

Syntheses, reactivities, and catalytic applications of low-valent compounds with *p*-block elements

विद्या वाचस्पति की
उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

A thesis submitted in partial fulfillment of the requirements of the degree of
Doctor of Philosophy

By
द्वारा
Nilanjana Sen
नीलांजना सेन

पंजीकरण सं. / Registration No.: २०१७३५२६/20173526

शोध प्रबंध पर्यवेक्षक / Thesis Supervisor:
Dr. Shabana Khan
डॉ॰ शबाना खान



भारतीय विज्ञान शिक्षा एवं अनुसंधान संस्थान पुणे

INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH PUNE

2023

Dedicated to...

Baba and Maa



Indian Institute of Science Education and Research

(IISER), Pune

Declaration by Student

I declare that this written submission represents my ideas in my own words and wherever others ideas have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented, fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will cause disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

Nilanjana Sen

Date: 4.10.2023

Signature of the Student



Indian Institute of Science Education and Research
(IISER), Pune

Certificate by Supervisor

It is hereby certified that the work described in this thesis entitled “*Syntheses, reactivities and catalytic applications of low-valent compounds with p-block elements*” submitted by *Ms. Nilanjana Sen* was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institution. I further certify that the above statement made by her in regard to her thesis is correct to the best of my knowledge.

Date: 4/10/2023

Signature of the supervisor

A handwritten signature in blue ink that reads 'Shabana Khan'.

(Dr. Shabana Khan)

Email: shabana@iiserpune.ac.in

Contact No.: +91 (20) 2590-8137

Acknowledgment

I would like to express my deepest gratitude and appreciation to my thesis supervisor, Dr. Shabana Khan, for her invaluable guidance and support throughout the course of my research. Her dedication, patience, and insightful feedback have been instrumental in shaping the outcome of this thesis.

I am highly grateful for her intense commitment to excellence and her willingness to invest her time and effort into my academic and personal development. Her guidance has not only enhanced my research skills but also broadened my perspective on the subject matter. I am also grateful for the opportunities she has provided me, such as participating and presenting at conferences and collaborating with other researchers in the field. These experiences have contributed immensely to my research growth and to my future academic and professional endeavors. Her contributions have been crucial to the successful completion of this thesis, and I am truly grateful for the opportunity to have worked under her guidance.

I consider myself to be fortunate to be a part of the Indian Institute of Science Education and Research, Pune, and thankful to each and everyone related to this institute. I express my gratitude to our former Directors Prof. K. N. Ganesh for founding this excellent institute and Prof. Jayant Udgaonkar for providing us with all outstanding research facilities.

I am also grateful to my Research Advisory Committee (RAC) members Dr. Sakya Singha Sen (NCL Pune) and Prof. R. Boomi Shankar (IISER, Pune) for their crucial suggestions during every annual meeting which actually helped intensely in my research work. I also express my gratitude to my collaborators Prof Swapan K. Pati, Dr. Srinu Tothadi and Dr. Pallavi Sarkar for helping me with their theoretical calculations and crystallographic expertise.

I also express my gratitude to all the technical staff, Mr. Parveen Nasa for providing us with the training in XRD measurements, Dr. Sandeep Mishra and Nitin Dalvi for NMR measurements, Sandeep Kanade for HRMS measurements, and Mahesh Jadhav for MALDI measurement. I am also thankful to other technicians and admin staff of IISER Pune for their cooperation and help especially Tushar sir, Mayuresh sir, and Sayalee ma'am.

Now I must acknowledge my labmates for always being there with me throughout my journey. Firstly, I would thank my seniors Shiv Pal and Neha Kathewad for helping me and teaching me the lab techniques. I am highly grateful to my senior Nasrina Parvin who has supported me and helped me throughout in all possible ways. I am also grateful to my labmates Md. Javed Hossain and Moushakhi Ghosh. I especially thank Ruksana Akhtar who apart from being my junior is my friend and for being the best support system since her joining. Lastly, I am thankful to all other lab members Sandeep Kaulage, Prachi Gothe, Vijay Kumar Mandal, Kumar Gaurav, and especially Brij Kumar Shah for helping me so much.

I have no words to express my immense gratitude for my parents Mrs. Reeta Sen and Mr. Angshu Prakash Sen. All my achievements till today are only because of their support and belief in me. They are the pillars of support in my life. Their selflessness and unconditional love are the constant source of my strength and inspiration. They not only supported me financially but also emotionally throughout my journey. Once again, their efforts, sacrifices and belief in my abilities have given me the confidence to chase my dreams and taught me to never give up. Other than my parents I am very much grateful to my aunt Mrs. Krishna Basu Roy. She has also motivated me in all possible ways and supported me when I needed the most. Apart from everyone friends are also important in everyone's life. Sometimes they become the support system like family when one is away from home. I consider myself to be very lucky to have some friends who are like my family and they have supported me whenever I needed them even if they were not present with me. Here I would start with Saikat Das and Sayak Saha Chowdhury, they are my childhood friends and they have been always there with me throughout my journey. Next Partha Pratim Mondal and Debabrata Bandhyopadhyay have been with me since my B.Sc time. They were always there whenever I needed them through all the ups and downs. I can share all my problems freely with them and many thanks to Partha for being my friend-philosopher and guide. Next, I am thankful to Sukanya Acharya, Papri Priya Basak, and Shreya Basu for putting up with me since childhood and always being supportive.

Other than my childhood friends I would like to thank very much to Surajit Metya. He is my batchmate from IISER. He has taught me many things and helped me in all possible ways throughout my Ph.D. journey. Next, I am grateful to Aman Chaturvedi for being one of my closest friends in IISER and always being there through thick and thin. I am also thankful to Manjeet Singh Pushpan and Lakshmi Goshwami for being my very good friends from the beginning of my Ph.D. journey. Lastly, I would like to thank my junior-cum-friend Sudipta

Majumder for making my last few months at IISER memorable.

I am thankful to the DST-INSPIRE, Government of India, for my research scholarship to support me financially during the course of my Ph.D. I thank to Science and Engineering Research Board (DST-SERB) and Infosys for giving me financial support to attend the International Conference of Organometallic Chemistry (ICOMC-2022) in Prague, Czech Republic. Along with this, MTIC-2019 and ICMGSC-2023 conference organizers have provided me the opportunity to present my work in oral and poster form. Moreover, I would like to thank the American Chemical Society (ACS), the Royal Society of Chemistry (RSC), and John Wiley & Sons for publishing research articles during the course of my research.

Thank you all for your help and support and would like to say...It was indeed a great and wonderful journey...

Contents

Synopsis	12-16
Abbreviations	17
List of Publications	18

Chapter 1: A brief introduction to low-valent main group p-block elements.	19-49
1.1. History of low-valent main group elements	20
1.2. What are tetrylenes?	20-21
1.3. General methods of preparation of tetrylenes	21-23
1.3.1. Dehydro halogenation of tetravalent (E^{IV}) precursors	
1.3.2. Reduction of the tetravalent precursor (IV)	
1.3.3. Substitution of divalent precursor	
1.4. Organotin compounds	23-24
1.5. Stannylenes	24-26
1.6. Selected reactivities of stannylenes	26-29
1.6.1. Reactivities of stannylenes with H_2 , NH_3 , P_4	
1.6.2. Reactivity of stannylenes with chalcogens	
1.7. Brief overview on disilenes	29
1.8. Structure and bonding of disilenes	29-31
1.9. Synthetic protocol of stable disilenes	32- 34
1.10. Examples of disilenes which remain in equilibrium	34-35
1.11. Reactivity of disilenes with transition metals	35-36
1.12. Reactivity of disilenes with small molecules	36-38
1.12.1. Treatment with H_2O , alcohol, ammonia	
1.12.2. Treatment with haloalkanes and halogens	
1.13. Low-valent compounds with Group 15 elements	39
1.14. Pnictinidenes	39-40
1.15. Pnictenium cations	40-41
1.16. Catalytic applications of pnictogenium cations	41-42
1.17. Motivation and Objective	43
1.18. References	44-49

Chapter 2: Cyclic Four-Membered Stanna Thio and Seleno Compounds **50-62**
from 2-Aminopyridinato Stannylenes

2.1. Introduction	51-52
2.2. Experimental Section	52-55
2.2.1. General remarks	
2.2.2. Synthesis of 2.3 to 2.10	
2.2.3. X-ray crystallographic details	
2.3. Results and Discussion	55-60
2.4. Conclusion	60
2.5 References	60-62

Chapter 3. Reactivity of $(\text{TMS})_2\text{N}(\eta^1\text{-Cp}^*)\text{Si}=\text{Si}(\eta^1\text{-Cp}^*)\text{N}(\text{TMS})_2$ toward the **63-83**
Halides of Groups 13-15

3.1. Introduction	64-65
3.2. Experimental Section	66-69
3.2.1. General remarks	
3.2.2. Synthesis of 3.2 to 3.10	
3.2.3. Xray-crystallographic details	
3.3. Results and Discussion	69-79
3.3.1. Reaction with halides of group 13 elements	
3.3.2. Reaction with halides of group 14 elements	
3.3.3. Reaction with halides of group 15 elements	
3.4. Conclusion	79
3.5. References	80-83

Chapter 4A. Donor-free stibenium cation as efficient cyanosilylation catalyst	84-108
4A.1. Introduction	85
4A.2. Experimental section	85-86
4A.2.1. General remarks	
4A.2.2. Synthesis of compounds 4A.1-4A.4	
4A.3. Results and discussion	87-90
4A.4. Estimation of Lewis acidity of 4A.2, 4A.3 and 4A.4	90-91
4A.5. Catalytic study	93-97
4A.6. Experimental data and theoretical calculations to propose mechanistic pathway of cyanosilylation reaction	98-101
4A.7. Computational details	102-105
4A.8. Conclusion	105
4A.9. References	106-108

Chapter 4B. Synthesis of stibine-manganese complex and its application in homogeneous catalysis	109-113
4B.1. Introduction	110
4B.2. Experimental section	111
4B.3. Results and discussion	111-112
4B.4. Conclusion	112
4B.5. References	113

Chapter 5. Donor-free bismuthenium cation as an efficient cyanosilylation catalyst	114-130
5.1. Introduction	115-116
5.2. Experimental section	117
5.2.1. General remarks	
5.2.2. Synthesis of compounds 5.1 and 5.2	
5.3. Results and discussion	118-120
5.4. Estimation of Lewis acidity	121

5.5. Catalytic application	124-126
5.6. Mechanistic cycle	126-128
5.7. Conclusion	128
5.8. Reference	129-130

Summary	131-132
----------------	----------------

Appendix	133-228
-----------------	----------------

Rights and Permissions	229-236
-------------------------------	----------------

Synopsis

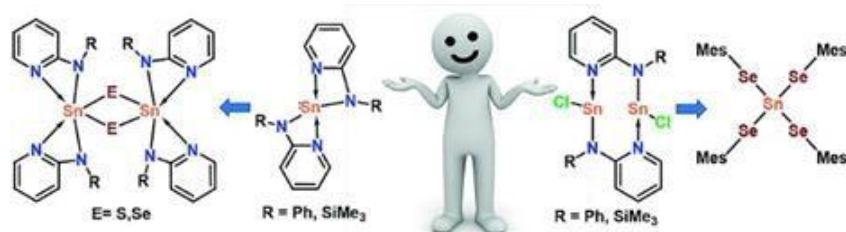
The thesis entitled “Syntheses, reactivity and catalytic applications of low valent compounds with p-block compounds” is mainly based on the synthesis of low valent compounds mainly involving groups 14 and 15 elements. Here primarily we have focused on the structural elucidation of main group low valent compounds. This thesis sheds light on the synthesis as well as reactivities of tetrylenes and disilene. Apart from that it also includes the development of donor-free pnictogenium cations and has explored the catalytic efficiency of those cationic species. This thesis is divided into five chapters starting with a brief introduction to low-valent main group compounds. In each chapter, we have elaborately discussed the experimental details and structural properties of the low-valent compounds that have been mentioned in the thesis.

Chapter 1: A brief introduction to low valent main group p-block elements

The discovery of the periodic system by Dmitri Mendeleev is remarkably the cornerstone in the science of chemistry. Mainly the *s*- and *p*- block elements are considered the main group elements that play a prominent role in the periodic table. Main group chemistry offers a wide aspect of both fundamental as well as applied chemistry. The main group elements are earth-abundant are low toxicity and less expensive and also exhibit versatile structural properties. The higher analogues of carbenes known as tetrylenes are highly reactive in nature. Recent times have witnessed various reactivities and major discoveries with the main group elements. It has been understood that if the main group compounds are properly designed, they can mimic the transition metals and will be able to activate small molecules like H₂, CO₂ even N₂. Main group compounds have also gained a strong foothold in the field of homogeneous catalysis. Along with these reactive low-valent main group elements, the *p*-block cations that are isoelectronic with that of carbenes have also attracted much attention. Group 15 cations known as pnictenium cations are well known for their alluring photophysical properties and also for their efficiency as potential homogeneous catalysis.

Chapter 2: Cyclic Four-Membered Stanna Thio and Seleno Compounds from 2-Aminopyridinato Stannylenes

As we descend the group the electronegativity decreases, size of the atomic radius increases for which the energy gap between the *ns* and *np* orbitals are higher and heavier tetrylenes are more stable than carbenes. Isolation of heavier tetrylenes requires both kinetic and electronic stabilization. Kinetic stabilization is provided from the steric protection of the ligand backbone whereas electronic stabilization comes from the presence of electron-withdrawing groups, in- or out-of-plane donation of the lone pair containing groups. In the 1st chapter we have discussed about the literature precedence of stannylenes and have shown the synthesis of both homoleptic as well as bischlorostannylenes. We have also explored the reactivity of the stannylenes. Here we have shown the small molecule activation by the homoleptic stannylenes. Here we have synthesized tin chalcogenide compounds via the reaction of the stannylenes with elemental sulphur and selenium. The reactivity pattern of stannylenes with chalcogenides mainly depends on the ligand backbone. If the ligand is bulkier in nature, then it prefers the form $\text{Sn}=\text{E}$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$), whereas cyclic four-membered Sn_2E_2 is obtained with a less bulky ligand system. We have employed 2-aminopyridinate ligands and in both cases, we have observed the formation of cyclic four-membered tin chalcogenide compounds.



Chapter 3: Reactivity of $(\text{TMS})_2\text{N}(\eta^1\text{-Cp}^*)\text{Si}=\text{Si}(\eta^1\text{-Cp}^*)\text{N}(\text{TMS})_2$ toward the Halides of Groups 13-15

In this chapter, we have shown the diverse reactivity of disilene with the halides of group 13-15 elements. Generally, disilenes are thermally stable compounds but in a few cases, it has been observed that there remains an equilibrium between the disilene and the corresponding silylene. In those cases, different types of reactivities are performed to understand the true nature of the disilene. Here, we have utilized the previously reported disilene $(\text{TMS})_2\text{N}(\eta^1\text{-Cp}^*)\text{Si}=\text{Si}(\eta^1\text{-Cp}^*)\text{N}(\text{TMS})_2$

$\text{Cp}^*\text{N}(\text{TMS})_2$ and have treated with Lewis acids like BCl_3 , BCy_2Cl , AlCl_3 , AlBr_3 . This study shows that the disilene shows oxidative addition, insertion, rearrangement and adduct formation. In each of the cases, we have observed different patterns of reactivity of the disilene. All these reactivities showed that the disilene actually behaves as the silylene. In addition, we have also treated the disilene with the halides of group 14 elements. Here we have shown that a totally new type of dendrimeric Si-Ge hybrid structure is obtained when the disilene is treated with GeCl_2 . On the other hand, when the disilene was reacted with SnCl_2 we obtained a different product due to the metal affinity of Cp^* group. Further, we have also shown that when PPh_2Cl was added to the disilene it afforded a similar type of insertion product like that with BCy_2Cl .

Following the reaction with PPh_2Cl we treated the disilene with PCl_3 which yielded a dichlorinated product via the 1,2-chloride addition to disilene. Overall, this work manifests the accessible routes for the synthesis of Si-E ($\text{E} = \text{B}, \text{Al}, \text{Ge}, \text{P}$) containing compounds.

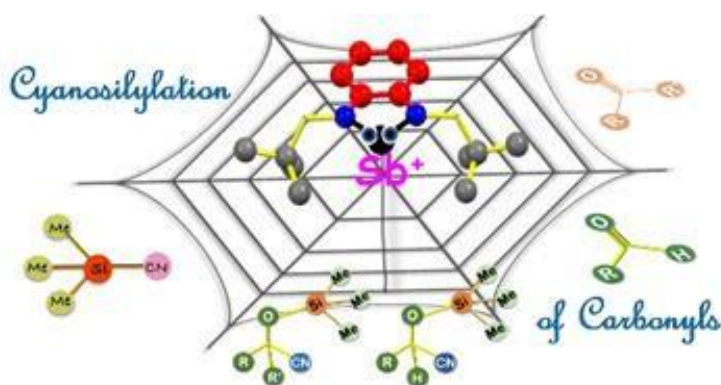


Chapter 4. Synthesis of donor free stibonium cation and stibine-manganese complex and their catalytic applications

The chemistry of cationic compounds as a homogeneous catalyst has not only flourished among the group 13 and 14 elements but has also stretched in the group 15 elements. Stibonium cations are amphoteric in nature due to the lone pair of electrons as well as the vacant p -orbital. Group 15 cationic compounds are highly Lewis acidic in nature as they are good π acceptors than σ donors. $\text{Sb}(\text{V})$ cationic species are well-known as Lewis acid catalysts. But $\text{Sb}(\text{III})$ cations are still less explored as potential Lewis acidic catalysts. In this chapter, we have demonstrated the synthesis of a donor-free stibonium cation utilizing N,N' -dineopentyl-1,2-phenylenediamine as the ligand backbone. Subsequently, we have also explored the donor-free stibonium cation as

the efficient catalyst for the cyanosilylation of carbonyls. We have also studied the photophysical properties of the stibenium cations. As mentioned earlier the Sb(III) compounds are Lewis acidic in nature, we have tried to quantify the Lewis acidity of our synthesized compounds following the Guttmann Beckett method using Et_3PO as the probe. Both the theoretical and experimental results suggest that the pathway of cyanosilylation follows the anchoring pathway. Donor-acceptor interaction takes place between the lone pair of electrons of TMSCN and the vacant p-orbital of the antimony center, followed by the nucleophilic attack of the carbonyl oxygen to the silicon center of TMSCN resulting in the formation of the four-membered transition state. Finally, rearrangement takes place yielding the required product and releasing the catalyst itself.

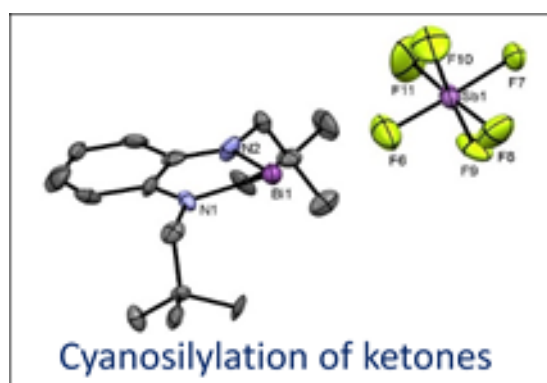
Following this we have also performed one reaction with the chlorostibine and $\text{NaMn}(\text{CO})_5$ to abstract the chloride atom. This reaction afforded the desired chloride abstraction with the formation of stibane-manganese complex which is a four membered dimeric compound. After this synthesis we have explored the catalytic efficiency of this complex in various organic transformations like hydroboration of amides, CO_2 and hydrosilylation of ketones.



Chapter 5. Donor free bismuthenium cation as an efficient cyanosilylation catalyst

According to the octet rule, we know that the presence of 8 valence electrons in the case of all atoms makes the main group elements most stable. So main group compounds where the total valence electron count is less than 8 it makes them more reactive species and they are short-lived intermediates in the chemical reaction. Carbenes and their higher analogs possess six valence electrons and hence they are highly reactive and electrophilic in nature. Tremendous

efforts have been made for the isolation of these types of intermediate species. Lappert and coworkers have isolated for the first time stannylene and plumbylene $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{E}$ ($\text{E} = \text{Sn}, \text{Pb}$). Although there were so many reports on the group 14 low valent species there were fewer studies done on organometallic cations of group 15 elements. The isolation of group 15 cationic species is difficult due to the presence of a positive charge, vacant p-orbital as well and a lone pair of electrons. In spite of all these difficulties, the first bismuthenium ion was isolated by using bulky meta-terphenyl substituents and weakly coordinating borate anions. After this, there have been few reports on bismuthenium ions. In this chapter, we have discussed the synthesis of a donor-free bismuthenium ion and have also studied its photophysical properties. Since bismuthenium ions are very much Lewis acidic in nature we have also estimated the Lewis acidity of all the compounds using Guttmann Beckett method. In this chapter, we have shown for the first time that bismuthenium ions can be also employed as a potential catalyst for cyanosilylation of ketones.



Abbreviations

Anal.	Analysis
Calcd	Calculated
CCDC	Cambridge Crystallographic Data Center
CIF	Crystallographic Information File
CDCl ₃	Deuterated chloroform
DCM	Dichloromethane
DFT	Density Functional Theory
HRMS	High-Resolution Mass Spectroscopy
Hz	Hertz
IR	Infrared Spectroscopy
<i>i</i> Pr	Isopropyl
min	Minutes
mmol	Milimoles
mg	Miligram
ml	Mililiter
NMR	Nuclear Magnetic Resonance
ppm	parts per million
RT	Room Temperature
TM	Transition metal
THF	Tetrahydrofuran
<i>t</i> Bu	Tertiary Butyl
XRD	X-ray diffraction

Publications

Publications included in thesis

1. 'Cyclic Four-Membered Stanna Thio and Seleno Compounds from 2-Aminopyridinato Stannylenes'. **Nilanjana Sen**, Shiv Pal, Vikas Vilas Khade and Shabana Khan, *Eur. J. Inorg. Chem.*, **2019**, 41, 4450-4454.
 2. 'Reactivity of $(\text{TMS})_2\text{N}(\eta^1\text{-Cp}^*)\text{Si}=\text{Si}(\eta^1\text{-Cp}^*)\text{N}(\text{TMS})_2$ towards the Halides of Group 13-15'. **Nilanjana Sen**, Nasrina Parvin, Srinu Tothadi, and Shabana Khan, *Organometallics*, **2021**, 40, 1874-1883.
 3. 'Donor-free stibenium cation as efficient cyanosilylation catalyst'. **Nilanjana Sen**, Prachi Gothe, Pallavi Sarkar, Shubhajit Das, Srinu Tothadi, Swapan K Pati and Shabana Khan, *Chem. Commun*, **2022**, 58, 10380-10383.
 4. 'Donor-free bismuthenium cation as efficient cyanosilylation catalyst'. **Nilanjana Sen**, Pallavi Sarkar and Shabana Khan (Manuscript under preparation).
 5. 'Synthesis of Stibane-Manganese complex and its application in homogeneous catalysis'. **Nilanjana Sen** and Shabana Khan (Mnauscript under preparation).
-

Publications not included in thesis

1. 'Coinage Metal Complexes of Germylene and Stannylene'. Moushakhi Ghosh[#], **Nilanjana Sen**[#] and Shabana Khan, *ACS Omega*, **2022**, 7, 6449-6454. ([#] equal contribution)
 2. 'Synthesis and Application of Silylene Stabilized Low-Coordinate Ag(I)-Arene Cationic Complexes'. Nasrina Parvin, **Nilanjana Sen**, Srinu Tothadi, Shahila Muhammed, Pattiyil Parameswaran and Shabana Khan, *Organometallics*, **2021**, 40, 1626-1632.
 3. 'The Diverse Reactivity of NOBF_4 towards Silylene, Disilene, Germylene and Stannylene'. Nasrina Parvin, **Nilanjana Sen**, Puthan Veetil Muhasina, Srinu Tothadi, Pattiyil Parameswaran and Shabana Khan, *Chem. Comm.*, **2021**, 57, 5008-5011.
 4. 'Heavier Tetrylenes as Single Site Catalysts'. **Nilanjana Sen** and Shabana Khan, *Chem. Asian J.*, **2021**, 16, 1-16.
-

Chapter 1

A brief introduction to low valent main group p-block elements

1.1. History of low-valent main group compounds

Main group chemistry has witnessed a tremendous uprise in the past decades. Main group elements involving *s*- and *p*-block elements offer a very large and diverse field in inorganic chemistry, which later paved the way to mimic transition metals. In terms of electronic properties, the lighter main group elements used to behave differently than their higher congeners. Previously it was believed that only transition metal chemistry is intrinsically richer than that of the main group elements. But gradually there has been a huge development in the field of main group chemistry which shows that main group compounds can also exhibit transition metal-like properties. The booming chemistry of main group elements targets to unveil some features that were unknown to the chemists and these are 1) multiple bond formation between the heavier main group elements such as Al, Si, Ge and their higher congeners¹, 2) stability of low valent compounds with open coordination sites^{2,3}, 3) stable paramagnetic electronic configuration i.e. radical bearing unpaired electron on the heavier main group elements as well as diradical electronic configuration.^{4,5,6} Main group compounds possess either fully occupied or empty valence *s*- and *p*-orbitals. They are mainly colorless in nature. Main group elements are not only limited to their unique structural features but also display a vast utilization in the fields of homogeneous catalysis, material science, photophysics and magnetism.^{7,8}

The growing interest in the main group elements has led to the development of many new and different types of compounds. Over the last few decades, this exploration involving the chemistry of group 14 and 15 elements has bloomed into a very large and diverse field. The low-valent main group chemistry has received significant attention following the first isolation of N-heterocyclic carbene by Arduengo and co-workers in 1991.⁹ Following the first synthesis N-heterocyclic carbenes play as a most important class of ligand in main group chemistry. In case of group 14 elements, the heavier congeners of carbene are known as ‘Tetrylenes.’ Both a lone pair of electrons and a vacant *p*-orbital on the same center make the tetrylenes entirely different from their analogues in the normal oxidation state. Over the past few decades, the chemistry of the tetrylenes has witnessed an upsurge in interest as a synthetic reagent and efficient catalyst.

1.2. What are tetrylenes?

Carbenes and their higher congeners like silylenes, germylenes, and stannylenes are considered the fundamental divalent species of group 14. The stability of these tetrylenes is mainly

achieved by the presence of sterically demanding substituents which is mainly considered as kinetic stabilization. On the other hand, thermodynamic stability is enabled by utilizing substituents allowing electron delocalization.¹⁰ In contrast to the carbenes as we proceed down the group the stability of the tetrylenes increases. This observation is mainly attributed to the inert pair effect for which SnCl_2 and PbCl_2 etc. are stable.^{11a} The presence of both vacant coordination site and lone pair of electrons tetrylenes can act as ambiphilic ligands.^{11b} Tetrylenes mainly prefer a singlet state since the outermost s orbital remains deeply seated to the nucleus and they are reluctant to participate in bonding hence the preferred electronic configuration is $(ns)^2(np)^2$. As we descend the 14th group, decrease in electronegativity of the elements, an increase in the atomic size and also the gap between ns and np orbitals become more prominent. These features are the reason behind the stability of the heavier tetrylenes than that of the carbenes. The highly reactive nature of the tetrylenes is due to the presence of empty p-orbital which are reactive and vulnerable. This uncommon electronic structure of the tetrylenes facilitates them to easily mimic the transition metals in the field of catalysis as well as small molecule activation.^{12,13}

1.3. General methods of preparation of tetrylenes

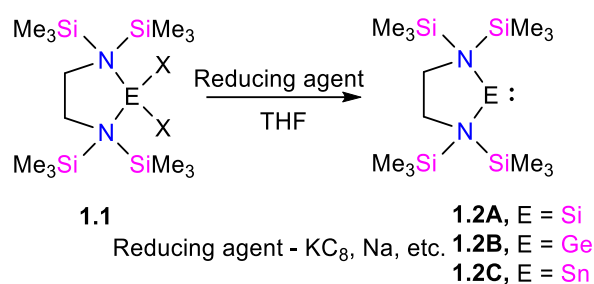
Generally, the methods for the preparation of tetrylenes can be classified into three classes: 1) Dehydro halogenation of tetravalent precursors. 2) Reduction of the tetravalent halogenated precursor. 3) Substitution of the divalent precursor.

1.3.1. Dehydro halogenation of tetravalent (E^{IV}) precursors

In this protocol for the synthesis of tetrylenes mainly strong bases like potassium or lithium bis(trimethylsilylamide) $[\text{KN}(\text{TMS})_2/\text{LiN}(\text{TMS})_2]$ or carbenes mainly N-heterocyclic carbenes (NHCs) and CAAC (cyclic alkyl amino carbene) are utilized to abstract the proton as well as the halogen from the starting precursors. In 2010 Roesky and co-workers modified an old procedure for the synthesis of chloro-amidinate silylene¹⁴ where the abstraction of HCl is done by using 2 equivalent of $\text{LiN}(\text{TMS})_2$ and yielded heteroleptic silylene followed by the elimination of 2 equivalent LiCl and $\text{HN}(\text{TMS})_2$.¹⁵ Similarly another report by Roesky and coworkers where they have shown the synthesis of base-stabilized chlorosilylene under the mild condition in presence of NHC by the reductive elimination of HCl from trichlorosilane.¹⁶

1.3.2. Reduction of the tetravalent precursor (IV)

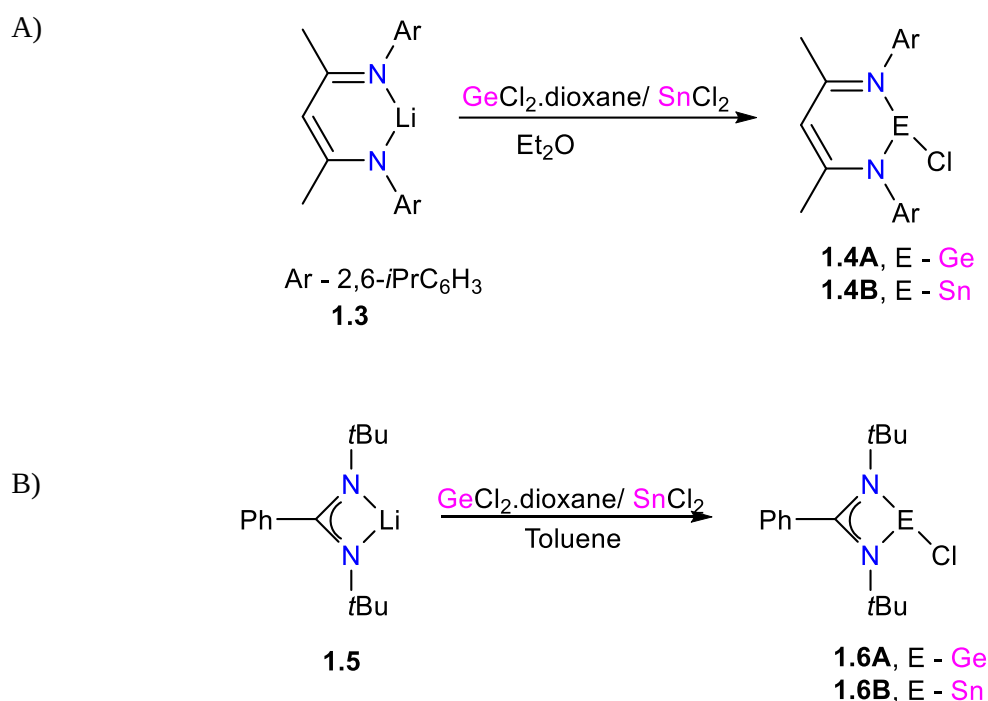
In this protocol mainly reducing agents like Na, K, KC_8 , Li naphthalenide (LiNaph), etc are used for the reduction of dihalo tetravalent precursors. West and co-workers reported the synthesis of five-membered monomeric silylene for the first time by using potassium metal as the reducing agent.¹⁷ The germanium analogue was synthesized by substitution of $GeCl_2$.dioxane with ligand followed by the reduction with lithium metal.¹⁸ Five-membered saturated cyclic tetrylenes were also synthesized by the reduction pathway using potassium graphite as the reducing agent (Scheme 1.1).^{19,20,21}



Scheme 1.1. Selected examples of synthesis of tetrylenes via reduction method.

1.3.3. Substitution of divalent precursor

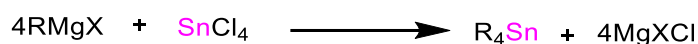
This protocol is mainly followed for the heavier elements of group 14 because their divalent precursors are commercially available like GeCl_2 , SnCl_2 , PbCl_2 , etc. In the case of silylene and carbene, their divalent precursors are not available, so this process is not followed for preparing carbenes or silylenes. The guadinate (**1.4A**, **1.4B**) and amidinate (**1.6A**, **1.6B**) germylene and stannylene are easily prepared by treating the lithiated salt of guadinate and amidinate ligand with GeCl_2 .dioxane and SnCl_2 respectively (Scheme 1.2).^{22,23}



Scheme 1.2. Selected examples of substitution methods

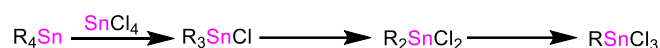
1.4. Organotin compounds

The symbol of tin Sn comes from the Latin word ‘stannum’ which means an alloy of silver and lead. The field of organotin had marked its existence by the isolation of diethyltindiodide by Frankland in 1849. In 1852, Lowich reported the synthesis of an alkyltin compound from the reaction between tin-sodium and alkyl halides. The compounds with at least one covalent Sn-C bond are considered organotin(IV) compounds. Organotin compounds are very much useful for new drug development as they have antitumoral and antimicrobial activities.²⁴ In the case of tin, two oxidation states are possible: Sn (+4) and Sn (+2). Bis(cyclopentadienyl) tin (II) is the first isolated divalent organotin compound.²⁵ Divalent organotin compounds are mainly less stable than organotin (IV) compounds. Organotin compounds are mainly prepared through the alkylation of SnCl₄ with Grignard reagents like organo-magnesium or aluminum compounds. In this type of reaction, the R group of the Grignard reagent has to be bulky enough for partial alkylation with SnCl₄. Otherwise, the end product of this type of reaction is R₄Sn (Scheme 1.3).



Scheme 1.3. Synthesis of organotin compound.

Again when this tetraalkylstannane is heated with SnCl₄ it results in redistribution producing different types of tin containing products like alkyltin chlorides (Kocheshkov reaction) (Scheme 1.4).²⁶



Scheme 1.4. Kocheshkov reaction for the formation of organotin compounds.

Organotin compounds are well known for their vast applications in industrial as well as in technological fields. Organotin compounds can be used as catalysts and also in polymer industry.²⁷ They are also very much useful in specific biological activities and also have pharmaceutical applications.²⁸

1.5. Stannylenes

Among the other tetrylenes, stannylenes are found to be more thermodynamically stable than their higher congeners. Almost 40 years back, Lappert reported the stable stannylene Sn[CH(SiMe₃)₂]₂ (**1.7**) for the first time.²⁹

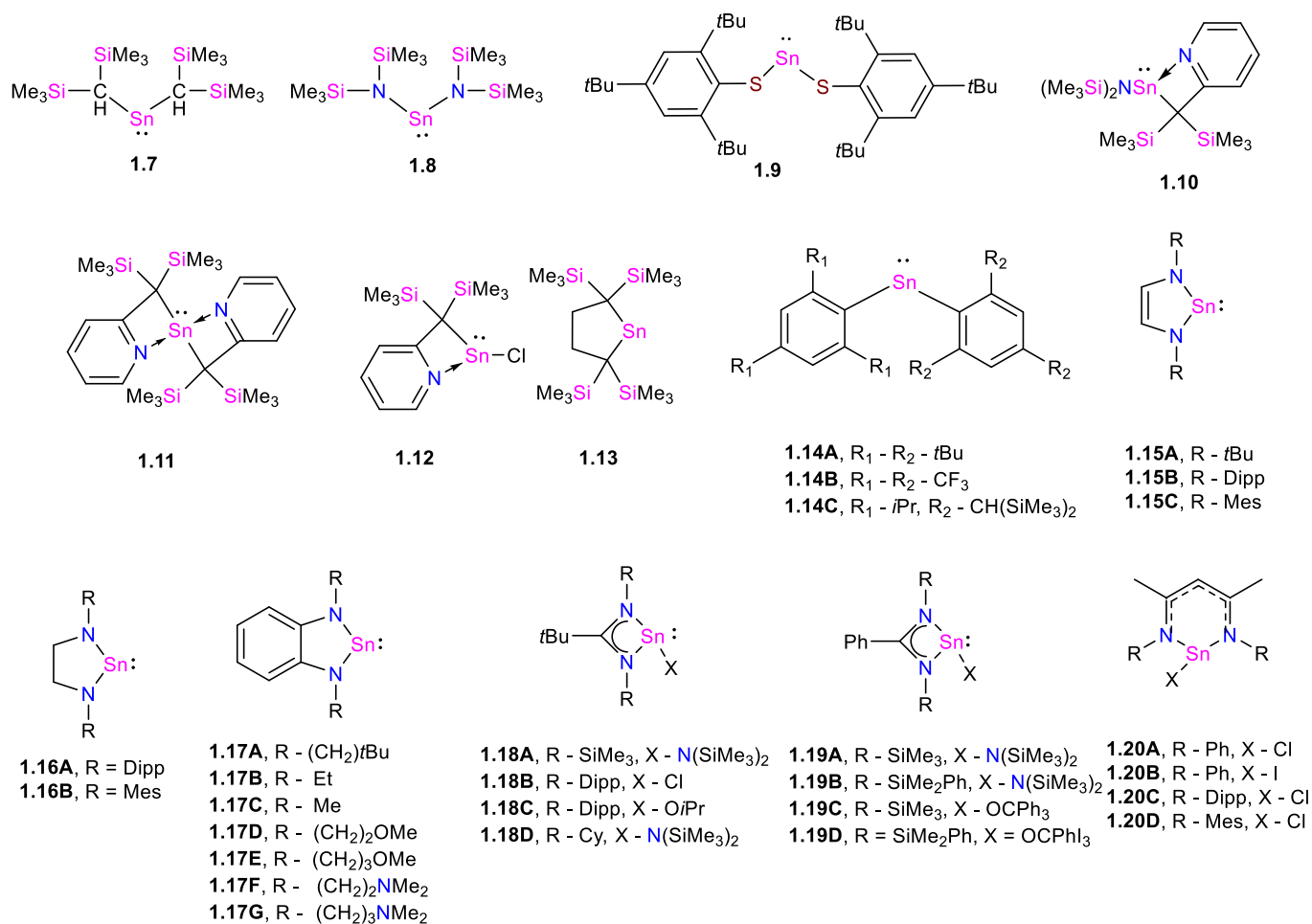


Chart 1.1. Selected examples of reported stannylenes

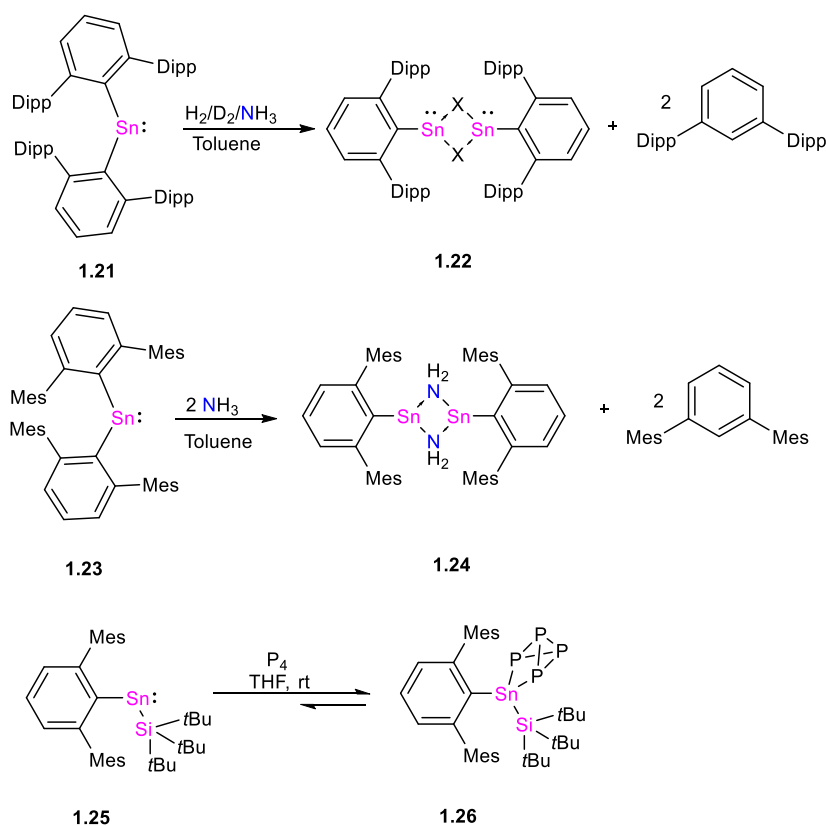
In 1983 Lappert reported the synthesis of dialkylbenzenedithiolate (**1.9**) and bis(trimethylsilyl)amide stabilized stannylenes (**1.8**).³⁰ In 1988 Lappert again synthesized the homoleptic monomeric stannylene (**1.10**) which is four coordinated in nature along with this they also reported the synthesis of two different types of heteroleptic stannylenes one Sn[PyClC(SiMe₃)₂] (**1.12**) and the other is Sn[PyN(SiMe₃)₂C(SiMe₃)₂] (**1.11**).³¹ Kira and co-workers in 1991 for the first time reported cyclic dialkyl stannylene 2,2,5,5-tetrakis(trimethylsilyl)-1-stannacyclopentane-1,1-diyl (**1.13**) which is monomeric in solid state and the coordination number is two.³² Later on, Weidenbruch isolated for the first time the diarylstannylene [2,4,6-(C(CH₃)₃)₃C₆H₂]₂Sn (**1.14A**) where no intramolecular donor stabilization is present as well as another diarylstannylene [2,4,6-(CF₃)₃C₆H₂]₂Sn (**1.14B**) was also synthesized where it was found that the close contact between the fluorine atoms of the ortho-CF₃ group and the low valent tin center provides the stability of the compound.³³ Following the above reports Gudat and co-workers isolated the cyclic five-membered unsaturated tin analogues of Arduengo's carbene (**1.15**).³⁴ Russell and coworkers reported a

similar type of five-membered saturated stannylene (**1.16**) as well as benzofused five-membered stannylene (**1.17**).³⁵ Amidinate, as well as quadinate ligands, have also been extensively utilized for the stabilization of cyclic four-membered and six-membered stannylenes respectively (**1.18-1.20**).³⁶

1.6. Selected reactivities of stannylenes

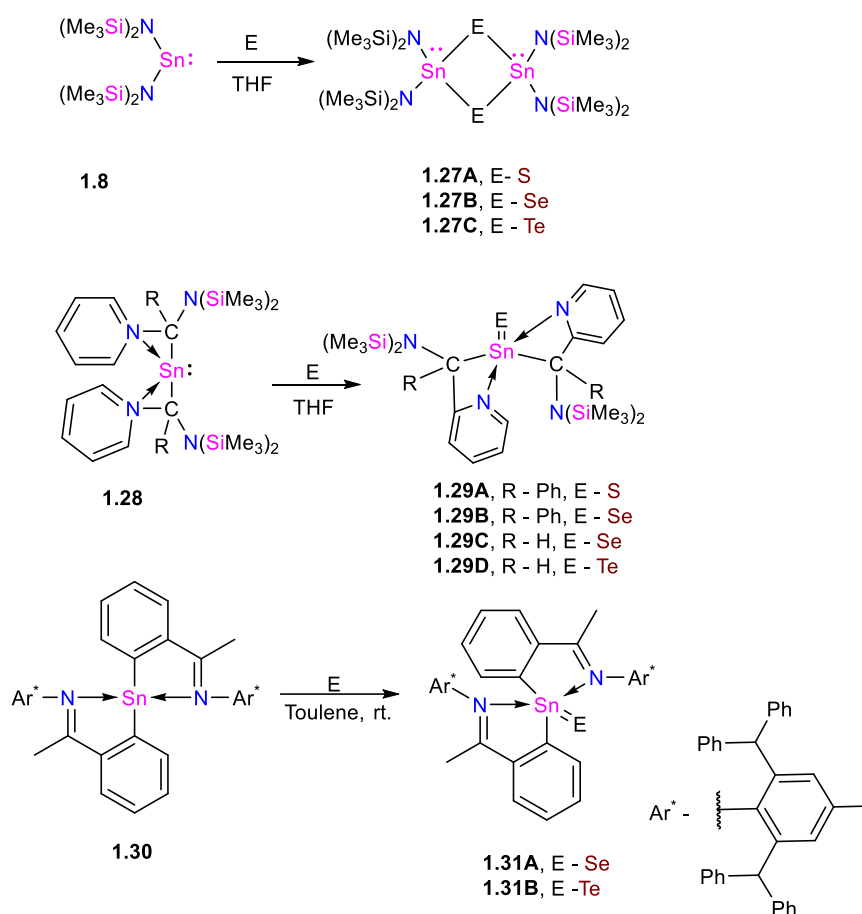
1.6.1. Reactivities of stannylenes with H₂, NH₃ and P₄

Activation of H₂ by transition metals is well-known in chemistry. Later the main group chemists targeted to mimic similar types of small molecule activations like H₂ and NH₃ activation by main group elements. In 2008 Power and co-workers reported for the first time the activation of H₂ and NH₃ by heavier congener of group 14 i.e. stannylene SnAr'₂ (Ar' = C₆H₃-2,6-(C₆H₃-2,6-*i*Pr₂)₂) under mild reaction condition along with arene elimination (Scheme 1.5A, 1.5B).³⁷ Similar to H₂ activation P₄ activation by main group elements remains very less explored. In recent years Inoue and coworkers reported activation of white phosphorus by silyl stannylene [2,6-(2,4,6-Me₃C₆H₂)₂C₆H₃Si(*t*Bu)₃Sn] (**1.25**) forming **1.26** (Scheme 1.5C).³⁸



Scheme 1.5. Activation of P₄, H₂, NH₃ by stannylenes.

