14.

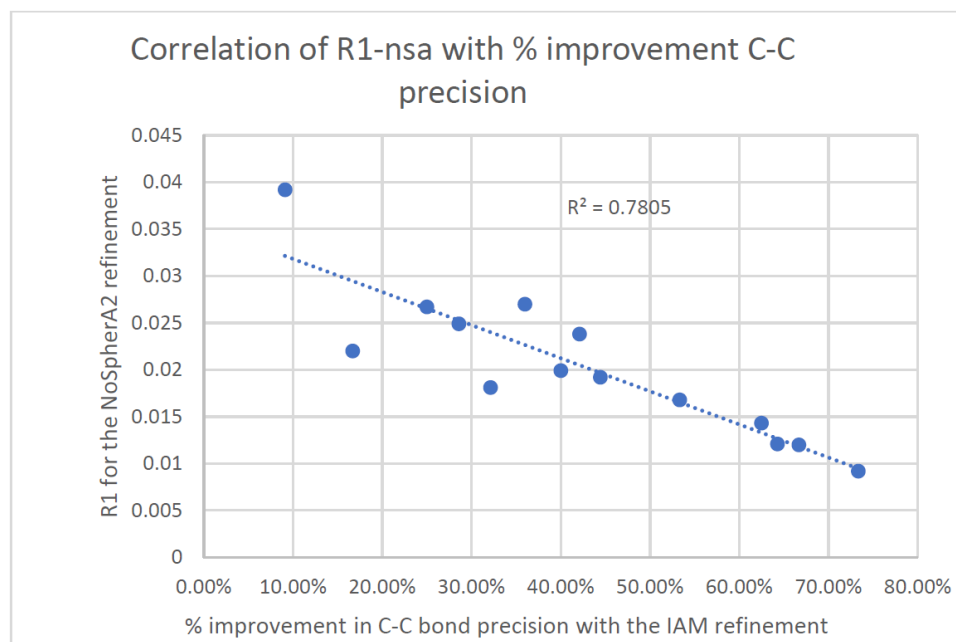


Figure A.3. Correlation of C-C bond distance precision improvement with R_1

The worst outlier seems to be associated with both poor data and a poor model (R_1 of 3.92% and $R_{\text{int}} = 9.8\%$). Satisfyingly, the better the data/model quality is, the bigger the improvement when refining all atoms using HAR/NoSpherA2.

Appendix B. Supporting Information for Chapter 4

Reproduced from the Supporting Information document accompanying “Hill, N.D.D.; Boéré, R.T., ‘*N,N'*-Diaryl-Sulfurdiimides are Strongly Redox Tuned’. *Chem. Eur. J.* **2024**, e202400563.”

B.1. Full Synthetic Experimental Details

B.1.1. Reagents and General Procedures

4-methoxyaniline, 4-fluoroaniline, 4-trifluoromethylaniline, *n*-butyllithium (1.6 M or 2.5 M in hexanes), hexamethyldisilazane, anhydrous dimethylformamide, and potassium *t*-butoxide were purchased from Sigma-Aldrich. 4-methylaniline, 4-chloroaniline were purchased from Eastman Organic Chemicals. 4-bromoaniline was purchased from Baker Chemicals, 4-nitroaniline was purchased from BDH, and thionyl chloride was purchased from Merck. All reagents were used as received. Benzene and heptane were dried by an MBraun solvent purification system. Literature methods were previously used to synthesize *bis*(*tert*-butyl)sulfur diimide (**10**)^[1] and *bis*(trimethylsilyl)sulfurdiimide (**11**)^[2], which were distilled under vacuum and checked for purity by ¹H NMR. Unless otherwise stated, all reactions were performed under N₂ using modified Schlenk and vacuum line techniques. NMR were obtained on either a 300 MHz Bruker Avance II spectrometer or a 700 MHz Bruker Avance III spectrometer. Low temperature NMR utilized the Bruker SmartCooler BCU II on the 700 MHz spectrometer. Deuterated chloroform dried over 0.4 Å molecular sieves was used as solvent. ¹H NMR spectra were referenced to residual chloroform at 7.27 ppm and ¹³C spectra were referenced to the CDCl₃ C nucleus at 77.23 ppm. ¹⁹F spectra were referenced to external CFCl₃ at 0.00 ppm.

B.1.2. Chemical Synthesis

Synthesis of 4-methoxyphenyl-N-trimethylsilylaniline (15). 4-methoxyaniline (5 g, 41 mmol) was added to a side-arm flask with neat hexamethyldisilazane (HMDS, 17.5 mL, 81

mmol) and saccharin (0.22 g, 1.2 mmol), then refluxed under N₂ flow for 5 hours, until evolution of ammonia subsided. The mixture was cooled to room temperature, and excess HMDS was removed by vacuum. The resulting liquid was distilled at 65-70°C under vacuum, and a colourless solid was recovered, which was pure 4-methoxyphenyl-*N*-trimethylsilylaniline. Yield: 6.62 g, 83%. ¹H NMR (300 MHz, CDCl₃): 0.27 ppm (s; 9H; Si(CH₃)₃), 3.24 ppm (s; 1H; NH) 3.76 ppm (s; 3H; OCH₃), 6.60 – 6.83 ppm (m; 4H; ArH)

Synthesis of bis(4-methoxyphenyl)sulfurdiimide (1). 4-methoxyphenyl-*N*-trimethylsilylaniline (6.62 g, 34 mmol) was dissolved in ~30 mL dry THF, and cooled to -65°C. To this was added *n*-butyllithium (1.6 M, 21.2 mL, 34 mmol), at which point there was a slight colour change from colourless to red, and solid precipitated after several minutes. The solution was again cooled to -65°C, and SOCl₂ (1.2 mL, 17 mmol) in 5 mL THF was added. The solution turned somewhat red, and was stirred for another hour, then warmed to room temperature. The solution then turned very dark red and was allowed to stir at room temperature for 3 hours. Diethyl ether was added to precipitate lithium chloride, the solution was filtered, and solvent removed, leaving a dark sludge. The reaction was determined by NMR to be incomplete, so the sludge was dissolved in toluene, and refluxed for 3 hours. After removing solvent, the crude product was separated on a chromatography column of 230-400 mesh silica in 2:3 hexane:CH₂Cl₂. Product was recrystallized from hexane and determined to be pure *bis*(4-methoxyphenyl)sulfurdiimide. Yield: 2.55 g, 55%. ¹H NMR (300 MHz, CDCl₃): 3.84 ppm (s; 6H; OCH₃), 6.75 ppm (d; ³J(H,H) = 8.7 Hz; 4H, *m*-ArH), 7.89 ppm (d; ³J(H,H) = 7.2 Hz; 4H, *o*-ArH). ¹³C{¹H} NMR (176 MHz, CDCl₃): 55 ppm (s; 2C; OCH₃), 114 ppm (s; 4C; *m*-ArC), 125 ppm (s; 4C; *o*-ArC), 140 ppm (s; 2C; *i*-ArC), 158 ppm (s; 2C; *p*-ArC). FTIR (cm⁻¹): 3008, 2963, 2940, 2905, 2835, 2048, 2027, 1898, 1879, 1588, 1565, 1492, 1459, 1439, 1420, 1314, 1292, 1268, 1239, 1182, 1163, 1106, 1057, 1027, 952, 933, 826, 743, 674, 635, 585, 530, 518, 502, 417. MP: 45.9-46.6°C. Anal. Calcd for C₁₄H₁₄N₂O₂S: C, 61.29; H, 5.14; N, 10.21; S, 11.69 %. Found: C, 62.09; H, 5.02; N, 10.66; S, 11.96 %.

Synthesis of 4-tolyl-N-sulfinylaniline. In a round-bottomed side-arm flask, 4-methylaniline (6.7 g, 62.5 mmol) was dissolved in ~40 mL dry benzene and stirred under N₂ flow. To this was added SOCl₂ (9.5 mL, 131 mmol) diluted in 30 mL of benzene. Solid anilinium chloride salt formed on addition of SOCl₂ but dissolved with heating. The reaction mixture was refluxed for ~30 minutes, until the evolution of HCl vapors ceased. The solvent was removed, leaving a dark yellow oil, which was highly pure 4-methyl-N-sulfinylaniline. Yield: 8.05 g, 84%. ¹H NMR (300MHz, CDCl₃): δ = 2.43 ppm (s; 3H; CH₃), 7.25 ppm (d; ³J(H,H) = 8.1 Hz; 2ArH), 7.85 ppm (d; ³J(H,H) = 8.4 Hz; 2ArH).

Synthesis of bis(4-tolyl)sulfurdiimide (2). Dissolved 4-tolyl-N-sulfinylaniline (5.0 g, 33 mmol) in dry benzene, and stirred under N₂ flow. On addition of potassium *tert*-butoxide (1.9 g, 17 mmol), the solution immediately turned dark red. Refluxed for 1.5 hours, then cooled to room temperature, and quenched with ~20 mL of dH₂O. Organic and aqueous phases were separated, and the organic phase was dried thoroughly, resulting in 3.4 g of dark red oil. Recrystallization from hexane yields crystals of the sulfur diimide. Yield: 0.95 g, 24% ¹H NMR (300 MHz, CDCl₃): δ = 2.36 ppm (s; 3H; CH₃), 7.15 ppm (d; ³J(H,H) = 8.1 Hz; 4H, *m*-ArH), 7.37 ppm (d; ³J(H,H) = 6.9 Hz; 4H, *o*-ArH). ¹³C{¹H} NMR (176 MHz, CDCl₃): δ = 21.5 ppm (s; 2C; CH₃), 123.4 ppm (s; 4C; *o*-ArC), 129.7 ppm (s; 4C; *m*-ArC), 137.1 ppm (s; 2C; *p*-ArC), 143.7 ppm (s; 2C; *i*-ArC). FTIR (cm⁻¹): 3071, 3022, 2983, 2947, 2914, 2853, 1890, 1594, 1562, 1495, 1446, 1377, 1293, 1263, 1223, 1172, 1107, 1062, 1036, 1018, 961, 937, 830, 809, 750, 709, 681, 638, 585, 512, 484, 411, 395, 386. MP: 45.2-46.6°C. Anal. Calcd for C₁₄H₁₄N₂S: C, 69.38; H, 5.82; N, 11.56; S, 13.23%. Found: C, 69.43; H, 6.15; N, 10.66; S, 13.75 %.

Synthesis of 4-fluorophenyl-N-trimethylsilylaniline. 4-fluoroaniline (5 mL, 53 mmol) was added to a side-arm flask with neat hexamethyldisilazane (7 mL, 33 mmol) and 6 drops of conc. sulfuric acid, then refluxed under N₂ flow for one hour, until evolution of ammonia subsided. The mixture was cooled to room temperature, and excess HMDS was

removed by vacuum. The resulting liquid was distilled at 92- 100°C under vacuum, and a colourless liquid was recovered, which was pure 4-fluorophenyl-N-trimethylsilylaniline. Yield: 6.87 g, 71%. ^1H NMR (300 MHz, CDCl_3): δ = 0.27 ppm (s; 9H; $\text{Si}(\text{CH}_3)_3$), 3.33 ppm (s; 1H; NH), 6.54-6.67 ppm (m; 2ArH), 6.81-6.91 ppm (m; 2ArH). ^{19}F NMR (282 MHz, CDCl_3): δ = -127 ppm.

Synthesis of bis(4-fluorophenyl)sulfurdiimide (3). 4-fluorophenyl-N-trimethylsilylaniline (1.86 g, 10mmol) was dissolved in ~25 mL dry THF, and cooled to -70°C. To this was added n-butyllithium (2.5 M, 6 mL, 15 mmol), and the mixture was stirred for 0.5 hours. This was then moved to an ice bath for 1 hour, during which it took on a dark brown colour. The solution was cooled again to -70°C, and SOCl_2 (0.36 mL, 6 mmol) diluted in ~3 mL dry THF was added, and stirred for 1 hour, then warmed to room temperature and stirred for 3 hours, during which the solution turned a vivid red. Diethyl ether was added, precipitating solid lithium chloride, then the solution was filtered, and solvent removed, leaving behind a red solid. The crude product was separated on a chromatography column of 230-400 mesh silica in 3:2 hexane: CH_2Cl_2 , and the collected fraction was recrystallized from heptane, yielding fine orange needles of *bis*(4-fluorophenyl)sulfurdiimide. Over several months, the colour of the crystals turned to dark yellow, but ^1H , ^{13}C , and ^{19}F NMR shows no degradation of the product. Yield: 0.292 g, 23%. ^1H NMR (300 MHz, CDCl_3): δ = 7.04 ppm (d; $^3\text{J}(\text{H,H})$ = 8.7 Hz; 4H, *m*-ArH), 7.45 ppm (d; $^3\text{J}(\text{H,H})$ = 8.1 Hz; 4H, *o*-ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3): δ = 116 ppm (d; $^2\text{J}(\text{C-F})$ = 22.6 Hz, 4C, *m*-ArC), 125 ppm (s; 4C; *o*-ArC), 142 ppm (d; $^4\text{J}(\text{C-F})$ = 3.0 Hz, 2C, *i*-ArC), 162 ppm (d; $^1\text{J}(\text{C-F})$ = 248 Hz), 2C, *p*-ArC). $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, CDCl_3): δ = -112.8 ppm. FTIR (cm^{-1}): 3061, 1883, 1579, 1489, 1412, 1306, 1294, 1270, 1206, 1152, 1102, 1093, 1061, 1044, 1016, 1009, 958, 826, 759, 707, 694, 675, 633, 581, 516, 488, 430, 410, 386. MP: 91.1-92.3°C. Anal. Calcd for $\text{C}_{12}\text{H}_8\text{F}_2\text{N}_2\text{S}$: C, 57.59; H, 3.22; N, 11.19; S, 12.81 %. Found: C, 59.03; H, 3.18; N, 11.67; S, 12.77 %.

Synthesis of 4-chlorophenyl-N-trimethylsilylaniline. 4-chloroaniline (11.8 g, 95 mmol) was added to a side-arm flask with neat hexamethyldisilazane (40 mL, 191 mmol) and 12 drops of conc. sulfuric acid, then refluxed under N₂ flow for 3 hours, until evolution of ammonia subsided. The mixture was cooled to room temperature, and excess HMDS was removed by vacuum. The resulting liquid was distilled at 62°C under vacuum, and a colourless liquid was recovered, which solidified overnight at -10°C as pure 4-chloro-N-trimethylsilylaniline. Yield: 5.0 g, 75% ¹H NMR (300 MHz, CDCl₃): δ = 0.27 ppm (s; 9H; Si(CH₃)₃), 3.44 ppm (s; 1H; NH), 6.56 ppm (d; ³J(H,H) = 8.7 Hz; 2ArH), 7.08 ppm (d; ³J(H,H) = 8.7 Hz; 2ArH).

Synthesis of bis(4-chlorophenyl)sulfur diimide (4). 4-chlorophenyl-N-trimethylsilylaniline (7.9 g, 40.4 mmol) was dissolved in ~70 mL dry THF, and cooled to -65°C. To this was added n-butyllithium (1.6 M, 27.8 mL, 44 mmol), and the mixture was stirred for 1.5 hours. White precipitate formed after ~10 minutes. SOCl₂ (1.5 mL, 20 mmol) diluted in ~10 mL dry THF was then added, quickly turning the solution a clear yellow, then red/orange in one hour. The solution was warmed to room temperature and stirred under N₂ flow for 2 days. Diethyl ether was added, precipitating significant amounts of solid, then the solution was filtered, and solvent removed, forming an orange solid. This was recrystallized from heptane, then separated on a chromatography column of 230-400 mesh silica in 3:2 hexane:CH₂Cl₂, and the collected fraction was recrystallized from hexane, yielding fine orange needles of bis(4-chlorophenyl)sulfur diimide. Yield: 1.3 g, 25%. ¹H NMR (700 MHz, CDCl₃): δ = 7.32 ppm (d; ³J(H,H) = 8.7 Hz; 4H, *m*-ArH), 7.41 ppm (d; ³J(H,H) = 8.1 Hz; 4H, *o*-ArH). ¹³C{¹H} NMR (176 MHz, CDCl₃): δ = 125 ppm (s; 4C; *o*-ArC), 129 ppm (s; 4C; *m*-ArC), 133 ppm (s; 2C; *p*-ArC), 144 ppm (s; 2C; *i*-ArC). FTIR (cm⁻¹): 3088, 3065, 3030, 1906, 1890, 1773, 1759, 1648, 1638, 1575, 1560, 1476, 1402, 1308, 1294, 1268, 1219, 1173, 1106, 1090, 1061, 1006, 957, 829, 815, 801, 762, 708, 683, 634, 602, 536, 518, 504, 437,

389. MP: 60.0-61.1°C. Anal. Calcd for $C_{12}H_8Cl_2N_2S$: C, 50.90; H, 2.85; N, 9.89; S, 11.32 %. Found: C, 50.85; H, 2.67; N, 10.03; S, 10.89 %.

Synthesis of 4-bromophenyl-N-sulfinylaniline. 4-bromoaniline (8.0 g, 46.5 mmol) was dissolved in ~60 mL dry benzene and stirred under N_2 flow. To this was added $SOCl_2$ (7.0 mL, 97 mmol) diluted in 30 mL of benzene. Anilinium chloride salt formed on addition of $SOCl_2$ but dissolved with heating. The reaction mixture was refluxed for ~3 hours, until the evolution of HCl vapors ceased. Green solid was present after reflux, which was filtered, and then the solvent was removed, leaving a purple/red solid, which was the 4-bromo-N-sulfinylaniline. Yield: 7.05 g, 70%. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.57 ppm (d; $^3J(H,H)$ = 8.7 Hz; 2ArH), 7.76 ppm (d; $^3J(H,H)$ = 8.7 Hz; 2ArH).

Synthesis of bis(4-bromophenyl)sulfur diimide (5). Dissolved 4-bromophenyl-N-sulfinylaniline (20.4 g, 94 mmol) in ~50 mL dry dimethylformamide, added potassium *tert*-butoxide (6.5 g, 57 mmol), and stirred under N_2 flow for 3 hours. Filtered resulting precipitate on a filter-stick and dried on high vacuum overnight. Washed in water to remove *t*-butoxide, and recrystallized from heptane, leaving orange/red crystals of the sulfur diimide. Yield: 5.1 g, 29%. ^1H NMR (700 MHz, $CDCl_3$): δ = 7.34 ppm (d; $^3J(H,H)$ = 7.8 Hz; 4H, *o*-ArH), 7.47 ppm (d; $^3J(H,H)$ = 8.7 Hz; 4H, *m*-ArH). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ = 121 ppm (s; 2C; *p*-ArC), 125 ppm (s; 4C; *o*-ArC), 132 ppm (s; 4C; *m*-ArC), 145 ppm (s; 2C; *i*-ArC). FTIR (cm^{-1}): 3084, 3061, 1888, 1638, 1571, 1474, 1458, 1397, 1307, 1293, 1267, 1221, 1172, 1115, 1101, 1071, 1058, 1003, 957, 863, 828, 814, 799, 750, 701, 666, 649, 628, 577, 544, 506, 493, 439, 419, 382. MP: 98.8-102.0°C. Anal. Calcd for $C_{12}H_8Br_2N_2S$: C, 38.73; H, 2.17; N, 7.53; S, 8.62 %. Found: C, 38.72; H, 2.12; N, 7.62; S, 8.46 %.

Synthesis of 4-trifluoromethylphenyl-N-sulfinylaniline. 4-trifluoromethylaniline (8.0 mL, 64 mmol) was dissolved in ~50 mL dry benzene and stirred under N_2 flow. To this was added $SOCl_2$ (10 mL, 138 mmol) diluted in 30 mL of benzene. Solid anilinium chloride salt formed on addition of $SOCl_2$ but dissolved with heating. The reaction mixture was refluxed

for ~3 hours, until the evolution of HCl vapors ceased. The solvent was removed, leaving a bright yellow oil, which was 4-trifluoromethyl-N-sulfinylaniline. Yield: 11.4 g, 86%. ^1H NMR (300 MHz, CDCl_3): δ = 7.68 ppm (d; $^3\text{J}(\text{H,H})$ = 8.7 Hz, 2ArH), 7.91 ppm (d; $^3\text{J}(\text{H,H})$ = 8.4 Hz, 2ArH). $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, CDCl_3): δ = -62 ppm (s, CF_3).

Synthesis of bis(4-trifluoromethylphenyl)sulfurdiimide (6). Dissolved 4-trifluoromethyl-N-sulfinylaniline (9.07 g, 43.8 mmol) in dry toluene, and stirred under N_2 flow. On addition of potassium *tert*-butoxide (3.68 g, 33 mmol), the solution immediately turned dark red. The mixture was refluxed for 4 hours, after which the toluene was removed. The remainder was dissolved in pentane, and then filtered under N_2 . The pentane was then removed, leaving a dark red oil. This was distilled under vacuum (115°C). The distillate contains the impurities of the crude product, leaving sulfur diimide behind in the boiling flask. Yield: 4.29 g, 56%. ^1H NMR (700 MHz, CDCl_3): δ = 7.42 ppm (d; $^3\text{J}(\text{H,H})$ = 8.1 Hz, 4H, *o*-ArH), 7.57 ppm (d; $^3\text{J}(\text{H,H})$ = 8.4 Hz, 4H, *m*-ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, CDCl_3): δ = 123.2 ppm (s, 4C, *o*-ArC), 124.1 ppm (q, $^1\text{J}(\text{C,F})$ = 272 Hz, 2C, CF_3), 126.4 ppm (q, $^3\text{J}(\text{C-F})$ = 3.7 Hz, 4C, *m*-ArC), 128.9 ppm (q, $^2\text{J}(\text{C-F})$ = 32.8 Hz, 2C, *p*-ArC), 147.7 ppm (q, $^5\text{J}(\text{C-F})$ = 1.4 Hz, 2C, *i*-ArC). ^{19}F NMR (282 MHz, CDCl_3): δ = -62 ppm (s, 6F, CF_3). FTIR (cm^{-1}): 3221, 2934, 1911, 1670, 1608, 1575, 1504, 1413, 1388, 1318, 1273, 1236, 1161, 1103, 1066, 1049, 1012, 967, 904, 874, 841, 755, 736, 717, 654, 636, 595, 570, 513, 436. MP: 37.2-39.5°C. Anal. Calcd for $\text{C}_{14}\text{H}_8\text{F}_6\text{N}_2\text{S}$: C, 48.00; H, 2.30; N, 8.00; S, 9.15 %. Found: C, 48.18; H, 2.09; N, 8.36; S, 8.90 %.

Synthesis of 4-nitrophenyl-N-sulfinylaniline. 4-nitroaniline (5 g, 36 mmol) was suspended in ~50 mL of dry benzene, and stirred under N_2 . SOCl_2 (5.5 mL, 76 mmol) was added, with little immediate effect. At first, the anilinium chloride salt formed when the mixture was heated but dissolved with further heating. After refluxing for 2.5 hours, solvent was removed until significant amounts of solid precipitated. This was redissolved in ~60 mL of benzene, and ~20 mL of ligroin was added. Light yellow crystals of pure 4-

nitro-N-sulfinylaniline began forming after a few minutes. This was stored at -10°C overnight, then filtered on a Büchner funnel, washed with cold ligroin, and dried. Yield: 4.8 g, 72%. ¹H NMR (300 MHz, CDCl₃): δ = 7.94 ppm (d; ³J(H,H) = 9.3 Hz; 2H, ArH), 8.31 ppm (d; ³J(H,H) = 9.0 Hz; 2H, ArH).

Synthesis of bis(4-nitrophenyl)sulfurdiimide (7). Dissolved 4-nitrophenyl-N-sulfinylaniline (4.8 g, 26 mmol) in meticulously dry dimethylformamide, and stirred under N₂ flow. On addition of potassium *tert*-butoxide (1.6 g, 14 mmol), the solution immediately turned dark red. The mixture was stirred at room temperature for 3 hours, then filtered on a filter-stick and dried on high vacuum for two days. Recrystallized from ~1.5:1 benzene:diethylether. Yield: 0.8 g, 20%. ¹H NMR (300 MHz, CDCl₃): δ = 7.60 ppm (d; ³J(H,H) = 9.0 Hz, 4H, *o*-ArH), 8.27 ppm (d; ³J(H,H) = 9.0 Hz, 4H, *m*-ArH). ¹³C{¹H} NMR (176 MHz, CDCl₃): δ = 124.0 ppm (s; 4C; *o*-ArC), 125.2 ppm (s; 4C; *m*-ArC), 146.2 ppm (s; 2C; *p*-ArC), 149.8 ppm (s; 2C; *i*-ArC). FTIR (cm⁻¹): 3479, 3359, 3220, 3101, 2909, 2827, 2436, 1708, 1630, 1593, 1580, 1504, 1471, 1445, 1331, 1314, 1296, 1271, 1175, 1106, 1059, 1000, 975, 967, 871, 850, 787, 751, 686, 676, 629, 585, 534, 515, 489, 456, 389. MP: 160.2-164.0°C. Anal. Calcd for C₁₂H₈N₄O₄S: C, 47.37; H, 2.65; N, 18.41; S, 10.54 %. Found: C, 48.19; H, 3.02; N, 17.98; S, 9.72 %.

Synthesis of 2,4,6-trifluorophenyl-N-sulfinylaniline. In a round-bottomed side-arm flask, 2,4,6- trifluoroaniline (2.04 g, 13.9 mmol) was dissolved in ~80 mL dry benzene and stirred under N₂ flow. To this was added SOCl₂ (2.2 mL, 30 mmol) diluted in ~20 mL of benzene. The reaction mixture was refluxed for ~2.5 hours, until the evolution of HCl vapors ceased. Removed solvent to yield a dark yellow oil, 2,4,6-trifluorophenyl-N-sulfinylaniline. Yield: 2.12 g, 79%. ¹H NMR (300 MHz, CDCl₃): δ = 6.83 ppm (m; 2ArH); ¹⁹F NMR (282 MHz, CDCl₃): δ = -105 ppm (m; 1F; *p*-ArF), -107 ppm (m; 2F; *o*-ArF).

Synthesis of bis(2,4,6-trifluorophenyl)sulfurdiimide (8). In a round-bottomed side-arm flask, 2,4,6-trifluorophenyl-N-sulfinylaniline (2.12 g, 11.0 mmol) was dissolved in ~100 mL

dry benzene, and potassium *tert*-butoxide (0.7 g, 6.2 mmol) was added. This was stirred at room temperature, changing colour from pale yellow to a medium orange solution. Upon reflux, the solution turned dark yellow. Refluxed for 2.5 hours, then cooled to room temperature, leaving a dark gel-like substance. This was washed three times with dH_2O , the organic phase was separated, dried over $MgSO_4$, and solvent was removed. The resulting brown crystals were > 99% pure sulfur diimide, as indicated by ^1H NMR. Yield: 1.49 g, 84%. ^1H NMR (700 MHz, $CDCl_3$): δ = 6.52 ppm (4H; t; *m*-ArH). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ = 99.9 ppm (ddd, $^2J(C-F)$ = 26.6 Hz, $^2J(C-F)$ =23.6 Hz, $^4J(C-F)$ = 4.8 Hz, 4C, *m*-ArC), 117.9 ppm (td, $^2J(C-F)$ = 17.7 Hz, $^4J(C-F)$ = 5.1 Hz, 2C, *i*-ArC), 153.6 ppm (ddd, $^1J(C-F)$ = 252.3 Hz, $^3J(C-F)$ = 14.7 Hz, $^3J(C-F)$ = 7.0 Hz, 4C, *o*-ArC), 160.3 ppm (dt, $^1J(C-F)$ = 250.6 Hz, $^3J(C-F)$ = 14.4 Hz, 2C, *p*-ArC). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -109 ppm (m; 2F; *p*-ArF), -113 ppm (m; 4F; *o*-ArF). FTIR (cm^{-1}): 510, 835, 985, 1038, 1123, 1267, 1443, 1486, 1605, 3105. MP: 95.9-96.5°C. Anal. Calcd for $C_{12}H_4F_6N_2S$: C, 44.73; H, 1.25; N, 8.69; S, 9.95 %. Found: C, 44.72; H, 1.11; N, 8.99; S, 11.61 %.

Synthesis of bis(2,4,6-tribromophenyl)sulfurdiimide (9). 2,4,6-tribromoaniline (1.42 g, 4.3 mmol) was dissolved in 60 mL dry $CHCl_3$ with DABCO (1,4-diazabicyclo[2.2.2]octane, 1.88 g, 16.8 mmol), and cooled to -30°C with stirring. S_2Cl_2 (0.65 mL, 8.1 mmol) was added dropwise, and the solution turned red. The solution was allowed to stir for 10 minutes, then warmed to room temperature and stirred for an hour, and then refluxed for an hour. After ~50 minutes of reflux, the solution turned brown. The reaction was cooled and filtered, isolating a red filtrate. Solvent was removed, and the resulting solid was dissolved in benzene and extracted with water to remove excess DABCO. The organic layer was dried over $MgSO_4$, separated, and the solvent removed. The product was columned on 230-400 mesh silica using 80:20 hexane:dichloromethane as eluent. The sulfur diimide was recrystallized from heptane. Yield: 0.21 g, 15%. ^1H NMR (700 MHz, $CDCl_3$): 7.56 ppm (s; 4H; *m*-ArH). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ = 117.3 ppm (s; 4C; *o*-ArC), 118.9 ppm (s; 2C; *p*-ArC), 134.0 ppm (s; 4C; *m*-ArC), 141.3 ppm (s; 2C; *i*-ArC). FTIR (cm^{-1}): 3090, 3064, 1731,

1607, 1554, 1522, 1456, 1422, 1406, 1366, 1287, 1248, 1240, 1186, 1109, 1093, 1070, 1042, 987, 871, 860, 851, 820, 786, 733, 714, 675, 617, 560, 543, 480. MP: 128.0-131.5°C. Anal. Calcd for $C_{12}H_4Br_6N_2S$: C, 20.96; H, 0.59; N, 4.07; S, 4.66 %. Found: C, 19.23; H, 0.58; N, 3.84; S, 4.62 %.

B.2. Full Crystallographic Details for 1 to 9, 15, and 16

Crystals were selected under the microscope and mounted on 100 μm MiTeGen supports using either Fomblin (1 – 9) or Paragon™ oils, and cooled to the temperature indicated (Table B.1) using the diffractometer Oxford 800 cooling wand. Diffraction image data were measured with a Rigaku-Oxford Diffraction SuperNova diffractometer equipped with a Pilatus P200 HPC detector, using $\text{CuK}\alpha$ ($\lambda = 1.54184 \text{ \AA}$, 1 - 15) or $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$, 16) radiation.

Table B.1. Crystal, Data Collection and Refinement Parameters for Crystallography of 1 – 9, 15, 16.

Parameter	1	2	3	4	5	6	7
Chemical Formula	$\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$	$\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$	$\text{C}_{12}\text{H}_8\text{N}_2\text{F}_2\text{S}$	$\text{C}_{12}\text{H}_8\text{Cl}_2\text{N}_2\text{S}$	$\text{C}_{12}\text{H}_8\text{Br}_2\text{N}_2\text{S}$	$\text{C}_{14}\text{H}_8\text{F}_6\text{N}_2\text{S}$	$\text{C}_{12}\text{H}_8\text{N}_4\text{O}_4\text{S}$
Formula Weight (g/mol)	274.346	242.347	250.274	283.182	372.084	350.289	304.28
Temperature (K)	99.98(13)	100.0(2)	100.0(3)	99.97(15)	100.0(3)	100.1(7)	103(5)
Crystal System	orthorhombic	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space Group	$\text{P}2_12_12_1$	$\text{P}-1$	$\text{Pca}2_1$	$\text{Pca}2_1$	$\text{C}2/\text{c}$	$\text{P}2_1/\text{c}$	$\text{Pna}2_1$
A (Å)	5.8160(2)	5.9009(3)	11.9782(5)	30.9892(8)	63.4775(16)	29.2783(12)	12.3801(3)
b (Å)	7.8340(3)	10.9280(4)	12.8933(5)	4.04825(10)	3.9565(1)	13.9144(4)	26.7982(5)
c (Å)	29.1661(12)	10.9347(4)	6.9647(2)	9.5656(3)	20.0452(5)	6.9053(3)	3.76337(13)
A (°)	90	113.980(4)	90	90	90	90	90
β (°)	90	103.805(4)	90	90	90.086(2)	91.229(4)	90
γ (°)	90	94.277(4)	90	90	90	90	90
Volume (Å³)	1328.88(9)	613.85(5)	1075.61(7)	1200.02(5)	5034.3(2)	2812.49(18)	1248.55(6)
Z	4	2	4	4	16	8	4
Z'	1	1	1	1	2	2	1
R^a [$I \geq 2\sigma(I)$]	0.0465	0.0537	0.0281	0.0395	0.0421	0.0706	0.0485
wR2 [all data]	0.1177	0.1464	0.0746	0.1072	0.1014	0.1977	0.1313
G.O.F.	1.033	1.048	1.046	1.051	1.047	1.056	1.042
Accession Code	1578020	1578021	1578022	1578023	1578024	2022775	1578025

Table B.1. Continued

Parameter	8	9	15	16
Chemical Formula	C ₁₂ H ₄ F ₆ N ₂ S	C ₁₂ H ₄ Br ₆ N ₂ S	C ₁₀ H ₁₇ NOSi	C ₆ H ₄ Br ₃ N
Formula Weight (g/mol)	322.235	687.666	195.338	329.816
Temperature (K)	159.8(2)	160.00(10)	100.00(12)	99.95(15)
Crystal System	monoclinic	triclinic	orthorhombic	orthorhombic
Space Group	P2 ₁ /n	P-1	Pbca	P2 ₁ 2 ₁ 2 ₁
A (Å)	10.4849(2)	8.5880(3)	11.34493(12)	4.2377(3)
b (Å)	10.0241(1)	8.9084(3)	11.85345(13)	13.3331(10)
c (Å)	12.3536(2)	12.3124(3)	17.04883(19)	14.4662(12)
A (°)	90	80.479(2)	90	90
β (°)	111.806(2)	82.867(2)	90	90
γ (°)	90	65.035(3)	90	90
Volume (Å³)	1205.48(4)	840.63(5)	2292.67(4)	817.35(10)
Z	4	2	8	4
Z'	1	1	1	1
R^a [$I \geq 2\sigma(I)$]	0.0168	0.0202	0.0192	0.0432
wR2 [all data]	0.0429	0.0431	0.0461	0.1061
G.O.F.	1.04	1.054	1.042	0.976
Accession Code	1889021	1889023	1578027	1961561

The images were integrated, the data processed and corrected for absorption using CrysAlisPro 1.171.38.43, (empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm). Structures were solved with SHELXT,^[3] and refined by full-matrix LS minimization using SHELXL-2014^[4] within the Olex2 suite of programs (release 1.5-alpha).^[5] For all structures, further refinement, also with full-matrix LS minimisation, was continued with olex2.refine to define the standard isolated atom model (IAM) refinement. Thereafter, Hirshfeld atom refinement (HAR) was undertaken in conjunction with tailor-made aspherical atom scattering factors computed by NoSpherA2 from Hirshfeld-partitioned electron densities (ED).^[6] The ED is calculated from a Gaussian basis set single determinant SCF wavefunction - DFT using selected functionals - for a fragment of the crystal. This fragment can be embedded in an electrostatic crystal field by employing cluster charges or modelled using implicit solvation models, depending on the software used. Quantum calculations to determine the electron densities were undertaken with the ORCA program system, version 5.0,^[7] at the R2SCAN/def2-TZVP level of theory for **1** - **8**, **15**; R2SCAN/def2-TZVPD for **9** and R2SCAN/Jorge-TSP for **16**.

These aromatic SDIs are very prone towards twinning, and many crystals were measured to obtain optimal data sets; in addition, the use of fluorinated cryo-oils was found essential as most SDIs are quite soluble in standard Paratone™, which adds to the difficulty as the Fomblin oil available to us was quite fluid at ambient temperature. In many cases, only the data from the main component of the twinned data could be used for refinement, leading in at least one case (**9**) to incompleteness (93% collected). In view of the importance of non-bonded interactions and dispersion in these structures, we decided to apply the newly developed HAR using NoSpherA2 because of its demonstrated improvement in overall structure accuracies.^[8-14] Thus, models were first refined fully using the same refinement engine (olex2.refine) in an IAM standard for comparison. The HAR/NoSphereA2 results were critically evaluated, and it was found that there were too many outliers in C–H bond lengths. It was therefore decided that for all the SDI structures, as well as for the known troublesome structure **16** (previous structure determinations CSD refcodes BRANIL, BRANIL01 and BRANIL02), the C–H distances are restrained at the distances determined from neutron diffraction data obtained in similar temperature ranges.^[15] Namely, C_{Ar}–H = 1.085 and C_{sp³}–H = 1.084 Å. Also, in most cases, the use of RIGU restraints applied to C,H pairs was found to be helpful. Frequent use of ISOR (approximate sphericity) was also applied to the anisotropic displacements of the H atoms. Similarly, the N–H distance in **16** was restrained to the neutron diffraction value of 1.040 Å.^[15] Upon review of the complete set of structures, we are confident that the refinements correspond to state-of-the-art results for SC-XRD. To our knowledge, no previous HAR structure models have ever been reported. The outcomes increase our confidence in the comparisons to DFT calculated structures and are important for the accurate molecular and lattice structures of these compounds. The comparisons to known data and analysis of interatomic distances and angles for **1** – **9** are dealt with in Section 4.2.2. For background and further discussion of the structures of **15** and **16**, which deal with reagents employed to prepare the former, see below after the structure image and derived parameter data tables for each structure.

Structures were visualized and analyzed using Mercury CSD Release 2021.2.0 as well as with PLATON.^[16-17] Crystal data and structure refinement details for all 11 structures are collected in Table B.1 including the CSD Accession Codes. Individual derived results for the structures of **1** – **9**, **15**, **16** are listed in Tables B.1 – B.25. Improvements from HAR/NoSpherA2 are in Table B.26. Selected averaged interatomic distances and angles are compiled in Table B.27 and comparisons of the calculated and computed geometrical parameters from DFT are made in Table B.28.

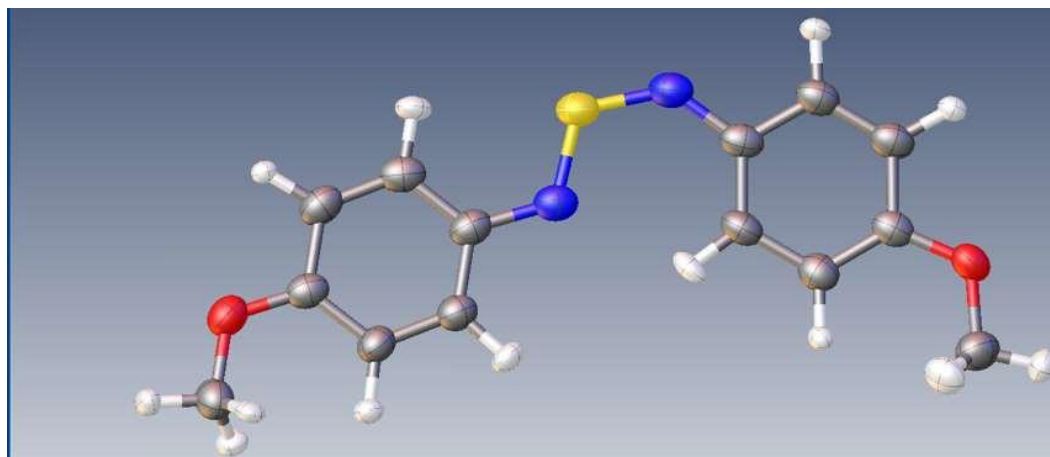


Figure B.1. Full view of a displacement ellipsoids plot of **1**

Table B.2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
S	6046.2(15)	1940.0(11)	3079.6(3)	44.8(2)
O1	4664(4)	5410(3)	5181.6(8)	42.0(6)
O2	-505(4)	2945(3)	1266.5(8)	47.3(6)
N1	6988(5)	2108(4)	3567.5(10)	48.1(7)
N2	3768(5)	2908(4)	2985.8(10)	43.9(7)
C1	6202(6)	3000(4)	3953.7(12)	39.7(7)
C2	7659(6)	2911(4)	4334.9(13)	43.1(8)
C3	7065(6)	3727(4)	4736.5(14)	42.3(9)
C4	5012(6)	4665(4)	4767.7(12)	38.2(8)
C5	3554(6)	4760(4)	4394.0(13)	41.9(8)
C6	4153(6)	3916(4)	3980.2(13)	41.9(8)
C7	2746(6)	2835(5)	2542.2(12)	41.7(8)
C8	3613(5)	1939(4)	2169.3(13)	43.3(8)
C9	2465(6)	1971(5)	1746.6(13)	45.0(8)
C10	458(5)	2931(4)	1688.9(12)	40.2(8)
C11	-412(6)	3814(4)	2066.0(12)	42.0(8)
C12	725(6)	3756(4)	2489.7(12)	42.0(8)
C13	2596(7)	6329(5)	5250.1(15)	51.6(10)
C14	-2310(7)	4122(5)	1186.8(15)	48.4(9)
H2a	9180(50)	2090(50)	4310(13)	58(9)
H3	8190(60)	3710(50)	5034(9)	47(8)
H5	2100(40)	5590(40)	4412(12)	42(7)
H6	3020(60)	4230(50)	3703(11)	60(10)
H8	5200(50)	1250(50)	2210(15)	70(11)
H9	2980(60)	1420(40)	1429(8)	39(7)
H11	-1970(50)	4580(50)	2039(13)	55(10)
H12	10(80)	4560(50)	2760(12)	71(12)
H13a	2410(90)	7310(60)	4997(16)	91(13)
H13b	1110(50)	5520(50)	5208(15)	67(10)
H13c	2550(80)	6710(70)	5605(8)	76(11)
H14a	-2650(70)	4000(60)	823(7)	58(10)
H14b	-3830(50)	3750(50)	1388(13)	58(10)
H14c	-1770(60)	5390(30)	1278(14)	52(9)

Table B.3. Bond lengths [Å], angles [°], and torsions [°] for **1**

Lengths	Atoms	Length/Å	Atoms	Length/Å
	S N1	1.530(3)	C6 H6	1.071(17)
	S N2	1.551(3)	C7 C8	1.389(5)
	O1 C4	1.356(4)	C7 C12	1.388(5)
	O1 C13	1.416(4)	C8 H8	1.076(17)
	O2 C10	1.353(4)	C8 C9	1.403(5)
	O2 C14	1.416(4)	C9 H9	1.065(17)
	N1 C1	1.402(4)	C9 C10	1.399(5)
	N2 C7	1.425(4)	C10 C11	1.394(5)
	C1 C2	1.399(5)	C11 H11	1.089(17)
	C1 C6	1.393(5)	C11 C12	1.402(5)
	C2 H2a	1.095(17)	C12 H12	1.089(17)
	C2 C3	1.379(5)	C13 H13a	1.074(18)
	C3 H3	1.088(17)	C13 H13b	1.080(18)
	C3 C4	1.405(5)	C13 H13c	1.078(18)
	C4 C5	1.383(5)	C14 H14a	1.083(17)
	C5 H5	1.071(17)	C14 H14b	1.103(18)
	C5 C6	1.420(5)	C14 H14c	1.076(17)
Angles	Atoms	Angle/°	Atoms	Angle/°
	N2 S N1	115.31(16)	C6 C5 C4	119.6(3)
	C13 O1 C4	118.1(3)	C5 C6 C1	119.8(3)
	C14 O2 C10	117.5(3)	C8 C7 N2	125.4(3)
	C1 N1 S	132.3(2)	C12 C7 N2	115.7(3)
	C7 N2 S	119.8(2)	C12 C7 C8	118.9(3)
	C2 C1 N1	114.6(3)	C9 C8 C7	120.4(3)
	C6 C1 N1	125.4(3)	C10 C9 C8	120.8(3)
	C6 C1 C2	119.9(3)	C9 C10 O2	117.3(3)
	C3 C2 C1	120.0(3)	C11 C10 O2	124.3(3)
	C4 C3 C2	120.7(3)	C11 C10 C9	118.3(3)
	C3 C4 O1	114.2(3)	C12 C11 C10	120.5(3)
	C5 C4 O1	125.9(3)	C11 C12 C7	120.9(3)
	C5 C4 C3	119.9(3)		
Torsions	Atoms	Angle/°	Atoms	Angle/°
	S N1 C1 C2	-176.1(3)	N2 C7 C8 C9	-179.5(3)
	S N1 C1 C6	4.2(4)	N2 C7 C12 C11	178.5(3)
	S N2 C7 C8	0.4(3)	C1 C2 C3 C4	-0.5(4)
	S N2 C7 C12	-179.3(3)	C1 C6 C5 C4	-0.0(4)
	O1 C4 C3 C2	-179.4(3)	C2 C3 C4 C5	0.6(4)
	O1 C4 C5 C6	179.7(3)	C3 C4 C5 C6	-0.4(3)
	O2 C10 C9 C8	177.7(3)	C7 C8 C9 C10	1.4(4)
	O2 C10 C11 C12	-178.7(3)	C7 C12 C11 C10	0.6(4)
	N1 C1 C2 C3	-179.6(3)	C8 C9 C10 C11	-2.0(4)
	N1 C1 C6 C5	179.8(3)	C9 C10 C11 C12	1.0(4)

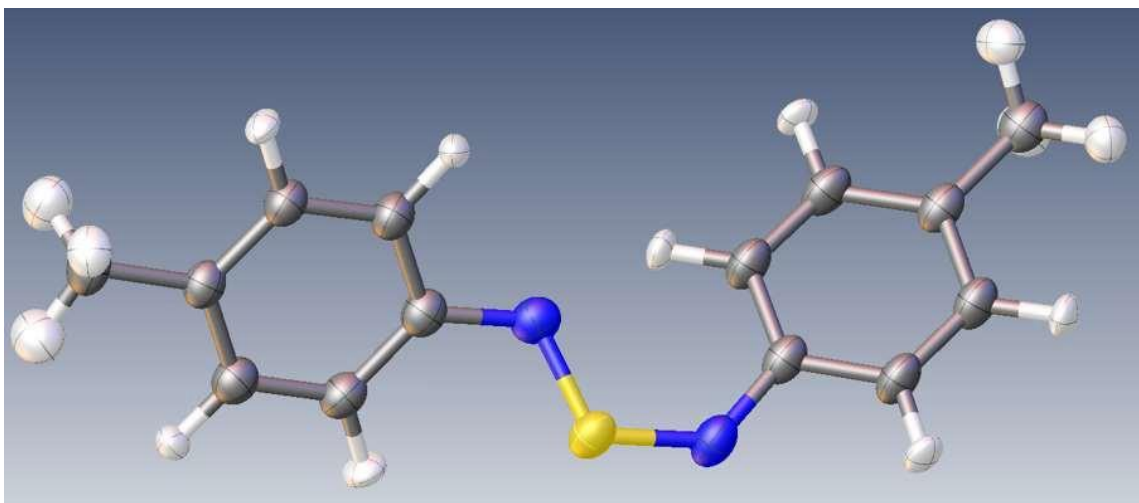


Figure B.2. Full view of a displacement ellipsoids plot of **2**

Table B.4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised UJ tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
S	1688.2(10)	2415.2(5)	786.1(5)	35.10(19)
N1	3559(4)	3418.9(19)	715(2)	37.1(4)
N2	2117(3)	2364.4(19)	2221.6(19)	35.3(4)
C1	5626(4)	4310(2)	1735(2)	32.4(4)
C2	7366(4)	4729(2)	1235(2)	35.2(5)
C3	9479(4)	5610(2)	2157(2)	35.5(5)
C4	9905(4)	6118(2)	3601(2)	33.2(4)
C5	8126(4)	5713(2)	4090(2)	36.2(5)
C6	6027(4)	4814(2)	3186(2)	35.0(5)
C7	440(4)	1398(2)	2280(2)	32.7(4)
C8	-2027(4)	1147(2)	1659(2)	34.3(5)
C9	-3544(4)	177(2)	1774(2)	34.6(5)
C10	-2658(4)	-553(2)	2516(2)	30.8(4)
C11	-199(4)	-268(2)	3146(2)	32.2(4)
C12	1322(4)	694(2)	3046(2)	33.9(4)
C13	12170(4)	7082(2)	4606(2)	37.8(5)
C14	-4262(4)	-1584(2)	2662(3)	39.8(5)
H2a	6980(60)	4350(30)	114(18)	57(8)
H3	10880(50)	5880(40)	1760(30)	61(8)
H5	8420(60)	6080(30)	5201(18)	56(8)
H6	4670(50)	4520(40)	3580(30)	56(8)
H8	-2770(60)	1730(30)	1110(40)	64(8)
H9	-5430(30)	-20(30)	1310(30)	52(7)
H11	520(50)	-820(30)	3740(30)	51(7)
H12	3230(30)	900(30)	3560(30)	51(7)
H13a	13510(50)	7140(40)	4120(40)	78(11)
H13b	11830(80)	8090(30)	5130(50)	102(15)
H13c	12910(70)	6790(40)	5430(30)	82(12)
H14a	-6070(40)	-1660(50)	2130(50)	110(16)
H14b	-3750(70)	-2570(20)	2270(40)	76(11)
H14c	-4330(90)	-1210(50)	3730(20)	105(15)

Table B.5. Bond lengths [Å], angles [°], and torsions [°] for 2

Lengths	Atoms	Length/Å	Atoms	Length/Å
	S N1	1.5353(19)	C7 C12	1.393(3)
	S N2	1.5539(19)	C8 H8	1.088(16)
	N1 C1	1.404(3)	C8 C9	1.401(3)
	N2 C7	1.424(3)	C9 H9	1.072(16)
	C1 C2	1.402(3)	C9 C10	1.397(3)
	C1 C6	1.403(3)	C10 C11	1.400(3)
	C2 H2a	1.080(16)	C10 C14	1.500(3)
	C2 C3	1.389(3)	C11 H11	1.095(16)
	C3 H3	1.093(16)	C11 C12	1.387(3)
	C3 C4	1.393(3)	C12 H12	1.091(16)
	C4 C5	1.405(3)	C13 H13a	1.064(18)
	C4 C13	1.501(3)	C13 H13b	1.080(18)
	C5 H5	1.078(16)	C13 H13c	1.081(18)
	C5 C6	1.386(3)	C14 H14a	1.068(18)
	C6 H6	1.078(16)	C14 H14b	1.079(17)
	C7 C8	1.404(3)	C14 H14c	1.081(18)
Angles	Atoms	Angle/°	Atoms	Angle/°
	N2 S N1	115.58(11)	C5 C6 C1	119.4(2)
	C1 N1 S	130.84(16)	C8 C7 N2	124.40(19)
	C7 N2 S	115.90(15)	C12 C7 N2	117.14(19)
	C2 C1 N1	116.13(19)	C12 C7 C8	118.4(2)
	C6 C1 N1	124.86(19)	C9 C8 C7	120.4(2)
	C6 C1 C2	119.0(2)	C10 C9 C8	121.3(2)
	C3 C2 C1	120.8(2)	C11 C10 C9	117.35(19)
	C4 C3 C2	120.9(2)	C14 C10 C9	121.9(2)
	C5 C4 C3	117.8(2)	C14 C10 C11	120.76(19)
	C13 C4 C3	121.3(2)	C12 C11 C10	121.99(19)
	C13 C4 C5	120.9(2)	C11 C12 C7	120.5(2)
	C6 C5 C4	122.1(2)		
Torsions	Atoms	Angle/°	Atoms	Angle/°
	S N1 C1 C2	158.3(2)	C1 C6 C5 C4	-1.4(2)
	S N1 C1 C6	-23.0(2)	C2 C3 C4 C5	-0.2(2)
	S N2 C7 C8	-41.56(18)	C2 C3 C4 C13	-179.3(2)
	S N2 C7 C12	140.59(16)	C3 C4 C5 C6	1.5(2)
	N1 C1 C2 C3	-180.00(19)	C7 C8 C9 C10	0.6(2)
	N1 C1 C6 C5	-178.6(2)	C7 C12 C11 C10	-1.2(2)
	N2 C7 C8 C9	-179.8(2)	C8 C9 C10 C11	0.5(2)
	N2 C7 C12 C11	-179.70(18)	C8 C9 C10 C14	179.3(2)
	C1 C2 C3 C4	-1.2(3)	C9 C10 C11 C12	-0.2(2)

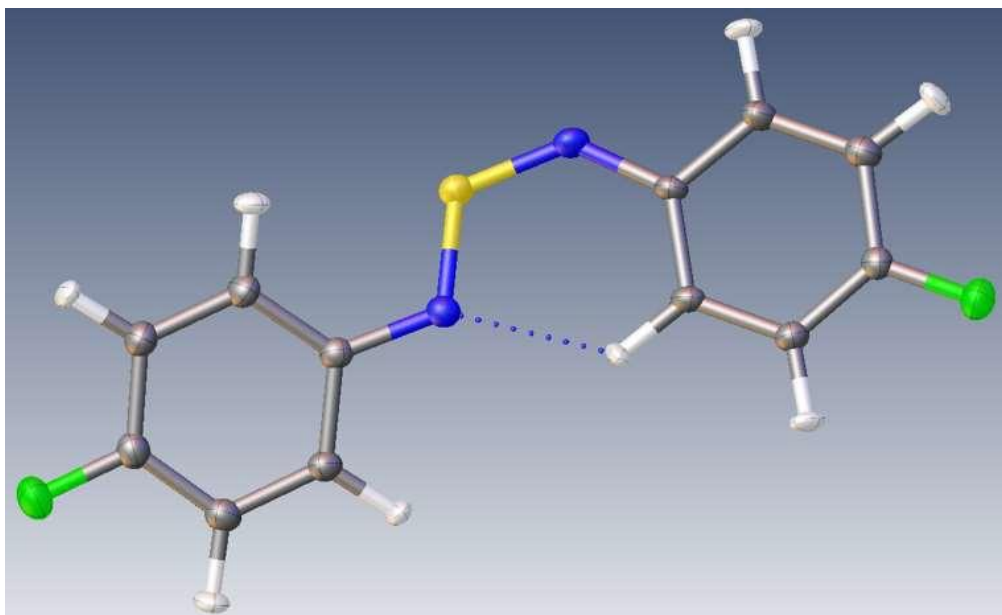


Figure B.3. Full view of a displacement ellipsoids plot of **3**

Table B.6. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
S	1560.9(3)	2993.9(3)	4191.2(8)	20.29(12)
F1	2887.2(10)	7813.2(9)	6906.4(18)	28.0(3)
F2	4757.8(10)	-998.5(9)	3186.0(17)	30.2(3)
N1	1096.3(13)	4066.2(13)	4707(2)	22.1(4)
N2	2852.3(12)	2851.0(11)	4391(3)	20.3(3)
C1	1618.7(15)	4978.6(15)	5306(3)	17.9(4)
C2	893.6(16)	5797.1(15)	5794(3)	22.2(4)
C3	1316.4(16)	6754.0(15)	6355(3)	23.0(4)
C4	2472.1(19)	6879.9(13)	6381(3)	19.8(4)
C5	3205.6(16)	6094.4(14)	5902(3)	20.6(4)
C6	2777.2(14)	5135.7(15)	5367(3)	18.7(4)
C7	3278.0(14)	1842.4(13)	4084(3)	18.3(3)
C8	2685.9(15)	924.9(14)	4451(3)	21.3(4)
C9	3179.4(15)	-39.1(13)	4143(3)	22.4(3)
C10	4270.6(16)	-68.3(14)	3460(3)	22.0(4)
C11	4883.2(16)	819.2(15)	3097(3)	22.4(4)
C12	4384.4(15)	1779.0(14)	3413(3)	20.6(4)
H2a	-11(14)	5650(20)	5720(50)	50(9)
H3	780(20)	7419(19)	6730(50)	46(8)
H5	4098(14)	6240(20)	5940(40)	39(8)
H6	3330(20)	4495(17)	4930(50)	39(8)
H8	1835(15)	970(20)	5010(40)	40(8)
H9	2759(19)	-768(14)	4450(50)	37(7)
H11	5732(16)	740(20)	2560(50)	52(10)
H12	4830(20)	2503(15)	3150(50)	41(8)

Table B.7. Bond lengths [Å], angles [°], and torsions [°] for **3**

Lengths	Atoms	Length/Å	Atoms	Length/Å
	S N1	1.5329(16)	C5 H5	1.086(16)
	S N2	1.5641(15)	C5 C6	1.389(3)
	F1 C4	1.352(2)	C6 H6	1.099(16)
	F2 C10	1.347(2)	C7 C8	1.403(2)
	N1 C1	1.396(2)	C7 C12	1.408(2)
	N2 C7	1.413(2)	C8 H8	1.093(16)
	C1 C2	1.408(3)	C8 C9	1.393(2)
	C1 C6	1.403(2)	C9 H9	1.088(15)
	C2 H2a	1.100(16)	C9 C10	1.392(3)
	C2 C3	1.390(3)	C10 C11	1.383(3)
	C3 H3	1.101(16)	C11 H11	1.087(16)
	C3 C4	1.394(3)	C11 C12	1.392(3)
	C4 C5	1.382(3)	C12 H12	1.090(16)
Angles	Atoms	Angle/°	Atoms	Angle/°
	N2 S N1	116.39(8)	C5 C6 C1	120.12(17)
	C1 N1 S	131.85(13)	C8 C7 N2	124.49(16)
	C7 N2 S	116.86(12)	C12 C7 N2	116.31(15)
	C2 C1 N1	115.28(15)	C12 C7 C8	119.18(16)
	C6 C1 N1	125.01(16)	C9 C8 C7	120.66(16)
	C6 C1 C2	119.65(17)	C10 C9 C8	118.38(16)
	C3 C2 C1	120.55(17)	C9 C10 F2	118.65(16)
	C4 C3 C2	117.97(17)	C11 C10 F2	118.74(17)
	C3 C4 F1	118.18(17)	C11 C10 C9	122.59(17)
	C5 C4 F1	118.93(19)	C12 C11 C10	118.63(17)
	C5 C4 C3	122.89(17)	C11 C12 C7	120.55(17)
	C6 C5 C4	118.82(17)		
Torsions	Atoms	Angle/°	Atoms	Angle/°
	S N1 C1 C2	-175.25(19)	N2 C7 C8 C9	-178.7(2)
	S N1 C1 C6	7.6(2)	N2 C7 C12 C11	178.98(17)
	S N2 C7 C8	-29.4(2)	C1 C2 C3 C4	1.2(2)
	S N2 C7 C12	152.32(16)	C1 C6 C5 C4	0.4(2)
	F1 C4 C3 C2	179.31(17)	C2 C3 C4 C5	-0.9(2)
	F1 C4 C5 C6	179.87(17)	C3 C4 C5 C6	0.1(2)
	F2 C10 C9 C8	179.06(18)	C7 C8 C9 C10	-0.2(2)
	F2 C10 C11 C12	-178.90(17)	C7 C12 C11 C10	-0.1(2)
	N1 C1 C2 C3	-178.02(17)	C8 C9 C10 C11	0.7(3)
	N1 C1 C6 C5	176.89(18)	C9 C10 C11 C12	-0.6(2)

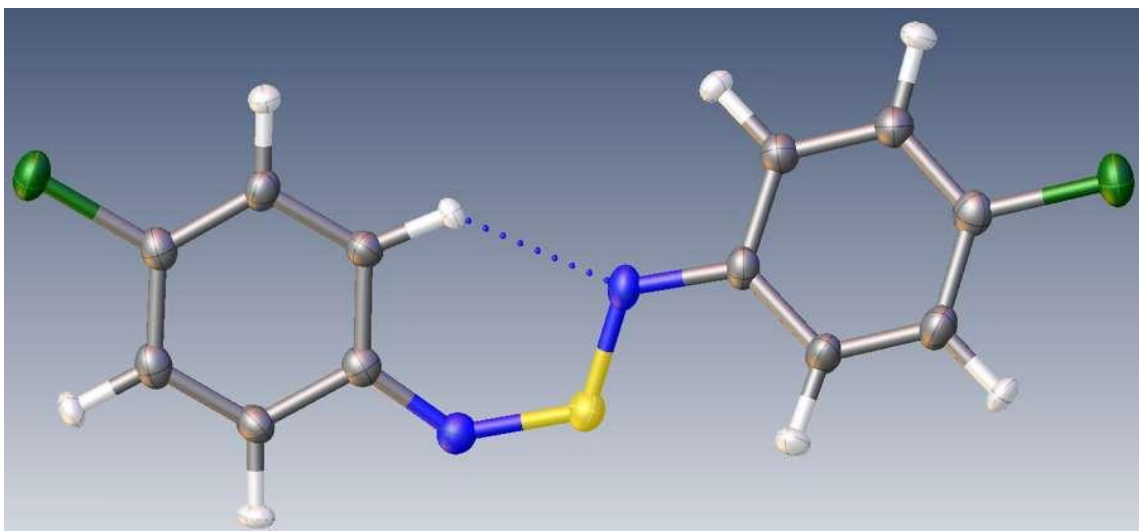


Figure B.4. Full view of a displacement ellipsoids plot of **4**

Table B.8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
Cl1	8751.5(2)	3782(2)	4539.1(9)	31.2(2)
Cl2	4702.1(2)	831(2)	3948.7(9)	33.7(2)
S	6586.5(2)	7876.2(18)	6247.4(8)	23.87(18)
N1	7063.0(9)	8495(7)	6579(3)	24.2(6)
N2	6491.0(8)	5327(7)	5061(3)	24.8(6)
C1	7444.5(10)	7216(7)	6042(3)	22.7(7)
C2	7823.8(10)	8202(8)	6742(3)	24.0(6)
C3	8225.7(10)	7136(8)	6290(4)	25.5(6)
C4	8248.8(10)	5111(8)	5116(4)	24.4(6)
C5	7880.3(10)	4098(8)	4408(3)	24.0(6)
C6	7476.0(10)	5129(8)	4878(3)	22.6(6)
C7	6056.1(9)	4406(8)	4843(3)	23.4(7)
C8	5730.2(10)	4686(9)	5851(3)	26.0(7)
C9	5314.1(11)	3642(9)	5572(4)	29.2(7)
C10	5222.0(11)	2262(8)	4276(4)	27.1(7)
C11	5538.7(11)	1950(9)	3260(4)	27.9(7)
C12	5954.7(11)	3018(9)	3542(4)	26.4(7)
H2a	7789(17)	9760(120)	7660(40)	41(11)
H3	8518(11)	8010(130)	6800(50)	42(11)
H5	7906(18)	2400(120)	3520(40)	40(11)
H6	7165(9)	4300(100)	4460(50)	26(9)
H8	5820(17)	5670(140)	6870(30)	42(11)
H9	5054(13)	4130(130)	6310(50)	46(12)
H11	5477(18)	720(130)	2260(30)	42(11)
H12	6212(13)	2710(130)	2770(40)	37(11)

Table B.9. Bond lengths [Å], angles [°], and torsions [°] for **4**

Lengths	Atoms	Length/Å	Atoms	Length/Å
	Cl1 C4	1.738(3)	C5 H5	1.095(18)
	Cl2 C10	1.740(3)	C5 C6	1.395(4)
	S N1	1.531(3)	C6 H6	1.095(18)
	S N2	1.562(3)	C7 C8	1.401(4)
	N1 C1	1.389(4)	C7 C12	1.401(5)
	N2 C7	1.414(4)	C8 H8	1.093(18)
	C1 C2	1.410(4)	C8 C9	1.383(5)
	C1 C6	1.401(5)	C9 H9	1.086(18)
	C2 H2a	1.087(18)	C9 C10	1.389(5)
	C2 C3	1.387(5)	C10 C11	1.387(5)
	C3 H3	1.088(18)	C11 H11	1.093(18)
	C3 C4	1.392(5)	C11 C12	1.386(5)
	C4 C5	1.389(4)	C12 H12	1.094(18)
Angles	Atoms	Angle/°	Atoms	Angle/°
	N2 S N1	116.19(14)	C5 C6 C1	119.9(3)
	C1 N1 S	133.1(2)	C8 C7 N2	124.4(3)
	C7 N2 S	117.5(2)	C12 C7 N2	116.8(3)
	C2 C1 N1	115.4(3)	C12 C7 C8	118.8(3)
	C6 C1 N1	125.3(3)	C9 C8 C7	121.0(3)
	C6 C1 C2	119.3(3)	C10 C9 C8	119.1(3)
	C3 C2 C1	120.8(3)	C9 C10 Cl2	119.0(3)
	C4 C3 C2	118.7(3)	C11 C10 Cl2	119.9(3)
	C3 C4 Cl1	119.0(2)	C11 C10 C9	121.1(3)
	C5 C4 Cl1	119.4(3)	C12 C11 C10	119.5(3)
	C5 C4 C3	121.6(3)	C11 C12 C7	120.4(3)
	C6 C5 C4	119.5(3)		
Torsions	Atoms	Angle/°	Atoms	Angle/°
	Cl1 C4 C3 C2	179.7(3)	N2 C7 C8 C9	-178.1(3)
	Cl1 C4 C5 C6	179.3(2)	N2 C7 C12 C11	177.9(3)
	Cl2 C10 C9 C8	178.0(3)	C1 C2 C3 C4	1.0(4)
	Cl2 C10 C11 C12	-178.3(3)	C1 C6 C5 C4	1.0(4)
	S N1 C1 C2	-173.7(3)	C2 C3 C4 C5	-1.1(4)
	S N1 C1 C6	7.3(4)	C3 C4 C5 C6	0.1(4)
	S N2 C7 C8	-22.3(3)	C7 C8 C9 C10	0.8(4)
	S N2 C7 C12	160.1(3)	C7 C12 C11 C10	-0.0(4)
	N1 C1 C2 C3	-178.9(3)	C8 C9 C10 C11	-0.7(4)
	N1 C1 C6 C5	177.7(3)	C9 C10 C11 C12	0.3(4)

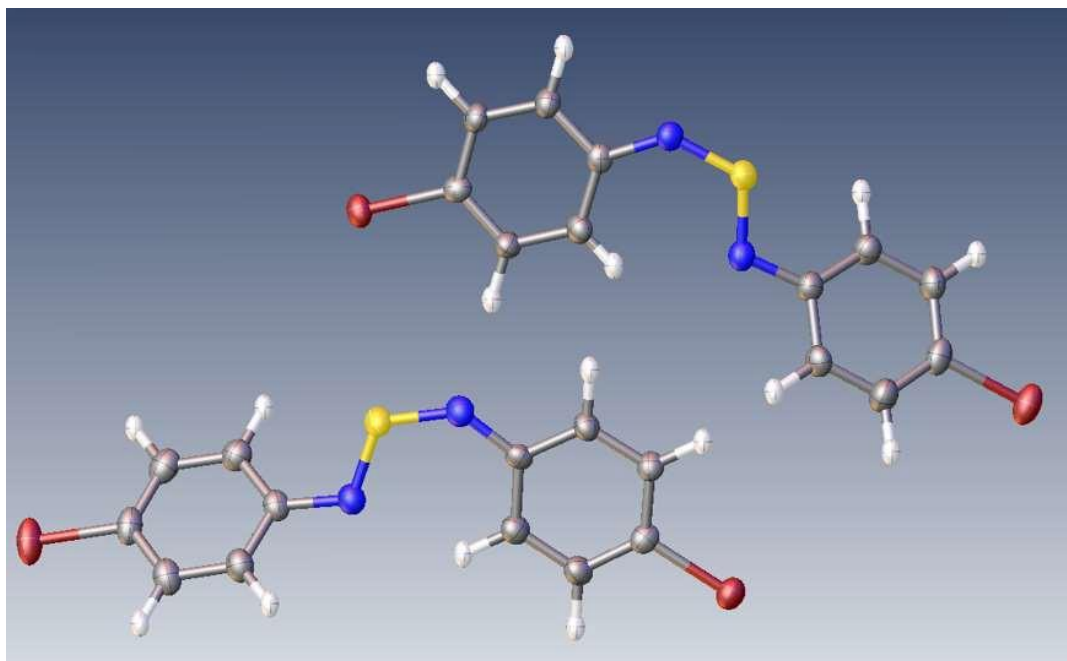


Figure B.5. Full view of a displacement ellipsoids plot of 5

Table B.10. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 5. Ueq is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Br1	5618.21(9)	8599.0(16)	8386.6(3)	33.07(17)
Br2	7653.43(10)	11424.2(15)	8936.1(5)	44.7(2)
S1	6713.4(2)	5919(3)	7513.5(8)	28.8(3)
N1	6484.3(7)	5296(12)	7310(2)	30.4(10)
N2	6750.6(7)	7807(12)	8186(3)	29.3(10)
C1	6292.4(9)	6187(13)	7589(3)	25.1(12)
C2	6113.2(8)	5078(14)	7246(3)	26.3(11)
C3	5911.3(9)	5727(13)	7478(3)	27.0(12)
C4	5890.8(9)	7572(14)	8071(3)	28.1(12)
C5	6065.4(10)	8724(14)	8424(3)	29.7(13)
C6	6266.5(9)	8042(14)	8181(3)	29.5(12)
C7	6964.1(9)	8565(13)	8329(3)	28.5(13)
C8	7104.8(9)	9924(15)	7854(3)	31.0(12)
C9	7309.1(10)	10743(14)	8036(4)	36.5(14)
C10	7374.7(8)	10222(14)	8687(3)	32.6(13)
C11	7238.1(10)	8884(13)	9172(4)	33.1(14)
C12	7034.7(9)	8083(15)	8984(3)	31.3(13)
H2	6136(10)	3670(60)	6785(11)	33(4)
H3	5762(6)	5010(90)	7260(30)	33(4)
H5	6062(10)	10130(100)	8887(15)	33(4)
H6	6399(7)	8920(120)	8480(30)	33(4)
H8	7085(10)	10450(80)	7319(10)	33(4)
H9	7408(8)	11770(40)	7640(20)	33(4)
H11	7315(9)	8640(120)	9654(17)	33(4)
H12	6936(8)	6970(120)	9380(20)	33(4)

Table B.10. Cont'd

Atom	x	y	z	U(eq)
Br3	6871.44(9)	1037.5(14)	5824.3(3)	30.13(16)
Br4	4863.5(1)	3709.0(15)	6363.2(4)	40.05(19)
S2	5786.7(2)	-3146(3)	5061.0(7)	26.7(3)
N3	6016.2(7)	-3768(11)	4852(3)	27.3(10)
N4	5752.3(7)	-964(12)	5703(3)	29.0(11)
C21	6207.0(8)	-2576(13)	5117(3)	23.3(11)
C22	6384.8(9)	-3161(13)	4714(3)	27.0(12)
C23	6583.0(9)	-2108(14)	4918(3)	28.4(12)
C24	6601.7(8)	-450(13)	5533(3)	24.8(11)
C25	6429.5(8)	148(15)	5940(3)	28.3(12)
C26	6230.7(9)	-902(14)	5726(3)	27.1(12)
C27	5542.9(8)	-15(13)	5827(3)	26.6(11)
C28	5400.0(9)	912(14)	5328(3)	30.7(13)
C29	5196.7(9)	1987(14)	5488(3)	32.1(13)
C30	5138.7(8)	2159(14)	6152(3)	31.8(13)
C31	5275.8(10)	1245(15)	6659(4)	36.7(15)
C32	5477.6(9)	222(15)	6497(3)	30.3(12)
H22	6392(10)	-4440(70)	4227(11)	33(4)
H23	6718(7)	-2590(80)	4600(20)	33(4)
H25	6459(10)	1390(100)	6419(15)	33(4)
H26	6083(6)	-620(140)	5990(30)	33(4)
H28	5444(9)	790(80)	4802(13)	33(4)
H29	5049(5)	2860(40)	5280(30)	33(4)
H31	5229(10)	1240(120)	7184(13)	33(4)
H32	5572(8)	-530(110)	6950(20)	33(4)

Table B.11. Bond lengths [Å], angles [°], and torsions [°] for 5

Lengths	Atoms	Length/Å	Atoms	Length/Å
	Br1 C4	1.887(6)	Br3 C24	1.901(5)
	Br2 C10	1.898(5)	Br4 C30	1.900(5)
	S1 N1	1.530(5)	S2 N3	1.536(5)
	S1 N2	1.559(5)	S2 N4	1.565(5)
	N1 C1	1.387(7)	N3 C21	1.403(7)
	N2 C7	1.417(7)	N4 C27	1.404(7)
	C1 C2	1.400(8)	C21 C22	1.408(8)
	C1 C6	1.404(8)	C21 C26	1.398(8)
	C2 H2	1.089(19)	C22 H22	1.100(19)
	C2 C3	1.387(8)	C22 C23	1.386(8)
	C3 H3	1.079(19)	C23 H23	1.087(19)
	C3 C4	1.402(8)	C23 C24	1.401(8)
	C4 C5	1.391(8)	C24 C25	1.385(8)
	C5 H5	1.083(19)	C25 H25	1.095(19)
	C5 C6	1.393(8)	C25 C26	1.396(8)
	C6 H6	1.092(19)	C26 H26	1.079(19)
	C7 C8	1.413(9)	C27 C28	1.398(8)
	C7 C12	1.399(9)	C27 C32	1.408(8)
	C8 H8	1.099(19)	C28 H28	1.094(19)
	C8 C9	1.385(9)	C28 C29	1.396(8)
	C9 H9	1.086(19)	C29 H29	1.079(19)
	C9 C10	1.385(10)	C29 C30	1.382(9)

Table B.11. Cont'd

Lengths	Atoms	Length/Å	Atoms	Length/Å
	C10 C11	1.406(9)	C30 C31	1.385(9)
	C11 H11	1.087(19)	C31 H31	1.094(19)
	C11 C12	1.381(8)	C31 C32	1.382(9)
	C12 H12	1.096(19)	C32 H32	1.131(19)
Angles	Atoms	Angle/°	Atoms	Angle/°
	N2 S1 N1	116.8(3)	N4 S2 N3	116.5(3)
	C1 N1 S1	133.3(4)	C21 N3 S2	131.4(4)
	C7 N2 S1	114.9(4)	C27 N4 S2	115.3(4)
	C2 C1 N1	115.8(5)	C22 C21 N3	114.9(5)
	C6 C1 N1	125.3(5)	C26 C21 N3	125.5(5)
	C6 C1 C2	118.9(5)	C26 C21 C22	119.6(5)
	C3 C2 C1	121.9(5)	C23 C22 C21	120.6(5)
	C4 C3 C2	117.9(5)	C24 C23 C22	118.5(5)
	C3 C4 Br1	118.9(4)	C23 C24 Br3	119.4(4)
	C5 C4 Br1	119.3(5)	C25 C24 Br3	118.5(4)
	C5 C4 C3	121.8(5)	C25 C24 C23	122.1(5)
	C6 C5 C4	119.3(6)	C26 C25 C24	118.8(5)
	C5 C6 C1	120.3(5)	C25 C26 C21	120.3(5)
	C8 C7 N2	123.3(5)	C28 C27 N4	123.8(5)
	C12 C7 N2	117.8(5)	C32 C27 N4	117.9(5)
	C12 C7 C8	118.8(5)	C32 C27 C28	118.2(5)
	C9 C8 C7	120.2(6)	C29 C28 C27	121.0(6)
	C10 C9 C8	119.6(6)	C30 C29 C28	118.9(5)
	C9 C10 Br2	119.3(5)	C29 C30 Br4	118.5(4)
	C11 C10 Br2	119.3(5)	C31 C30 Br4	119.8(5)
	C11 C10 C9	121.5(5)	C31 C30 C29	121.7(5)
	C12 C11 C10	118.4(6)	C32 C31 C30	119.0(6)
	C11 C12 C7	121.5(6)	C31 C32 C27	121.2(5)
Torsions	Atoms	Angle/°	Atoms	Angle/°
	Br1 C4 C3 C2	178.3(4)	Br3 C24 C23 C22	-179.7(4)
	Br1 C4 C5 C6	-178.3(4)	Br3 C24 C25 C26	179.3(4)
	Br2 C10 C9 C8	-178.9(4)	Br4 C30 C29 C28	178.8(4)
	Br2 C10 C11 C12	178.8(4)	Br4 C30 C31 C32	-178.0(4)
	S1 N1 C1 C2	-179.3(5)	S2 N3 C21 C22	-168.1(5)
	S1 N1 C1 C6	-0.0(7)	S2 N3 C21 C26	11.6(6)
	S1 N2 C7 C8	45.0(5)	S2 N4 C27 C28	-38.3(5)
	S1 N2 C7 C12	-138.1(4)	S2 N4 C27 C32	145.9(4)
	N1 C1 C2 C3	178.6(4)	N3 C21 C22 C23	-179.9(4)
	N1 C1 C6 C5	-178.5(5)	N3 C21 C26 C25	179.5(5)
	N2 C7 C8 C9	177.2(5)	N4 C27 C28 C29	-176.9(5)
	N2 C7 C12 C11	-177.5(5)	N4 C27 C32 C31	177.9(5)
	C1 C2 C3 C4	0.5(6)	C21 C22 C23 C24	-0.1(6)
	C1 C6 C5 C4	-0.5(6)	C21 C26 C25 C24	1.0(6)
	C2 C3 C4 C5	-0.2(6)	C22 C23 C24 C25	0.3(6)
	C3 C4 C5 C6	0.2(6)	C23 C24 C25 C26	-0.8(6)
	C7 C8 C9 C10	-0.0(7)	C27 C28 C29 C30	0.7(6)
	C7 C12 C11 C10	0.2(7)	C27 C32 C31 C30	-2.2(7)
	C8 C9 C10 C11	-0.2(6)	C28 C29 C30 C31	-1.0(6)
	C9 C10 C11 C12	0.1(6)	C29 C30 C31 C32	1.7(6)

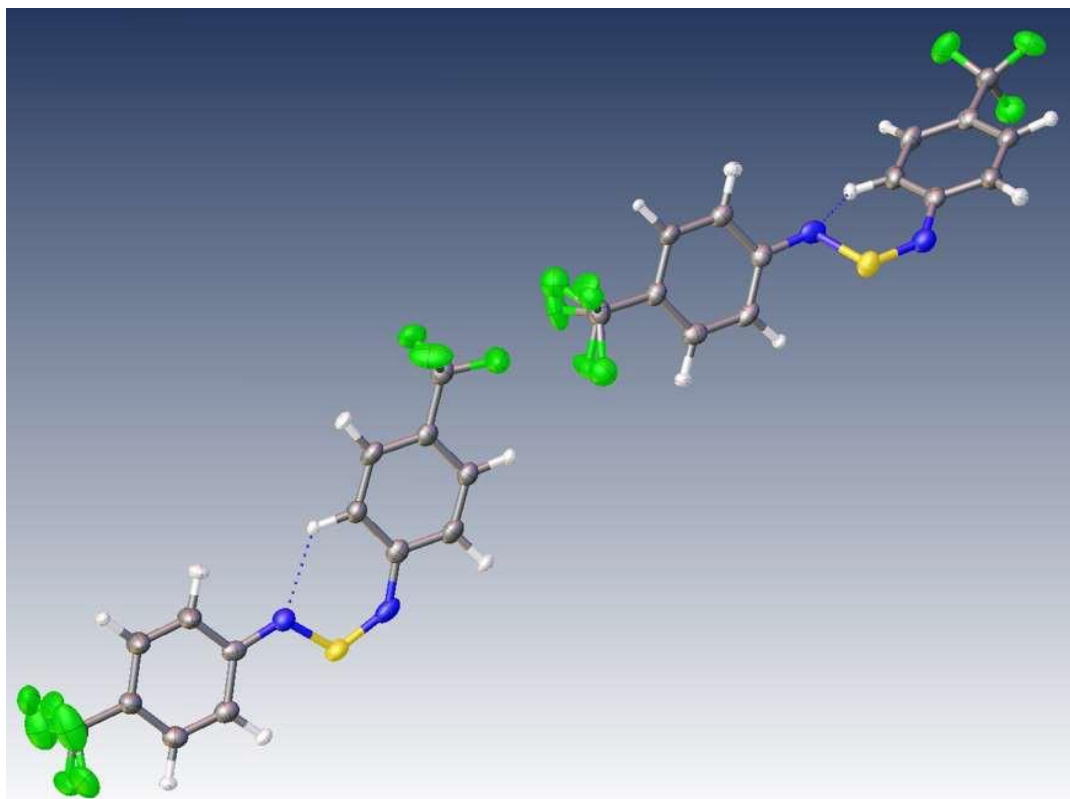


Figure B.6. Full view of a displacement ellipsoids plot of **6**

Table B.12. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **6**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
S1	1434.4(4)	1644.6(7)	1893(2)	33.9(3)
F1	3880.0(10)	3545(2)	2441(7)	63.6(10)
N1	1950.0(14)	1537(3)	1826(6)	33.8(8)
C1	2310.1(15)	2189(3)	1910(6)	27.9(9)
F2	3532.4(11)	4565(2)	671(5)	47.7(8)
N2	1258.3(12)	2700(3)	2084(6)	31.1(8)
C2	2747.1(16)	1792(3)	1945(7)	29.7(9)
F3	3461.3(13)	4611(3)	3716(5)	63.5(10)
C3	3130.7(14)	2364(3)	2034(7)	28.0(9)
F4	-834(8)	3262(19)	3600(50)	75(8)
F4A	-907.0(15)	3218(3)	2286(16)	79(3)
C4	3082.2(14)	3369(3)	2093(7)	27.9(9)
F5	-745(8)	4000(30)	860(30)	82(8)
F5A	-694.1(15)	4583(5)	1357(10)	65(2)
C5	2648.8(15)	3771(3)	2044(7)	29.5(9)
F6	-636(6)	4616(12)	3540(40)	49(6)
F6A	-668(2)	4248(8)	4300(9)	84(3)
C6	2260.6(14)	3199(3)	1960(7)	28.7(9)
C7	792.7(14)	2908(3)	2183(6)	27.3(9)
C8	434.1(15)	2232(3)	2239(7)	31.7(10)
C9	-13.9(15)	2533(3)	2328(7)	32.0(10)

Table B.12. Cont'd

Atom	x	y	z	U(eq)
C10	-116.2(15)	3517(4)	2410(7)	35.1(11)
C11	238.5(16)	4189(4)	2391(8)	42.4(13)
C12	685.0(16)	3885(3)	2291(8)	39.1(12)
C13	3489.3(15)	4011(3)	2218(7)	32.1(9)
C14	-592.8(17)	3866(4)	2579(8)	41.5(12)
H2	2783(19)	1024(14)	2130(90)	44(11)
H3	3475(8)	2090(40)	2040(80)	35(10)
H5	2640(20)	4552(12)	2120(90)	44(11)
H6	1918(8)	3480(30)	1840(70)	25(7)
H8	530(19)	1481(16)	2350(80)	41(11)
H9	-291(14)	2020(30)	2320(80)	39(12)
H11	144(16)	4942(15)	2490(70)	30(7)
H12	978(14)	4360(40)	2220(90)	52(13)
S2	6495.8(4)	1270.4(8)	7885.0(18)	32.5(3)
N3	6964.0(13)	845(3)	7514(6)	36.4(9)
N4	6353.8(13)	2123(3)	6584(6)	31.8(8)
F7	8348.7(11)	359(2)	854(5)	43.9(7)
F8	8276.4(12)	1884(2)	577(5)	57.4(9)
F9	8755.4(9)	1286(2)	2643(5)	49.7(8)
F10	4258.2(18)	3260(5)	7650(30)	61(4)
F10A	4299(4)	3185(8)	8600(20)	50(3)
F11	4526(4)	4482(7)	6177(13)	55(2)
F11A	4404(4)	4109(16)	6127(14)	61(4)
F12	4588(4)	4389(9)	9237(17)	37(3)
F12A	4622(6)	4548(10)	8960(30)	43(3)
C21	7290.3(15)	1022(3)	6070(7)	29.3(10)
C22	7724.1(15)	665(3)	6491(7)	30.9(9)
C23	8069.9(16)	748(3)	5146(7)	29.9(9)
C24	7972.4(15)	1173(3)	3361(7)	27.7(9)
C25	7536.9(16)	1527(3)	2946(7)	30.9(9)
C26	7195.1(15)	1464(3)	4304(7)	31.6(10)
C27	5908.8(15)	2504(3)	6938(6)	28.9(10)
C28	5519.2(16)	1933(3)	7092(6)	29.2(9)
C29	5088.9(15)	2355(3)	7351(7)	29.4(9)
C30	5053.2(14)	3352(3)	7412(7)	28.5(9)
C31	5442.6(14)	3918(3)	7296(6)	26.3(9)
C32	5865.3(16)	3505(3)	7041(6)	28.8(9)
C33	8338.0(16)	1197(3)	1877(7)	32.1(10)
C34	4603.7(16)	3835(4)	7670(8)	37.2(11)
H22	7767(19)	320(40)	7890(50)	45(11)
H23	8423(8)	540(40)	5400(80)	32(8)
H25	7479(15)	1740(30)	1460(30)	23(7)
H26	6859(9)	1780(40)	4130(80)	34(11)
H28	5583(16)	1169(14)	6880(70)	28(10)
H29	4782(11)	1920(30)	7430(80)	36(11)
H31	5402(14)	4690(13)	7410(60)	19(8)
H32	6172(13)	3940(40)	6950(80)	41(12)

Table B.13. Bond lengths [Å], angles [°], and torsions [°] for **6**

Lengths	Atoms	Length/Å	Atoms	Length/Å
	S1 N1	1.519(4)	S2 N3	1.520(4)
	S1 N2	1.564(4)	S2 N4	1.540(4)
	F1 C13	1.321(5)	N3 C21	1.417(6)
	N1 C1	1.392(6)	N4 C27	1.432(6)
	C1 C2	1.393(6)	F7 C33	1.363(6)
	C1 C6	1.413(6)	F8 C33	1.322(6)
	F2 C13	1.325(6)	F9 C33	1.327(6)
	N2 C7	1.397(6)	F10 C34	1.289(8)
	C2 H2	1.081(16)	F10A C34	1.433(11)
	C2 C3	1.377(6)	F11 C34	1.383(10)
	F3 C13	1.333(6)	F11A C34	1.263(10)
	C3 H3	1.081(16)	F12 C34	1.330(13)
	C3 C4	1.406(6)	F12A C34	1.334(15)
	F4 C14	1.31(2)	C21 C22	1.388(6)
	F4A C14	1.301(7)	C21 C26	1.389(7)
	C4 C5	1.387(6)	C22 H22	1.082(17)
	C4 C13	1.491(6)	C22 C23	1.393(7)
	F5 C14	1.27(2)	C23 H23	1.085(16)
	F5A C14	1.336(7)	C23 C24	1.392(6)
	C5 H5	1.088(16)	C24 C25	1.391(6)
	C5 C6	1.388(6)	C24 C33	1.498(6)
	F6 C14	1.245(17)	C25 H25	1.077(16)
	F6A C14	1.325(8)	C25 C26	1.389(7)
	C6 H6	1.080(16)	C26 H26	1.081(16)
	C7 C8	1.411(6)	C27 C28	1.396(6)
	C7 C12	1.398(6)	C27 C32	1.401(6)
	C8 H8	1.085(17)	C28 H28	1.089(16)
	C8 C9	1.379(7)	C28 C29	1.405(6)
	C9 H9	1.078(16)	C29 H29	1.081(16)
	C9 C10	1.404(7)	C29 C30	1.393(6)
	C10 C11	1.398(7)	C30 C31	1.389(6)
	C10 C14	1.484(7)	C30 C34	1.492(6)
	C11 H11	1.086(16)	C31 H31	1.085(16)
	C11 C12	1.377(7)	C31 C32	1.379(6)
	C12 H12	1.083(17)	C32 H32	1.089(17)
Angles	Atoms	Angle/°	Atoms	Angle/°
	N2 S1 N1	115.2(2)	N4 S2 N3	115.8(2)
	C1 N1 S1	133.4(3)	C21 N3 S2	132.5(4)
	C2 C1 N1	115.9(4)	C27 N4 S2	114.9(3)
	C6 C1 N1	124.9(4)	C22 C21 N3	114.7(4)
	C6 C1 C2	119.2(4)	C26 C21 N3	124.7(4)
	C7 N2 S1	121.5(3)	C26 C21 C22	120.5(4)
	C3 C2 C1	121.3(4)	C23 C22 C21	120.4(4)
	C4 C3 C2	119.6(4)	C24 C23 C22	119.2(4)
	C5 C4 C3	119.6(4)	C25 C24 C23	120.2(4)
	C13 C4 C3	121.1(4)	C33 C24 C23	118.6(4)
	C13 C4 C5	119.3(4)	C33 C24 C25	121.1(4)
	C6 C5 C4	121.2(4)	C26 C25 C24	120.6(4)
	C5 C6 C1	119.2(4)	C25 C26 C21	119.1(4)
	C8 C7 N2	126.2(4)	C28 C27 N4	123.4(4)
	C12 C7 N2	115.2(4)	C32 C27 N4	117.4(4)
	C12 C7 C8	118.6(4)	C32 C27 C28	119.1(4)
	C9 C8 C7	120.5(4)	C29 C28 C27	120.6(4)
	C10 C9 C8	120.1(4)	C30 C29 C28	119.2(4)
	C11 C10 C9	119.6(4)	C31 C30 C29	120.1(4)
	C14 C10 C9	121.6(4)	C34 C30 C29	121.3(4)

Table B.13. Cont'd

Angles	Atoms	Angle/°	Atoms	Angle/°
	C14 C10 C11	118.8(5)	C34 C30 C31	118.6(4)
	C12 C11 C10	120.1(5)	C32 C31 C30	120.7(4)
	C11 C12 C7	121.1(4)	C31 C32 C27	120.2(4)
	F2 C13 F1	106.4(4)	F8 C33 F7	105.7(4)
	F3 C13 F1	106.5(4)	F9 C33 F7	104.8(4)
	F3 C13 F2	105.7(4)	F9 C33 F8	108.3(4)
	C4 C13 F1	113.7(4)	C24 C33 F7	111.1(4)
	C4 C13 F2	113.0(4)	C24 C33 F8	113.0(4)
	C4 C13 F3	111.0(4)	C24 C33 F9	113.3(4)
	F4A C14 F4	41.6(14)	F10A C34 F10	27.9(6)
	F5 C14 F4	114(2)	F11 C34 F10	106.3(7)
	F5 C14 F4A	73.8(17)	F11 C34 F10A	130.6(6)
	F5A C14 F4	134.6(13)	F11A C34 F10	80.3(8)
	F5A C14 F4A	105.8(5)	F11A C34 F10A	106.7(9)
	F5A C14 F5	40.1(18)	F11A C34 F11	27.0(8)
	F6 C14 F4	101.0(16)	F12 C34 F10	108.9(8)
	F6 C14 F4A	125.8(10)	F12 C34 F10A	88.1(7)
	F6 C14 F5	109.8(19)	F12 C34 F11	102.8(7)
	F6 C14 F5A	71.7(13)	F12 C34 F11A	119.2(9)
	F6A C14 F4	71.0(15)	F12A C34 F10	119.1(9)
	F6A C14 F4A	106.7(6)	F12A C34 F10A	100.7(9)
	F6A C14 F5	135.9(15)	F12A C34 F11	91.0(9)
	F6A C14 F5A	103.2(6)	F12A C34 F11A	110.5(11)
	F6A C14 F6	33.4(11)	F12A C34 F12	13.4(10)
	C10 C14 F4	110.5(11)	C30 C34 F10	114.4(5)
	C10 C14 F4A	115.1(5)	C30 C34 F10A	109.2(6)
	C10 C14 F5	106.6(12)	C30 C34 F11	109.7(6)
	C10 C14 F5A	113.0(4)	C30 C34 F11A	115.4(6)
	C10 C14 F6	114.9(9)	C30 C34 F12	113.9(7)
	C10 C14 F6A	112.1(5)	C30 C34 F12A	113.1(8)
Torsions	Atoms	Angle/°	Atoms	Angle/°
	S1 N1 C1 C2	175.4(5)	S2 N3 C21 C22	164.5(4)
	S1 N1 C1 C6	-4.6(5)	S2 N3 C21 C26	-19.0(5)
	S1 N2 C7 C8	3.9(5)	S2 N4 C27 C28	-48.3(4)
	S1 N2 C7 C12	-178.1(4)	S2 N4 C27 C32	134.8(3)
	F1 C13 C4 C3	-5.8(5)	N3 C21 C22 C23	176.7(4)
	F1 C13 C4 C5	173.9(4)	N3 C21 C26 C25	-174.9(4)
	N1 C1 C2 C3	-179.8(4)	N4 C27 C28 C29	-177.0(4)
	N1 C1 C6 C5	180.0(5)	N4 C27 C32 C31	177.2(4)
	C1 C2 C3 C4	0.1(5)	F7 C33 C24 C23	84.1(4)
	C1 C6 C5 C4	-0.4(5)	F7 C33 C24 C25	-92.9(4)
	F2 C13 C4 C3	115.7(4)	F8 C33 C24 C23	-157.2(4)
	F2 C13 C4 C5	-64.7(5)	F8 C33 C24 C25	25.8(5)
	N2 C7 C8 C9	-179.7(5)	F9 C33 C24 C23	-33.6(5)
	N2 C7 C12 C11	179.9(5)	F9 C33 C24 C25	149.4(4)
	C2 C3 C4 C5	-0.6(5)	F10 C34 C30 C29	-5.8(11)
	C2 C3 C4 C13	179.1(4)	F10 C34 C30 C31	176.3(10)
	F3 C13 C4 C3	-125.8(4)	F10A C34 C30 C29	23.8(8)
	F3 C13 C4 C5	53.8(5)	F10A C34 C30 C31	-154.1(7)
	C3 C4 C5 C6	0.7(5)	F11 C34 C30 C29	-125.0(6)
	F4 C14 C10 C9	32.9(19)	F11 C34 C30 C31	57.0(6)
	F4 C14 C10 C11	-145.1(19)	F11A C34 C30 C29	-96.4(13)
	F4A C14 C10 C9	-12.1(8)	F11A C34 C30 C31	85.7(13)
	F4A C14 C10 C11	169.8(7)	F12 C34 C30 C29	120.4(7)
	F5 C14 C10 C9	-92(2)	F12 C34 C30 C31	-57.5(8)
	F5 C14 C10 C11	90(2)	F12A C34 C30 C29	135.0(10)
	F5A C14 C10 C9	-133.9(6)	F12A C34 C30 C31	-42.9(11)
	F5A C14 C10 C11	48.1(7)	C21 C22 C23 C24	-1.4(5)

Table B.13. Cont'd

Torsions	Atoms	Angle/°	Atoms	Angle/°
F6 C14 C10 C9		146.4(16)	C21 C26 C25 C24	-1.5(5)
F6 C14 C10 C11		-31.6(16)	C22 C23 C24 C25	1.2(5)
F6A C14 C10 C9		110.0(7)	C22 C23 C24 C33	-175.8(4)
F6A C14 C10 C11		-68.0(7)	C23 C24 C25 C26	0.3(5)
C7 C8 C9 C10		-1.6(5)	C27 C28 C29 C30	1.3(5)
C7 C12 C11 C10		0.8(6)	C27 C32 C31 C30	-1.4(5)
C8 C9 C10 C11		0.3(6)	C28 C29 C30 C31	-2.5(5)
C8 C9 C10 C14		-177.7(5)	C28 C29 C30 C34	179.6(4)
C9 C10 C11 C12		0.1(6)	C29 C30 C31 C32	2.6(5)

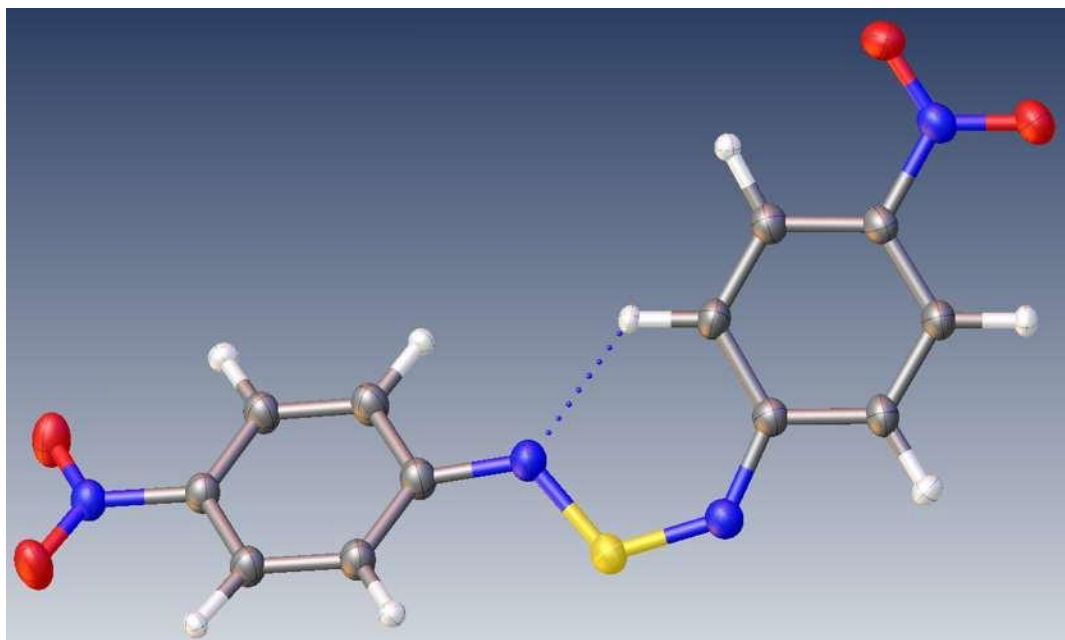


Figure B.7. Full view of a displacement ellipsoids plot of 7

Table B.14. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 7. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
S	8499.2(6)	6123.6(2)	6648(2)	28.8(2)
O1	6728(2)	3654.8(9)	-1279(8)	44.9(8)
O2	5434(2)	4172.1(9)	-2366(8)	43.7(7)
O3	5964(2)	8487.7(8)	10321(7)	41.5(7)
O4	4616.9(19)	8069.7(8)	12337(7)	38.1(7)
N1	8759(2)	5604.3(10)	5166(8)	29.5(7)
N2	7303(2)	6283.3(9)	6277(8)	31.6(7)
N3	6338(2)	4071.9(10)	-1158(8)	31.2(7)
N4	5502(2)	8094.7(9)	10831(7)	27.6(7)
C1	8106(3)	5247.4(11)	3534(9)	27.1(7)
C2	8611(3)	4791.3(11)	2752(10)	29.3(7)
C3	8045(3)	4400.5(10)	1201(10)	29.9(8)
C4	6954(3)	4475.6(11)	443(9)	27.9(7)
C5	6437(3)	4926.7(11)	1121(10)	29.1(8)
C6	7003(3)	5312.3(11)	2680(10)	29.3(7)

Table B.14. Cont'd

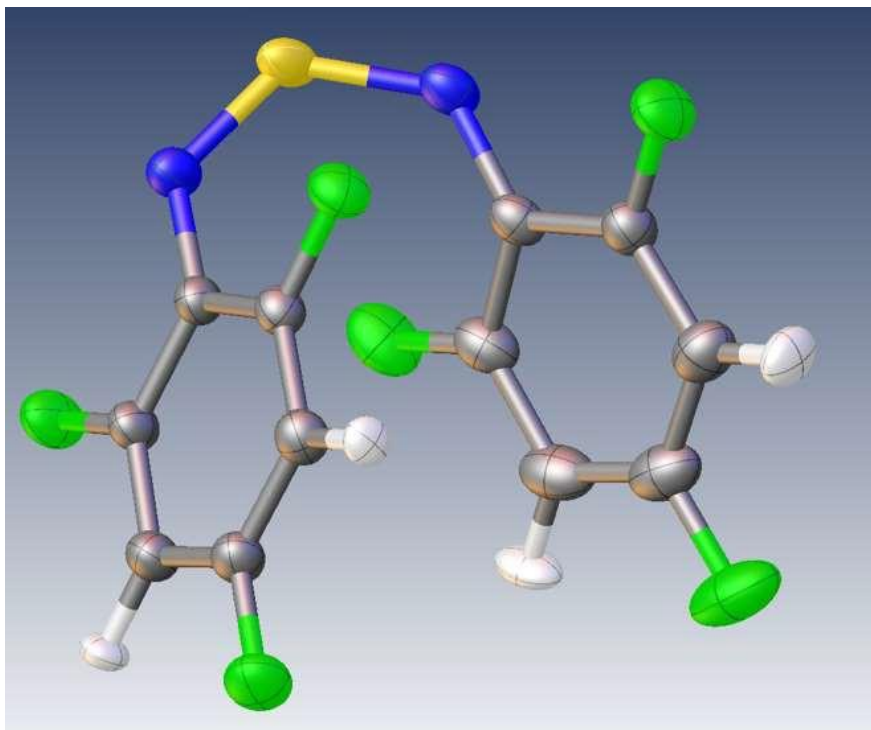
Atom	x	y	z	U(eq)
C7	6927(3)	6752.4(11)	7466(9)	27.7(7)
C8	7508(3)	7198.2(11)	7187(10)	28.8(7)
C9	7032(3)	7645.2(11)	8286(9)	27.6(7)
C10	5997(2)	7631.8(11)	9667(9)	25.5(7)
C11	5416(3)	7190.9(11)	9987(10)	29.0(7)
C12	5879(3)	6750.8(12)	8829(10)	30.0(7)
H2	9456(18)	4733(15)	3370(140)	41(8)
H3	8440(30)	4040(9)	850(120)	33(8)
H5	5610(17)	4975(14)	220(100)	28(7)
H6	6610(30)	5652(9)	3320(110)	29(7)
H8	8301(19)	7211(14)	5910(100)	30(7)
H9	7420(30)	8006(8)	7990(110)	27(7)
H11	4610(20)	7195(15)	11170(120)	36(8)
H12	5460(30)	6393(9)	8870(120)	28(7)

Table B.15. Bond lengths [Å], angles [°], and torsions [°] for 7

Lengths	Atoms	Length/Å	Atoms	Length/Å
	S N1	1.534(3)	C3 C4	1.395(4)
	S N2	1.548(3)	C4 C5	1.391(4)
	O1 N3	1.219(4)	C5 H5	1.087(18)
	O2 N3	1.237(4)	C5 C6	1.380(5)
	O3 N4	1.214(3)	C6 H6	1.063(17)
	O4 N4	1.235(4)	C7 C8	1.398(4)
	N1 C1	1.395(4)	C7 C12	1.395(5)
	N2 C7	1.413(4)	C8 H8	1.093(18)
	N3 C4	1.454(4)	C8 C9	1.398(4)
	N4 C10	1.451(4)	C9 H9	1.087(17)
	C1 C2	1.404(4)	C9 C10	1.383(5)
	C1 C6	1.413(4)	C10 C11	1.388(4)
	C2 H2	1.083(18)	C11 H11	1.095(18)
	C2 C3	1.389(4)	C11 C12	1.382(5)
	C3 H3	1.089(17)	C12 H12	1.089(17)
Angles	Atoms	Angle/°	Atoms	Angle/°
	N2 S N1	114.76(15)	C5 C4 N3	118.8(3)
	C1 N1 S	131.3(2)	C5 C4 C3	122.2(3)
	C7 N2 S	122.1(2)	C6 C5 C4	119.7(3)
	O2 N3 O1	122.9(3)	C5 C6 C1	119.7(3)
	C4 N3 O1	119.3(3)	C8 C7 N2	124.6(3)
	C4 N3 O2	117.7(3)	C12 C7 N2	114.8(3)
	O4 N4 O3	122.5(3)	C12 C7 C8	120.5(3)
	C10 N4 O3	119.7(3)	C9 C8 C7	119.6(3)
	C10 N4 O4	117.8(2)	C10 C9 C8	118.7(3)
	C2 C1 N1	115.5(3)	C9 C10 N4	118.8(3)
	C6 C1 N1	125.1(3)	C11 C10 N4	118.9(3)
	C6 C1 C2	119.3(3)	C11 C10 C9	122.3(3)
	C3 C2 C1	121.3(3)	C12 C11 C10	119.0(3)
	C4 C3 C2	117.8(3)	C11 C12 C7	119.9(3)
	C3 C4 N3	119.0(3)		
Torsions	Atoms	Angle/°	Atoms	Angle/°
	S N1 C1 C2	-175.2(3)	N2 C7 C8 C9	176.6(4)
	S N1 C1 C6	4.2(4)	N2 C7 C12 C11	-178.3(3)
	S N2 C7 C8	37.8(3)	N3 C4 C3 C2	-179.6(3)
	S N2 C7 C12	-145.4(3)	N3 C4 C5 C6	179.2(3)
	O1 N3 C4 C3	11.8(4)	N4 C10 C9 C8	179.6(3)
	O1 N3 C4 C5	-169.1(3)	N4 C10 C11 C12	179.0(3)
	O2 N3 C4 C3	-167.7(3)	C1 C2 C3 C4	-0.0(4)

Table B.15. Cont'd

Torsions	Atoms	Angle/°	Atoms	Angle/°
	O2 N3 C4 C5	11.4(4)	C1 C6 C5 C4	0.8(4)
	O3 N4 C10 C9	5.8(4)	C2 C3 C4 C5	1.4(4)
	O3 N4 C10 C11	-174.4(3)	C3 C4 C5 C6	-1.8(4)
	O4 N4 C10 C9	-173.8(3)	C7 C8 C9 C10	0.8(4)
	O4 N4 C10 C11	6.0(3)	C7 C12 C11 C10	2.0(4)
	N1 C1 C2 C3	178.5(3)	C8 C9 C10 C11	-0.2(4)
	N1 C1 C6 C5	-178.8(4)	C9 C10 C11 C12	-1.2(4)

Figure B.8. Full view of a displacement ellipsoids plot of **8**Table B.16. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **8**. Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
S	1978.4(3)	-469.4(2)	5262.6(2)	33.07(8)
F1	2496.4(7)	2536.4(6)	7563.5(5)	38.71(15)
F2	1656.1(7)	6074.4(6)	4908.5(6)	40.62(16)
F3	509.7(6)	1703.6(6)	3553.6(5)	32.37(14)
F4	4501.8(7)	1322.3(7)	6266.4(5)	44.04(17)
F5	5255.7(8)	4239.1(7)	3601.3(8)	61.4(2)
F6	2438.6(7)	503.4(6)	2264.4(5)	39.87(16)
N1	1507.0(9)	701.7(8)	5830.3(7)	31.9(2)
N2	2801.8(9)	-294.7(8)	4466.2(7)	31.64(19)
C1	1543.7(10)	2056.4(9)	5567.6(8)	24.82(19)
C2	2033.6(10)	2992.9(10)	6466.3(8)	27.0(2)
C3	2100.5(11)	4346.1(10)	6275.4(9)	29.6(2)
C4	1613.9(10)	4768.1(9)	5125.6(9)	28.2(2)
C5	1064.6(10)	3911.2(10)	4185.7(9)	27.9(2)
C6	1043.0(9)	2567.7(9)	4434.8(8)	24.66(19)
C7	3408.3(10)	880.3(9)	4274.8(8)	26.4(2)

Table B.16. Cont'd

Atom	x	y	z	U(eq)
C8	4266.9(10)	1691.3(10)	5165.0(9)	31.8(2)
C9	4903.9(11)	2826.1(11)	4970.8(11)	40.0(3)
C10	4665.4(11)	3143.3(11)	3823.5(11)	40.5(3)
C11	3846.0(12)	2380.1(11)	2887.2(10)	37.9(2)
C12	3249.2(10)	1257.2(10)	3143.6(8)	29.4(2)
H3	2534(15)	5031(13)	6998(10)	52(4)
H5	665(14)	4279(13)	3288(10)	48(4)
H9	5567(15)	3423(15)	5702(12)	69(5)
H11	3657(18)	2681(17)	1990(11)	72(5)

Table B.17. Bond lengths [Å], angles [°], and torsions [°] for 8

Lengths	Atoms	Length/Å	Atoms	Length/Å
	S N1	1.5400(9)	C3 H3	1.083(11)
	S N2	1.5410(9)	C3 C4	1.3852(14)
	F1 C2	1.3392(11)	C4 C5	1.3860(14)
	F2 C4	1.3406(11)	C5 H5	1.093(10)
	F3 C6	1.3401(10)	C5 C6	1.3835(13)
	F4 C8	1.3416(12)	C7 C8	1.3947(14)
	F5 C10	1.3384(13)	C7 C12	1.3964(13)
	F6 C12	1.3368(12)	C8 C9	1.3844(16)
	N1 C1	1.4000(12)	C9 H9	1.091(11)
	N2 C7	1.3998(13)	C9 C10	1.3817(17)
	C1 C2	1.3979(13)	C10 C11	1.3867(17)
	C1 C6	1.3967(13)	C11 H11	1.093(12)
	C2 C3	1.3830(13)	C11 C12	1.3806(15)
Angles	Atoms	Angle/°	Atoms	Angle/°
	N2 S N1	123.69(5)	C5 C6 C1	123.29(9)
	C1 N1 S	126.35(7)	C8 C7 N2	123.91(9)
	C7 N2 S	126.93(7)	C12 C7 N2	120.25(9)
	C2 C1 N1	120.06(8)	C12 C7 C8	115.69(9)
	C6 C1 N1	123.76(8)	C7 C8 F4	117.42(9)
	C6 C1 C2	116.09(8)	C9 C8 F4	118.92(9)
	C1 C2 F1	117.55(8)	C9 C8 C7	123.64(10)
	C3 C2 F1	119.04(8)	C10 C9 C8	116.85(10)
	C3 C2 C1	123.38(9)	C9 C10 F5	118.55(11)
	C4 C3 C2	116.86(9)	C11 C10 F5	118.17(11)
	C3 C4 F2	118.46(9)	C11 C10 C9	123.28(10)
	C5 C4 F2	118.17(9)	C12 C11 C10	116.84(10)
	C5 C4 C3	123.36(9)	C7 C12 F6	117.63(9)
	C6 C5 C4	116.94(9)	C11 C12 F6	118.68(9)
	C1 C6 F3	117.70(8)	C11 C12 C7	123.66(10)
	C5 C6 F3	119.00(8)		
Torsions	Atoms	Angle/°	Atoms	Angle/°
	S N1 C1 C2	-134.82(9)	F5 C10 C11 C12	-179.89(10)
	S N1 C1 C6	48.79(10)	F6 C12 C7 N2	3.92(11)
	S N2 C7 C8	50.52(10)	F6 C12 C7 C8	179.74(9)
	S N2 C7 C12	-134.02(9)	F6 C12 C11 C10	179.22(10)
	F1 C2 C1 N1	2.09(11)	N1 C1 C2 C3	-179.97(9)
	F1 C2 C1 C6	178.75(8)	N1 C1 C6 C5	178.94(9)
	F1 C2 C3 C4	179.76(9)	N2 C7 C8 C9	177.55(10)

Table B.17. Cont'd

Torsions	Atoms	Angle/°	Atoms	Angle/°
	F2 C4 C3 C2	179.64(9)	N2 C7 C12 C11	-178.14(9)
	F2 C4 C5 C6	179.55(9)	C1 C2 C3 C4	1.85(11)
	F3 C6 C1 N1	-0.61(10)	C1 C6 C5 C4	-0.15(11)
	F3 C6 C1 C2	-177.13(8)	C2 C3 C4 C5	0.69(12)
	F3 C6 C5 C4	179.40(9)	C3 C4 C5 C6	-1.50(12)
	F4 C8 C7 N2	-0.98(11)	C7 C8 C9 C10	-0.49(12)
	F4 C8 C7 C12	-176.63(9)	C7 C12 C11 C10	1.29(12)
	F4 C8 C9 C10	178.02(10)	C8 C9 C10 C11	-0.68(13)
	F5 C10 C9 C8	179.51(10)	C9 C10 C11 C12	0.29(13)

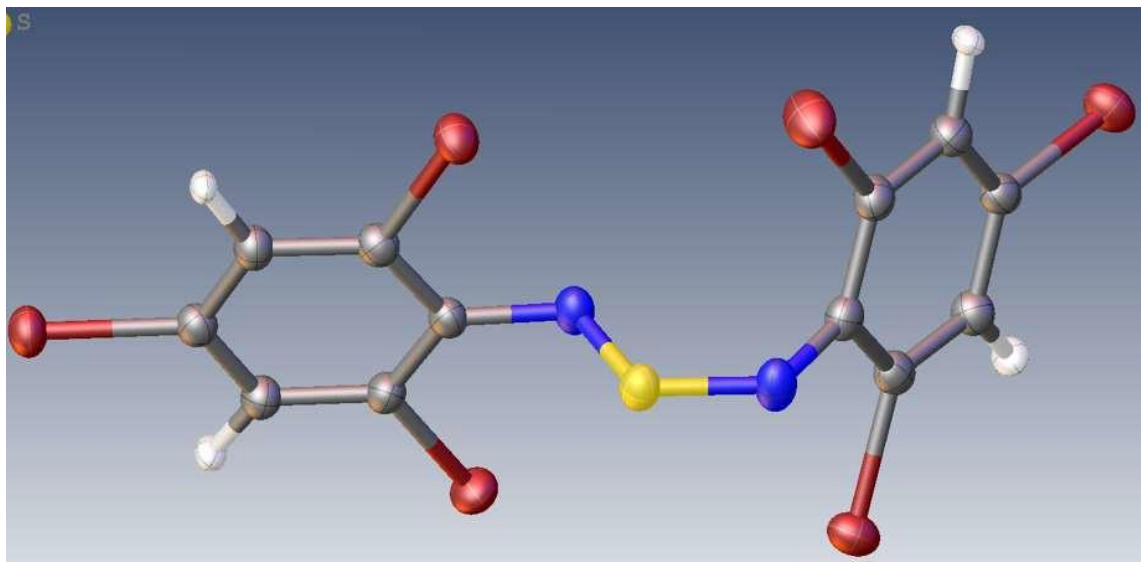


Figure B.9. Full view of a displacement ellipsoids plot of 9

Table B.18. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 9. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Br1	6365.2(5)	544.7(4)	1003.9(3)	41.83(9)
Br2	9660.2(3)	4098.1(4)	-1821.4(2)	32.45(8)
Br3	5527.0(4)	6871.3(3)	1926.1(2)	32.12(8)
Br4	7191.9(4)	-1608.2(3)	4077.2(2)	31.53(8)
Br5	9022.5(4)	-1315.6(3)	8269.3(2)	31.57(8)
Br6	7845.9(4)	4158.4(3)	4950.2(2)	33.82(8)
S	5255.5(7)	2839.2(7)	3350.7(5)	26.13(13)
N1	4866(3)	3713(3)	2185.0(18)	31.1(5)
N2	7180(3)	1934(3)	3574.5(17)	28.5(4)
C1	6100(3)	3735(3)	1319(2)	25.2(5)
C2	6844(3)	2448(3)	655(2)	26.9(5)
C3	7924(3)	2540(3)	-266(2)	27.6(5)
C4	8248(3)	3964(3)	-535(2)	25.2(5)
C5	7551(3)	5271(3)	105(2)	26.5(5)
C6	6490(3)	5130(3)	1029(2)	25.3(5)
C7	7537(3)	1189(3)	4671.6(19)	23.6(5)
C8	7642(3)	-426(3)	5050(2)	25.2(5)

Table B.18. Cont'd

Atom	x	y	z	U(eq)
C9	8081(3)	-1185(3)	6113(2)	25.5(5)
C10	8433(3)	-317(3)	6820(2)	25.7(5)
C11	8374(3)	1268(3)	6483(2)	26.3(5)
C12	7928(3)	2003(3)	5413(2)	25.5(5)
H3	8480(40)	1470(30)	-730(20)	38(8)
H5	7830(50)	6350(30)	-100(30)	44(8)
H9	8190(40)	-2460(30)	6360(30)	33(7)
H11	8710(50)	1860(40)	7070(20)	40(8)

Table B.19. Bond lengths [Å], angles [°], and torsions [°] for 9

Lengths	Atoms	Length/Å	Atoms	Length/Å
	Br1 C2	1.879(2)	C3 H3	1.091(17)
	Br2 C4	1.891(2)	C3 C4	1.390(3)
	Br3 C6	1.889(2)	C4 C5	1.389(4)
	Br4 C8	1.890(2)	C5 H5	1.072(17)
	Br5 C10	1.885(2)	C5 C6	1.390(3)
	Br6 C12	1.884(2)	C7 C8	1.404(3)
	S N1	1.519(2)	C7 C12	1.404(3)
	S N2	1.540(2)	C8 C9	1.388(3)
	N1 C1	1.411(3)	C9 H9	1.095(17)
	N2 C7	1.412(3)	C9 C10	1.390(3)
	C1 C2	1.398(4)	C10 C11	1.385(3)
	C1 C6	1.399(3)	C11 H11	1.087(17)
	C2 C3	1.388(4)	C11 C12	1.392(3)
Angles	Atoms	Angle/°	Atoms	Angle/°
	N2 S N1	115.25(12)	C5 C6 C1	122.1(2)
	C1 N1 S	125.69(18)	C8 C7 N2	122.4(2)
	C7 N2 S	115.15(17)	C12 C7 N2	120.5(2)
	C2 C1 N1	121.3(2)	C12 C7 C8	117.0(2)
	C6 C1 N1	120.7(2)	C7 C8 Br4	118.93(18)
	C6 C1 C2	117.7(2)	C9 C8 Br4	118.97(18)
	C1 C2 Br1	119.58(19)	C9 C8 C7	122.1(2)
	C3 C2 Br1	118.75(19)	C10 C9 C8	118.7(2)
	C3 C2 C1	121.7(2)	C9 C10 Br5	119.52(18)
	C4 C3 C2	118.6(2)	C11 C10 Br5	118.89(19)
	C3 C4 Br2	117.96(19)	C11 C10 C9	121.6(2)
	C5 C4 Br2	120.19(18)	C12 C11 C10	118.6(2)
	C5 C4 C3	121.8(2)	C7 C12 Br6	119.18(18)
	C6 C5 C4	118.1(2)	C11 C12 Br6	118.80(18)
	C1 C6 Br3	118.46(19)	C11 C12 C7	122.0(2)
	C5 C6 Br3	119.44(18)		
Torsions	Atoms	Angle/°	Atoms	Angle/°
	Br1 C2 C1 N1	-6.1(2)	S N1 C1 C2	85.4(2)
	Br1 C2 C1 C6	-179.97(18)	S N1 C1 C6	-101.0(2)
	Br1 C2 C3 C4	178.72(18)	S N2 C7 C8	85.9(2)
	Br2 C4 C3 C2	-177.91(18)	S N2 C7 C12	-98.74(19)
	Br2 C4 C5 C6	178.61(18)	N1 C1 C2 C3	173.3(2)
	Br3 C6 C1 N1	7.0(2)	N1 C1 C6 C5	-172.6(2)
	Br3 C6 C1 C2	-179.07(18)	N2 C7 C8 C9	176.6(2)
	Br3 C6 C5 C4	179.63(18)	N2 C7 C12 C11	-176.6(2)

Table B.19. Cont'd

Torsions	Atoms	Angle/°	Atoms	Angle/°
	Br4 C8 C7 N2	-2.8(2)	C1 C2 C3 C4	-0.7(3)
	Br4 C8 C7 C12	-178.31(18)	C1 C6 C5 C4	-0.7(3)
	Br4 C8 C9 C10	179.18(18)	C2 C3 C4 C5	1.3(3)
	Br5 C10 C9 C8	179.73(18)	C3 C4 C5 C6	-0.6(3)
	Br5 C10 C11 C12	-179.64(18)	C7 C8 C9 C10	-0.2(3)
	Br6 C12 C7 N2	3.5(2)	C7 C12 C11 C10	0.1(3)
	Br6 C12 C7 C8	179.05(18)	C8 C9 C10 C11	-0.8(3)
	Br6 C12 C11 C10	179.99(18)	C9 C10 C11 C12	0.9(3)

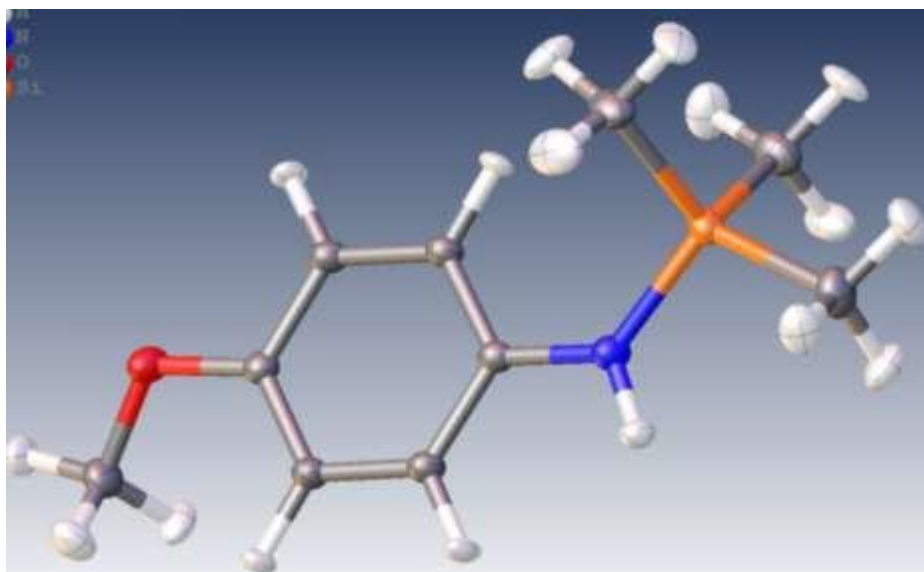


Figure B.10. Full view of a displacement ellipsoids plot of 15

Table B.20. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 15. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Si	4512.92(17)	4947.14(17)	3055.27(12)	17.49(7)
O	9430.2(5)	2442.0(4)	4565.8(3)	23.50(13)
N	5628.3(6)	5192.6(6)	3734.6(4)	19.04(14)
C1	6577.7(6)	4514.7(6)	3944.9(4)	15.25(14)
C2	7301.1(7)	4807.7(6)	4579.7(4)	17.21(15)
C3	8254.9(7)	4137.3(6)	4803.6(4)	17.69(15)
C4	8507.8(6)	3151.9(6)	4389.9(4)	16.21(15)
C5	7796.5(6)	2842.9(6)	3759.7(4)	17.21(15)
C6	6847.7(6)	3516.4(6)	3538.8(4)	16.70(15)
C7	10403.7(8)	2907.8(8)	4969.9(5)	24.88(18)
C8	3733.5(8)	3593.6(8)	3277.8(5)	25.90(18)
C9	5094.7(8)	4924.7(8)	2029.1(5)	27.01(18)
C10	3495.3(8)	6173.7(8)	3166.8(6)	28.03(19)
H	5536(10)	5884(9)	4066(7)	38(3)
H2	7119(9)	5569(9)	4910(6)	37(3)
H3	8792(9)	4392(9)	5303(6)	38(3)
H5	8008(9)	2064(8)	3441(6)	36(3)
H6	6308(9)	3261(9)	3038(5)	32(3)

Table B.20. Cont'd

Atom	x	y	z	U(eq)
H7a	10708(10)	3661(9)	4679(8)	56(4)
H7b	10170(11)	3120(12)	5568(6)	58(4)
H7c	11085(10)	2264(9)	4977(8)	50(3)
H8a	4251(12)	2869(9)	3114(9)	62(4)
H8b	3551(15)	3520(12)	3891(7)	75(5)
H8c	2913(10)	3545(12)	2963(8)	61(4)
H9a	5568(11)	5696(11)	1900(7)	57(4)
H9b	5671(12)	4217(12)	1917(8)	69(4)
H9c	4376(10)	4878(11)	1615(7)	51(4)
H10a	3085(11)	6183(11)	3740(7)	55(4)
H10b	3973(12)	6964(9)	3091(8)	59(4)
H10c	2800(11)	6148(12)	2722(7)	58(4)

Table B.21. Bond lengths [Å], angles [°], and torsions [°] for 15

Lengths	Atoms	Length/Å	Atoms	Length/Å
	Si N	1.7399(7)	C5 H5	1.098(9)
	Si C8	1.8709(9)	C5 C6	1.3921(10)
	Si C9	1.8701(9)	C6 H6	1.093(8)
	Si C10	1.8662(9)	C7 H7a	1.079(10)
	O C4	1.3759(9)	C7 H7b	1.084(10)
	O C7	1.4139(10)	C7 H7c	1.086(10)
	N H	1.001(10)	C8 H8a	1.077(11)
	N C1	1.3908(9)	C8 H8b	1.069(11)
	C1 C2	1.4019(10)	C8 H8c	1.076(10)
	C1 C6	1.4049(10)	C9 H9a	1.083(11)
	C2 H2	1.084(9)	C9 H9b	1.081(11)
	C2 C3	1.3957(10)	C9 H9c	1.080(10)
	C3 H3	1.091(9)	C10 H10a	1.083(10)
	C3 C4	1.3944(10)	C10 H10b	1.090(11)
	C4 C5	1.3928(10)	C10 H10c	1.094(10)
Angles	Atoms	Angle/°	Atoms	Angle/°
	C8 Si N	110.62(4)	C6 C1 N	121.90(7)
	C9 Si N	111.62(4)	C6 C1 C2	117.49(7)
	C9 Si C8	110.14(4)	C3 C2 C1	121.59(7)
	C10 Si N	104.59(4)	C4 C3 C2	119.88(7)
	C10 Si C8	110.80(4)	C3 C4 O	123.96(6)
	C10 Si C9	108.95(4)	C5 C4 O	116.61(6)
	C7 O C4	117.48(6)	C5 C4 C3	119.42(7)
	C1 N Si	129.66(5)	C6 C5 C4	120.39(7)
	C2 C1 N	120.61(7)	C5 C6 C1	121.22(7)
Torsions	Atoms	Angle/°	Atoms	Angle/°
	Si N C1 C2	-171.96(7)	N C1 C6 C5	-179.56(7)
	Si N C1 C6	7.73(8)	C1 C2 C3 C4	0.22(9)
	O C4 C3 C2	179.76(7)	C1 C6 C5 C4	-0.44(9)
	O C4 C5 C6	-179.63(6)	C2 C3 C4 C5	-0.52(9)
	N C1 C2 C3	179.68(7)	C3 C4 C5 C6	0.63(8)

Table B.22. Hydrogen Bonds Bond lengths [Å], angles [°], and torsions [°] for **15**

Donor	H	Acceptor	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N	H	O ¹	1.001(10)	2.034(10)	3.0202(9)	167.9(11)

¹ 3/2-X, 1/2+Y, +Z

The CSD (release 2023.3.0)^[18] lists 28 monotrimethylsilyl aniline crystal structures, of which twenty are simple molecular compounds, seven are coordination complexes involving some or all N donors and one is an organometallic diaryl-Cr complex with pendant NHTMS substituents. The geometries w.r.t. the bonds CAr-N and N-Si, and the angles associated with the NTMS substituents, do not average very well. The variance is not primarily between molecular and coordinated exemplars either. Rather, specific structural features affect these values, so that the Si-N distance is particularly short for the diaryl-Cr complex (refcode: ENEZUS),^[19] the CAr-N distance is particularly short for a para-arylsulfoxide (refcode: SIYLIX).^[20] Regarding the angles and torsions of the substituent w.r.t. the aromatic ring, it is noteworthy that 10 of the 20 molecule compounds, unusually, are those with large di-*ortho* flanking groups that cause the aniline group to be orthogonal to the ring plane. The closest comparative structures are two other cases of aryl ethers, namely the 2-methoxy isomer of **12** (refcode: XAZJOX)^[21] and 2-phenoxy analogue (refcode: UCIYAG).^[22] The values for $d(\text{C-N})$, $d(\text{Si-N})$, $\angle(\text{C-N-Si})$ and the two C-C-N-Si torsion angles are indistinguishable from these at the 99% confidence level. The mean values over four (eight) independent values are $d(\text{C-N}) = 1.3917(19)$ Å, $d(\text{Si-N}) = 1.740(3)$ Å, $\angle(\text{C-N-Si}) = 130.1(5)^\circ$, and C-C-N-Si = $6(3)^\circ$. Evidently, the constraints on the torsion angles, i.e. the degree of co-planarity of the -NSiMe₃ group and the aryl ring are low, but constrained in the range of 0 - 10°, in the absence of significant steric constraints from the *ortho* positions. Notably, the values in **15** are higher than in the *ortho*-substituted UCIYAG, so that no specific meaning should be attached to these values, save that they will be close to co-planar in the absence of significant, di-*ortho* position occupancies.

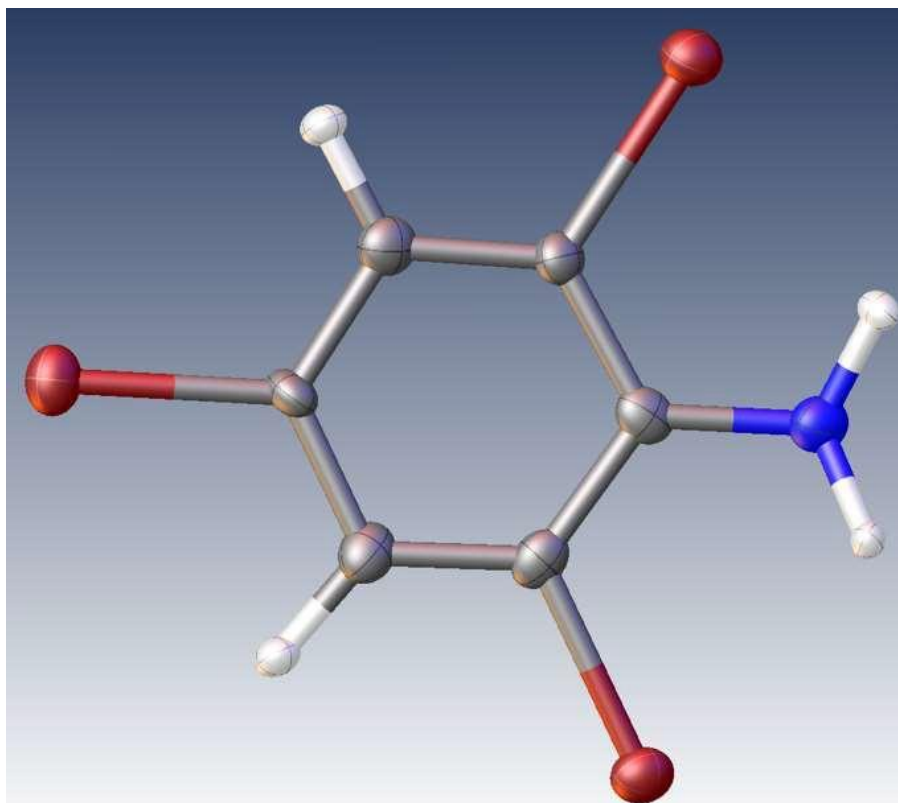


Figure B.11. Full view of a displacement ellipsoids plot of **16**

Table B.23. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **16**. U_{eq} is defined as $1/3$ of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Br1	8044.4(19)	5239.1(6)	5969.6(6)	25.8(2)
Br2	3099.5(19)	3199.1(6)	9096.8(6)	26.6(2)
Br3	10080.1(17)	1048.5(6)	6417.1(6)	24.3(2)
N1	10626(14)	3146(5)	5497(5)	24.8(15)
C1	8950(15)	3154(6)	6322(6)	20.0(16)
C2	7488(15)	4036(6)	6655(5)	19.0(16)
C3	5718(16)	4055(6)	7449(6)	23.0(17)
C4	5359(17)	3178(5)	7956(5)	18.8(15)
C5	6662(19)	2272(6)	7654(6)	23.3(17)
C6	8398(18)	2287(6)	6850(6)	20.6(16)
H1a	11200(200)	3860(30)	5280(60)	25(15)
H1b	12200(180)	2550(50)	5470(70)	23(17)
H3	4700(200)	4740(40)	7710(60)	33(14)
H5	5900(200)	1620(40)	8050(60)	33(14)

Table B.24. Bond lengths [Å], angles [°], and torsions [°] for **16**

Lengths	Atoms	Length/Å	Atoms	Length/Å
	Br1 C2	1.900(8)	C1 C6	1.406(11)
	Br2 C4	1.908(7)	C2 C3	1.373(11)
	Br3 C6	1.904(8)	C3 H3	1.084(19)
	N1 H1a	1.035(19)	C3 C4	1.389(11)
	N1 H1b	1.043(19)	C4 C5	1.398(10)
	N1 C1	1.389(10)	C5 H5	1.086(19)
	C1 C2	1.414(10)	C5 C6	1.376(12)
Angles	Atoms	Angle/°	Atoms	Angle/°
	C2 C1 N1	121.6(7)	C3 C4 Br2	119.9(6)
	C6 C1 N1	123.1(7)	C5 C4 Br2	118.8(6)
	C6 C1 C2	115.2(7)	C5 C4 C3	121.3(7)
	C1 C2 Br1	118.0(6)	C6 C5 C4	117.6(7)
	C3 C2 Br1	119.3(6)	C1 C6 Br3	118.2(6)
	C3 C2 C1	122.7(7)	C5 C6 Br3	117.8(6)
	C4 C3 C2	119.1(7)	C5 C6 C1	124.0(7)
Torsions	Atoms	Angle/°	Atoms	Angle/°
	Br1 C2 C1 N1	-3.0(6)	Br3 C6 C5 C4	-178.3(6)
	Br1 C2 C1 C6	-178.8(5)	N1 C1 C2 C3	177.4(7)
	Br1 C2 C3 C4	-179.0(6)	N1 C1 C6 C5	-177.9(7)
	Br2 C4 C3 C2	176.7(6)	C1 C2 C3 C4	0.6(9)
	Br2 C4 C5 C6	-177.2(6)	C1 C6 C5 C4	0.4(9)
	Br3 C6 C1 N1	0.8(7)	C2 C3 C4 C5	-2.5(9)
	Br3 C6 C1 C2	176.6(5)	C3 C4 C5 C6	1.9(8)

The structure determination and refinement of **16** has proven difficult, and this is reflected in the past history of this compound. Three separate structure determinations are already deposited in the CSD (release 2023.3.0)^[18], BRANIL (determined by photographic methods; noted that it is an ‘overcrowded’ molecule and isostructural with that of plain 1,3,5-tribromobenzene),^[23] BRANIL01 (also photographic methods but only the unit cell was reported, same as BRANIL),^[24] and BRANIL02 (the first diffractometer structure, at 173 K, confirms the cell and space group but also shows the distorting effects on some displacement ellipsoids that we observed).^[25] Our attempts proved quite challenging, using multiple crystals and both Cu and Mo radiation. The best result, from a Mo dataset, is reported, and could after much effort be refined using HAR/NoSpherA2 to a very nice, restrained, model with almost all artefacts sufficiently modelled. Rather poor crystal quality is the probable culprit ($R_{\text{int}} = 8.2\%$) along with racemic twinning, resulting in ‘ghost’ peaks for Br1,3 in the refinement model. Rather low intensities lead to capping the refinement to a resolution of $52^\circ \sin\theta/\lambda$. The structure forms a classic ‘herringbone’ packing

of the almost-symmetrical 1,3,5-tribromo aryl rings, but despite this overall similarity to the parent tribromobenzene, the aniline functional groups are still engaged in H-bonding between molecules and stacks of molecules (Figure B.12).

Table B.25. Hydrogen Bonds for **16**

Donor	H	Acceptor	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	Br	1.035(19)	2.49(9)	3.075(7)	115(6)
N1	H1b	N1 ¹	1.043(19)	2.21(7)	3.086(10)	140(7)

¹1/2+X,1/2-Y,1-Z

Table B.26. Comparative geometrical parameters from the SC-XRD refinements of **1** – **9**

Lengths											
Compound	1	2	3	4	5(a)	5(b)	6(a)	6(b)	7	8	9
N-C(E)	1.425	1.424	1.413	1.414	1.417	1.404	1.397	1.432	1.413	1.4000	1.412
SD	0.004	0.003	0.002	0.004	0.007	0.007	0.006	0.006	0.004	0.0012	0.003
N-C(E)	1.425(4)	1.424(3)	1.413(2)	1.414(4)	1.417(7)	1.404(7)	1.397(6)	1.432(6)	1.413(4)	1.4000(12)	1.412(3)
S-N(E)	1.551	1.5539	1.5641	1.562	1.559	1.565	1.564	1.540	1.548	1.5400	1.540
SD	0.003	0.0019	0.0015	0.003	0.005	0.005	0.004	0.004	0.003	0.0009	0.002
S-N(E)	1.551(3)	1.5539(19)	1.5641(15)	1.562(3)	1.559(5)	1.565(5)	1.564(4)	1.540(4)	1.548(3)	1.5400(9)	1.540(2)
S-N(Z)	1.530	1.5353	1.5329	1.531	1.530	1.536	1.519	1.520	1.534	1.5410	1.519
SD	0.003	0.0019	0.0016	0.003	0.005	0.005	0.004	0.004	0.003	0.0009	0.002
S-N(Z)	1.530(3)	1.5353(19)	1.5329(16)	1.531(3)	1.530(5)	1.536(5)	1.519(4)	1.520(4)	1.534(3)	1.5410(9)	1.519(2)
N-C(Z)	1.402	1.404	1.396	1.389	1.387	1.403	1.392	1.417	1.395	1.3998	1.411
SD	0.004	0.003	0.002	0.004	0.007	0.007	0.006	0.006	0.004	0.0013	0.003
N-C(Z)	1.402(4)	1.404(3)	1.396(2)	1.389(4)	1.387(7)	1.403(7)	1.392(6)	1.417(6)	1.395(4)	1.3998(13)	1.411(3)
Angles											
Compound	1	2	3	4	5(a)	5(b)	6(a)	6(b)	7	8	9
S-N-C(E)	119.8	115.90	116.86	117.5	114.9	115.3	121.5	114.9	122.1	126.35	115.15
SD	0.2	0.15	0.12	0.2	0.4	0.4	0.3	0.3	0.2	0.07	0.17
S-N-C(E)	119.8(2)	115.90(15)	116.86(12)	117.5(2)	114.9(4)	115.3(4)	121.5(3)	114.9(3)	122.1(2)	126.35(7)	115.15(17)
N-S-N	115.31	115.58	116.39	116.19	116.8	116.5	115.2	115.8	114.76	123.69	115.25
SD	0.16	0.11	0.08	0.14	0.3	0.3	0.2	0.2	0.15	0.05	0.12
N-S-N	115.31(16)	115.58(11)	116.39(8)	116.19(14)	116.8(3)	116.5(3)	115.2(2)	115.8(2)	114.76(15)	123.69(5)	115.25(12)
S-N-C(Z)	132.3	130.84	131.85	133.1	133.3	131.4	133.4	132.5	131.3	126.93	125.69
SD	0.2	0.16	0.13	0.2	0.4	0.4	0.3	0.4	0.2	0.07	0.18
S-N-C(Z)	132.3(2)	130.84(16)	131.85(13)	133.1(2)	133.3(4)	131.4(4)	133.4(3)	132.5(4)	131.3(2)	126.93(7)	125.69(18)
Torsions											
Compound	1	2	3	4	5(a)	5(b)	6(a)	6(b)	7	8	9
S-N-C-C(E1)	0.4	-41.56	-29.4	-22.3	45.0	-38.3	3.9	-48.3	37.8	48.79	85.9
SD	0.3	0.18	0.2	0.3	0.5	0.5	0.5	0.4	0.3	0.10	0.2
S-N-C-C(E1)	0.4(3)	-41.56(18)	-29.4(2)	-22.3(3)	45.0(5)	-38.3(5)	3.9(5)	-48.3(4)	37.8(3)	48.79(10)	85.9(2)
S-N-C-C(E2)	-179.3	140.59	152.32	160.1	-138.1	145.9	-178.1	134.8	-145.4	-134.82	-98.74
SD	0.3	0.16	0.16	0.3	0.4	0.4	0.4	0.3	0.3	0.09	0.19
S-N-C-C(E2)	-179.3(3)	140.59(16)	152.32(16)	160.1(3)	-138.1(4)	145.9(4)	-178.1(4)	134.8(3)	-145.4(3)	-134.82(9)	-98.74(19)
N-S-N-C(E)	180.0	-177.7	174.6	172.6	-175.2	170.9	-179.3	179.1	-179.3	11.3	177.2
SD	0.3	0.2	0.1	0.2	0.4	0.4	0.3	0.3	0.2	0.1	0.2
N-S-N-C(E)	180.0(3)	-177.7(2)	174.6(1)	172.6(2)	-175.2(4)	170.9(4)	-179.3(3)	179.1(3)	-179.3(2)	11.3(1)	177.2(2)
N-S-N-C(Z)	-1.0	0.2	1.5	-0.6	3.1	-3.7	0.4	-6.5	0.0	10.0	0.8
SD	0.4	0.3	0.2	0.4	0.6	0.6	0.6	0.5	0.4	0.1	0.3
N-S-N-C(Z)	-1.0(4)	0.2(3)	1.5(2)	-0.6(4)	3.1(6)	-3.7(6)	0.4(6)	-6.5(5)	0.0(4)	10.0(1)	0.8(3)
S-N-C-C(Z1)	4.2	-23.0	7.6	7.3	0.0	11.6	-4.6	-19.0	4.2	50.52	85.4
SD	0.4	0.2	0.2	0.4	0.7	0.6	0.5	0.5	0.4	0.10	0.2
S-N-C-C(Z1)	4.2(4)	-23.0(2)	7.6(2)	7.3(4)	0.0(7)	11.6(6)	-4.6(5)	-19.0(5)	4.2(4)	50.52(10)	85.4(2)
S-N-C-C(Z2)	-176.1	158.3	-175.25	-173.7	-179.3	-168.1	175.4	164.5	-175.2	-134.02	-101.0
SD	0.3	0.2	0.19	0.3	0.5	0.5	0.5	0.4	0.3	0.09	0.2
S-N-C-C(Z2)	-176.1(3)	158.3(2)	-175.25(19)	-173.7(3)	-179.3(5)	-168.1(5)	175.4(5)	164.5(4)	-175.2(3)	-134.02(9)	-101.0(2)
C-O-C-C(E)	9.5							O-N-C-C(E)	5.8		
	0.5								0.4		
	9.5(5)								5.8(4)		
C-O-C-C(Z)	2.2							O-N-C-C(Z)	11.8		
	0.5								0.4		
	2.2(5)								11.8(4)		
Angle b/n rings	4.58	56.96	25.22	22.73	48.16	40.19	4.55	67.91	38.18	27.38	52.81

Moreover, there are fairly strong non-classical H-bonds linking the C-H atoms to Br atoms on neighbouring molecules (Table B.25). The interatomic distances and angles in our model have a considerable improvement in accuracy compared to the earlier BRANIL results and most noticeably better than that of BRANIL02.

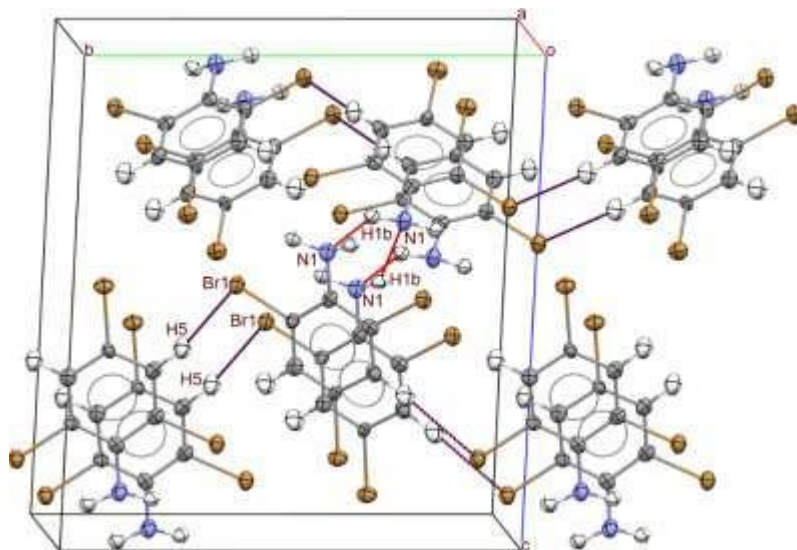


Figure B.12. Classical and non-classical H-bonding found in the lattice of **16**

B.3. Assessment of the HAR/NoSpherA2 refinement approach

In keeping with practices established in our prior publications, we have monitored the degree of improvement in the average derived parameter (via the most commonly recurring bond distance in each structure).^[8-14] This set of structures stands out from those previously processed with HAR/NoSpherA2 (NSA) in that several structures show very low or zero improvement (entries for **1**, **4**, **6** in column 6 of Table B.27) over the independent atom model (IAM), but the *average* improvement in structure precision remains 13%, and the best dataset (**15**) has an impressive 41% improvement in structure precision. We continue to collect this type of data when multiple comparisons on closely related structures are determined with the HAR approach. The same conclusions apply: the best datasets improve the most.

Table B.27. Improvement in average C-C (or C-Br where noted) bond precision in NoSpherA2 vs. IAM refinement

Comp.	NSA R1 %	Rint %	IAM C-C	NSA C-C	%impr C-C	Ord/Disord
15	1.92	4.17	0.0017	0.0010	41.2%	ordered
8	1.68	2.07	0.0022	0.0015	31.8%	ordered
9*	2.02	3.30	0.0030	0.0022	27.8%	ordered
2	5.37	4.36	0.0035	0.0030	14.3%	ordered
7	4.85	4.98	0.0050	0.0046	8.0%	inv. Twin
3	2.81	6.39	0.0030	0.0028	6.7%	inv. Twin
16#	4.66	8.19	0.0080	0.0077	4.2%	inv. Twin
5	4.21	10.93	0.0086	0.0083	3.5%	Z' =2
1	4.97	6.90	0.0051	0.0050	2.0%	inv. Twin
4	3.96	4.09	0.0045	0.0045	0.0%	inv. Twin
6	7.04	9.03	0.0063	0.0063	0.0%	disordered
Avg impr =					12.7%	

9*, 16# Using avg. C-Br bond precision, C-C is 0% impr.

A major reason to implement HAR with NoSpherA2 in this project was the ability to place the H-atoms more accurately, and to define their displacements realistically, by allowing for anisotropic displacement ellipsoids, as is of course commonly done for the heavier elements in most modern crystal structure determinations. For the heavy atoms, which tend to be central atoms, a major motivation for using the displacement tensors is the ability to better describe the electron density (ED) for the purpose of improving the calculated structure factors and get a better match to the measured structure factors from the diffraction intensities. This leads to improvement in the so-called residuals, like the well-known conventional R_1 , the 'R-factor' that is commonly used as a quality marker for structures. In actual fact, the precision of the atom positions and the bonds and angles that are derived from them are better measures of model accuracy, and that is why we monitor the precision of the most common bond distances in our structures with versus without HAR/NoSpherA2 as done in Table B.27.

Certainly, allowing the H-positions to be described by a 6-term displacement tensor, rather than just x,y,z, or, as is common in the IAM, just 'riding' on their attached atom coordinates with fixed offset distances and angles, tends to lead to lower R -factors. However, that is not the motivation. Rather, we were interested in having a truer picture

of the ED arising from the H-atom electrons, since these tend to be on the periphery of the molecules. This is important for modelling intermolecular interactions, especially dipoles and dispersion interactions.

In many of the structures for which we have used HAR with NoSpherA2,^[8] we have actually allowed the H-atoms to be placed freely and have found that the positions so described correspond very well with the positions typically found via neutron diffraction experiments. These data have been compiled in many of these prior publications. In the set of compounds measured here, that was usually not possible as the diffraction data was of insufficient quality to get reliable H-atom placements. Instead, in this work we have consistently undertaken a restrained refinement, with targeted distance restraints, often along with RIGU restraints for E-H bonds when the displacements required additional shape restrictions. The target distances employed are those taken from neutron diffraction studies in the same temperature range (near to 100 K) for the different E atom types. For aryl C-H, 1.085, for methyl C-H, 1.084 and for N-H, 1.04 Å.^[9]

The appropriateness of these choices is bolstered by our previous experiences where the E-H distances were freely refined and found to agree very well with these neutron predictions. In addition, for the very well-behaved dataset and model for **15**, we have undertaken additional refinement cycles with all the distance restraints removed and found that the model did not perceptibly alter. Nevertheless, proving H-atom placement from NoSpherA2 was not a goal of this work and we feel that it remained better to apply the restraints uniformly over all the refinements in this paper.

A detailed description of the work flow we typically employ for HAR with NoSpherA2 has been published in an Open Access publication for easy access by all interested readers.^[8d] This cited article also provides a detailed description of the method, and many literature references that interested readers can follow to learn more about the promise, achievements and possible limitations of the approach.

B.4. Comparison of SC-XRD Data to DFT Computed Geometries

Table B.28. Comparison of crystal structures of **1** – **9** to DFT-optimized geometries (distances, Å; angles & torsions, °).^{a,b,c,d}

	1	2	3	4	5(a,b)^e	6(a,b)^e	7	8	9	Average^f
N-C{E}	1.425(4)	1.424(3)	1.413(2)	1.414(4)	1.417(7), 1.404(7)	1.397(6), 1.432(6)	1.413(4)	1.4000(12)	1.412(3)	1.415(10)
	<i>1.401</i>	<i>1.402</i>	<i>1.402</i>	<i>1.4</i>	<i>1.4</i>	<i>1.4</i>	<i>1.396</i>	<i>1.391</i>	<i>1.362</i>	<i>1.400(2)</i>
S-N{E} (Å)	1.551(3)	1.5539(19)	1.5641(15)	1.562(3)	1.559(5), 1.565(5)	1.564(4), 1.540(4)	1.548(3)	1.5400(9)	1.540(2)	1.556(8)
	<i>1.578</i>	<i>1.575</i>	<i>1.575</i>	<i>1.575</i>	<i>1.575</i>	<i>1.573</i>	<i>1.573</i>	<i>1.551</i>	<i>1.546</i>	<i>1.575(2)</i>
S-N{Z} (Å)	1.530(3)	1.5353(19)	1.5329(16)	1.531(3)	1.530(5), 1.536(5)	1.519(4), 1.520(4)	1.534(3)	1.5410(9)	1.519(2)	1.530(6)
	<i>1.546</i>	<i>1.543</i>	<i>1.542</i>	<i>1.543</i>	<i>1.542</i>	<i>1.54</i>	<i>1.54</i>	<i>1.551</i>	<i>1.553</i>	<i>1.542(2)</i>
N-C{Z} (Å)	1.402(4)	1.404(3)	1.396(2)	1.389(4)	1.387(7), 1.403(7)	1.392(6), 1.417(6)	1.395(4)	1.3998(13)	1.411(3)	1.398(9)
	<i>1.381</i>	<i>1.384</i>	<i>1.384</i>	<i>1.383</i>	<i>1.383</i>	<i>1.385</i>	<i>1.382</i>	<i>1.391</i>	<i>1.402</i>	<i>1.383(1)</i>
S-N-C{E} (°)	119.8(2)	115.90(15)	116.86(12)	117.5(2)	114.9(4), 115.3(4)	121.5(3), 114.9(3)	122.1(2)	126.35(7)	115.15(17)	118(3)
	<i>118.22</i>	<i>118.03</i>	<i>118.18</i>	<i>118.38</i>	<i>118.38</i>	<i>118.18</i>	<i>118.73</i>	<i>127.28</i>	<i>136.51</i>	<i>118.3(2)</i>
N-S-N (°)	115.31(16)	115.58(11)	116.39(8)	116.19(14)	116.8(3), 116.5(3)	115.2(2), 115.8(2)	114.76(15)	123.69(5)	115.25(12)	115.8(6)
	<i>115.95</i>	<i>116.16</i>	<i>115.99</i>	<i>115.96</i>	<i>115.96</i>	<i>116.11</i>	<i>115.95</i>	<i>123.42</i>	<i>109.96</i>	<i>116.0(1)</i>
S-N-C{Z} (°)	132.3(2)	130.84(16)	131.85(13)	133.1(2)	133.3(4), 131.4(4)	133.4(3), 132.5(4)	131.3(2)	126.93(7)	125.69(18)	132.2(9)
	<i>131.94</i>	<i>132.02</i>	<i>132.07</i>	<i>132.12</i>	<i>132.12</i>	<i>132.27</i>	<i>132.54</i>	<i>127.28</i>	<i>120.83</i>	<i>132.2(2)</i>
S-N-C-C{E1} (°)	0.4(3)	-41.56(18)	-29.4(2)	-22.3(3)	45.0(5), -38.3(5)	3.9(5), -48.3(4)	37.8(3)	48.79(10)	85.9(2)	
	<i>-33.92</i>	<i>-36.05</i>	<i>-36.02</i>	<i>-35.24</i>	<i>-35.39</i>	<i>-38.42</i>	<i>-36.55</i>	<i>51.49</i>	<i>0</i>	
S-N-C-C{E2} (°)	-179.3(3)	140.59(16)	152.32(16)	160.1(3)	-138.1(4), 145.9(4)	-178.1(4), 134.8(3)	-145.4(3)	-134.82(9)	-98.74(19)	
	<i>148.14</i>	<i>145.93</i>	<i>146.12</i>	<i>146.9</i>	<i>146.77</i>	<i>143.8</i>	<i>145.71</i>	<i>-131.68</i>	<i>180</i>	

Table B.28. Cont'd

	1	2	3	4	5(a,b)^e	6(a,b)^e	7	8	9
N-S-N-C{E} (°)	180.0(3) <i>173.87</i>	-177.7(2) <i>173.99</i>	174.6(1) <i>174.27</i>	172.6(2) <i>174.22</i>	-175.2(4), 170.9(4) <i>174.19</i>	-179.3(3), 179.1(3) <i>174.08</i>	-179.3(2) <i>174.11</i>	11.3(1) <i>9</i>	177.2(2) <i>179.99</i>
N-S-N-C{Z} (°)	-1.0(4) <i>-2.14</i>	0.2(3) <i>-2.42</i>	1.5(2) <i>-2.19</i>	-0.6(4) <i>-2.33</i>	3.1(6), -3.7(6) <i>-2.35</i>	0.4(6), -6.5(5) <i>2.59</i>	0.0(4) <i>-2.67</i>	10.0(1) <i>8.99</i>	0.8(3) <i>0</i>
S-N-C-C{Z1} (°)	4.2(4) <i>1.24</i>	-23.0(2) <i>1.39</i>	7.6(2) <i>1.18</i>	7.3(4) <i>1.08</i>	0.0(7), 11.6(6) <i>1.06</i>	-4.6(5), -19.0(5) <i>1.21</i>	4.2(4) <i>0.79</i>	50.52(10) <i>51.5</i>	85.4(2) <i>90.12</i>
S-N-C-C{Z2} (°)	-176.1(3) <i>-178.52</i>	158.3(2) <i>-178.33</i>	-175.25(19) <i>-178.58</i>	-173.7(3) <i>-178.68</i>	-179.3(5), -168.1(5) <i>-178.7</i>	175.4(5), 164.5(4) <i>-178.6</i>	-175.2(3) <i>-178.99</i>	-134.02(9) <i>-131.68</i>	-101.0(2) <i>-90.14</i>
Angle b/n rings (°)	4.58 <i>37.92</i>	56.96 <i>40.14</i>	25.22 <i>39.79</i>	22.73 <i>39.24</i>	48.16, 40.19 <i>39.44</i>	4.55, 67.91 <i>42.57</i>	38.18 <i>41.01</i>	27.38 <i>25.18</i>	52.81 <i>89.99</i>

^a Geometry optimized using Gaussian 16w v1.1, computed at B3LYPD3BJ/6-311G++(2d,p). Conformation of computed structure used is based on conformation obtained in crystal structures, i.e. **1-7, 9** in E/Z conformation, and **8** in Z/Z conformation. ^b Errors given for bond lengths, angles, and torsions are s.u. from crystallographic data. Errors for averages are s.d. for the series. ^c Range of bond lengths (longest – shortest = range, given in Å): N-C{E}, 0.035; S-N{E}, 0.025; S-N{Z}, 0.022; N-C{Z}, 0.030. Range of bond angles (°): S-N-C{E}, 7.2; N-S-N, 2.0; S-N-C{Z}, 2.6. ^d Italicized entries are values taken from computed geometries optimized using B3LYPD3BJ/6-311++G(2d,p) ^e **5** and **6** each contain two molecules in the asymmetric unit (*Z'* = 2), values for each independent molecule are tabulated. ^f Averages are taken from **1 – 7**, since **8** and **9** have significantly different conformations. Averages of torsions are not given, due to inconsistency of sign and large variation of magnitude (e.g. averaging torsions of 11.6 and -19.0)

B.5. Computation of the aryl ring orientation in 9

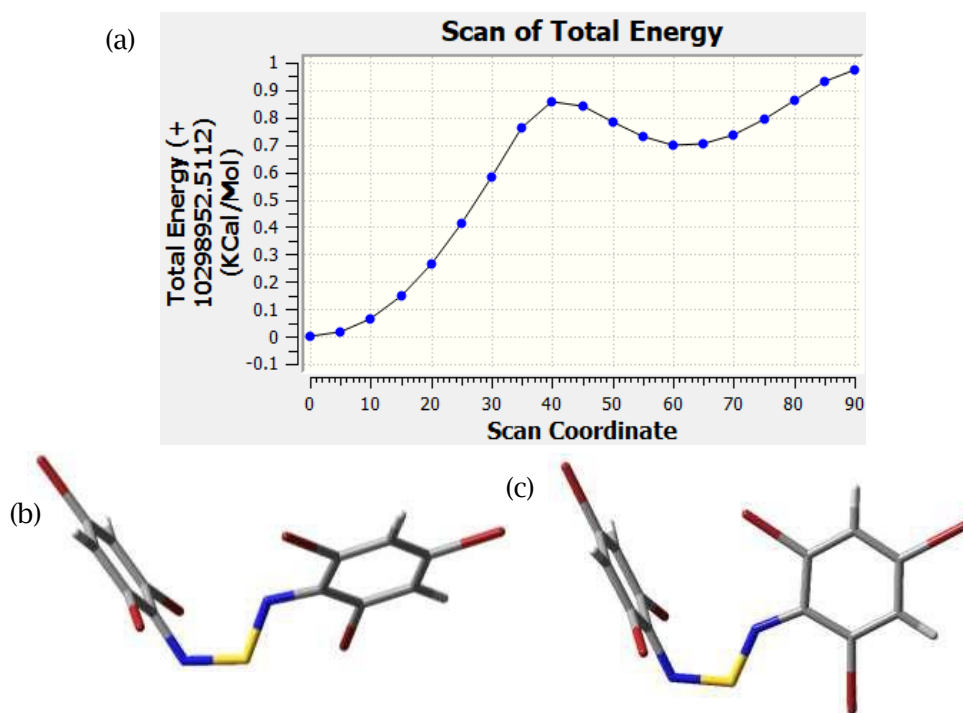


Figure B.13. (a) Relaxed scan DFT calculation at the B3LYP-D3BJ/6-311++G(2d,p) level of theory. (b) Computed local minimum conformation at 60°, close to the SC-XRD geometry. (c) Global minimum conformation with the torsion at 0°.