1.6.2. Reactivity of stannylenes with chalcogens

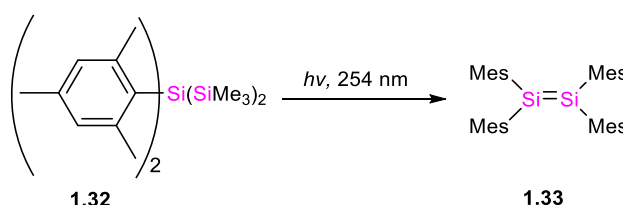
**Scheme 1.6.** Selected examples of reactivity of stannylenes with chalcogens.

In case of the reactions between stannylenes and chalcogenides different bonding patterns have been observed. When the ligand backbone on the Sn(II) center is bulky it leads to the formation of Sn=E (E = S, Se, Te), whereas with less bulky ligands four-membered cyclic Sn₂E₂ type of compounds are formed.

In 1995 Lappert and co-workers for the first time reported the Sn(IV) cyclic chalcogenide complexes (Scheme 1.6A). They treated bis[bis(trimethylsilyl)amido]stannylene with elemental chalcogens and it afforded the desired cyclic tin chalcogenide compound (**1.27**).³⁹ Next, in 1999 Leung and coworkers reported the formation of Sn=E (E = S, Se, Te) compounds (**1.29**) utilizing bulky ligand backbone (Scheme 1.6B).⁴⁰ In the last year our group also reported four coordinate tin chalcogenides compounds (**1.31**) with sterically crowded ligand system (Scheme 1.6C).⁴¹

1.7. Brief overview of disilenes

The last few decades have witnessed tremendous growth in the field of organometallic chemistry of the heavier group 14 elements ($E = \text{Si}, \text{Ge}, \text{Sn}$). Initially, the ‘double bond’ rule states that other than carbon, the elements possessing three or higher valence principal quantum numbers cannot effectively take part in π bond formation.⁴² Later on, West and co-workers isolation of the first stable disilene $\text{Mes}_2\text{Si}=\text{SiMes}_2$ ($\text{Mes} = 2,4,6$ trimethylphenyl) (Scheme 1.7) superseded the idea that multiple bonded silicon compounds are non-existent or highly unstable.⁴³ Following this breakthrough, huge attention has been directed to the chemistry of disilene which includes structure and bonding, spectroscopic properties as well as reactivities.⁴⁴ In some cases, disilenes are thermally stable and do not revert back to their corresponding silylenes. However, in a few cases, it has been observed that disilenes can easily undergo thermal dissociation to their singlet silylene fragment ($\text{R}_2\text{Si:}$).



Scheme 1.7. Synthesis of the first disilene by Jutzi and coworkers.

1.8. Structure and bonding of disilenes

Although disilenes are higher analogues of alkenes it is noteworthy to mention that there is an intrinsic difference $\text{Si}=\text{Si}$ double bond and the $\text{C}=\text{C}$ double bond. In the case of alkenes, the $\text{C}=\text{C}$ double bond mainly comprises of σ bond formed by the σ overlap of two sp^2 hybridized orbitals and another π bond which is formed due to the π overlap of two pure $p\pi$ -orbitals resulting in planar geometry. Whereas the geometry of disilene is found to be trans-bent in nature differing from that of the linear geometry of ethylene (Figure 1.1). Disilenes are found

to be much more reactive owing to the low HOMO-LUMO gap and the diradical character of the π bond.⁴⁵

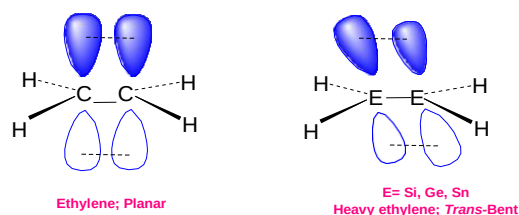


Figure 1.1. Orbital representation of linear and trans-bent geometry.

In accordance with the Carter-Goddard-Malrieu-Trinquier (CGMT) model⁴⁶ when the in-plane n -orbitals and the out-of-plane $p\pi$ orbitals of the two EH_2 groups approach each other to form a planar $\text{E}=\text{E}$ double then the overlap between two n orbitals and two $p\pi$ orbitals give rise to σ and σ^* bonds and π and π^* orbitals respectively. The energy gap between n and $p\pi$ orbitals is denoted as ΔE_{ST} . Again, the σ - σ^* and π - π^* orbital splitting energies are considered as E_σ ($\epsilon_{\sigma^*} - \epsilon_\sigma$) E_π ($\epsilon_{\pi^*} - \epsilon_\pi$). When a double bond is formed $\epsilon_\pi < \epsilon_{\sigma^*}$ and $\epsilon_\sigma < \epsilon_{\pi^*}$. According to PMO (perturbation molecular orbital) theory⁴⁷ ϵ_{σ^*} and ϵ_π are close to each other effective π - σ^* mixing takes place which is the reason for *trans*-bent geometry in the case of disilenes (Figure 1.2).

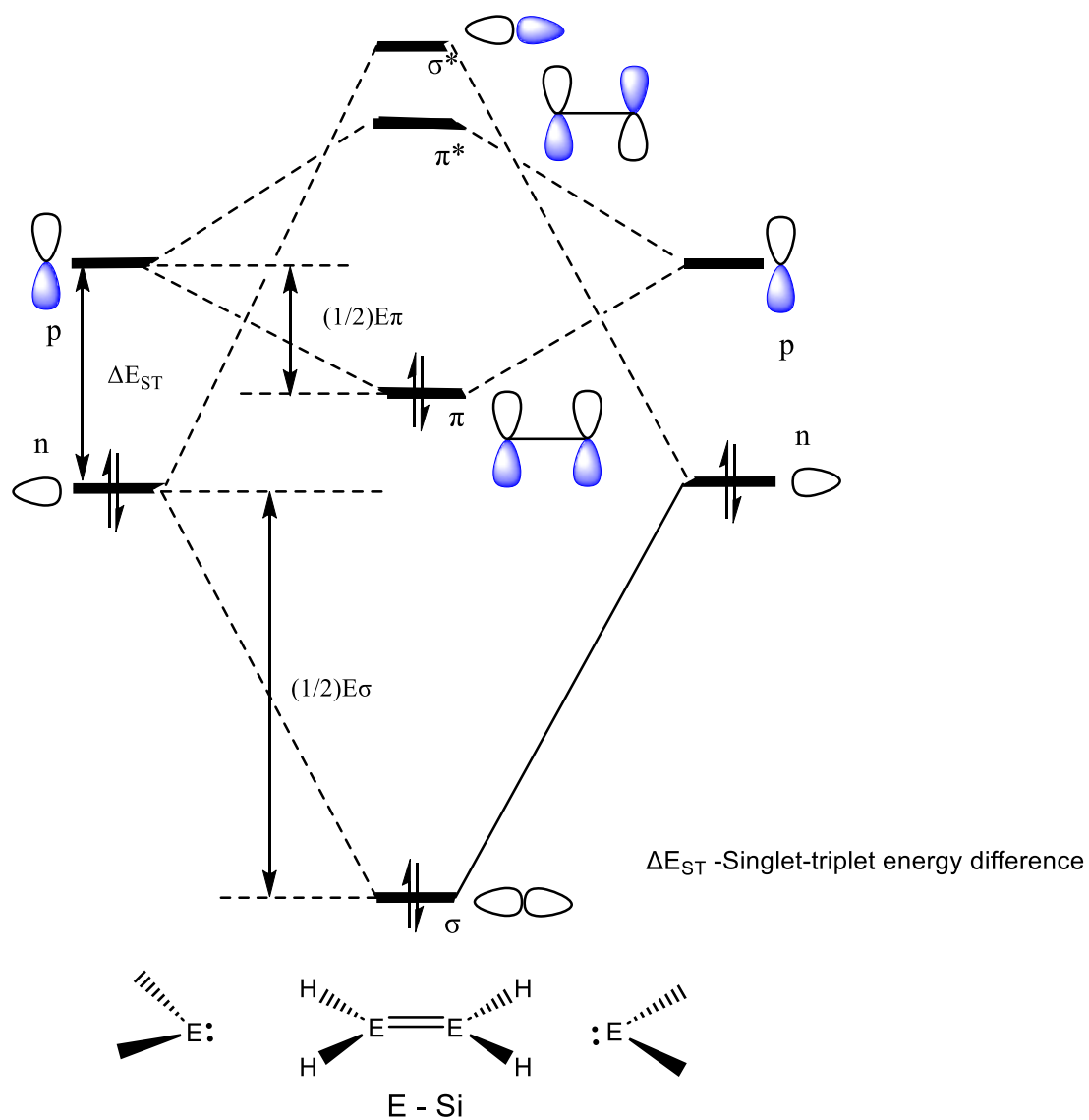
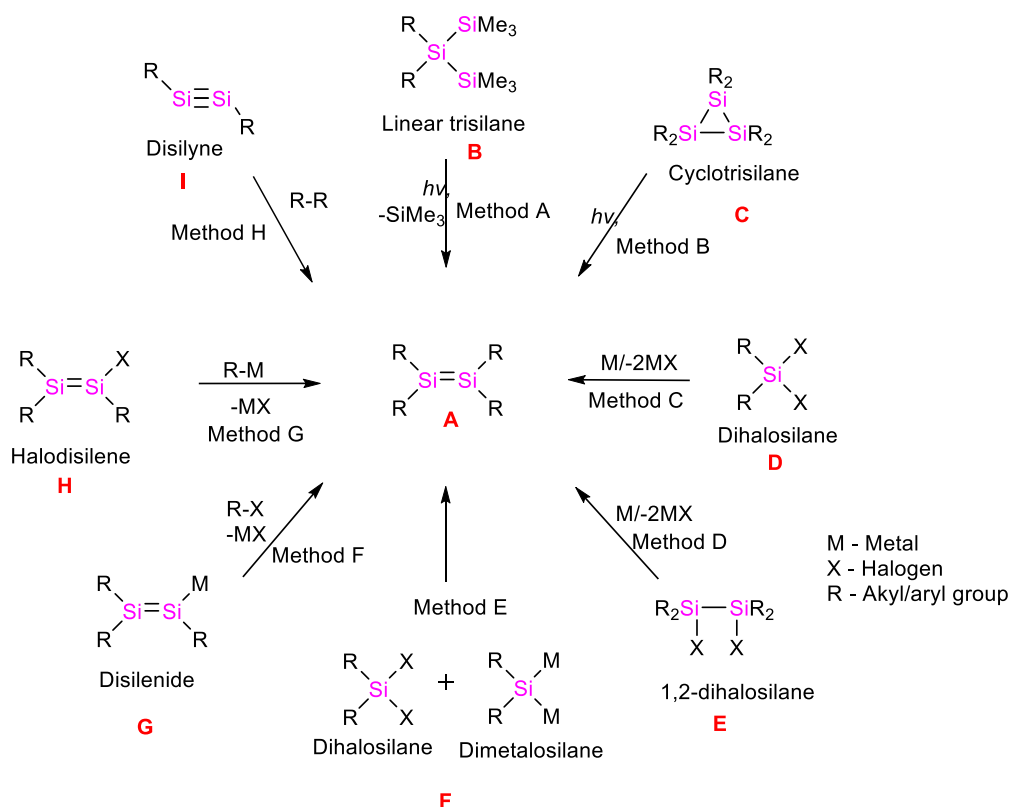
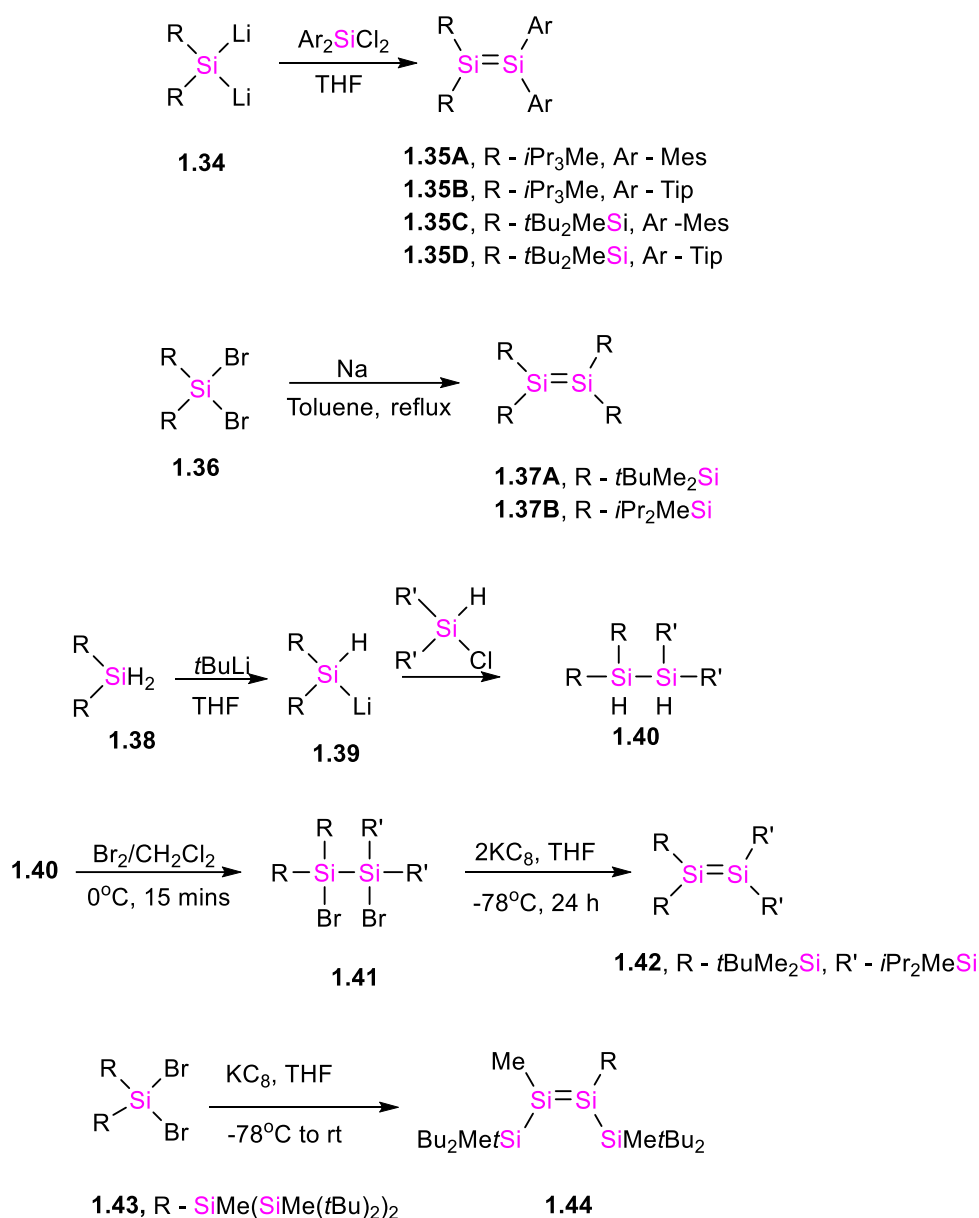


Figure 1.2. Schematic MO representation of the formation of dimetallenes by the dimerisation of corresponding metallylenes.

1.9. Synthetic protocol of stable disilenes

**Chart 1.2.** Synthetic routes for the preparation of stable disilenes.

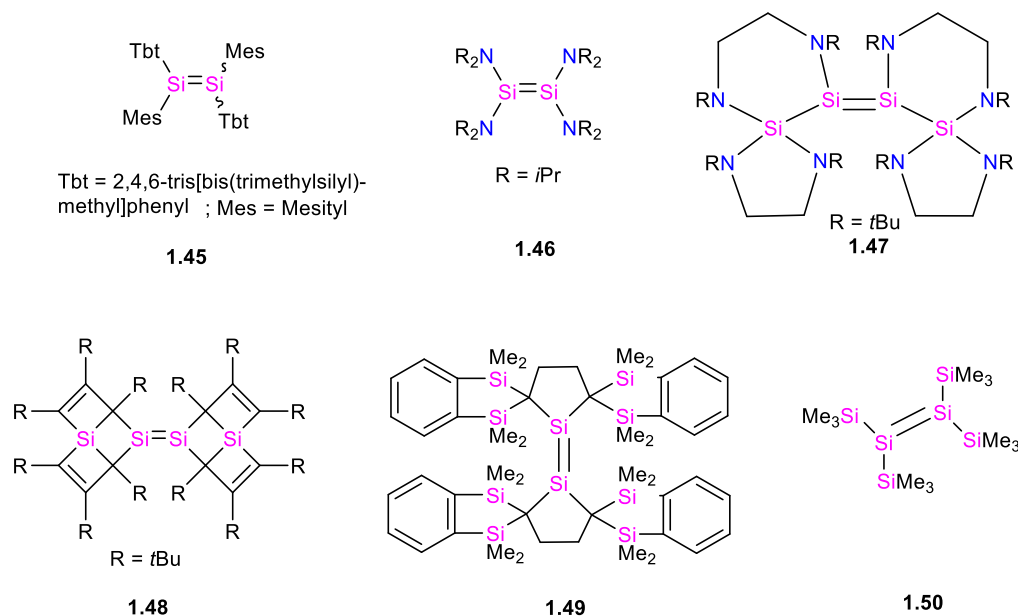
There are various synthetic protocols reported for the synthesis of stable disilenes (Chart 1.2). Disilenes can be synthesized through photolysis linear trisilanes (Method A). Disilenes are also formed from the photolysis of cyclic trisilanes (Method B). Reductive dehalogenation of dihalosilanes using metals (Method C). Another pathway is reductive dehalogenation of 1,2-dihalosilanes using metals (Method D). Other than these above synthetic protocols metathesis of 1,1-dihalosilanes and 1,1-dimetalated silanes also results in the formation of disilenes (Method E). Furthermore, substitution at the sp^2 silicon center of disilenide with electrophile (Method F) and in the case of halogen substituted disilenes with nucleophiles also yield disilenes (Method G). Another versatile and useful way for the synthesis of disilene is the 1,2 cross-addition across the silicon-silicon triple bonds (Method H).



Scheme 1.8. Some selected synthetic routes of disilenes.

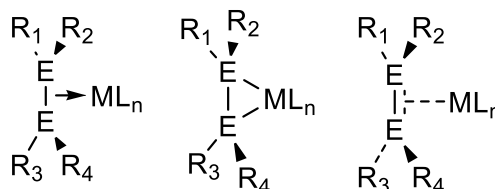
Different types of disilenes have been reported over the years. $\text{A}_2\text{Si}=\text{SiB}_2$ types of disilenes have been prepared by treating dilithiosilane (**1.34**) with dichlorosilane resulting in the formation of corresponding disilene (**1.35**).⁴⁸ Bis(*t*-butyldimethylsilyl)hydridosilyllithium (**1.39**) was synthesized through silametallation of the corresponding dihydridosilane (**1.40**) with *t*-butyllithium and then with bis(diisopropylmethylsilyl)chlorosilane it afforded 1,1-bis(*t*-butyldimethylsilyl)-2,2-bis(diisopropylmethylsilyl)disilane (**1.41**). Bromination of the dihydridosilane with bromine resulted in the formation of dibromosilane which was finally reduced with KC_8 giving the desired disilene (**1.42**).⁴⁹ Another way of synthesizing acyclic disilene is the reduction of the dihalosilanes using different reducing agents like sodium/potassium metals and KC_8 . Tetrakis(trialkylsilyl)disilenes (**1.37**) have been synthesized by reducing bis(trialkylsilyl)dibromosilanes with sodium metal.⁵⁰

1.10. Examples of disilenes which remain in equilibrium

**Chart 1.3.** Reported examples of disilenes which remain in equilibrium.

Silylenes dimerizes into the corresponding disilenes but disilenes generally do not revert back to the silylenes due to their thermal stability. However, few reports on disilenes remain in equilibrium with their corresponding silylenes (Chart 1.3). In 1993 Okazaki and co-workers for the first time reported the extremely sterically hindered and kinetically stable disilene $\text{Tb}(\text{Mes})\text{Si}=\text{Si}(\text{Mes})\text{Tb}$ (**1.45**) {Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = mesityl} from TbMesSiBr_2 and reducing it with LiNaph which under mild condition readily decomposes into its corresponding silylene TbMesSi .⁵¹ Kira and coworkers in 1998 generated bis(diisopropylamine)silylene photochemically at room temperature which gives the corresponding disilene (**1.46**) at low temperature.⁵² In 1999 West and coworkers isolated the crystal structure of diaminodisilyl disilene (**1.47**) which surprisingly exists in equilibrium with its silylene.⁵³ Sakamoto and coworkers reported the synthesis of tetraalkyl disilene (**1.48**) through the reduction of (tri-*tert*-butylcyclopropenyl)tribromosilane with KC_8 .⁵⁴ This disilene dissociates into the corresponding silylene. In recent times Inoue and co-workers isolated the (hypersilyl)(supersilyl)silylene which also remains in equilibrium with the disilene (**1.50**).⁵⁵

1.11. Reactivity of disilenes with transition metals



R_1, R_2 - Alkyl group

E - Si, M - Transition metals

Chart 1.4. Bonding pattern of disilene with transition metals.

The bonding pattern in the case of alkenes with the transition metals are well-known study and according to the Dewar-Chatt-Duncanson (DCD) model, it is described as the synergistic metal-to-alkene σ -donation and alkene to metal π -back donation (Chart 1.4).⁵⁶ The structure of the alkene metal complex is mainly dependent on the relative importance of the σ -donation and π -back donation. When the σ -donation from the alkene to the metal center is strong then the complex is known as the π -complex and it becomes a metallacycle when the π -back donation is more dominant. There is an intermediate structure between the π -complex and the metallacycle where the actual character and the structure of the alkene are not well known. In the case of disilenes-transition metal complexes, it is also assumed that it will also follow the DCD model.

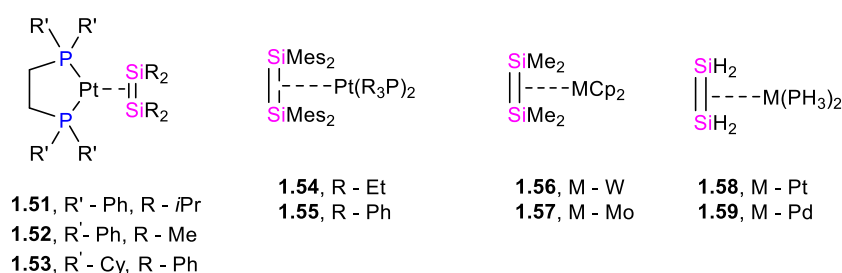
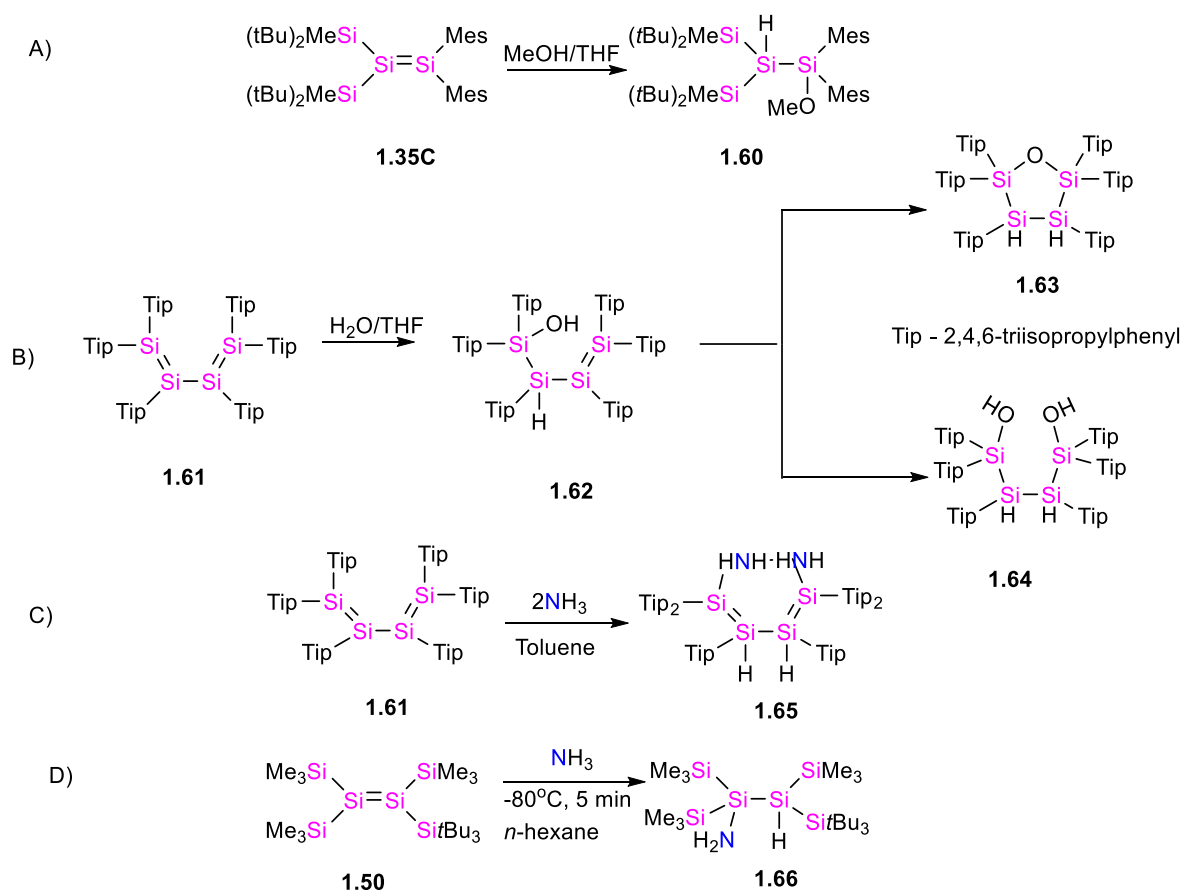


Chart 1.5. Selected examples of disilene-transition metal complexes.

West and co-workers reported the first examples of disilene platinum complexes. Upon irradiation of (oxalate)bis(phosphine)platinum complexes in the presence of tetramesityldisilene the desired platinum disilene complexes are formed.⁵⁷ In the case of the other complexes direct utilization of disilene is not involved rather the reaction between bis(phosphine)metal dichlorides and 1,2-dihydrodisilanes or metal-lithium salts with 1,2-dichlorodisilanes followed by the reduction of magnesium metal itself afforded the metal disilene complexes. Among all these the tungsten complex has been only characterized by X-ray crystallography (**1.56**).⁵⁸ In 2004 for the first time Kira and coworkers reported the synthesis of iron complexes of both (*E*)- and (*Z*)- dichlorodisilene.⁵⁹

1.12. Reactivity of disilenes with small molecules

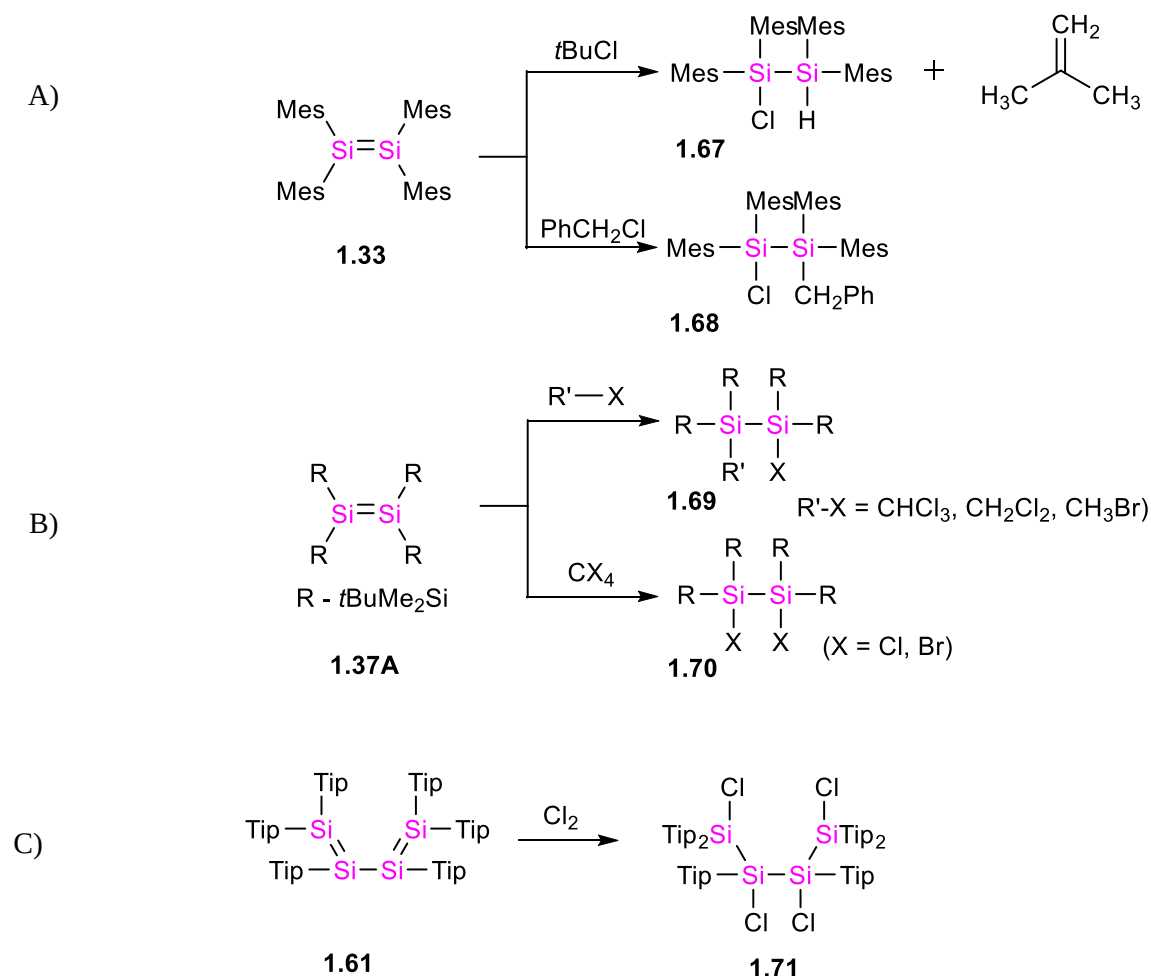
1.12.1. Treatment with H₂O, alcohol, ammonia



Scheme 1.9. Some selected examples of reactivity of disilenes.

In 2001 Sekiguchi and co-workers reported the treatment of methanol with 1,1-dimesityl-2,2-bis[di-tertbutyl(methyl)silyl]disilene (Scheme 1.9A) which afforded 1,2-addition where the methoxy group is attached to one silicon center and the hydrogen is attached to the other silicon center (**1.60**).⁶⁰ Again, Weidenbruch and co-workers reported the formation of oxatetrasilacyclopentane (**1.63**) in the treatment of H₂O with disilene.⁶¹ In this case, they have mentioned that in the first step, 1,2-addition of water takes place in one of the Si=Si double bonds followed by the hydrogen shift and ring closure leading to the formation of the desired 5-membered cyclic product. The reactivity of disilene with ammonia (NH₃) is less known. The same group reported the formation of 1,4-diamminotetrasilane (**1.65**) by the addition of 2 equivalent of ammonia with the same tetrasilene-1,3-diene (Scheme 1.9C).⁶² In recent years Inoue and co-workers reported the 1,2-addition of NH₃ across the double bond of tetrasilyldisilene (Scheme 1.9D).⁶³

1.12.2. Treatment with haloalkanes and halogens



Scheme 1.10. Selected examples of reactivity of disilenes with haloalkanes and halogens.

West and co-workers for the first time reported the reactivity of tetramesityldisilene with haloalkanes like *tert*-butylchloride which afforded a normal hydrogen chloride adduct and with benzyl chloride which resulted in the formation of benzyl-2-chlorodisilane (**1.67**) (Scheme 1.10A).⁶⁴ Kira and co-workers also showed that the addition of carbon tetrachloride and carbon tetrabromide gives the desired dihalodisilene (**1.70**) (Scheme 1.10B).⁶⁵ Another example of only chlorine addition to disilene (Scheme 1.10C). In this case, tetrasilyldisilene (**1.61**) was treated with chlorine which resulted in the formation of 1,2,3,4-tetrachlorotetrasilane (**1.71**).⁶²

1.13. Low-valent compounds with group 15 elements

Group 15 elements are nitrogen (N), phosphorus (P), antimony (Sb) and bismuth (Bi) and they are known as pnictogens. Pnictogens comes from a Greek word pnigein which means choking. Phosphorus was discovered by German alchemist Hennig Brand in 1669 which eventually assisted the discovery of the higher congeners of group 15.⁶⁶ Among the group 15 elements amines and phosphine play versatile roles as ligand systems for the coordination of both *d* and *f*-block metals and *p*-block elements as well.⁶⁷ Pnictogen elements can act as both donors i.e. Lewis bases and Lewis acids also. Generally, the pnictogens are found in the +3 and +5 oxidation states. When the pnictogens are in +5 oxidation state there is one lone pair of electrons present on the central atom only covalent bonds with the adjacent atoms are observed. In the case of the +3 oxidation state, the central pnictogen atom bears a lone pair of electrons. Other than these two oxidation states another most common oxidation state is the +1 oxidation state where four non-bonding electrons are present. Phosphorus compounds with +1 oxidation state are known as phosphinidenes.⁶⁸ Neutral phosphinidenes with the general formula R-P, are monocoordinated phosphorus atoms with two lone pairs of electrons and a vacant *p*-orbital. Phosphinidenes are considered the building blocks for the synthesis of various organophosphorus compounds as well as different transition metal complexes.

1.14. Pnictinidenes

Pnictinidenes are the low-valent monomeric species with the central atom group 15 elements bearing +1 oxidation state.⁶⁹ In the case of pnictinidenes the central atom remains attached to a single substituent through a σ -bond. Pnictinidenes can be either singlet or triplet, the singlet state has two lone pairs of electrons and one vacant *p*-orbital whereas the triplet state bears one lone pair of electrons and two singly occupied *p*-orbitals (Figure 1.3). Generally, free pnictinidenes are stabilized using Lewis bases or transition metals. Pnictinidenes have a strong propensity towards triplet state. Triplet phosphinidenes belong to those highly reactive class of species and their isolation still remains a challenge. Free phosphinidenes are very unstable and remain in a triplet state. In the absence of steric protection phosphinidenes are prone to undergo dimerization resulting in the formation of the corresponding diphosphene.⁷⁰ Singlet-free phosphinidenes remained uncharacterized before 2016 when Bertrand and co-workers reported for the first time the synthesis of singlet phosphinidene.⁷¹ All these precedents encourage the main group chemists to accept the challenge of synthesizing and isolating single-centered diradicals which can open the pathway to mimic the transition metals with main group elements.

Very recently Cornella and co-workers have reported the triplet bismuthinidene.⁷² Here they have shown that the bismuth center is flanked by the rigid, non-coordinating and bulky ligand backbone that provides steric protection to the Bi(I) center which forms a single bond with the carbon atom.

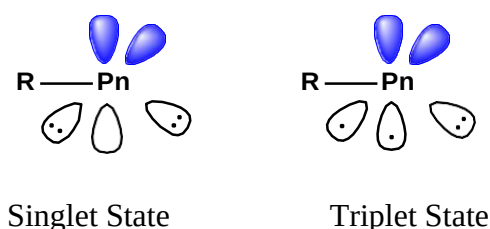


Figure 1.3. Representation of singlet and triplet states of pnictinidenes (Pn – P, As, Sb, Bi).

1.15. Pnictenium cations

The first stable phosphonium cation was isolated 40 years ago.⁷³ Following that isolation there has been a huge interest in the chemistry of heavier pnictogenium cations. The bonding pattern in case of heavier congeners of group 15 elements i.e. Sb and Bi exhibits a huge difference from that of the lighter elements of the group and so they are more reactive in nature.

Pnictogenium cations are dicoordinate, six-electron systems containing a lone pair of electrons and a vacant *p* orbital. These cations are amphoteric in nature and isoelectronic to carbenes. Due to the presence of a positive charge, these pnictogenium cations exhibit enhanced π acceptor abilities and less σ donation properties.⁷⁴ Following the isolation of N-heterocyclic carbenes (NHCs) similar types of isoelectronic, heteroatom bonding with both saturated and unsaturated backbone pnictogenium cations have been also reported. Different types of N-heterocyclic phosphonium,^{74,75} arsenium,⁷⁶ stibonium^{76c, 77} cations have been isolated to date. Other than these N-heterocyclic pnictogenium cations, donor-free diaryl stibonium and bismuthenium cations have been also reported (Chart 1.6).^{77B,7}

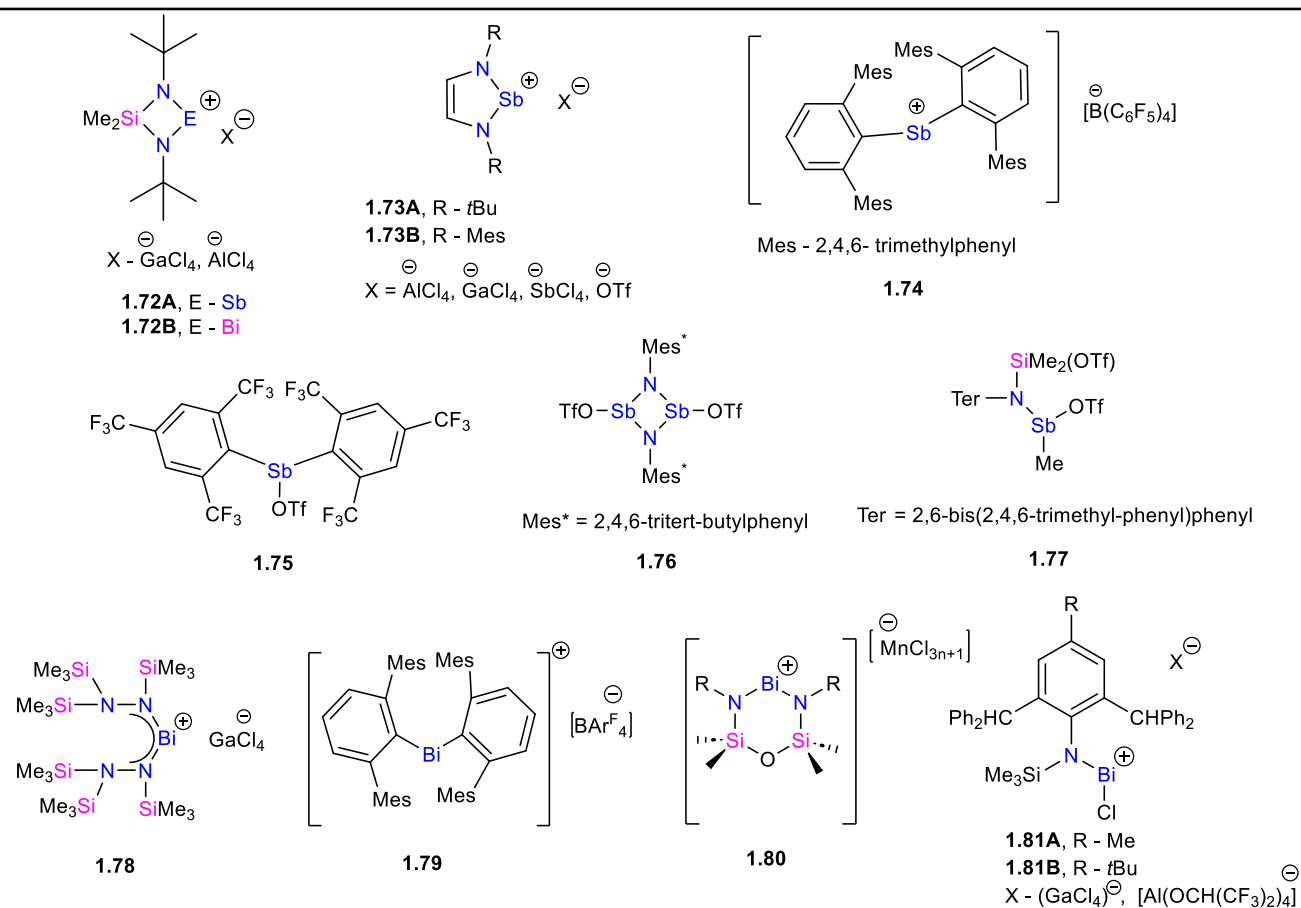


Chart 1.6. Some selected examples of donor free stibonium and bismuthenium cations.

Although various donor-stabilized as well as donor-free stibenium cations are known but they have not been explored in the field of homogeneous catalysis. Recently our group has reported a donor-free stibenium cation and has explored it as a potential cyanosilylation catalyst which we have mentioned in detail in Chapter 4A of this thesis. The next congener bismuth being the non-toxic, cheap, cationic bismuth compounds have been used widely in the field of homogeneous catalysis. Bismuth halides and triflate complexes act as Lewis acid catalysts in various organic reactions. A variety of organobismuth compounds are also reported in the literature which are utilized as potential homogeneous catalysis (Chart 1.7).