In view of the discrepancy in the DFT geometry for the E/Z isomer of the tribromophenyl SDI **9** from what is found in the crystal structure, we have undertaken a relaxed scan DFT simulation for rotation of the *E*-branch phenyl ring from zero (Scan Coordinate (SC) #1) to 90 degrees (SC #19). The local minimum near 60° is fairly close to the torsional angle found experimentally in the crystal lattice (86°), Figure B.13(b), whereas the global minimum has this ring co-planar with the -NSN- moiety, Figure B.13(c). However, the energy differences, and indeed the barriers, are very low. The 60° geometry is computed at only 2.9 kJ/mol above the lowest conformation, and the interconversion barriers between the two are low (3.6/0.7 kJ/mol). Moreover, the barrier at the fully orthogonal conformation is only 4.1 kJ/mol, i.e. well within *kT* at RT. Importantly, these are expected to the *highest* aryl ring rotation barriers for the whole series, as the 2,6-dibromo substitution will have the greatest steric hindrance. We can assume free rotation of the aryl rings in all the neutral SDIs considered in this work.

B.6. NMR Spectroscopy Data Tables and Discussion

Table B.29. ^1H , ^{13}C , and ^{19}F NMR spectroscopic data for **1** – **9**

Cmpd	$\text{H}_1(\text{X})^f$	H_2	$\text{X}_1(^1\text{H or } ^{19}\text{F})$	C_1	C_2	C_3	C_4	$\text{X}_1(^{13}\text{C})$
1	6.75, d (8.3)	7.49, s	3.84, s	140.2, s	125.0, s	114.3, s	158.5, s	55.7, s
2	7.15, d (8.1)	7.37, d (7.2)	2.36, s	143.7, s	123.4, s	129.6, s	136.9, s	21.4, s
3	7.03, s	7.44, s	-112.8	142.1, d (1.9)	125.1, s	116.0, d (22.6)	161.3, d (248)	–
4	7.32, d (8.7)	7.41, d (7.8)	–	144.1, s	124.7, s	129.3, s	132.7, s	–
5	7.34, d (7.9)	7.47, d (8.6)	–	144.5, s	125.0, s	132.3, s	120.7, s	–
6	7.43, s	7.57, d (8.2)	-61.9	147.7, q (1.4)	123.2, s	126.4, q (3.7)	128.9, q (32.8)	124.1, q (272)
7	7.60, d (8.7)	8.27, d (9.0)	–	149.8, s	124.0, s	125.2, s	146.2, s	–
8	-112.6 (19F)	6.52, m (abb'xx')	-109.0	117.9, td (17.7, 5.1)	153.6, ddd (252, 14.7, 7.0)	99.9, ddd (26.6, 23.6, 4.8)	160.3, dt (251, 14.4)	–
9	–	7.56, s	–	141.0, s	133.8, s	133.8, s	118.7, s	–

^aIn CDCl₃; format: δ (ppm), multiplicity, (J (Hz)). ^bNumbering Scheme shown below. ^c $\delta(^1\text{H})$, relative to residual CHCl₃ at 7.27 ppm. ^d $\delta(^{13}\text{C}\{^1\text{H}\})$, relative to residual CHCl₃ at 77.23 ppm. ^e $\delta(^{19}\text{F}\{^1\text{H}\}(3,6)$ or ^{19}F (**8**)), relative to external CFCl₃ at 0.00 ppm. ^fH₁ signals are broadened by exchange, so the expected doublet from *ortho* protons is not resolved in **1**-**7**.

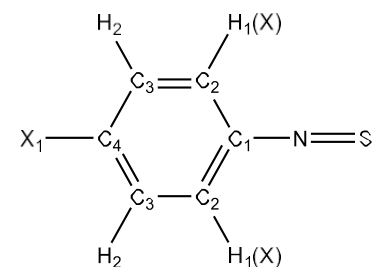
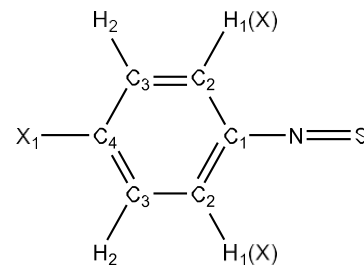


Table B.30. Low-temperature (233 K – 240 K) $^1\text{H}^{\text{a,b,c}}$ and $^{13}\text{C}^{\text{a,b,d}}$ NMR data for **1** – **9**.^e

Cmpd	H ₁	H ₂	X ₁ (¹ H)	C ₁	C ₂	C ₃	C ₄	X ₁ (¹³ C)
1	7.09, s; 8.20, s	6.90, s	3.83, s	139.3, s; 140.8, s	121.4, s; 128.1, s	113.7, s; 114.5, s	157.9, s	55.6, s
2	~6.9, s; 7.91, s	7.01, s	2.20, s	143.5, s	120.6, s; 126.3, s	129.8, s	136.4, s; 138.3, s	21.7, s
3	8.18, s; obscured by H ₂	7.08, s	–	141.6, s; 142.5, s	121.8, s; 128.5, s	115.9, s	161.0, d (248)	–
4	7.04, s; 8.08, s	7.33, s	–	143.8, s	121.8, s; 127.8, s	129.2, s	132.0, s; 133.1, s	–
5	6.98, s; 8.01, s	7.48, s	–	144.3, s	122.0, s; 127.9, s	132.0, s	120.0, s	–
6	7.19, s; 8.16, s	7.59, s	–	147.4, s	120.8, s; obscured by C3	126.2, s	128.4, s	123.8, q (27)
7	Lost in baseline	8.30, d (7.3)	–	149.7, s	121.2, s; obscured by C3	125.2, s	145.7, s	–
8	–	6.53, m	–	117.4, m	153.0, m	99.8, m	160.0, dt (251, 14)	–
9	–	7.54, s	–	140.6, s	117.0, s	133.4, s	118.7, s	–

^aIn CDCl₃; format: δ (ppm), multiplicity (J (Hz)); entries in double lines for asymmetric cases. ^bNumbering Scheme below. ^c $\delta(^1\text{H})$, relative to residual CHCl₃ at 7.27 ppm. ^d $\delta(^{13}\text{C}\{^1\text{H}\})$, relative to residual CHCl₃ at 77.23 ppm. ^eLow-temperature NMR was performed on a spectrometer that did not have a ¹⁹F probe, so no ¹⁹F NMR was obtained below room temperature.



The temperature range of these experiments (-40°C to ~22°C) reach neither the high nor the low exchange limits, as the signals remain broad and unresolved. In contrast to the solution-state behaviour of compounds **1-7**, measurements of compounds **8** and **9** indicate that they are symmetrical and non-fluxional in solution. Over the same temperature range, the ¹H and ¹³C signals of **8** and **9** remain sharp and well resolved, show the expected coupling patterns, and show no indication of splitting at low temperatures due to inhibition of exchange. There are several examples in the literature which have explored this phenomenon by NMR at lower temperatures (-90°C to -110°C).^[26-29] The expected doublets of *para*-substituted aryl sulfur diimides which are not resolved at -40°C are fully resolved at -90°C and below. These signals split from one singlet at room temperature to two singlets of equal integration at low temperature, lending credibility to the claim that the dominant conformation in solution is E/Z. There is a minor component of these compounds seen at low temperatures, which Grunwell, Vrieze, and Webb attributed to the E/E conformer.^[26, 28-29, 36] Grunwell makes this assertion based on CNDO/2 calculations on various sulfur diimides,^[29] and ‘chemical intuition’. Vrieze makes an argument based primarily on steric considerations for the preference of the sulfur diimides to adopt the E/E conformation.^[26, 36] Webb compares the ortho-¹H shift of *bis*(2-methylphenyl)sulfur diimide (5.92 ppm) to a series of sulfinylanilines (R-PhNSO), which are claimed to adopt the *cis* (Z) conformation in solution, and argues that based on the shielding of the ortho-¹H signal of the analogous 2-methylsulfinylaniline (8.36 ppm), the sulfur diimide must necessarily have adopted the *trans* (E) conformation.^[28] However, NMR and computational evidence suggest that the assignment of this conformer as E/E is in error.

The preponderance of computational results for sulfur diimides – from the parent compound, H-NSN-H, to alkyl and aryl derivatives – strongly indicates that E/E is universally the least stable conformation for sulfur diimides.^[27, 37-40] E/Z and Z/Z conformations are found to be close in energy, most often within +/- 5-10 kJ/mol for our

series **1** to **9**, while the E/E conformation is typically found 30-40kJ/mol higher in energy. While this does not preclude the sulfur diimides in solution adopting the E/E conformation at least transiently, it implies that if a symmetrical conformer is seen in solution, it is much more likely to be the Z/Z conformer. Further, there is no example in literature of a sulfur diimide that crystallizes in the E/E conformation. Sandblom et al.^[37] undertook a careful analysis of DFT computations of 1,3-dimethylsulfurdiimide, H₃C-NSN-CH₃, making a strong argument that sterics are not the dominant driving force in the conformation of sulfur diimides. They conclude that electronic factors and orbital interactions are the main contributors to the geometry of these molecules. This gives us latitude to move beyond the limitations of our chemical intuition and set aside Vrieze's reasoning that led to the assignment of the symmetrical conformer as E/E. Webb's argument of the chemical shifts is logically consistent, but it does not consider the significant effects of anisotropic ring shielding that would be present in the Z/Z conformation. We believe that ring shielding is an alternate and sufficient explanation for the chemical shifts, is furthermore consistent with the computational determination of sulfur diimide energies in the respective conformations, and also with the similarly shielded signals of the methyl ¹H signals in both the 2-methylphenyl- and 2,4,6-trimethylphenylsulfur diimides in both Webb and Vrieze's work.

Table B.31. Incremental Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5 ppm). "Carbon Atom of Substituents in parts per million from TMS" Modified by the authors to incorporate typical diaryl sulfur diimides for the sole purpose of assigning C13 NMR signals of the latter species.*

Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH ₃	9.3	0.7	-0.1	-2.9	21.3
CH ₂ CH ₃	15.6	-0.5	0.0	-2.6	29.2 (CH ₂), 15.8 (CH ₃)
CH(CH ₃) ₂	20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH ₃)
C(CH ₃) ₃	22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH ₃)
CH=CH ₂	9.1	-2.4	0.2	-0.5	137.1 (CH), 113.3 (CH ₂)
C≡CH	-5.8	6.9	0.1	0.4	84.0 (C), 77.8 (CH)
C ₆ H ₅	12.1	-1.8	-0.1	-1.6	
CH ₂ OH	13.3	-0.8	-0.6	-0.4	64.5
CH ₂ O(C=O)CH ₃	7.7	-0.0	-0.0	-0.0	20.7 (CH ₃), 66.1 (CH ₂), 170.5 (C=O)
OH	26.6	-12.7	1.6	-7.3	
OCH ₃	31.4	-14.4	1.0	-7.7	54.1
OC ₆ H ₅	29.0	-9.4	1.6	-5.3	
O(C=O)CH ₃	22.4	-7.1	-0.4	-3.2	23.9 (CH ₃), 169.7 (C=O)
(C=O)H	8.2	1.2	0.6	5.8	192
(C=O)CH ₃	7.8	-0.4	-0.4	2.8	24.6 (CH ₃), 195.7 (C=O)
(C=O)C ₆ H ₅	9.1	1.5	-0.2	3.8	196.4 (C=O)
(C=O)F ₃	-5.6	1.8	0.7	6.7	
(C=O)OH	2.9	1.3	0.4	4.3	168
(C=O)OCH ₃	2.0	1.2	-0.1	4.8	51.0 (CH ₃), 166.8 (C=O)
(C=O)Cl	4.6	2.9	0.6	7.0	168.5
(C=O)NH ₂	5.0	-1.2	0.0	3.4	
C≡N	-16	3.6	0.6	4.3	119.5
NH ₂	19.2	-12.4	1.3	-9.5	
N(CH ₃) ₂	22.4	-15.7	0.8	-11.8	40.3
NH(C=O)CH ₃	11.1	-9.9	0.2	-5.6	
NO ₂	19.6	-5.3	0.9	6.0	
N=C=O	5.7	-3.6	1.2	-2.8	129.5
F	35.1	-14.3	0.9	-4.5	
Cl	6.4	0.2	1.0	-2.0	
Br	-5.4	3.4	2.2	-1.0	
I	-32.2	9.9	2.6	-7.3	
CF ₃	2.6	-3.1	0.4	3.4	
SH	2.3	0.6	0.2	-3.3	
SCH ₃	10.2	-1.8	0.4	-3.6	15.9
SO ₂ NH ₂	15.3	-2.9	0.4	3.3	
-N=S=N-	17.0	-5.3	0.3	-1.9	
Si(CH ₃) ₃	13.4	4.4	-1.1	-1.1	

* See Ewing, D.E., (1979). *Org. Magn. Reson.*, **12**, 499, for 709 chemical shifts of monosubstituted benzenes.

* Adapted from Table 4.12 in the 7th edition of Robert M. Silverstein, Francis X. Webster and David J. Kiemle, *Spectrometric Identification of Organic Compounds*, Wiley, 2005.^[20] The highlighted line provides the incremental shifts for diaryl sulfur diimides, based on reliable data for Ph-NSN-Ph, as reported in Kresze *et al.*^[21]

B.7. Computed Isomerization Pathways for the SDIs

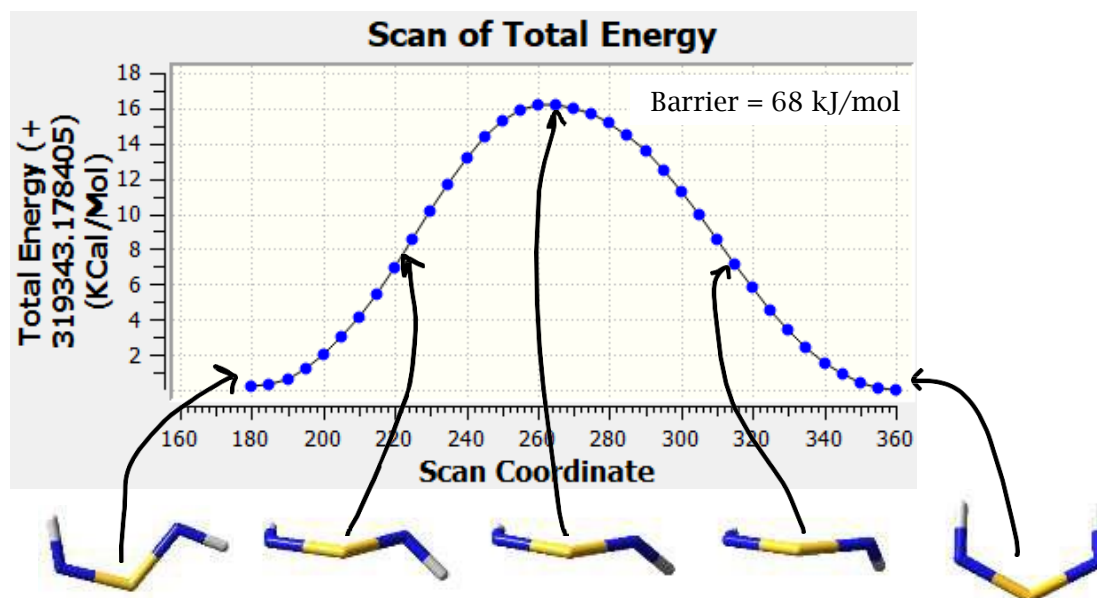


Figure B.14. B3LYP-D3BJ/6-311++G(2d,p) calculation of relaxed scan of HNSNH from E/Z to Z/Z

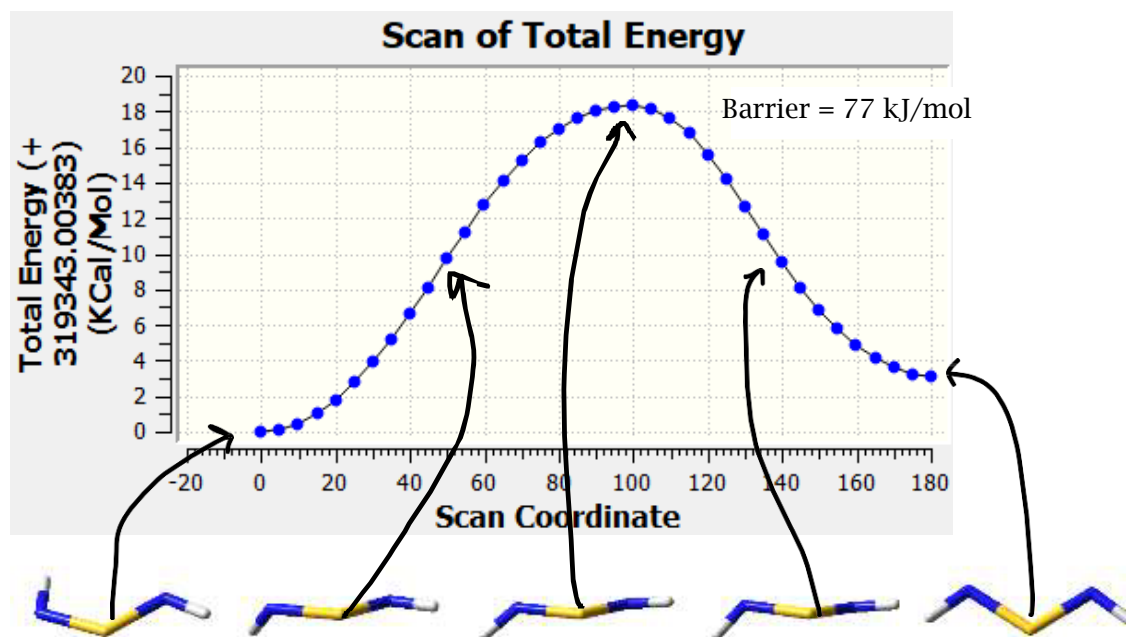


Figure B.15. B3LYP-D3BJ/6-311++G(2d,p) calculation of relaxed scan of HNSNH from E/Z to E/E

Relaxed scans, driven by rotations of the internal coordinates for the N-S-N-H torsion angles, are indeed able to convert the E/Z conformer to both Z/Z and E/E, as originally proposed by Raghavachari and Haddon.^[26d] Figure B.14 provides plots of the energies along these paths and provide vignettes for some conformations along these paths. IRC calculations, starting from the transition states (TS) of the scans shown above and driven both forwards and backwards, reproduce the essential features of the relaxed scans, although as is normal for the IRC approach do not arrive at the fully optimized starting and ending geometries. Thus, the indicated barriers are computed from the difference between the optimized ground states and the optimized and frequency-monitored TS (the latter showing the expected single imaginary frequency associated with a saddle point). By contrast, the same approach when applied to a model diaryl-SDI, PhNSNPh, results in a TS with a greatly enlarged S-N-*Cipso* bond angle for the E branch phenyl ring (central vignette in Figure B.16 below). An IRC calculation driven forward and backwards from this TS identifies a path involving far less large-body motion of the phenyl rings than naively imagined in the original relaxed scan. After considerable opening of the S-N-*Cipso* bond angles, a multidirectional nuclear motion of the -NSN- atoms finesse Z/Z to E/Z transformation in an elegant re-arrangement that illustrates the principle of least nuclear motion (PLNM)

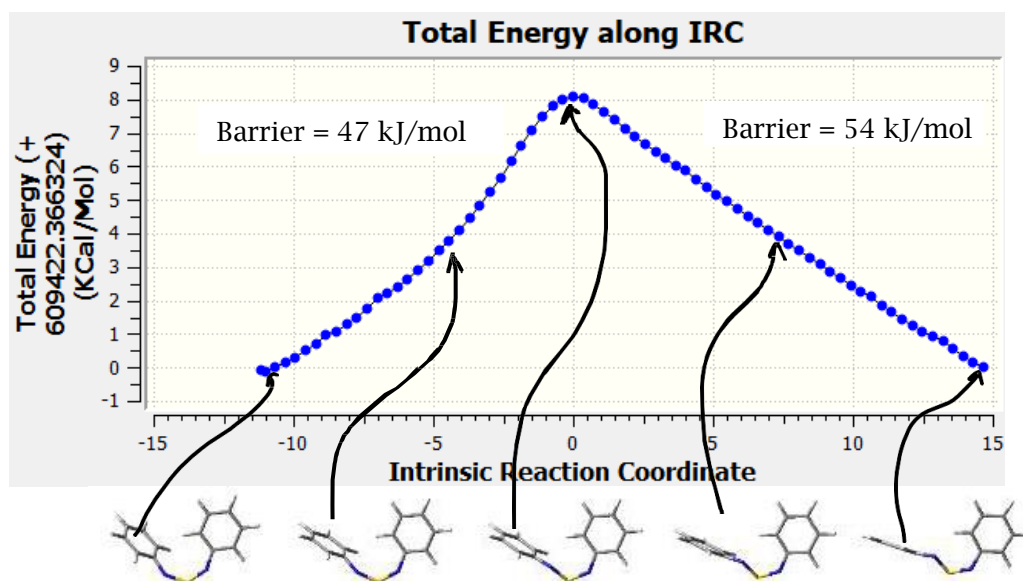


Figure B.16. B3LYP-D3BJ/6-311++G(2d,p) calculation of IRC path calculation for PhNSNPh from Z/Z to E/Z.

Here too, the two end points along the IRC path are far from fully optimized, and the barrier is therefore higher than appears from the energy scale of Figure B.16. For PhNSNPh, as for **1** – **7** in Table 4.1, inclusion of D3BJ dispersion correction results in a computed energy of Z/Z somewhat lower than E/Z, contrary to the experimental evidence from NMR or UV-vis spectroscopies. Nevertheless, the better estimation of the geometry of the Z/Z isomer by inclusion of dispersion effects has led us to favour the inclusion of the correction in the models used in this paper. Notably, the barrier heights, which are therefore different for the forward and reverse reactions, unlike the case for the effectively degenerate HNSNH, are significantly *lower* for PhNSNPh, illustrating the high effectiveness of the PLNM principle. As a key difference in the computed paths for the two molecules is the wide opening of S-N-*Cipso* bond angles, we suspect that delocalization into the aryl ring vibrations, which is so strongly evident in the computed vibrational spectra of PhNSNPh plays an important role in finessing the isomer interconversions in diaryl-SDIs studied in this work. These computed barriers align well with estimates for SDI interconversion in solution previously obtained from variable temperature NMR measurements.

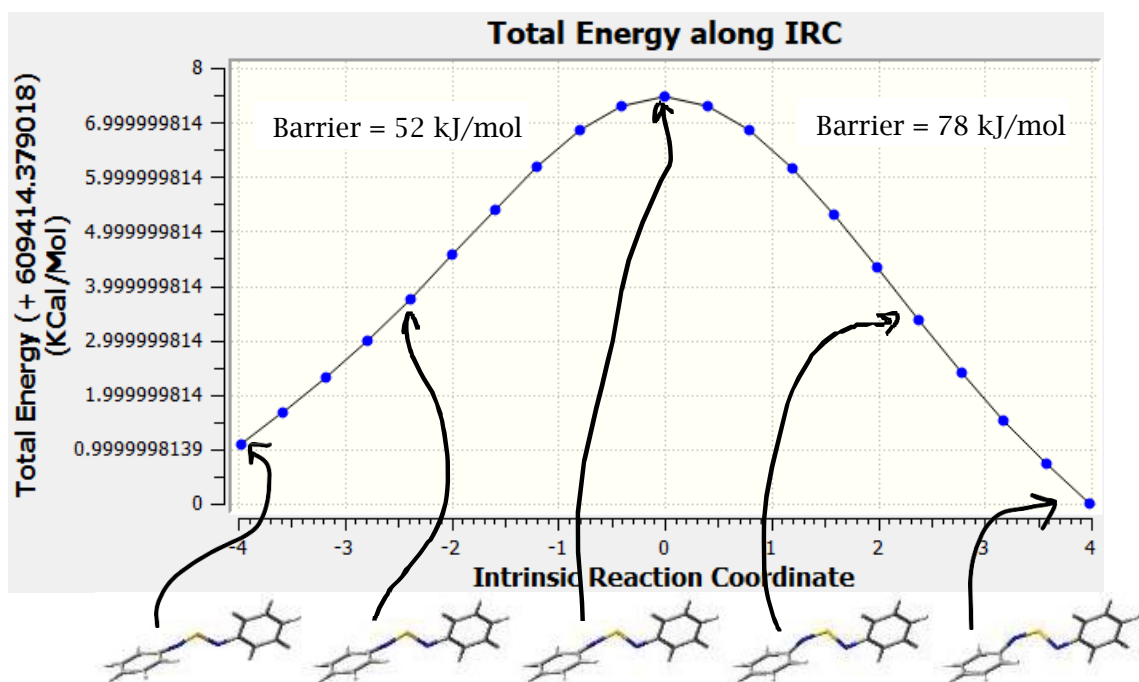


Figure B.17. B3LYP-D3BJ/6-311++G(2d,p) calculation of IRC path calculation for PhNSNPh from E/E to Z/E.

The barrier heights are even more asymmetrical here (Figure B.17, again as expected from Table 4.1, since the E/E conformer is the highest in energy for all known neutral SDIs), and at +52 and +78 kJ/mol corroborate the notion that the easiest path between isomers will be $E/Z \leftrightarrow Z/Z \leftrightarrow Z/E$. However, we are emphatic in noting that the barrier to E/E is only slightly higher in these IRC paths and relaxed scans. Whereas the energy difference is sufficient to ensure that the *population* of E/E could be much less than 1%,* it is highly likely that E/E is also *available* at any point. These low barrier heights, for isomerisations that at least start with some rotation about the N-S bonds, are consistent with a π -bond order of ~ 0.5 . Evidently, the bond shortening in SDIs attributed to an ionic bonding component is expected to be non-directional and will not contribute to rigidity of the bonds.

Finally, although the IRC paths discovered for PhNSNPh are fully consistent with the PLNM, it will be foolish to put too much weight on them. At the ambient temperatures employed for most of the solution experiments in this work, it is evident that the

molecules have plenty of thermal motion to enable many possible paths interconnecting these isomers. Here we remember the sage advice of Shaik et al.:^[22]

Although intrinsic reaction coordinates like minima, maxima and saddle points comprise geometrical or mathematical features of energy surfaces, considerable care must be exercised not to attribute chemical or physical significance to them. Real molecules have more than infinitesimal kinetic energy, and will not follow the IRC.

* (At T = 298.15 K, if their energies differ by 12 kJ/mol the corresponding populations are in the 99:1 ratio.)

B.8. Cyclic and Square Wave Voltammetry Data Tables and Figures

Table B.32A. Electrochemical characterization data for compounds **1** – **9**.^a

Process:		-1/-2			0/-1						+1/0				
Cmpd.	Conc ^b (mM)	E_p^{c2} (V)	E_{SW}^2 (V)	$\Delta E_p^{c(1-2)}$	E_p^{c1} (V)	E_p^{a1} (V)	E_m^1 (V)	ΔE_{pp} (V)	I_a/I_c^c	E_{SW}^1 (V)	E_p^{a3} (V)	E_p^{c3} (V)	$E_p^{a(3-1)}$ (V)	I_a/I_c	E_{SW}^2 (V)
1	4.5	-2.131	-2.034	0.414	-1.717	-1.589	-1.653	0.128	0.52	-1.642	0.749	0.623	2.338	0.34	0.677
2	4.4	-2.036	-1.966	0.391	-1.645	-1.527	-1.586	0.118	0.64	-1.566	1.081	0.829	2.608	0.28	0.976
3	4.5	-1.987	-2.047	0.391	-1.596	-1.453	-1.525	0.143	0.65	-1.547	1.209		2.662		1.125
4	4.5	-1.871	-1.765	0.404	-1.467	-1.335	-1.401	0.132	0.67	-1.394	1.229		2.564		1.217
5	4.9	-1.889	-1.917	0.430	-1.459	-1.330	-1.395	0.129	0.73	-1.408	1.247		2.577		1.189
6	4.4	-1.720	-1.653	0.407	-1.313	-1.175	-1.244	0.138	0.70	-1.254	0.969, 1.547		2.144		0.907
7	4.0 ^d	-1.871 ^e	-1.793	0.886	-0.985	-0.863	-0.924	0.122	0.83	-0.912	1.109, 1.741		1.972		0.906
8	6.3	-2.157	-2.064	0.678	-1.479	-1.279	-1.379	0.200	1.00	-1.404	No data		—		1.422
9	5.5	-1.721	-1.706	0.319	-1.402	-1.255	-1.328	0.147	0.64	-1.334	1.143		2.398		1.116, 1.614
10		—	—	—	-2.571	—	—	—	—	-2.627	—		—		
11		—	—	—	-2.717	—	—	—	—	-2.347	—		—		

^a GC electrode, A = 7.1 mm², ν = 0.2 V s⁻¹, T = 22°C, with 0.4M [tBu₄N][PF₆] supporting electrolyte in CH₂Cl₂. All potentials are vs. Fc^{+/0}. ^b Nominal concentrations, +/- 0.5 mM. ^c I_a/I_c ratios are estimated except for **3**, **7**, and **8**, due to unsatisfactory baseline for anodic process (-/2- process disrupted baseline for all other compounds). ^d Concentration of **7** is overestimated due to limited solubility in CH₂Cl₂. ^e E^{a2} = -1.714 V; I_a/I_c = 0.55.

Table B.32B. Electrochemical data for the reduction of **10**.

Scan rate dependence of tBu SDI Red1 Ec					
Scan rate (	Red1 Ec	Fc Ea	Fc Ec	Fc E	adj. Red1 Ec
50	-2.24839	0.401517	0.3174	0.359459	-2.60785
100	-2.28601	0.420333	0.306332	0.363333	-2.64934
200	-2.35812	0.42808	0.293051	0.360566	-2.71869
500	-2.4318	0.446896	0.279769	0.363333	-2.79513
1000	-2.49764	0.466818	0.26206	0.364439	-2.86208

For this irreversible reduction (Figure B.59) the apparent peak potential is strongly dependent on the applied scan rate. Similar results are obtained for the reduction of **11** (Figure B.61). The E_p^{c1} values for the apparent peak potentials as a function of scan rate are shown in the right-most column of the Table at left. The potentials shift by 0.25 V from 50 mV/s to 1 V/s.

Table B.33. Reversibility indicators^a for the E¹ process in aryl SDIs

Cmpd	I _{pa} /I _{pc}	Confidence	E _{1/4}	E _{3/4}	ΔE (mV)	Moving avg.	Deviation
1	0.52	low	-1.5900	-1.6578	67.8	67.8	0.0
2	0.64	low	-1.5235	-1.5904	66.9	67.3	-0.4
3	0.65	high	-1.4717	-1.5387	67.0	67.2	-0.2
4	0.67	med	-1.3475	-1.4085	61.0	65.7	-4.7
5	0.73	med	-1.3251	-1.399	73.9	67.3	6.6
6	0.70	med	-1.185	-1.2494	64.4	66.8	-2.4
7	0.83	med	-0.875	-0.935	60.0	65.9	-5.9
8	1.00	high	-1.3305	-1.4097	79.2	67.5	11.7
9	0.64	low	-1.2715	-1.3395	68.0	67.6	0.4

^aEvaluation of *electrochemical* reversibility for the E^{c1} process via the Tomeš criterion based the potential differences measured at the ¼ and ¾ current heights. See: Oldham *et al.*, *Electrochemical Science and Technology: Fundamentals and Applications*, pgs 253-254.^[23] and Bard and Faulkner, *Electrochemical Methods: Fundamentals and Applications*.^[24] Notes:

- The I_{pa}/I_{pc} ratios were determined from the CV scans via the *apparent* ratios of the forward and reverse peak currents.
- The Confidence indicator reflects the relative ability to accurately describe the reverse current baseline, which is moderately to severely compromised and hard to define, with the exceptions of **3** and **8**, due to interference from the onset of the (closely spaced) E² process.
- Theory predicts that ΔE(¼ - ¾) should be 56.5 mV, at 298.15 K and in aqueous solution. With a low-dielectric solvent like CH₂Cl₂, all voltammetric peaks tend to be considerably wider, an effect that is experimentally mitigated by using the high (0.4 M) supporting electrolyte concentration, but cannot be eliminated. With this in mind, an average ΔE(¼ - ¾) = 68 mV is indicative of electrochemical reversibility or close-to-reversibility for all cases.
- The largest deviations occur for **5** and **8** but at 7-12 mV larger than the average, it seems unwise to draw a confident exception.
- When the Tomeš criterion is compared with the clear trends in I_{pa}/I_{pc} the logical conclusion is that an EC process is operative, and that for the series **1** - **7**, the instability (i.e. rate of follow up chemical reaction) increases with the electron donating power of the *para* substituents, and the stability of 7⁻ in particular stands out by the appearance of a well-defined E² process (with return wave) that is 0.89 V more negative, indicating a large voltammetric stability range, and hence lifetime, for the radical anion.
- The I_{pa}/I_{pc} ratio for **8**, presumed to be Z/Z in solution, is the best of the series; like **7**, the separation between processes ΔE^{c(1-2)} is large, leading to a well-defined reverse current baseline; unlike **7** the E² process is very distorted and highly irreversible.
- For the non-aryl SDIs **10** and **11**, the I_{pa}/I_{pc} ratios are both zero over the scan rates investigated in this work.

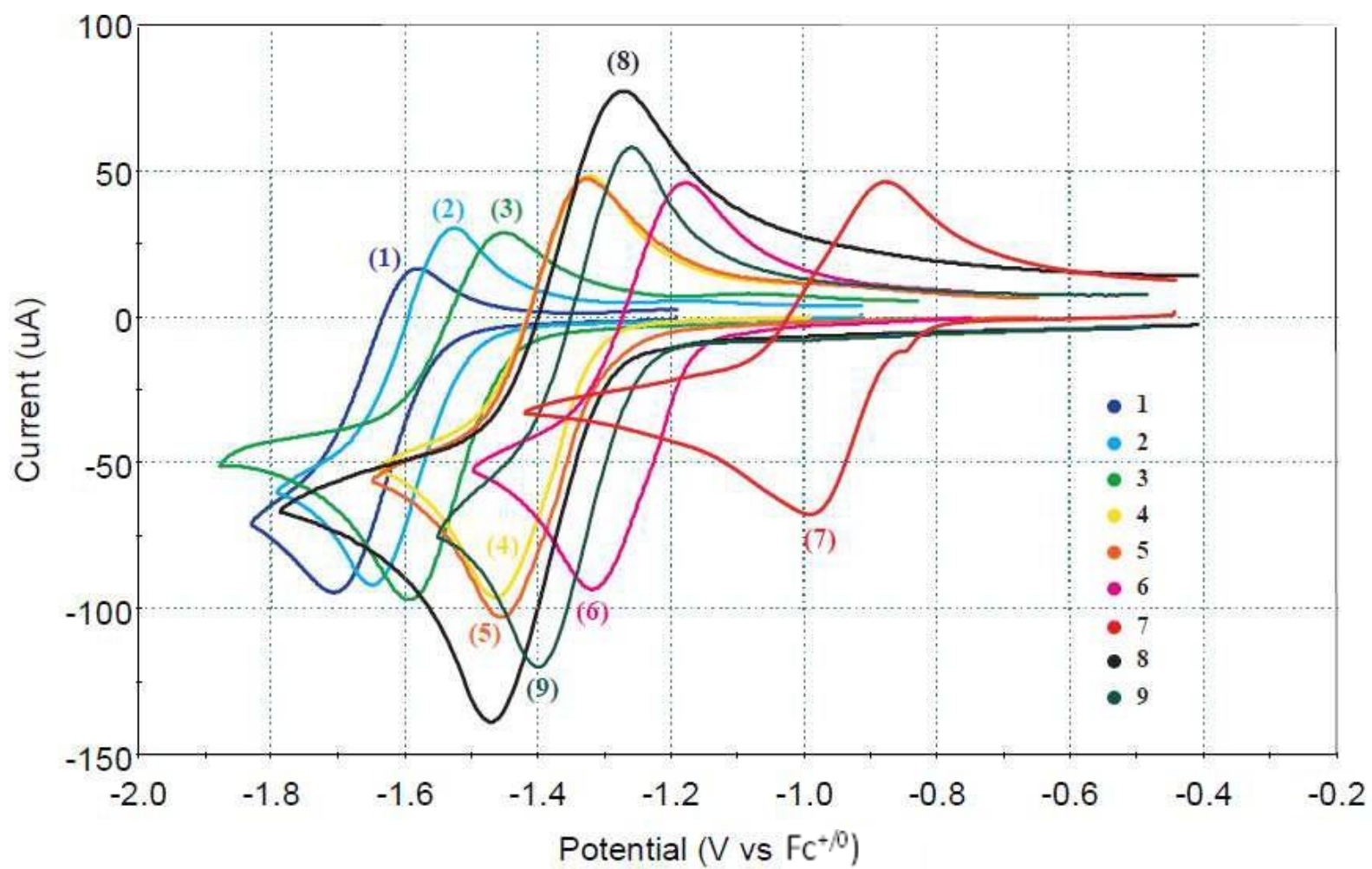


Figure B.18. Compiled cyclic voltammograms of the 0/- redox process for compounds 1-9 before concentration correction

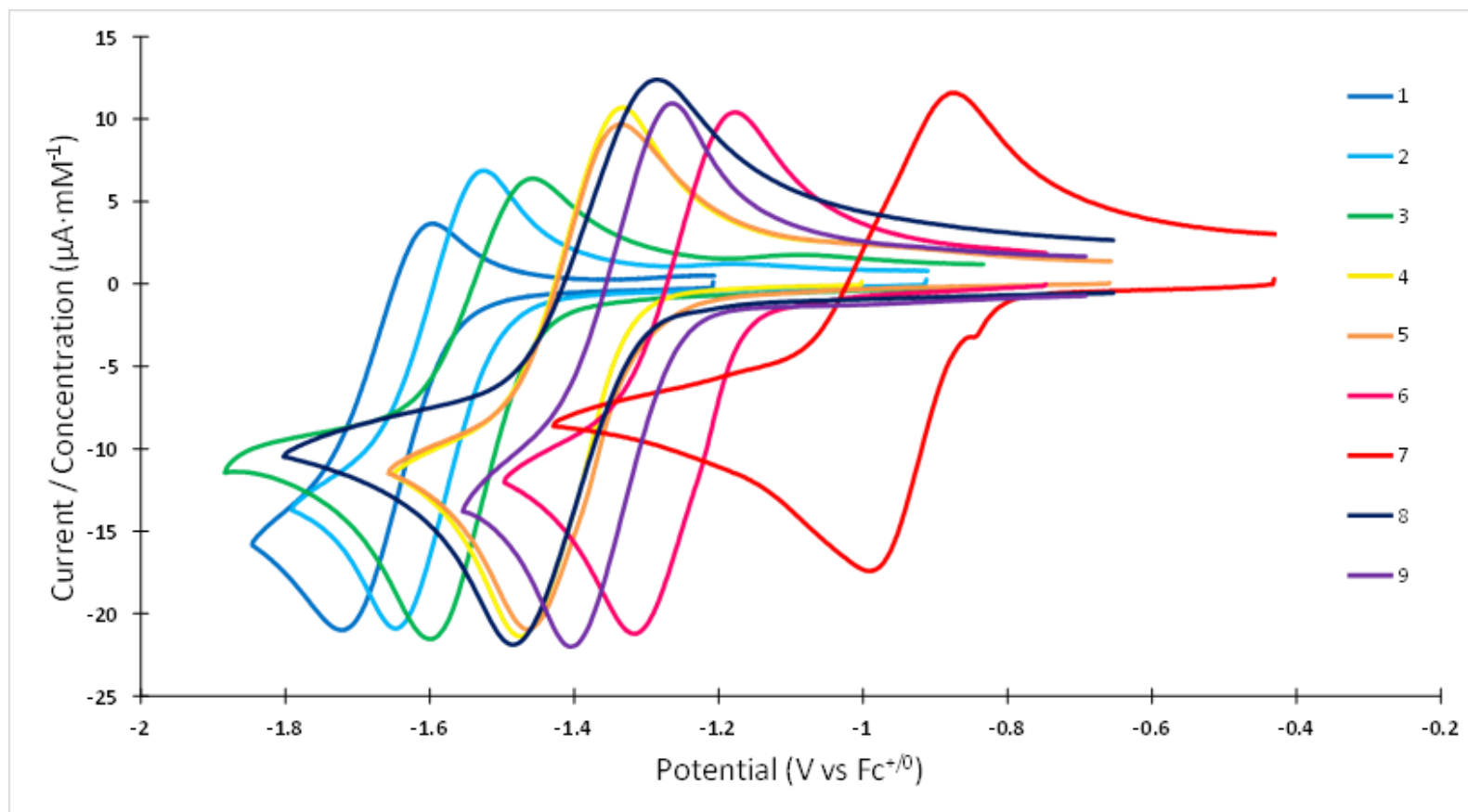


Figure B.19. Overlays of cyclic voltammograms of the 0/- redox process for compounds 1-9 after concentration correction*

* To achieve some accuracy in concentration when working in the glove box, analyte was weighed by difference before and after addition of a small number of crystals to the voltammetric solutions. Thereby, the weights could be measured on a 5-figure analytical balance outside the box. Hence, the concentrations are more accurate but cover a rather wide range, which influences the currents. Dividing the CV currents by the concentrations normalizes this effect to give more comparable CVs in the overlay figure. Compound 7 stands out and the lower current is probably due to incomplete dissolution as it is the least soluble of all the samples in the CH_2Cl_2 /electrolyte medium.

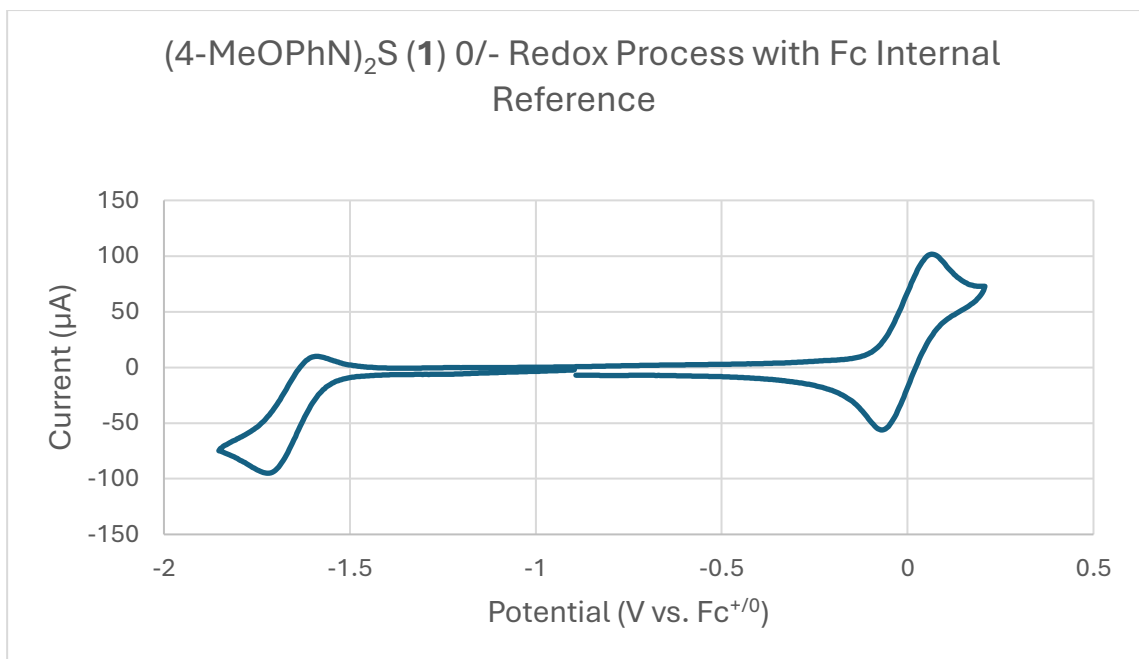


Figure B.20. Cyclic voltammogram (CV) of the 0/- redox process of **1**, showing the $\text{Fc}^{+/0}$ process used as an internal reference, scan rate 0.200 V/s. All subsequent CVs are referenced to $\text{Fc}^{+/0}$ (individually referenced for each figure), but Fc is not included in the figure. All CVs and SWVs were taken on glassy carbon electrode (7.1 mm²) in CH_2Cl_2 with ~0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ supporting electrolyte.

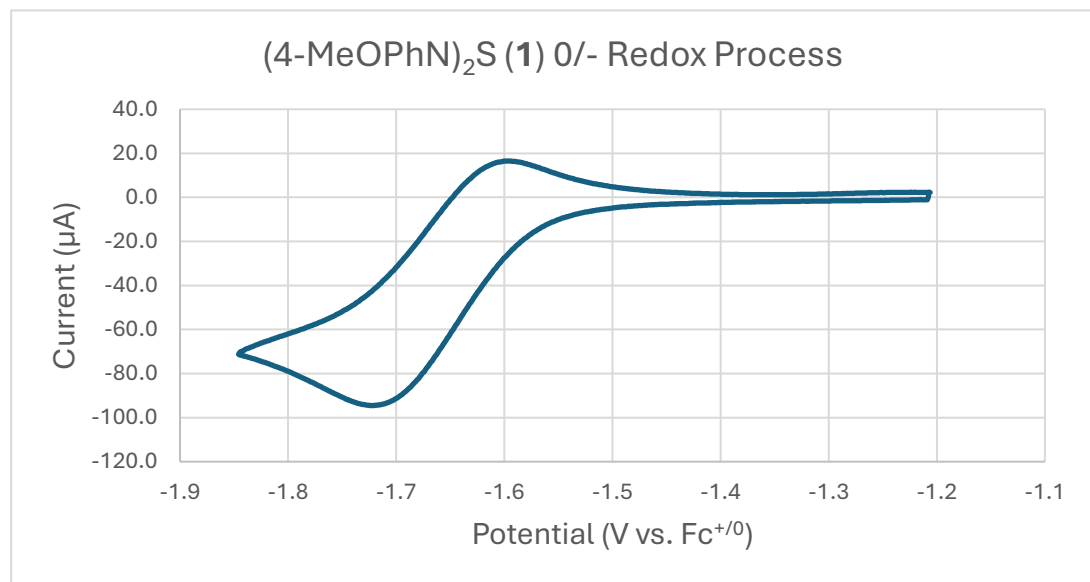


Figure B.21. CV of the 0/- redox process of **1**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.200 V/s

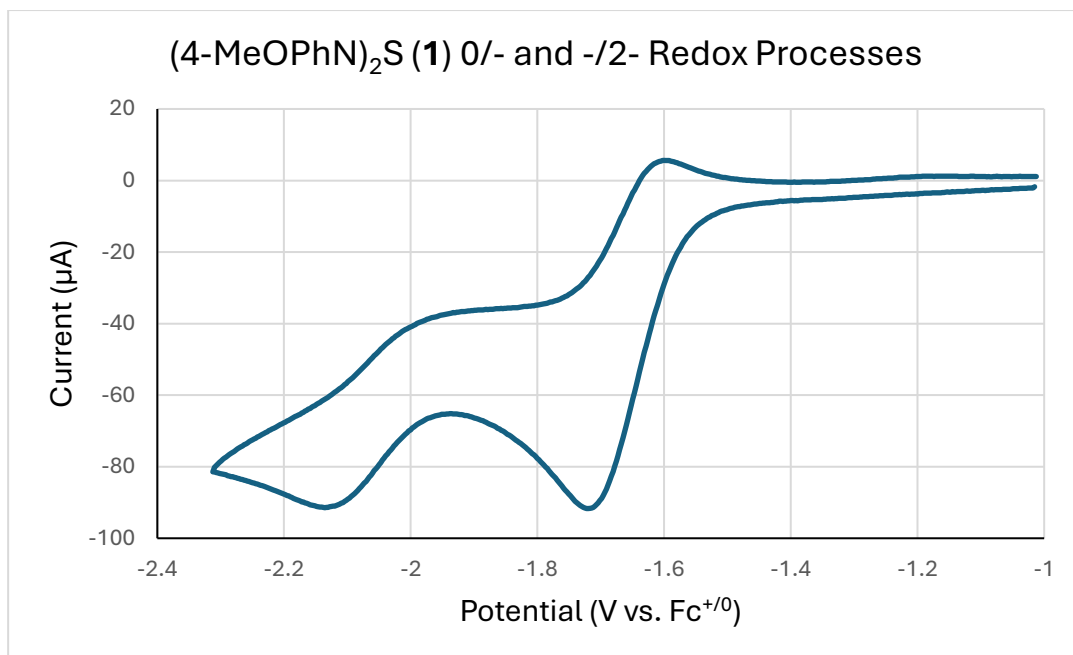


Figure B.22. CV of the 0/- and -/2- redox processes of **1**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ at 0.200 V/s

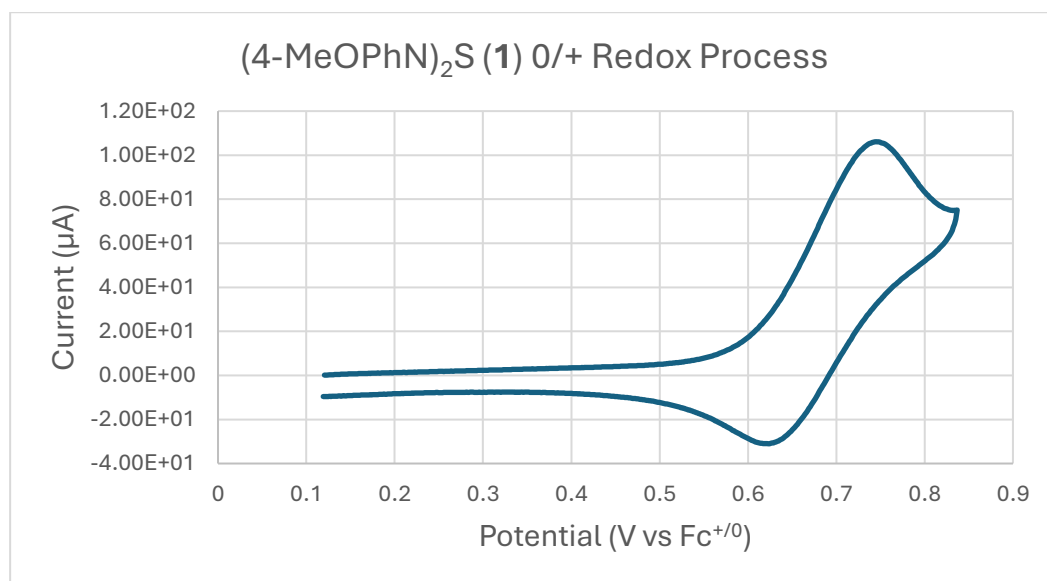


Figure B.23. CV of the +/0 redox process of **1**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ at 0.200 V/s

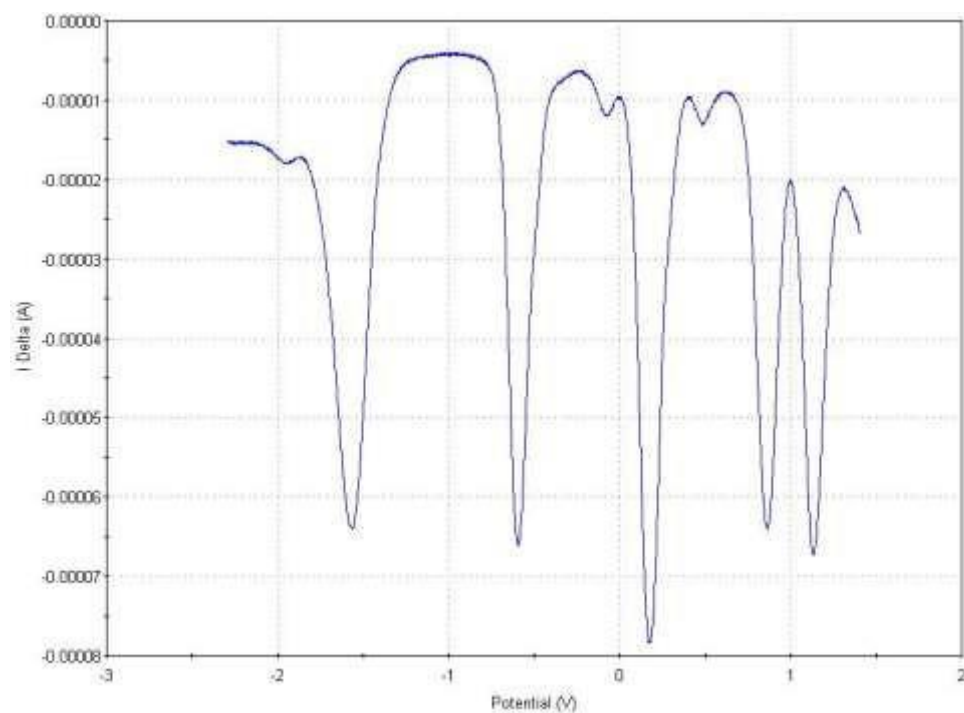


Figure B.24. Square wave voltammogram (SW) of **1** + ferrocene, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻

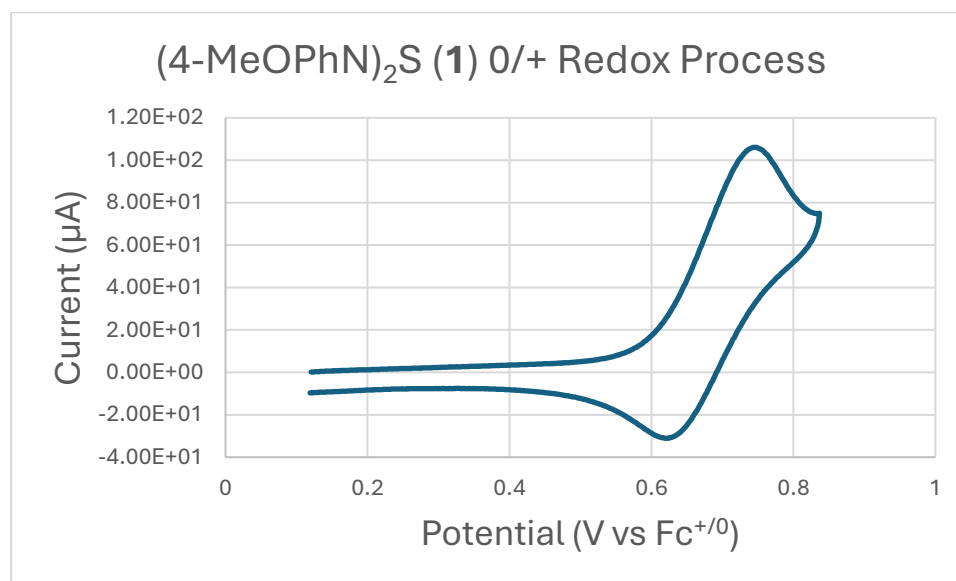


Figure B.25. CV of the 0/+ redox process of **2**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 0.200 V/s

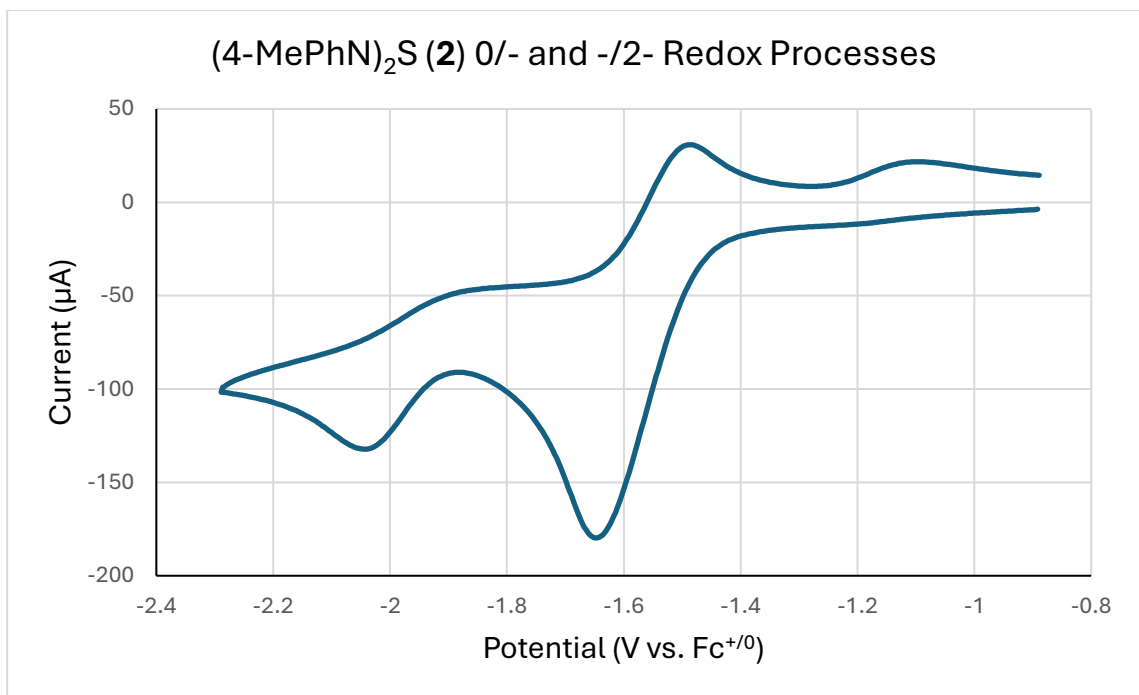


Figure B.26. CV of the 0/- and -/2- redox processes of **2**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 0.700 V/s

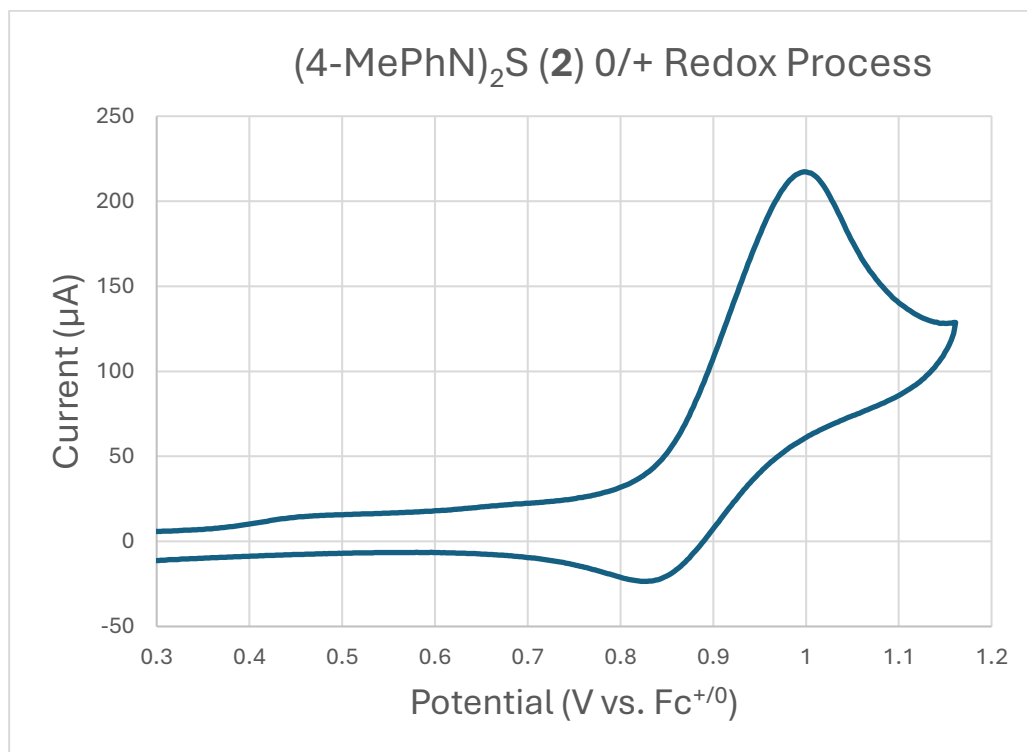


Figure B.27. CV of the +/0 redox process of **2**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 1.000 V/s

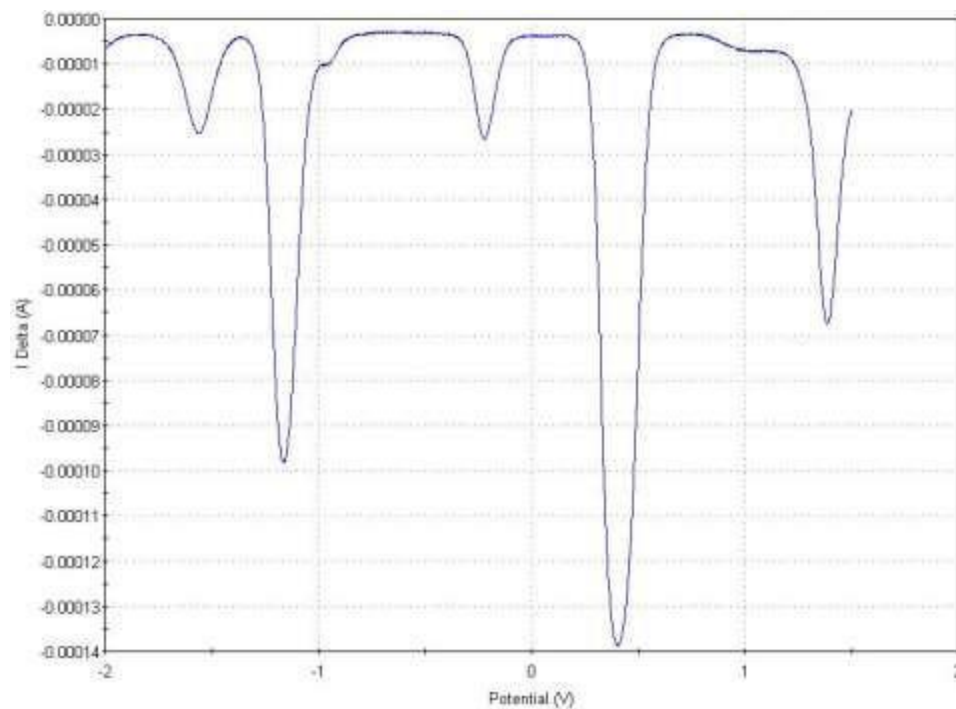


Figure B.28. SW of **2** + ferrocene, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻

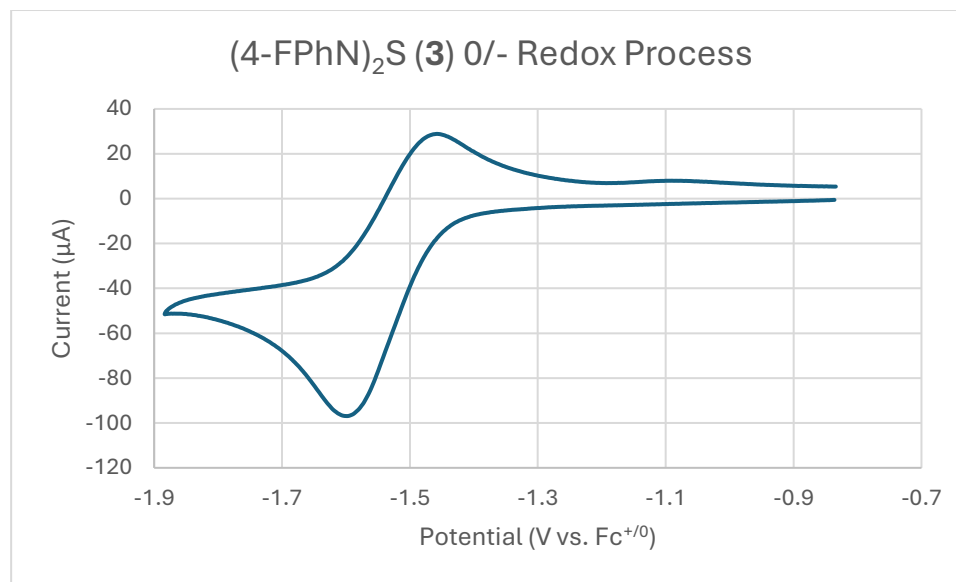


Figure B.29. CV of the 0/- redox process of **3**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 0.200 V/s

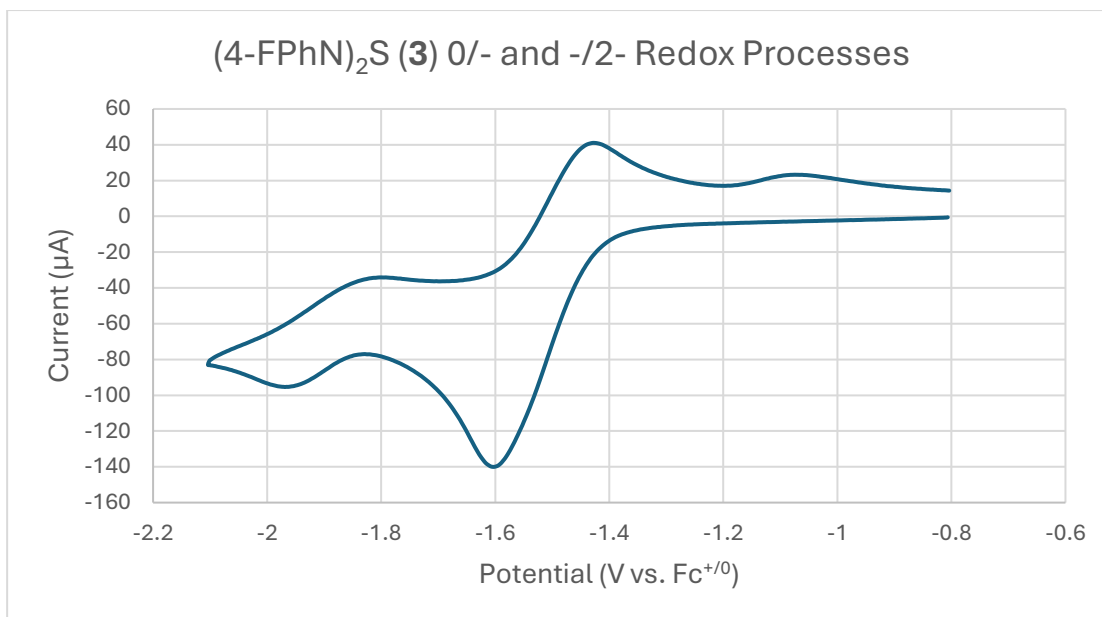


Figure B.30. CV of the 0/- and -/2- redox processes of **3**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.500 V/s

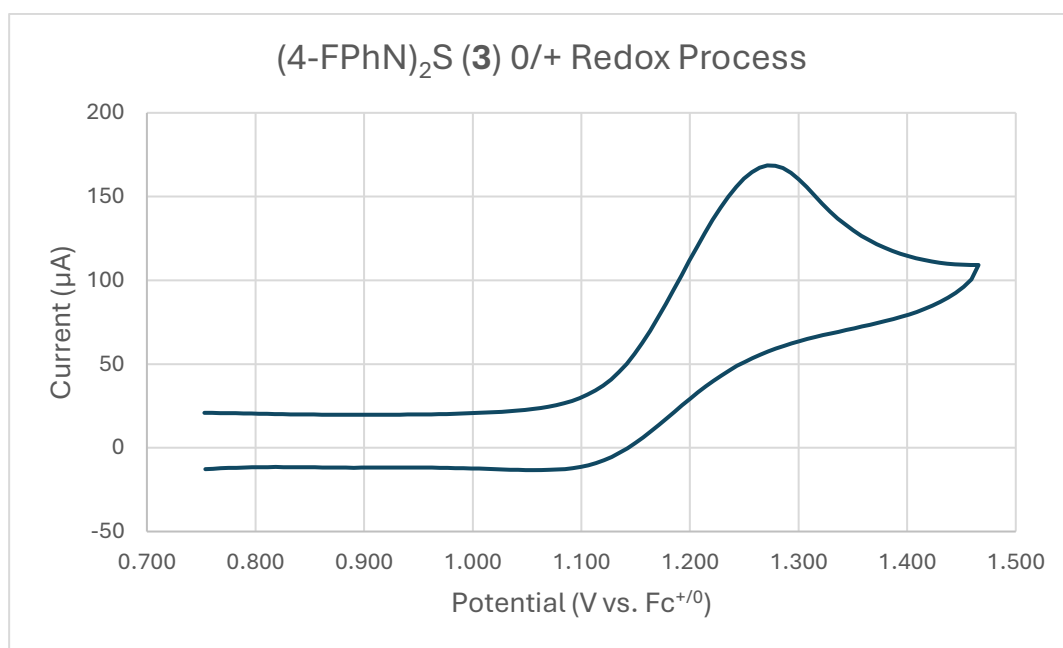


Figure B.31. CV of the +/0 redox process of **3**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.500 V/s

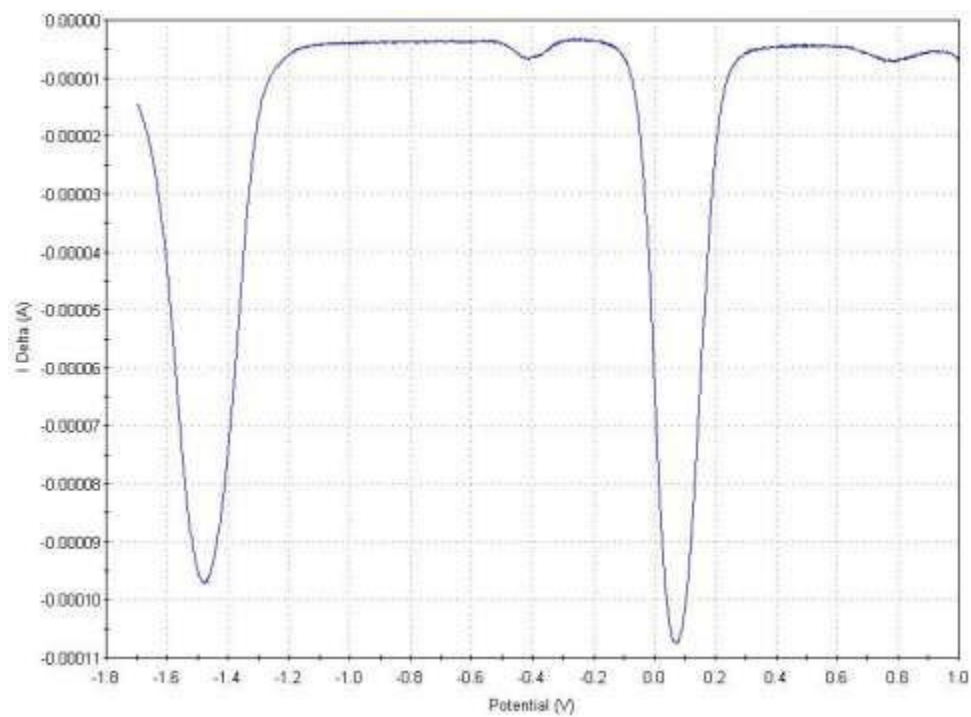


Figure B.32. SW of **3**, showing $\text{Fc}^{+/0}$ and **3** $0/-$ redox processes, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$

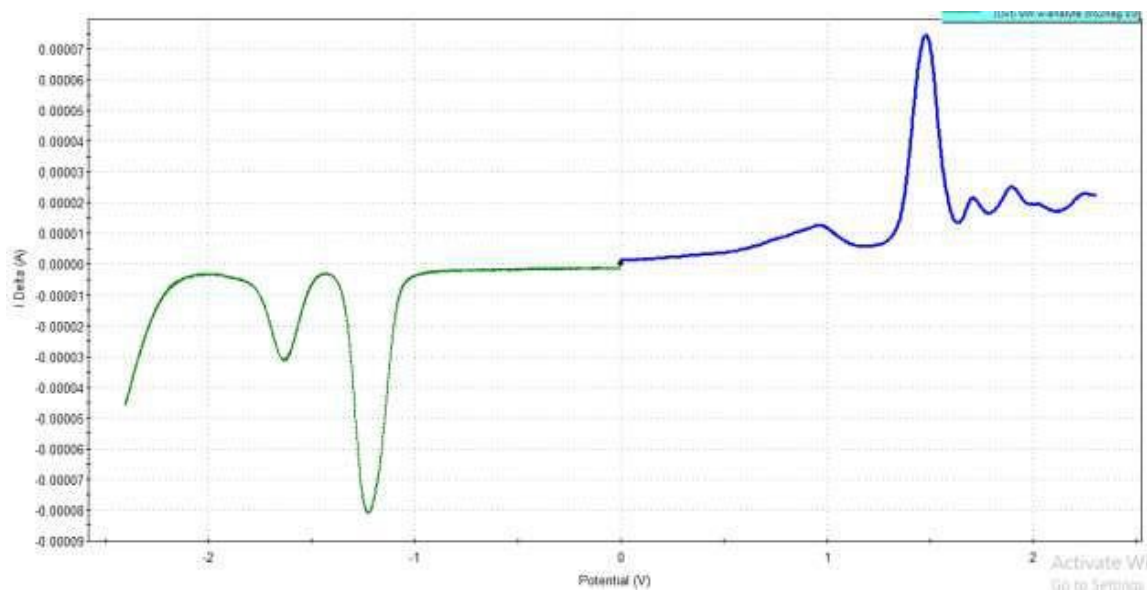


Figure B.33. SW of **3**, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$

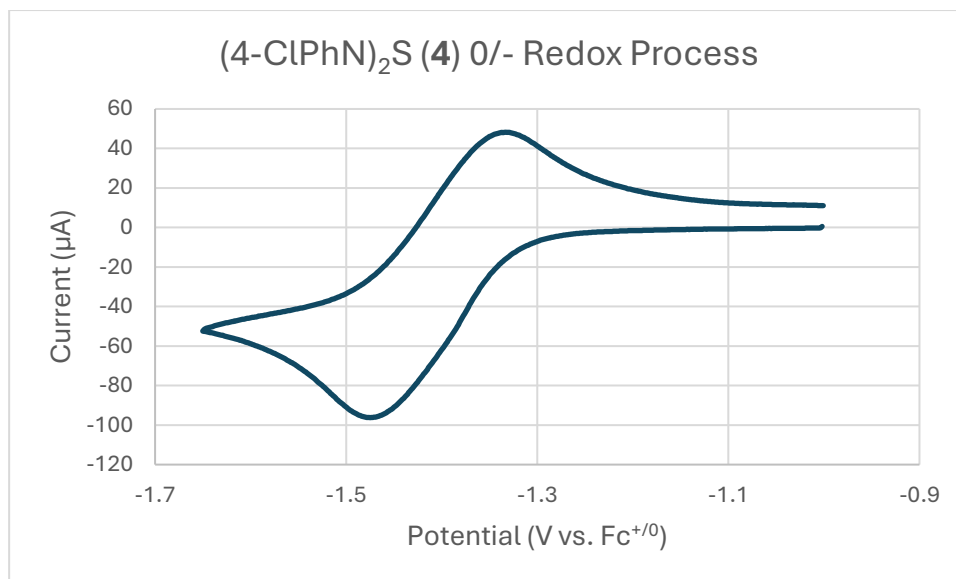


Figure B.34. CV of the 0/- redox process of **4**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.200 V/s

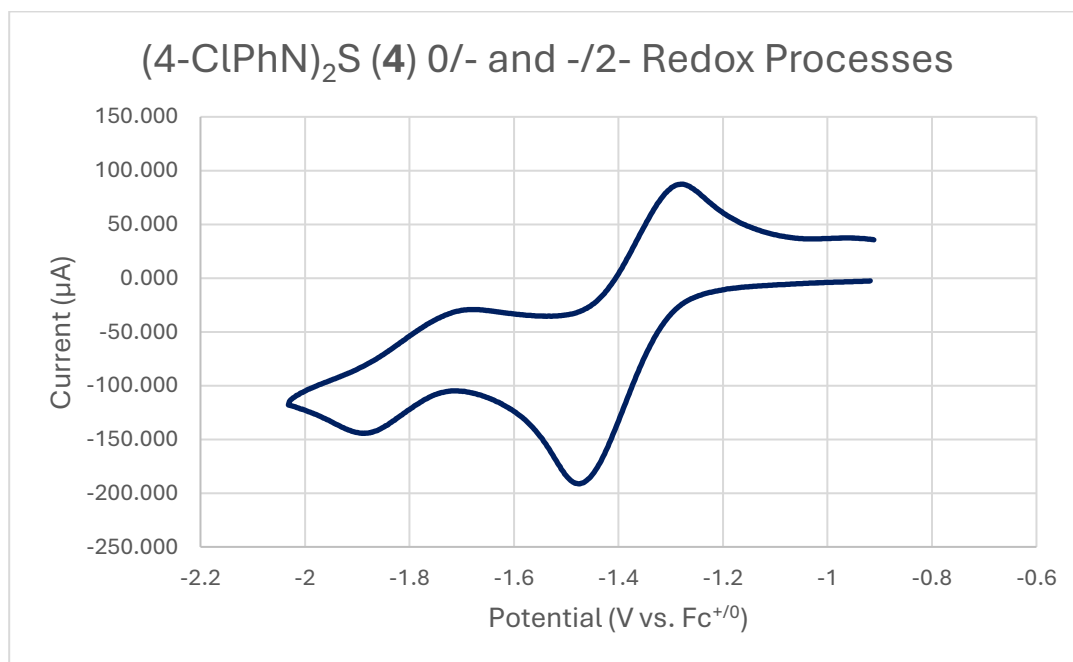


Figure B.35. CV of the 0/- and -/2- redox processes of **4**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 1.000 V/s

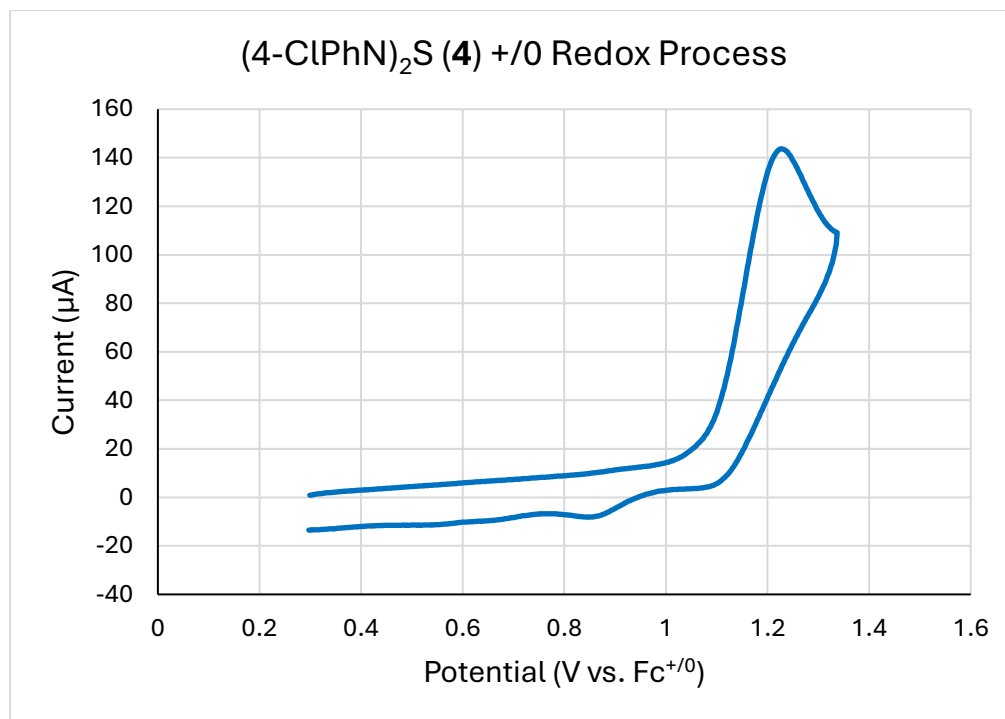


Figure B.36. CV of the +/0 redox process of **4**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.400 V/s.

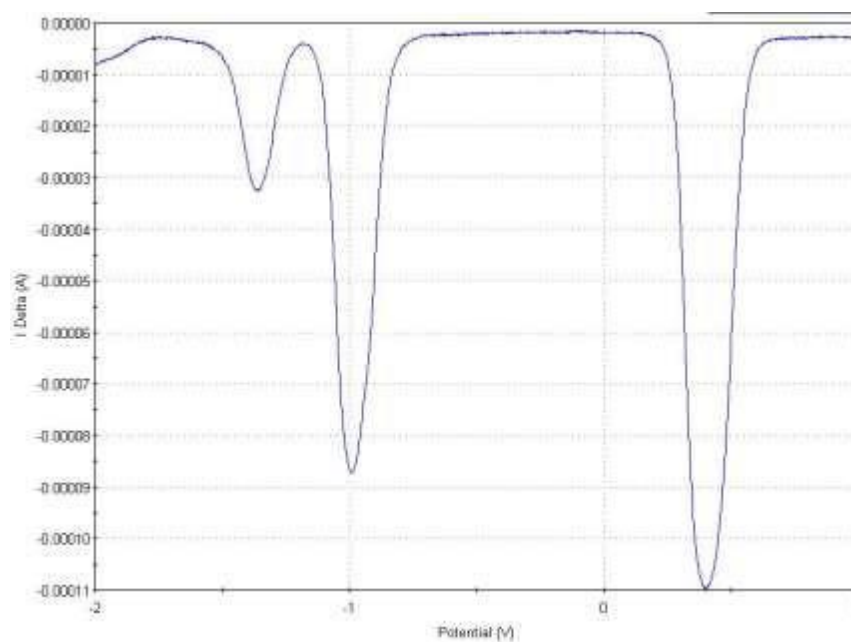


Figure B.37. SW of **4** + ferrocene, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$

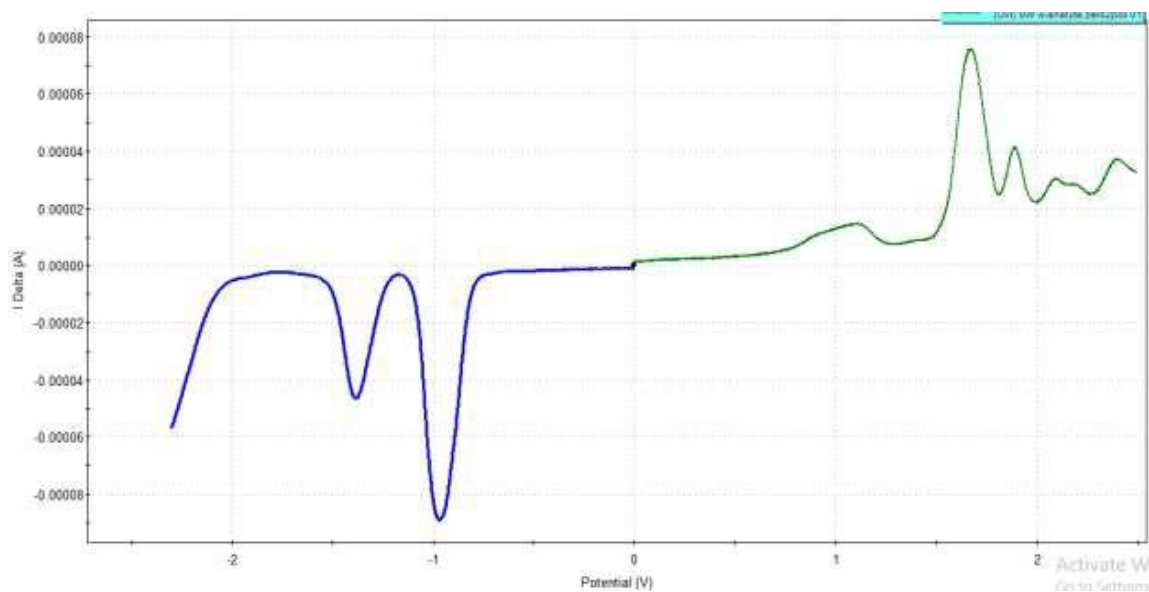


Figure B.38. SW of **4**, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻

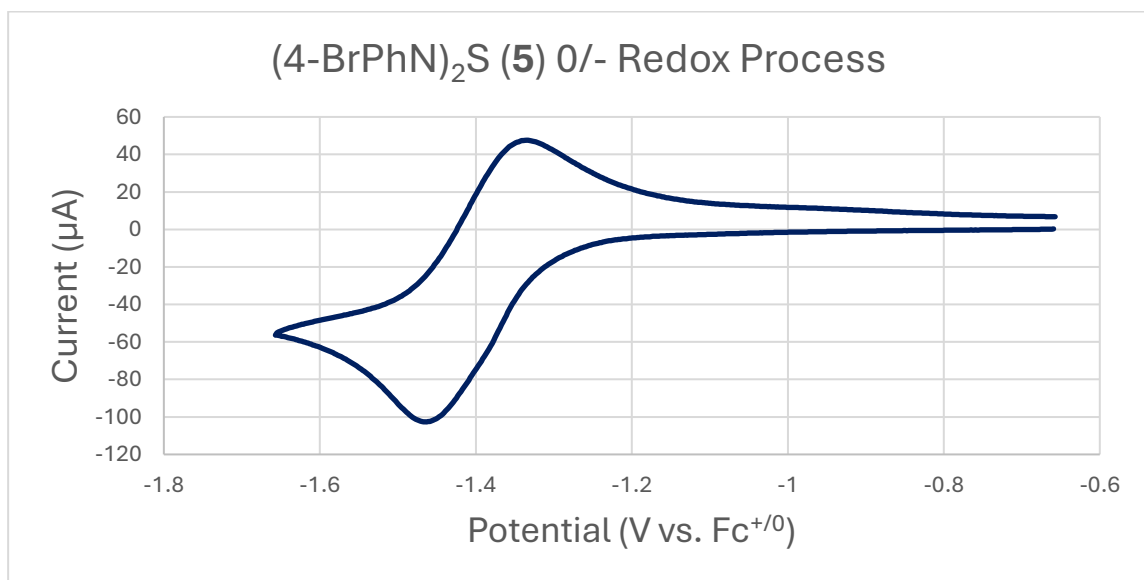


Figure B.39. CV of the 0/- redox process of **5**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 0.200 V/s

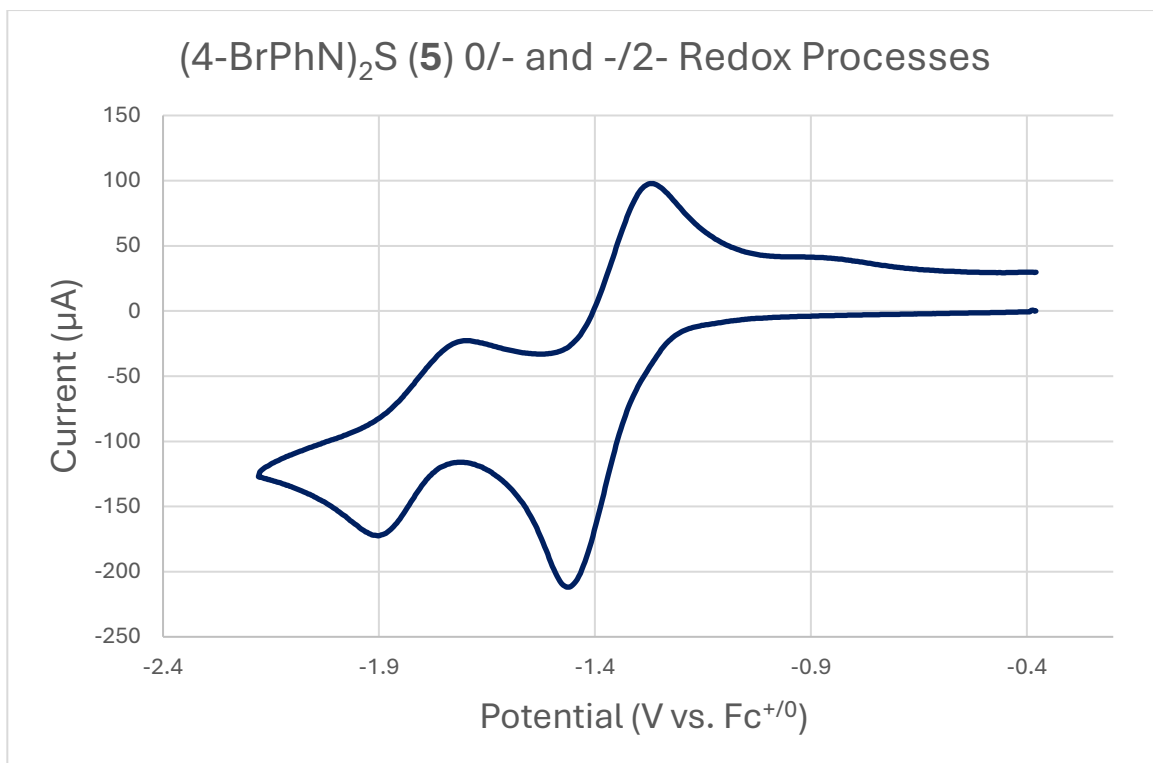


Figure B.40. CV of the 0/- and -/2- redox processes of **5**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 1.000 V/s

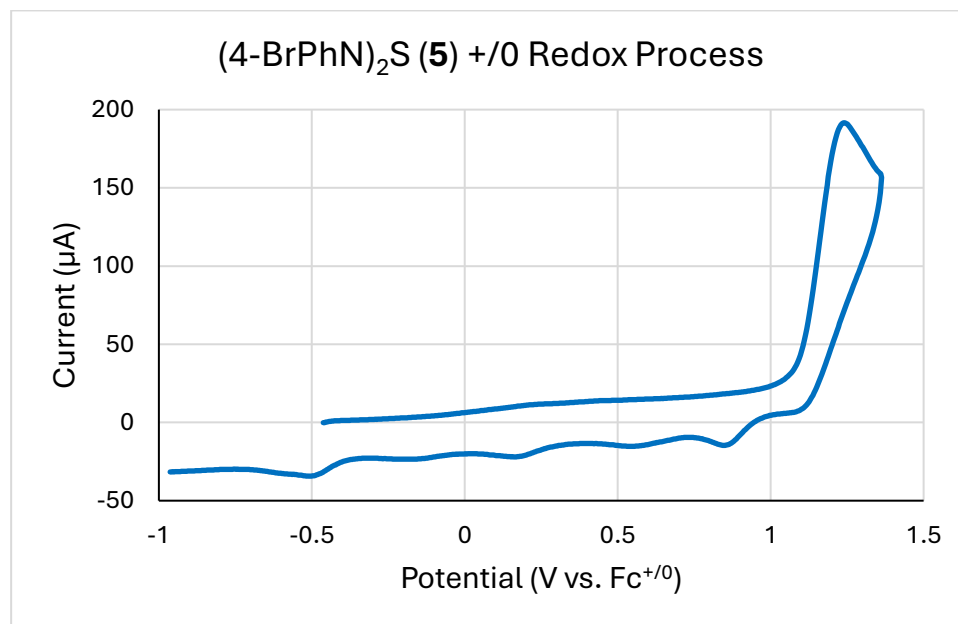


Figure B.41. CV of the +/0 redox process of **5**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 0.600 V/s.

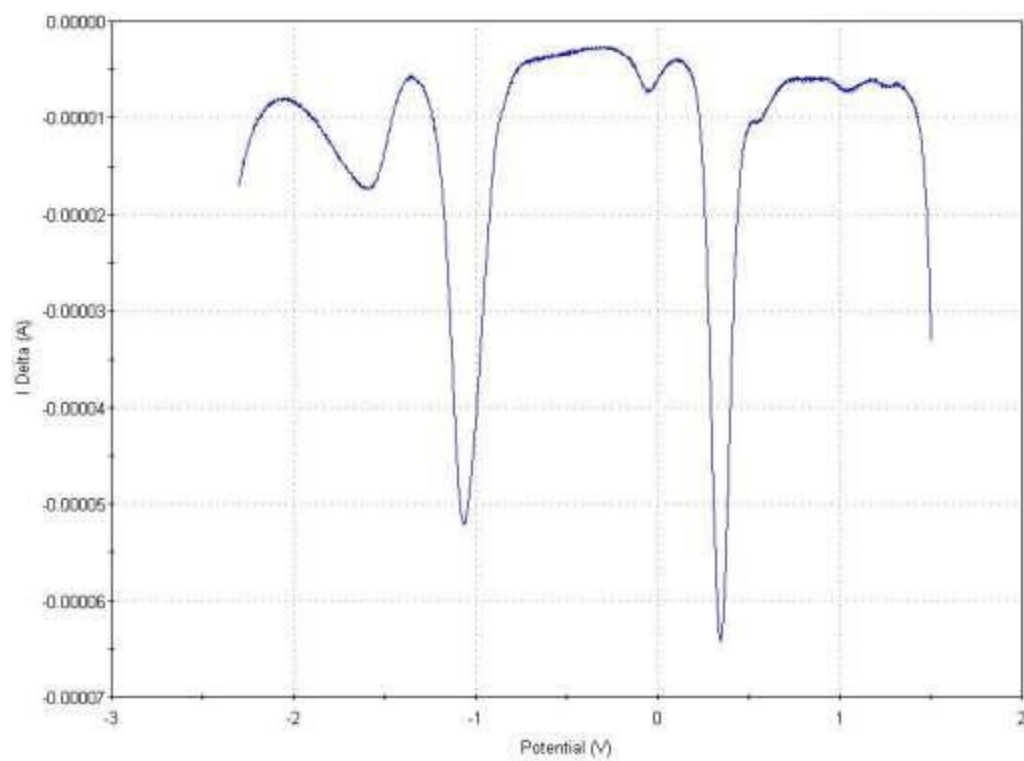


Figure B.42. SW of 5 + ferrocene, recorded in 0.4M [Bu₄N]⁺[PF₆]⁻

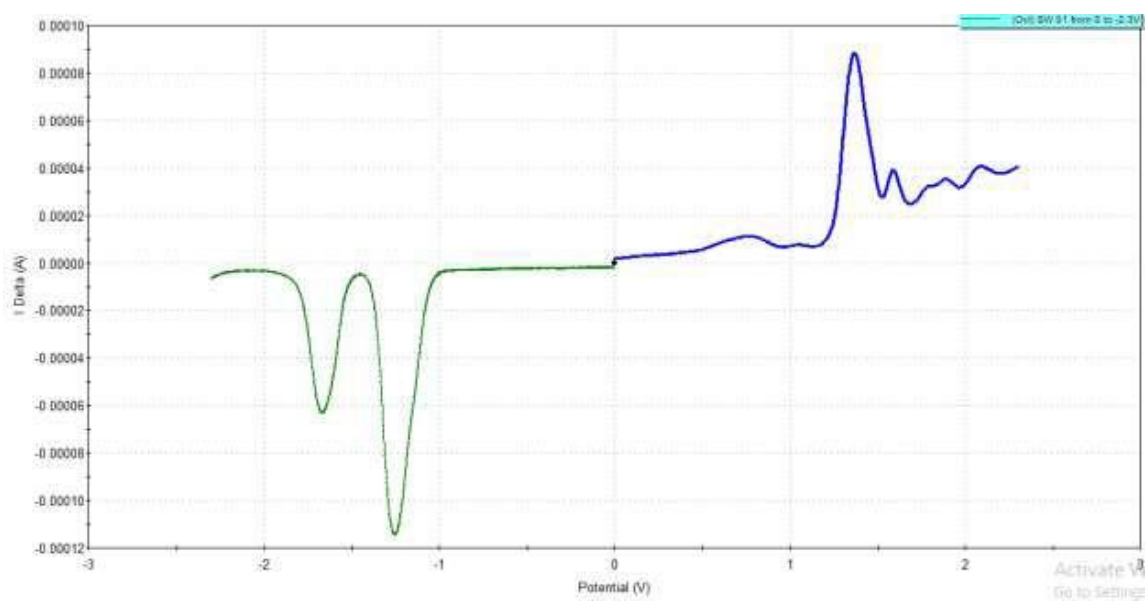


Figure B.43. SW of 5, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻

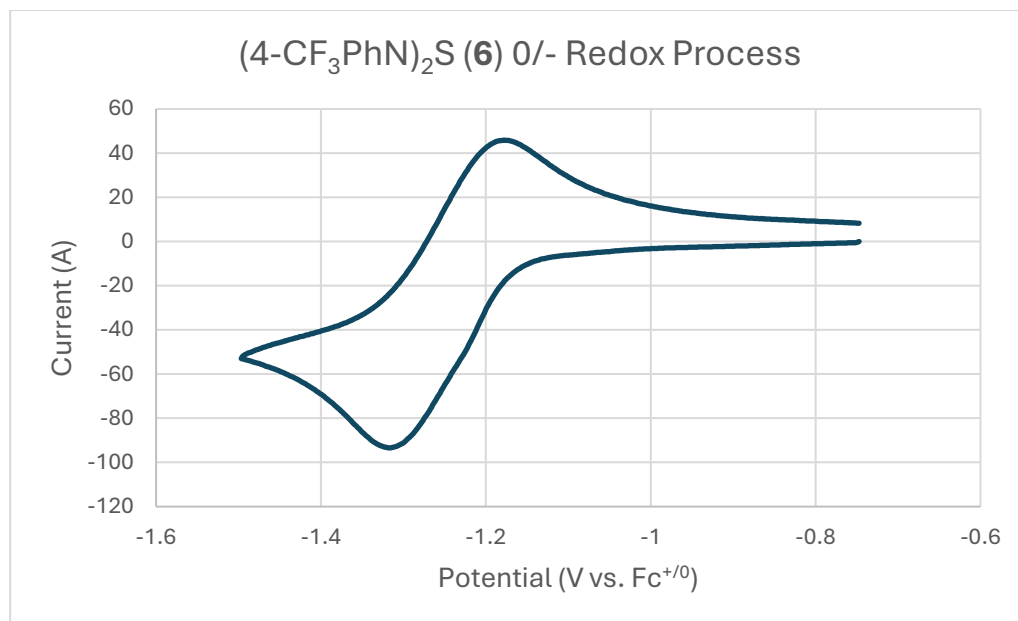


Figure B.44. CV of the 0/- redox process of **6**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.200 V/s

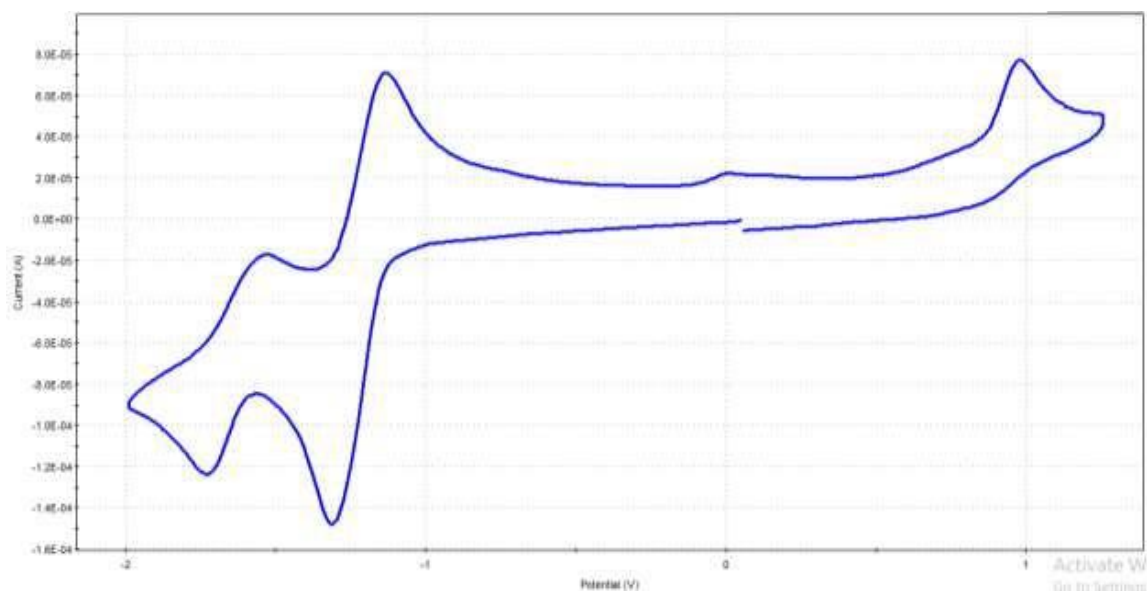


Figure B.45. CV of the +/0, 0/-, and -/2- redox processes of **6**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.500 V/s

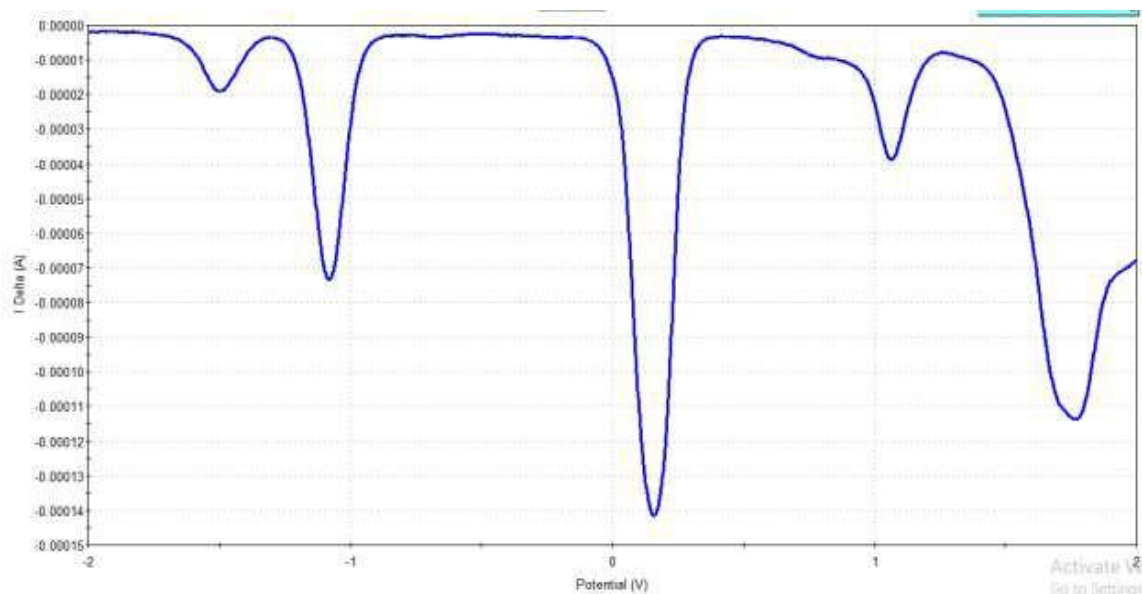


Figure B.46. SW of **6** + ferrocene, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻

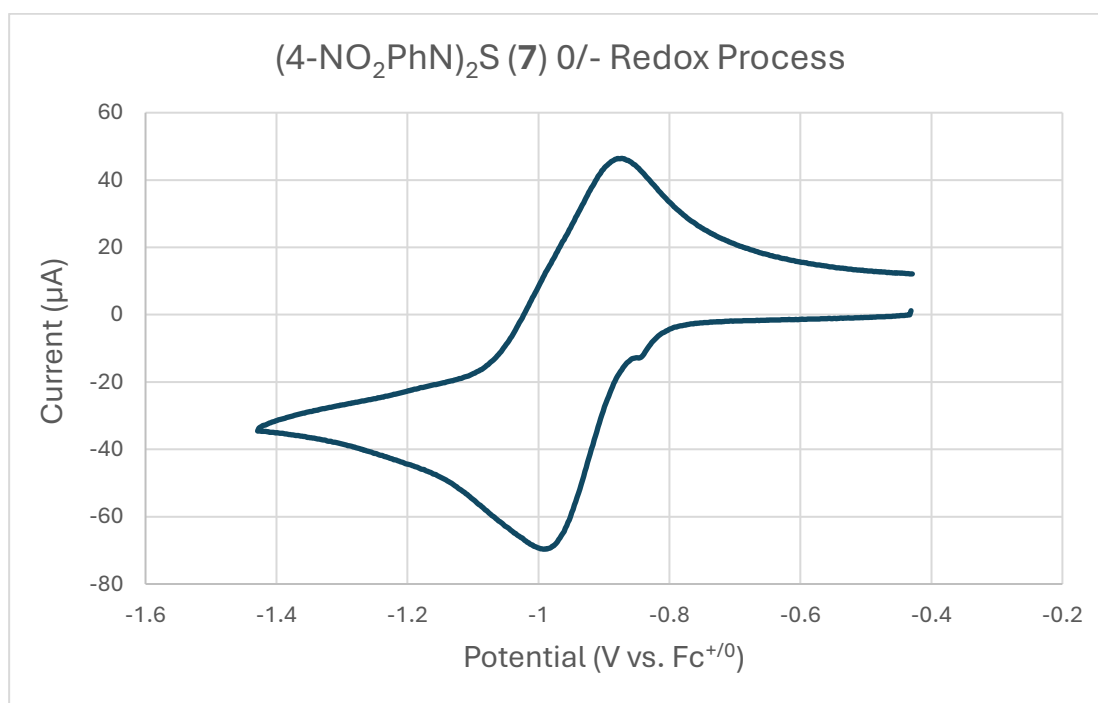


Figure B.47. CV of the 0/- redox process of **7**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 0.200 V/s

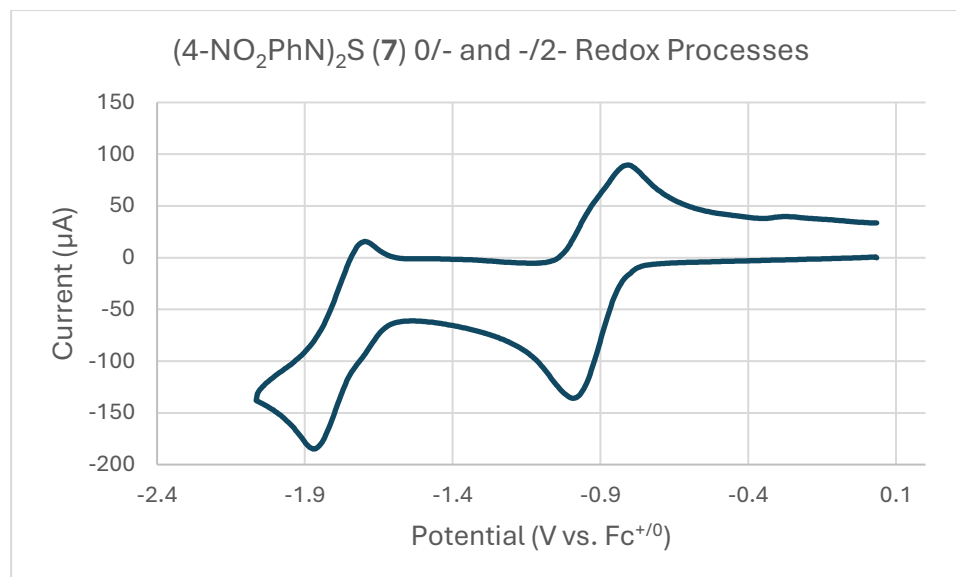


Figure B.48. CV of the 0/- and -/2- redox processes of **7**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 1.000 V/s

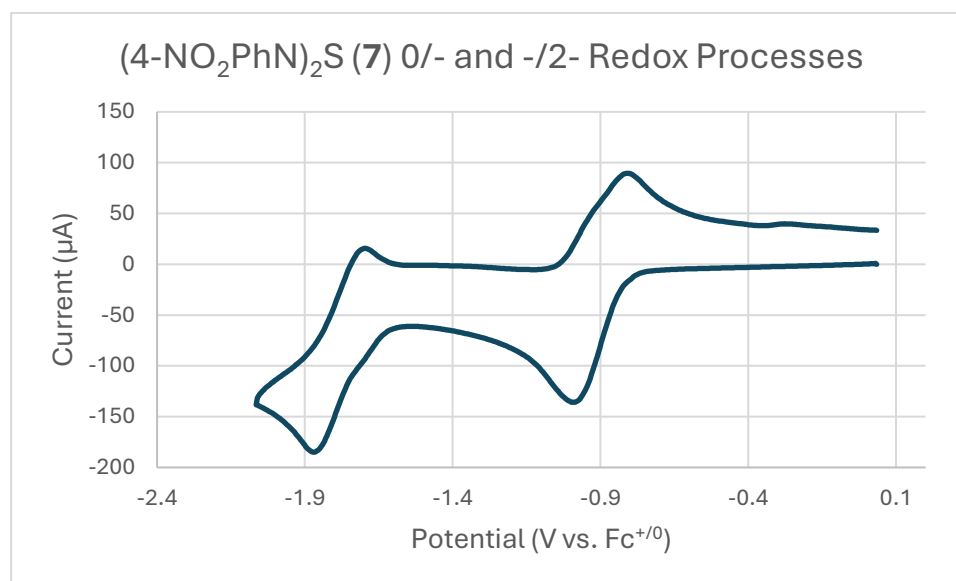


Figure B.49. CV of the +/0 redox process of **7**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 0.200 V/s. This scan also shows the 0/- redox process.

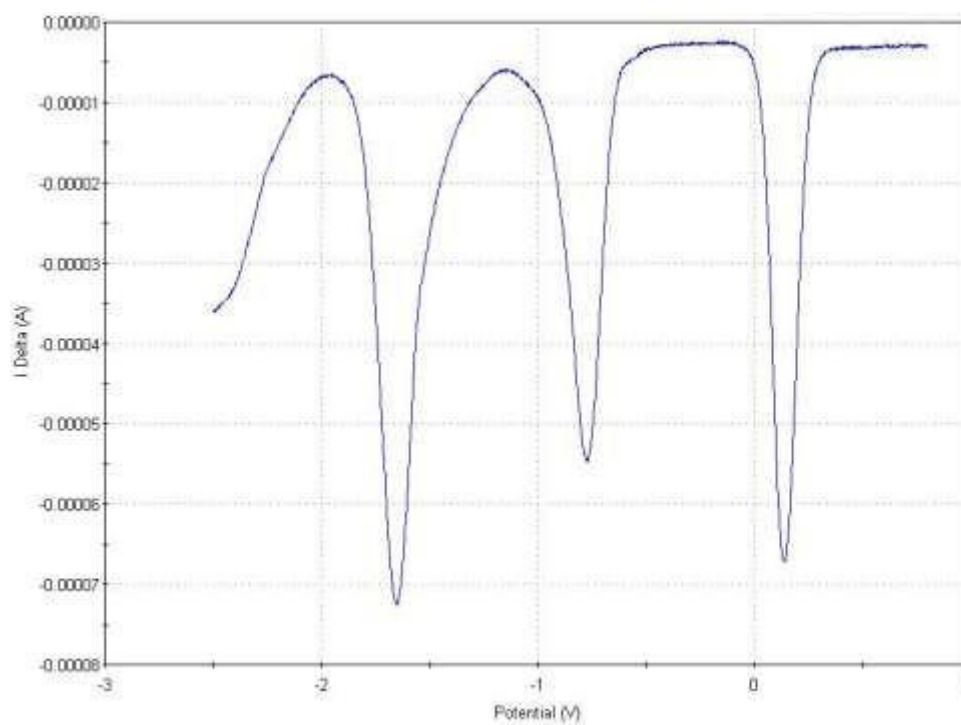


Figure B.50. SW of **7** + ferrocene, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻

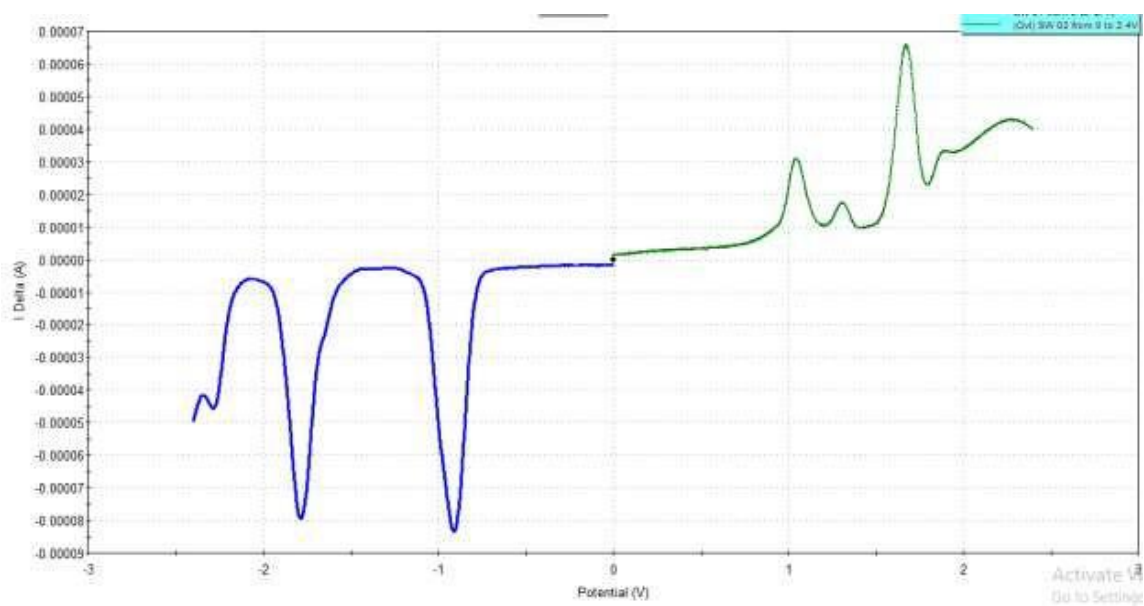


Figure B.51. SW of **7**, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻

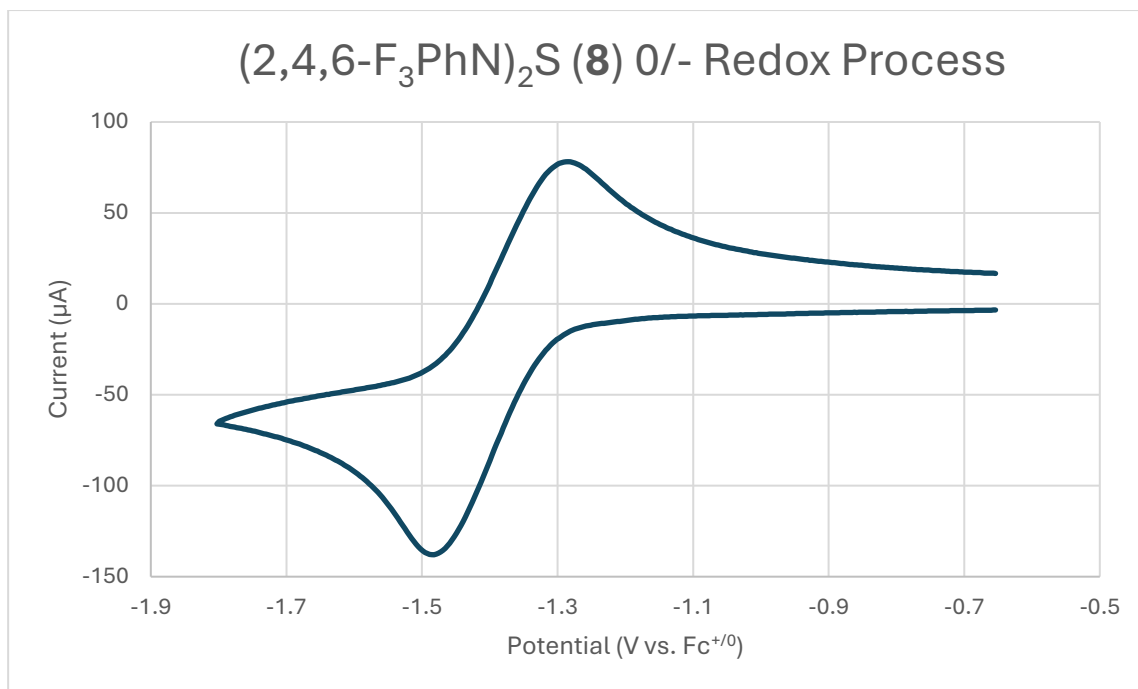


Figure B.52. CV of the 0/- redox process of **8**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 0.200 V/s

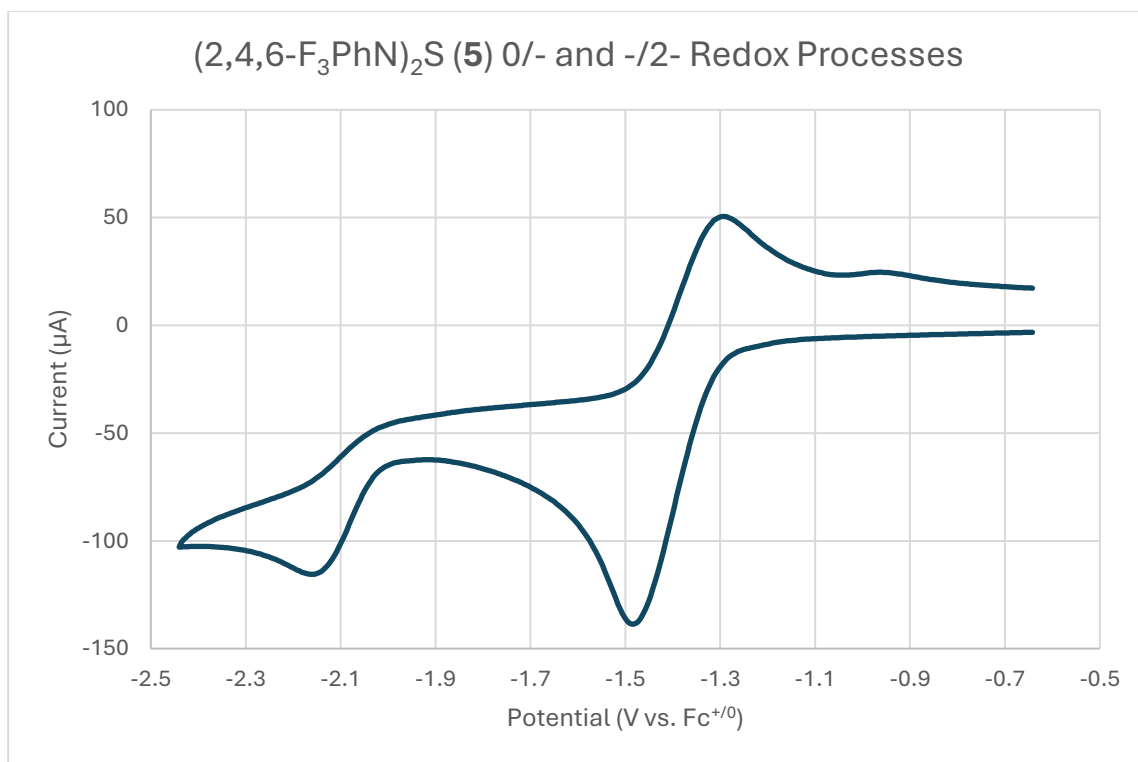


Figure B.53. CV of the 0/- and -/2- redox processes of **8**, referenced to Fc^{+/0}, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻ at 0.200 V/s

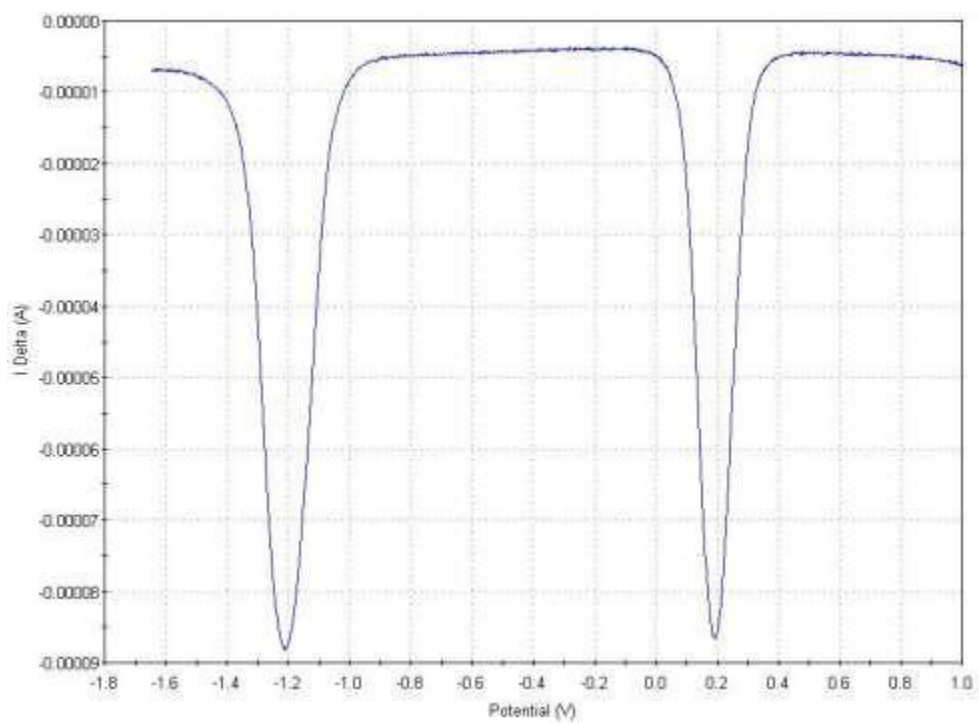


Figure B.54. SW of **8**, showing Fc $+/-$ and **8** $0/-$ redox processes, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻

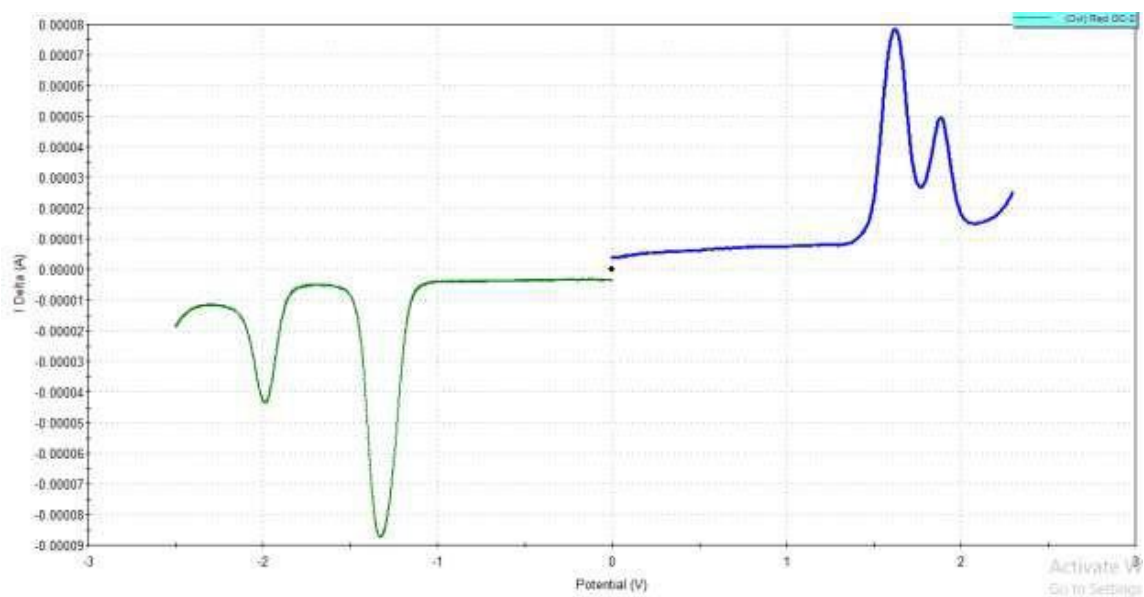


Figure B.55. SW of **8**, recorded in 0.4 M [Bu₄N]⁺[PF₆]⁻

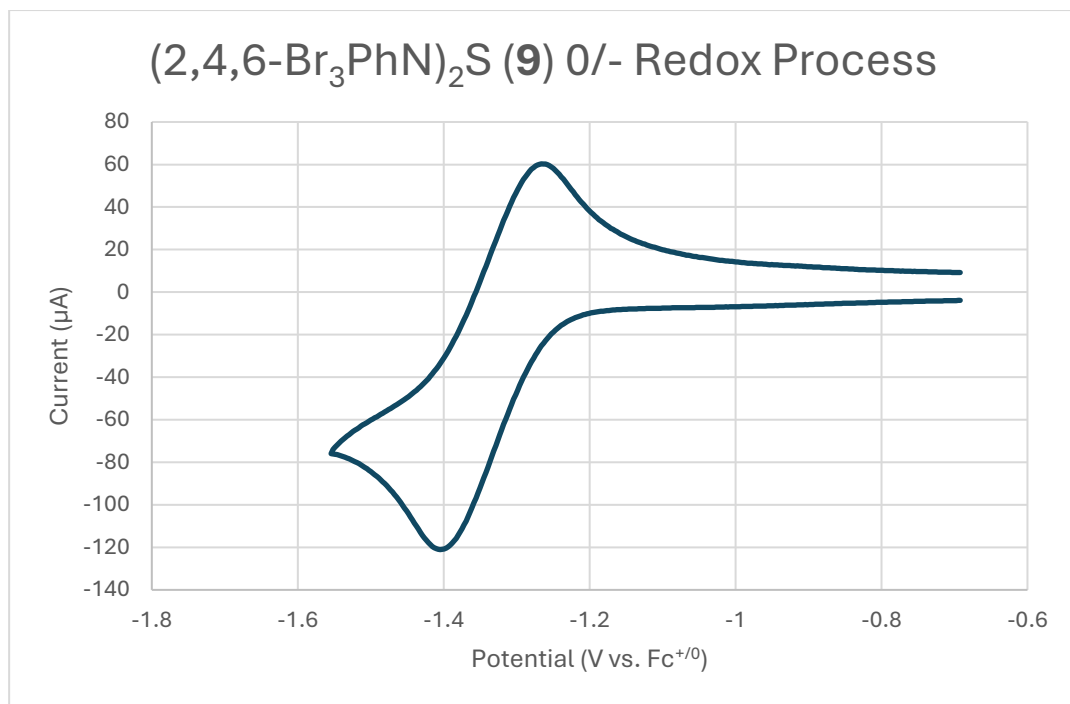


Figure B.56. CV of the 0/- redox process of **9**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.200 V/s

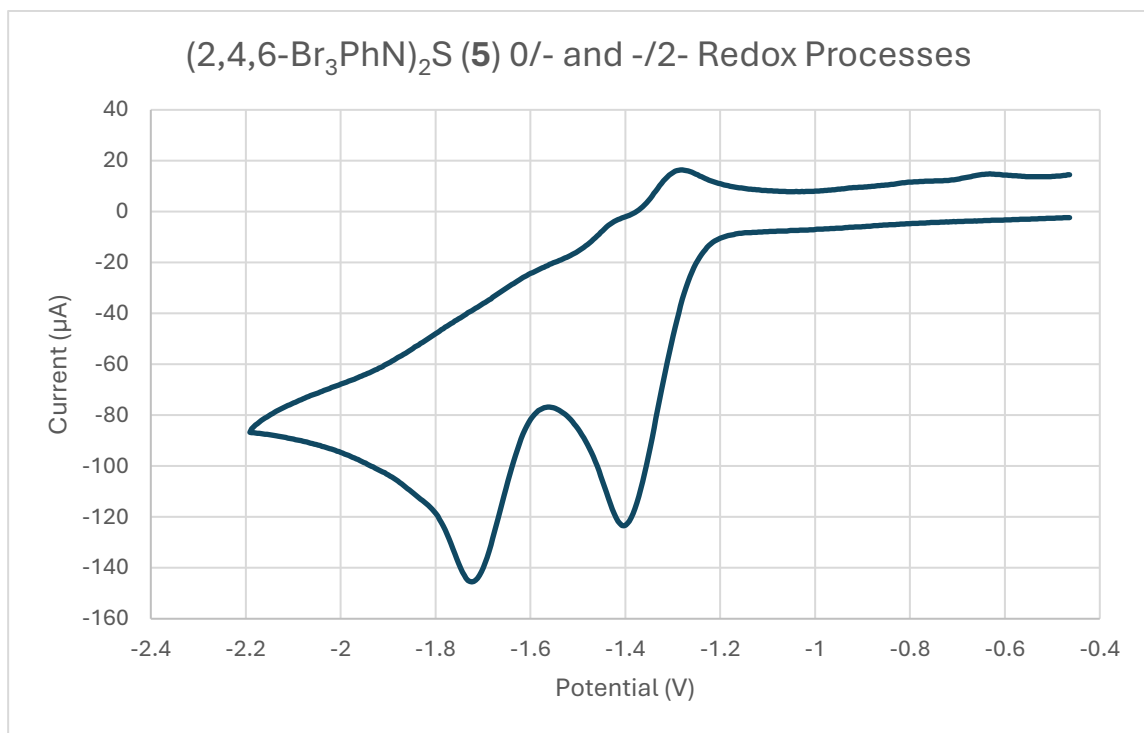


Figure B.57. CV of the 0/- and -/2- redox processes of **9**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.200 V/s

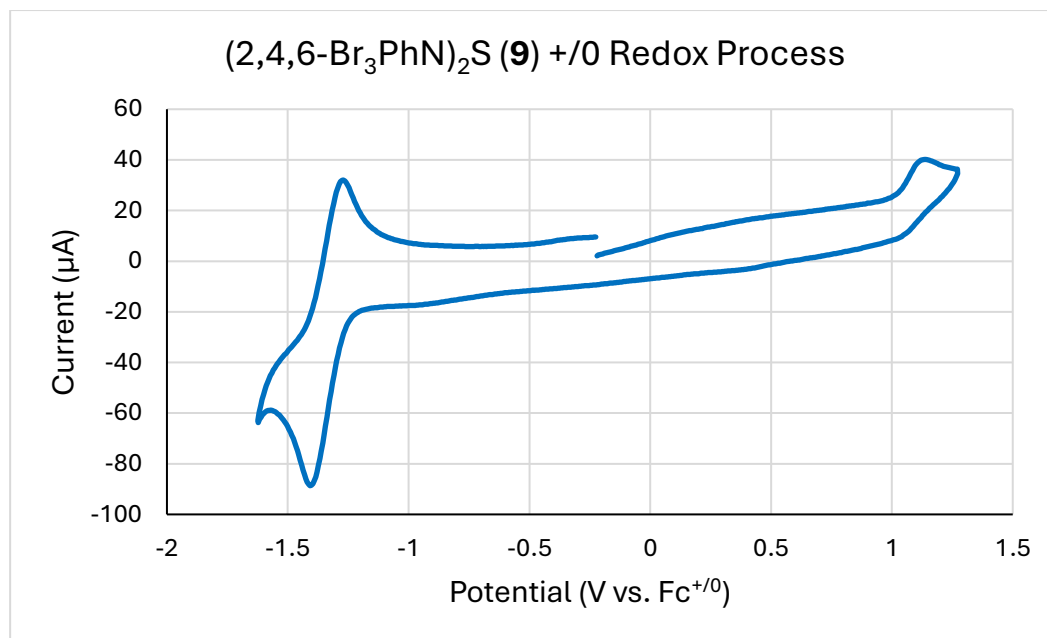


Figure B.58. CV of the +/0 redox process of **9**, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.200 V/s. This scan also shows the 0/- redox process.

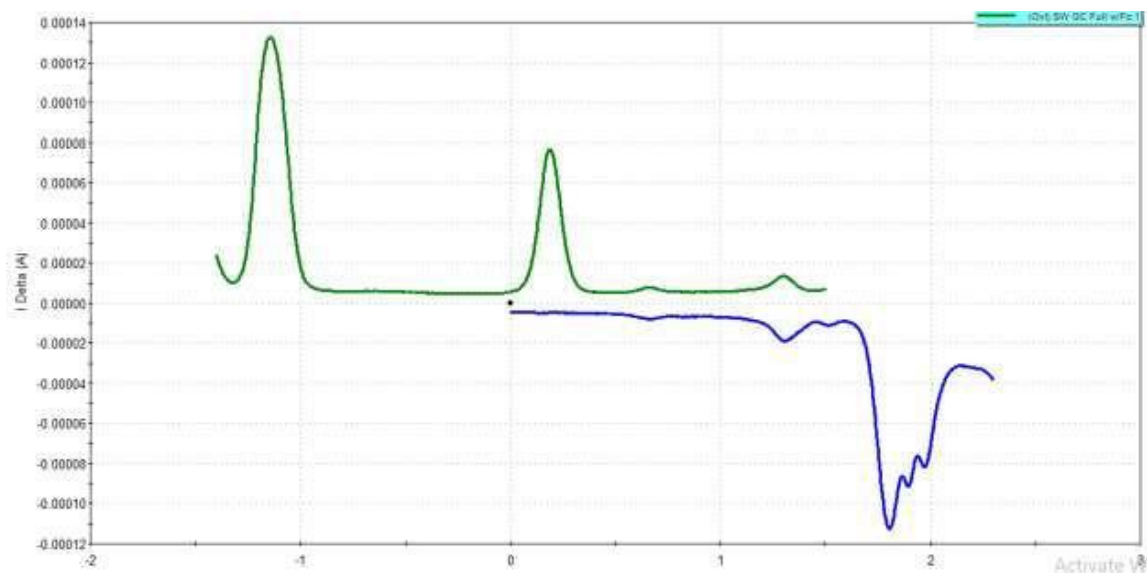


Figure B.59. SW of **9** + ferrocene, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$

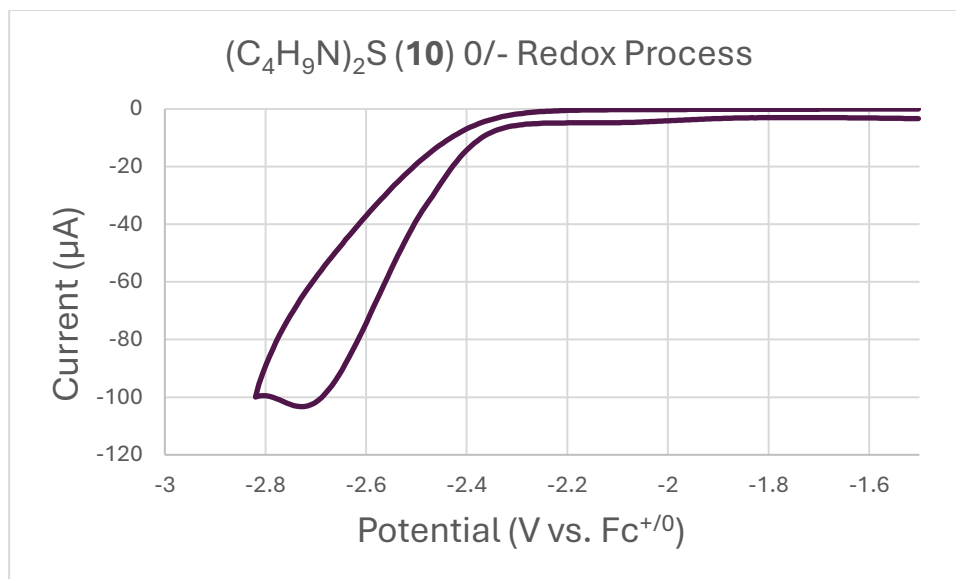


Figure B.60. CV of the 0/- redox process of *bis(tert-butyl)sulfur diimide (10)*, referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.200 V/s

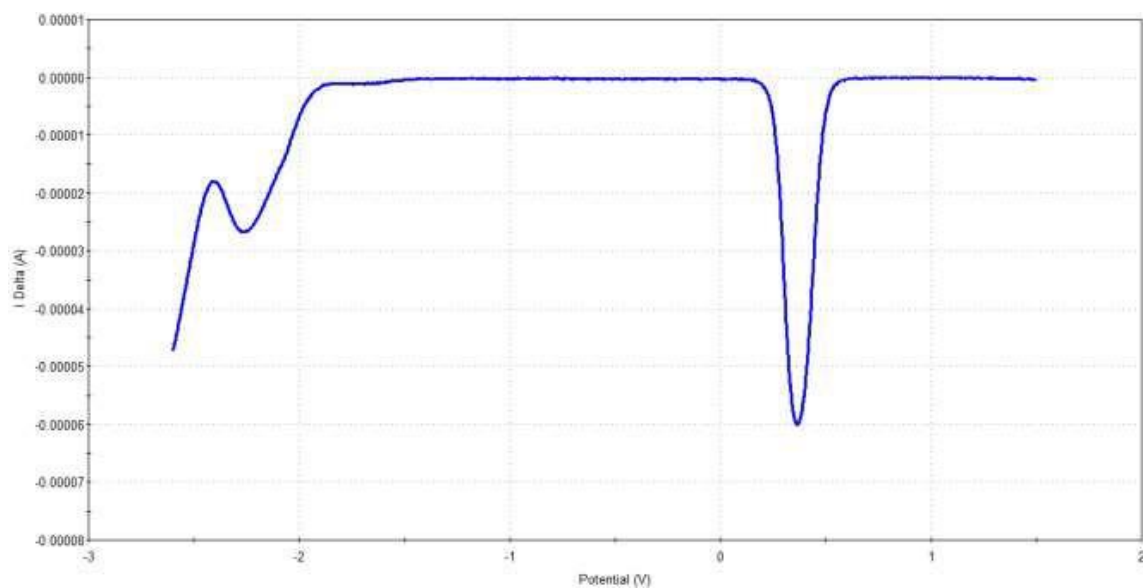


Figure B.61. SW of **10** + ferrocene, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$

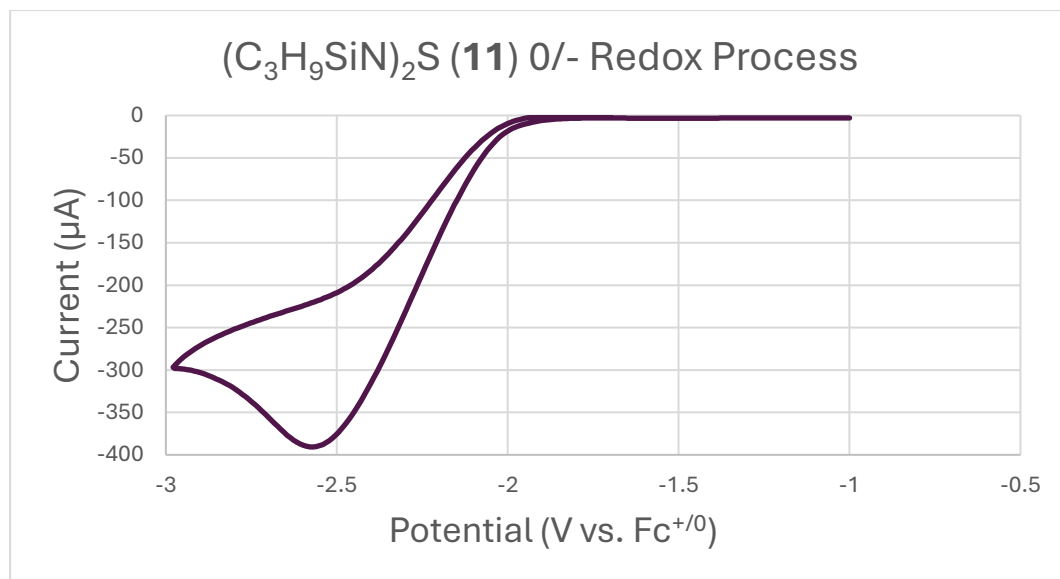


Figure B.62. CV of the 0/- redox process of *bis*(trimethylsilyl)sulfur diimide (**11**), referenced to $\text{Fc}^{+/0}$, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 0.200 V/s

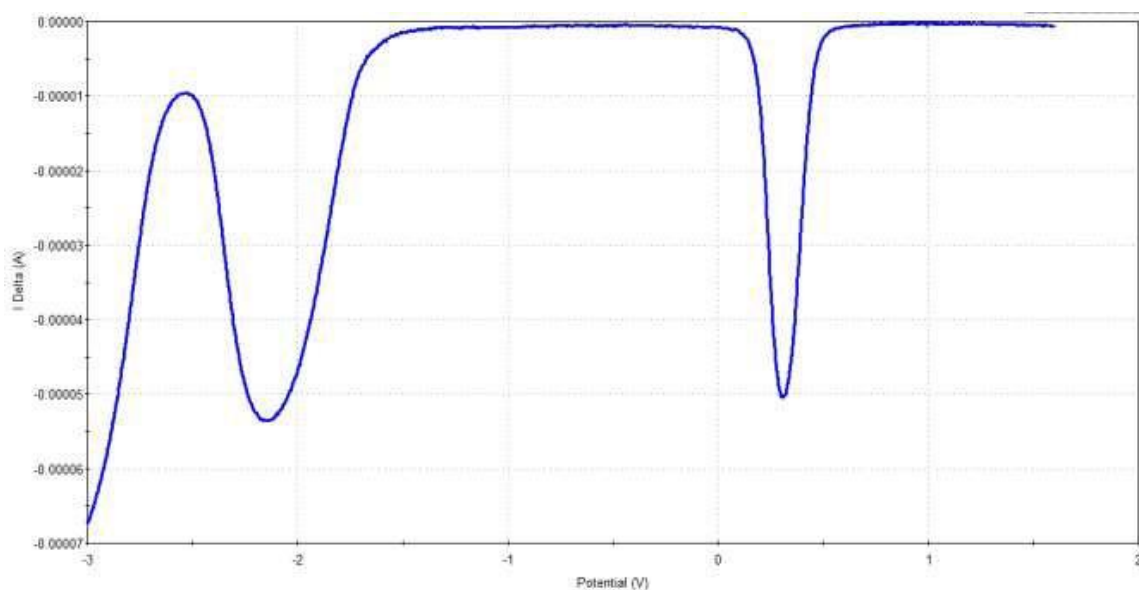


Figure B.63. SW of **11** + ferrocene, recorded in 0.4 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$

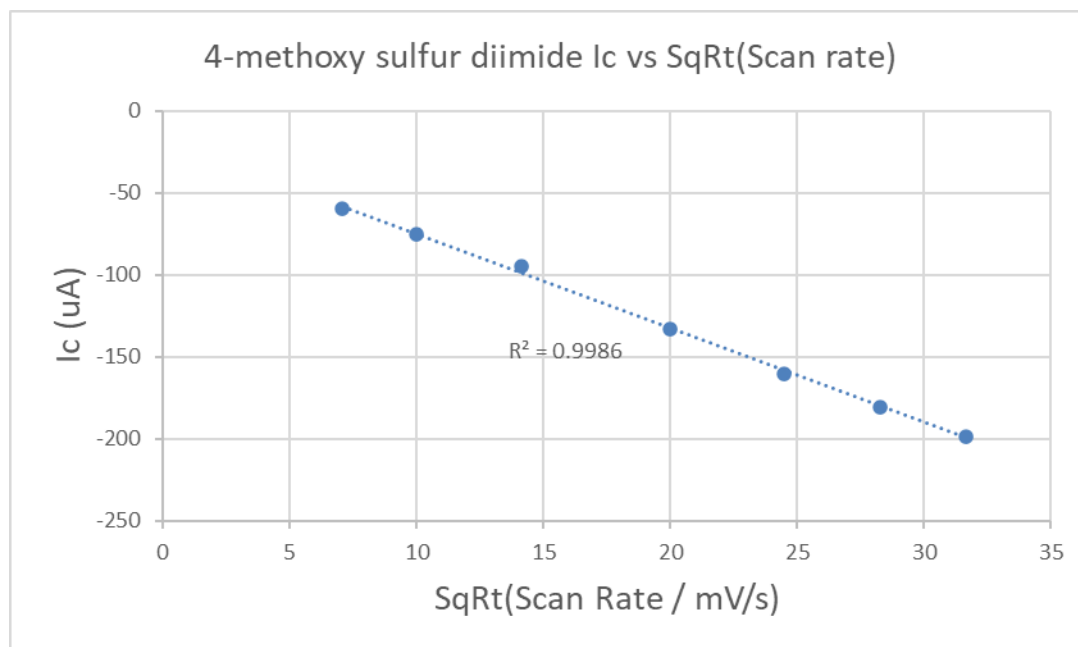


Figure B.64. Cathodic peak current (I_c) vs square root of scan rate for **1**. Linearity of this plot shows that electrochemical characterization was performed under diffusion-controlled conditions.

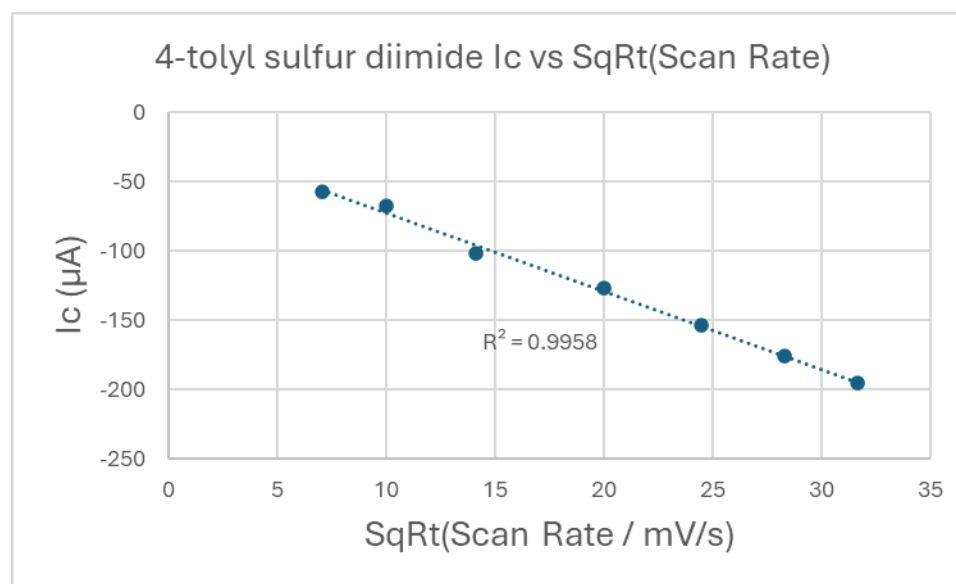


Figure B.65. Cathodic peak current (I_c) vs square root of scan rate for **2**. Linearity of this plot shows that electrochemical characterization was performed under diffusion-controlled conditions.

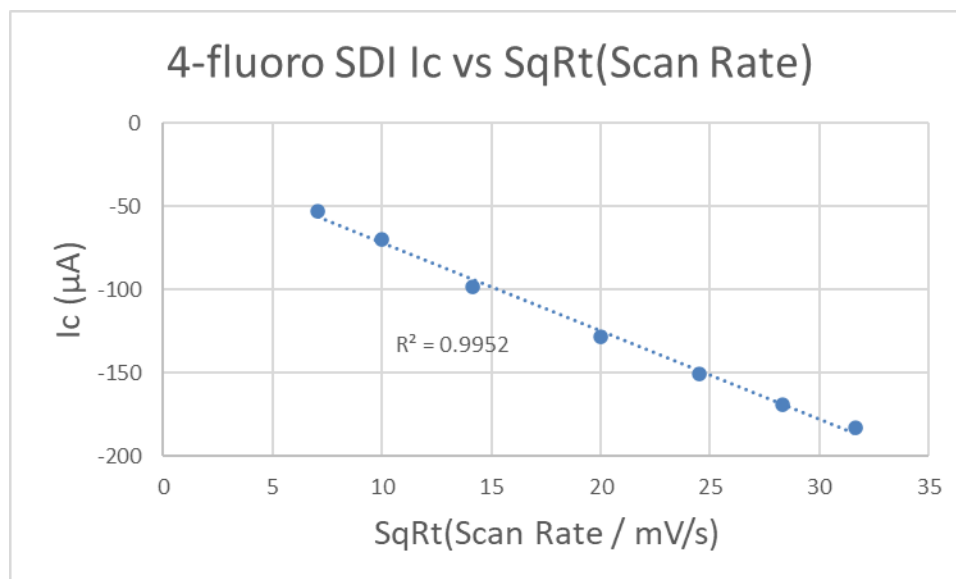


Figure B.66. Cathodic peak current (I_c) vs square root of scan rate for 3. Linearity of this plot shows that electrochemical characterization was performed under diffusion-controlled conditions.

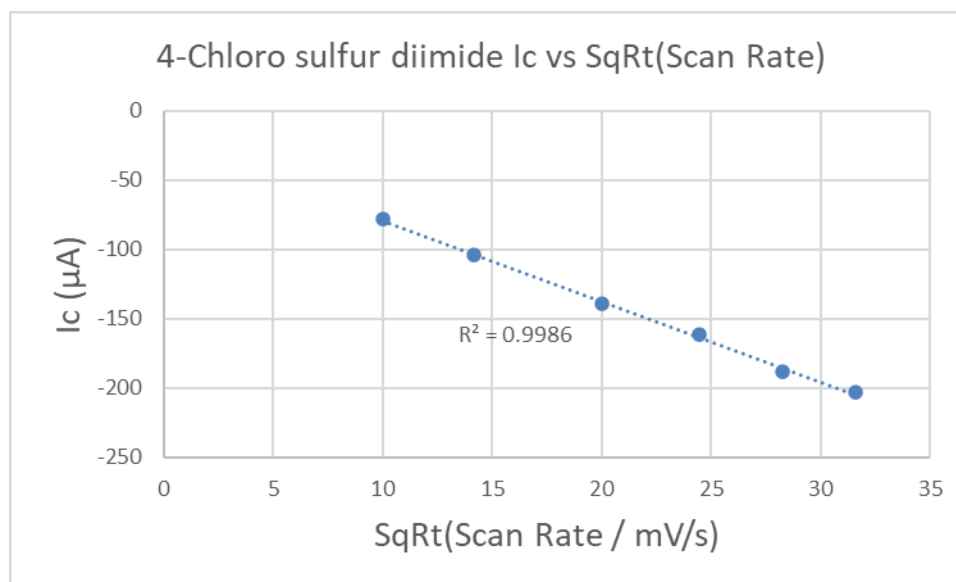


Figure B.67. Cathodic peak current (I_c) vs square root of scan rate for 4. Linearity of this plot shows that electrochemical characterization was performed under diffusion-controlled conditions.

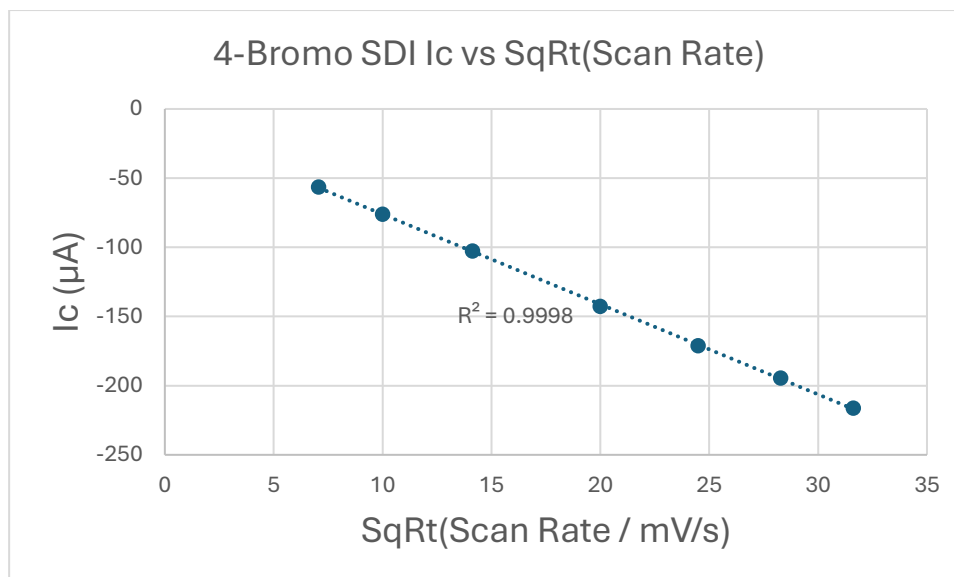


Figure B.68. Cathodic peak current (I_c) vs square root of scan rate for **5**. Linearity of this plot shows that electrochemical characterization was performed under diffusion-controlled conditions.