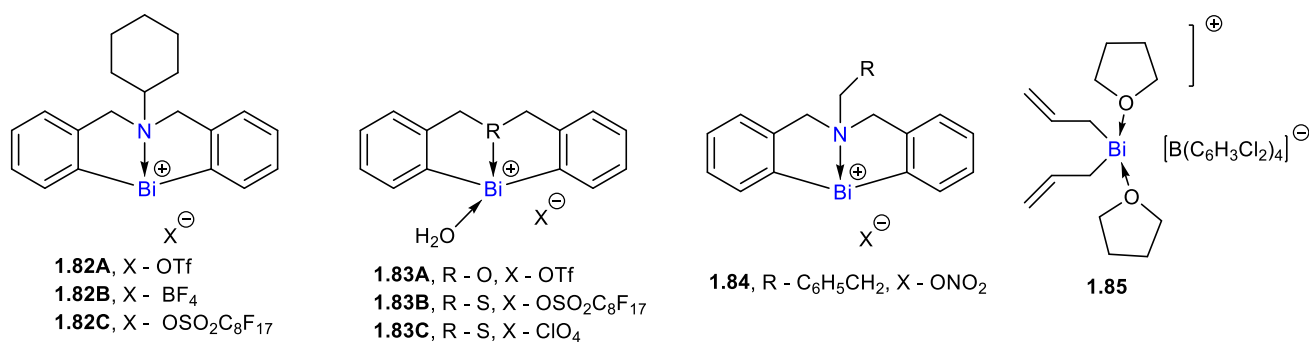


Chart 1.7. Selected examples of bismuthenium cations utilised as catalysts.

Organobismuth(III) perfluorooctanesulfonate ($\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}(\text{OSO}_2\text{C}_8\text{F}_{17})$) (**1.82C**) and organobismuth(III) tetrafluoroborate ($\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}(\text{BF}_4)$) (**1.82B**) have been utilized as a potential catalyst for Mannich reaction^{82a} and allylation of aldehyde^{82b} respectively. Another organobismuth triflate complex $[\text{O}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}(\text{OH}_2)]^+[\text{OSO}_2\text{CF}_3]^-$ (**1.83A**) has been

synthesized and its catalytic efficiency has been examined in the ring opening of epoxides with aromatic rings.⁸³ Other cationic organobismuth compounds with a similar type of framework have been utilized for the synthesis of α , β -unsaturated ketones by crossed condensation of ketones and aldehydes and oxidative coupling of thiophenol to diphenyl sulfide.⁸⁴ Another Lewis acid bis(allyl)bismuth cation $[\text{Bi}(\text{C}_3\text{H}_5)_2(\text{THF})_2]^+[\text{B}(\text{C}_6\text{H}_3\text{Cl}_2)_4]^-$ acts as allyl transfer reagent leading to carbometalation product (**1.85**).⁸⁵

1.17. Motivation and objective

Over the last few decades, the main group chemistry has drawn considerable attention due its unique structural properties, bonding patterns and catalytic efficiency. It is evident that main group chemistry is not limited to the synthesis of different types of coordinated compounds with the transition metals but the main group *p*-block elements are useful for small molecule activation, synthesis of cationic compounds and in homogeneous catalysis. So far, we have discussed various aspects of group 14 and group 15 low valent species and have studied their structure and bonding patterns. We have understood the importance of the main group elements which are very useful for the development of new materials and catalysts which can mimic the transition metals chemistry. My thesis is mainly focused on the synthesis of new low-valent main-group 14 and 15 compounds. Recent years have witnessed tremendous growth in the field of the development of main group element based catalysts for the sustainable catalysis. Many low-valent main group compounds of group 13-15 have been synthesized and utilized for the catalytic application. However, they are still developing. We were keen to develop some efficient main group based catalysts for important organic transformation. Hence, my work is mainly focused on the synthesis and application of group 14 and group 15 elements based low valent compounds.

1.18. References

1. Power, P.P. *Chem. Rev.* **1999**, 99, 3463–3503.
2. Mizuhata, Y.; Sasamori, T.; Tokito, N. *Chem. Rev.* **2009**, 109, 3479–3511.
3. Linti, G.; Schnöckel, H. *Coordination Chemistry Reviews* **2000**, 285–319.
4. Power, P.P. *Chem. Rev.* **2003**, 103, 789–809.
5. Hicks, R. G. *Org. Biomol. Chem.* **2007**, 5, 1321–1338.
6. Lee, V. Y.; Nakamoto, M.; Sekiguchi, A. *Chemistry Letters* **2008**, 37, 128–133.
7. Bertrand, G. *Chem. Rev.* **2010**, 110, 3851.
8. Bourissou, D. *Chem. Rev.* **2019**, 119, 14, 8229–8230.
9. Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, 113, 361–363.
10. Nechaev, M. S. *Organometallics* **2021**, 40, 3408–3423.
11. a) Sanderson, R. T. *Inorg. Chem.* **1986**, 25, 1856–1858. b) Chu, T.; Nikonov, G.; T. *Chem. Rev.* **2018**, 118, 3608–3680
12. Oberdorf, K.; Lichtenberg, C. *Chem. Commun.* **2023**, 59, 8043–8058.
13. Weetman, C. *Encyclopedia of Inorganic and Bioinorganic Chemistry* (Ed.: R. A. Scott), John Wiley & Sons, pp 1–27.
14. So, C-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem. Int. Ed.* **2006**, 45, 3948–3950.
15. Sen, S. S.; Roesky, H. W.; Stern, D.; Henn, J.; Stalke, D. *J. Am. Chem. Soc.* **2010**, 132, 1123–1126.
16. Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem. Int. Ed.* **2009**, 48, 5683–5686.
17. Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, 116, 2691–2692.
18. Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 1485.
19. Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, 121, 9722–9723.
20. Kira, M.; Ishida, S.; Iwamoto, T.; Ichinohe, M.; Kabuto, C.; Ignatovich, L.; Sakurai, H. *Chem. Lett.* **1999**, 263–264.
21. Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H.; *J. Am. Chem. Soc.* **1991**, 113, 7785–7787.
22. Akkari, A.; Byrne, J. J.; Saur, I.; Rima, G.; Gornitzka, H.; Barrau, J. J. *Organomet. Chem.* **2001**, 622, 190–198.

-
-
23. Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 1190-1194.
24. Shah, S. S. A.; Ashfaq, M.; Waseem, A.; Ahmed, M. M.; Najam, T.; Shaheen, S.; Rivera, G. *Mini-Reviews in Medicinal Chemistry* **2015**, *15*, 406-426.
25. Fischer, E. O.; Fritz, H. P. *Advances in Inorganic Chemistry and Radiochemistry* **1959**, *1*, 55-115.
26. Portnyagin, I. A.; Lunin, V. V.; Nechaev, M. S. *Journal of Organometallic Chemistry* **2008**, *693*, 3847-3850.
27. a) Arkis, E.; Balkose, D. *Polymer Degradation and Stability* **2005**, *88*, 46-51. b) *J. Org. Chem.* **1991**, *56*, 5307-5311.
28. a) Ghazi, D.; Yousif, E. *International Journal of Research in Engineering and Innovation* **2017**, *1*, 63-65. b) Yousif, E.; Mehdi, B. I.; Yusop, R.; Salimon, J.; Salih, N.; Abdullah, B. M. *Journal of Taibah University for Science* **2014**, *8*, 276-281.
29. Davidson, P. J.; Lappert, M. F. *J. Chem. Soc. Chem. Commun.* **1973**, 317.
30. Hitchcock, P. B.; Lappert, M. F.; Samways, B. J.; Weinberg, E. L. *J. Chem. Soc., Chem. Commun.* **1983**, 1492-1494.
31. Engelhardt, L. M.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; White, A. H.; *J. Chem. Soc. Chem. Commun.* **1988**, 336-338.
32. Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H.; *J. Am. Chem. Soc.* **1991**, *113*, 7785-7787.
33. Weidenbruch, M.; Schlaefke, J.; Schäfer, A.; Peters, K.; Schnering, H. G. V.; Marsmann, H.; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1846-1848.
34. Gans-Eichler, T.; Gudat, D.; Nieger, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 1888-1891.
35. Mansell, S. M.; Russell, C. A.; Wass, D. F. *Inorg. Chem.* **2008**, *47*, 11367-11375.
36. A) Nimitsiriwat, N.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Dale, S. H.; Elsegood, M. R. *J. Dalton Trans.* **2007**, 4464-4471. b) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **1999**, *18*, 4700-4705. c) Aubrecht, K. B.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules*, **2002**, *35*, 644-650. d) Sen, S. S.; Kritzler-Kosch, M. P.; Nagendran, S.; Roesky, H. W.; Beck, T.; Pal, A.; Herbst-Irmer, R. *Eur. J. Inorg. Chem.* **2010**, 5304-5311. e) Dove, A. P.; Gibson, V. C.; Marshall, E. L.; Rzepa, H. S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2006**, *128*, 9834-9843. f) Jana, A.; Roesky, H. W.; Schulzke, C.; Doering, A.; Beck, T.; Pal, A.; Herbst-Irmer, R. *Inorg. Chem.* **2009**, *48*, 193-197.
-

-
37. Peng, Y.; Ellis, B. D.; Wang, X.; Power, P. P. *J. Am. Chem. Soc.* **2008**, *130*, 12268–12269.
38. Sarkar, D.; Weetman, C.; Munz, D.; Inoue, S. *Angew. Chem. Int. Ed.* **2021**, *60*, 3519 – 3523.
39. Hitchcock, P. B.; Jang, E.; Lappert, M. F. *J. Chem. Soc. Dalton Trans.* **1995**, 3179–3187.
40. Leung, W-P.; Kwok, W-H.; Zhou, Z-Y.; Mak, T. C. W. *Organometallics* **2000**, *19*, 296–303.
41. Hossain, J.; Parvin, N.; Shah, B. K.; Khan, S. Z. *Anorg.Allg. Chem.* **2022**, *648*, e202200164.
42. a) Jutzi, P. *Angew. Chem. Int. Ed.* **1975**, *14*, 232–245. b) Guselnikov, L. E.; Nametkin, N. S. *Chemical Reviews* **1979**, *79*, 529–577.
43. West, R.; Fink, M. *J. Science* **1981**, *214*, 1343–1344.
44. a) West, R. *Polyhedron*, **2002**, *21*, 467–472; b) Power, P. P. *Chem. Commun.*, **2003**, 2091–2101. c) Power, P. P. *Organometallics*, **2007**, *26*, 4362–4372.
45. Kira, M. *Proc. Jpn. Acad., Ser. B* **2012**, *88*, 167–191.
46. a) Carter, E. A.; Goddard, W. A. *The Journal of Physical Chemistry* **1986**, *90*, 998–1001. b) Trinquier, G.; Malrieu, J-P. *J. Am. Chem. Soc.* *109*, **1987**, 5303–5315. c) Malrieu, J-P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916–5921. d) Trinquier, G.; Malrieu, J-P. *J. Phys. Chem.* **1990**, *94*, 6184–6196.
47. Dougherty, R. C. *J. Chem. Phys.* **1997**, *106*, 2621–2626.
48. Ichinohe, M.; Arai, Y.; Sekiguchi, A. *Organometallics* **2001**, *20*, 4141–4143.
49. Iwamoto, T.; Okita, J.; Kabuto, C.; Kira, M. *Journal of Organometallic Chemistry* **2003**, *686*, 105–111.
50. Kira, M.; Maruyama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1489–1491.
51. Tokitoh, N.; Suzuki, H.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 10428–10429.
52. Tsutsui, S.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 9955–9956.
53. Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479–9480.
54. Tsutsui, S.; Tanaka, H.; Kwon, E.; Matsumoto, S.; Sakamoto, K. *Organometallics* **2004**, *23*, 5659–5661.
55. Reiter, D.; Holzner, R.; Porzelt, A.; Altmann, P. J.; Frisch, P.; Inoue, S. *J. Am. Chem. Soc.* **2019**, *141*, 13536–13546.
-

56. a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.*, **1951**, 18, C71-C7. b) Chatt, J.; Duncanson, L. *A. J. Chem. Soc.* **1953**, 2939–29.
57. Pham, E. K.; West, R. *Organometallics* **1990**, 9, 1517–1523.
58. Berry, D. H.; Chey, J. H.; Zipin, H. S.; Carroll, P. H. *J. Am. Chem. Soc.* **1990**, 112, 452–453; Hong, P.; Damrauer, N. H.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, 12, 3698–3704.
59. Hashimoto, H.; Suzuki, K.; Setaka, W.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2004**, 126, 13628–13629.
60. Ichinohe, M.; Arai, Y.; Sekiguchi, A. *Organometallics* **2001**, 20, 4141–4143.
61. Willms, S.; Grybat, A.; Saak, W.; Weidenbruch, M. *Z. Anorg. Allg. Chem.* **2000**, 626, 1148–1152.
62. Boomgaarden, S.; Saak, W.; Weidenbruch, M. *Z. Anorg. Allg. Chem.* **2001**, 627, 349–352.
63. Reiter, D.; Holzner, R.; Porzelt, A.; Altmann, P. J.; Frisch, P.; Inoue, S. *J. Am. Chem. Soc.* **2019**, 141, 13536–13546.
64. Fanta, A. D.; Belzner, J.; Powell, D. R.; West, R. *Organometallics* **1993**, 12, 2177–2181.
65. Iwamoto, T.; Sakurai, H.; Kira, M. *Bull. Chem. Soc. Jpn.* **1998**, 71, 2741–2747.
66. Wisniak J. *Indian J Chem Technol.* **2005**, 12, 108–22.
67. a) Gopalakrishnan, J. *Appl. Organometal. Chem.* **2009**, 23, 291–318. b) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. *Chem. Rev.* **2010**, 110, 4023–4078. c) Fujii, T.; Kitagawa, Y.; Hasegawa, Y.; Imoto, H.; Naka, K. *Inorg.Chem.* **2022**, 61, 17662–17672.
68. a) Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, 1127–1138. b) Aktaş, H.; Slootweg, J. C.; Lammertsma, K. *Angew. Chem. Int. Ed.* **2010**, 49, 2102–2113. c) Dostál, L. *Coordination Chemistry Reviews* **2017**, 353, 142–158.
69. a) Ellis, B. D.; Macdonald, C. L. B. *Coordination Chemistry Reviews* **2007**, 251, 936–973. b) Mitchell, E. C.; Wolf, M. E.; Turney, J. M.; Schaefer, H. F. *Chem.Eur. J.* **2021**, 27, 14461–14471.
70. Weber, L. *Chem. Rev.* **1992**, 92, 1839–1906.
71. Liu, L.; Ruiz, D. A.; Munz, D.; Bertrand, G. *Chem* **2016**, 1, 147–153.
72. Pang, Y.; Nöthling, N.; Leutzsch, M.; Kang, L.; Bill, E.; Gastel, M. V.; Reijerse, E.; Goddard, R.; Wagner, L.; SantaLucia, D.; DeBeer, S.; Neese, F.; Cornella, J. *Science* **2023**, 380, 1043–1048.

73. Dimroth, K.; Hoffmann, P. *Angew. Chem., Int. Ed. Engl.* **1964**, 3, 384.
74. a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, 85, 367-382.
75. a) Caputo, C. A.; Price, J. T.; Jennings, M. C.; McDonald, R.; Jones, N. D. *Dalton Trans.*, **2008**, 3461–3469. b) Lundrigan, T.; Welsh, E. N.; Hynes, T.; Tien, C-H.; Adams, M. R.; Roy, K. R.; Robertson, K. N.; Speed, A. W. H. *J. Am. Chem. Soc.* **2019**, 141, 14083–14088. c) Pop, L-C.; Katir, N.; Castel, A.; Dumitrescu, L. S.; Delpech, F.; Dumitrescu, I. S.; Gornitzka, H.; Carey, D. M.; Saffon, N. *Journal of Organometallic Chemistry* **2009**, 694, 1562–1566. d) Vidovic, D.; Lu, Z.; Reeske, G.; Moore, J. A.; Cowley, A. H. *Chem. Commun.* **2006**, 6, 3501–3503. e) Reeske, G.; Hoberg, C. R.; Hill, N. J.; Cowley, A. H. *J. Am. Chem. Soc.* **2006**, 128, 2800.
76. a) Burford, N.; Parks, T. M.; Royan, B. W.; Borecka, B.; Cameron, T. S.; Richardson, J. F.; Gabe, E. J.; Haynes, R. *J. Am. Chem. Soc.* **1992**, 114, 8147. b) Reeske, G.; Cowley, A. H. *Chem. Commun.*, **2006**, 1784-1786. c) Spinney, H. A.; Korobkov, I.; Richeson, D. S. *Chem. Commun.*, **2007**, 1647–1649. d) Burck, S.; Daniels, J.; Gans-Eichler, T.; Gudat, D.; Nättinen, K.; Nieger, M. *Z. Anorg. Allg. Chem.* **2005**, 631, 1403-1412.
77. a) Price, J. T.; Lui, M.; Jones, N. D.; Ragona, P. J. *Inorg. Chem.* **2011**, 50, 12810–12817. b) Gudat, D.; Eichler, T. G.; Nieger, M. *Chem. Commun.*, **2004**, 2434–2435.
78. a) Olaru, M.; Duvinage, D.; Lork, E.; Mebs, S.; Beckmann, J. *Angew. Chem. Int. Ed.* **2018**, 57, 10080–10084. b) Lehmann, M.; Schulz, A.; Villinger, A. *Eur. J. Inorg. Chem.* **2010**, 5501–5508. c) Burford, N.; Macdonald, C. L. B.; LeBlanc, D. J.; Cameron, T. S. *Organometallics* **2000**, 19, 152-155. d) Veith, M.; Bertsch, B.; Huch, V. *Z. anorg. Allg. Chem.* **1988**, 559, 73-88. e) Baumann, W.; Schulz, A.; Villinger, A. *Angew. Chem. Int. Ed.* **2008**, 47, 9530 –9532. f) Schwamm, R. J.; Coles, M. P.; Fitchett, C. M. *Dalton Trans.*, **2017**, 46, 4066–4074. g) Junghans, C. H.; Thomas, M.; Villinger, A.; Schulz, A. *Chem. Eur. J.* **2015**, 21, 6713–6717.
79. a) Mukherjee, A.; Milstein, D. *ACS Catal.* **2018**, 8, 11435–11469. b) Chirik, P. J. *Acc. Chem. Res.* **2015**, 48, 1687–1695. c) Wu, X-F.; Fang, X.; Wu, L.; Jackstell, R.; Neumann, H.; Beller, M. *Acc. Chem. Res.* **2014**, 47, 1041–1053.
80. Pérez, M.; Qu, Z-W.; Caputo, C. B.; Podgorny, V.; Hounjet, L. J.; Hansen, A.; Dobrovetsky, R.; Grimme, S.; Stephan, D. W. *Chem. Eur. J.* **2015**, 21, 6491–6500.
81. a) Mehta, M.; Holthausen, M. H.; Mallov, I.; Pérez, M.; Qu, Z-W.; Grimme, S.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2015**, 54, 8250–8254. b) Pérez, M.; Hounjet, L. J.; Caputo, C. B.; Dobrovetsky, R.; Stephan, D. W. *J. Am. Chem. Soc.* **2013**, 135,

- 18308–18310. c) Holthausen, M. H.; Mehta, M.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2014**, *53*, 6538–6541. d) Gasperini, D.; Neale, S. E.; Mahon, M. F.; Macgregor, S. A.; Webster, R. L. *ACS Catal.* **2021**, *11*, 5452–5462.
82. a) Zhang, X.; Yin, S.; Qiu, R.; Xia, J.; Dai, W.; Yu, Z.; Au, C-T.; Wong, W-Y. *Journal of Organometallic Chemistry* **2009**, *694*, 3559–3564. b) Zhang, X.; Qiu, R.; Tan, N.; Yin, S.; Xia, J.; Luo, S.; Au, C-T. *Tetrahedron Letters* **2010**, *51*, 153–156.
83. Tan, N.; Yin, S.; Li, Y.; Qiu, R.; Meng, Z.; Song, X.; Luo, S.; Au, C-T.; Wong, W-Y. *Journal of Organometallic Chemistry* **2011**, *696*, 1579–1583.
84. Toma, A. M.; Raț, C. I.; Pavel, O. D.; Hardacre, C.; Rüffer, T.; Lang, H.; Mehring, M.; Silvestru, A.; Pârvulescu, V. I. *Catal. Sci. Technol.*, **2017**, *7*, 5343–5353.
85. Lichtenberg, C.; Pan, F.; Spaniol, T. P.; Englert, U.; Okuda, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 13011–13015.

Chapter 2

Cyclic Four-Membered Stanna Thio and Seleno Compounds from 2-Aminopyridinato Stannylenes

2.1. Introduction

Network compounds featuring group 14 elements with sulfur or selenium linkers exhibit intriguing chemical and physical properties as well as applications.^{1–3} One of the common protocols to access thiostannates is the solvothermal route that utilizes different amines as a structure-directing agent such as $(\text{C}_2\text{H}_{10}\text{N}_2)(\text{C}_2\text{H}_9\text{N}_2)_2[\text{Sn}_2\text{S}_6]$,⁴ $\text{R}_2\text{Sn}_3\text{S}_7$ [R = tetramethylammonium (TMA),⁵ $[\text{SnS}_2 \cdot \text{en}]$ (en = ethylenediamine),⁶ $(\text{C}_6\text{H}_{20}\text{N}_4)_2[\text{SnS}_2] \cdot 2\text{H}_2\text{O}$,⁷ diazabicyclooctane (DABCO),⁸ ammonium/tetraethylammonium (ATEA), tetraethylammonium (TEA)],⁹ $\text{R}'_2\text{Sn}_4\text{S}_9$ [R' = tetrapropylammonium (TPA), tetrabutylammonium (TBA)],⁹ and $(\text{enH})_4[\text{Sn}_2\text{S}_6]$.¹⁰ An alternative approach to access SnS/Se system is the introduction of organic ligands with a designed functionality, which has been widely used by synthetic chemists in recent years (vide infra). Due to our interest in group 14/16 chemistry, we aimed to synthesize stannylene-based chalcogen complexes.

Synthesis of tin chalcogenides complexes via the reaction of stannylenes with elemental chalcogen has shown distinct bonding, which includes the formation of $\text{Sn}=\text{E}$ (E = S, Se, Te) double bonds when the substituents on tin are bulky (Chart 2.1).¹¹ However, the decrease in the bulkiness of the aryl substituents on tin results in the formation of bridging Sn-E-Sn moiety or four-membered Sn_2E_2 species (Chart 2.1).¹²

2-Aminopyridinate ligands have found extensive usage in transition metal chemistry¹³ as they can blend anionic amide and a neutral pyridine in a chelating ligand and offer a wide range of substitution patterns. However, it has been ignored as a ligand in low-valent main-group chemistry because the steric bulk of aminopyridinato ligands is rather small in comparison to the related amidinate or -diketiminato ligands. Nevertheless, aminopyridinato ligands have also started to gain a foothold in main group chemistry, as the group of Ding already prepared silicon (IV) and Ge (II) compounds^{14a,14b} using the same ligand and used them for CVD studies. To the best of our knowledge, there is no report so far on the synthesis of tin(II) compounds containing aminopyridinato ligands. Herein, we report synthesizing two types of stannylenes using aminopyridinato ligand and their subsequent reactivity with sulfur and selenium.

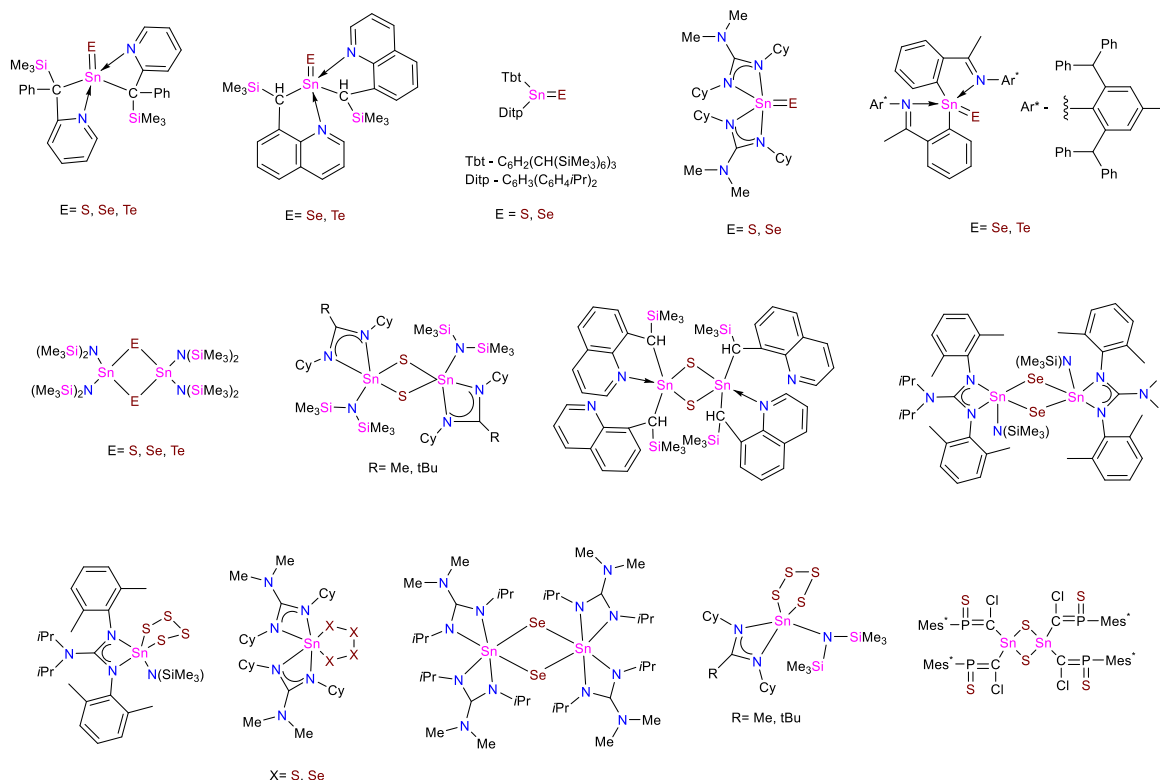


Chart 2.1. Previously reported tin-chalcogenide compounds.

2.2. Experimental Section

2.2.1 General Remarks

Ligand syntheses were carried out under air and metallation reactions were carried out under an inert atmosphere of argon applying standard Schlenk techniques or in a glove box. The solvents used were purified by an MBRAUN solvent purification system MBSPS-800. All chemicals purchased from Sigma Aldrich, Alfa-Aesar were used without further purification. Ligands **2.1** and **2.2** were prepared by the previously reported methods.¹⁵ ^1H and ^{13}C NMR spectra were recorded in CDCl_3 , C_6D_6 and $[\text{D}_6]$ DMSO using a Bruker AvanceDRX500 spectrometer and were referenced to external SiMe_4 . ^{77}Se NMR and ^{119}Sn NMR were referenced to external Me_2Se and Me_4Sn , respectively.

2.2.2. Synthesis of compounds 2.3-2.10

Synthesis of 2.3. Ligand **2.1** (1 g, 5.88 mmol) was taken in a 100 mL Schlenk flask and dried under a high vacuum at 60 °C for 4 h. Then 40 mL of dry Et_2O was added to the flask. Subsequently, the flask was cooled to -70 °C, and $n\text{BuLi}$ (3 mL of 2 M solution) was added to the flask drop by drop. The reaction mixture was slowly brought to room temperature and stirred for 3 h. The reaction mixture was again cooled to 0 °C and it was transferred to another Schlenk

flask containing Et₂O (10 mL) solution of SnCl₂ (0.56 g, 2.94 mmol). The reaction was stirred overnight which afforded a white ppt (LiCl). The solution was filtered and concentrated till some crystalline particles were visible on the surface of the flask. Storage of the concentrated solution of **2.3** at 0 °C resulted in the yellow crystals of **2.3**. Yield = 0.74 g (55 %). Mp: 112 °C. ¹H NMR (400 MHz, C₆D₆, 289 K, ppm): δ = 7.31 (d, *J* = 4.8 Hz, 2H), 7.18 (s, 2H), 7.14 (s, 2H), 7.04 (d, *J* = 7.3 Hz, 4H), 6.91 (t, *J* = 7.3 Hz, 2H), 6.80 (t, *J* = 6.9 Hz, 2H), 6.46 (d, *J* = 8.7 Hz, 2H), 5.90 (t, *J* = 5.8 Hz, 2H); ¹³C{¹H} NMR (101 MHz, C₆D₆, 298 K, ppm): δ = 163.7, 146.4, 144.7, 139.0, 127.8, 123.4, 122.4, 109.9, 107.5; ¹¹⁹Sn{¹H} NMR (149.18 MHz, C₆D₆, 298 K, δ) –262.5 ppm; MALDI MS *m/z*: 457.5848 [M]⁺.

Synthesis of 2.4. To the solution of **2.2** (1 g, 6.02 mmol) in 40 mL of Et₂O, 3.01 mL (6 mmol) of *n*BuLi at –70 °C was added slowly. After stirring the reaction mixture for 3 h, 0.57 g (3.01 mmol) of SnCl₂ was added at –70 °C. After the addition of SnCl₂, the reaction mixture was warmed to room temperature slowly and left for stirring overnight. Then the solution was filtered off, concentrated to 8 mL and kept at 0 °C for crystallization. The colorless crystals of **2.4** suitable for X-ray analysis were observed after one day. Yield: 0.813 g (60 %), mp: 97 °C. ¹H NMR (400 MHz, CDCl₃, 298 K, ppm): δ = 7.71 (s, 2H), 7.52–7.48 (m, 2H), 6.57–6.51 (m, 4H); ¹³C{¹H} NMR (101 MHz, CDCl₃, 298 K, ppm): δ = 162.2, 141.69, 111.4, 110.9, 1.1; ¹¹⁹Sn (149.18 MHz, CDCl₃, 298 K, ppm): δ = –426.0; MALDI MS *m/z*: 451.4435 ([M + H]⁺).

Synthesis of 2.5. To the mixture of 0.200 g (0.437 mmol) of **2.3** and 0.014 g (0.437 mmol) of powder elemental sulfur, 25 mL of DCM was added at room temperature. After stirring the reaction mixture for 10 min, the yellow-colored solution was filtered off and reduced to 10 mL. The yellow-colored crystals of **2.5** suitable for X-ray analysis were obtained at room temperature. Yield: 0.15 g (70 %), mp: 189.3 °C. ¹H NMR (400 MHz, [D₆]DMSO, 298 K, ppm): δ = 8.99 (s, 3H), 8.14 (d, *J* = 3.6 Hz, 4H), 7.67 (d, *J* = 7.9 Hz, 7H), 7.57–7.52 (m, 4H), 7.27–7.23 (m, 8H), 6.89–6.81 (m, 7H), 6.74–6.71 (m, 3H); ¹³C{¹H} (101 MHz, CDCl₃, 298 K, ppm): δ = 129.4, 123.8, 66.0, 29.8, 15.4, 1.1; ¹¹⁹Sn{¹H} (149.18 MHz, CDCl₃, 298 K, ppm): δ = –446.6; MALDI MS *m/z*: 980.2598 [M⁺].

Synthesis of 2.6. To the mixture of 0.034 g (0.437 mmol) of elemental selenium and **2.3** (0.200 g, 0.437 mmol), 25 mL of DCM was added at room temperature and the reaction mixture was stirred for an additional 48 h. The golden yellow-colored solution was then filtered off and reduced to 10 mL. To this solution, 5 mL of *n*-pentane was added. Yellow-colored crystals of

2.6 suitable for X-ray analysis were grown at 0 °C. Yield: 0.173 g (74 %), mp: 240 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): = 8.22 (d, J = 4.4 Hz, 4H), 7.48 (t, J = 7.8 Hz, 4H), 7.34 (d, J = 4.2 Hz, 16H), 7.06–7.04 (m, 4H), 6.89 (d, J = 8.3 Hz, 4H), 6.74–6.71 (m, 4H) ppm. $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3 , 298 K, ppm): δ = 129.0, 123.9, 66.0, 15.4, 1.1; MALDI MS m/z : 1075.6656 [M^+].

Synthesis of 2.7. **2.4** (0.200 g, 0.444 mmol) and 0.014 g (0.444 mmol) of elemental sulfur was taken in a 100 mL Schlenk flask and to that 30 mL of DCM was added at room temperature. After stirring the reaction mixture for an additional 24 h, a yellow-colored solution was obtained which was filtered under argon and the solvent was reduced to 15 mL. **2.7** was obtained as a yellow solid. Yield: 0.113 g (53 %). ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): δ = 8.07–8.06 (m, 3H), 7.36 (dd, J = 15.5, 2.0 Hz, 6H), 6.57 (ddd, J = 7.2, 5.0, 0.9 Hz, 3H), 6.49 (dd, J = 14.0, 8.4 Hz, 2H), 6.43–6.41 (m, 2H), 0.28 (s, 36H SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3 , 298 K, ppm): δ = 159.8, 148.4, 137.3, 113.2, 109.6, 1.1; $^{119}\text{Sn}\{^1\text{H}\}$ (149.18 MHz, CDCl_3 , 298 K, ppm): δ = 30.9; MALDI MS m/z : 964.5907 [M^+].

Synthesis of 2.8. To the mixture of 0.035 g (0.444 mmol) of elemental selenium and **2.4** (0.200 g, 0.444 mmol), 25 mL of DCM was added at room temperature and the reaction mixture was stirred for an additional 48 h. The golden yellow-colored solution was then filtered off and reduced to 8 mL. Yellow-colored crystals of **2.8** suitable for X-ray analysis were grown at room temperature. Yield: 0.105 g (45 %), mp: 75 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): δ = 8.07 (d, J = 4.0 Hz, 2H), 7.38 (dd, J = 16.0, 7.6 Hz, 6H), 6.59–6.56 (m, 2H), 6.46–6.41 (m, 6H), 0.28 (s, 36H, SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3 , 298 K, δ) 148.4, 137.3, 113.2, 110.9, 109.6, 1.1; MALDI MS m/z : 1060.4114 [$\text{M} + \text{H}^+$].

Synthesis of 2.9. 1g of **2.1** (5.88 mmol) was taken in a Schlenk flask and to that 40 mL of Et_2O was added. Subsequently, the flask was cooled to –70 °C and $n\text{BuLi}$ (3 mL of 2 M solution) was added to the flask. The reaction mixture was slowly brought to room temperature and stirred for 3 h. The reaction mixture was again cooled to 0 °C and it was transferred to another Schlenk flask containing Et_2O (10 mL) solution of SnCl_2 (1.117 g, 5.88 mmol). The reaction was stirred overnight which afforded a white ppt (LiCl). The solution was filtered and concentrated till some crystalline particles were visible on the surface of the flask. Storage of the concentrated solution of **9** at 0 °C resulted in pale yellow crystals of **2.9**. Yield: 1.50 g (79 %), mp: 80.7 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): δ = 8.21 (s, 1H), 7.88–7.79 (s, 2H), 7.42 (s, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 7.2 Hz, 7H), 6.74 (s, 2H), 6.52 (s, 2H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 298 K, ppm): δ = 144.6, 141.9, 139.9, 129.4, 124.5, 122.9, 112.1, 107.3; $^{119}\text{Sn}\{^1\text{H}\}$ (149.18 MHz, CDCl_3 , 298 K, ppm): δ = -509.2; MALDI MS m/z 647.1318. $[\text{M}^+]$.

Synthesis of 2.10. **2.10** was prepared by following the synthetic method used for **2.9**. **2.2** (1 g, 6.02 mmol), $n\text{BuLi}$ (3 mL of 2 M solution) and SnCl_2 (1.143 g, 6.02 mmol). Yield: 1.5 g (79 %), mp: 125 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): δ = 7.99 (d, J = 5.8, Hz, 2H), 7.70 (t, J = 6.8 Hz, 2H), 7.10 (d, J = 8.3 Hz, 2H), 6.68 (t, J = 6.5 Hz, 2H), 0.33 (s, 18H, SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 298 K, ppm): δ = 162.8, 147.4, 143.7, 141.0, 138.2, 123.5, 117.5, 113.4, 110.5, 66.0, 15.4, 2.0, 1.1; $^{119}\text{Sn}\{^1\text{H}\}$ (149.18 MHz, CDCl_3 , 298 K, ppm): δ = -283.7; MALDI MS m/z : 639.1292 $[\text{M}^+]$.

Synthesis of 2.11. 40 mL of THF was added to the mixture of 0.200 g (0.310 mmol) of **2.9/2.10** and 0.188 g (0.626 mmol) Mes-SeMgBr at room temperature and left for stirring for an additional 12 h. The solvent was then evaporated under a vacuum and the residue was extracted with 40 mL of DCM and filtered off. The bright yellow solution was reduced to 10 mL and to that 5 mL n -pentane was added. Bright yellow crystals of **2.11** suitable for X-ray analysis were obtained at room temperature. Yield: 0.085 g (30 %), mp: 90 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): δ = 6.88 (s, 8H), 2.28 (s, 24H), 2.25 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 298 K, ppm): δ = 144.4, 138.1, 128.5, 66.0, 26.1, 21.1, 15.4; $^{119}\text{Sn}\{^1\text{H}\}$ (149.18 MHz, CDCl_3 , 298 K, ppm): δ = -147.7; MALDI MS m/z 914.1752 $[\text{M}^+]$.

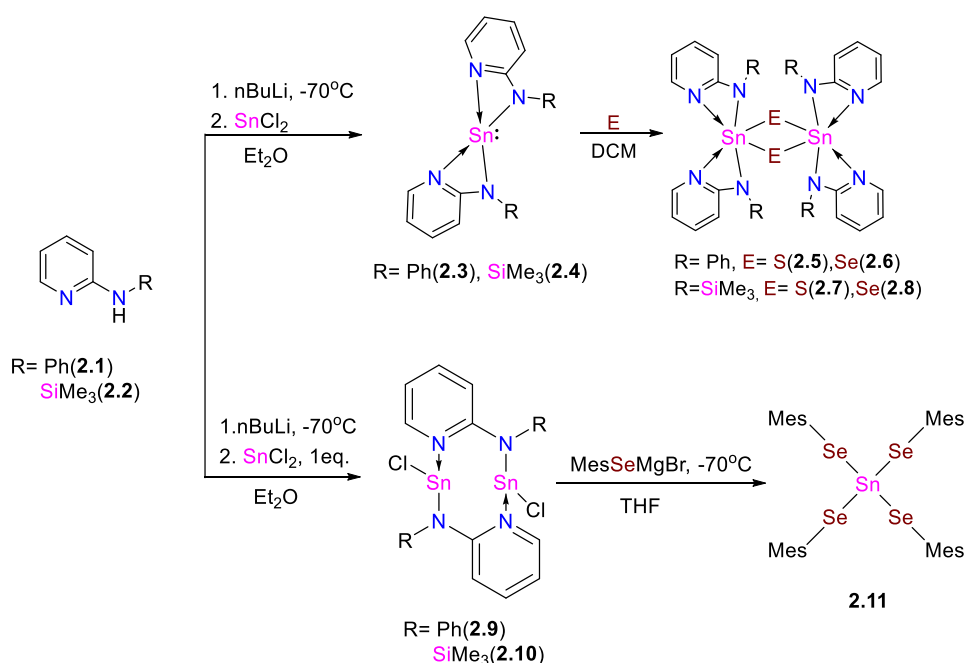
2.2.3. X-ray crystallographic details

Crystallography reflections were collected on a Bruker Smart Apex Duo diffractometer at 150 K using $\text{Mo K}\alpha$ radiation (λ = 0.71073 Å) for **2.3**, **2.4**, **2.5**, **2.6**, **2.8**, **2.9**, **2.10**, **2.11**.²¹ Collected data were integrated by using SAINT and then absorption correction was done by a multi-scan method using SADABS program. The structures were solved by direct method and refined by full-matrix least-squares methods against F^2 (SHELXL-2014/6). Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC.

2.3. Result and Discussion

The lithium salts of both the ligands **2.1** and **2.2** were treated with 0.5 equivalent of SnCl_2 in Et_2O at -70 °C, which afforded $[\text{Sn}\{\text{NPh}(\text{py})_2\}_2]$ (**2.3**) and $[\text{Sn}\{\text{N}(\text{SiMe}_3)\text{py}\}_2]$ (**2.4**) (Scheme 2.1), respectively. When the lithium salts of ligands **2.1** and **2.2** were treated with one equiv. of

SnCl_2 in Et_2O under the same reaction conditions, they afforded the desired bis(chlorostannylene) derivatives, (**2.9** and **2.10**) which are dimeric in nature (vide infra). To the best of our knowledge, there is only one example of such dimeric chlorostannylene $[\text{PhS}(\text{NSiMe}_3)_2(\eta^1\text{-}\eta^1\text{-SnCl})_2[\mu\text{-NSPh}(\text{NHSiMe}_3)]$ reported by Ishii and co-workers.^{14c} The characterization of all these stannylenes has been done by NMR spectroscopy, elemental analysis, and single-crystal X-ray crystallography. The ^{119}Sn NMR resonances for **2.3** appear at $\delta = -262.5$ ppm which falls within the range of $[\text{CyNC}(\text{Me})\text{NCy}]_2\text{Sn}$ (-272.0 ppm) and $[\text{CyNC}(\text{tBu})\text{NCy}]_2\text{Sn}$ (-223.0 ppm)^{11e} and for **2.4** it is at $\delta = -124.1$ ppm which is in the close proximity of the previously reported heteroleptic Sn(II) amido guanidines.^{12f} The molecular structures of **2.3** and **2.4** are determined by single-crystal X-ray studies, which reveal the presence of a four-coordinated Sn atom (Figure 2.1). The small angles of the aminopyridinato four-membered rings (**2.3**: $57.6(2)$ and $58.4(2)^\circ$; **2.4**: $58.24(7)$ and $57.96(7)^\circ$) led to the distortion of the four-membered rings and the Sn atom can be best described as distorted square pyramid considering the lone pair on Sn in **2.3** and **2.4**. The coordination bond between pyridyl nitrogen and the Sn atoms in **2.3** ($2.416(6)$ and $2.368(5)$ Å) and **2.4** ($2.440(2)$ and $2.440(2)$ Å) are significantly longer than the Sn–N covalent single bonds (**2.3**: $2.189(6)$ and $2.190(5)$ Å; **2.4**: $2.186(2)$ and $2.170(2)$ Å) but in both the compounds Sn1–N3 and Sn1–N4 bond lengths are consistent with the previously reported Sn(II) amino guanidines.¹²



Scheme 2.1. Synthesis of homoleptic stannylene complexes, **2.3** and **2.4** and their reactions with S and Se (above). The synthesis of bischlorostannylenes (**2.9** and **2.10**) and the reaction of **2.9** and **2.10** with MesSeMgBr is depicted below

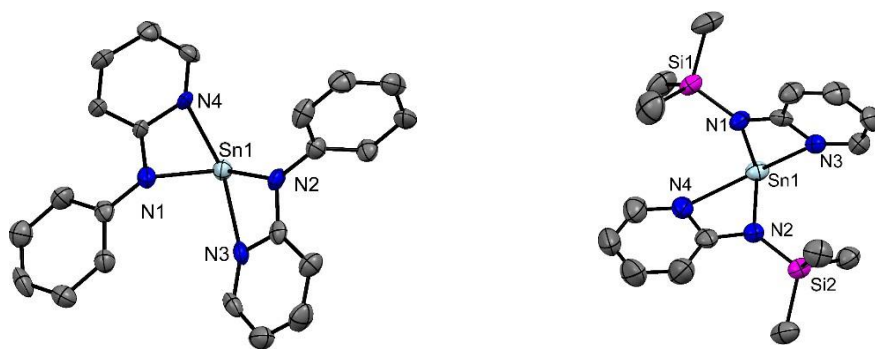


Figure 2.1. Molecular structures of **2.3**(left) and **2.4**(right) with anisotropic displacement parameters are depicted at a 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths(Å) and bond angles (°) for **2.3**: N2–Sn1 2.190(5), N4–Sn1 2.416(6), N1–Sn12.189(6), N3–Sn1 2.368(5); N1–Sn1–N3 85.8(2), N4–Sn1–N285.0(2), N1–Sn1–N4 57.6(2), N3–Sn1–N2 58.4(2); Selected bond lengths(Å) and bond angles (°) for **2.4**: 1–Sn1 2.170(2), N4–Sn1 2.440(2), N3–Sn12.440(2), N2–Sn1 2.186(2); N1–Sn1–N4 84.08(7), N3–Sn1–N283.31(7), N1–Sn1–N3 58.24(7), N4–Sn1–N2 57.96(7)

We further performed the reactions of **2.3** and **2.4** with S and Se, which resulted in the formation of **2.5–2.8**. The ^{119}Sn NMR of **2.5** appears at $\delta = -446.68$ and is much more upfield than those of the previous similar types of Sn_2S_2 bridged dimeric complexes like for $\{\text{Sn}[\text{N}(\text{SiMe}_3)_2](\mu\text{-S})\}_2$ appears at -106.6 ppm^{12c} and $[\{\text{CH}(\text{SiMe}_3)\text{C}_9\text{H}_6\text{N}\}_2\text{Sn}(\mu\text{-S})]_2$ appears at -100.48 ppm.^{12g} This upfield shifting is mainly due to the greater π donation from the Ph group of the ligand backbone. In contrast to the above-mentioned examples, ^{119}Sn NMR of **2.7** is visible at 30.90 ppm which is highly de-shielded than the previously reported Sn-S complexes. All these compounds were characterized by single-crystal X-ray studies (except **2.7**), which disclose the formation of a four-membered ring with bridging chalcogens (Figure 2.2). Two tin atoms are arranged opposite to each other in the Sn_2E_2 (E = S and Se) four-membered ring. The structural parameters of compounds of **2.5**, **2.6** and **2.8** are similar and the slight differences in the bond lengths and bond angles are mainly due to different chalcogens. The coordination geometry around the Sn centers in all the compounds is a distorted octahedral.