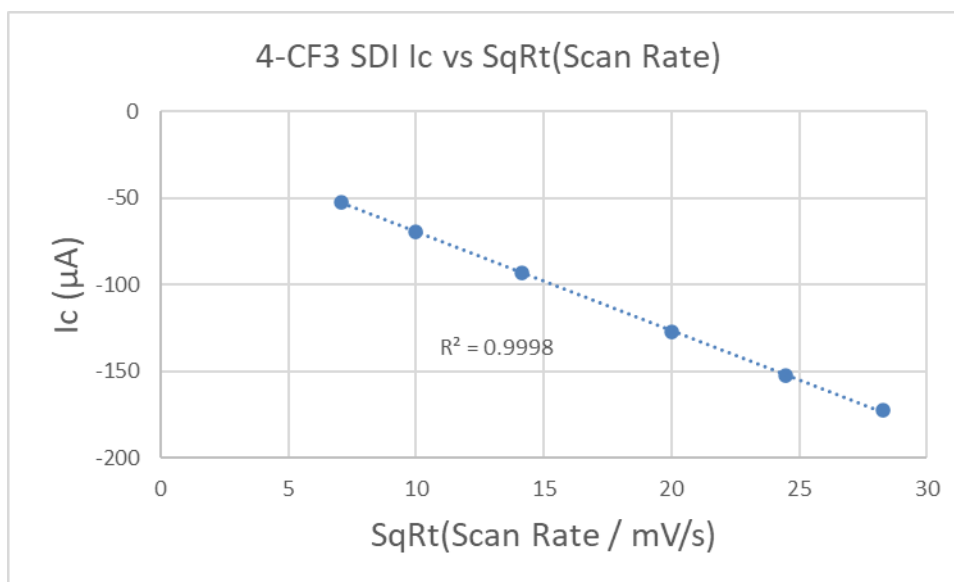


Figure B.69. Cathodic peak current (I_c) vs square root of scan rate for **6**. Linearity of this plot shows that electrochemical characterization was performed under diffusion-controlled conditions.

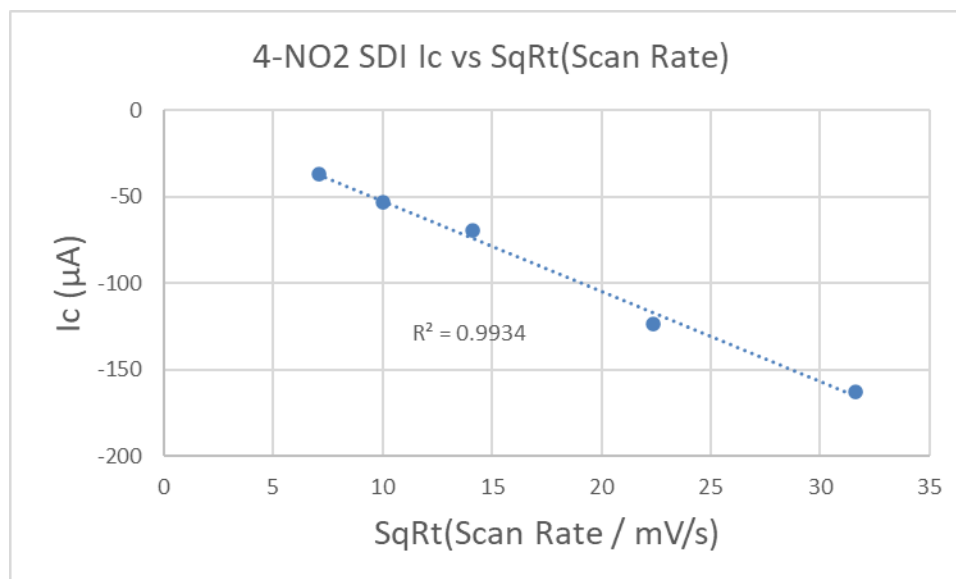


Figure B.70. Cathodic peak current (I_c) vs square root of scan rate for **7**. Linearity of this plot shows that electrochemical characterization was performed under diffusion-controlled conditions.

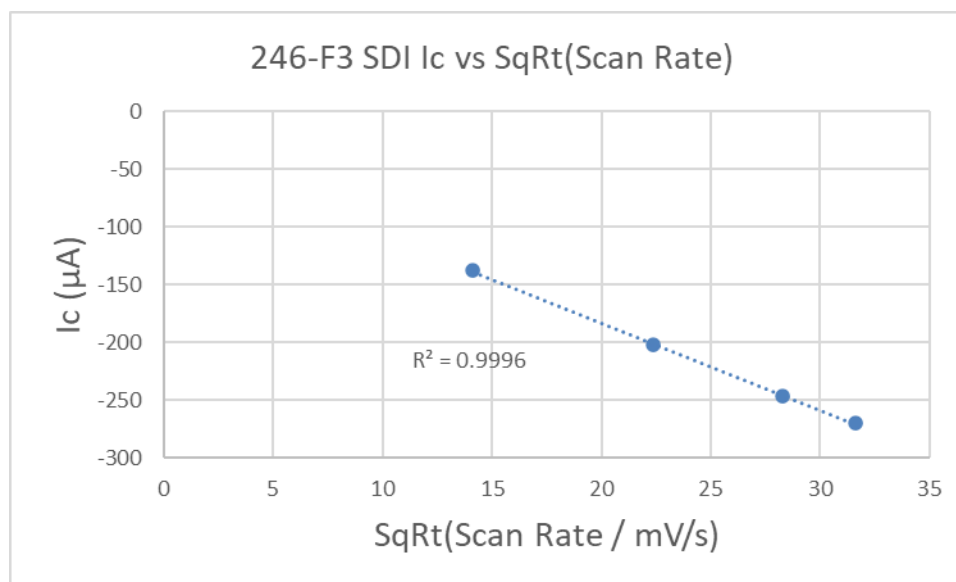


Figure B.71. Cathodic peak current (I_c) vs square root of scan rate for **8**. Linearity of this plot shows that electrochemical characterization was performed under diffusion-controlled conditions.

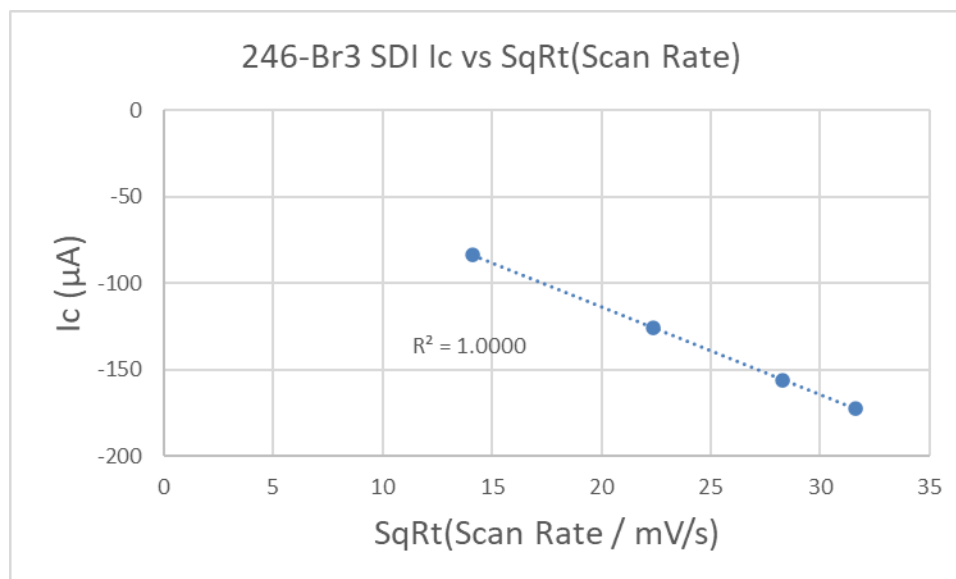
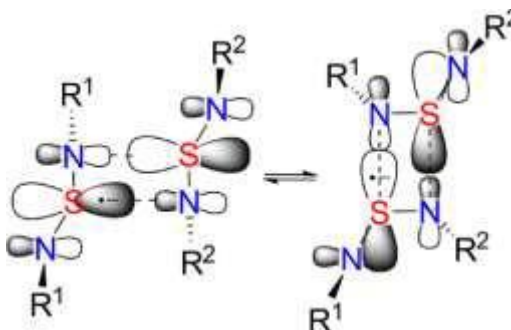


Figure B.72. Cathodic peak current (I_c) vs square root of scan rate for **9**. Linearity of this plot shows that electrochemical characterization was performed under diffusion-controlled conditions.



Scheme B.1. Radical anion scrambling of sulfur diimines following Bestari *et al.*

Although originally proposed as *radical couplings* via their π^* SOMOs, a similar process that leads to scrambling may conceivably operate between one radical and a neutral SDI. While there are no reports that higher aggregated ring- or (branch)chained radicals can be formed by such a process, there are many known examples of rapid changes in molecularity of thiazyl compounds under redox conditions. This *may* therefore account for the highly unusual appearances of the redox waves we determined for the E^2 processes in **1** – **6** and **8**, **9** (see Section 4.2.9).

B.9. Frontier Molecular Orbitals for the Aryl SDIs 1 - 9

B3LYP-D3BJ/6-311++G(2d,p) computations have been adopted as the model chemistry method for the work reported in this paper. This triple-zeta basis set, using the highly attested B3LYP functional and the now also very well characterized Grimme post-SCF empirical dispersion correction (as modified by Becke-Johnson damping) proved to be a reliable method to obtain computed structures that are verified by the experimental XRD and fit with the dominant solution species of **1** - **9** as determined by NMR and UV-vis spectroscopies in solutions (CDCl_3 and CH_2Cl_2). The relevant frontier molecular orbitals (FMOs) of these computed structures in their dominant solution conformation are presented here.

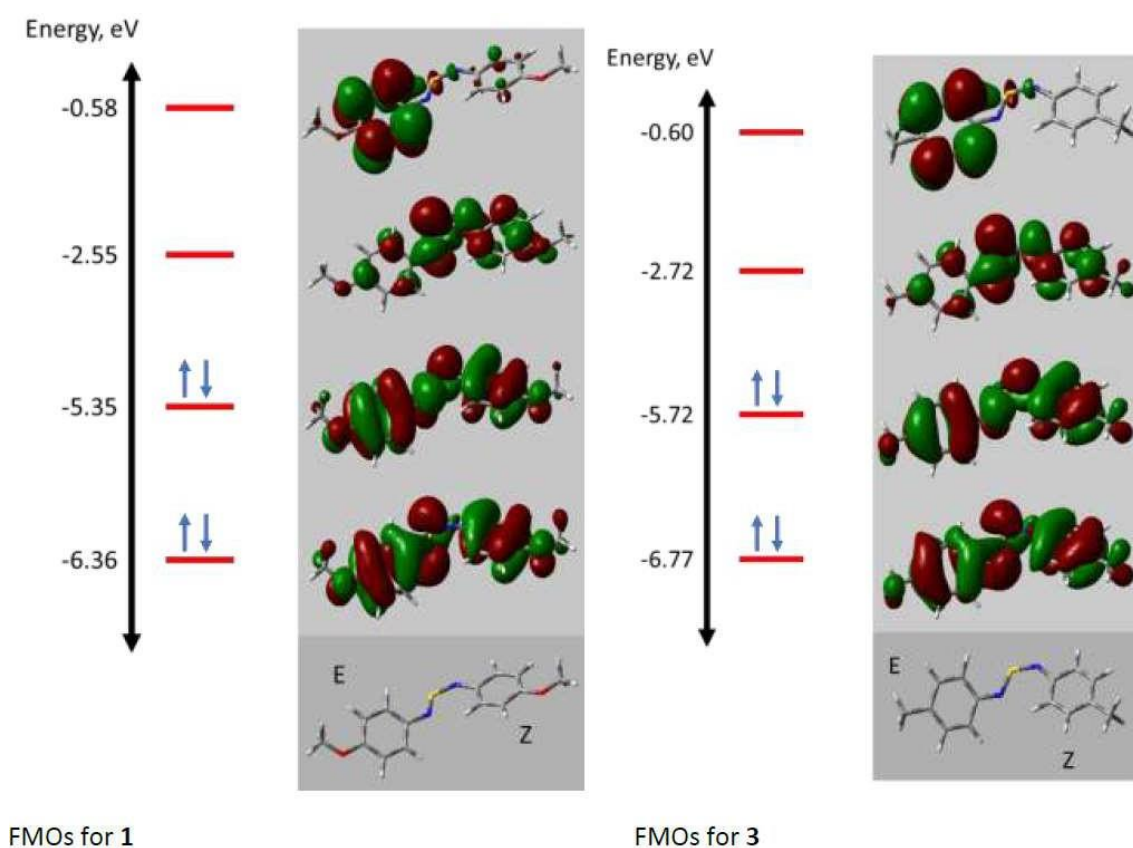


Figure B.73. Frontier molecular orbitals for **1** - **9** in their experimentally most stable configuration.

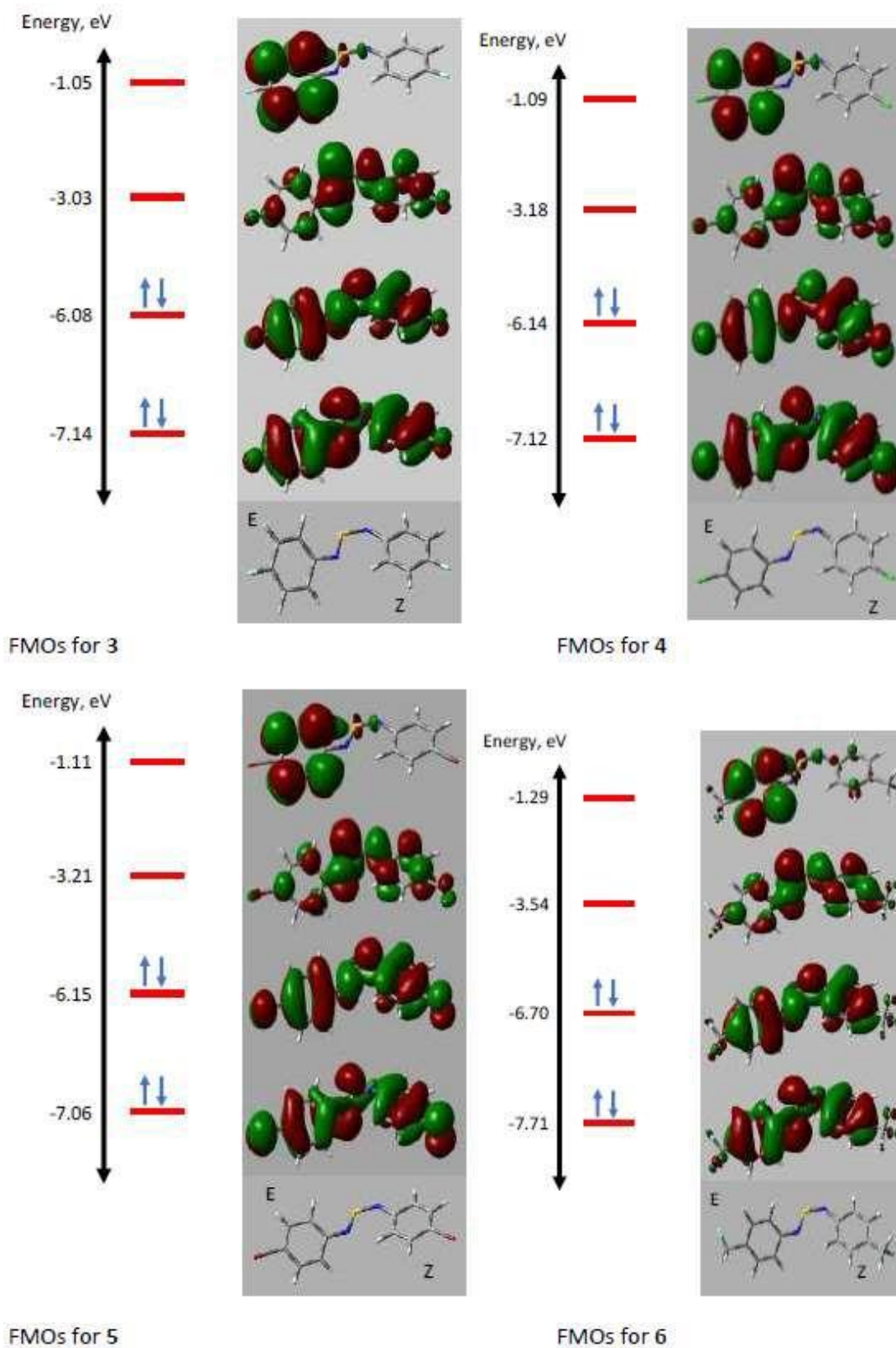


Figure B.73. Cont'd. Frontier molecular orbitals for 1 - 9 in their experimentally most stable configuration.

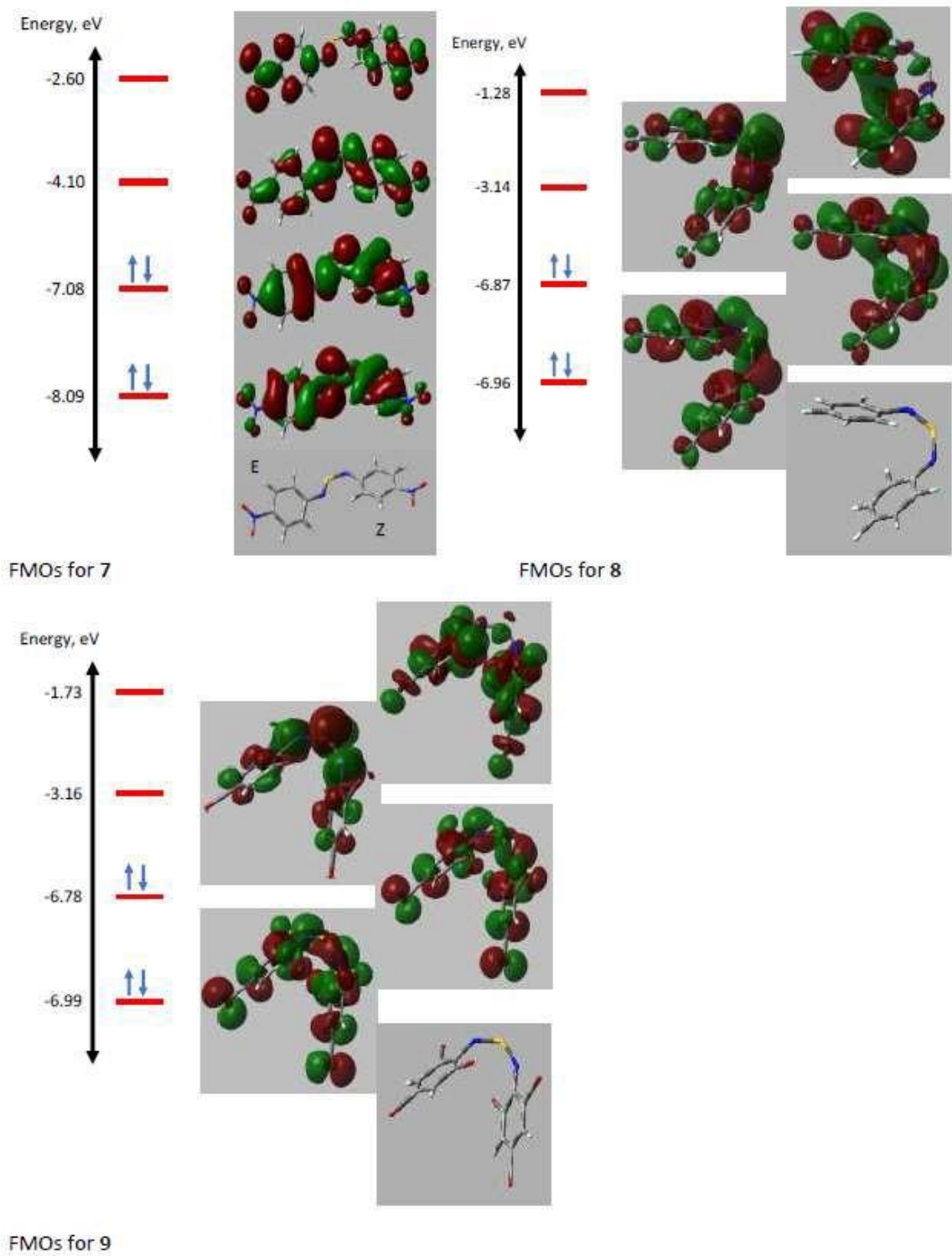


Figure B.73. cont'd. Frontier molecular orbitals for 1 – 9 in their experimentally most stable configuration.

B.10. Electron Paramagnetic Resonance Spectroscopy Data and Figures

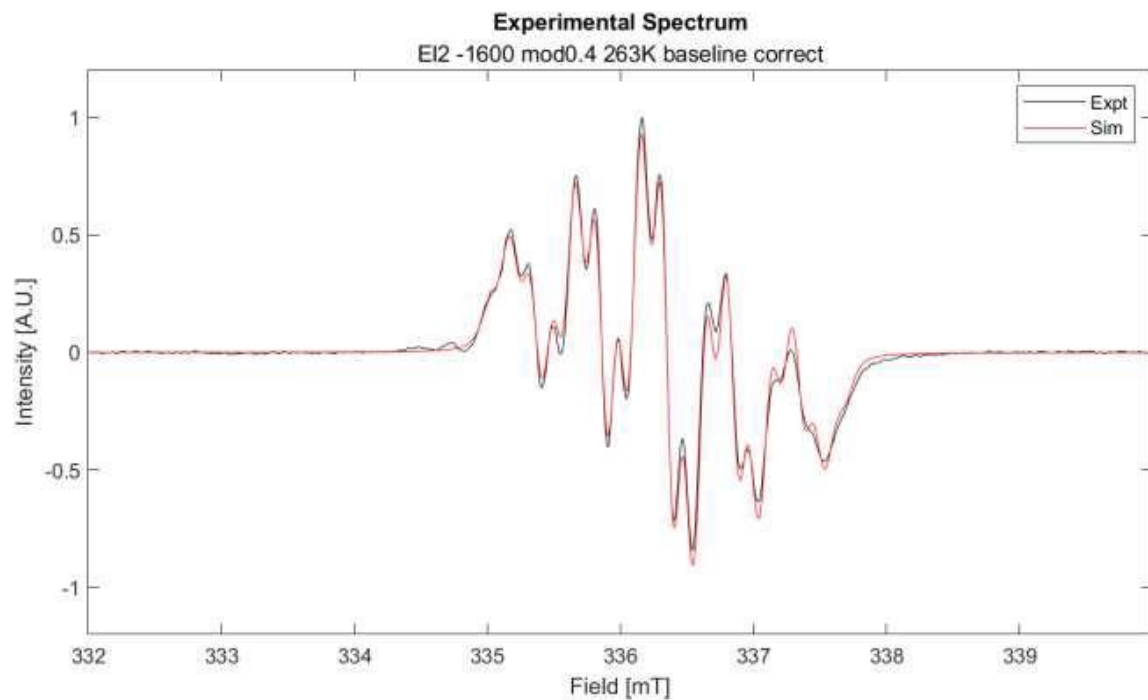


Figure B.74. SEPR spectrum of **1** (black) with simulated spectrum (red). Simulations were performed using EasySpin software

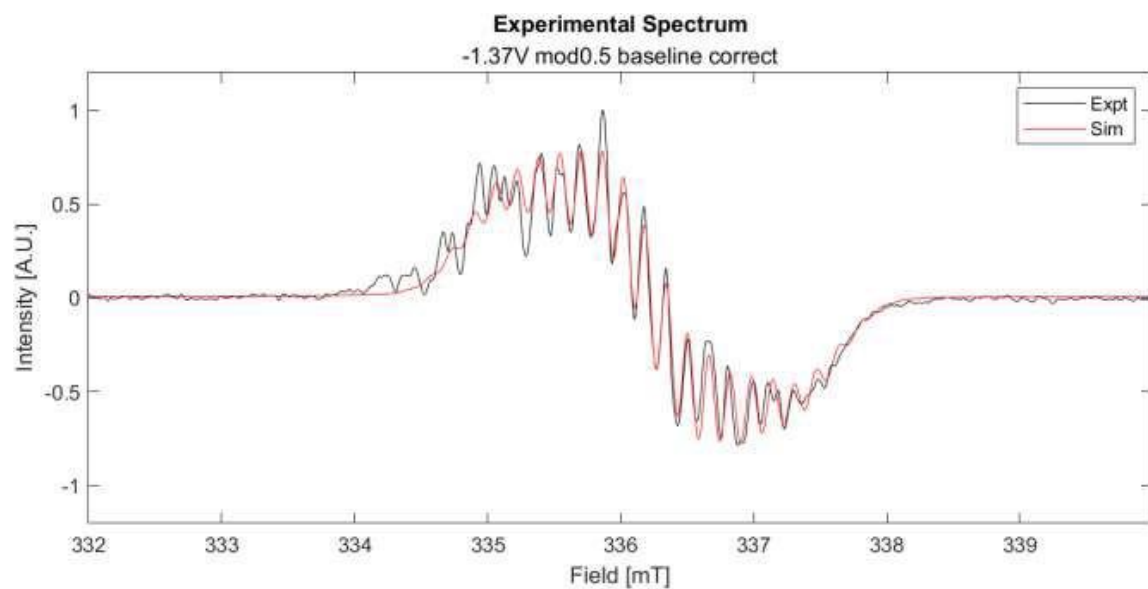


Figure B.75. SEPR spectrum of **2** (black) with simulated spectrum (red).

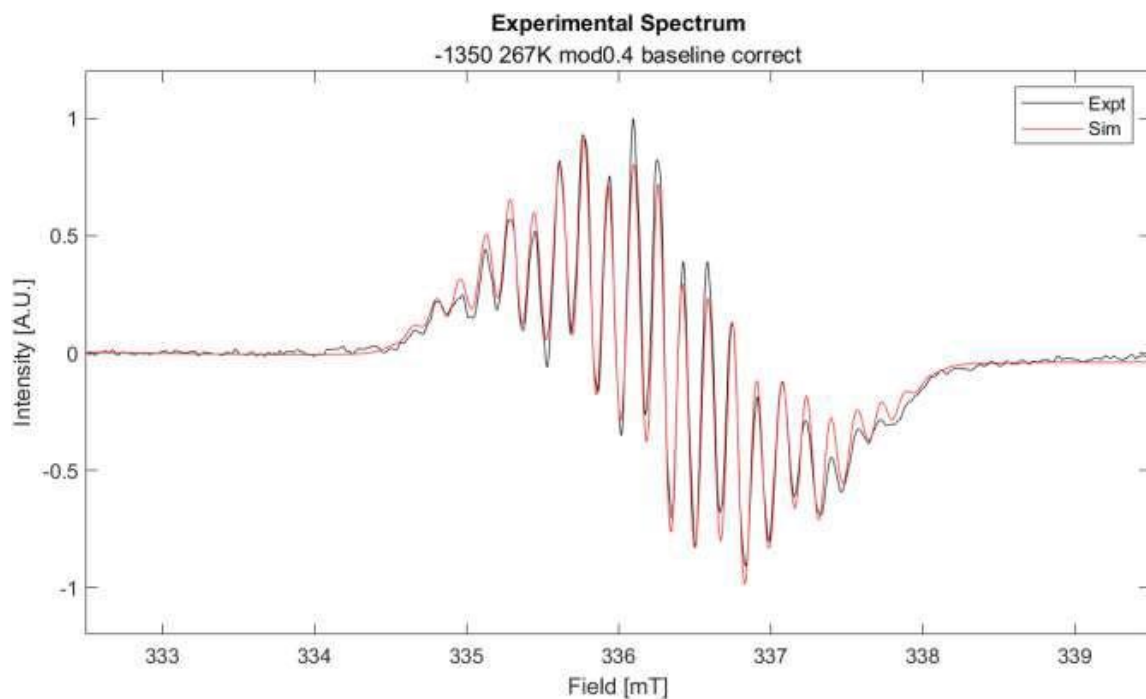


Figure B.76. SEEPR spectrum of 3 (black) with simulated spectrum (red).

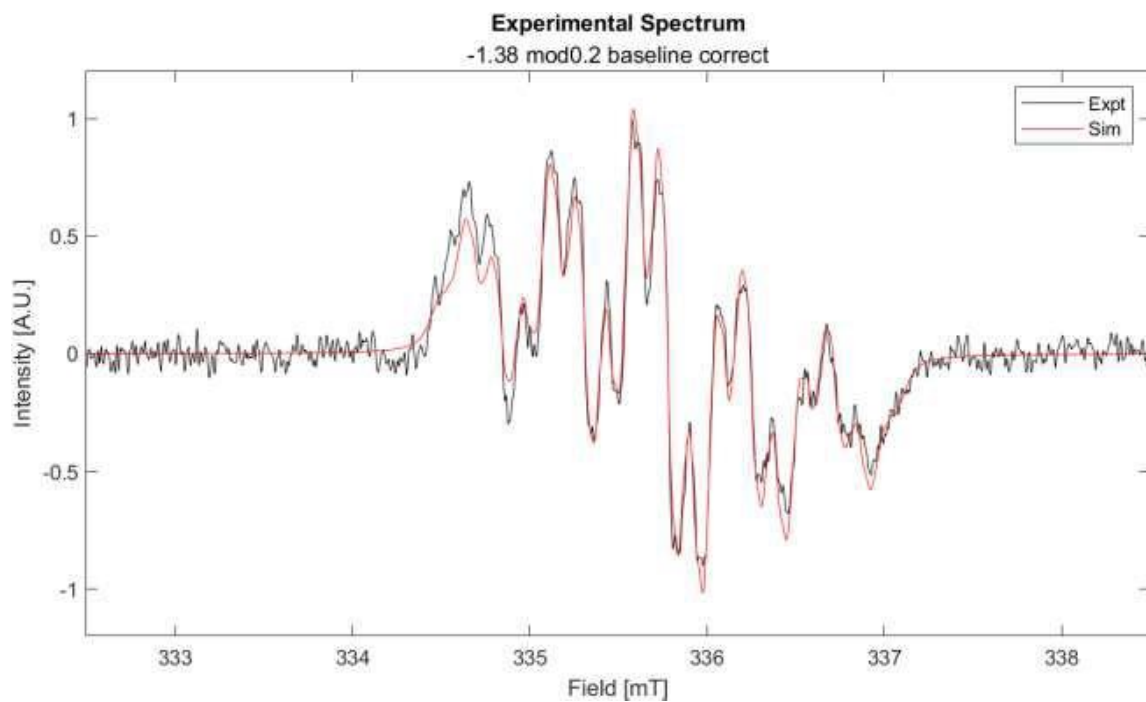


Figure B.77. SEEPR spectrum of 4 (black) with simulated spectrum (red).

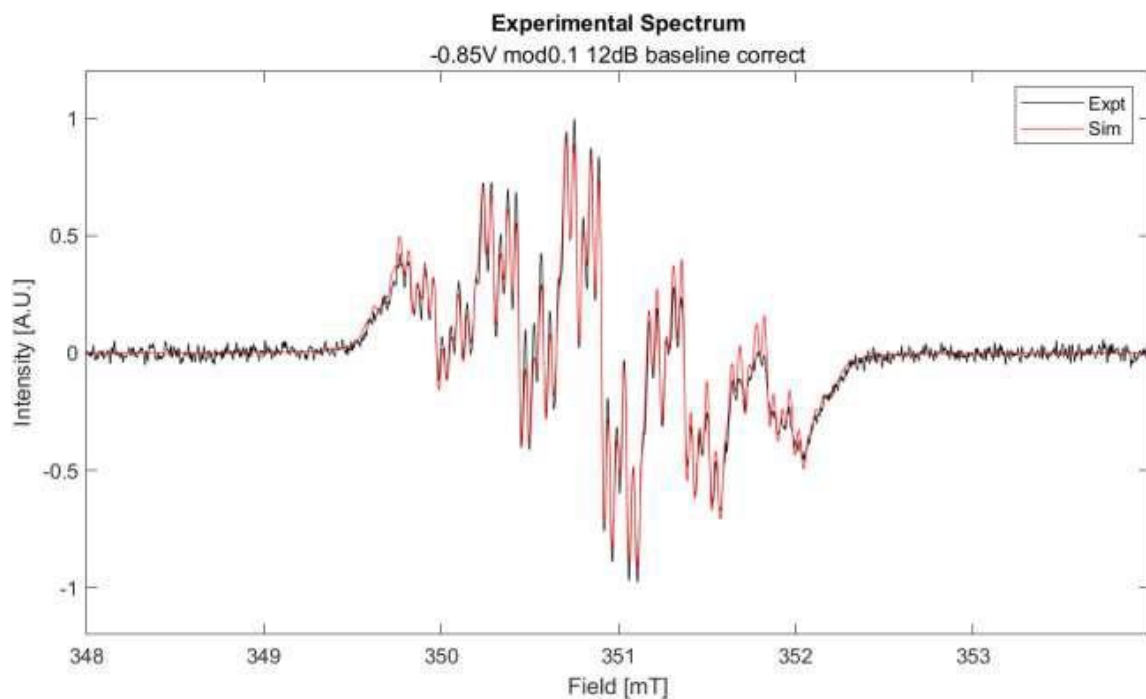


Figure B.78. SEEPR spectrum of 5 (black) with simulated spectrum (red).

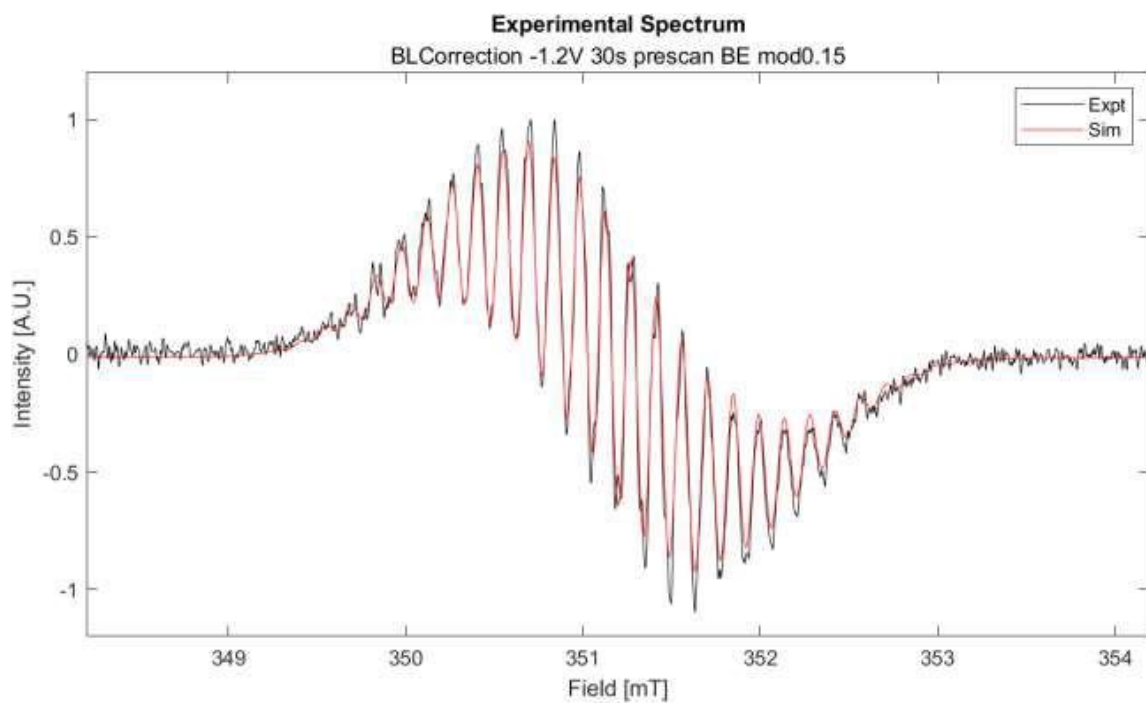


Figure B.79. SEEPR spectrum of 6 (black) with simulated spectrum (red).

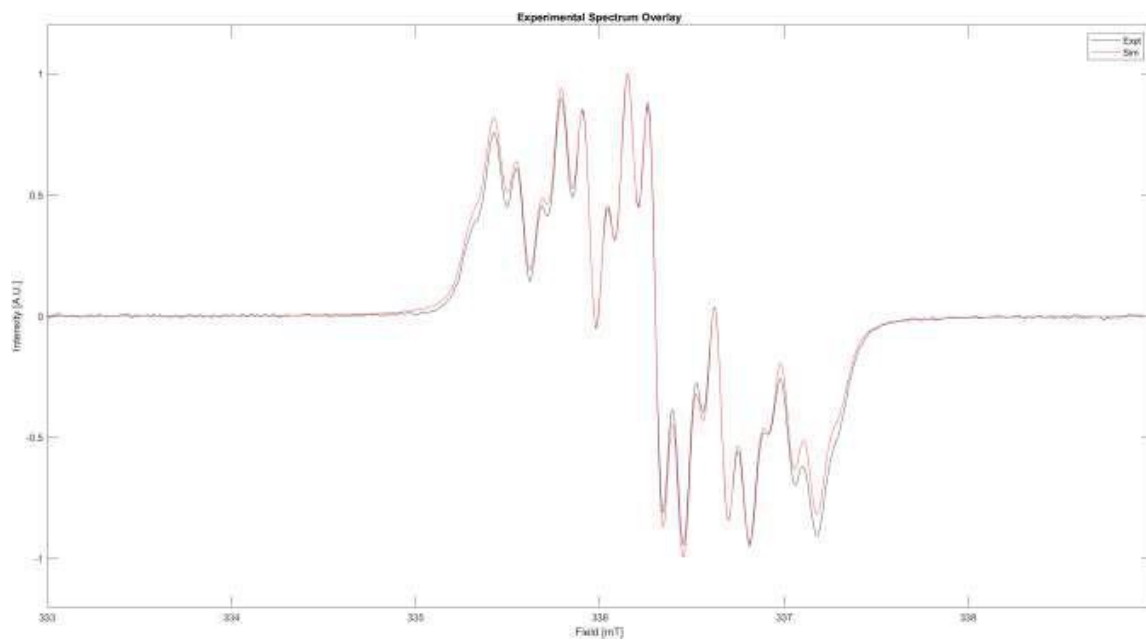


Figure B.80. SEEPR spectrum of **7** (black) with simulated spectrum (red).

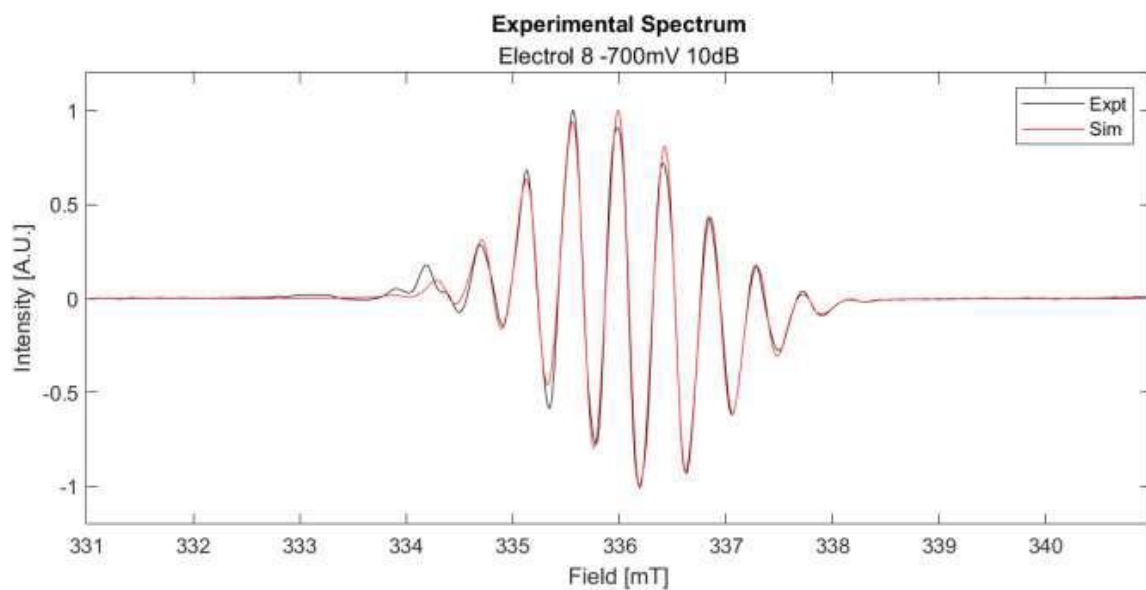


Figure B.81. SEEPR spectrum of **8** (black) with simulated spectrum (red).

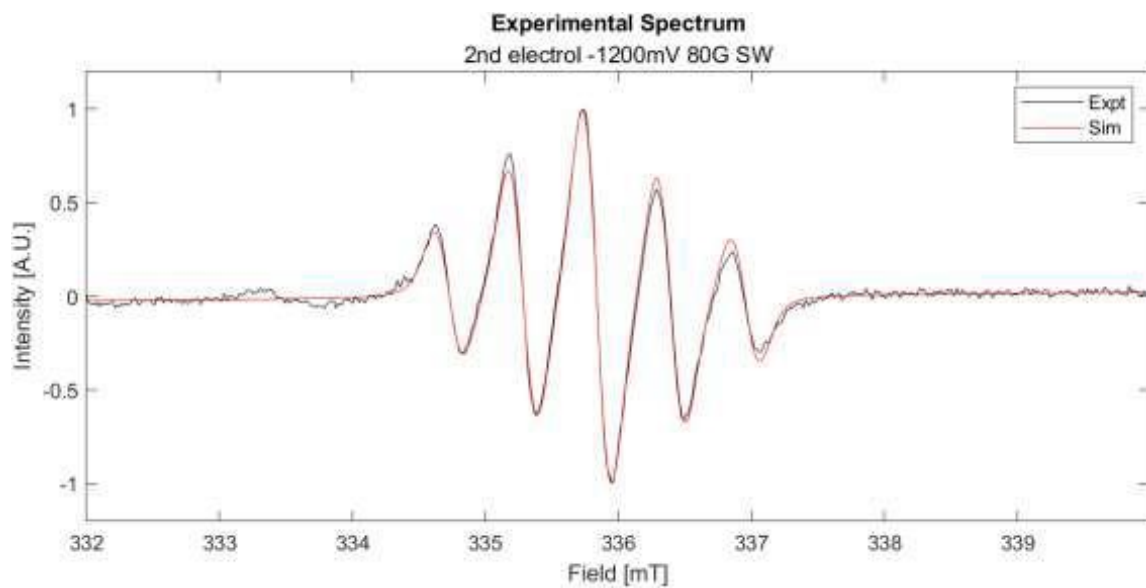


Figure B.82. SEEPR spectrum of **9** (black) with simulated spectrum (red).

Table B.34. EPR simulation data from best fit in EasySpin to experimental data

	1 - MeO	2 - Me	3 - F	4 - Cl	5 - Br	6 - CF3	7 - NO2	8 - F3	9 - Br3
g-value	2.0062	2.0063	2.0064	2.0065	2.0070	2.0063	2.0063	2.0065	2.0090
LW(G)^a	0.0941	0.0771	0.1045	0.0264	0.0060	0.0660	0.0625	0.1068	0.1298
LW(L)^b	0.0808	0.0804	0.0951	0.0922	0.0778	0.0665	0.0529	0.1737	0.1502
LW(hh)^c	0.1749	0.1575	0.1996	0.1186	0.0838	0.1325	0.1154	0.2805	0.2800
%G^d	53.8	49.0	52.4	22.3	7.2	49.8	54.2	38.1	46.4
%L^e	46.2	51.0	47.6	77.7	92.8	50.2	45.8	61.9	53.6
HFS (mT)^f									
2N	0.4925	0.4722	0.4877	0.4698	0.4667	0.4374	0.3562	0.4555	0.5565
2H	0.1540	0.2010	0.1467	0.1494	0.0570	0.1471	0.1329	0.0505	0.0673
2H	0.1344	0.1744	0.1467	0.1333	0.1429	0.1033	0.1071	0.0504	0.0581
2H	0.0414	0.1328	0.1308	0.0479	0.1392	0.0377	0.0149		
2H	0.0414	0.0565	0.0278	0.0421	0.0422	0.0317	0.0069		
6H		0.1511							
2F			0.3409						
6F						0.2820		0.4051	
2N							0.0228		
HFS (MHz)									
2N	13.8289	13.2609	13.6959	13.1929	13.1097	12.2830	10.0016	12.7922	15.648
2H	4.3238	5.6430	4.1188	4.1944	1.6020	4.1293	3.7320	1.4182	1.8934
2H	3.7746	4.8971	4.1188	3.7446	4.0131	2.9015	3.0084	1.4145	1.6337
2H	1.1626	3.7291	3.6745	1.34449	3.9114	1.0582	0.4181		
2H	1.1626	1.5875	0.7801	1.1825	1.1842	0.8913	0.1945		
6H		4.2431							
2F			9.5745						
6F						7.9186		11.3760	
2N							0.6394		

^aLinewidth, Gaussian component; ^bLinewidth, Lorentzian component; ^cLinewidth at half height: LW(hh) = LW(G) + LW(L); ^dPercentage of Gaussian contribution to lineshape: LW(G) / (LW(G) + LW(L)); ^ePercentage of Lorentzian contribution to lineshape: LW(L) / (LW(G) + LW(L)); ^fAll mT values were calculated from MHz using individual g factors.

Table B.35. Comparison of our EPR values vs Hunter et al.^[41]

Values in mT	[(4-MePhN) ₂ S] ^{•-}		[(4-O ₂ NPhN) ₂ S] ^{•-}	
	Hunter	Us	Hunter	Us
g-value	2.0063	2.0063	2.0064	2.0063
N	0.444	0.4720	0.361	0.3562
H - 2,2',6,6'	0.140	0.2010	0.124	0.1329
	0.187 our avg	0.1744	0.061 our avg	0.1071
H - 3,3',5,5'	0.046	0.1328	0.031	0.0149
	0.095 our avg	0.0565	0.011 our avg	0.0069
H - CH ₃	0.143	0.1511		

After correcting the mHz → mT conversion, our values for **2** and **7** compare very favourably with Hunter's. The values for AN in particular are very close. The smaller values for H splittings are somewhat further off, possibly due to the different conditions (counterion, solvent)? Possibly due to limitations of 1980 instrumentation and simulation software? Like our old simulations on WinSim, Hunter groups all ortho- and meta-hydrogens together (2 x 4H), whereas with EasySpin we were able to parse these into 4 x 2H. Worth noting that Hunter also combines both N, as we did, implying equivalence of the nitrogen atoms and symmetry of the solution state conformation of the monoanion.

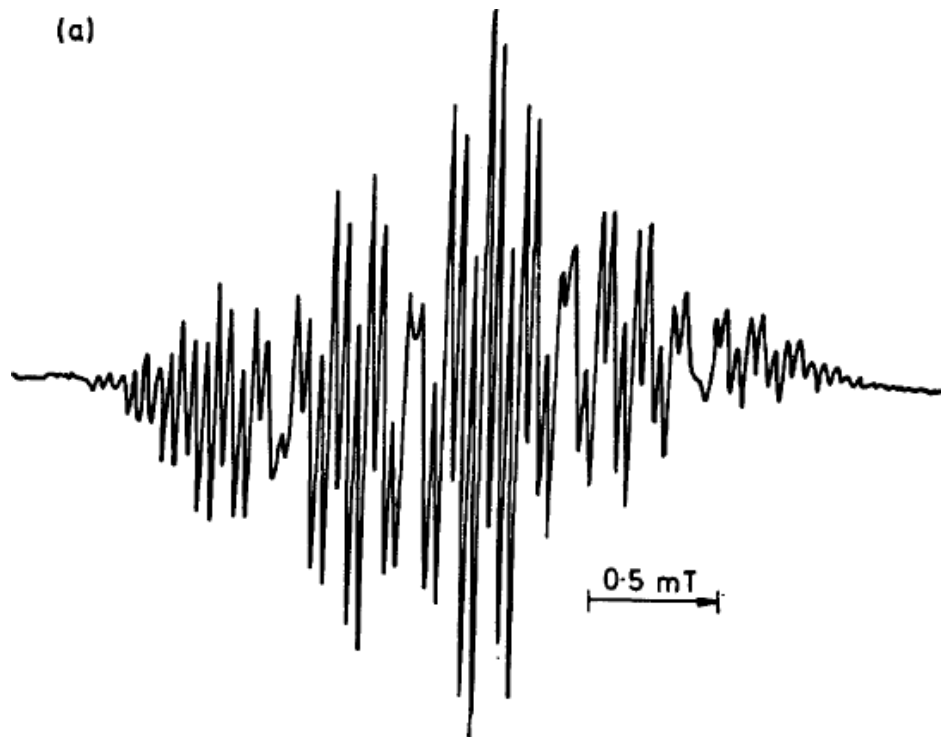


Figure B.83. Hunter's EPR spectrum of *bis*-(4-MePhN)₂S, clearly shows 1:2:3:2:1 splitting from 2 equiv. N atoms. Shows similar issues with symmetry as seen in ours above (Figure B.75).

Table B.36. Computed HFC constants for **1** to **9** with fitting to experimental values

1 •• Isotropic EPR hypfine coupling simulations																	
EZconf1-pMeO-PhNSN-b3lypD3bj-6311++G2dp_anion_OF						ZZconf1-pMeO-PhNSN-b3lypD3bj-6311++G2dp_anion_OF						EEconf1-pMeO-conf1-PhNSN-b3lypD3bj-6311++G2dp_anion_O					
Isotropic	Fermi	Couplings				Isotropic	Fermi	Couplings				Isotropic	Fermi	Couplings			
Label	Atom	MegaHertz		EasySpin	Agreemer	Label	Atom	MegaHertz		EasySpin	Agreemer	Label	Atom	MegaHertz		EasySpin	Agreemer
1 S(33)		10.67708	ScalFact	1.33		1 S(33)		13.20105	ScalFact	1.49		1 S(33)		9.81293	ScalFact	1.07	
2 N(14)		9.42716	8.16	13.83	-5.67	2 N(14)		19.52611	19.24	13.83	5.41	2 N(14)		7.62461	7.62	13.83	-6.21
3 N(14)		6.88401			-41.0%	3 N(14)		18.9601			39.1%	3 N(14)		7.62462			-44.9%
20 H(1)		7.42555	7.01	4.32	2.69	10 H(1)		6.41006	5.65	4.32	1.33	20 H(1)		5.71649	5.72	4.32	1.40
10 H(1)		6.59382			62.3%	20 H(1)		4.89307			30.8%	10 H(1)		5.71649			32.3%
18 H(1)		6.07734	4.45	3.77	0.68	18 H(1)		4.86438	4.64	3.77	0.87	8 H(1)		3.53731	3.54	3.77	-0.23
22 H(1)		2.82828			18.1%	8 H(1)		4.40994			23.0%	18 H(1)		3.53731			-6.2%
23 H(1)		2.74397	2.57	1.16	1.41	12 H(1)		2.12686	2.11	1.16	0.95	22 H(1)		1.4903	1.49	1.16	0.33
8 H(1)		2.40241			121.8%	13 H(1)		2.08624			81.6%	12 H(1)		1.4903			28.5%
13 H(1)		1.31301	1.21	1.16	0.05	22 H(1)		2.00778	1.96	1.16	0.80	13 H(1)		1.45925	1.46	1.16	0.30
12 H(1)		1.11634			4.7%	23 H(1)		1.91416			69.0%	23 H(1)		1.45924			25.8%
27 H(1)		-0.26413	0.57	0		27 H(1)		-0.16262	0.59	0		27 H(1)		-0.1421	0.75	0	
28 H(1)		1.35446				28 H(1)		1.05384				28 H(1)		1.19541			
29 H(1)		1.35428				29 H(1)		0.88884				29 H(1)		1.19538			
31 H(1)		-0.18252				31 H(1)		-0.16521				31 H(1)		-0.1421			
32 H(1)		0.569				32 H(1)		0.83203				32 H(1)		1.19538			
33 H(1)		0.56903				33 H(1)		1.12209				33 H(1)		1.19541			
4 C(13)		-8.57842	not observed			4 C(13)		5.10038				4 C(13)		-10.4608			
5 C(13)		1.79474				5 C(13)		4.72167				5 C(13)		3.36214			
6 C(13)		6.17057				6 C(13)		9.20067				6 C(13)		5.48097			
7 C(13)		-4.43134				7 C(13)		-6.67674				7 C(13)		-5.43256			
9 C(13)		-6.07471				9 C(13)		-5.8502				9 C(13)		-5.85726			
11 C(13)		5.77216				11 C(13)		7.38702				11 C(13)		6.16333			
14 C(13)		-15.0985				14 C(13)		9.27518				14 C(13)		-10.4608			
15 C(13)		7.21221				15 C(13)		7.17173				15 C(13)		3.36214			
16 C(13)		8.47237				16 C(13)		5.09004				16 C(13)		5.48096			
17 C(13)		-8.88398				17 C(13)		-4.94151				17 C(13)		-5.43256			
19 C(13)		-9.62433				19 C(13)		-6.56693				19 C(13)		-5.85726			
21 C(13)		10.44304				21 C(13)		6.77513				21 C(13)		6.16333			
26 C(13)		-0.51443				26 C(13)		-0.36331				26 C(13)		-0.42273			
30 C(13)		-0.24676				30 C(13)		-0.29365				30 C(13)		-0.42273			
24 O(17)		-0.97631	not observed			24 O(17)		-1.37097				24 O(17)		-1.34895			
25 O(17)		-1.87164				25 O(17)		-1.27124				25 O(17)		-1.34895			



Table B.36. Cont'd

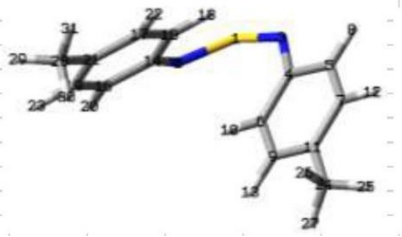
2 •-					Isotropic EPR hypofine coupling simulations									
EZconf3-pCH3-PhNSN-b3lypD3bj-6311++G2dp_ANION_OF					ZZconf1-pCH3-PhNSN-b3lypD3bj-6311++G2dp_ANION_OF					EEconf1-pCH3-PhNSN-b3lypD3bj-6311++G2dp_anion_OF				
Isotropic	Fermi	Couplings			Isotropic	Fermi	Couplings			Isotropic	Fermi	Couplings		
Label	Atom	MegaHertz	EasySpin	Agreemer	Label	Atom	MegaHertz	EasySpin	Agreemer	Label	Atom	MegaHertz	EasySpin	Agreemer
1 S(33)		11.24011	ScalFact	0.97	1 S(33)		13.589	ScalFact	1.07	1 S(33)		10.22592	ScalFact	0.78
2 N(14)		8.92761	7.79	13.26	-5.47	2 N(14)	18.94416	18.94	13.26	5.68	2 N(14)	7.23628	7.24	13.26
3 N(14)		6.65121			-41.3%	3 N(14)	18.93117			42.8%	3 N(14)	7.23628		-45.4%
18 H(1)		6.86841	6.51	5.64	0.87	10 H(1)	5.52677	5.52	5.64	-0.12	10 H(1)	5.95189	5.95	5.64
20 H(1)		6.14619			15.4%	18 H(1)	5.52266			-2.0%	20 H(1)	5.95189		5.5%
10 H(1)		5.92265	4.33	4.9	-0.57	8 H(1)	4.36001	4.36	4.9	-0.54	8 H(1)	3.06304	3.06	4.9
8 H(1)		2.73852			-11.6%	20 H(1)	4.357			-11.1%	18 H(1)	3.06304		-37.5%
22 H(1)		2.75291	2.73	3.73	-1.00	22 H(1)	2.10998	2.11	3.73	-1.62	13 H(1)	1.6728	1.67	3.73
23 H(1)		2.70896			-26.8%	13 H(1)	2.10991			-43.4%	23 H(1)	1.6728		-55.2%
13 H(1)		1.64715	1.29	1.59	-0.30	12 H(1)	1.91804	1.92	1.59	0.33	12 H(1)	1.16343	1.16	1.59
12 H(1)		0.94229			-18.6%	23 H(1)	1.91624			20.6%	22 H(1)	1.16343		-26.8%
25 H(1)		8.24304	6.89	4.24	2.65	25 H(1)	4.62454	5.78	4.24	1.54	25 H(1)	7.85902	5.33	4.24
26 H(1)		7.35767			62.6%	26 H(1)	11.02624			36.4%	26 H(1)	7.83176		25.7%
27 H(1)		0.32185				27 H(1)	1.70009				27 H(1)	0.29206		
29 H(1)		8.51201				29 H(1)	4.61505				29 H(1)	7.85895		
30 H(1)		1.4769				30 H(1)	11.02002				30 H(1)	7.83183		
31 H(1)		15.44989				31 H(1)	1.70258				31 H(1)	0.29206		
4 C(13)		-7.931	not observed			4 C(13)	7.50393				4 C(13)	-9.75542		
5 C(13)		2.02429				5 C(13)	4.79428				5 C(13)	2.68054		
6 C(13)		5.58344				6 C(13)	8.00319				6 C(13)	5.77657		
7 C(13)		-4.67529				7 C(13)	-6.51887				7 C(13)	-5.00902		
9 C(13)		-6.30237				9 C(13)	-5.40043				9 C(13)	-6.32832		
11 C(13)		6.558				11 C(13)	7.60983				11 C(13)	6.57754		
14 C(13)		-14.2081				14 C(13)	7.52843				14 C(13)	-9.75542		
15 C(13)		7.91581				15 C(13)	7.99799				15 C(13)	2.68054		
16 C(13)		7.0603				16 C(13)	4.79327				16 C(13)	5.77657		
17 C(13)		-9.46482				17 C(13)	-5.39535				17 C(13)	-5.00902		
19 C(13)		-9.15427				19 C(13)	-6.51423				19 C(13)	-6.32831		
21 C(13)		11.16209				21 C(13)	7.60478				21 C(13)	6.57754		
24 C(13)		-3.2421				24 C(13)	-3.47124				24 C(13)	-3.18959		
28 C(13)		-5.09648				28 C(13)	-3.46869				28 C(13)	-3.18959		
														

Table B.36. Cont'd

3 •-						ZZconf1-pF-PhNSN-b3lypd3bj-6311++G2dp_anion_OF						EEconf1-FPhNSN-b3lypd3bj-6311++G2dp_anion_OF					
EZ-pFPhNSN-b3lypd3bj-6311++G2dp_anion_OF						ZZconf1-pF-PhNSN-b3lypd3bj-6311++G2dp_anion_OF						EEconf1-FPhNSN-b3lypd3bj-6311++G2dp_anion_OF					
Isotropic	Fermi	Couplings				Isotropic	Fermi	Couplings				Isotropic	Fermi	Couplings			
Label	Atom	MegaHertz	ScalFact	EasySpin	Agreemer	Label	Atom	MegaHertz	ScalFact	EasySpin	Agreemer	Label	Atom	MegaHertz	ScalFact	EasySpin	Agreemer
1 S(33)		11.26539		1.18		1 S(33)		13.69663		1.34		1 S(33)		10.23562		0.98	
2 N(14)		9.17703	8.00	13.7	-5.70	2 N(14)		19.35965	19.36	13.7	5.66	2 N(14)		7.37877	7.38	13.7	-6.32
3 N(14)		6.81939			-41.6%	3 N(14)		19.35965			41.3%	3 N(14)		7.37877			-46.1%
18 H(1)		6.94009	6.87	4.12	2.75	10 H(1)		5.71367	5.71	4.12	1.59	22 H(1)		6.25021	6.25	4.12	2.13
20 H(1)		6.8041			66.8%	18 H(1)		5.71367			38.7%	25 H(1)		6.25021			51.7%
10 H(1)		6.26706	4.58	4.12	0.46	8 H(1)		4.63517	4.64	4.12	0.52	23 H(1)		3.21802	3.22	4.12	-0.90
8 H(1)		2.89909			11.2%	20 H(1)		4.63517			12.5%	24 H(1)		3.21802			-21.9%
22 H(1)		2.88753	2.87	3.67	-0.80	13 H(1)		2.11176	2.11	3.67	-1.56	11 H(1)		1.61034	1.61	3.67	-2.06
23 H(1)		2.85063			-21.8%	22 H(1)		2.11176			-42.5%	19 H(1)		1.61034			-56.1%
13 H(1)		1.59812	1.36	0.78	0.58	12 H(1)		2.01218	2.01	0.78	1.23	10 H(1)		1.3195	1.32	0.78	0.54
12 H(1)		1.12091			74.3%	23 H(1)		2.01218			158.0%	18 H(1)		1.3195			69.2%
24 F(19)		13.93447	11.17	9.57	1.60	24 F(19)		9.41114	9.41	9.57	-0.16	20 F(19)		8.54337	8.54	9.57	-1.03
25 F(19)		8.41354			16.8%	25 F(19)		9.41114			-1.7%	21 F(19)		8.54337			-10.7%
21 C(13)		11.94478	not observed			6 C(13)		8.38375				9 C(13)		6.93771			
15 C(13)		7.98944				15 C(13)		8.38375				17 C(13)		6.93771			
16 C(13)		7.66406				4 C(13)		8.00971				6 C(13)		5.97716			
11 C(13)		6.93062				14 C(13)		8.00971				14 C(13)		5.97716			
6 C(13)		5.83912				11 C(13)		7.95074				5 C(13)		2.8139			
5 C(13)		2.18351				21 C(13)		7.95074				13 C(13)		2.8139			
7 C(13)		-4.81897				5 C(13)		4.7885				7 C(13)		-5.12624			
9 C(13)		-6.30418				16 C(13)		4.7885				15 C(13)		-5.12624			
4 C(13)		-8.3447				9 C(13)		-5.46962				8 C(13)		-6.30029			
17 C(13)		-9.4539				17 C(13)		-5.46962				16 C(13)		-6.30029			
19 C(13)		-9.4602				7 C(13)		-6.62895				4 C(13)		-10.1014			
14 C(13)		-14.7792				19 C(13)		-6.62895				12 C(13)		-10.1014			

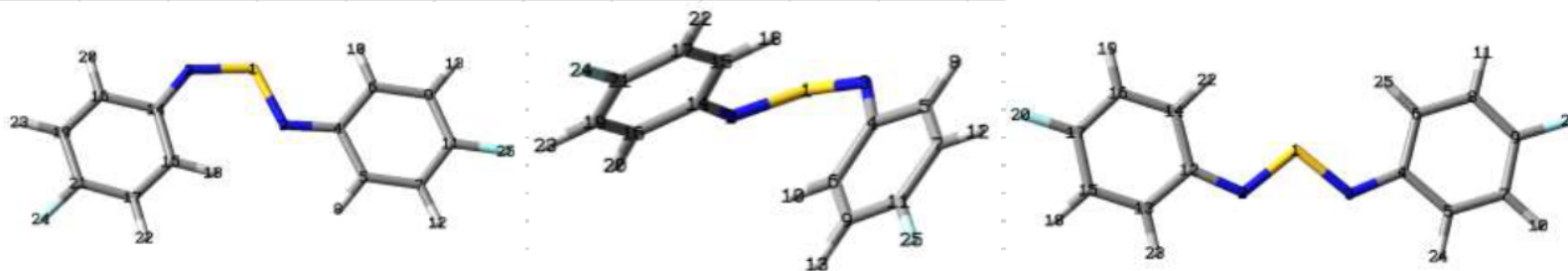


Table B.36. Cont'd

4 •- Isotropic EPR hypofine coupling simulations														
EZconf1-pClPhNSN-b3lypd3bj-6311++G2dp_anion_OF					ZZconf1-pClPhNSN-b3lypd3bj-6311++G2dp_anion_FR					EEconf1-pCl-PhNSN-b3lypd3bj-6311++G2dp_anion_OP				
Isotropic	Fermi	Couplings			Isotropic	Fermi	Couplings			Isotropic	Fermi	Couplings		
Label	Atom	MegaHertz	EasySpin	Agreemer	Label	Atom	MegaHertz	EasySpin	Agreemer	Label	Atom	MegaHertz	EasySpin	Agreemer
1 S(33)		11.70844	ScalFact	1.32	1 S(33)		13.9504	ScalFact	1.45	1 S(33)		10.74714	ScalFact	1.04
2 N(14)		8.62944	7.53	13.19	-5.66	2 N(14)	18.65685	18.66	13.19	5.47	2 N(14)	7.05177	7.05	13.19
3 N(14)		6.4353			-42.9%	3 N(14)	18.65685			41.4%	3 N(14)	7.05177		-46.5%
18 H(1)		6.74291	6.63	4.19	2.44	10 H(1)	5.56464	5.56	4.19	1.37	10 H(1)	5.92969	5.93	4.19
20 H(1)		6.5076			58.1%	18 H(1)	5.56464			32.8%	20 H(1)	5.92969		41.5%
10 H(1)		5.84885	4.39	3.74	0.65	8 H(1)	4.50574	4.51	3.74	0.77	8 H(1)	3.27584	3.28	3.74
8 H(1)		2.94076			17.5%	20 H(1)	4.50574			20.5%	18 H(1)	3.27584		-12.4%
22 H(1)		2.84861	2.83	1.34	1.49	13 H(1)	2.20131	2.20	1.34	0.86	13 H(1)	1.84958	1.85	1.34
23 H(1)		2.81338			111.3%	22 H(1)	2.20131			64.3%	23 H(1)	1.84958		38.0%
13 H(1)		1.79927	1.36	1.18	0.18	12 H(1)	1.97841	1.98	1.18	0.80	12 H(1)	1.15469	1.15	1.18
12 H(1)		0.91871			15.2%	23 H(1)	1.97841			67.7%	22 H(1)	1.15469		-2.1%
21 C(13)		13.68459	not observed			24 Cl(35)	0.20228				24 Cl(35)	0.1829		
11 C(13)		8.09843				25 Cl(35)	0.20228				25 Cl(35)	0.1829		
15 C(13)		7.72984				11 C(13)	9.24358				11 C(13)	8.14519		
16 C(13)		7.30176				21 C(13)	9.24358				21 C(13)	8.14519		
6 C(13)		5.49609				6 C(13)	8.29555				6 C(13)	5.76215		
5 C(13)		2.1106				15 C(13)	8.29555				16 C(13)	5.76215		
7 C(13)		-4.68692				4 C(13)	7.64545				5 C(13)	2.78094		
9 C(13)		-6.29713				14 C(13)	7.64545				15 C(13)	2.78094		
4 C(13)		-7.65332				5 C(13)	4.86419				7 C(13)	-5.04708		
19 C(13)		-9.28279				16 C(13)	4.86419				17 C(13)	-5.04708		
17 C(13)		-9.31017				9 C(13)	-5.53113				9 C(13)	-6.37499		
14 C(13)		-13.9046				17 C(13)	-5.53113				19 C(13)	-6.37499		
24 Cl(35)		0.14086	not observed			7 C(13)	-6.57358				4 C(13)	-9.56419		
25 Cl(35)		0.28151				19 C(13)	-6.57358				14 C(13)	-9.56419		



Table B.36. Cont'd

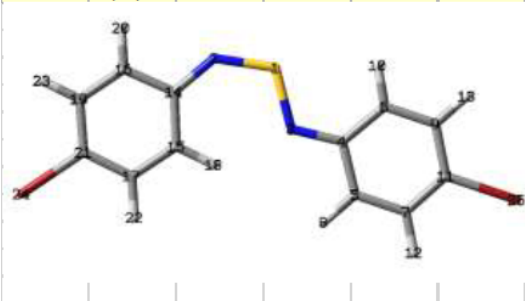
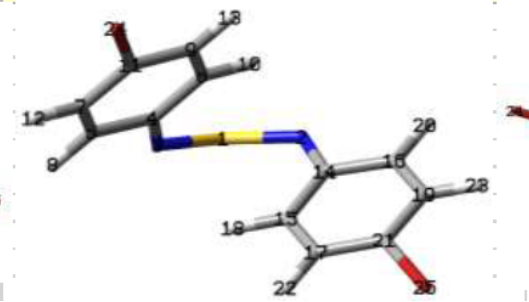
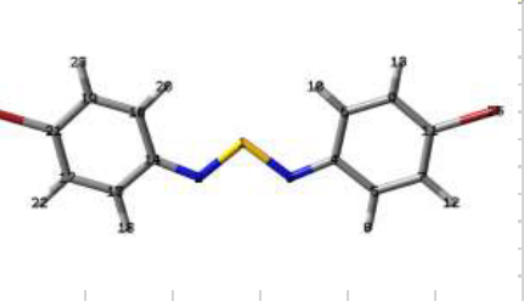
5 •-						Isotropic EPR hypofine coupling simulations											
EZconf1-pBr-PhNSN-b3lypD3bj-6311++G2dp_anion_OP						ZZconf1-pBr-PhNSN-b3lypD3bj-6311++G2dp_anion_OF						EEconf1-pBr-PhNSN-b3lypD3bj-6311++G2dp_ANION_OF					
Isotropic	Fermi	Couplings				Isotropic	Fermi	Couplings				Isotropic	Fermi	Couplings			
Label	Atom	MegaHertz		EasySpin	Agreemer	Label	Atom	MegaHertz		EasySpin	Agreemer	Label	Atom	MegaHertz		EasySpin	Agreemer
1 S(33)		11.81177	ScalFact	1.24		1 S(33)		14.07663	ScalFact	1.37		1 S(33)		10.85812	ScalFact	0.99	
2 N(14)		8.55943	7.47	13.11	-5.64	2 N(14)		18.69315	18.69	13.11	5.58	2 N(14)		6.99464	6.99	13.11	-6.12
3 N(14)		6.38023			-43.0%	3 N(14)		18.69315			42.6%	3 N(14)		6.99464			-46.6%
18 H(1)		6.69079	6.57	4.01	2.56	10 H(1)		5.46337	5.46	4.01	1.45	10 H(1)		5.87677	5.88	4.01	1.87
20 H(1)		6.44407			63.8%	18 H(1)		5.46337			36.2%	20 H(1)		5.87677			46.6%
10 H(1)		5.7814	4.35	3.91	0.44	8 H(1)		4.38782	4.39	3.91	0.48	8 H(1)		3.25808	3.26	3.91	-0.65
8 H(1)		2.91743			11.2%	20 H(1)		4.38782			12.2%	18 H(1)		3.25808			-16.7%
22 H(1)		2.81482	2.80	1.6	1.20	13 H(1)		2.1465	2.15	1.6	0.55	13 H(1)		1.86977	1.87	1.6	0.27
23 H(1)		2.7825			74.9%	22 H(1)		2.1465			34.2%	23 H(1)		1.86977			16.9%
13 H(1)		1.81035	1.34	1.18	0.16	12 H(1)		1.89801	1.90	1.18	0.72	12 H(1)		1.10501	1.11	1.18	-0.07
12 H(1)		0.86394			13.3%	23 H(1)		1.89801			60.8%	22 H(1)		1.10501			-6.4%
21 C(13)		14.13644	not observed			11 C(13)		9.30263				11 C(13)		8.44878			
11 C(13)		8.39002				21 C(13)		9.30263				21 C(13)		8.44878			
15 C(13)		7.68735				6 C(13)		8.22416				6 C(13)		5.74107			
16 C(13)		7.24565				15 C(13)		8.22416				16 C(13)		5.74107			
6 C(13)		5.45485				4 C(13)		8.00892				5 C(13)		2.74704			
5 C(13)		2.06894				14 C(13)		8.00892				15 C(13)		2.74704			
7 C(13)		-4.56705				5 C(13)		4.72251				7 C(13)		-4.93587			
9 C(13)		-6.20163				16 C(13)		4.72251				17 C(13)		-4.93587			
4 C(13)		-7.50882				9 C(13)		-5.26299				9 C(13)		-6.29655			
19 C(13)		-9.11222				17 C(13)		-5.26299				19 C(13)		-6.29655			
17 C(13)		-9.14464				7 C(13)		-6.30778				4 C(13)		-9.43692			
14 C(13)		-13.7326				19 C(13)		-6.30778				14 C(13)		-9.43692			
24 Br(79)		1.03404	not observed			24 Br(79)		0.74361				24 Br(79)		0.6693			
25 Br(79)		0.53855				25 Br(79)		0.74361				25 Br(79)		0.6693			
																	

Table B.36. Cont'd

6 •-					ZZconf1-pCF3-PhNSN-b3lypD3bj-6311++G2dp_ANION_OF					EEconf1-pCF3-PhNSN-b3lypD3bj-6311++G2dp_anion_OF				
EZconf2-pCF3-PhNSN-b3lypD3bj-6311++G2dp_ANION_OF														
Isotropic	Fermi	Couplings			Isotropic	Fermi	Couplings			Isotropic	Fermi	Couplings		
Label	Atom	MegaHertz	EasySpin	Agreemer	Label	Atom	MegaHertz	EasySpin	Agreemer	Label	Atom	MegaHertz	EasySpin	Agreemer
1 S(33)		12.50908	ScalFact	1.44	1 S(33)		14.51278	ScalFact	1.51	1 S(33)		11.64035	ScalFact	1.10
2 N(14)		7.81983	6.82	12.28	3 N(14)		17.93792	17.94	12.28	2 N(14)		6.49748	6.50	12.28
3 N(14)		5.82257		-44.5%	2 N(14)		17.93544		46.1%	3 N(14)		6.49748		-47.1%
20 H(1)		6.40724	6.05	4.13	18 H(1)		5.22023	5.22	4.13	10 H(1)		5.52515	5.53	4.13
18 H(1)		5.69269		46.5%	10 H(1)		5.21968		26.4%	20 H(1)		5.52515		33.8%
10 H(1)		5.28448	3.98	2.9	20 H(1)		3.8489	3.85	2.9	8 H(1)		3.01726	3.02	2.9
8 H(1)		2.67606		37.3%	8 H(1)		3.84848		32.7%	18 H(1)		3.01726		4.0%
23 H(1)		2.33393	2.29	1.06	13 H(1)		1.91886	1.92	1.06	13 H(1)		1.86275	1.86	1.06
22 H(1)		2.24244		115.9%	22 H(1)		1.91877		81.0%	23 H(1)		1.86275		75.7%
13 H(1)		1.73385	1.01	0.89	23 H(1)		1.45297	1.45	0.89	12 H(1)		0.57369	0.57	0.89
12 H(1)		0.29175		13.8%	12 H(1)		1.45274		63.2%	22 H(1)		0.57369		-35.5%
28 F(19)		38.20753	15.51	7.92	28 F(19)		21.94359	12.26	7.92	29 F(19)		15.62268	10.42	7.92
29 F(19)		21.48015		95.8%	29 F(19)		21.94058		54.8%	31 F(19)		15.61988		31.6%
26 F(19)		17.04512			27 F(19)		13.48835			30 F(19)		15.61421		
30 F(19)		11.91139			30 F(19)		13.48703			28 F(19)		15.61148		
27 F(19)		3.25898			31 F(19)		1.3405			26 F(19)		0.03445		
31 F(19)		1.156			26 F(19)		1.34035			27 F(19)		0.03445		
21 C(13)		10.25063			4 C(13)		8.1258			11 C(13)		6.15071		
16 C(13)		6.91312	not observed		14 C(13)		8.12245			21 C(13)		6.1507		
11 C(13)		6.00131			15 C(13)		7.8072			6 C(13)		5.2037		
15 C(13)		5.97561			6 C(13)		7.80646			16 C(13)		5.2037		
6 C(13)		4.72371			21 C(13)		6.68941			5 C(13)		2.08022		
5 C(13)		1.38134			11 C(13)		6.68863			15 C(13)		2.08022		
24 C(13)		-3.83017			5 C(13)		4.13757			24 C(13)		-3.86138		
7 C(13)		-3.96817			16 C(13)		4.13743			25 C(13)		-3.86138		
25 C(13)		-6.04536			24 C(13)		-3.98929			7 C(13)		-4.40799		
9 C(13)		-6.07306			25 C(13)		-3.98972			17 C(13)		-4.40799		
4 C(13)		-6.24222			9 C(13)		-4.90424			19 C(13)		-6.31388		
17 C(13)		-8.39734			17 C(13)		-4.90489			9 C(13)		-6.31389		
19 C(13)		-8.67503			7 C(13)		-5.70154			4 C(13)		-8.32976		
14 C(13)		-12.1683			19 C(13)		-5.70221			14 C(13)		-8.32976		

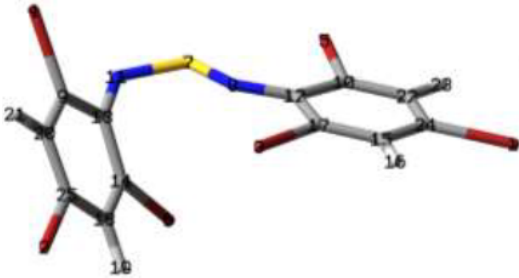
Table B.36. Cont'd

7 •-					Isotropic EPR hypofine coupling simulations										
EZconf1-pNO3-PhNSN-b3lypd3bj-6311+G2dp_anion_OF2					ZZconf1-pNO3-PhNSN-b3lypd3bj-6311++G2dp_anion_OF2					EEconf1-pNO2-PhNSN-b3lypd3bj-6311++G2dp_anion_OF					
Isotropic	Fermi	Couplings			Isotropic	Fermi	Couplings			Isotropic	Fermi	Couplings			
	Atom	MegaHertz	ScalFact	EasySpin	Agreements	Atom	MegaHertz	ScalFact	EasySpin	Agreements	Atom	MegaHertz	ScalFact	EasySpin	Agreemen
	1 S(33)	12.06655		1.99		1 S(33)	13.62248		1.99		1 S(33)	11.89031		1.47	
	2 N(14)	5.61656	4.87	10	-5.13	3 N(14)	14.56937	14.57	10	4.57	2 N(14)	5.1695	5.17	10	-4.83
	3 N(14)	4.12165			-51.3%	2 N(14)	14.56579			45.7%	3 N(14)	5.16947			-48.3%
	24 N(14)	-0.72199	-0.98	-0.64	-0.34	24 N(14)	-0.90676	-0.91	-0.64	-0.27	27 N(14)	-0.96781	-0.97	-0.64	-0.33
	27 N(14)	-1.24746			53.9%	27 N(14)	-0.90679			41.7%	24 N(14)	-0.96783			51.2%
	18 H(1)	4.62645	4.43	3.73	0.70	18 H(1)	3.88803	3.89	3.73	0.16	20 H(1)	4.13513	4.14	3.73	0.41
	20 H(1)	4.23811			18.8%	10 H(1)	3.88779			4.2%	10 H(1)	4.13512			10.9%
	10 H(1)	3.49115	2.76	3.01	-0.25	20 H(1)	3.02489	3.02	3.01	0.01	18 H(1)	2.67581	2.68	3.01	-0.33
	8 H(1)	2.02845			-8.3%	8 H(1)	3.02477			0.5%	8 H(1)	2.6758			-11.1%
	22 H(1)	1.34603	1.32	0.42	0.90	13 H(1)	1.36665	1.37	0.42	0.95	13 H(1)	1.67059	1.67	0.42	1.25
	13 H(1)	1.29306			214.2%	22 H(1)	1.36608			225.3%	23 H(1)	1.67059			297.8%
	23 H(1)	1.15574	0.88	0.19	0.69	23 H(1)	0.71152	0.71	0.19	0.52	12 H(1)	0.15856	0.16	0.19	-0.03
	12 H(1)	0.61254			365.3%	12 H(1)	0.71146			274.5%	22 H(1)	0.15855			-16.6%
	21 C(13)	8.06474	not observed			4 C(13)	7.23436				21 C(13)	5.52513			
	11 C(13)	4.57094				14 C(13)	7.23236				11 C(13)	5.52506			
	15 C(13)	4.53515				15 C(13)	5.95984				16 C(13)	3.72826			
	16 C(13)	3.82271				6 C(13)	5.95914				6 C(13)	3.72825			
	6 C(13)	2.74709				11 C(13)	5.58669				15 C(13)	1.37169			
	5 C(13)	0.33156				21 C(13)	5.58666				5 C(13)	1.37168			
	7 C(13)	-2.41041				5 C(13)	3.20435				7 C(13)	-3.27927			
	4 C(13)	-3.40083				16 C(13)	3.20244				17 C(13)	-3.27929			
	9 C(13)	-4.4834				9 C(13)	-3.63524				9 C(13)	-5.24483			
	19 C(13)	-6.01242				17 C(13)	-3.63541				19 C(13)	-5.24485			
	17 C(13)	-6.22428				7 C(13)	-4.18988				4 C(13)	-6.11111			
	14 C(13)	-8.30527				19 C(13)	-4.19026				14 C(13)	-6.11114			
	26 O(17)	-1.49861	not observed			26 O(17)	-1.50949				26 O(17)	-1.30117			
	25 O(17)	-1.91704				28 O(17)	-1.50955				29 O(17)	-1.3012			
	28 O(17)	-2.41545				25 O(17)	-1.66877				25 O(17)	-1.74203			
	29 O(17)	-2.47996				29 O(17)	-1.66887				28 O(17)	-1.74207			

Table B.36. Cont'd

8 •- Isotropic EPR hypofine coupling simulations																	
EZ-F3PhNSN-b3lypd3bj-6311++G2dp_anion_OF						ZZ-F3-PhNSN-b3lypd3bj-6311++G2dp_anion_OF						EEconf1-F3PhNSN-b3lypd3bj-6311++G2dp_anion_OF					
Isotropic	Fermi	Couplings				Isotropic	Fermi	Couplings				Isotropic	Fermi	Couplings			
	Atom	MegaHertz		EasySpin	Agreements		Atom	MegaHertz		EasySpin	Agreements		Atom	MegaHertz		EasySpin	Agreemen
	1 S(33)	12.80373	ScalFact	1.07			1 S(33)	15.29346	ScalFact	1.21			1 S(33)	12.11444	ScalFact	1.03	
	2 N(14)	16.67047	11.29	12.79	-1.50		2 N(14)	18.39721	18.40	12.79	5.61		2 N(14)	6.87384	6.87	12.79	-5.92
	3 N(14)	5.91941			-11.7%		3 N(14)	18.39721			43.8%		3 N(14)	6.87384			-46.3%
	18 H(1)	2.50028	2.32	1.42	0.90		11 H(1)	2.67015	2.67	1.42	1.25		11 H(1)	2.18347	2.18	1.42	0.76
	11 H(1)	2.14781			63.7%		18 H(1)	2.67015			88.0%		19 H(1)	2.18347			53.8%
	10 H(1)	1.78147	1.60	1.41	0.19		10 H(1)	1.56506	1.57	1.41	0.16		10 H(1)	1.87509	1.88	1.41	0.47
	19 H(1)	1.41606			13.4%		19 H(1)	1.56506			11.0%		18 H(1)	1.87509			33.0%
	20 F(19)	5.59576					20 F(19)	6.72392					20 F(19)	10.47014			
	21 F(19)	10.35235	6.96	11.38	-4.42		21 F(19)	6.72392	4.66	11.38	-6.72		21 F(19)	10.47014	8.16	11.38	-3.22
	22 F(19)	1.23765	in plane		-38.8%		22 F(19)	5.47318			-59.0%		22 F(19)	4.70934			-28.3%
	23 F(19)	6.25828	9.56	11.38	-1.82		23 F(19)	1.78867	4.66	11.38	-6.72		23 F(19)	9.31167	8.16	11.38	-3.22
	24 F(19)	4.51895			-16.0%		24 F(19)	1.78867			-59.0%		24 F(19)	9.31167			-28.3%
	25 F(19)	13.79814					25 F(19)	5.47318					25 F(19)	4.70934			
	4 C(13)	-9.67501	not observed				4 C(13)	-2.86988					4 C(13)	-11.5197			
	5 C(13)	5.11563					5 C(13)	12.98648					5 C(13)	5.59218			
	6 C(13)	7.68689					6 C(13)	12.69397					6 C(13)	8.01292			
	7 C(13)	-6.47934					7 C(13)	-4.93764					7 C(13)	-6.59063			
	8 C(13)	-7.40322					8 C(13)	-2.64486					8 C(13)	-7.53627			
	9 C(13)	8.5687					9 C(13)	5.80218					9 C(13)	8.53026			
	12 C(13)	-5.27185					12 C(13)	-2.86988					12 C(13)	-11.5197			
	13 C(13)	15.24909					13 C(13)	12.69397					13 C(13)	5.59218			
	14 C(13)	12.79205					14 C(13)	12.98648					14 C(13)	8.01292			
	15 C(13)	-2.07455					15 C(13)	-2.64486					15 C(13)	-6.59063			
	16 C(13)	-3.84539					16 C(13)	-4.93764					16 C(13)	-7.53627			
	17 C(13)	4.61771					17 C(13)	5.80218					17 C(13)	8.53026			

Table B.36. Cont'd

9 •-					Isotropic EPR hpefine coupling simulations									
Br3phNSN-B3LYPd3bj-6311++2dp-anion_OF2					EZCONF1-BISBr3PhNSN-B3LYPd3bj-6311++G2dp_Anion_OF					EEconf1-Br3-PhNSN-b3lypD3bj-6311++G2dp_ANION_OF				
Isotropic	Fermi	Couplings			Isotropic	Fermi	Couplings			Isotropic	Fermi	Couplings		
Atom	MegaHertz		EasySpin	Agreements	Atom	MegaHertz		EasySpin	Agreements	Atom	MegaHertz		EasySpin	Agreemer
7 S(33)	13.87698	ScalFact	0.93		7 S(33)	14.46781	ScalFact	1.40		1 S(33)	13.89145	ScalFact	1.01	
11 N(14)	18.07817	10.80	15.65	-4.85	8 N(14)	17.38798	17.37	15.65	1.72	3 N(14)	5.53155	5.53	15.65	-10.12
8 N(14)	3.52034			-31.0%	11 N(14)	17.35737			11.0%	2 N(14)	5.53151			-64.7%
19 H(1)	2.57484	2.34	1.89	0.45	21 H(1)	4.32615	4.32	1.89	2.43	11 H(1)	2.60492	2.60	1.89	0.71
23 H(1)	2.09881			23.6%	16 H(1)	4.32374			128.8%	19 H(1)	2.6049			37.8%
16 H(1)	1.60377	1.43	1.63	-0.20	19 H(1)	1.28782	1.29	1.63	-0.34	10 H(1)	2.11238	2.11	1.63	0.48
21 H(1)	1.25908			-12.2%	23 H(1)	1.28446			-21.1%	18 H(1)	2.11238			29.6%
9 C(13)	28.27477	not observed			14 C(13)	28.90391				9 C(13)	11.25135			
14 C(13)	20.49696				10 C(13)	28.87901				17 C(13)	11.25128			
24 C(13)	9.6312				9 C(13)	10.61887				6 C(13)	10.37862			
10 C(13)	8.15322				17 C(13)	10.58325				14 C(13)	10.37849			
17 C(13)	4.39462				25 C(13)	7.2204				5 C(13)	6.47462			
25 C(13)	3.97649				24 C(13)	7.21155				13 C(13)	6.4746			
18 C(13)	0.45785				15 C(13)	-1.93906				15 C(13)	-6.74793			
20 C(13)	-2.00704				20 C(13)	-1.95147				7 C(13)	-6.74796			
12 C(13)	-4.30567				22 C(13)	-4.39286				16 C(13)	-7.87039			
15 C(13)	-5.50266				18 C(13)	-4.39646				8 C(13)	-7.87045			
22 C(13)	-6.53716				12 C(13)	-5.56012				12 C(13)	-10.2077			
13 C(13)	-10.935				13 C(13)	-5.64054				4 C(13)	-10.2078			
5 Br(79)	1.64328	not observed			2 Br(79)	0.7735				21 Br(79)	1.28706			
6 Br(79)	1.06276				1 Br(79)	0.77213				20 Br(79)	1.28705			
1 Br(79)	0.91571				6 Br(79)	-0.07525				25 Br(79)	0.85642			
3 Br(79)	0.3876				5 Br(79)	-0.07604				22 Br(79)	0.8564			
2 Br(79)	0.38281				4 Br(79)	-1.10196				23 Br(79)	-0.31569			
4 Br(79)	0.16446				3 Br(79)	-1.12111				24 Br(79)	-0.31605			
														

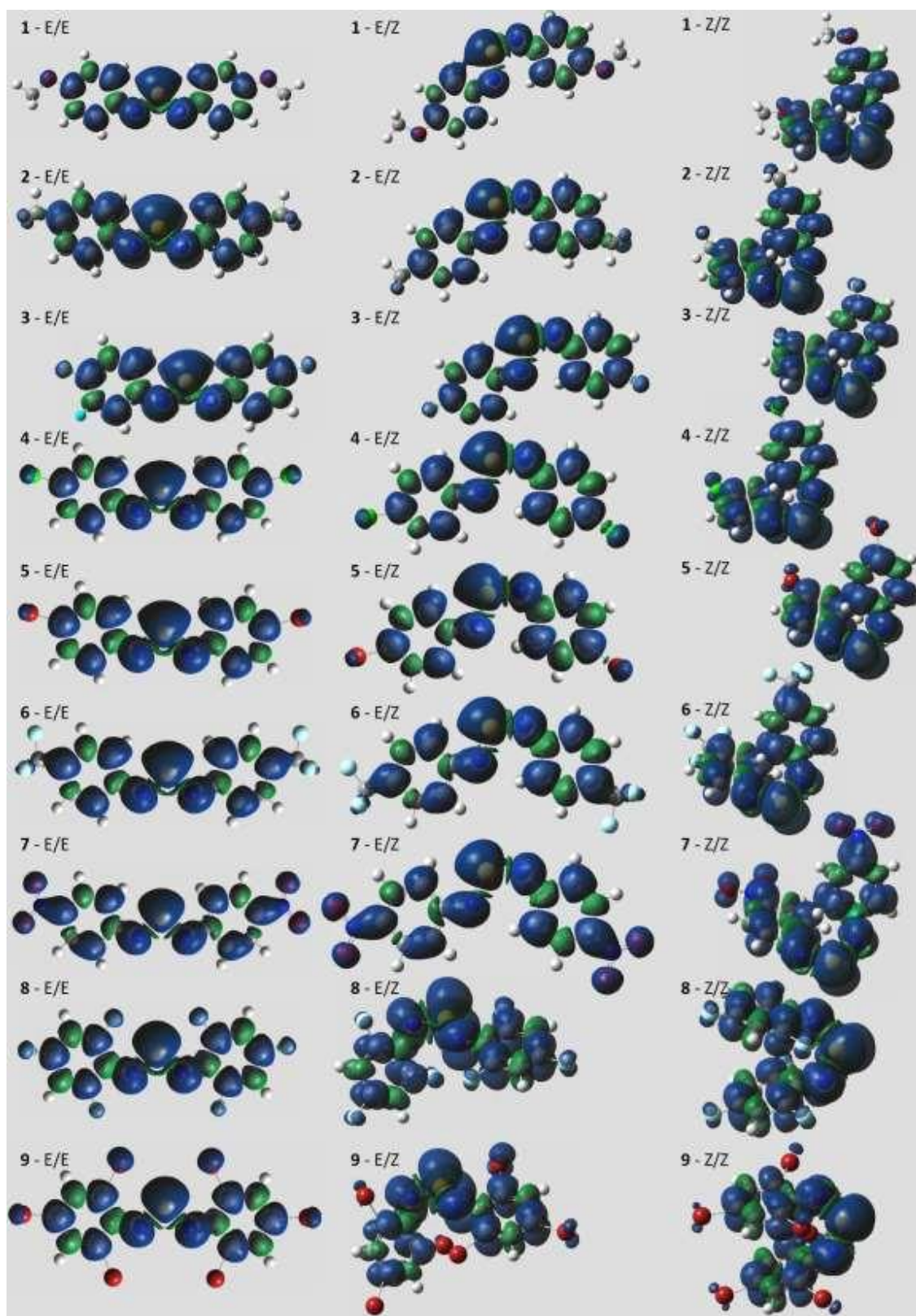


Figure B.84. Spin density surface plots from DFT computation at the 6311++G(2d,p) level of theory for each of the three possible conformations of $[1^{\cdot-}-9^{\cdot-}]$.

B.11. UV-Visible Spectroscopy Data Tables and Figures

Table B.37. UV-visible spectroscopy data of **1-9**.

Compound	MW (g/mol)	Conc (mol/L)	λ max (nm)	λ max Abs	ϵ at λ max
1	274.3288	0.000110	453.1	1.624	1.48×10^4
2	242.33	0.000172	431.0	1.911	1.11×10^4
3	250.2594	0.000192	418.3	1.585	8.26×10^3
4	283.168	0.000226	427.0	2.025	8.96×10^3
5	372.0706	0.000113	427.9	1.494	1.32×10^4
6	350.273	0.000191	406.2	1.429	7.49×10^3
7	304.2736	0.000166	425.9	0.922	5.57×10^3
8	322.2214	0.000340	350.1	1.677	4.93×10^3
9	687.655	0.000156	353.4	0.562	3.59×10^3

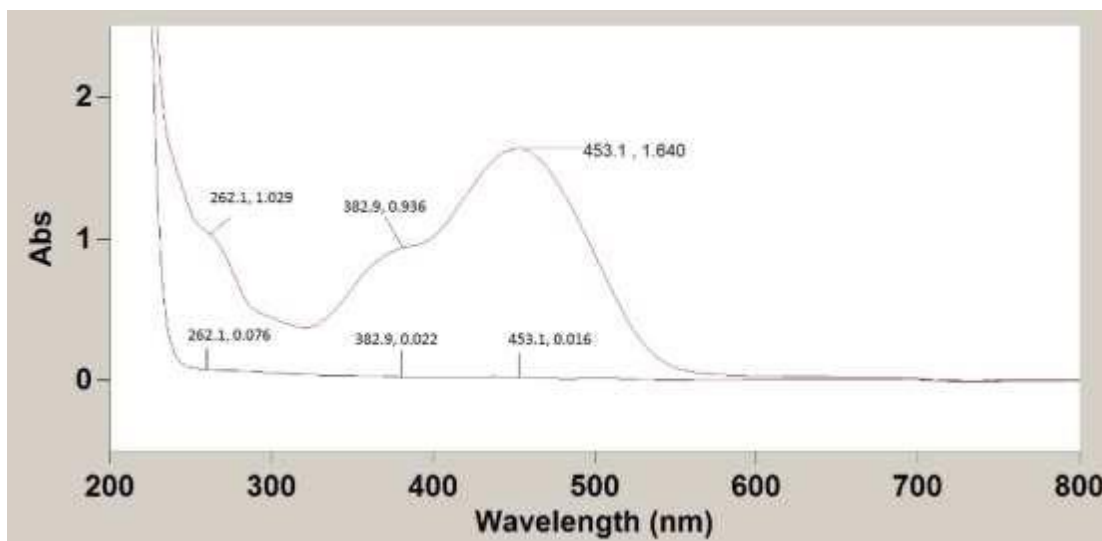


Figure B.85. UV-visible spectrum of 1.1×10^{-4} M solution of **1** in CH_2Cl_2 . Experimental and Blank runs.

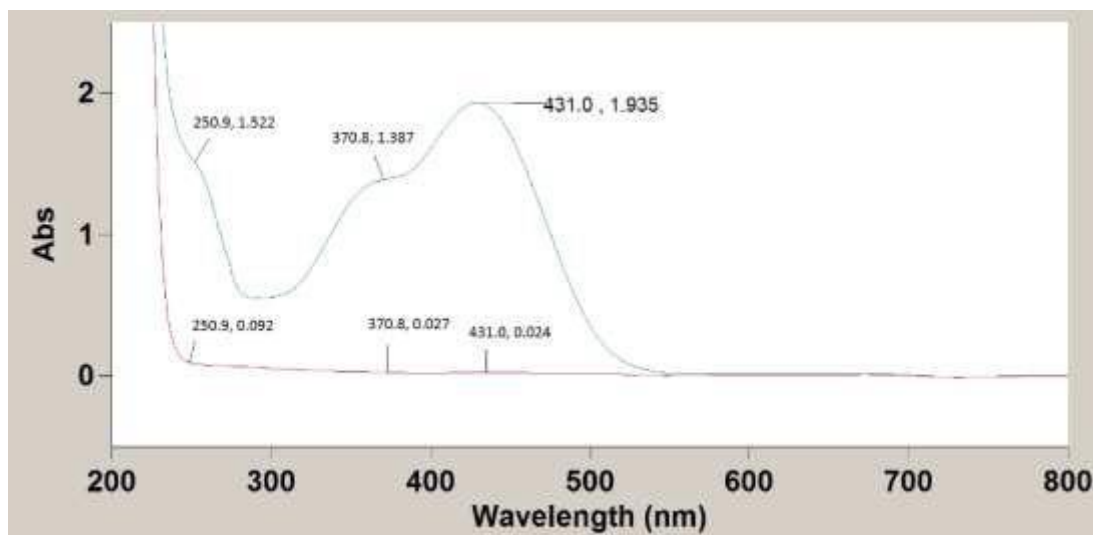


Figure B.86. UV-visible spectrum of 1.7×10^{-4} M solution of **2** in CH_2Cl_2 . Experimental and Blank runs.

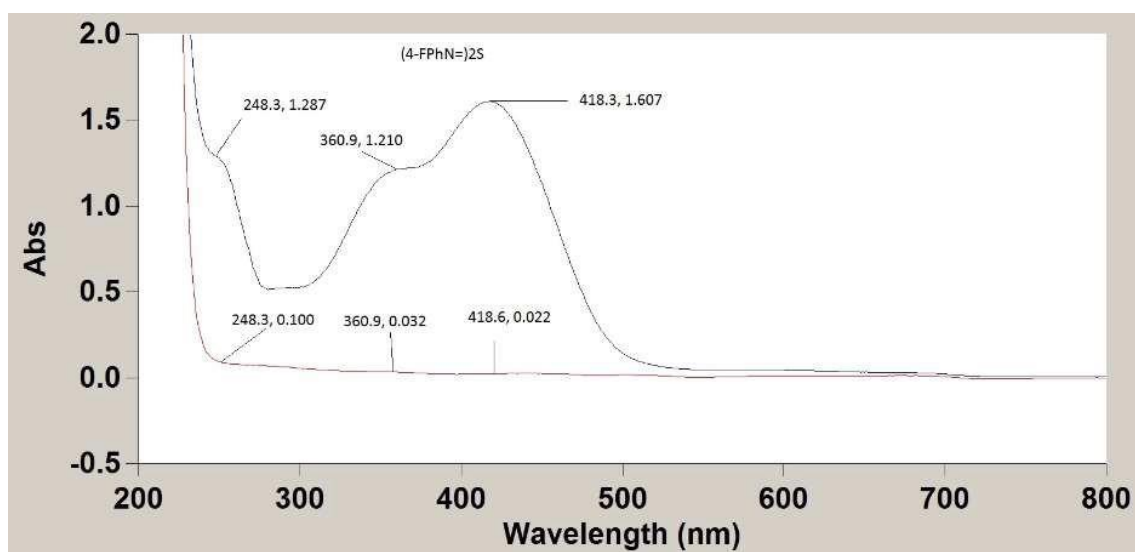


Figure B.87. UV-visible spectrum of 1.9×10^{-4} M solution of **3** in CH_2Cl_2 . Experimental and Blank runs.

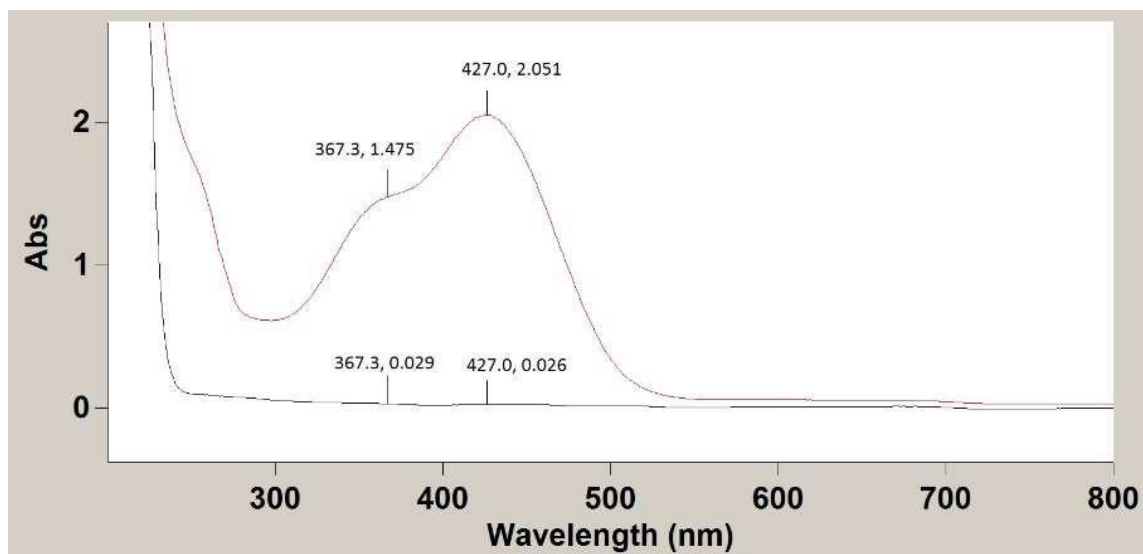


Figure B.88. UV-visible spectrum of 2.3×10^{-4} M solution of **4** in CH_2Cl_2 . Experimental and Blank runs.

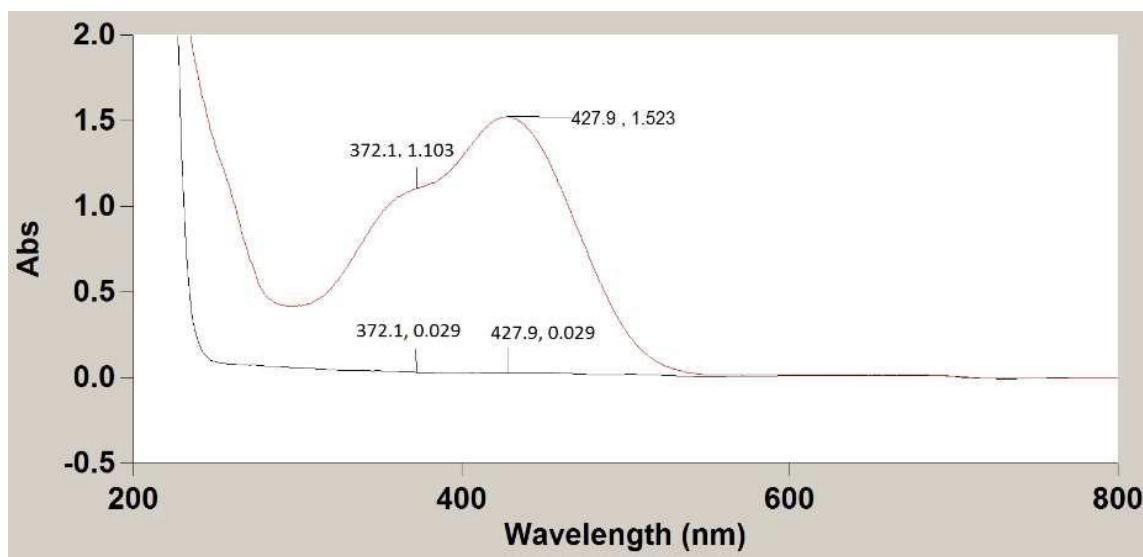


Figure B.89. UV-visible spectrum of 1.1×10^{-4} M solution of **5** in CH_2Cl_2 . Experimental and Blank runs included.

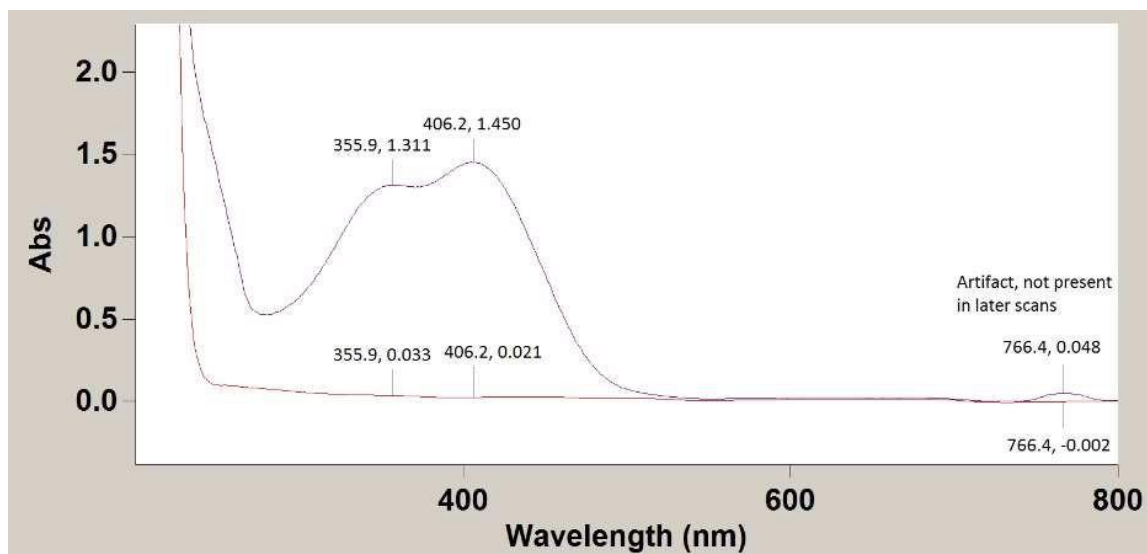


Figure B.90. UV-visible spectrum of 1.9×10^{-4} M solution of **6** in CH_2Cl_2 . Experimental and Blank runs included.

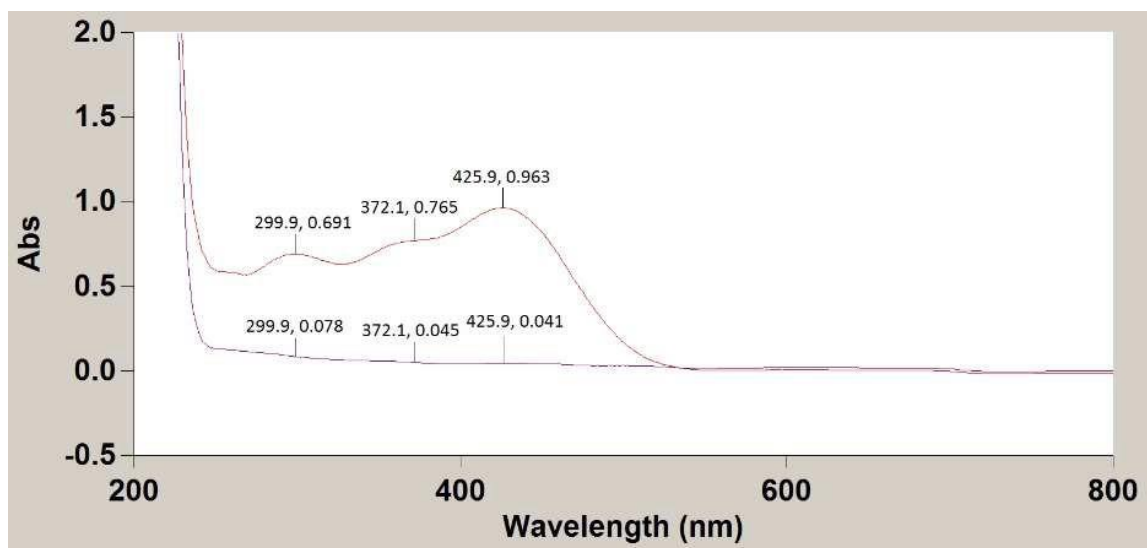


Figure B.91. UV-visible spectrum of 1.7×10^{-4} M solution of **7** in CH_2Cl_2 . Experimental and Blank runs included.

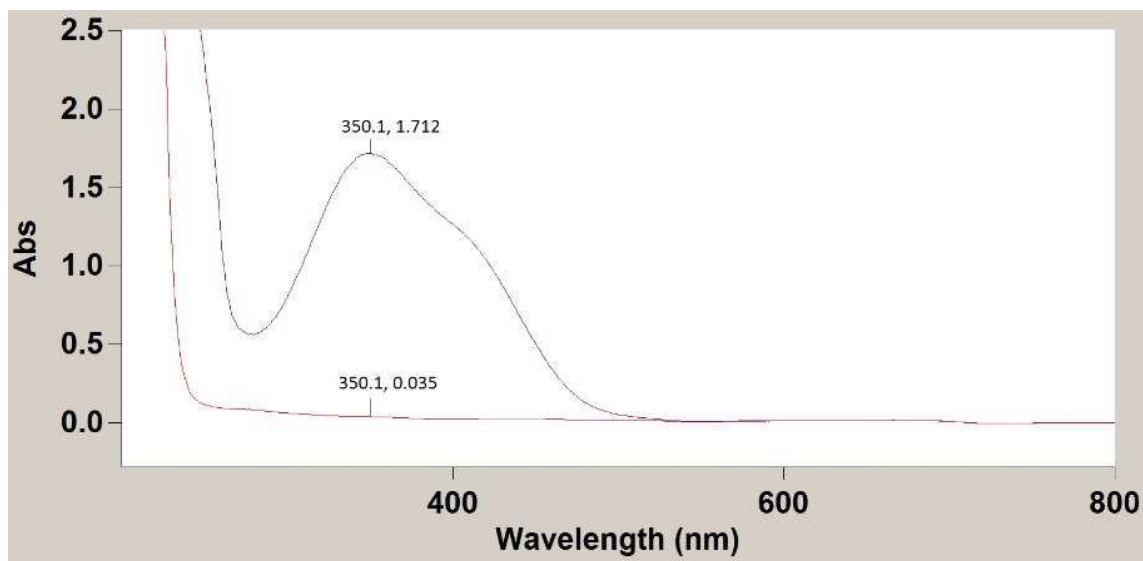


Figure B.92. UV-visible spectrum of 3.4×10^{-4} M solution of **8** in CH_2Cl_2 . Experimental and Blank runs included.

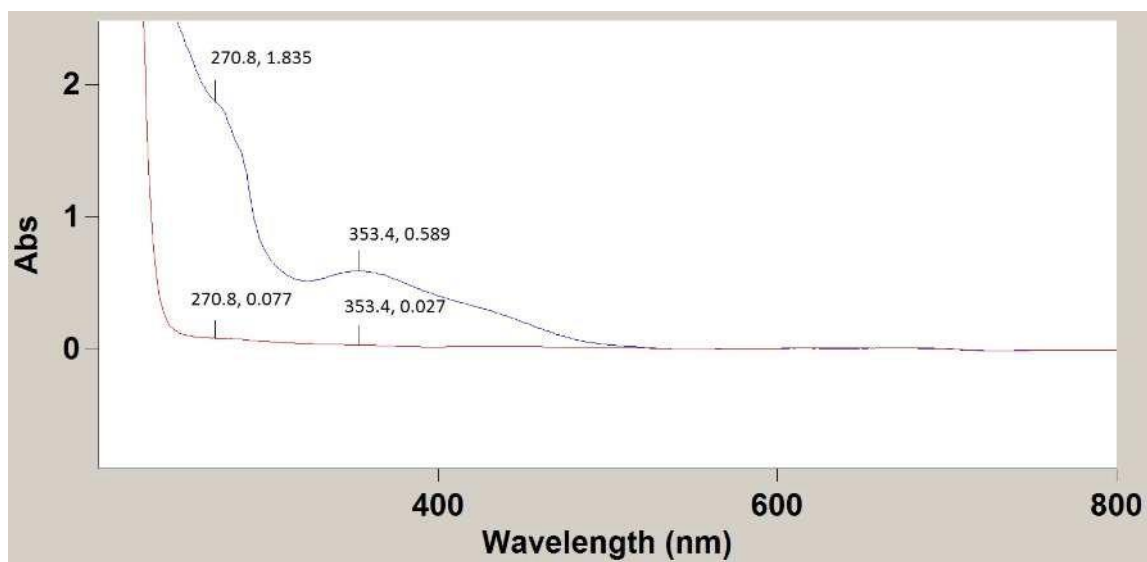


Figure B.93. UV-visible spectrum of 1.6×10^{-4} M solution of **9** in CH_2Cl_2 . Experimental and Blank runs included.

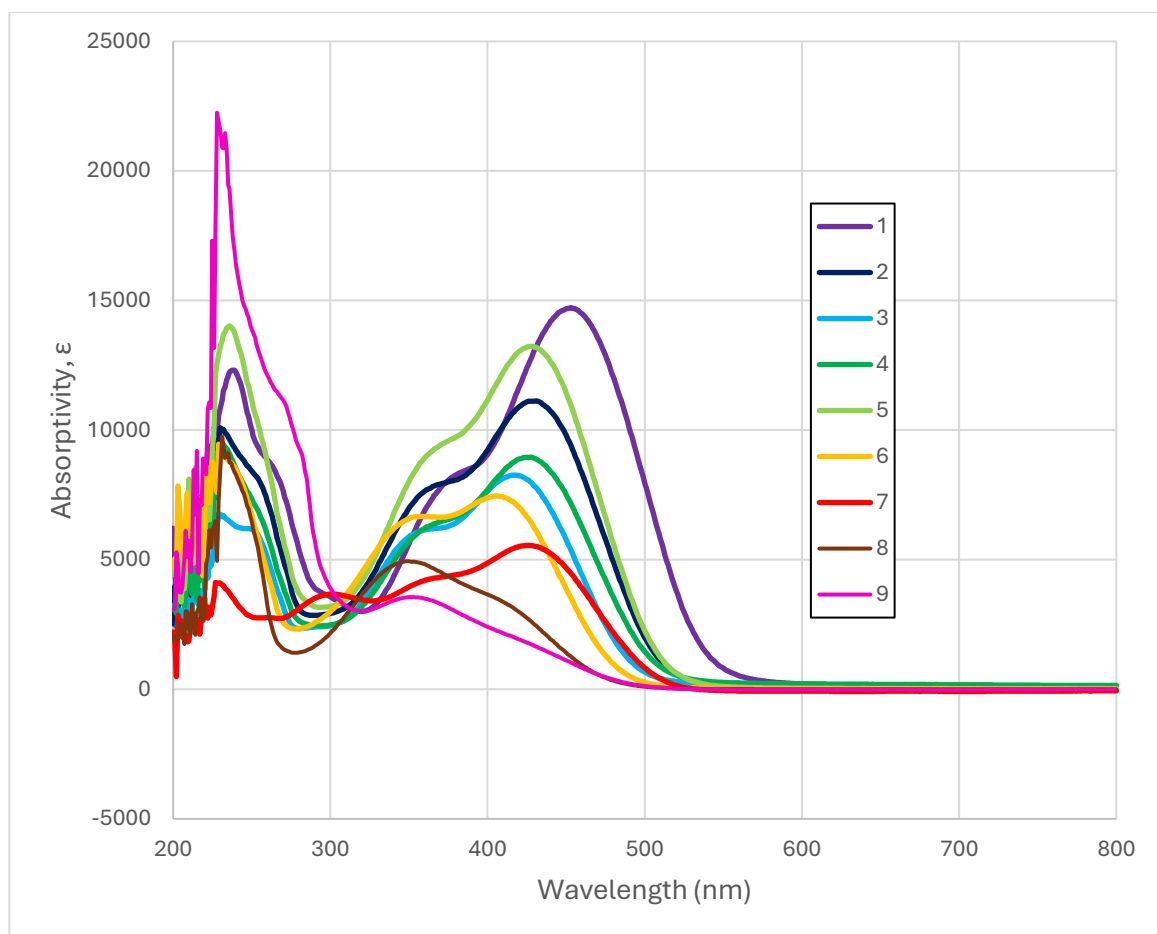


Figure B.94. Composite UV-visible spectrum of **1-9**. Y-axis in units of molar absorptivity, ϵ .

B.12. TD-DFT Derived Simulations for UV-visible Spectroscopy, Data Tables and Figures

Table B.38. TD-DFT calculated peaks and oscillator strengths (OS)

Compound	Conformation	$\lambda_{1/4}$ (nm)	OS	$\lambda_{2/5}$ (nm)	OS	$\lambda_{3/6}$ (nm)	OS
1	EZ	456.51	0.7965	339.83	0.1631	278.93	0.0329
2	EZ	433.09	0.7132	336.54	0.1706	282.00	0.0147
3	EZ	421.73	0.6269	331.88	0.1561	275.87	0.0125
		272.34	0.0048	267.48	0.0040	257.69	0.0434
4	EZ	429.59	0.7715	336.66	0.1715	279.93	0.0177
5	EZ	430.57	0.8178	337.56	0.1814	280.71	0.0208
6	EZ	409.85	0.6740	334.88	0.1945	282.94	0.0126
7	EZ	432.16	0.9445	345.40	0.1779	311.93	0.0007
8	ZZ	719.12	0.0000*	510.32	0.0000*	401.12	0.0556
		353.20	0.0000*	342.51	0.1774	337.13	0.0000*
9	ZZ	412.77	0.0326	333.83	0.1151	291.36	0.0004

*Peaks with zero oscillator strength included for completeness

Table B.39. Principal experimental peaks and absorbances

Compound	λ_1	$\epsilon_1 (\times 10^3)$	λ_2	$\epsilon_2 (\times 10^3)$
1	453.1	14.8	382.9	8.33
2	431.0	11.1	370.8	7.92
3	418.3	8.26	360.9	6.14
4	427.0	8.96	367.3	6.40
5	427.9	13.2	372.1	9.51
6	406.2	7.49	355.9	6.70
7	425.9	5.57	372.1	4.35
8	407*	3.5	350.1	4.93
9	428*	1.8	353.4	3.59

* λ_1 and ϵ_1 for **8** and **9** are estimated due to poorly resolved peaks

Table B.40. Experimental vs TD-DFT (EE conformation) UV-vis peak data

Compound	Experimental		TD-DFT		Difference (nm)		Difference (%)	
	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2
1	453.1	382.9	519.73	347.23	66.6	35.7	14.7	4.2
2	431.0	370.8	479.14	341.12	48.1	29.7	11.2	3.3
3	418.3	360.9	468.5	335.97	50.2	24.9	12.0	3.6
4	427.0	367.3	474.28	340.64	47.3	26.7	11.1	3.3
5	427.9	372.1	474.87	341.32	47.0	30.8	11.0	3.2
6	406.2	355.9	447.57	336.32	41.4	19.6	10.2	3.0
7	425.9	372.1	464.91	350.33	39.0	21.8	9.2	2.6
8	407*	350.1	473.23	372.82	66	22.7	18.9	5.1
9	428*	353.4	427.09	295.67	1	57.7	0.3	0.1
				Average	45.2	29.9	10.9	3.1
				Std Dev	18.1	10.9	4.7	1.3

* λ_1 for **8** and **9** are estimated due to poorly resolved peaks

Table B.41. Experimental vs TD-DFT (EZ conformation) UV-vis peak data

Compound	Experimental		TD-DFT		Difference (nm)		Difference (%)	
	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2
1	453.1	382.9	456.51	339.83	3.4	43.1	0.8	0.2
2	431.0	370.8	433.09	336.54	2.1	34.3	0.5	0.1
3	418.3	360.9	421.73	331.88	3.4	29.0	0.8	0.2
4	427.0	367.3	429.59	336.66	2.6	30.6	0.6	0.2
5	427.9	372.1	430.57	337.56	2.7	34.5	0.6	0.2
6	406.2	355.9	409.85	334.88	3.7	21.0	0.9	0.3
7	425.9	372.1	432.16	345.4	6.3	26.7	1.5	0.4
8	407*	350.1	409.02	322.94	2	27.2	0.5	0.2
9	428*	353.4	390.18	349.75	38	3.6	8.8	2.5
				Average	7.1	27.8	1.7	0.5
				Std Dev	10.9	10.3	2.6	0.7

* λ_1 for 8 and 9 are estimated due to poorly resolved peaks

Table B.42. Experimental vs TD-DFT (ZZ conformation) UV-vis peak data

Compound	Experimental		TD-DFT		Difference (nm)		Difference (%)	
	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2
1	453.1	382.9	414.39	405.69	38.7	22.8	8.5	2.1
2	431.0	370.8	402.74	385.3	28.3	14.5	6.6	1.7
3	418.3	360.9	394.08	379.39	24.2	18.5	5.8	1.5
4	427.0	367.3	407.66	367.05	19.3	0.3	4.5	1.2
5	427.9	372.1	411.85	358.41	16.1	13.7	3.8	1.0
6	406.2	355.9	396.65	336.03	9.6	19.9	2.4	0.7
7	425.9	372.1	398.58	352.47	27.3	19.6	6.4	1.8
8	407*	350.1	401.12	353.2	6	3.1	1.4	0.4
9	428*	353.4	412.77	333.83	15	19.6	3.6	1.1
				Average	20.5	14.7	4.8	1.3
				Std Dev	9.6	7.4	2.1	0.5

* λ_1 for 8 and 9 are estimated due to poorly resolved peaks

Table B.43. Experimental vs Best Fit TD-DFT UV-vis peak data

Compd	Conf	Experimental		TD-DFT		Difference (nm)		Difference (%)	
		λ_1	λ_2	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2
1	EZ	453.1	382.9	456.51	339.83	3.4	43.1	0.8	0.2
2	EZ	431.0	370.8	433.09	336.54	2.1	34.3	0.5	0.1
3	EZ	418.3	360.9	421.73	331.88	3.4	29.0	0.8	0.2
4	EZ	427.0	367.3	429.59	336.66	2.6	30.6	0.6	0.2
5	EZ	427.9	372.1	430.57	337.56	2.7	34.5	0.6	0.2
6	EZ	406.2	355.9	409.85	334.88	3.7	21.0	0.9	0.3
7	EZ	425.9	372.1	432.16	345.4	6.3	26.7	1.5	0.4
8	ZZ	407*	350.1	401.12	353.2	6	3.1	1.7	0.5
9	ZZ	428*	353.4	412.77	333.83	15	19.6	4.3	1.3
					Average	5.0	26.9	1.3	0.4
					Std Dev	3.9	10.8	1.1	0.3

* λ_1 for 8 and 9 are estimated due to poorly resolved peaks

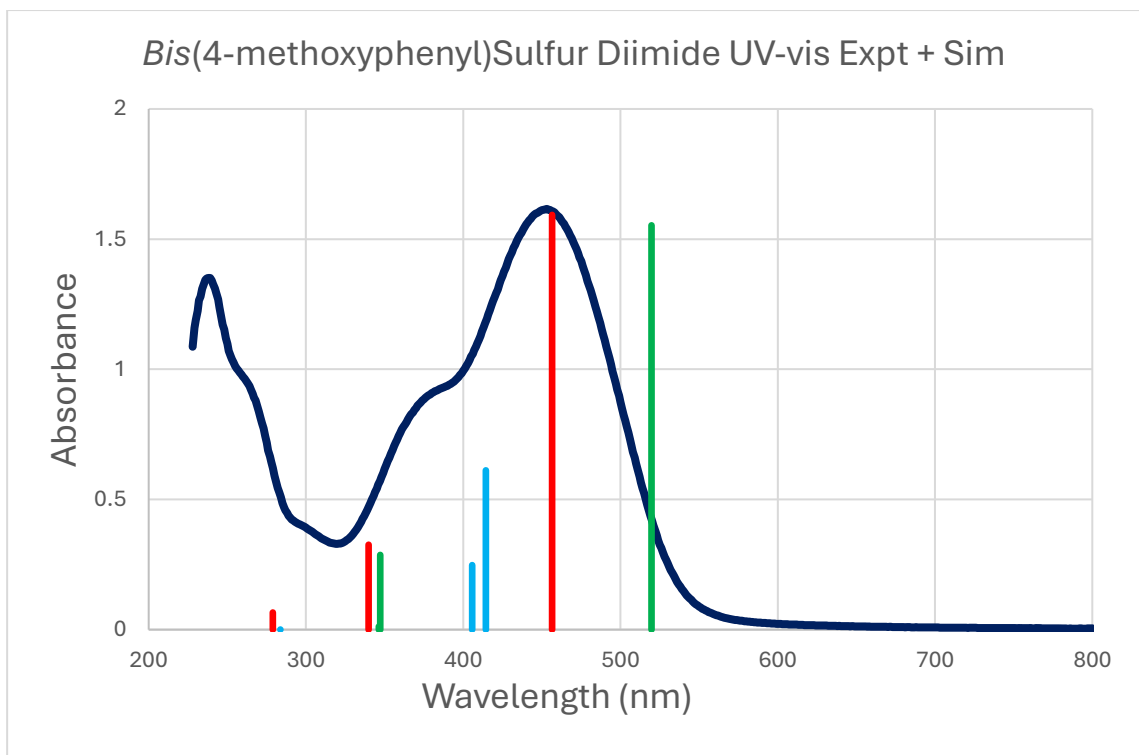


Figure B.95. UV-vis spectrum of **1** (dark blue trace) with simulated peaks from TD-DFT calculations of the possible conformers (EE = Green, EZ = Red, ZZ = Light Blue)

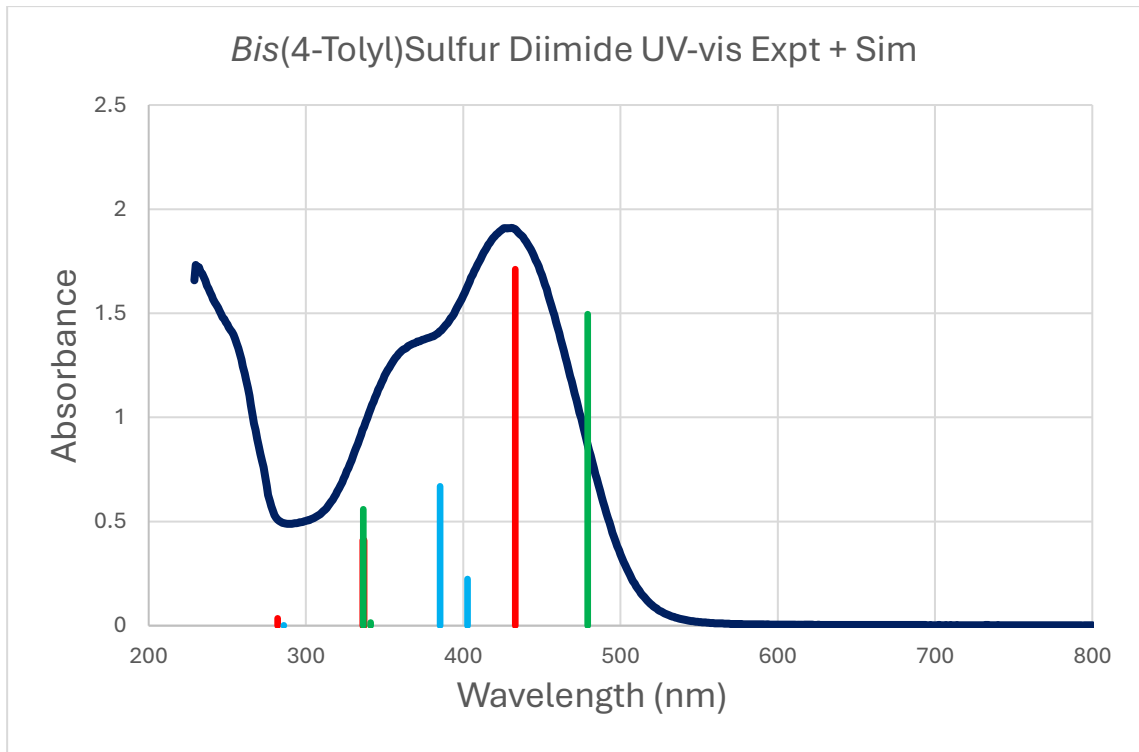


Figure B.96. UV-vis spectrum of **2** (dark blue trace) with simulated peaks from TD-DFT calculations of the possible conformers (EE = Green, EZ = Red, ZZ = Light Blue)

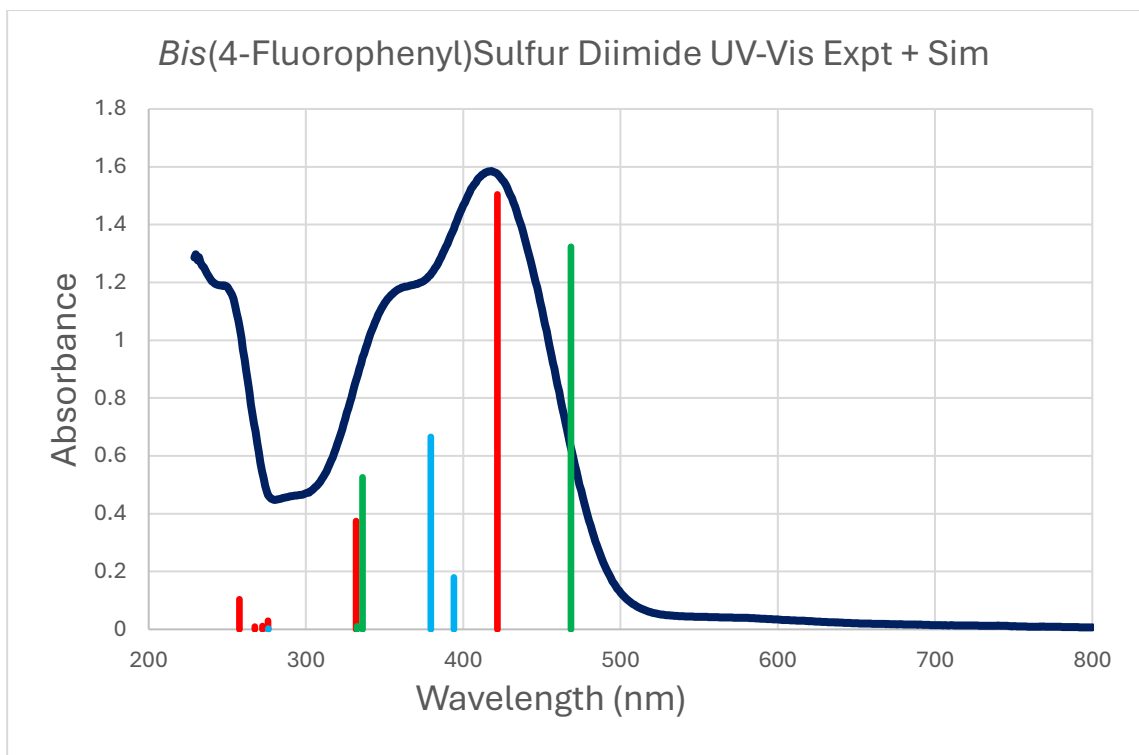


Figure B.97. UV-vis spectrum of **3** (dark blue trace) with simulated peaks from TD-DFT calculations of the possible conformers (EE = Green, EZ = Red, ZZ = Light Blue)

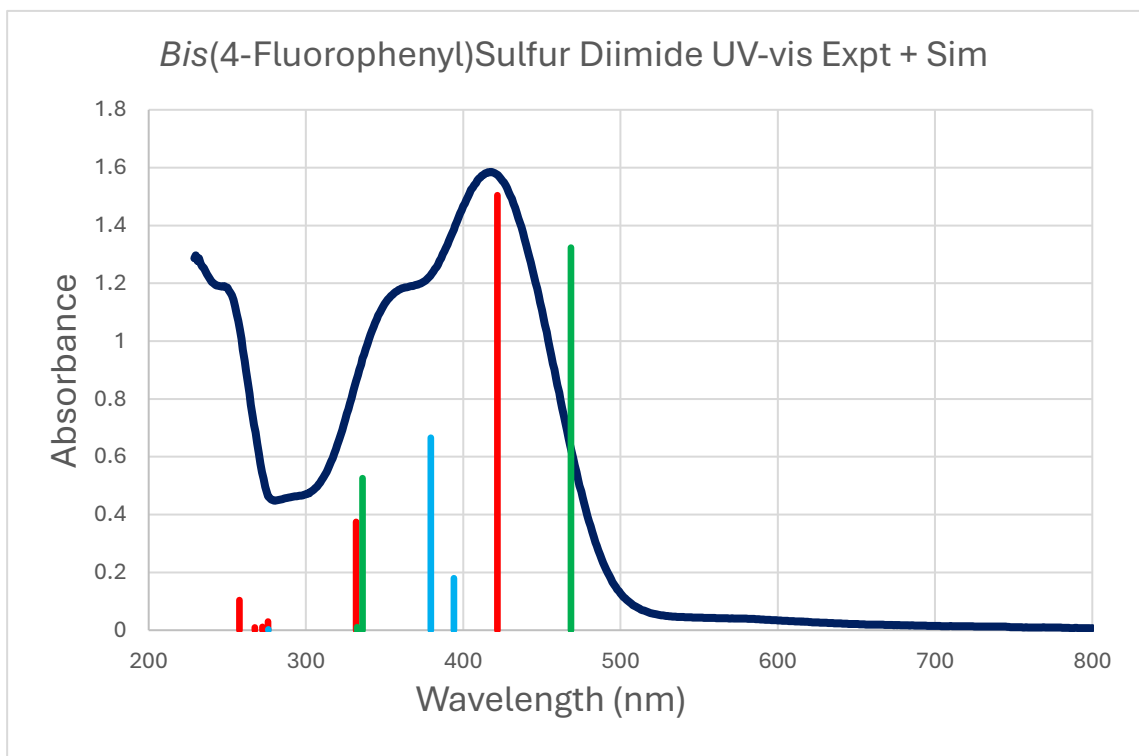


Figure B.98. UV-vis spectrum of **4** (dark blue trace) with simulated peaks from TD-DFT calculations of the possible conformers (EE = Green, EZ = Red, ZZ = Light Blue)

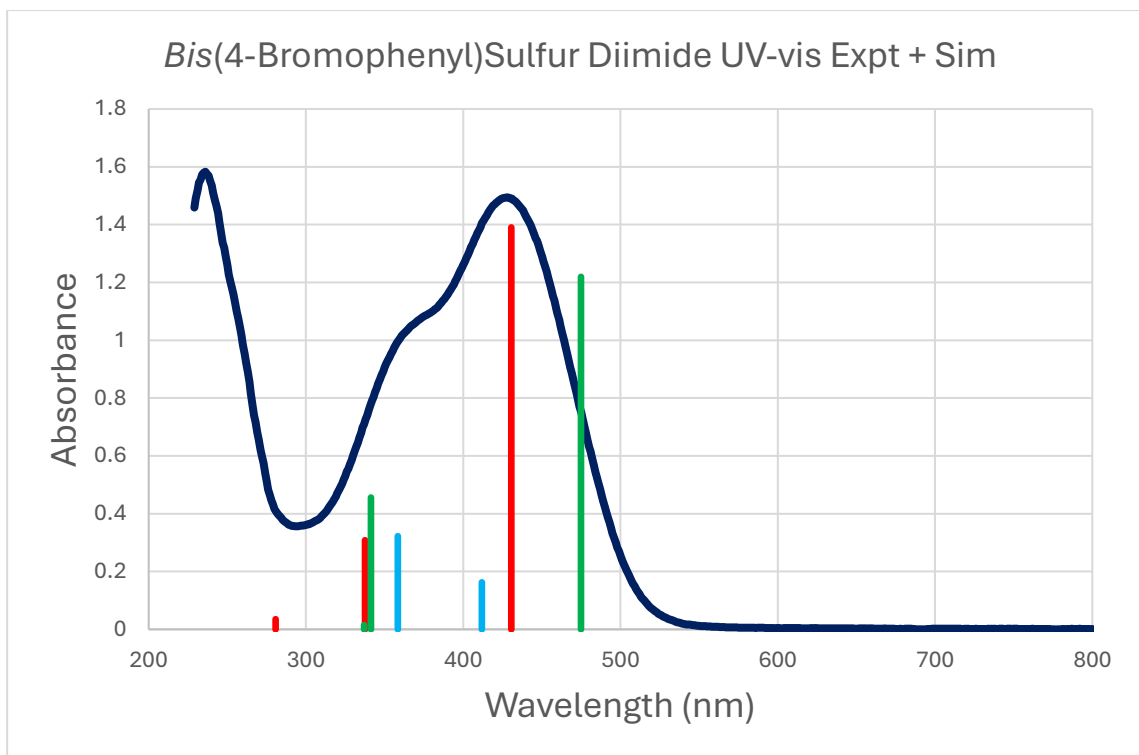


Figure B.99. UV-Vis spectrum of **5** (dark blue trace) with simulated peaks from TD-DFT calculations of the possible conformers (EE = Green, EZ = Red, ZZ = Light Blue)

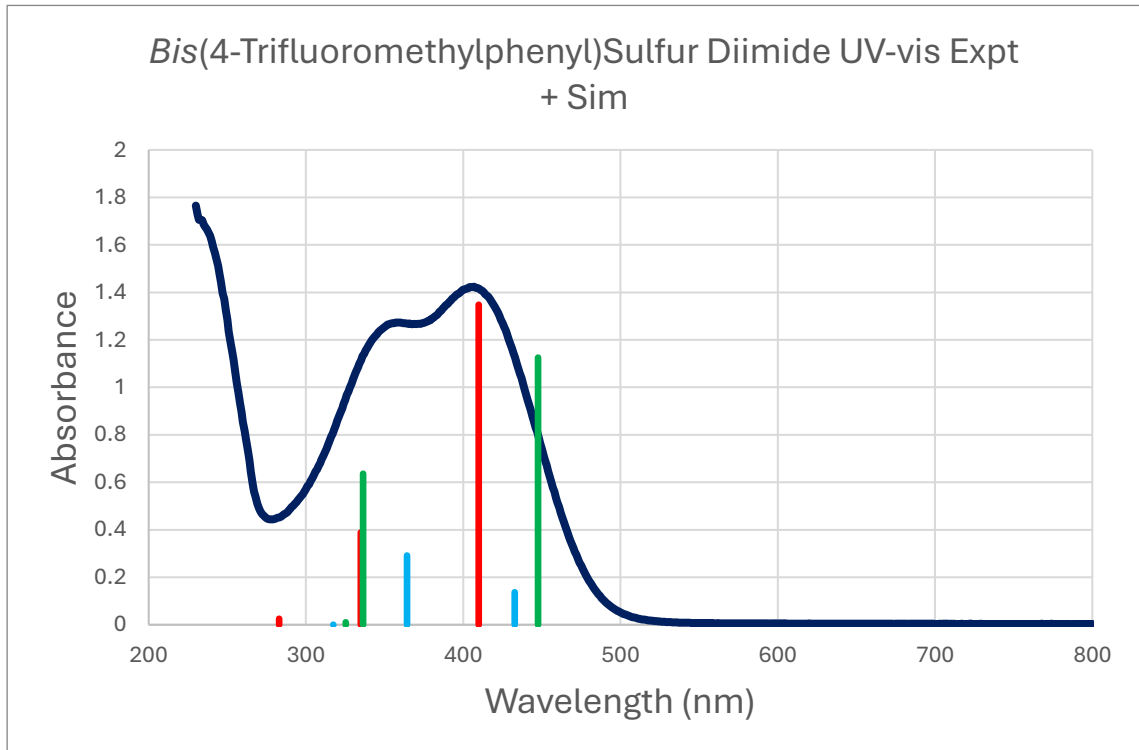


Figure B.100. UV-Vis spectrum of **6** (dark blue trace) with simulated peaks from TD-DFT calculations of the possible conformers (EE = Green, EZ = Red, ZZ = Light Blue)

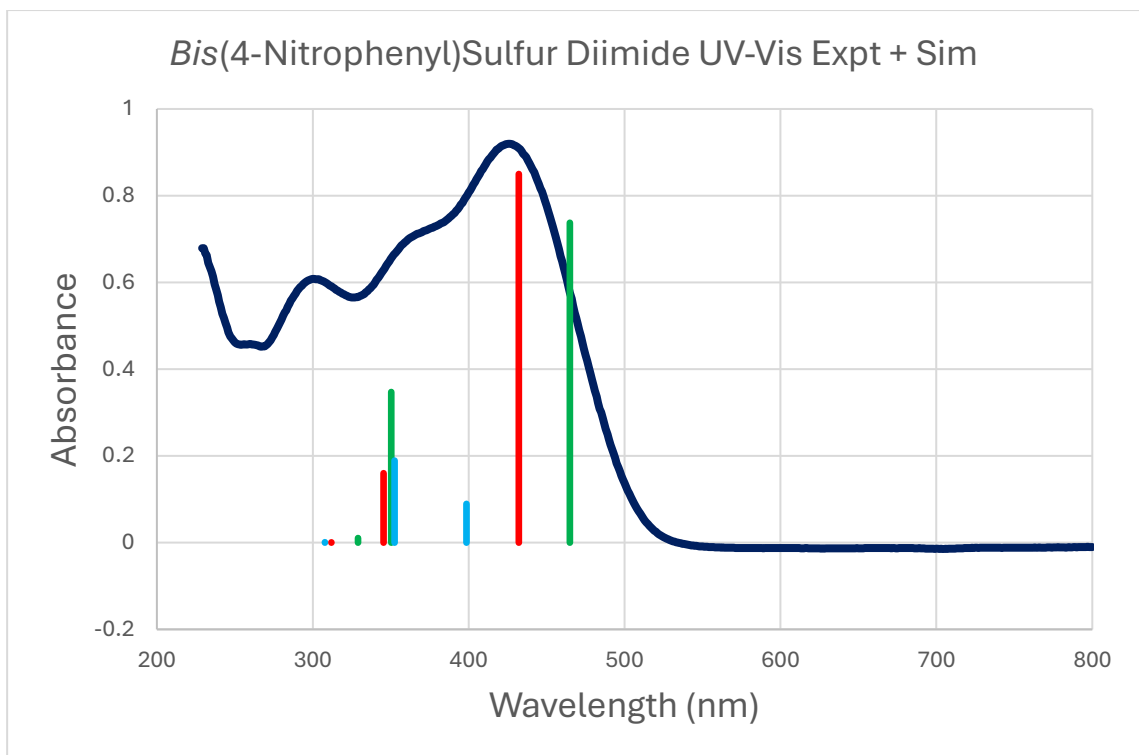


Figure B.101. UV-Vis spectrum of **7** (dark blue trace) with simulated peaks from TD-DFT calculations of the possible conformers (EE = Green, EZ = Red, ZZ = Light Blue)

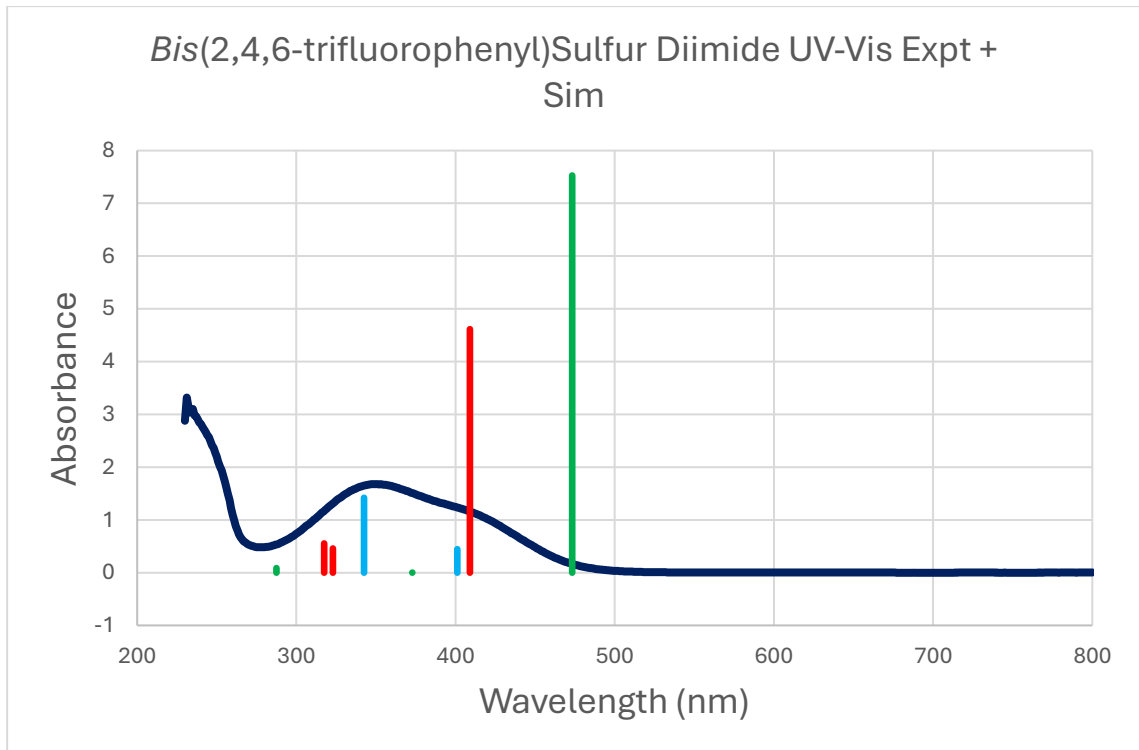


Figure B.102. UV-Vis spectrum of **8** (dark blue trace) with simulated peaks from TD-DFT calculations of possible conformers (EE = Green, EZ = Red, ZZ = Light Blue)

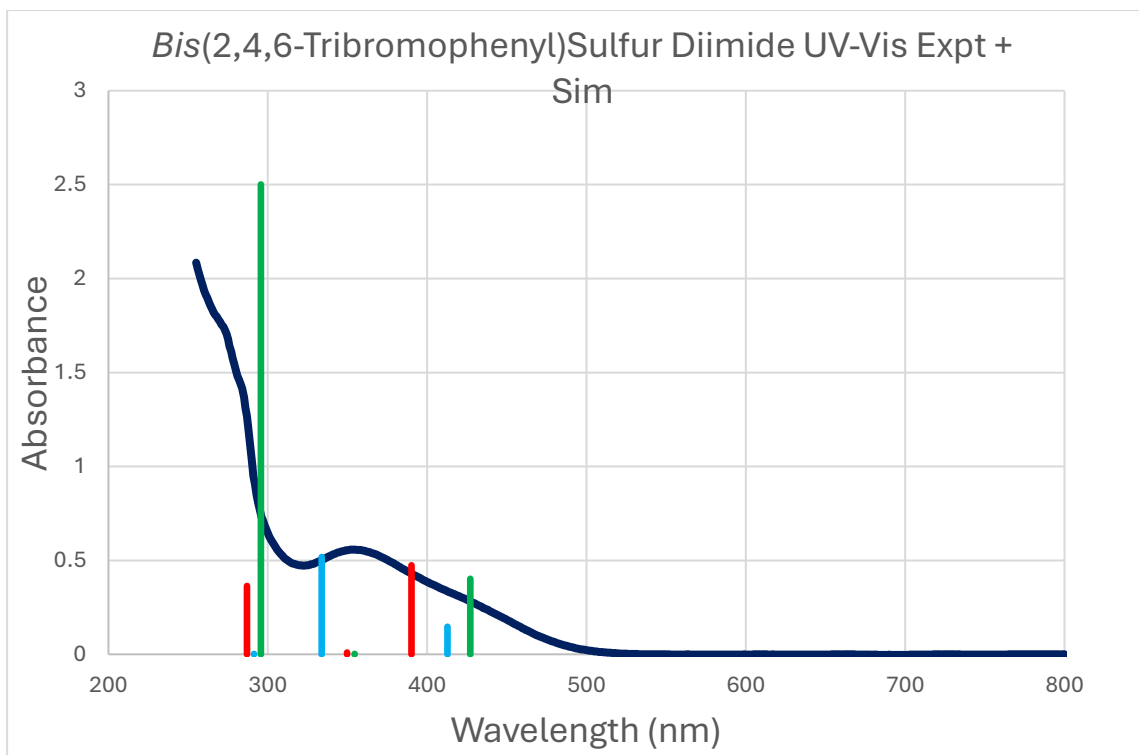


Figure B.103. UV-Vis spectrum of **9** (dark blue trace) with simulated peaks from TD-DFT calculations of the possible conformers (EE = Green, EZ = Red, ZZ = Light Blue)

B.13. FTIR Data Tables and Figures

Table B.44. IR Assignment with DFT computed spectra for the E/Z and Z/Z isomers of HNSNH

E/Z Isomer

Mode	Exp IR	Int	Cint	ScalFrq ¹⁴ N	ScalFrq ¹⁵ N	Cint	DifC ^a	Assignment - EZ
9	3295	w	15%	3353	3345	16%	7	v(N-H),Z branch
8	3287	w	9%	3331	3323	10%	7	v(N-H),E branch
7	1181	s	13%	1166	1154	10%	12	v(NSN), asym
6	1037	vs	100%	1040	1024	100%	15	δN-H, asym
5	998	m	17%	1009	1004	36%	5	δN-H, sym
4	934	m	11%	935	912	12%	24	v(NSN), sym
3	718	m	11%	718	714	12%	4	ρH, asym (o.o.p. wrt stationary NSN)
2	615	vs	69%	598	597	80%	2	ρH, sym (o.o.p. wrt stationary NSN)
1	410	w	17%	416	409	19%	7.5	δ(NSN)sym

Z/Z Isomer

Mode	Exp IR	Int	Cint	ScalFrq ¹⁴ N	ScalFrq ¹⁵ N	Cint	DifC ^a	Assignment - ZZ
9	3292	s	8%	3348	3340	8%	8	v(N-H), asym
8	3292	s	6%	3347	3339	5%	7	v(N-H), sym
7	1157	m	65%	1121	1103	54%	18	v(NSN), asym
6	unobs		0%	1101	1093	0%	8	δN-H, sym
5	913	s	100%	931	926	100%	5	δN-H, asym
4	unobs		9%	907	883	9%	24	v(NSN), sym
3	677	s	79%	676	670	75%	6	ρH, asym (o.o.p. wrt stationary NSN)
2	unobs		0%	649	647	0%	1	ρH, sym (o.o.p. wrt stationary NSN)
1	unobs		17%	412	405	15%	7	δNSN

^a Difference in the computed ¹⁴N and ¹⁵N vibrational mode energies.

Data from Haas *et al.*, 1999.^[42] Under matrix conditions, reactions of MNSNM (M = Ag, Tl) or INSNI with HX under optimized conditions give consistent spectral signals assignable to an isomeric mixture of HNSNH.

Computed at the B3LYP-D3BJ/6-311++G(2d,p) level of theory in Gaussian 16w. Vibrations were visualized in GaussView 6.0.16, resulting in unambiguous assignments of the fundamental vibrational modes.

Agreement between the experimental and computed frequencies averages to ± 10 cm⁻¹.