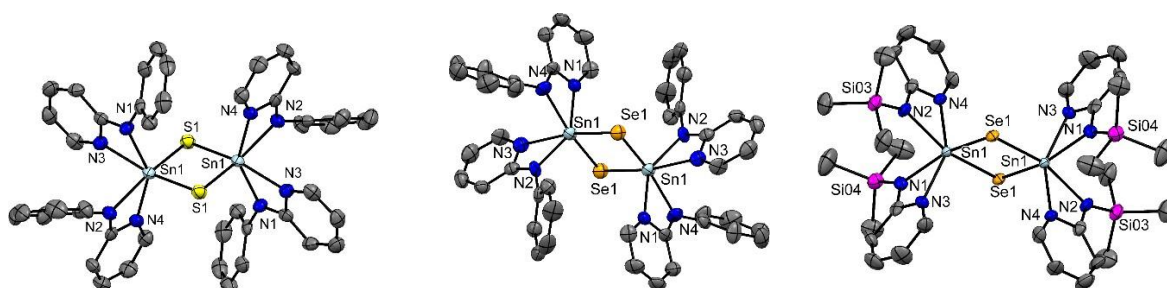


Figure 2.2. Molecular structures of **2.5**(left), **2.6**(middle) and **2.8**(right) with anisotropic displacement parameters are depicted at a 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths(Å) and bond angles (°) for **2.5**: Sn1–S1 2.4515(9), Sn1–S1 2.4111(8), N4–Sn1 2.247(3), N2–Sn1 2.194(3), N3–Sn1 2.291(3), N1–Sn1 2.145(3); Sn1–S1–Sn1 86.58(3), S1–Sn1–S1 93.42(3), N2–Sn1–N4 59.7(1), N3–Sn1–N1 59.9(1); Selected bond lengths(Å) and bond angles (°) for **2.6**: Sn1–Se1 2.529(1); Sn1–Se1 2.575(1); N4–Sn1 2.187(7); N1–Sn1 2.249(7); N3–Sn1 2.291(6); N2–Sn1 2.144(7); Sn1–Se1–Sn1 84.68(3), Se1–Sn1–Se1 95.32(3), N1–Sn1–N4 59.3(2), N2–Sn1–N3 59.8(2). Selected bond lengths(Å) and bond angles (°) for **2.8**: Sn1–Se1 2.561(1), N1–Sn1 2.215(3), N2–Sn1 2.209(3), N4–Sn1 2.215(3), N3–Sn1 2.229(3), Sn1–Sn1 3.517(1), Se1–Sn1 2.568(1); Sn1–Se1–Sn1 86.59(2), Se1–Sn1–Se1 93.41(2), N4–Sn1–N2 60.8(1), N1–Sn1–N3 60.5(1), N2–Sn1–N1 88.3(1).

The Sn–S bond lengths in **2.5** (2.4515(9) and 2.4111(8) Å) are significantly longer than Parkin's terminal tin sulfido complexes [η^4 -Me₈taa]Sn=S (2.274(3) Å) (Me₈taa = octamethyldibenzo-tetraaza[14]annulene),¹⁶ but match well with the Sn–S distance in [(Tbt)(Mes)Sn(μ -S)]₂ (2.44 Å) (Tbt = 2,4,6-tris[bis(trimethyl-silyl)methyl]phenyl).¹⁷ The Sn–Se bond lengths in **2.6** (2.529(1) and 2.575(1) Å) and **2.8** [2.561(1) and 2.568(1) Å] are in well agreement with a Sn–Se single bond length (2.55–2.60 Å),¹⁸ but longer than that in tbt(Ditip)Sn=Se (2.373(3) Å) (Ditip= 2,2''-diisopropyl-m-terphenyl-2'-yl).^{11a}

Further, the treatment of lithium salt of both the ligands **2.1** and **2.2** with 1 equivalent of SnCl₂ led to the formation of bis(chlorostannylenes), **2.9** and **2.10**, respectively (Scheme 2.1). The Sn atoms in **2.9** and **2.10** are three-coordinated, adopting a distorted trigonal pyramidal geometry with a lone pair of electrons on their apexes (Figure 2.3). We assume that the dimerization takes place due to the instability of the mono-chlorostannylenes ([Sn{N(R)py}Cl]). In the ¹¹⁹Sn NMR, **2.9** exhibits a peak at δ = –509.3 ppm, while **2.10** shows a peak at δ = –283.8 ppm. Their molecular structures are shown in Figure 2.3. The Sn–Cl bond lengths in **2.9** (2.504(3) and 2.529(2) Å) and **2.10** (2.521(3) Å) are matching well with the values reported for [PhS(NSiMe₃)₂(η^1 - η^1 -SnCl)₂][μ -NSPh(NHSiMe₃)] (Sn–Cl(2.5083(9) Å and 2.5126(8) Å)^{14c} and commensurable with that in another three coordinated stannylene, PhC(NtBu)₂SnCl (2.4831(9) Å).¹⁹

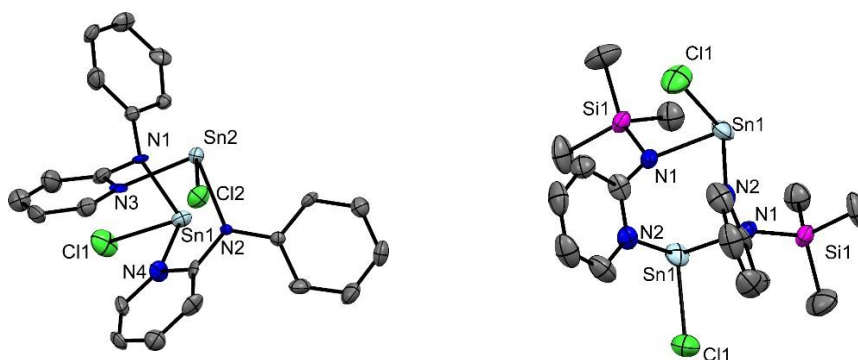


Figure 2.3. Molecular structures of **2.9**(left) and **2.10**(right) with anisotropic displacement parameters are depicted at a 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths(Å) and bond angles (°) for **2.9**: Sn2 2.277(8), Sn1–N1 2.213(7), Sn1–Cl12.504(3), Sn2–N3 2.249(9), Sn1–N4 2.229(9), Sn2–Cl2 2.529(2), Sn1–Cl12.504(3); N2–Sn2–N3 87.8(3), Cl2–Sn2–N2 86.7(2), N3–Sn2–Cl2 86.2(2), N4–Sn1–N1 87.8(3), N1–Sn1–Cl1 91.3(2), N4–Sn1–Cl1 89.1(2); Selected bond lengths(Å) and bond angles (°) for **2.10**: Sn1–Cl1 2.521(3), N2–Sn1 2.233(6), N1–Sn1 2.217(6); N1–Sn1–Cl1 91.7(2), N2–Sn1–Cl1 88.5(2), N2–Sn1–N1 91.0(2).

In order to functionalize the chloride atom with mesityl selenium moiety, we reacted **2.9** and **2.10** with MesSeMgBr at low temperatures. However, instead of a metathesis reaction, oxidation of the Sn center takes place leading to mesityltetraseleno tin(IV)derivative, **2.11** in both cases. This is important to mention here that this product has been isolated regardless of the ratio of the reaction partners. The molecular structure of **2.11** has been depicted in Figure 2.4. The Sn atom assumes a distorted tetrahedral geometry with four SeMes occupying the four vertices of the tetrahedron. The Sn–Se bond lengths vary between 2.522(2) to 2.545(3) Å, which are in good agreement with those reported in Dehnen’s bis[tris(arylselenolato)tin] compounds (2.5248(10)–2.5493(8) Å).²⁰ The ⁷⁷Se NMR displays a resonance at $\delta = 88.14$ ppm, while the ¹¹⁹Sn NMR shows a signal at $\delta = -147.73$ ppm.

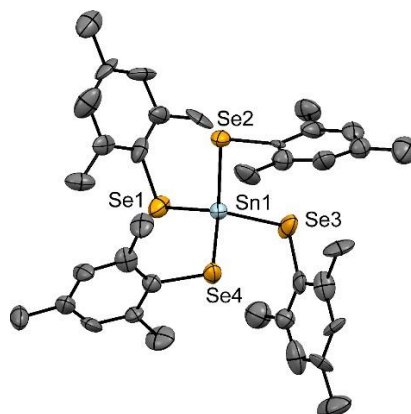


Figure 2.4. Molecular structures of **2.11** with anisotropic displacement parameters are depicted at a 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths(Å) and bond angles (°) for **2.11**: Se4–Sn1 2.522(2), Se1–Sn1 2.523(2), Se3–Sn1 2.545(3), Se2–Sn1 2.535(2); Se1–Sn1–Se4 113.92(8), Se2–Sn1–Se3 111.17(8), Se4–Sn1–Se3 102.75(7), Se1–Sn1–Se2 106.02(7).

2.4. Conclusion

In summary, we have prepared two four-coordinated stannylenes (**2.3** and **2.4**) and two bis(chlorostannylenes) (**2.9** and **2.10**). The difference in the formation of two different types of stannylenes can be attributed to the stoichiometry of SnCl_2 . The reactions of **2.3** and **2.4** with sulfur and selenium have been performed which led to the formation of compounds with four-membered Sn_2E_2 (E = S and Se) cycle (**2.5–2.8**). The reaction of **2.9** and **2.10** with MesSeMgBr resulted in the oxidation of the Sn(II) center and the formation of a mesityltetraseleno tin(IV) derivative, **2.11**. The formation of **2.3–2.6** and **2.8–2.11** was unequivocally established by single-crystal X-ray diffraction studies.

2.5. References

1. Fard, Z. H.; Müller, C.; Harmening, T.; Pöttgen, R.; Dehnen, S. *Angew. Chem.Int. Ed.* **2009**, *48*, 4441–4444; *Angew. Chem. Int. Ed.* **2009**, *121*, 4507–4511
2. Fard, Z. H.; Xiong, L.; Müller, C.; Holynska, M.; Dehnen, S. *Chem. Eur. J.* **2009**, *15*, 6595–6604.
3. Halvagar, M. R.; Fard, Z. H.; Xiong, L.; Dehnen, S. *Inorg. Chem.* **2009**, *48*, 7373–7377.
4. Puls, A.; Näther, C.; Bensch, W. *Acta Crystallogr., Sect. E* **2005**, *61*, m868–m870.
5. Parise, J. B.; Rijssenbeek, Y. Ko, J.; Nellis, D. M.; Tan, K.; Koch, S. *J. Chem.Soc., Chem. Commun.* **1994**, 527–528.
6. Behrens, M.; Näther, C.; Bensch, W.; *Z. Anorg. Allg. Chem.* **2002**, *628*, 2160.
7. Näther, C.; Scherb, S.; Bensch, W. *Acta Crystallogr., Sect. E* **2003**, *59*, m280–m282.
8. Jiang, T.; Lough, A.; Ozin, G. A. *Adv. Mater.* **1998**, *10*, 42–46.
9. a) Jiang, T.; Lough, A.; Ozin, G. A.; Bedard, R. L.; Broach, R. *J. Mater. Chem.* **1998**, *8*, 721–732; b) Dehnen, S.; Zimmermann, C. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2436–2439.
10. Parvin, N.; Pal, S. Khan, S.; Das, S.; Pati, S. K.; Roesky, H. W. *Inorg. Chem.* **2017**, *56*, 1706–1712.
11. a) Saito, M.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **2004**, *126*, 15572–15582; b) Saito, M.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 11124–11125; c) Chivers, T.; Eisler, D. J. *Angew. Chem. Int. Ed.* **2004**, *43*, 6686–6689; *Angew. Chem. Int.*

- Ed.* **2004**, 116, 6854–6857; d) Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Severn, J. R. *Dalton Trans.* **2004**, 4193–4201; e) Zhou, Y.; Richeson, D. S. *J. Am. Chem. Soc.* **1996**, 118, 10850–10852.
12. a) Mansell, S. M.; Russell, C. A.; Wass, D. F. *Dalton Trans.* **2015**, 44, 9756–9765; b) Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J. M.; Protchenko, A. V.; Uiterweerd, P. G. H. *Dalton Trans.* **2009**, 4578–4585; c) Hitchcock, P. B.; Jang, E.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1995**, 3179–3187; d) R. Guillard, R.; Ratti, C.; Barbe, J. M.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1991**, 30, 1537–1542; e) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **1999**, 18, 4700–4705; f) Ahmet, I. Y.; Hill, M. S.; Raithby, P. R.; Johnson, A. L. *Dalton Trans.* **2018**, 47, 5031–5048; g) Leung, W. P.; Kwok, W. H.; Zhou, Z. Y.; Mak, T. C. W. *Organometallics* **2000**, 19, 296–303; h) Kocsor, T. G.; Matioszek, D.; Nemes, G.; Castel, A.; Escudie, J.; Petrar, P. M.; Saffon, N.; Haiduc, I. *Inorg. Chem.* **2012**, 51, 7782–7787
13. a) Ortu, F.; Moxey, G. J.; Blake, A. J.; Lewis, W.; Kays, D. L. *Inorg. Chem.* **2013**, 52, 12429–12439; b) Noor, A.; Kretschmer, W. P.; Glatz, G.; Kempe, R. *Inorg. Chem.* **2011**, 50, 4598–4606; c) Noor, A.; Kretschmer, W. P.; Kempe, R. *Eur. J. Inorg. Chem.* **2006**, 2683–2689. For review articles on aminopyridinatoligands, see d) Kempe, R.; Noss, H.; Irrgang, T. *J. Organomet. Chem.* **2002**, 647, 12–20; e) Kempe, R. *Eur. J. Inorg. Chem.* **2003**, 2003, 791–803.
14. a) Du, L.; Chu, W. Xu, C.; Miao, H.; Ding, Y. *RSC Adv.* **2015**, 5, 59991–59996; b) Du, L.; Wang, H.; Ding, Y. *Polyhedron* **2017**, 134, 282–286; c) Nakata, N.; Hosoda, N.; Takahashi, S.; Ishii, A. *Dalton Trans.* **2018**, 47, 481–490; d) Wagner, C.; Merzweiler, K. *Z. Anorg. Allg. Chem.* **2017**, 643, 938–944; e) Xu, H.; Chao, Z.; Sang, Y.; Hou, H.; Fan, Y. *Inorg. Chem. Commun.* **2008**, 11, 1436–1440; f) Gallego, D.; Inoue, S.; Blom, B.; Driess, M. *Organometallics* **2014**, 33, 6885–6897; g) Wey, Y. T.; Yang, F. S.; Yu, H. C.; Kuo, T. S.; Tsai, Y. C. *Angew. Chem. Int. Ed.* **2017**, 56, 15108–15112; *Angew. Chem. Int. Ed.* **2017**, 129, 15304–15308; h) Jones, C.; Junk, P. C.; Leary, S. G.; Smithies, N. A.; Steed, J. W. *Inorg. Chem. Commun.* **2002**, 5, 533–536.
15. a) Mishra, N. K.; Choi, M.; Jo, H.; Oh, Y.; Sharma, S.; Han, S. H.; Jeong, T.; Han, S.; Lee, S. Y.; Kim, I. S. *Chem. Commun.* **2015**, 51, 17229–17232; b) Liddle, S. T.; Clegg, W. J. *Chem. Soc., Dalton Trans.* **2001**, 402–408.
16. Kuchta, M. C.; Parkin, G. *J. Am. Chem. Soc.* **1994**, 116, 8372–8373.
17. Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M. *Organometallics* **1993**, 12, 2573–2583.

-
-
18. The average length of a Sn–Se single bond in X–Sn–Se–X systems (428 examples) is 2.579 Å (Cambridge Structural Database).
 19. Sen, S. S.; Kritzler-Kosch, M. P.; Nagendran, S.; Roesky, H. W.; Beck, T.; Pal, A.; Herbst-Irmer, R. *Eur. J. Inorg. Chem.* **2010**, 5304–5311.
 20. Nayek, H. P.; Niedermeyer, H.; Dehnen, S. Z. *Anorg. Allg. Chem.* **2008**, 634, 2805–2810.
 21. a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, 26, 615–619; b) Stalke, D. *Chem. Soc. Rev.* **1998**, 27, 171–178; c) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, 64, 112–122; d) Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Graf, J.; Michaelsen, C.; Ruf, M.; Sheldrick, G. M.; Stalke, D. *J. Appl. Crystallogr.* **2009**, 42, 885–891; e) Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *J. Appl. Crystallogr.* **2015**, 48, 3–10.

Chapter 3

Reactivity of $(\text{TMS})_2\text{N}(\eta^1\text{-Cp}^*)\text{Si}=\text{Si}(\eta^1\text{-Cp}^*)\text{N}(\text{TMS})_2$ toward the Halides of Groups 13-15

3.1. Introduction

Silicon analogues of carbene were not experimentally realized until 1986, when Jutzi and co-workers reported the synthesis of the first stable decamethylsilicocene (Cp^*_2Si).¹ Since then, a huge variety of silylenes have been documented and explored for their application in small molecule activation, and several other bond activation reactions.^{2–14} It is well evident from the literature that the Si(II) atom of N-heterocyclic silylenes can easily insert into the E–X bonds (E = C, B, Si, etc.; X = H, halide, N, etc.) due to their high nucleophilicity.^{15–23} The resultant products are mainly derived from oxidative addition, auto-ionization, and sometimes insertion into the Si–N bonds, followed by rearrangements.^{20,21} Among the reported Si(II) compounds, there is an interesting class of disilenes, which can exist in equilibrium with their singlet silylene fragments (Chart 3.1).^{24–29} Disilenes are generally synthesized through dimerization of their corresponding silylenes, and in most cases, they do not revert to their respective silylenes because of their thermal stability. In this regard, a notable contribution was made by Jutzi et al., where a disilene $\text{E}[(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si}=\text{Si}(\eta^1\text{-Me}_5\text{C}_5)\text{N}(\text{TMS})_2]$ (**3.1**) was found to be in equilibrium with its corresponding silylene $[(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si}]$.³⁰ It was demonstrated that **3.1** exists as a yellow-colored crystalline solid, whereas in solution, it dissociates to the silylene, $[(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{-Si}]$. Such an equilibrium will entice further reactivity, but the synthetic constraints associated with **3.1** hampered the progress. **3.1** was later reproduced by Roesky and co-workers in 68% yield by utilizing $(\text{Me}_5\text{C}_5)\text{SiHCl}_2$ precursor with $\text{KN}(\text{TMS})_2$ in a single-step procedure.³¹ This modified procedure of **3.1** boosted further exploration of its reactivity and led to the isolation of Si_2O_2 and Si_2S_2 ring compounds along with P_4 and As_4 activation.^{32–34} Nonetheless, the reactivity of **3.1** is only limited to this handful of examples (Chart 3.2), but they are different than the usual disilenes.

Motivated by the unique reaction behavior of **3.1**, we planned to study it further for its properties. We chose to explore the reaction of **3.1** with the halides of the main group, especially groups 13–15, in the quest to form compounds with Si–E bonds (E = B, Al, Ge, Sn, P, Sb, etc.). These halides have never been studied systematically with any such unique Si(II) system (Chart 3.1). Interestingly, there is only one report on Cp^* substituted silicon(II) compound (Cp^*_2Si), where it reacts with group-13 element halides, demonstrating several important reactions such as insertion, rearrangement, and elimination reactions.³⁵ However, there is no reactivity study of any disilene with different p-block halides. In this work, we have explored the reactivity

behaviour of **3.1** with different halides of group 13–15 elements, which led to the formation of unique products. Our results are reported herein.

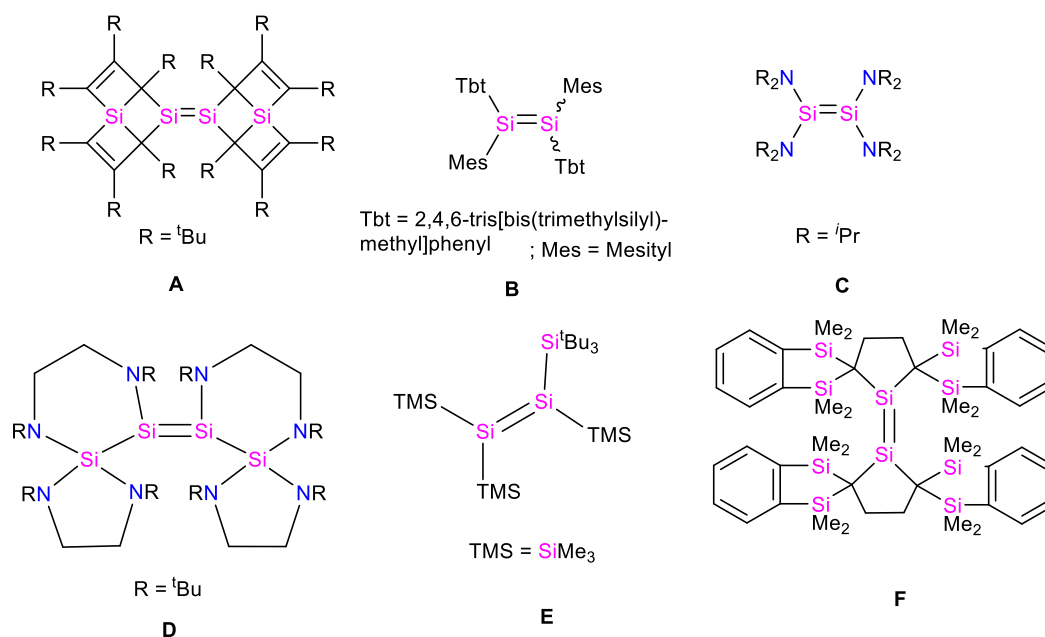


Chart 3.1. Reported examples of disilenes, which exist in equilibrium with the corresponding silylene.

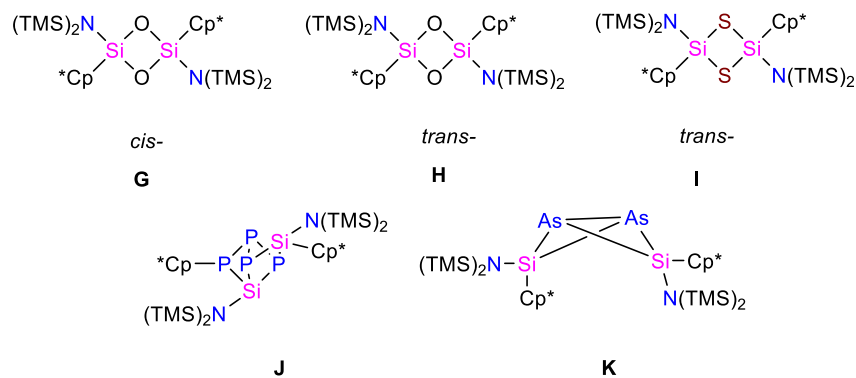


Chart 3.2. Reported reaction products **3.1** generated from the reactions of oxygen, sulfur, phosphorus and arsenic.

3.2. Experimental Section

3.2.1. General remarks

The whole process was executed under an inert atmosphere of argon using standard Schlenk techniques or in a glovebox. Solvents used were purified using an MBRAUN solvent purification system MBSPS800. BCl_3 , BCy_2Cl , AlCl_3 , AlBr_3 , GeCl_2 , SnCl_2 , and PPh_2Cl were purchased from Sigma-Aldrich and Alfa Aesar. They were used without further purification. ^1H , ^{13}C , ^{29}Si , ^{11}B , ^{31}P , and ^{119}Sn NMR spectra were recorded on a Bruker spectrometer in CDCl_3 as the solvent with an external standard (SiMe_4 for ^1H , ^{13}C , ^{29}Si ; $\text{BF}_3 \cdot \text{Et}_2\text{O}$ for ^{11}B ; 85% H_3PO_4 for ^{31}P ; and Me_4Sn for ^{119}Sn). Mass spectra were recorded using an AB Sciex, 4800 MALDI TOF/TOF, and HRMS was recorded on a Waters Synapt, USA. Yields are calculated based on the isolated crystals.

Synthesis of 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 3.10

Synthesis of 3.2. Toluene (30 mL) was added to the mixture of **3.1** (0.200 g, 0.31 mmol) and BCl_3 (0.62 mL of 1 M solution) in a 100 mL Schlenk flask, and after stirring the reaction mixture for 10–15 min, the bright yellow color of the solution became pale. The reaction mixture was stirred overnight at room temperature. The colorless solution was evaporated under reduced pressure to 10 mL and kept at 0 °C. Storage of the concentrated solution at 0 °C afforded the colorless crystals of **3.2**. Yield: 60% (0.122 g). Mp: 228 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 0.31 (s, 18H, TMS) ppm, 2.30 (s, 15H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.613 MHz, CDCl_3 , 298 K): δ 5.7, 9.7, 114.4 ppm. ^{11}B (128.387 MHz, CDCl_3 , 298 K): δ 3.0 and –54.1 ppm. $^{29}\text{Si}\{^1\text{H}\}$ (79.495 MHz, CDCl_3 , 298 K) δ 9.0 (SiMe_3) ppm. HRMS: Calcd for ($\text{C}_{16}\text{H}_{33}\text{N}_2\text{Si}_4\text{B}_2\text{Cl}_8$): m/z 667.9619. Found m/z 668.8983 [$\text{M} + \text{H}$] $^+$.

Synthesis of 3.3. To the solution of **3.1** (0.323 g, 0.5 mmol) in 30 mL of toluene was added Cy_2BCl (1 mL of 1 M solution) in a 100 mL Schlenk flask, and the solution became colorless after 30 min. The reaction mixture was stirred overnight at room temperature. The solution was filtered and concentrated until it afforded some crystalline particles on the surface of the flask. The concentrated solution was kept at 0 °C, which resulted in colorless crystals of **3.3**. Yield: 23% (0.120 g). Mp: 89.5 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 0.21 (s, 18H, TMS) ppm, 1.29 (br, 15H, CH_3), 1.80 (br, 22H, C_6H_{11}). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.613 MHz, CDCl_3 , 298 K): δ 6.1 (SiMe_3), 11.5 (SiMe_3), 13.0 (Me_5C_5), 16.3 (Me_5C_5), 26.7 (C_6H_{12}), 27.1 (C_6H_{12}), 27.2 (C_6H_{12}), 27.8 (C_6H_{12}), 27.8 (C_6H_{12}), 28.1 (C_6H_{12}), 137.0 (Me_5C_5), 138.8 (Me_5C_5) ppm. ^{11}B (128.387 MHz, CDCl_3 , 298 K): δ 76.2 ppm. $^{29}\text{Si}\{^1\text{H}\}$ (79.495 MHz, CDCl_3 , 298 K):

δ 7.1 (s, -SiMe₃), -5.8 (s, -SiClBCy₂Cp*) ppm. HRMS: Calcd for [C₂₈H₅₅NSi₃BCl]: m/z 535.3424. Found m/z 574.2534 ([M + K]⁺).

Synthesis of 3.4. 30 mL of toluene was added to the mixture of **3.1** (0.323 g, 0.5 mmol) and AlCl₃ (0.133 g, 1 mmol) in a 100 mL Schlenk flask, and the solution was stirred overnight at room temperature. The colorless solution was filtered and reduced under vacuum to 10 mL. Storage of the concentrated solution at 0 °C afforded colorless crystals of **3.4**. Yield: 35% (0.159 g). Mp: 230 °C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 0.34 (s, 18H, TMS), 2.11 (s, 15H, CH₃) ppm. ¹³C{¹H} NMR (100.613 MHz, CDCl₃, 298 K): δ 4.4, 12.6, 130.4 ppm. ²⁹Si{¹H} (79.495 MHz, CDCl₃, 298 K): δ 4.2 (SiMe₃), -12.6 (SiN(SiMe₃)₂) ppm. MALDI: Calcd for [C₁₆H₃₃NSi₃AlCl₃]: m/z 455.0802. Found: m/z 455.2372 [M]⁺.

Synthesis of 3.5. Toluene (30 mL) was added to a mixture of **3.1** (0.323 g, 0.5 mmol) and AlBr₃ (0.266 g, 1 mmol) in a 100 mL Schlenk flask, and after some time, a brown-colored oily precipitate was formed. The reaction mixture was stirred overnight at room temperature, and then the toluene was evaporated under a vacuum. Subsequently, the reaction residue was extracted with DCM (30 mL). The solution was filtered and reduced to 5 mL, and to this, 5 mL of pentane was added. Colorless crystals of **3.5** were grown at 0 °C. Yield: 34% (0.190 g). Mp: 145.5 °C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 0.37 (s, 18H, TMS), 2.12 (s, 15H, CH₃) ppm. ¹³C NMR (100.613 MHz, CDCl₃, 298 K): δ 4.5, 13.2 ppm. ²⁹Si{¹H} (149.18 MHz, CDCl₃, 298 K): δ 4.3 (SiMe₃), -17.8 (SiN(SiMe₃)₂) ppm. MALDI: Calcd for [C₁₆H₃₃NSi₃AlBr₃]: m/z 586.9286. Found: m/z 611.3051 ([M + Na + H₂]⁺).

Synthesis of 3.6. Toluene (30 mL) was added to a mixture of **3.1** (0.200 g, 0.31 mmol) and GeCl₂·dioxane (0.090 g, 0.62 mmol) in a 100 mL Schlenk flask, and the solution became golden yellow immediately. The reaction mixture was further stirred for 30 min at room temperature and then filtered and reduced to 5 mL. The storage of the solution at 0 °C afforded colorless crystals of **3.6**. Yield: 55% (0.144 g). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 0.39 (s, 54H, TMS), 4.59 (s, 1H, GeH) ppm. ¹³C{¹H} NMR (100.613 MHz, CDCl₃, 298 K): δ 5.7 ppm. ²⁹Si{¹H} (79.495 MHz, CDCl₃, 298 K): δ 7.4 (-SiMe₃), 7.6 (-SiCl₂) ppm. HRMS: Calcd for [C₁₈H₅₅N₃Si₉Cl₆Ge]: m/z 848.9662. Found: m/z 847.4979 [M]⁺.

Synthesis of 3.7. Upon adding 30 mL of toluene to a mixture of **3.1** (0.200 g, 0.31 mmol) and SnCl₂ (0.117 g, 0.62 mmol) in a 100 mL Schlenk flask, the color of the solution immediately changed to green. The reaction mixture was stirred at room temperature for an additional 30 min. The solution was then filtered and concentrated to 5 mL. Storage of the solution at 0 °C

yielded the colorless crystals of **3.7**. Yield: 64% (0.057 g). ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 2.15 (s, 15H, CH_3) ppm. ^{13}C NMR (100.613 MHz, CDCl_3 , 298 K): δ 1.1, 5.6, 9.9 (s, Me_5C_5) and 119.9 (s, Me_5C_5) ppm. $^{119}\text{Sn}\{^1\text{H}\}$ (149.18 MHz CDCl_3 , 298 K): δ 86.1 ppm. HRMS: Calcd for $[\text{C}_{10}\text{H}_{15}\text{SnCl}]$: m/z 289.9884. Found: 289.1483 $[\text{M}]^+$.

Synthesis of 3.8. Toluene (30 mL) was added to the reaction mixture of **3.1** (0.323 g, 0.5 mmol) and AlCl_3 (0.133 g, 1 mmol) in a 100 mL Schlenk flask, and the color of the solution became pale yellow after 1 h. Subsequently, $\text{GeCl}_2 \cdot \text{dioxane}$ (0.232 g, 1 mmol) was added to the reaction mixture, changing the color from pale yellow to orange after 30 min. It was stirred overnight at room temperature, and then the volatiles were removed under vacuum, followed by the addition of DCM (30 mL) to the reaction mixture. The solution was filtered off and concentrated to 5 mL, and to this, 5 mL of pentane was added. Colorless crystals of **3.8** were obtained after 1 day at room temperature. Yield: 50% (0.102 g). Mp: 110 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 2.19 (s, 15H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.613 MHz, CDCl_3 , 298 K): δ 9.5, 122.0 ppm. MALDI: Calcd for $[(\text{C}_{10}\text{H}_{15}\text{Ge})^+ (\text{AlCl}_4)]$: m/z 375.8955. Found: m/z 377.2650 $[\text{M} + \text{H}_2]^+$.

Synthesis of 3.9. **3.1** (0.200 g, 0.31 mmol) and Ph_2PCl (0.0136 g, 0.110 mL, 0.62 mmol) were taken in a 100 mL Schlenk flask, and 30 mL of toluene was added to it at room temperature. The reaction mixture was stirred overnight at room temperature. Then the solution was filtered and concentrated until some crystalline particles were observed on the surface of the flask. The concentrated solution was kept at 0 °C, which yielded colorless crystals of **3.9**. Yield: 36% (0.117 g). Mp: 130–135 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 0.36 (s, 18H, TMS), 1.96–1.86 (m, 15H, CH_3), 7.85–7.77 (m, 10H, Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.613 MHz, CDCl_3 , 298 K): δ 6.8 (SiMe_3), 6.9 (SiMe_3), 7.4 (SiMe_3), 11.7 (C), 12.6 (C_5Me_5), 14.4 (C_5Me_5), 16.4 (C_5Me_5), 127.3 (C_5Me_5), 127.4 (C_5Me_5), 128.4 (C_5Me_5), 128.5 (C_5Me_5), 128.5 (C_5Me_5), 128.8 (Ph), 137.2 (Ph), 137.5 (Ph), 137.7 (Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ (161.976 MHz, CDCl_3 , 298 K): δ -55.6 ppm. $^{29}\text{Si}\{^1\text{H}\}$ (79.495 MHz, CDCl_3 , 298 K): δ 4.3 (SiMe_3), 6.3 (SiMe_3), and 7.1–7.1 (d, J = 3.2 Hz, SiPPH_2) ppm. HRMS: Calcd for $(\text{C}_{28}\text{H}_{43}\text{PClInSi}_3)$: m/z 543.2129. Found: m/z 543.1151 $[\text{M}]^+$.

Synthesis of 3.10. **3.1** (0.200 g, 0.31 mmol) and PCl_3 (0.042 g, 0.054 mL, 0.62 mmol) were taken in a 100 mL Schlenk flask, and 30 mL of toluene was added to it at room temperature. The mixture was kept on stirring overnight. Then the solution was filtered and concentrated to 5 mL. The concentrated solution was kept at 0 °C, which yielded colorless crystals of **3.10**. Yield: 45% (0.100 g). ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 0.32 (18H, TMS), 1.84 (15H,

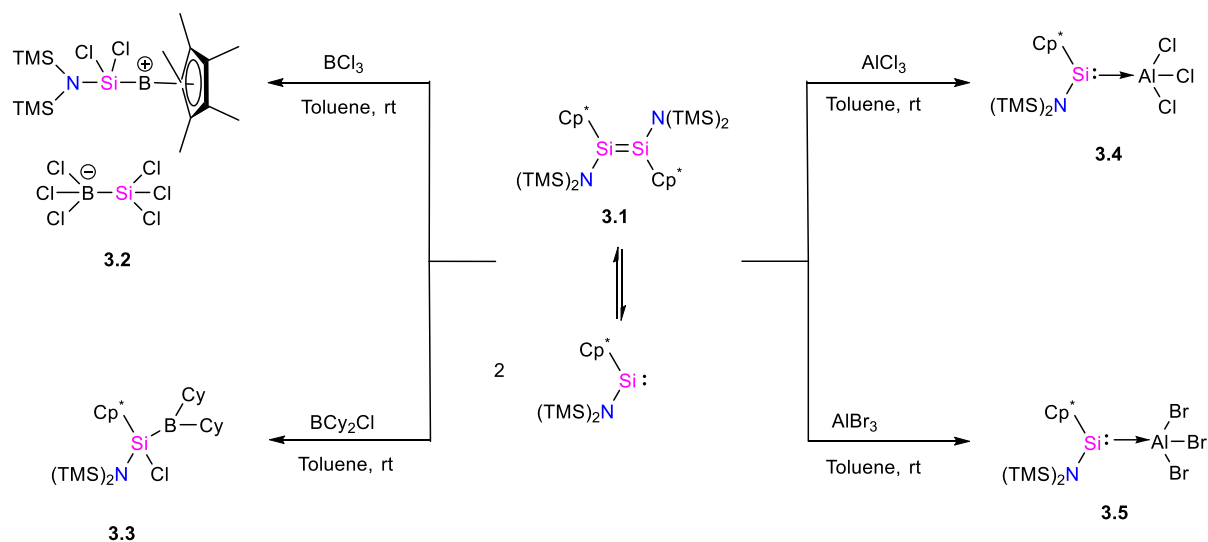
CH₃) ppm. ¹³C{¹H} NMR (100.613 MHz, CDCl₃, 298 K): δ 1.2, 3.7, 5.0, 5.5, 5.6, 5.7, 6.3 ppm. ²⁹Si{¹H} (79.495 MHz, CDCl₃, 298 K): δ 1.9, 3.4, 5.1, 7.2, 7.5, 14.6 ppm. HRMS: Calcd for (C₃₂H₆₆Cl₂N₂Si₆): *m/z* 716.3219. Found: *m/z* 717.5989 [M + H]⁺.

3.3. Result and discussion

Our investigation is based on the reactivity of **3.1** toward different halides of group 13–15 elements, which include BCl₃, BCy₂Cl, AlX₃ (X = Cl, Br), GeCl₂(dioxane), SnCl₂, and PPh₂Cl. The reactions proceeded smoothly in all the cases under mild conditions and resulted in various products via adduct formation, oxidative addition, or rearrangement.

3.3.1. Reaction with Halides of Group 13 Elements.

After the first report of a silylene-borane adduct, followed by the Si insertion into the B–C bond by Metzler and Denk,³⁶ a stock of compounds with the Si–B bonds have been isolated by utilizing different boron sources.^{15,16,37–43} It is noteworthy to mention that access to silylboranes via the reaction of silylene with borane precursors is very much desired, which otherwise involves a tedious synthetic approach.^{17–19} However, the reported reactions mainly utilized either RBX₂ or R₃B type of precursors.^{15–17,20,21,42} There are very few reports where BX₃ or R₂BX (X = F, Cl, Br) boron substrates are reacted with the Si(II) compounds,^{17–21,35,38} and only one report on disilene reaction with haloboranes (B-chlorocatecholborane and B-chloropinacolborane) reported by Tokitoh and co-workers.³⁸ Recently, few reports appeared on the oxidative addition of the Lewis acidic boron halides to the Si(II) center of NHSi and amidinato bis-silylene, resulting in the ring expansion via the insertion of boron atom into the Si(II)–N bond.^{20,21,44} Therefore, we planned to explore the reactivity of **3.1** toward some other boron halides. Treatment of **3.1** with 2 equiv of BCl₃ in toluene at room temperature led to the formation of **3.2** as a major product (Scheme 3.1) with some unidentified products in a small amount. The ¹H NMR spectrum of **3.2** displays a sharp singlet at δ 0.31 ppm, which corresponds to 18 TMS protons, while another singlet at δ 2.30 ppm corresponds to 15 Cp* methyl protons.³¹ The ¹¹B NMR spectrum of **3.2** reveals two resonances at δ 3.03 ppm and δ –54.16 ppm, which are in good agreement with those in [(Me₅C₅)SiCl₂B(Me₅C₅)] [Me₅C₅BCl₃] (δ 6.1 and –54.6 ppm).³⁵ In the ²⁹Si NMR spectrum, a sharp singlet peak at 9.08 ppm was observed.



Scheme 3.1. Reactivity of **3.1** with the halides of group 13 elements.

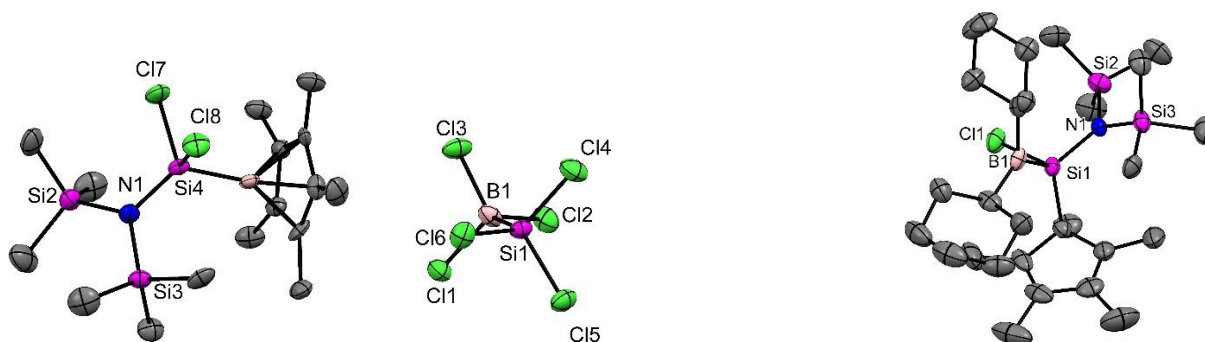
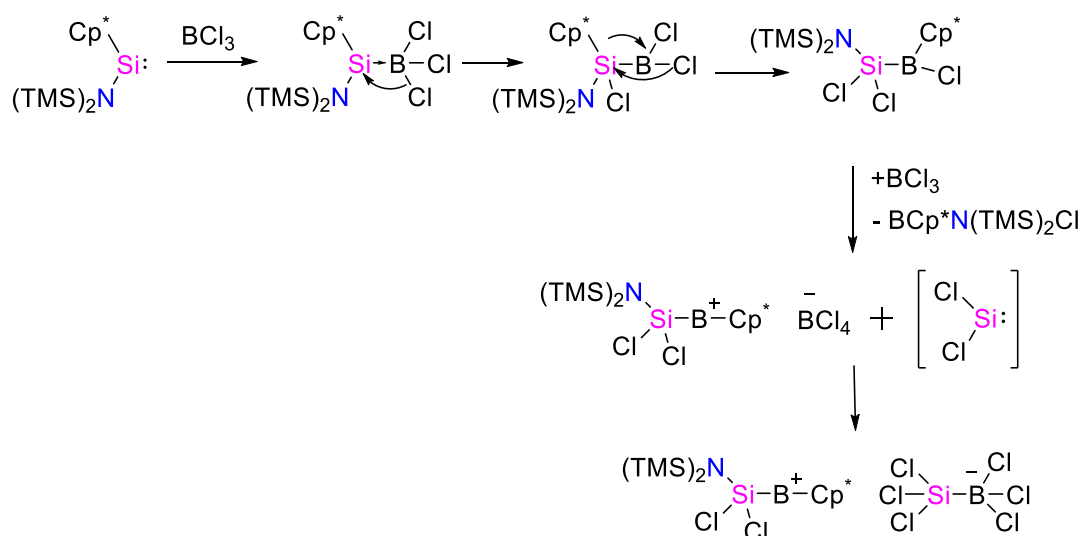


Figure 3.1. Molecular structures of **3.2**(left) and **3.3**(right) with anisotropic displacement parameters are depicted at a 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths(Å) and bond angles (°) for **3.2**: Cl7–Si4 2.065(2), Cl8–Si4 2.051(2), Si4–N1 1.690(4), Si4–B2 1.991(6), C2–B2 1.741(8), C1–B2 1.748(7), C5–B2 1.736(8), C4–B2 1.773(8), C3–B2 1.754(7), Cl6–Si1 2.058(2), Cl11–B1 1.874(6), Cl3–B1 1.856(6), Cl4–Si1 2.051(2), Cl5–Si1 2.055(2), Cl2–B1 1.852(6), Si1–B1 2.004(6); Cl7–Si4–Cl8 102.71(8), Cl7–Si4–N1 111.9(2), Cl7–Si4–B2 101.3(2), Cl8–Si4–N1 114.2(2), Cl8–Si4–B2 106.0(2), N1–Si4–B2 118.8(2), Si4–N1–Si3 118.6(2), Si4–N1–Si2 120.6(2), Si4–B2–C2 135.6(4), Si4–B2–C1 144.9(4), Si4–B2–C5 140.5(4), Si4–B2–C4 130.2(4), Si4–B2–C3 126.8(4). Selected bond lengths(Å) and bond angles (°) for **3.3**: Cl11–Si1 2.119(1), Si1–N1 1.750(3), Si1–C14 1.943(4), Si1–B1 2.064(4), C7–B1 1.591(5), C1–B1 1.582(5); Cl11–Si1–N1 106.4(1), Cl11–Si1–C14 101.2(1), Cl11–Si1–B1 95.8(1), N1–Si1–C14 114.4(1), N1–Si1–B1 113.8(1), C14–Si1–B1 121.1(2), C12–C7–B1 116.2(3), C8–C7–B1 111.7(3).

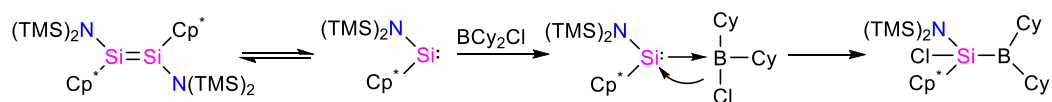
Single crystals of **3.2** suitable for the X-ray diffraction studies were obtained in toluene at 0 °C. **3.2** crystallizes in the monoclinic space group *P21/c* (Figure 3.1). The molecular structure of **3.2** reveals a pentacarba-nido-hexaboronium salt type structure, matching well with the

structure of the reported silylborane compound $[(\text{Me}_5\text{C}_5)\text{SiCl}_2\text{B}(\text{Me}_5\text{C}_5)][\text{Me}_5\text{C}_5\text{BCl}_3]$.³⁵ It is important to note that this is the only report where a similar pattern of the reactivity of a silylene (Cp^*Si) with BCl_3 was observed, and the reason could be attributed to the presence of a Cp^* group on the Si(II) center in **3.1** like Cp^*Si . The structure of **3.2** reveals that the Cp^* ring is bonded in η^5 fashion to the boron atom, and the bond lengths between the boron center and the carbon atoms of the Cp^* ring range from 1.736 to 1.773 Å, which is comparable to those of $[(\text{Me}_5\text{C}_5)_2\text{SiCl}_2\text{B}][\text{Me}_5\text{C}_5\text{BCl}_3]$ (1.738–1.768 Å).³⁵ In the cationic part, the Si–Cl bond lengths are 2.051(2) and 2.065(2) Å, respectively, which matches well with the Si–Cl bonds in $[(\text{Me}_5\text{C}_5)_2\text{SiCl}_2\text{B}][\text{Me}_5\text{C}_5\text{BCl}_3]$ (2.066–2.067 Å). Similarly, the Si–B bond length in **3.2** is 1.992(6) Å, which is in good agreement with the Si–B bond length in $[(\text{Me}_5\text{C}_5)_2\text{SiCl}_2\text{B}][\text{Me}_5\text{C}_5\text{BCl}_3]$ (1.973 Å).³⁵ Although we have not performed a detailed mechanistic study, we would like to propose a tentative mechanism based on the previous reports and observations. We assume that the formation of **3.2** involves a number of steps, Scheme 3.2). The first step can be proposed as the simple Lewis acid-base adduct formation by the nucleophilic attack of the **3.1** on the electron-deficient boron center, followed by the migration of the chloride atom as proposed by Jutzi and coworkers too.³⁵ Final steps can be suggested to follow two important reactions: (a) generation of a BCl_4^- anion and the desired cationic product; (b) migration of the $\text{N}(\text{TMS})_2$ group to the boron atom to form $\text{BCp}^*\text{N}(\text{TMS})_2\text{Cl}$ with the in situ generation of $[\text{SiCl}_2]$, which further reacts with BCl_4^- to form the desired anionic counterpart.³⁵



Scheme 3.2. Proposed mechanism for formation of **3.2**.

Further, when **3.1** was treated with 2 equiv of BCy_2Cl in toluene at room temperature, it yielded **3** in 23% yield (Scheme 3.1) through the oxidative addition of the B–Cl bond at the Si(II) center. The formation of **3.3** was confirmed by routine NMR spectroscopy and single-crystal X-ray diffraction studies. The ^{29}Si NMR spectrum of **3.3** displays two peaks at -5.85 and 7.16 ppm for the central silicon atom and the SiMe_3 groups, respectively. A single resonance at δ 76.28 ppm was detected in the ^{11}B NMR spectrum of **3.3**, which is in good accordance with the silylborane compound $(\text{NHSi}(\text{Cl})\text{BCl}-(\text{Duryl})) = 81$ ppm; $\text{NHSi} = [(\text{CH})_2(\text{NXyl})_2]\text{Si}$; Duryl = 2,3,5,6-tetramethylphenyl) reported by Braunschweig and coworkers.¹⁷ Single crystals suitable for X-ray analysis were grown from toluene at 0°C . **3.3** crystallizes in the monoclinic space group C2/c with the central silicon atom in a distorted tetrahedral geometry (Figure 2). The molecular structure of **3.3** reveals the Si–B bond length of $2.064(4)$ Å, which is marginally longer than the Si–B bond length in $\text{NHSi}(\text{Cl})-\text{BCl}(\text{Duryl})$ (2.019 Å).³⁶ The Si–Cl bond distance in **3.3** is $2.119(1)$ Å and also matches well with the Si–Cl bond in $\text{NHSi}(\text{Cl})\text{BCl}(\text{Duryl})$ (2.1079 Å).¹⁷ The reaction pattern of **3.1** with BCy_2Cl is different from the reaction with BCl_3 . The formation of **3.3** can be explained as the insertion of the Si(II) atom into the B–Cl bond via the donation of σ electrons from the Si atom to the positive BCy_2 group and the electrons of X (Cl) into the empty p orbital on the Si atom (Scheme 3.3). It is presumed that the large cyclohexyl groups hinder the migration of the Cp^* group from the silicon center to the boron center.



Scheme 3.3. Proposed mechanism for the formation of **3.3**.

After the successful reaction of **3.1** with BCl_3 and BCy_2Cl , we turned our attention toward aluminum halides. In contrast to the silicon-boron compounds, very few examples of siliconaluminum compounds have been isolated to date.^{22,23,45,46} The reaction of **3.1** with AlCl_3 in toluene at room temperature afforded **3.4** in 35% yield (Scheme 3.1). The analogous reaction with AlBr_3 led to **3.5** in 34% yield (Scheme 3.1). The ^{29}Si NMR spectra of **3.4** and **3.5** display two resonances for each at δ -12.62 and 4.23 ppm (for **3.4**) and δ -17.87 and 4.37 ppm (for **3.5**), respectively. The resonances at δ -12.62 (for **3.4**) and -17.87 ppm (for **3.5**) are assigned for the central silicon atom, which is upfield shifted than **3.1** (δ 15.06 ppm).³¹ The other two resonances correspond to the TMS groups of the respective compounds.

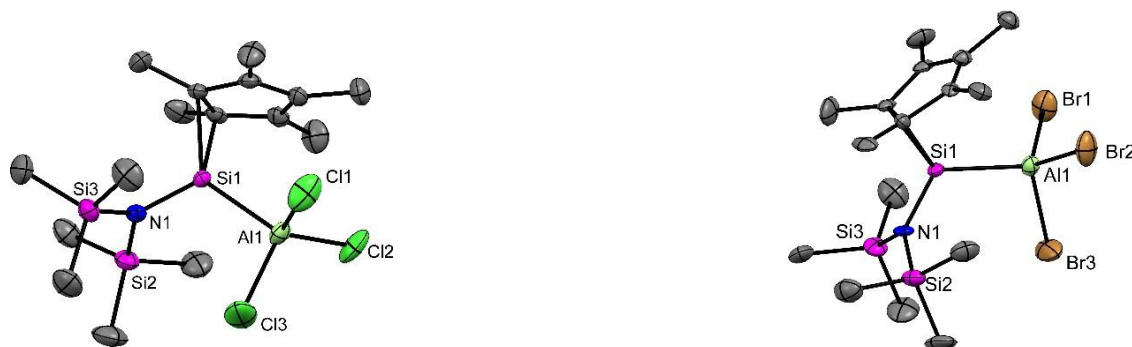


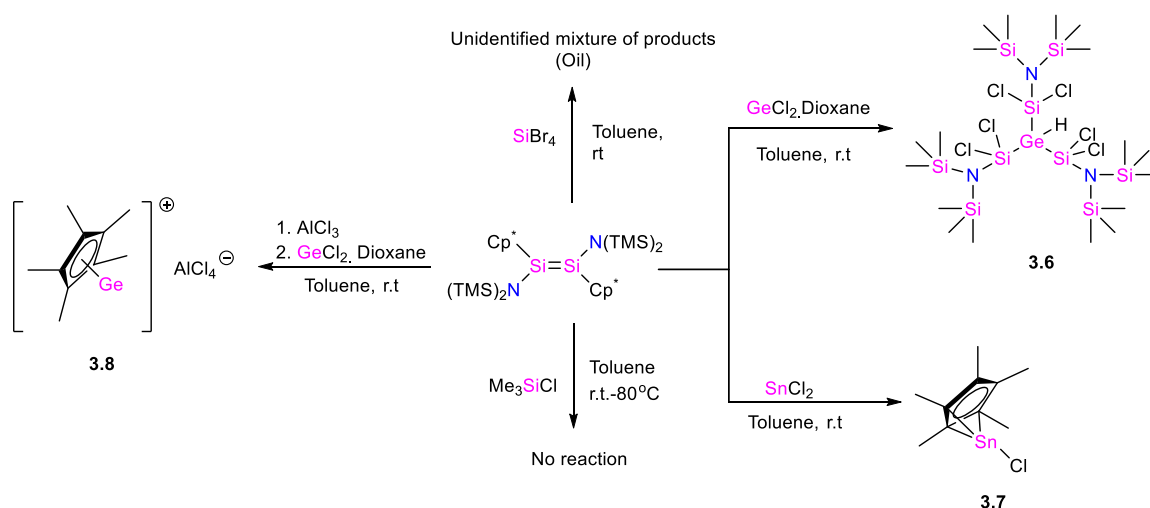
Figure 3.2. Molecular structures of **3.3**(left) and **3.4**(right) with anisotropic displacement parameters are depicted at a 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths(Å) and bond angles (°) for **3.3**: Si1–Al1 2.4675(9), Si1–N1 1.720(2), Si1–C2 2.033(2), Si1–C1 2.031(2), Cl2–Al1 2.134(1), Cl1–Al1 2.134(1), Al1–Cl3 2.139(1); Al1–Si1–N1 116.77(7), Al1–Si1–C2 123.51(8), Al1–Si1–C1 123.72(8), N1–Si1–C2 114.7(1), N1–Si1–C1 114.9(1), C2–Si1–C1 42.5(1), Si1–Al1–Cl2 113.06(4), Si1–Al1–Cl1 111.41(4), Si1–Al1–Cl3 103.31(4), Cl2–Al1–Cl1 110.24(4), Cl2–Al1–Cl3 109.28(4), Cl1–Al1–Cl3 109.26(4), Si1–N1–Si3 117.1(1), Si1–N1–Si2 117.7(1), Si3–N1–Si2 124.1(1), Si1–C2–C3 97.1(2), Si1–C2–C1 68.7(1). *Selected bond lengths(Å) and bond angles (°) for 3.4*: Br1–Al1 2.293(5), Br2–Al1 2.291(5), Br3–Al1 2.296(4), Si1–Al1 2.463(4), Si1–N1 1.73(1), Si1–C6 2.04(1), Si1–C5 2.03(1); Al1–Si1–N1 116.7(4), Al1–Si1–C6 124.3(4), Al1–Si1–C5 123.7(4), N1–Si1–C6 114.0(5), N1–Si1–C5 115.0(5), C6–Si1–C5 42.6(5), Br1–Al1–Br2 110.7(2), Br1–Al1–Br3 108.4(2), Br1–Al1–Si1 112.7(2), Br2–Al1–Br3 108.4(2), Br2–Al1–Si1 111.7(2), Br3–Al1–Si1 104.6(2), Si1–N1–Si3 118.8(6), Si1–N1–Si2 115.7(6).

The single-crystal X-ray diffraction analysis further confirms the molecular composition of **3.4** and **3.5**. Both **3.4** and **3.5** crystallize in the monoclinic space group P21/n (Figures 3.2). The molecular structure of **3.4** reveals a donor-acceptor complex of **3.1**→AlCl₃ composition, where the silicon center is coordinated with the Lewis acid AlCl₃ as well as bonded to the Cp* ring in η^2 fashion. The Si–Al bond length in **3.4** is 2.4675(9) Å, which is almost commensurable with the Si–Al bond length of the recently reported complex RSi→AlCl₃ [R = PhC–(NtBu)₂C₆H₄PPh₂] (2.4509 Å) by Roesky and co-workers.²³ The structure of **5** in the solid state (Figure 3.2) is very similar to that of **4**. The bond distance between the silicon and the aluminum center (2.463(4) Å) in **3.5** is closely matching with the Si–Al bond distance of **3.4** (2.4675 Å). The silicon center is also bonded in η^2 fashion with the Cp* ring. It is noteworthy to mention that **3.5** is the first example of a silylene→AlBr₃ adduct.

3.3.2. Reactions with Halides of Group 14 Elements.

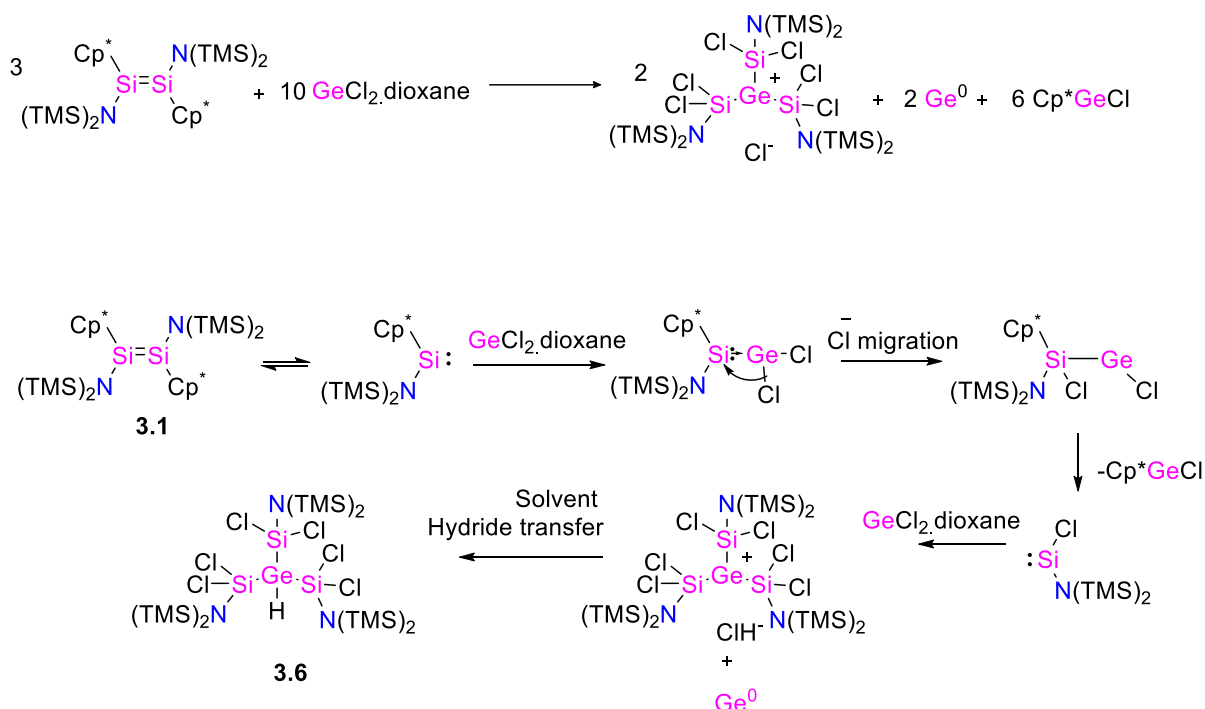
After studying the reactivity of **3.1** with group 13 halides, we shifted our focus to group 14 halides. We performed some reactions of **3.1** with the dihalides of germanium (II) and tin (II).

In most of the cases, the reaction of silylene with $\text{GeCl}_2 \cdot \text{dioxane}$ furnishes silicon(II)-germanium(II) adducts like $\text{PhC}(\text{NtBu})_2\text{N}(\text{PPh}_2)-(\text{Ar})\text{Si} \rightarrow \text{GeCl}_2$ [$\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$] and $\text{PhC}(\text{NtBu})_2\text{N}-(\text{TMS})_2\text{Si} \rightarrow \text{GeCl}_2$.^{47,48} When **3.1** was treated with 2 equiv of $\text{GeCl}_2 \cdot \text{dioxane}$ in toluene at room temperature, **3.6** was obtained in 55% yield (Scheme 3.4) along with some unidentified transient species. The molecular structure of **3.6** (Figure 3.3) disclosed a dendrimeric compound $[\{\text{N}(\text{TMS})_2\}_3(\text{SiCl}_2)_3\text{GeH}]$. In **3.6**, both the silicon and germanium centers have been oxidized, and it is comparable to group-14-based hybrid first-generation dendrimers.^{49–55} Generally, silicon-based dendrimers are synthesized via multistep procedures, and they require different types of silanes as the starting precursors. It is evident from the molecular structure of **3.6** that the germanium center is bonded with three $[\text{SiCl}_2\text{N}(\text{TMS})_2]$ moieties and one hydrogen atom. The germanium center in **3.6** adopts a distorted tetrahedral geometry and is comparable with the previously reported compound $[\{(\text{GeMe}_3)_2\text{SiMeGeMe}_2\}_3\text{SiMe}]$ (av Si–Ge–Si is 115.4°).⁵⁰ The Ge–Si bond lengths of **3.6** are equivalent with a bond length of 2.381 Å, which is shorter than those reported for Si $\rightarrow$ Ge coordinate bonds, e.g., $\text{PhC}(\text{NtBu})_2\text{N}(\text{PPh}_2)(\text{Ar})\text{Si} \rightarrow \text{GeCl}_2$ (2.4863 Å) and $\text{PhC}(\text{NtBu})_2\text{N}(\text{TMS})_2\text{Si} \rightarrow \text{GeCl}_2$ (2.5259 Å). The constitution of **3.6** was further established by NMR spectroscopic studies. The ^1H NMR spectrum of **3.6** reveals a singlet at δ 4.59 ppm that can be assigned to the hydride bound to the Ge(IV) center, which is comparable to the reported values of Ge(IV) hydrides (4–6 ppm).^{56–59} It is of note that we tried the reaction in several solvents, e.g., THF, hexane, Et_2O , etc., to understand the source of the hydride, but in each case, we obtained the same product.



Scheme 3.4. Reactivity of **3.1** with $\text{GeCl}_2 \cdot \text{dioxane}$, SiBr_4 , SnCl_2 .

Further, we performed a reaction in toluene- d_8 solvent and recorded the ^1H NMR spectrum, which revealed the absence of the peak at δ 4.59 ppm. Hence, we can propose that the hydride is coming from the solvent. We suggest that the initial steps of the formation of **3.6** involve the Si(II) $\rightarrow$ GeCl₂ adduct formation, followed by the migration of the Cp* group from the Si to Ge atom (Scheme 3.5). Subsequent in situ generation of a silylene probably leads the way to the formation of **3.6**.



Scheme 3.5. Proposed mechanism for the formation of **3.6**.

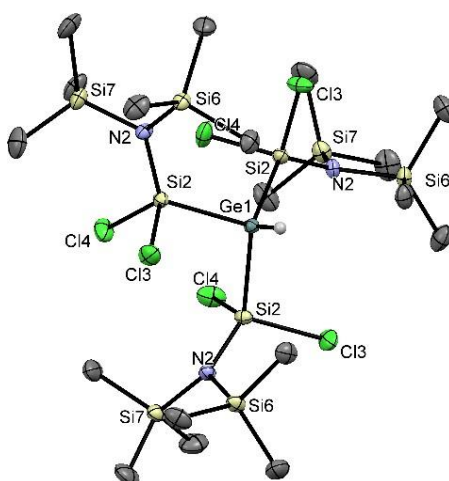
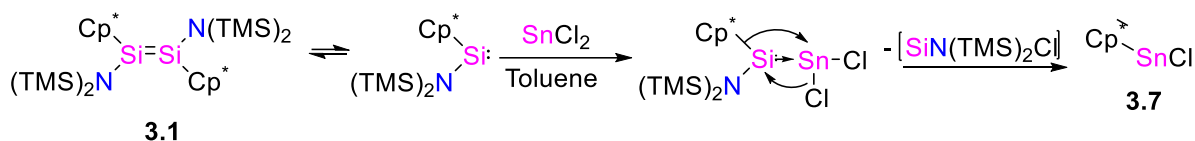


Figure 3.3. Molecular structures of **3.6** with anisotropic displacement parameters are depicted at a 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths(Å) and bond *angles*

(°) for **3.6**: Ge1–H1 0.9778, Ge1–Si2 2.381, Ge1–Si2 2.380, Ge1–Si2 2.381, Cl1–Si2 2.078(1), Cl2–Si2 2.052(1), Si2–N1 1.699(5); H1–Ge1–Si2 109.67, Si2–Ge1–Si2 109.28, Ge1–Si2–Cl1 104.06, Ge1–Si2–Cl2 102.86, Ge1–Si2–N1 122.8, Cl1–Si2–Cl2 103.61(7), Cl1–Si2–N1 110.3(1), Cl2–Si2–N1 111.3(1).

Motivated by the results of the GeCl_2 reaction, we sought to synthesize a similar type of compound with tin. It is well known in the literature that the reaction of two-coordinate silylene $[\{\text{HCN}(\text{tBu})\}_2\text{Si}]$ with SnCl_2 results in a disproportionation reaction forming $[\{\text{HCN}(\text{tBu})\}_2\text{Si}]_3\text{SnCl}$ and Sn .⁶⁰ Amidinato silicon(II) amide $[\text{PhC}(\text{NtBu})_2\text{N}(\text{TMS})_2\text{Si}]$ with SnCl_2 gives a simple adduct formation $[\text{PhC}(\text{NtBu})_2\text{N}(\text{TMS})_2\text{Si} \rightarrow \text{SnCl}_2]$.⁶¹ However, the reaction of **3.1** with SnCl_2 led to a metathesis product **3.7** in 64% yield (Scheme 3.4) along with some decomposition products (Scheme 3.6). The formation of this product can be reasoned due to the metal affinity of Cp^* group. The molecular structure of **3.7** (Figure 3.4) revealed an $\text{Sn}(\text{II})$ center attached to the Cp^* ring in η^3 fashion with the average $\text{Sn}-\text{C}$ bond length of 2.483(9) Å, matching well with the $\text{Sn}-\text{C}$ bond length in $(\text{C}_5\text{Me}_5\text{Sn})^+(\text{BF}_4)^-$ (2.462 Å).⁶²



Scheme 3.6. Proposed mechanism for the formation of **3.7**.

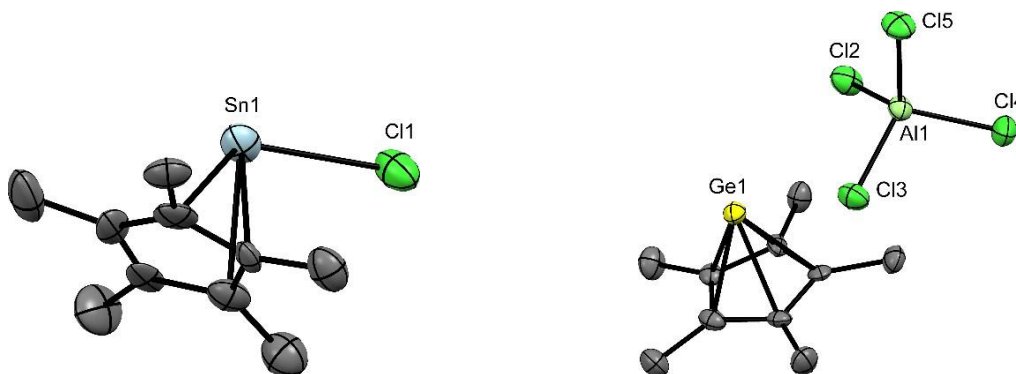


Figure 3.4. Molecular structures of **3.7**(left) and **3.8**(right) with anisotropic displacement parameters are depicted at a 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths(Å) and bond angles (°) for **3.7**: Sn1–Cl1 2.703(3), Sn1–C2 2.412(9), Sn1–C3 2.472(9), Sn1–C1 2.56(1), Sn1–C5 2.677, Sn1–C4 2.647; Cl1–Sn1–C2 92.6(2), Cl1–Sn1–C3 87.7(2), Cl1–Sn1–C1 124.5(2), C2–Sn1–C3 33.6(3), C2–Sn1–C1 32.9(3), C3–Sn1–C1 53.8(3), Sn1–C2–C3 75.5(5), Sn1–C2–C1 79.4(5). Selected bond lengths(Å) and bond angles (°) for **3.8**: Ge1–C5 2.271(5), Ge1–C4 2.272(5), Ge1–C2 2.263(4), Ge1–C3 2.267(4), Ge1–C1 2.267(4), Cl3–Al1 2.136(2) Cl5–Al1 2.137(2), Cl2–Al1 2.139(2), Cl4–Al1 2.146(2); C5–Ge1–C4 36.6(2), C5–Ge1–C2 61.5(2), C5–Ge1–C3 61.4(2),

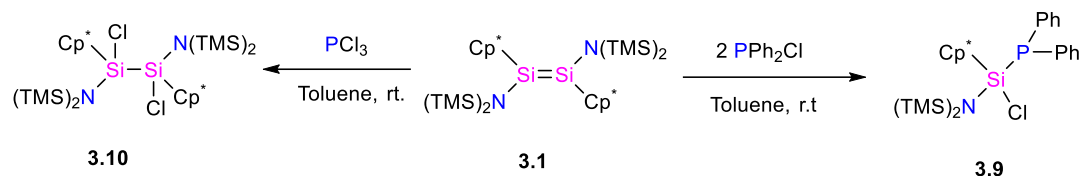
C5–Ge1–C1 36.8(2), C4–Ge1–C2 61.6(2), C4–Ge1–C3 36.9(2), C4–Ge1–C1 61.2(2), C2–Ge1–C3 36.9(2), C2–Ge1–C1 36.7(2), C3–Ge1–C1 61.2(2), Cl3–Al1–Cl5 111.32(8), Cl3–Al1–Cl2 108.76(8), Cl3–Al1–Cl4 109.17(8), Cl5–Al1–Cl2 109.57(8), Cl5–Al1–Cl4 108.58(8), Cl2–Al1–Cl4 109.42(8).

Further, we probed the reaction of **3.1** with two different halides in one pot. Our assumption was to dehalogenate from **3.4** to make an aluminum cation, which has a modicum of precedence. However, the treatment of **3.1** with 2 equiv of AlCl₃ in toluene, followed by the addition of 2 equiv of GeCl₂·dioxane, afforded a cationic Ge(II) center with AlCl₄ anion (**3.8**). In the ¹H NMR spectrum of **3.8**, only one sharp singlet at δ 2.19 ppm appeared, corresponding to the 15 CH₃ protons of the Cp* group. The molecular structure of **3.8** was confirmed by single-crystal X-ray diffraction analysis (Figure 3.4). **3.8** crystallizes in the orthorhombic space group Pbca. The molecular structure of **3.8** reveals a Ge(II) center bound to the Cp* ring in η^5 fashion with all the Ge–C bond lengths ranging from 2.263 to 2.272(4) Å. A similar type of cationic compound [Cp*Ge]⁺ [BF₄][–] was reported by Jutzi and co-workers by the reaction of Cp*₂Ge with HBF₄.^{62,63} We also checked the reactivity of **3.1** with SiBr₄ and Me₃SiCl (Scheme 3.4). In doing that, **3.1** was treated with 2 equiv of SiBr₄ in toluene at room temperature. The NMR studies revealed a mixture of products (as oil), which could not be crystallized. On the contrary, Me₃SiCl did not react with **3.1** even at elevated temperatures. The probable explanation for this could be the steric hindrance of the substrate.

3.3.3. Reaction with the Halides of Group 15.

Moving our investigation to the halides of group 15, we planned to explore the commonly available halides of phosphorus and antimony. It is interesting to note that the reaction of Si(II) compounds with phosphorus/antimony halides is not known to the best of our knowledge. However, the reaction of SbCl₃ with **3.1** could only afford decomposition products. When we treated **3.1** with 2 equiv of PPh₂Cl in toluene at room temperature (Scheme 3.7), it afforded **3.9** in 36% yield. There is only one report where the Si–P bond is formed via the reaction of West's silylene [{HC(*t*BuN)}₂Si:] and a phosphonium ion [P(NC₂H₅)₂]⁺ [AlCl₄][–].⁶⁴ The ²⁹Si NMR spectrum of **3.9** displays three peaks at δ 7.16, 4.34, and 6.32 ppm. The peak at δ 7.16 ppm is assigned to the central silicon atom, which is upfield shifted compared to the parent compound **3.1** (δ 15.06 ppm). The remaining two peaks (δ 4.34 and 6.32 ppm) correspond to TMS groups. The ³¹P NMR spectrum of **3.9** reveals a single peak at δ –55.62 ppm, which further confirmed the formation of a single product. **3.9** crystallizes in the triclinic space group P $\bar{1}$ (Figure 3.5). The molecular structure of **3.10** reveals that the Si–P bond length is 2.289 Å, which is

marginally longer than those in $[\{HC(tBuN)\}_2(Cl)Si-P(NCy_2)_2]$ (2.255 Å).⁶⁴ We presume that the formation of **3.10** follows the same pathway like **3.3**.



Scheme 3.7. Reactivity of **3.1** with PPh_2Cl and PCl_3 .

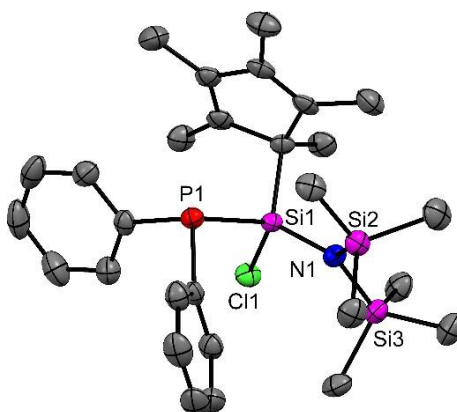


Figure 3.5. Molecular structures of **3.9** with anisotropic displacement parameters are depicted at a 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths(Å) and bond angles (°) for **3.9**. Cl1–Si1 2.0981(7), P1–Si1 2.2890(8), P1–C7 1.849(2), P1–Cl1 1.844(2), Si1–N1 1.738(1), Si1–C17 1.925(2). Selected bond angles (deg) for **3.9**: Si1–P1–C7 101.99(6), Si1–P1–Cl1 106.01(6), C7–P1–Cl1 102.06(9), Cl1–Si1–P1 108.87(3), Cl1–Si1–N1 106.22(6), Cl1–Si1–C17 102.63(6), P1–Si1–N1 112.74(6), P1–Si1–C17 108.41(6), N1–Si1–C17 117.21(8).

Following the reaction with PPh_2Cl , we further treated **3.1** with 2 equiv of PCl_3 in toluene at room temperature, which afforded a dichlorinated compound **3.10** in 45% yield (Scheme 3.7). In this reaction, 1,2-chloride addition to the disilene is observed. The molecular structure of **3.10** (Figure 3.6) shows the placement of two chloride atoms opposite to each other on two different silicon centers. Similar reactivity of **3.1** with NOBF_4 has been recently reported by our group, resulting in the formation of $[\text{N}(\text{TMS})_2\text{Cp}^*_2\text{Si}_2\text{F}_2]$.⁶⁵

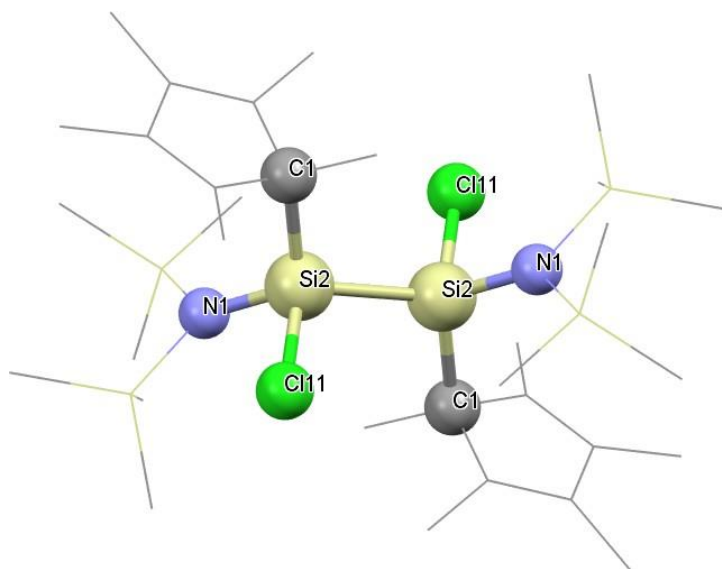


Figure 3.6. Molecular structure of **3.10** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) for **3.10**: Si2-Cl11 2.118(8), Si2-Si2 2.433(2).

3.4. CONCLUSION

In summary, we have shown a diverse set of reactions of **3.1** toward the halides of groups 13–15. The reaction of **3.1** with BCl_3 and Cy_2BCl resulted in the oxidation of the silicon center, followed by rearrangement (**3.2** and **3.3**), whereas reaction with AlX_3 ($\text{X} = \text{Cl}, \text{Br}$) afforded simple $(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si} \rightarrow \text{AlX}_3$ adducts (**3.4** and **3.5**). Surprisingly, the reaction of **1** with GeCl_2 led to the isolation of an unprecedented hybrid dendrimer **3.6**, where the central Ge(IV) atom is connected to three Si(IV) atoms. Lastly, the treatment of **1** with PPh_2Cl afforded a phosphasilane (**3.9**), which can be described as the insertion of a Si(II) atom into a P-Cl bond. Overall, our work demonstrates an accessible route for the synthesis of Si-E ($\text{E} = \text{B}, \text{P}, \text{Ge}$) functionalized compounds.

3.5. Reference

1. Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 164–164.
2. Grev, R. S.; Schaefer III, H. F.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, 113, 5638–5643.
3. Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, 33, 704–714.
4. Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, 109, 3479–3511.
5. Kira, M. *Chem. Commun.* **2010**, 46, 2893–2903.
6. Sen, S.S.; Khan, S.; Nagendran, S.; Roesky, H.W. *Acc. Chem. Res.* **2012**, 45, 578–587.
7. Sen, S. S.; Khan, S.; Samuel, P. P.; Roesky, H. W. *Chem. Sci.* **2012**, 3, 659–682.
8. Roesky, H. W. Chemistry of low valent silicon. *J. Organomet. Chem.* **2013**, 730, 57–62.
9. Benedek, Z.; Szilvási, T. *RSC Adv.* **2015**, 5, 5077–5086.
10. Raoufmoghaddam, S.; Zhou, Y.-P.; Wang, Y.; Driess, M. *J. Organomet. Chem.* **2017**, 829, 2–10.
11. Chu, T.; Nikonov, G. I. *Chem. Rev.* **2018**, 118, 3608–3680.
12. Zhou, Y. P.; Driess, M. *Angew. Chem., Int. Ed.* **2019**, 58, 3715–3728.
13. Fujimori, S.; Inoue, S. *Eur. J. Inorg. Chem.* **2020**, 2020, 3131–3142.
14. Shan, C.; Yao, S.; Driess, M. *Chem. Soc. Rev.* **2020**, 49, 6733–6754.
15. Junold, K.; Baus, J. A.; Burschka, C.; Guerra, C. F.; Bickelhaupt, F. M.; Tacke, R. *Chem. Eur. J.* **2014**, 20, 12411–12415.
16. Cui, H.; Wu, M.; Teng, P. *Eur. J. Inorg. Chem.* **2016**, 2016, 4123–4127.
17. Gackstatter, A.; Braunschweig, H.; Kupfer, T.; Voigt, C.; Arnold, N. *Chem. Eur. J.* **2016**, 22, 16415–16419.
18. Suzuki, Y.; Ishida, S.; Sato, S.; Isobe, H.; Iwamoto, T. *Angew. Chem., Int. Ed.* **2017**, 56, 4593–4597.
19. Dübek, G.; Franz, D.; Eisenhut, C.; Altmann, P. J.; Inoue, S. *Dalton Trans.* **2019**, 48, 5756–5765.
20. Bisai, M. K.; Swamy, V.; Raj, K. V.; Vanka, K.; Sen, S. S. *Inorg. Chem.* **2021**, 60, 1654–1663.
21. Li, J.; Liu, Y.; Kundu, S.; Keil, H.; Zhu, H.; Herbst-Irmer, R.; Stalke, D.; Roesky, H. W. *Inorg. Chem.* **2020**, 59, 7910–7914.
22. Mück, F. M.; Baus, J. A.; Bertermann, R. d.; Burschka, C.; Tacke, R. *Organometallics* **2016**, 35, 2583–2588.

-
-
23. Nazish, M.; Siddiqui, M. M.; Sarkar, S. K.; Münch, A.; Legendre, C. M.; Herbst-Irmer, R.; Stalke, D.; Roesky, H. W. *Chem. Eur. J.* **2021**, *27*, 1744–1752.
 24. Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, *115*, 10428–10429.
 25. Tsutsui, S.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 9955–9956.
 26. Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479–9480.
 27. Tsutsui, S.; Tanaka, H.; Kwon, E.; Matsumoto, S.; Sakamoto, K. *Organometallics* **2004**, *23*, 5659–5661.
 28. Abe, T.; Tanaka, R.; Ishida, S.; Kira, M.; Iwamoto, T. *J. Am. Chem. Soc.* **2012**, *134*, 20029–20032.
 29. Reiter, D.; Holzner, R.; Porzelt, A.; Altmann, P. J.; Frisch, P.; Inoue, S. *J. Am. Chem. Soc.* **2019**, *141*, 13536–13546.
 30. Jutzi, P.; Mix, A.; Neumann, B.; Rummel, B.; Schoeller, W. W.; Stämmler, H.-G.; Rozhenko, A. *J. Am. Chem. Soc.* **2009**, *131*, 12137–12143.
 31. Khan, S.; Sen, S. S.; Roesky, H. W.; Kratzert, D.; Michel, R.; Stalke, D. *Inorg. Chem.* **2010**, *49*, 9689–9693.
 32. Khan, S.; Sen, S. S.; Roesky, H. W.; Kratzert, D.; Michel, R.; Stalke, D. *Inorg. Chem.* **2010**, *49*, 9689–9693.
 33. Khan, S.; Michel, R.; Sen, S. S.; Roesky, H. W.; Stalke, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 11786–11789.
 34. Seitz, A. E.; Eckhardt, M.; Sen, S. S.; Erlebach, A.; Peresypkina, E. V.; Roesky, H. W.; Sierka, M.; Scheer, M. Different reactivity of As₄ towards disilenes and silylenes. *Angew. Chem., Int. Ed.* **2017**, *56*, 6655–6659.
 35. Holtmann, U.; Jutzi, P.; Kühler, T.; Neumann, B.; Stämmler, H.-G. *Organometallics* **1999**, *18*, 5531–5538.
 36. Metzler, N.; Denk, M. *Chem. Commun.* **1996**, 2657–2658.
 37. Takeda, N.; Kajiwar, T.; Tokitoh, N. *Chem. Lett.* **2001**, *30*, 1076–1077.
 38. Kajiwar, T.; Takeda, N.; Sasamori, T.; Tokitoh, N. *Organo-metallics* **2004**, *23*, 4723–4734.
 39. Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Stalke, D. *Chem. Eur. J.* **2010**, *16*, 85–88.
 40. Azhakar, R.; Tavčar, G.; Roesky, H. W.; Hey, J.; Stalke, D. *Eur. J. Inorg. Chem.* **2011**, *2011*, 475–477.
 41. Inoue, S.; Leszczyńska, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8589–8593.
-

-
-
42. Wendel, D.; Porzelt, A.; Herz, F. A.; Sarkar, D.; Jandl, C.; Inoue, S.; Rieger, B. *J. Am. Chem. Soc.* **2017**, *139*, 8134–8137.
 43. Kaufmann, S.; Schäfer, S.; Gamer, M. T.; Roesky, P. W. *Dalton Trans.* **2017**, *46*, 8861–8867.
 44. Khoo, S.; Shan, Y.-L.; Yang, M.-C.; Li, Y.; Su, M.-D.; So, C.-W. *Inorg. Chem.* **2018**, *57*, 5879–5887.
 45. Belzner, J.; Ronneberger, V.; Schär, D.; Brönnecke, C.; Herbst-Irmer, R.; Noltemeyer, M. *J. Organomet. Chem.* **1999**, *577*, 330–336.
 46. Li, J.; Zhong, M.; Keil, H.; Zhu, H.; Herbst-Irmer, R.; Stalke, D.; De, S.; Koley, D.; Roesky, H. W. *Chem. Commun.* **2019**, *55*, 2360–2363.
 47. Shan, Y. L.; Yim, W. L.; So, C. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 13155–13158.
 48. Ismail, M. L. B.; So, C.-W. *Chem. Commun.* **2019**, *55*, 2074–2077.
 49. Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2575–2576.
 50. Nanjo, M.; Sekiguchi, A. *Organometallics* **1998**, *17*, 492–494.
 51. Frey, H.; Schlenk, C. *Top. Curr. Chem.* **2000**, *210*, 69–129.
 52. Dvornic, P. R. PAMAMOS: *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2755–2773.
 53. Kim, C.; Hong, J. H. *Molecules* **2009**, *14*, 3719–3730.
 54. Abbasi, E.; Aval, S. F.; Akbarzadeh, A.; Milani, M.; Nasrabadi, H. T.; Joo, S. W.; Hanifehpour, Y.; Nejati-Koshki, K.; Pashaei-Asl, R. *Nanoscale Res. Lett.* **2014**, *9*, 247.
 55. Najafi, F.; Salami-Kalajahi, M.; Roghani-Mamaqani, H. *J. Iran. Chem. Soc.* **2021**, *18*, 503–517.
 56. Brelière, C.; Carré, F.; Corriu, R.; Royo, G. *Organometallics* **1988**, *7*, 1006–1008.
 57. Castel, A.; Riviere, P.; Satge, J.; Ko, H. *Organometallics* **1990**, *9*, 205–210.
 58. Riedmiller, F.; Wegner, G. L.; Jockisch, A.; Schmidbaur, H. *Organometallics* **1999**, *18*, 4317–4324.
 59. Richards, A. F.; Phillips, A. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 3204–3205.
 60. Gehrhus, B.; Hitchcock, P. B.; Jansen, H. J. *Organomet. Chem.* **2006**, *691*, 811–816.
 61. Shan, Y.-L.; Leong, B.-X.; Xi, H.-W.; Ganguly, R.; Li, Y.; Lim, K. H.; So, C.-W. *Dalton Trans.* **2017**, *46*, 3642–3648.
 62. Jutzi, P.; Kohl, F.; Hofmann, P.; Krüger, C.; Tsay, Y. H. *Chem. Ber.* **1980**, *113*, 757–769.
 63. Tholen, P.; Dong, Z.; Schmidtman, M.; Albers, L.; Müller, T. *Angew. Chem., Int. Ed.* **2018**, *57*, 13319–13324.
-

64. Pietschnig, R. *Chem. Commun.* **2004**, 546–547.
65. Parvin, N.; Sen, N.; Muhasina, P.V.; Tothadi, S.; Parameswaran, P.; Khan, S. *Chem. Commun.* **2021**, 57, 5008–5011.