Table B.45. Vibrational data and assignment using DFT computed spectra for Z-PhNSO

Mode	ExpIRN14	Int	Cint	ExpRamN14	Int	Cint	Calc N14	ExpIRN15	Int	Cint	Difc	Difc	ExpRamN15	Int	Cint	Difc	Calc N15	Assignment
36	not listed by I	2%	not listed by Meij				3122	not listed by Meij					not listed by Meij				3122	vCH ortho towards the O of NSO
35	not listed by I	4%	not listed by Meij				3093	not listed by Meij					not listed by Meij				3093	vCH sym all four remaining not ortho to O
34	not listed by I	8%	not listed by Meij				3084	not listed by Meij					not listed by Meij				3084	vCH asym four other CH
33	not listed by I	5%	not listed by Meij				3074	not listed by Meij					not listed by Meij				3074	vCH asym meta CH
32	not listed by I	0%	not listed by Meij				3065	not listed by Meij					not listed by Meij				3065	vCH asym para CH
31	unobs		4%	1585	m	57%	1578	unobs		4%			1585	m	46%		1577	v(ring), sym, NSO stationary
30	1576	m	2%	1576	sh	5%	1555	1576	m	2%			unobs		4%		1555	v(ring), asym, NSO stationary
29	1486	s	4%	1483	m	15%	1470	1484	s	4%	2		1483	m	10%		1469	v(ring), sym, small asym vNSO
28	1454	m	2%	unobs		1%	1438	1454		2%			unobs		1%		1438	v(ring), ssym, normal to NSO
27	unobs		0%	unobs		4%	1319	unobs		0%			unobs		2%		1318	v(ring) and vCH
26	1299	m	1%	1299	s	57%	1283	unobs		0%	3		1292	s	13%	7	1280	v(ring), asym, weakly coupled to Ph-N, with v(NS) character
25	1284	s	23%	1284	s	100%	1267	1272	s	23%	12	16	1272	s	100%	12	1251	v(ring), asym, strongly coupled to Ph-N, with v(NSO) character
24	1181	m	2%	unobs		13%	1163	1178	m	2%	3		unobs		13%		1162	δ C-H
23	1161	sh	3%	unobs		2%	1148	1160	sh	3%			unobs		2%		1148	δ C-H
22	1155	s	#####	1158	s	24%	1122	1153	s	#####			1154	s	18%		1122	v(ring), asym, strongly coupled with dominant v(NSO) character
	1100	w	0%	unobs		0%		1100	w	0%			unobs		0%			Suspect band! (this reported IR only band is not in the computation)
21	1074	m	8%	unobs		0%	1071	1070	m	8%	4		unobs		0%		1070	δ C-H, weak asym n(NSO)
20	1035	m	3%	1034	m	15%	1017	1031	m	2%	4	2	1030	m	8%	4	1015	v(ring) and δ C-H weakly coupled to sym v(NSO)
19	1020	m	10%	1020	w	16%	1003	1016	m	9%	4	8	1015	w	24%	5	995	v(ring) and C-H def strongly coupled to sym v(NSO)
18	1000	w	0%	999	w	9%	987	1000	w	0%		1	1000	m	3%		986	v(ring) and C-H def weakly coupled to sym vn(NSO)
17	unobs		0%	unobs		0%	970	unobs		0%			unobs		0%		970	δ C-H, out of plane
16	unobs		0%	unobs		0%	952	unobs		0%			unobs		0%		952	δ C-H, out of plane
15	920	m	4%	unobs		0%	914	920	m	4%			unobs		0%		914	δ C-H, out of plane
14	unobs		0%	unobs		0%	823			0%		823	unobs		0%			δ C-H, out of plane
13	767	s	27%	unobs		0%	760	765	s	26%	2		unobs		0%		760	δ C-H, out of plane, slight N wag
12	748	w	4%	747	m	6%	741	740	w	3%	8	6	739	m	5%	8	734	δ (ring), in plane, coupled to sym δ NSO
11	683	s	23%	unobs		0%	677	682	s	23%			unobs		0%		677	δ C-H, out of plane
10	638	w	3%	638	m	3%	627	631	w	2%	7	6	630	m	2%	8	621	δ (ring), in plane, coupled to sym δ NSO
9	606	w	2%	606	w	1%	603	604	w	3%	2	4	606	w	1%		599	δ (ring), in plane, coupled to ssym δ NSO
8	533	w	1%	unobs		0%	530	530	w	1%	3	4	unobs		0%		527	δ (ring), in plane, coupled to sym δ NSO
7	436	m	7%	437	m	2%	433	434	m	7%	2	2	438	m	1%		431	δ (ring), in plane, coupled to asym δ NSO
6	unobs		0%	unobs		0%	405	unobs		0%			unobs		0%		405	δ (ring), in plane δ NSO (isolated from NSO)
5	368	w	4%	unobs		0%	359	362	w	4%	6	5	unobs		0%		354	p(ring) coupled to pNSO
4	300	w	3%	300	w	1%	302	300	w	3%			300	w	1%		302	δ (ring) i.p. strongly coupled to pNSO
3	unobs		2%	166	w	1%	150	unobs		2%			unobs		0%		150	δ (ring), in plane, strongly coupled to sym δ NSO
2	unobs		2%	146	w	0%	149	unobs		2%			unobs		0%		149	p(ring) coupled to pNSO
1	not meas			non meas			59	not meas		0%			not meas				59	p(ring) coupled to pNSO
																	Averages:	12 cm ⁻¹

Table B.46. Vibrational data and assignment using DFT computed spectra for E/Z PhNSNPh

Mode	Exptl	IR N14	Int	Cint	ExpRamN14	Int	Cint	ScalFrc	Exptl	IR N14	ExpIRN15	Int	Cint	Diffr	Diffr	Exptl	IR N15	Int	Cint	Diffr	ScalFrc	Exptl	IR N15	Int	Cint	Assignment
69				4%				0%	3132				4%						0%		3132	vCH, Z ortho towards the N of NSN				
68				12%				6%	3090				10%					7%		3090	vCH, Z sym all four remaining not ortho to N					
67				13%				7%	3089				11%					8%		3089	vCH, E sym all CH					
66				15%				3%	3083				12%					4%		3083	vCH, E ssym all CH					
65	3080 vs			18%				5%	3082				15%					6%		3082	vCH, Z asym o,p CH					
64				10%				3%	3075				8%					3%		3075	vCH, E ssym all CH					
63				9%				3%	3070				8%					4%		3070	vCH, Z asym meta CH					
62	unobs			3%				3%	3066				3%					3%		3066	vCH, E asym all CH					
61	unobs			1%				1%	3061				1%					1%		3061	vCH, Z asym all CH					
60	unobs			6%				1%	3059				5%					1%		3059	vCH, E asym all CH					
59				5%				8%	1577				4%					9%		1576	v(both rings), asym, uncoupled fom NSN					
58	1598 s			17%				48%	1575				14%					57%		1575	v(both rings), sym, uncoupled fom NSN					
57	unobs			5%				1%	1554				4%					1%		1554	v(E ring), asym, uncoupled fom NSN					
56	unobs			1%				3%	1550				1%					3%		1550	v(Z ring), asym, uncoupled fom NSN					
55	1480 s			37%				8%	1468				27%					8%		1468	v(Z ring), sym, uncoupled fom NSN					
54	1448 s			42%				13%	1467				36%					14%		1467	v(E ring), sym, uncoupled fom NSN					
53	unobs			5%				0%	1436				4%					0%		1436	v(Z ring), asym, uncoupled fom NSN					
52	unobs			1%				0%	1435				1%					0%		1435	v(E ring), asym, uncoupled fom NSN					
51	unobs			2%				3%	1318				1%					2%		1318	v(Z ring), asym, uncoupled fom NSN					
50	unobs			0%				0%	1313				0%					0%		1313	v(E ring), asym, uncoupled fom NSN					
49	1300/1298 s			46%	1300 m			35%	1293	1296 m		13%	4	7.6		1295 m		24%	5	1285	v(Ph-N), Z branch					
48	unobs			4%				2%	1268				1%					1%		1268	v(E ring) weakly coupled to (NSN)					
47	1268/1265 s			98%	1268 m			20%	1258	1257 s		100%	11	12		1258 m		35%	10	1246	v(Ph-N-S), Z branch					
46	1222/1218 s			100%	1222 m			100%	1216	1213 s		78%	9	10		1213 s		100%	9	1205	v(Ph-N), E branch					
45	unobs			0%				4%	1161				1%					4%		1161	v(both rings), sym in plane, coupled to δ (CH)					
44	1170 m			8%				24%	1158				8%				m	35%		1157	v(both rings), sym in plane, coupled to δ (CH)					
43	1185 m			1%				0%	1145				1%					1%		1145	v(Z ring), asym in plane, coupled to δ (CH)					
42				1%				1%	1144				1%				m	2%		1144	v(E ring), asym in plane, coupled to δ (CH)					
41	unobs			4%				0%	1070				4%				w	0%		1070	v(Z ring), asym in plane, coupled to δ (CH)					
40	unobs			7%				0%	1068				5%					0%		1068	v(E ring), asym in plane, coupled to δ (CH)					
39	1070 s			83%				0%	1050				76%		9.1		m	0%		1041	v(NSN) asym, coupled to v(ring) & δ (CH)					
38	1025 m			3%				2%	1014				3%					2%		1014	v(E ring), coupled with δ (CH), isolated from NSN					
37	unobs			2%				0%	1011				2%					0%		1011	v(Z ring), coupled with δ (CH), isolated from NSN					
36	997 m			1%				10%	986				0%				w	11%		986	v(E ring), coupled with δ (CH), isolated from NSN					
35	972 w			3%				4%	984				4%					4%		984	v(Z ring), coupled with δ (CH), isolated from NSN					
34	unobs			0%				0%	963				0%					0%		963	δ (C-H)					
33	unobs			0%				0%	957				0%					0%		957	δ (C-H)					
32	unobs			0%				0%	949				0%					0%		949	δ (C-H)					
31	960/957 m			24%	960 s			17%	943				1%	0				0%	960	938.76 v(N-S)s, for N14						
30	unobs			1%				3%	938.21	960 m		23%		13		942 m		27%		925.17 v(N-S)s, for N15						
29	913 m			5%				0%	904				4%					0%		904	δ (C-H)					
28	900 m			4%				1%	882				3%					1%		881	δ (C-H)					
27	unobs			0%				0%	820				0%					0%		820	δ (C-H)					
26	828 w			1%				1%	807				1%					2%		807	δ (C-H)					
25	802/803 m			21%	803 w			2%	790	792 m		18%	11	10		791 w		2%	12	780	δ (N-S-N)s					
24	758 s			40%				0%	754				34%					0%		754	δ (C-H)					
23	731 m			24%				1%	748				21%					1%		747	δ (C-H)					
22	unobs			12%				5%	725				8%		4.4			6%		721	δ (C-H) coupled to δ (NSN)s					
21	unobs			40%				0%	680				34%					0%		680	δ (C-H)					
20	unobs			27%				0%	676				22%					0%		676	δ (C-H)					
19	634 s			21%				1%	631				14%		6.4			1%		625	δ (N-S-N)s					
18	unobs			0%				0%	613				0%					0%		613	δ (E ring)					
17	below NaCl			7%				0%	606				9%		2.1			0%		604	δ (Z ring)					
16	below NaCl			6%				1%	532				6%		7.6			2%		525	δ (both rings)					
15	below NaCl			2%				0%	514				3%		2.9			0%		511	δ (Z ring) o.o.p.					
14	below NaCl			7%				1%	498				5%		2.5			1%		495	δ (E ring) o.o.p.					
13	below NaCl			12%				0%	423				10%		1.9			0%		421	δ (both rings)					
12	below NaCl			1%				0%	408				1%					0%		408	p(both rings) o.o.p.					
11	below NaCl			0%				1%	406				0%					1%		406	p(E ring) o.o.p.					
10	below NaCl			1%				0%	387				1%		3.3			0%		383	p(E ring)					
9	337 w			5%	338 w			0%	333	328 w		4%	10	5.5		324 w		0%	14	327	p(NSN)					
8	below NaCl			0%				2%	253				0%		2.2			2%		251	p(E ring)					
7	below NaCl			0%				0%	241				0%					0%		240	δ (both rings)					
6	below NaCl			2%				1%	151				2%					1%		151	p(NSN)					
5	below NaCl			1%				0%	138				1%					0%		137	δ (both rings)					
4	below NaCl			1%				1%	101				0%		1.2			1%		100	p(Z ring)					
3	below NaCl			0%				0%	52				0%					0%		52	p(NSN)					
2	below NaCl			0%				0%	37				0%					0%		37	δ (both rings)					
1	below NaCl			0%				0%	28				0%					0%		28	δ (both rings)					

Experimental IR data from Cramer, J. Org. Chem., 1961; IR and Raman data for principal modes are from Meij, et al., J. Mol. Struct., 1979.

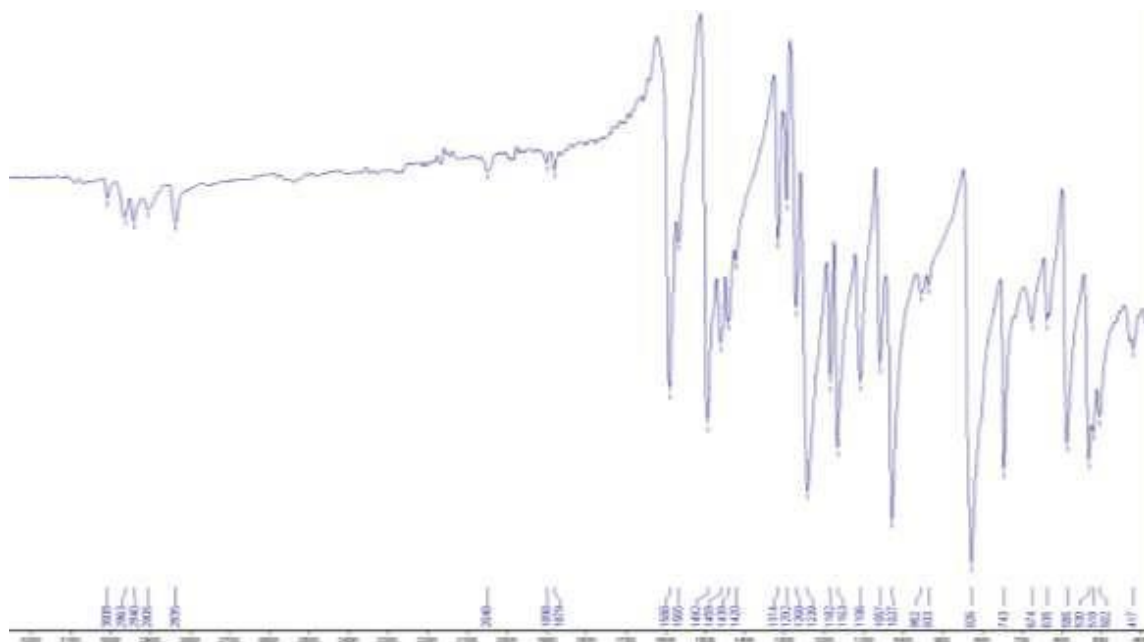


Figure B.104. FTIR spectrum of **1**

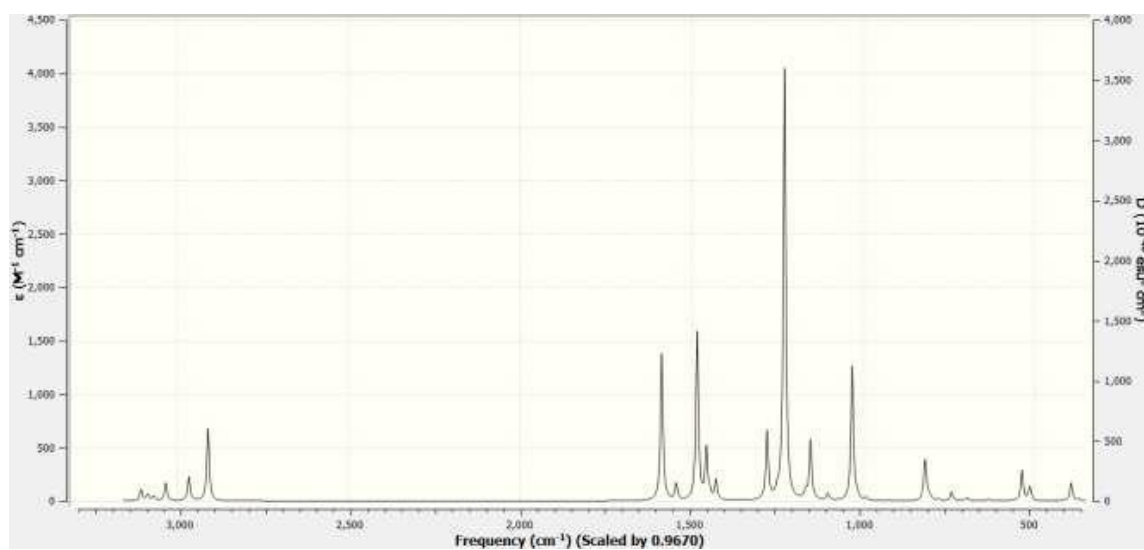


Figure B.105. Simulated vibrational spectrum of **1** in E/E conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

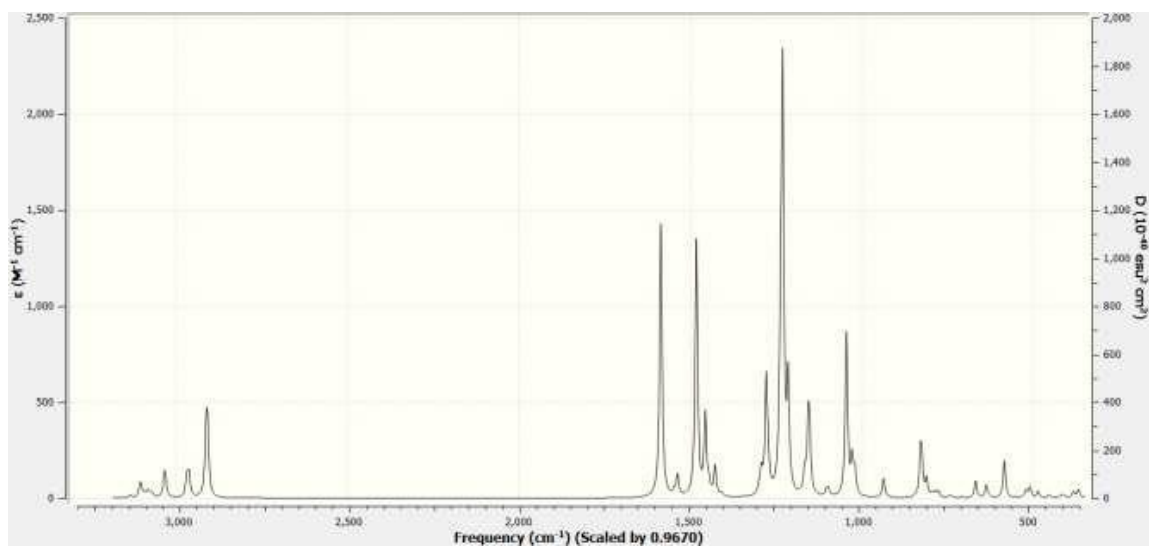


Figure B.106. Simulated vibrational spectrum of **1** in E/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

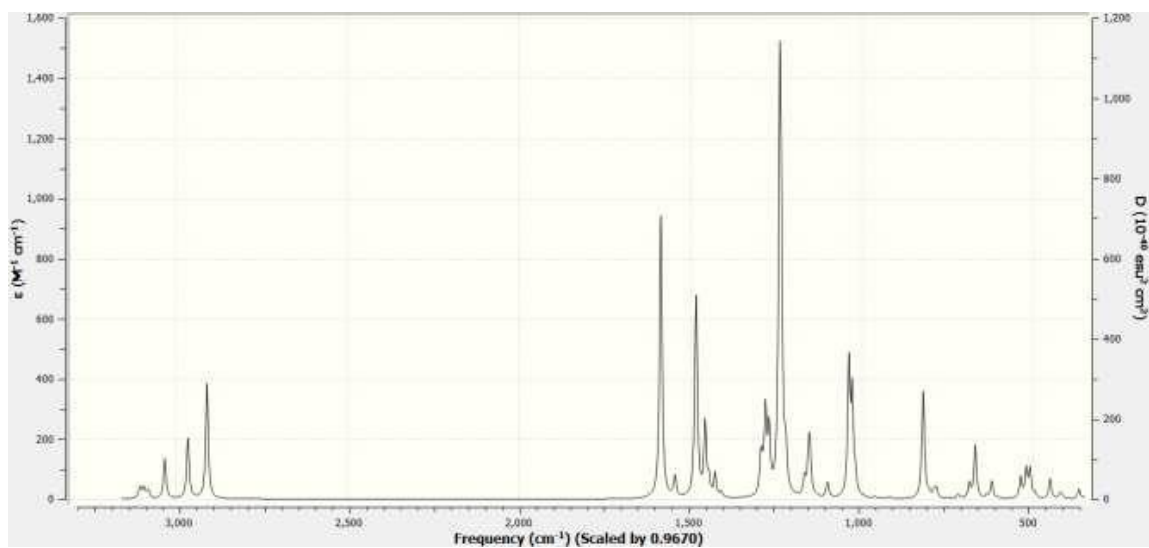


Figure B.107. Simulated vibrational spectrum of **1** in Z/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

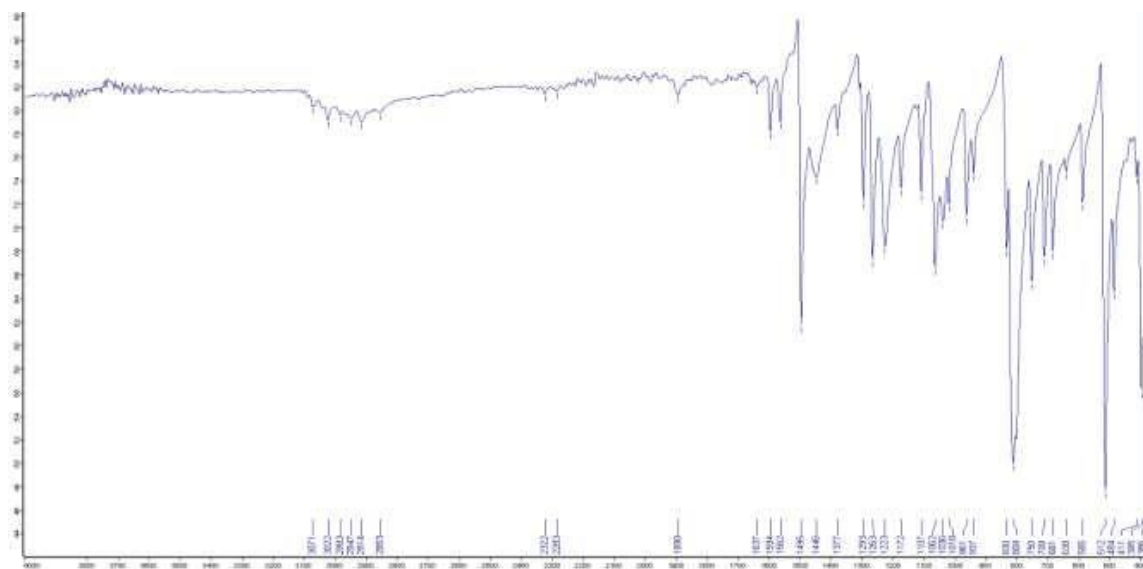


Figure B.108. FTIR spectrum of **2**

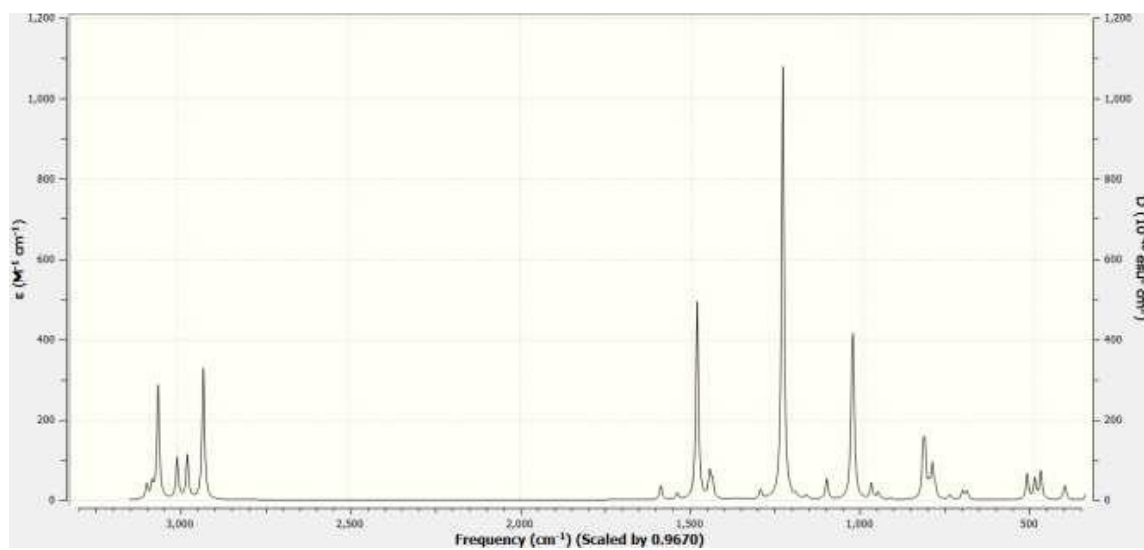


Figure B.109. Simulated vibrational spectrum of **2** in E/E conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

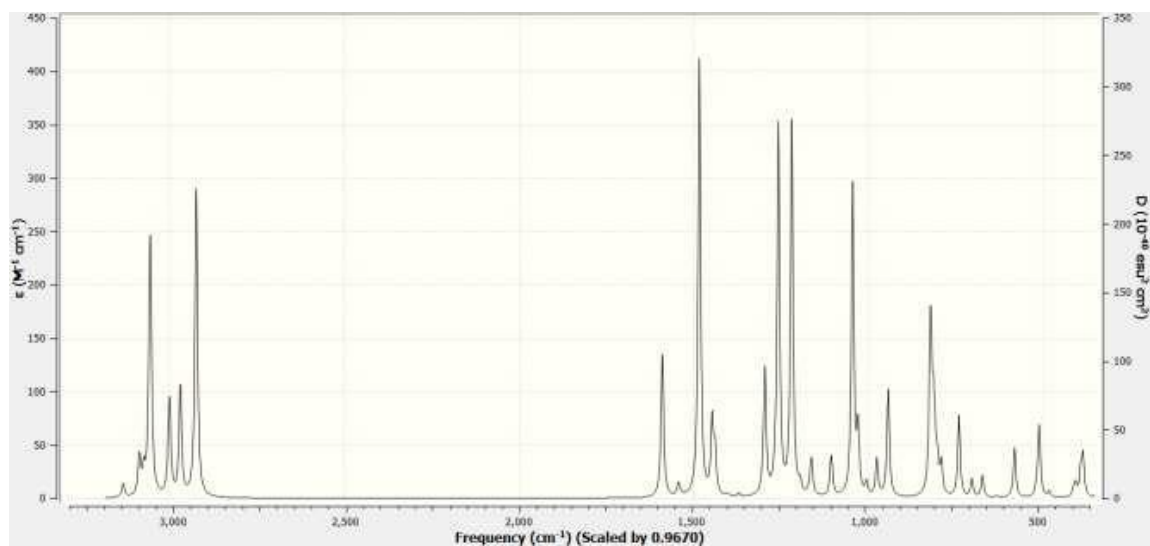


Figure B.110. Simulated vibrational spectrum of **2** in E/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

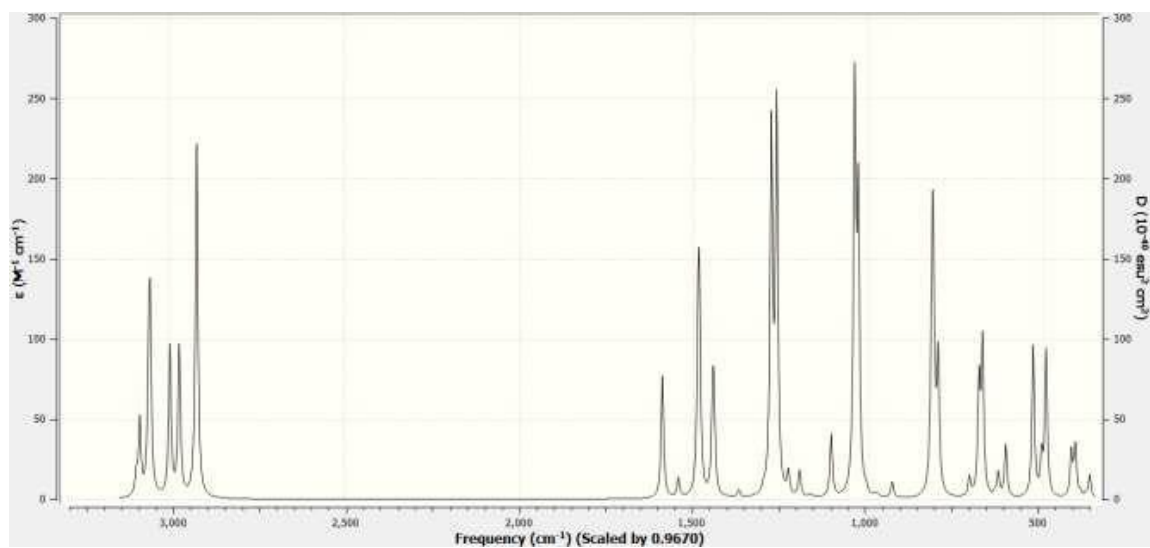


Figure B.111. Simulated vibrational spectrum of **2** in Z/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

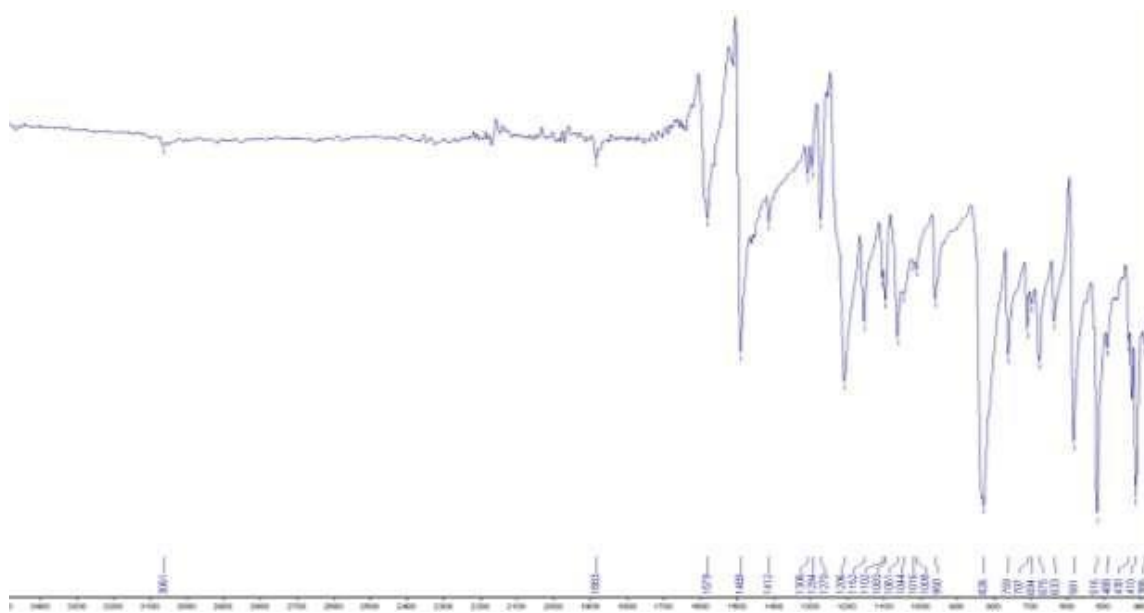


Figure B.112. FTIR spectrum of **3**

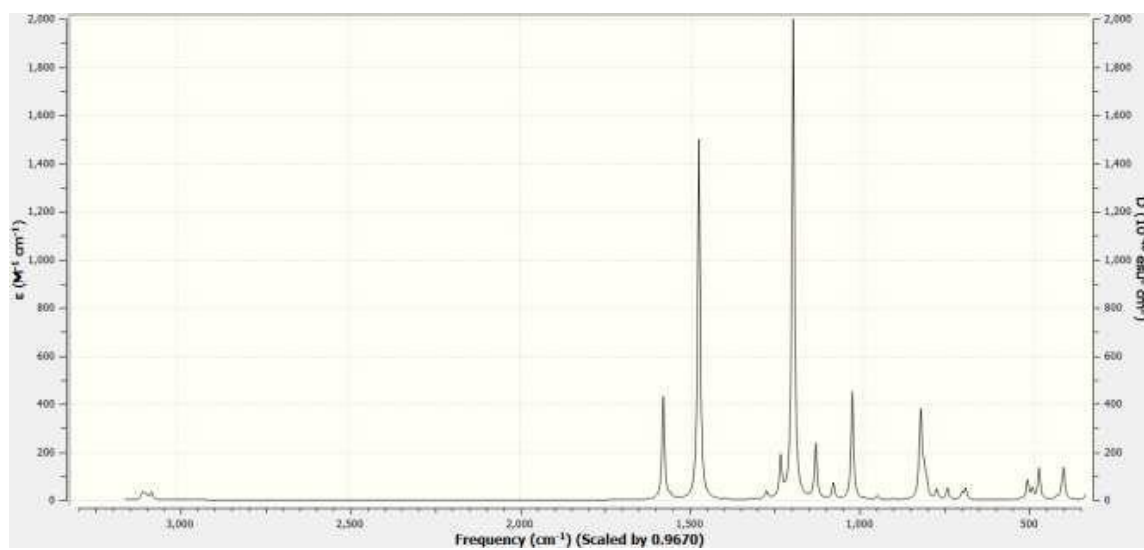


Figure B.113. Simulated vibrational spectrum of **3** in E/E conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

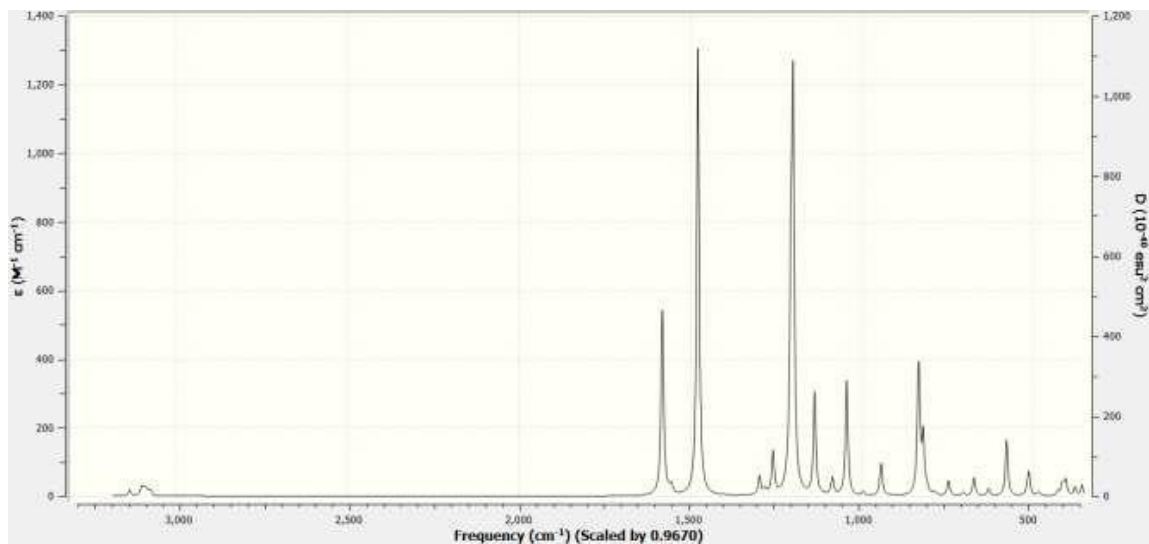


Figure B.114. Simulated vibrational spectrum of **3** in E/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

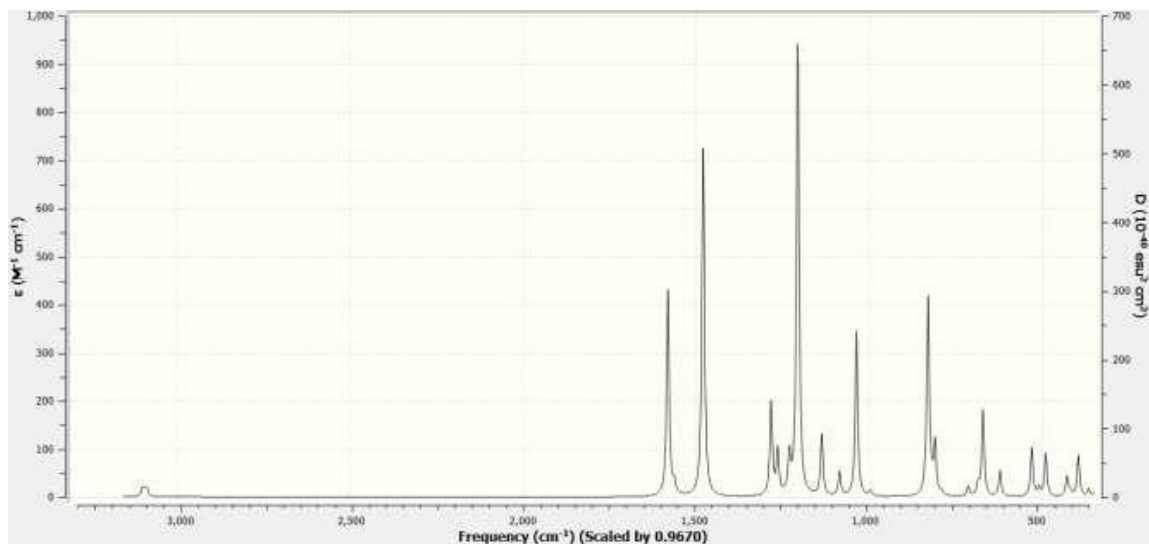


Figure B.115. Simulated vibrational spectrum of **3** in Z/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

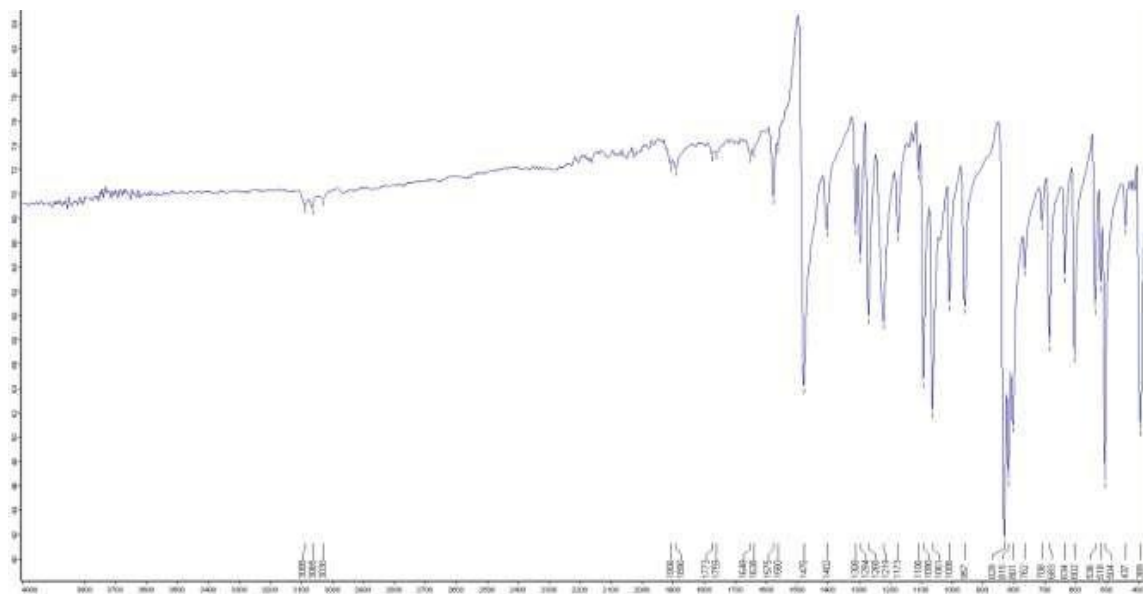


Figure B.116. FTIR spectrum of **4**

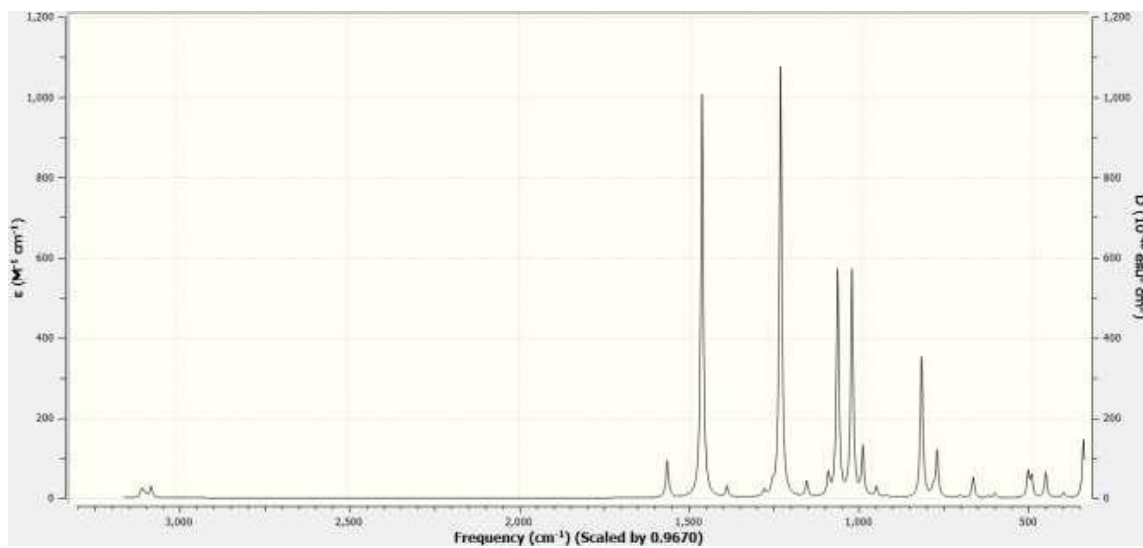


Figure B.117. Simulated vibrational spectrum of **4** in E/E conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

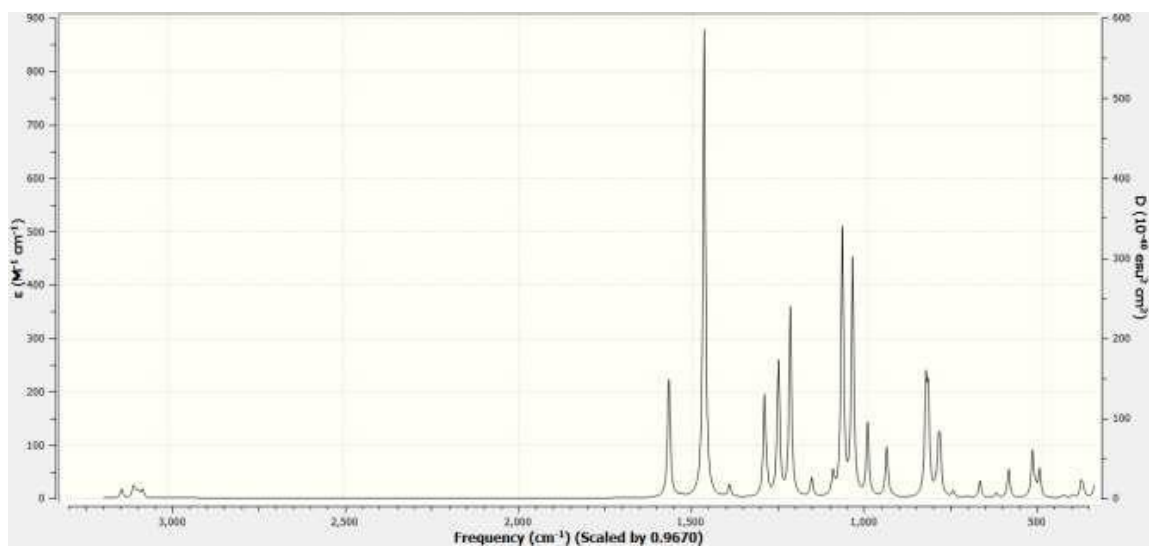


Figure B.118. Simulated vibrational spectrum of **4** in E/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

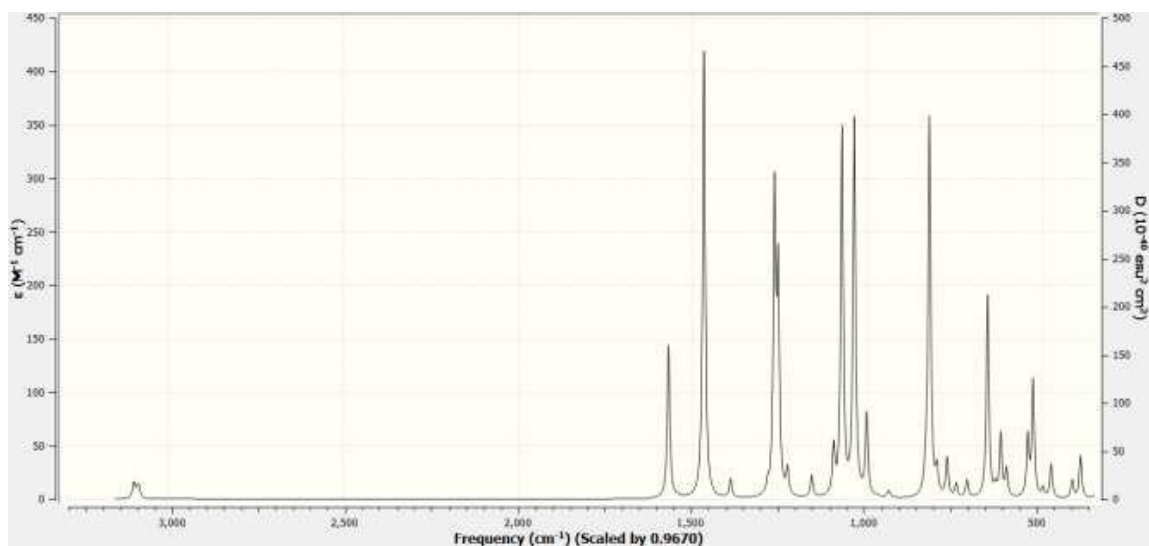


Figure B.119. Simulated vibrational spectrum of **4** in Z/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

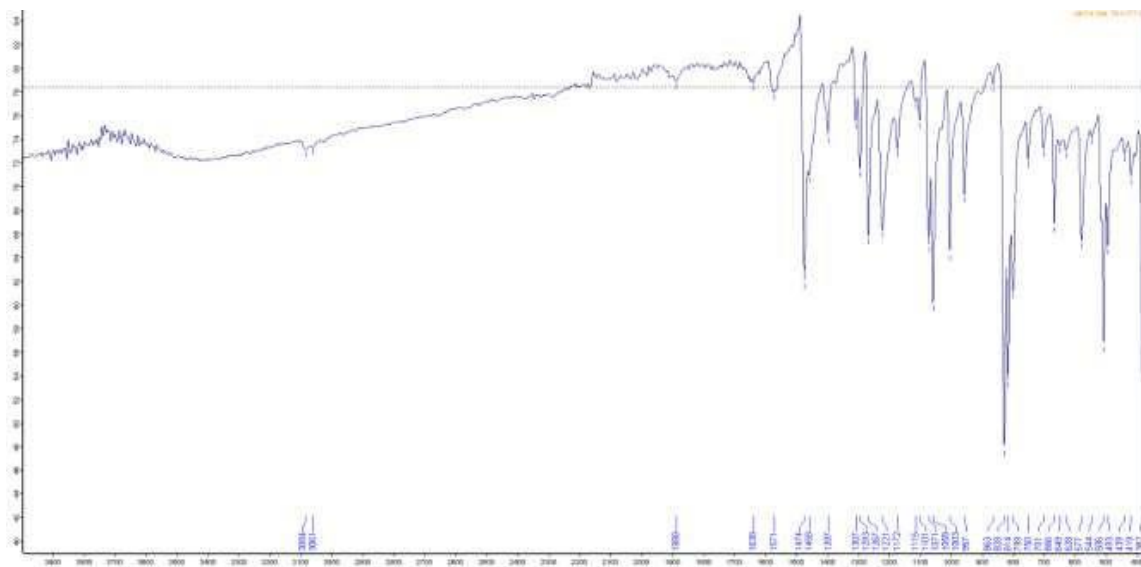


Figure B.120. FTIR spectrum of 5

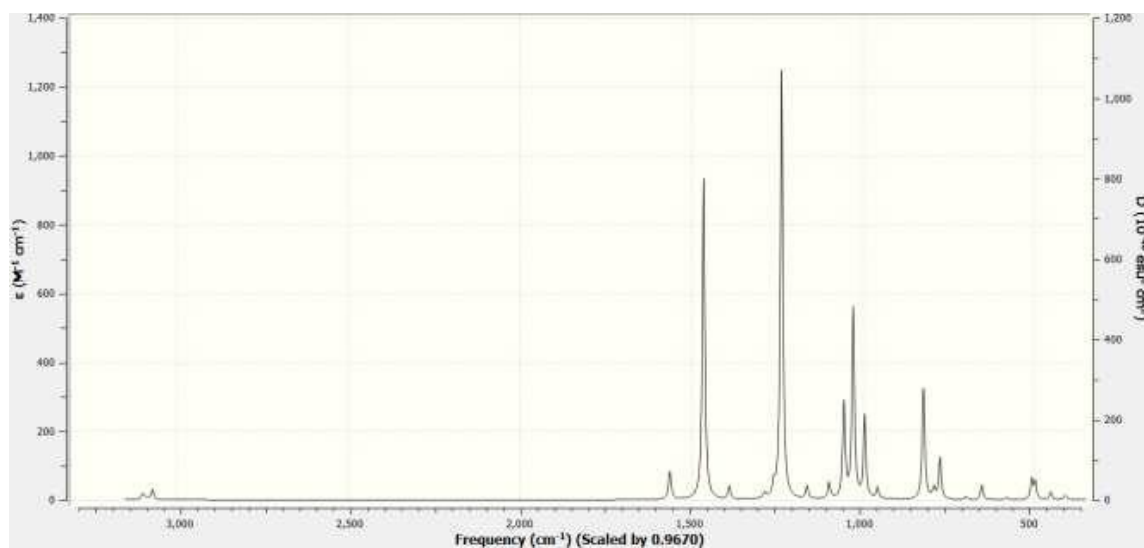


Figure B.121. Simulated vibrational spectrum of 5 in E/E conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

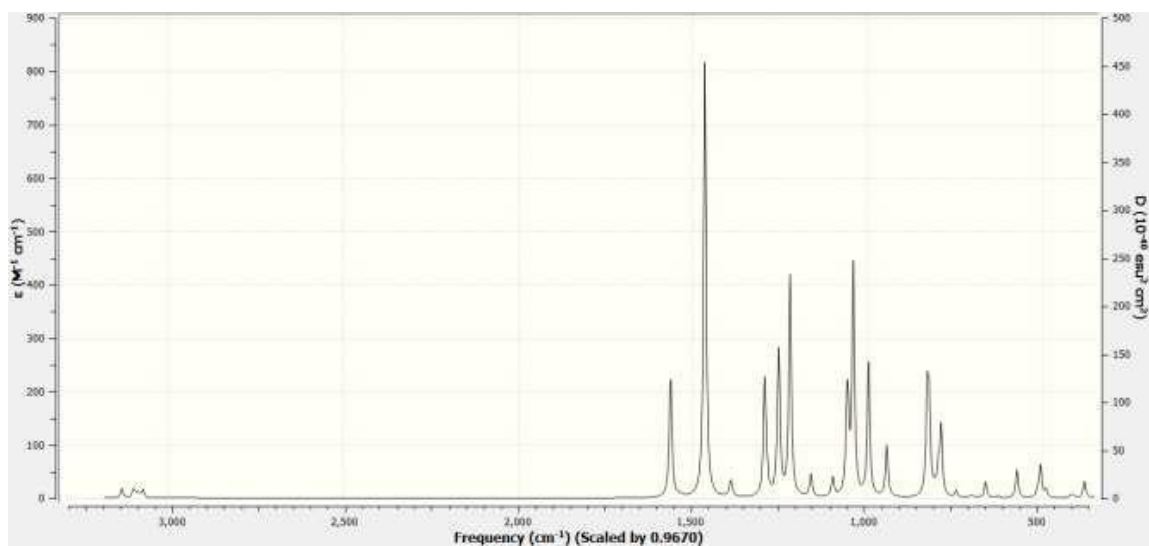


Figure B.122. Simulated vibrational spectrum of **5** in E/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

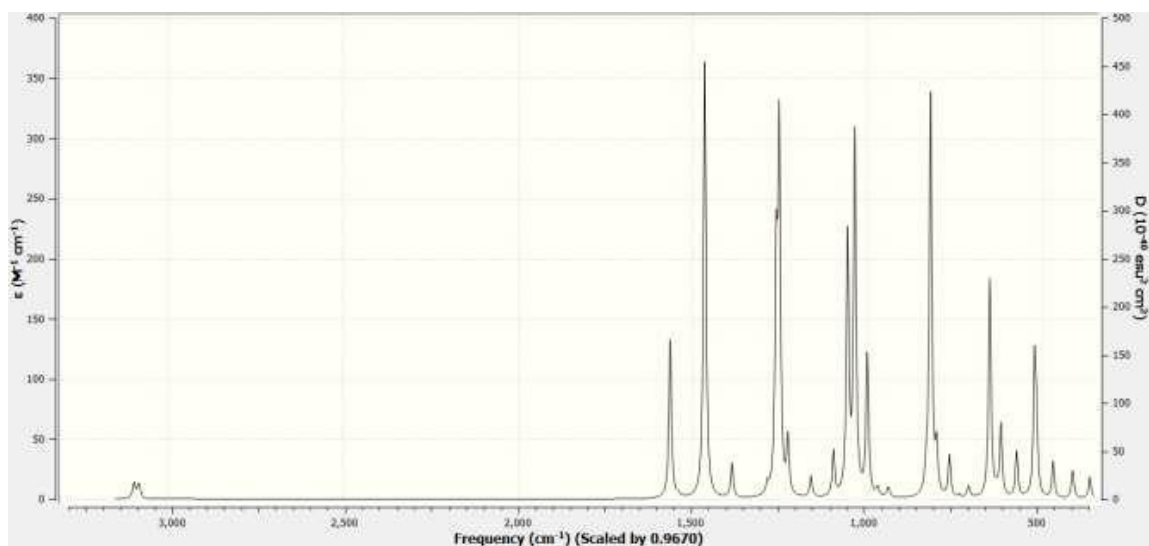


Figure B.123. Simulated vibrational spectrum of **5** in Z/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

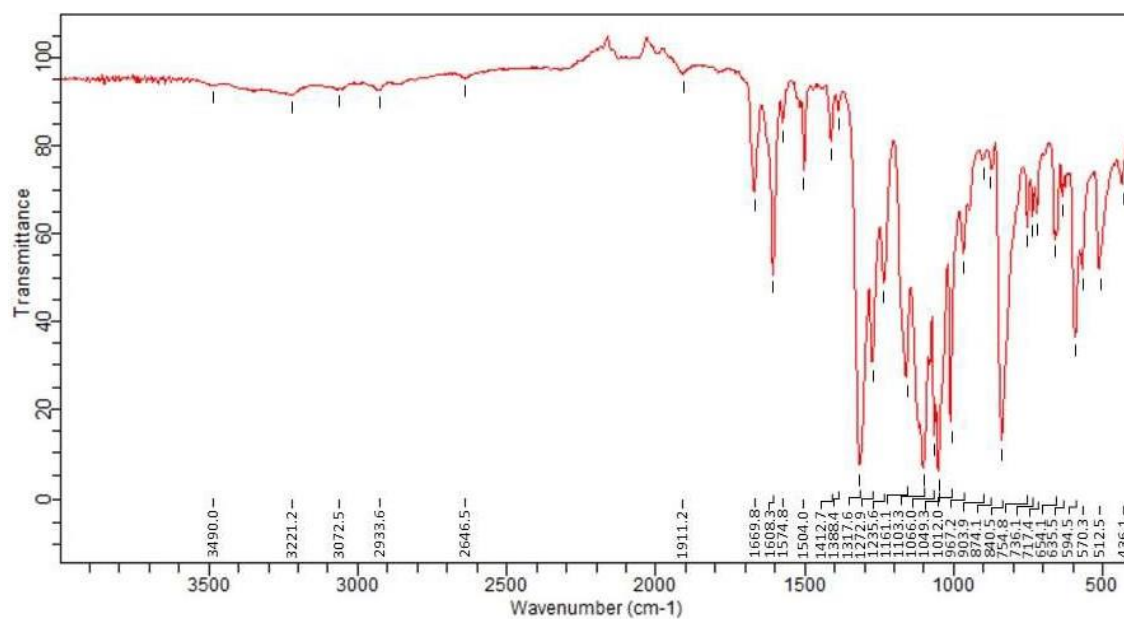


Figure B.124. FTIR spectrum of 6

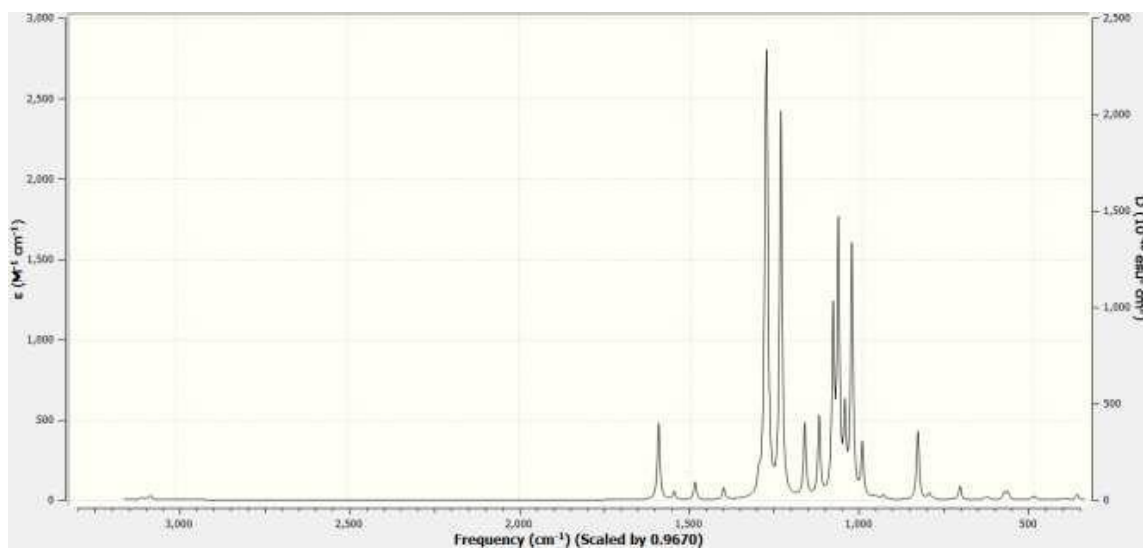


Figure B.125. Simulated vibrational spectrum of 6 in E/E conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

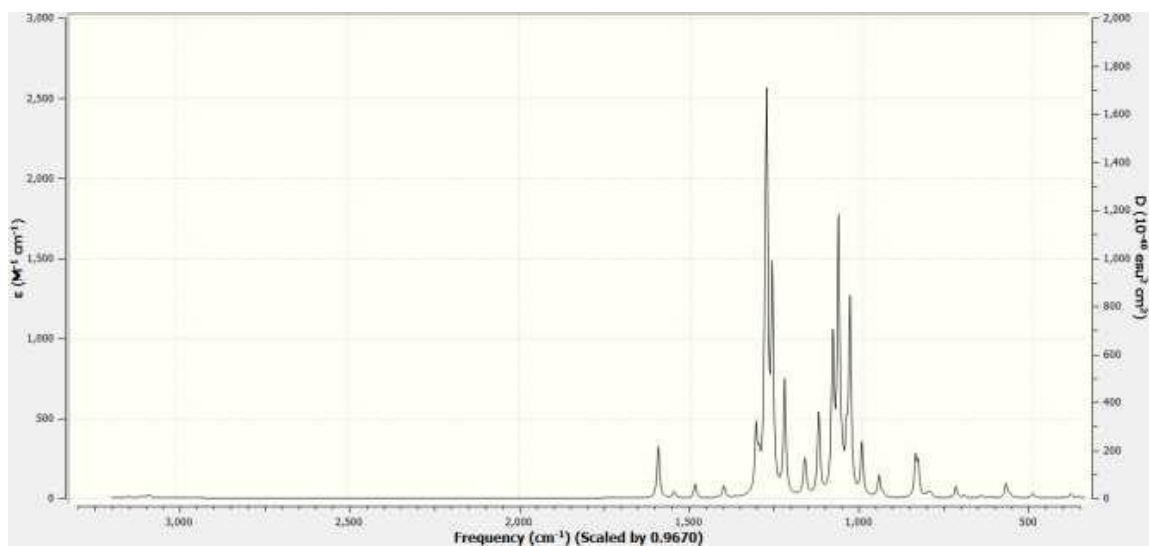


Figure B.126. Simulated vibrational spectrum of **6** in E/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

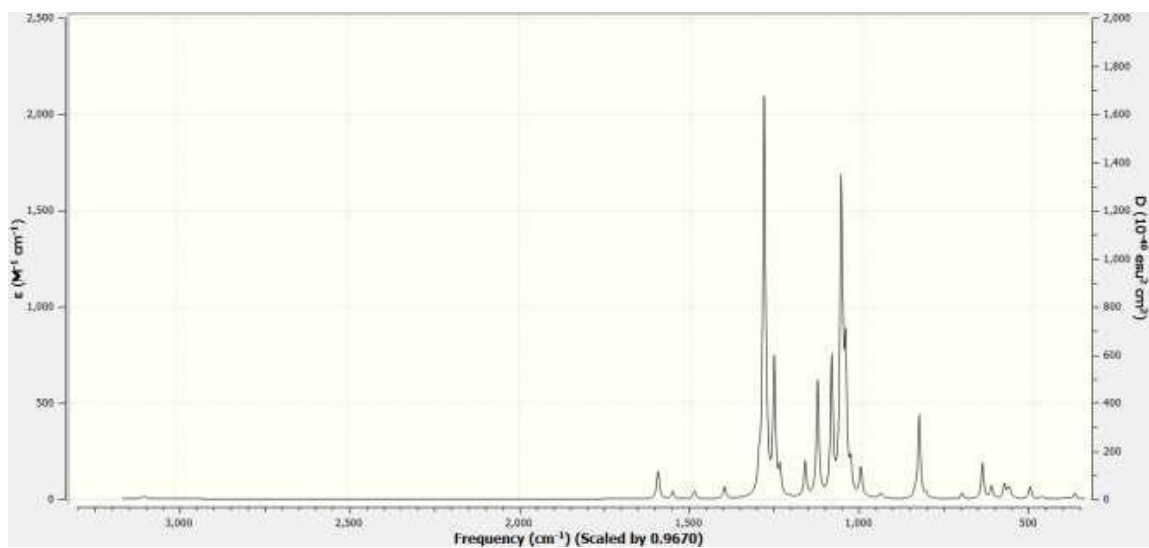


Figure B.127. Simulated vibrational spectrum of **6** in Z/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

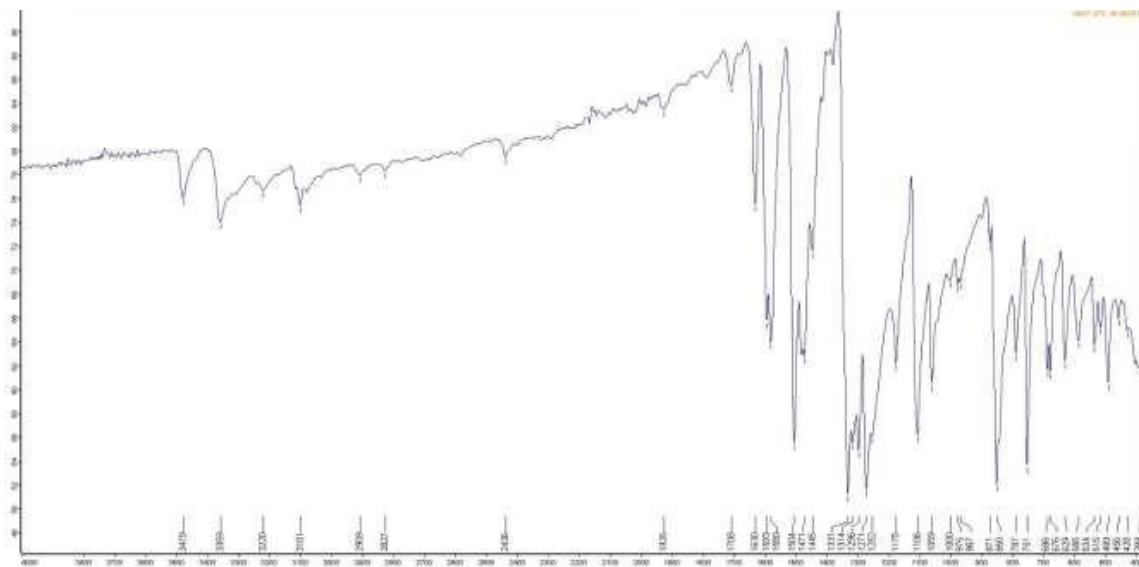


Figure B.128. FTIR spectrum of **7**

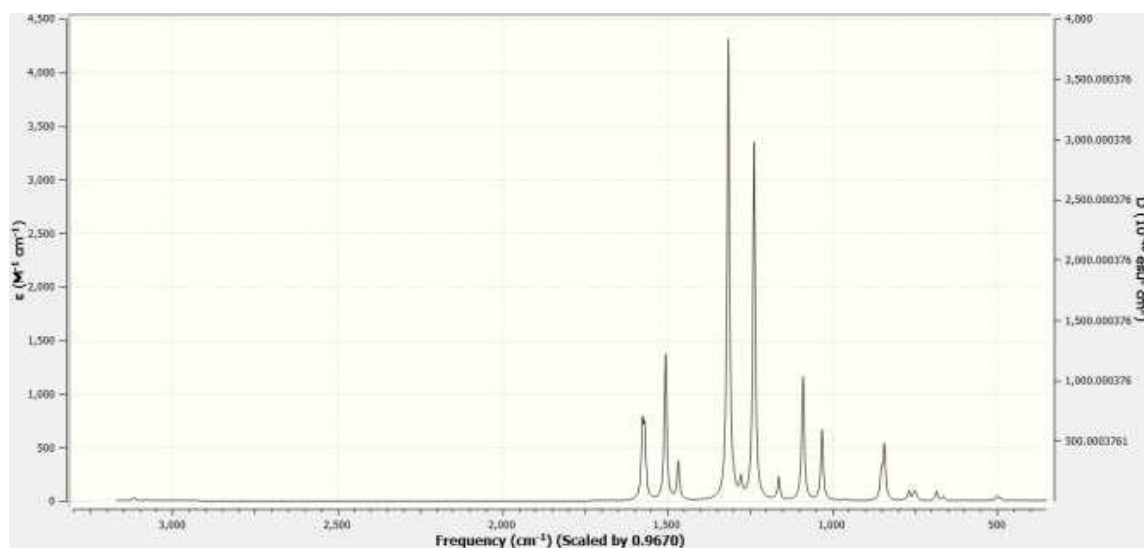


Figure B.129. Simulated vibrational spectrum of **7** in E/E conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

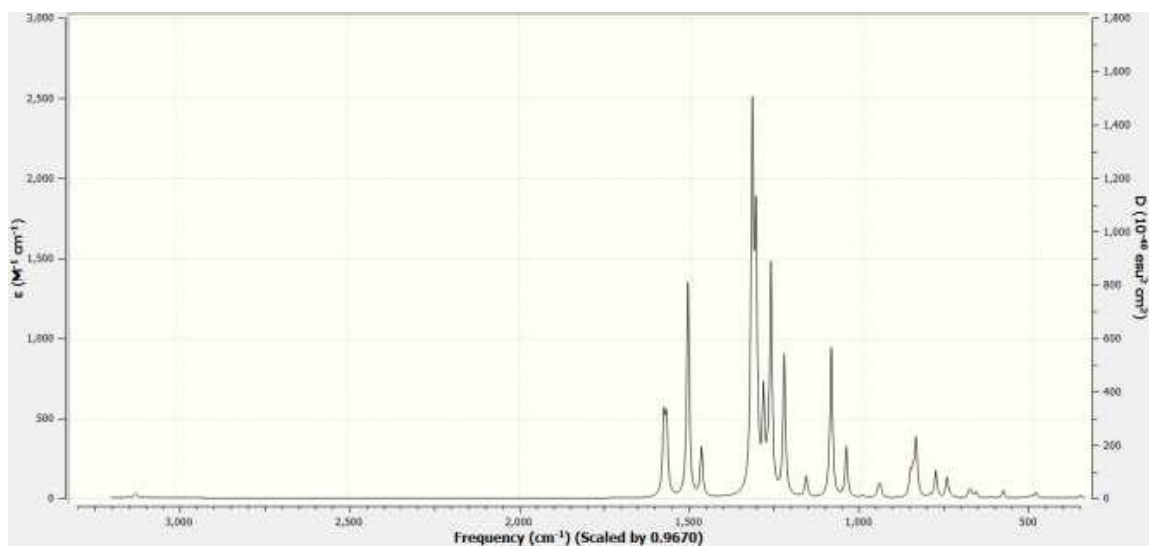


Figure B.130. Simulated vibrational spectrum of **7** in E/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

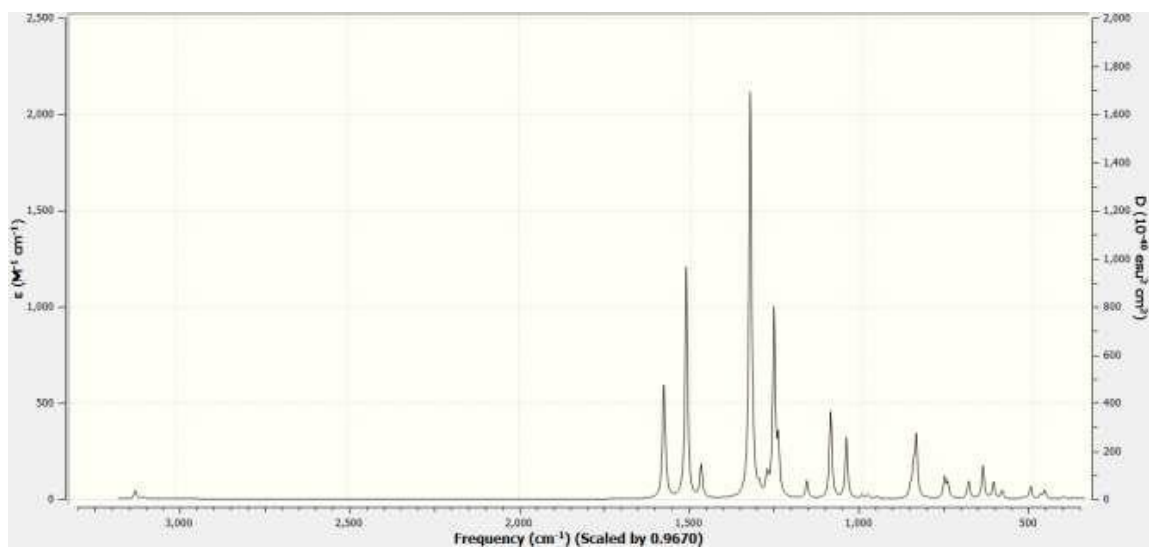


Figure B.131. Simulated vibrational spectrum of **7** in Z/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

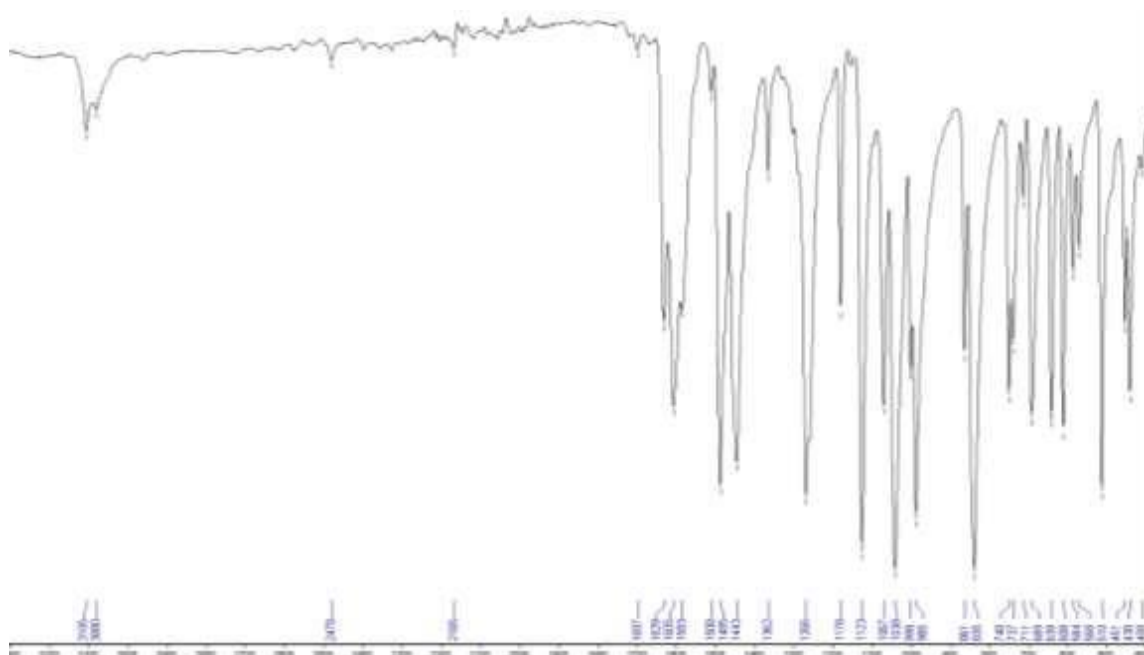


Figure B.132. FTIR spectrum of **8**

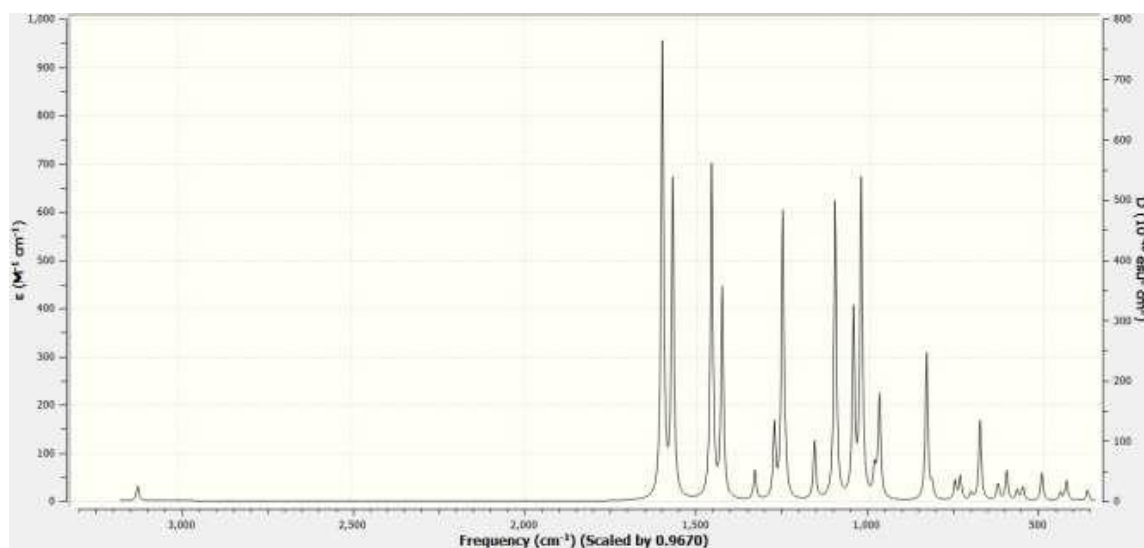


Figure B.133. Simulated vibrational spectrum of **8** in Z/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

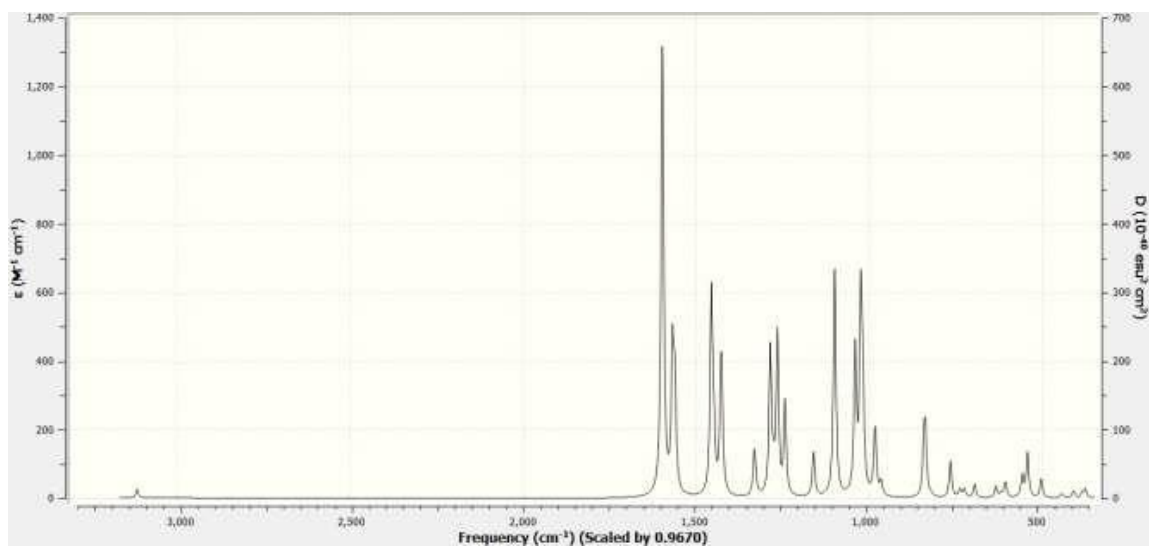


Figure B.134. Simulated vibrational spectrum of **8** in E/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

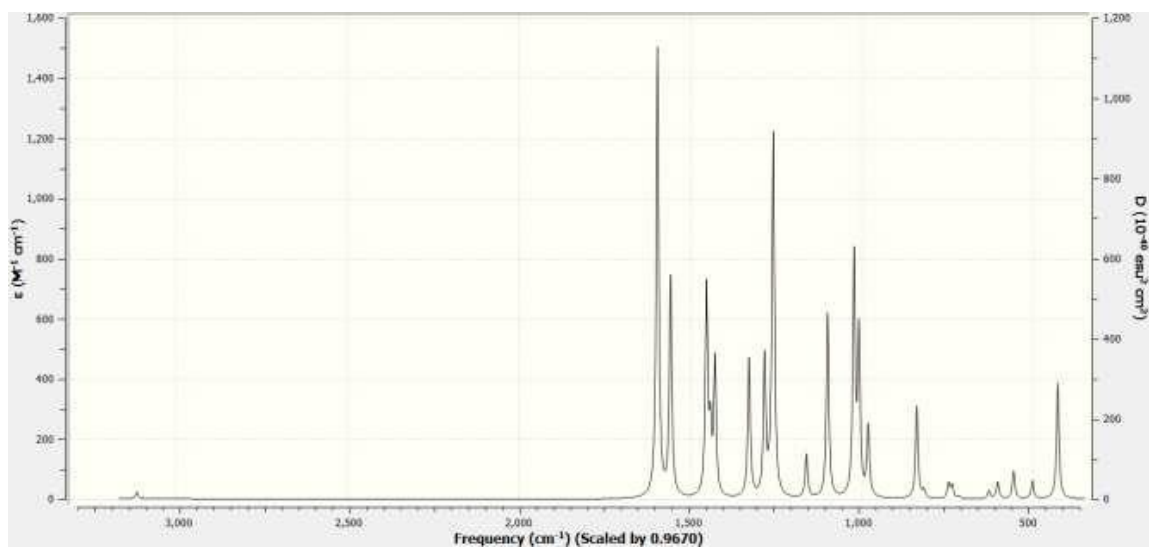


Figure B.135. Simulated vibrational spectrum of **8** in E/E conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

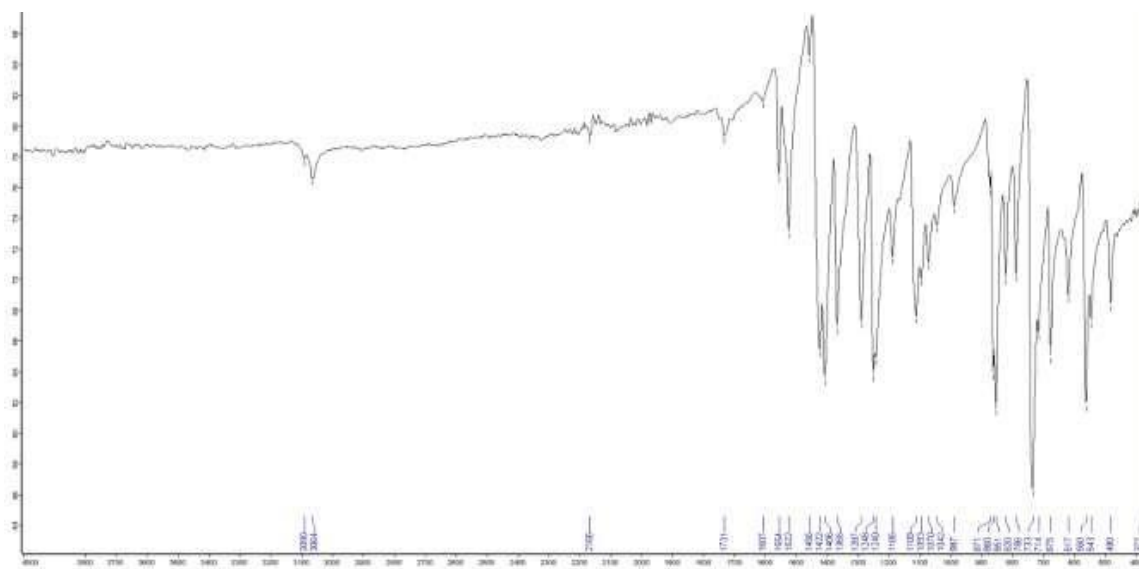


Figure B.136. FTIR Spectrum of **9**

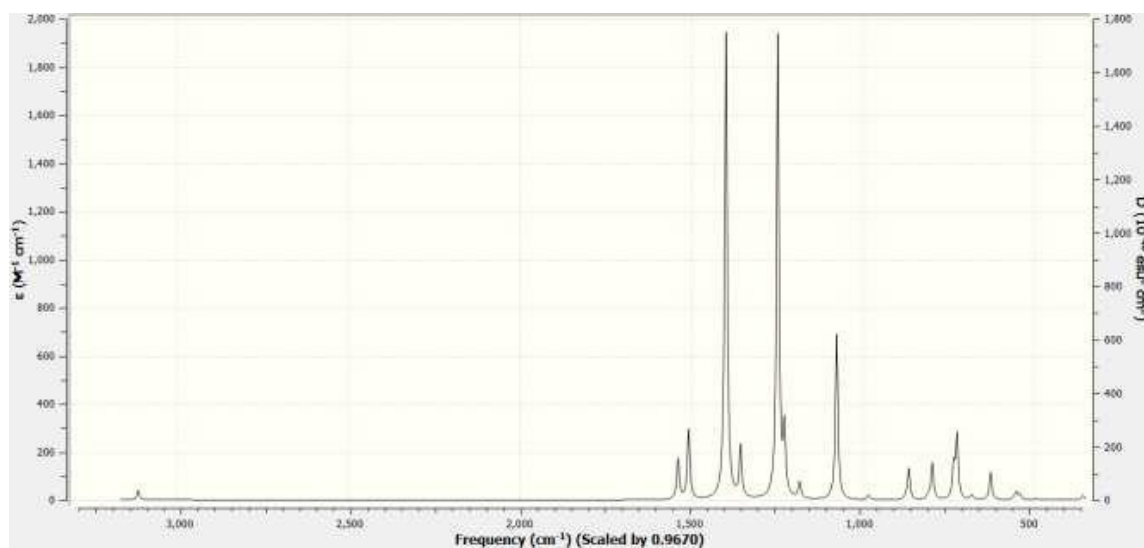


Figure B.137. Simulated vibrational spectrum of **9** in E/E conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

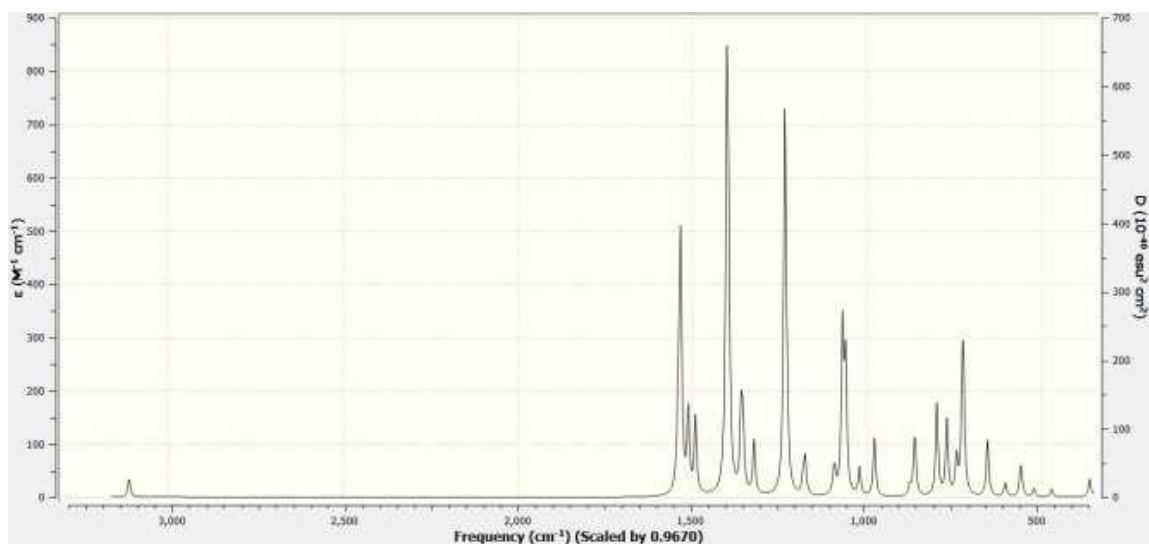


Figure B.138. Simulated vibrational spectrum of **9** in E/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

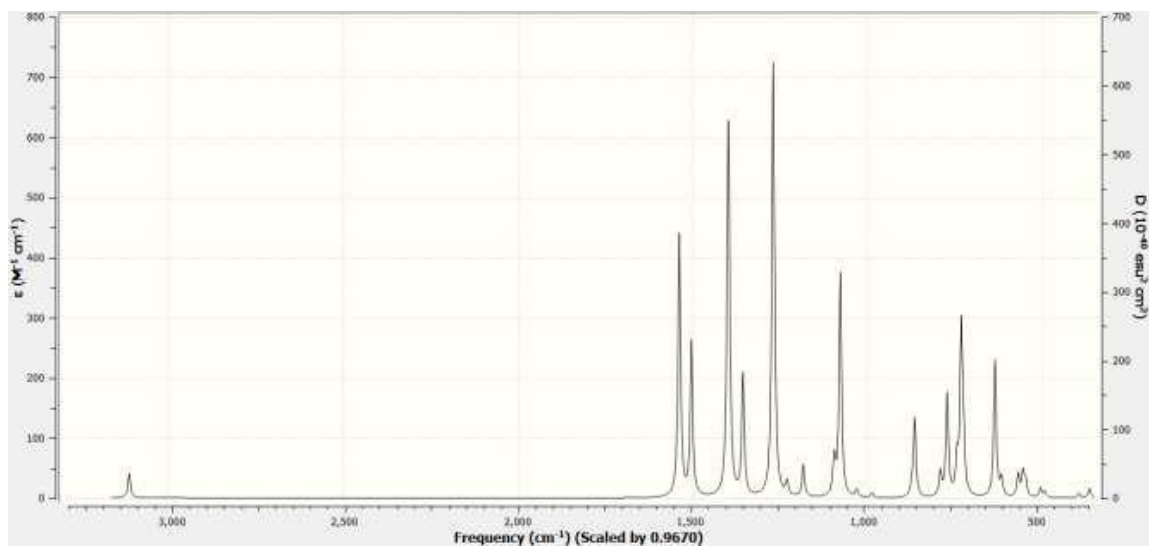


Figure B.139. Simulated vibrational spectrum of **9** in Z/Z conformation, obtained from frequency calculation at B3LYPD3BJ/6-311G++(2d,p) level of theory. X-axis scaled by 0.967.

B.14. Archival NMR Spectra

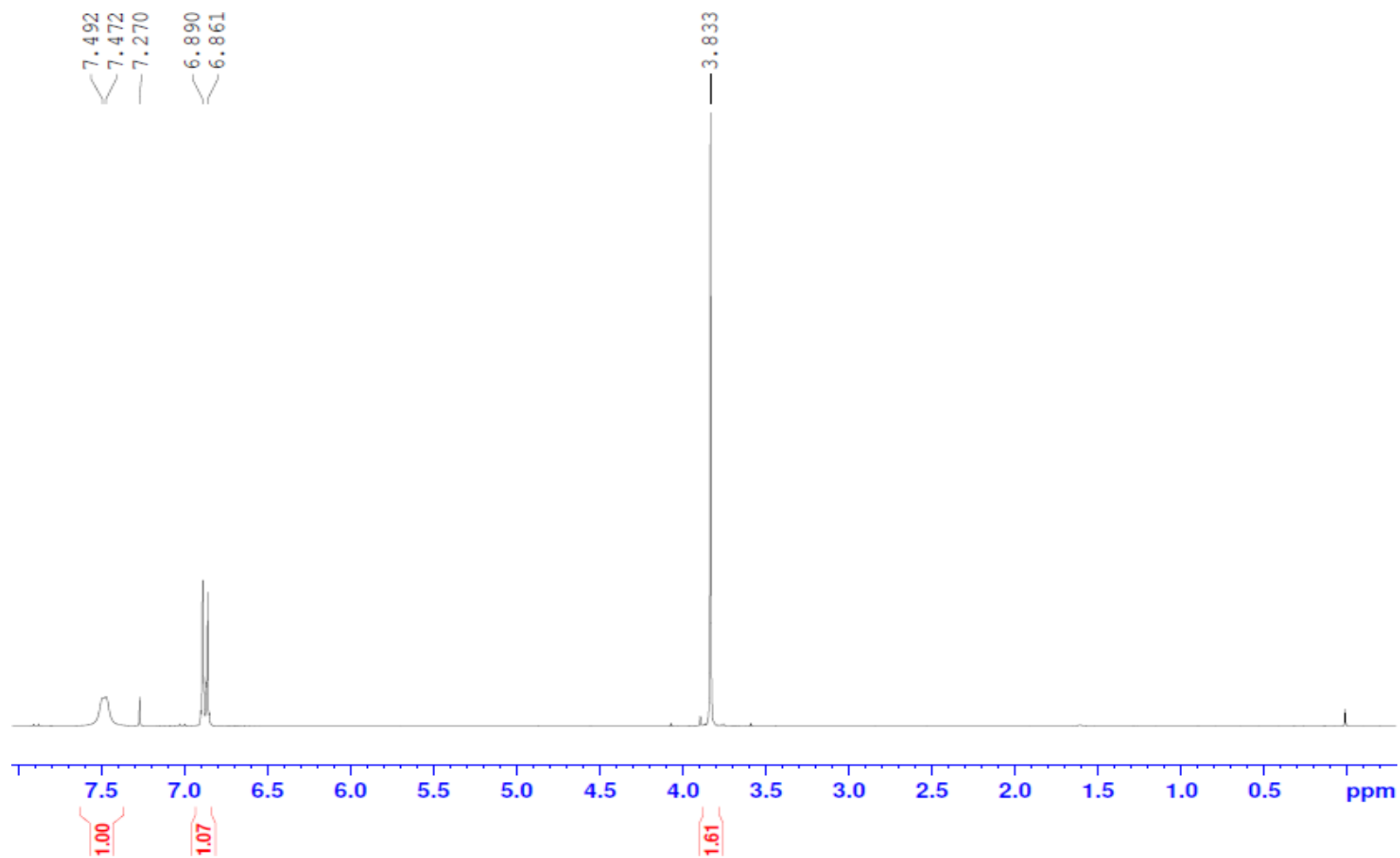


Figure B.140. ^1H NMR of **1** in CDCl_3 taken at room temperature, referenced to residual solvent at 7.27 ppm

700MHz 1D Proton with no Decoupling
bis(4-methoxyphenyl)sulfur diimide 1H CDCl3 w/TMS -33C

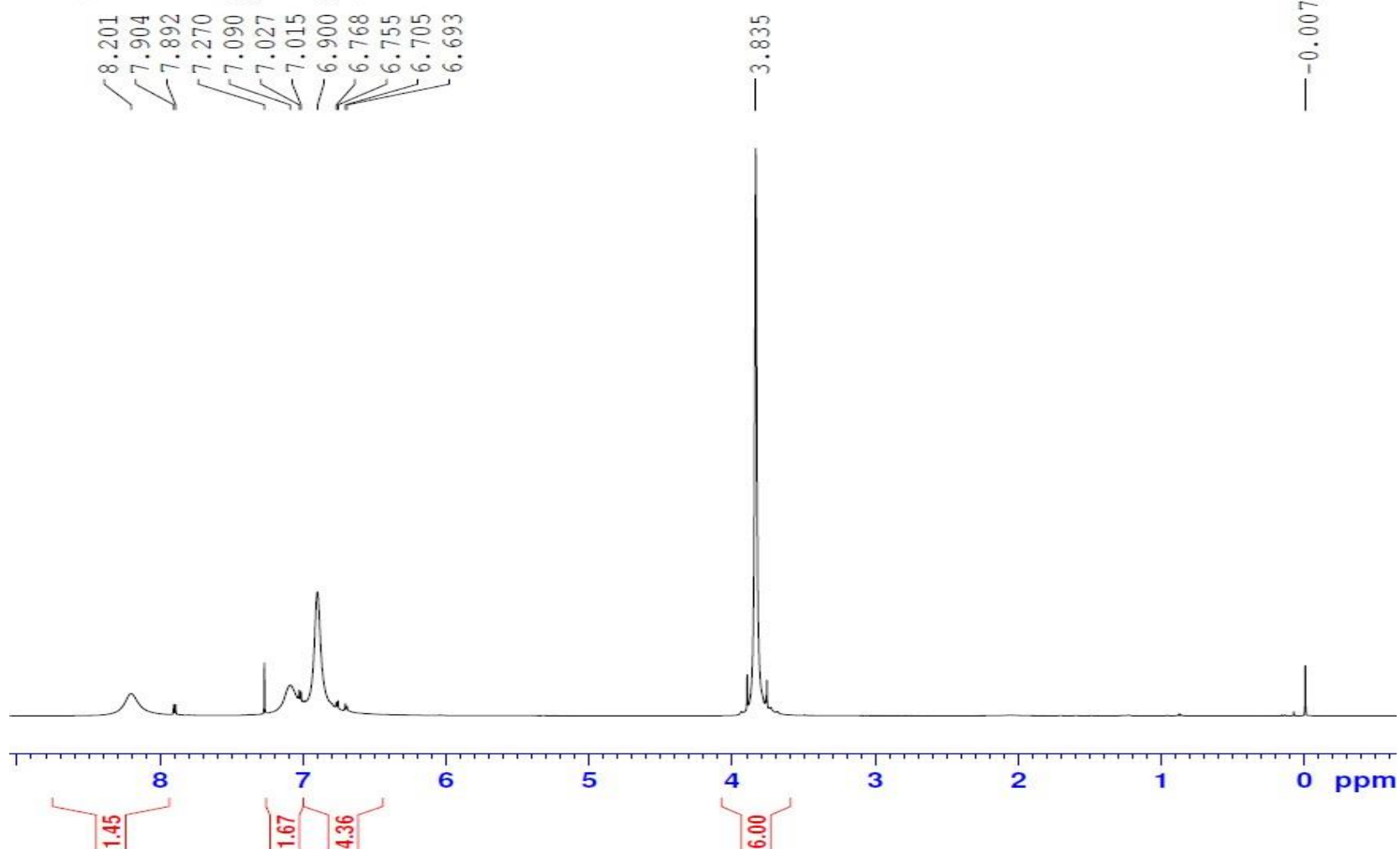


Figure B.141. ^1H NMR of **1** in CDCl_3 taken at 240 K, referenced to residual solvent at 7.27 ppm

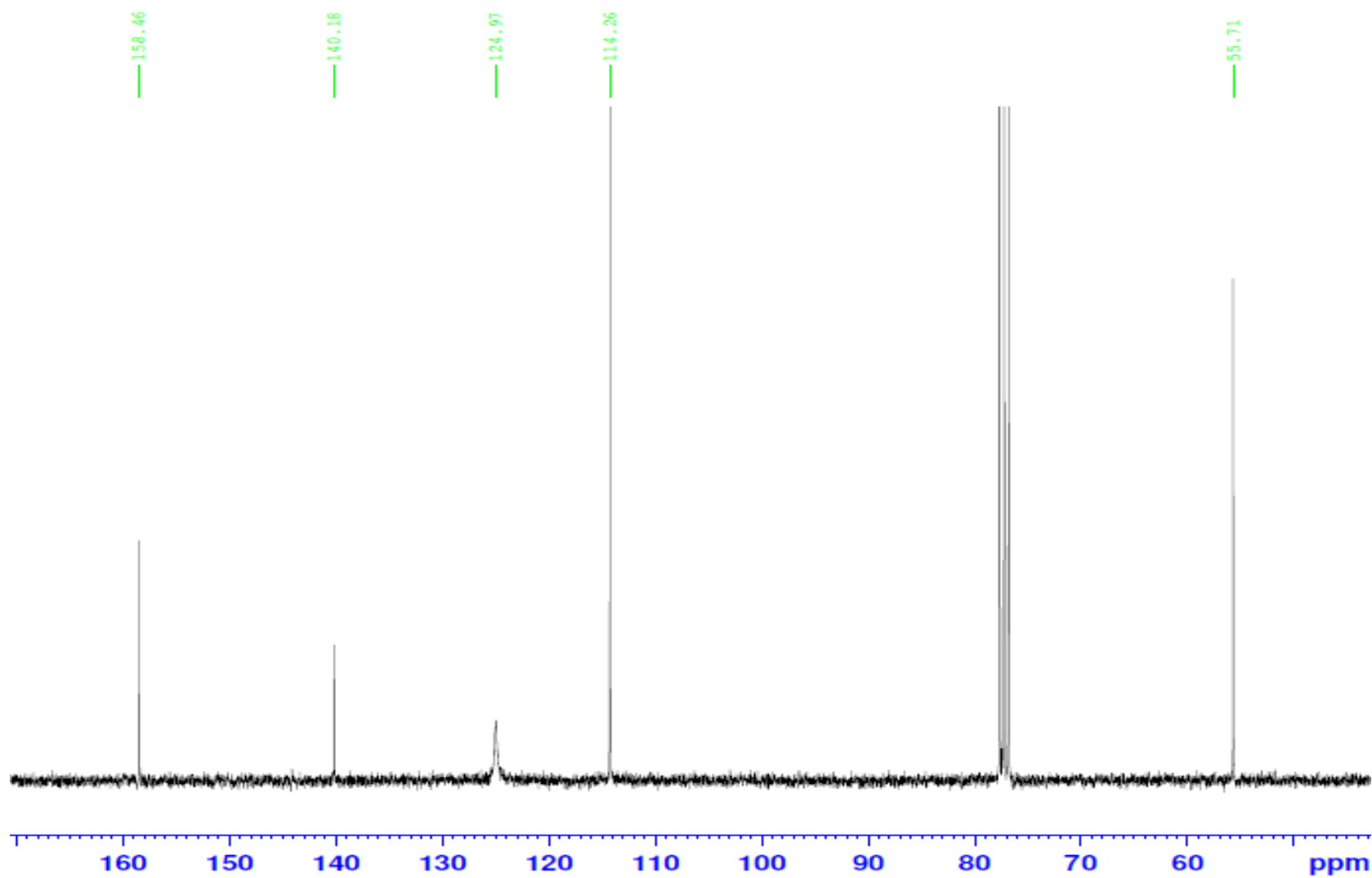


Figure B.142. ¹³C{¹H} NMR of **1** in CDCl₃ taken at room temperature, referenced to residual solvent at 77.23 ppm

^{13}C with ^1H Decoupling
bis(4-methoxyphenyl)sulfur diimide, CDCl_3 , -33°C

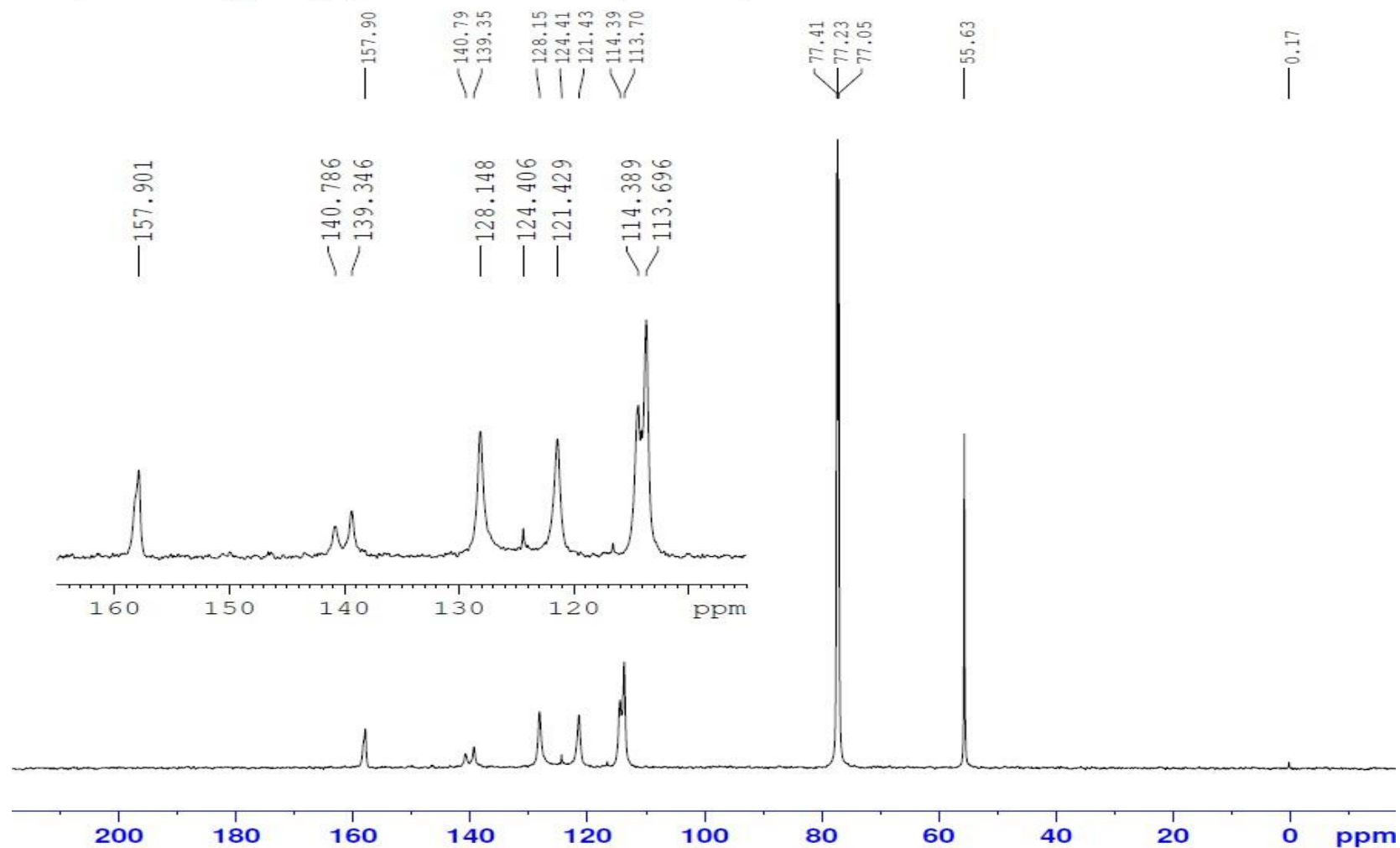


Figure B.143. $^{13}\text{C}\{^1\text{H}\}$ NMR of **1** in CDCl_3 taken at 240 K, referenced to residual solvent at 77.23 ppm

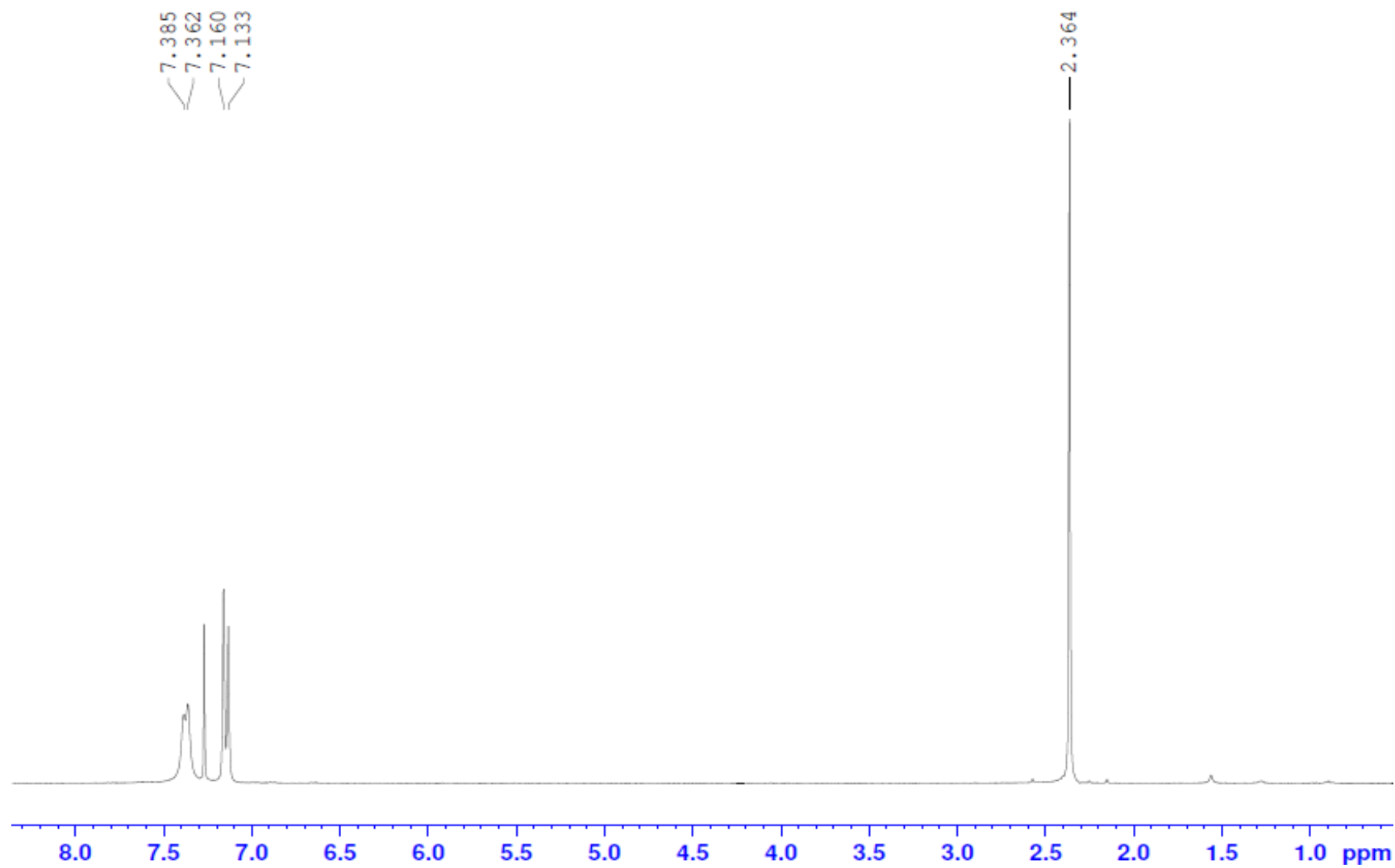


Figure B.144. ^1H NMR of **2** in CDCl_3 taken at room temperature, referenced to residual solvent at 7.27 ppm

1D Proton with no Decoupling
bis(4-tolyl)sulfur diimide, CDCl₃, -40C

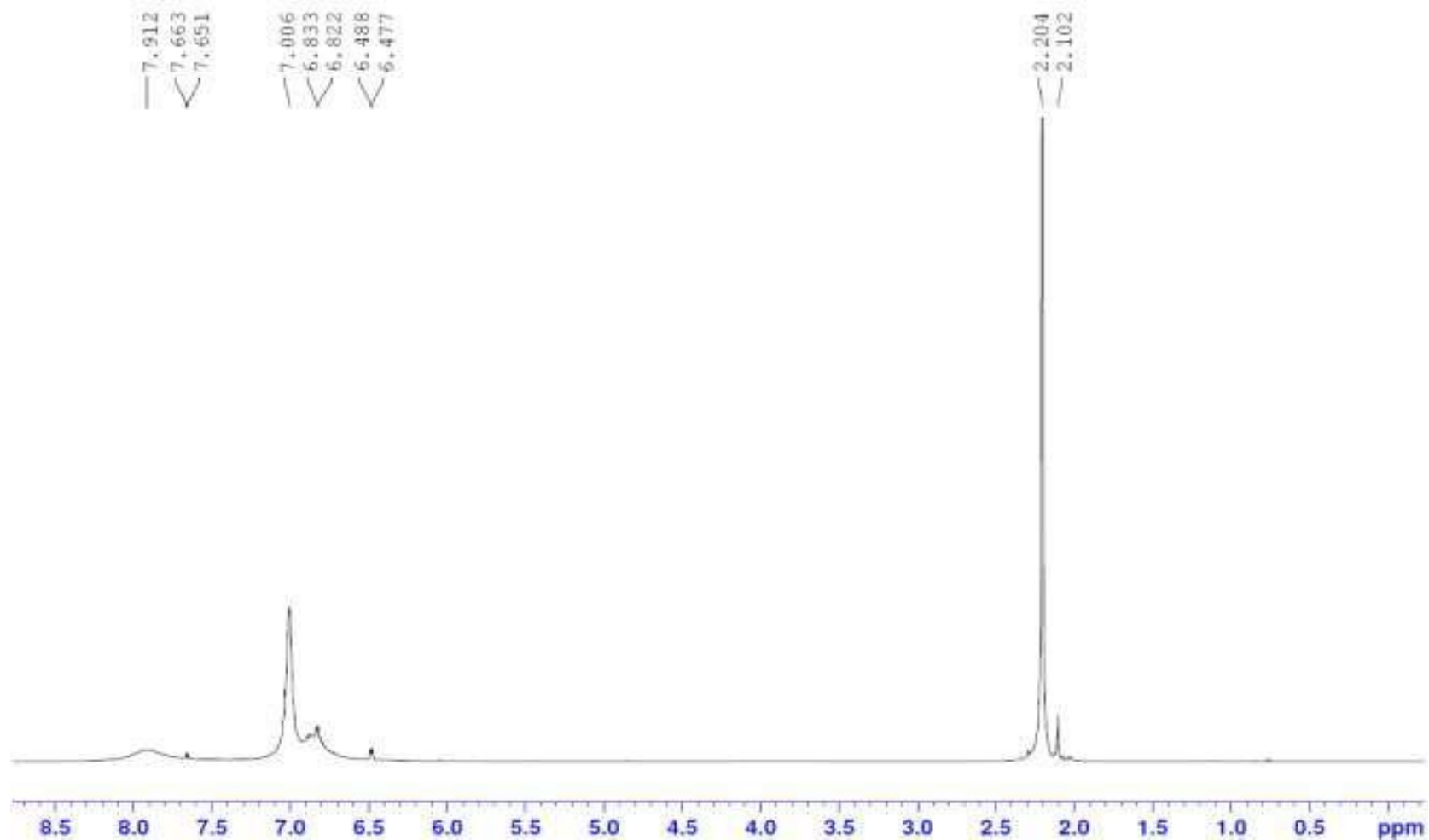


Figure B.145. ¹H NMR of 2 in CDCl₃ taken at 233 K, referenced to residual solvent at 7.27 ppm

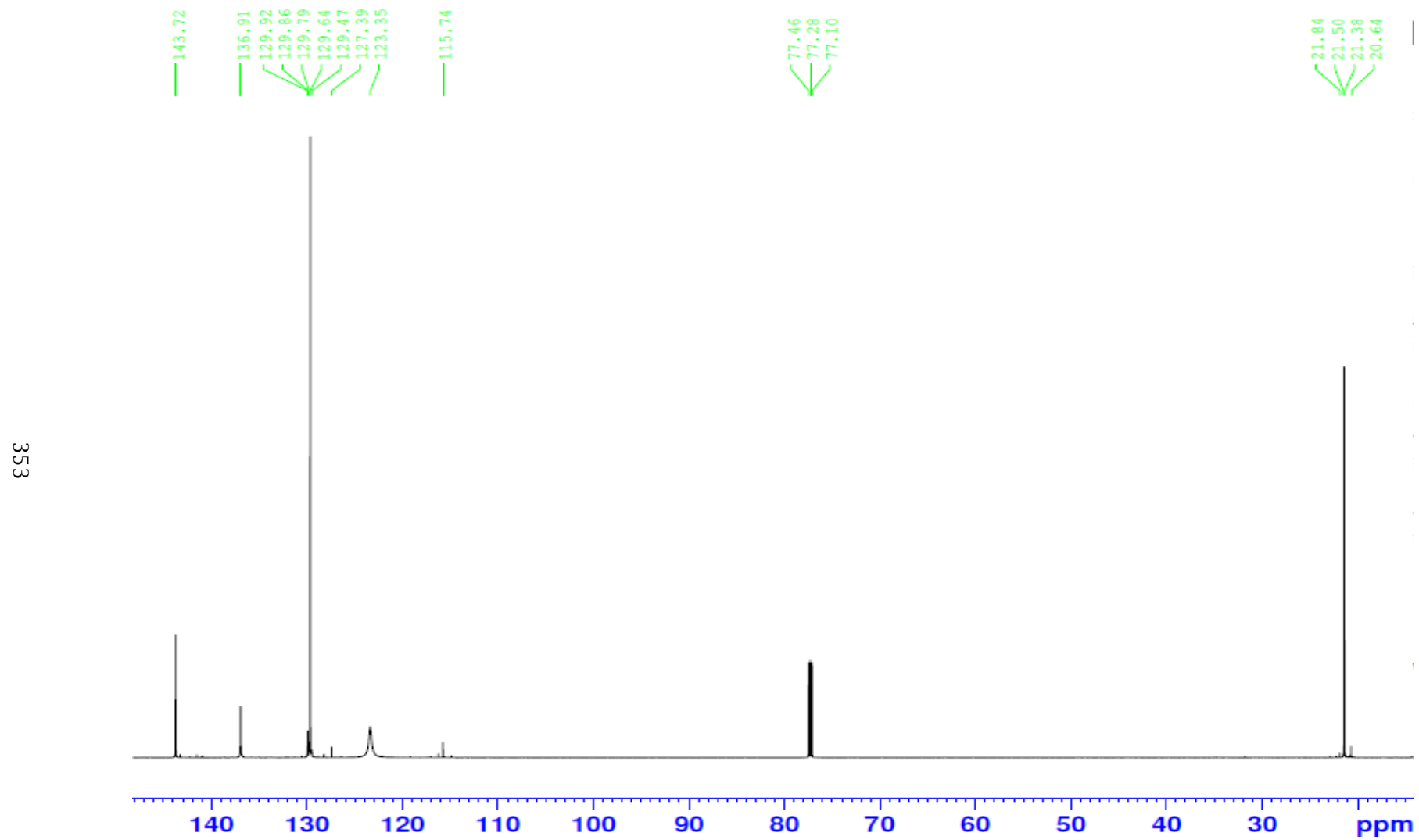


Figure B.146. $^{13}\text{C}\{^1\text{H}\}$ NMR of **2** in CDCl_3 at room temperature, referenced to residual solvent at 77.23 ppm

$^{13}\text{C}\{^1\text{H}\}$ bis(4-tolyl)sulfur diimide -40 Deg C

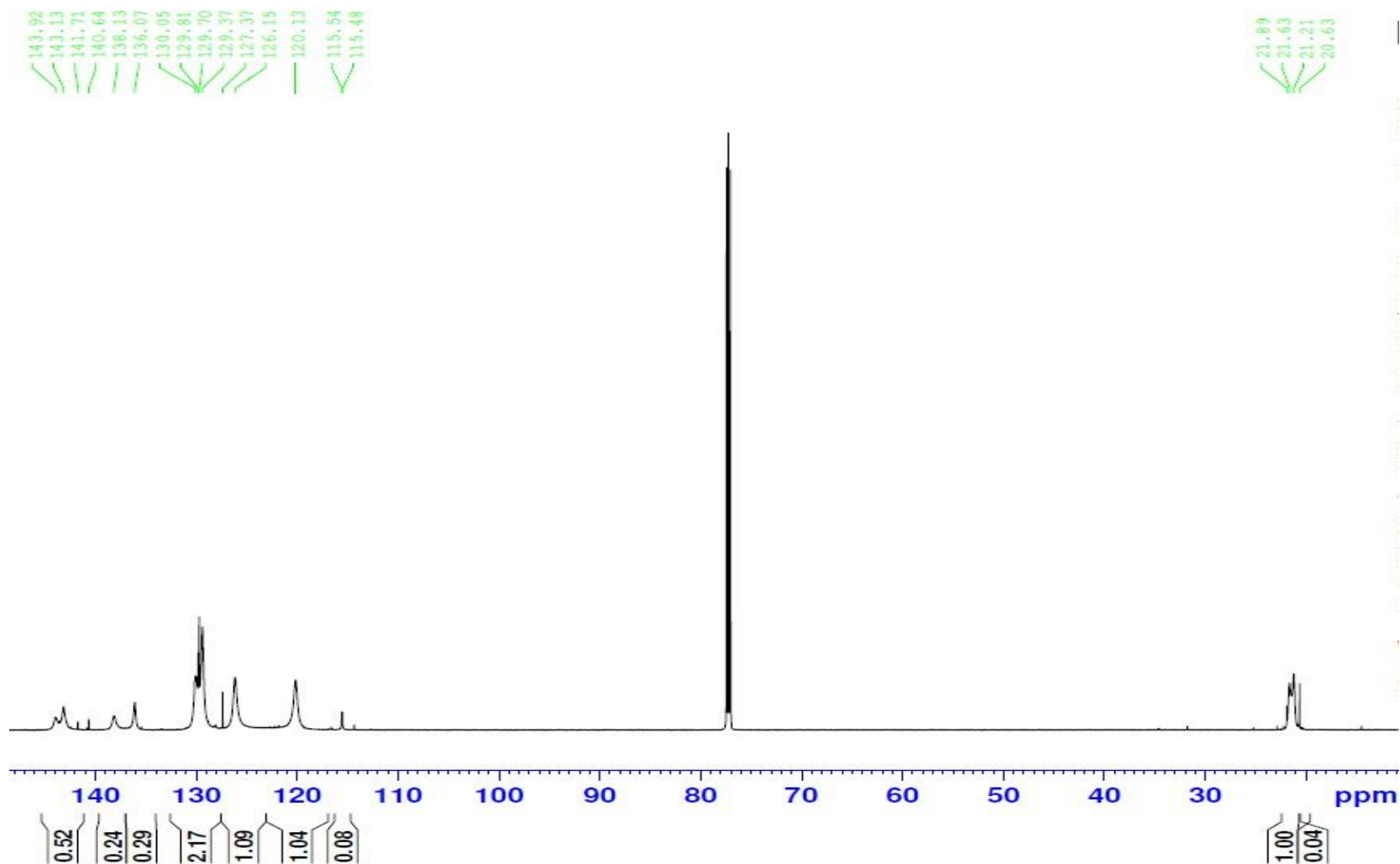


Figure B.147. $^{13}\text{C}\{^1\text{H}\}$ NMR of **2** in CDCl_3 at 233 K, referenced to residual solvent at 77.23 ppm

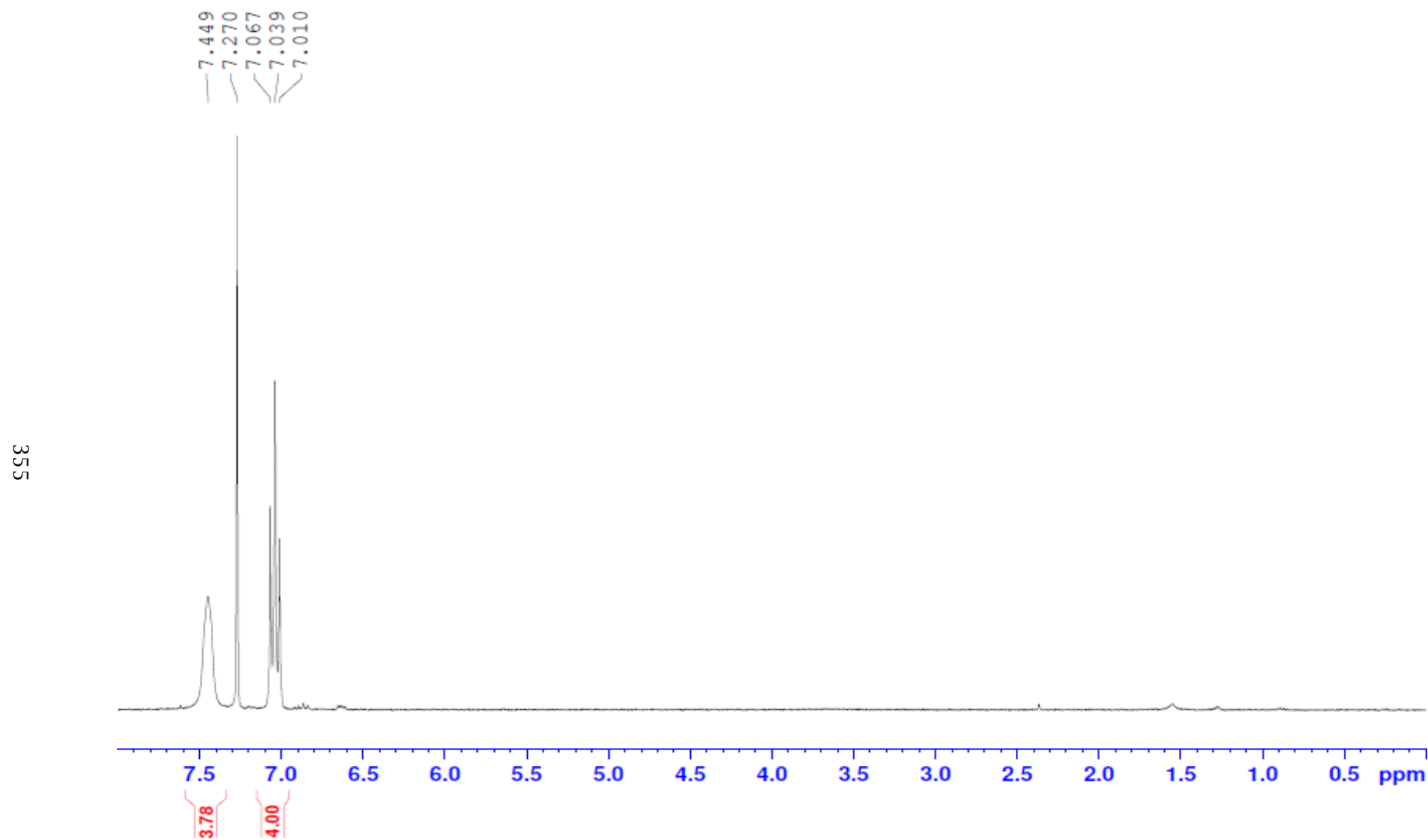


Figure B.148. ¹H NMR of 3 in CDCl₃ taken at room temperature, referenced to residual solvent at 7.27 ppm

^1H (4-FPhN)2S in CDCl_3 with TMS 233K

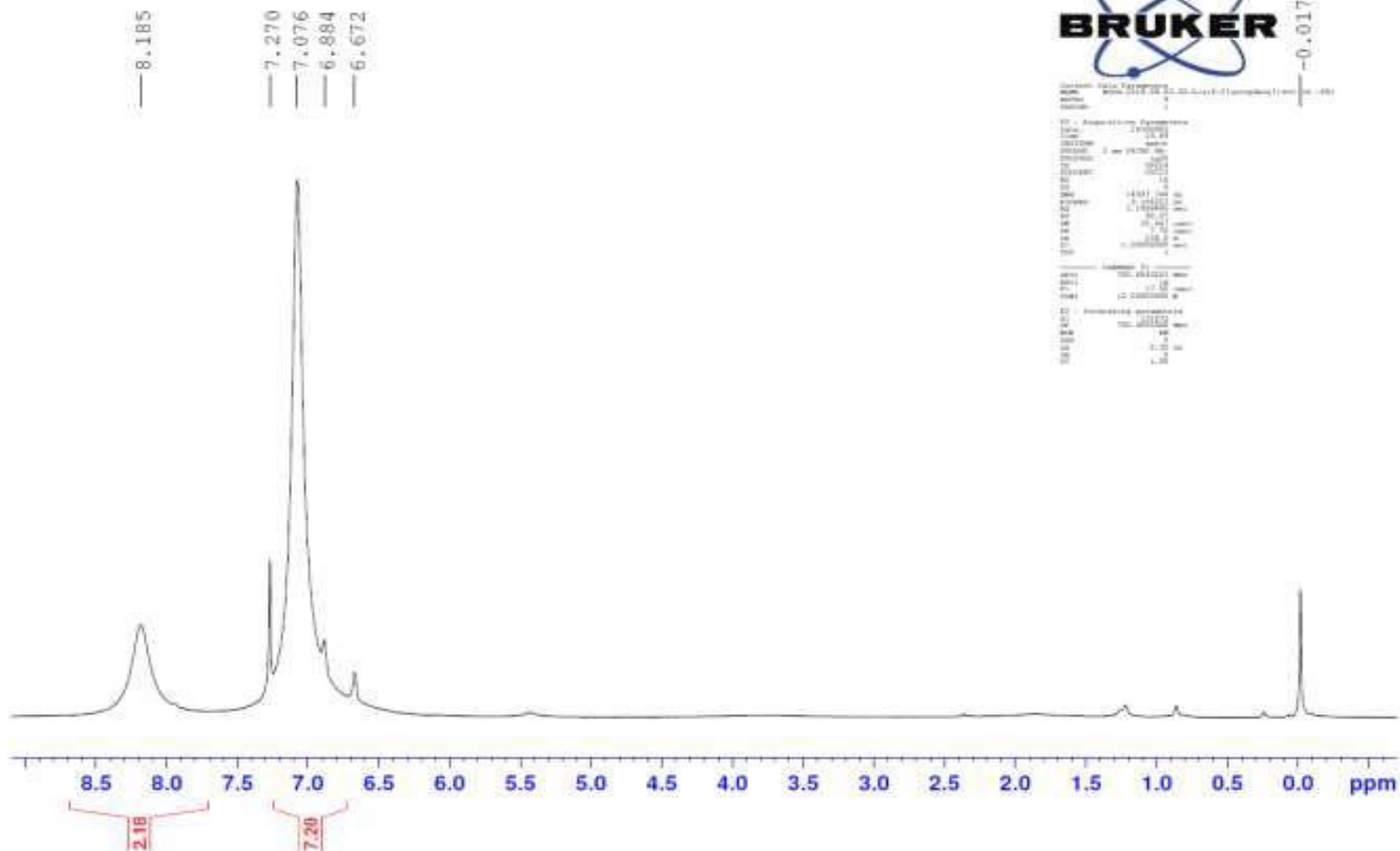


Figure B.149. ^1H NMR of **3** in CDCl_3 taken at 233 K, referenced to residual solvent at 7.27 ppm

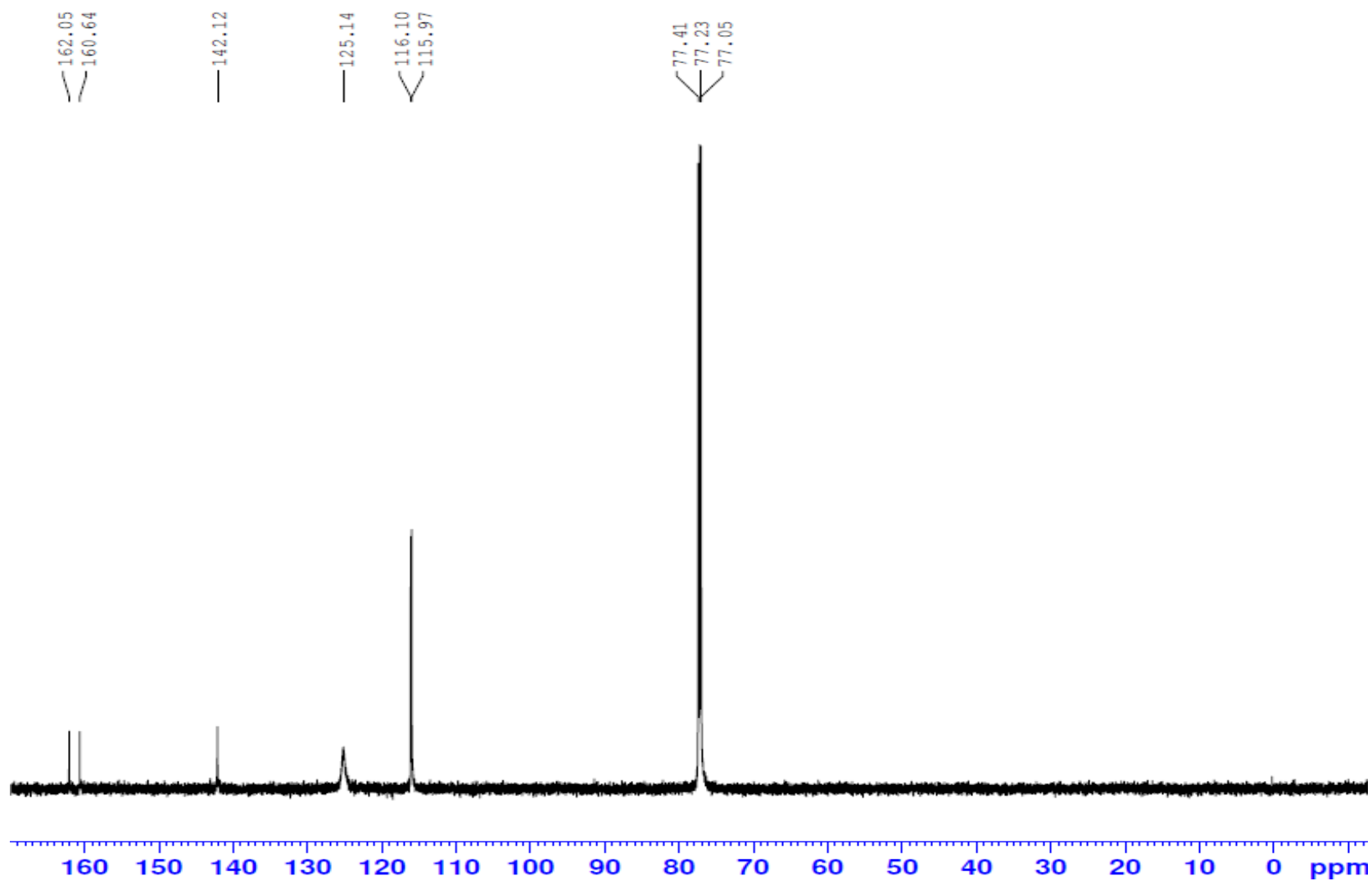


Figure B.150. $^{13}\text{C}\{^1\text{H}\}$ NMR of 3 in CDCl_3 taken at room temperature, referenced to residual solvent at 77.23 ppm

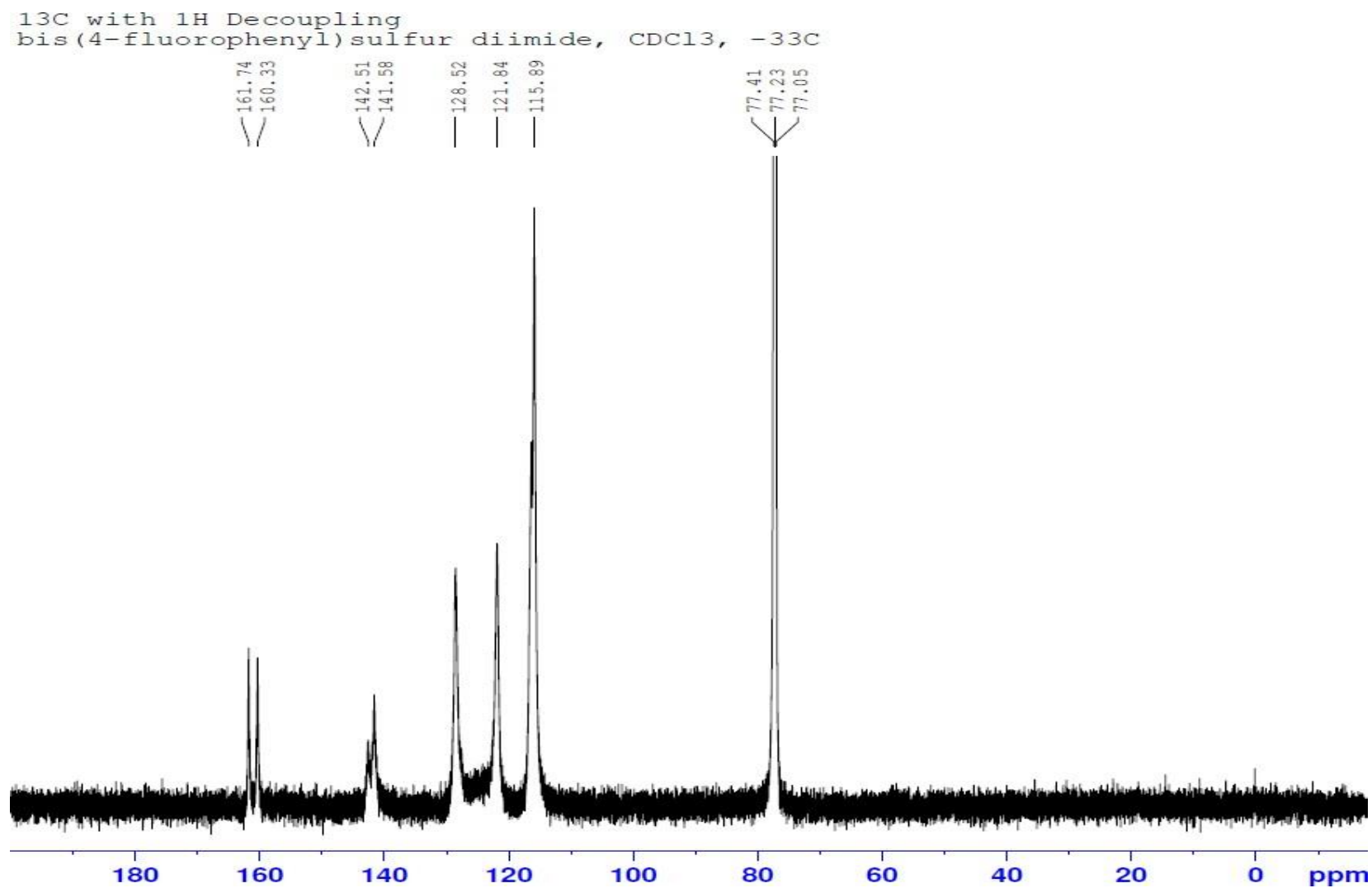


Figure B.151. $^{13}\text{C}\{^1\text{H}\}$ NMR of **3** in CDCl_3 taken at 240 K, referenced to residual solvent at 77.23 ppm

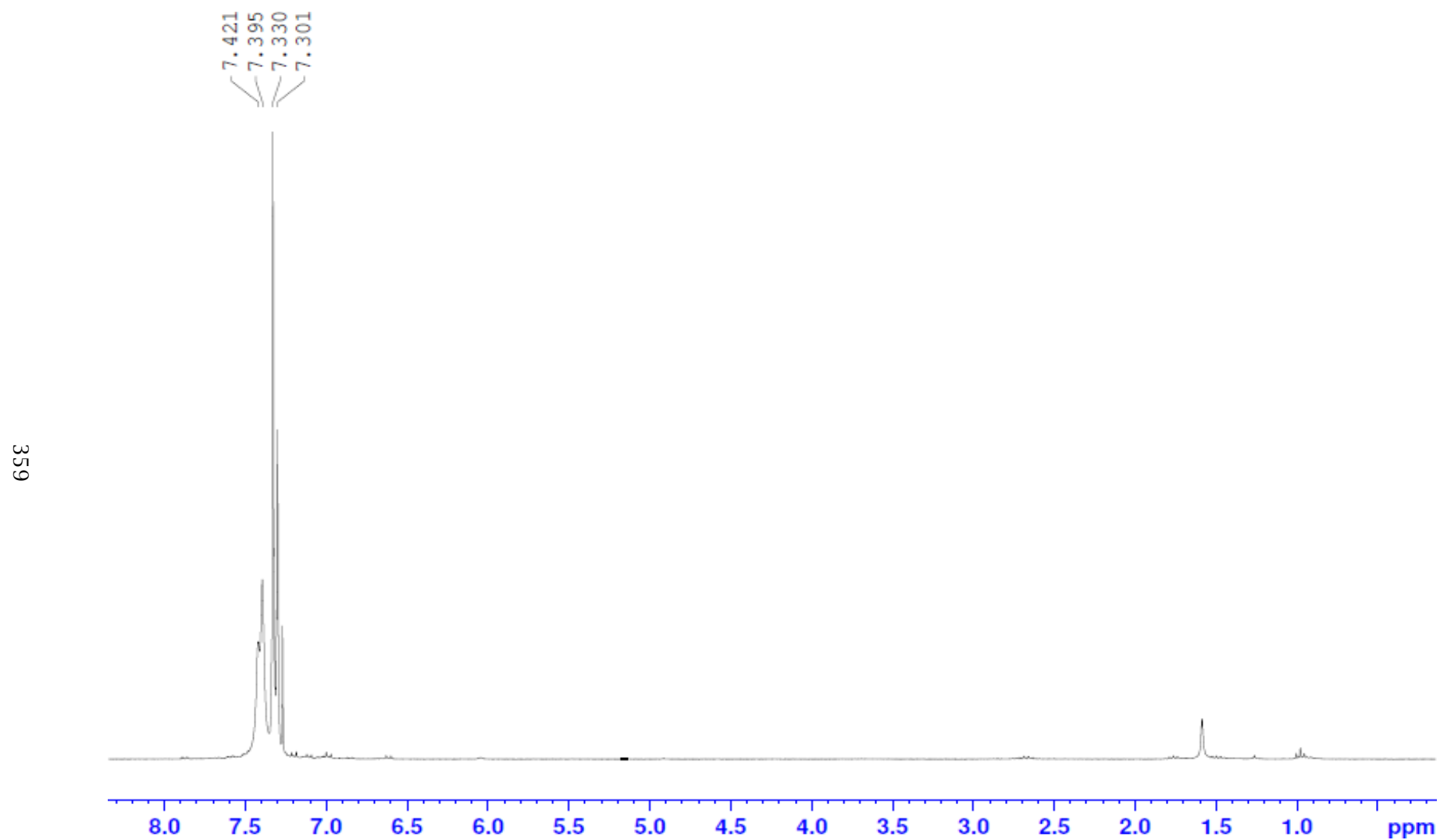


Figure B.152. ^1H NMR of **4** in CDCl_3 taken at room temperature, referenced to residual solvent at 7.27 ppm

1D Proton with no Decoupling
bis(4-chlorophenyl)sulfur diimide, CDCl₃, -33C

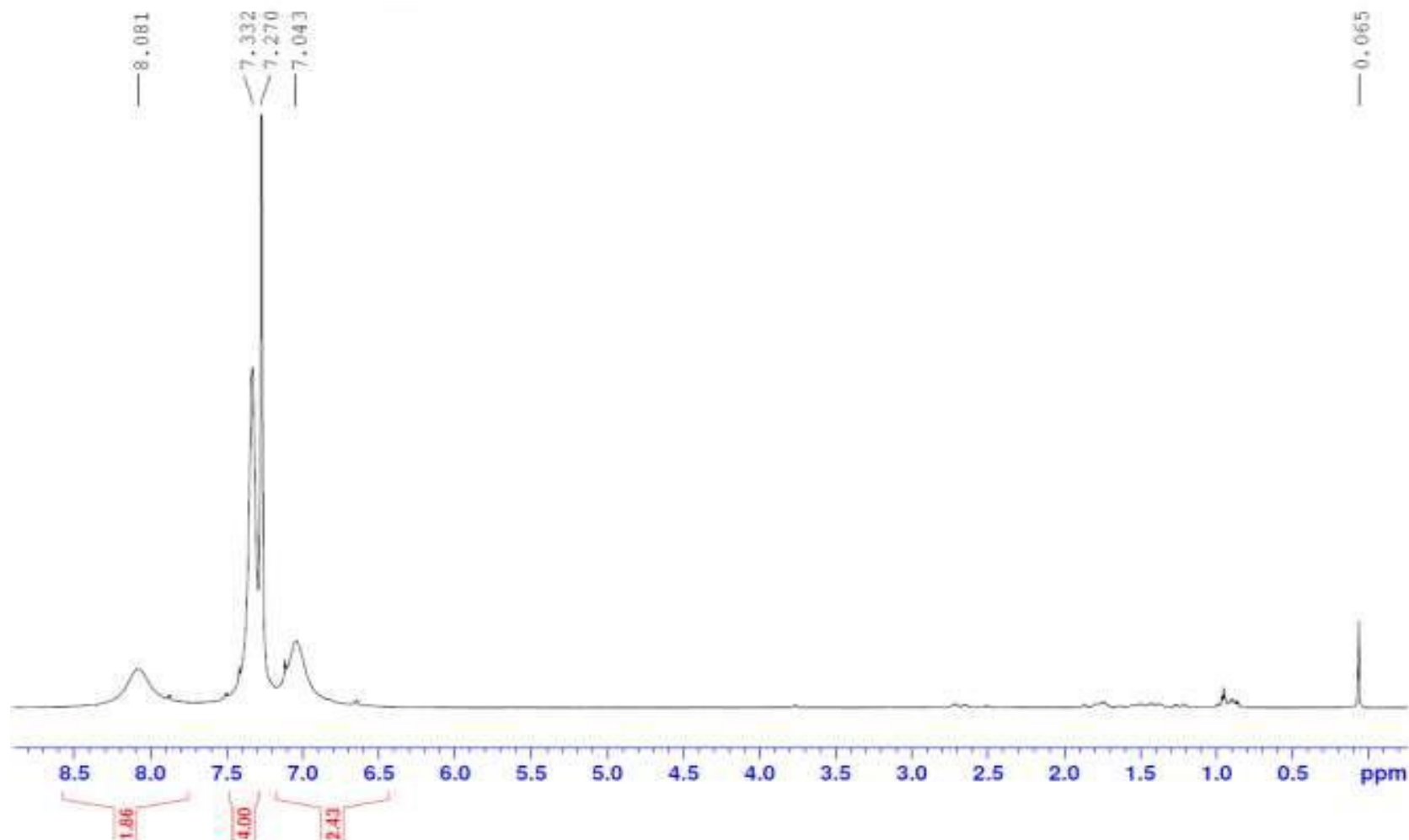


Figure B.153. ¹H NMR of **4** in CDCl₃ taken at 240 K, referenced to residual solvent at 7.27 ppm

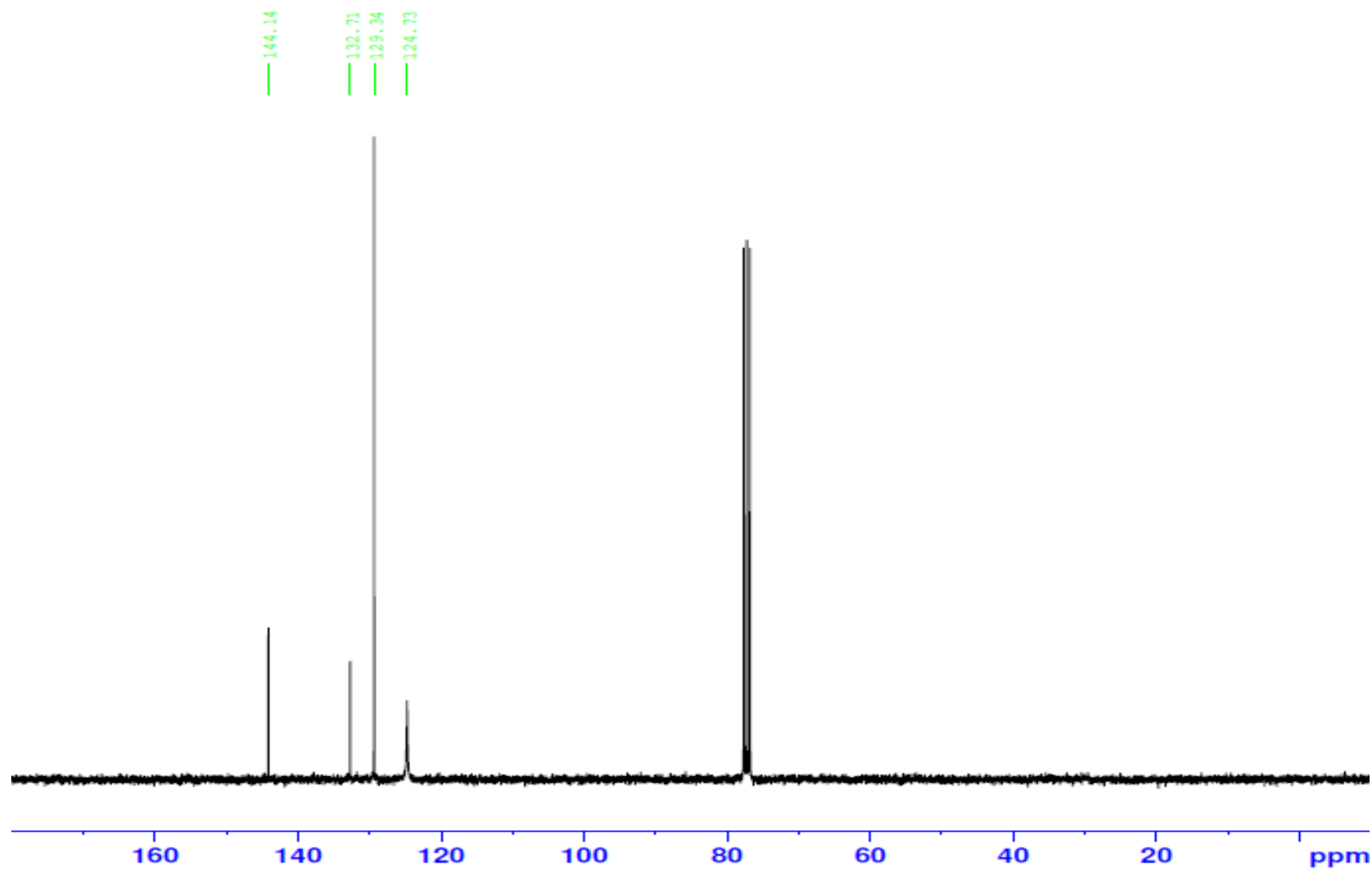


Figure B.154. $^{13}\text{C}\{^1\text{H}\}$ NMR of **4** in CDCl_3 taken at room temperature, referenced to residual solvent at 77.23 ppm

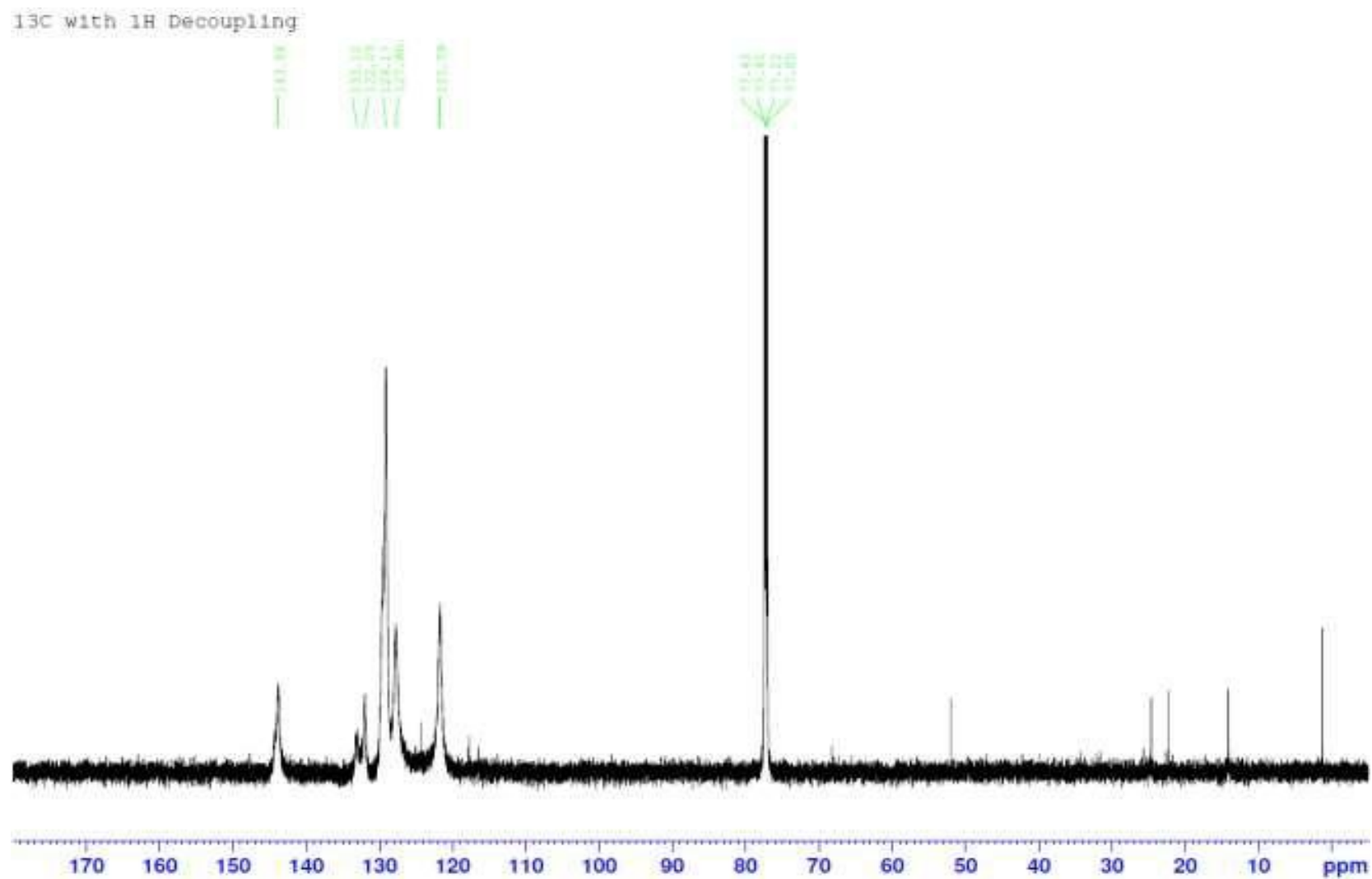


Figure B.155. $^{13}\text{C}\{^1\text{H}\}$ NMR of **4** in CDCl_3 taken at 240 K, referenced to residual solvent at 77.23 ppm

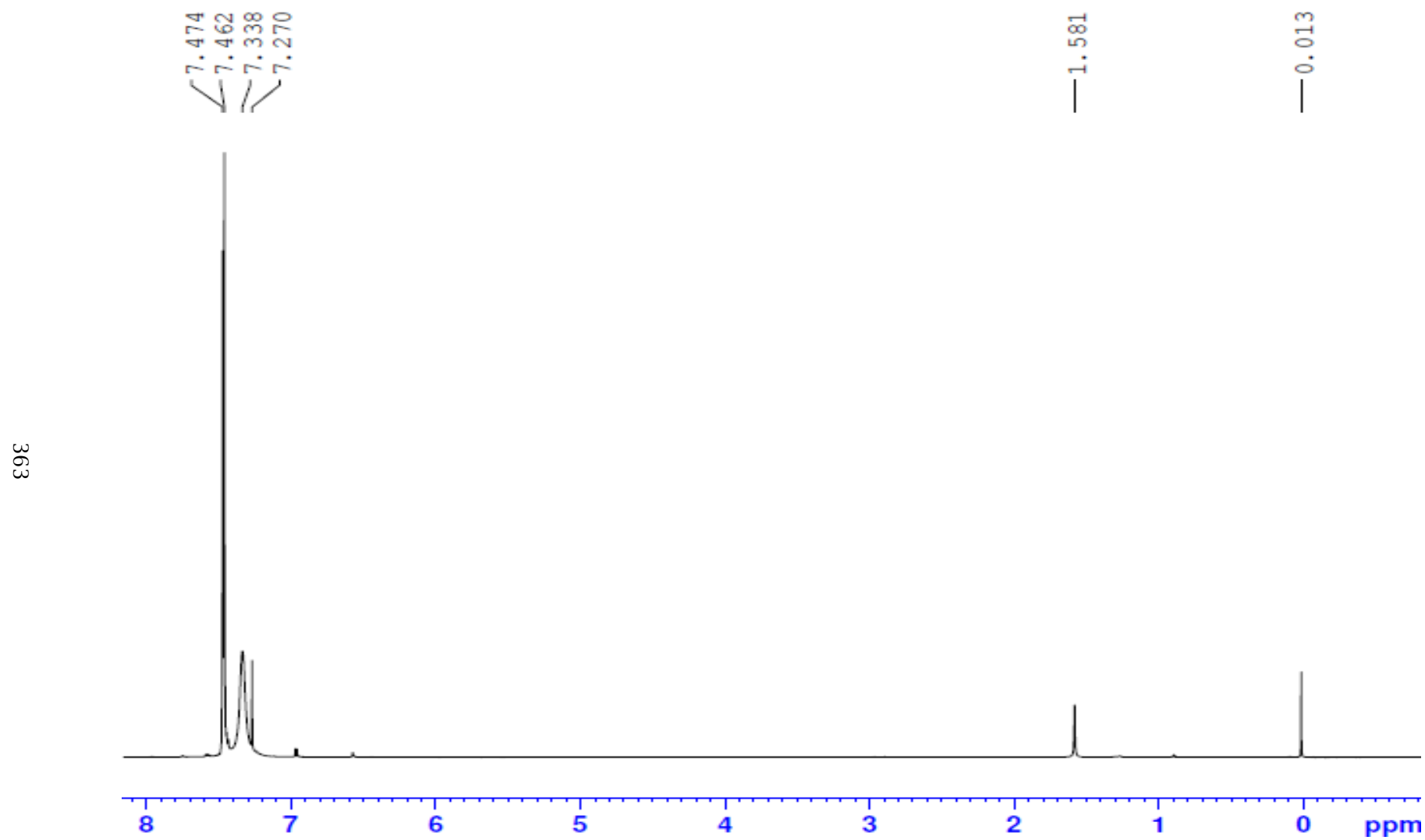


Figure B.156. ^1H NMR of **5** in CDCl_3 taken at room temperature, referenced to residual solvent at 7.27 ppm

1D Proton with no Decoupling
bis(4-bromophenyl)sulfur diimide, CDCl₃, -33C

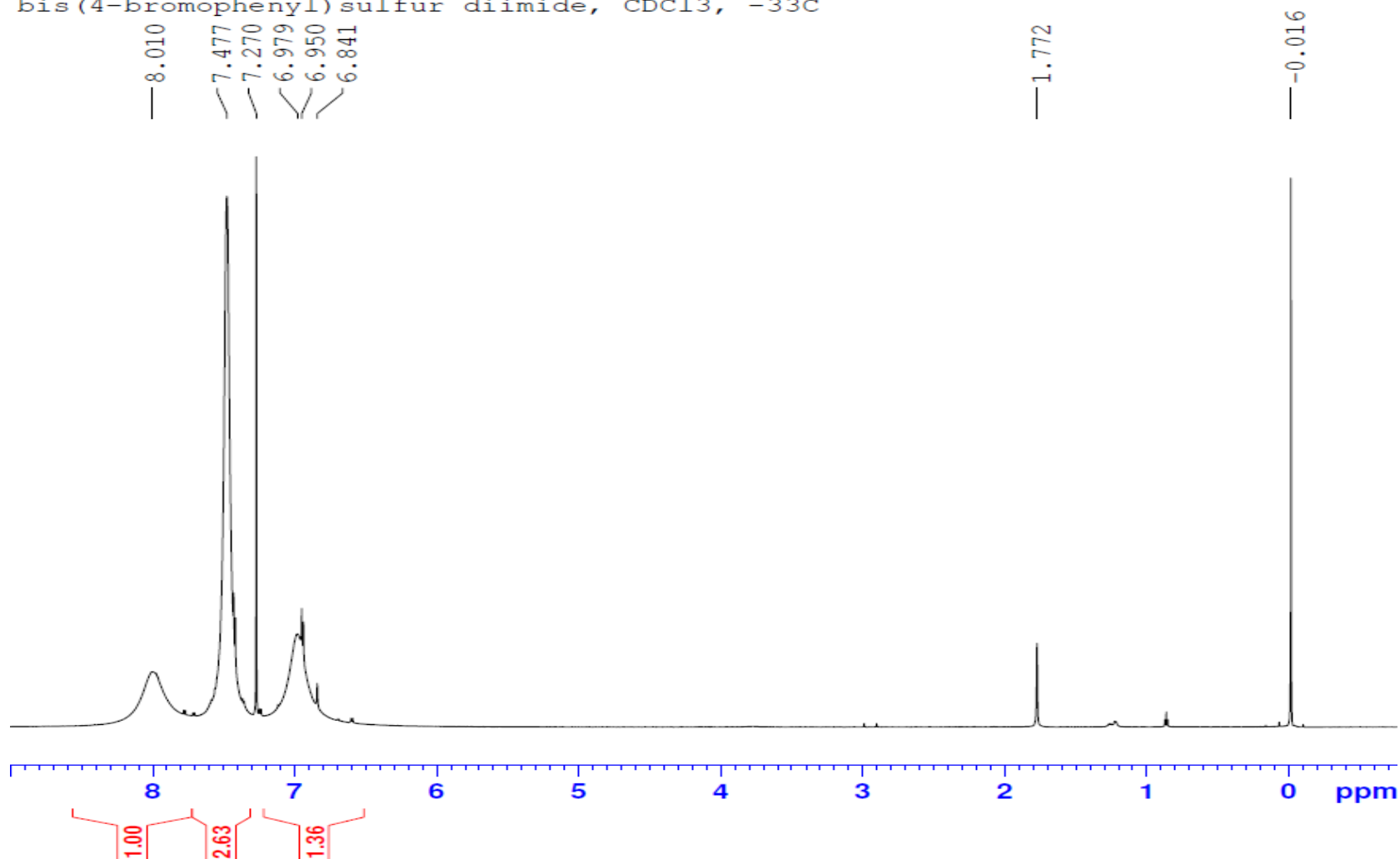


Figure B.157. ¹H NMR of **5** in CDCl₃ taken at 240 K, referenced to residual solvent at 7.27 ppm

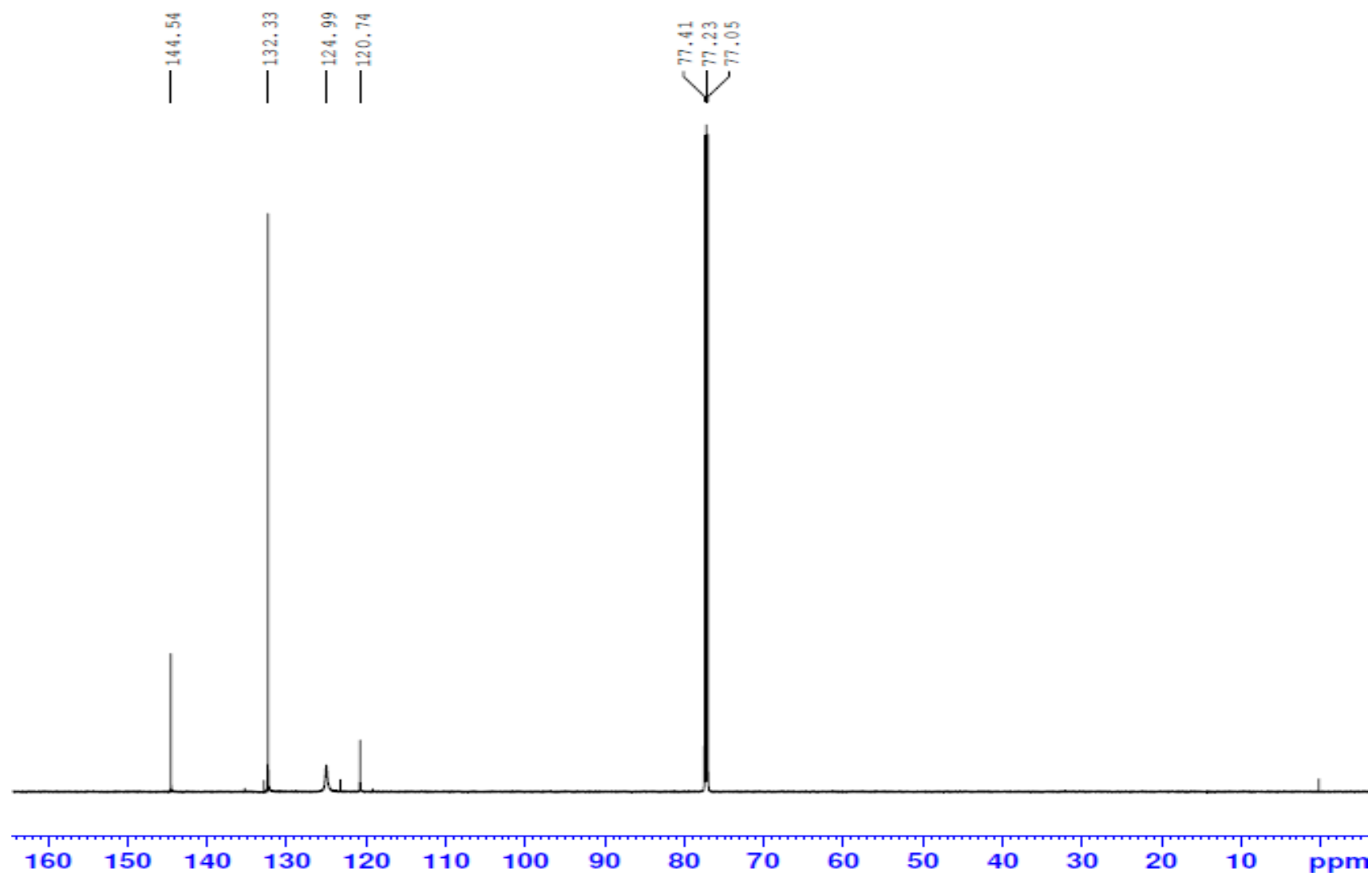


Figure B.158. $^{13}\text{C}\{^1\text{H}\}$ NMR of 5 in CDCl_3 taken at room temperature, referenced to residual solvent at 77.23 ppm

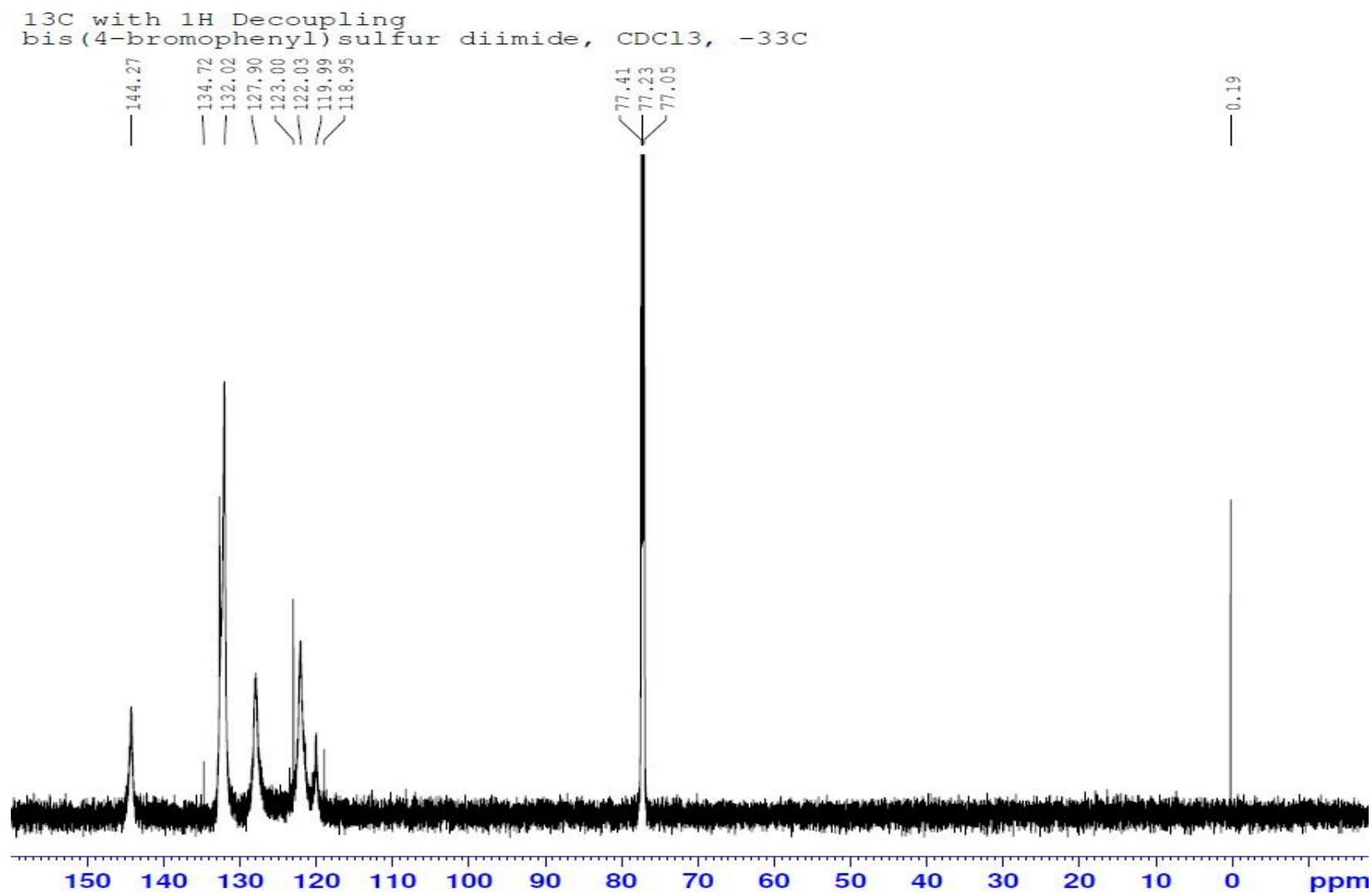


Figure B.159. $^{13}\text{C}\{^1\text{H}\}$ NMR of **5** in CDCl_3 taken at 240 K, referenced to residual solvent at 77.23 ppm

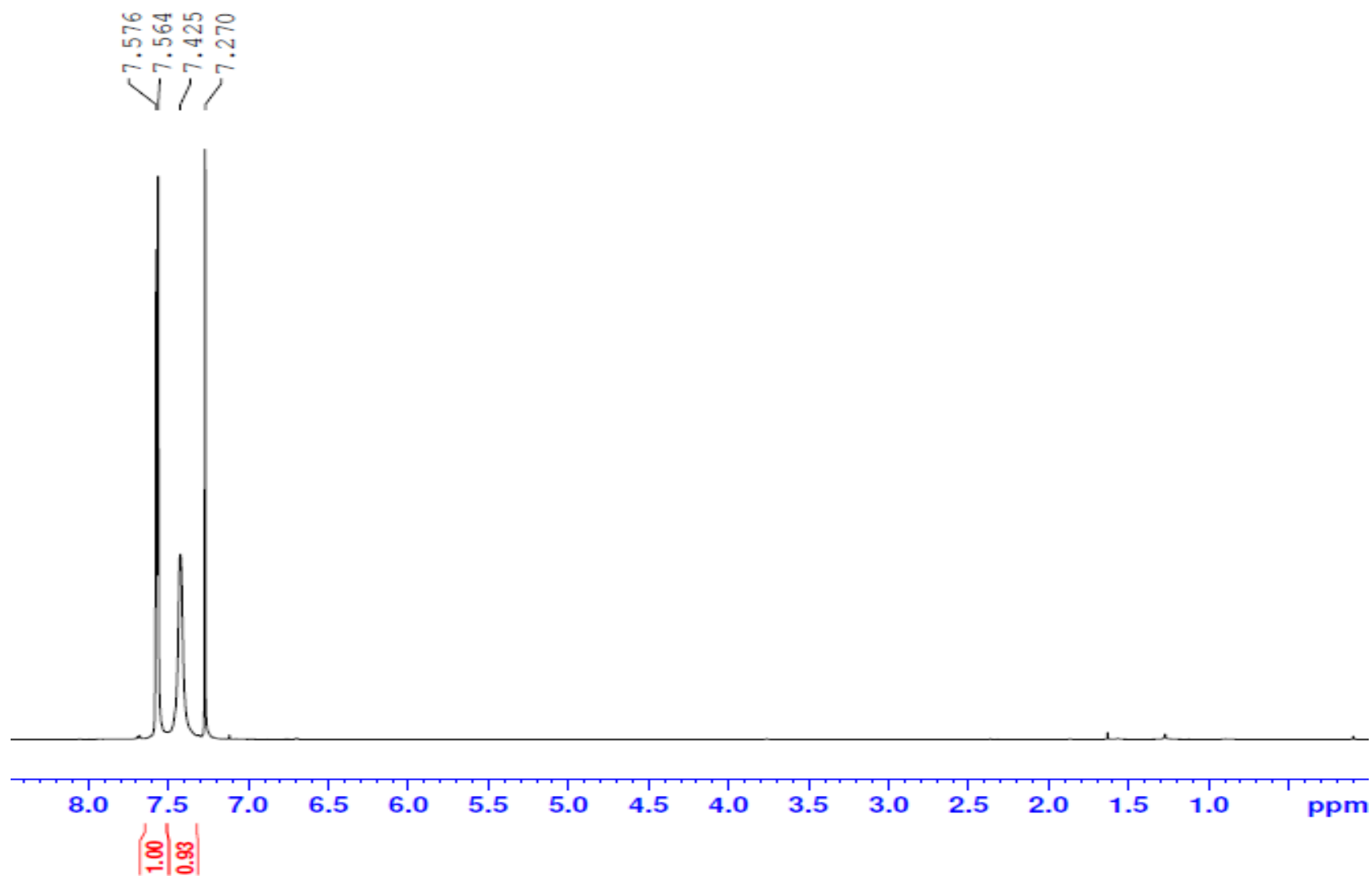


Figure B.160. ¹H NMR of 6 in CDCl₃ taken at room temperature, referenced to residual solvent at 7.27 ppm

1D Proton with no Decoupling
bis(4-trifluoromethylphenyl)sulfur diimide, CDCl₃, -33C

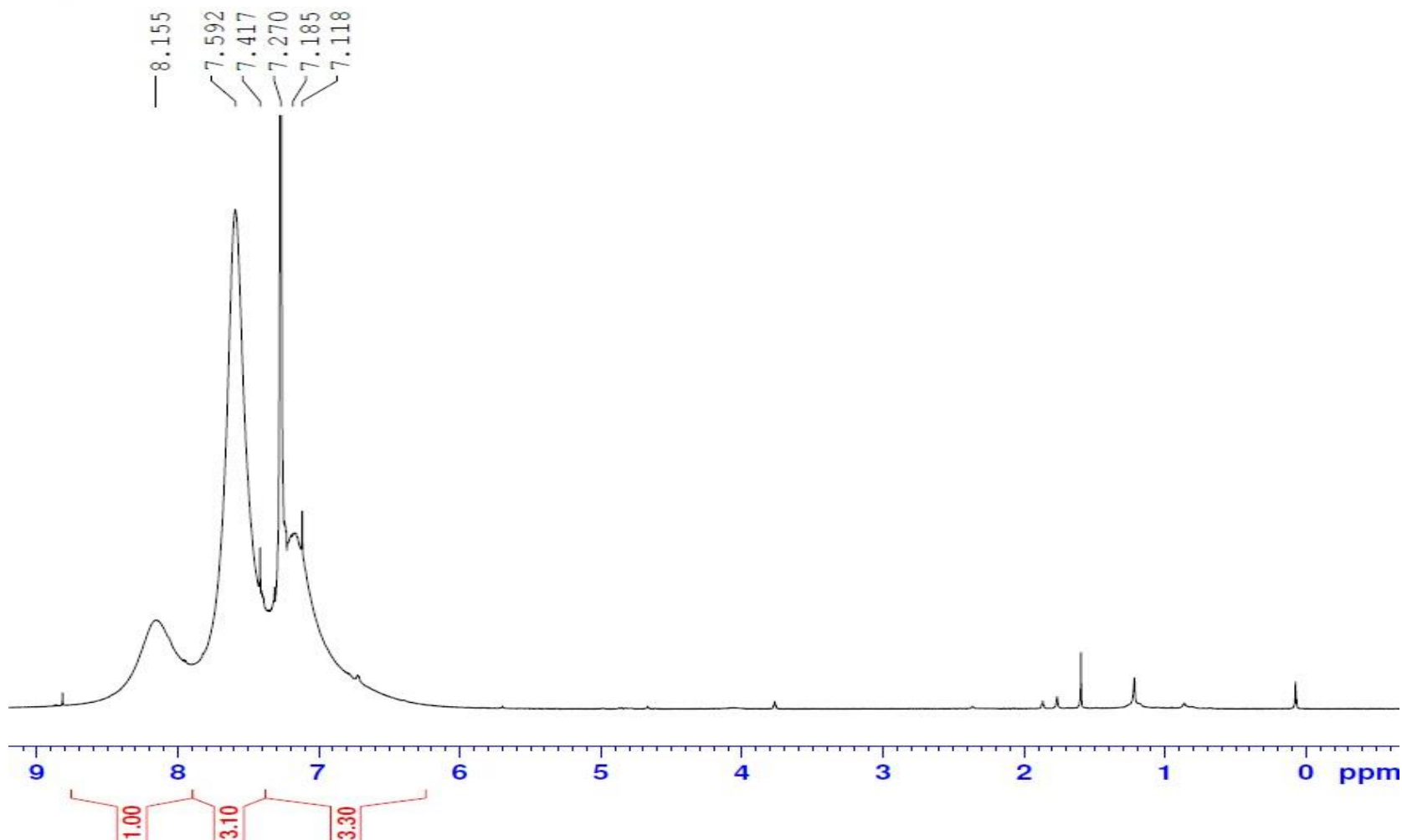


Figure B.161. ¹H NMR of **6** in CDCl₃ taken at 240 K, referenced to residual solvent at 7.27 ppm

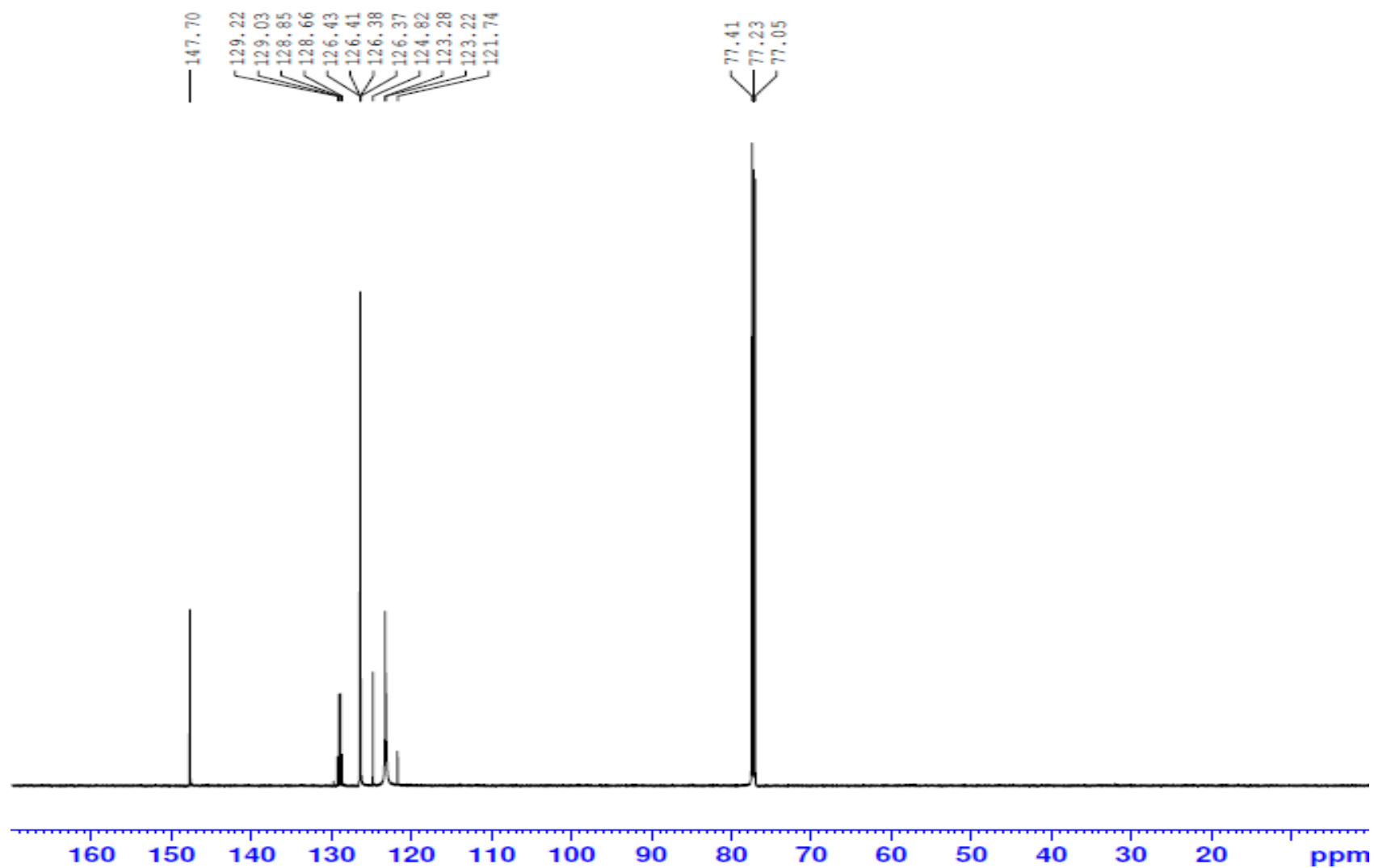


Figure B.162. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6** in CDCl_3 taken at room temperature, referenced to residual solvent at 77.23 ppm

^{13}C with ^1H Decoupling
 bis(4-trifluoromethylphenyl)sulfur diimide, CDCl_3 , -33°C

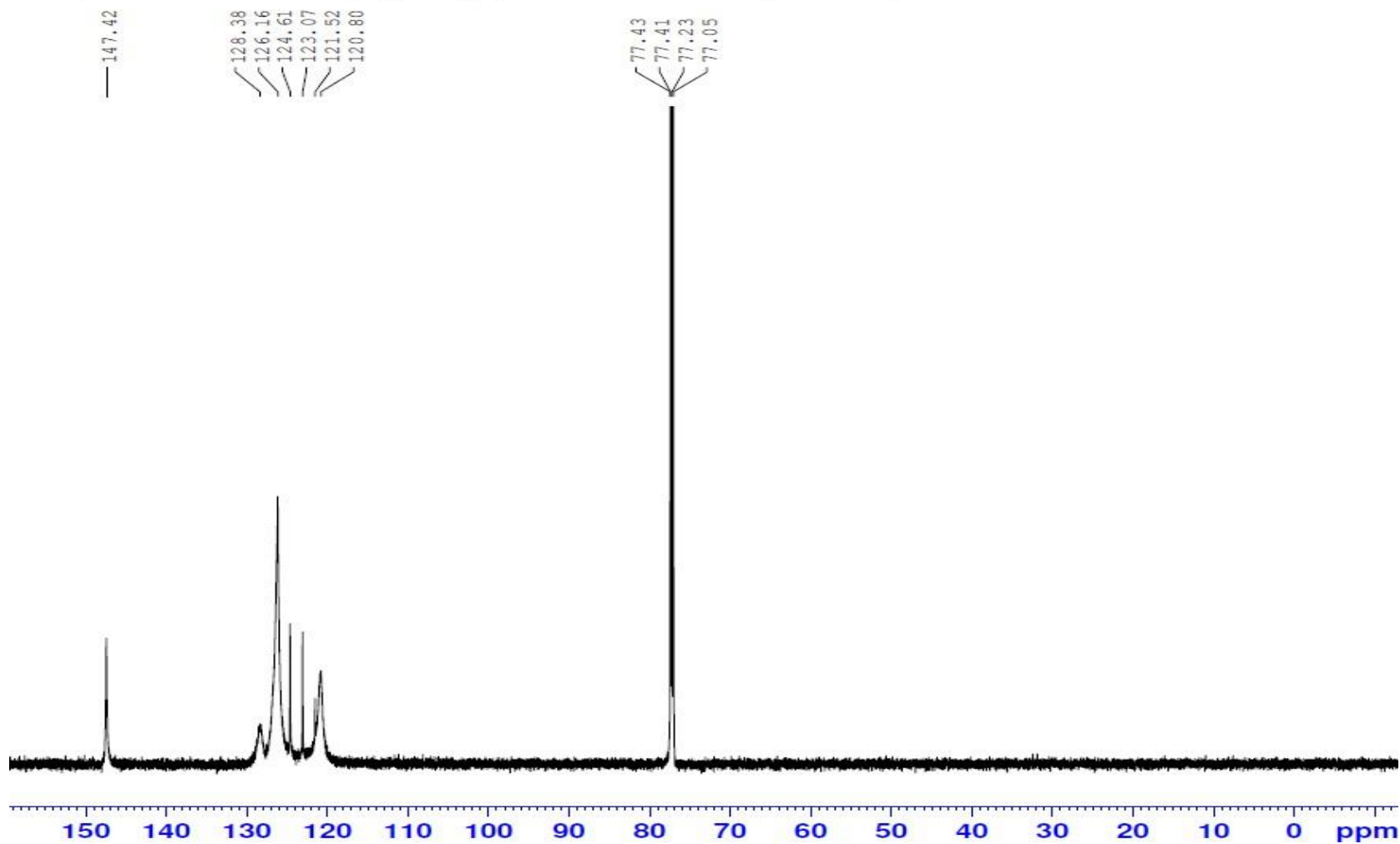


Figure B.163. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6** in CDCl_3 taken at 240 K, referenced to residual solvent at 77.23 ppm

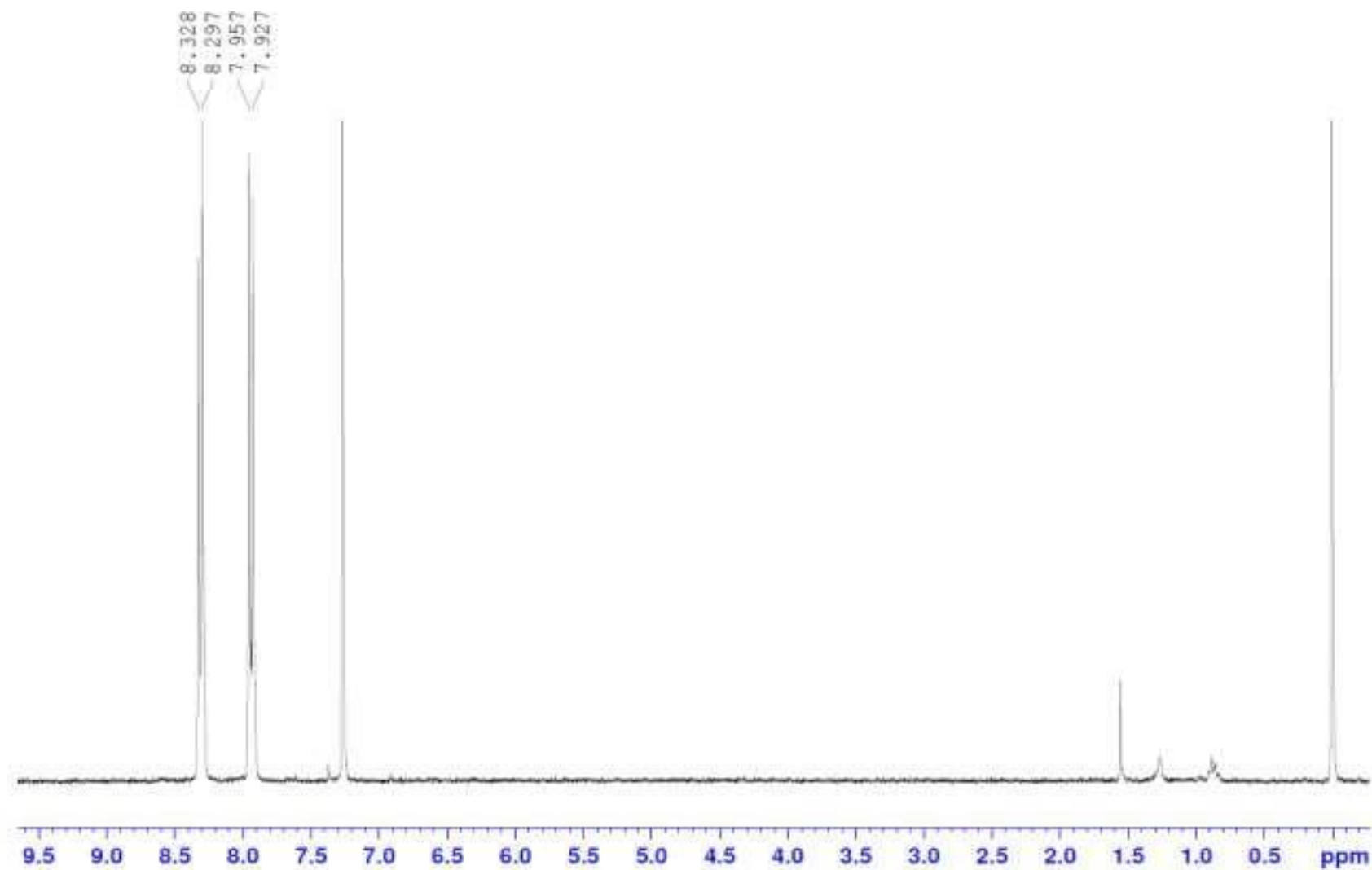


Figure B.164. ^1H NMR of 7 in CDCl_3 taken at room temperature, referenced to residual solvent at 7.27 ppm

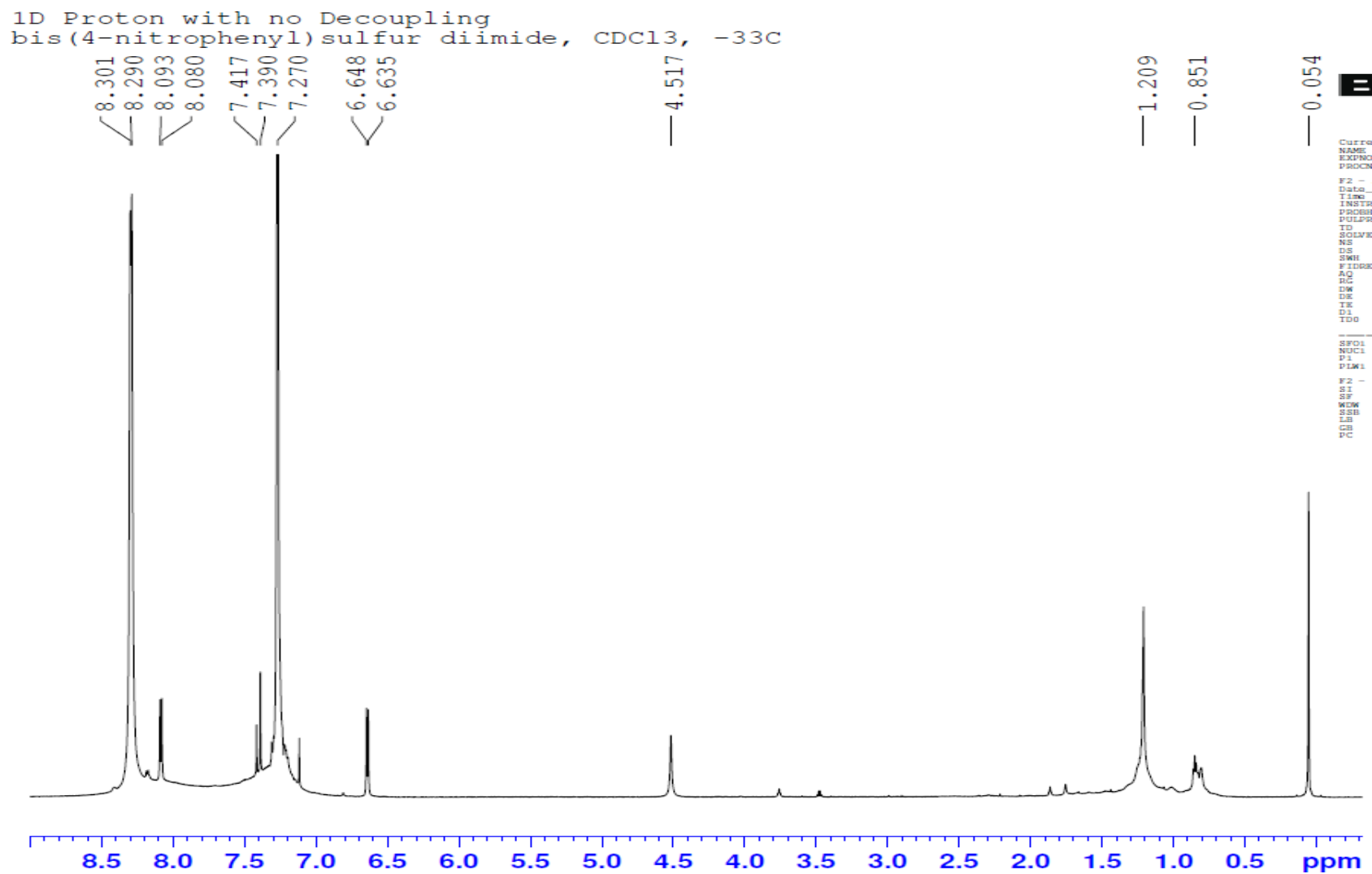


Figure B.165. ¹H NMR of **7** in CDCl₃ taken at 240 K, referenced to residual solvent at 7.27 ppm

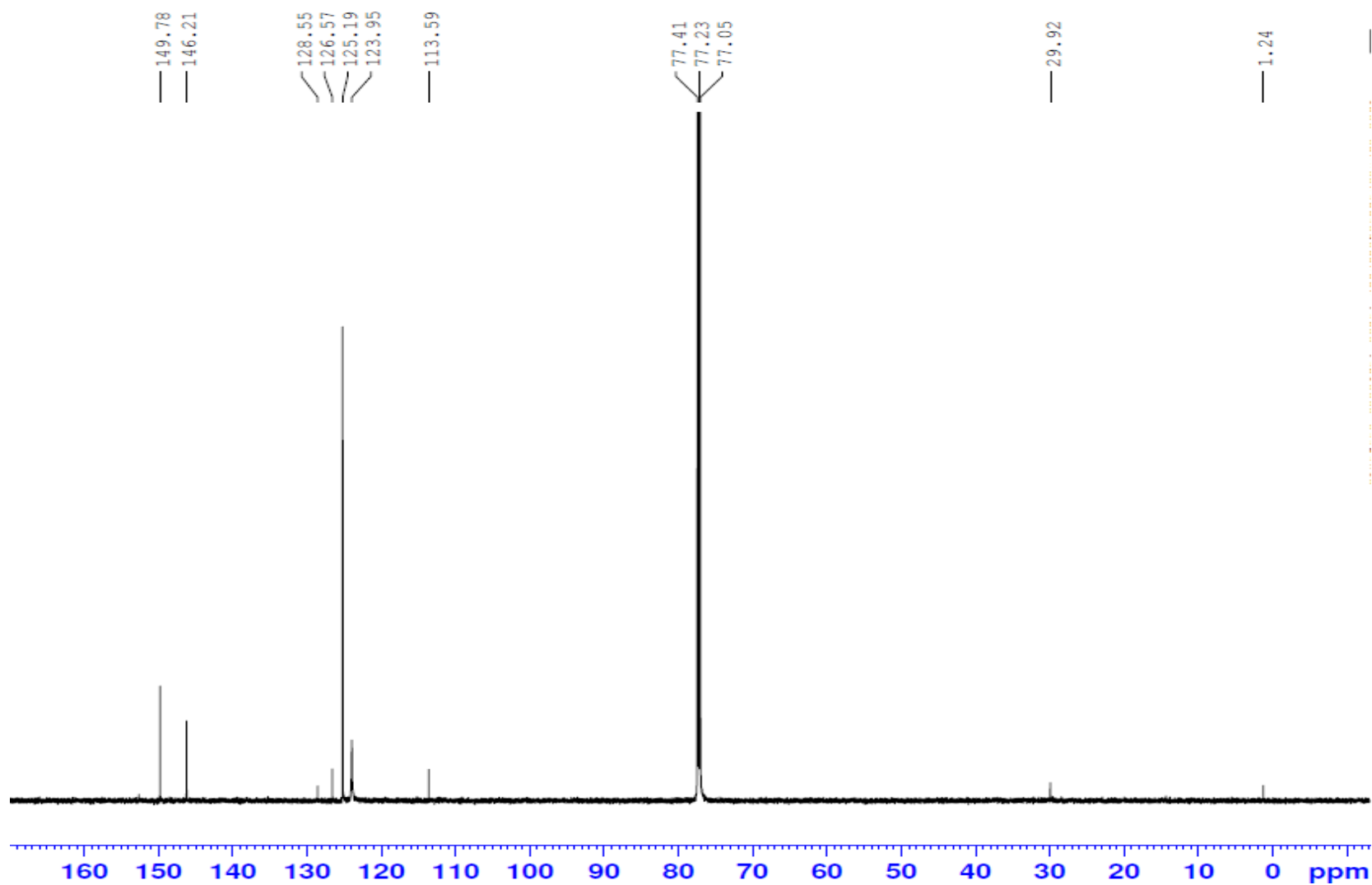


Figure B.166. $^{13}\text{C}\{^1\text{H}\}$ NMR of **7** in CDCl_3 taken at room temperature, referenced to residual solvent at 77.23 ppm

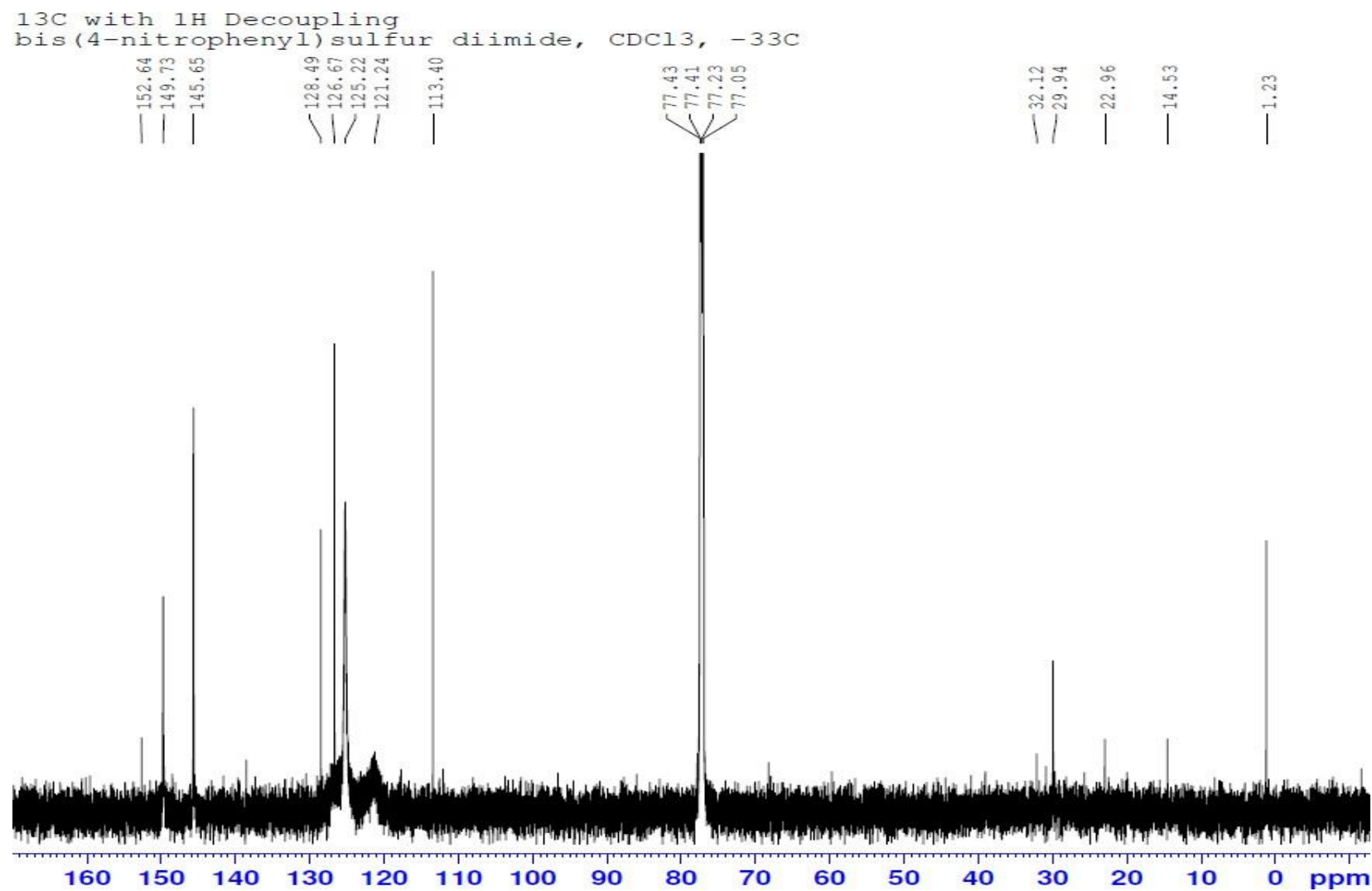


Figure B.167. $^{13}\text{C}\{^1\text{H}\}$ NMR of **7** in CDCl_3 taken at 240 K, referenced to residual solvent at 77.23 ppm

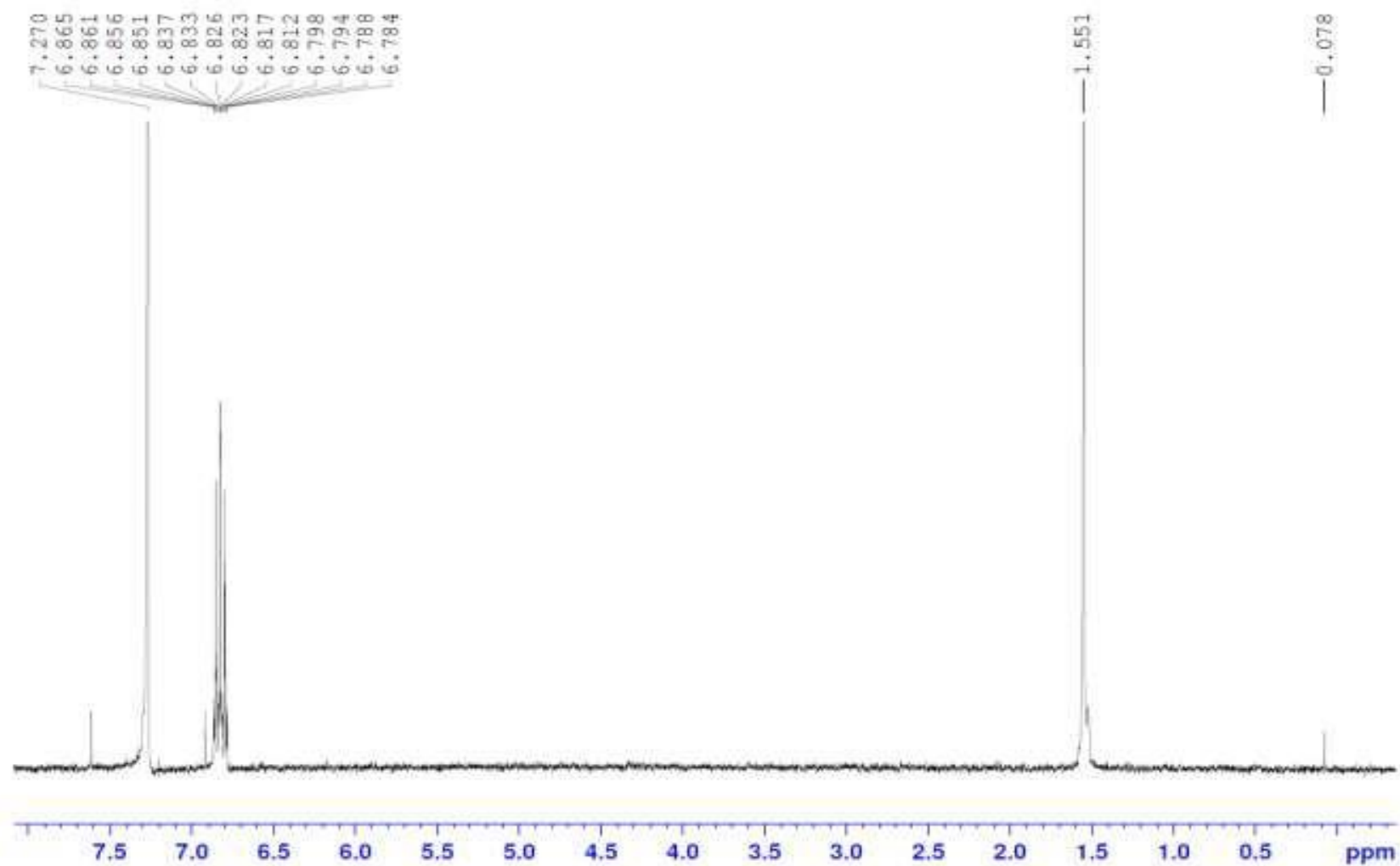


Figure B.168. ^1H NMR of 2,4,6-trifluoro-N-sulfinyl aniline in CDCl_3 taken at room temperature, referenced to residual solvent at 7.27 ppm

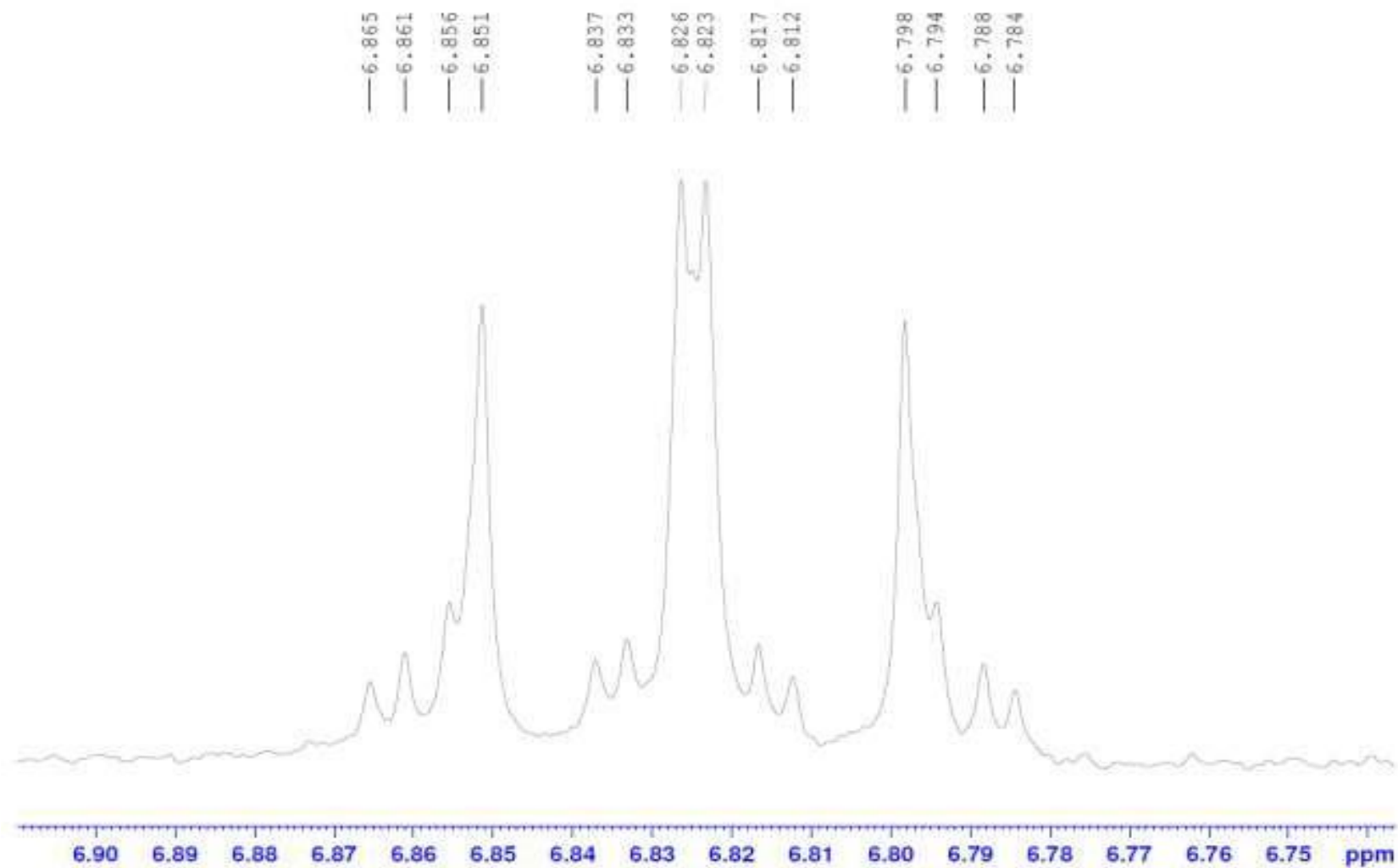


Figure B.169. ^1H NMR of 2,4,6-trifluoro-N-sulfinyl aniline in CDCl_3 , referenced to residual solvent at 7.27 ppm. Close-up of signal exhibiting highly symmetrical ^1H - ^{19}F coupling in ABB'XX' spin system.

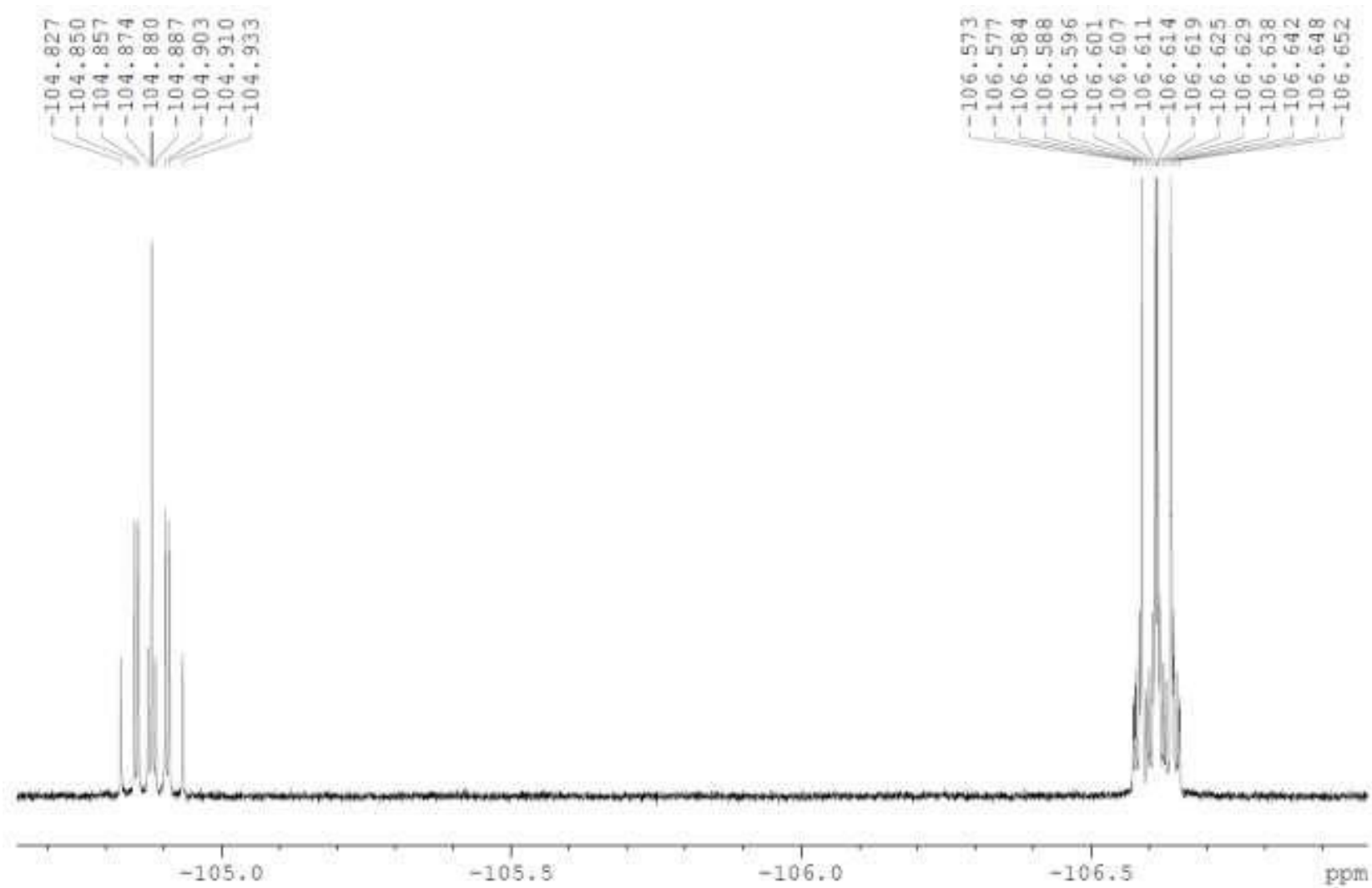


Figure B.170. ^{19}F NMR of 2,4,6-trifluoro-N-sulfinyl aniline in CDCl_3 , referenced to external CFCl_3 at 0.0 ppm.

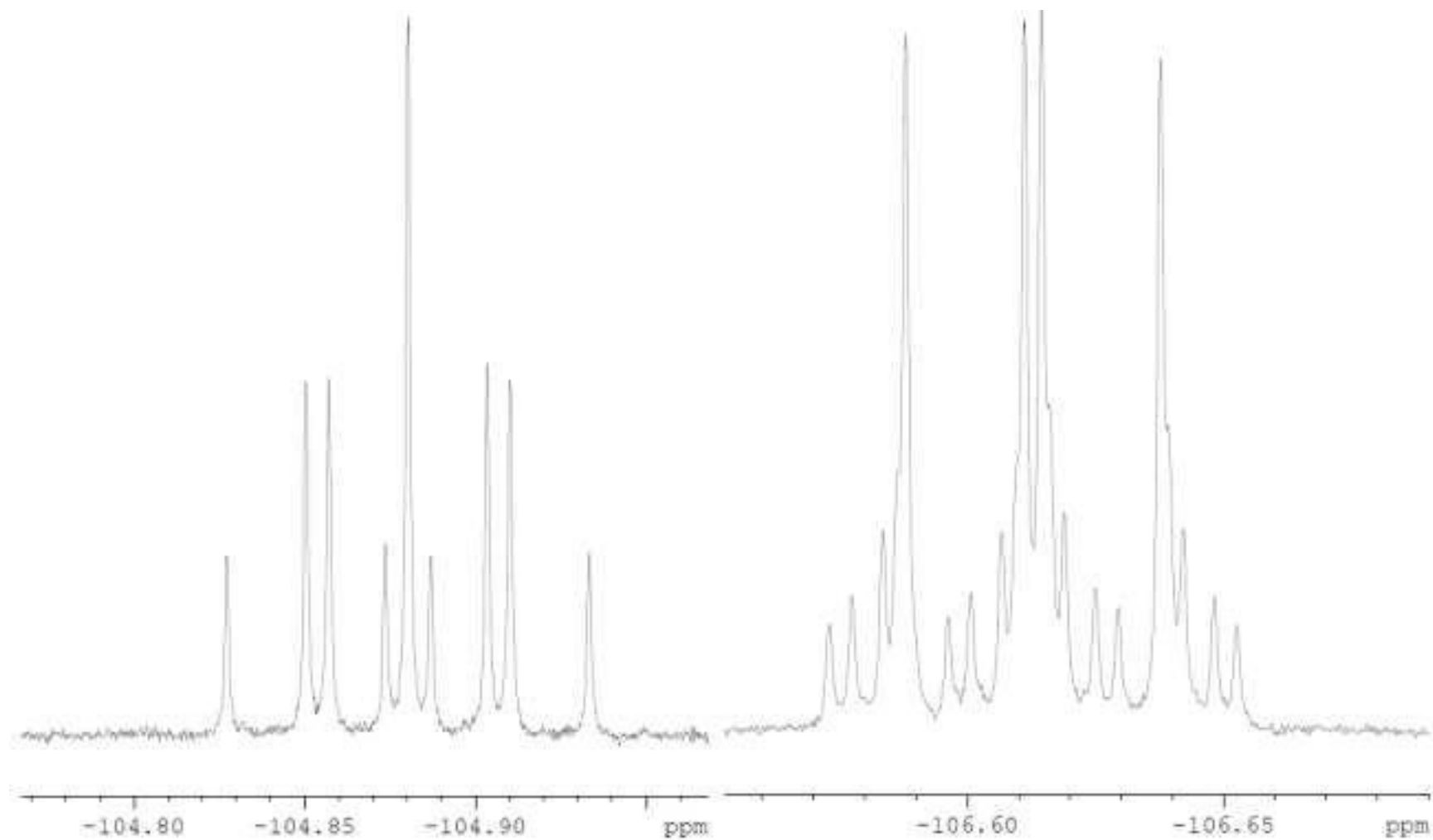


Figure B.171. ^{19}F NMR of 2,4,6-trifluoro-N-sulfinyl aniline in CDCl_3 , referenced to external CFCl_3 at 0.0 ppm. Window restricted and truncated for close-up of signals exhibiting highly symmetrical ^{19}F - ^{19}F and ^{19}F - ^1H coupling.

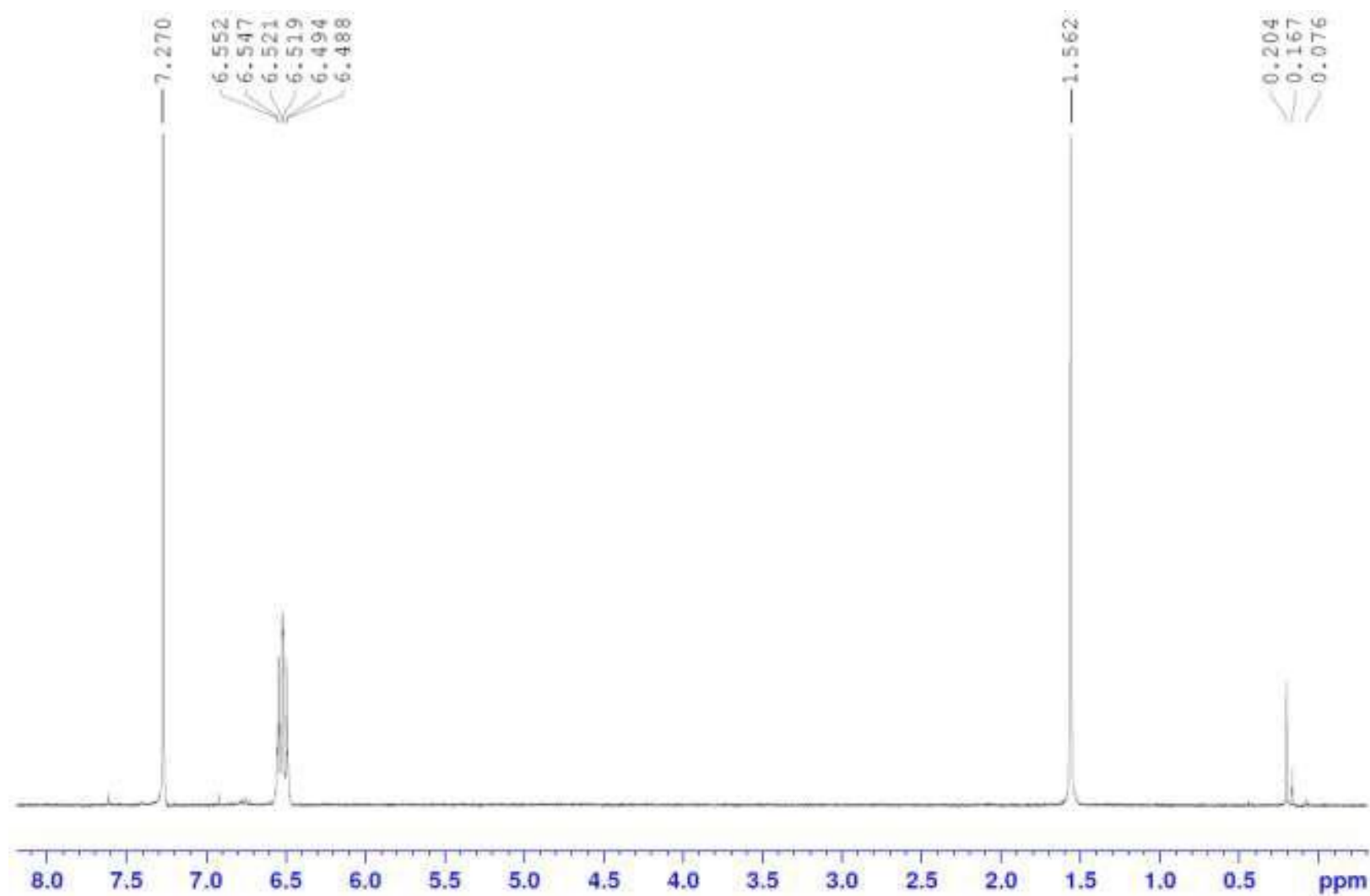


Figure B.172. ^1H NMR of **8** in CDCl_3 taken at room temperature, referenced to residual solvent at 7.27 ppm

1D Proton with no Decoupling
bis(2,4,6-trifluorophenyl)sulfur diimide, CDCl₃, 240 K

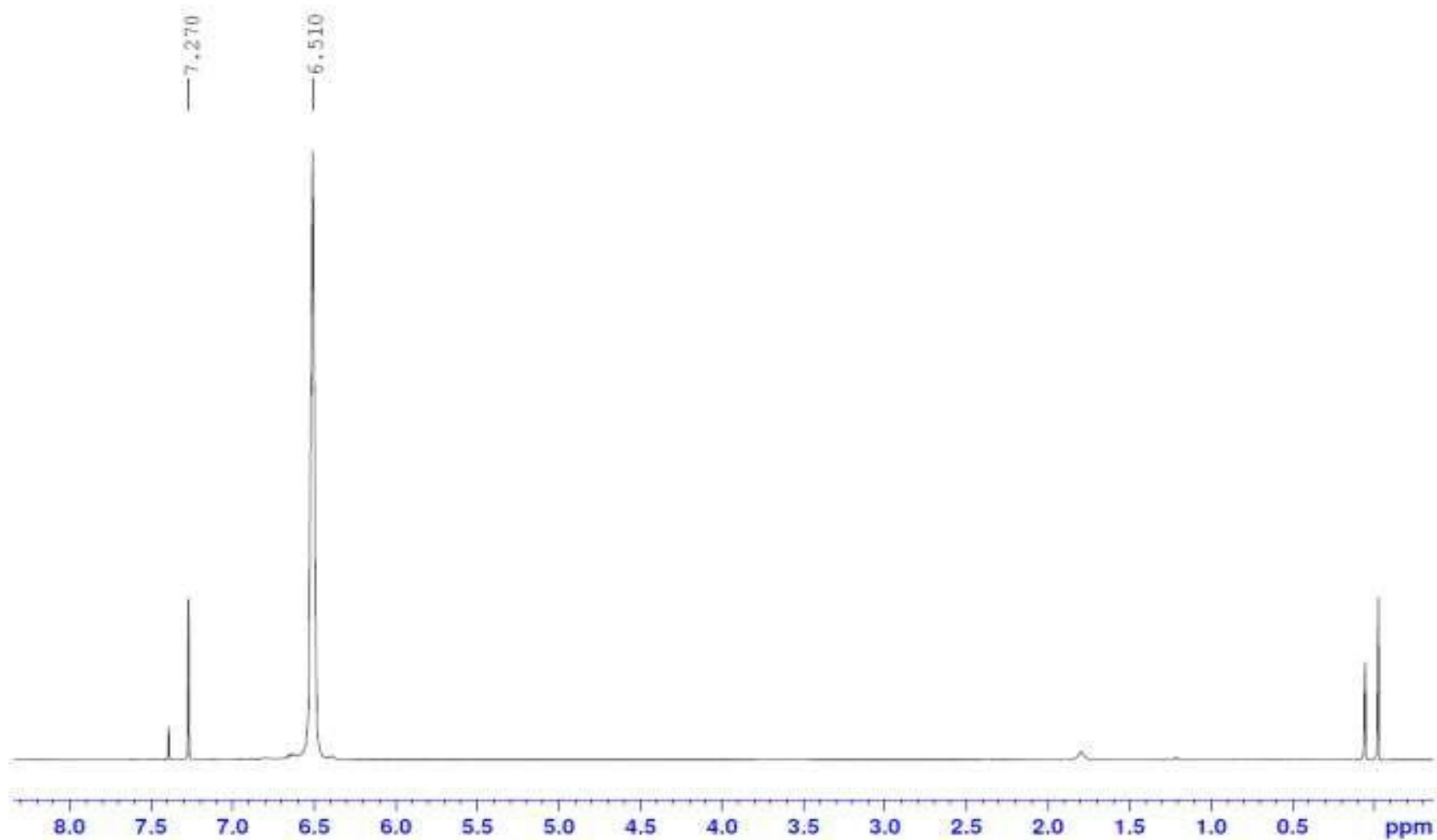


Figure B.173. ¹H NMR of **8** in CDCl₃ taken at 240 K, referenced to residual solvent at 7.27 ppm

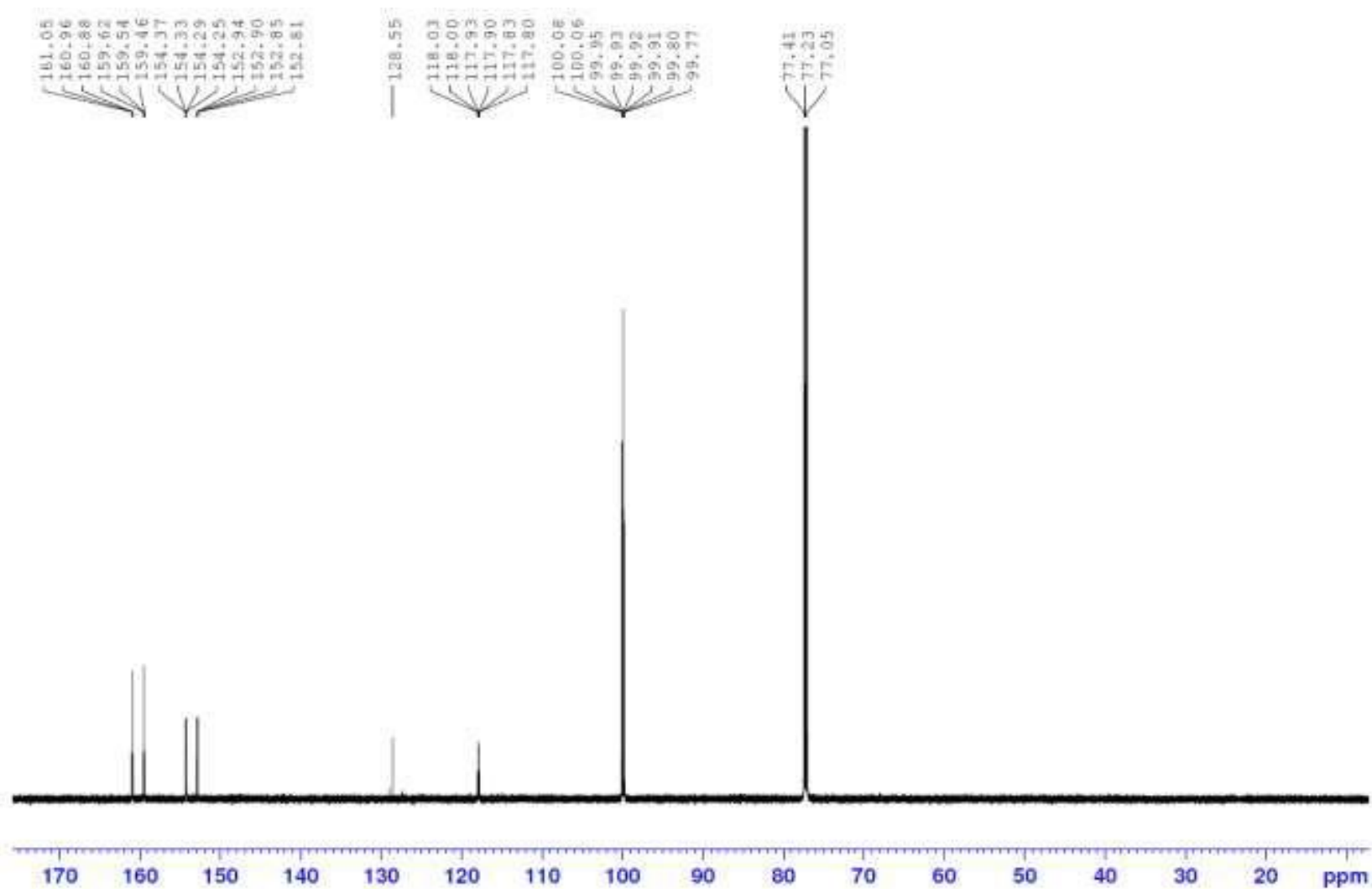


Figure B.174. $^{13}\text{C}\{^1\text{H}\}$ NMR of **8** in CDCl_3 taken at room temperature, referenced to residual solvent at 77.23 ppm

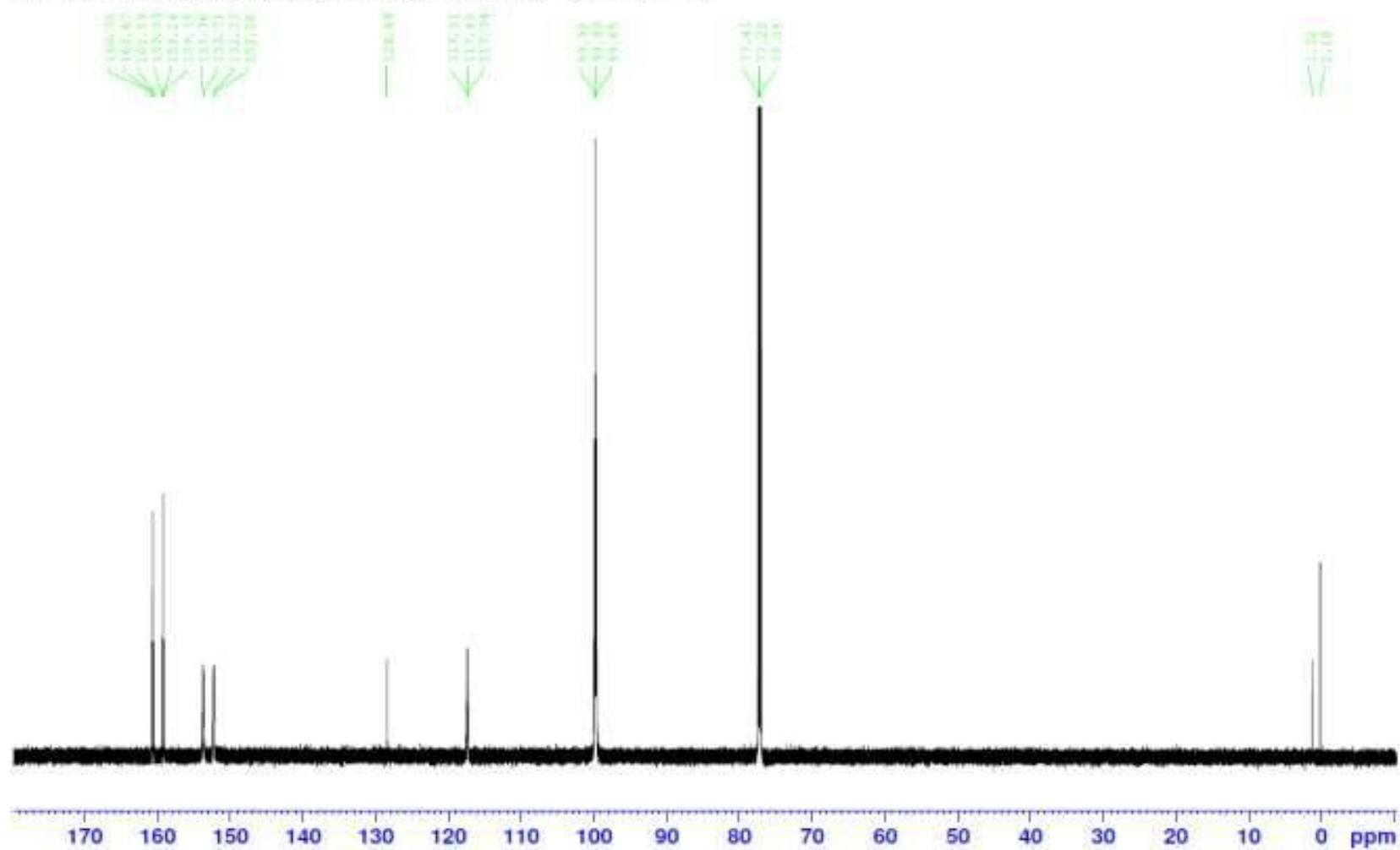


Figure B.175. $^{13}\text{C}\{^1\text{H}\}$ NMR of **8** in CDCl_3 taken at 240 K, referenced to residual solvent at 77.23 ppm

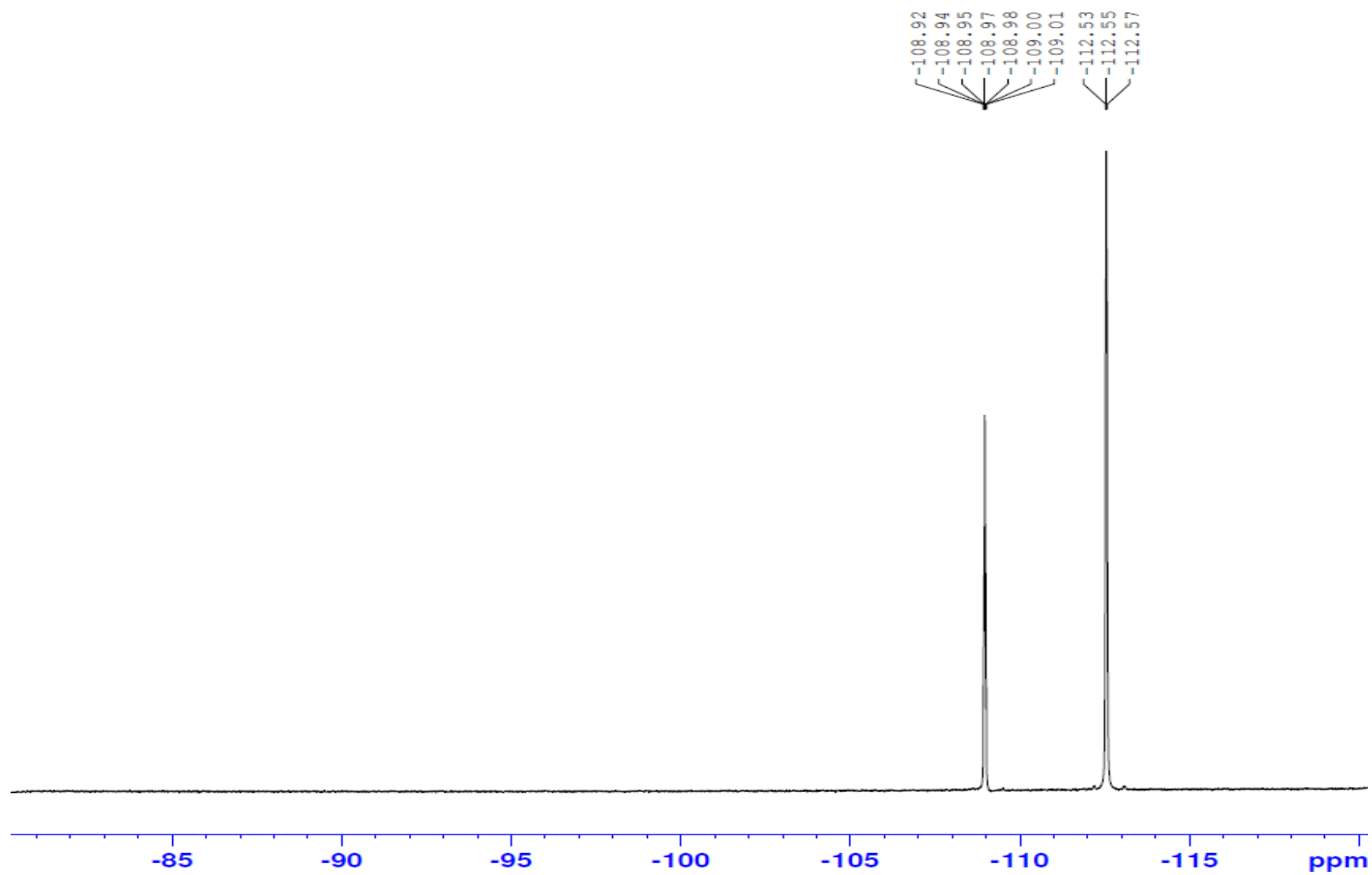


Figure B.176. ¹⁹F NMR of **8** in CDCl₃ taken at room temperature, referenced to external CFCl₃ at 0.0 ppm.

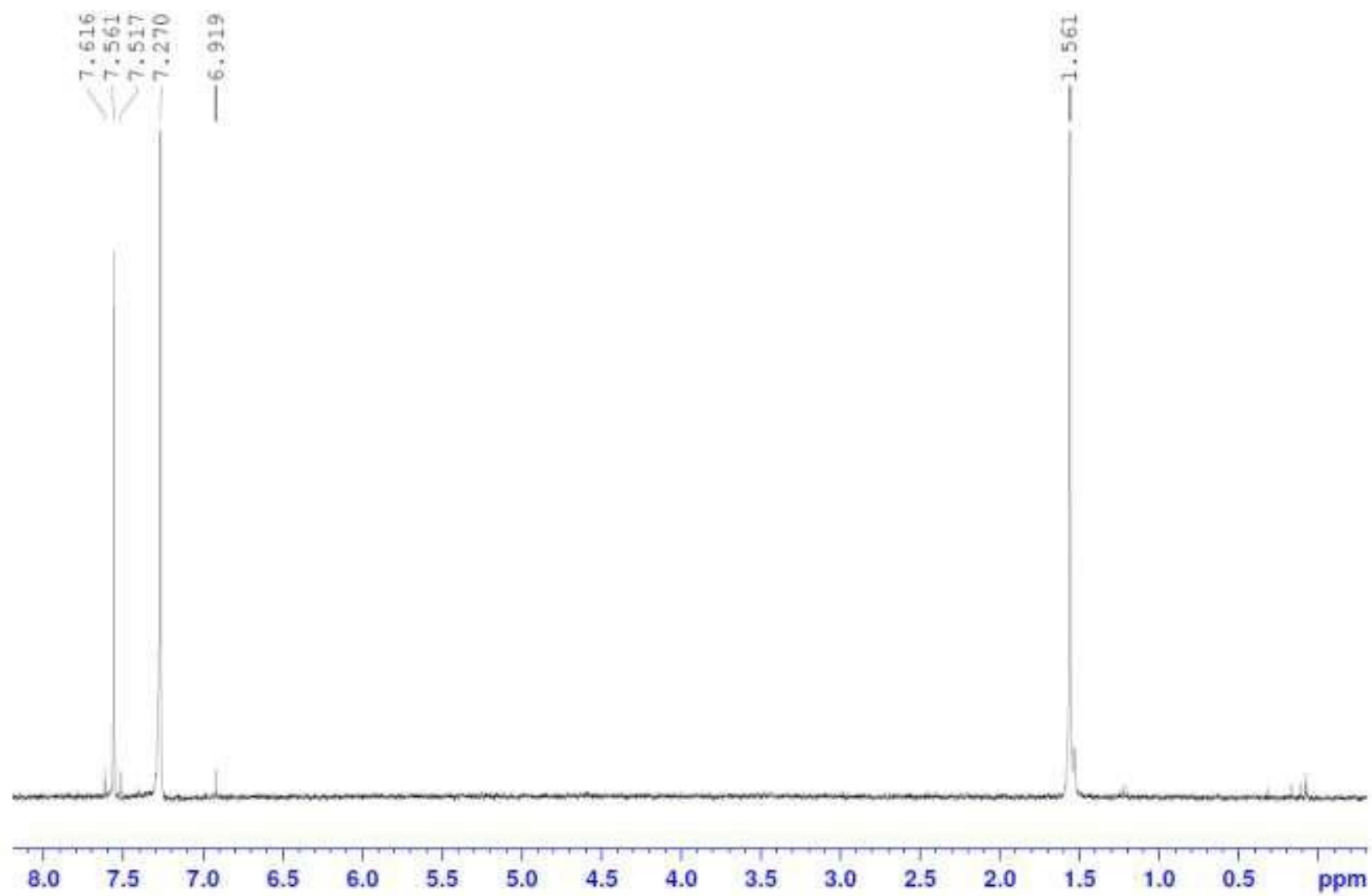


Figure B.177. ¹H NMR of **9** in CDCl₃ taken at room temperature, referenced to residual solvent at 7.27 ppm

1D Proton with no Decoupling
bis(2,4,6-tribromophenyl)sulfur diimide, CDCl₃, -33C

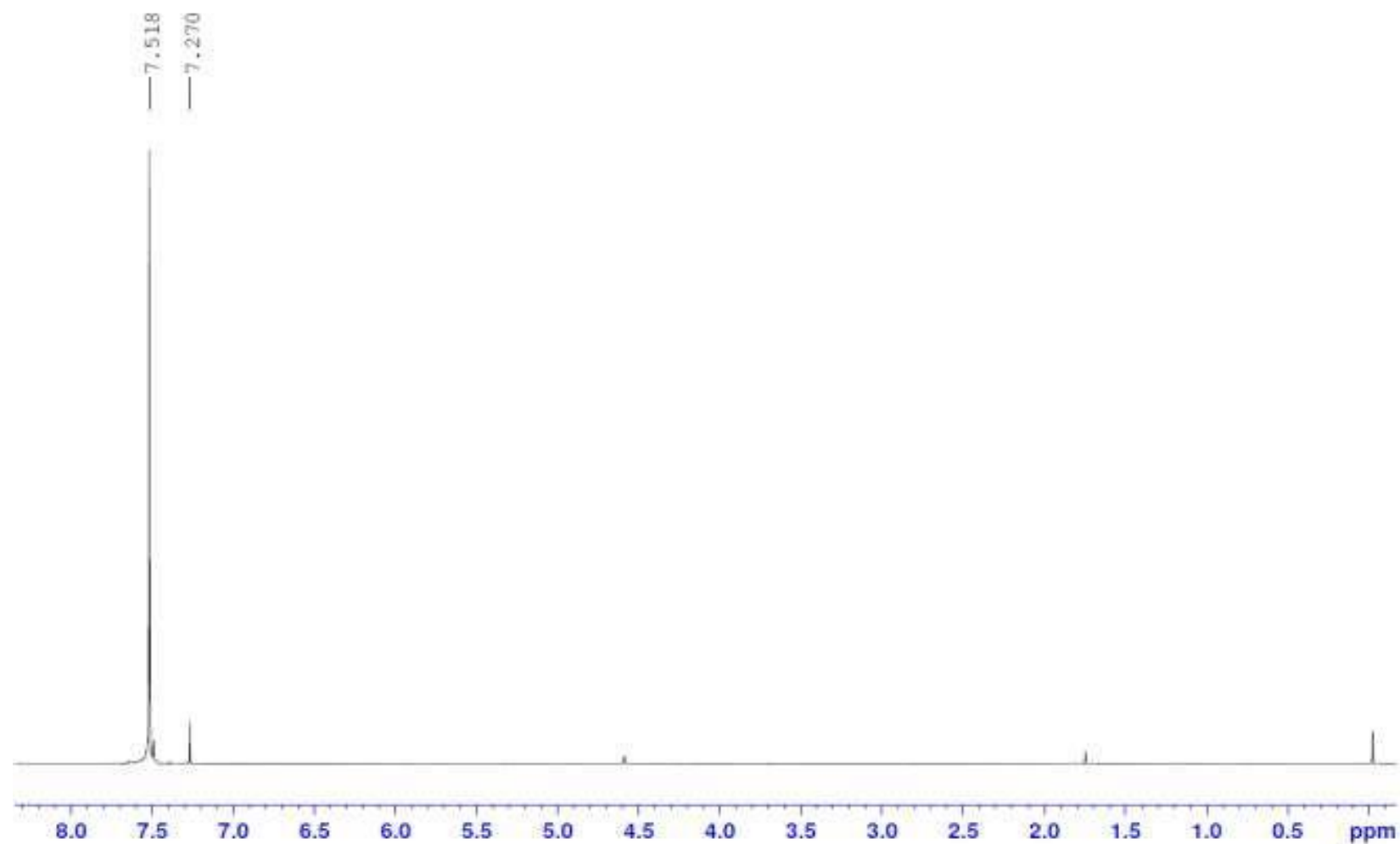


Figure B.178. ¹H NMR of **9** in CDCl₃ taken at 240 K, referenced to residual solvent at 7.27 ppm

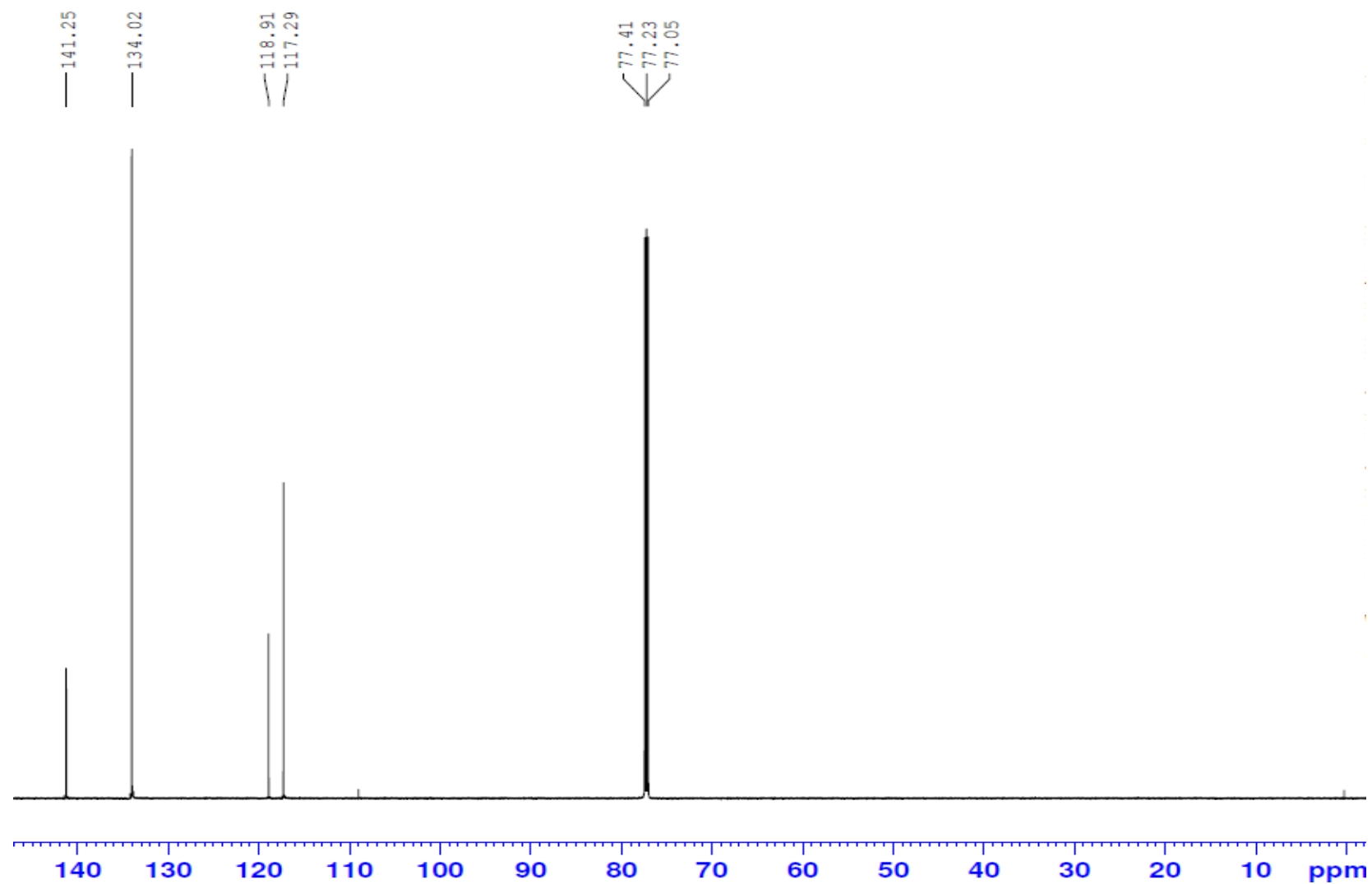


Figure B.179. $^{13}\text{C}\{^1\text{H}\}$ NMR of **9** in CDCl_3 taken at room temperature, referenced to residual solvent at 77.23 ppm

VT ^{13}C with ^1H Decoupling, 233K
(246-Br3PhN) 2S

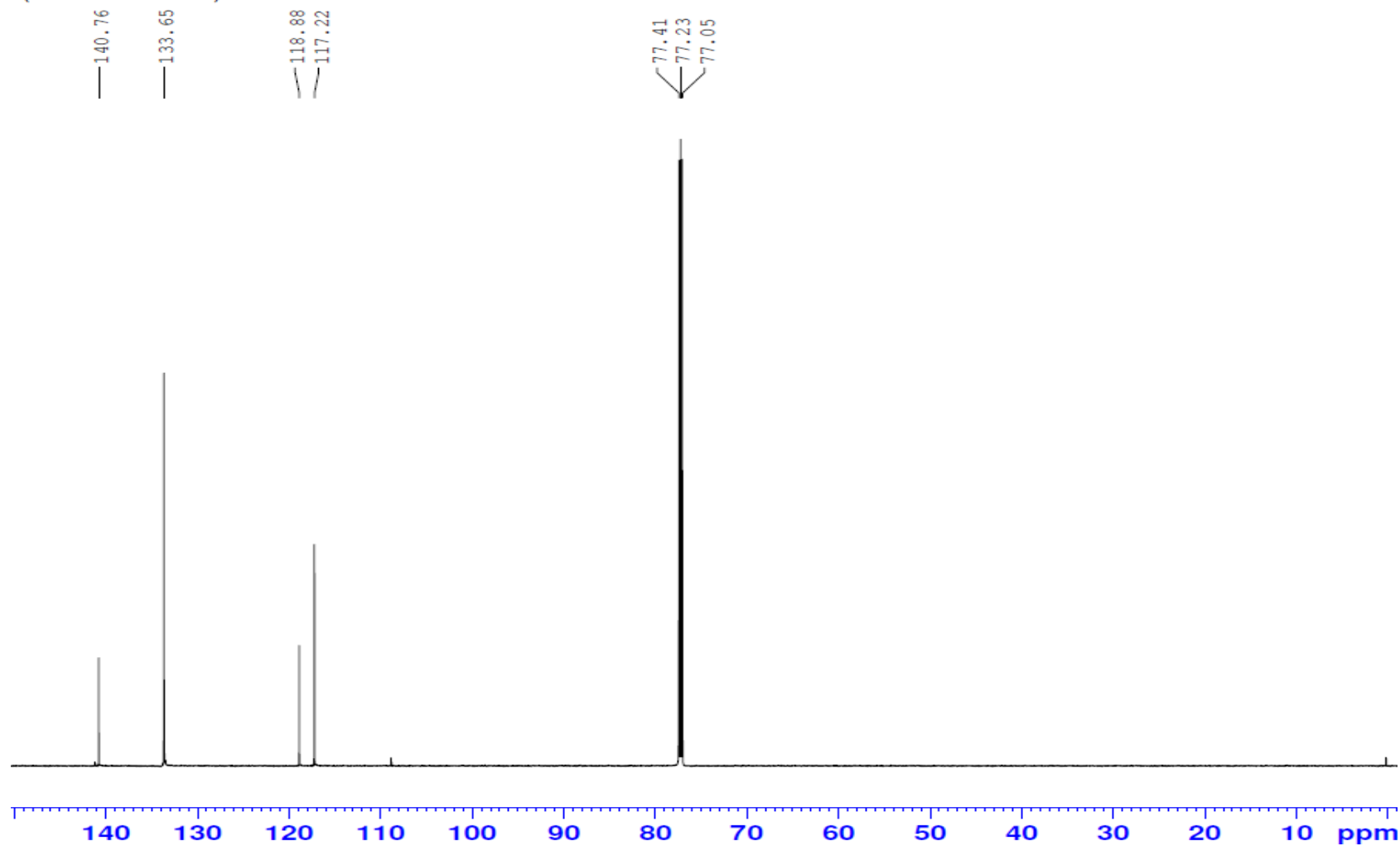


Figure B.180. $^{13}\text{C}\{^1\text{H}\}$ NMR of **9** in CDCl_3 taken at 240 K, referenced to residual solvent at 77.23 ppm

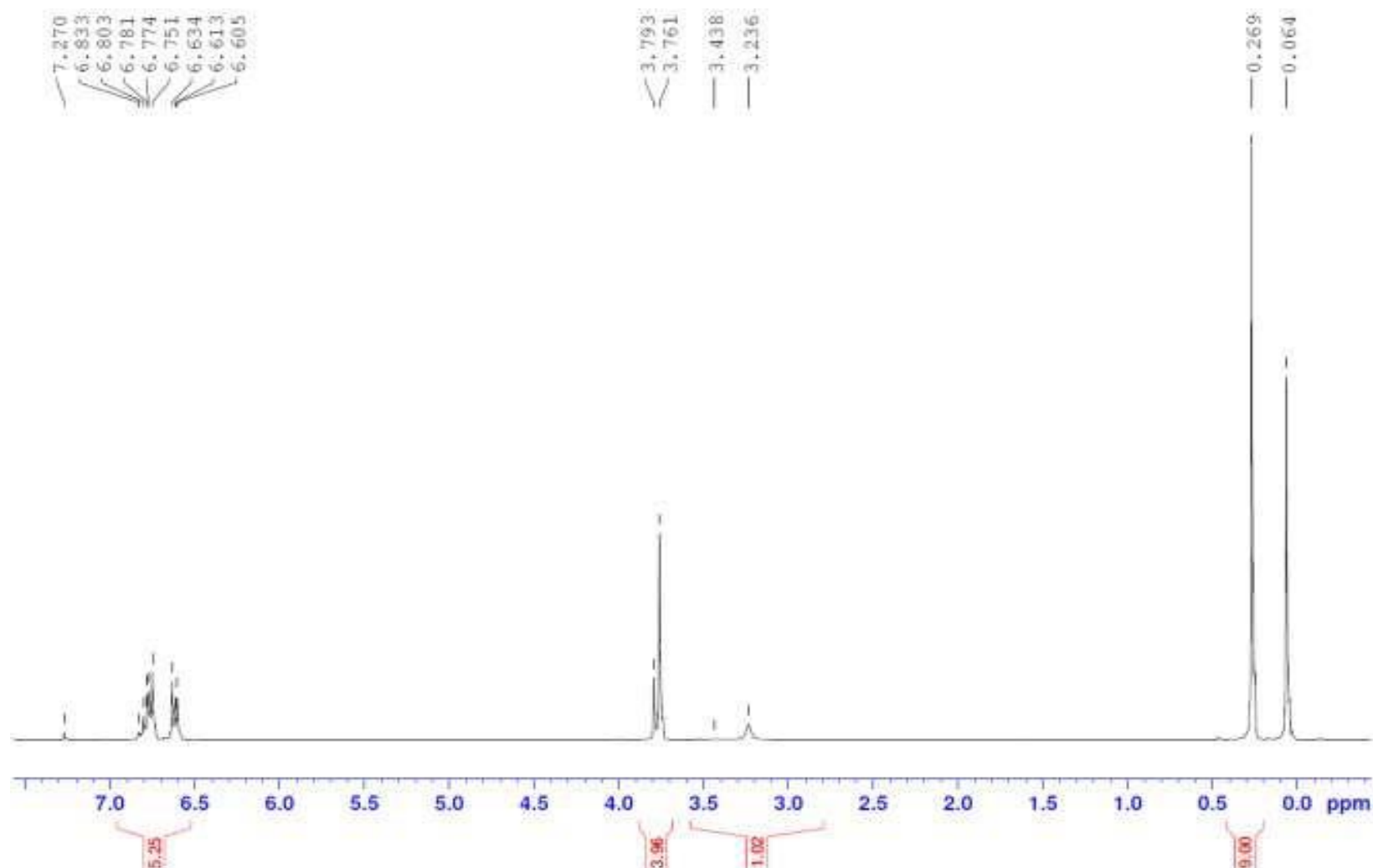


Figure B.181. ¹H NMR of 4-MeOPhNH(TMS) (15) in CDCl₃, referenced to residual solvent at 7.27 ppm. This was from a distillation fraction which was a mixture of **15** and 4-methoxyaniline in a proportion of approximately 3:1, respectively.

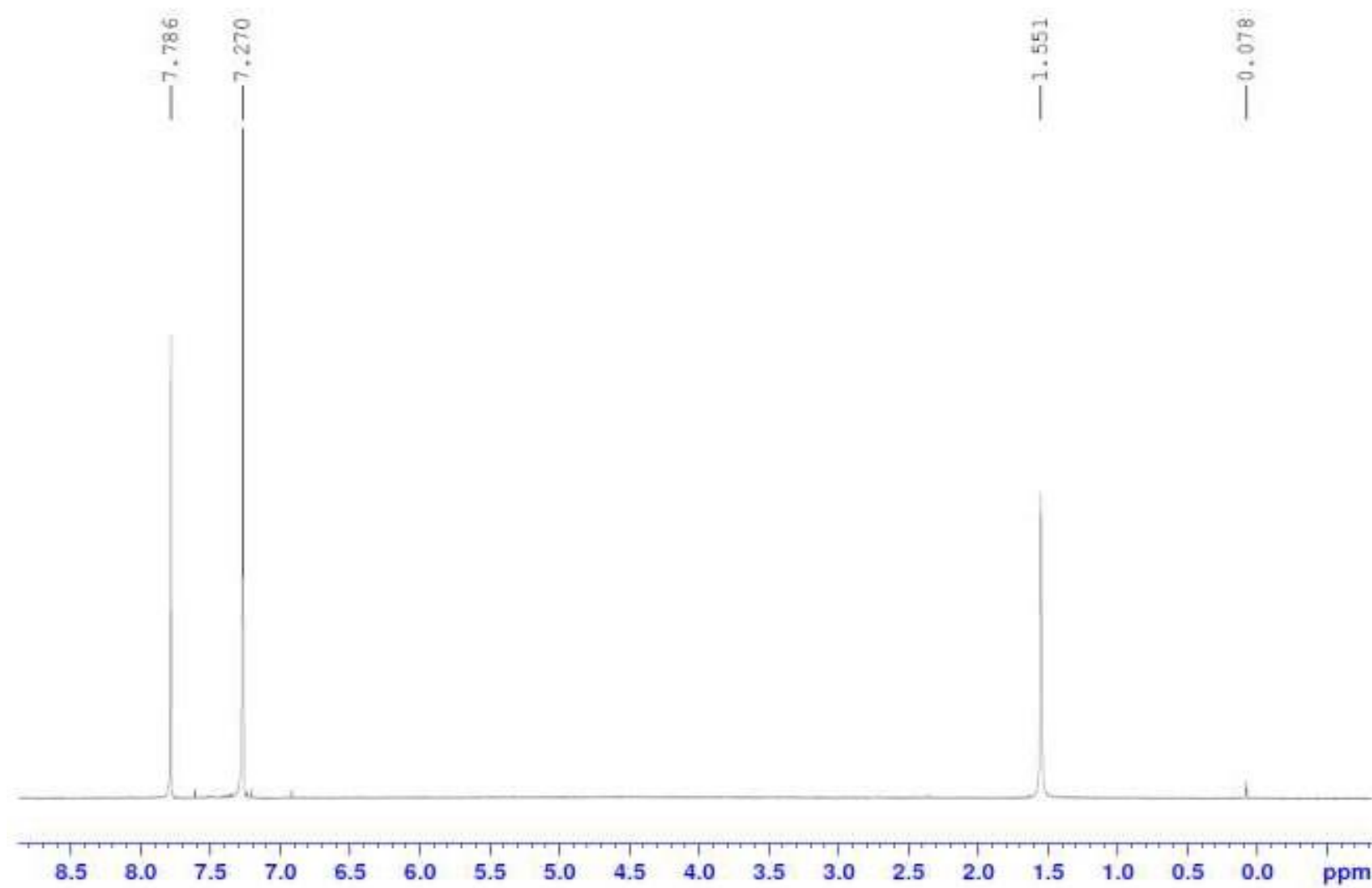


Figure B.182. ^1H NMR of 2,4,6- Br_3PhNSO (16) in CDCl_3 , referenced to residual solvent at 7.27 ppm

B.15. DFT Neutral and Anion Optimized Geometry Cartesian Coordinates and Plots

Table B.47. DFT Computed Cartesian Geometries of neutral sulfur diimides with Structure Plots

1 - *bis*(4-methoxyphenyl)sulfur diimide

EE-PMEO-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	x	y	z
S	0.000001	0.111706	0.000003
N	1.255093	1.041736	-0.096808
N	-1.255093	1.041721	0.096931
C	-2.529376	0.492742	-0.029031
C	-3.583892	1.238970	0.510323
C	-2.844399	-0.723507	-0.667990
C	-4.894266	0.784160	0.461965
H	-3.351496	2.183885	0.983895
C	-4.145329	-1.179804	-0.720825
H	-2.064800	-1.298217	-1.152736
C	-5.182784	-0.435898	-0.149860
H	-5.676748	1.388333	0.897748
H	-4.388980	-2.108126	-1.221542
C	2.529377	0.492744	0.029093
C	3.583892	1.239028	-0.510184
C	2.844401	-0.723573	0.667920
C	4.894265	0.784212	-0.461880
H	3.351496	2.183996	-0.983653
C	4.145330	-1.179880	0.720701
H	2.064802	-1.298334	1.152610
C	5.182784	-0.435915	0.149811
H	5.676747	1.388430	-0.897601
H	4.388981	-2.108256	1.221316
O	-6.429936	-0.971852	-0.260228
O	6.429935	-0.971882	0.260115
C	7.520721	-0.239429	-0.277792
H	8.407514	-0.837417	-0.081478
H	7.409124	-0.097021	-1.356755
H	7.622803	0.734648	0.209660
C	-7.520723	-0.239455	0.277755
H	-8.407516	-0.837419	0.081370
H	-7.409131	-0.097166	1.356733
H	-7.622800	0.734676	-0.209591



EZ-PMEO-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	-0.180361	1.652880	-0.319953
N	1.354377	1.832339	-0.277337
N	-0.704478	0.167235	-0.234947
C	-2.085985	-0.043433	-0.137633
C	-2.600550	-1.211706	-0.725757
C	-2.978059	0.800141	0.534477
C	-3.948716	-1.499024	-0.677152
H	-1.914957	-1.878309	-1.232860
C	-4.338309	0.514911	0.589205
H	-2.605090	1.675229	1.052332
C	-4.832977	-0.634455	-0.024240
H	-4.344864	-2.395025	-1.137637
H	-4.992666	1.184559	1.128464
C	2.386360	0.924927	-0.138192
C	2.253685	-0.475447	-0.018035
C	3.678729	1.473588	-0.112133
C	3.373217	-1.269493	0.127897
H	1.270580	-0.917217	-0.043468
C	4.801111	0.677388	0.032767
H	3.779360	2.547029	-0.206823
C	4.652446	-0.707470	0.155184
H	3.280394	-2.344050	0.220921
H	5.778203	1.137853	0.049204
O	-6.143773	-1.009219	-0.025455
O	5.683701	-1.580828	0.300517
C	7.005777	-1.061779	0.329473
H	7.660350	-1.921655	0.449748
H	7.249162	-0.546191	-0.603935
H	7.144261	-0.377793	1.171682
C	-7.080093	-0.159152	0.617961
H	-8.051369	-0.630390	0.486501
H	-6.863278	-0.065837	1.686462
H	-7.092848	0.835080	0.161224



ZZ-PMEO-NSN-B3LYPD3BJ-6311++G2DP_OF

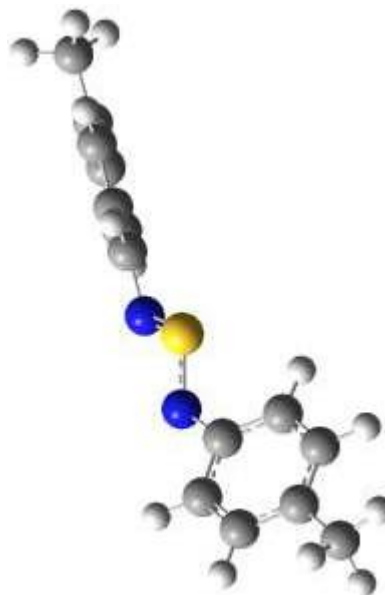
Atom Type	X	Y	Z
S	-1.070194	-3.289557	-0.181151
N	0.446097	-2.966261	-0.369898
N	-2.182052	-2.235126	0.118302
C	-2.142778	-0.849907	0.041000
C	-2.993035	-0.123055	0.893267
C	-1.357461	-0.136692	-0.873201
C	-3.012712	1.254912	0.867957
H	-3.620108	-0.670096	1.585323
C	-1.394210	1.250310	-0.922785
H	-0.723223	-0.670120	-1.566661
C	-2.207412	1.955517	-0.037886
H	-3.649274	1.817562	1.538591
H	-0.773410	1.764134	-1.641886
C	1.157422	-1.810841	-0.077459
C	0.840697	-0.936718	0.979610
C	2.297321	-1.535533	-0.840602
C	1.621909	0.170666	1.238783
H	-0.011962	-1.144067	1.610146
C	3.070889	-0.408588	-0.602257
H	2.559732	-2.216865	-1.639651
C	2.732594	0.455406	0.441773
H	1.379729	0.841234	2.052978
H	3.932853	-0.219793	-1.225566
O	-2.293404	3.312554	0.017370
O	3.422857	1.585465	0.761716
C	4.580288	1.899687	0.002046
H	4.974066	2.820798	0.425239
H	5.333774	1.110759	0.082631
H	4.332667	2.059938	-1.051633
C	-1.473665	4.069075	-0.861517
H	-1.683199	5.112933	-0.640254
H	-0.413379	3.863865	-0.687042
H	-1.718189	3.862753	-1.907677



2 - bis(4-tolyl)sulfur diimide

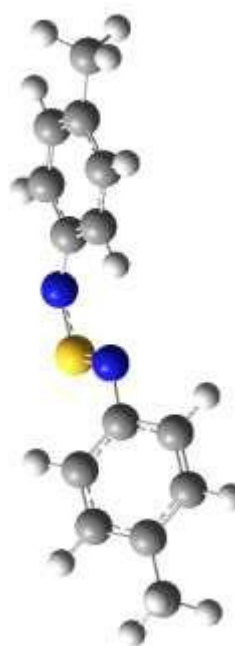
EE-PCH3-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	0.000001	0.167060	0.000033
N	-1.250820	1.089403	0.154614
N	1.250817	1.089407	-0.154561
C	2.520020	0.515012	-0.040686
C	3.556159	1.131979	-0.758453
C	2.834629	-0.597262	0.754264
C	4.842256	0.624802	-0.714632
H	3.319799	2.002435	-1.356646
C	4.130419	-1.092508	0.789332
H	2.070422	-1.052340	1.372708
C	5.157316	-0.499019	0.056160
H	5.623137	1.113170	-1.287249
H	4.350550	-1.949857	1.415536
C	-2.520021	0.515009	0.040706
C	-3.556171	1.131965	0.758467
C	-2.834619	-0.597252	-0.754267
C	-4.842267	0.624789	0.714619
H	-3.319820	2.002412	1.356677
C	-4.130407	-1.092498	-0.789361
H	-2.070403	-1.052321	-1.372706
C	-5.157315	-0.499020	-0.056195
H	-5.623157	1.113148	1.287232
H	-4.350530	-1.949837	-1.415581
C	6.567904	-1.019654	0.120146
H	7.007998	-1.094248	-0.876984
H	7.208042	-0.354213	0.707243
H	6.605905	-2.007323	0.581414
C	-6.567902	-1.019654	-0.120211
H	-7.008012	-1.094261	0.876911
H	-7.208032	-0.354205	-0.707309
H	-6.605897	-2.007316	-0.581492



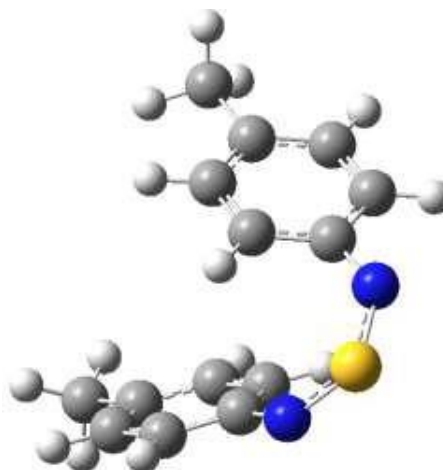
EZ-PCH3-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	0.135713	-1.585133	-0.284274
N	-1.401395	-1.721428	-0.265119
N	0.704549	-0.120891	-0.168374
C	2.092733	0.039479	-0.052291
C	2.661505	1.171358	-0.653752
C	2.935195	-0.830225	0.654034
C	4.024466	1.399237	-0.579417
H	2.012707	1.852220	-1.189787
C	4.300318	-0.586904	0.721511
H	2.515183	-1.680610	1.177306
C	4.873391	0.525254	0.106841
H	4.441253	2.276512	-1.062150
H	4.930927	-1.271321	1.277963
C	-2.412636	-0.787629	-0.119948
C	-2.242310	0.599706	0.027949
C	-3.721122	-1.307592	-0.118578
C	-3.353207	1.418978	0.176732
H	-1.248206	1.016720	0.023283
C	-4.811353	-0.475153	0.029614
H	-3.846320	-2.376515	-0.233770
C	-4.649955	0.908083	0.180427
H	-3.204651	2.486838	0.291593
H	-5.809576	-0.898914	0.029672
C	6.349560	0.802324	0.206532
H	6.766670	1.082031	-0.763631
H	6.550972	1.627965	0.895795
H	6.893386	-0.070990	0.569001
C	-5.846825	1.806409	0.330891
H	-6.486350	1.477653	1.154166
H	-5.548482	2.837025	0.525368
H	-6.459557	1.799783	-0.575251



ZZ-PCH3-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	-0.000007	3.091768	-0.000013
N	-1.369494	2.371780	-0.177660
N	1.369485	2.371789	0.177646
C	1.698924	1.031476	-0.003906
C	2.682005	0.478673	0.827097
C	1.140177	0.226069	-1.006148
C	3.053535	-0.848134	0.688233
H	3.126975	1.103984	1.590469
C	1.542129	-1.091844	-1.150155
H	0.397160	0.637906	-1.674786
C	2.493090	-1.659565	-0.302357
H	3.798169	-1.263026	1.358517
H	1.091996	-1.696891	-1.928898
C	-1.698928	1.031467	0.003902
C	-1.140153	0.226060	1.006127
C	-2.682032	0.478664	-0.827075
C	-1.542099	-1.091854	1.150142
H	-0.397116	0.637897	1.674744
C	-3.053557	-0.848143	-0.688204
H	-3.127024	1.103976	-1.590434
C	-2.493082	-1.659575	0.302371
H	-1.091944	-1.696902	1.928872
H	-3.798209	-1.263035	-1.358467
C	2.928116	-3.090607	-0.469313
H	3.821605	-3.158616	-1.097879
H	3.171744	-3.546792	0.492025
H	2.148563	-3.689375	-0.943014
C	-2.928102	-3.090619	0.469328
H	-3.821723	-3.158614	1.097707
H	-3.171515	-3.546873	-0.492033
H	-2.148631	-3.689334	0.943229



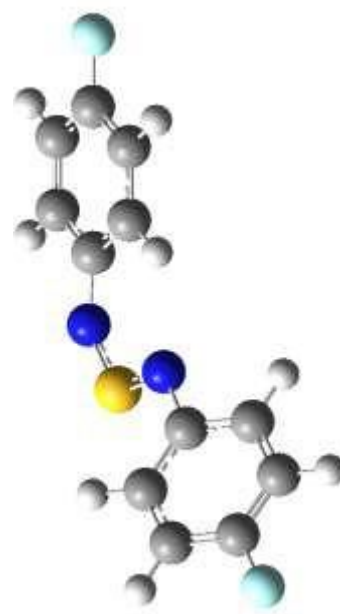
3 - bis(4-fluorophenyl)sulfur diimide EE-PF-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	-0.000003	0.136434	-0.000112
N	-1.250765	1.059507	0.141507
N	1.250774	1.059515	-0.141540
C	2.522263	0.490584	-0.030921
C	3.555509	1.135689	-0.728213
C	2.836402	-0.638143	0.744791
C	4.850620	0.646189	-0.693840
H	3.314492	2.018771	-1.304672
C	4.131813	-1.132297	0.784926
H	2.071057	-1.110076	1.347993
C	5.115967	-0.486130	0.058236
H	5.651997	1.132036	-1.234425
H	4.387232	-1.994403	1.386721
C	-2.522259	0.490585	0.030923
C	-3.555463	1.135623	0.728340
C	-2.836443	-0.638066	-0.744880
C	-4.850577	0.646129	0.693992
H	-3.314413	2.018650	1.304869
C	-4.131857	-1.132214	-0.784988
H	-2.071133	-1.109939	-1.348172
C	-5.115969	-0.486116	-0.058178
H	-5.651923	1.131925	1.234670
H	-4.387312	-1.994260	-1.386853
F	-6.381178	-0.961090	-0.103425
F	6.381173	-0.961109	0.103509



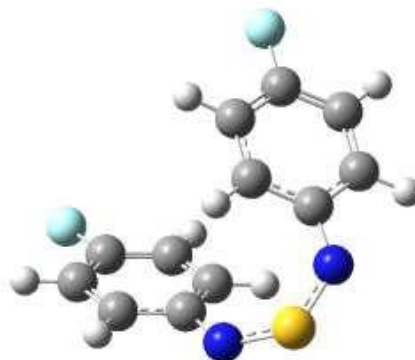
EZ-PF-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	0.129341	-1.570056	-0.290338
N	-1.407914	-1.693711	-0.272709
N	0.706034	-0.110608	-0.157110
C	2.095217	0.044872	-0.044728
C	2.659080	1.186991	-0.631472
C	2.935911	-0.840553	0.648234
C	4.022925	1.422408	-0.563968
H	2.007755	1.876994	-1.151399
C	4.302555	-0.610274	0.721386
H	2.513898	-1.695765	1.160766
C	4.823763	0.514507	0.108335
H	4.467978	2.296953	-1.019692
H	4.958221	-1.280704	1.261072
C	-2.411913	-0.753736	-0.120712
C	-3.722762	-1.267210	-0.130122
C	-2.224948	0.632435	0.042150
C	-4.814922	-0.434759	0.022792
H	-3.854455	-2.333318	-0.258321
C	-3.320828	1.468743	0.197195
H	-1.225839	1.036877	0.043782
C	-4.592328	0.924503	0.185147
H	-5.826614	-0.817781	0.018153
H	-3.197229	2.536114	0.324327
F	-5.655729	1.743665	0.333830
F	6.154561	0.745692	0.185063



ZZ-PF-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	0.000228	3.024639	-0.000029
N	-1.369200	2.306333	-0.179761
N	1.369585	2.306191	0.179668
C	1.717338	0.972280	-0.003224
C	2.741512	0.452637	0.801786
C	1.147149	0.150332	-0.988197
C	3.154262	-0.862478	0.663123
H	3.194683	1.096631	1.543729
C	1.574315	-1.158370	-1.150610
H	0.380596	0.544049	-1.640117
C	2.560175	-1.646573	-0.312587
H	3.930544	-1.280833	1.289830
H	1.143235	-1.800604	-1.906752
C	-1.717145	0.972477	0.003181
C	-1.147294	0.150541	0.988365
C	-2.741240	0.452910	-0.801978
C	-1.574689	-1.158081	1.150818
H	-0.380848	0.544212	1.640433
C	-3.154214	-0.862129	-0.663274
H	-3.194168	1.096900	-1.544073
C	-2.560443	-1.646219	0.312633
H	-1.143873	-1.800301	1.907122
H	-3.930431	-1.280428	-1.290098
F	-2.965331	-2.927867	0.455311
F	2.964838	-2.928297	-0.455220



4 - *bis*(4-chlorophenyl)sulfur diimide

EE-PCL-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	0.000011	0.266170	0.000296
N	1.249125	1.190967	-0.148846
N	-1.249147	1.190995	0.148900
C	-2.521388	0.627171	0.045424
C	-3.551308	1.280581	0.739150
C	-2.843663	-0.506184	-0.719880
C	-4.847218	0.795321	0.710569
H	-3.307846	2.167398	1.309056
C	-4.140652	-0.993378	-0.752637
H	-2.083388	-0.988320	-1.321696
C	-5.133918	-0.344769	-0.030971
H	-5.634457	1.298679	1.254917
H	-4.385188	-1.861253	-1.349774
C	2.521378	0.627168	-0.045436
C	3.551197	1.280375	-0.739506
C	2.843761	-0.505961	0.720154
C	4.847112	0.795127	-0.710967
H	3.307653	2.167026	-1.309634
C	4.140756	-0.993143	0.752869
H	2.083571	-0.987913	1.322226
C	5.133918	-0.344747	0.030868
H	5.634273	1.298326	-1.255574
H	4.385380	-1.860840	1.350229
Cl	6.775635	-0.955008	0.079822
Cl	-6.775628	-0.955046	-0.079980



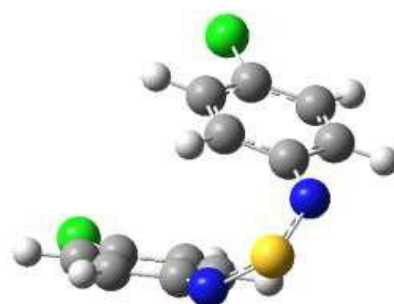
EZ-PCL-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	-0.144372	1.761329	-0.252974
N	1.389237	1.926361	-0.233878
N	-0.679370	0.281684	-0.182667
C	-2.060185	0.077870	-0.072663
C	-2.589029	-1.062702	-0.693344
C	-2.929270	0.911866	0.648290
C	-3.943536	-1.343303	-0.630799
H	-1.918498	-1.715856	-1.236189
C	-4.285980	0.633243	0.715132
H	-2.537114	1.764893	1.187762
C	-4.786439	-0.489191	0.070077
H	-4.346169	-2.220425	-1.118721
H	-4.949923	1.274616	1.278549
C	2.419313	1.010527	-0.123784
C	2.274450	-0.385384	-0.016410
C	3.715227	1.559197	-0.116979
C	3.394657	-1.194137	0.099798
H	1.288587	-0.821151	-0.026996
C	4.829880	0.752038	-0.002496
H	3.818793	2.632826	-0.202088
C	4.660647	-0.625112	0.106259
H	3.285787	-2.266875	0.183443
H	5.823624	1.178187	0.003100
Cl	-6.500071	-0.847224	0.161207
Cl	6.069329	-1.654733	0.250326



ZZ-PCL-NSN-B3LYPD3BJ-6311++G2DP_OF

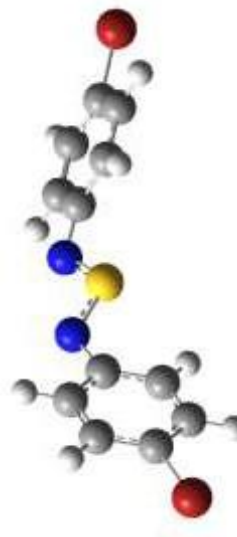
Atom Type	X	Y	Z
S	0.000000	0.000000	3.528214
N	1.061059	0.872534	2.796367
N	-1.061059	-0.872534	2.796367
C	-1.126501	-1.184077	1.437877
C	-2.378664	-1.166686	0.813726
C	0.000000	-1.545798	0.685525
C	-2.495053	-1.431288	-0.541902
H	-3.251989	-0.914995	1.401033
C	-0.114860	-1.834308	-0.663345
H	0.969580	-1.597157	1.161115
C	-1.359362	-1.754183	-1.273968
H	-3.459503	-1.390502	-1.029363
H	0.758044	-2.099814	-1.243350
C	1.126501	1.184077	1.437877
C	0.000000	1.545798	0.685525
C	2.378664	1.166686	0.813726
C	0.114860	1.834308	-0.663345
H	-0.969580	1.597157	1.161115
C	2.495053	1.431288	-0.541902
H	3.251989	0.914995	1.401033
C	1.359362	1.754183	-1.273968
H	-0.758044	2.099814	-1.243350
H	3.459503	1.390502	-1.029363
Cl	-1.500205	-2.073723	-2.990423
Cl	1.500205	2.073723	-2.990423



5 - *bis*(4-bromophenyl)sulfur diimide

EE-PBR-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	0.000002	0.476572	0.000072
N	1.248139	1.401515	-0.155575
N	-1.248142	1.401505	0.155719
C	-2.520976	0.838252	0.058747
C	-3.546869	1.491836	0.758031
C	-2.847554	-0.294494	-0.705494
C	-4.843734	1.007306	0.735410
H	-3.300331	2.378256	1.327348
C	-4.145446	-0.781030	-0.732259
H	-2.090673	-0.776948	-1.311434
C	-5.134120	-0.131937	-0.005370
H	-5.624548	1.514077	1.285501
H	-4.388557	-1.648904	-1.329700
C	2.520974	0.838256	-0.058665
C	3.546851	1.491873	-0.757943
C	2.847570	-0.294525	0.705516
C	4.843717	1.007343	-0.735373
H	3.300300	2.378319	-1.327212
C	4.145462	-0.781062	0.732228
H	2.090702	-0.777006	1.311452
C	5.134119	-0.131936	0.005347
H	5.624519	1.514138	-1.285458
H	4.388586	-1.648964	1.329624
Br	6.926472	-0.796266	0.051341
Br	-6.926471	-0.796265	-0.051436



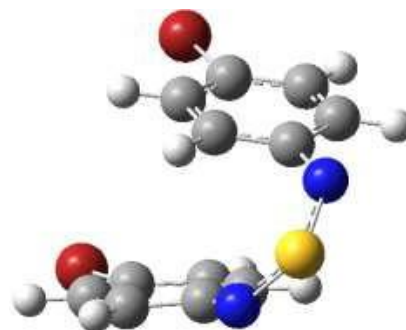
EZ-PBR-NSN-B3LYPD3BJ-6311++G2DP_NEU_OPT+FRQ

Atom Type	X	Y	Z
S	0.151813	2.042215	0.224651
N	-1.376708	2.248074	0.201701
N	0.646315	0.547083	0.208319
C	2.020618	0.301983	0.103180
C	2.520879	-0.827055	0.766924
C	2.908812	1.083336	-0.652437
C	3.867633	-1.146385	0.711767
H	1.835332	-1.440279	1.337022
C	4.257798	0.765785	-0.712062
H	2.537689	1.924698	-1.224260
C	4.729759	-0.343214	-0.024429
H	4.243888	-2.014958	1.234457
H	4.932735	1.369510	-1.303045
C	-2.431484	1.357081	0.126478
C	-2.324525	-0.045031	0.069545
C	-3.711937	1.940060	0.101840
C	-3.466872	-0.827244	-0.015717
H	-1.350913	-0.507095	0.094365
C	-4.848739	1.159444	0.018335
H	-3.786612	3.018516	0.148167
C	-4.716437	-0.224382	-0.040797
H	-3.382120	-1.904317	-0.060482
H	-5.828383	1.616328	-0.000844
Br	-6.283918	-1.311399	-0.154889
Br	6.588178	-0.787749	-0.113846



ZZ-PBr-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	0.000000	0.000000	4.222809
N	-0.362884	1.323227	3.487330
N	0.362884	-1.323227	3.487330
C	0.598991	-1.488760	2.120044
C	0.000000	-2.569595	1.465690
C	1.422253	-0.623518	1.386530
C	0.143311	-2.730462	0.095313
H	-0.610238	-3.255990	2.038065
C	1.585771	-0.792572	0.022484
H	1.922141	0.194069	1.887488
C	0.922851	-1.830303	-0.618869
H	-0.350970	-3.547025	-0.412632
H	2.202371	-0.106428	-0.540837
C	-0.598991	1.488760	2.120044
C	-1.422253	0.623518	1.386530
C	0.000000	2.569595	1.465690
C	-1.585771	0.792572	0.022484
H	-1.922141	-0.194069	1.887488
C	-0.143311	2.730462	0.095313
H	0.610238	3.255990	2.038065
C	-0.922851	1.830303	-0.618869
H	-2.202371	0.106428	-0.540837
H	0.350970	3.547025	-0.412632
Br	1.084261	-2.016755	-2.514086
Br	-1.084261	2.016755	-2.514086



6 - *bis*(4-trifluoromethylphenyl)sulfur diimide

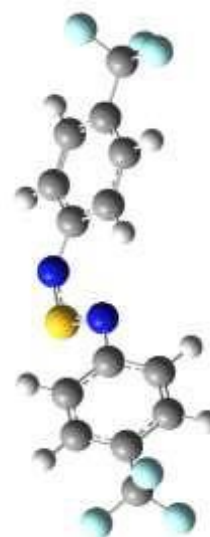
EE-PCF3-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	0.000000	0.471163	-0.000007
N	-1.246521	1.392749	0.163049
N	1.246522	1.392750	-0.163046
C	2.517285	0.822074	-0.066451
C	3.532327	1.424193	-0.826720
C	2.843315	-0.266851	0.756833
C	4.819315	0.922846	-0.798732
H	3.280113	2.277274	-1.442034
C	4.136707	-0.764011	0.783090
H	2.090949	-0.700842	1.403285
C	5.125509	-0.178217	0.001184
H	5.591805	1.385428	-1.399027
H	4.379419	-1.602381	1.421420
C	-2.517284	0.822074	0.066452
C	-3.532324	1.424184	0.826732
C	-2.843318	-0.266842	-0.756844
C	-4.819312	0.922837	0.798743
H	-3.280108	2.277257	1.442055
C	-4.136709	-0.764001	-0.783102
H	-2.090954	-0.700825	-1.403304
C	-5.125509	-0.178216	-0.001186
H	-5.591800	1.385412	1.399046
H	-4.379424	-1.602363	-1.421442
C	6.538465	-0.676195	0.050997
C	-6.538465	-0.676194	-0.050995
F	6.631590	-1.905796	0.595920
F	-6.631598	-1.905773	-0.595967
F	7.335450	0.137936	0.784917
F	7.092821	-0.741150	-1.180121
F	-7.335463	0.137966	-0.784868
F	-7.092800	-0.741200	1.180129



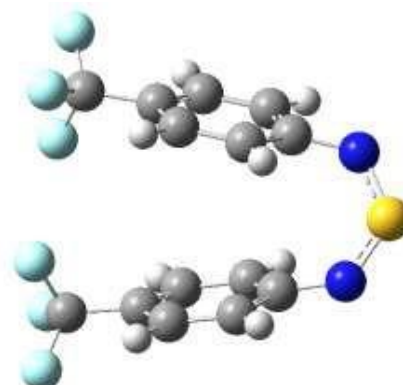
EZ-PCF3-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	-0.151464	2.001792	-0.242084
N	1.375631	2.200244	-0.219754
N	-0.656442	0.512560	-0.218208
C	-2.033392	0.283020	-0.109898
C	-2.557884	-0.807815	-0.819935
C	-2.893919	1.045327	0.693184
C	-3.906366	-1.101817	-0.756617
H	-1.888235	-1.402600	-1.426661
C	-4.246148	0.744508	0.755529
H	-2.496747	1.853215	1.294530
C	-4.757529	-0.322975	0.027760
H	-4.303480	-1.937771	-1.317723
H	-4.901998	1.336203	1.379138
C	2.429680	1.306403	-0.135415
C	2.316176	-0.092546	-0.068594
C	3.710447	1.891224	-0.113485
C	3.459553	-0.873752	0.023558
H	1.341465	-0.551557	-0.091391
C	4.839833	1.106050	-0.022946
H	3.783523	2.969057	-0.168097
C	4.716323	-0.283426	0.046595
H	3.369799	-1.949839	0.075983
H	5.820052	1.564551	-0.006407
C	-6.208901	-0.687702	0.110335
C	5.962934	-1.112196	0.146283
F	-6.951593	0.278448	0.686074
F	-6.405534	-1.816726	0.833960
F	-6.738379	-0.924225	-1.111383
F	5.705822	-2.433226	0.185641
F	6.790507	-0.898980	-0.903314
F	6.674717	-0.812554	1.258085



ZZ-PCF3-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	4.167741	0.000001	0.000013
N	3.434915	-1.366341	0.079023
N	3.434912	1.366341	-0.079011
C	2.064896	1.608058	0.057151
C	1.433461	2.406457	-0.903183
C	1.316627	1.099883	1.125377
C	0.066911	2.614646	-0.842548
H	2.024258	2.825242	-1.706887
C	-0.047893	1.324619	1.191319
H	1.805788	0.514292	1.891415
C	-0.679426	2.062432	0.196613
H	-0.423259	3.207934	-1.603499
H	-0.625648	0.907606	2.004077
C	2.064900	-1.608056	-0.057145
C	1.316631	-1.099854	-1.125358
C	1.433464	-2.406476	0.903172
C	-0.047890	-1.324588	-1.191305
H	1.805793	-0.514242	-1.891380
C	0.066914	-2.614662	0.842532
H	2.024260	-2.825279	1.706867
C	-0.679423	-2.062423	-0.196617
H	-0.625644	-0.907553	-2.004053
H	-0.423258	-3.207966	1.603470
C	-2.167870	2.244484	0.199632
C	-2.167866	-2.244486	-0.199642
F	-2.729090	-1.895627	-1.371477
F	-2.760354	-1.495549	0.762299
F	-2.520301	-3.526861	0.048550
F	-2.520320	3.526827	-0.048696
F	-2.760362	1.495436	-0.762219
F	-2.729079	1.895746	1.371512



7 - *bis*(4-nitrophenyl)sulfur diimide

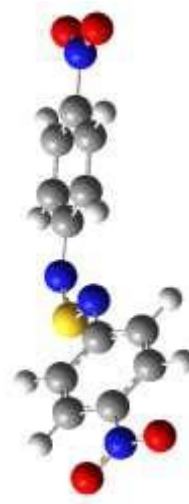
EE-PNO2-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	0.000001	-0.328394	-0.000005
N	-1.245664	-1.254435	-0.150401
N	1.245662	-1.254423	0.150490
C	2.518944	-0.700640	0.049203
C	3.536599	-1.348288	0.770126
C	2.846621	0.414574	-0.744277
C	4.832108	-0.870967	0.739543
H	3.279653	-2.219734	1.356677
C	4.142844	0.893034	-0.778371
H	2.089962	0.881541	-1.361782
C	5.120980	0.250170	-0.030442
H	5.622922	-1.352077	1.296009
H	4.412318	1.744990	-1.385243
C	-2.518944	-0.700644	-0.049151
C	-3.536605	-1.348357	-0.770007
C	-2.846616	0.414643	0.744231
C	-4.832114	-0.871033	-0.739456
H	-3.279663	-2.219856	-1.356481
C	-4.142838	0.893106	0.778292
H	-2.089952	0.881666	1.361687
C	-5.120981	0.250173	0.030429
H	-5.622933	-1.352194	-1.295873
H	-4.412308	1.745117	1.385088
N	-6.497279	0.755441	0.071717
O	-6.721690	1.740127	0.767406
O	-7.340251	0.164639	-0.594075
N	6.497279	0.755434	-0.071765
O	6.721696	1.740056	-0.767543
O	7.340246	0.164692	0.594086



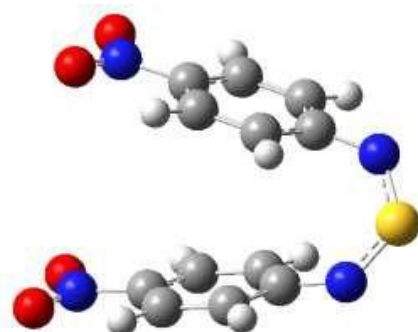
EZ-PNO2-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	-0.146504	1.859453	-0.305491
N	1.383912	2.033339	-0.289846
N	-0.672140	0.379712	-0.213359
C	-2.046067	0.161667	-0.097356
C	-2.563844	-0.982902	-0.725426
C	-2.912419	0.988152	0.640317
C	-3.912065	-1.274523	-0.654016
H	-1.888206	-1.623322	-1.276034
C	-4.262261	0.697775	0.715567
H	-2.517790	1.838352	1.181682
C	-4.749302	-0.426917	0.062790
H	-4.326650	-2.145911	-1.139168
H	-4.940656	1.319401	1.281348
C	2.425295	1.133636	-0.161604
C	2.290972	-0.261362	-0.019570
C	3.712781	1.705069	-0.174766
C	3.419545	-1.052142	0.109812
H	1.309742	-0.706514	-0.014391
C	4.836019	0.915441	-0.046950
H	3.797615	2.777404	-0.286486
C	4.674086	-0.459002	0.094664
H	3.340964	-2.123601	0.221160
H	5.829785	1.337949	-0.054668
N	-6.180261	-0.737458	0.147127
O	-6.891541	0.025077	0.792426
O	-6.580132	-1.739831	-0.434700
N	5.866742	-1.307172	0.230551
O	6.960692	-0.754659	0.215566
O	5.695364	-2.514751	0.350748



ZZ-PNO2-NSN-B3LYPD3BJ-6311++G2DP_OF

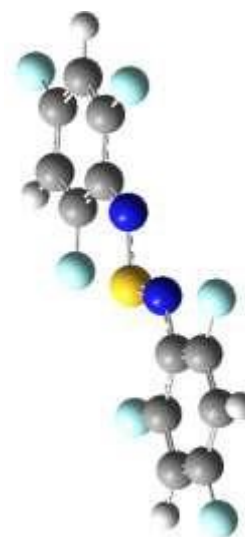
Atom Type	X	Y	Z
S	-3.805492	-0.000055	0.000002
N	-3.067998	-1.363021	-0.077495
N	-3.068054	1.362945	0.077495
C	-1.703166	1.607977	-0.071441
C	-1.065377	2.416497	0.877516
C	-0.968197	1.097036	-1.151959
C	0.296352	2.646363	0.793819
H	-1.647591	2.830858	1.689445
C	0.388578	1.337379	-1.247090
H	-1.466385	0.504433	-1.906549
C	1.009650	2.093673	-0.261704
H	0.813834	3.243368	1.530327
H	0.975417	0.936913	-2.060474
C	-1.703105	-1.608016	0.071440
C	-0.968150	-1.097066	1.151964
C	-1.065294	-2.416512	-0.877523
C	0.388631	-1.337376	1.247096
H	-1.466354	-0.504481	1.906558
C	0.296440	-2.646342	-0.793827
H	-1.647497	-2.830882	-1.689456
C	1.009723	-2.093645	0.261702
H	0.975458	-0.936906	2.060486
H	0.813940	-3.243324	-1.530342
N	2.458383	2.321508	-0.344763
O	3.061817	1.798646	-1.274133
O	2.974040	3.018712	0.520991
N	2.458462	-2.321446	0.344762
O	2.974145	-3.018591	-0.521024
O	3.061873	-1.798620	1.274167



8 - *bis*(2,4,6-trifluorophenyl)sulfur diimide

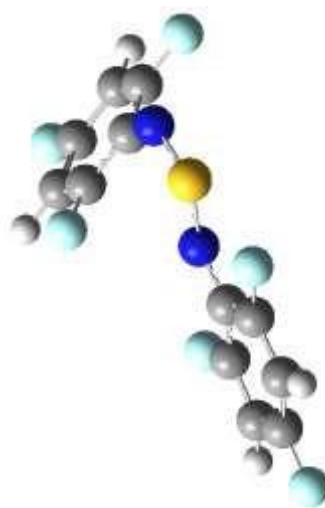
EETWIST-BIS-F3-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	-0.000015	-0.291430	-0.000321
N	-1.233585	0.670668	0.000563
N	1.233579	0.670617	-0.000157
C	2.543733	0.266887	-0.000040
C	3.532870	1.274577	-0.000688
C	3.050308	-1.046352	0.000624
C	4.888374	1.015259	-0.000621
C	4.392007	-1.360740	0.000739
C	5.291717	-0.308432	0.000127
H	5.604997	1.823872	-0.001120
H	4.721958	-2.389597	0.001310
C	-2.543734	0.266910	0.000129
C	-3.532893	1.274583	0.000718
C	-3.050283	-1.046333	-0.000532
C	-4.888389	1.015241	0.000579
C	-4.391978	-1.360747	-0.000668
C	-5.291708	-0.308460	-0.000139
H	-5.605025	1.823842	0.001003
H	-4.721901	-2.389614	-0.001207
F	-6.608455	-0.585214	-0.000248
F	6.608468	-0.585162	0.000169
F	-3.133108	2.549074	0.001192
F	-2.157953	-2.057695	-0.001180
F	2.157995	-2.057726	0.001337
F	3.133064	2.549060	-0.001167

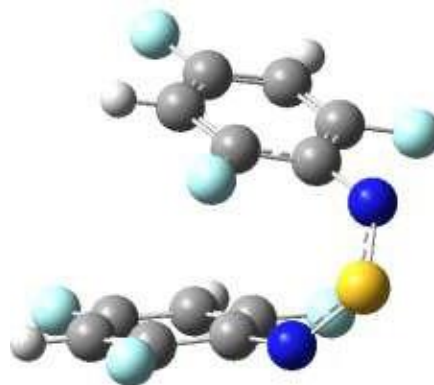


EZ-BIS-F3-NSN-B3LYPD3BJ-6311++G2DP_OF

Atom Type	X	Y	Z
S	-0.058457	-1.882532	0.268985
N	-0.636296	-0.461555	-0.013828
C	2.189310	0.393670	0.948427
C	-3.077741	-0.942492	0.071473
N	1.490883	-1.891115	0.311291
C	-1.960849	-0.104448	-0.082199
C	2.315096	-0.780604	0.193032
C	3.419508	-0.831281	-0.668539
C	-3.556010	1.731292	-0.431005
H	-3.741497	2.777481	-0.626999
C	-2.266795	1.246851	-0.336152
C	4.316247	0.208254	-0.816430
H	5.141381	0.135624	-1.509993
C	3.062676	1.458737	0.845081
H	2.933198	2.341807	1.453806
C	-4.384738	-0.513107	-0.011188
H	-5.207387	-1.201839	0.116131
C	-4.594715	0.832053	-0.264429
C	4.110507	1.341795	-0.049642
F	4.972233	2.369472	-0.173056
F	1.210422	0.461152	1.862966
F	3.592824	-1.936615	-1.407107
F	-2.842160	-2.246992	0.315608
F	-1.252394	2.104074	-0.492234
F	-5.859534	1.281332	-0.351680



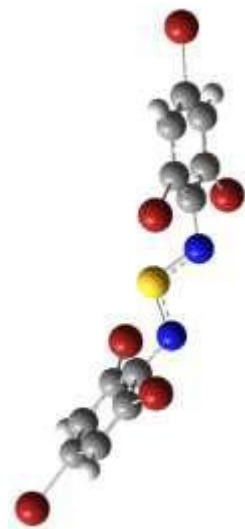
Atom Type	X	Y	Z
S	-0.000098	2.923899	0.000013
N	-1.356608	2.188831	0.156983
N	1.356459	2.188915	-0.156947
C	1.558950	0.827446	-0.354519
C	2.490898	0.127023	0.420156
C	0.918353	0.085142	-1.353217
C	2.738129	-1.223106	0.263405
C	1.136225	-1.261883	-1.561939
C	2.044549	-1.891919	-0.730662
H	3.445364	-1.734494	0.900290
H	0.615494	-1.795714	-2.343369
C	-1.559009	0.827346	0.354532
C	-0.918287	0.085049	1.353156
C	-2.490981	0.126891	-0.420086
C	-1.136067	-1.261994	1.561858
C	-2.738125	-1.223255	-0.263351
C	-2.044427	-1.892056	0.730641
H	-0.615238	-1.795819	2.343228
H	-3.445383	-1.734665	-0.900192
F	-2.267936	-3.208677	0.898898
F	2.268147	-3.208522	-0.898938
F	0.058168	0.732198	-2.160231
F	-0.058057	0.732127	2.160104
F	-3.139720	0.792254	-1.383181
F	3.139523	0.792397	1.383321



9 - *bis*(2,4,6-tribromophenyl)sulfur diimide

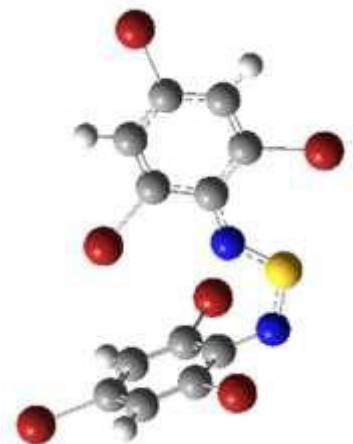
EE-BR3PHNSN-B3LYP-D3BJ-6311++G2DP_OF2

Atom Type	X	Y	Z
S	0.000062	-0.000420	0.148468
N	-1.247277	0.059559	1.057191
N	1.247319	-0.059362	1.057430
C	2.506636	0.026761	0.451352
C	3.019040	1.201828	-0.121424
C	3.371485	-1.077208	0.504116
C	4.316528	1.280061	-0.604924
C	4.669236	-1.026504	0.023505
C	5.129151	0.160509	-0.525603
H	4.683029	2.201139	-1.032041
H	5.304129	-1.898009	0.076371
C	-2.506628	-0.026776	0.451334
C	-3.371482	1.077252	0.504095
C	-3.019031	-1.201817	-0.121372
C	-4.669198	1.026524	0.023515
C	-4.316574	-1.280064	-0.604884
C	-5.129158	-0.160547	-0.525583
H	-5.304132	1.898004	0.076312
H	-4.683005	-2.201183	-1.031968
Br	6.918882	0.254906	-1.187197
Br	1.933426	2.774975	-0.223299
Br	2.726499	-2.713400	1.239211
Br	-1.933442	-2.774995	-0.223342
Br	-2.726512	2.713455	1.239197
Br	-6.918891	-0.254791	-1.187178



BR3PHNSN-ORTHOGONAL-B3LYPD3BJ-6311++2DP_OF

Atom Type	X	Y	Z
Br	-5.658473	2.399490	-0.000188
Br	4.806483	2.587936	0.000237
Br	-0.009915	1.967802	-0.000593
Br	2.028189	-1.454162	2.858461
Br	-3.315282	-2.741975	0.000140
Br	2.029402	-1.454906	-2.858117
S	-0.125181	-2.433408	0.000066
N	-0.590368	-0.959574	-0.000112
C	2.598206	-0.718079	1.193043
C	-3.081880	-0.849980	-0.000042
N	1.426096	-2.499716	0.000176
C	-1.781606	-0.299558	-0.000159
C	2.195189	-1.327776	0.000193
C	2.598719	-0.718396	-1.192648
C	-2.842527	1.916629	-0.000354
H	-2.748499	2.991955	-0.000481
C	-1.714761	1.118151	-0.000344
C	3.375536	0.429110	-1.208542
H	3.666624	0.877869	-2.146144
C	3.375020	0.429427	1.208971
H	3.665707	0.878430	2.146582
C	-4.224610	-0.068215	-0.000046
H	-5.200421	-0.529860	0.000059
C	-4.091874	1.311667	-0.000195
C	3.753795	0.991128	0.000223



ZZ-BR3PHNSN-B3LYP-D3BJ-6311++G2DP_OF3

Atom Type	X	Y	Z
S	-0.000096	-3.206484	-0.000012
N	-1.123394	-2.487125	-0.782491
N	1.123239	-2.487183	0.782469
C	1.332614	-1.123091	0.959991
C	2.514346	-0.532092	0.485112
C	0.442135	-0.283990	1.651521
C	2.718080	0.837669	0.533592
C	0.627791	1.086610	1.720794
C	1.750019	1.637433	1.121703
H	-0.092290	1.708844	2.230009
C	-1.332679	-1.123017	-0.959984
C	-0.442127	-0.283968	-1.651477
C	-2.514371	-0.531946	-0.485097
C	-0.627685	1.086649	-1.720728
C	-2.718011	0.837835	-0.533561
C	-1.749888	1.637540	-1.121652
H	0.092429	1.708837	-2.229949
H	-3.614442	1.268584	-0.113900
Br	3.877042	-1.627330	-0.272747
Br	1.036690	-1.039011	-2.586970
Br	-1.036765	-1.038924	2.586968
Br	-3.877171	-1.627107	0.272696
Br	-1.975723	3.533325	-1.129762
Br	1.975958	3.533203	1.129786
H	3.614524	1.268367	0.113898

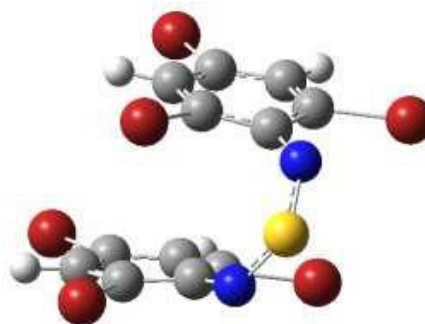
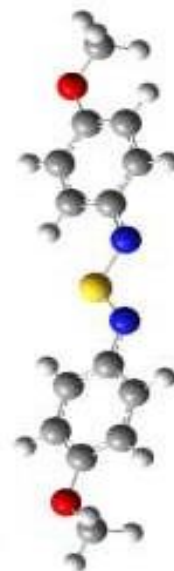


Table B.48. DFT Computed Cartesian Geometries of anionic sulfur diimides with Structure Plots

1 - *bis*(4-methoxyphenyl)sulfur diimide

EECONF1-PMEO-CONF1-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.000000	0.034650	-0.000013
N	-1.270337	-0.991848	-0.000017
N	1.270337	-0.991848	-0.000001
C	2.525057	-0.453881	-0.000003
C	3.612257	-1.359641	0.000012
C	2.875099	0.926530	-0.000018
C	4.935354	-0.940537	0.000012
H	3.379583	-2.417676	0.000024
C	4.196216	1.342548	-0.000016
H	2.093807	1.675826	-0.000030
C	5.239565	0.421364	-0.000001
H	5.718568	-1.687484	0.000023
H	4.438507	2.399726	-0.000028
C	-2.525057	-0.453881	-0.000015
C	-3.612257	-1.359641	-0.000028
C	-2.875099	0.926530	0.000000
C	-4.935354	-0.940537	-0.000027
H	-3.379583	-2.417676	-0.000038
C	-4.196216	1.342548	0.000001
H	-2.093807	1.675826	0.000012
C	-5.239565	0.421364	-0.000013
H	-5.718568	-1.687484	-0.000039
H	-4.438507	2.399726	0.000013
O	6.527109	0.944619	-0.000007
O	-6.527109	0.944619	-0.000017
C	-7.590458	0.023675	0.000047
H	-8.507974	0.612229	0.000073
H	-7.574477	-0.617110	-0.890454
H	-7.574399	-0.617072	0.890573
C	7.590458	0.023675	0.000071
H	8.507974	0.612229	0.000087
H	7.574400	-0.617057	0.890608
H	7.574476	-0.617125	-0.890418



EZCONF1-PMEO-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	-0.195497	1.793371	-0.000172
N	1.407413	1.940685	-0.000227
N	-0.707373	0.224807	-0.000150
C	-2.054863	-0.000138	-0.000093
C	-2.485796	-1.354474	-0.000120
C	-3.087073	0.971397	-0.000008
C	-3.819484	-1.704698	-0.000069
H	-1.720876	-2.121993	-0.000185
C	-4.436097	0.614948	0.000043
H	-2.834337	2.023859	0.000025
C	-4.813833	-0.721368	0.000013
H	-4.118601	-2.746940	-0.000091
H	-5.178382	1.402957	0.000107
C	2.390469	1.002283	-0.000114
C	2.239794	-0.413384	0.000049
C	3.722845	1.486691	-0.000161
C	3.342475	-1.249069	0.000163
H	1.240868	-0.820489	0.000079
C	4.823691	0.641965	-0.000051
H	3.866559	2.560565	-0.000285
C	4.640218	-0.740585	0.000114
H	3.209981	-2.325572	0.000290
H	5.815415	1.075415	-0.000097
O	-6.126861	-1.177677	0.000053
O	5.669548	-1.672894	0.000223
C	6.984871	-1.174259	0.000313
H	7.643798	-2.042682	0.000465
H	7.190434	-0.567196	-0.890310
H	7.190241	-0.567023	0.890861
C	-7.139599	-0.201623	0.000194
H	-8.087534	-0.740004	0.000238
H	-7.088470	0.437534	0.890680
H	-7.088616	0.437643	-0.890222



ZZCONF1-PMEO-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

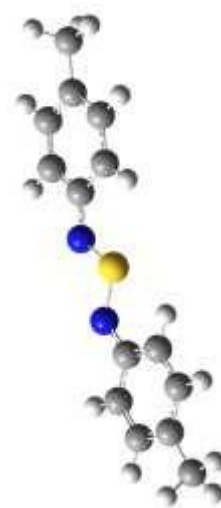
Atom Type	X	Y	Z
S	-0.287017	-3.285335	-0.241584
N	0.938700	-2.469876	-0.958434
N	-1.432084	-2.496005	0.621680
C	-1.888636	-1.233612	0.371987
C	-2.850569	-0.701964	1.270969
C	-1.520541	-0.400308	-0.709073
C	-3.393291	0.555737	1.105600
H	-3.151446	-1.321390	2.107634
C	-2.074082	0.866282	-0.877301
H	-0.787327	-0.750766	-1.420092
C	-3.008006	1.356770	0.027881
H	-4.122322	0.943424	1.808412
H	-1.747011	1.462719	-1.718787
C	1.559015	-1.366811	-0.444560
C	1.307523	-0.771093	0.820347
C	2.568309	-0.760457	-1.226070
C	2.022936	0.330524	1.253960
H	0.538116	-1.187096	1.454464
C	3.280514	0.350420	-0.791713
H	2.781681	-1.193382	-2.196261
C	3.010634	0.905862	0.458098
H	1.811885	0.773919	2.220554
H	4.040624	0.769722	-1.438112
O	-3.602049	2.609012	-0.046761
O	3.659305	2.015631	0.984651
C	4.627807	2.634395	0.174039
H	5.008087	3.483718	0.741826
H	5.459204	1.956790	-0.058171
H	4.198500	2.994929	-0.769135
C	-3.177195	3.454608	-1.089681
H	-3.725562	4.389164	-0.970491
H	-2.100906	3.656420	-1.033789
H	-3.402118	3.029091	-2.075462



2 - bis(4-methylphenyl)sulfur diimide

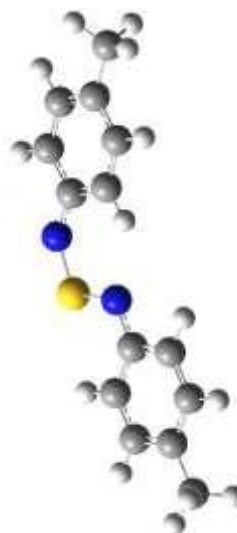
EECONF1-PCH3-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.000000	0.028475	0.000001
N	-1.269458	-0.998604	0.000043
N	1.269458	-0.998604	-0.000044
C	2.523375	-0.463933	-0.000030
C	3.608034	-1.382053	-0.000137
C	2.879927	0.911344	0.000043
C	4.922474	-0.961185	-0.000144
H	3.364343	-2.437917	-0.000238
C	4.209808	1.312178	0.000034
H	2.103280	1.665786	0.000088
C	5.263733	0.399890	-0.000045
H	5.713909	-1.706575	-0.000241
H	4.433748	2.376020	0.000080
C	-2.523375	-0.463933	0.000030
C	-3.608034	-1.382053	0.000136
C	-2.879927	0.911344	-0.000044
C	-4.922474	-0.961184	0.000144
H	-3.364343	-2.437917	0.000237
C	-4.209808	1.312178	-0.000034
H	-2.103280	1.665786	-0.000089
C	-5.263733	0.399890	0.000044
H	-5.713909	-1.706575	0.000240
H	-4.433747	2.376020	-0.000081
C	6.702920	0.845087	0.000161
H	7.245036	0.482094	0.881269
H	7.246010	0.479567	-0.879284
H	6.774932	1.935481	-0.001341
C	-6.702920	0.845087	-0.000160
H	-7.245038	0.482088	-0.881265
H	-7.246007	0.479573	0.879289
H	-6.774932	1.935481	0.001335



EZCONF3-PCH3-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	-0.138274	-1.736578	0.002031
N	1.468319	-1.821374	0.004776
N	-0.711550	-0.190363	0.002439
C	-2.063390	-0.012412	0.001124
C	-2.541697	1.325685	0.001164
C	-3.062158	-1.023468	-0.001336
C	-3.889850	1.621398	-0.000280
H	-1.803202	2.119026	0.001669
C	-4.413780	-0.702567	-0.002732
H	-2.770583	-2.066167	-0.003119
C	-4.868106	0.615012	-0.001775
H	-4.200414	2.663344	-0.000630
H	-5.141384	-1.510492	-0.005015
C	2.415734	-0.849502	0.000636
C	2.219154	0.557149	-0.008881
C	3.767822	-1.294514	0.000735
C	3.303196	1.423647	-0.013714
H	1.208478	0.933540	-0.014646
C	4.827033	-0.410050	-0.004275
H	3.941684	-2.364254	0.001450
C	4.625891	0.977553	-0.009445
H	3.110048	2.493527	-0.022663
H	5.841707	-0.800646	-0.005910
C	-6.336353	0.951913	0.003893
H	-6.631900	1.491806	0.911642
H	-6.615315	1.585051	-0.846436
H	-6.945422	0.046039	-0.049138
C	5.787491	1.936074	0.015348
H	6.566801	1.647472	-0.697998
H	5.465996	2.949323	-0.238460
H	6.262577	1.984331	1.003481



ZZCONF1-PCH3-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

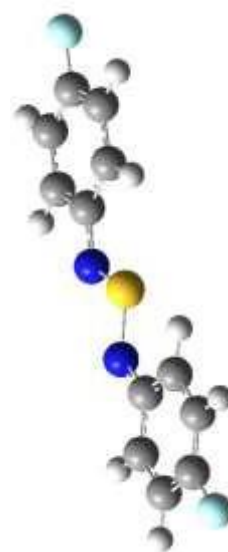
Atom Type	X	Y	Z
S	0.000477	2.940125	-0.000108
N	-1.225303	2.137138	-0.726558
N	1.226283	2.137183	0.726329
C	1.748937	0.944446	0.322767
C	2.778376	0.381795	1.120356
C	1.390028	0.216994	-0.839762
C	3.390166	-0.811065	0.784217
H	3.076871	0.924524	2.009827
C	2.023108	-0.973913	-1.161705
H	0.610705	0.600143	-1.482336
C	3.027082	-1.525286	-0.364545
H	4.173219	-1.203330	1.428378
H	1.714821	-1.499727	-2.061425
C	-1.748428	0.944648	-0.322841
C	-1.390534	0.217597	0.840264
C	-2.777516	0.381956	-1.120854
C	-2.024148	-0.973005	1.162270
H	-0.611623	0.600841	1.483268
C	-3.389843	-0.810609	-0.784642
H	-3.075295	0.924407	-2.010735
C	-3.027712	-1.524459	0.364648
H	-1.716632	-1.498508	2.062435
H	-4.172577	-1.202925	-1.429159
C	3.662540	-2.850168	-0.697356
H	4.728773	-2.858062	-0.450278
H	3.199644	-3.678985	-0.146947
H	3.566657	-3.078241	-1.762207
C	-3.663722	-2.849047	0.697573
H	-4.729667	-2.856953	0.449266
H	-3.200298	-3.678275	0.148227
H	-3.569100	-3.076462	1.762679