Chapter 4A

Donor free stibenium Cation as efficient cyanosilylation catalyst

4A.1. Introduction

In the last few years, p-block elements have gained significant attention in catalysis due to their cost-effectiveness and environmentally friendly nature.¹ Among them, cations of p-block elements have been identified as potent and versatile Lewis acid catalysts due to their enhanced electrophilic nature.² This burgeoning chemistry of cationic compounds as efficient catalysts is not only limited to groups 13 and 14 elements but has also extended to group 15 elements.³ For example, the phosphonium cations were shown to perform asymmetric organocatalysis as well as regio- and chemoselective hydroboration.⁴ While Lewis acid catalysis has been demonstrated with Sb(V) cations,⁵ the antimony analogues of phosphonium cations, namely stibenium (Sb(III)) cations have not been investigated in the field of catalysis.

Owing to a lone pair of electrons and the vacant p-orbital stibenium cations are amphoteric in nature.⁶ It has been established that group 15 cationic species are weak s-donor and better p-acceptor.⁶ Most of the reported stibenium cations typically feature stabilization from Lewis bases,^{6a-d} thereby reflecting their greater electrophilic nature. The untapped potential of stibenium cation in catalysis motivated our pursuit of such a compound, which can easily be accessible. Hence, we turned our attention towards *N,N'*-dineopentyl-1,2-phenylenediamine ligand,⁷ which was utilized to stabilize heavier tetrylenes.⁸ Consequently, we also used *N,N'*-dineopentyl-1,2-phenylenediamine ligand to stabilize the donor-free stibenium cations. Herein, we report a novel donor-free stibenium cation, which was subsequently utilized as a catalyst for the cyanosilylation of carbonyl compounds. It is noteworthy to mention that this is the first catalytic application of any stibenium cation.

4A.2. Experimental Section

4A.2.1. General remarks

The whole process was executed under an inert atmosphere of argon using standard Schlenk techniques or in a glovebox. Solvents used were purified using an MBRAUN solvent purification system MBSPS-800. SbCl₃, AgOTf, AgSbF₆ were purchased from Sigma-Aldrich and Alfa Aesar. They were used without further purification. ¹H, ¹³C, ²⁹Si, ¹¹B and ³¹P spectra were recorded on a Bruker spectrometer in CDCl₃ as the solvent with an external standard (SiMe₄ for ¹H, ¹³C,). Mass spectra were recorded using an AB Sciex, 4800 MALDI TOF/TOF, and HRMS was recorded on a Waters Synapt, USA. Yields are calculated based on the isolated crystals.

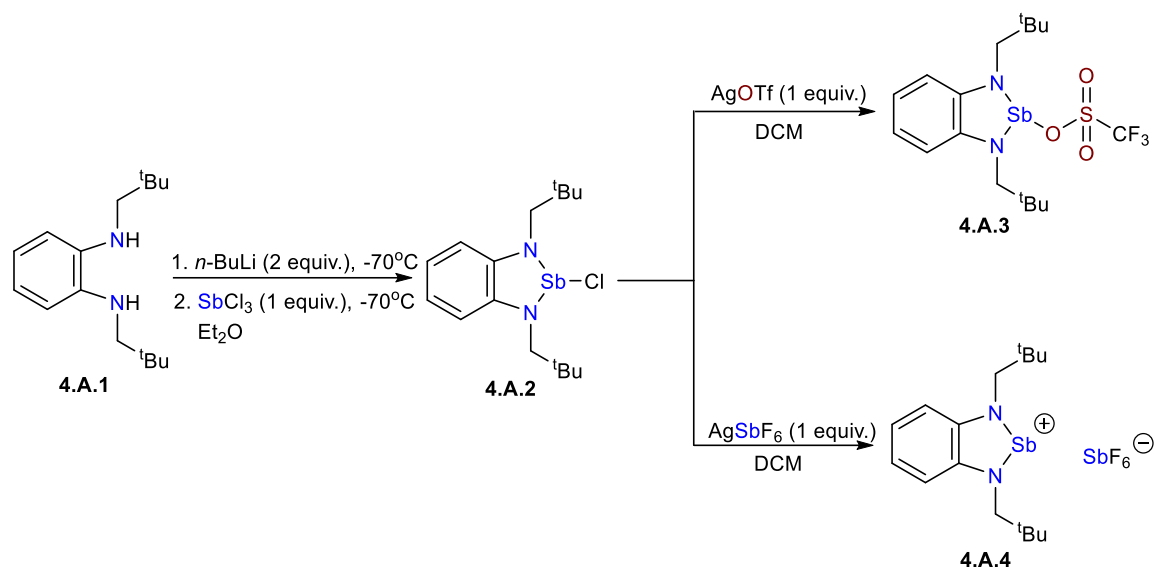
4A.2.2. Synthesis of compounds 4A.2-4A.4.

Synthesis of 4A.2. Ligand **4A.1** (1 g, 4.03 mmol) was taken in a 100 ml Schlenk flask and 60 ml of dry Et₂O was added to it. Subsequently, the flask was cooled to -70°C and 3.22 ml of *n*BuLi (2.5 M solution) was added to it drop by drop. The reaction mixture was slowly allowed to come to room temperature and kept on stirring for 8 h. The reaction mixture was again cooled to -40°C and SbCl₃ (918 mg, 4.03 mmol) was added to it directly and the solution became orange in colour with colorless precipitate after 30 min. The reaction mixture was stirred overnight. The solution was filtered and concentrated till some orange-colored crystalline particles appeared on the wall of the flask. Storage of the concentrated solution at 0 °C afforded the orange crystals of **4A.2**. Yield: 800 mg (49 %) Mp: 120°C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 1.06 (s, 18H, CH₃), 3.72 (s, 4H, -CH₂), 6.92-6.82 (m, 4H, Ph) ppm. ¹³C NMR (100.613 MHz, CDCl₃, 298 K): δ 27.8, 28.3, 33.5, 57.7, 111.5, 118.2, 143.6 ppm. HRMS: Calcd for compound **4A.2**: m/z 402.08. Found m/z 403.0484 [M+H]⁺.

Synthesis of 4A.3. A 100 ml Schlenk flask charged with **4A.2** (0.403 g, 1 mmol) and AgOTf (0.257 g, 1 mmol) and 40 ml of DCM was added to it at room temperature. The solution turned dark red immediately. The dark red colored solution was kept on stirring for 12 h which afforded a white precipitate. The reaction mixture was filtered and concentrated to 5 ml DCM and 5 ml of pentane was added to it and stored at 0°C which resulted in the dark red colored crystals of **4A.3**. Yield: 300 mg (58%) Mp: 188°C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 1.05 (s, 18H, -CH₃), 7.37-7.18 (m, 4H, Ph) ppm. ¹⁹F{¹H} NMR (376.66 MHz, CDCl₃, 298 K): δ -78.0 ppm. HRMS: Calcd for compound **4A.3**: m/z 516.07. Found m/z 516.0612 [M⁺].

Synthesis of 4A.4. A 100 ml Schlenk flask charged with **4A.2** (0.403 g, 1 mmol) and AgSbF₆ (0.344 g, 1 mmol) and 40 ml DCM was added to it at room temperature. The solution turned dark red in color immediately. The dark red colored solution was kept on stirring for 12 h which afforded white precipitate. The reaction mixture was filtered and concentrated to 5 ml DCM and 5 ml of pentane was added to it and stored at 0°C which resulted in the dark red colored crystals of **4A.4**. Yield: 250 mg (41.5%) Mp: 215°C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 1.06 (s, 18H -CCH₃), 4.77 (s, 4H, -CH₂), 7.53-7.50 and 7.33-7.31 (m, 4H, Ph) ppm. ¹³C{¹H} NMR (100.613 MHz, CDCl₃, 298 K): δ 27.9, 32.9, 59.9, 114.7, 124.7, 147.0 ppm. ¹⁹F{¹H} NMR (376.66 MHz, CDCl₃, 298 K): δ -167.5 (br) ppm. HRMS: Calcd for compound **4A.4**: 602.00. Found m/z 602.0012 [M⁺].

4A.3. Results and discussion

**Scheme 4A.1.** Syntheses of complexes **4A.2-4A.4**.

The lithium salt of *N,N'*-neopentyl-1,2-phenylenediamine (**4A.1**) was treated with one equiv of SbCl_3 in Et_2O at 70 °C, which resulted in chlorostibine **4A.2** (70% yield) (Scheme 4.A.1). The chemical composition of **4A.2** was established by NMR spectroscopy and single-crystal X-ray diffraction studies. The ^1H NMR spectrum of **4A.2** displays a sharp singlet at δ 1.06 ppm for 18 ^tBu protons and another singlet at δ 3.72 ppm for four $-\text{CH}_2-$ protons. **4A.2** is found to be crystallized in monoclinic space group *P21/c*. The molecular structure of **4A.2** is given in Figure 4.1.

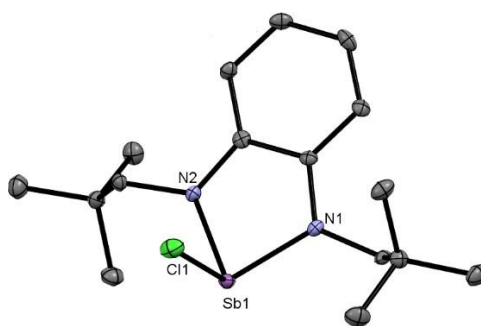


Figure 4A.1. Molecular structure of **4A.2** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) for **4A.2**: Sb1-Cl1 2.565(1), Sb1-N1 1.988(3), Sb1-N2 1.992(3). Selected bond angles (°) for **4A.2**: Cl1-Sb1-N1 102.29(1), Cl1-Sb1-N2 92.28(1), N1-Sb1-N2 81.67(1).

Single crystals suitable for X-ray diffraction studies were obtained from DCM/pentane mixture at room temperature. **4A.2** is found to be crystallized in monoclinic space group $P2_1/c$. From the molecular structure (Figure 4.1), it is evident that the geometry around the antimony centre is trigonal pyramidal and the five-membered C_2N_2Sb ring is planar whereas the chloride atom is flanked from the antimony centre and remains slightly above the plane of the ring. The Sb-Cl bond length is observed to be 2.565(1) Å which is in good agreement with the bithiophene based diaminochlorostibine by Ragogna and co-workers (2.5129(6) Å)^{6d} but longer than the other previously reported five-membered N-heterocyclic chlorostibines^{6a,6b, 9, 10, 11} and much shorter than the previously reported Sb-Cl bond length of cyclo $[(CH)_2(N^tBu)_2SbCl]$ (2.646(2) Å).^{6f} Sb-N bond distances are 1.990(3) and 1.985(3) Å are also comparable to Sb-N distances of the first reported cyclo $[Me_2Si(N^tBu)_2SbCl]$ (1.995(6) Å)¹¹ and the cyclo $[(CH)_2(N^tBu)_2SbCl]$ (1.998(4), 2.000(4) Å)^{6f} and lastly in case of the bond angles it is observed that both N-Sb-N bond angle (81.60(1)°) which is almost equivalent to phosphine containing N-heterocyclic chlorostibine by Chiu and coworkers (80.1°)¹⁰ and N-Sb-Cl bond angles (92.30(1)° and 102.24(1)°) is akin to the cyclo $[Me_2Si(N^tBu)_2SbCl]$ (99.4(2)°)¹¹ and $[(NMe_s^*)_2(SbCl)_2]$ (95.85(3)° and 102.11(3)°).⁹



Figure 4A.2. a) Molecular structure of **4A.3** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) for **4A.3**: Sb1-O1 2.457(5), Sb1-N2 1.995(4), Sb1-N1 1.986(4). Selected bond angles (°) for **4A.3**: O1-Sb1-N2 93.8(2), O1-Sb1-N1 101.6(2), N2-Sb1-N1 81.9(2), Sb1-O1-S1 144.4(3), Sb1-N2-C1 122.4(3), Sb1-N2-C2 113.6(3), Sb1-N1-C1 113.7(3), Sb1-N1-C7 123.0(3). b) Representation of the extended head-to-tail cation chains observed for compound **4A.3**. Hydrogen atoms are not shown for clarity. Short contacts are shown in green dotted lines.

Subsequently, the treatment of **4A.2** with one equivalent of AgOTf and AgSbF₆ afforded the stibonium cations, **4A.3** and **4A.4**, respectively. **4A.3** crystallizes in the monoclinic space group *P*2₁ as red crystals. The molecular structure of **4A.3** (Fig. 4.2a) reveals the close contact of triflate anion with the antimony center with the Sb–O bond distance of 2.463(5) Å, which is shorter than those in (Me₂NH)SbOTf(*i*PrN)₂C₁₀H₆ (Sb–O=2.823(9)Å),^{6a} but longer than those in C₁₀H₄Sb(OTf)(CF₃)₃ (2.082(8) Å).^{12, 13} **4A.3** exhibits cation–arene interactions in the solid state, where an extended zigzag chain is formed due to Sb⋯ π interactions ranging from 3.539(3) to 3.584(4) Å (Fig. 4.A.2b).

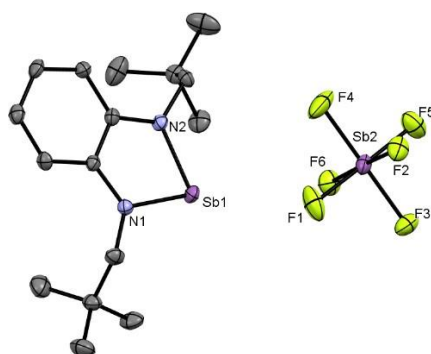


Figure 4A.3. Molecular structure of **4A.4** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) for **4A.4**: Sb1–N1 1.997(2), Sb1–N2 1.988(2), Sb1–F1 3.158. Selected bond angles (°) for **4A.4**: N1–Sb1–N2 81.71(7), Sb1–N1–C1 113.5(1), Sb1–N1–C7 123.1(1), Sb1–N2–C2 114.0(1), Sb1–N2–C12 123.6(1)

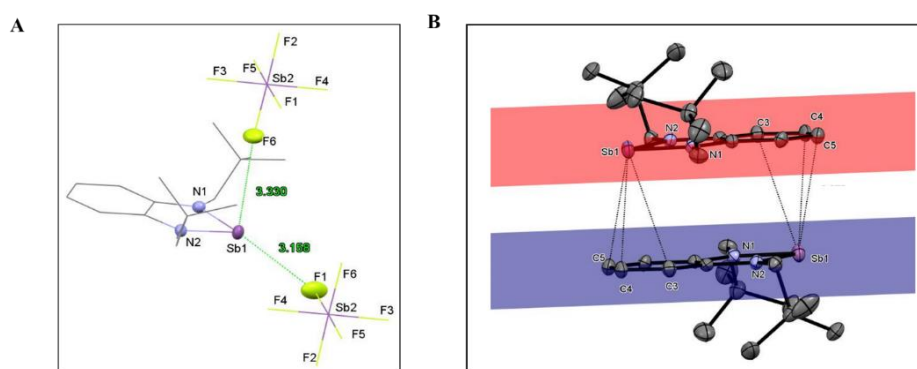


Figure 4A.4. A) Representation of the interactions with the central cationic antimony with the adjacent fluorine atoms of compound **4A.4**. B) Representation of π -stacked cation-cation interactions (antiparallel dimers) of compound **4A.4**. Hydrogen atoms are not shown for clarity.

4A.4 crystallizes in the monoclinic space group $P21/n$. The molecular structure of **4A.4** reveals an Sb(III) cationic center with a discrete SbF_6 anion (Fig. **4A.3**), displaying two long contacts with the two fluorine atoms of hexafluoroantimonate anions with the Sb-F bond distances of 3.155(2) and 3.329(1) Å (Fig. **4A.4A**).

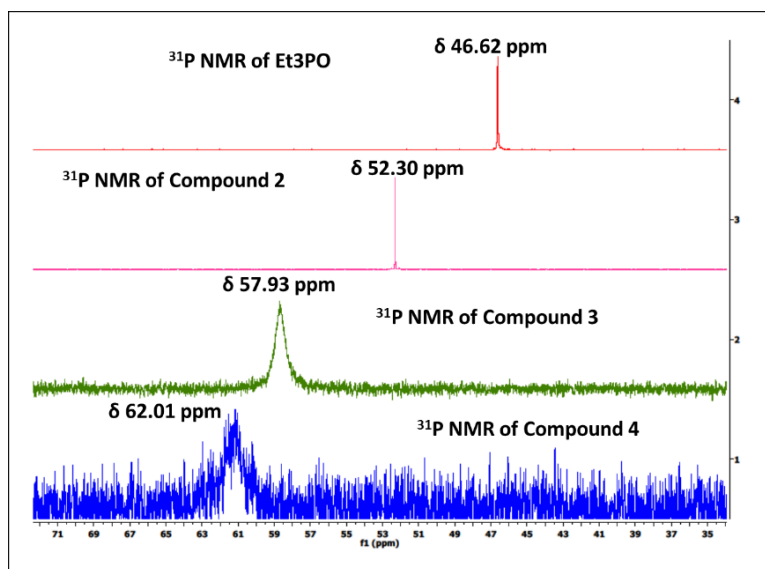


Figure 4A.5. Stacked ^{31}P NMR of compounds **4A.2**, **4A.3** and **4A.4** in presence of Et_3PO (Guttmann-Beckett method).

4A.4. Estimation of Lewis acidity of 4A.2, 4A.3 and 4A.4. Further to quantify the Lewis acidic nature of both the stibonium cations, we followed the standard Guttmann-Beckett method.¹⁴ For this experiment we used OPet_3 (Triethylphosphineoxide) and checked the chemical shift of ^{31}P . OPet_3 was treated with each compound **4A.3** and **4A.4** in a 1:1 ratio. Since both **4A.3** and **4A.4** being cationic in nature will interact with the lone pair of oxygen of OPet_3 , resulting in the chemical shifting of ^{31}P NMR. It should be mentioned that the more the downfield shifting in ^{31}P NMR more is the Lewis acidity of the compound. So, by evaluating the ^{31}P NMR, we can determine the Lewis acidity of both the compounds. In the case of compound **4A.4** ^{31}P NMR appears at δ 62.01 ppm and for compound **4A.3** it is observed at δ 57.93 ppm and for compound **4A.2** ^{31}P NMR is highly upfield shifted appearing at δ 52.30 ppm. So, from the NMR data it can be concluded that the Lewis acidity trend is like **4A.4** > **4A.3** > **4A.2** (Figure 4.5). Although from the chemical shift it can be said that compound **4A.4** is more Lewis acidic than compound **4A.3** but this small range of difference can be attributed due to the different types of interactions present in both the compounds as mentioned in the above section which is the reason for the reduction of the Lewis acidity. Further, we compared

the ^{31}P NMR values of our compounds with the previously reported boron, phosphorus, and silicon based Lewis acids (Table 4A.1), which reveals the moderate Lewis acidic character of **4A.4** as compared to them.¹⁵

Table 4A.1. Comparison of **4A.2-4A.4** with some reported Lewis acids (Guttmann Beckett method)

Entry	Compound	^{31}P NMR
1	4A.2 (OPEt_3)	52.30
2	4A.3 (OPEt_3)	57.93
3	4A.4 (OPEt_3)	61.03
4	$(\text{C}_6\text{F}_5)_3\text{B}(\text{OPEt}_3)$	76.8
5	$(\text{Me}_5\text{C}_6)\text{Si}(\text{OPEt}_3)$	85.4
6	$(\text{C}_6\text{F}_5)_3\text{PF}(\text{OPEt}_3)$	91.1

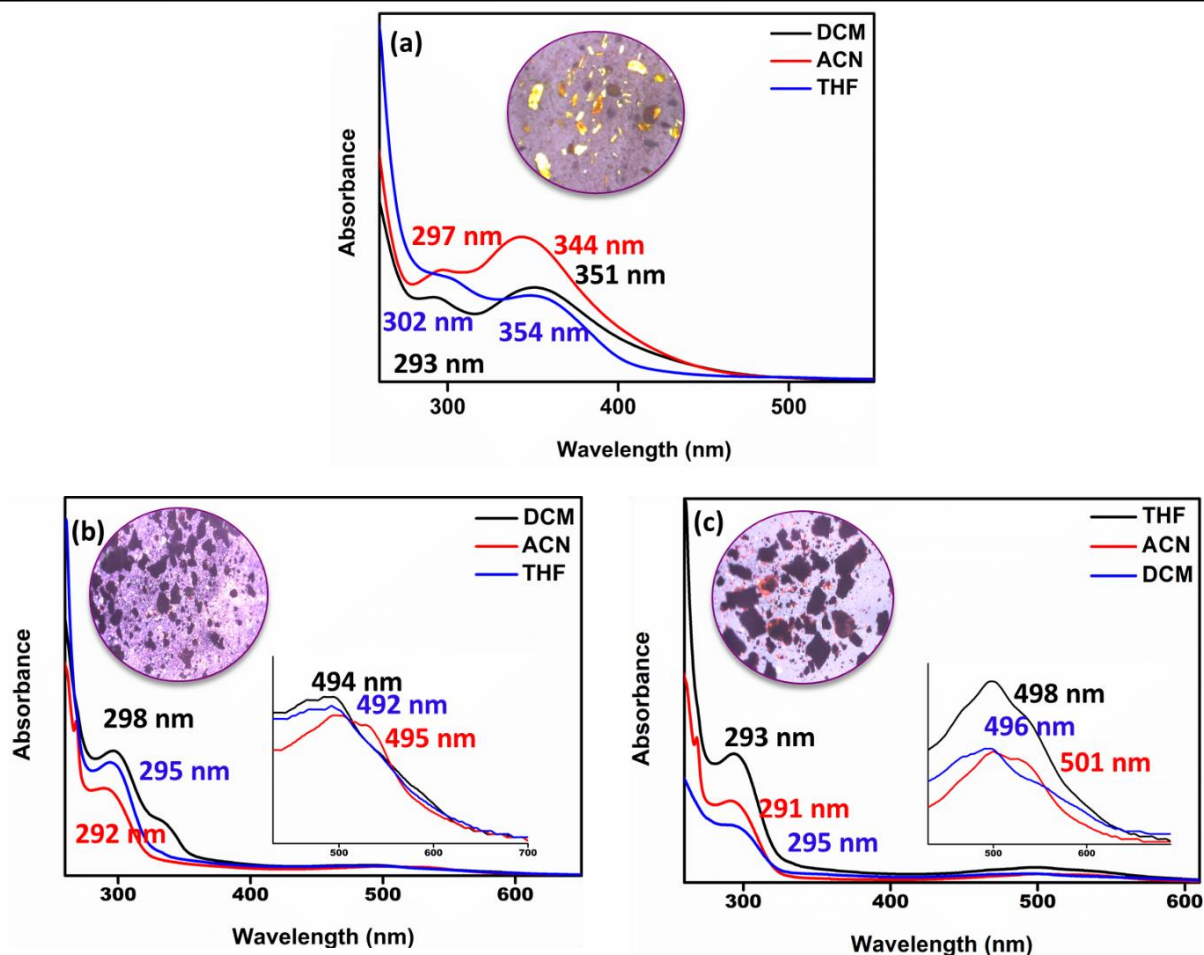


Figure 4A.6. UV-vis absorption spectra of compounds **4A.2** (a), **4A.3** (b), **4A.4** (c).

We also recorded UV-Vis absorption spectra for **4A.2–4A.4** (Figure 4.6)¹³ and performed the TD-DFT [B3LYP-D3/def2-TZVP(Sb), 6-311+G(d,p) for lighter atoms] level of theory. Our results reveal that the absorptions are due to the charge transfer from the p-electron density of the aromatic ring to the vacant p orbital of the antimony atom (Fig. 3 and Table S2, ESI†). Furthermore, the computed nucleus-independent chemical shift (NICS(0)) values of **4A.3** (10.7) and **4A.4** (11.1) reveal their aromatic character.

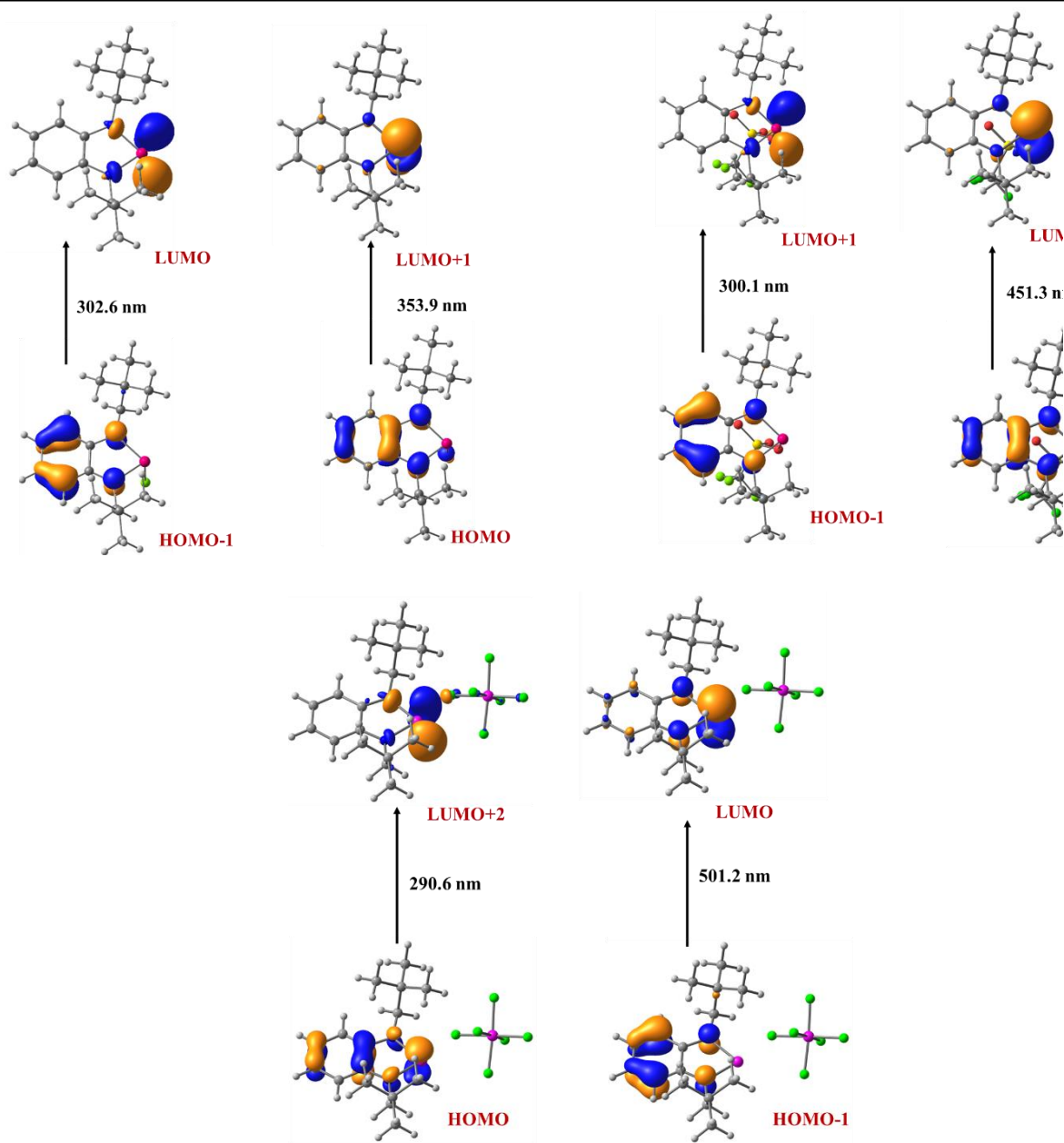
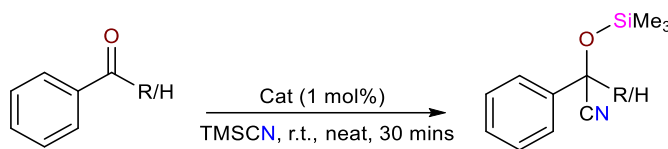


Figure 4A.7. Frontier molecular orbitals of **4A.2**, **4A.3**, **4A.4**.

4A.5. Catalytic study

Compounds **4A.2**–**4A.4** were used as catalysts for the cyanosilylation of both aldehydes and ketones using the optimized reaction conditions (Scheme 4A.2, Table 4A.1). Although a range of compounds with main-group elements has been studied for the cyanosilylation of carbonyl compounds,¹⁶⁻¹⁷ this is the first example of any antimony(III) compound to date. Among these compounds, **4A.4** was found to be the most efficient catalyst, which is in accordance with the Lewis acidic nature of **4A.2**–**4A.4**. To understand the superior behavior of **4A.4** over others the mechanism of cyanosilylation

was studied using density functional theory (DFT) with two model catalysts 3m/4m and benzaldehyde as substrate (Fig. 4A.12). The reaction begins with the coordination of TMSCN with the catalyst molecule leading to the formation of INT1, which features a donor–acceptor interaction between the nitrogen lone pair of TMSCN and the vacant p orbital of the Sb atom of the catalyst. The interaction is stronger in 4m (Sb–N distance 2.689 Å) compared to 3m (Sb–N distance 2.807 Å, Fig. 4A.14, 4A.15 and Table 4A.3,) due to more residual Lewis acidity of Sb center in 4m.



Scheme 4A.2. Cyanosilylation of carbonyls by catalyst **4A.4**.

Table 4A.2. Optimisation of benzaldehyde with catalyst **4.4**.

Entry	Catalyst	Mol (%)	Reaction time	TMSCN (equiv.)	Temperature	Yield (%)
1	4A.4	1	8 hrs	1.5 equ	60°C	>99
					RT	>99
2	4A.4	1	4 hrs	1.5	60°C	96
					RT	94
3	4A.4	1	2 hrs	1.5	60°C	98
					RT	93
4	4A.4	1	30 min	1.5	60°C	>99
	4A.4	1	30 min	1.5	RT	>99
5	4A.4	0.5	30 min	1.5	RT	No reaction
6	4A.4	1	30 min	1	RT	64
7	No catalyst		30 min	1.5	RT	Trace amount

The addition of benzaldehyde to INT1 occurs through a nucleophilic attack of the carbonyl oxygen center to the silicon center of TMSCN, which leads to the transfer of the CN group via a four-

membered transition state, TS1. At TS1, the catalysts unit anchor to TMSCN more strongly, which is reflected by the lowering of the Sb–N distance. This anchoring is more effective in 4m (Sb–N distance of 2.420 Å) in comparison to 3m (Sb–N distance of 2.516 Å), which results in a lower free energy activation barrier in the former catalyst (20.2 kcal mol⁻¹ vs. 26.3 kcal mol⁻¹ in 3m). In INT2, the anchoring becomes much weaker (Sb–N distances are 2.843 Å, and 2.872 Å for 3m and 4m, respectively). In all the intermediates and transition states, the anion remains loosely associated with the Sb center. Finally, INT2 dissociates to regenerate the catalyst molecules and releases the desired cyanohydrin product.

We further performed the solution-state NMR studies to understand the mechanism and recorded the ¹H, ¹³C, and ²⁹Si NMR spectra of the 1:1 stoichiometric reaction of **4A.4** and TMSCN (see SI for the spectra). In the ²⁹Si NMR spectrum, a new peak at δ 7.6 ppm was detected, which is downfield shifted with respect to free TMSCN (δ 11.3 ppm). The ¹H NMR spectrum shows the appearance of a new resonance at δ 0.06 ppm and a residual TMSCN peak at δ 0.34 ppm. A new peak appeared in the ¹³C spectrum at δ 2.04 ppm (–CH₃), which is different from the free TMSCN (δ = 2.26 ppm for –CH₃). In the IR spectrum, the CN stretching frequency of the intermediate appears at ν = 1686.67 cm⁻¹, which is lower than that of free TMSCN. This decrease in the IR stretching frequency indicates the decrease of the CN triple bond character, which is almost comparable to that of CN double bond,¹⁹ and there is a delocalization of electron density in the intermediate 3m/4m.

Consequently, we explored **4A.4** for the cyanosilylation of other carbonyl compounds as a catalyst (Chart 4A.1). Mainly aromatic aldehydes have been utilized for the cyanosilylation reaction, and it has been observed that both electron-donating and electron-withdrawing groups were well tolerated and afforded cyanohydrin trimethylsilyl ethers in good to excellent yields. The presence of the bromo group in ortho/meta/para (**4A.5f**: 93%, **4A.5g**: 98%, **4.5h**: 99%) positions resulted in good conversion within 30 min at the room temperature, reflecting little influence of the substitution position. In fact, no yield drop was noticed when two methyl groups were installed at the 2,6-position of the phenyl moiety (**4.5b**). Similarly, aromatic ketones afforded corresponding cyanosilylated products with 1 mol% of the catalyst loading in 30 min. A variety of substituted acetophenone with electron-withdrawing and electron-donating groups like Br– (**4.6e** and **4.6f**: 99%), OH– (**4.6d**: 94%), MeO– (**4.6b**: 99%), Me– (**4.6a**: 99%) gave excellent yields of the products (99%). Benzophenone (**4.6h**: 99%) and cyclopentanone (**4.6i**: 97%) also led to full conversion with 1 mol% of the catalyst. Aliphatic ketones such as cyclopentanone also undergo smooth reduction (**4.6i**). Further, selective

cyanosilylation of aldehydes over ketones was also observed in both intermolecular and intramolecular reactions (Scheme 4A.3). It must be noted here that among previously reported p-block cyanosilylation catalysts, only Roesky's aluminum hydride^{17c} and Inoue's germylenium cation^{17g} were capable of cyanosilylating both aldehydes and ketones.

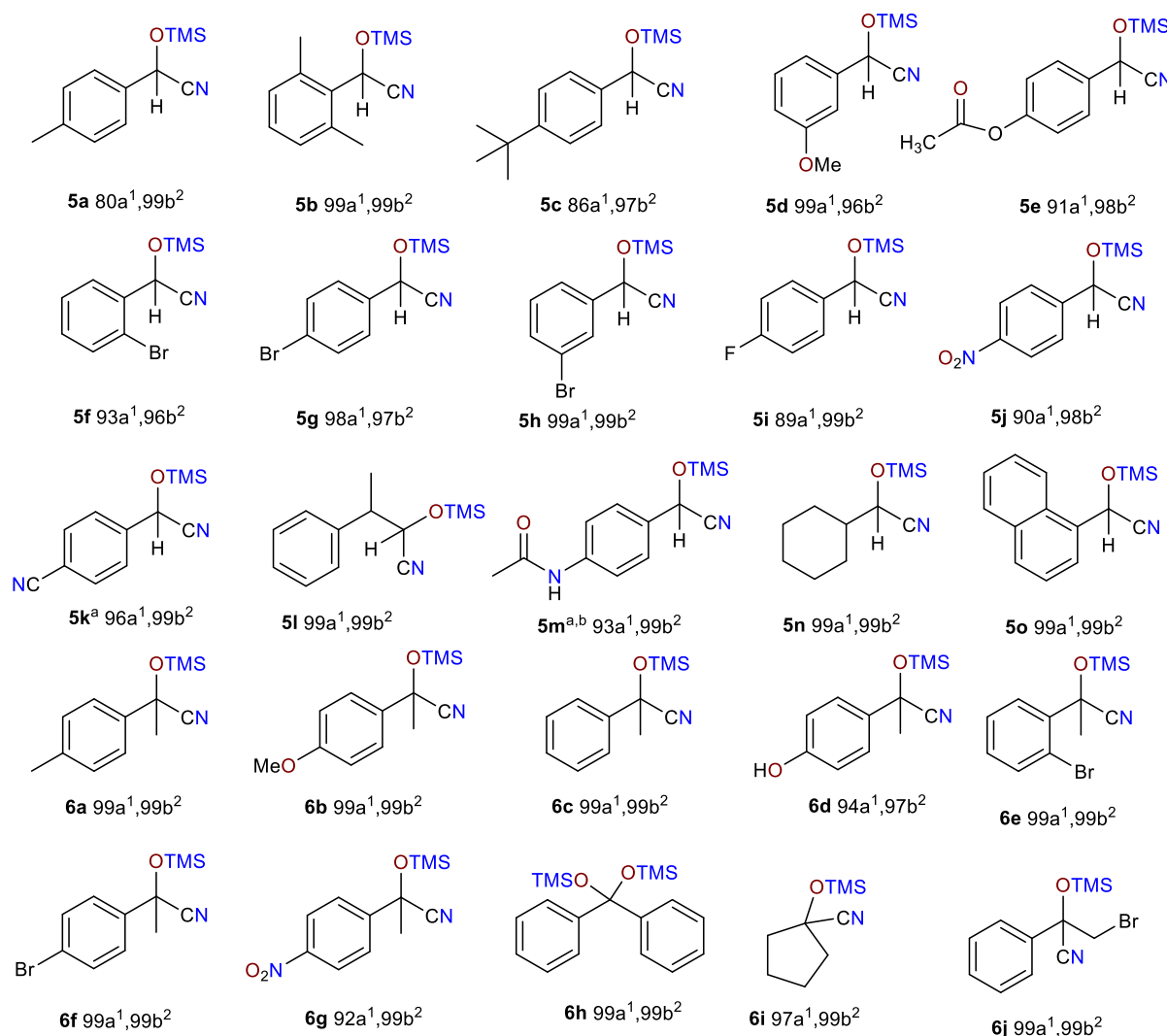
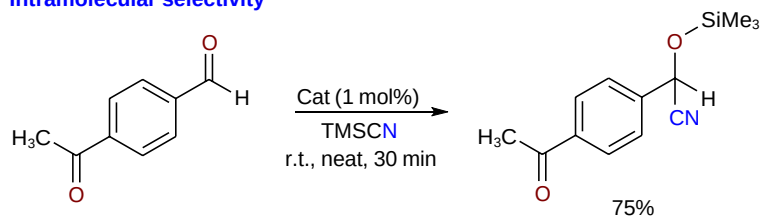


Chart 4A.1. Substrate scope for cyanosilylation of aldehydes and ketones using catalyst **4A.4**. Reaction conditions: aldehydes/ketones (0.25 mmol), TMSCN (0.38 mmol, 1.5 equiv.), neat reaction at room temperature. The catalyst loading is 1 mol%. Reaction time: 30 min. ¹Yield (%) determined by ¹H NMR spectroscopy using mesitylene as an internal standard. ²Only conversion (%) without using internal standard.

Intermolecular selectivity



Intramolecular selectivity

**Scheme 4A.3.** Selective cyanosilylation of aldehydes using **4A.4**.

4A.5. Experimental data and theoretical calculations to propose mechanistic pathway of cyanosilylation reaction.

^1H , ^{13}C and ^{29}Si NMR and IR spectra's to experimentally prove the mechanism of cyanosilylation reaction:

Figure 4A.8. ^{29}Si NMR of 1:1 reaction of catalyst **4A.4** and TMSCN in DMSO- d_6 .