3 - *bis*(4-fluorophenyl)sulfur diimide

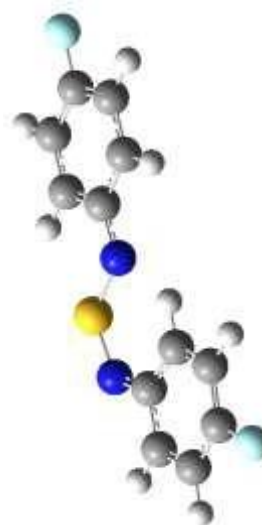
EECONF1-FPHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.000000	0.000000	0.039330
N	0.000000	1.268609	-0.986273
N	0.000000	-1.268609	-0.986273
C	0.000000	-2.523221	-0.451412
C	0.000000	-3.604669	-1.371938
C	0.000000	-2.873315	0.927708
C	0.000000	-4.925273	-0.958821
C	0.000000	-4.200245	1.342012
C	0.000000	-5.208214	0.398765
H	0.000000	-5.736826	-1.676742
H	0.000000	-4.453315	2.395871
C	0.000000	2.523221	-0.451412
C	0.000000	3.604669	-1.371938
C	0.000000	2.873315	0.927708
C	0.000000	4.925273	-0.958821
C	0.000000	4.200245	1.342012
C	0.000000	5.208214	0.398765
H	0.000000	5.736826	-1.676742
H	0.000000	4.453315	2.395871
F	0.000000	6.520675	0.811208
F	0.000000	-6.520675	0.811208
H	0.000000	2.093845	1.678283
H	0.000000	3.360503	-2.426894
H	0.000000	-3.360503	-2.426894
H	0.000000	-2.093845	1.678283



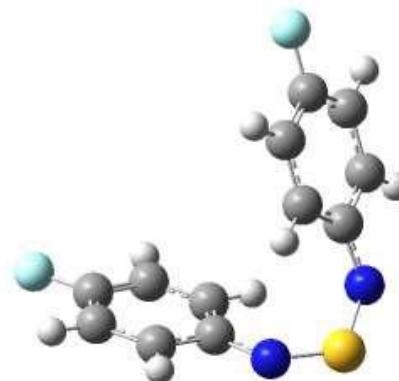
EZ-PFPHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.133908	-1.718160	-0.000090
N	-1.472441	-1.795646	0.000089
N	0.710647	-0.173018	0.000342
C	2.064031	-0.000107	0.000171
C	2.544435	1.336406	0.000715
C	3.054495	-1.022073	-0.000496
C	3.895411	1.635924	0.000613
H	1.809940	2.132432	0.001230
C	4.411877	-0.720274	-0.000594
H	2.754062	-2.061609	-0.000958
C	4.816833	0.599111	-0.000040
H	4.241573	2.662720	0.001037
H	5.155955	-1.508441	-0.001106
C	-2.414069	-0.817046	0.000036
C	-2.200864	0.588993	-0.000018
C	-3.767455	-1.256519	0.000030
C	-3.270833	1.474791	-0.000097
H	-1.185760	0.952970	0.000020
C	-4.828878	-0.369381	-0.000037
H	-3.948033	-2.324354	0.000074
C	-4.565528	0.991479	-0.000104
H	-3.100519	2.545222	-0.000142
H	-5.854265	-0.719713	-0.000044
F	-5.618801	1.876352	-0.000169
F	6.161062	0.895221	-0.000139



ZZCONF1-PF-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.000000	0.000000	2.888493
N	-1.262154	-0.654566	2.080864
N	1.262154	0.654566	2.080864
C	1.185975	1.319858	0.892006
C	2.405333	1.772973	0.326222
C	0.000000	1.627805	0.176280
C	2.444577	2.483421	-0.861793
H	3.321122	1.547045	0.858598
C	0.039589	2.346399	-1.011335
H	-0.951753	1.295170	0.563232
C	1.255924	2.762223	-1.516576
H	3.383522	2.821488	-1.283887
H	-0.871388	2.572308	-1.552563
C	-1.185975	-1.319858	0.892006
C	0.000000	-1.627805	0.176280
C	-2.405333	-1.772973	0.326222
C	-0.039589	-2.346399	-1.011335
H	0.951753	-1.295170	0.563232
C	-2.444577	-2.483421	-0.861793
H	-3.321122	-1.547045	0.858598
C	-1.255924	-2.762223	-1.516576
H	0.871388	-2.572308	-1.552563
H	-3.383522	-2.821488	-1.283887
F	-1.292652	-3.463664	-2.698688
F	1.292652	3.463664	-2.698688



4 - bis(4-chlorophenyl)sulfur diimide

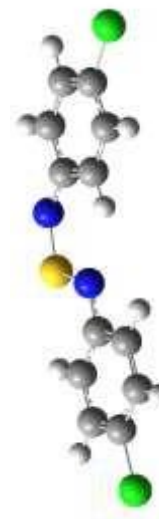
EECONF1-PCL-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.000000	0.066168	-0.000001
N	1.267137	1.094198	0.000001
N	-1.267137	1.094199	-0.000002
C	-2.520718	0.566024	-0.000004
C	-3.599951	1.490163	-0.000004
C	-2.877471	-0.811997	-0.000006
C	-4.919380	1.082263	-0.000007
H	-3.353869	2.544779	-0.000003
C	-4.202876	-1.220047	-0.000008
H	-2.102287	-1.567301	-0.000006
C	-5.219963	-0.277621	-0.000009
H	-5.718621	1.812815	-0.000007
H	-4.445884	-2.275548	-0.000010
C	2.520718	0.566024	0.000004
C	3.599951	1.490163	0.000005
C	2.877471	-0.811998	0.000006
C	4.919380	1.082263	0.000007
H	3.353869	2.544779	0.000004
C	4.202876	-1.220047	0.000008
H	2.102287	-1.567301	0.000006
C	5.219963	-0.277621	0.000009
H	5.718621	1.812815	0.000008
H	4.445884	-2.275548	0.000010
Cl	6.913200	-0.804481	0.000012
Cl	-6.913200	-0.804481	-0.000012



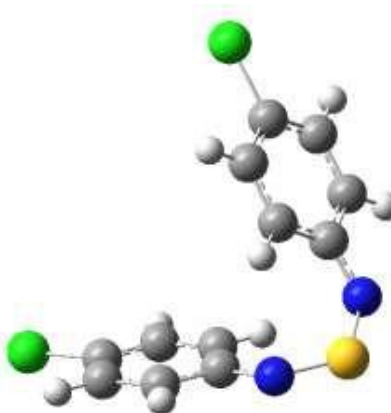
EZCONF1-PCLPHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	-0.148316	1.912546	-0.000016
N	1.454046	2.030623	0.000098
N	-0.683069	0.353245	0.000351
C	-2.026934	0.139171	0.000181
C	-2.467947	-1.211387	0.000686
C	-3.049187	1.130260	-0.000452
C	-3.806833	-1.550257	0.000583
H	-1.711209	-1.986388	0.001173
C	-4.393366	0.788395	-0.000551
H	-2.782169	2.179056	-0.000887
C	-4.771466	-0.545408	-0.000035
H	-4.108736	-2.590163	0.000981
H	-5.150316	1.563195	-0.001038
C	2.421481	1.082190	0.000050
C	2.250805	-0.329998	0.000043
C	3.762292	1.560219	0.000009
C	3.344330	-1.182099	-0.000027
H	1.247914	-0.726461	0.000105
C	4.846936	0.706272	-0.000051
H	3.913278	2.632712	0.000020
C	4.634133	-0.669396	-0.000072
H	3.191853	-2.254427	-0.000037
H	5.855988	1.099133	-0.000085
Cl	-6.491966	-0.977123	-0.000163
Cl	6.024564	-1.770655	-0.000148



ZZCONF1-PCLPHNSN-B3LYPD3BJ-6311++G2DP_ANION_OPT+FRQ

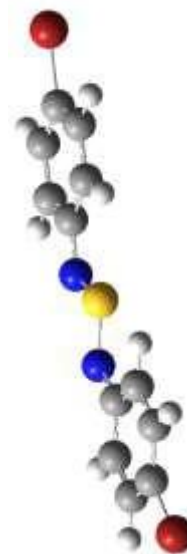
Atom Type	X	Y	Z
S	0.000000	0.000000	3.277065
N	-0.865757	-1.127000	2.470373
N	0.865757	1.127000	2.470373
C	0.526649	1.694030	1.280789
C	1.446452	2.616688	0.718064
C	-0.674058	1.474650	0.556237
C	1.192689	3.272297	-0.471763
H	2.369078	2.799312	1.255351
C	-0.930459	2.138759	-0.632910
H	-1.403835	0.776660	0.939124
C	0.000000	3.030358	-1.145748
H	1.913701	3.969547	-0.879742
H	-1.852597	1.952582	-1.168819
C	-0.526649	-1.694030	1.280789
C	0.674058	-1.474650	0.556237
C	-1.446452	-2.616688	0.718064
C	0.930459	-2.138759	-0.632910
H	1.403835	-0.776660	0.939124
C	-1.192689	-3.272297	-0.471763
H	-2.369078	-2.799312	1.255351
C	0.000000	-3.030358	-1.145748
H	1.852597	-1.952582	-1.168819
H	-1.913701	-3.969547	-0.879742
Cl	-0.326414	3.865600	-2.675474
Cl	0.326414	-3.865600	-2.675474



5 - *bis*(4-bromophenyl)sulfur diimide

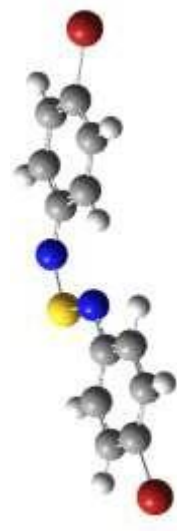
EECONF1-PBR-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.000000	0.000000	0.242517
N	0.000001	-1.266342	1.271102
N	-0.000001	1.266342	1.271102
C	-0.000001	2.519598	0.744073
C	-0.000003	3.598110	1.669092
C	0.000001	2.876829	-0.633939
C	-0.000003	4.918093	1.262503
H	-0.000005	3.351743	2.723671
C	0.000001	4.202254	-1.042007
H	0.000003	2.102174	-1.389854
C	-0.000001	5.217145	-0.097479
H	-0.000004	5.713797	1.996462
H	0.000003	4.441561	-2.098050
C	0.000001	-2.519598	0.744073
C	0.000003	-3.598110	1.669092
C	-0.000001	-2.876829	-0.633939
C	0.000003	-4.918093	1.262503
H	0.000005	-3.351743	2.723671
C	-0.000001	-4.202254	-1.042007
H	-0.000003	-2.102174	-1.389854
C	0.000001	-5.217145	-0.097479
H	0.000004	-5.713797	1.996462
H	-0.000003	-4.441561	-2.098050
Br	0.000001	-7.061653	-0.670958
Br	-0.000001	7.061653	-0.670958



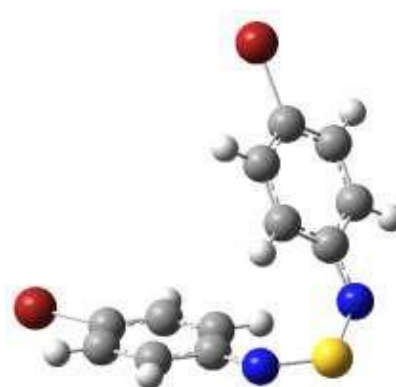
EZCONF1-PBR-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.154126	2.211577	0.000228
N	-1.444373	2.371223	0.000242
N	0.647281	0.638725	0.000072
C	1.984367	0.388774	0.000058
C	2.388828	-0.973224	-0.000084
C	3.032684	1.352414	0.000169
C	3.718200	-1.348539	-0.000112
H	1.611794	-1.727929	-0.000171
C	4.367545	0.975456	0.000140
H	2.794085	2.408098	0.000280
C	4.707682	-0.368425	0.000001
H	3.987975	-2.396901	-0.000221
H	5.141746	1.732562	0.000228
C	-2.435760	1.448525	0.000135
C	-2.301582	0.032410	-0.000025
C	-3.763600	1.961514	0.000189
C	-3.416616	-0.791802	-0.000122
H	-1.309444	-0.390406	-0.000069
C	-4.870701	1.136493	0.000092
H	-3.886870	3.037585	0.000311
C	-4.691550	-0.243758	-0.000064
H	-3.287755	-1.866900	-0.000244
H	-5.867225	1.559283	0.000137
Br	-6.236834	-1.404106	-0.000200
Br	6.568615	-0.888160	-0.000039



ZZCONF1-PBR-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

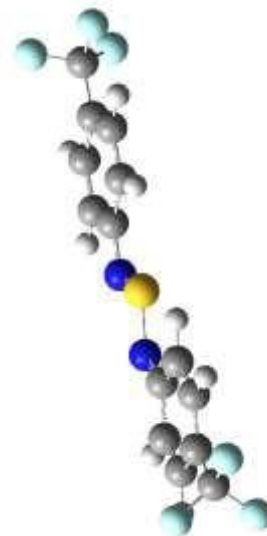
Atom Type	X	Y	Z
S	0.000000	0.000000	3.862832
N	-1.243296	-0.687184	3.055864
N	1.243296	0.687184	3.055864
C	1.158977	1.342443	1.866783
C	2.371183	1.819323	1.303654
C	-0.029709	1.622998	1.143482
C	2.401245	2.523048	0.114398
H	3.290219	1.616595	1.839958
C	0.000000	2.335212	-0.045338
H	-0.978092	1.276385	1.526815
C	1.210157	2.779528	-0.556682
H	3.342805	2.871592	-0.290302
H	-0.921955	2.532892	-0.576862
C	-1.158977	-1.342443	1.866783
C	0.029709	-1.622998	1.143482
C	-2.371183	-1.819323	1.303654
C	0.000000	-2.335212	-0.045338
H	0.978092	-1.276385	1.526815
C	-2.401245	-2.523048	0.114398
H	-3.290219	-1.616595	1.839958
C	-1.210157	-2.779528	-0.556682
H	0.921955	-2.532892	-0.576862
H	-3.342805	-2.871592	-0.290302
Br	1.247338	3.758555	-2.221460
Br	-1.247338	-3.758555	-2.221460



6 - *bis*(4-trifluoromethylphenyl)sulfur diimide

EECONF1-PCF3-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.000000	0.182629	-0.000005
N	1.264303	1.213285	-0.000005
N	-1.264302	1.213285	0.000003
C	-2.517399	0.695721	-0.000010
C	-3.589610	1.632962	0.000004
C	-2.883600	-0.680590	-0.000040
C	-4.904106	1.232485	-0.000009
H	-3.330394	2.684143	0.000023
C	-4.208853	-1.072862	-0.000051
H	-2.112730	-1.440088	-0.000058
C	-5.238488	-0.131628	-0.000039
H	-5.691667	1.977237	-0.000001
H	-4.451099	-2.128039	-0.000075
C	2.517398	0.695722	0.000005
C	3.589610	1.632962	-0.000004
C	2.883600	-0.680590	0.000026
C	4.904106	1.232485	0.000005
H	3.330394	2.684143	-0.000017
C	4.208853	-1.072862	0.000033
H	2.112730	-1.440088	0.000038
C	5.238488	-0.131628	0.000025
H	5.691667	1.977237	0.000000
H	4.451098	-2.128039	0.000049
C	-6.662521	-0.531411	-0.000002
C	6.662521	-0.531411	0.000008
F	-6.843244	-1.874297	-0.000322
F	6.843244	-1.874297	0.000173
F	-7.356260	-0.057869	-1.080648
F	-7.356064	-0.058428	1.081021
F	7.356211	-0.058005	1.080747
F	7.356113	-0.058293	-1.080922



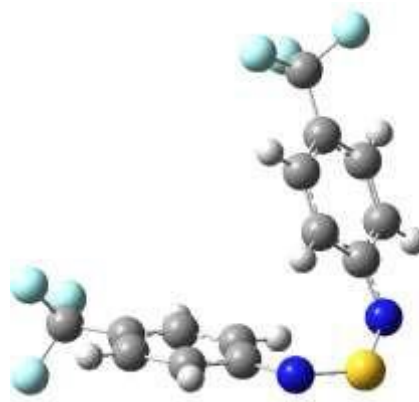
EZCONF-PCF3-PHNSN-B3LYP6311D3BJ-G++2DP_ANION_OF

Atom Type	X	Y	Z
S	-0.148730	2.187966	0.000144
N	1.449975	2.326699	0.000017
N	-0.661823	0.622747	-0.000331
C	-1.997289	0.384149	-0.000213
C	-2.409057	-0.978974	-0.000707
C	-3.038671	1.356075	0.000360
C	-3.735470	-1.337848	-0.000653
H	-1.633667	-1.734832	-0.001148
C	-4.369890	0.984724	0.000410
H	-2.790572	2.409303	0.000765
C	-4.743378	-0.359353	-0.000104
H	-4.007232	-2.387150	-0.001057
H	-5.135315	1.750390	0.000846
C	2.432606	1.399078	-0.000038
C	2.289773	-0.016197	-0.000230
C	3.764941	1.909007	0.000084
C	3.400954	-0.839166	-0.000264
H	1.295747	-0.432896	-0.000360
C	4.858891	1.078775	0.000034
H	3.887904	2.984742	0.000210
C	4.694871	-0.315534	-0.000156
H	3.261826	-1.912774	-0.000411
H	5.856472	1.502714	0.000113
C	-6.161810	-0.776365	0.000072
C	5.891984	-1.185312	0.000062
F	-7.028402	0.265616	-0.000146
F	-6.499345	-1.545823	1.080996
F	-6.499400	-1.546395	-1.080398
F	5.597497	-2.506797	-0.001691
F	6.707922	-0.979352	-1.079851
F	6.705808	-0.981853	1.082090



ZZCONF2-PCF3-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

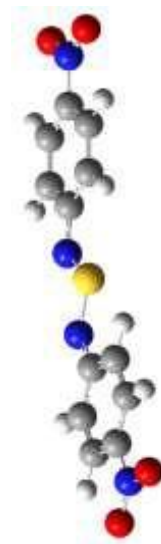
Atom Type	X	Y	Z
S	-0.148924	-2.188492	-0.007762
N	1.448893	-2.328813	-0.001218
N	-0.659940	-0.623101	-0.005716
C	-1.994722	-0.382114	-0.010941
C	-2.404899	0.981266	-0.011871
C	-3.037368	-1.353196	-0.017490
C	-3.731198	1.341737	-0.019061
H	-1.628751	1.736399	-0.009118
C	-4.367822	-0.980441	-0.023931
H	-2.790083	-2.406677	-0.019207
C	-4.739902	0.364502	-0.028073
H	-4.002136	2.391111	-0.022648
H	-5.134334	-1.745268	-0.029605
C	2.433539	-1.403749	0.009559
C	3.764704	-1.915258	0.014179
C	2.292389	0.012391	0.019428
C	4.860410	-1.086262	0.026709
H	3.886547	-2.991155	0.009953
C	3.404152	0.833238	0.031174
H	1.298649	0.429986	0.018867
C	4.698258	0.307471	0.039223
H	5.857332	-1.510848	0.033431
H	3.266681	1.907381	0.039732
C	-6.159140	0.777481	0.002452
C	5.888801	1.185295	0.000986
F	6.895124	0.753647	0.814483
F	5.624555	2.464297	0.364737
F	6.465012	1.272430	-1.241564
F	-6.549430	1.307360	1.206177
F	-6.452696	1.752223	-0.907657
F	-7.020011	-0.241715	-0.240926



7 - *bis*(4-nitrophenyl)sulfur diimide

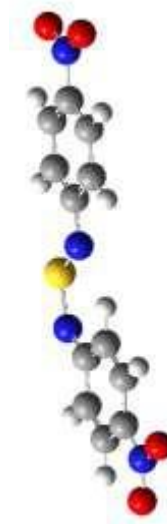
EECONF1-PNO2-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	-0.000001	0.058340	0.000002
N	1.259546	1.088600	-0.000007
N	-1.259548	1.088600	0.000020
C	-2.515299	0.594098	0.000043
C	-3.571147	1.552674	0.000047
C	-2.897451	-0.782935	0.000063
C	-4.889465	1.177189	0.000068
H	-3.292223	2.598378	0.000033
C	-4.218914	-1.156979	0.000083
H	-2.134235	-1.550218	0.000063
C	-5.227293	-0.185354	0.000087
H	-5.681748	1.911668	0.000071
H	-4.502338	-2.199839	0.000099
C	2.515297	0.594099	-0.000032
C	3.571144	1.552675	-0.000031
C	2.897450	-0.782934	-0.000060
C	4.889463	1.177189	-0.000054
H	3.292220	2.598378	-0.000011
C	4.218912	-1.156978	-0.000083
H	2.134234	-1.550217	-0.000064
C	5.227293	-0.185353	-0.000080
H	5.681744	1.911670	-0.000053
H	4.502336	-2.199838	-0.000104
N	6.599086	-0.582603	-0.000104
O	6.869517	-1.794647	-0.000121
O	7.472744	0.299540	-0.000097
N	-6.599083	-0.582604	0.000109
O	-6.869510	-1.794651	0.000084
O	-7.472741	0.299543	0.000072



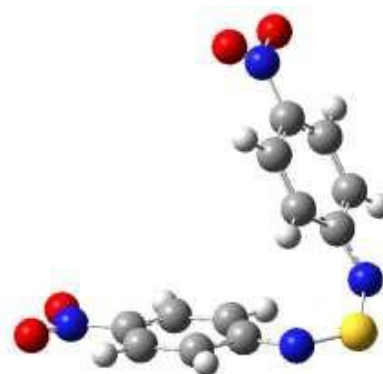
EZCONF1-PNO2-PHNSN-B3LYPD3BJ-6311+G2DP_ANION_OF

Atom Type	X	Y	Z
S	-0.143884	-2.026820	-0.000064
N	1.447660	-2.133966	-0.000054
N	-0.684039	-0.480362	0.000009
C	-2.015854	-0.244818	-0.000020
C	-2.427870	1.119246	0.000086
C	-3.051464	-1.228766	-0.000150
C	-3.751839	1.476141	0.000070
H	-1.653209	1.875299	0.000182
C	-4.377269	-0.870002	-0.000165
H	-2.793412	-2.279766	-0.000243
C	-4.742611	0.481756	-0.000054
H	-4.052930	2.513695	0.000153
H	-5.156739	-1.618531	-0.000264
C	2.423151	-1.205795	-0.000014
C	2.264794	0.212136	0.000043
C	3.757785	-1.713770	-0.000031
C	3.362484	1.040639	0.000078
H	1.267101	0.619506	0.000058
C	4.846739	-0.883097	0.000005
H	3.882579	-2.788950	-0.000074
C	4.657522	0.507924	0.000059
H	3.243342	2.114667	0.000121
H	5.853579	-1.274570	-0.000009
N	-6.122985	0.846223	-0.000071
O	-6.978517	-0.054699	-0.000164
O	-6.419108	2.052219	0.000044
N	5.790066	1.379235	0.000097
O	6.926641	0.876332	0.000139
O	5.598924	2.606185	0.000205



ZZCONF1-PNO2-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

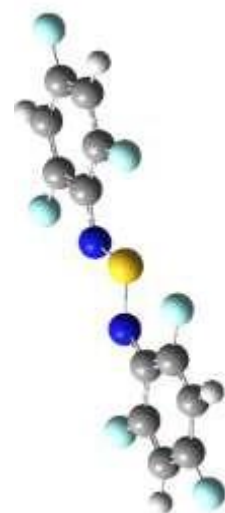
Atom Type	X	Y	Z
S	0.000179	3.479658	-0.000036
N	1.204879	2.686044	0.747182
N	-1.204519	2.686015	-0.747225
C	-1.740602	1.492800	-0.414966
C	-2.751961	0.979464	-1.277418
C	-1.420993	0.723494	0.740778
C	-3.398106	-0.199624	-1.008853
H	-2.999399	1.557409	-2.158529
C	-2.081353	-0.450683	1.015596
H	-0.662528	1.079625	1.421425
C	-3.069622	-0.923797	0.146212
H	-4.163450	-0.583821	-1.667407
H	-1.845496	-1.025287	1.899636
C	1.740852	1.492775	0.414947
C	1.420941	0.723367	-0.740641
C	2.752327	0.979446	1.277265
C	2.081157	-0.450890	-1.015469
H	0.662340	1.079473	-1.421155
C	3.398330	-0.199719	1.008694
H	2.999975	1.557461	2.158271
C	3.069571	-0.923980	-0.146237
H	1.845073	-1.025575	-1.899396
H	4.163772	-0.583908	1.667140
N	-3.757558	-2.144418	0.441163
O	-3.463388	-2.757936	1.477383
O	-4.628498	-2.539523	-0.349894
N	3.757358	-2.144681	-0.441200
O	4.628221	-2.539922	0.349873
O	3.462726	-2.758436	-1.477149



8 - *bis*(2,4,6-trifluorophenyl)sulfur diimide

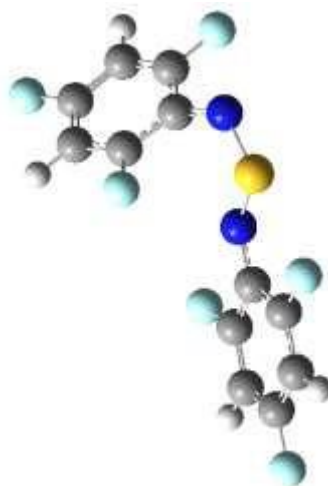
EECONF1-F3PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.000000	0.000000	0.363669
N	0.000000	1.248299	-0.690633
N	0.000000	-1.248299	-0.690633
C	0.000000	-2.531616	-0.276669
C	0.000000	-3.551299	-1.272481
C	0.000000	-3.077154	1.034898
C	0.000000	-4.907471	-1.023630
C	0.000000	-4.426907	1.338462
C	0.000000	-5.330440	0.295593
H	0.000000	-5.611329	-1.844314
H	0.000001	-4.750396	2.370266
C	0.000000	2.531616	-0.276669
C	0.000000	3.551299	-1.272481
C	0.000000	3.077154	1.034898
C	0.000000	4.907471	-1.023630
C	0.000000	4.426907	1.338462
C	0.000000	5.330440	0.295593
H	0.000000	5.611329	-1.844314
H	-0.000001	4.750396	2.370266
F	0.000000	6.671500	0.567586
F	0.000000	-6.671500	0.567586
F	0.000000	3.161345	-2.565724
F	-0.000001	2.216314	2.089481
F	0.000001	-2.216314	2.089481
F	0.000000	-3.161345	-2.565724



EZ-F3PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.054235	2.003667	-0.134686
N	-1.559473	1.977802	0.005656
N	0.603604	0.527279	0.315650
C	1.892963	0.151598	0.223592
C	2.239585	-1.178113	0.596747
C	3.026889	0.895136	-0.195747
C	3.512648	-1.706999	0.564014
C	4.322243	0.413495	-0.250700
C	4.547899	-0.892884	0.133668
H	3.685079	-2.731237	0.864415
H	5.126850	1.054335	-0.584213
C	-2.297796	0.832294	-0.090458
C	-2.101878	-0.240455	-0.989165
C	-3.452359	0.679018	0.705178
C	-2.912999	-1.358536	-1.064177
C	-4.303903	-0.410494	0.665236
C	-4.006870	-1.425137	-0.223922
H	-2.696299	-2.141904	-1.776924
H	-5.160343	-0.463397	1.322635
F	-4.825224	-2.518693	-0.281425
F	5.820361	-1.396235	0.089939
F	-1.095766	-0.156546	-1.885794
F	-3.748826	1.660755	1.589308
F	1.242076	-1.987940	1.016744
F	2.837324	2.191373	-0.569403



ZZ-F3-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	0.000000	0.000000	2.968624
N	-0.339470	-1.364583	2.143311
N	0.339470	1.364583	2.143311
C	0.000000	1.608347	0.849133
C	0.858451	2.384971	0.035617
C	-1.177213	1.207907	0.173744
C	0.636381	2.672863	-1.296920
C	-1.443535	1.455902	-1.160811
C	-0.518413	2.184064	-1.881079
H	1.358529	3.245185	-1.862279
H	-2.356848	1.093085	-1.610958
C	0.000000	-1.608347	0.849133
C	1.177213	-1.207907	0.173744
C	-0.858451	-2.384971	0.035617
C	1.443535	-1.455902	-1.160811
C	-0.636381	-2.672863	-1.296920
C	0.518413	-2.184064	-1.881079
H	2.356848	-1.093085	-1.610958
H	-1.358529	-3.245185	-1.862279
F	0.754213	-2.443183	-3.201971
F	-0.754213	2.443183	-3.201971
F	-1.999105	-2.856579	0.589192
F	2.130213	-0.559410	0.879776
F	-2.130213	0.559410	0.879776
F	1.999105	2.856579	0.589192



9 - bis(2,4,6-tribromophenyl)sulfur diimide

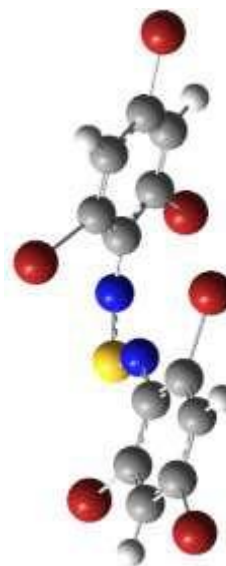
EECONF1-BR3-PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
S	-0.000008	0.665419	0.000000
N	-1.233647	-0.393945	0.000000
N	1.233642	-0.393932	0.000000
C	2.540422	-0.127614	0.000000
C	3.422822	-1.268097	-0.000001
C	3.262622	1.111407	0.000000
C	4.796468	-1.198817	-0.000001
C	4.645300	1.203632	0.000000
C	5.407863	0.050363	-0.000001
H	5.384193	-2.104515	-0.000001
H	5.116602	2.175255	0.000000
C	-2.540425	-0.127625	0.000000
C	-3.422836	-1.268101	0.000000
C	-3.262612	1.111402	0.000000
C	-4.796481	-1.198806	0.000001
C	-4.645289	1.203642	0.000000
C	-5.407863	0.050379	0.000001
H	-5.384216	-2.104498	0.000001
H	-5.116581	2.175269	0.000000
Br	-7.327936	0.172888	0.000001
Br	7.327937	0.172851	-0.000001
Br	2.631572	-3.013386	-0.000001
Br	2.340474	2.804480	0.000001
Br	-2.340437	2.804460	-0.000001
Br	-2.631604	-3.013398	0.000000



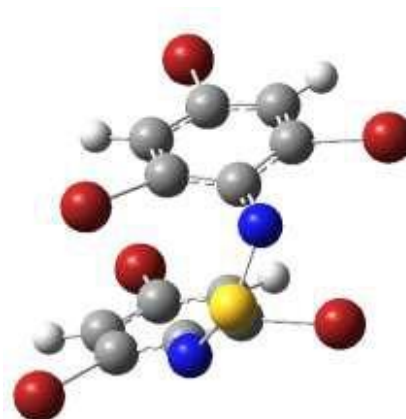
EZ-BR3PHNSN-B3LYPD3BJ-6311++2DP-ANION_OF

Atom Type	X	Y	Z
S	-0.106930	2.216134	0.163346
N	-0.739547	0.781950	-0.058278
C	3.492101	1.076940	-0.530394
C	-3.207182	1.044582	0.075890
N	1.459545	2.067240	0.146336
C	-1.988632	0.331338	-0.177195
C	2.271664	1.004904	0.227679
C	2.089056	-0.161289	1.044326
C	-3.360729	-1.646284	-0.692829
H	-3.440291	-2.680473	-0.993124
C	-2.130493	-1.046913	-0.572424
C	2.988707	-1.198906	1.008233
H	2.852864	-2.058261	1.648092
C	4.372942	0.022162	-0.585091
H	5.255394	0.077985	-1.205039
C	-4.436840	0.442918	-0.035533
H	-5.339838	0.998969	0.169083
C	-4.509156	-0.899713	-0.420860
C	4.106491	-1.119795	0.169509
Br	-6.195820	-1.714848	-0.578034
Br	5.299737	-2.572204	0.099852
Br	-0.587637	-2.069458	-0.950658
Br	3.845605	2.613025	-1.565352
Br	-3.148651	2.862177	0.595492
Br	0.764342	-0.228416	2.401078



ZZCONF1-BISBR3PHNSN-B3LYPD3BJ-6311++G2DP_ANION_OF

Atom Type	X	Y	Z
Br	-1.697576	3.554970	-1.344548
Br	1.693626	3.556329	1.344939
Br	0.920715	-1.303667	-2.602922
Br	-0.919295	-1.305297	2.602768
Br	-4.014791	-1.355955	0.330861
Br	4.016364	-1.351888	-0.330698
S	0.001920	-3.291482	-0.000826
N	-1.305934	-2.476356	-0.513357
C	0.450351	-0.408890	1.605510
C	-2.539851	-0.423666	-0.469709
N	1.308600	-2.475370	0.513276
C	-1.387905	-1.170312	-0.848875
C	1.389127	-1.169165	0.848666
C	2.540280	-0.421269	0.469666
C	-0.522692	0.965896	-1.749737
H	0.248760	1.495456	-2.288484
C	-0.449999	-0.408887	-1.605624
C	2.648006	0.947207	0.612874
H	3.521753	1.464835	0.246682
C	0.521540	0.965957	1.749775
H	-0.250476	1.494625	2.288586
C	-2.649082	0.944697	-0.612763
H	-3.523376	1.461321	-0.246457
C	-1.608035	1.638767	-1.214937
C	1.606165	1.640054	1.215063



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Appendix C. Supporting Information for Chapter 5

Reproduced from the Supporting Information document accompanying “Hill, N.D.D.; Boéré, R.T., ‘*N,N*’-Diaryl-Sulfurdiimide and *N,N*’-Tert-butyl-Sulfurdiimide Complexes of Tin(IV) Chloride’, *Chem. Eur. J.*, 2025, e02342.”

C.1. Full Crystallographic Details for 1 – 4 and 10

Crystals were selected under a polarizing microscope, checked for optical extinction, mounted in Paratone™ oil on 100 μm MiTeGen loops, and cooled to 100 K using the diffractometer Oxford 800 cooling wand. Diffraction image data were measured with a Rigaku-Oxford Diffraction SuperNova diffractometer equipped with a Pilatus P200 HPC detector, using $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$, **1, 3, 4, 10**) or $\text{CuK}\alpha$ ($\lambda = 1.54184 \text{ \AA}$, **2**) radiation. Data collection and reduction was controlled with CrysAlisPro 1.171.38.43. The data were processed and corrected for Lorentz and polarization effects by standard methods and corrected for absorption by semi-empirical methods from equivalents. Structures were solved with ShelXT^[1] and refined with olex2.refine within the Olex2 suite of programs.^[2] The final rounds of refinements employed NoSpherA2 (Non-Spherical Atom form factors in Olex2),^[3] also available within Olex2, which uses DFT calculations (by ORCA v5.0^[4-5] at the PBE/def2-TZVP level of theory, in this work) during refinement to assign tailor-made aspherical atomic form factors to greatly improve hydrogen atom placements to nearly neutron diffraction accuracy, detailed in several of our previous works.^[6-10] Crystal data and structure refinement parameters are summarized in Table C.1, and full archival data is available in CIF format.

Table C.1. Crystal, Data Collection, and Refinement Parameters for Crystallography of **1–4** and **10**.

Parameter	1	2	3	4	10
Chemical Formula	C ₁₄ H ₁₄ Cl ₄ N ₂ O ₂ SSn	C ₁₄ H ₁₄ Cl ₄ N ₂ SSn	C ₁₂ H ₈ Cl ₄ F ₂ N ₂ SSn	C ₁₂ H ₈ Cl ₆ N ₂ SSn	C ₁₂ H ₁₀ Cl ₄ N ₂ O ₂ S ₂ Sn
Formula Weight (g/mol)	534.866	502.867	510.794	543.65	538.878
Temperature (K)	100.01(10)	100.15	100.00(10)	99.9(3)	99.99(10)
Radiation	Mo K α	Cu K α	Mo K α	Mo K α	Mo K α
Crystal System	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic
Space Group	<i>Pbcn</i>	<i>Pbcn</i>	<i>P2₁/c</i>	<i>Pbcn</i>	<i>P</i> $\bar{1}$
a (Å)	9.6674(4)	10.7039(1)	8.0272(5)	10.7493(12)	7.2598(2)
b (Å)	8.5852(4)	7.9361(1)	12.4599(8)	7.8567(8)	10.0511(3)
c (Å)	22.8975(14)	20.9108(2)	17.4259(11)	20.7528(18)	13.7203(4)
α (°)	90	90	90	90	103.524(2)
β (°)	90	90	99.199(6)	90	104.014(2)
γ (°)	90	90	90	90	94.250(2)
Volume (Å³)	1900.41(17)	1776.31(3)	1720.49(19)	1752.6(3)	935.31(5)
Z	4	4	4	4	2
R₁^a [<i>I</i> $\geq$ 2σ(<i>I</i>)]	0.0266	0.0234	0.0359	0.1501	0.0212
wR₂ [all data]	0.0439	0.0611	0.0759	0.3703	0.0397
G.O.F.	1.001	1.051	1.004	1.137	1.030
CCDC Code	2417095	2417096	2417097	2417098	2417099

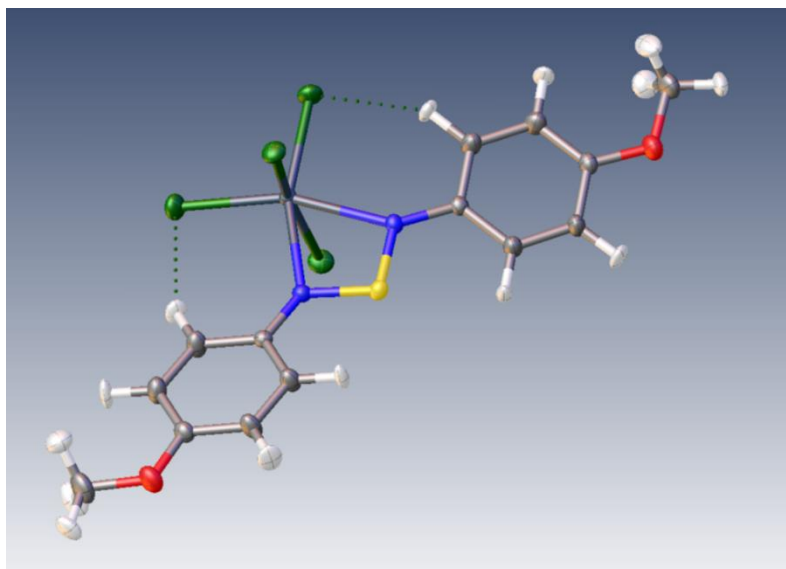


Figure C.1. Full view of a displacement ellipsoids plot of **1**

Table C.2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1**. U_{eq} is defined as $1/3$ of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
Sn1	5000	5947.5(2)	7500	14.79(6)
Cl1	2764.5(5)	5582.1(6)	7075.3(2)	24.66(12)
Cl2	4199.6(6)	7700.6(6)	8210.7(3)	28.03(13)
S1	5000	2436.0(7)	7500	17.35(14)
O1	6521.2(16)	1551.8(18)	4758.6(7)	29.7(4)
N1	5420.2(16)	3626.0(18)	7004.3(7)	16.6(3)
C1	5654.5(19)	3111(2)	6432.1(9)	16.6(4)
C2	6146(2)	4170(2)	6020.8(10)	27.6(5)
H2	6350(30)	5410(30)	6166(12)	55(9)
C3	6429(2)	3694(3)	5450.4(10)	27.4(5)
H3	6800(30)	4520(30)	5142(12)	65(9)
C4	6244(2)	2146(2)	5293.6(9)	20.8(4)
C5	5744(2)	1083(3)	5705.1(10)	27.3(5)
H5	5560(30)	-100(30)	5557(13)	64(9)
C6	5439(2)	1557(2)	6266.6(10)	25.5(5)
H6	5070(30)	730(30)	6583(12)	52(8)
C7	7029(3)	2569(3)	4317.5(11)	36.2(6)
H7a	7200(30)	1840(30)	3954(12)	62(9)
H7b	6260(30)	3460(40)	4259(14)	75(10)
H7c	7980(30)	3110(40)	4449(14)	83(11)

Table C.3. Bond Lengths [Å], Angles [°], and Torsions [°] for **1**

Lengths	Atoms	Length/Å	Atoms	Length/Å
	Sn1 Cl1 ¹	2.3905(5)	C1 C6	1.403(3)
	Sn1 Cl1	2.3905(5)	C2 H2	1.13(2)
	Sn1 Cl2 ¹	2.3478(5)	C2 C3	1.396(3)
	Sn1 Cl2	2.3478(5)	C3 H3	1.06(2)
	Sn1 N1 ¹	2.3293(16)	C3 C4	1.388(3)
	Sn1 N1	2.3293(16)	C4 C5	1.398(3)
	S1 N1 ¹	1.5803(17)	C5 H5	1.08(2)
	S1 N1	1.5803(17)	C5 C6	1.380(3)
	O1 C4	1.354(3)	C6 H6	1.07(2)
	O1 C7	1.423(3)	C7 H7a	1.06(3)
	N1 C1	1.401(3)	C7 H7b	1.07(3)
	C1 C2	1.393(3)	C7 H7c	1.07(3)
Angles	Atoms	Angle/°	Atoms	Angle/°
	Cl1 Sn1 Cl1 ¹	164.92(3)	N1 ¹ S1 N1	99.44(12)
	Cl2 Sn1 Cl1 ¹	95.75(2)	C7 O1 C4	118.66(18)
	Cl2 ¹ Sn1 Cl1 ¹	93.906(19)	S1 N1 Sn1	99.11(8)
	Cl2 ¹ Sn1 Cl1	95.75(2)	C1 N1 Sn1	138.92(13)
	Cl2 Sn1 Cl1	93.906(19)	C1 N1 S1	120.61(13)
	Cl2 Sn1 Cl2 ¹	100.26(3)	C2 C1 N1	118.79(17)
	N1 Sn1 Cl1	81.21(4)	C6 C1 N1	121.92(19)
	N1 ¹ Sn1 Cl1	85.89(4)	C6 C1 C2	119.3(2)
	N1 Sn1 Cl1 ¹	85.89(4)	C3 C2 C1	120.6(2)
	N1 ¹ Sn1 Cl1 ¹	81.21(4)	C4 C3 C2	119.8(2)
	N1 Sn1 Cl2	160.69(4)	C3 C4 O1	124.7(2)
	N1 ¹ Sn1 Cl2	98.82(4)	C5 C4 O1	115.65(19)
	N1 ¹ Sn1 Cl2 ¹	160.69(4)	C5 C4 C3	119.7(2)
	N1 Sn1 Cl2 ¹	98.82(4)	C6 C5 C4	120.6(2)
	N1 ¹ Sn1 N1	62.34(8)	C5 C6 C1	120.0(2)
Torsions	Atoms	Angle/°	Atoms	Angle/°
	Sn1 N1 S1 N1 ¹	-0.00(11)	S1 N1 C1 C6	4.36(18)
	Sn1 N1 ¹ S1 ¹ N1	0.00(11)	O1 C4 C3 C2	-178.1(2)
	Sn1 N1 C1 C2	22.4(2)	O1 C4 C5 C6	179.36(19)
	Sn1 ¹ N1 C1 C2	22.4(2)	N1 C1 C2 C3	178.3(2)
	Sn1 N1 C1 C6	-159.1(2)	N1 C1 C6 C5	-177.0(2)
	Sn1 ¹ N1 C1 C6	-159.1(2)	S1 ¹ N1 C1 C2	-174.12(16)
	S1 N1 C1 C2	-174.12(16)	S1 ¹ N1 C1 C6	4.36(18)

¹1-X,+Y,3/2-Z

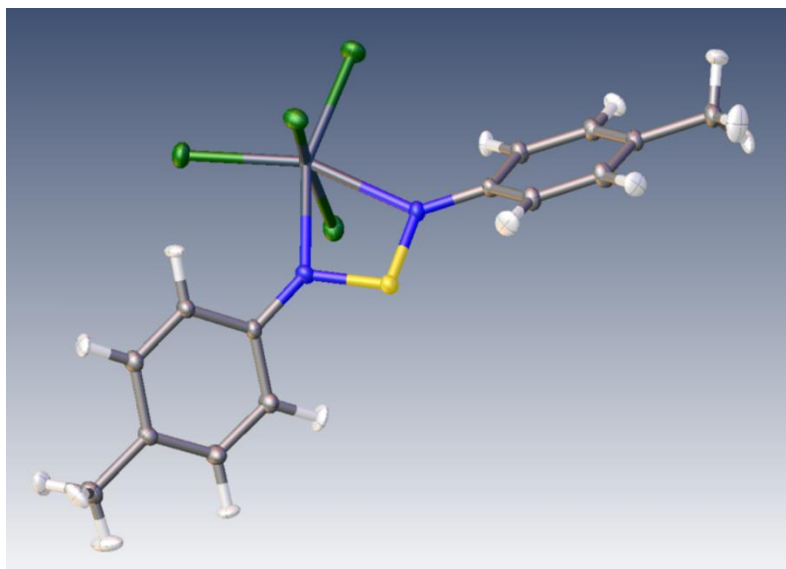


Figure C.2. Full view of a displacement ellipsoids plot of **2**

Table C.4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Sn1	5000	5224.1(2)	7500	11.61(9)
Cl1	2854.0(4)	4850.5(6)	7202.9(2)	19.08(12)
Cl2	4549.7(5)	7025.5(6)	8354.65(19)	21.28(12)
S1	5000	1420.6(10)	7500	13.86(17)
N1	5219.5(15)	2713(2)	6940.8(7)	14.2(3)
C1	5616.2(16)	2223(2)	6325.8(8)	13.6(3)
C2	5111.8(16)	3095(3)	5801.6(10)	15.2(4)
H2	4460(20)	4120(30)	5884(11)	31(6)
C3	5454.1(19)	2627(2)	5184.5(8)	16.0(4)
H3	5050(20)	3260(40)	4791(16)	38(10)
C4	6315.6(17)	1315(2)	5081.2(8)	14.7(3)
C5	6808(2)	479(3)	5612.6(9)	18.0(4)
H5	7470(30)	-540(40)	5547(15)	40(8)
C6	6472.4(17)	917(2)	6231.5(8)	16.4(4)
H6	6890(30)	300(30)	6636(13)	46(8)
C7	6693(2)	821(3)	4414.9(8)	18.8(4)
H7a	5930(30)	360(30)	4127(11)	40(7)
H7b	7110(30)	1860(30)	4161(13)	50(8)
H7c	7350(40)	-90(40)	4403(18)	65(12)

Table C.5. Bond Lengths [Å], Angles [°], and Torsions [°] for 2.

Lengths	Atoms	Length/Å	Atoms	Length/Å
	Sn1 Cl1	2.3980(5)	C2 C3	1.392(3)
	Sn1 Cl1 ¹	2.3980(5)	C3 H3	1.06(3)
	Sn1 Cl2	2.3388(4)	C3 C4	1.407(3)
	Sn1 Cl2 ¹	2.3388(4)	C4 C5	1.398(3)
	Sn1 N1 ¹	2.3222(17)	C4 C7	1.503(2)
	Sn1 N1	2.3222(17)	C5 H5	1.08(3)
	S1 N1 ¹	1.5732(17)	C5 C6	1.387(2)
	S1 N1	1.5732(17)	C6 H6	1.07(2)
	N1 C1	1.409(2)	C7 H7a	1.08(3)
	C1 C2	1.404(3)	C7 H7b	1.08(3)
	C1 C6	1.397(3)	C7 H7c	1.01(3)
	C2 H2	1.09(2)		
Angles	Atoms	Angle/°	Atoms	Angle/°
	Cl1 ¹ Sn1 Cl1	165.80(2)	N1 ¹ S1 N1	98.60(13)
	Cl2 Sn1 Cl1	94.367(16)	S1 N1 Sn1	99.80(8)
	Cl2 ¹ Sn1 Cl1	94.302(17)	C1 N1 Sn1	136.63(13)
	Cl2 ¹ Sn1 Cl1 ¹	94.367(16)	C1 N1 S1	122.91(14)
	Cl2 Sn1 Cl1 ¹	94.302(17)	C2 C1 N1	117.42(17)
	Cl2 Sn1 Cl2 ¹	104.64(2)	C6 C1 N1	122.08(15)
	N1 Sn1 Cl1	81.97(4)	C6 C1 C2	120.50(16)
	N1 ¹ Sn1 Cl1	85.84(4)	C3 C2 C1	119.40(19)
	N1 ¹ Sn1 Cl1 ¹	81.97(4)	C4 C3 C2	120.81(17)
	N1 Sn1 Cl1 ¹	85.84(4)	C5 C4 C3	118.45(16)
	N1 Sn1 Cl2	158.45(4)	C7 C4 C3	120.75(16)
	N1 ¹ Sn1 Cl2	96.83(4)	C7 C4 C5	120.80(17)
	N1 ¹ Sn1 Cl2 ¹	158.45(4)	C6 C5 C4	121.66(18)
	N1 Sn1 Cl2 ¹	96.83(4)	C5 C6 C1	119.17(16)
	N1 ¹ Sn1 N1	61.80(8)		
Torsions	Atoms	Angle/°	Atoms	Angle/°
	Sn1 N1 S1 N1 ¹	0.00(12)	S1 ¹ N1 C1 C6	-36.83(17)
	Sn1 N1 ¹ S1 ¹ N1	0.00(12)	N1 C1 C2 C3	-178.48(17)
	Sn1 ¹ N1 C1 C2	-48.56(18)	N1 C1 C6 C5	178.92(18)
	Sn1 N1 C1 C2	-48.56(18)	C1 C2 C3 C4	-1.2(2)
	Sn1 ¹ N1 C1 C6	131.77(17)	C1 C6 C5 C4	0.3(2)
	Sn1 N1 C1 C6	131.77(17)	C2 C3 C4 C5	0.8(2)
	S1 N1 C1 C2	142.84(15)	C2 C3 C4 C7	-179.48(18)
	S1 ¹ N1 C1 C2	142.84(15)	C3 C4 C5 C6	-0.4(2)
	S1 N1 C1 C6	-36.83(17)		

¹1-X,+Y,3/2-Z

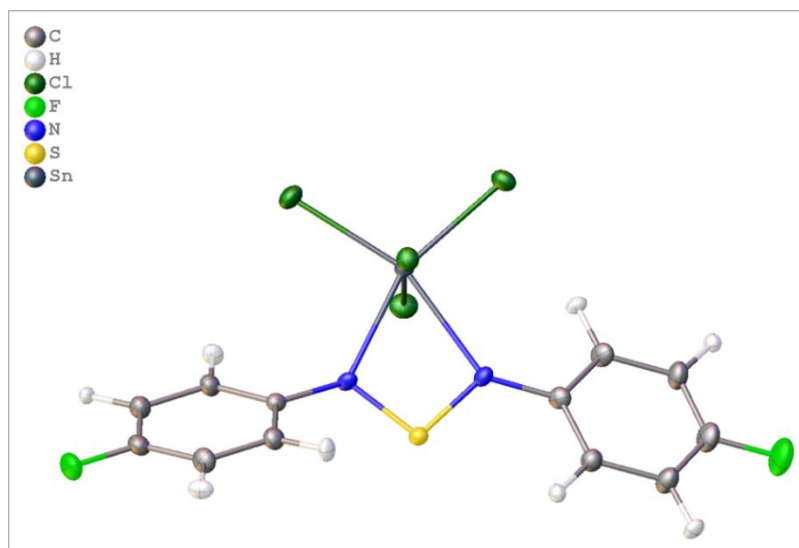


Figure C.3. Full view of a displacement ellipsoids plot of **3**

Table C.6. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
Sn1	3047.3(4)	4204.6(2)	6553.49(17)	11.49(7)
Cl1	3272.8(15)	3735.3(9)	5251.0(6)	20.3(2)
Cl2	3005.1(15)	2398.7(8)	6954.5(7)	19.7(2)
Cl3	3335.3(14)	4912.8(8)	7841.8(6)	15.6(2)
Cl4	208.7(13)	4713.1(9)	6240.6(7)	17.8(2)
S1	6115.6(13)	5592.6(8)	6504.6(6)	12.9(2)
F1	11128(3)	2402(2)	8669.9(16)	25.2(6)
F2	2028(4)	9505(2)	4597.1(18)	37.4(8)
N1	5905(4)	4399(3)	6782(2)	13.9(8)
N2	4193(4)	5874(3)	6239.8(19)	13.6(7)
C1	7238(5)	3888(3)	7288(2)	11.7(9)
C2	7544(5)	2811(3)	7162(3)	16.7(9)
H2	6740(5)	2364(3)	6696(3)	32(12)
C3	8872(5)	2303(4)	7629(3)	18.1(10)
H3	9158(5)	1451(4)	7537(3)	25(11)
C4	9839(5)	2896(4)	8219(3)	18.2(10)
C5	9517(5)	3959(3)	8365(3)	18.3(10)
H5	10293(5)	4395(3)	8845(3)	33(12)
C6	8191(5)	4464(3)	7892(3)	16.3(9)
H6	7893(5)	5312(3)	7993(3)	33(12)
C7	3662(5)	6820(3)	5835(2)	15.4(9)
C8	2181(5)	6767(4)	5293(3)	17.7(10)
H8	1458(5)	6012(4)	5204(3)	28(12)
C9	1627(6)	7683(3)	4864(3)	21.5(10)
H9	471(6)	7663(3)	4426(3)	26(6)
C10	2560(7)	8615(4)	5000(3)	23.5(10)
C11	4022(6)	8694(4)	5544(3)	20.9(10)
H11	4720(6)	9457(4)	5640(3)	33(12)
C12	4579(6)	7776(3)	5966(2)	16.5(9)
H12	5738(6)	7802(3)	6401(2)	26(6)

Table C.7. Bond Lengths [Å], Angles [°], and Torsions [°] for **3**.

Lengths	Atoms	Length/Å	Atoms	Length/Å
	Sn1 Cl1	2.3786(11)	C3 H3	1.103
	Sn1 Cl2	2.3581(10)	C3 C4	1.396(6)
	Sn1 Cl3	2.3888(10)	C4 C5	1.381(6)
	Sn1 Cl4	2.3438(11)	C5 H5	1.103
	Sn1 N1	2.277(3)	C5 C6	1.388(6)
	Sn1 N2	2.373(3)	C6 H6	1.103
	S1 N1	1.582(3)	C7 C8	1.397(6)
	S1 N2	1.578(3)	C7 C12	1.399(6)
	F1 C4	1.345(5)	C8 H8	1.103
	F2 C10	1.345(5)	C8 C9	1.397(6)
	N1 C1	1.422(5)	C9 H9	1.103
	N2 C7	1.405(5)	C9 C10	1.382(6)
	C1 C2	1.389(6)	C10 C11	1.389(6)
	C1 C6	1.397(6)	C11 H11	1.103
	C2 H2	1.103	C11 C12	1.394(6)
	C2 C3	1.386(6)	C12 H12	1.103
Angles	Atoms	Angle/°	Atoms	Angle/°
	Cl2 Sn1 Cl1	93.16(4)	C7 N2 S1	122.5(3)
	Cl3 Sn1 Cl1	167.67(4)	C2 C1 N1	118.0(4)
	Cl3 Sn1 Cl2	94.46(4)	C6 C1 N1	120.3(3)
	Cl4 Sn1 Cl1	93.67(4)	C6 C1 C2	121.7(4)
	Cl4 Sn1 Cl2	105.51(4)	C3 C2 C1	119.2(4)
	Cl4 Sn1 Cl3	93.62(4)	C4 C3 C2	118.4(4)
	N1 Sn1 Cl1	87.99(10)	C3 C4 F1	118.2(4)
	N1 Sn1 Cl2	96.38(9)	C5 C4 F1	118.7(4)
	N1 Sn1 Cl3	81.54(9)	C5 C4 C3	123.0(4)
	N1 Sn1 Cl4	157.90(9)	C6 C5 C4	118.3(4)
	N2 Sn1 Cl1	84.50(9)	C5 C6 C1	119.3(4)
	N2 Sn1 Cl2	158.29(8)	C8 C7 N2	117.2(4)
	N2 Sn1 Cl3	84.83(8)	C12 C7 N2	121.5(4)
	N2 Sn1 Cl4	96.19(8)	C12 C7 C8	121.3(4)
	N2 Sn1 N1	62.01(11)	C9 C8 C7	119.1(4)
	N2 S1 N1	98.68(18)	C10 C9 C8	118.5(4)
	S1 N1 Sn1	101.55(16)	C9 C10 F2	119.0(4)
	C1 N1 Sn1	134.2(3)	C11 C10 F2	117.5(4)
	C1 N1 S1	120.2(3)	C11 C10 C9	123.5(4)
	S1 N2 Sn1	97.76(16)	C12 C11 C10	117.8(4)
	C7 N2 Sn1	138.9(3)	C11 C12 C7	119.8(4)
Torsions	Atoms	Angle/°	Atoms	Angle/°
	Sn1 N1 S1 N2	-0.48(19)	N1 C1 C6 C5	-178.2(4)
	Sn1 N1 C1 C2	65.9(4)	N2 S1 N1 C1	-161.1(3)
	Sn1 N1 C1 C6	-113.8(4)	N2 C7 C8 C9	-178.5(4)
	Sn1 N2 S1 N1	0.46(18)	N2 C7 C12 C11	179.1(4)
	Sn1 N2 C7 C8	-20.0(4)	C1 C2 C3 C4	1.0(5)
	Sn1 N2 C7 C12	160.3(4)	C1 C6 C5 C4	-0.2(5)
	S1 N1 C1 C2	-141.2(3)	C2 C1 C6 C5	2.2(5)
	S1 N1 C1 C6	39.1(4)	C2 C3 C4 C5	1.0(5)
	S1 N2 C7 C8	146.9(4)	C3 C2 C1 C6	-2.6(5)
	S1 N2 C7 C12	-32.8(4)	C3 C4 C5 C6	-1.4(5)
	F1 C4 C3 C2	-179.9(4)	C7 C8 C9 C10	-0.8(5)
	F1 C4 C5 C6	179.6(4)	C7 C12 C11 C10	-0.3(5)

Table C.7. Cont'd				
Torsions	Atoms	Angle/°	Atoms	Angle/°
	F2 C10 C9 C8	-179.3(4)	C8 C7 C12 C11	-0.6(5)
	F2 C10 C11 C12	179.9(4)	C8 C9 C10 C11	-0.2(6)
	N1 S1 N2 C7	-170.9(3)	C9 C8 C7 C12	1.2(5)
	N1 C1 C2 C3	177.8(4)	C9 C10 C11 C12	0.8(6)

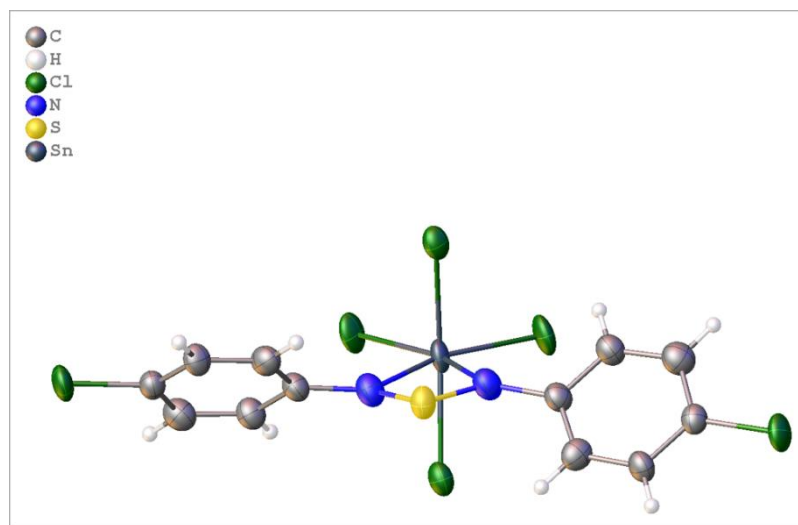


Figure C.4. Full view of a displacement ellipsoids plot of **4**

Table C.8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
Sn1	5000	4964(3)	2500	31.0(8)
Cl1	7146(6)	5363(7)	2762(3)	35.5(14)
Cl2	5393(7)	3141(8)	1630(3)	45.0(16)
Cl3	3156(6)	9266(8)	5696(3)	42.4(15)
S1	5000	8817(10)	2500	34.6(18)
N1	4825(19)	7540(30)	3039(10)	39(5)
C1	4400(20)	7960(30)	3681(11)	33(5)
C2	4870(20)	7100(30)	4210(11)	37(5)
C3	4530(20)	7490(30)	4833(13)	44(6)
C4	3640(20)	8780(30)	4920(11)	32(5)
C5	3170(20)	9700(30)	4389(11)	34(5)
C6	3550(20)	9240(30)	3798(12)	37(5)
H2	5458.06	6205.78	4139.69	44
H3	4887.59	6906.66	5190.91	52
H5	2599.76	10612.82	4448.5	41
H6	3214.23	9840.3	3438.87	45

Table C.9. Bond Lengths [Å], Angles [°], and Torsions [°] for **4**.

Lengths	Atoms	Length/Å	Atom	Length/Å
	Sn1 Cl1	2.391(6)	C1 C2	1.39(3)
	Sn1 Cl1 ¹	2.391(6)	C1 C6	1.38(3)
	Sn1 Cl2 ¹	2.342(6)	C2 H2	0.95
	Sn1 Cl2	2.342(6)	C2 C3	1.38(3)
	Sn1 N1	2.32(2)	C3 H3	0.95
	Sn1 N1 ¹	2.32(2)	C3 C4	1.41(4)
	Cl3 C4	1.73(2)	C4 C5	1.41(3)
	S1 N1	1.51(2)	C5 H5	0.95
	S1 N1 ¹	1.51(2)	C5 C6	1.34(3)
	N1 C1	1.45(3)	C6 H6	0.95
Angles	Atoms	Angle/°	Atoms	Angle/°
	Cl1 ¹ Sn1 Cl1	164.9(3)	N1 ¹ S1 N1	97.1(16)
	Cl2 Sn1 Cl1	94.7(2)	S1 N1 Sn1	102.2(10)
	Cl2 ¹ Sn1 Cl1 ¹	94.7(2)	C1 N1 Sn1	131.8(16)
	Cl2 ¹ Sn1 Cl1	94.5(2)	C1 N1 S1	124.8(17)
	Cl2 Sn1 Cl1 ¹	94.5(2)	C2 C1 N1	120(2)
	Cl2 ¹ Sn1 Cl2	104.6(3)	C6 C1 N1	122(2)
	N1 Sn1 Cl1	85.2(5)	C6 C1 C2	117(2)
	N1 ¹ Sn1 Cl1 ¹	85.2(5)	C3 C2 C1	122(2)
	N1 ¹ Sn1 Cl1	81.6(5)	C2 C3 C4	117(2)
	N1 Sn1 Cl1 ¹	81.6(5)	C3 C4 Cl3	118.6(18)
	N1 Sn1 Cl2	156.8(5)	C5 C4 Cl3	120.5(18)
	N1 Sn1 Cl2 ¹	98.5(5)	C5 C4 C3	121(2)
	N1 ¹ Sn1 Cl2	98.5(5)	C4 C5 C6	118(2)
	N1 ¹ Sn1 Cl2 ¹	156.8(5)	C1 C6 C5	124(2)
	N1 ¹ Sn1 N1	58.5(10)		
Torsions	Atoms	Angle/°	Atoms	Angle/°
	Sn1 N1 C1 C2	51(3)	N1 C1 C6 C5	-177(2)
	Sn1 N1 C1 C6	-132(2)	C1 C2 C3 C4	2(4)
	Cl3 C4 C5 C6	-178.4(19)	C2 C1 C6 C5	0(4)
	S1 N1 C1 C2	-144(2)	C2 C3 C4 Cl3	178.3(19)
	S1 N1 C1 C6	33(3)	C2 C3 C4 C5	-4(4)
	N1 ¹ S1 N1 Sn1	0.000(3)	C3 C4 C5 C6	4(4)
	N1 ¹ S1 N1 C1	-169(2)	C4 C5 C6 C1	-2(4)
	N1 C1 C2 C3	177(2)	C6 C1 C2 C3	0(4)

¹1-X,+Y,1/2-Z

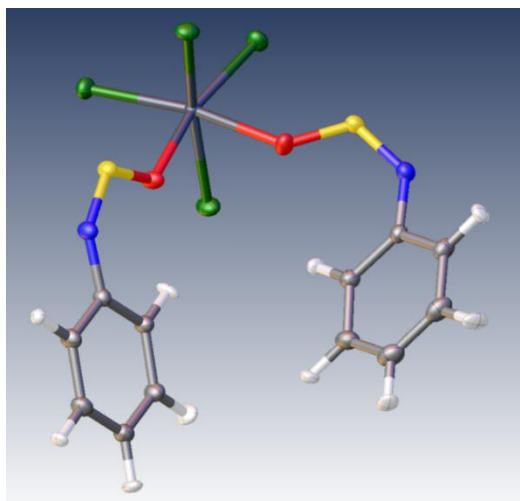


Figure C.5. Full view of a displacement ellipsoids plot of **10**

Table C.10. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **10**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
Sn1	9034.89(15)	10002.06(10)	7562.55(8)	11.57(3)
Cl1	11212.1(6)	8666.3(4)	8320.7(3)	22.45(8)
Cl2	6263.3(6)	10765.5(4)	6679.2(3)	20.23(8)
Cl3	9632.2(6)	11851.8(4)	9081.1(3)	20.48(8)
Cl4	11083.8(6)	10829.7(4)	6673.3(3)	19.74(8)
S1	6395.6(6)	9271.7(4)	9140.6(3)	16.24(8)
S2	7018.7(6)	7817.6(4)	5192.6(3)	16.95(8)
O1	7037.7(18)	8850.7(11)	8172.6(9)	21.2(2)
O2	8103.2(17)	8067.7(11)	6315.5(8)	18.4(2)
N1	5545(2)	8108.2(14)	9483.6(11)	18.5(3)
N2	6727(2)	6347.2(14)	4550.0(10)	18.1(3)
C1	5291(2)	6671.0(16)	9059.3(12)	15.7(3)
C2	3627(2)	5923.6(18)	9106.5(14)	20.8(3)
H2	2670(30)	6480(20)	9453(18)	41(6)
C3	3281(3)	4497.1(19)	8685.2(14)	26.5(4)
H3	1970(30)	3920(20)	8730(20)	54(7)
C4	4643(3)	3822.6(18)	8268.9(14)	27.3(4)
H4	4380(40)	2700(20)	7951(18)	49(7)
C5	6326(3)	4572.1(17)	8254.7(14)	23.8(4)
H5	7430(30)	4040(20)	7940(18)	38(6)
C6	6652(2)	6002.3(17)	8631.7(13)	19.1(3)
H6	7940(30)	6600(20)	8619(17)	35(5)
C7	7221(2)	5105.3(15)	4745.9(12)	14.9(3)
C8	6662(2)	3948.3(17)	3882.7(13)	18.9(3)
H8	5870(30)	4082(19)	3119(15)	26(4)
C9	7093(2)	2660.5(17)	3995.6(13)	20.2(3)
H9	6670(30)	1755(19)	3352(15)	28(5)
C10	8082(2)	2524.0(17)	4968.0(13)	19.8(3)
H10	8360(40)	1490(20)	5026(17)	42(6)
C11	8652(2)	3677.4(17)	5825.6(13)	19.8(3)
H11	9460(40)	3550(20)	6589(17)	45(7)
C12	8230(2)	4973.7(16)	5727.5(12)	16.7(3)
H12	8660(30)	5900(20)	6391(16)	36(6)

Table C.11. Bond Lengths [Å], Angles [°], and Torsions [°] for **10**.

Lengths	Atoms	Length/Å	Atoms	Length/Å
	Sn1 Cl1	2.3568(4)	C3 C4	1.398(3)
	Sn1 Cl2	2.3641(4)	C4 H4	1.09(2)
	Sn1 Cl3	2.3700(4)	C4 C5	1.394(3)
	Sn1 Cl4	2.3586(4)	C5 H5	1.11(2)
	Sn1 O1	2.2213(11)	C5 C6	1.390(2)
	Sn1 O2	2.2031(11)	C6 H6	1.08(2)
	S1 O1	1.4922(12)	C7 C8	1.405(2)
	S1 N1	1.5039(14)	C7 C12	1.410(2)
	S2 O2	1.5029(12)	C8 H8	1.109(19)
	S2 N2	1.5034(14)	C8 C9	1.388(2)
	N1 C1	1.405(2)	C9 H9	1.074(18)
	N2 C7	1.391(2)	C9 C10	1.397(2)
	C1 C2	1.398(2)	C10 H10	1.089(19)
	C1 C6	1.402(2)	C10 C11	1.398(2)
	C2 H2	1.06(2)	C11 H11	1.11(2)
	C2 C3	1.393(2)	C11 C12	1.390(2)
	C3 H3	1.11(2)	C12 H12	1.104(19)
Angles	Atoms	Angle/°	Atoms	Angle/°
	Cl2 Sn1 Cl1	164.074(15)	C1 N1 S1	130.79(11)
	Cl3 Sn1 Cl1	95.371(15)	C7 N2 S2	134.94(12)
	Cl3 Sn1 Cl2	94.329(14)	C2 C1 N1	116.69(14)
	Cl4 Sn1 Cl1	94.928(15)	C6 C1 N1	122.22(14)
	Cl4 Sn1 Cl2	95.555(14)	C6 C1 C2	121.07(15)
	Cl4 Sn1 Cl3	101.133(14)	C3 C2 C1	119.40(17)
	O1 Sn1 Cl1	82.17(3)	C4 C3 C2	119.74(17)
	O1 Sn1 Cl2	85.31(3)	C5 C4 C3	120.38(16)
	O1 Sn1 Cl3	89.52(3)	C6 C5 C4	120.47(17)
	O1 Sn1 Cl4	169.20(3)	C5 C6 C1	118.85(16)
	O2 Sn1 Cl1	82.44(3)	C8 C7 N2	115.39(14)
	O2 Sn1 Cl2	85.43(3)	C12 C7 N2	124.04(14)
	O2 Sn1 Cl3	167.88(3)	C12 C7 C8	120.57(14)
	O2 Sn1 Cl4	90.94(3)	C9 C8 C7	119.88(15)
	O2 Sn1 O1	78.38(4)	C10 C9 C8	119.73(15)
	N1 S1 O1	115.48(7)	C11 C10 C9	120.40(15)
	N2 S2 O2	115.57(7)	C12 C11 C10	120.65(16)
	S1 O1 Sn1	130.23(7)	C11 C12 C7	118.76(15)
	S2 O2 Sn1	130.53(6)		
Torsions	Atoms	Angle/°	Atoms	Angle/°
	Sn1 O1 S1 N1	-161.44(9)	N2 C7 C12 C11	-179.60(16)
	Sn1 O2 S2 N2	176.77(9)	C1 C2 C3 C4	3.23(19)
	S1 N1 C1 C2	-143.75(15)	C1 C6 C5 C4	2.23(19)
	S1 N1 C1 C6	37.85(17)	C2 C3 C4 C5	-1.3(2)
	S2 N2 C7 C8	-179.10(17)	C3 C4 C5 C6	-1.5(2)
	S2 N2 C7 C12	0.20(19)	C7 C8 C9 C10	-0.08(19)
	N1 C1 C2 C3	179.07(14)	C7 C12 C11 C10	-0.19(18)
	N1 C1 C6 C5	178.11(15)	C8 C9 C10 C11	-0.43(19)
	N2 C7 C8 C9	179.79(14)	C9 C10 C11 C12	0.57(19)

C.2. On the XRD Identification of NSO Complex 12b

The claim for the existence of “(Ph₃P)₂Pt(OSNH)₂” is made in two different publications from Turner *et al.*^[11-12] Despite good data quality, the supposed H atoms attached to the purported Pt-O=S=N-H ligands were not identified in a final difference Fourier map. The bond lengths from Pt-O and O-S are also unusual and diverse. The 1981 article even proposes that the coordinated entities might actually be ONSH and NSOH. A search for the natural H-bonding geometries expected for the purported complex are quite unconvincing (Figure C.6).

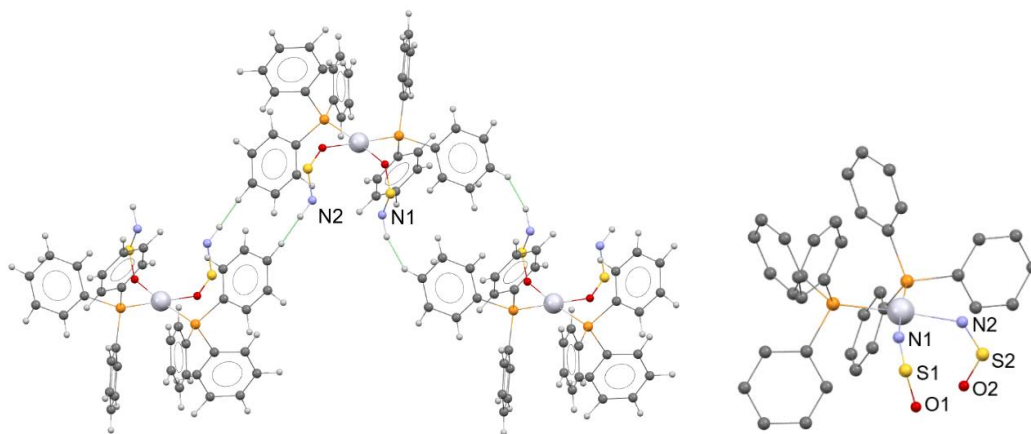


Figure C.6. (left) Plot of the H-bonding environment of the N1 and N2 atoms reported for refcode TIPHPT10. The H-atoms supposedly bonded at N1 and N2 have been added at calculated positions, leading to the unrealistic short H · · · H contacts.

Figure C.7. (right) Corrected atom identification for the structure of **12b**.

In view of the absence of expected H-bonding, the unusually small displacement ellipsoids of the supposed O1 and O2 in Fig. 1 of the Holt paper, and the weird bond distance involving the supposed O1 and O2 atomic sites, we argue that the correct identification of this structure is (Ph₃P)₂Pt(NSO)₂. Metal complexes of the monoanionic [NSO]⁻ ligand are well-known, display similar geometries and are fully consistent with the reported geometry as a Pt(II), rather than Pt(0), complex. This necessary correction to a faulty claim that has persisted in the literature for 45 years is greatly overdue. McGeachie *et al.* provide further commentary on this structure claim.^[13]

C.3. Comparison of SC-XRD Data to DFT Computed Geometries

Table C.12. Comparison of crystal structures of **1** – **4** to DFT-optimized geometries (distances, Å; angles & torsions, °)^{a,b,c}

	1	2	3^d	4	Average^e
Sn-Cl(ax) (Å)	2.3905(5) <i>2.3848</i>	2.3980(5) <i>2.3821</i>	2.3786(11), 2.3888(10) <i>2.3801</i>	2.391(6) <i>2.3781</i>	2.391(6) <i>2.381(2)</i>
Sn-Cl(eq) (Å)	2.3478(5) <i>2.3477</i>	2.3388(4) <i>2.3424</i>	2.3581(10), 2.3438(11) <i>2.3402</i>	2.342(6) <i>2.3395</i>	2.345(6) <i>2.342(3)</i>
Sn-N (Å)	2.3293(16) <i>2.4046</i>	2.3222(17) <i>2.4220</i>	2.277(3), 2.373(3) <i>2.4316</i>	2.32(2) <i>2.4397</i>	2.32(2) <i>2.424(13)</i>
S-N (Å)	1.5803(17) <i>1.571</i>	1.5732(17) <i>1.563</i>	1.582(3), 1.578(3) <i>1.562</i>	1.51(2) <i>1.562</i>	1.56(3) <i>1.565(4)</i>
N-C (Å)	1.401(3) <i>1.3835</i>	1.409(2) <i>1.3882</i>	1.422(5), 1.405(5) <i>1.3882</i>	1.45(3) <i>1.3869</i>	1.418(19) <i>1.387(2)</i>
Cl-Sn-Cl (ax) (°)	164.92(3) <i>160.07</i>	165.80(2) <i>158.91</i>	167.67(4) <i>158.26</i>	164.9(3) <i>157.94</i>	165.8(11) <i>158.8(8)</i>
Cl-Sn-Cl (eq) (°)	100.26(3) <i>106.57</i>	104.64(2) <i>107.89</i>	105.51(4) <i>108.49</i>	104.6(3) <i>108.46</i>	104(2) <i>107.9(8)</i>
N-Sn-N (°)	62.34(8) <i>60.14</i>	61.80(8) <i>59.54</i>	62.01(11) <i>59.26</i>	58.5(10) <i>59.07</i>	61.2(15) <i>59.5(4)</i>
N-S-N (°)	99.44(12) <i>100.17</i>	98.60(13) <i>100.56</i>	98.68(18) <i>100.63</i>	97.1(16) <i>100.67</i>	98.5(8) <i>100.5(2)</i>
S-N-C (°)	120.61(13) <i>122.83</i>	122.91(14) <i>122.87</i>	120.2(3), 122.5(3) <i>123.05</i>	124.8(17) <i>123.05</i>	122.4(17) <i>122.9(1)</i>
S-N-C-C (°)	-174.12(16) <i>155.67</i>	142.84(15) <i>152.21</i>	-141.2(3), 146.9(4) <i>151.98</i>	-144(2) <i>152.56</i>	
S-N-C-C' (°)	4.36(18) <i>-24.86</i>	-36.83(17) <i>-28.56</i>	39.1(4), -32.8(4) <i>-29.15</i>	33(3) <i>-28.45</i>	
Ring-Ring (°)^f	24.48 <i>76.88</i>	81.95 <i>80.94</i>	31.46 <i>81.54</i>	82.96 <i>79.27</i>	

^a Computed geometries were optimized using Gaussian 16w v1.1, computed at B3PW91-D3BJ/def2TZVP, shown as italicized entries below experimental values. ^b Errors given for bond lengths, angles, and torsions are s.u. from crystallographic data. Errors for averages are s.d. for the series. ^c Range of experimental bond lengths (largest – smallest = range; Å): Sn-Cl(ax), 0.019; Sn-Cl(eq), 0.019; Sn-N, 0.096; S-N, 0.072; N-C, 0.049. Range of bond angles (°): Cl-Sn-Cl(ax), 2.8; Cl-Sn-Cl(eq), 5.3; N-Sn-N, 3.8; N-S-N, 2.3; S-N-C, 4.6. ^d **1**, **2**, and **4** are bisected by a C₂ rotation axis, such that symmetry equivalent atoms have identical bond lengths, angles, and torsions. This is not the case for **3**, which reports two entries in these cases. ^e Averages of torsions are not given, due to inconsistency of sign and large variation of magnitude (e.g. averaging torsions of 65.7 and -32.6) ^f Angle between mean planes of the aryl rings.

Table C.13. Differences (Å/° and %) between experimental and DFT bond lengths and angles of **1** – **4**.^a

	1	2	3	4	Average
Sn-Cl(ax) (Å)	0.006 0.2%	0.016 0.7%	0.004 0.2%	0.013 0.5%	0.009 0.4%
Sn-Cl(eq) (Å)	0.000 0.0%	0.004 0.2%	0.011 0.5%	0.003 0.1%	0.004 0.2%
Sn-N (Å)	0.075 3.2%	0.100 4.3%	0.107 4.6%	0.120 5.2%	0.100 4.3%
S-N (Å)	0.010 0.6%	0.010 0.6%	0.018 1.1%	0.052 3.5%	0.022 1.5%
N-C (Å)	0.018 1.2%	0.021 1.5%	0.025 1.8%	0.063 4.4%	0.032 2.2%
Cl-Sn-Cl(ax) (°)	4.85 2.9%	6.89 4.2%	9.41 5.6%	6.96 4.2%	7.03 4.2%
Cl-Sn-Cl(eq) (°)	6.31 6.3%	3.25 3.1%	2.98 2.8%	3.86 3.7%	4.10 4.0%
N-Sn-N (°)	2.20 3.5%	2.26 3.7%	2.75 4.4%	0.57 1.0%	1.95 3.2%
N-S-N (°)	0.73 0.7%	1.96 2.0%	1.95 2.0%	3.57 3.7%	2.05 2.1%
S-N-C (°)	2.22 1.8%	0.04 0.0%	1.70 1.4%	1.75 1.4%	1.43 1.2%

^aDifferences are given for bond lengths and bond angles only. They are calculated based on average of entries, if there are more than one, and %difference is with reference to the experimental (SC-XRD) values.

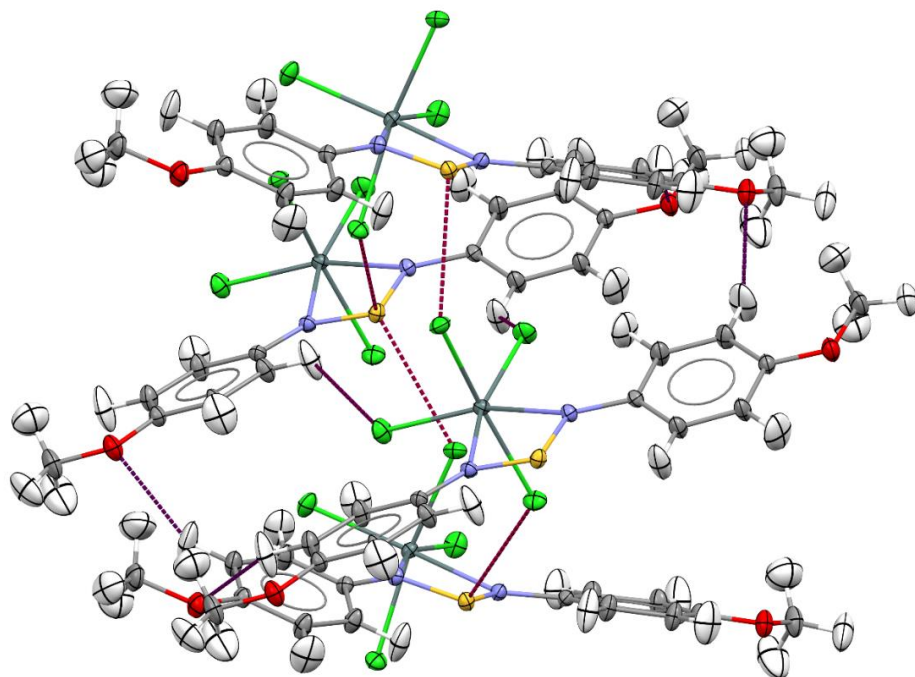
Table C.14. Comparison of crystal structures of **10** to DFT-optimized geometries (distances, Å; angles & torsions, °),^{a,b} and differences (Å/° and %) between experimental and DFT values.^c

	10	Difference
Sn-Cl(ax) (Å)	2.3568(4), 2.3641(4) <i>2.3705, 2.3733</i>	0.011 Å 0.5%
Sn-Cl(eq) (Å)	2.3700(4), 2.3586(4) <i>2.3451, 2.3266</i>	0.028 Å 1.2%
Sn-O (Å)	2.2213(11), 2.2031(11) <i>2.3872, 2.3641</i>	0.163 Å 7.4%
O-S (Å)	1.4922(12), 1.5029(12) <i>1.4884, 1.4889</i>	0.009 Å 0.2%
S-N (Å)	1.5039(14), 1.5034(14) <i>1.5092, 1.5070</i>	0.004 Å 0.3%
N-C (Å)	1.405(2), 1.391(2) <i>1.383, 1.381</i>	0.016 Å 1.1%
Cl-Sn-Cl(ax)	164.074(15) <i>154.570</i>	9.50° 5.8%
Cl-Sn-Cl(eq)	101.133(14) <i>106.061</i>	4.93° 4.9%
Sn-O-S (°)	130.23(7), 130.53(6) <i>125.27, 127.10</i>	4.19° 3.2%
O-S-N (°)	115.48(7), 115.57(7) <i>115.90, 117.55</i>	1.20° 1.0%
S-N-C (°)	130.79(11), 134.94(12) <i>132.86, 134.46</i>	0.79° 0.6%
O-S-N-C (°)	1.9(2), 0.6(2) <i>3.9, 0.8</i>	
S-N-C-C (°)	-143.75(15), -179.10(17) <i>166.64, 173.05</i>	
S-N-C-C' (°)	37.85(17), 0.20(19) <i>-13.81, -6.23</i>	

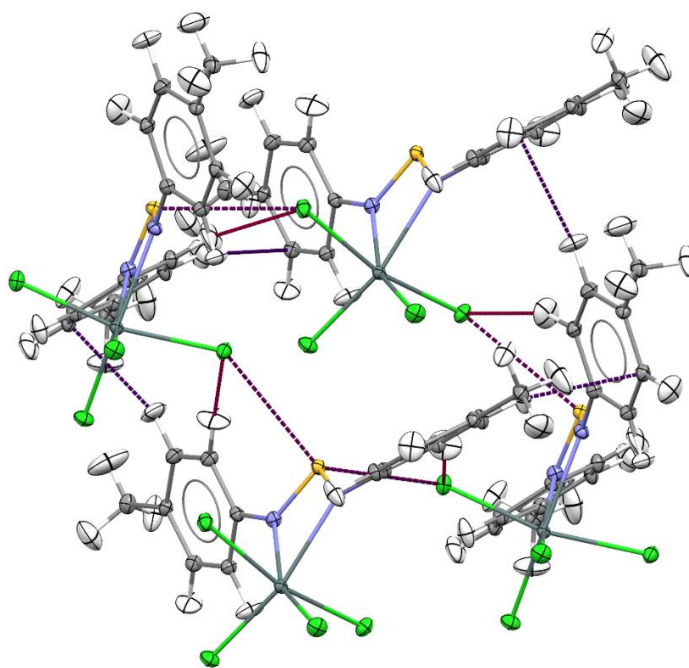
^a Computed geometries were optimized using Gaussian 16w v1.1, computed at B3PW91-D3BJ/def2TZVP, shown as italicized entries below experimental values. ^b Errors given for bond lengths, angles, and torsions are s.u. from crystallographic data. Errors for averages are s.d. for the series. ^c Differences are given for bond lengths and bond angles only. They are calculated based on average of entries, if there are more than one, and %difference is calculated against the experimental (SC-XRD) values.

C.4. Lattice Structures and Intermolecular Contacts

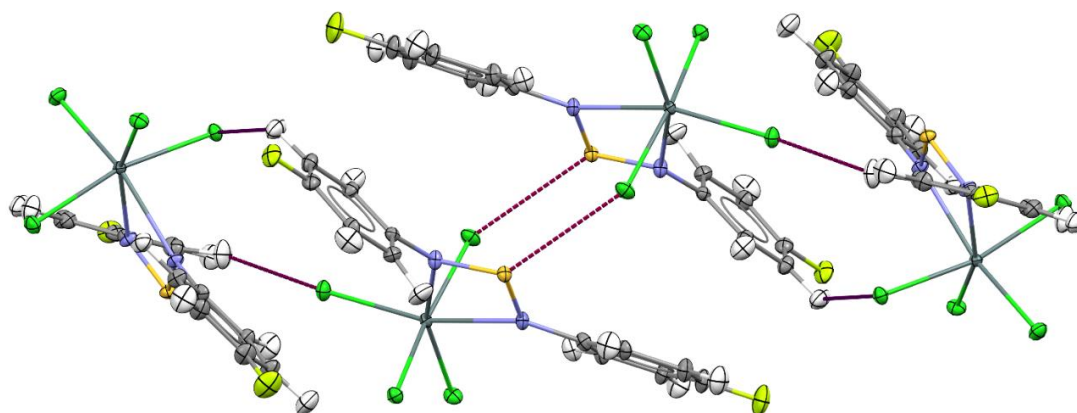
(a)



(b)



(c)



(d)

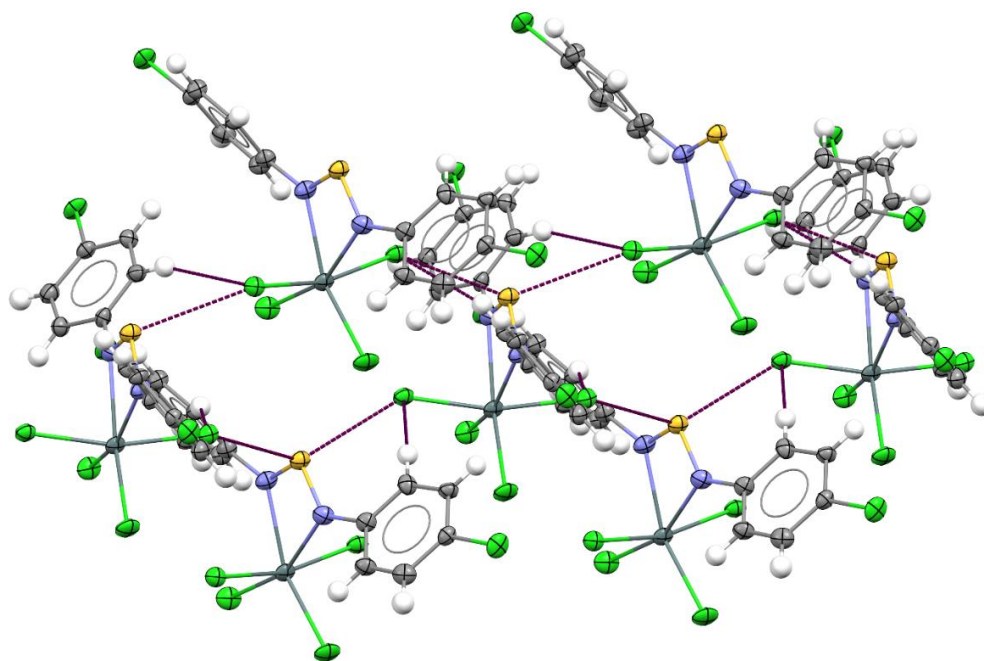


Figure C.8. Lattice structure diagrams for 1-4. Displacement ellipsoids plots (40% probability) with short contacts in purple dashed lines for $d = (r_{\text{vdw}} - 0.2 \text{ \AA})$. (a) 1; (b) 2; (c) 3; (d) 4.

Table C.15. Short Intermolecular Contacts (Å) in Complexes **1–4**, **6**, and **10**.

Cmpd	Atom1	Atom2	Length	Length-VdW	Symm. op. 1	Symm. op. 2
1	S1	Cl1	3.259	-0.291	x,y,z	1/2-x,-1/2+y,z
1	O1	H5	2.474	-0.246	x,y,z	1-x,-y,1-z
1	H6	Cl2	2.735	-0.215	x,y,z	1-x,-1+y,1.5-z
1	O1	H3	2.529	-0.191	1-x,y,1.5-z	-1/2+x,-1/2+y,1.5-z
1	C5	H7c	2.781	-0.119	x,y,z	-1/2+x,1/2-y,1-z
2	H6	Cl1	2.662	-0.288	1-x,y,1.5-z	1/2-x,-1/2+y,z
2	S1	Cl1	3.357	-0.193	x,y,z	1/2-x,-1/2+y,z
2	H5	C3	2.762	-0.138	1-x,y,1.5-z	-1/2+x,-1/2+y,1.5-z
2	C1	H7a	2.800	-0.100	x,y,z	1-x,-y,1-z
3	F2	H5	2.225	-0.445	x,y,z	-1+x,1.5-y,-1/2+z
3	Cl1	S1	3.284	-0.266	x,y,z	1-x,1-y,1-z
3	Cl2	H6	2.704	-0.246	x,y,z	1-x,-1/2+y,1.5-z
3	H3	Cl3	2.773	-0.177	x,y,z	1-x,-1/2+y,1.5-z
3	Cl4	H8	2.805	-0.145	x,y,z	-x,1-y,1-z
4	Cl1	S1	3.344	-0.206	1-x,y,1/2-z	-1/2+x,-1/2+y,1/2-z
4	Cl1	H6	2.772	-0.178	1-x,y,1/2-z	1/2-x,-1/2+y,z
4	Cl1	Cl3	3.392	-0.108	1-x,y,1/2-z	1/2-x,1.5-y,-1/2+z
6	S1	Cl2	3.201	-0.349	x,y,z	-1+x,y,z
6	S1	Cl1	3.398	-0.152	x,y,z	x,y,-1+z
10	C6	H8	2.624	-0.276	x,y,z	1-x,1-y,1-z
10	H3	Cl3	2.788	-0.162	x,y,z	-1+x,-1+y,z
10	H4	Cl4	2.845	-0.105	x,y,z	-1+x,-1+y,z

C.5. Computational Data for NBO Analysis, Complexation Energies, and Lattice Energies

Table C.16. Select NBO charges calculated for **1** – **5**, sorted small-to-large by [SnCl₄].^a

Cmpd	Ligand	N	S	Sn	[SnCl ₄] ^b
4	(4-ClPhN) ₂ S	-0.714	1.192	1.550	-0.256
2	(4-MePhN) ₂ S	-0.715	1.189	1.554	-0.272
3	(4-FPhN) ₂ S	-0.715	1.191	1.551	-0.261
1	(4-MeOPhN) ₂ S	-0.716	1.145	1.556	-0.292
5	(^t BuN) ₂ S	-0.766	1.293	1.573	-0.285

^aNBO charges are taken from geometry optimizations of the indicated compound at the B3PW91-D3BJ/def2TZVP level of theory. Table entries are sorted by NBO charges on N atoms. ^b [SnCl₄] values are the sum of NBO charges on Sn and 4Cl atoms.

Table C.17. Calculated NBO charges^a of [SnCl₄] fragment and complexation energies^b of **1** – **5**, sorted small-to-large by E_{Complexation}.

Cmpd	Ligand	E _{Complexation} (kJ·mol ⁻¹)	NBO Charge [SnCl ₄]
4	(4-ClPhN) ₂ S	-176.9	-0.256
3	(4-FPhN) ₂ S	-182.7	-0.261
2	(4-MePhN) ₂ S	-192.4	-0.272
1	(4-MeOPhN) ₂ S	-209.5	-0.292
5	(^t BuN) ₂ S	-237.9	-0.285

^a NBO charges are taken from geometry optimizations of the indicated compound at the B3PW91-D3BJ/def2TZVP level of theory. ^b Complexation energies are calculated by dividing DFT-optimized structures into [Cl₄Sn] and [Ligand] fragments, and running a single-point energy calculation with counterpoise enabled. Counterpoise calculations return the complexation energy, which is the difference in energy between the complex ([Cl₄Sn-Ligand]) and the sum of the individual fragments ([Cl₄Sn] + [Ligand]) after correction for Basis Set Superposition Energy (BSSE).

Lattice energies reported in Table C.19 are derived from interaction energies calculated in CrystalExplorer v21.5, and have been shown to compare favourably to experimental estimates from sublimation enthalpies with accuracy comparable or superior to more computationally expensive methods.^[14] CrystalExplorer (CE) extracts atomic coordinates and symmetry data from CIF files to calculate (among other things) interaction energies between discrete molecules in a crystal structure using counterpoise calculations, similarly to complexation energy calculations as explained in Table C.17, footnote b. CE calculates interaction energies from four energy terms: E_{ele}, E_{pol}, E_{dis}, and E_{rep}. The first two are electrostatic terms; E_{ele} is the unperturbed coulombic interaction between fragments (can be negative or positive), and E_{pol} is the energy associated with the polarization of electron density of each fragment by the other (always negative). E_{dis} is the

energy associated with dispersion effects (always negative, and E_{rep} is the repulsive interaction from overlap of molecular wavefunctions (always positive). To calculate the total energy of an interaction, E_{tot} , CE applies scale factors, k , to each energy term, such that the final calculation is: $E_{\text{tot}} = E_{\text{ele}}k_{\text{ele}} + E_{\text{pol}}k_{\text{pol}} + E_{\text{dis}}k_{\text{dis}} + E_{\text{rep}}k_{\text{rep}}$

The lattice energy of a molecule cluster is calculated as half of the sum of all interaction energies in the molecule cluster (w.r.t. the originating molecule of the cluster, as in Figure C.9, and Table C.19):

$$E_{\text{Lattice}} = \frac{1}{2} \sum E_{\text{tot}}$$

Table C.18. Output of CrystalExplorer interaction energy calculations for **1** using a molecule cluster generated in a 3.8 Å radius from the originating molecule.^{a,b}

	N ^c	Symop	R ^d	Electron Density ^e	E_ele	E_pol	E_dis	E_rep	E_tot	N*E_tot ^f
	4	x+1/2, y+1/2, -z+1/2	6.46	B3LYP/D GDZVP	-20.91	-10.99	-48.09	63.55	-32.86	-131.44
	2	x, y, z	8.59	B3LYP/D GDZVP	-24.85	-5.58	-18.69	24.47	-31.57	-63.14
	4	-x+1/2, -y+1/2, z+1/2	12.85	B3LYP/D GDZVP	-8.75	-2.20	-15.93	0.00	-24.75	-99
	2	-x,-y,-z	13.72	B3LYP/D GDZVP	-2.58	-1.42	-16.33	0.00	-18.00	-36
	2	-x,-y,-z	11.49	B3LYP/D GDZVP	-29.95	-7.53	-29.07	24.75	-47.27	-94.54
									E _{Lattice} ^g	-212.06

^a CE generates this cluster by identifying any atoms within 3.8 Å of the originating molecule and adding their parent molecules to the cluster. ^b All energies reported in kJ · mol⁻¹. ^c N denotes the number of molecules in the cluster which are symmetry-related to the originating molecule by the same symmetry operation shown in the 'Symop' column. ^d Distance (Å) from the originating molecule to the symmetry-related (red-coloured) molecules in the lattice. ^e Computational methods used by CE (determines scale factors (k) applied to energy terms (E_{ele} , E_{pol} , E_{dis} , E_{rep}). ^f Individual interaction energy (E_{tot}) multiplied by N (# of identical interactions). Column added manually (after CE calculation) to determine E_{Lattice} . ^g Sum of interaction energies divided by 2: $E_{\text{Lattice}} = \Sigma(N*E_{\text{tot}})/2$

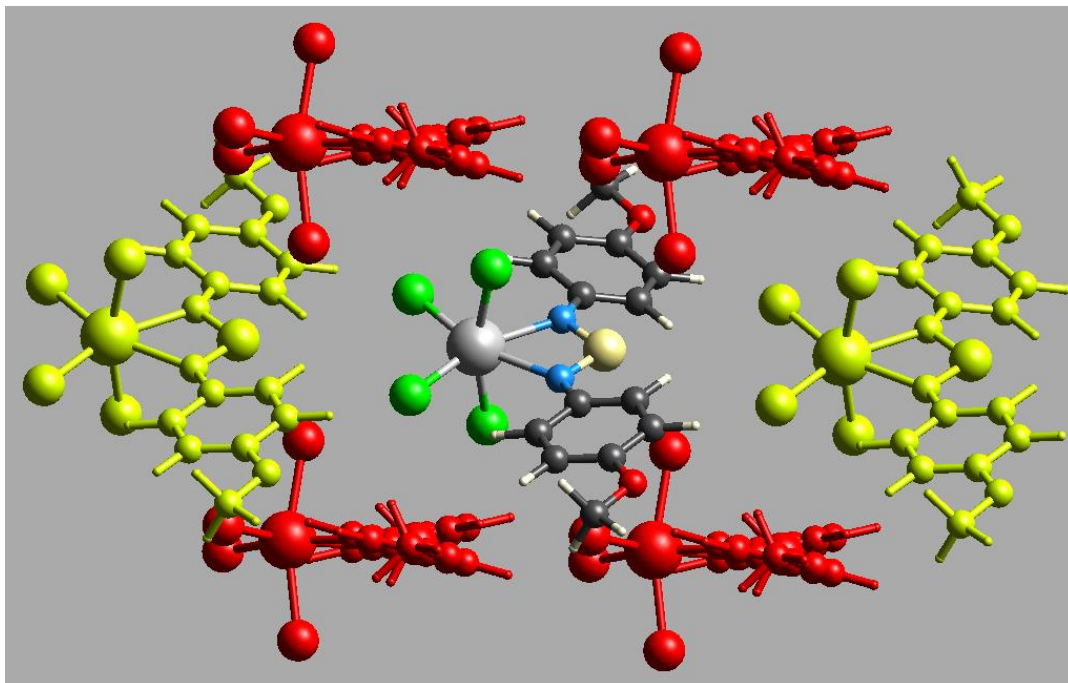


Figure C.9. Partial molecule cluster of **1** used by CrystalExplorer in interaction energy calculation. Red and yellow molecules correspond to the colour coding in Table C.18. Other molecules in the cluster (green, blue, purple) were hidden for clarity. The originating molecule is in the centre of the cluster, coloured by element.

Table C.19. Calculated lattice energies for compounds of the form $\text{Cl}_4\text{Sn-L}$.

Complex	Ligand	E_{Lattice} (kJ/mol)
3	(4-FPhN) ₂ S	-154.2
4	(4-ClPhN) ₂ S	-157.7
2	(4-MePhN) ₂ S	-188.9
1	(4-MeOPhN) ₂ S	-212.1

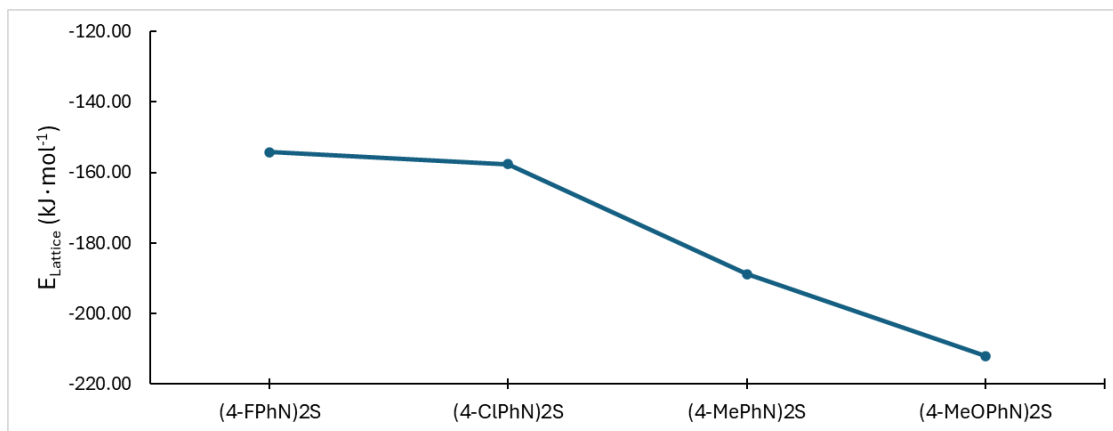


Figure C.10. Graph of lattice energies from Table C.19, derived from interaction energies calculated in CrystalExplorer at the B3LYP/DGDZVP level of theory, applying D2 dispersion correction.

C.6. FTIR and Raman Spectroscopy Data Tables and Spectra

C.6.1. Experimental FTIR and Raman Data and Assignments, and Comparison to DFT Computed Vibrational Spectra

Table C.20. Experimental and computed IR and Raman spectroscopic data for **1**. Calculated IR vibrational frequencies and modes for the free SDI ligand in the *EE* conformation are reported in blue.

IR Expt	IR DFT ^a	Lig. DFT ^b	Mode	Raman Expt ^c	Raman DFT ^a	Mode ^d	Assignment ^e
3179, <i>w</i>	3115, 1%	3103, 24%	92			107	$\nu_{as}(\text{C-H, Ar})$
3095, <i>w</i>	3096, 2%	3067, 1%	86		3096, 2%	103	$\nu_{as}(\text{C-H, Ar})$
3067, <i>sh</i>	3044, 3%	3031, 4%	84		3044, 1%	99	$\nu_{as}(\text{C-H, CH}_3)$
3013, <i>w</i>	2981, 4%	2964, 6%	83,82		2981, 1%	98,97	$\nu_{as}(\text{C-H, CH}_3)$
2974, <i>w</i>	2916, 2%	2908, 1%	81		2916, 7%	96	$\nu_{as}(\text{C-H, CH}_3)$
2933, <i>w</i>	2915, 14%	2908, 15%	80			95	$\nu_{as}(\text{C-H, CH}_3)$
1586, <i>s</i>	1592, 100%	1586, 34%	79		1592, 2%	93	$\nu_{as}(\text{C-C, Ar})$
1569, <i>s</i>	1551, 7%	1543, 3%	76			91	$\nu_{as}(\text{C-C, Ar})$
1501, <i>vs</i>	1487, 25%	1482, 38%	75			90	$\nu_{as}(\text{N-C, Ar})$
Not obs.	1485, 1%	1481, 1%	74		1485, 33%	89	$\nu_s(\text{N-C, Ar})$
1452, <i>m</i>	1445, 10%	1455, 12%	72			87	$\delta_{as}(\text{C-H, CH}_3)$
1440, <i>m</i>	1423, 5%	1409, <1%	67			83	$\delta_{as}(\text{C-H, Ar})$
1429, <i>m</i>	1419, 1%	1427, 4%	68			81	$\delta_{as}(\text{C-H, CH}_3)$
1306, <i>m</i>	1312, 11%	1278, 16%	63		1312, 1%	79	$\delta_{as}(\text{C-C, Ar})$
1254, <i>vs</i>	1275, 83%	1249, 2%	61		1275, 1%	75	$\nu_{as}(\text{S=N+CAr})$
1230, <i>sh</i>	1256, 44%	1227, 100%	58			73	$\nu_{as}(\text{N-CAr})$
1165, <i>vs</i>	1148, 38%	1152, 14%	55			69	$\delta_{as}(\text{C-H, Ar})$
1132, <i>m</i>	1101, <1%	1101, 1%	51			66	$\delta_{as}(\text{C-H, Ar})$
1021, <i>vs</i>	1040, 20%	1030, 31%	49			64	$\nu_{as}(\text{O-CH}_3)$
1000, <i>m</i>	1022, 6%	1016, 1%	47			62	$\nu_{as}(\text{NSN})$
972, <i>w</i>	994, <1%	949, <1%	44		994, 29%	61	$\nu_s(\text{NSN})$
826, <i>vs</i>	833, 5%	820, 2%	39		833, 17%	54	$\delta_s(\text{NSN})$
777, <i>vs</i>	782, 2%	779, <1%	34			49	$\rho_{as}(\text{C-H, Ar})$
726, <i>w</i>	757, 2%	740, 2%	33		757, 10%	48	$\delta_s(\text{NSN})$
712, <i>w</i>	721, 1%	695, 1%	30			47	$\delta_{as}(\text{NSN})$
631, <i>m</i>	626, 2%	632, <1%	29			44	$\delta_{as}(\text{ring, in-plane})$
553, <i>s</i>	546, 11%	535, 7%	26			41	$\rho_{as}(\text{NSN})$
520, <i>s</i>	516, 4%	513, 3%	25			40	$\rho_s(\text{C-H})$
423, <i>w</i>	411, 1%	416, 1%	21			36	$\rho_{as}(\text{C-C, Ar})$
388, <i>s</i>	385, 7%	392, 4%	19			32	$\rho_{as}(\text{ring, in-plane})$

^a Computed at the B3PW91-D3BJ/def2TZVP level of theory $\times 0.964$. [Scaled average] agreement to experiment $\pm 18 \text{ cm}^{-1}$. ^b Computed at the B3LYP-D3BJ/6311G++(2d,p) level of theory $\times 0.967$. ^c The Raman spectrum of **1** had very poor signal-to-noise due to extreme fluorescence; no useable results were obtained. ^d Compound **1** has 108 normal modes of vibration of which 30 are observed and the remainder are either very weak or below the 385 cm^{-1} cutoff of our spectrometer. ^e Assignments made by visual assessment of vibration animations in the GaussView 6.0.16 GUI.

Table C.21. Experimental and computed IR and Raman spectroscopic data for **2**. Calculated IR vibrational frequencies and modes for the free SDI ligand in the *EE* conformation are reported in blue.

IR Expt	IR DFT ^a	Lig. DFT ^b	Mode	Raman Expt	Raman DFT ^a	Mode ^c	Assignment ^d
3086, <i>w</i>	3070, 9%	3054, 15%	82			97	$\nu_{as}(\text{C-H, Ar})$
3033, <i>w</i>	3019, 5%	2922, 30%	74			94	$\nu_{as}(\text{C-H, CH}_3)$
1592, <i>s</i>	1595, 100%	1588, 3%	73			88	$\nu_{as}(\text{C-C, Ar})$
				1592, <i>s</i>	1595, 54%	87	$\nu_s(\text{C-C, Ar})$
1494, <i>m</i>	1482, 9%	1482, 44%	69			84	$\nu_{as}(\text{N-C, Ar})$
				1494, <i>m</i>	1480, 17%	83	$\nu_s(\text{N-C, Ar})$
1439, <i>w, br</i>	1433, 6%	1446, 3%	66			81	$\delta_{as}(\text{C-H, CH}_3)$
				1445, <i>vw</i>	1425, 1%	80	$\delta_s(\text{C-H, CH}_3)$
				1380, <i>vw</i>	1355, 2%	76	$\delta_s(\text{CH}_3)$
				1314, <i>vw</i>	1304, 8%	74	$\nu_{as}(\text{C-C, Ar})$
1287, <i>w</i>	1302, 14%	1297, 18%	59			73	$\nu_{as}(\text{C-C, Ar})$
				1288, <i>vw</i>	1289, 9%	72	$\delta_{as}(\text{C-H, Ar})$
1250, <i>w</i>	1268, 1%	1232, 100%	54	1250, <i>vs</i>	1268, 100%	70	$\nu_s(\text{S=N+CAr})$
				Not obs.	1262, 2%	69	$\nu_{as}(\text{S=N+CAr})$
1213, <i>w</i>	1203, 8%	1194, <1%	53			67	$\nu_{as}(\text{C-CH}_3)$
				1182, <i>s</i>	1160, 14%	66	$\delta_s(\text{C-H, Ar})$
1178, <i>m</i>	1160, 17%	1164, <1%	51			65	$\delta_{as}(\text{C-H, Ar in-plane})$
1119, <i>w</i>	1105, 6%	1104, 3%	48			63	$\delta_{as}(\text{C-H, Ar in-plane})$
1034, <i>w</i>	1035, 38%	1031, 19%	47			62	$\nu_{as}(\text{NSN})$
1019, <i>s</i>	1017, 22%	1027, 29%	45			60	$\delta_{as}(\text{C-H, CH}_3)$
				1018, <i>vw</i>	1006, 5%	59	$\nu_s(\text{NSN})$
982, <i>m</i>	988, 4%	955, 2%	40	984, <i>m</i>	988, 9%	57	$\nu_s(\text{NSN})$
938, <i>m</i>	946, 1%	941, 1%	39			54	$\delta_{as}(\text{C-H, Ar})$
849, <i>vs</i>	832, 20%	823, 11%	35	851, <i>m</i>	832, 9%	50	$\delta_s(\text{NSN})$
815, <i>s</i>	809, 6%	806, 2%	32			47	$\delta_{as}(\text{C-H, Ar})$
803, <i>vs</i>	796, 14%	797, 7%	31			46	$\delta_{as}(\text{C-H, Ar})$
				807, <i>m</i>	789, 6%	45	$\delta_{as}(\text{C-H, Ar})$
776, <i>w</i>	759, 2%	746, 1%	29	777, <i>w</i>	759, 3%	44	$\delta_s(\text{NSN})$
727, <i>m</i>	717, 13%	709, 2%	28			43	$\delta_{as}(\text{NSN})$
699, <i>s</i>	695, 3%	699, <1%	27	699, <i>w</i>	695, <1%	41	$\delta_{as}(\text{ring, oop})$
				634, <i>w</i>	626, <1%	40	$\delta_{as}(\text{ring, in-plane})$
541, <i>s</i>	532, 10%	520, 6%	22			37	$\rho_{as}(\text{NSN})$
				506, <i>w</i>	497, 1%	36	$\delta_{as}(\text{ring, oop})$
504, <i>vs</i>	495, 13%	480, 7%	20			35	$\rho_s(\text{NSN})$
407, <i>s</i>	402, 9%	412, 2%	18			33	$\delta_{as}(\text{ring, in-plane})$
				408, <i>w</i>	401, 1%	31	$\delta_s(\text{ring, oop})$
389, <i>m</i>	377, 3%	347, 2%	15			30	$\rho_{as}(\text{NSN})$
				348, <i>w</i>	347, 1%	28	$\rho_s(\text{NSN})$
				331, <i>w</i>	333, 1%	26	$\nu_s(\text{Sn-Cl}_{eq})$
				292, <i>w</i>	290, 1%	23	$\nu_s(\text{Sn-Cl}_{ax})$

^a Computed at the B3PW91-D3BJ/def2TZVP level of theory $\times 0.964$. [Scaled average] agreement to experiment $\pm 10 \text{ cm}^{-1}$. ^b Computed at the B3LYP-D3BJ/6311G++(2d,p) level of

theory $\times 0.967$. ^c Compound 2 has 102 normal modes of vibration of which 39 are observed and the remainder are either very weak or, for FTIR, below the 385 cm⁻¹ cutoff of our spectrometer. ^d Assignments made by visual assessment of vibration animations in the GaussView 6.0.16 GUI.

Table C.22. Experimental and computed IR and Raman spectroscopic data for 3. Calculated IR vibrational frequencies and modes for the free SDI ligand in the *EE* conformation are reported in blue.

IR Expt	IR DFT ^a	Lig. DFT ^b	Mode	Raman Expt	Raman DFT ^a	Mode ^c	Assignment ^d
3225-2962, <i>vw</i> ^e	3112-3074 ^e					84-77	$\nu_{as}(\text{C-H, Ar})$
				1589, <i>m</i>	1591, 66%	76	$\nu_s(\text{C-C, Ar})$
1584, <i>vs</i>	1590, 100%	1581, 20%	61			75	$\nu_{as}(\text{C-C, Ar})$
1491, <i>vs</i>	1481, 51%	1477, 72%	57			72	$\nu_{as}(\text{N-C, Ar})$
				1493, <i>m</i>	1480, 26%	71	$\nu_s(\text{N-C, Ar})$
				Not obs.	1306, 16%	68	$\nu_s(\text{C-C, Ar})$
1292, <i>m</i>	1304, 6%	1268, <1%	51			67	$\nu_{as}(\text{C-C, Ar})$
				1249, <i>vs</i>	1278, 100%	66	$\nu_s(\text{S=N+CAr})$
1262, <i>w</i>	1268, 17%	1238, 9%	49			63	$\nu_{as}(\text{S=N+CAr})$
				1228, <i>w</i>	1234, 12%	62	$\nu_s(\text{F-C, Ar})$
1235, <i>vs</i>	1230, 71%	1202, 100%	46			61	$\nu_{as}(\text{S=N+C-F})$
				1158, <i>s</i>	1136, 10%	60	$\delta_s(\text{C-H, Ar})$
1153, <i>vs</i>	1134, 29%	1136, 11%	45			59	$\delta_{as}(\text{C-H, Ar})$
1100, <i>s</i>	1087, 3%	1085, 2%	42			57	$\delta_{as}(\text{C-H, Ar})$
1013, <i>s</i>	1034, 21%	1030, 23%	41			56	$\nu_{as}(\text{NSN})$
				984, <i>s</i>	998, 11%	55	$\nu_s(\text{NSN})$
984, <i>w</i>	988, 1%	957, <1%	38			53	$\nu_s(\text{NSN})$
856, <i>s</i>	843, 10%	834, 5%	33	858, <i>m</i>	843, 11%	48	$\delta_s(\text{NSN})$
830, <i>vs</i>	837, 11%	830, 16%	32			47	$\delta_{as}(\text{C-H, Ar})$
798, <i>s</i>	827, 8%	820, 5%	31			46	$\delta_{as}(\text{C-H, Ar})$
				833, <i>m</i>	820, 9%	45	$\delta_{as}(\text{C-H, Ar})$
748, <i>w</i>	784, 4%	783, 1%	28			43	$\delta_{as}(\text{C-H, Ar})$
733, <i>w</i>	768, 3%	753, 3%	27	793, <i>m</i>	768, 9%	42	$\delta_s(\text{NSN})$
701, <i>w</i>	702, 1%	699, <1%	24	702, <i>w</i>	702, 2%	39	$\delta_{as}(\text{ring, oop})$
				631, <i>w</i>	622, 1%	37	$\delta_s(\text{C-C, Ar})$
539, <i>s</i>	530, 7%	519, 4%	20			35	$\delta_s(\text{ring, oop})$
517, <i>vs</i>	508, 4%	505, 2%	19	520, <i>w</i>	508, 1%	34	$\delta_s(\text{ring, oop})$
498, <i>vs</i>	500, 11%	485, 7%	18			33	$\rho_s(\text{NSN})$
426, <i>s</i>	418, 3%	420, 2%	16			31	Ring twist
				415, <i>w</i>	418, 1%	30	Ring twist
405, <i>s</i>	408, 7%	414, 7%	14	406, <i>w</i>	408, 1%	29	Ring twist
				335, <i>m</i>	336, 1%	22	$\nu_s(\text{Sn-Cl}_{eq})$
				300, <i>w</i>	293, <1%	21	$\nu_s(\text{Sn-Cl}_{ax})$
						19	NSNtwist+ $\nu_s(\text{Sn-Cl}_{eq})$
				269, <i>w</i>	226, 1%	19	
				145, <i>w</i>	144, 1%	16	$\delta_s(\text{Sn-Cl}_{ax})$

^a Computed at the B3PW91-D3BJ/def2TZVP level of theory $\times 0.964$. [Scaled average] agreement to experiment ± 12 cm⁻¹. ^b Computed at the B3LYP-D3BJ/6311G++(2d,p) level of theory $\times 0.967$. ^c Compound 3 has 84 normal modes of vibration of which 36 are observed and the remainder are either very weak or, for FTIR, below the 385 cm⁻¹ cutoff of our spectrometer. ^d Assignments made by visual assessment of vibration animations in the GaussView 6.0.16 GUI. ^e Several small, mostly broad, signals appear in the FTIR spectrum. Peaks at 3093, 3060, 3043 cm⁻¹ have possible corresponding calculated peaks, all <1% intensity.

Table C.23. Experimental and computed IR and Raman spectroscopic data for **4**. Calculated IR vibrational frequencies and modes for the free SDI ligand in the *EE* conformation are reported in blue.

IR Expt	IR DFT ^a	Lig. DFT ^b	Mode	Raman Expt	Raman DFT ^a	Mode ^c	Assignment ^d
3212, <i>m</i>	3111, 1%	3099, 2%	68			84,83	$\nu_{as}(\text{C-H, Ar})$
3174, <i>m</i>	3100, 1%	3095, 1%	66			79-82	$\nu_{as}(\text{C-H, Ar})$
3101, <i>m</i>	3072, 1%	3071, 3%	62			78,77	$\nu_{as}(\text{C-H, Ar})$
1567, <i>m</i>	1577, 100%	1567, 8%	61			76	$\nu_{as}(\text{C-C, Ar})$
				1574, <i>s</i>	1576, 61%	75	$\nu_s(\text{C-C, Ar})$
1481, <i>s</i>	1463, 39%	1465, 89%	57			72	$\nu_{as}(\text{N-C, Ar})$
				1482, <i>m</i>	1462, 15%	71	$\nu_s(\text{N-C, Ar})$
1410, <i>m</i>	1401, 2%	1393, 2%	55			70	$\nu_{as}(\text{C-C, Ar})$
				1305, <i>w</i>	1295, 15%	68	$\nu_{as}(\text{C-C, Ar})$
1277, <i>w</i>	1293, 6%	1260, 2%	51			67	$\nu_{as}(\text{C-C, Ar})$
				1277, <i>w</i>	1276, 18%	66	$\nu_s(\text{S=N+CAr})$
				1249, <i>vs</i>	1268, 100%	64	$\nu_s(\text{S=N+CAr})$
				Not obs.	1263, 2%	63	$\nu_{as}(\text{S=N+CAr})$
1159, <i>m</i>	1158, 1%	1160, 3%	47			62	$\delta_s(\text{C-H})$
				1181, <i>m</i>	1157, 10%	61	$\delta_s(\text{C-H, Ar})$
1116, <i>w</i>	1097, 5%	1096, 3%	44			59	$\delta_{as}(\text{C-H, Ar})$
				1093, <i>m</i>	1083, 9%	58	$\nu_s(\text{Cl-C, Ar})$
1094, <i>vs</i>	1081, 94%	1070, 49%	43			57	$\nu_{as}(\text{Cl-C, Ar})$
1014, <i>vs</i>	1033, 43%	1028, 53%	41			56	$\nu_{as}(\text{NSN})$
				Not obs.	1003, 5%	55	$\nu_s(\text{NSN})$
987, <i>w</i>	994, 10%	996, 11%	39			54	$\delta_{as}(\text{C-C, Ar})$
958, <i>w</i>	985, 4%	957, 2%	38	987, <i>s</i>	985, 12%	53	$\nu_s(\text{NSN})$
943, <i>w</i>	948, 1%	942, <1%				52	$\delta_{as}(\text{C-H, Ar})$
830, <i>vs</i>	834, 18%	826, 12%	33	851, <i>m</i>	834, 4%	48	$\delta_s(\text{NSN})$
819, <i>s</i>	828, 16%	824, 22%	32			47	$\delta_s(\text{C-H, Ar})$
				808, <i>s</i>	804, 4%	46	$\delta_s(\text{NSN})$
784, <i>m</i>	786, 17%	780, 11%	28			44	$\delta_{as}(\text{NSN})$
695, <i>m</i>	689, 5%	675, 5%	25	696, <i>vw</i>	689, 2%	40	$\delta_s(\text{NSN})$
650, <i>s</i>	642, 1%	630, 1%				39	$\delta_{as}(\text{NSN})$
				627, <i>vw</i>	618, <1%	38	$\delta_s(\text{C-C, Ar})$
520, <i>s</i>	516, 4%	514, 6%	21			36	$\delta_s(\text{ring, oop})$
506, <i>vs</i>	503, 7%	504, 5%	20	508, <i>vw</i>	503, 1%	35	$\delta_s(\text{ring, oop})$
482, <i>m</i>	478, 11%	463, 6%	19			34	$\rho_s(\text{NSN})$
394, <i>s</i>	404, 2%	412, 1%	16			31	$\delta_{as}(\text{ring, oop})$
				409, <i>w</i>	403, 1%	30	$\delta_{as}(\text{ring, oop})$
				358, <i>vw</i>	342, 1%	25	$\text{NSNtwist}+\nu_s(\text{Sn-Cl}_{eq})$
				341, <i>w</i>	333, 2%	24	$\nu_s(\text{Sn-Cl}_{eq})$
				146, <i>w</i>	143, 1%	16	$\delta_s(\text{Sn-Cl})$

^a Computed at the B3PW91-D3BJ/def2TZVP level of theory $\times 0.964$. [Scaled average] agreement to experiment $\pm 17 \text{ cm}^{-1}$. ^b Computed at the B3LYP-D3BJ/6311G++(2d,p) level of

theory $\times 0.967$. ^c Compound **4** has 84 normal modes of vibration of which 40 are observed and the remainder are very weak or, for FTIR, below the 385 cm⁻¹ cutoff of our spectrometer. ^d Assignments made by visual assessment of vibration animations in the GaussView 6.0.16 GUI.

Table C.24. Experimental and computed IR and Raman spectroscopic data for **5**. Calculated IR vibrational frequencies and modes for the free SDI ligand in the *EE* conformation are reported in blue.

IR Expt	IR DFT ^a	Lig. DFT ^b	Mode	Raman Expt	Raman DFT ^a	Mode ^c	Assignment ^d
				2981, s	3024, 70%	92	$\nu_s(\text{C-H, 'Bu})$
2980, <i>m</i>	3023, 28%	2995, 49%	76			91	$\nu_{as}(\text{C-H, 'Bu})$
				2932, <i>m, br</i>	2946, 100%	84	$\nu_s(\text{C-H, 'Bu})$
2930, <i>w</i>	2946, 17%	2933, 15%	68			83	$\nu_{as}(\text{C-H, 'Bu})$
1471, <i>m</i>	1453, 8%	1455, 5%	61			77	$\delta_{as}(\text{C-H, 'Bu})$
1457, <i>w</i>	1442, 7%	1447, 3%	59			76	$\delta_{as}(\text{C-H, 'Bu})$
1366, <i>s</i>	1344, 11%	1353, 7%	49			62	$\delta_{as}(\text{C-H, 'Bu})$
1245, <i>w</i>	1228, 15%	1213, 6%	45			60	$\delta_{as}(\text{C-'Bu})$
1228, <i>m</i>	1218, 14%	1201, 5%	43			59	$\delta_{as}(\text{C-'Bu})$
				not obs.	1188, 32%	56	$\nu_s(\text{S=N+C'Bu})$
1176, <i>vs</i>	1171, 100%	1178, 100%	40			55	$\nu_{as}(\text{S=N+C'Bu})$
1116, <i>vs</i>	1151, 14%	1138, 54%	39			54	$\nu_{as}(\text{NSN})$
Not obs.	1123, 2%	1076, <1%	38	1109, <i>vs</i>	1123, 26%	53	$\nu_s(\text{NSN})$
1040, <i>s</i>	1014, 2%	1015, 2%	35			50	$\delta_{as}(\text{C-'Bu})$
930, <i>w</i>	906, 2%	892, 1%	31	931, <i>w</i>	906, 1%	46	$\delta_s(\text{C-H, 'Bu})$
872, <i>s</i>	855, 13%	827, 6%	27			42	$\delta_s(\text{NSN})$
787, <i>m</i>	828, 1%	824, <1%	26			41	$\delta_{as}(\text{NSN})$
760, <i>m, br</i>	764, 5%	739, 2%	25	789, <i>m</i>	764, 8%	40	$\delta_s(\text{NSN})$
499, <i>s</i>	489, 7%	458, 3%	21			36	$\rho_{as}(\text{'BuN})_2\text{S}$
				332, <i>vs</i>	324, 3%	26	$\rho_s(\text{SnN}_2\text{S})$
				295, <i>m</i>	286, 2%	23	$\delta_s(\text{'Bu})$

^a Computed at the B3PW91-D3BJ/def2TZVP level of theory $\times 0.964$. [Scaled average] agreement to experiment ± 20 cm⁻¹. ^b Computed at the B3LYP-D3BJ/6311G++(2d,p) level of theory $\times 0.967$. ^c Compound **5** has 96 normal modes of vibration of which 20 are observed and the remainder are either very weak or, for FTIR, below the 385 cm⁻¹ cutoff of our spectrometer. ^d Assignments made by visual assessment of vibration animations in the GaussView 6.0.16 GUI.

Table C.25. Experimental and computed IR and Raman spectroscopic data for **6**.^a Calculated IR vibrational frequencies and modes for the free SDI ligand in the *EE* conformation are reported in blue.

IR Expt	IR DFT ^b	Lig. (<i>EE</i>) DFT ^c	Lig. Mode(s)	Mode(s) ^d	Assignment ^e
1258	1236, 15%	1245, 8%	47	59	$\delta_{as}(\text{C-SiMe}_3)$
1155	1188, 95%	1193, 100%	45	60	$\nu_{as}(\text{S=N+SiMe}_3)$
	844, 45%	840, 17%	42	58	$\delta_s(\text{NSN})$
852	842, 25%	839, 18%	41	57	$\delta_{as}(\text{C-H, SiMe}_3)$
	822, 100%	836, 52%	38	53	$\delta_{as}(\text{C-H, SiMe}_3)$

^a Very limited IR and zero Raman data reported for this complex in the literature.^[15] ^b Computed at the B3PW91-D3BJ/def2TZVP level of theory $\times 0.964$. [Scaled average] agreement to experiment ± 21 cm⁻¹. ^c Computed at the B3LYP-D3BJ/6311G++(2d,p) level of theory $\times 0.967$. ^d Compound **6** has 96 normal modes of vibration of which the three most intense are reported; we assume that modes 38, 41, and 42 will merge in solid-state IR spectrum. ^e Assignments made by visual assessment of vibration animations in the GaussView 6.0.16 GUI.

C.6.2. Experimental Methods

IR spectra of **1–5** were collected in a N₂-filled glovebox with oxygen and moisture rigorously excluded, and Raman spectra were collected by sealing samples in ~1 mm O.D. capillary tubes. Simulated IR and Raman spectra derived from DFT calculations undertaken for this work used B3PW91-D3BJ/def2-TZVP.

C.6.3. Results

The average agreement between experimental and simulated peaks was $\pm 10\text{--}21\text{ cm}^{-1}$ over the series, and this excellent result allows a high degree of confidence in our peak assignments. There are very few strong calculated peaks (arbitrarily, greater than 10% calculated intensity vs. highest intensity peak) that are experimentally unobserved, exclusively in the Raman spectra, notably mode 56 from complex **5** (Table C.24). Lattice-based selection rules can affect Raman spectra of crystalline solids and are not accounted for by gas-phase computations.^[16] The noted omissions are probably attributable to such effects. The structure of **6** in *P2/m* is centered on a crystallographic mirror plane and it is quite possible that **5** may share similar site symmetry. The overall agreement between experimental and computational spectra was exceptional, and suggests satisfactory purity of the bulk samples. As was found in our investigation of the free sulfur diimides,^[7] complexes **1–5** exhibit strong mixing of vibrational modes between the R groups and the –NSN– atoms, such that many of the assignments in Tables C.20–C.25 are judiciously simplified.

There is a single literature entry of vibrational data for tetrachlorotin-SDI complexes, that of *bis*-trimethylsilyl sulfur diimide, **6**, which notes three IR peaks without assignments.^[15] As with **1–5**, these peaks were assigned by comparing to a simulated spectrum which also found good agreement.

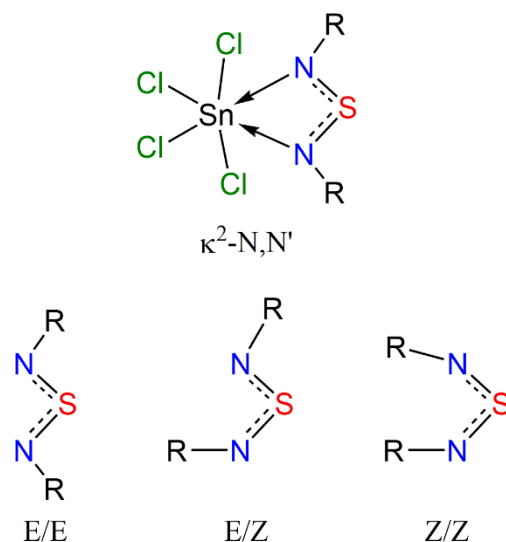


Figure C.11. Possible conformations of sulfur diimides.

Our previous work reported IR spectra for a series of aryl sulfur diimides ($R\text{-NSN-}R$, $R = \text{Ar}$) which were mostly in *EZ* conformation, with one ($R = 2,4,6\text{-F}_3\text{Ph}$) found in *ZZ* conformation (see Figure C.11).^[7] The series included the unbound SDI ligands of complexes **1–4**, all of which are found in *EZ* conformation. While a direct comparison of peak data is not possible because $\kappa^2\text{-N,N'}$ coordinated SDIs are constrained to *EE* geometry, some broad trends can be meaningfully noted. The experimental bands which are dominated by $\nu(\text{S=N-R})$ vibrations are found between $1200\text{--}1300\text{ cm}^{-1}$ in both the free aryl SDIs and in complexes **1–4**. Stretching vibrations centred on the NSN atoms, $\nu(\text{NSN})$, are very similar between **1–4** and their unbound analogs, while bending (δ) and wagging (ρ) modes of the coordinated SDIs are found at $\sim 50\text{--}100\text{ cm}^{-1}$ higher frequencies than free SDIs. This appears to be consistent with the intuitively sensible notion that 1) IR bands dominated by N-R vibrations would be less affected by coordination to Sn compared to vibrations that deform the NSN moiety w.r.t. the SnCl_4 fragment, and 2) N,N' -bidentate coordination would increase the amount of energy needed to induce such vibrations.

The experimental IR data for *tert*-butyl and trimethylsilyl SDI complexes **5** and **6** and their corresponding free SDIs is limited by data quality and, for the latter, reporting. As laid out in Table 5.2, their $\nu(\text{S=N-R})$ bands are $\sim 100\text{ cm}^{-1}$ lower frequency than the aryl SDI

complexes **1-4**, while $\nu(\text{NSN})$ bands are $\sim 100\text{ cm}^{-1}$ higher frequency. The frequencies of the bending (δ) and wagging (ρ) bands observed for **5** and **6** are found within the range of the same vibrations of **1-4**.

Because *EE* is the globally highest energy conformation for SDIs, only their *EZ* and *ZZ* isomers can be directly observed by IR, such that simulated spectra from computational models of *EE* SDIs are the only tool available to probe their vibrational properties. An intriguing finding from our analysis is that simulated IR spectra of the free SDIs in their *EE* conformation produce peaks that are a remarkably good fit to the computed IR peaks of the complexes, as seen in Tables C.20–C.25. While the intrinsic differences between experimental spectra from crystalline solids and computational spectra from gas-phase calculations must be emphasized, as well as the different computational methods used to perform the necessary frequency calculations (B3PW91-D3BJ/def2-TZVP for the complexes vs. B3LYP-D3BJ/6311G++(2d,p) for the free *EE* SDIs), this may imply that coordination of the SDI to the Sn metal centre has a relatively small impact on the SDI vibrational modes. Thus, we *tentatively* suggest that the experimental vibrational spectra of these complexes may serve as an indirect method to obtain at least an approximation of vibrational data for SDIs in *EE* conformation.

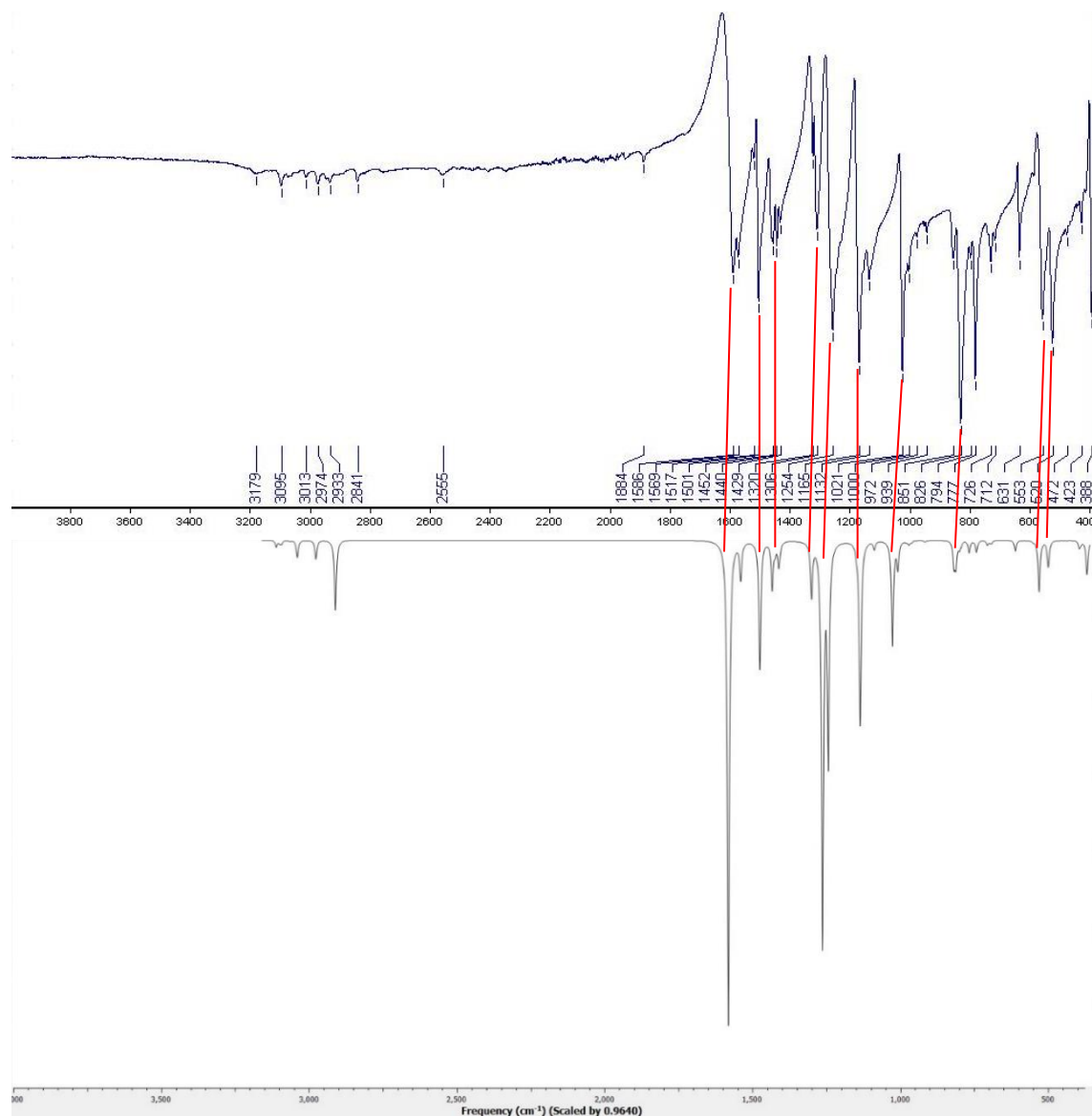


Figure C.12. Experimental (top) and simulated (bottom) FTIR spectra of **1** (top) with correlation lines drawn between simulated and experimental peaks. Simulated spectrum was obtained from frequency calculation at B3PW91-D3BJ/def2TZVP. X-axis scaled by 0.964.

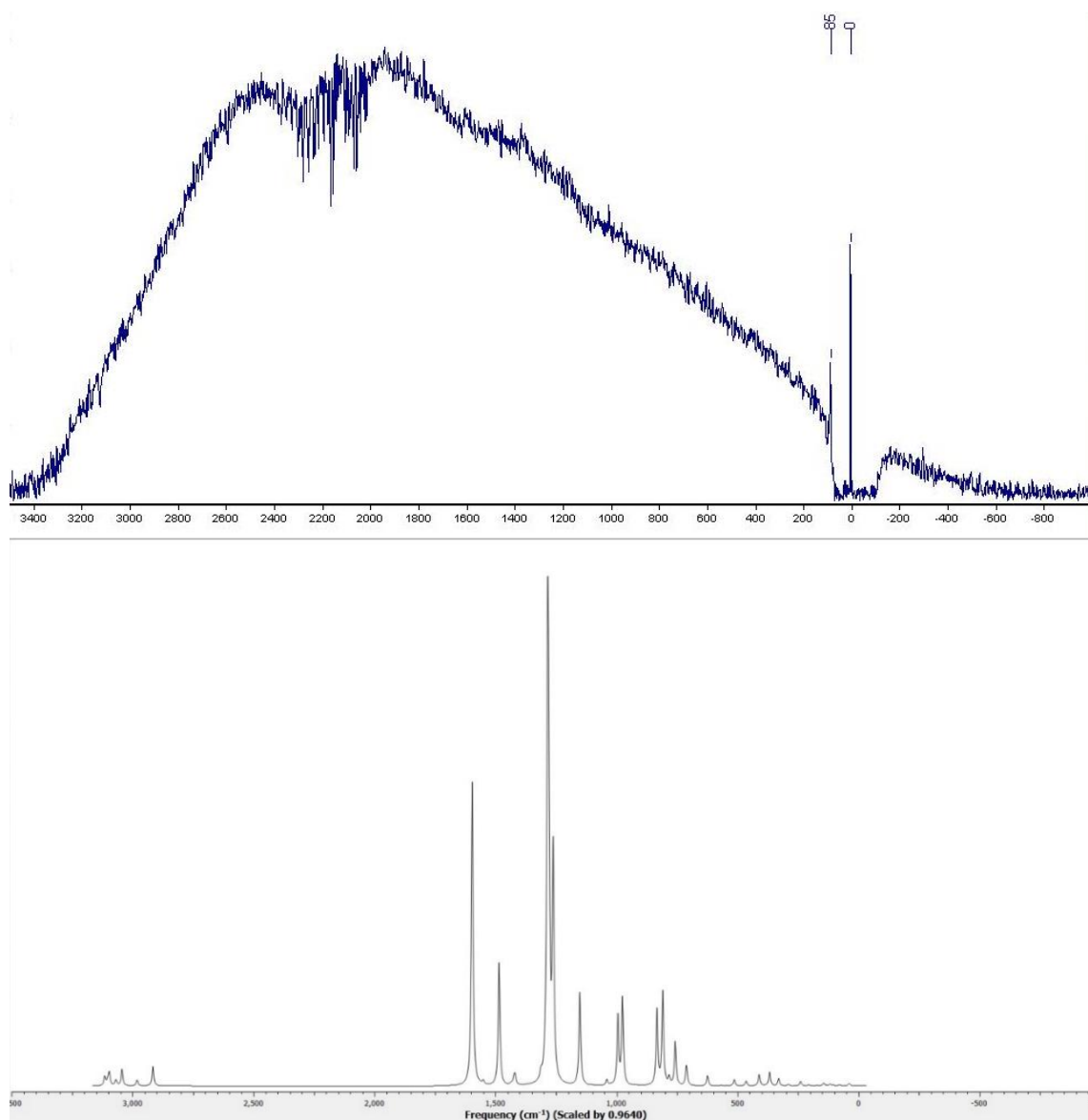


Figure C.13. Experimental (top) and simulated (bottom) Raman spectra of **1** (top). Simulated spectrum was obtained from frequency calculation at B3PW91-D3BJ/def2TZVP. X-axis scaled by 0.964.

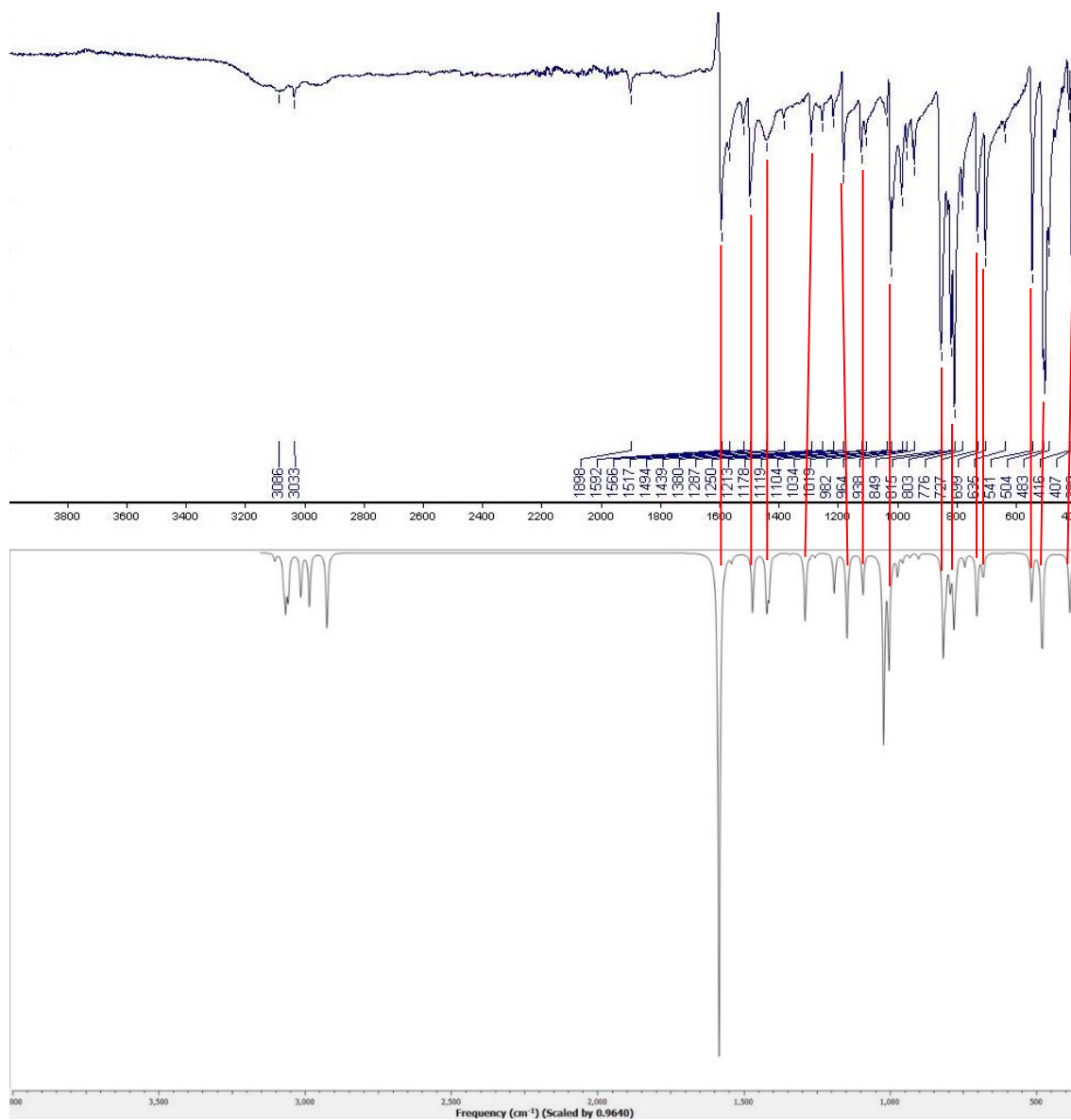


Figure C.14. Experimental (top) and simulated (bottom) FTIR spectra of **2** (top) with correlation lines drawn between simulated and experimental peaks. Simulated spectrum was obtained from frequency calculation at B3PW91-D3BJ/def2TZVP. X-axis scaled by 0.964.

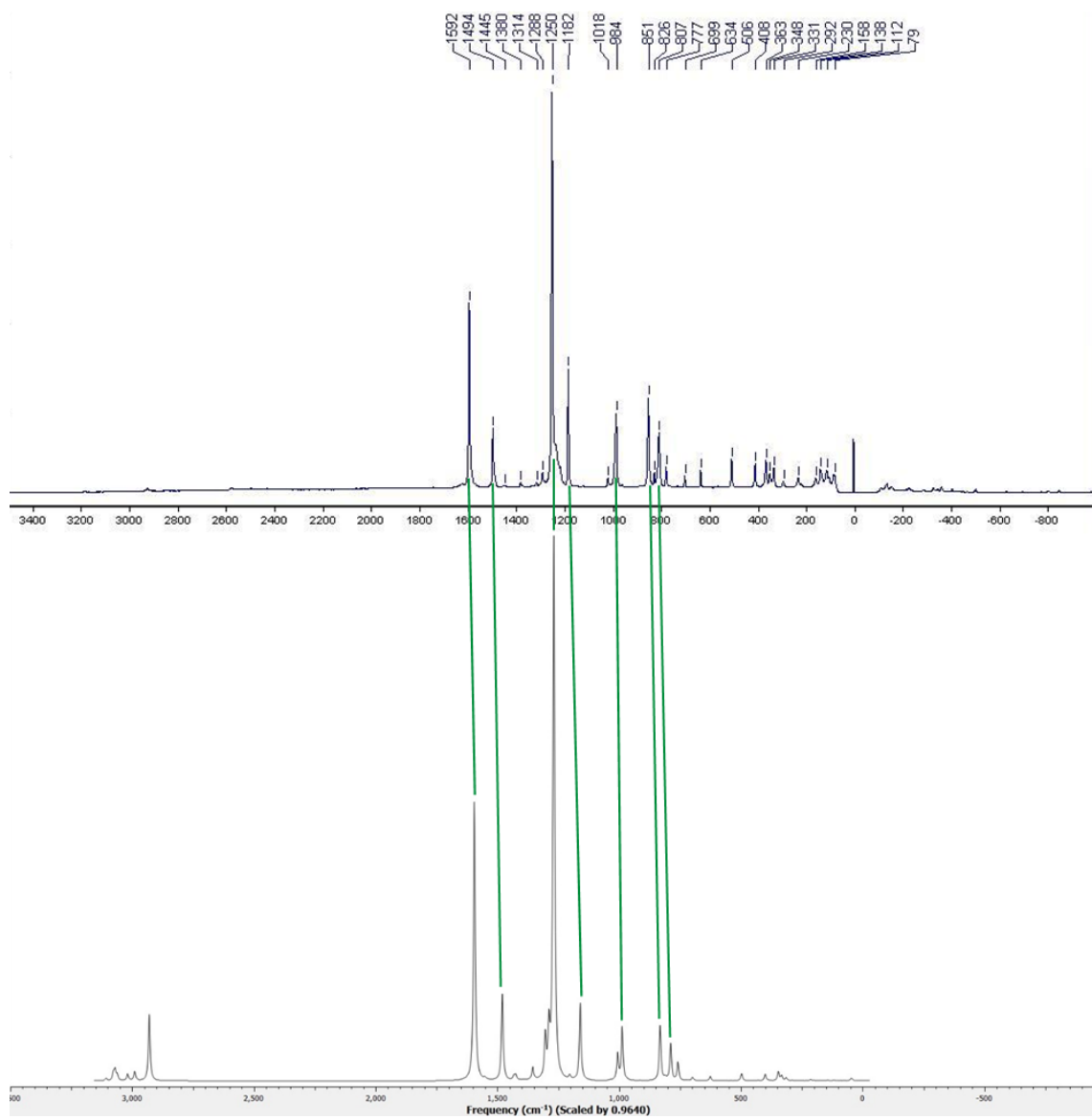


Figure C.15. Experimental (top) and simulated (bottom) Raman spectra of **2** (top) with correlation lines drawn between simulated and experimental peaks. Simulated spectrum was obtained from frequency calculation at B3PW91-D3BJ/def2TZVP. X-axis scaled by 0.964.

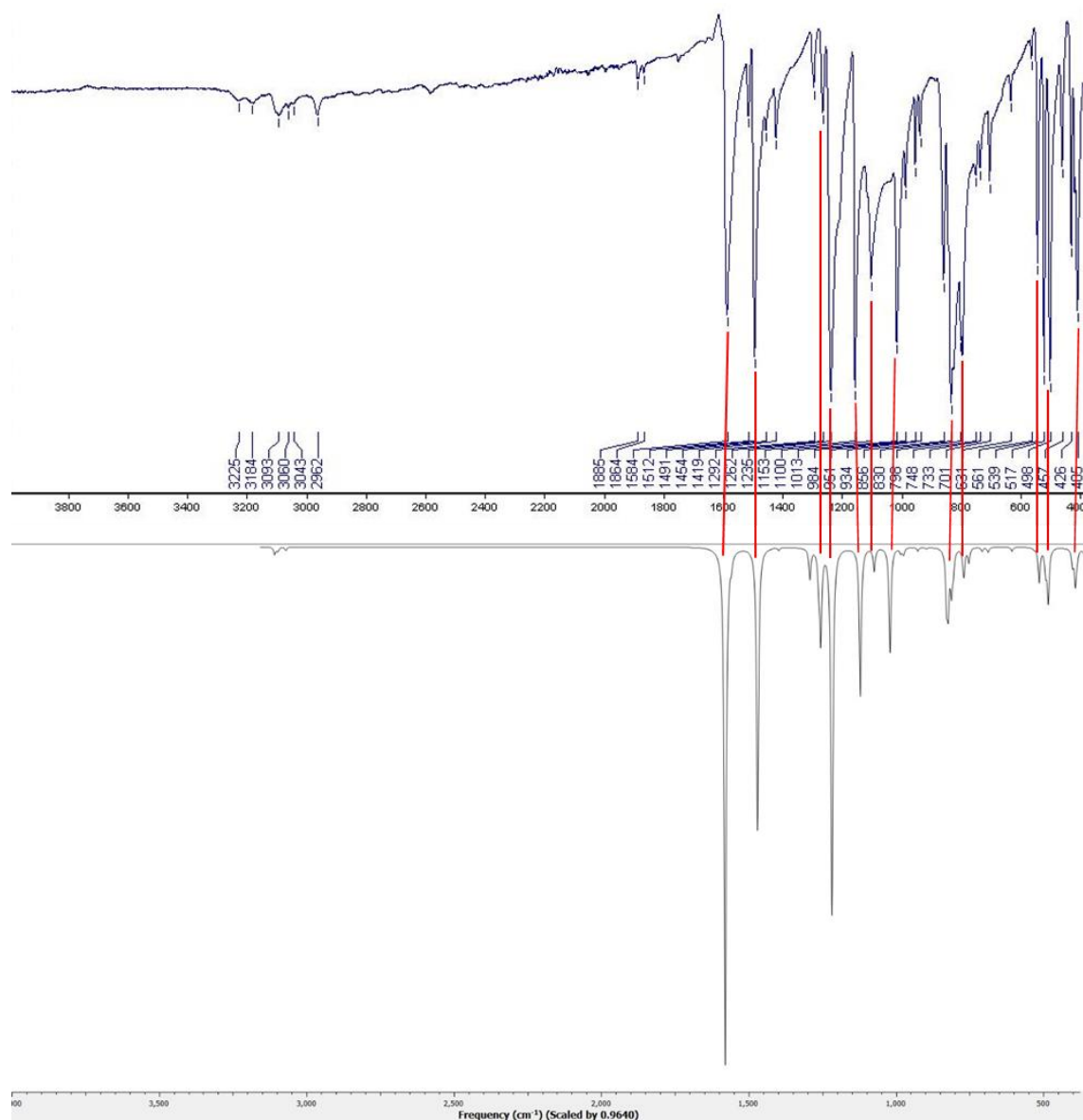


Figure C.16. Experimental (top) and simulated (bottom) FTIR spectra of **3** (top) with correlation lines drawn between simulated and experimental peaks. Simulated spectrum was obtained from frequency calculation at B3PW91-D3BJ/def2TZVP. X-axis scaled by 0.964.

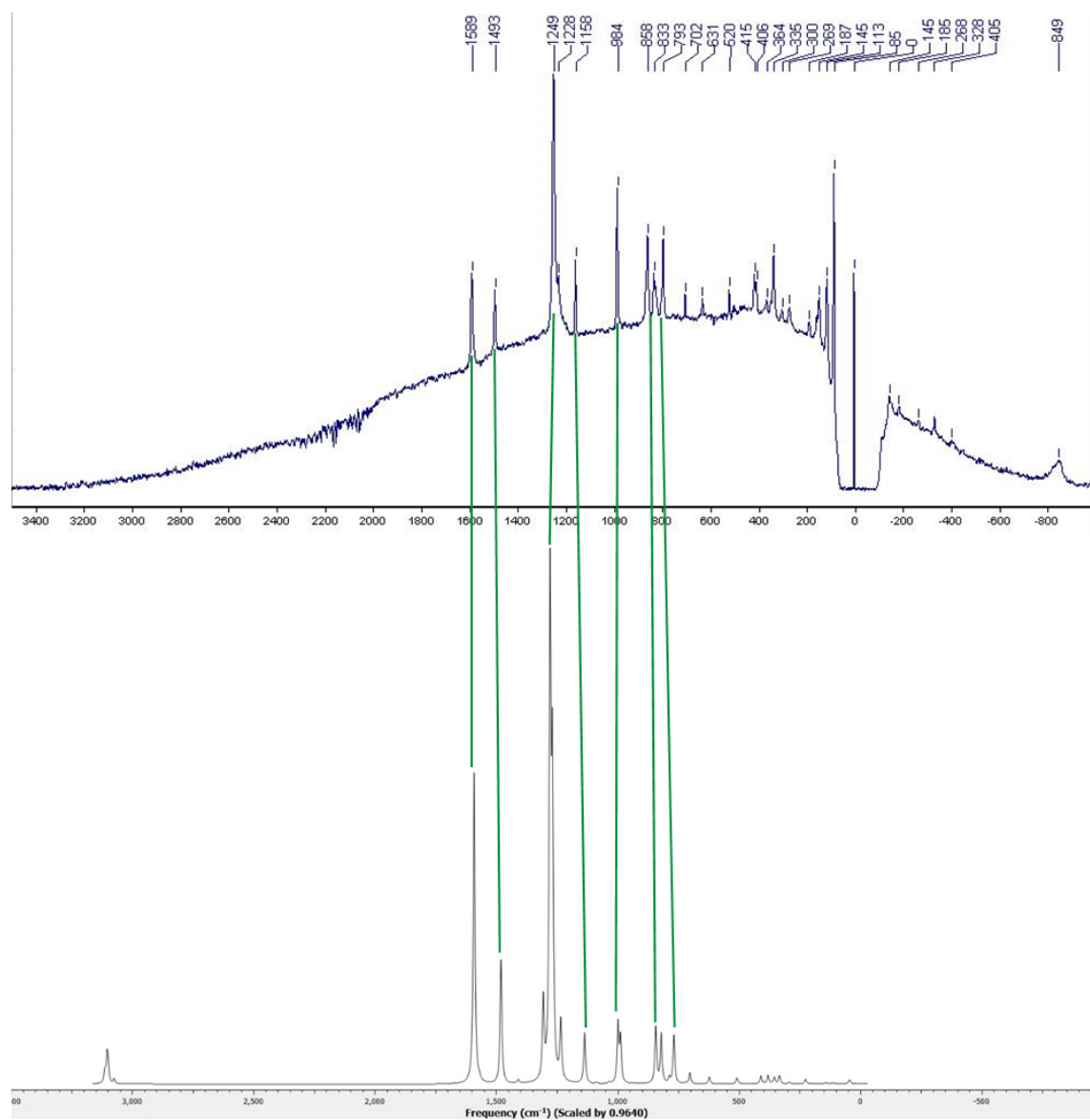


Figure C.17. Experimental (top) and simulated (bottom) Raman spectra of **3** (top) with correlation lines drawn between simulated and experimental peaks. Simulated spectrum was obtained from frequency calculation at B3PW91-D3BJ/def2TZVP. X-axis scaled by 0.964.

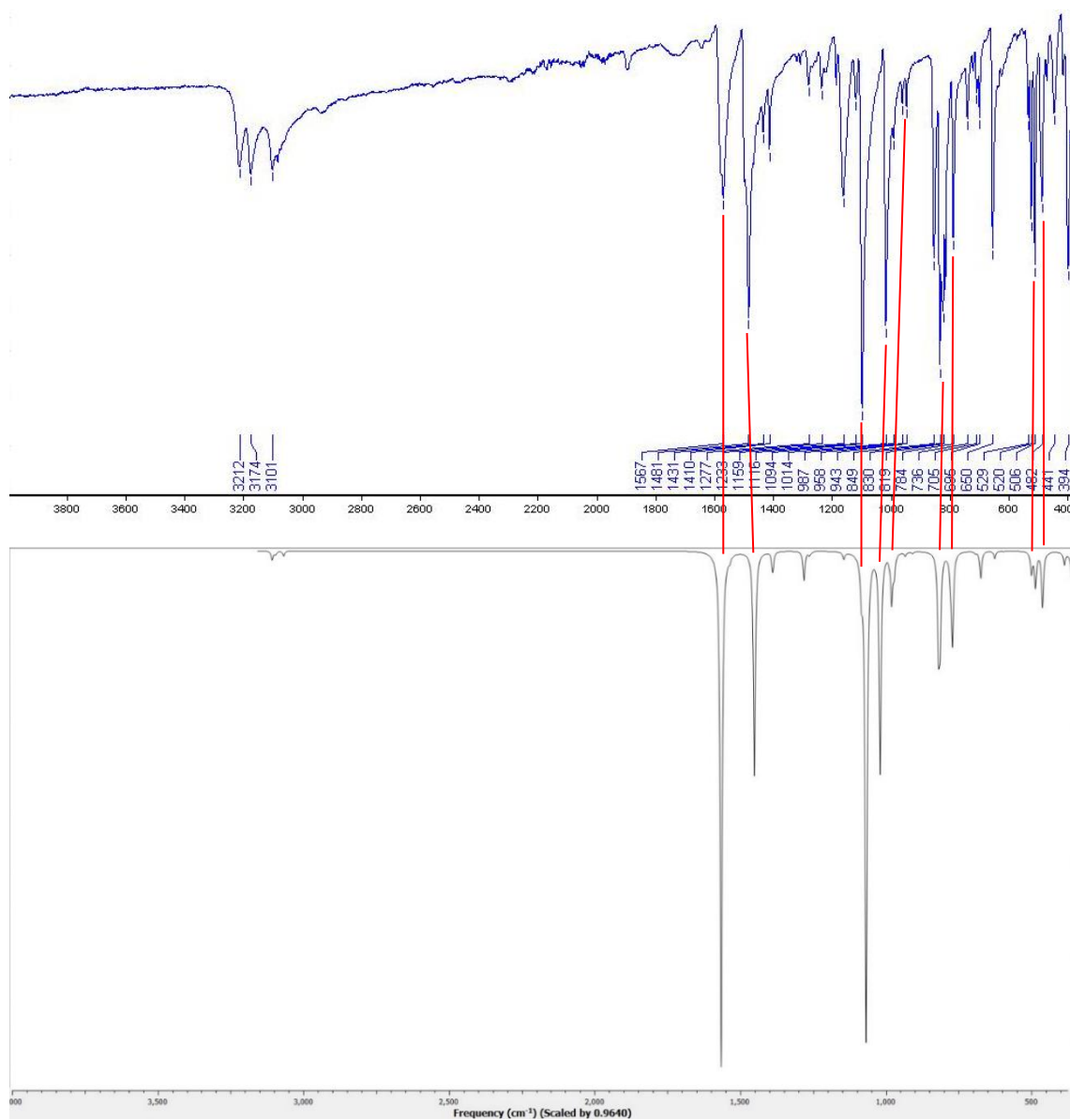


Figure C.18. Experimental (top) and simulated (bottom) FTIR spectra of **4** (top) with correlation lines drawn between simulated and experimental peaks. Simulated spectrum was obtained from frequency calculation at B3PW91-D3BJ/def2TZVP. X-axis scaled by 0.964.

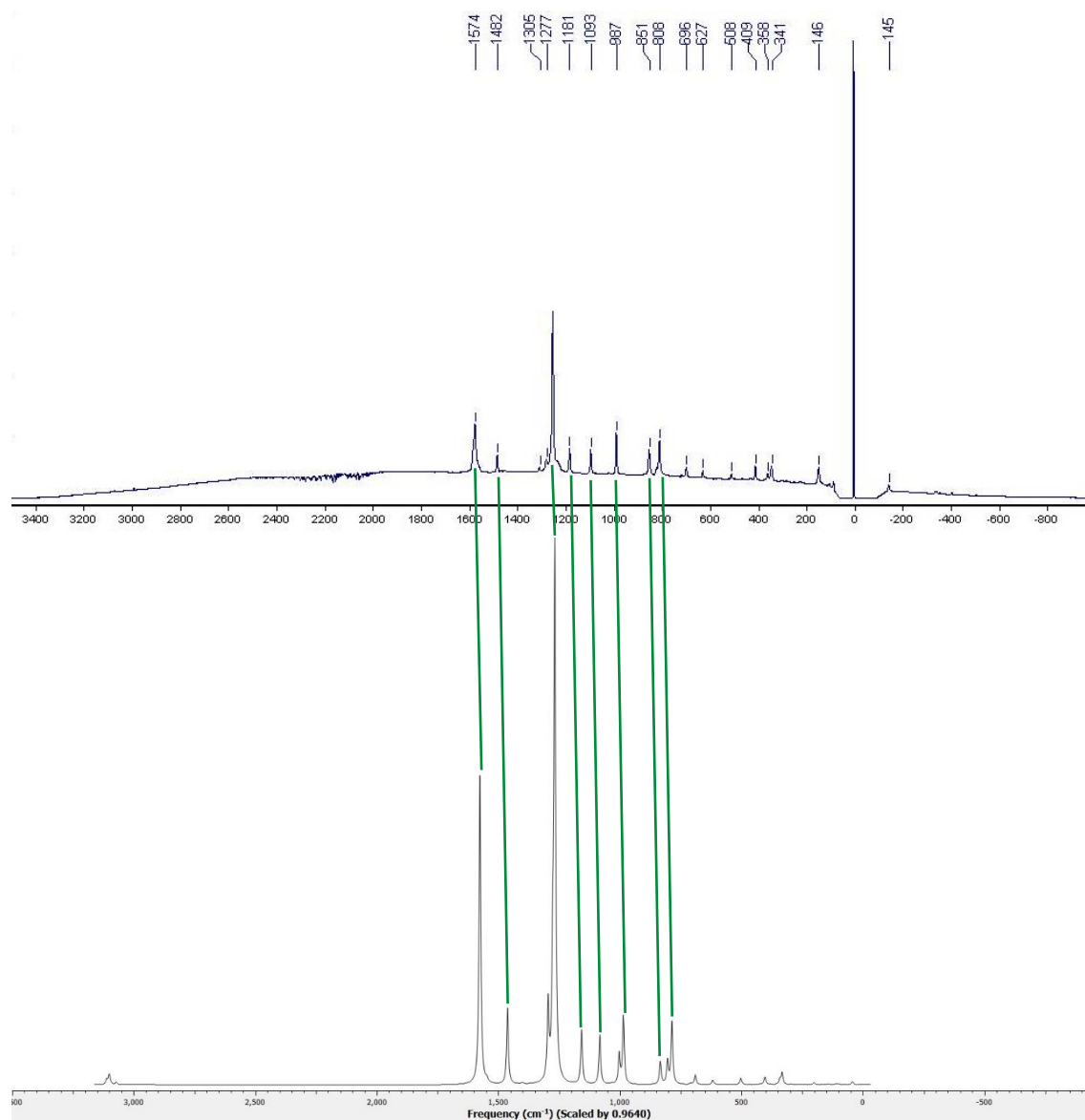


Figure C.19. Experimental (top) and simulated (bottom) Raman spectra of **4** (top) with correlation lines drawn between simulated and experimental peaks. Simulated spectrum was obtained from frequency calculation at B3PW91-D3BJ/def2TZVP. X-axis scaled by 0.964.

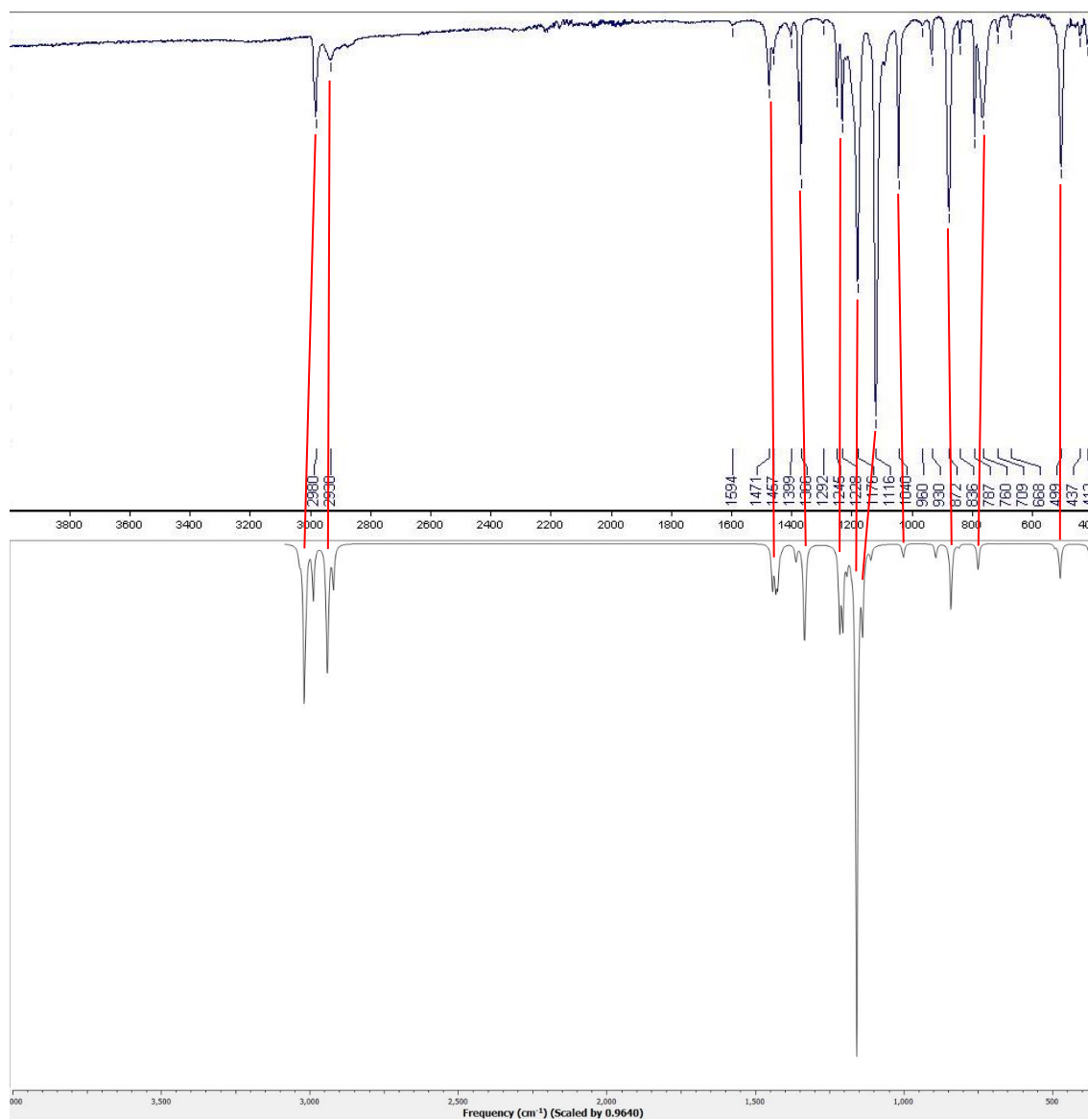


Figure C.20. Experimental (top) and simulated (bottom) FTIR spectra of 5 (top) with correlation lines drawn between simulated and experimental peaks. Simulated spectrum was obtained from frequency calculation at B3PW91-D3BJ/def2TZVP. X-axis scaled by 0.964.

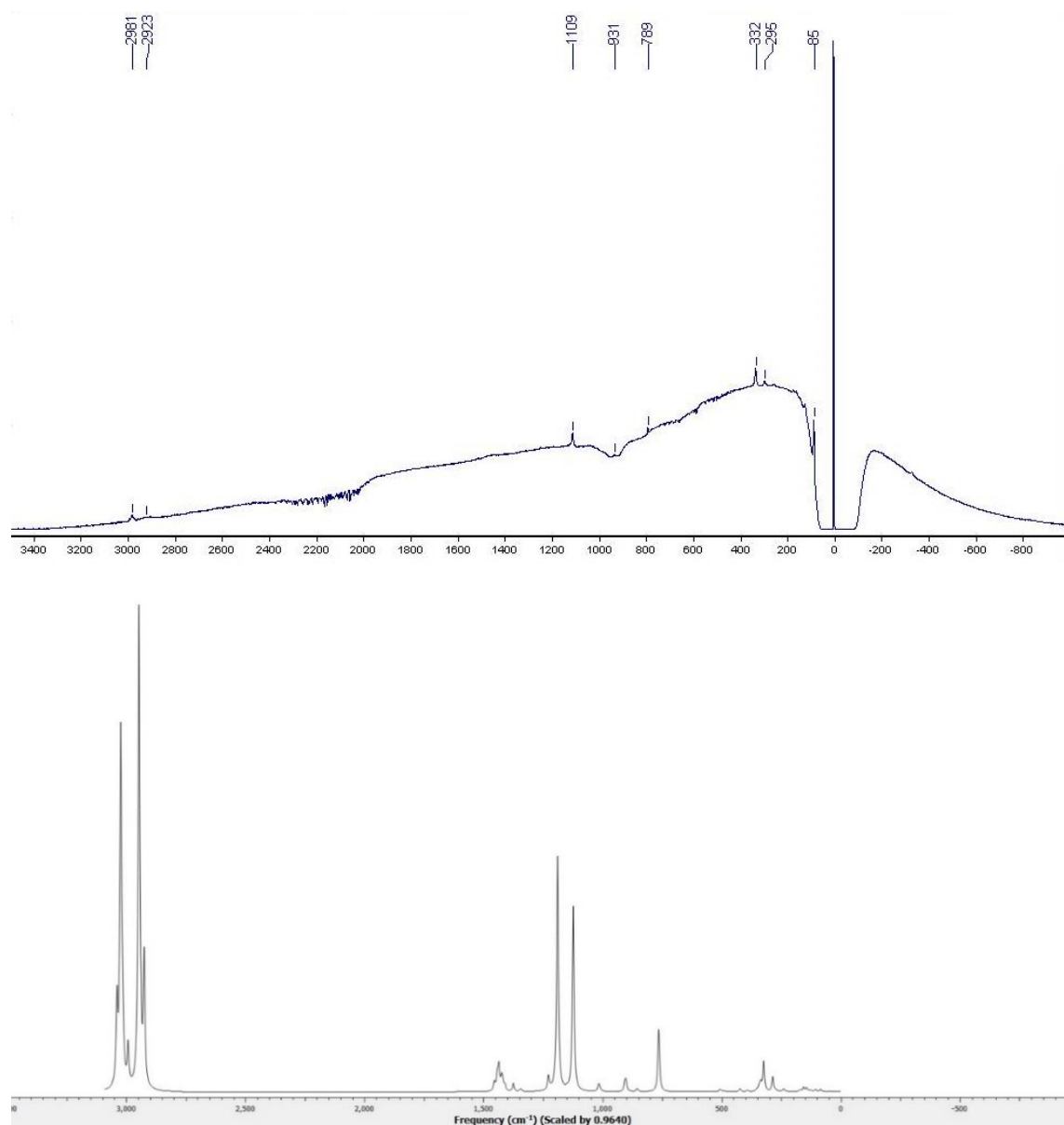


Figure C.21. Experimental (top) and simulated (bottom) Raman spectra of **5** (top). Simulated spectrum was obtained from frequency calculation at B3PW91-D3BJ/def2TZVP. X-axis scaled by 0.964.

C.7. Solution Speciation from NMR Evidence

^{119}Sn NMR was a vital tool in identifying the presence of $\text{Cl}_4\text{Sn}(\text{NCMe})_2$ in solution, which led to the deduction that **1-5** are subject to a ligand exchange equilibrium in acetonitrile. There is only one other report of the ^{119}Sn NMR signal of $\text{Cl}_4\text{Sn}(\text{NCMe})_2$ from Lassigne in 1977,^[17] which assigns it to -775 ppm (after reversing the sign to follow current IUPAC convention), a considerable difference of 92 ppm from our data. After taking exhaustive scans across much of the frequency range of ^{119}Sn NMR and finding no other signals present, and verifying our SnMe_4 reference against the well known -150 ppm signal of neat SnCl_4 (Figure C.74),^[18-20] we are confident in asserting that our assignment of the -683 ppm signal to $\text{Cl}_4\text{Sn}(\text{NCMe})_2$ is correct. Depending on how Lassigne truncated their spectral windows, it is possible that they ran into issues with signal folding, which could account for the difference between their assignment and ours. Differences in spectrometer frequency (15 MHz vs 261 MHz) and the dependence of ^{119}Sn NMR chemical shift on concentration (noted by Hunter^[21]) were also noted, but were not considered sufficiently explanatory. It may be that the disparity is due to a combination of multiple issues, or another factor that we have not considered. The possibility of signal folding remains the most likely cause, in our opinion.

The concentration-dependence of the ligand exchange equilibrium was demonstrated by running low-concentration and saturated NMR samples of **1-5** and comparing the ratios between the ^{119}Sn NMR signals for Sn-SDI and $\text{Sn}(\text{NCMe})_2$ from each concentration, detailed in Table C.26 and Figure C.22 below (Table C.26 repeats Table 5.3 for the reader's convenience).

Table C.26. ^{119}Sn NMR^a chemical shifts and integration ratios of 1–5 and other relevant compounds.

Cmpd	δ (ppm)	ratio (low conc/sat'd.) ^b
1	-615	1:3 / 1:2
2	-617	1:4 / 1:3.5
3	-616	1:8 / 1:6
4	-618	1:3 / 8:1
5	-563	1:1.5 / 4:1
$\text{Cl}_4\text{Sn}(\text{NCMe})_2$	-683	
SnCl_4 (neat)	-150	

^a In CD_3CN ; ^{119}Sn spectra are referenced to external SnMe_4 (90% in C_6D_6) at 0.0 ppm.

^b Approximate integration ratio of high frequency peak (Sn-coordinated SDI) to low frequency peak ($\text{Cl}_4\text{Sn}(\text{NCMe})_2$) in low concentration and saturated samples.

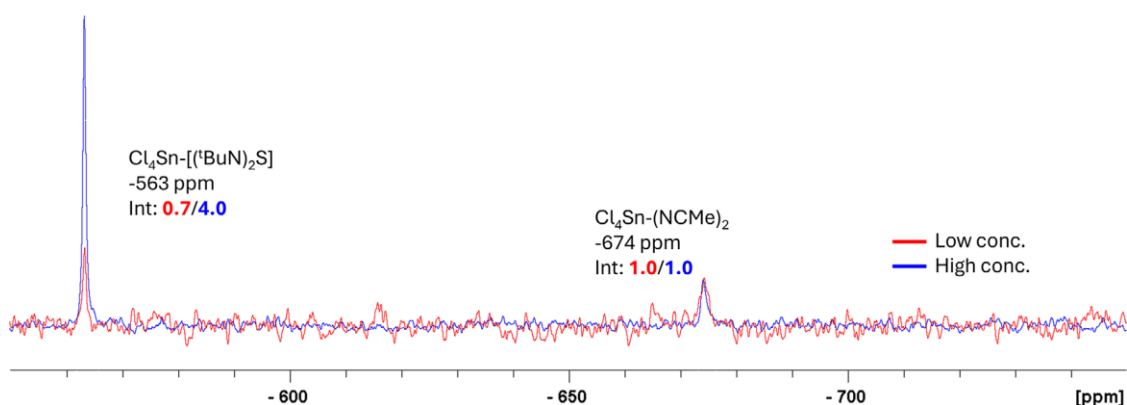


Figure C.22. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra of 5, overlay of low conc. (red trace) and high conc. (blue trace), showing difference in ratio between Sn-SDI complex (left, -563 ppm) and $\text{Sn}(\text{NCMe})_2$ complex (right, -675 ppm).

Farcasiu *et al.* studied $\text{SnCl}_4\text{-(Et}_2\text{O)}_n$ ($n = 1\text{--}2$) complexes, which bear similarities to the $\text{SnCl}_4\text{-(NCMe)}_n$ system.^[22] They observed incomplete complexation of SnCl_4 with Et_2O , which was dependent on both temperature and relative concentrations of SnCl_4 and Et_2O . They show that SnCl_4 is not a sufficiently strong Lewis acid to shift complexation equilibria fully towards complex (in the case of their $\text{SnCl}_4/\text{Et}_2\text{O}$ system), which implies that competition of Lewis bases of similar basicity may be facile by ligand displacement. This study differs from our system significantly in that they were working with well-defined ratios of $\text{SnCl}_4\text{:Et}_2\text{O}$ in a non-coordinating solvent, dichloromethane, whereas our experiments were done in acetonitrile due to solubility limitations in other solvents. Farcasiu assigns a peak at -579 ppm to a 1:1 $\text{Cl}_4\text{Sn-OEt}_2$ complex. While the strong influence of coordination number on ^{119}Sn chemical shifts would make this a more normative range for a

hexacoordinated species,^[23-28] Farcasiu makes convincing arguments in favour of their assignment.

Compound **4** is vastly more soluble in acetonitrile than the other complexes, and so perhaps unsurprisingly sees the most dramatic differences between the low- and high-concentration samples, especially when comparing ^{119}Sn NMR spectra. At low concentration, it is substantially similar to **1-3** and **5**, containing two signals from $\text{Cl}_4\text{Sn-SDI}$ and $\text{Cl}_4\text{Sn}(\text{NCMe})_2$. However, at high concentration the latter signal broadens and shifts to slightly higher frequency compared to a low-concentration sample ($\Delta\delta \approx 3$ ppm; Figure C.23, red trace), and an additional low-intensity tin peak appears at -579 ppm, conspicuously similar to a 5-coordinate Sn(IV) species in Farcasiu's work discussed above. Low-temperature NMR spectra of **4** were acquired at 263 K and 233 K, and there are several noteworthy changes, illustrated in Figure C.23. The broad $\text{Sn}(\text{NCMe})_2$ peak (-679 ppm) shifts to lower frequency and splits into two equal-intensity peaks. These are assigned to the *cis* and *trans* isomers, which seem in other Sn-SDI cases at room temperature to coalesce, consistent with Knight and Merbach's investigation of Cl_4SnL_2 *cis/trans* isomerization where $\text{L} = \text{Me}_2\text{S}$.^[29] Both of these signals are shifted to lower frequency relative to the broad peak, whereas the peak at -579 ppm shifts to higher frequency. No other significant peak shifts take place, and this leads us to believe that the -579 peak is likely a five-coordinate species in equilibrium with the -680 peaks, which would be a mono-acetonitrile complex, $\text{Cl}_4\text{Sn-NCMe}$, consistent with Farcasiu's work with $\text{Sn-Et}_2\text{O}$ complexes.^[22] These signals are separated by approximately 115 ppm, which is a reasonable change in chemical shift between a five- and six-coordinate tin species.^[23-24]

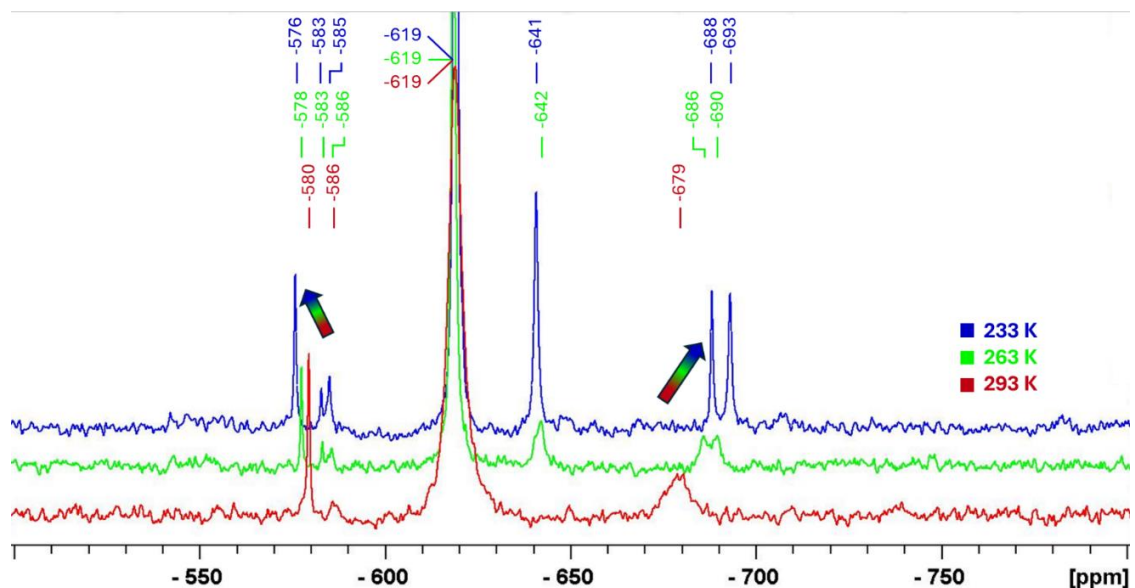


Figure C.23. ^{119}Sn NMR spectra of saturated samples of **4** at room temperature (red trace), 263 K (green trace), and 233 K (blue trace). Spectra are vertically offset for clarity, but keep the same ppm scale (x-axis) for accurate comparison.

At both 263 and 233 K, a new signal appears around -640 ppm, intermediate between the signals for the $\text{Cl}_4\text{Sn-SDI}$ and $\text{Cl}_4\text{Sn-(NCMe)}_2$ complexes. The signal is broad and fairly low-intensity at 263 K, becoming quite sharp and well resolved at 233 K. We do not have a confident assignment of this species, but considering the dramatically narrower FWHM of the $\text{Cl}_4\text{Sn-SDI}$ peak at low temperature (1050 Hz @ RT, 350 Hz @ 263 K, 177 Hz @ 233 K), we suggest that this may show the displacement of one end of the bidentate SDI ligand by acetonitrile, resulting in a complex like $\text{Cl}_4\text{Sn}(\kappa^1\text{-N-4})(\text{NCMe})$. Alternatively, it is conceivable that this could be something like $[\text{Cl}_5\text{Sn-NCMe}]$. Lastly, there are two peaks around -585 ppm, present at all three temperatures, which are very close together at RT and split further apart at 263 and 233 K. The identity of these species are unknown. Given the small splitting of these peaks at low temperatures, and that they do not seem to correlate with other identified species, it is possible that this is a Cl_4Sn species with monodentate ligands in a *cis/trans* isomerization, or perhaps a $[\text{Cl}_5\text{Sn}]^-$ species in a trigonal bipyramidal $\leftrightarrow$ square pyramidal isomerization.

Recognition of the concentration-dependent equilibrium proved extremely useful in identifying signals in ^1H and ^{13}C NMR spectra, allowing us to differentiate between Sn-coordinated SDI (e.g. C1), free SDI (e.g. L1), and other species. An example of the side-by-side comparison of low- and high-concentration spectra used to confer assignments is provided below in Figure C.24.

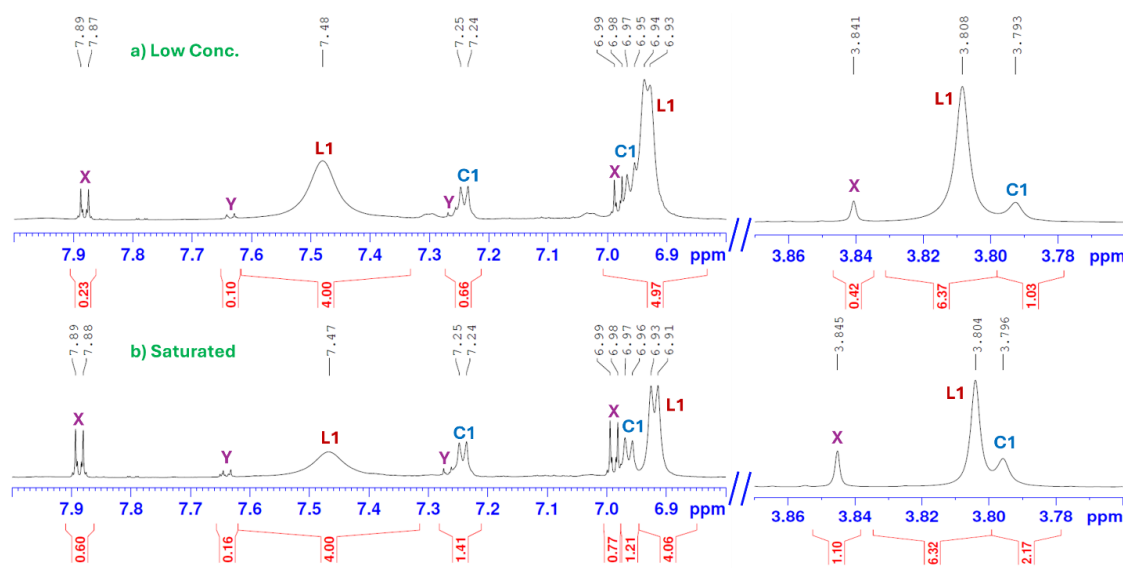
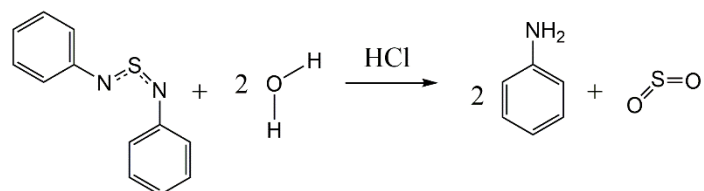
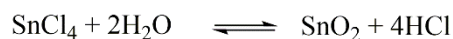


Figure C.24. Side-by-side comparison of ^1H NMR spectra of a) low concentration and b) saturated samples of C1 in CD_3CN , referenced to residual solvent at 1.94 ppm. As specified in Table 5.4, signals marked C1 are from Cl_4Sn -coordinated $(4\text{-MeOPhN})_2\text{S}$, and L1 are from free $(4\text{-MeOPhN})_2\text{S}$. X and Y are unknown species.

As evidenced in ^1H NMR experiments, all samples of **1**–**5** contained at least one species in addition to Sn-coordinated SDI and free SDI. In the case of **3**, this species was positively identified as 4-FPhNSO. The most likely source is incomplete purification during the synthesis of the corresponding SDI, $(4\text{-FPhN})_2\text{S}$, in which 4-FPhNSO is an intermediate of one of the viable synthesis routes.^[7] In the remaining compounds, the unidentified species does not fit well to the corresponding -NSO, and we suspect a hydrolysis product is more likely. Tin(IV) halides are known to be highly sensitive to hydrolysis,^[26, 30–31] releasing HCl which will readily decompose sulfur diimides by protonation of nitrogen followed by nucleophilic attack at sulfur.^[32–34] Appel determined the major products of acidic hydrolysis of aliphatic sulfur diimides to be the corresponding amines and sulfur dioxide, a mechanism which is likely operative in aryl SDI analogs as in Scheme C.1 below.



Scheme C.1. Hydrolysis of SnCl_4 , and subsequent acid-catalyzed hydrolysis of an aryl sulfur diimide

1 and **2** contained an unidentified species of significant integration (50 – 80% vs. coordinated SDI, ~10% overall), which qualitatively fits the profile of a (4-RPh)- fragment. Its methyl and aromatic peaks are not a good fit for either the aniline (4-RPhNH₂) or N-sulfinylaniline (4-RPhNSO). In the case of **1**, the unidentified species has peaks at 3.85 (CH₃, s), 6.90 (Ar-H, d), and 7.89 (Ar-H, d). By contrast, the ¹H spectrum of the parent aniline has signals at 3.34 (NH₂, bs), 3.76 (CH₃, s), 6.66 (Ar-H, d), and 6.76 (Ar-H, d), and the N-sulfinylaniline's spectrum is 4.20 (CH₃, s), 7.20 (Ar-H, d), and 8.20 (Ar-H, d). One alternative possibility is that the unidentified species is the protonated aniline. Protonation of the NH₂ precludes delocalization of the nitrogen lone pair into the ring, significantly deshielding the *ortho*-H and moderately deshielding the *meta* positions, which could match well with the observed shifts, and is consistent with Naudin et al., who characterized anilinium tetrafluoroborate.^[35] This tentative assignment has one issue, in that there is not a clear signal corresponding to NH₃⁺, which should be found around 8 ppm according to Naudin. However, there are a number of examples of this and other protonated anilines, mostly hydrochloride adducts, whose ¹H NMR spectra were obtained in various solvents (methanol-*d*₄, CDCl₃, DMSO-*d*₆), and the NH₃⁺ peaks were reported around 10.4 ppm, or not reported/detected,^[36-38] indicating that the chemical shift and ability to detect the NH₃⁺ signal may be highly dependent on solvent and chemical environment. In all Sn-arylSDI ¹H spectra, there is a broad singlet found at 6.6 – 6.8 ppm for which we do not have a confident assignment.

All ^1H NMR spectra collected contain a 1:1:1 triplet ($J = 52.5$ Hz), strongly indicative of ^1H - ^{14}N coupling. The triplet is found between 5.8 – 5.9 ppm in **1** – **4** (*extremely* small), and at 6.18 ppm in **5** (small, but *much* larger than in **1** – **4**). These closely resemble protonated polyanilines,^[39-40] as well as NH_4^+ salts.^[33, 41] The triplet is found around 7 ppm in most reported cases, but Haas found their NH_4^+ peaks at ~ 5.6 ppm. Acetonitrile can polymerize/oligomerize in acidic conditions, which are expected in solution due to HCl present, but are even more likely with Lewis acids like ZnCl_2 and TiCl_4 ,^[42] and presumably SnCl_4 . So, these triplets could potentially be some protonated polynitrile, which could conceivably incorporate SDIs. Almost certainly these triplets would arise from protonated nitrogens, since NH^+ protons exchange much slower than neutral NH .^[39] In an effort to narrow the candidate explanations for these triplets, we dissolved samples of 4-bromoaniline, *bis*(4-bromophenyl)sulfurdiimide, and 4-methylaniline in dichloromethane, acidified each with an excess of concentrated HCl, and obtained ^1H NMR of the resulting solid anilinium salts in CDCl_3 and in CD_3CN . Also of relevance is a sample of $\text{Cl}_4\text{Sn}(\text{NCMe})_2$ made by adding acetonitrile to tin tetrachloride from an old bottle with no septum which has been repeatedly exposed to atmosphere, and thus expected to contain HCl as a byproduct of reaction with water vapour. The 1:1:1 triplet under investigation was not observed in any spectra in CDCl_3 , but was present in all CD_3CN spectra, always with the same coupling constant. Notably, the chemical shift of the triplet varied from 6.8 – 6.9 ppm in the acidified anilines, to 6.3 ppm in the acidified SDI, to 5.8 ppm in a sample of $\text{Cl}_4\text{Sn}(\text{NCMe})_2$, indicating a considerable variability of the chemical shift based on other species in solution. The presence of the triplet only in samples using CD_3CN as a solvent, and irrespective of the presence of aniline or SDI, leads us to suggest the most likely identity is a protonated nitrile or polynitrile originating from solvent.

The ^1H NMR spectrum of **5** (Figure C.63) contains a sharp, low-intensity peak at 7.58 ppm with satellites at 214 Hz, indicative of a $^2J(^1\text{H}\text{-}^{119}\text{Sn})$ coupling.^[43] This seems likely to be a peak from a Sn-OH fragment, such as in $\text{Cl}_3(\text{OH})\text{Sn-L}$.

There are two unidentified peaks in the methyl region of the ^1H NMR spectrum of 5 at 1.35 and 1.40 ppm. From the 2D-HSQC experiment, Figure C.66, the 1.35 ppm peak is from a hydrogen connected to carbon, correlating to the 27.5 ppm ^{13}C NMR signal. The HSQC also showed that the 1.40 ppm ^1H peak is not connected to carbon, which combined with the broadened lineshape identifies it as an exchangeable proton. These signals are in approximately the correct chemical shift range to be *tert*-butylamine produced by hydrolysis, however the 1.40 ppm signal integrates 1:1.7 with the 1.35 ppm signal, which precludes such an assignment.

C.8. Possible Speciation Pathways of SnCl_4 Dissolved in Acetonitrile

Previous NMR studies have demonstrated that solutions of SnX_4 undergo facile halogen exchange with e.g. mixtures of $\text{SnCl}_4/\text{SnBr}_4$,^[19-20, 44] or SnCl_4 with $^n\text{Bu}_4\text{NCl}$ acting as a source of Cl^- .^[45] Solutions of SnCl_4 with neutral Lewis base ligands have been shown to undergo ligand exchange with either free ligand^[22, 46-47] or with solvent (this work). As such, a solution of SnCl_4 in acetonitrile can be expected to be in dynamic equilibrium even in unperturbed conditions. This has implications for voltammetric experiments on $\text{SnCl}_4/\text{CH}_3\text{CN}$ solutions, as a wide variety of species may be present or accessible, presenting myriad possibilities for E (electrochemical) or C (chemical) processes. Figure C.25 shows some of these possibilities and potential E-C pathways for various SnX_nL_m species. Many of these may be transitional states, and it is not known which paths may be stepwise or concerted, but several species are known and structurally confirmed as highlighted in the figure.

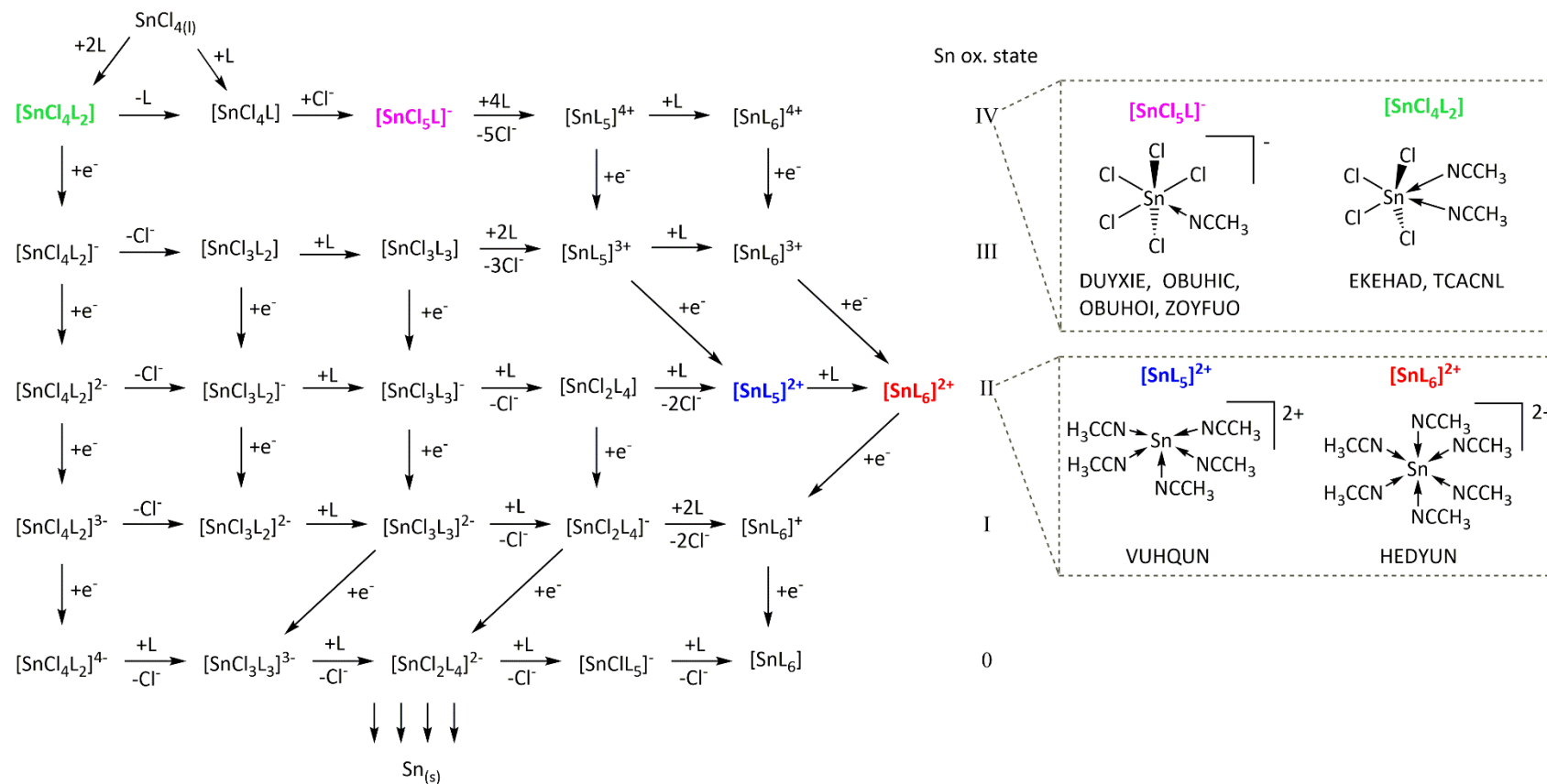


Figure C.25. Diagram of possible pathways in the redox speciation of SnCl_4 dissolved in CH_3CN ($\text{L} = \text{CH}_3\text{CN}$). C-steps are horizontal, E-steps are vertical. Structurally characterized species are colour-coded to the line structures on the right-hand side with CSD reftypes indicated.

C.9. Compilation of NMR Spectra

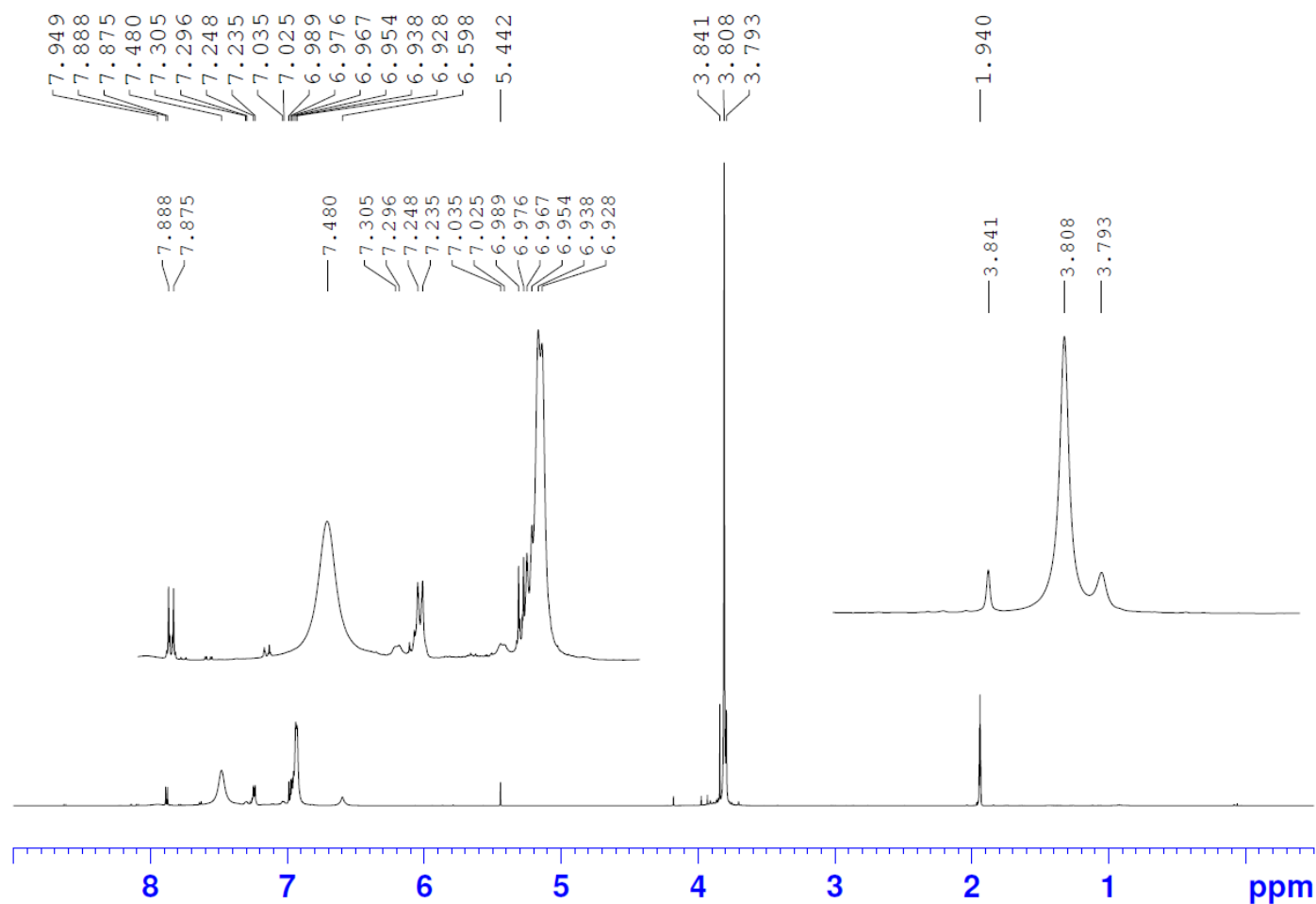


Figure C.26. ^1H NMR of **C1** in CD_3CN , low concentration, referenced to residual solvent at 1.94 ppm. As set out in Table 5.4, **C1** refers to a sample of the $\text{Cl}_4\text{Sn-L}$ complex (in the case of **C1**, $\text{L} = (4\text{-MeOPhN})_2\text{S}$) in acetonitrile solution. Likewise, **L1** will refer to a sample of only **L**.

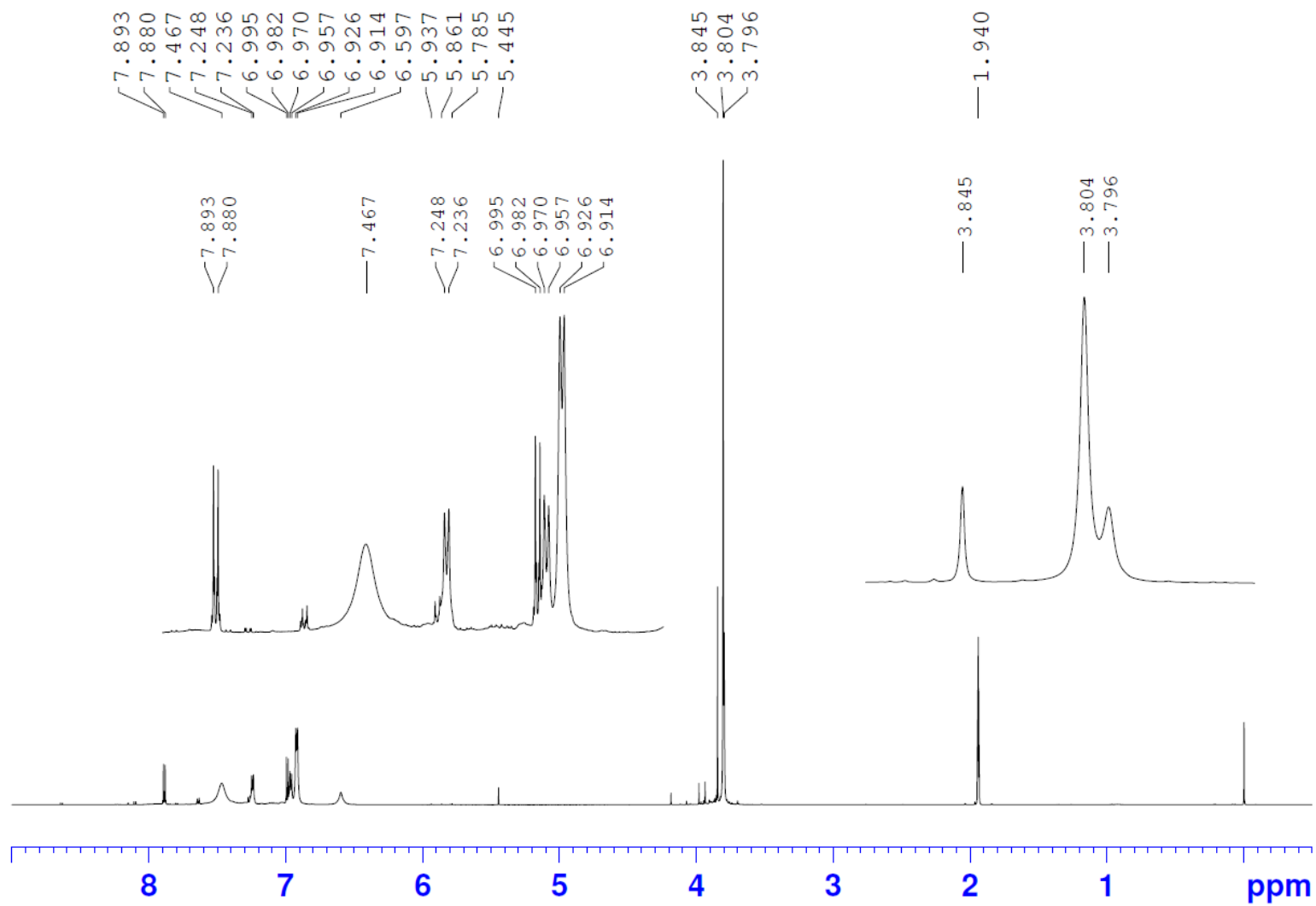


Figure C.27. ^1H NMR of C1 in CD_3CN , saturated, referenced to residual solvent at 1.94 ppm

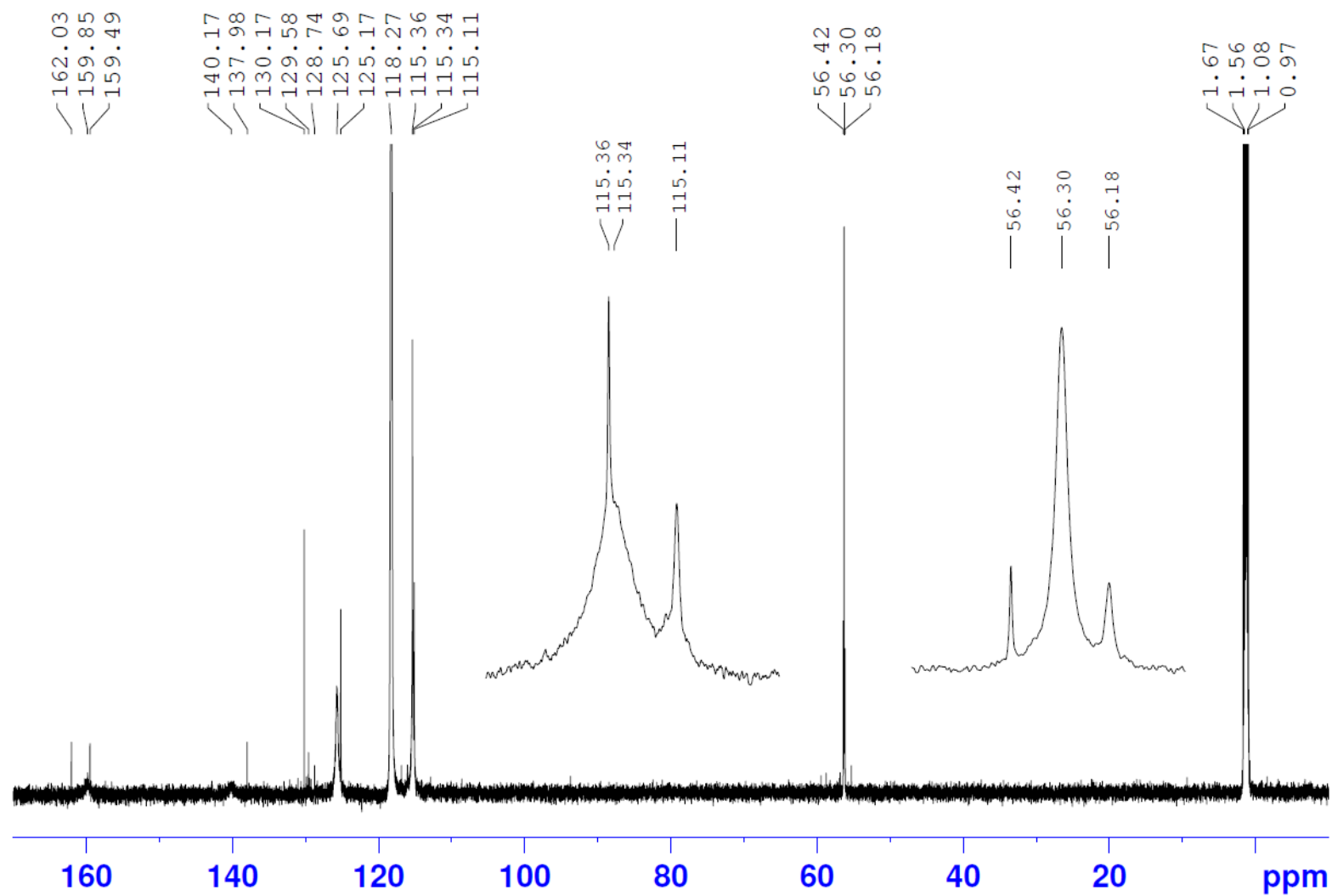


Figure C.28. $^{13}\text{C}\{^1\text{H}\}$ NMR of C1 in CD_3CN , low concentration, referenced to residual solvent at 1.32 ppm

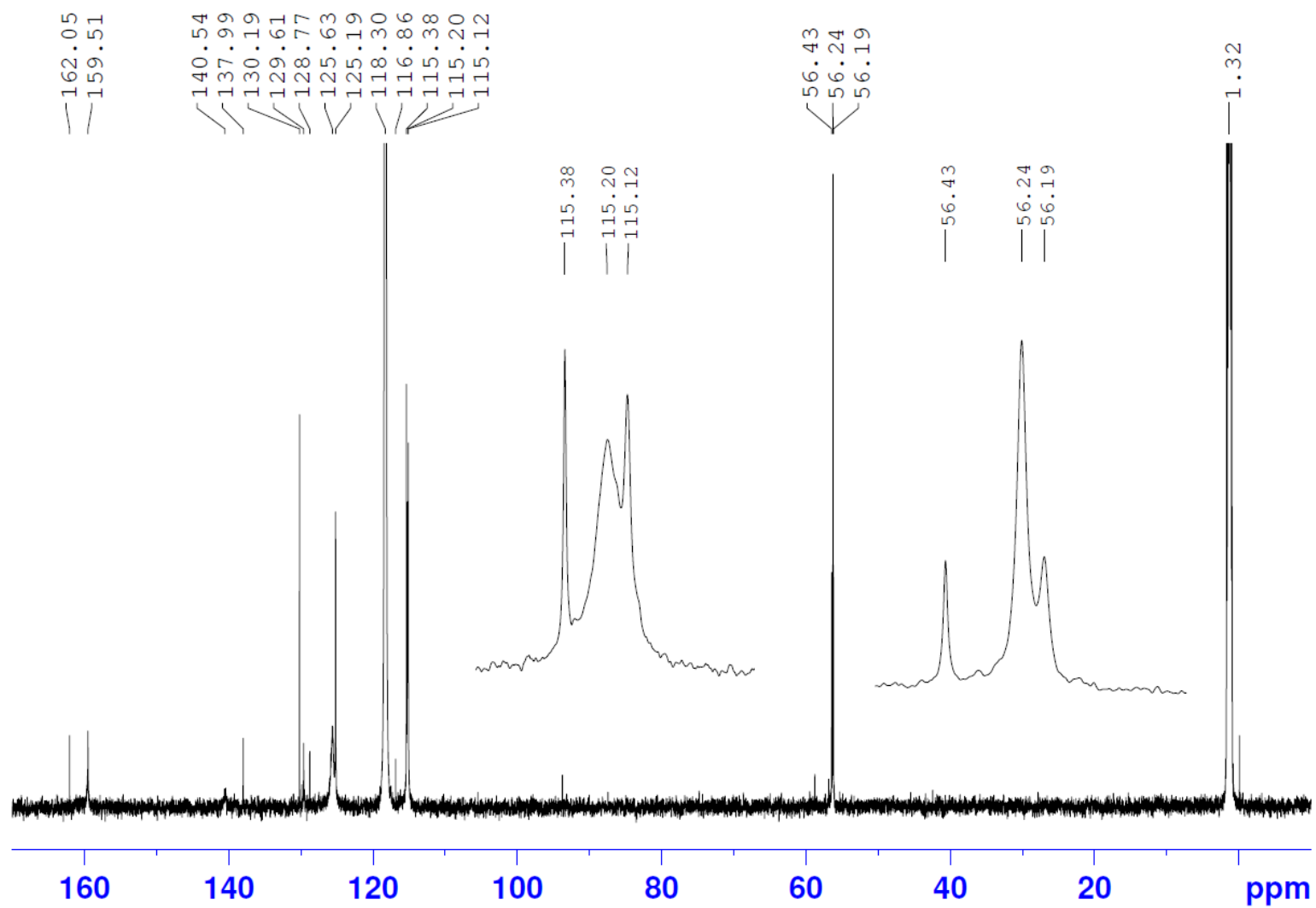


Figure C.29. $^{13}\text{C}\{^1\text{H}\}$ NMR of C1 in CD_3CN , saturated, referenced to residual solvent at 1.32 ppm

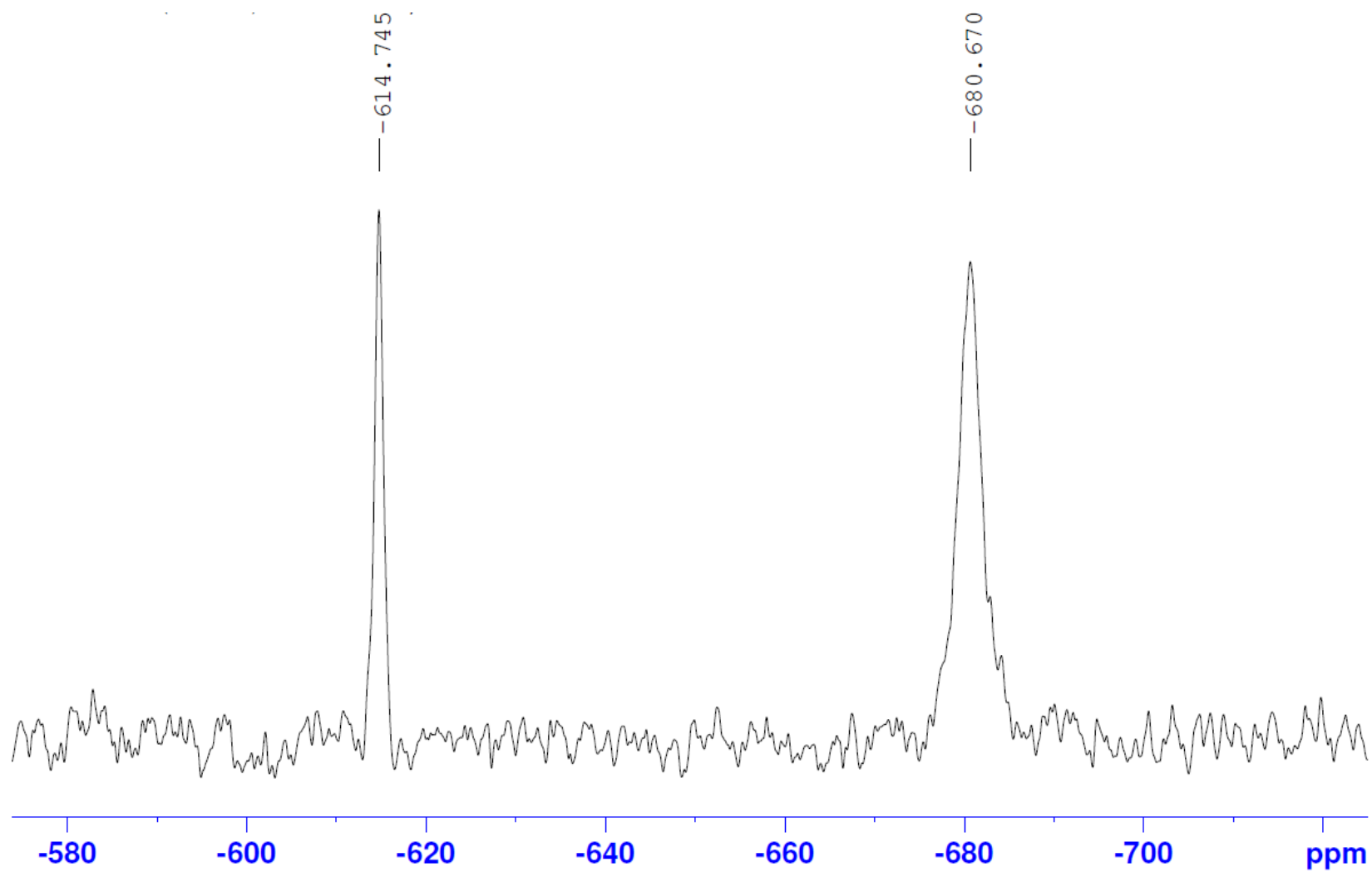


Figure C.30. ^{119}Sn NMR of C1 in CD_3CN , low concentration, referenced to external SnMe_4 at 0.0 ppm

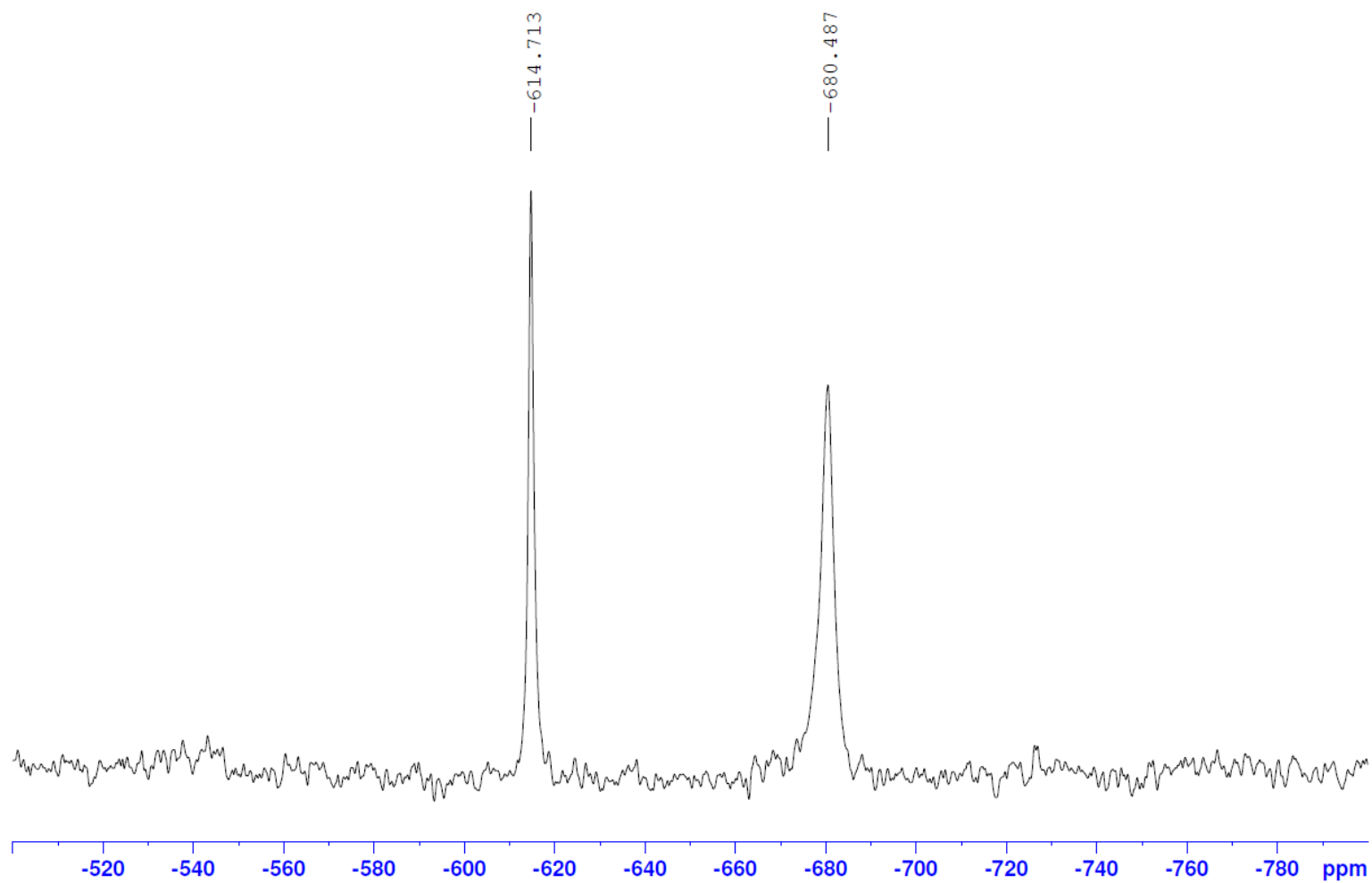


Figure C.31. ^{119}Sn NMR of **C1** in CD_3CN , saturated, referenced to external SnMe_4 at 0.0 ppm

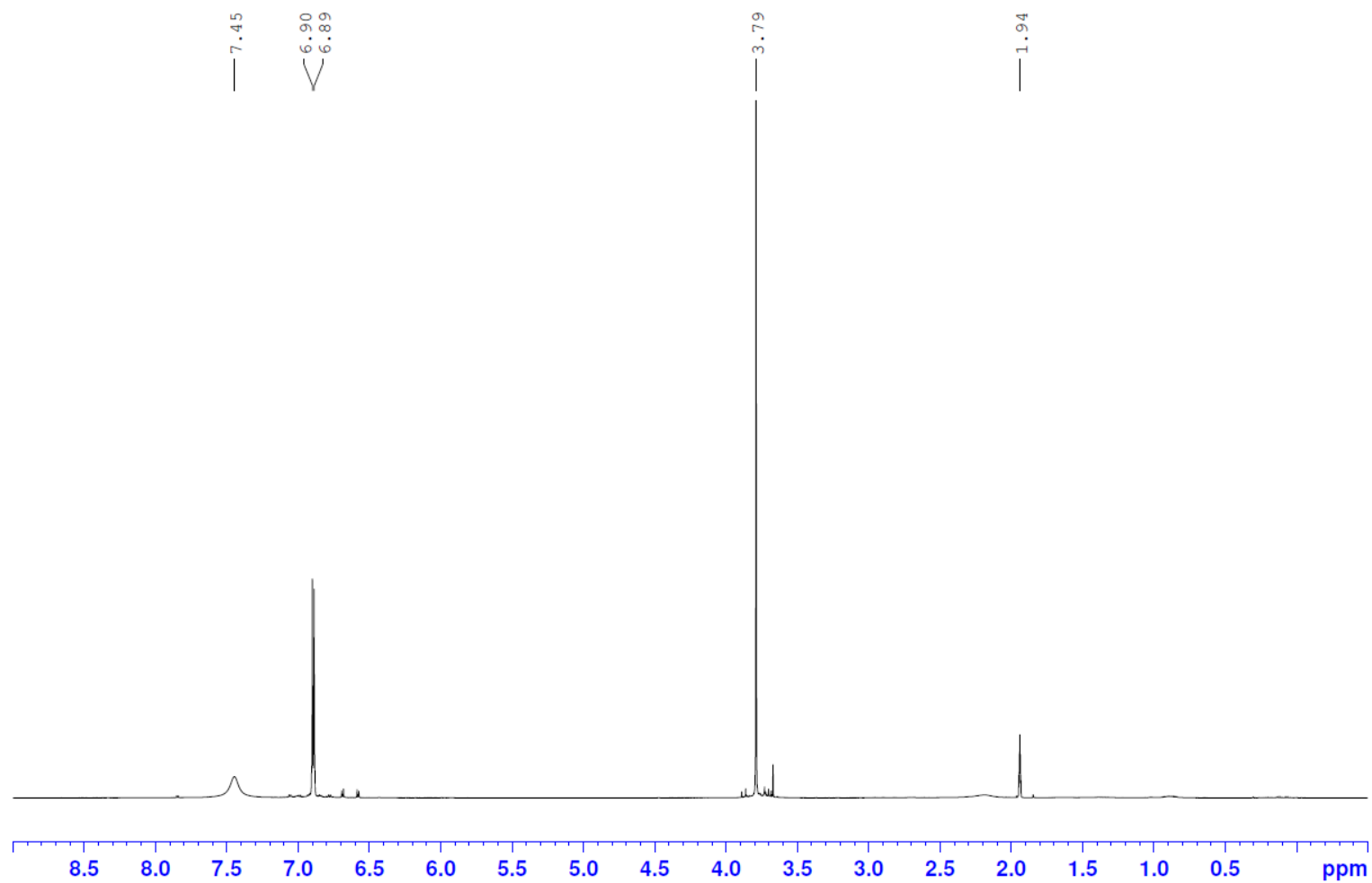


Figure C.32. ^1H NMR of L1 in CD_3CN , referenced to residual solvent at 1.94 ppm

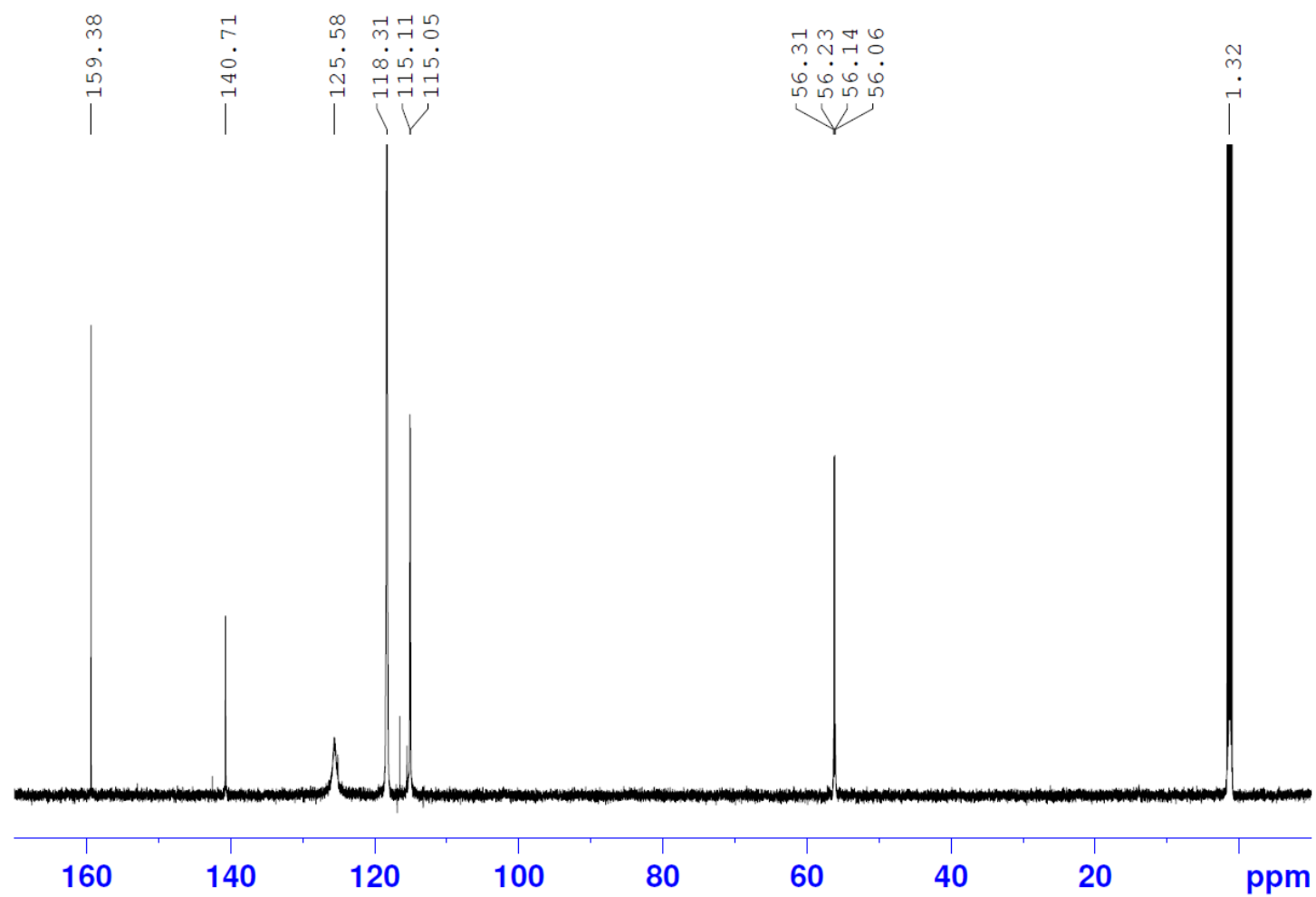


Figure C.33. $^{13}\text{C}\{^1\text{H}\}$ NMR of L1 in CD_3CN , referenced to residual solvent at 1.32 ppm

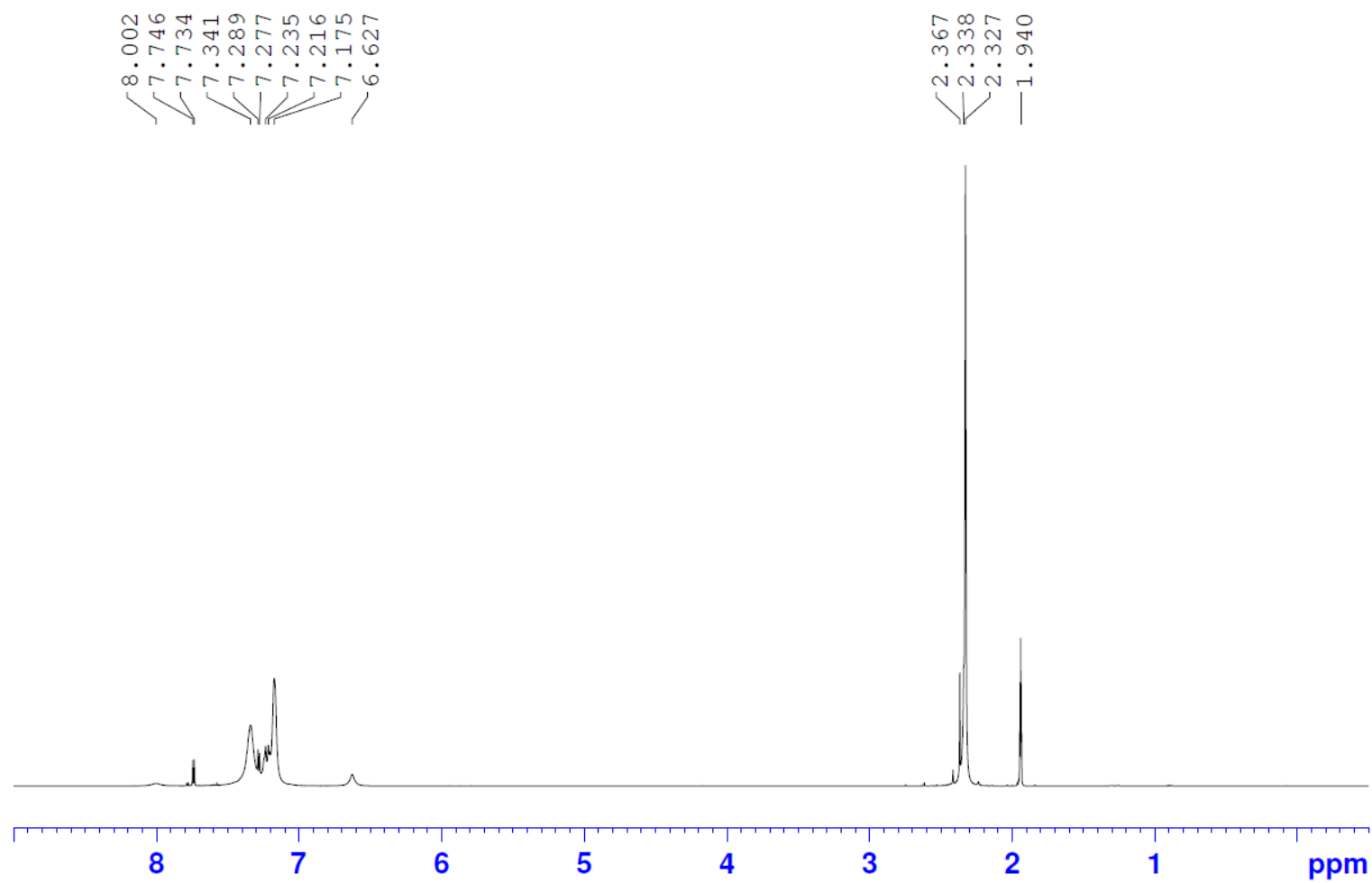


Figure C.34. ^1H NMR of C2 in CD_3CN , low concentration, referenced to residual solvent at 1.94 ppm

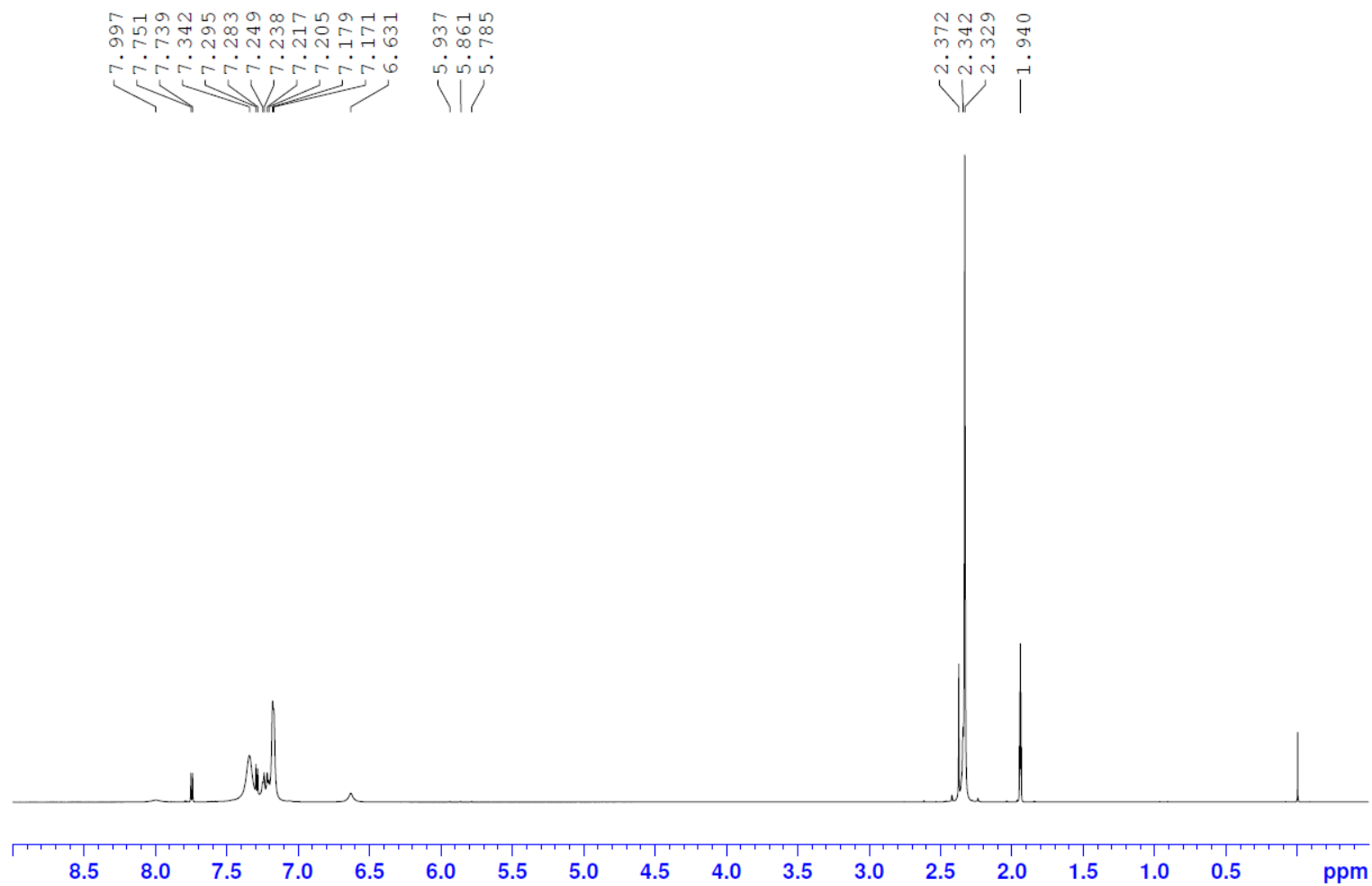


Figure C.35. ^1H NMR of C2 in CD_3CN , saturated, referenced to residual solvent at 1.94 ppm

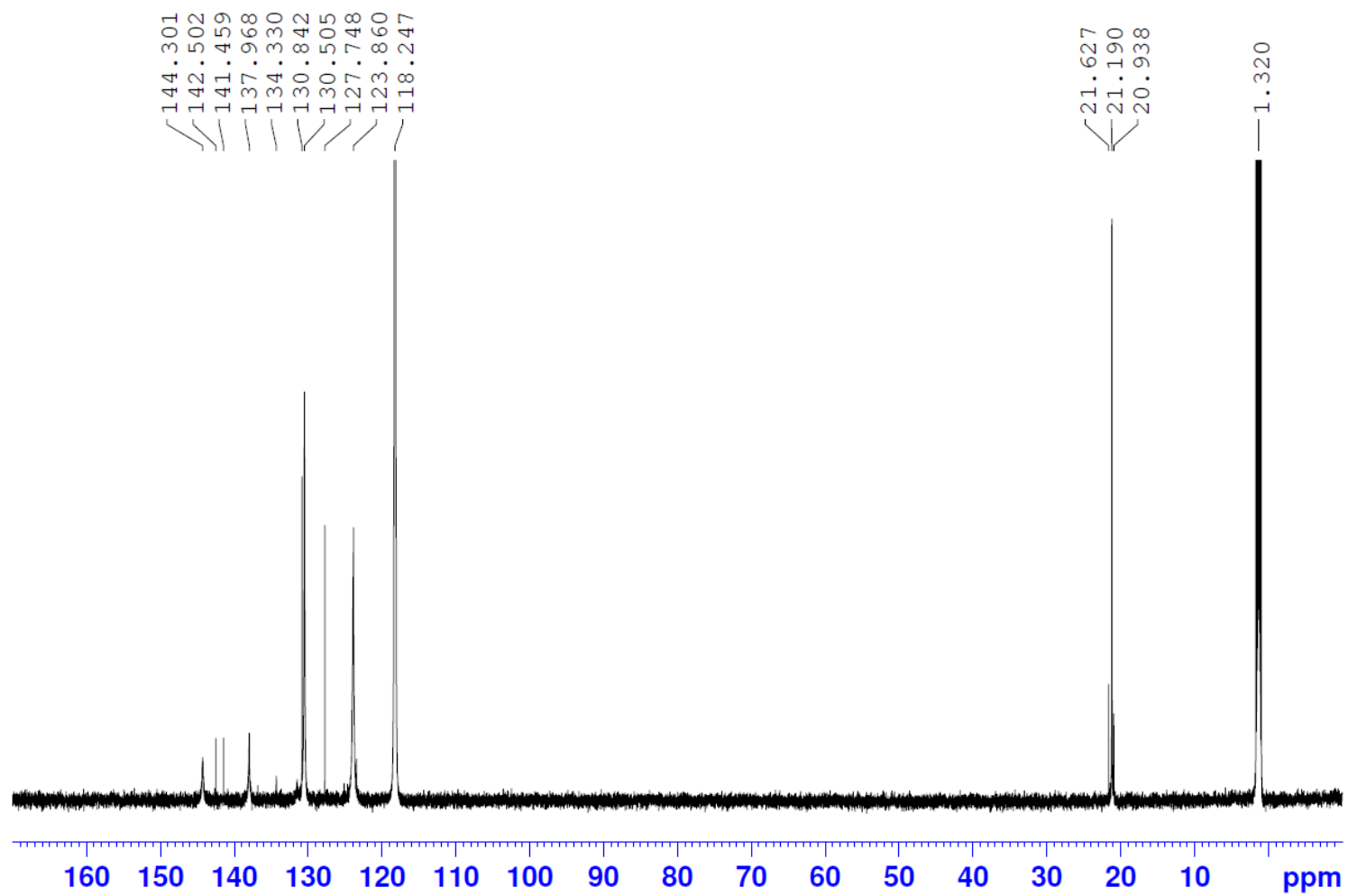


Figure C.36. $^{13}\text{C}\{^1\text{H}\}$ NMR of C2 in CD_3CN , low concentration, referenced to residual solvent at 1.32 ppm

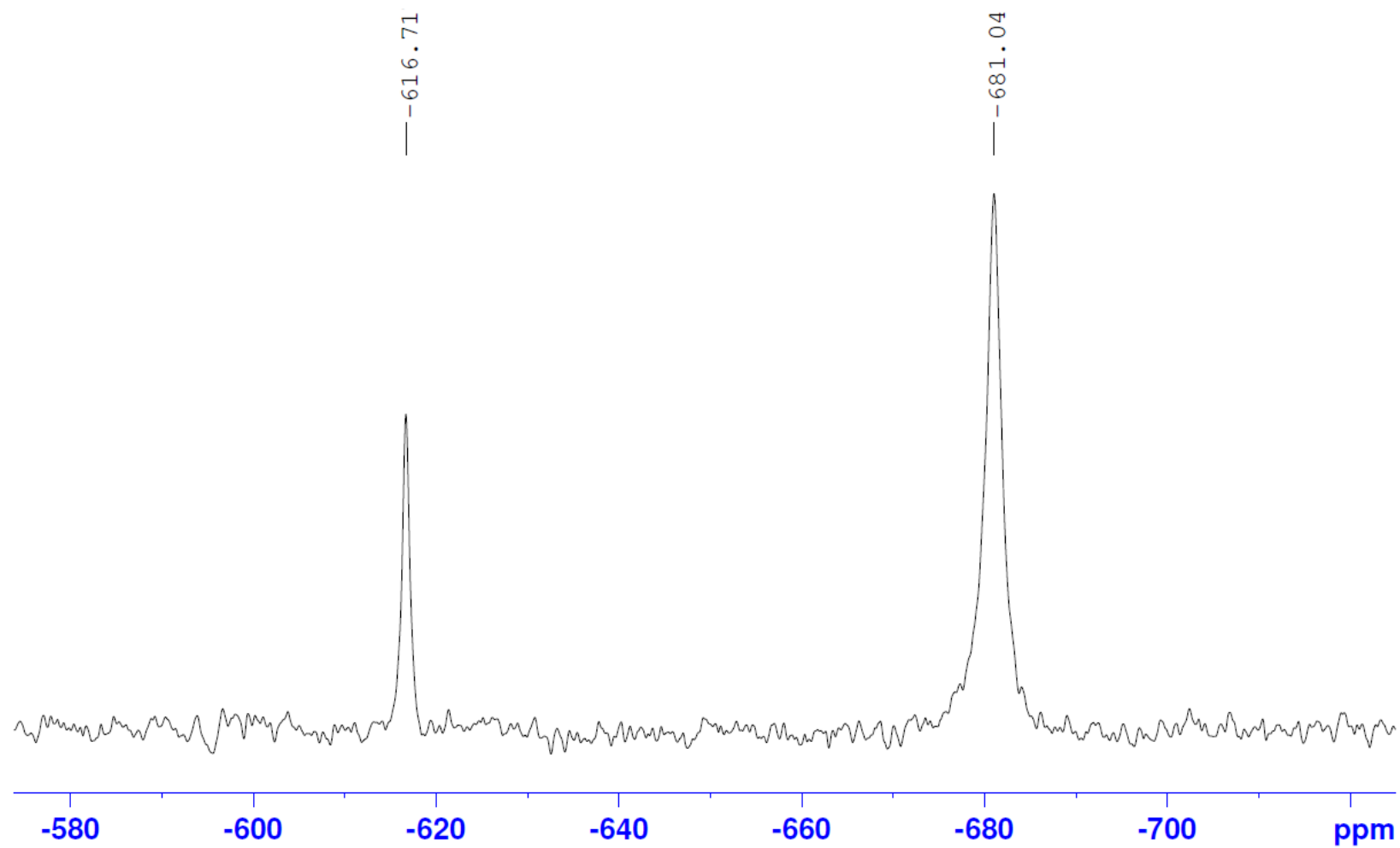


Figure C.37. ^{119}Sn NMR of C2 in CD_3CN , low concentration, referenced to external SnMe_4 at 0.0 ppm

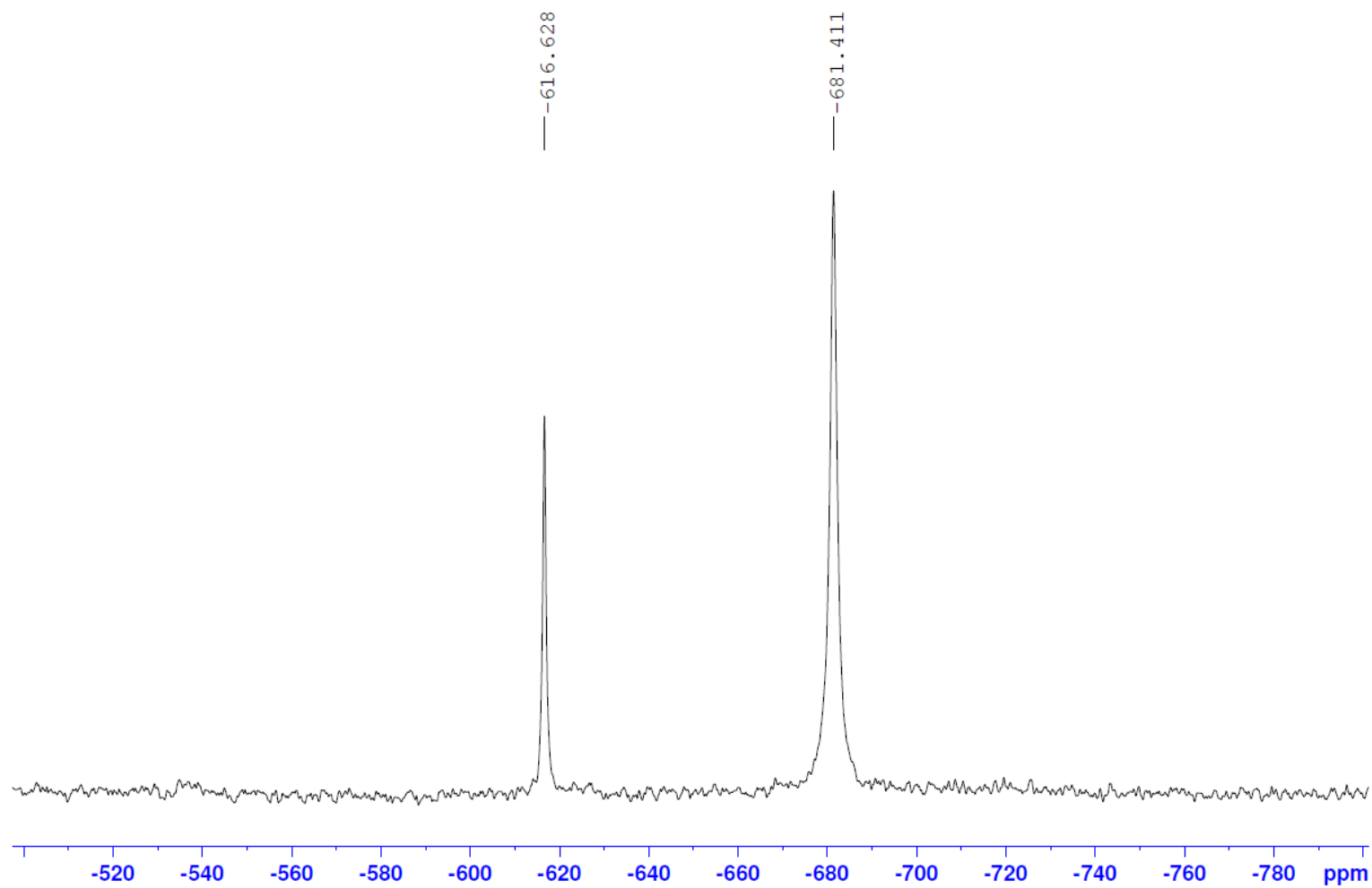


Figure C.38. ^{119}Sn NMR of C2 in CD_3CN , saturated, referenced to external SnMe_4 at 0.0 ppm

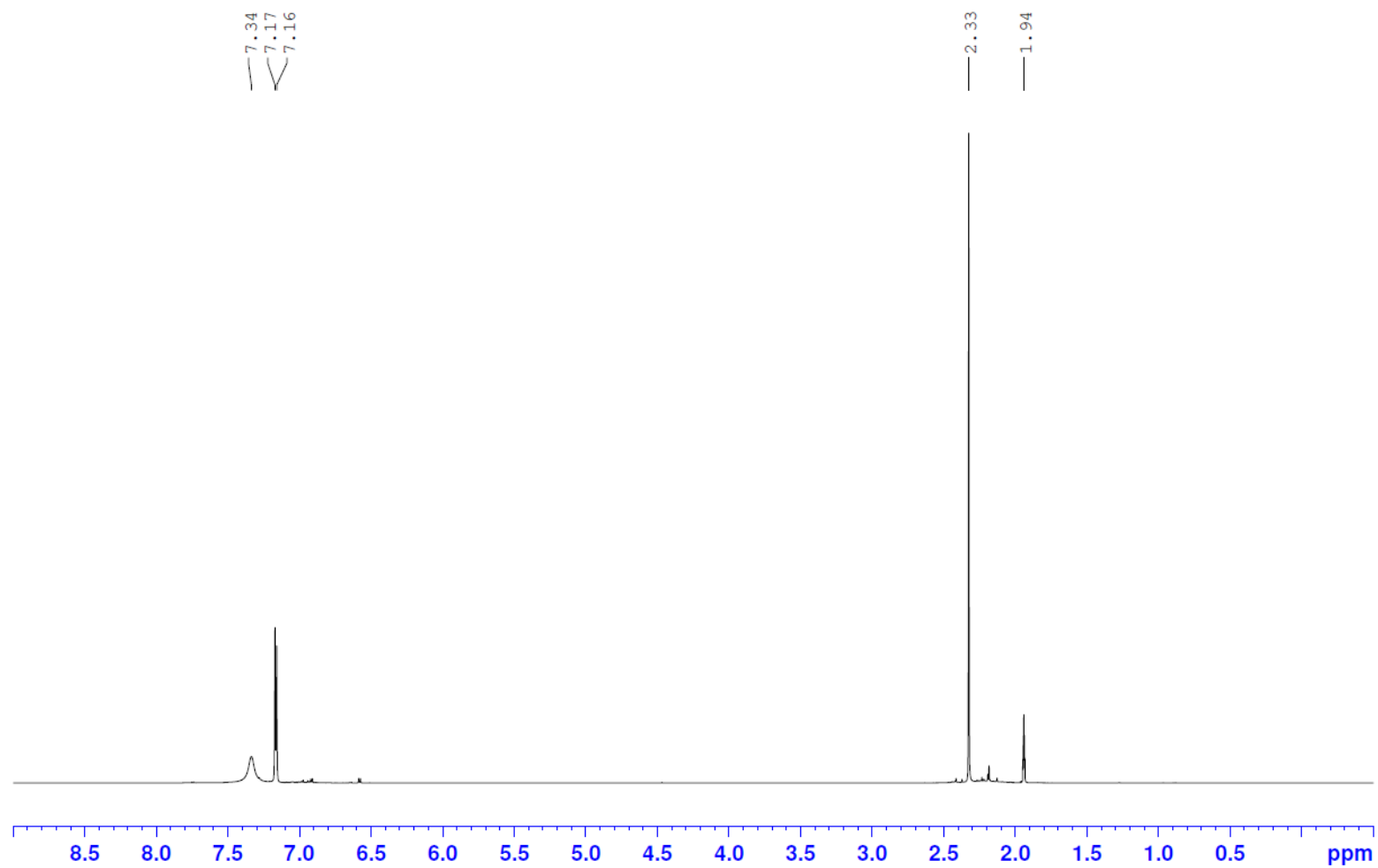


Figure C.39. ^1H NMR of L2 in CD_3CN , referenced to residual solvent at 1.94 ppm

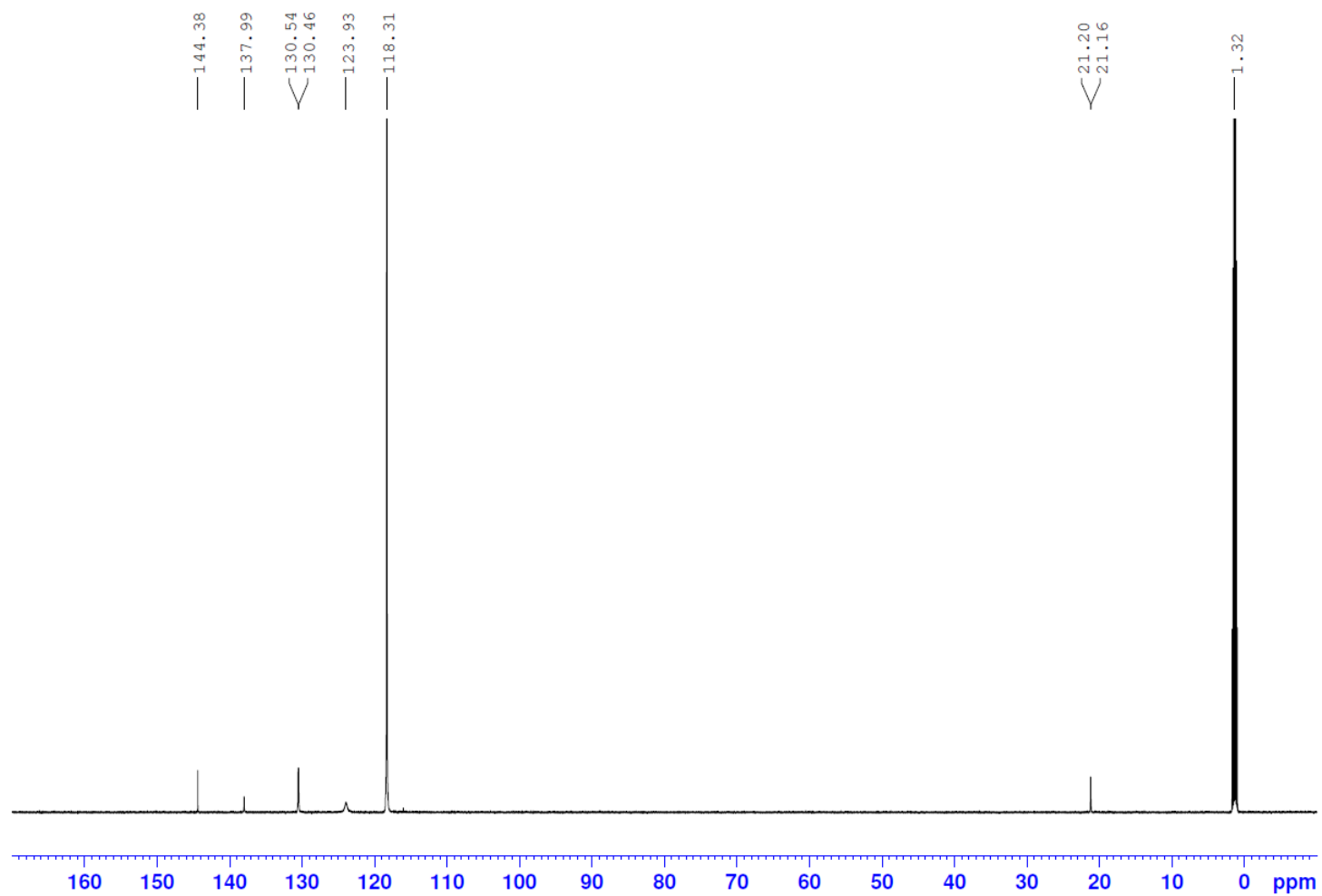


Figure C.40. $^{13}\text{C}\{^1\text{H}\}$ NMR of L2 in CD_3CN , referenced to residual solvent at 1.32 ppm

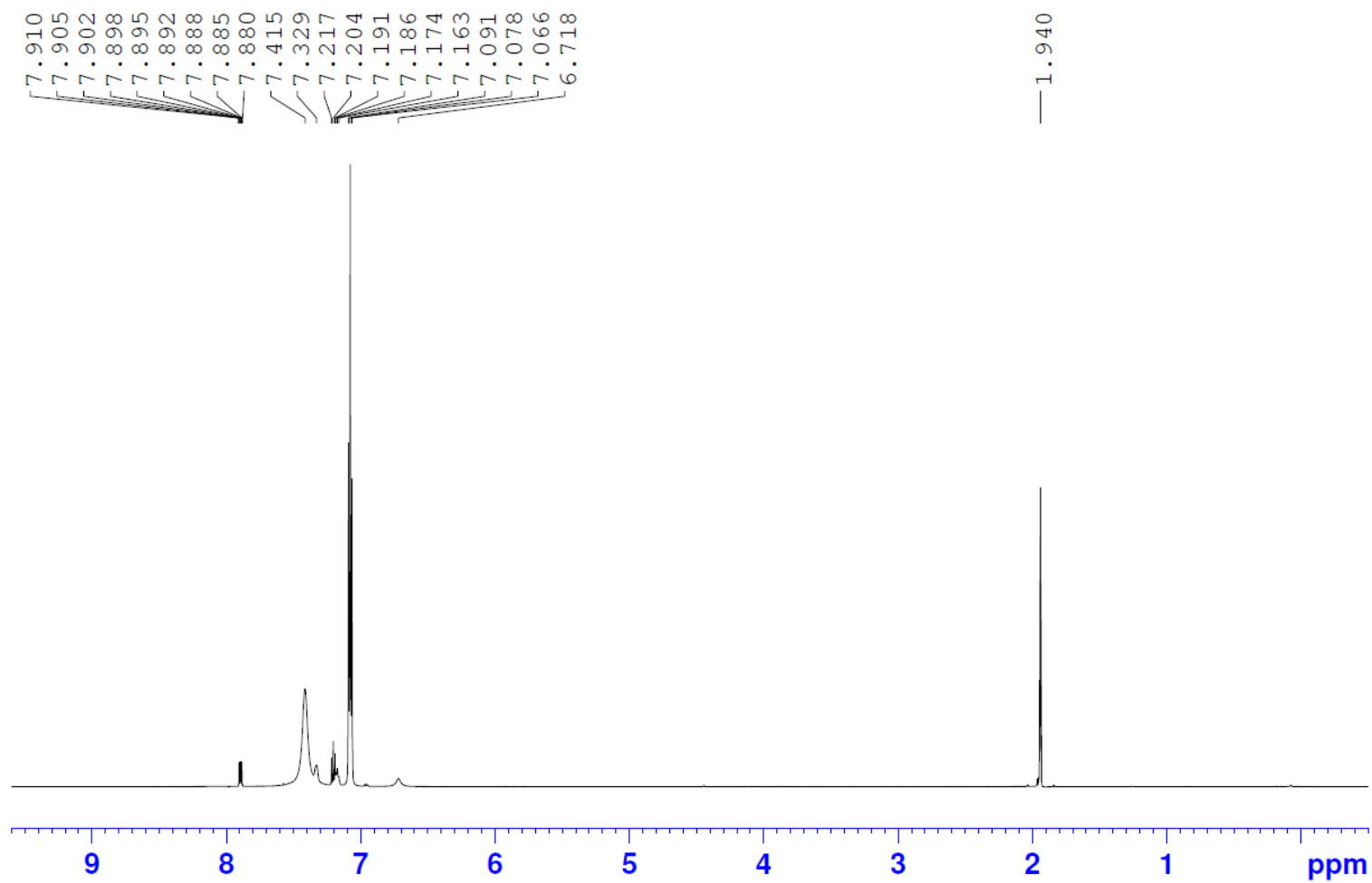


Figure C.41. ^1H NMR of C3 in CD_3CN , low concentration, referenced to residual solvent at 1.94 ppm

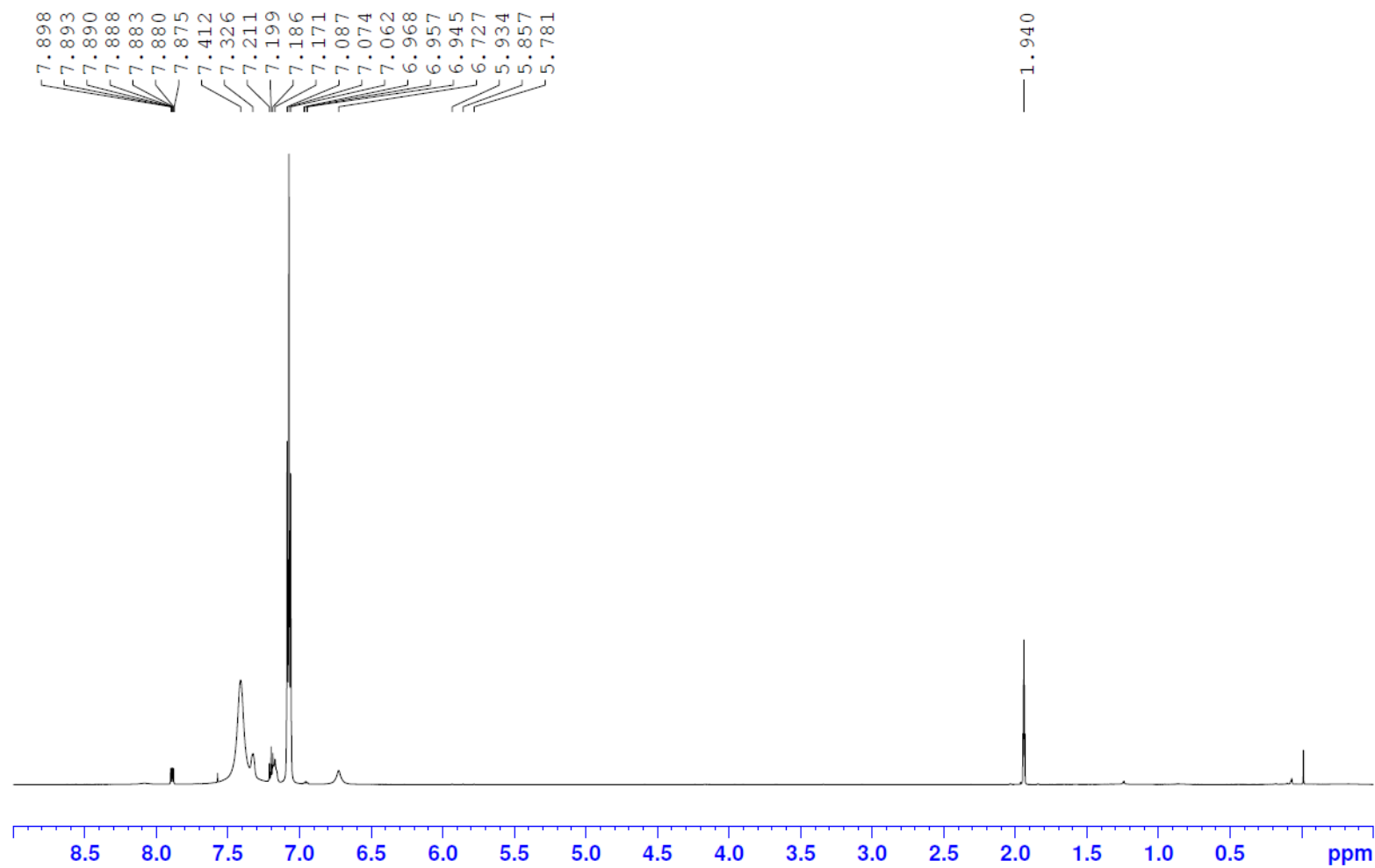


Figure C.42. ^1H NMR of C3 in CD_3CN , saturated, referenced to residual solvent at 1.94 ppm

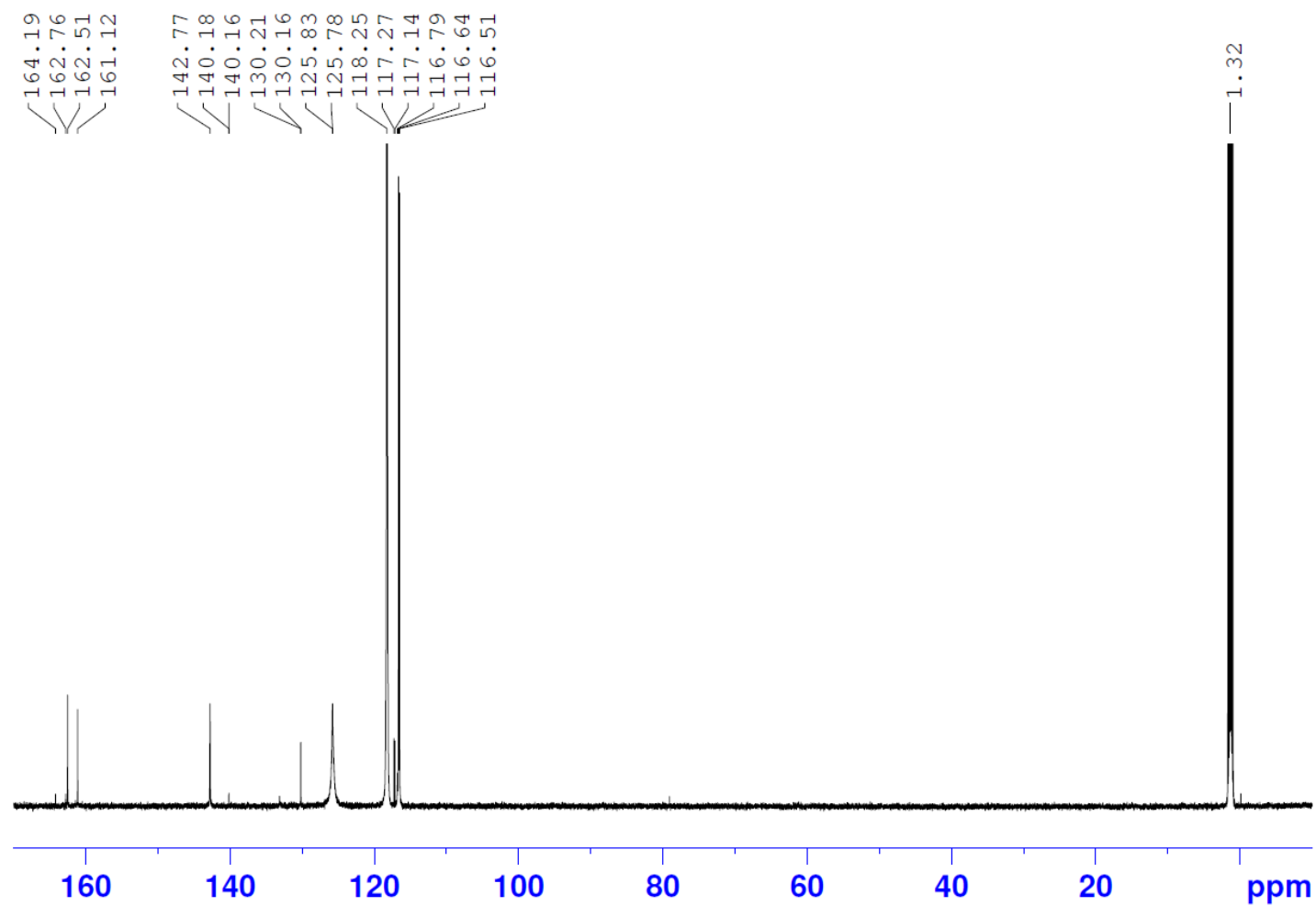


Figure C.43. $^{13}\text{C}\{^1\text{H}\}$ NMR of C3 in CD_3CN , saturated, referenced to residual solvent at 1.32 ppm

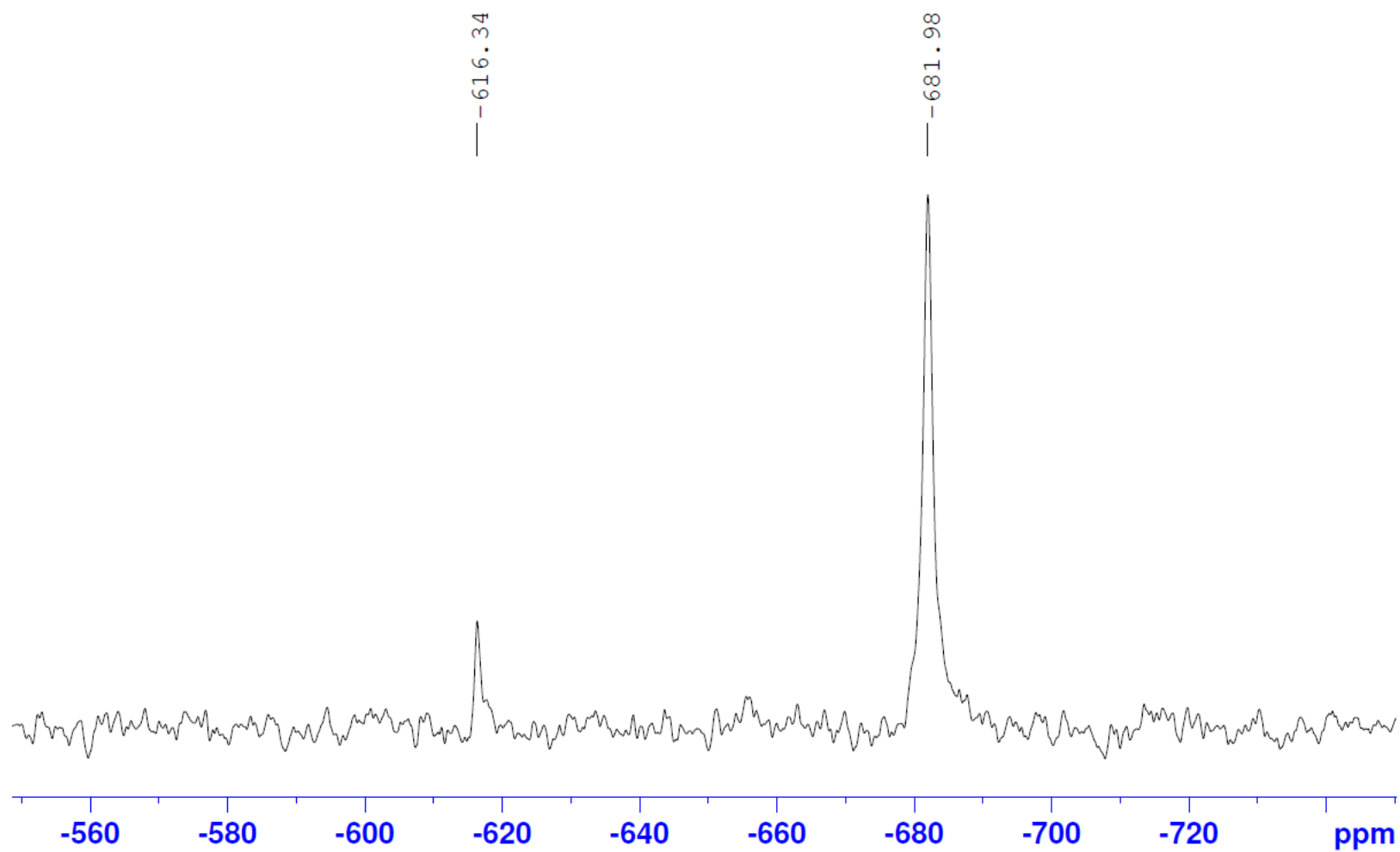


Figure C.44. ^{119}Sn NMR of C3 in CD_3CN , low concentration, referenced to external SnMe_4 at 0.0 ppm

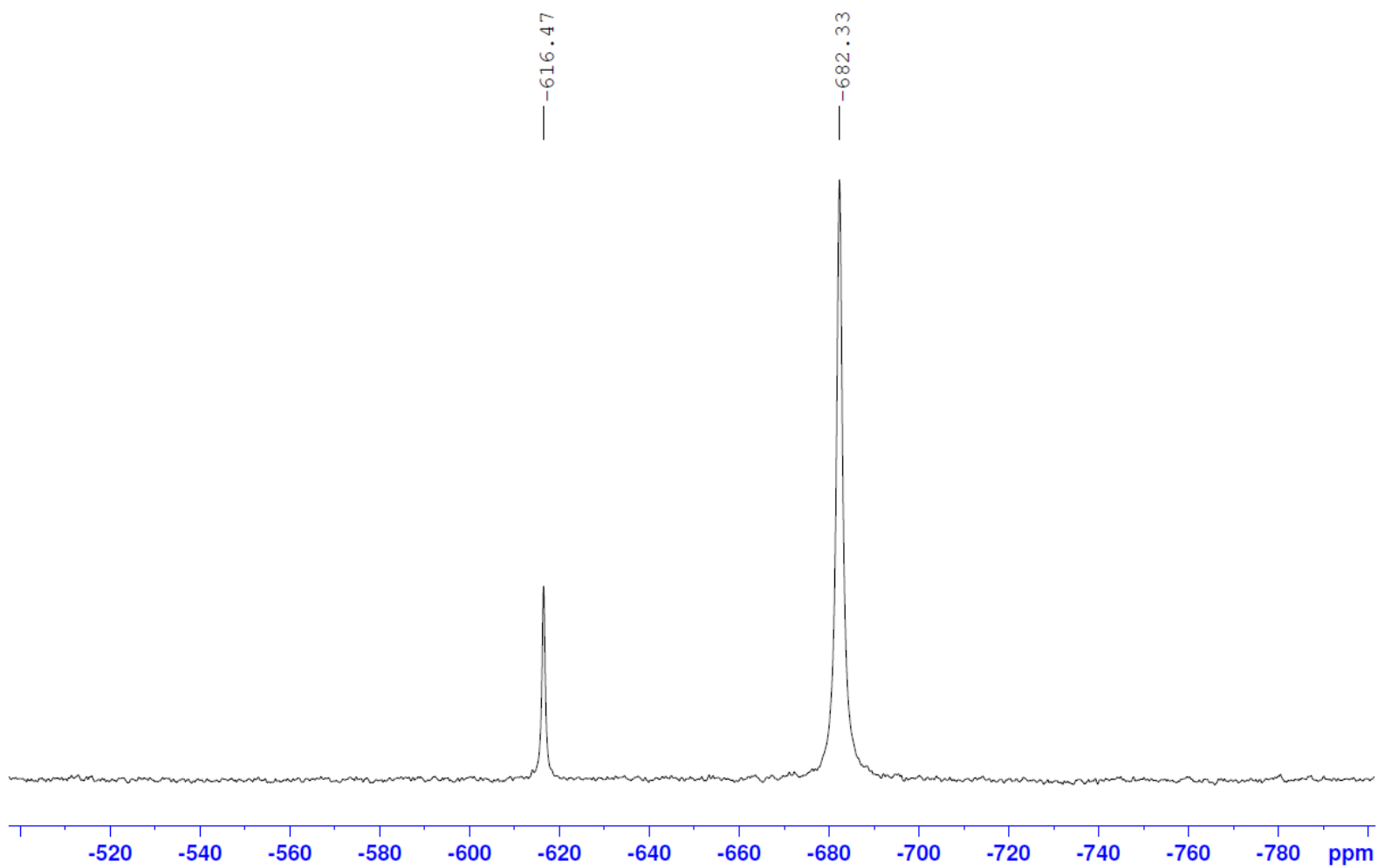


Figure C.45. ^{119}Sn NMR of C3 in CD_3CN , saturated, referenced to external SnMe_4 at 0.0 ppm

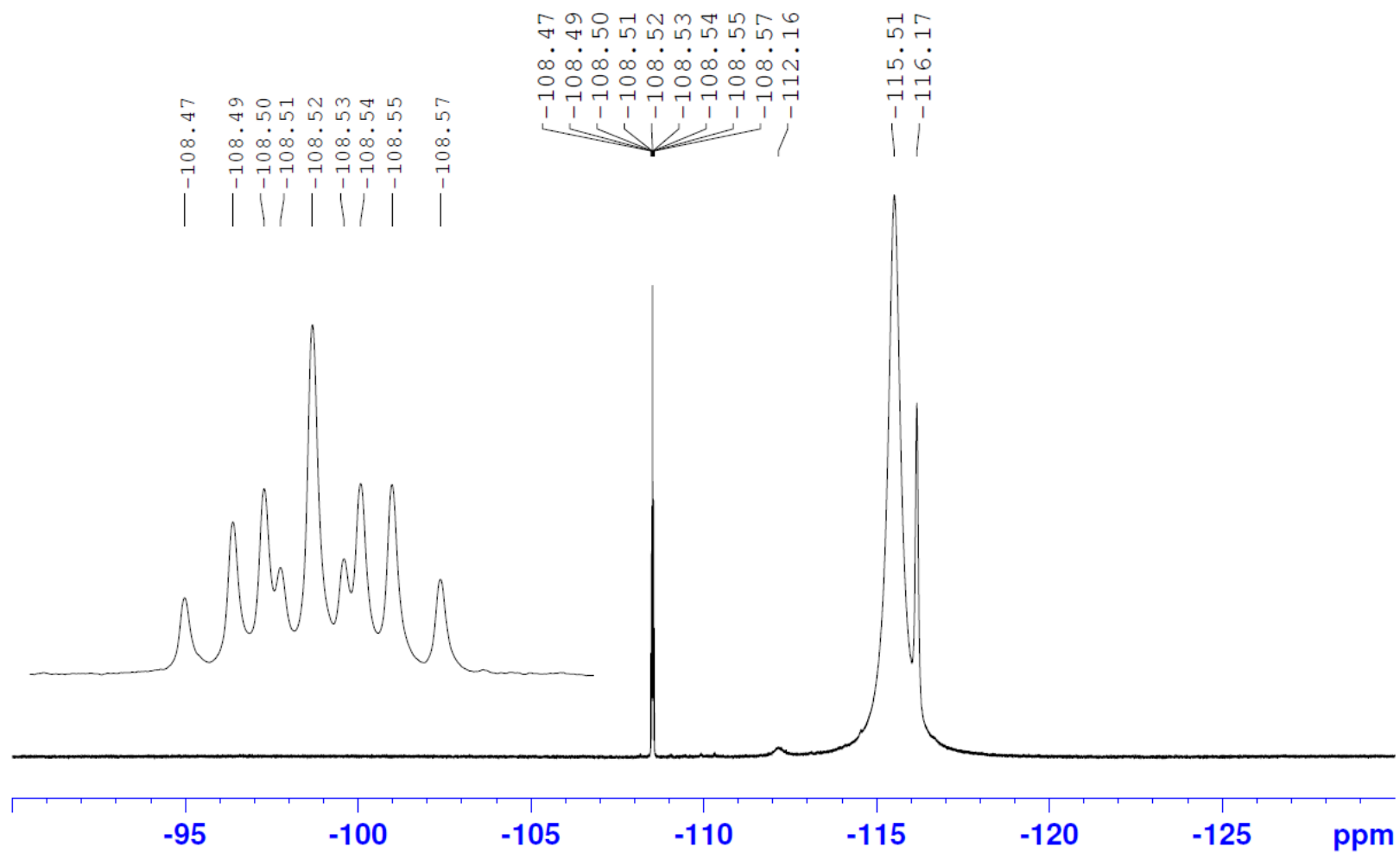


Figure C.46. ^{19}F NMR of C3 in CD_3CN , saturated, referenced to external CFCl_3 at 0.0 ppm

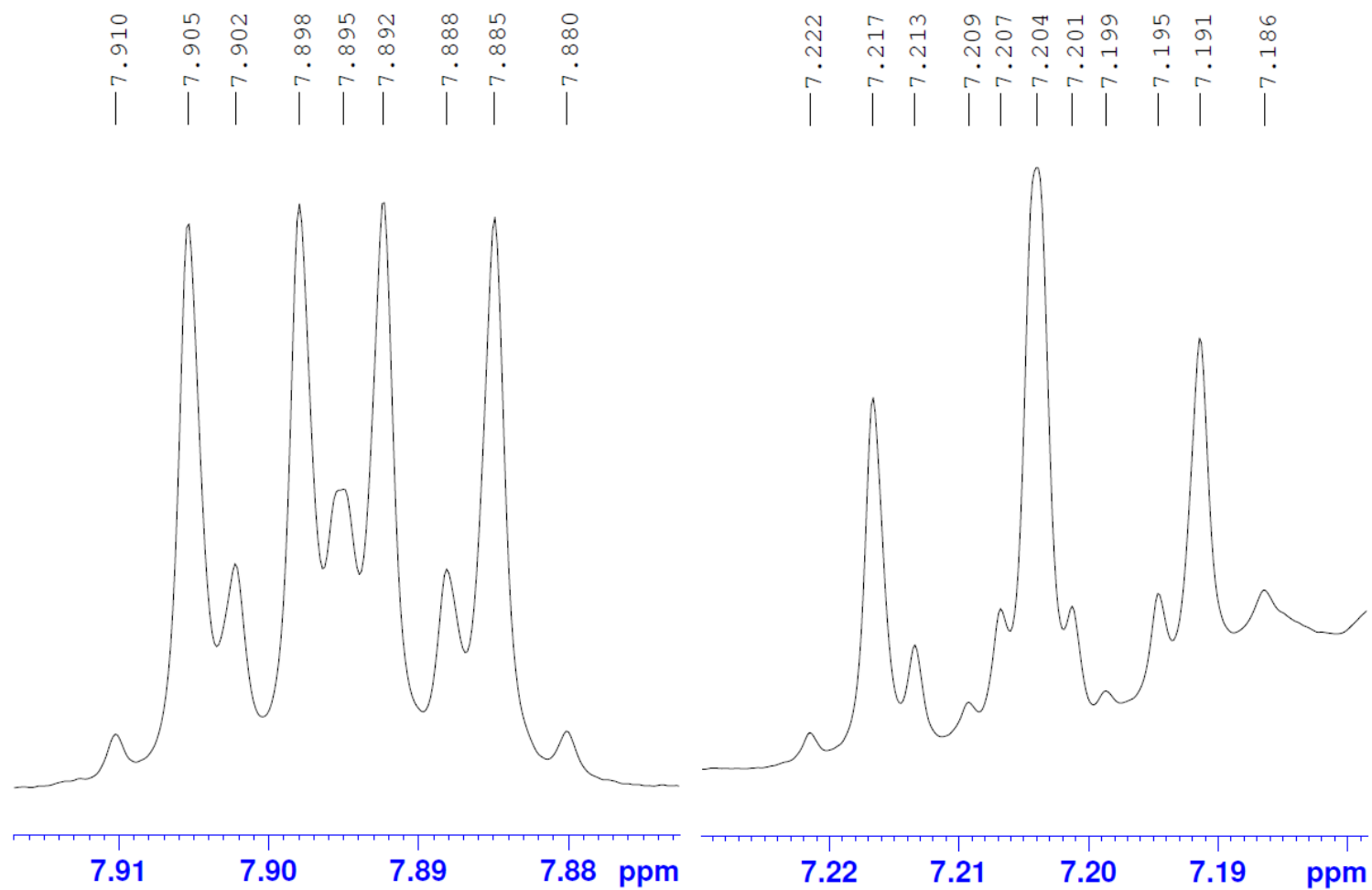


Figure C.47. ^1H NMR of C3 in CD_3CN , saturated, closeup of 4-FPhNSO signals, referenced to residual solvent at 1.94 ppm

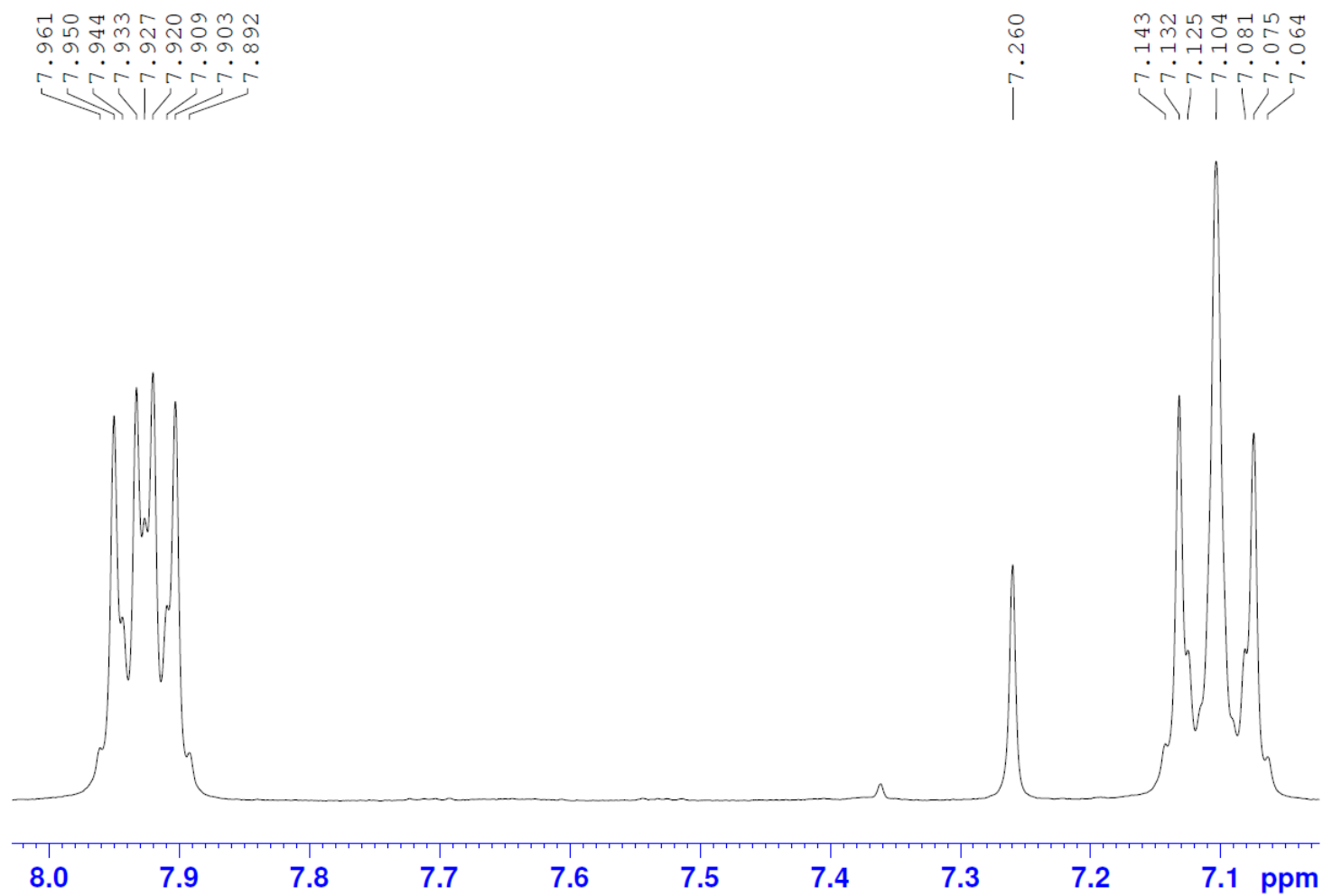


Figure C.48. ^1H NMR of 4-FPhNSO in CDCl_3 , referenced to residual solvent at 7.26 ppm

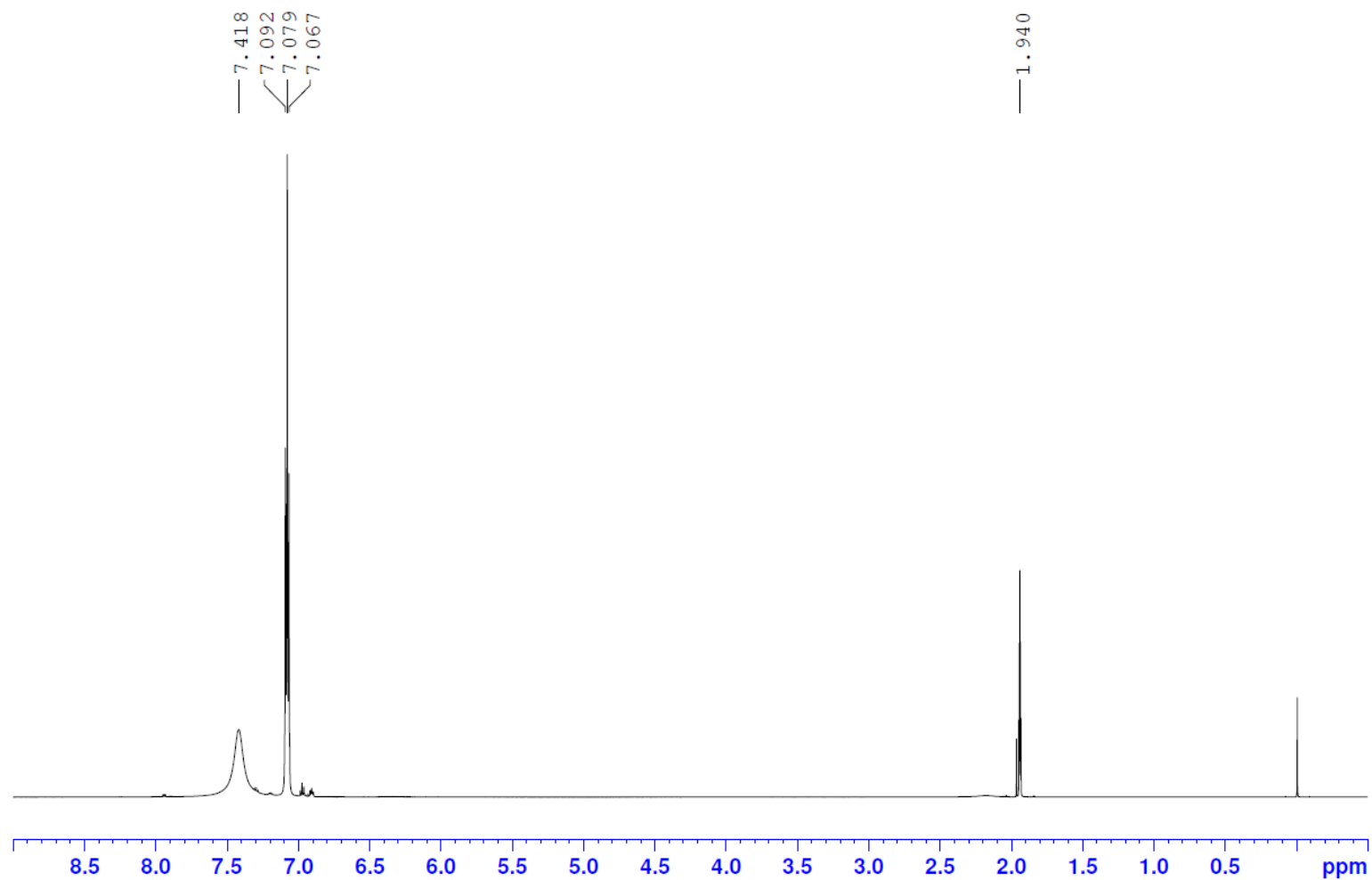


Figure C.49. ^1H NMR of L3 in CD_3CN , referenced to residual solvent at 1.94 ppm

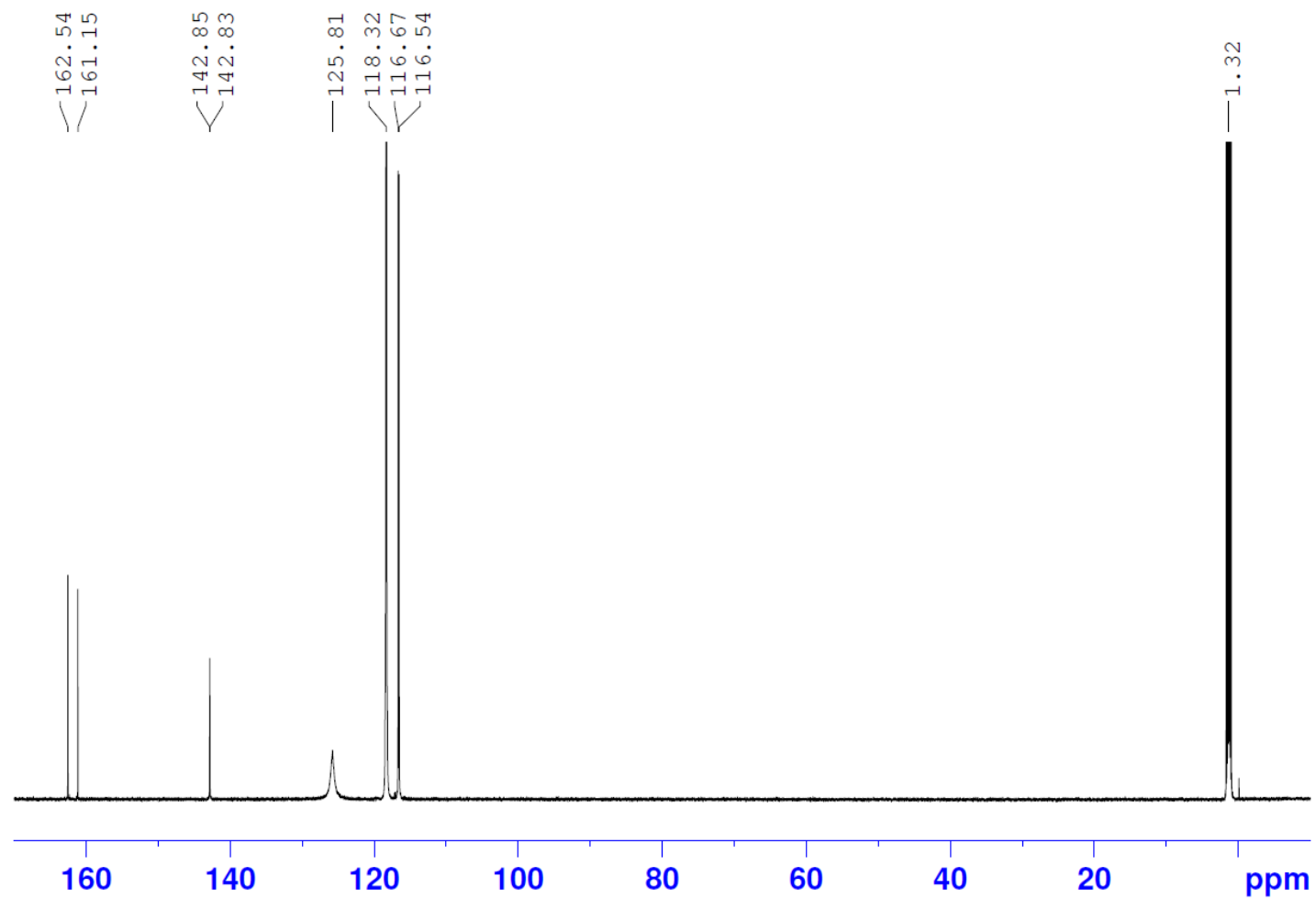


Figure C.50. $^{13}\text{C}\{^1\text{H}\}$ NMR of L3 in CD_3CN , referenced to residual solvent at 1.32 ppm

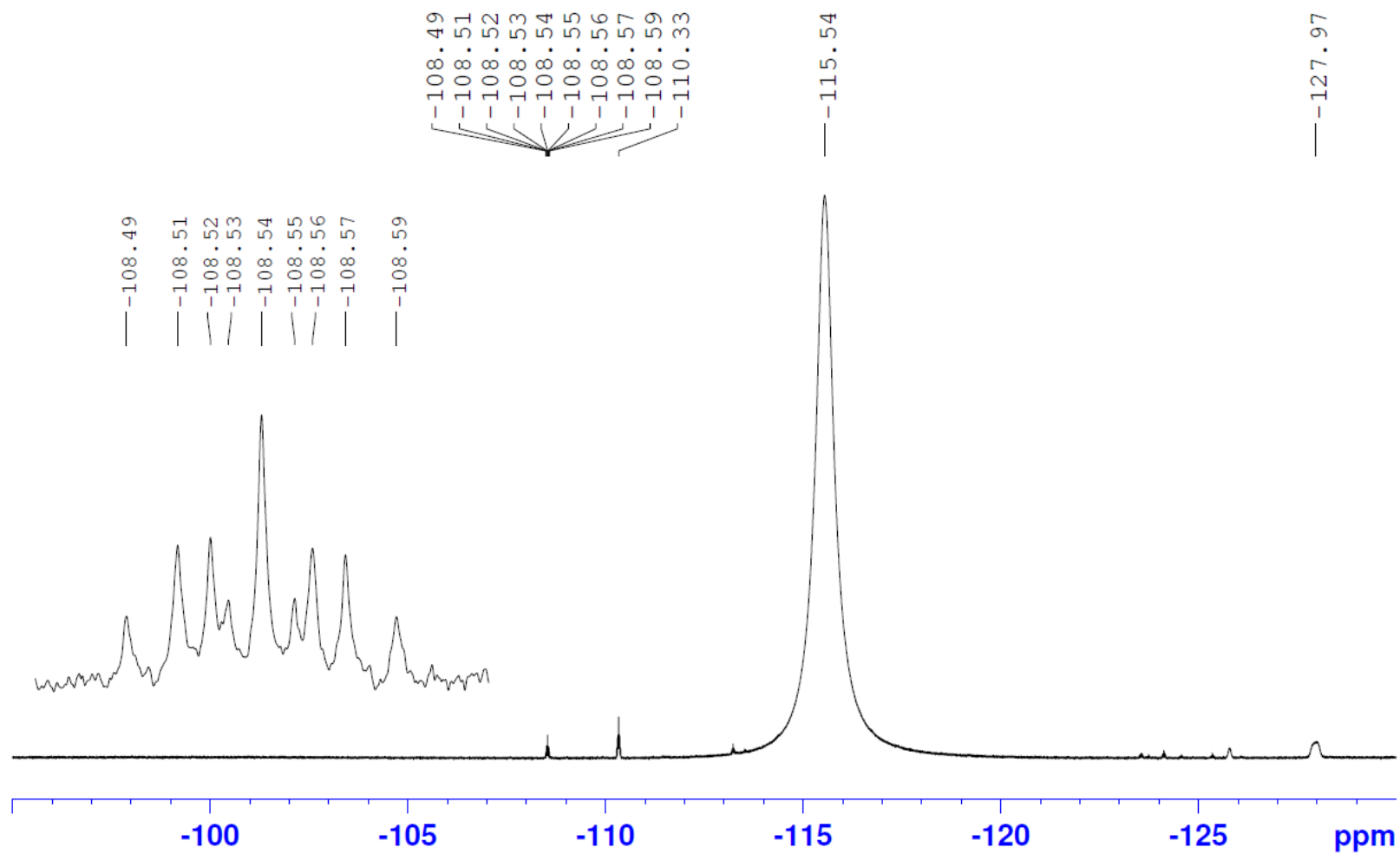


Figure C.51. ^{19}F NMR of L3 in CD_3CN , referenced to external CFCl_3 at 0.0 ppm

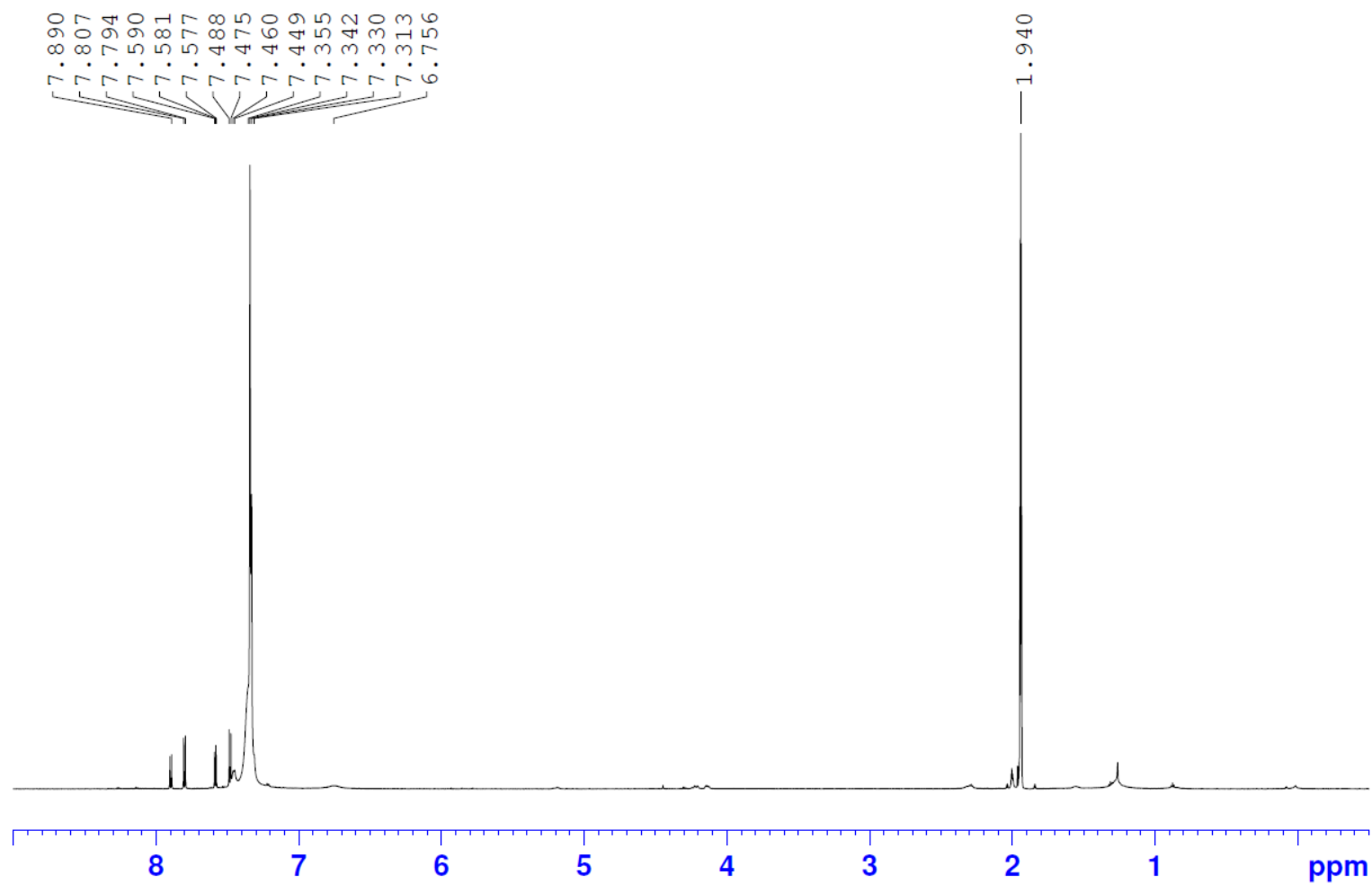


Figure C.52. ^1H NMR of C4 in CD_3CN , low concentration, referenced to residual solvent at 1.94 ppm

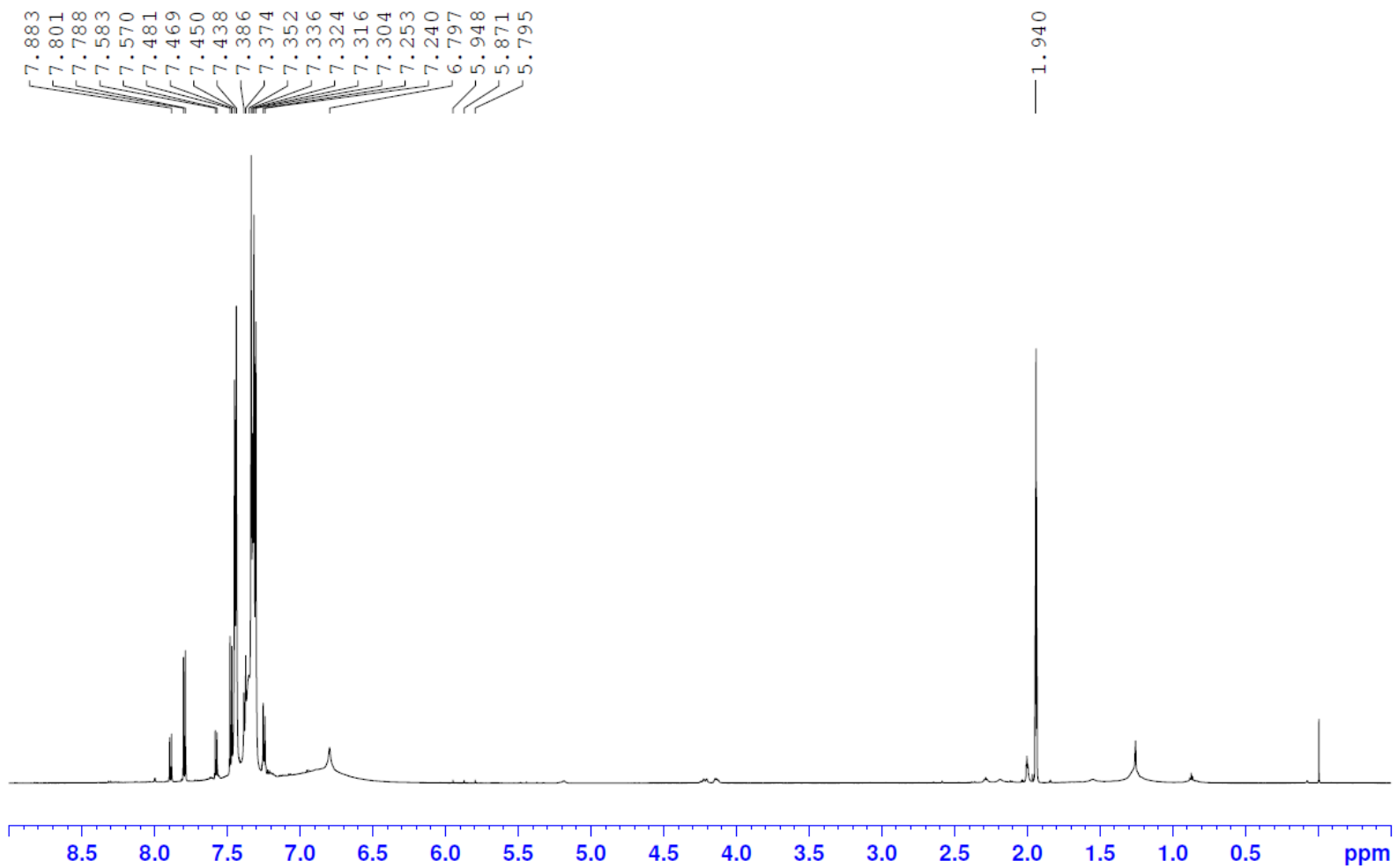


Figure C.53. ^1H NMR of C4 in CD_3CN , saturated, referenced to residual solvent at 1.94 ppm