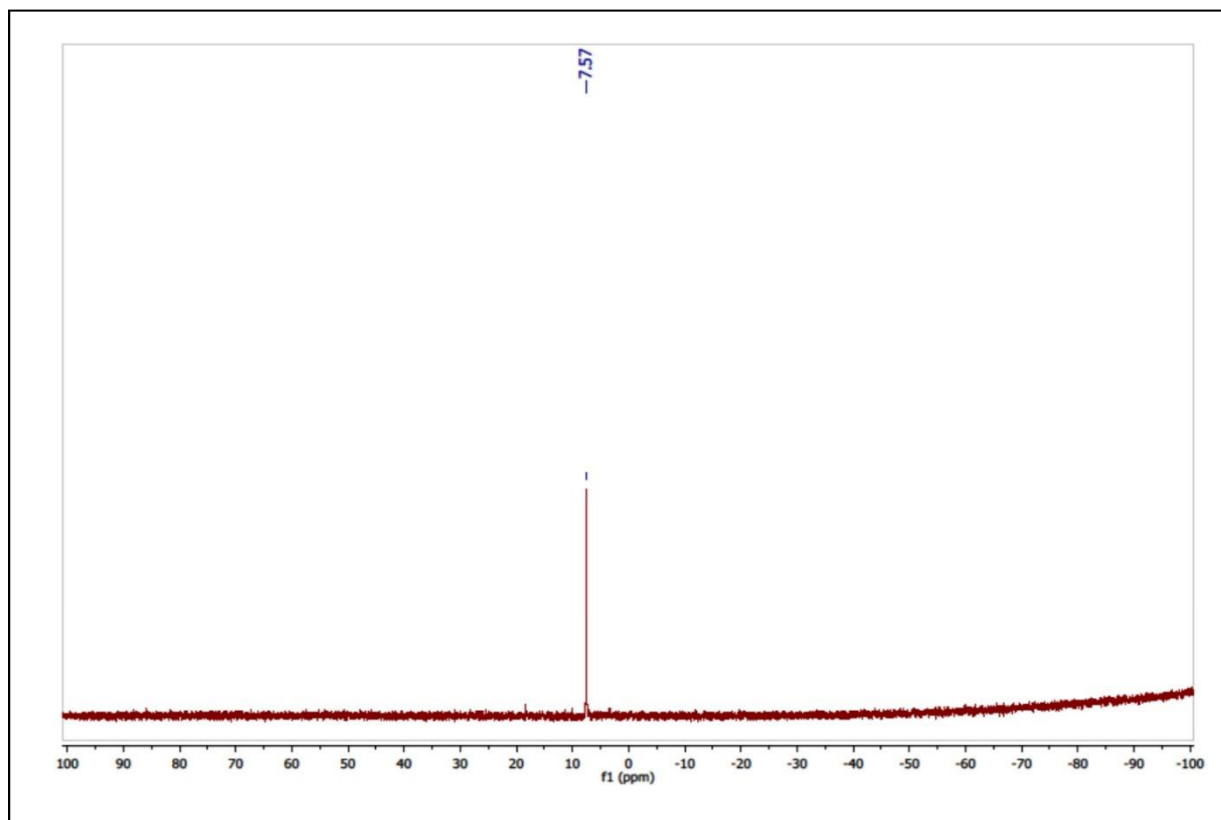
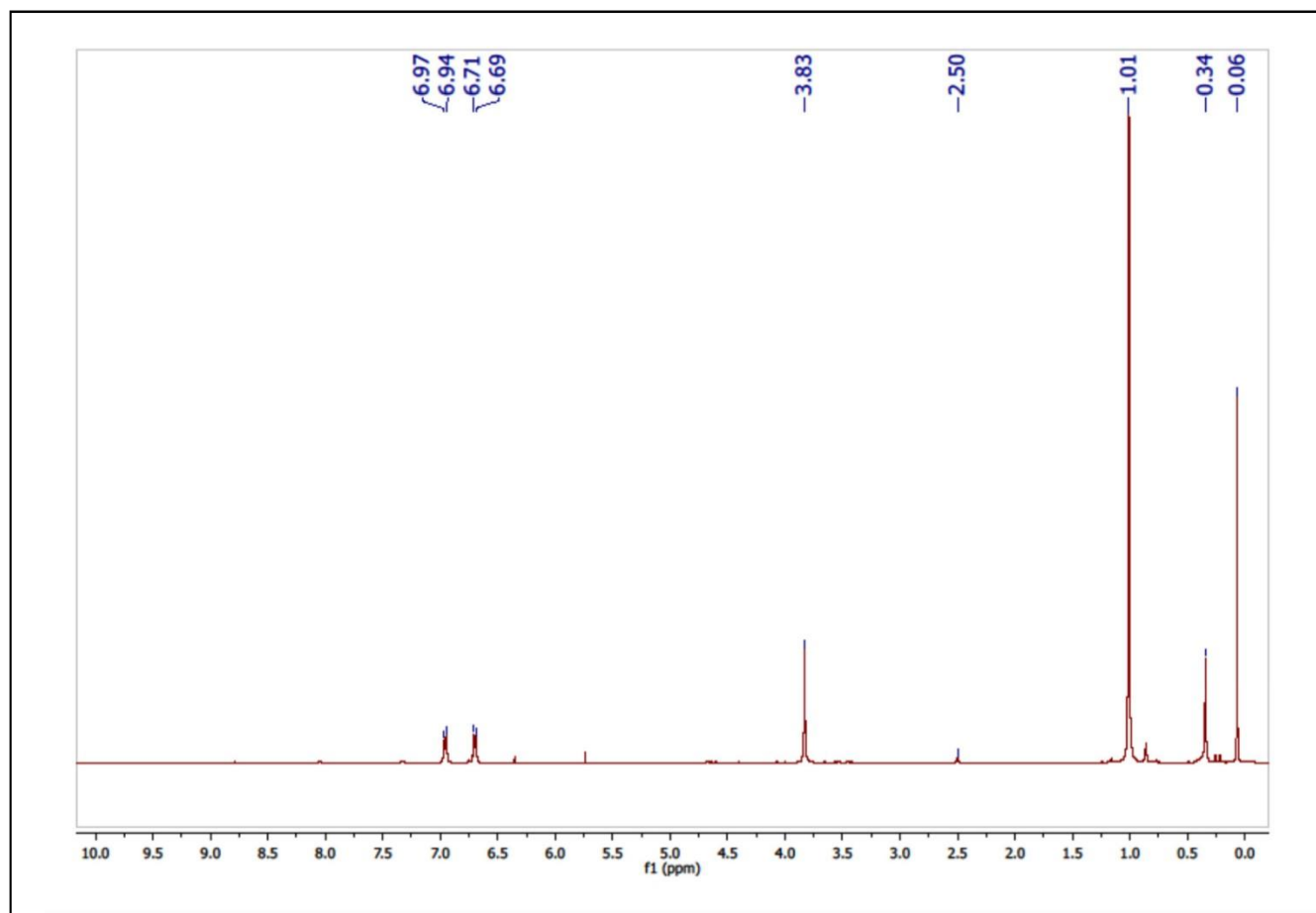


Figure 4A.9. ^1H NMR of 1:1 reaction of catalyst **4A.4** and TMS-CN in DMSO- d_6 .



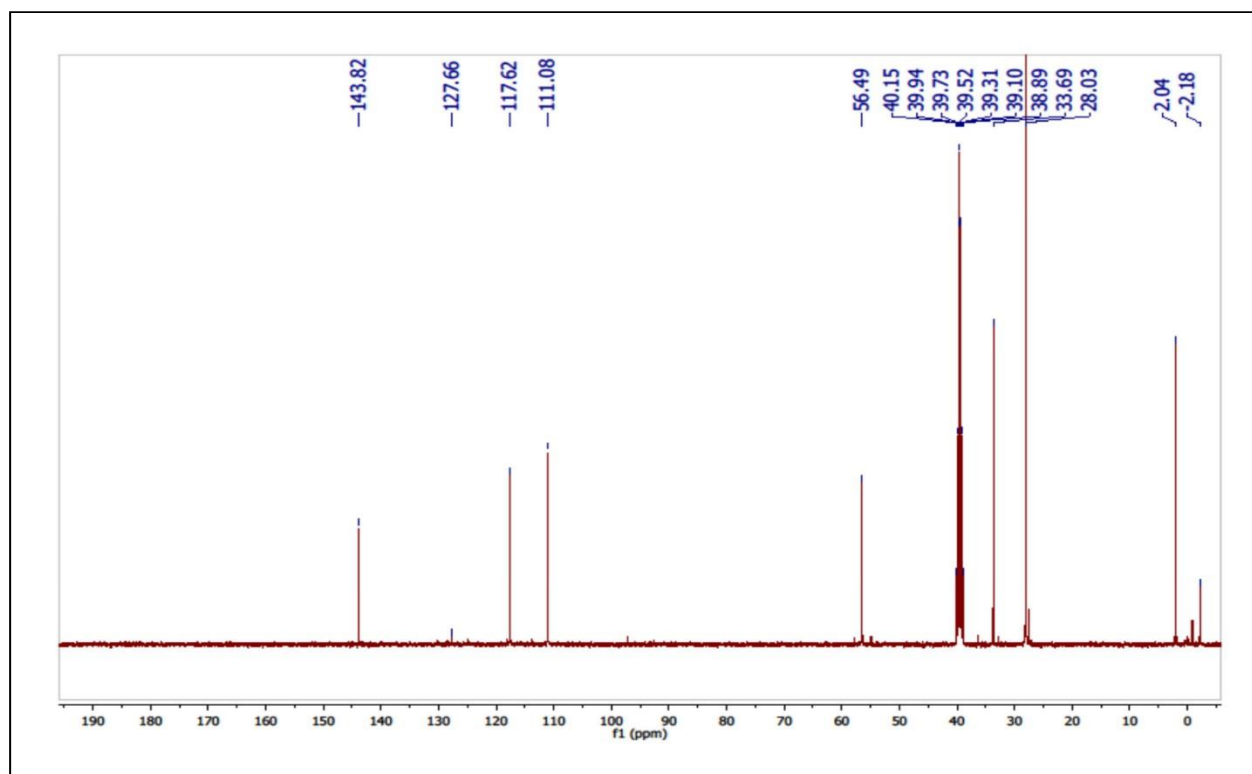


Figure 4A.10. ^{13}C NMR of 1:1 reaction of catalyst **4A.4** and TMSCN in DMSO- d_6 .

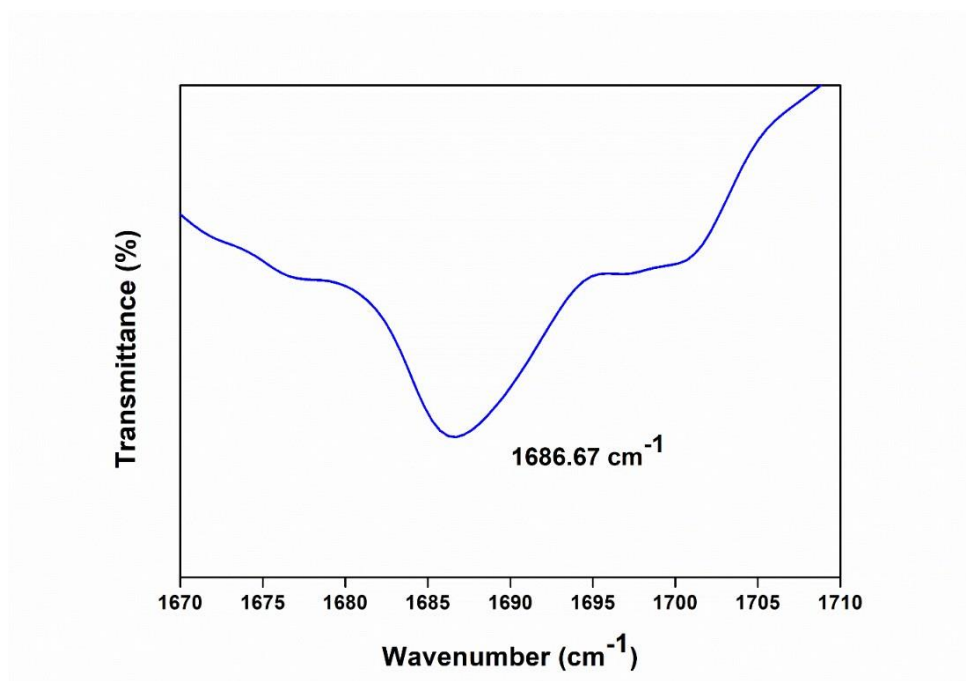


Figure 4A.11. IR spectrum of 1:1 reaction of catalyst **4A.4** and TMSCN.

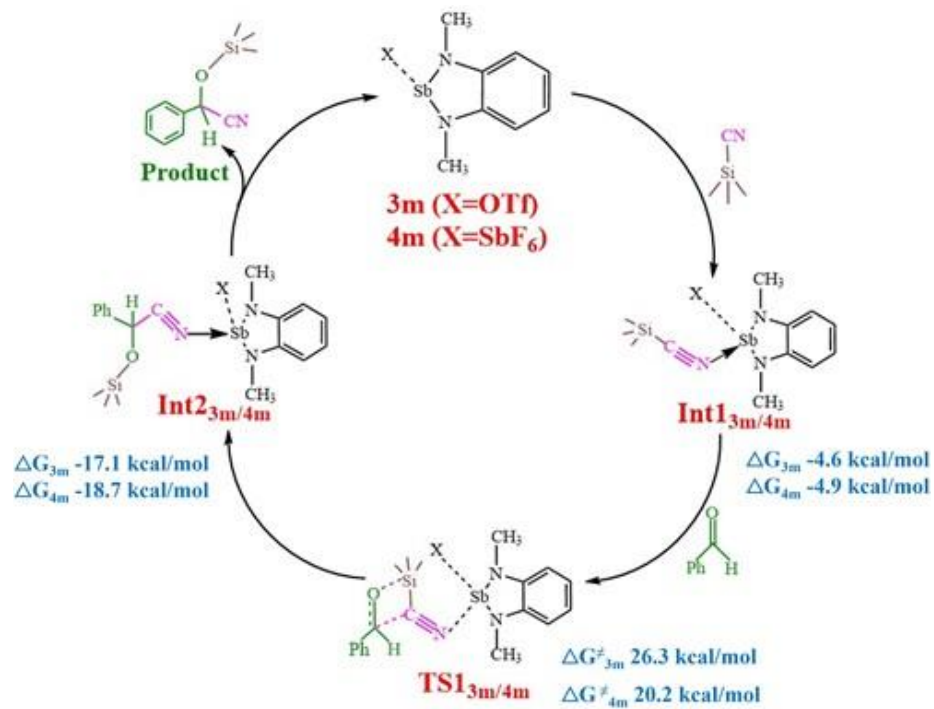


Figure 4A.12. Proposed catalytic cycle for cyanosilylation of benzaldehyde using model catalysts **3m** and **4m**.

4A.6. Computational Details:

Geometry optimized structures of the all-reaction intermediates & transition states:

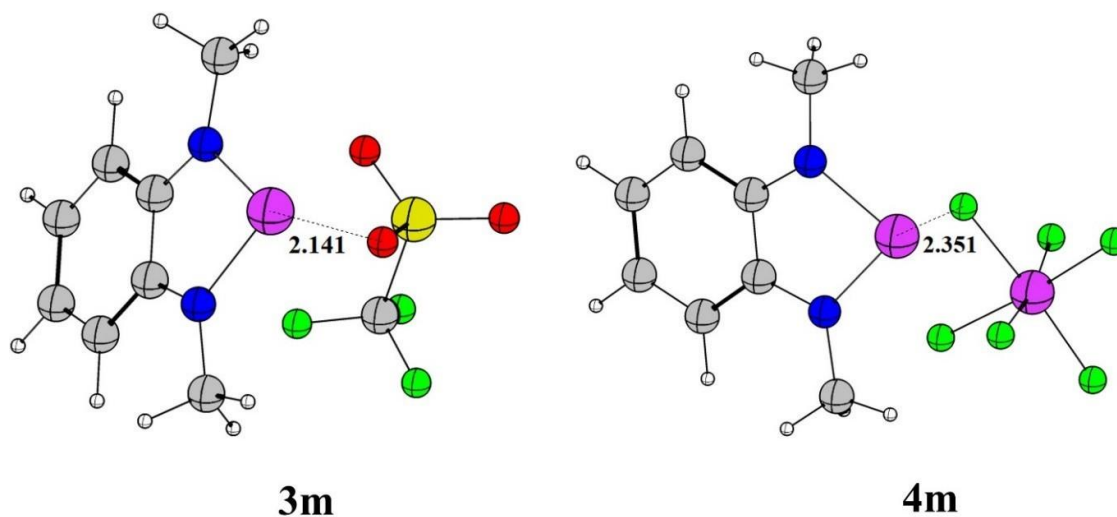


Figure 4A.13: Geometry optimized structures of catalyst **3m** and **4m**. All distances are shown in Å unit

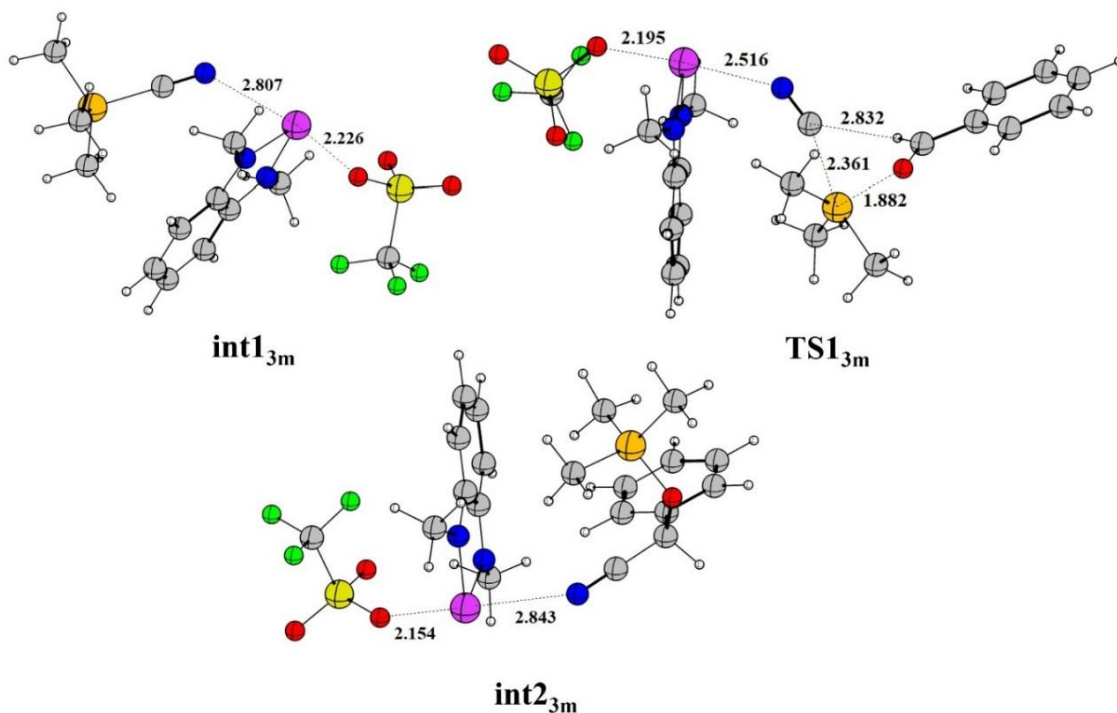


Figure 4A.14: Geometry optimized structures of various intermediates and transition states for cyanosilylation of benzaldehyde catalysed by **3m**. All distances are shown in Å unit.

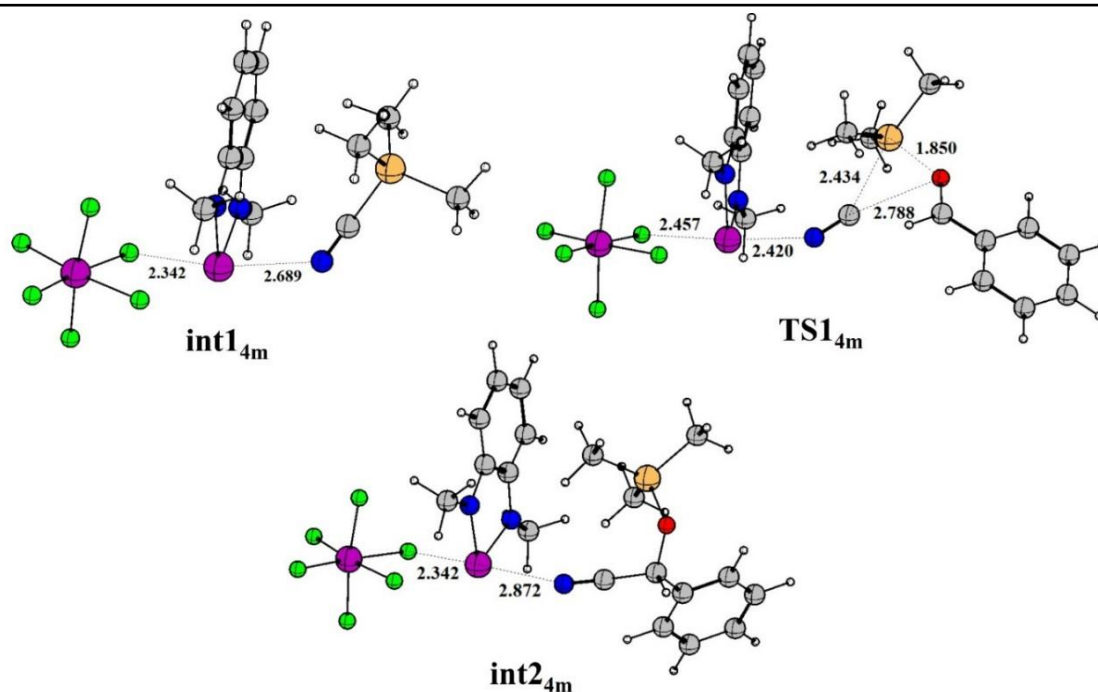


Figure 4A.15: Geometry optimized structures of various intermediates and transition states for cyanosilylation of benzaldehyde catalysed by **4m**. All distances are shown in Å unit.

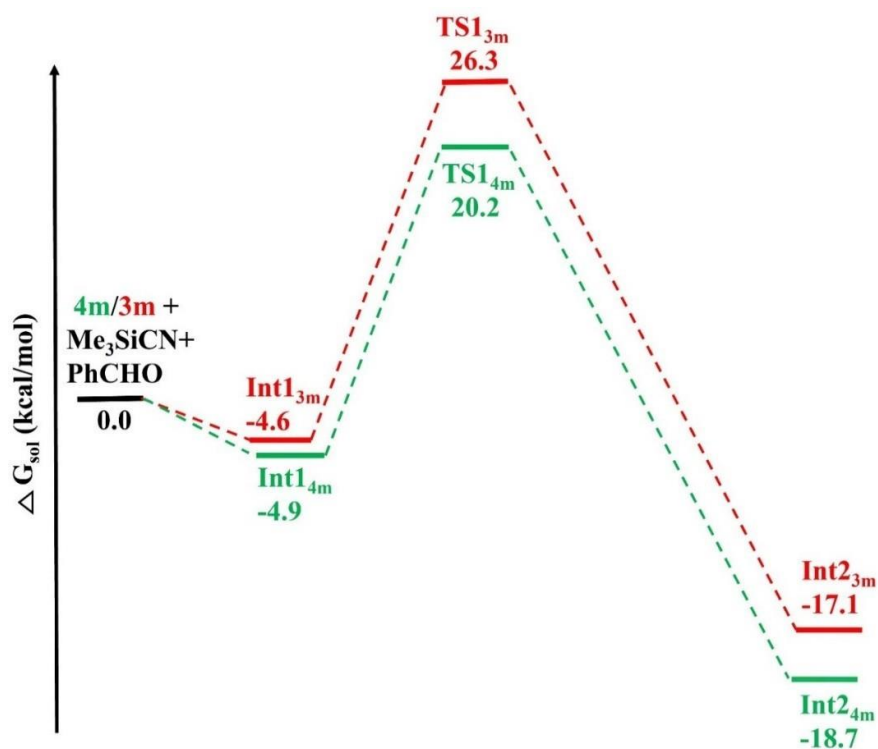


Figure 4A.16: Relative solvent-corrected Gibbs free energy profiles for the cyanosilylation of PhCHO catalyzed by **3m** and **4m**.

Table 4A.3: Selected NBO interaction energies (estimated at the second order perturbation level) in the reaction intermediates/transition states of cyanosilylation catalysed by 3m/4m. All the energies are in kcal/mol.

RI/TS	NBO interaction energy (kcal/mol)
INT1_{3m}	$\Delta E^{\text{int}}_{\text{N(p)} \rightarrow \text{Sb(p}^*\text{1)}} = 14.9$ $\Delta E^{\text{int}}_{\text{O1(p1)} \rightarrow \text{Sb(p}^*\text{1)}} = 10.1$ $\Delta E^{\text{int}}_{\text{O1(p1)} \rightarrow \text{Sb(p}^*\text{2)}} = 3.6$ $\Delta E^{\text{int}}_{\text{O1(p2)} \rightarrow \text{Sb(p}^*\text{1)}} = 2.6$ $\Delta E^{\text{int}}_{\text{O2(p1)} \rightarrow \text{Sb(p}^*\text{1)}} = 47.9$ $\Delta E^{\text{int}}_{\text{O2(p1)} \rightarrow \text{Sb(p}^*\text{2)}} = 27.5$
TS1_{3m}	$\Delta E^{\text{int}}_{\text{N(p)} \rightarrow \text{Sb(p}^*\text{1)}} = 39.9$ $\Delta E^{\text{int}}_{\text{N(p)} \rightarrow \text{Sb(p}^*\text{2)}} = 2.6$ $\Delta E^{\text{int}}_{\text{O1(p1)} \rightarrow \text{Sb(p}^*\text{1)}} = 20.4$ $\Delta E^{\text{int}}_{\text{O1(p1)} \rightarrow \text{Sb(p}^*\text{2)}} = 5.8$ $\Delta E^{\text{int}}_{\text{O2(p1)} \rightarrow \text{Sb(p}^*\text{1)}} = 64.8$ $\Delta E^{\text{int}}_{\text{O2(p1)} \rightarrow \text{Sb(p}^*\text{2)}} = 18.9$
INT14_m	$\Delta E^{\text{int}}_{\text{N(p)} \rightarrow \text{Sb(p}^*\text{1)}} = 21.4$
TS14_m	$\Delta E^{\text{int}}_{\text{N(p)} \rightarrow \text{Sb(p}^*\text{1)}} = 38.8$ $\Delta E^{\text{int}}_{\text{N(p)} \rightarrow \text{Sb(p}^*\text{2)}} = 15.9$

Electronic structure of all the systems studied are done by density functional theory. For geometry optimization M062X²⁰⁻²¹ exchange-correlation functional along with 6-311G(d,p) basis set is used for lighter atoms (C, H, B, N, O, F). For Sb, we have used def2TZVP basis set in combination with Stuttgart-Dresden pseudopotential.²² All optimized geometries are characterized by harmonic vibrational analysis to recognize the structures as minima (all positive frequencies) or transition state (one negative frequency). Transition states (TS) are verified through intrinsic reaction coordinate (IRC) calculations. All thermochemical data are estimated within the ideal gas-rigid rotor-harmonic oscillator approximation at 298.15 K and 1 atm pressure. SMD model is used to take into account solvent effects as proposed by Truhlar and Cramer. The computed entropic corrections are further scaled to 75% in order to take into

account the quenching of translational and rotational degrees of freedom in the solution phase.²³⁻²⁶ Photophysical properties of these catalysts are calculated using time-dependent density functional theory (TD-DFT) methods using B3LYP-D3²⁷⁻³¹ exchange-correlation functional.

The model catalysts 3m and 4m are used for the mechanistic study wherein the substituent on the N centres in **4A.3** and **4A.4** are replaced by methyl groups, which does not impose major changes in the electronic and structural properties of the catalysts. The obvious change in the steric environment also does not affect the reactivity as found in our initial test calculations with full catalyst structures. Note that, we have previously used similar model structures to study the bonding properties of silylene chalcogenone complexes.

We have also calculated the anion dissociation energies, which run as **4A.2** > **4A.3** > **4A.4**. Note that this trend is in agreement with the experimentally measured Lewis acidity trend (**4A.4** > **4A.3** > **4A.2**). Thus, it can be said that for catalyst **4A.4**, the anion SbF_6^- is loosely bound with the cationic Sb centre. As a consequence, **4A.4** possess higher Lewis acidity compared to **4A.2** and **4A.3**. This result is also in agreement with the Natural bonding analysis (NBO) results which shows the absence of any interaction between the anion SbF_6^- and the cationic Sb centre in catalyst **4A.4**.

Anion dissociation energies-

Compound **4A.2** = [cationic Sb moiety] + Cl^- $\Delta G = 62.6 \text{ kcal/mol}$

Compound **4A.3** = [cationic Sb moiety] + OTf $\Delta G = 42.0 \text{ kcal/mol}$

Compound **4A.4** = [cationic Sb moiety] + SbF_6^- $\Delta G = 27.8 \text{ kcal/mol}$

4A.7. Conclusion

In summary, we have synthesized two novel stibonium cations, **4A.3** and **4A.4** via the heterolysis of Sb–Cl bond of the chlorostibine (**4A.2**). The molecular structures of **4A.2–4A.4** are established by single-crystal X-ray diffraction studies. Further, **4A.4** was found to be an efficient catalyst for the cyanosilylation of both aldehydes and ketones. To understand the mechanism, DFT calculations and NMR experiments were performed.

4A.8. References

1. See recent reviews; (a) Lipshultz, J. M.; Li, G.; Radosevich, A. T. *J. Am. Chem. Soc.* **2021**, *143*, 1699–1721; (b) Sen, N.; Khan, S. *Chem. Asian J.*, **2021**, *16*, 705–719; (c) Shegavi, M. L.; Bose, S. K. *Catal. Sci. Technol.*, **2019**, *9*, 3307–3336; (d) Pahar, S.; Kundu, G.; Sen, S. S. *ACS Omega*, **2020**, *5*, 25477–25484.
2. (a) Hsu, C.-P.; Liu, Y.-H.; Boobalan, R.; Lin, Y.-F.; Chein, R.-J.; Chiu, C.-W. *Organometallics*, **2021**, *40*, 1244–1251; (b) Franz, D.; Inoue, S. *Chem. Eur. J.*, **2019**, *25*, 2898–2926; (c) Friedrich, A.; Eyselein, J.; Elsen, H.; Langer, J.; Pahl, J.; Wiesinger, M.; Harder, S. *Chem. Eur. J.*, **2021**, *27*, 7756–7763; (d) Sarkar, D.; Dutta, S.; Weetman, C.; Schubert, E.; Koley, D.; Inoue, S. *Chem. Eur. J.*, **2021**, *27*, 13072–13078.
3. (a) Dagorne, S.; Atwood, D. A. *Chem. Rev.*, **2008**, *108*, 4037–4071; (b) Engesser, T. A.; Lichtenthaler, M. R.; Schleep, M.; Krossing, I. *Chem. Soc. Rev.*, **2016**, *45*, 789–899; (c) Koelle, P.; Noeth, H. *Chem. Rev.*, **1985**, *85*, 399–418.
4. (a) Miaskiewicz, S.; Reed, J. H.; Donets, P. A.; Oliveira, C. C.; Cramer, N. *Angew. Chem., Int. Ed.*, **2018**, *57*, 4039–4042; (b) Rao, B.; Chong, C. C.; Kinjo, R. *J. Am. Chem. Soc.*, **2018**, *140*, 652–656; (c) Lundrigan, T.; Welsh, E. N.; Hynes, T.; Tien, C.-H.; M. Adams, R.; Roy, K. R.; Robertson, K. N.; Speed, A. W. H. *J. Am. Chem. Soc.*, **2019**, *141*, 14083–14088.
5. (a) Pan, B.; Gabbaï, F. P. *J. Am. Chem. Soc.*, **2014**, *136*, 9564–9567; (b) Yang, M.; Gabbaï, F. P. *Inorg. Chem.*, **2017**, *56*, 8644–8650; (c) Hirai, M.; Cho, J.; Gabbaï, F. P. *Chem. Eur. J.*, **2016**, *22*, 6537–6541.
6. (a) Spinney, H. A.; Korobkov, I.; Richeson, D. S. *Chem. Commun.*, **2007**, 1647–1649; (b) Spinney, H. A.; Korobkov, I.; DiLabio, G. A.; Yap, G. P. A.; Richeson, D. S. *Organometallics*, **2007**, *26*, 4972–4982; (c) Lehmann, M.; Schulz, A.; Villinger, A. *Angew. Chem., Int. Ed.*, **2012**, *51*, 8087–8091; (d) Price, J. T.; Lui, M.; Jones, N. D.; Ragogna, P. J. *Inorg. Chem.*, **2011**, *50*, 12810–12817; (e) Tulchinsky, Y.; Kozuch, S.; Saha, P.; Mauda, A.; Nisnevich, G.; Botoshansky, M.; Shimon, L. J. W.; Gandelman, M. *Chem. Eur. J.*, **2015**, *21*, 7099–7110; (f) Gudat, D.; Gans-Eichler T.; Nieger, M. *Chem. Commun.*, **2004**, 2434–2435; (g) Olaru, M.; Duvinage, D.; Lork, E.; Mebs, S.; Beckmann, J. *Angew. Chem., Int. Ed.*, **2018**, *57*, 10080–10084.
7. Hahn, F. E.; Wittenbecher, L.; Boese, R.; Blaßer, D. *Chem. Eur. J.*, **1999**, *5*, 1931–1935.

-
-
8. (a) H. Braunschweig, B. Gehrhus, P. B. Hitchcock and M. F. Lappert, *Z. Anorg. Allg. Chem.*, **1995**, 621, 1922–1928; (b) O. Ku^uhl, P. Lo^onnecke and J. Heinicke, *Polyhedron*, **2001**, 20, 2215–2222.
 9. Lehmann, M.; Schulz, A.; Villinger, A., Synthesis and Characterization of 1,3-Dihalogeno-2,4-bis (2,4,6-tri-tert-butylphenyl)-cyclo-1,3-distiba-2,4-diazanes, $[X-Sb(\mu-NR)]_2$ (X= F, Cl, Br, and I). *Eur. J. Inorg. Chem.* **2010**, 5501-5508
 10. Srungavruksham, N. K.; Liu, Y.-H.; Tsai, M.-K.; Chiu, C.-W., PSb⁺P Ligand: Platform for a Stibonium to Transition-Metal Interaction. *Inorg. Chem.* **2020**, 59, 4468-4474.
 11. Ma, X.; Ding, Y.; Roesky, H. W.; Sun, S.; Yang, Z., Synthesis and crystal structures of antimony (III) complexes with a bis (amino) silane ligand. *Z. Anorg. Allg. Chem.* **2013**, 639, 49-52.
 12. Ould, D. M. C.; Rigby, A. C.; Wilkins, L. C.; Adams, S. J.; Platts, J. A.; Pope, S. J. A.; Richards, E.; Melen, R. L. *Organometallics*, **2018**, 37, 712–719.
 13. Burford, N.; Macdonald, C. L. B.; LeBlanc, D. J.; Cameron, T. S. *Organometallics*, **2000**, 19, 152–155.
 14. (a) Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.*, **1975**, 106, 1235–1257; (b) Beckett, M. A.; Strickland, G. C.; Holland, J. R.; Varma, K. S. *Polymer*, **1996**, 37, 4629–4631.
 15. Grobekappenberg, H.; Reibmann, M.; Schmidtman, M.; Muller, T. *Organometallics*, **2015**, 34, 4952–4958.
 16. Siwatch, R. K.; Nagendran, S. *Chem. Eur. J.*, **2014**, 20, 13551–13556.
 17. (a) Bisai, M. K.; Das, T.; Vanka, K.; Sen, S. S. *Chem. Commun.*, **2018**, 54, 6843–6846; (b) Wang, W.; Luo, M.; Li, J.; Pullarkat, S. A.; Ma, M. *Chem. Commun.*, **2018**, 54, 3042–3044; (c) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem., Int. Ed.*, **2015**, 54, 10225–10229; (d) Zeng, X.-P.; Cao, Z.-Y.; Wang, X.; Chen, L.; Zhou, F.; Zhu, F.; Wang, C.-H.; Zhou, J. *J. Am. Chem. Soc.*, **2016**, **138**, 416–425; (e) Martin, A. L. L.; Bergman, R. G.; Tilley, T. D. *J. Am. Chem. Soc.*, **2015**, 137, 5328–5331; (f) Swamy, V. S. V. S. N.; Bisai, M. K.; Das, T.; Sen, S. S. *Chem. Commun.*, **2017**, 53, 6910–6913; (g) Sarkar, D.; Dutta, S.; Weetman, C.; Schubert, E.; Koley, D.; Inoue, S. *Chem. Eur. J.*, **2021**, 27, 13072–13078.
 18. Dasgupta, R.; Das, S.; Hiwase, S.; Pati, S. K.; Khan, S. *Organometallics*, **2019**, 38, 1429–1435.
 19. Suydam, F. H. *Anal. Chem.*, **1963**, 35, 193–195.
 20. Zhao, Y.; Truhlar, D. G. *Theoretical chemistry accounts* **2008**, 120, 215-241.
 21. Zhao, Y.; Truhlar, D. G. *Accounts of chemical research* **2008**, 41, 157-167
-

22. Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theoretica chimica acta* **1990**, 77, 123-141.
23. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *The Journal of Physical Chemistry B* **2009**, 113, 6378- 6396.
24. Wertz, D. H. *J. Am. Chem. Soc.* **1980**, 102, 5316-5322.
25. Deubel, D. V. *J. Am. Chem. Soc.* **2008**, 130, 665- 675.
26. Rios, P.; Rodriguez, A.; Lopez-Serrano, J. *ACS Catalysis* **2016**, 6, 5715-5723.
27. Lee, C.; Yang, W.; Parr, R. G. *Physical review B* **1988**, 37, 785.
28. Grimme, S. *Journal of computational chemistry* **2004**, 25, 1463- 1473.
29. Grimme, S. *Journal of computational chemistry* **2006**, 27, 1787-1799.
30. Grimme, S.; Antony, J. Ehrlich, S.; Krieg, H. *The Journal of Chemical Physics* **2010**, 132, 154104.
31. Grimme, S.; Ehrlich, S.; Goerigk, L. *Journal of computational chemistry* **2011**, 32, 1456-1465.

Chapter 4b

Synthesis of stibane-manganese complex and its application in homogeneous catalysis

4B.1. Introduction

To date, transition metal stibine complexes have not been reported. Organometallic chemistry mainly flourishes on the base of a single metal centre in a compound and those metal centres can exhibit different chemical reactivities and homogeneous catalysis as well. Recent times have witnessed the chemistry of heterobimetallic complexes as they have attracted much attention with their significant role in coordination chemistry as well as in catalysis.¹ The synthesis of heterobimetallic complexes mainly involves ditopic ligand backbone because ditopic ligands have two binding sites that can bind two metal centres.² Heterobimetallic complexes are utilized also in various fields like material chemistry,³ medicinal chemistry,⁴ photoredox catalysis⁵ and photoactive polymers⁶, etc. Nowadays heterobimetallic complexes containing both main group elements and transition metals have attracted much attention in the field of homogeneous catalysis.⁷

In our work, we have employed the previously reported chlorostibine along with NaMn(CO)_5 which resulted in the formation of a cyclic four-membered heterobimetallic complex containing both antimony center as well as manganese. There is only one report with bismuthane-transition metal complexes.⁸ Here we have reported the synthesis of the stibine-transition metal complex for the first time. We have also investigated the catalytic potential of our synthesized heterobimetallic Sb-Mn complex.

4B.2. Experimental Section

4B.2.1. General remarks

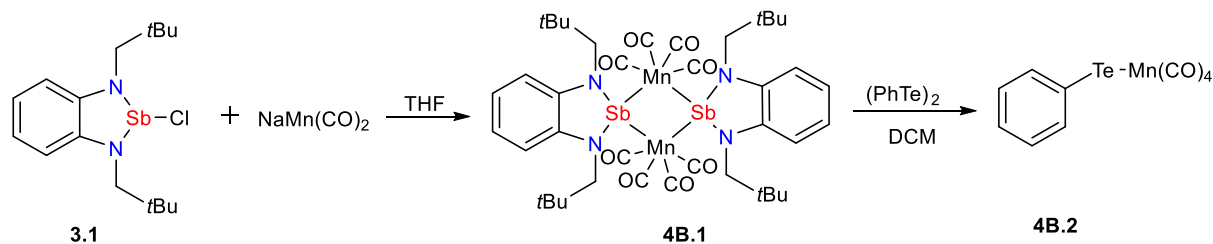
The whole process was executed under an inert atmosphere of argon using standard Schlenk techniques or in a glovebox. Solvents used were purified using an MBRAUN solvent purification system MBSPS-800. SbCl_3 , AgOTf , AgSbF_6 were purchased from Sigma-Aldrich and Alfa Aesar. They were used without further purification. ^1H , ^{13}C , ^{29}Si , NMR spectra were recorded on a Bruker spectrometer in CDCl_3 as the solvent with an external standard (SiMe_4 for ^1H , ^{13}C ,). Mass spectra were recorded using an AB Sciex, 4800 MALDI TOF/TOF, and HRMS was recorded on a Waters Synapt, USA. Yields are calculated based on the isolated crystals.

4B.2.2. Synthesis of compounds 4B.1-4B.2.

Synthesis of compound 4B.1. THF (30 ml) was added to a 100 ml flask containing both compound 3.1 and $\text{NaMn}(\text{CO})_5$ and kept on stirring for overnight. The color of the solution immediately became dark brown. THF was evaporated and then toluene (30 ml) was added to the reaction mixture and the extraction was done in toluene itself. The solution was reduced to 5 ml and dropwise pentane was added to it. Then the reaction mixture was kept at 0°C for crystallization. Brown-colored crystals were grown at 0°C .

Synthesis of compound 4B.2. Toluene (30 ml) was taken in a 100 ml Schenk flask containing both compound 4B.1 and $(\text{PhTe})_2$ and the reaction mixture was kept and stirring for overnight. The color of the solution immediately became red from dark brown. The extraction was done in toluene itself. The solution was evaporated, reduced to 5 ml, and kept at room temperature for crystallization. Red-coloured crystals were grown at room temperature.

4B.3. Results and Discussion



Scheme 4B.1. Synthesis of compounds 4B.1 and 4B.2.

After the successful generation of stibonium cations, we aimed to functionalize the chloride atom of compound **3.1** with transition metal salt. In doing so we treated compound **3.1** with 1 equivalent of NaMn(CO)_5 and it afforded the desired compound **4B.1**. We recorded the IR spectrum of the compound **4B.1** and the peaks appeared at 2090 cm^{-1} and 1946 cm^{-1} which are almost similar to that of the previously reported bismuth-manganese compound ($2083, 1995\text{ cm}^{-1}$) by Lichtenberg and co-workers.⁸ After the synthesis of compound **4B.1** we treated it with diphenyl ditelluride in 1:1 ratio in DCM which afforded compound **4B.2**.

4B.4. Conclusion

Here we have synthesized a new antimony-manganese complex which is dimeric in nature. Further we have tried some reactivities like bond activation. Due to the presence of both antimony and manganese, we expect this complex to show efficient catalytic activity. So we are further studying the catalytic activities with the newly synthesized antimony-manganese compound.

4B.5. References

1. a) Kamboj, R. C.; Chaudhury, A. *Chem Sci Rev Lett* **2016**, 5, 170-192. b) Bullock, R. M. *Acc. Chem. Res.* **1987**, 20, 167-173.
2. Parker, D. J. *Chem. Soc. Chem. Commun.* **1985**, 1129-1131. b) Bratanovici, B. I.; Nicolescu, A.; Shova, S.; Dascălu, I. A.; Ardeleanu, R.; Lozan, V.; Roman, G. *Research on Chemical Intermediates* **2020**, 46, 1587–1611.
3. Hardy, M.; Lutzen, A. *Chem. Eur. J.* **2020**, 26, 13332–13346.
4. Chaudhary, A.; Singh, A.; Rawat, E.; Singh, R. V. *Chem Sci Rev Lett* **2016**, 5, 98-119.
5. Bayer, L.; Birenheide, B. S.; Krämer, F.; Lebedkin, S.; Breher, F. *Chem. Eur. J.* **2022**, 28, doi.org/10.1002/chem.202201856.
6. Bera, M. K.; Ninomiya, Y.; Higuchi, M. *Molecules* **2020**, 25, 5261-5270.
7. a) Nekoueishahraki, B.; Jana, A.; Roesky, H. W.; Mishra, L.; Stern, D.; Stalke, D. *Organometallics* **2009**, 28, 5733–573. b) Levent, E.; Sala, O.; Wilm, L. F. B.; Löwea, P.; Dielmann, F. *Green Chem.* **2021**, 23, 2747–2755.
8. Ramler, J.; Krummenacher, I.; Lichtenberg, C. *Angew. Chem. Int. Ed. Engl.* **2019**, 58, 12924-12929.

Chapter 5

Donor free bismuthenium cation as an efficient cyanosilylation catalyst

5.1. Introduction

The role of transition metals in the field of homogeneous catalysis has been well-known for years.¹ Recently, there has been an urge to surrogate the transition metals by more earth-abundant and less toxic main group elements. Cyanosilylation is a well-established organic transformation of carbonyl moieties to the cyanohydrin product through forming C-C bonds. The first example of cyanohydrin synthesis was reported in 1832 by Winkler and coworkers.² Due to the less toxicity and ease of handling than the other cyanide sources like HCN and NaCN, Me₃SiCN has mainly been used for cyanosilylation.³ A wide variety of biologically important compounds like β -amino alcohols, α -hydroxy acids, α -hydroxy ketones, and α -amino acids can be easily acquired through the cyanosilylation of carbonyls.⁴ The field of homogeneous catalysis has witnessed a large number of reports on cyanosilylation mainly by transition metals.⁵ Later on, the main group elements proved to be very efficient homogeneous catalysts because of their low cost, low toxicity, and sustainability. In view of this development of the main group elements, several main group catalysts have been developed as efficient homogeneous catalysts for cyanosilylation utilizing Me₃SiCN.⁶

Cyanosilylation of carbonyls has been well reported by groups 13 and 14 elements (Chart 5.1). Among the various earth-abundant elements aluminum being the 3rd most earth-abundant element, it has been extensively utilized as an efficient Lewis acidic cyanosilylation catalyst.⁷ Parallel to group 13 elements there has been recent development by the group 14 elements. The first report of silicon compound as cyanosilylation catalyst is by Tilley and coworkers.⁸ After that Sen and coworkers also reported cyanosilylation by benz-amidinato chlorosilane.⁹ Following this Nagendran and coworkers for the first time reported cyanosilylation of aldehydes by cyanogermylene.¹⁰ Our group also reported the same by N-heterocyclic germylene and stannylene.¹¹ Coming to group 15 only three reports are there to date. Other than the previously reported aluminum cation as a cyanosilylation catalyst our group has recently reported stibonium cation as an efficient Lewis acid catalyst for the cyanosilylation of carbonyls.¹² Based on the previous literature survey it has been observed that although various bismuthenium ions¹³ have been reported, only one Bi-based siloxane has been utilized for cyanosilylation.¹⁴ So bismuthenium cations still remain untouched as the Lewis acid catalyst for the cyanosilylation of carbonyls. Bismuth is the heaviest non-radioactive element. The structural feature of bismuth is mainly guided by the 6p orbitals. In this work, we have mainly focused on synthesizing a mono-cationic bismuthenium compound that is donor-free in nature and has been employed in the

cyanosilylation of ketones for the first time. The cationic bismuth compounds have 6 valence electrons and are isoelectronic to that of tetrylenes. The presence of a lone pair of electrons and vacant p orbital in bismuthenium cations renders the amphoteric nature. The presence of a +ve charge makes it more Lewis acidic. Due to this Lewis acidic nature bismuth (III) compounds have been utilized as Lewis acids in various stoichiometric as well as catalytic reactions. Bismuth (III) compounds are classified into three classes depending on the counter anion attached to the metal center: A) R_2Bi-X where X is an electronegative atom which remains directly attached to the metal center.¹⁵ B) $R_2Bi \cdots X$, where X is a weakly coordinated counter anion like $AlCl_4^-$, $(O_3SCF_3)^-$.^{13a,16} C) R_2BiWCA (WCA is the weakly coordinated counter anion like SbF_6^- , $[B(C_6F_5)]^-$ where there is no direct interaction with the metal center.^{13d,13e,17} Lewis acidity of the Bi(III) compounds arises mainly due to the σ -type interactions with the Lewis bases.