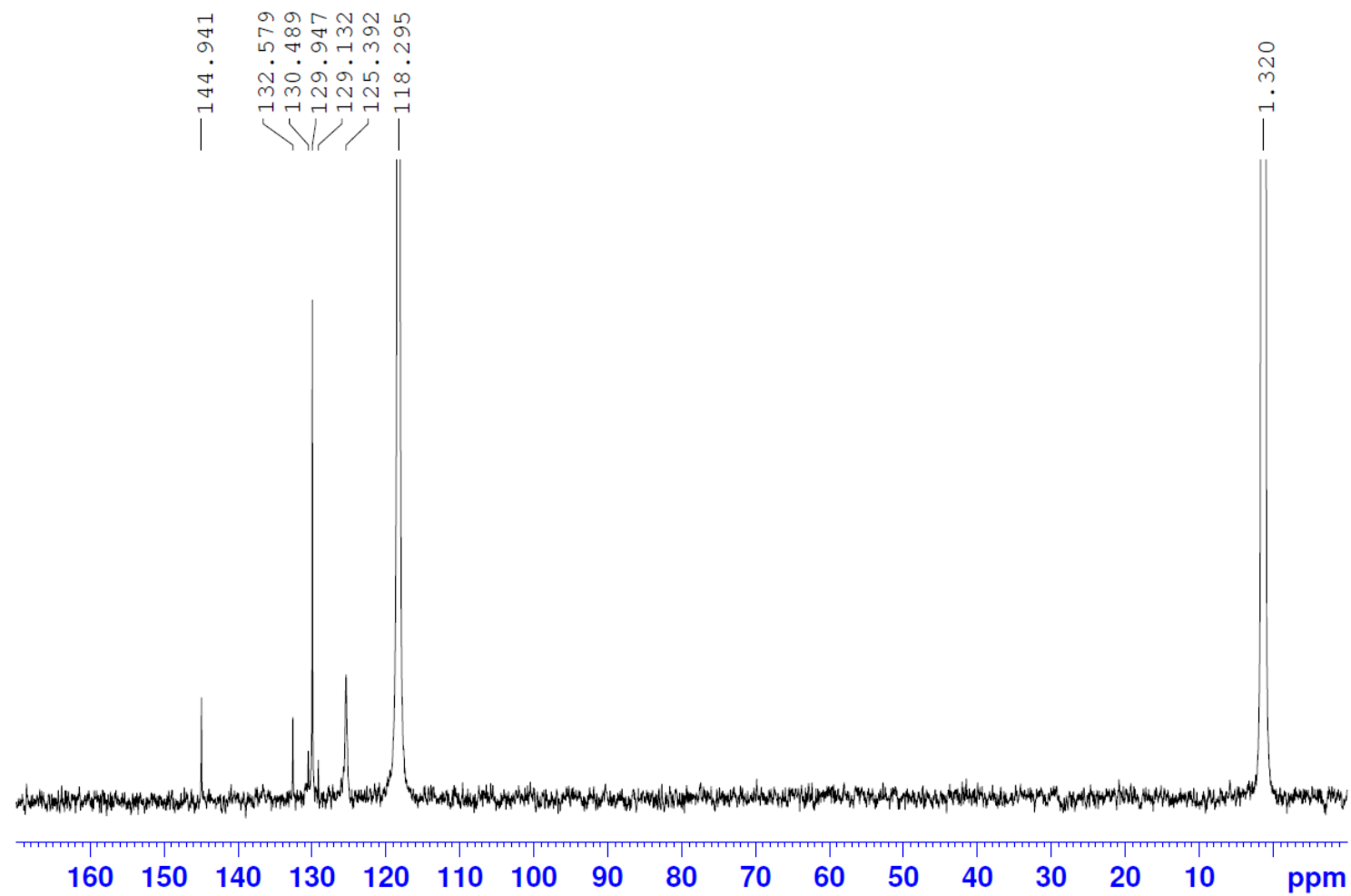


Figure C.54. $^{13}\text{C}\{^1\text{H}\}$ NMR of C4 in CD_3CN , low concentration, referenced to residual solvent at 1.32 ppm

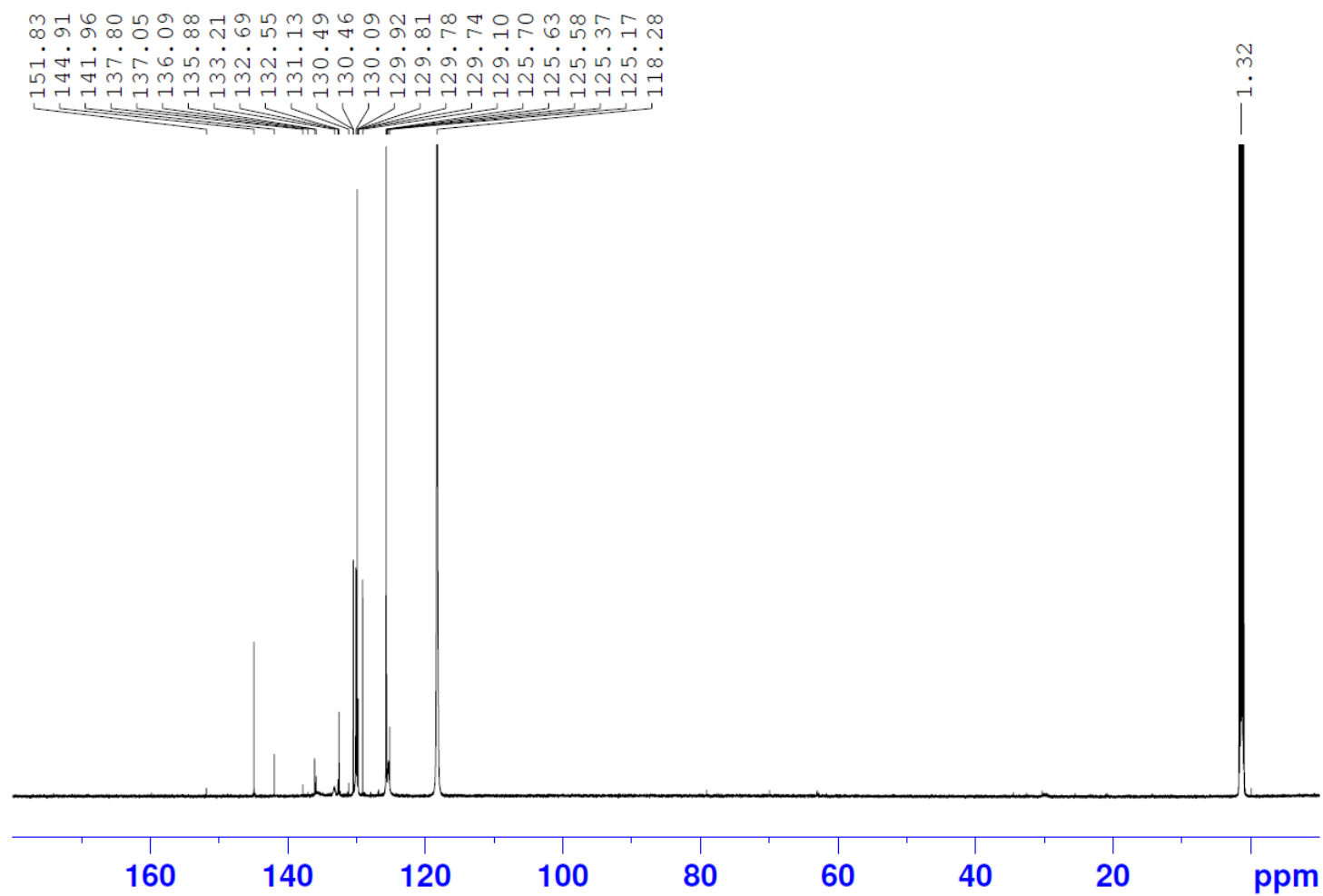


Figure C.55. $^{13}\text{C}\{^1\text{H}\}$ NMR of C4 in CD_3CN , saturated, referenced to residual solvent at 1.32 ppm

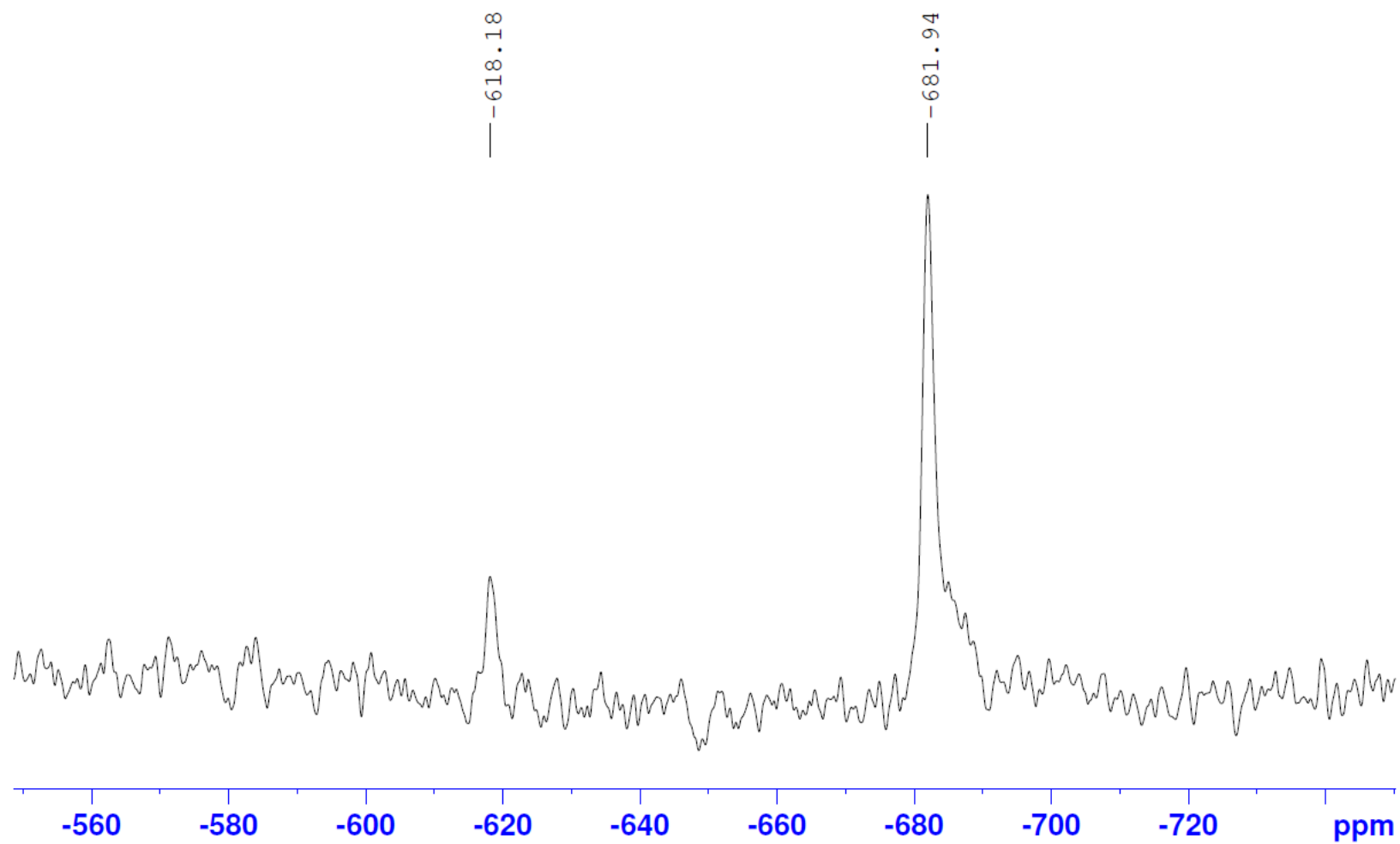


Figure C.56. ^{119}Sn NMR of C4 in CD_3CN , low concentration, referenced to external SnMe_4 at 0.0 ppm

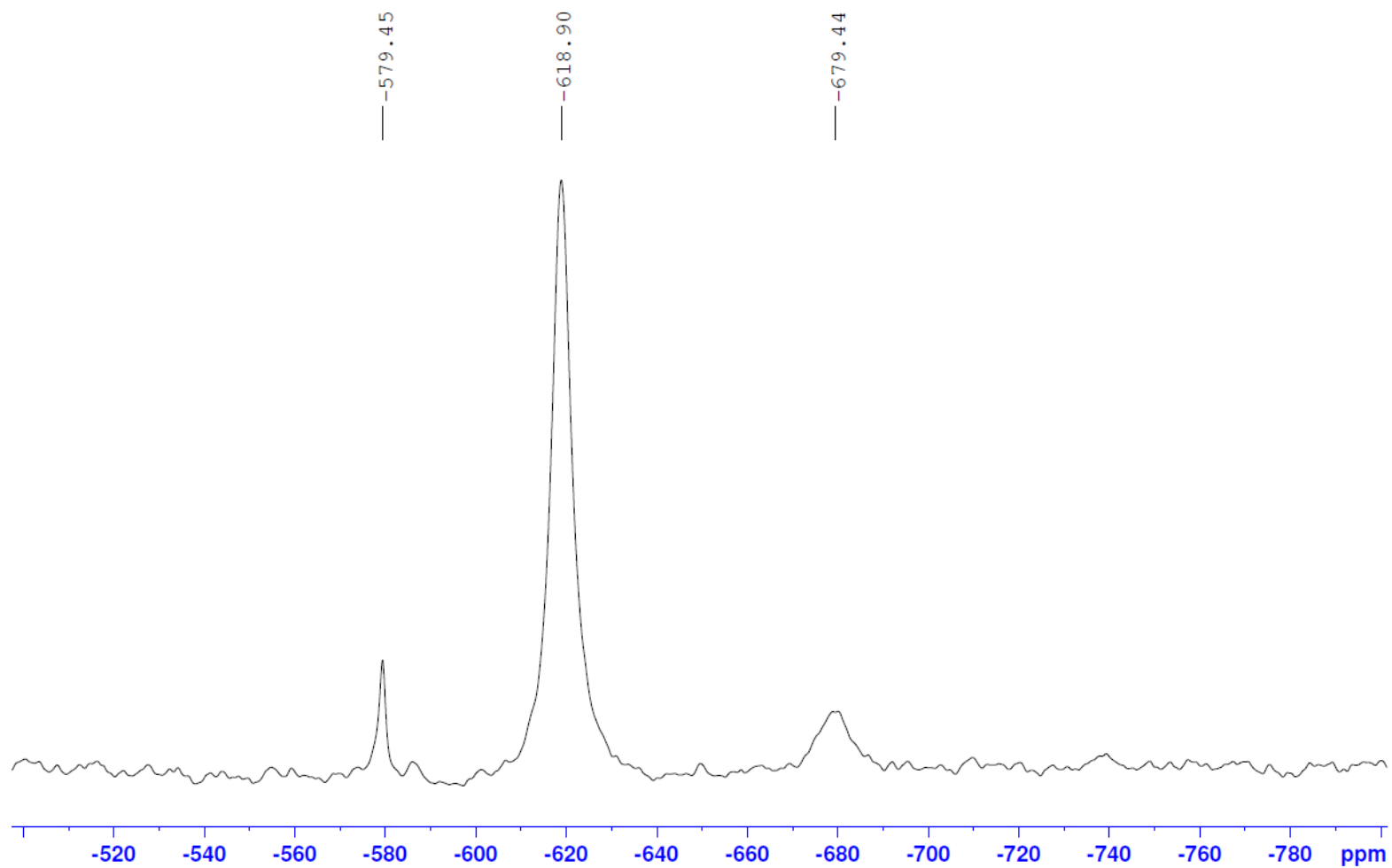


Figure C.57. ^{119}Sn NMR of C4 in CD_3CN , saturated, room temperature ($\sim 293\text{ K}$), referenced to external SnMe_4 at 0.0 ppm

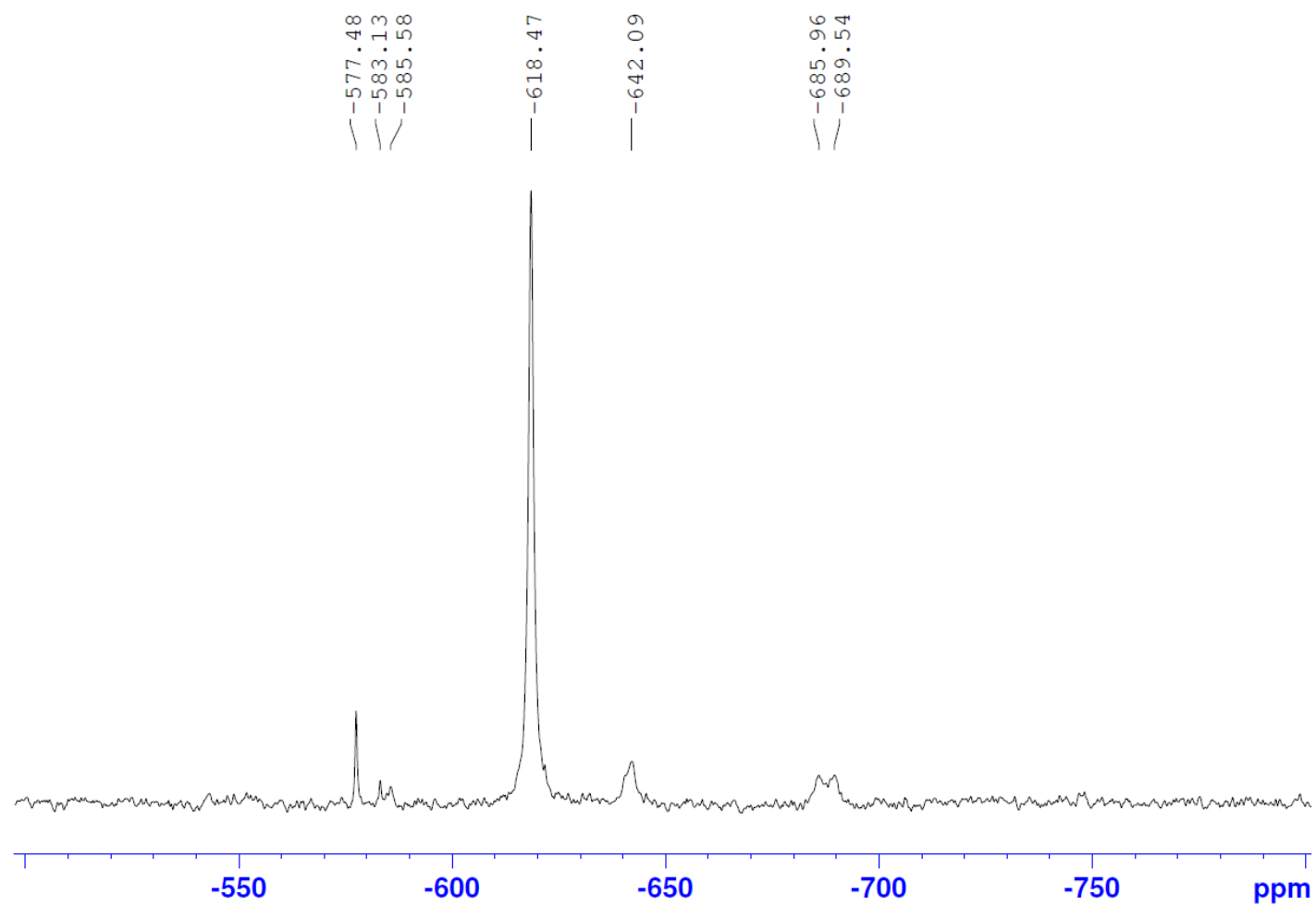


Figure C.58. ^{119}Sn NMR of C4 in CD_3CN , saturated, 263 K, referenced to external SnMe_4 at 0.0 ppm

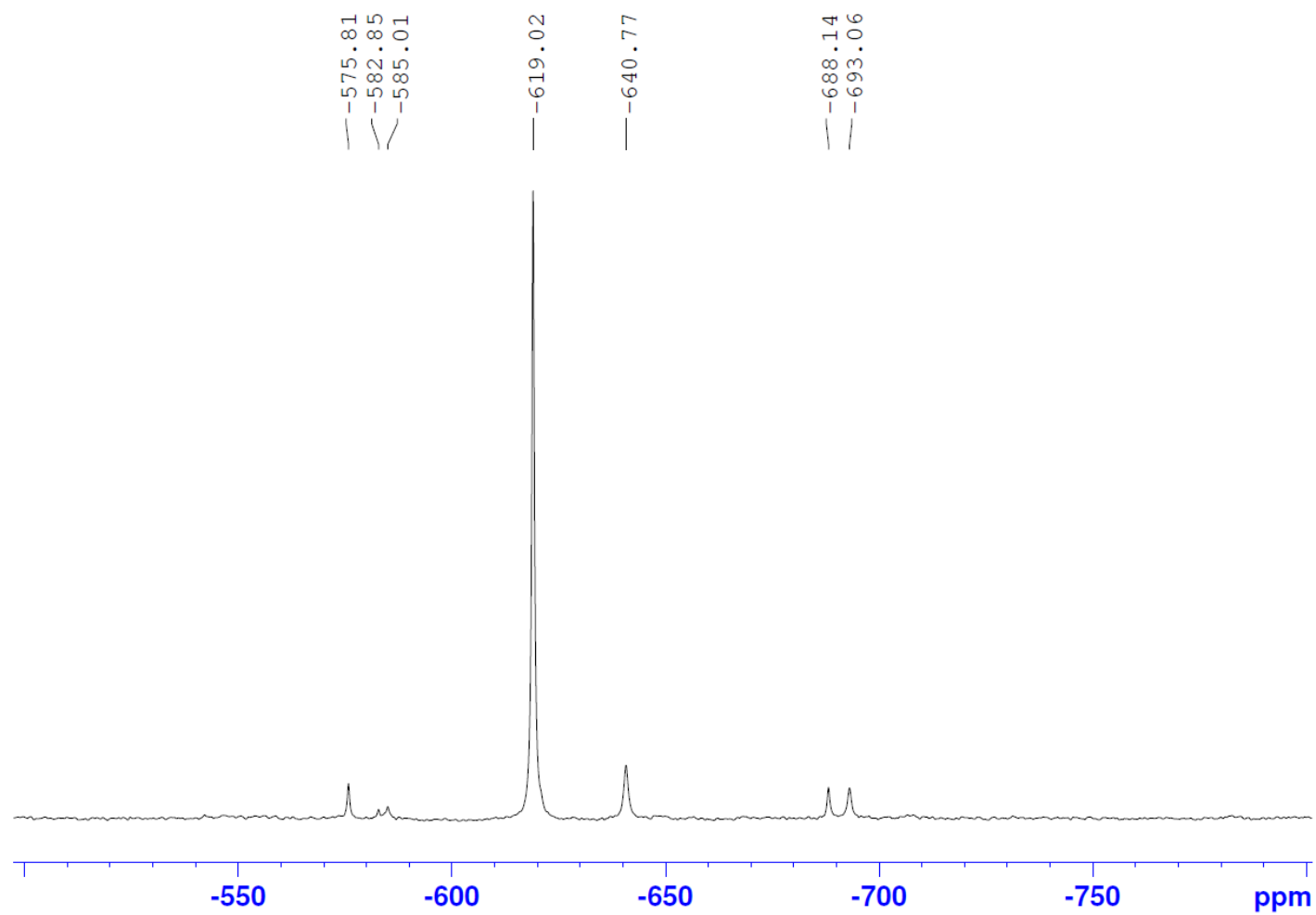


Figure C.59. ^{119}Sn NMR of C4 in CD_3CN , saturated, 233 K, referenced to external SnMe_4 at 0.0 ppm

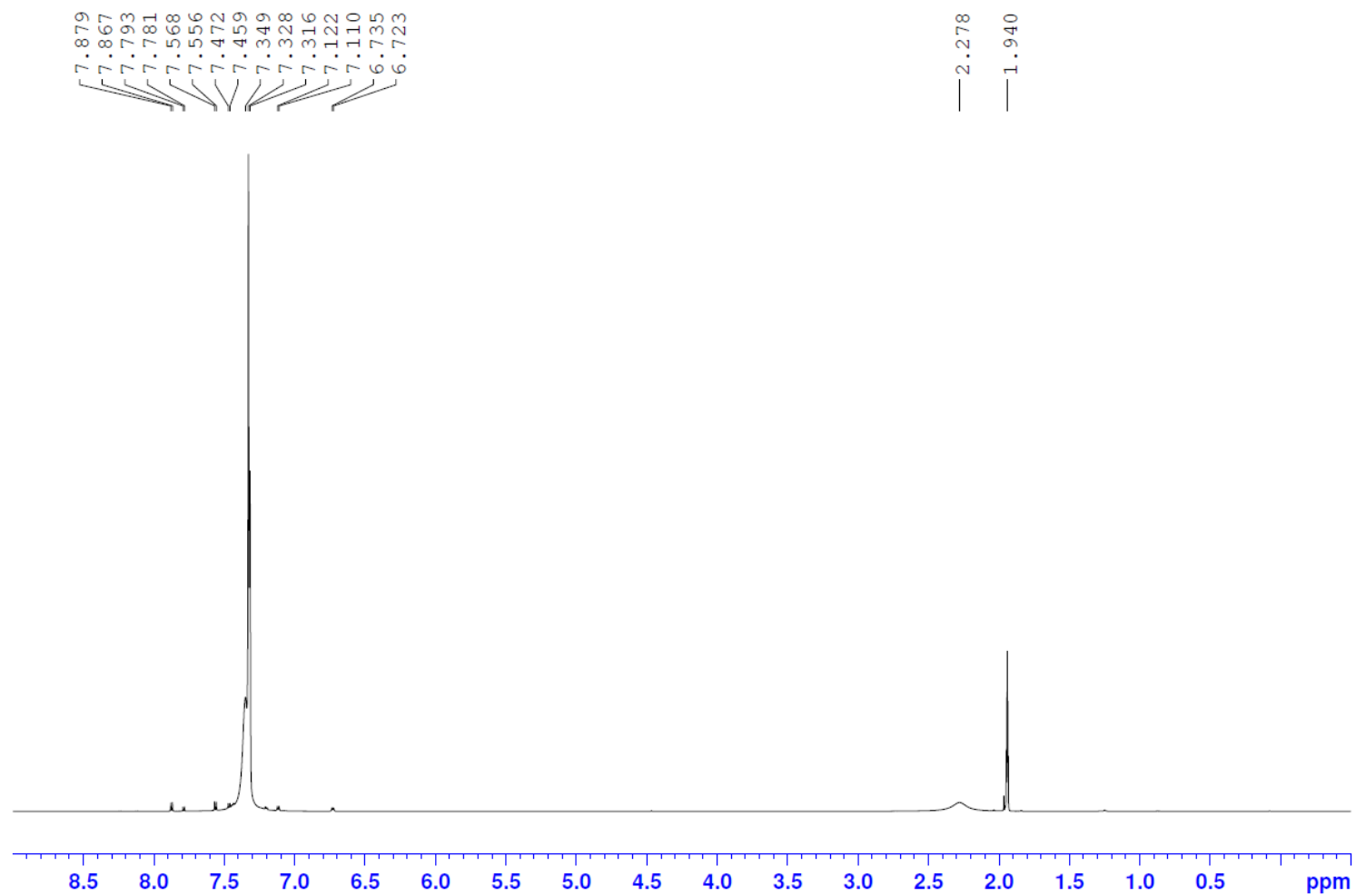


Figure C.60. ^1H NMR of **L4** in CD_3CN , referenced to residual solvent at 1.94 ppm

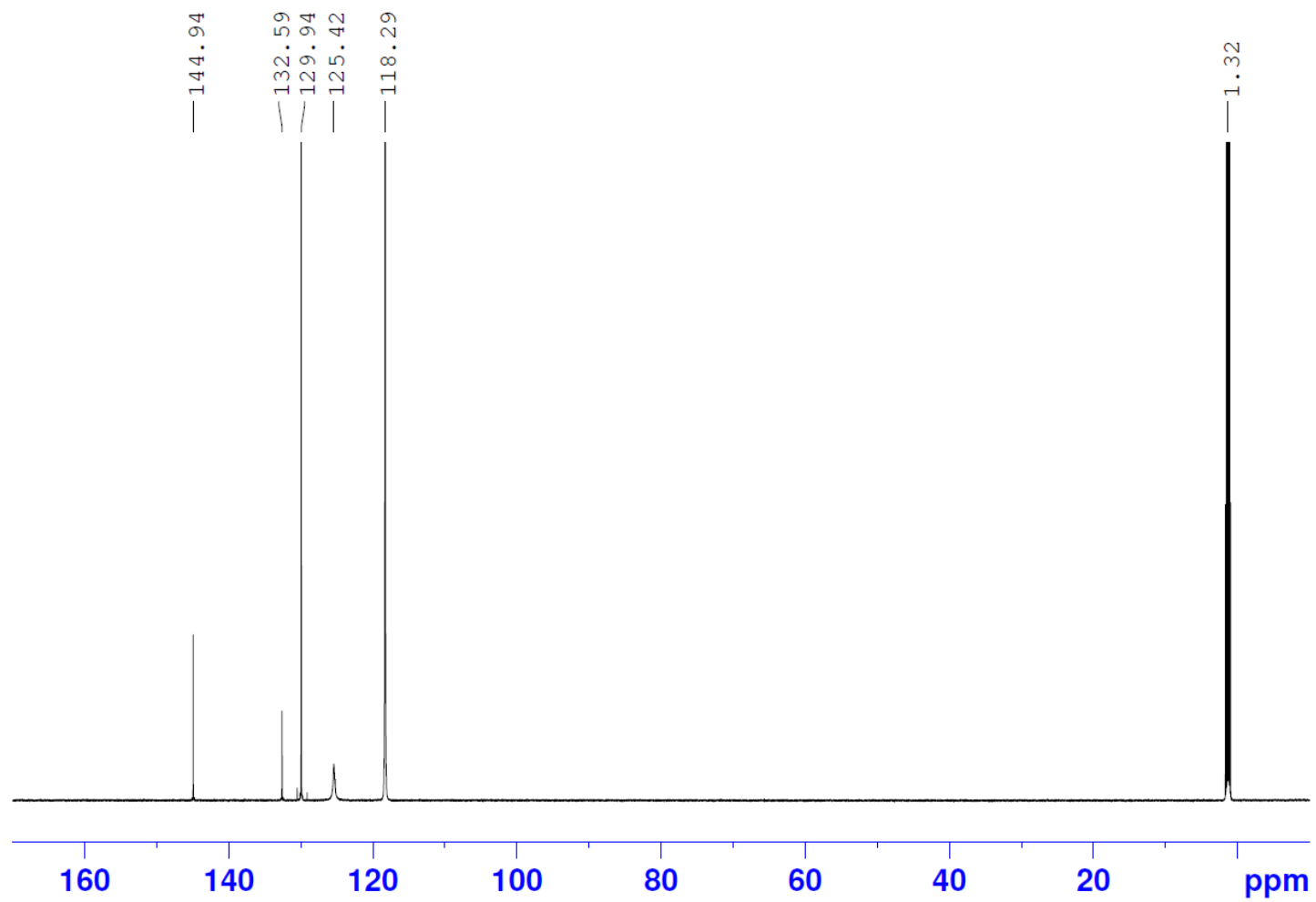


Figure C.61. $^{13}\text{C}\{^1\text{H}\}$ NMR of L4 in CD_3CN , referenced to residual solvent at 1.32 ppm

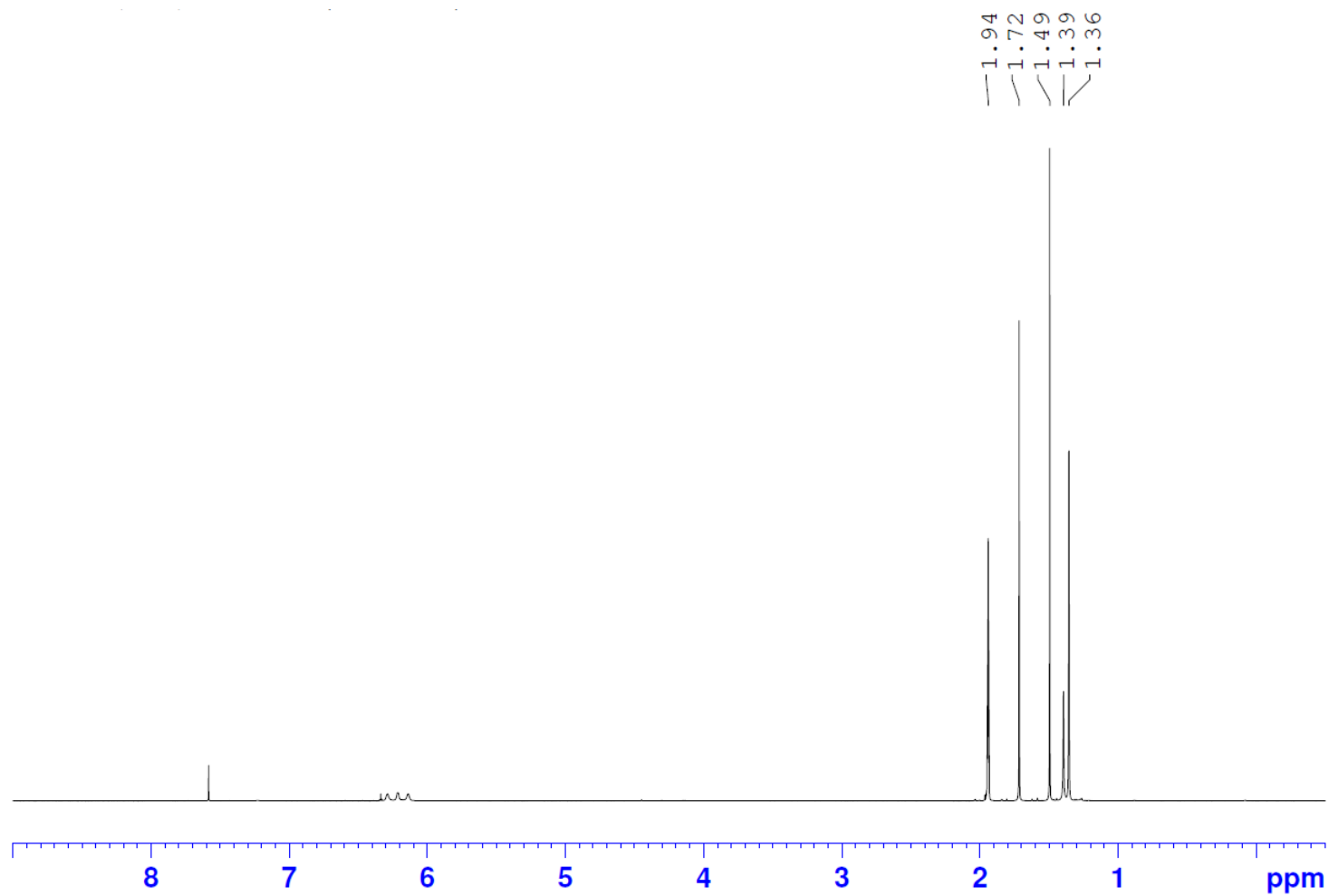


Figure C.62. ^1H NMR of C5 in CD_3CN , low concentration, referenced to residual solvent at 1.94 ppm

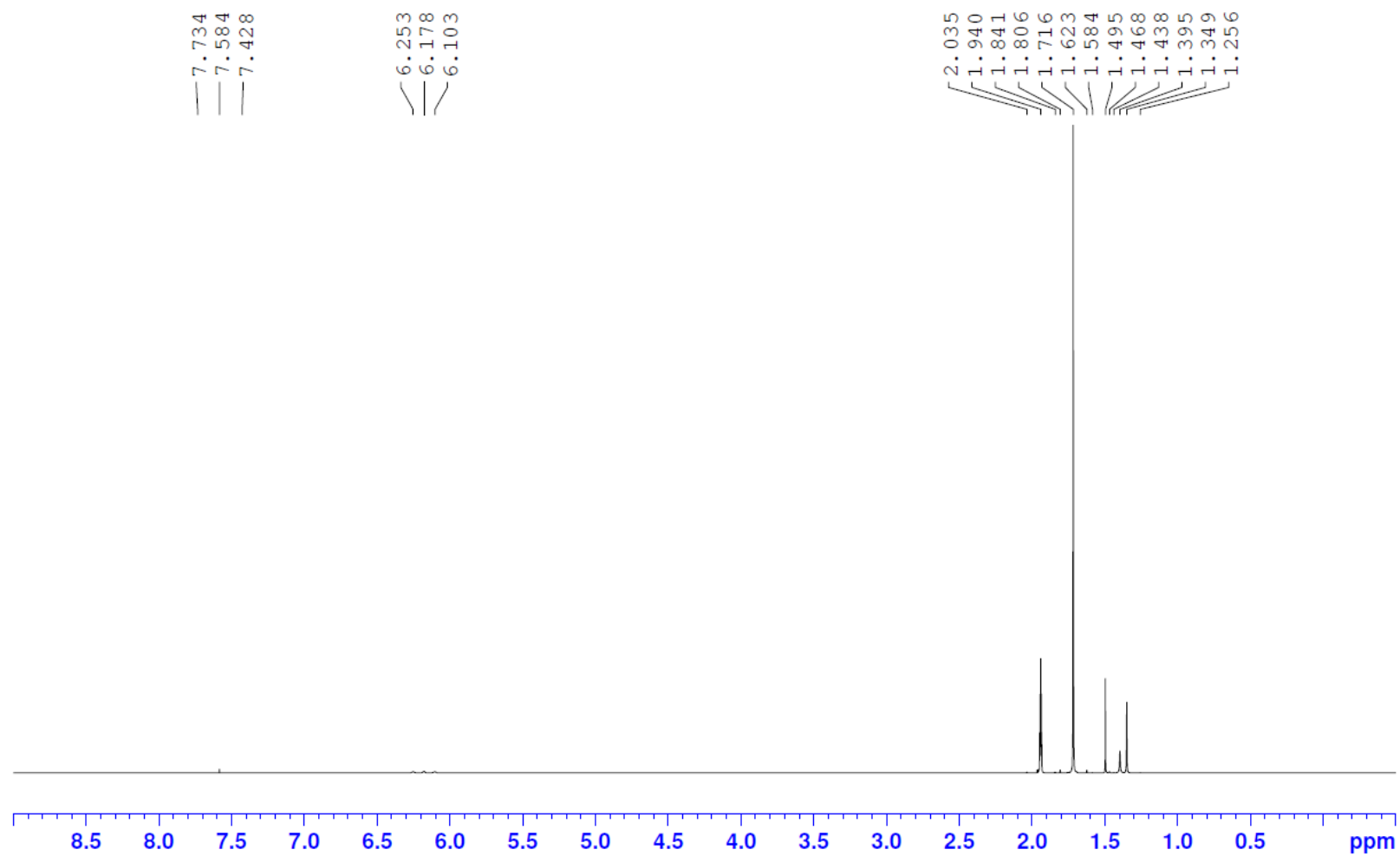


Figure C.63. ^1H NMR of C5 in CD_3CN , saturated, referenced to residual solvent at 1.94 ppm

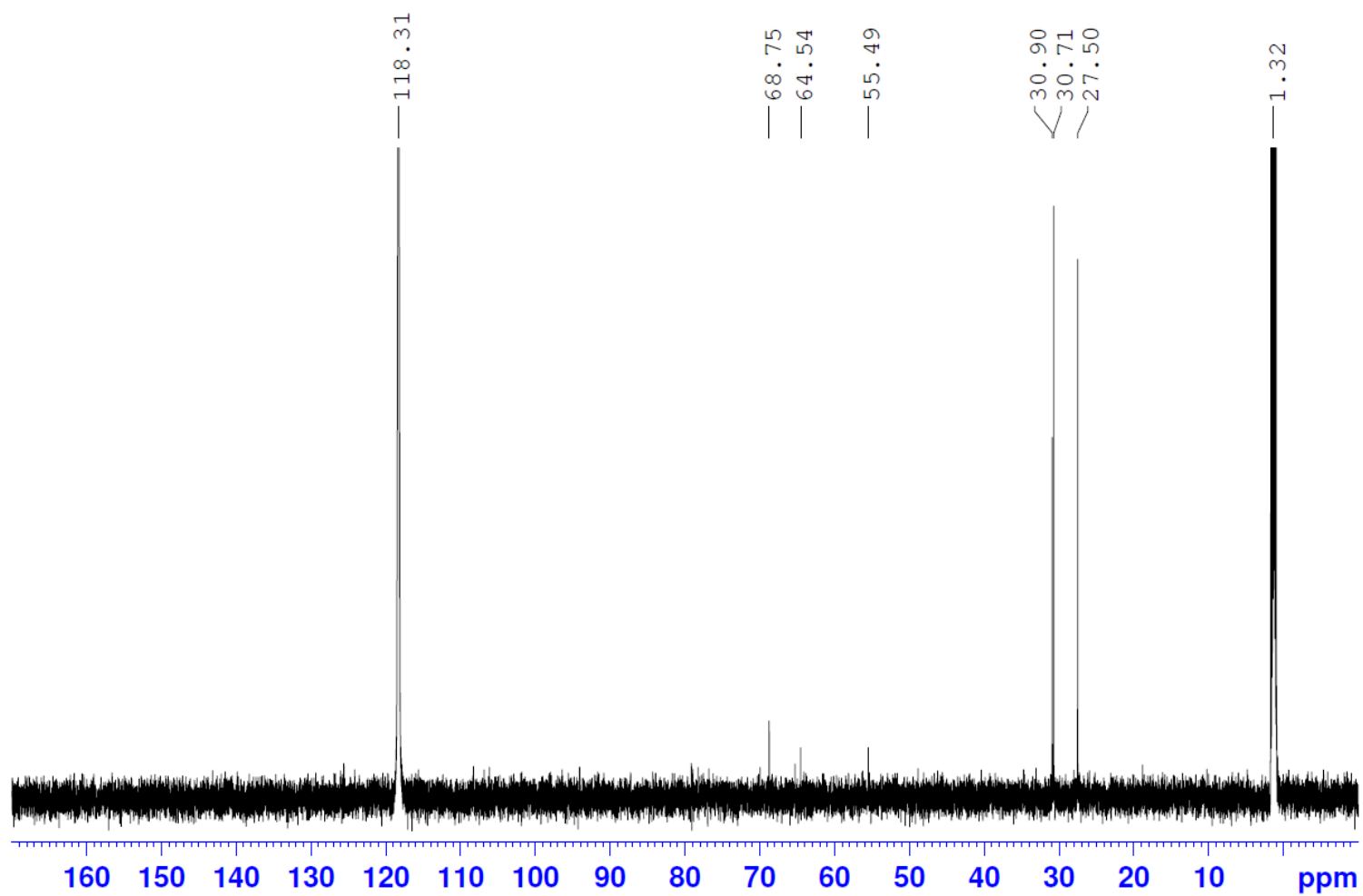


Figure C.64. $^{13}\text{C}\{^1\text{H}\}$ NMR of C5 in CD_3CN , low concentration, referenced to residual solvent at 1.32 ppm

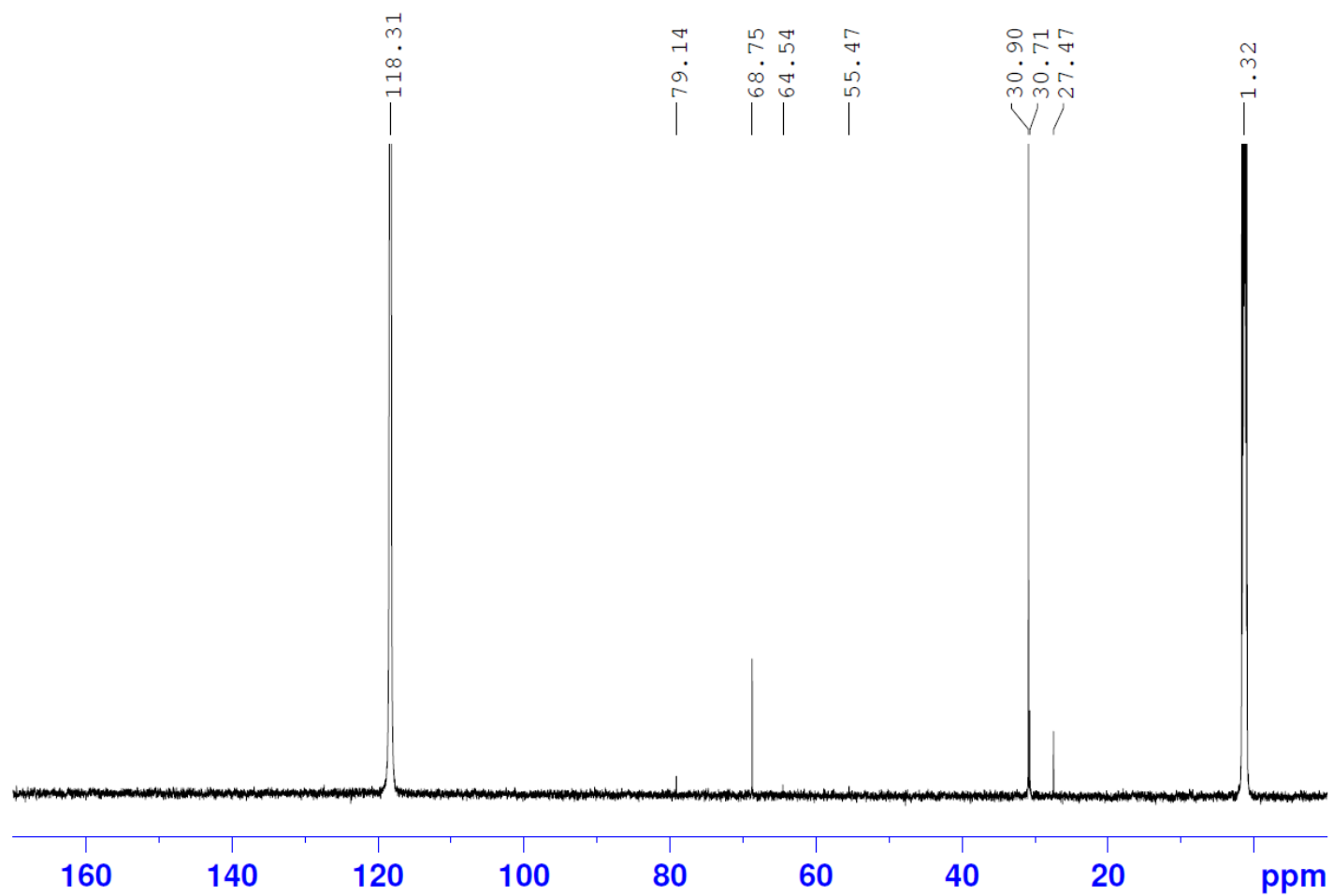


Figure C.65. $^{13}\text{C}\{^1\text{H}\}$ NMR of C5 in CD_3CN , saturated, referenced to residual solvent at 1.32 ppm

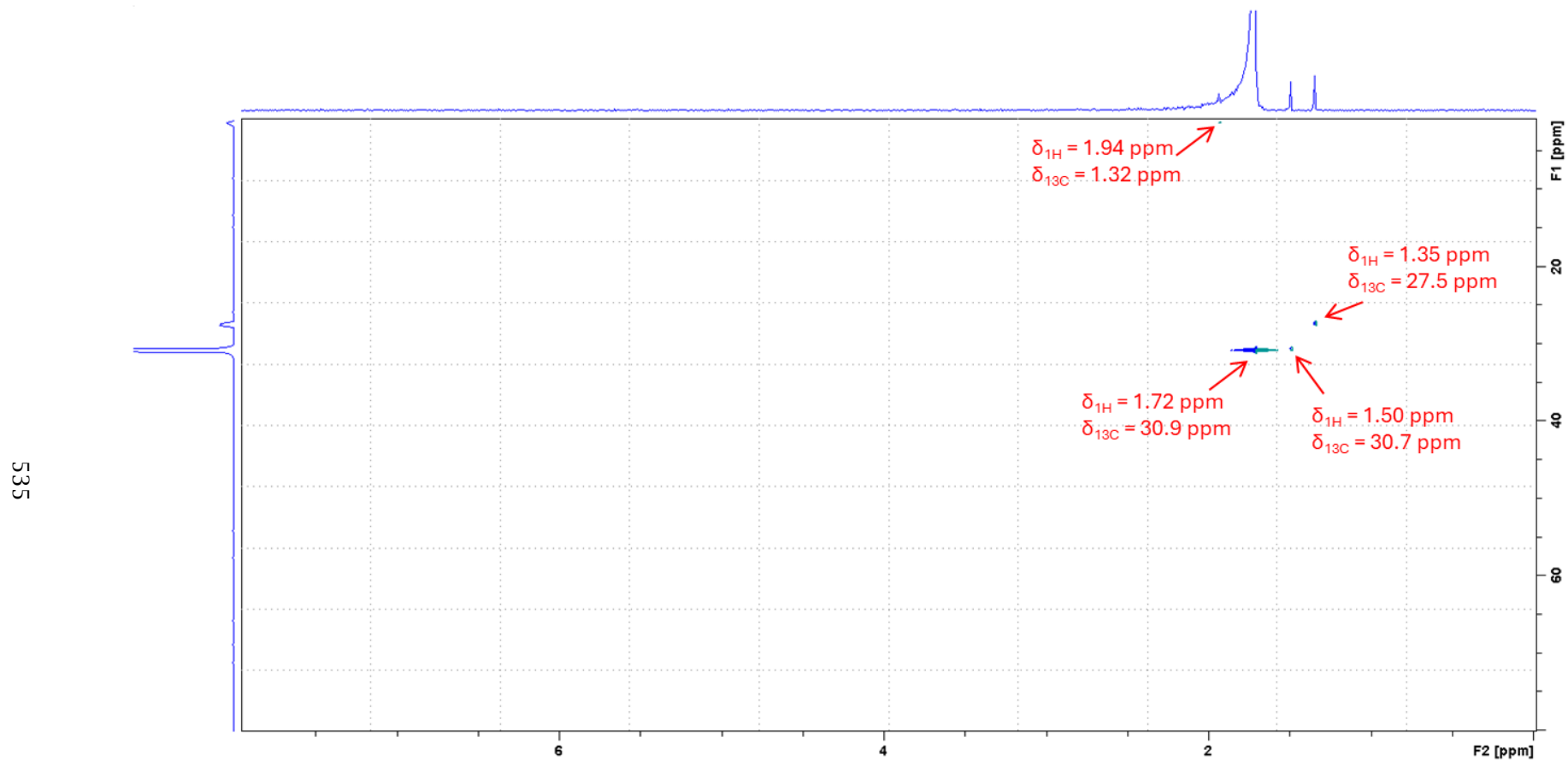


Figure C.66. ^1H - ^{13}C HSQC 2D-NMR of C5 in CD_3CN , saturated, referenced to residual solvent at 1.94 ppm (^1H , x-axis) and 1.32 ppm (^{13}C , y-axis)

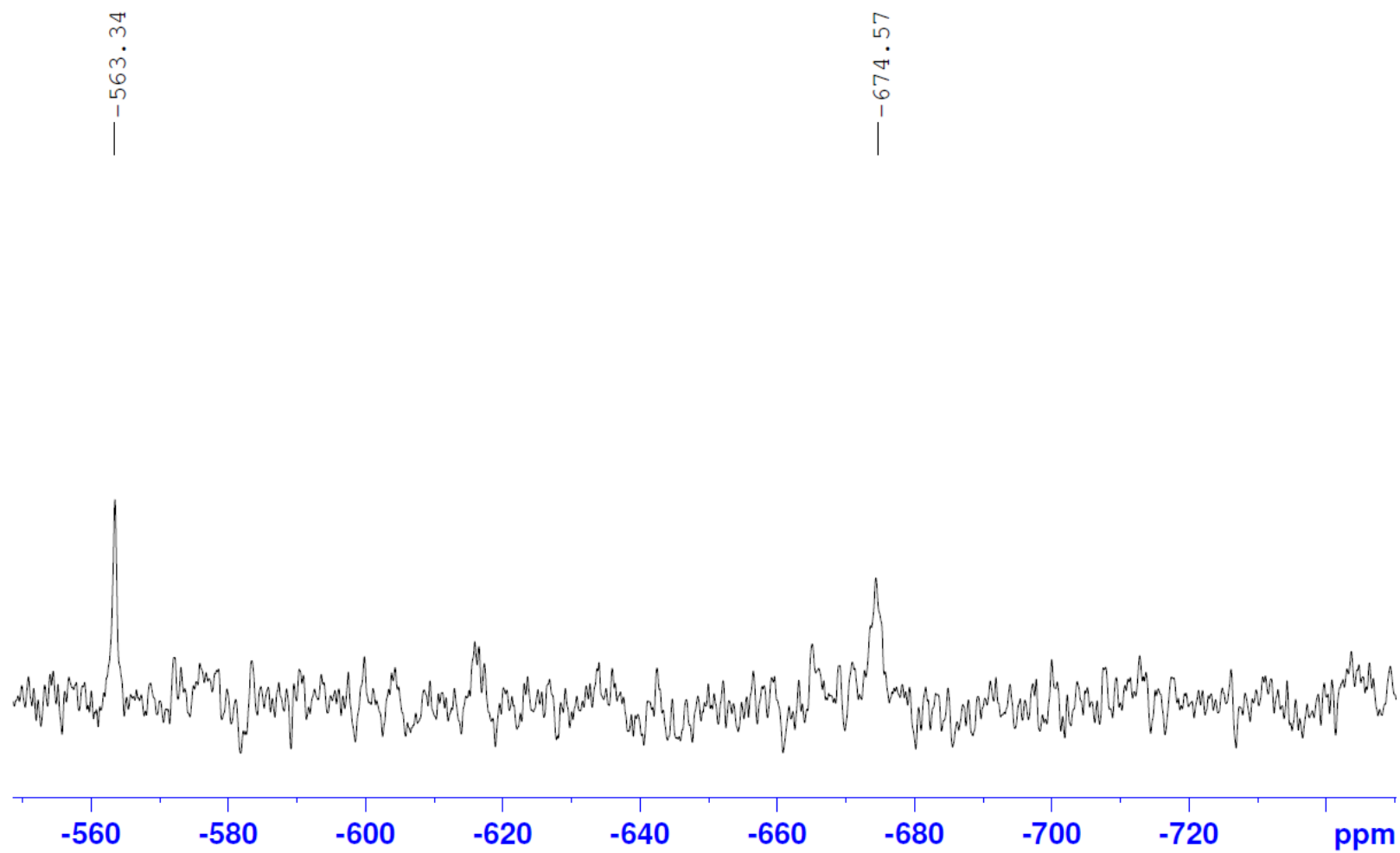


Figure C.67. ^{119}Sn NMR of C5 in CD_3CN , low concentration, referenced to external SnMe_4 at 0.0 ppm

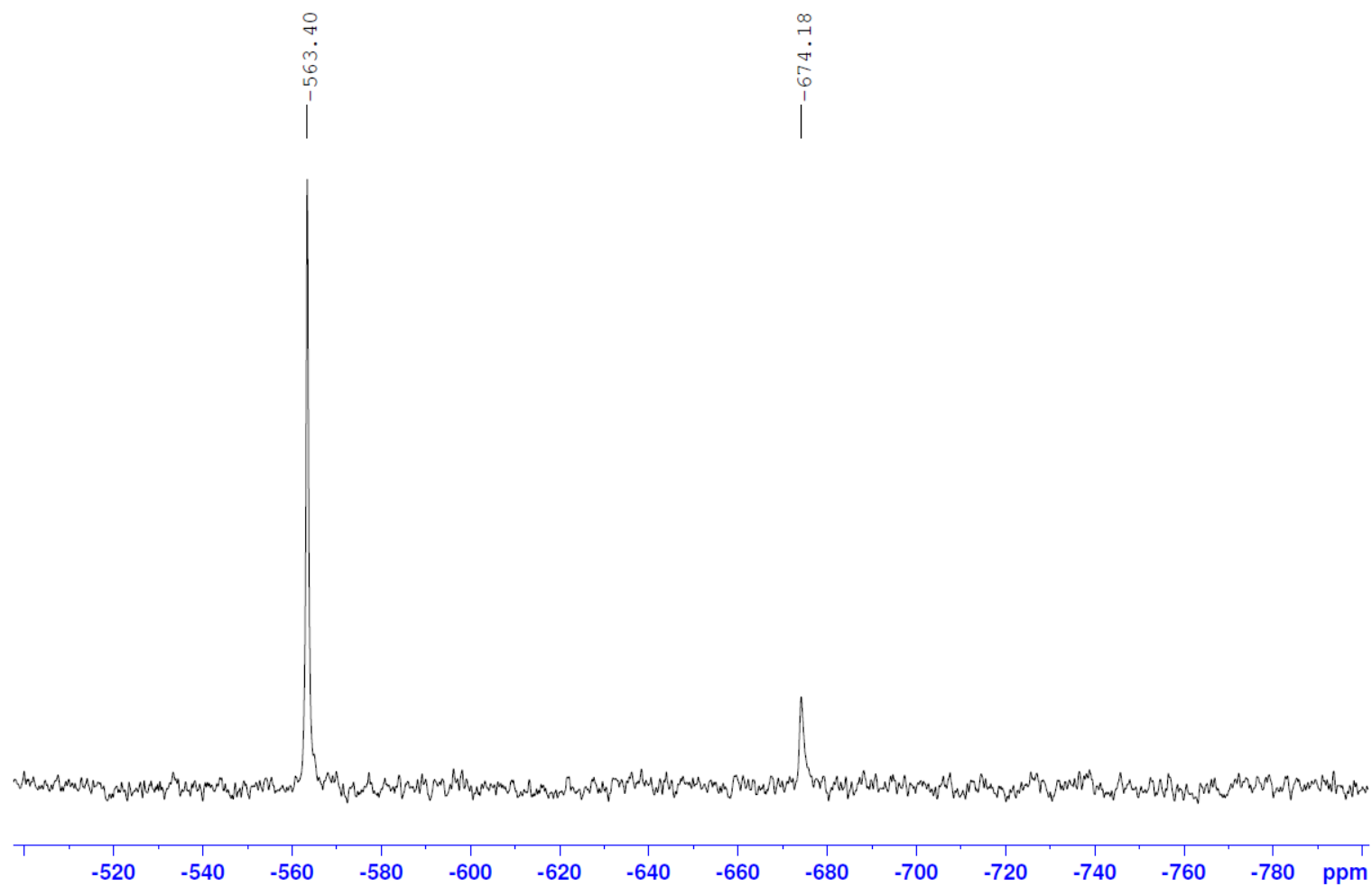


Figure C.68. ^{119}Sn NMR of C5 in CD_3CN , saturated, referenced to external SnMe_4 at 0.0 ppm

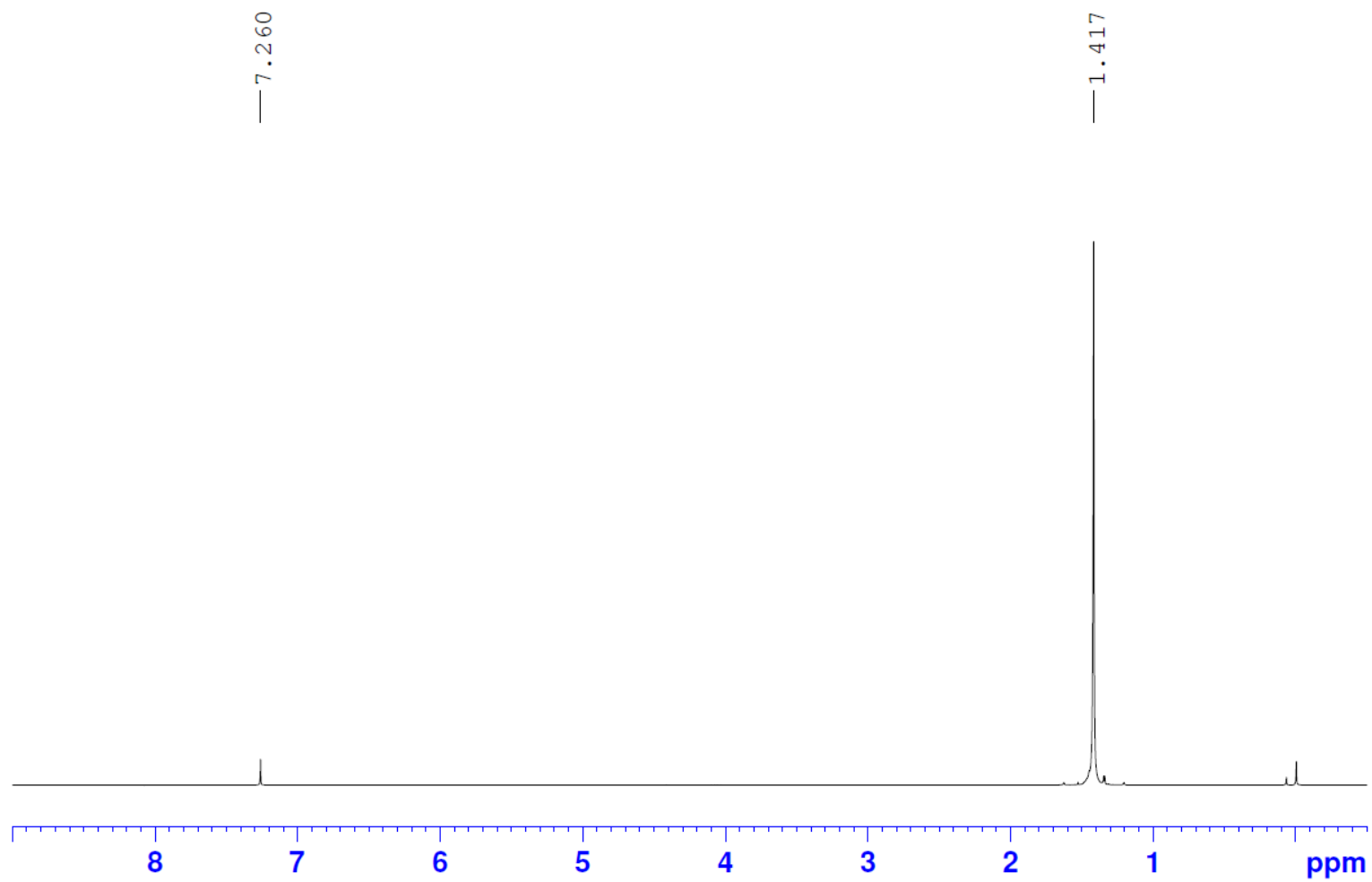


Figure C.69. ^1H NMR of L5 in CDCl_3 , referenced to residual solvent at 7.26 ppm

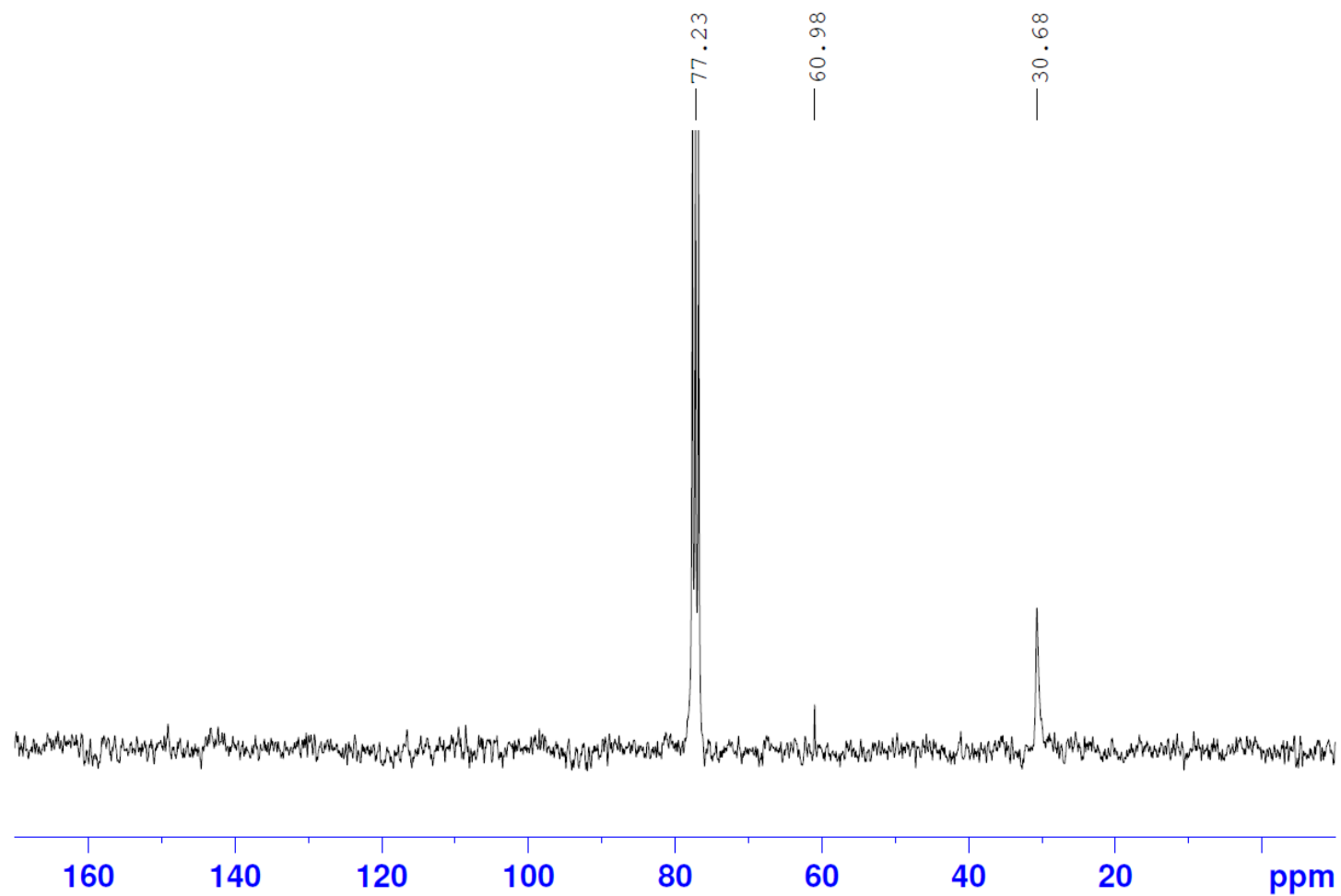


Figure C.70. $^{13}\text{C}\{^1\text{H}\}$ NMR of L5 in CDCl_3 , referenced to residual solvent at 77.23 ppm

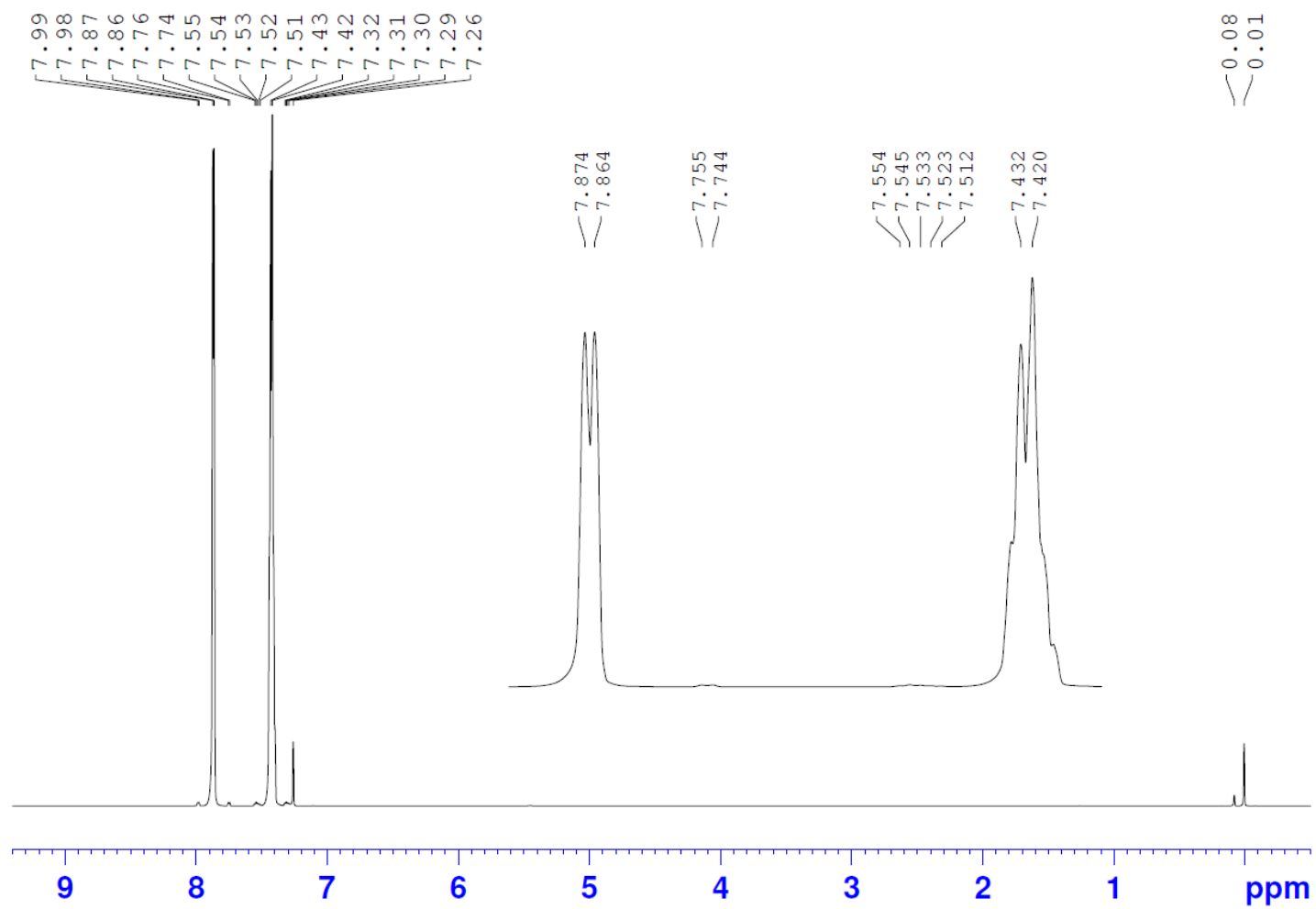


Figure C.71. ¹H NMR of C10 in CDCl₃, referenced to residual solvent at 7.26 ppm

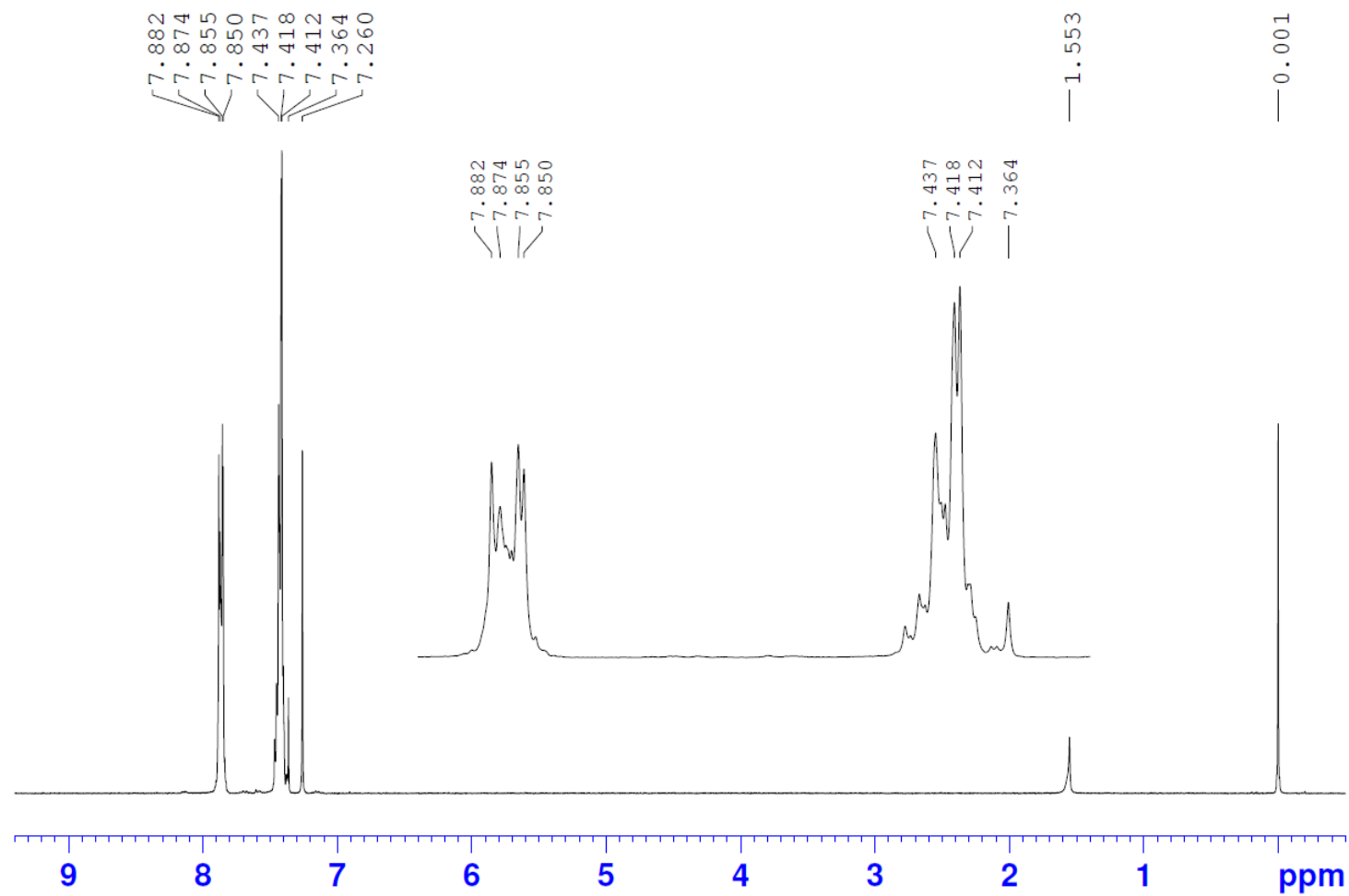


Figure C.72. ¹H NMR of L10 in CDCl₃, referenced to residual solvent at 7.26 ppm

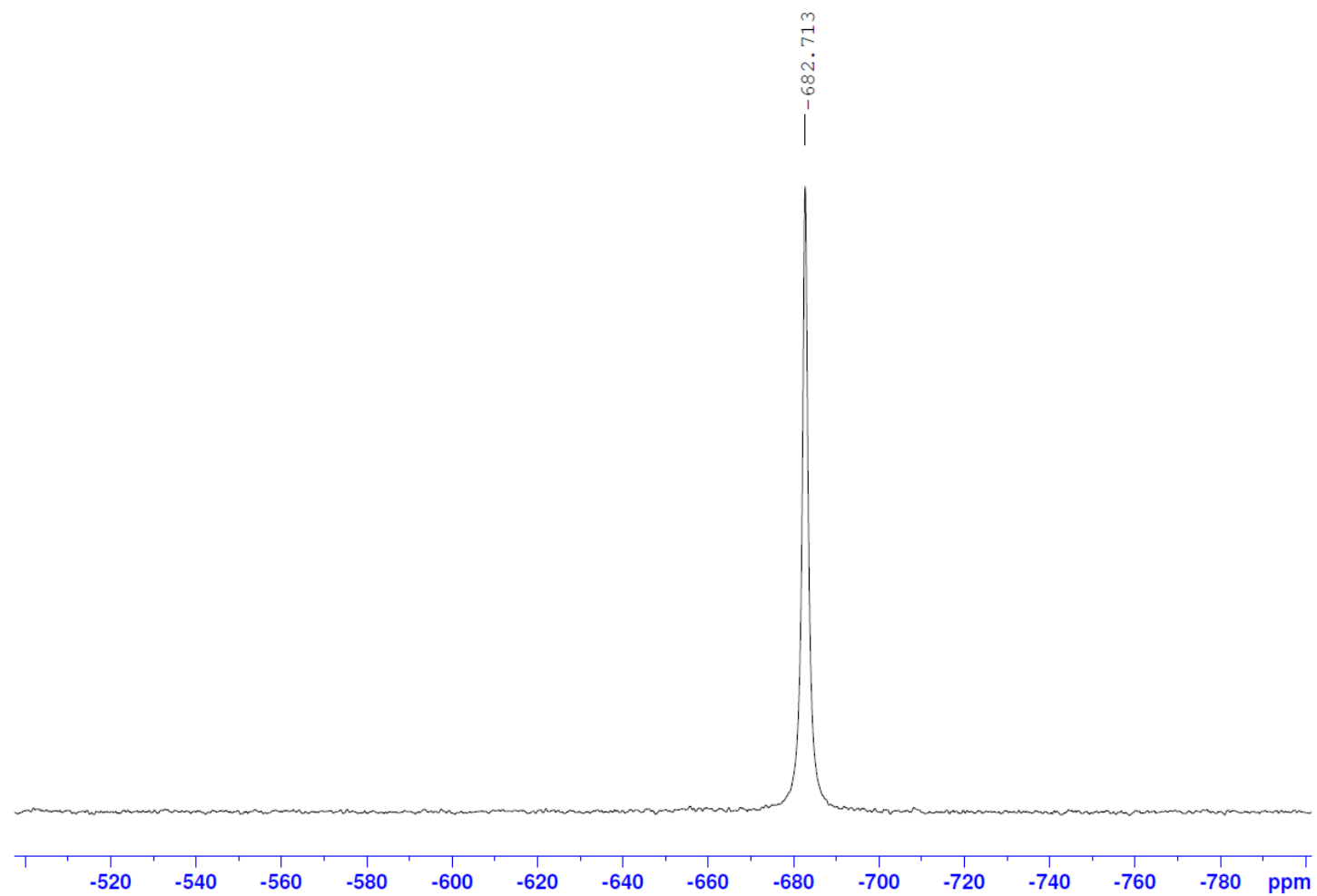


Figure C.73. ^{119}Sn NMR of **9** in CD_3CN , saturated, referenced to external SnMe_4 at 0.0 ppm

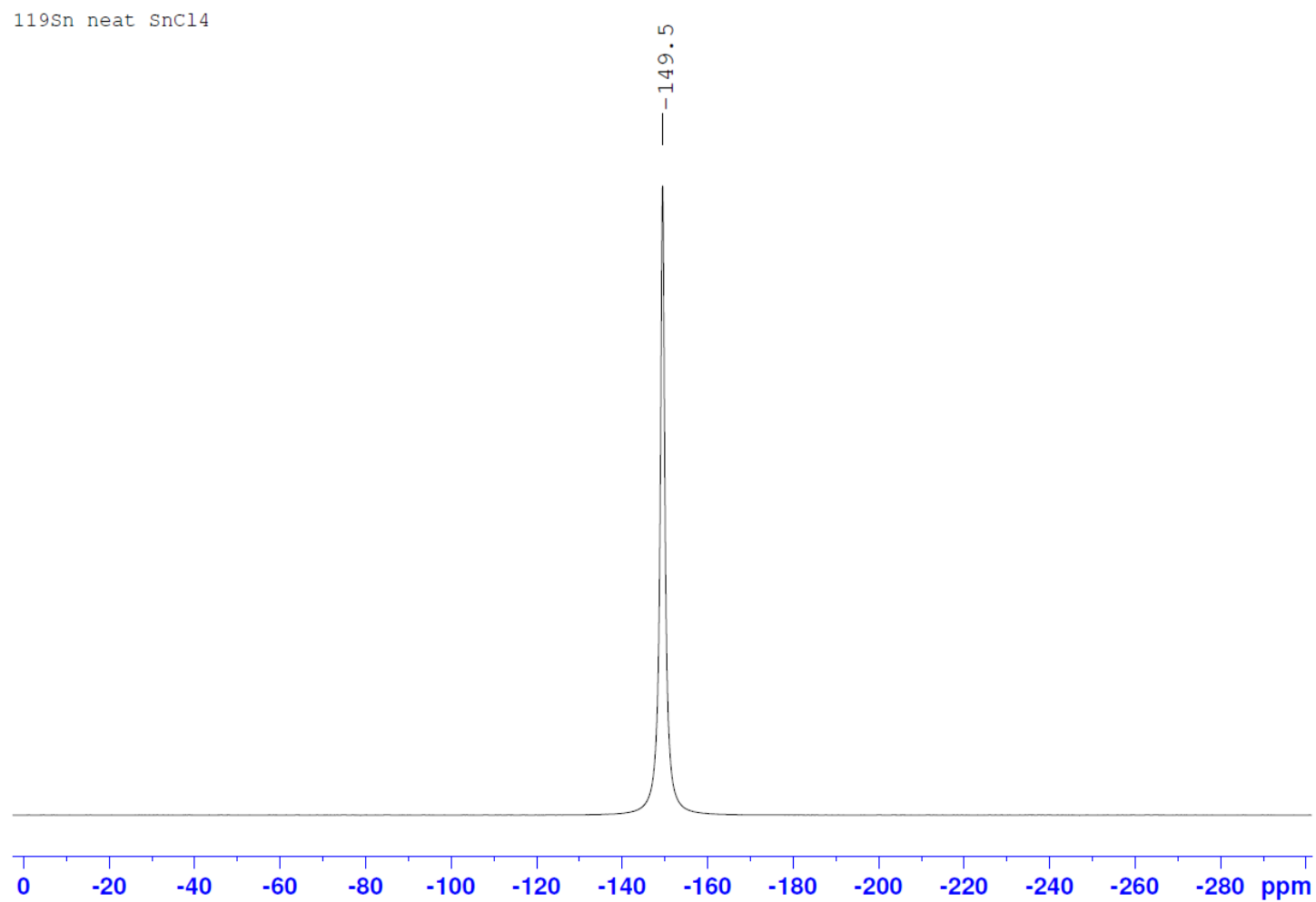
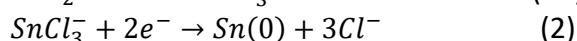
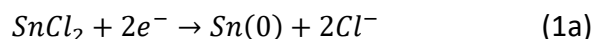


Figure C.74. ^{119}Sn NMR of neat SnCl_4 , referenced to external SnMe_4 at 0.0 ppm

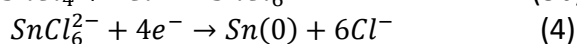
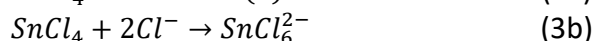
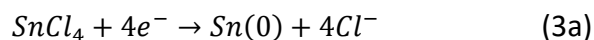
C.10. Polarography and Voltammetry of Sn(IV) and Sn(II) Halides

Sn(IV) and Sn(II) chlorides have highly similar electrochemical behaviours, and their polarography and voltammetry have been repeatedly and thoroughly documented. Thomas and Kolthoff,^[48] followed by Brajer *et al.*^[49] and Pool *et al.*,^[50] meticulously investigated the electrochemical profile of Sn(II) chloride in acetonitrile, resulting in a postulated mechanism where the first reduction process is a two-electron reduction of SnCl₂ with deposition of Sn(0) (or amalgamation, with a mercury electrode) and concurrent formation of Cl⁻ (Equation 1a below). Brajer demonstrates that Cl⁻ is a strong ligand toward Sn(II) in acetonitrile^[49] which will rapidly form SnCl₃⁻, a stable species whose reduction potential is more negative than that of SnCl₂. As such, the first reduction is current-limited by the formation of SnCl₃⁻, which reduces the availability of SnCl₂, as in equation 1b. The second cathodic process found is then attributed to the reduction of SnCl₃⁻, either in a one-electron process to a stable and soluble ionic species, or, in the presence of excess Cl⁻, a two-electron process which deposits Sn(0) metal. This mechanism is succinctly described by the reaction equations:



Scheme C.2. Reduction mechanism of Sn(II) chloride

In their earlier work, Thomas and Kolthoff suggested that Sn(IV) chlorides undergo two successive two-electron reductions, Sn(IV)→Sn(II)→Sn(0).^[48] However, Young *et al.* showed that the polarographic behaviour of Sn(IV) chloride is more consistent with a mechanism that is directly analogous to Sn(II) chloride, invoking two four-electron reductions in the following mechanistic equations:^[51]



Scheme C.3. Reduction mechanism of Sn(IV) chloride

C.11. Voltammetry Data Tables and Compilation of Voltammograms

Table C.27. Principal redox potentials of solutions containing Sn-complexes in CH₃CN, C1-C5 (E_c^2), compared to solutions of only their corresponding unbound ligands in CH₂Cl₂ or CH₃CN as indicated, L1-L5 (E_c^1). CV data report cathodic peak potentials, since C1-C5 processes are irreversible. All values are internally referenced to Fc^{+/0}.

Cyclic Voltammetry				
<i>n</i>	Scan rate (V·s ⁻¹)	Ln E_c^1 (V)	Cn E_c^2 (V) ^c	ΔE (V)
1	0.200	-1.717 ^a / -1.608 ^b	-1.659	0.058 / -0.051
2	0.200	-1.645 ^a / -1.576 ^b	-1.618	0.027 / -0.042
3	0.200	-1.596 ^a	-1.718	-0.122
4	0.200	-1.467 ^a	-1.360	0.107
5	0.500	-2.770 ^a	-2.620	0.150
Square-Wave Voltammetry				
<i>n</i>		Ln E_{sw}^1 (V)	Cn E_{sw}^2 (V) ^c	ΔE (V)
1		-1.642 ^a / -1.576 ^b	-1.602	0.040 / -0.026
2		-1.566 ^a / -1.516 ^b	-1.536	0.030 / -0.020
3		-1.547 ^a	-1.610	-0.063
4		-1.394 ^a	-1.322	0.072
5		-2.627 ^a	-2.450	0.177

^a 0.004 – 0.007 M analyte, 0.4 M [ⁿBu₂N][PF₆] in CH₂Cl₂; working electrode: glassy carbon (GC) (7.1 mm²), reference electrode: Ag wire, counter electrode: coiled Pt wire. ^b 0.004 M analyte, 0.2 M [ⁿBu₂N][PF₆] in CH₃CN; working electrode: Pt (7.1 mm²), reference electrode: Ag wire, counter electrode: coiled Pt wire. ^c 0.003 – 0.006 M analyte, 0.2 M [ⁿBu₂N][PF₆] in CH₃CN; working electrode: Pt (7.1 mm²), reference electrode: Ag wire, counter electrode: coiled Pt wire.

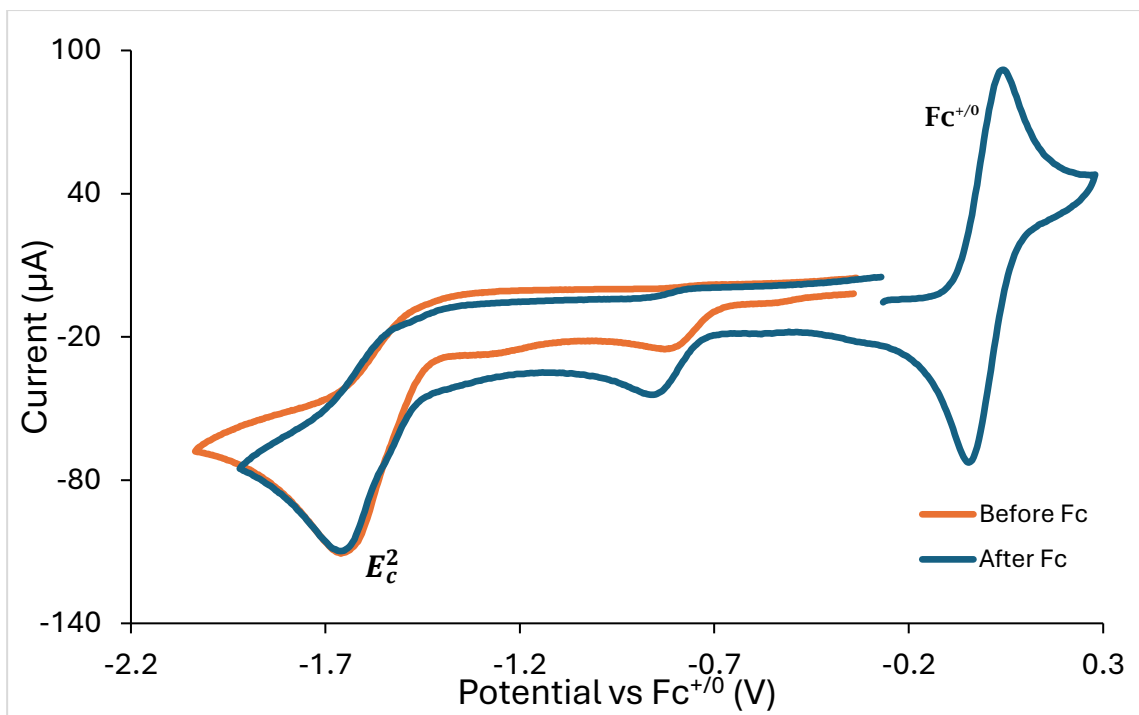


Figure C.75. Overlay of cyclic voltammograms (CVs) of **1**, showing experiments with a switching potential negative of the E_c^2 peak before (orange trace) and after (blue trace) addition of ferrocene (Fc). Voltammograms of **1**–**5** are internally referenced to the midpoint of the $\text{Fc}^{+/0}$ process at 0.0 V. Voltammograms without Fc are calibrated to the E_c^2 peak potential from an analogous voltammogram containing Fc, as in the blue trace above. Because the voltammograms sometimes change after Fc is added, overlays are provided for all compounds. All CVs and square-wave voltammograms (SWVs) were taken on a 7.1 mm² Pt working electrode in CH₃CN with ~0.2 M [Bu₄N][PF₆] supporting electrolyte. The scan rate of CVs was 0.200 V/s unless otherwise specified.

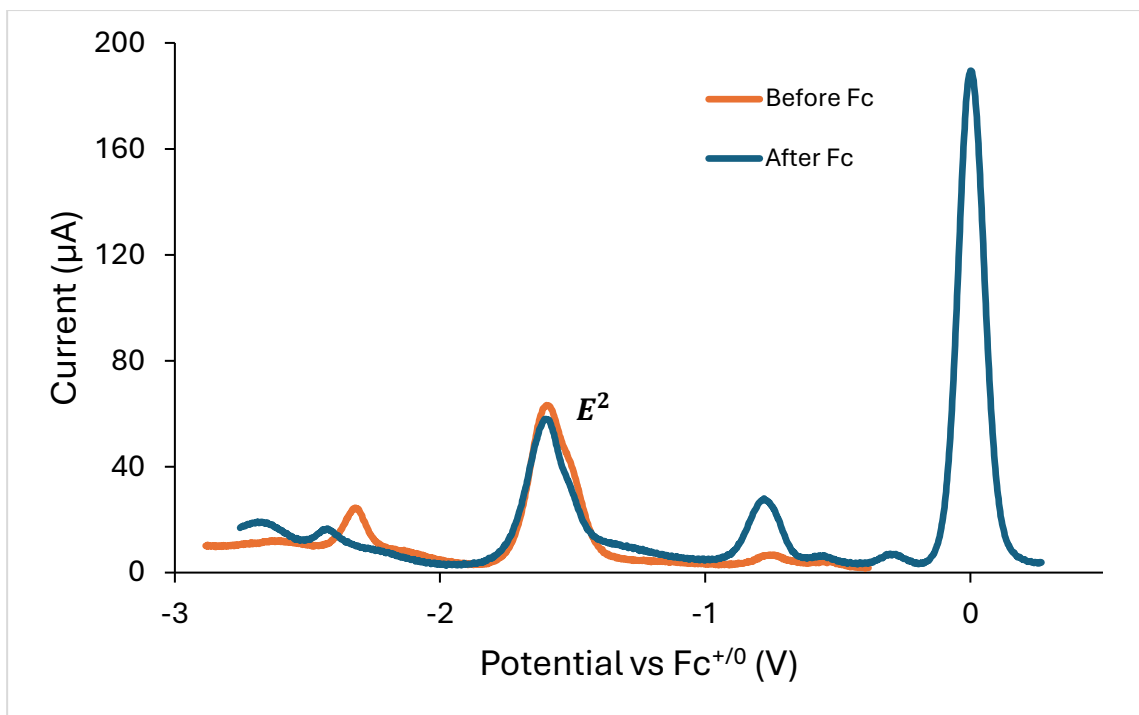


Figure C.76. Overlay of SWVs of **1** before and after addition of Fc.

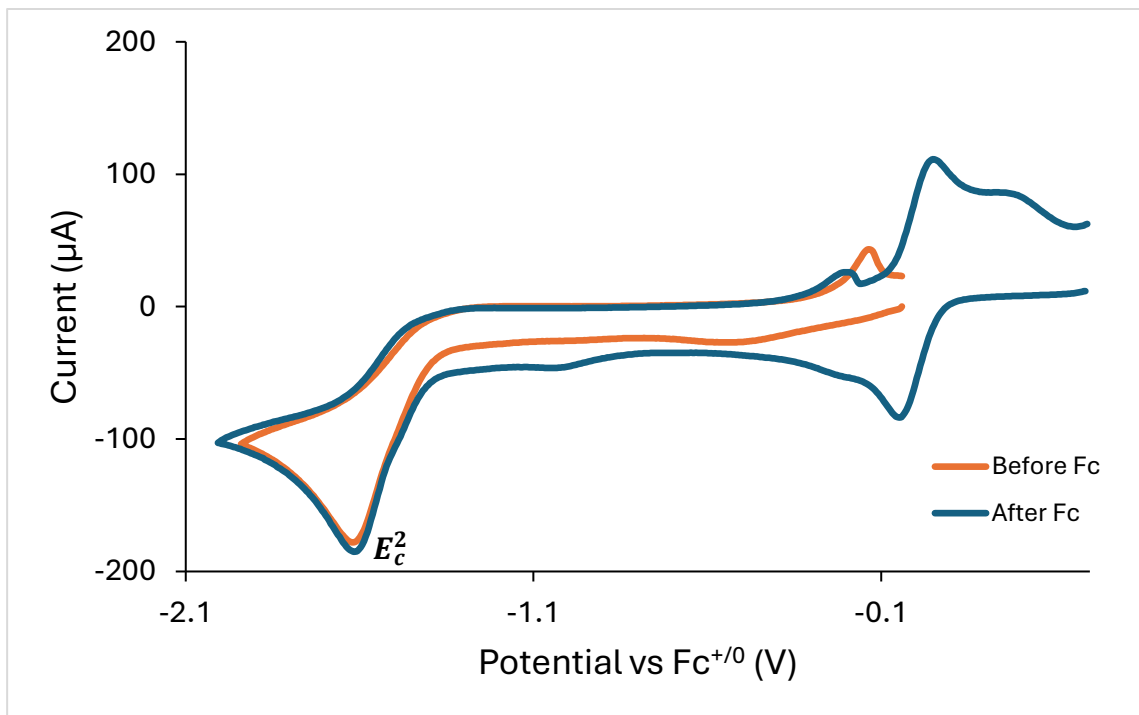


Figure C.77. Overlay of CVs of **2** before and after addition of Fc.

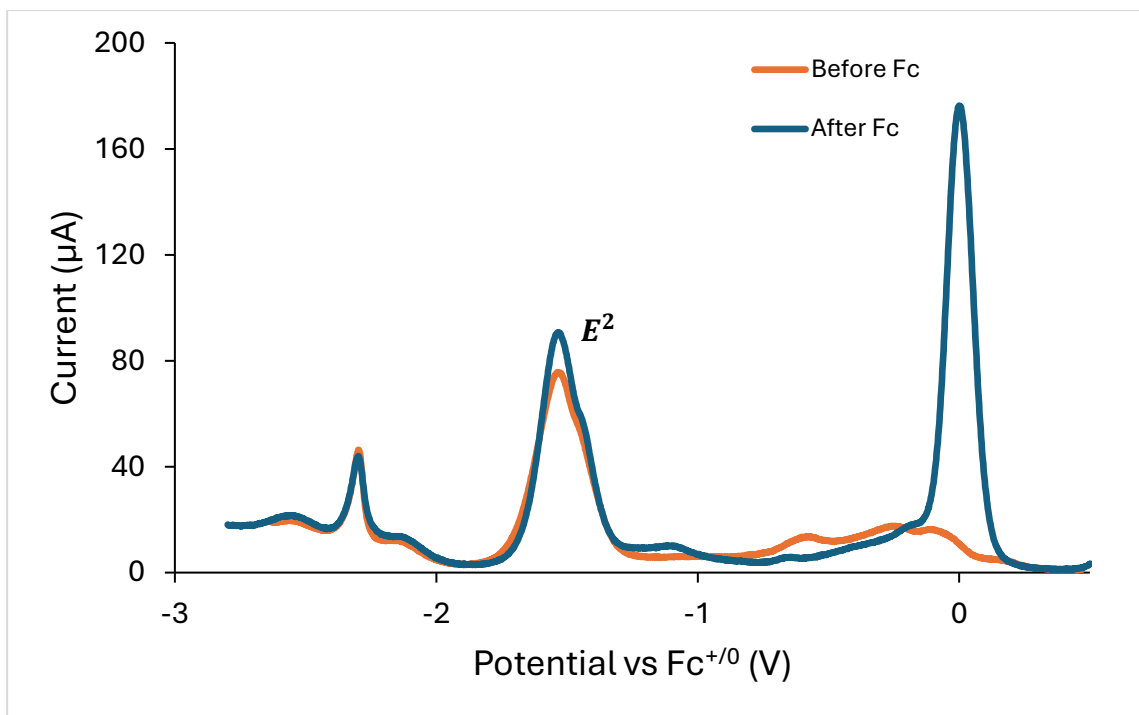


Figure C.78. Overlay of SWVs of **2** before and after addition of Fc.

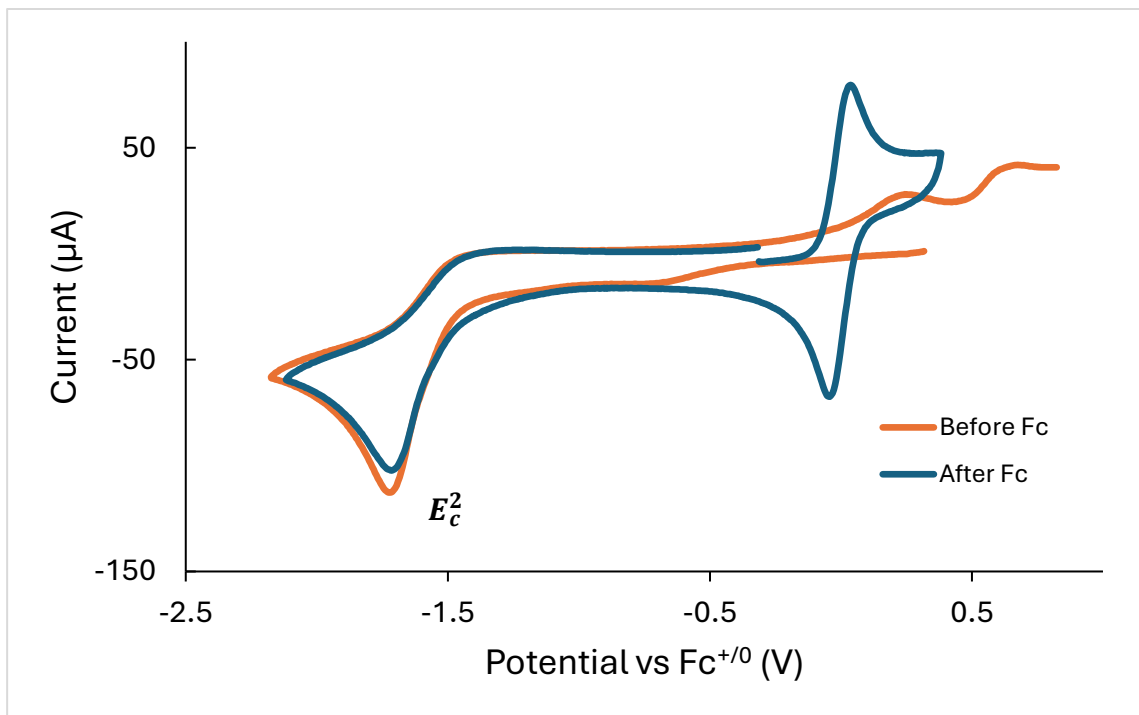


Figure C.79. Overlay of CVs of **3** before and after addition of Fc.

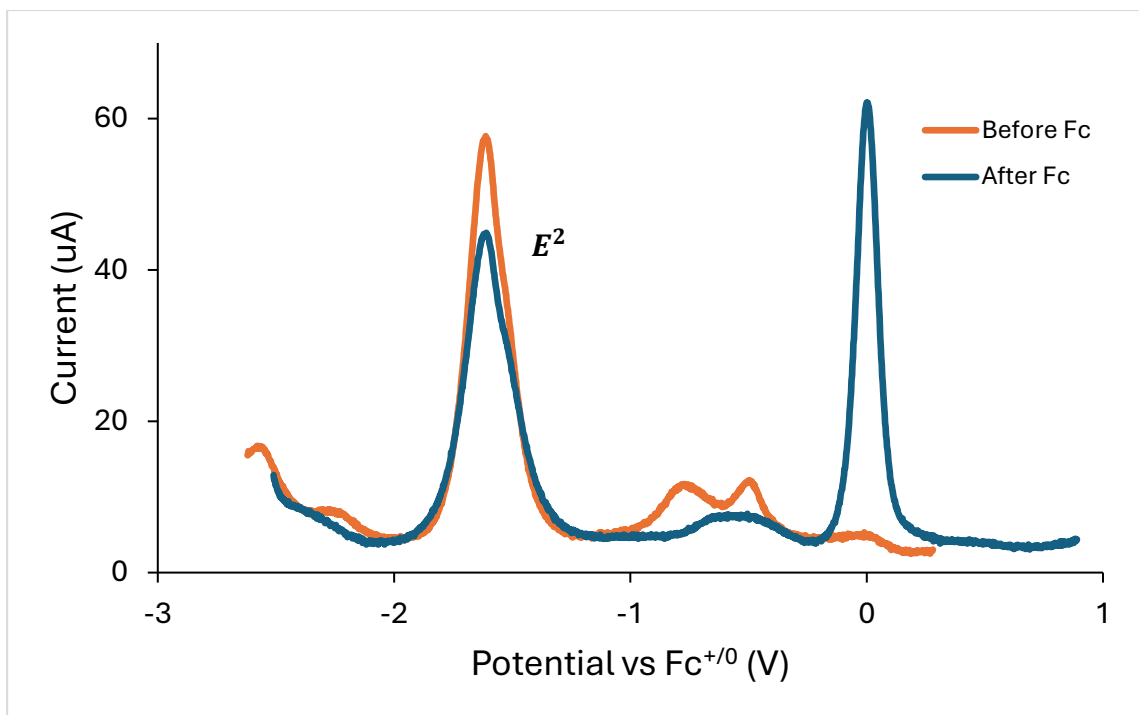


Figure C.80. Overlay of SWVs of 3 before and after addition of Fc.

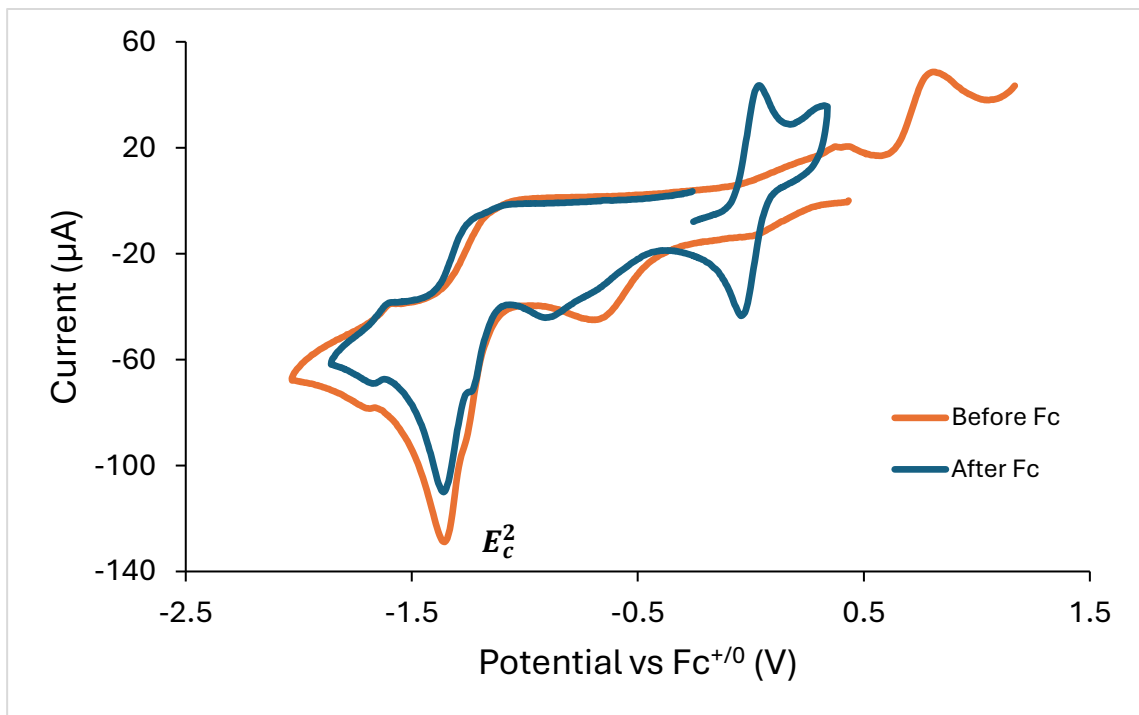


Figure C.81. Overlay of CVs of 4 before and after addition of Fc.

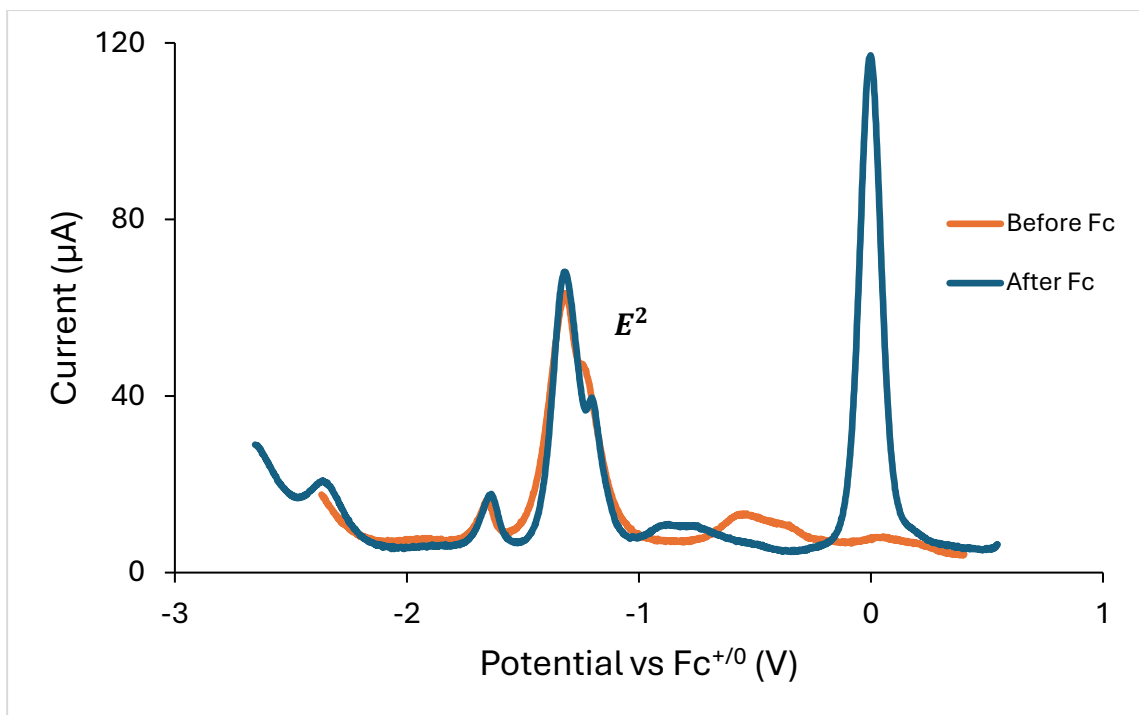


Figure C.82. Overlay of SWVs of **4** before and after addition of Fc.

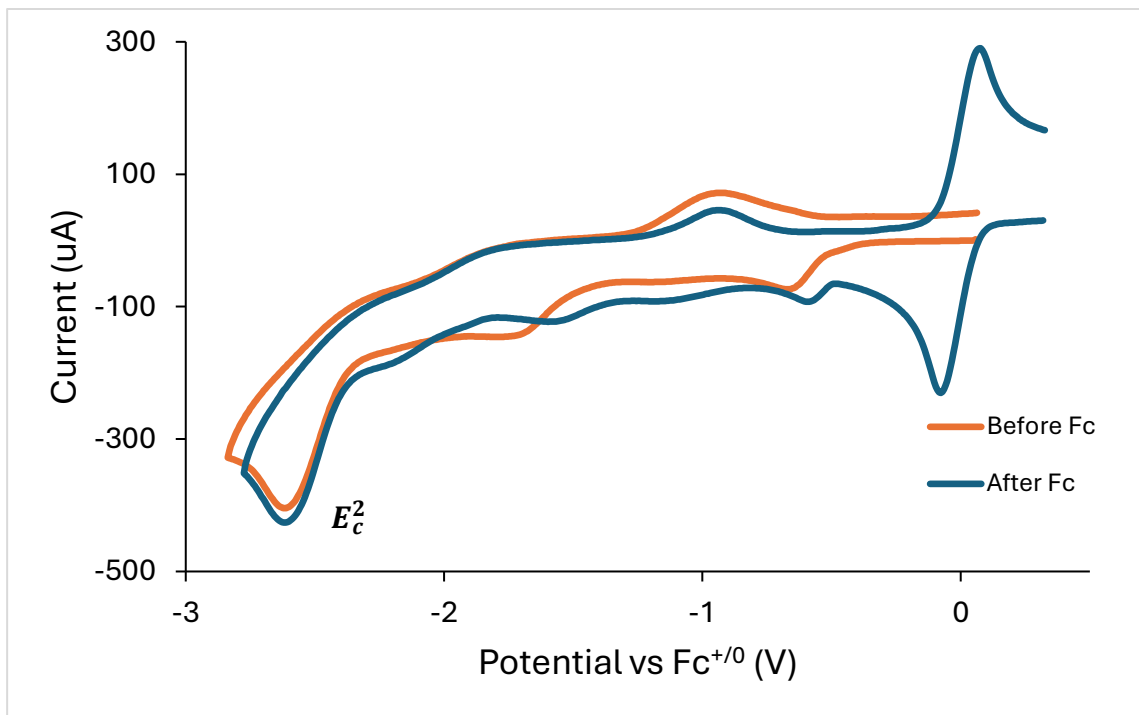


Figure C.83. Overlay of CVs of **5** before and after addition of Fc. CV scan rate for **5** was 0.500 V/s.

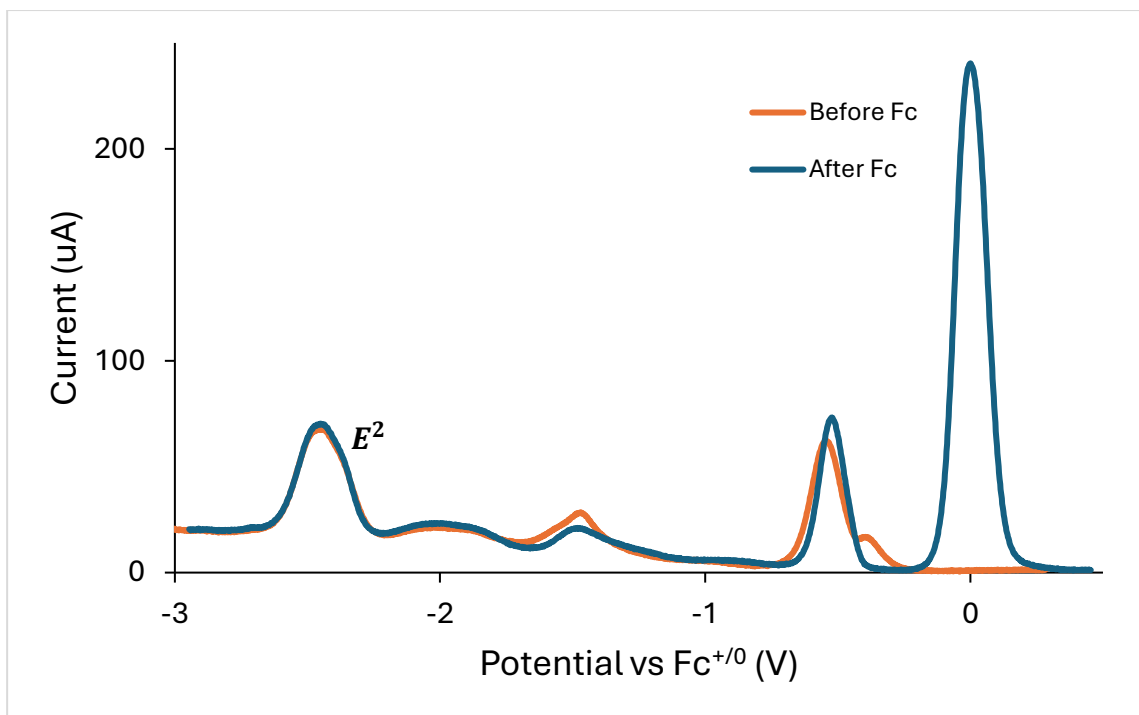


Figure C.84. Overlay of SWVs of 5 before and after addition of Fc.

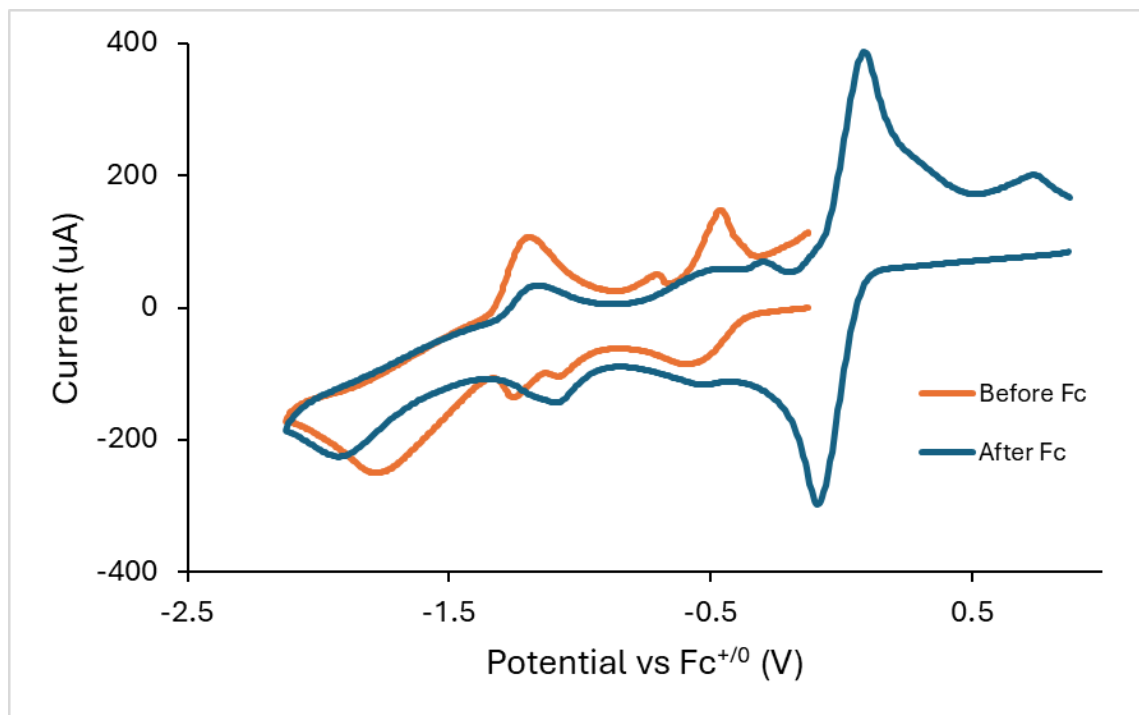


Figure C.85. Overlay of CVs of 9 before and after addition of Fc. Because of significant changes in redox behaviour after Fc was added, the 'Before Fc' voltammogram (orange trace) here is treated differently than 1–5. Instead of calibrating it to a peak value vs $\text{Fc}^{+/0}$, it is referenced by applying the same offset as was applied to the 'After Fc' voltammogram (blue trace) to set $\text{Fc}^{+/0}$ to 0.0 V.

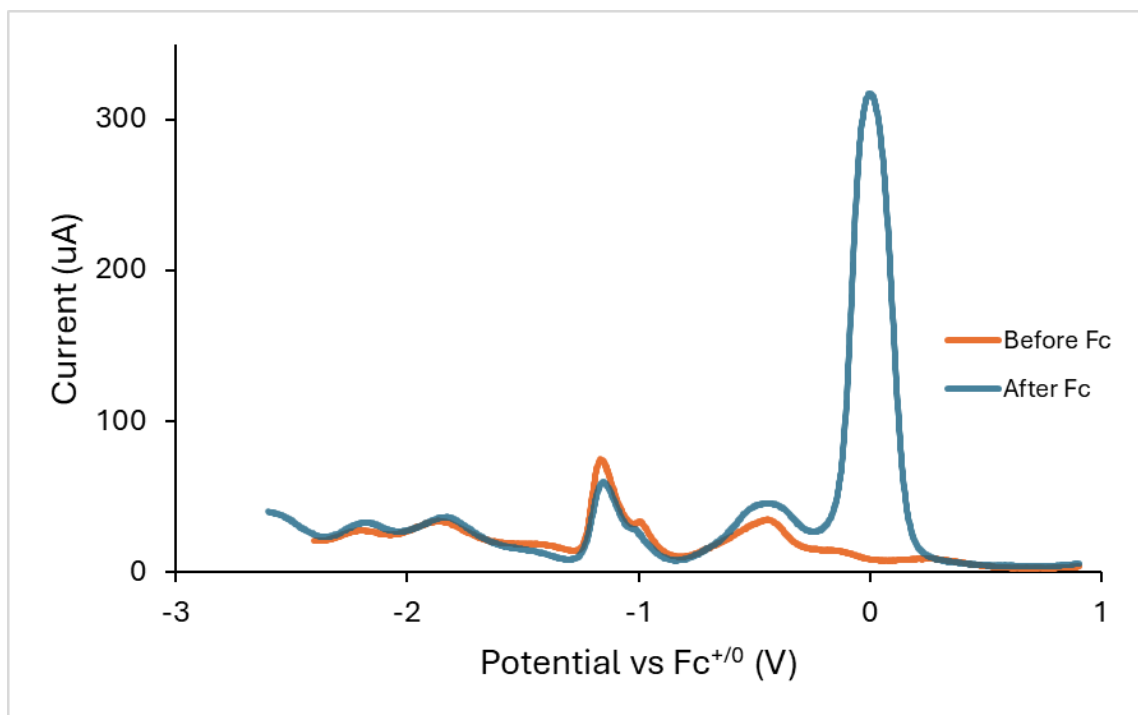


Figure C.86. Overlay of SWVs of **9** before and after addition of Fc. 'Before Fc' (orange trace) is referenced to $\text{Fc}^{+/0}$ by applying the same offset as was applied to 'After Fc' (blue trace) to set $\text{Fc}^{+/0}$ to 0.0 V.

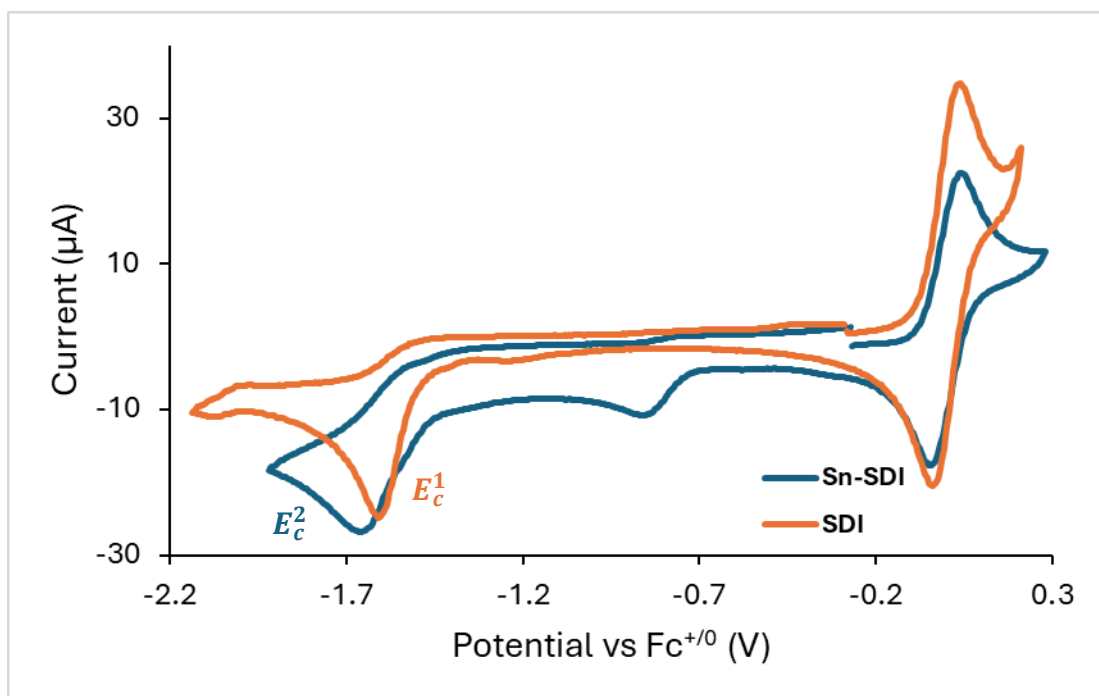


Figure C.87. Overlay of CVs of $(4\text{-MeOPhN})_2\text{S}$ (orange trace) and its corresponding tetrachlorotin complex, **1** (blue trace). Both CVs were taken in CH_3CN with a 7.1 mm^2 Pt inlaid-disk working electrode at 0.200 V/s .

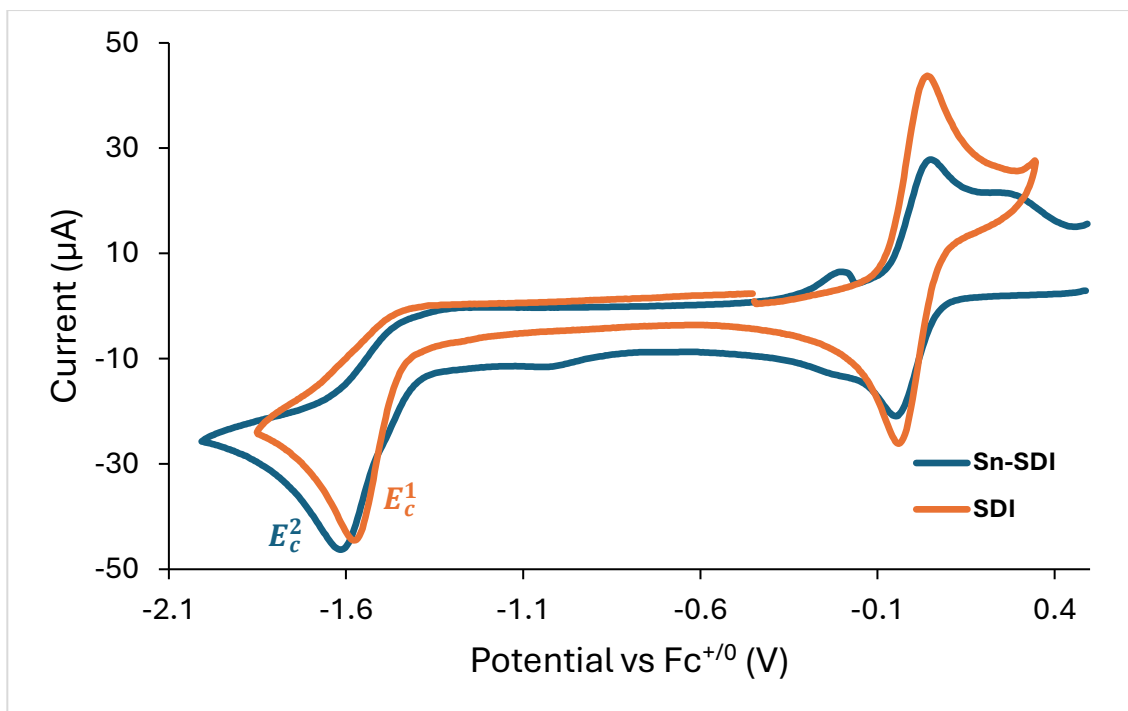


Figure C.88. Overlay of CVs of (4-MePhN)₂S (orange trace) and its corresponding tetrachlorotin complex, 2 (blue trace). Both CVs were taken in CH₃CN with a 7.1 mm² Pt inlaid-disk working electrode at 0.200 V/s.

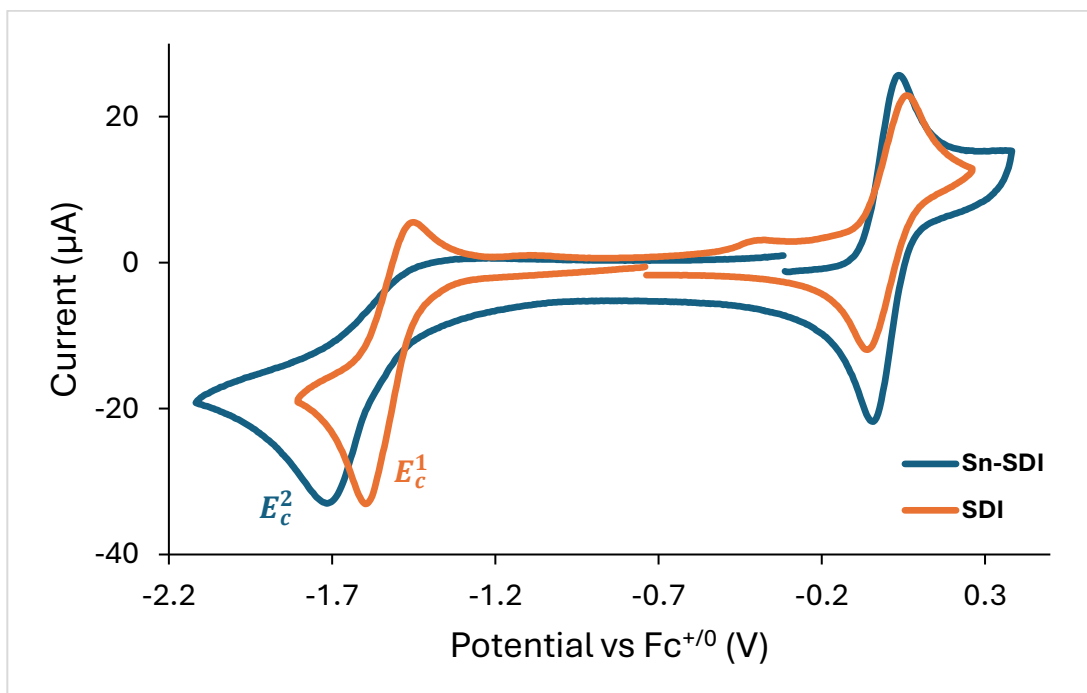


Figure C.89. Overlay of CVs of (4-FPhN)₂S (orange trace) and its corresponding tetrachlorotin complex, 3 (blue trace). The CV of (4-FPhN)₂S was taken in CH₂Cl₂ with a 7.1 mm² glassy-carbon inlaid-disk working electrode at 0.200 V/s. The CV of 3 was taken in CH₂Cl₂ with a 7.1 mm² Pt inlaid-disk working electrode at 0.200 V/s.

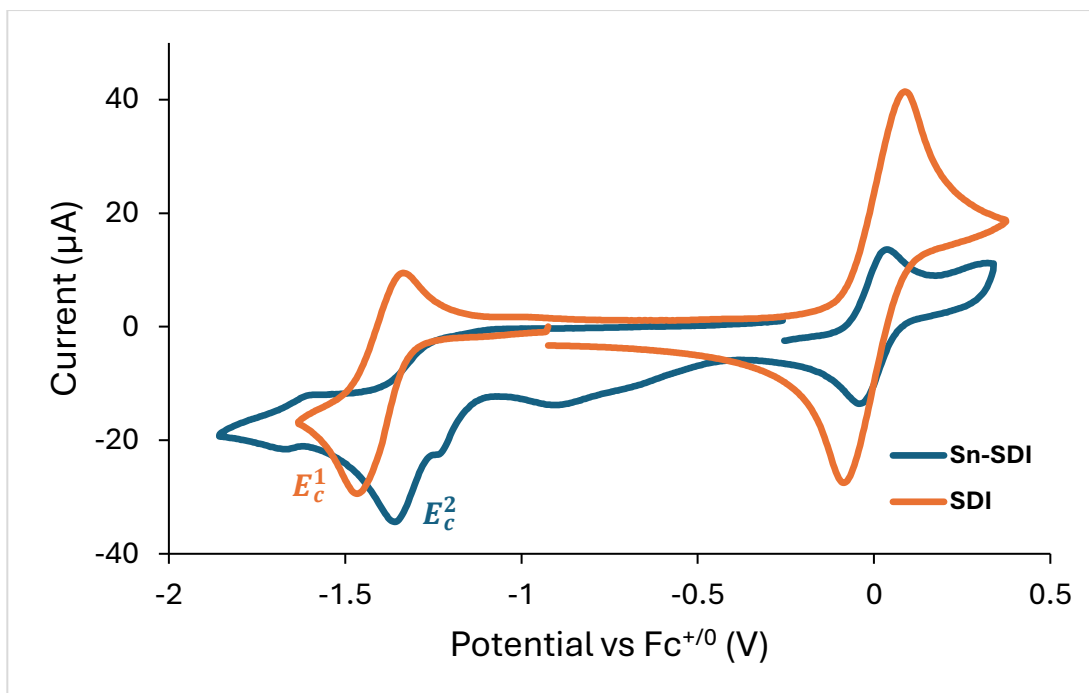


Figure C.90. Overlay of CVs of (4-ClPhN)₂S (orange trace) and its corresponding tetrachlorotin complex, 4 (blue trace). The CV of (4-ClPhN)₂S was taken in CH₂Cl₂ with a 7.1 mm² glassy-carbon inlaid-disk working electrode at 0.200 V/s. The CV of 4 was taken in CH₂Cl₂ with a 7.1 mm² Pt inlaid-disk working electrode at 0.200 V/s.

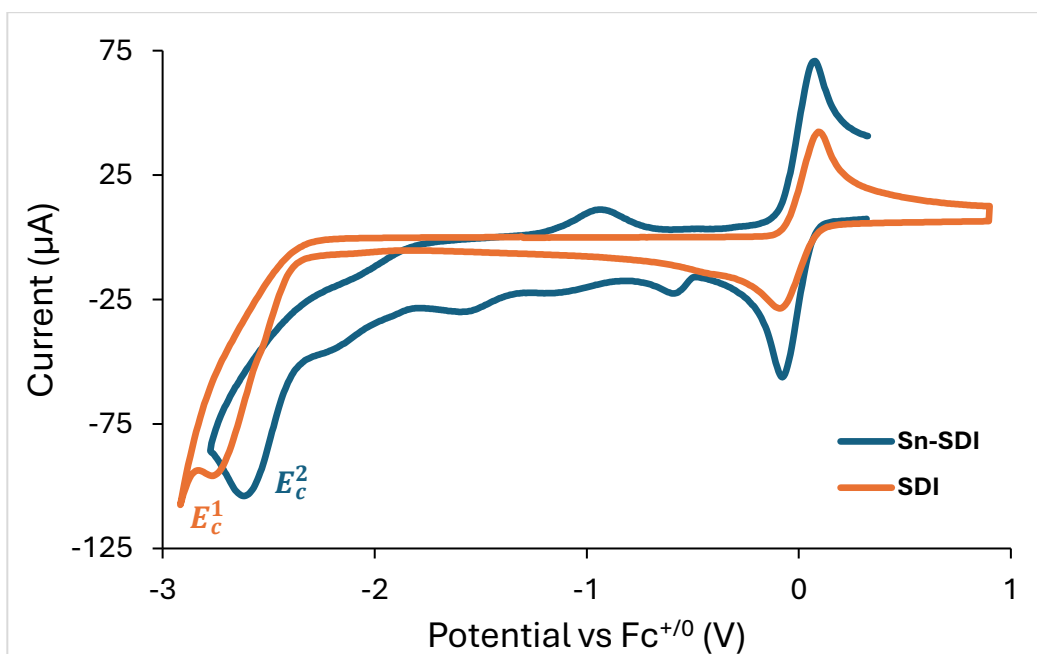


Figure C.91. Overlay of CVs of (t-BuN)₂S (orange trace) and its corresponding tetrachlorotin complex, 5 (blue trace). The CVs of (t-BuN)₂S and 5 were taken in CH₂Cl₂ and CH₃CN, respectively. Both CVs used a 7.1 mm² Pt inlaid-disk working electrode at 0.500 V/s.

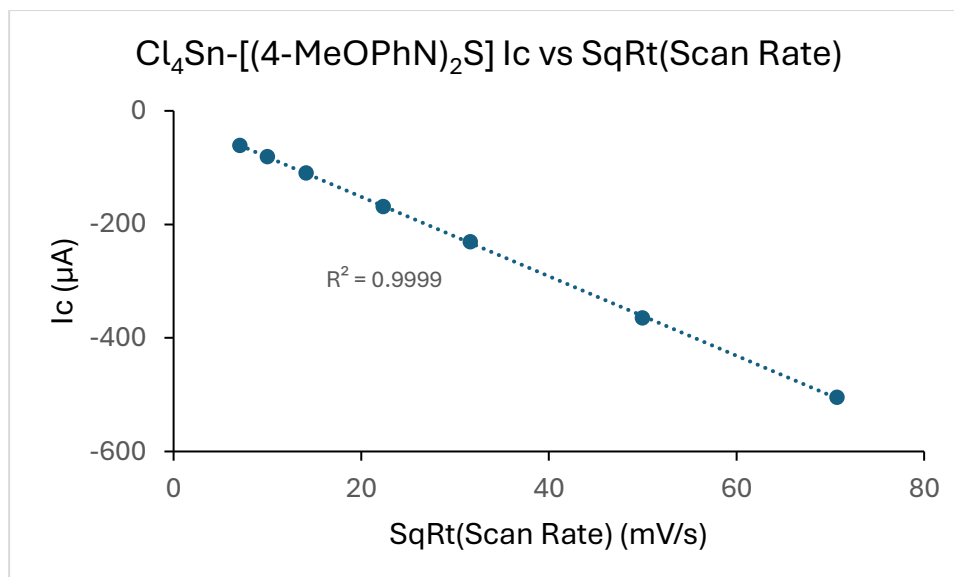


Figure C.92. Cathodic peak current (Ic) vs square root of scan rate for **1**. Linearity of this plot shows that voltammetry was performed under diffusion-controlled conditions.

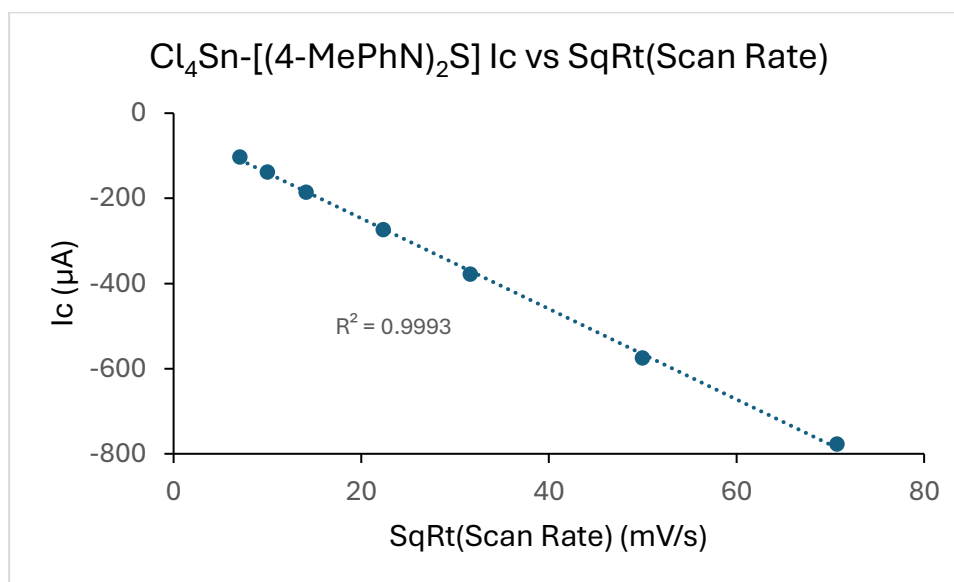


Figure C.93. Cathodic peak current (Ic) vs square root of scan rate for **2**.

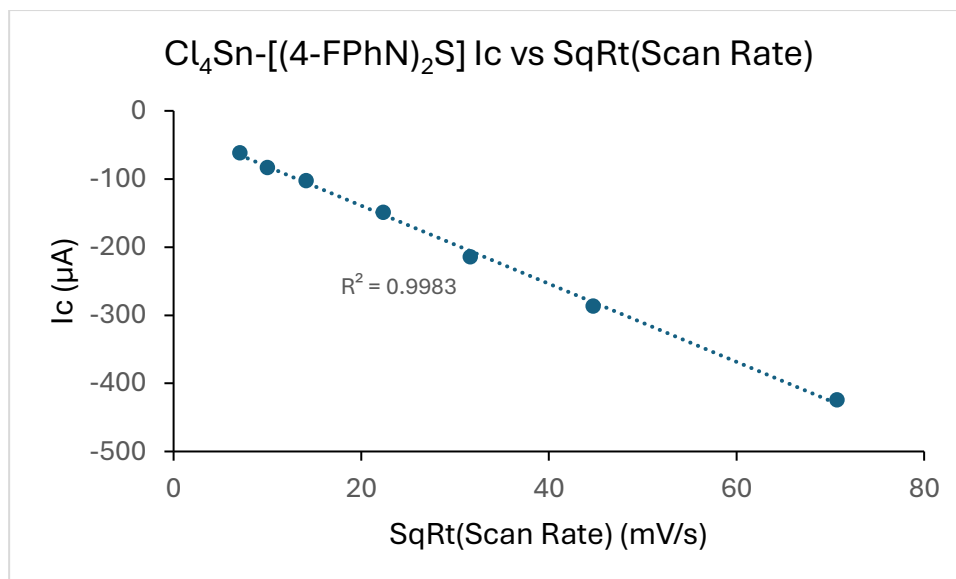


Figure C.94. Cathodic peak current (I_c) vs square root of scan rate for 3.

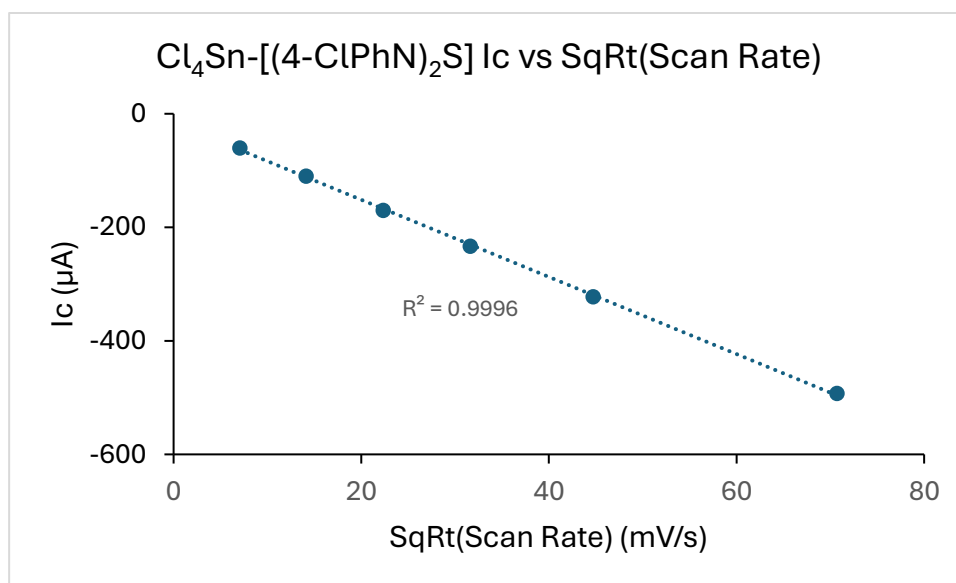


Figure C.95. Cathodic peak current (I_c) vs square root of scan rate for 4.

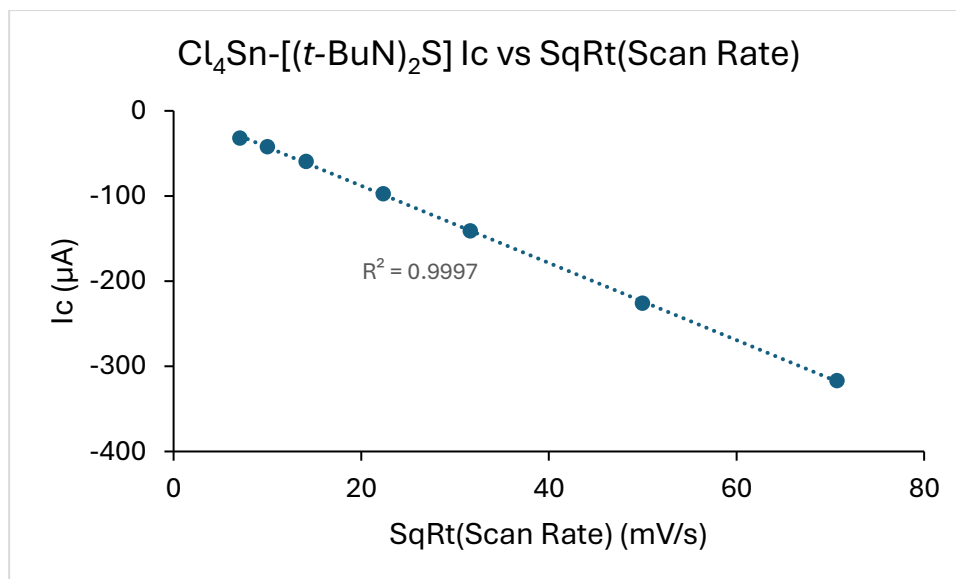


Figure C.96. Cathodic peak current (I_c) vs square root of scan rate for 5.

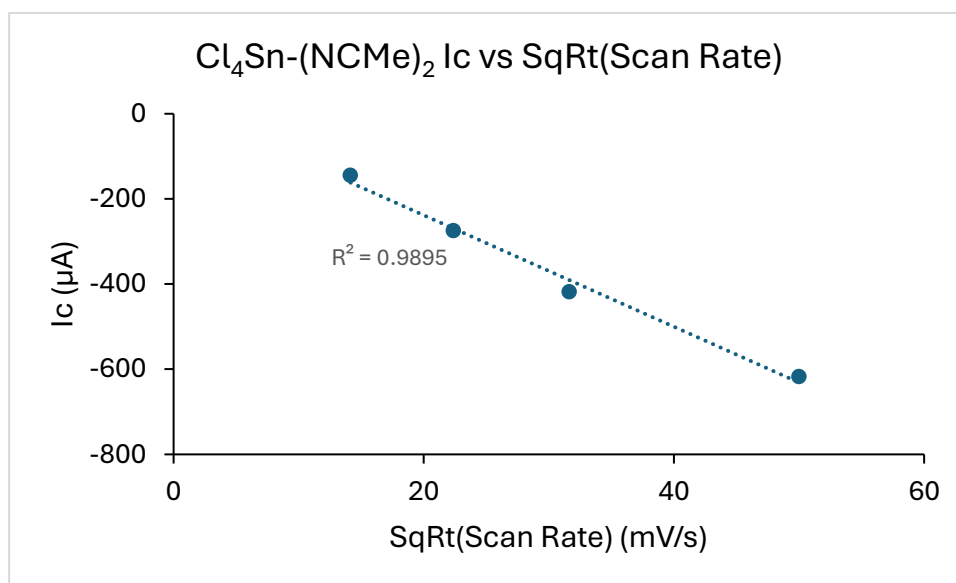


Figure C.97. Cathodic peak current (I_c) vs square root of scan rate for 9.

C.12. DFT Optimized Geometry Cartesian Coordinates

Table C.28. DFT computed Cartesian coordinates of **1**

Atom Type	X	Y	Z
Sn	-0.00024	1.402345	-2.2E-05
Cl	1.845347	2.806204	-0.36711
Cl	0.462365	0.990384	2.302922
S	0.000099	-1.68655	0.00063
N	-1.1851	-0.67849	0.216317
C	-2.51182	-1.03461	0.05223
C	-2.93227	-2.09153	-0.76908
H	-2.20675	-2.62623	-1.37154
C	-4.26543	-2.40951	-0.86249
H	-4.60672	-3.20808	-1.50854
C	-5.2176	-1.66879	-0.15231
C	-4.80812	-0.598	0.64472
H	-5.52671	-0.00322	1.190124
C	-3.46707	-0.28357	0.740342
H	-3.13768	0.541932	1.356273
N	1.185374	-0.67874	-0.21547
C	2.512117	-1.03476	-0.05171
C	2.932851	-2.09226	0.768732
H	2.207512	-2.62762	1.370834
C	4.26607	-2.41008	0.86174
H	4.60757	-3.2091	1.507115
C	5.218047	-1.66866	0.152008
C	4.808281	-0.59735	-0.64418
H	5.52669	-0.00205	-1.18925
C	3.467175	-0.28306	-0.73938
H	3.137573	0.542853	-1.35465
Cl	-1.84634	2.805645	0.366348
Cl	-0.46219	0.989114	-2.30289
O	-6.49705	-2.0469	-0.31744
O	6.497564	-2.04673	0.316682
C	-7.50742	-1.2998	0.333725
H	-8.4502	-1.76377	0.053333
H	-7.39151	-1.34052	1.420791
H	-7.50216	-0.25694	0.003857
C	7.507811	-1.29888	-0.33383
H	8.450678	-1.76285	-0.05374
H	7.392	-1.33877	-1.42094
H	7.502266	-0.25628	-0.00314

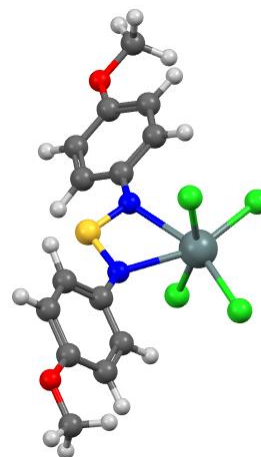


Table C.29. DFT computed Cartesian coordinates of **2**

Atom Type	X	Y	Z
Sn	-4E-06	1.356428	-1E-06
Cl	1.854291	2.735101	-0.38402
Cl	0.47887	0.920556	2.292433
S	0.000002	-1.74488	0.000013
N	-1.18122	-0.74593	0.225105
C	-2.51386	-1.11657	0.108371
C	-2.94804	-2.14567	-0.7313
H	-2.23869	-2.64714	-1.38011
C	-4.28889	-2.4742	-0.77847
H	-4.61893	-3.26586	-1.44141
C	-5.22911	-1.78218	-0.01516
C	-4.78072	-0.74186	0.801575
H	-5.49611	-0.18605	1.396968
C	-3.44568	-0.40062	0.865109
H	-3.09926	0.404411	1.498766
N	1.181219	-0.74593	-0.22509
C	2.513866	-1.11657	-0.10836
C	2.948056	-2.14567	0.731307
H	2.238714	-2.64715	1.380115
C	4.2889	-2.4742	0.778468
H	4.618953	-3.26586	1.441402
C	5.22912	-1.78217	0.015151
C	4.780717	-0.74186	-0.80158
H	5.4961	-0.18604	-1.39697
C	3.445678	-0.40061	-0.8651
H	3.099255	0.404418	-1.49875
Cl	-1.85431	2.735095	0.384003
Cl	-0.47887	0.920532	-2.29243
C	6.686733	-2.10923	0.105433
H	7.17	-2.03474	-0.87035
H	7.197515	-1.40959	0.774136
H	6.847265	-3.11511	0.494561
C	-6.68673	-2.10924	-0.10545
H	-7.17	-2.03474	0.870329
H	-7.1975	-1.40961	-0.77417
H	-6.84725	-3.11512	-0.49458

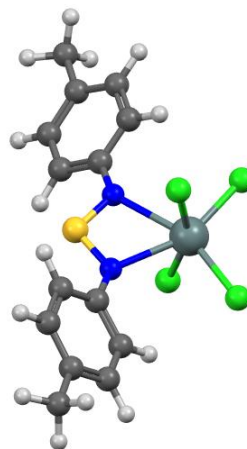


Table C.30. DFT computed Cartesian coordinates of **3**

Atom Type	X	Y	Z
Sn	-8E-06	1.356964	-1E-06
Cl	-1.86147	2.724346	0.376404
Cl	-0.4665	0.908167	-2.29037
S	0.000007	-1.75417	0.000016
N	1.182133	-0.75665	-0.21893
C	2.515249	-1.12485	-0.09971
C	2.949362	-2.1482	0.749343
H	2.240629	-2.64602	1.400739
C	4.288964	-2.47958	0.80757
H	4.651495	-3.25549	1.468754
C	5.184229	-1.76817	0.025741
C	4.78293	-0.73094	-0.80047
H	5.518815	-0.19106	-1.38148
C	3.443126	-0.40473	-0.85909
H	3.092462	0.398314	-1.49265
N	-1.18212	-0.75665	0.21895
C	-2.51524	-1.12485	0.09972
C	-2.94934	-2.14819	-0.74935
H	-2.2406	-2.64599	-1.40075
C	-4.28894	-2.47958	-0.80759
H	-4.65147	-3.25548	-1.46879
C	-5.18421	-1.76818	-0.02575
C	-4.78292	-0.73097	0.800477
H	-5.51881	-0.1911	1.381499
C	-3.44312	-0.40475	0.859116
H	-3.09246	0.398284	1.492685
Cl	1.861432	2.724366	-0.37642
Cl	0.466499	0.9082	2.290374
F	-6.48136	-2.07936	-0.08933
F	6.481383	-2.07934	0.089311

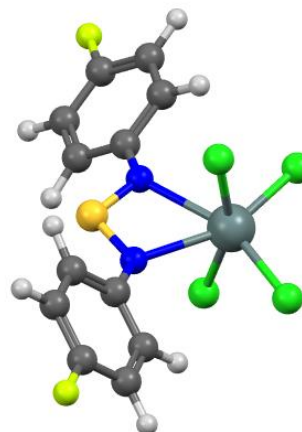


Table C.31. DFT computed Cartesian coordinates of **4**

Atom Type	X	Y	Z
Sn	-4E-06	1.506163	0
Cl	-1.86161	2.873612	0.371148
Cl	-0.45996	1.05115	-2.28837
S	0.000003	-1.61374	0.000003
N	1.183224	-0.61649	-0.2157
C	2.51497	-0.98793	-0.10648
C	2.951587	-2.02868	0.719701
H	2.245676	-2.54147	1.362758
C	4.290334	-2.36137	0.76689
H	4.639313	-3.15512	1.413605
C	5.199417	-1.64199	-0.00068
C	4.781493	-0.58675	-0.80392
H	5.505728	-0.02926	-1.38239
C	3.442893	-0.25588	-0.85321
H	3.094316	0.560156	-1.47127
N	-1.18322	-0.61649	0.215698
C	-2.51496	-0.98793	0.106482
C	-2.95158	-2.02867	-0.71971
H	-2.24567	-2.54145	-1.36278
C	-4.29033	-2.36136	-0.7669
H	-4.63931	-3.1551	-1.41363
C	-5.19941	-1.64199	0.000677
C	-4.78149	-0.58677	0.803934
H	-5.50572	-0.02929	1.382414
C	-3.44289	-0.25589	0.853228
H	-3.09431	0.560136	1.471292
Cl	1.861589	2.873623	-0.37115
Cl	0.45996	1.051159	2.288368
Cl	-6.87257	-2.04756	-0.06859
Cl	6.872578	-2.04755	0.068593

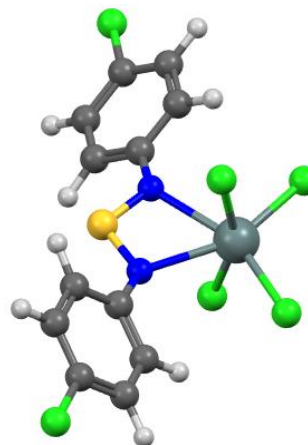


Table C.32. DFT computed Cartesian coordinates of 5

Atom Type	X	Y	Z
Sn	-4E-06	0.998776	0.000155
S	0.000006	-2.03451	-0.0003
Cl	-3E-06	0.603559	2.355862
Cl	-2E-06	0.604293	-2.35568
Cl	-1.88146	2.404187	0.000378
N	1.198259	-1.06832	-0.00017
C	2.744683	-3.00677	-0.00027
C	3.23827	-0.89287	-1.25708
C	3.238374	-0.89292	1.256591
H	3.802415	-3.27131	-0.00032
H	2.291617	-3.45193	-0.89024
H	2.291695	-3.45197	0.889711
H	4.302566	-1.13432	-1.27307
H	3.122875	0.190052	-1.26748
H	2.768383	-1.29618	-2.1547
H	4.302672	-1.13436	1.272476
H	2.768564	-1.29627	2.154235
H	3.122977	0.190002	1.267045
Cl	1.881448	2.404194	0.000378
N	-1.19825	-1.06833	-0.00017
C	-2.74466	-3.00678	-0.00027
C	-3.23826	-0.89288	-1.25708
C	-3.23837	-0.89293	1.256591
H	-3.80239	-3.27133	-0.00032
H	-2.2916	-3.45195	-0.89024
H	-2.29167	-3.45199	0.88971
H	-4.30256	-1.13434	-1.27307
H	-3.12287	0.190037	-1.26748
H	-2.76837	-1.29619	-2.1547
H	-4.30266	-1.13439	1.272476
H	-2.76855	-1.29628	2.154235
H	-3.12298	0.189985	1.267046
C	2.606865	-1.49019	-0.00023
C	-2.60685	-1.49021	-0.00023

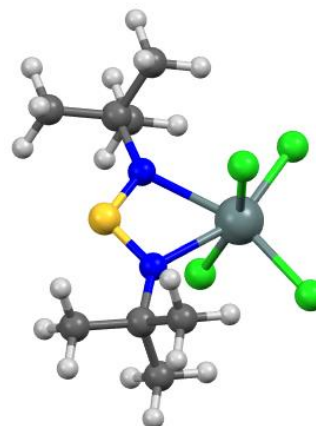
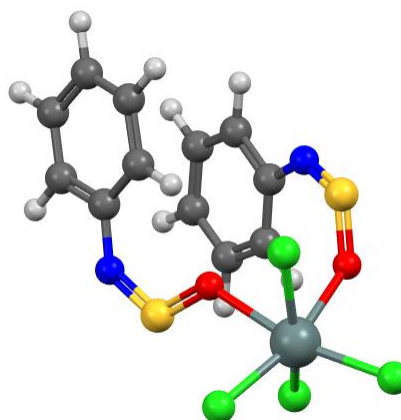


Table C.33. DFT computed Cartesian coordinates of **10**

Atom Type	X	Y	Z
Sn	2.341148	-0.16306	0.028537
Cl	1.828	-0.19356	2.345477
Cl	1.856345	0.173739	-2.26724
Cl	4.345707	1.012561	0.140515
Cl	2.925986	-2.42566	-0.16701
S	0.197649	2.28577	1.236002
S	-0.57508	-1.73455	-0.99443
O	1.134215	1.865581	0.158218
O	0.060998	-0.86988	0.037292
N	-1.27707	2.294342	0.915039
N	-2.0472	-2.00111	-0.81347
C	-2.03008	1.926428	-0.18236
C	-3.42014	1.958399	-0.01201
H	-3.81479	2.280559	0.942184
C	-4.25161	1.560354	-1.03892
H	-5.32481	1.568718	-0.89848
C	-3.70697	1.140419	-2.24753
H	-4.35901	0.822569	-3.05217
C	-2.32867	1.132128	-2.43002
H	-1.90623	0.813836	-3.37512
C	-1.48259	1.522855	-1.40897
H	-0.41185	1.512585	-1.55181
C	-2.96898	-1.5883	0.131694
C	-4.3145	-1.8062	-0.18612
H	-4.55006	-2.27757	-1.13148
C	-5.30549	-1.41181	0.691188
H	-6.34614	-1.57353	0.438524
C	-4.96371	-0.81764	1.900835
H	-5.74055	-0.51552	2.592993
C	-3.62797	-0.61907	2.229743
H	-3.36345	-0.16216	3.175306
C	-2.62567	-0.99142	1.3538
H	-1.58786	-0.83154	1.605196



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