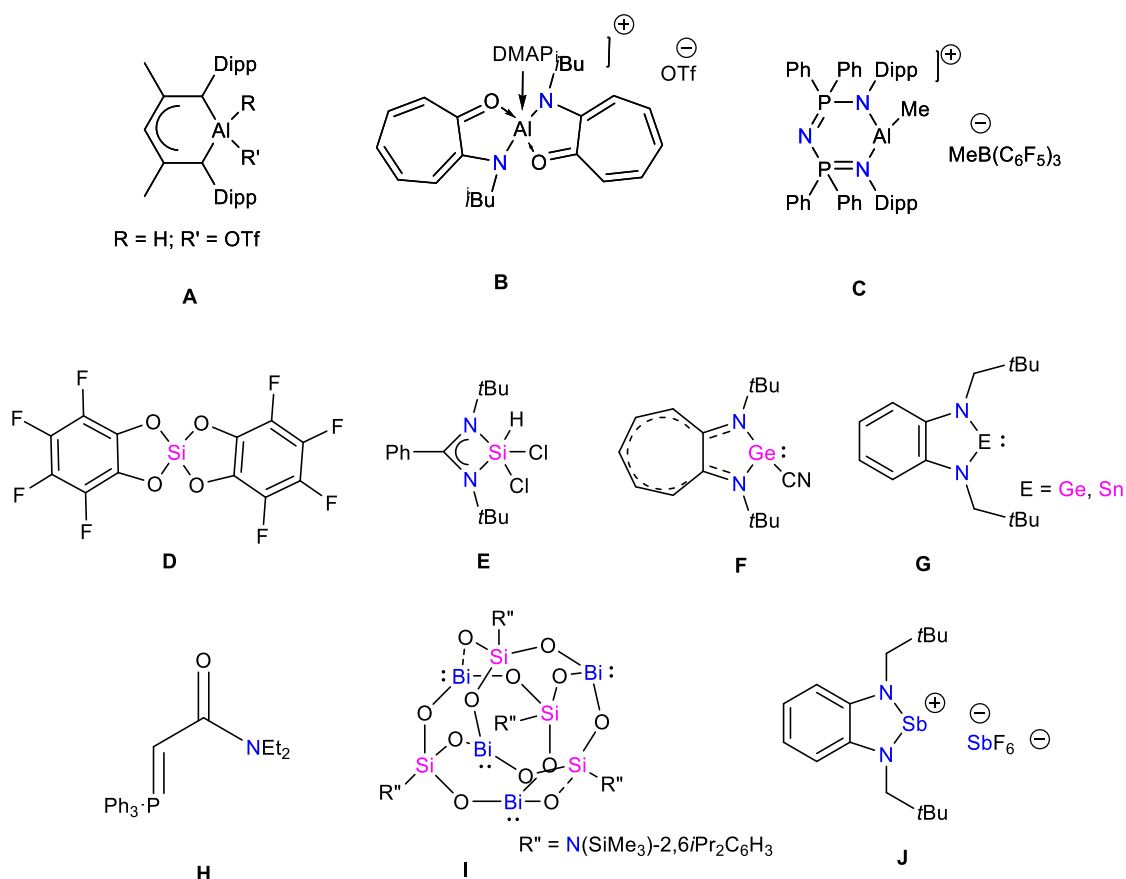


Chart 5.1. Reported examples of main group compounds used as cyanosilylation catalysts.

5.2. Experimental Section

5.2.1. General remarks

The whole process was executed under an inert atmosphere of argon using standard Schlenk techniques or in a glovebox. Solvents used were purified using an MBRAUN solvent purification system MBSPS-800. SbCl_3 , AgSbF_6 were purchased from Sigma-Aldrich and Alfa Aesar. They were used without further purification. ^1H , ^{13}C , ^{29}Si , NMR spectra were recorded on a Bruker spectrometer in CDCl_3 as the solvent with an external standard (SiMe_4 for ^1H , ^{13}C ,). Mass spectra were recorded using an AB Sciex, 4800 MALDI TOF/TOF, and HRMS was recorded on a Waters Synapt, USA. Yields are calculated based on the isolated crystals.

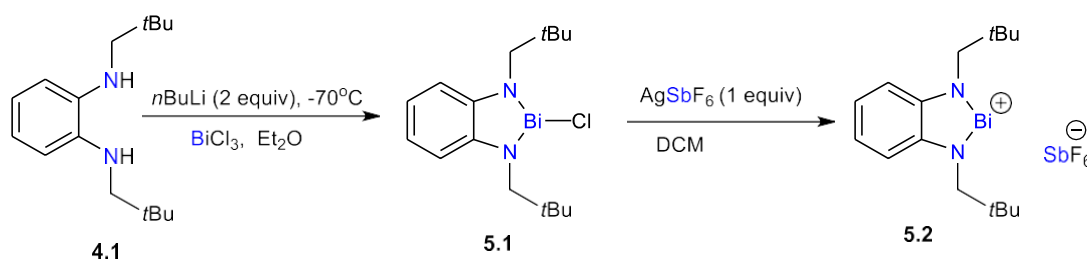
5.2.2. Synthesis of compounds 5.1 and 5.2.

Synthesis of 5.1. Compound 4.1 (1 gm, 4.11 mmol) was taken in a 100 ml Schlenk flask, and 60 ml of Et_2O was added at room temperature. Subsequently the flask was cooled to -60°C and $n\text{BuLi}$ (3.29 ml, 2.5 M) was added to it slowly. Then the reaction mixture was allowed to come at room temperature and kept on stirring for 6 h. The reaction mixture was cooled again and transferred to another flask containing THF solution (20 ml) of BiCl_3 (1.294 gm, 4.11 mmol). The reaction mixture was again kept on stirring for overnight. Extraction was done with DCM and concentrated to 5 ml followed by the addition of few drops of pentane and kept for crystallization at 0°C . Yield (%): 61.22% (300 mg) ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 1.05 (s, 18H, *t*Bu group), 2.86 (s, 4H, $-\text{CH}_2$), 6.69-6.80 (m, 4H, Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.613 MHz, CDCl_3 , 298 K): δ 1.1, 27.9, 31.6, 56.5, 112.2, 119.3, 138.4 ppm.

Synthesis of 5.2. To the mixture of compound 5.1 (490 mg, 1 mmol) and AgSbF_6 (344 mg, 1 mmol) 40 ml of DCM was added in a 100 ml Schlenk flask and kept on stirring. After 10 min of stirring the color of the reaction mixture immediately changed to dark purple from reddish purple. After 12 h of stirring, the solvent was evaporated. The extraction was done in DCM and concentrated to 5 ml followed by adding 5 ml pentane and kept at room temperature for crystallization. Yield (%): 72% (500 mg) ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 1.10 (s, 18H, *t*Bu), 3.02 (s, 4H, $-\text{CH}_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.613 MHz, CDCl_3 , 298 K): δ 1.1, 25.7, 27.3, 31.4, 68.1, 120.1, 126.2, 134.8 ppm. HRMS: Calcd for $[\text{C}_{16}\text{H}_{26}\text{BiN}_2\text{SbF}_6]$: m/z 690.0842. Found m/z 690.1079.

5.3. Results and discussion

The lithiated salt of *N,N'*-dineopentyl-1,2-phenylenediamine(**4.1**) was treated with one equiv. of BiCl₃ in Et₂O/THF mixture at -70°C which afforded the desired compound **5.1** (Scheme 1). The formation of compound **5.1** was confirmed through NMR spectroscopy study. The NMR spectrum of compound **5.1** shows the appearance of a sharp singlet at δ 1.04 ppm, corresponding to 18 *t*Bu protons and a second peak at δ 2.85 ppm for four -CH₂- protons. **5.1** crystallizes in monoclinic space group *P1*.



Scheme 5.1. Syntheses of compounds **5.1** and **5.2**.

Since our target was to generate the bismuthenium cation we treated compound **5.1** with 1 equiv of AgSbF₆ in DCM. Treatment of compound **5.1** with AgSbF₆ yielded the desired bismuthenium cation **5.2**. Compound **5.2** has been characterized well through NMR spectroscopy and single crystal X-ray diffraction study. The ¹⁹F NMR spectrum exhibits a peak at -169.42 ppm corresponding to the SbF₆ anionic moiety. Diffusion of pentane to the DCM solution of **5.2** actually resulted in the formation of dark violet-colored crystals of **5.2**. It is found that **3** crystallizes in the monoclinic space group. The molecular structure of **5.2** unveils the presence of Bi (III) cationic center along with a discrete SbF₆ anionic counterpart where it is observed that the Bi-N distances are 2.117(2), 2.163(2) Å which is commensurable to that of the previously reported bis[*N,N',N'*-tris(trimethylsilyl)hydrazino]bismuthenium cation (2.150(2), 2.115(2) Å) by Schulz and coworkers^{13b} but is longer than that of the previous report [Bi(NON)^{Ar}][AlCl₄] (2.113(12), 2.111(12) Å) by Coles and coworkers.^{13a} The N-Bi-N bond angle of **3** is observed to be 77.79(8) ° which is found to be much smaller than both the previously mentioned reported bismuthenium cationic species (100.28(5), 111.9(1)°).^{13a,13b}

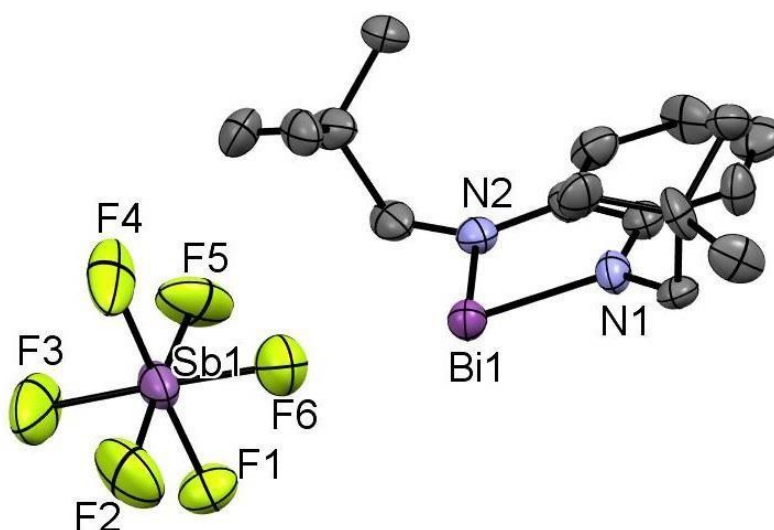


Figure 5.1. Molecular structure of compound **5.2** with anisotropic displacement parameters depicted at 50% probability level. Hydrogen atoms are shown for clarity. Selected bond lengths(Å) for **5.2**: Bi1-N1 2.117(2), Bi1-N2 2.163(2). Selected bond angles (°) for **5.2**: N1-Bi1-N2 77.79(6).

The cationic Bi (III) center displays long contacts with two fluorine atoms of two SbF_6 anions. The Bi-F distances are 2.848 and 2.973 Å, almost similar to that of the previously reported carbodicarbene stabilized bismuthenium ion (2.904(2) Å) by Gilliard and coworkers.¹⁸

Apart from these two interactions between the Bi (III) cationic center and the fluorine atoms it has been observed that **5.2** exhibits a different pattern of cation-cation interaction in solid state which similar to that of the previously reported stibenium cation by Khan and coworkers.¹² The molecular structure reveals that the bismuth center comprises π -stacked dimers which are antiparallel to each other in orientation and the Bi center displays an intermolecular π interaction with the arene ring of the adjacent moiety in η^3 fashion (Bi $\cdots$ C4 is 3.468 Å, Bi $\cdots$ C5 is 3.364 Å, Bi $\cdots$ C6 is 3.540 Å).

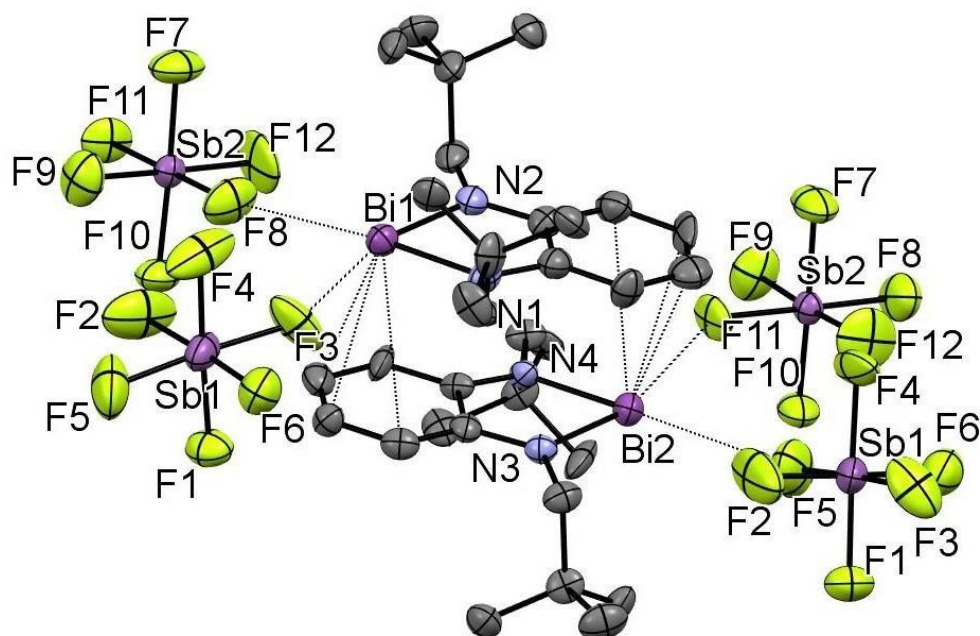


Figure 5.2. Representation of the interactions with the central cationic bismuth with the adjacent fluorine atoms of compound 5.2 and π stacked cation-cation interactions (antiparallel dimers) of compound 5.2. Hydrogen atoms are shown for clarity.

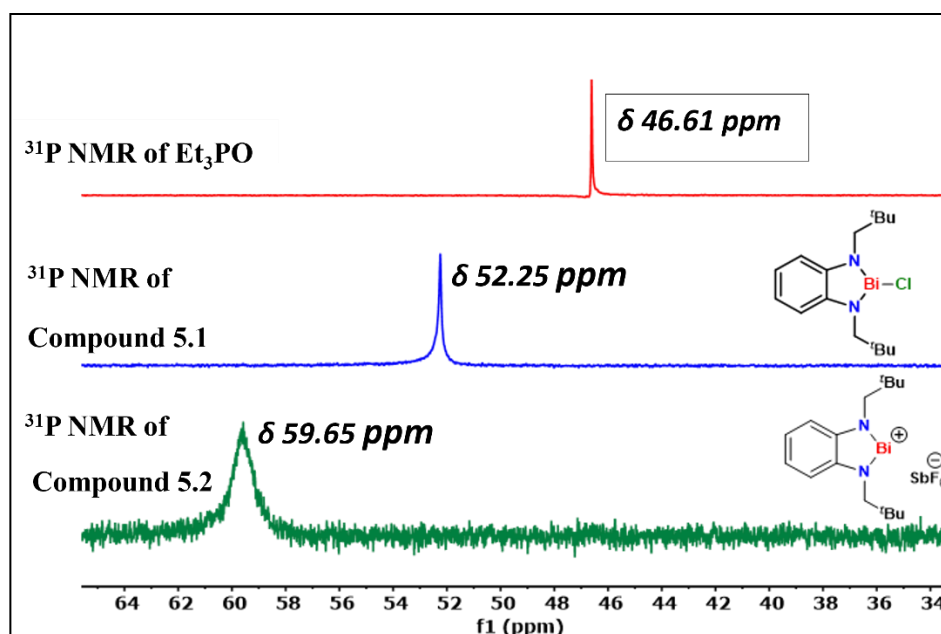


Figure 5.3. Stacked ³¹P NMR of compounds **5.1** and **5.2** in the presence of Et₃PO (Guttmann-Beckett method)

5.4. Estimation of Lewis acidity: Guttmann Beckett method is generally employed for the estimation of Lewis acidity in the case of cationic compounds.¹⁹ In the case of our compound **5.1** the presence of Cl atom will reduce its Lewis acidity than compound **5.2** as it is a cationic bismuth compound. We followed the Guttmann-Beckett method to estimate the Lewis acidity of **5.1** and **5.2**. We utilized OPEt₃ as the probe to quantify the Lewis acidity. We treated OPEt₃ with both compounds in a 1:1 ratio and checked the chemical shift in ³¹P NMR spectra. More the downfield shift in ³¹P NMR spectra more is the Lewis acidity of the compound. In compound **5.1**, the ³¹P NMR appears at δ 52.25 ppm; similarly, in the case of compound **5.2**, it is observed at δ 59.65 ppm. So, from the chemical shift of ³¹P NMR spectra, it can be concluded that the Lewis acidity order is **5.2**>**5.1**.

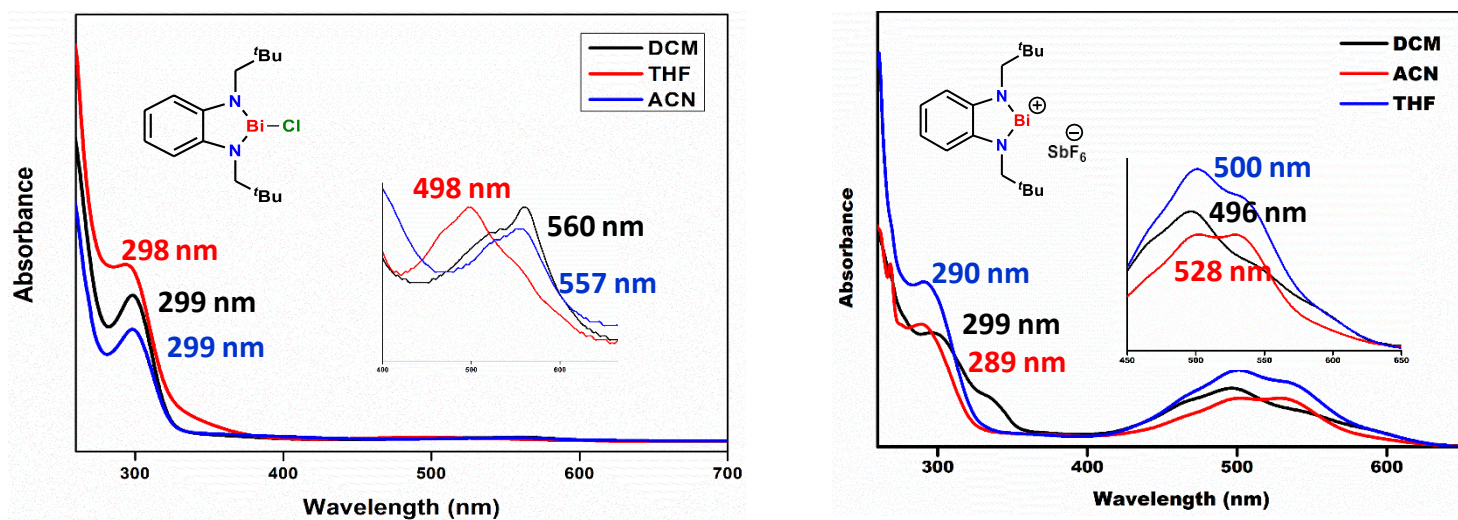


Figure 5.4. UV-vis absorption spectra of compounds 5.1 and 5.2.

Entry	Compound	Solvent	λ_{Max} (nm)
1	5.1	THF	498
		ACN	557
		DCM	560
2	5.2	THF	500
		ACN	528
		DCM	496

Our both the compounds being highly coloured we were motivated to study the photophysical properties of these compounds. Since the compounds were soluble in polar solvents, we recorded the UV-Vis spectra of both the compounds in three different polar solvents like THF, ACN and DCM. Compound **5.1** exhibits a dark purple color and the observed UV-Vis spectrum appears at 299 nm and 560 nm in DCM, 298 nm and 498 nm in THF, 299 nm and 557 nm in ACN. Compound **5.2** also appeared to be dark violet in color and from UV-Vis spectrometry study it is observed that two peaks at 290 nm and 500 nm appear in THF, 299 nm and 496 nm in DCM, 289 nm and 528 nm in ACN. We have performed the TD-DFT [B3LYP-D3/def2-TZVP(Bi), 6-311+G(d,p) for lighter atoms] level of theory. The results reveal that the absorptions are due to the charge transfer from the p-electron density of the aromatic ring to the vacant p orbital of the bismuth atom.

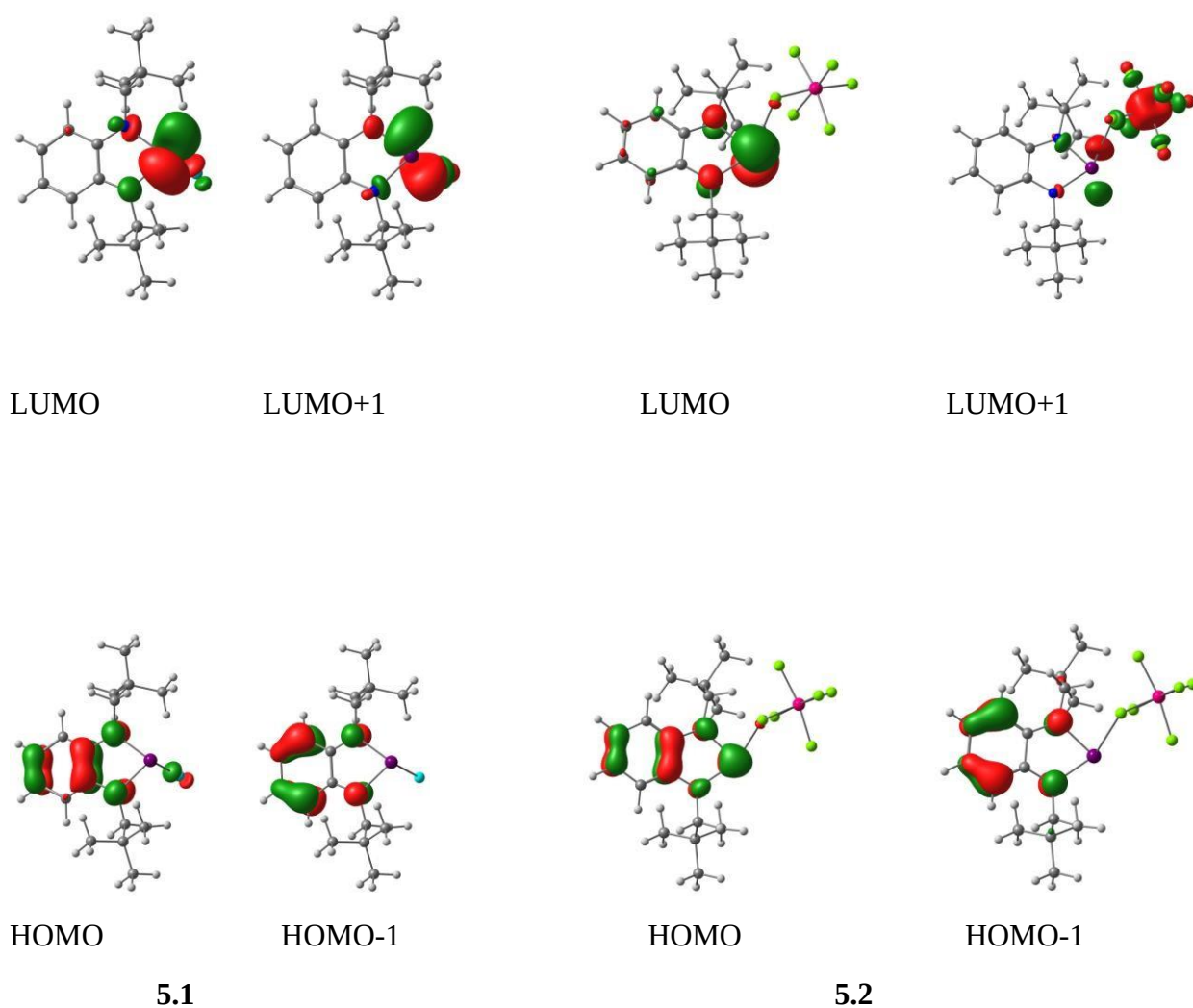


Figure 5.5. Frontier molecular orbitals of compounds **5.1** and **5.2**.

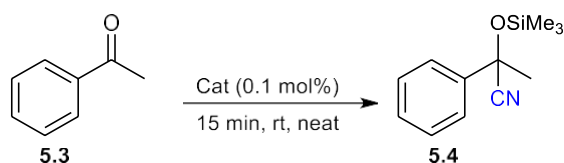
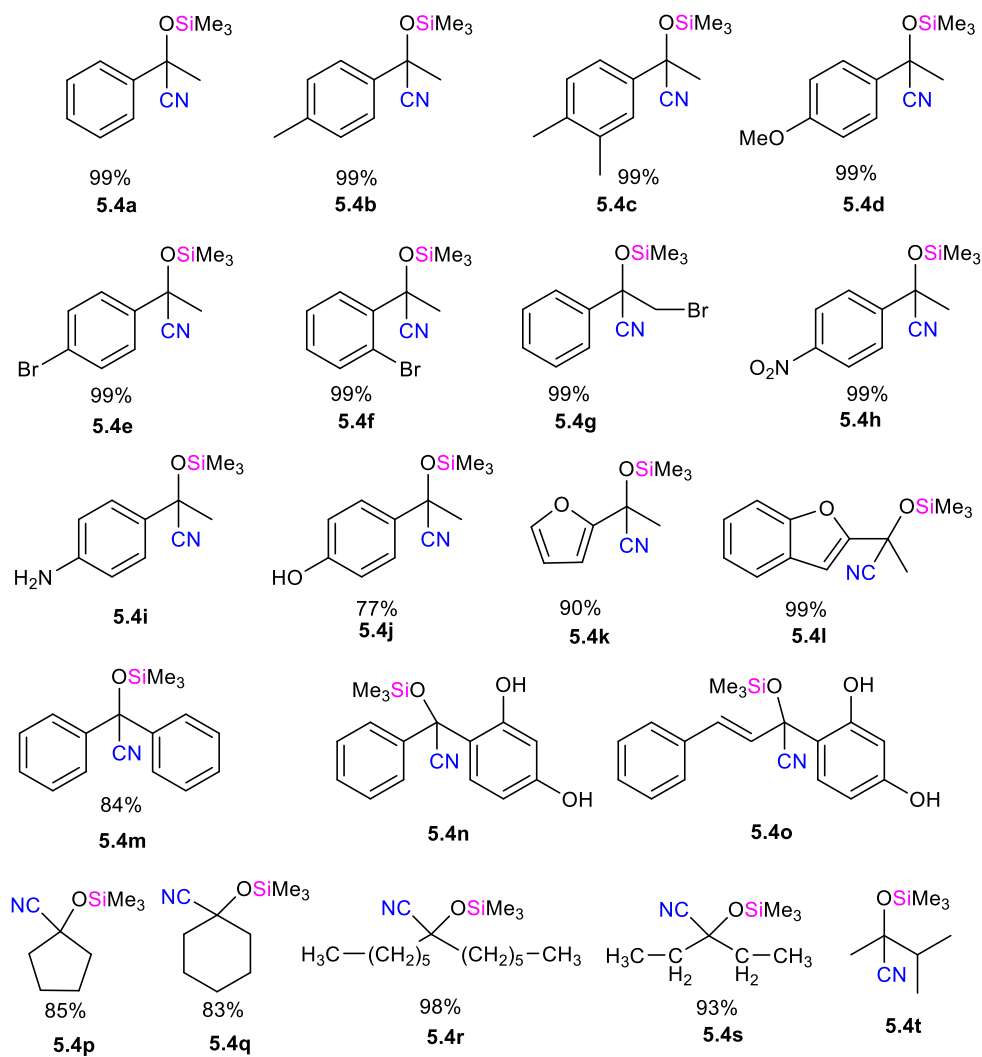
5.5. Catalytic application

Since cyanosilylation of carbonyls by group 15 elements we were interested in investigating the catalytic efficiency of our newly synthesized bismuth mono cation, we began with the optimization of the reaction conditions. The optimization was performed using acetophenone as the model substrate. We carried out a brief screening of the catalyst loading, temperature, and time for cyanosilylation of acetophenone using 1.2 equivalent TMSCN to get the best conversion of the product. We started with 0.5 mol% of the catalyst and within 30 min we observed 99 % product formation. Next, the same reaction was repeated within 15 min, and in this case, 99 % product formation was achieved. Gradually both the mol% of the catalyst and the time of the reaction were reduced and it was found that with 0.1 mol% within 15 min very good product conversion was taking place. So, with these optimization conditions in our hands, we began to explore the catalytic efficiency of compound **5.2** on various substrates of ketones.

We started with the derivatives of acetophenone. Both the electron-donating containing groups and electron-withdrawing groups underwent cyanosilylation to form the corresponding cyanohydrin product in moderate to good yield (Scheme 5.2). Along with the aromatic ketones, the aliphatic ketones also showed good product conversion under the same reaction conditions.

Table 5.1. Optimization table for cyanosilylation of acetophenone with catalyst **5.2**.

Entry	Catalyst	Mol (%)	Time (Min)	TMSCN (Equiv.)	Temperature	Yield (%)
1	5.2	0.5	30	1.5	RT	>99
	5.2	0.5	15	1.5	RT	>99
2	5.2	0.25	30	1.5	RT	>99
	5.2	0.25	15	1.5	RT	>99
3	5.2	0.1	30	1.5	RT	>99
	5.2	0.1	15	1.5	RT	>99
4	5.2	0.05	30	1.5	RT	<50

**Scheme 5.2.** Cyanosilylation of acetophenone with catalyst 5.2.**Chart 5.1.** Substrate scope of ketones for cyanosilylation.

Following the aforementioned optimization condition, we expanded the substrate scope. Chart 5.1 delineates the scope of ketones we have studied in this work. Here we have employed both aromatic as well as aliphatic ketones for the cyanosilylation. The commonly available aromatic ketones with electron-donating groups like 4-methylacetophenone (**5.4b**), 3,4-dimethylacetophenone (**5.4c**) as well as with electron-withdrawing groups like the bromoacetophenones gave very good product conversion. We employed 2-acetylfuran (**5.4k**) and 2-acetylbenzofuran (**5.4l**) and in both cases, we observed good product formation. Following the aromatic ketones, we focused on the aliphatic ketones like dihexyl ketone (**5.4r**), diethyl ketone (**5.4s**), and 3-methylbutanone (**5.4t**) along with the cyclic ketones like cyclopentanone (**5.4p**) and cyclohexanone (**5.4q**) gave their corresponding cyanohydrin product in moderate to good yield under the same optimized conditions. Along with benzophenone we have employed benzoescorcinol which is bulkier than benzophenone and, in both cases, we have a good percentage of product yield. We have also calculated the TOF value which is 66 min^{-1} . With this TOF value, it can be said that our catalyst is the 2nd most efficient catalyst after the cationic aluminum reported by Singh and coworkers.^{7d}

5.6. Mechanistic cycle

To understand the mechanistic pathway of our catalysis we performed solution-state NMR studies and recorded the ^1H , ^{13}C , and ^{29}Si NMR spectra of the intermediate which was afforded from 1:1 stoichiometric reaction of the catalyst and TMSCN. The ^{29}Si NMR spectrum of the intermediate exhibits a peak at δ 7.33 ppm which is downfield shifted than that of only TMSCN which appears at δ -11.31 ppm. From the ^1H NMR spectrum we observed a new peak at δ 0.05 ppm along with some amount of residual TMSCN which appears at δ 0.21 ppm. In the ^{13}C NMR spectrum also we observed the appearance of a new peak at δ 2.00 ppm ($-\text{CH}_3$) which differs from that of the free TMSCN (δ -2.26 ppm).

To support our experimental data, we have performed theoretical studies to get more insight into the mechanistic pathway. In this case, mainly donor-acceptor interaction between the bismuth center of the catalyst and the TMSCN takes place. The first step of the mechanistic cycle is the coordination of TMSCN with that of the bismuth center where interaction between the nitrogen center of TMSCN and the vacant p orbital of the cationic bismuth center takes place resulting in the formation of the INT1. Then in the presence of the substrate acetophenone, a four-membered transition state is formed where the oxygen atom of the substrate gets coordinated with the silicon center of $-\text{SiMe}_3$ of TMSCN and the carbon atom of the cyanide gets coordinated to the carbonyl center of acetophenone. Finally, in the next step, rearrangement takes place and $-\text{SiMe}_3$ moiety gets attached to the oxygen atom of the substrate and the CN group forms a bond with the carbonyl carbon of the substrate and there remains a coordination between the nitrogen center and the bismuth center forming the INT2. From this INT2 the product gets dissociated from the INT2 and also reproduces the catalyst back.

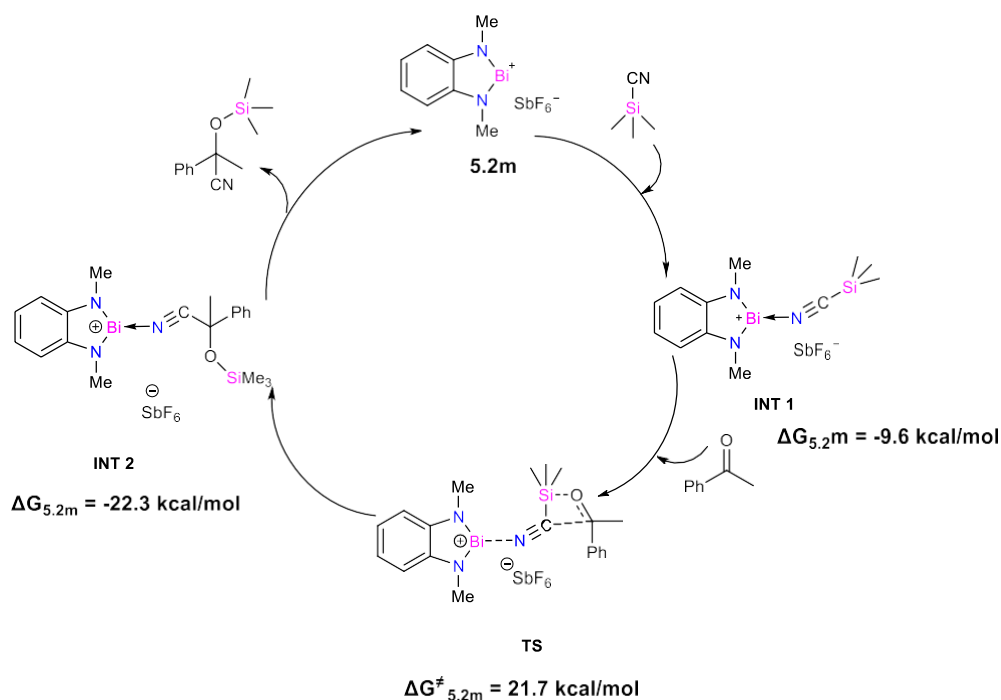


Figure 5.6. Proposed catalytic cycle for the cyanosilylation of acetophenone using model catalyst **5.2m**

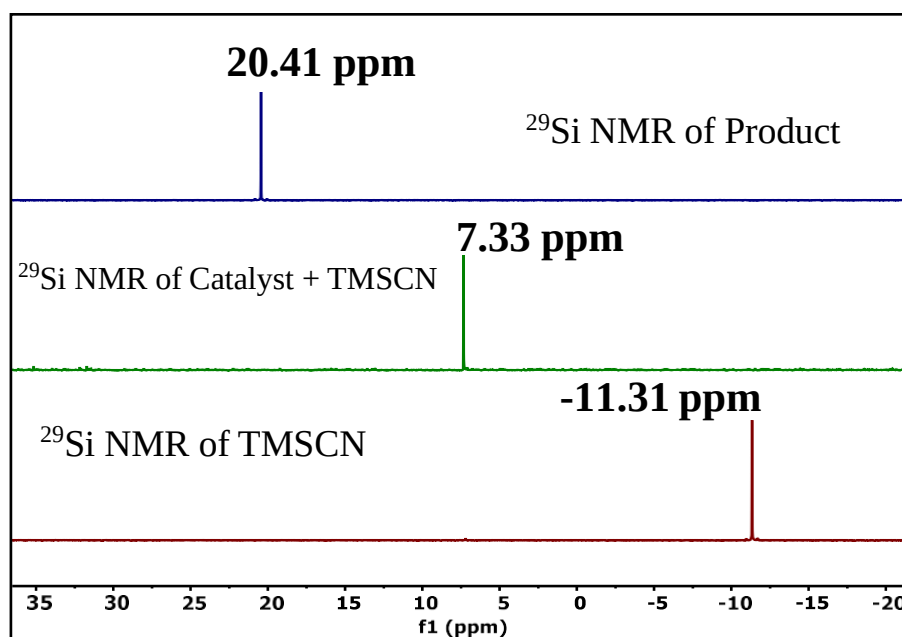


Figure 5.7. Stacked ^{29}Si NMR of cyanosilylation product, 1:1 reaction of TMSCN and catalyst and only TMSCN

5.7. Conclusion

Herein, we have synthesized a donor-free mono-cationic bismuth compound, and the molecular structure was established by a single-crystal X-ray diffraction study. We have estimated the Lewis acidity of both the chloro bismuthine and bismuthenium cation. For the first time, we have reported the efficiency of the bismuthenium cation as a homogeneous catalyst for cyanosilylation of ketones under very mild conditions and with low catalyst loading within very little time. We also proposed a catalytic pathway for the cyanosilylation reaction. Our experimental as well as theoretical results disclose the fact that the cyanosilylation of ketones occurs through the formation of a weak adduct between the cationic bismuth center of the catalyst and the TMSCN. Our study has opened a new province in the field of homogeneous catalysis by main group cationic species.

5.8. References

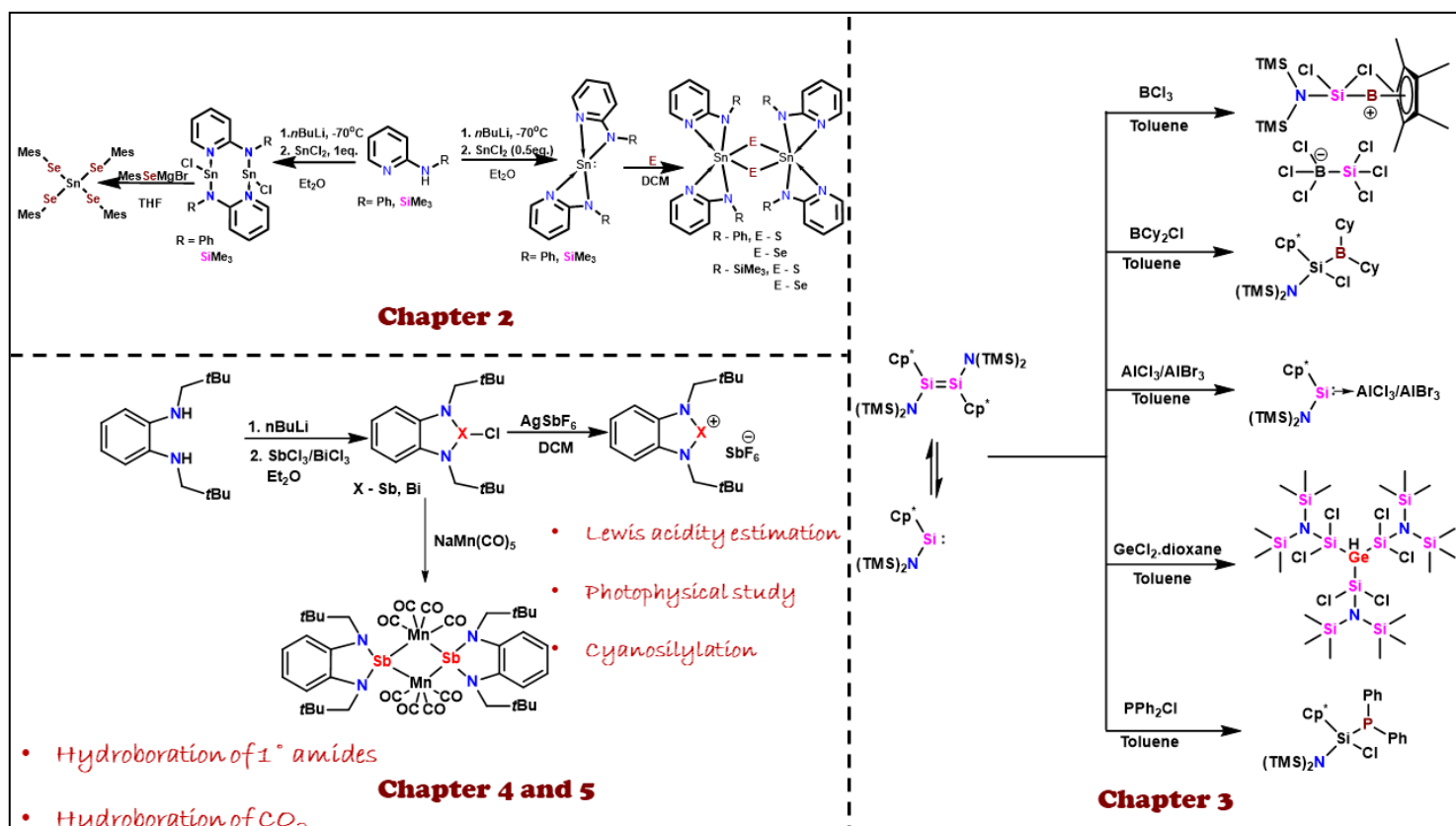
1. A) Mukherjee, A.; Milstein, D. *ACS Catal.* **2018**, *8*, 11435–11469; B) Chirik. P. J. *Acc. Chem. Res.* **2015**, *48*, 1687–1695; Wu, X-F.; C) Fang, X.; Wu, L.; Jackstell, R.; Neumann, H.; Beller, M. *Acc. Chem. Res.* **2014**, *47*, 1041–1053.
2. Winkler, F. W. *Liebigs Ann. Chem.* **1832**, *4*, 246-249.
3. Tiago, G. A. O.; Mahmudov, K. T.; Silva, M. F. C. G. D.; Ribeiro, A.P.C.; Branco, L. C.; Zubkov, F. I.; Pombeiro, A. J. L. *Catalysts* **2019**, *9*, 284-300.
4. North, M.; Usanov, D. L.; Young, C. *Chem. Rev.* **2008**, *108*, 5146– 5226.
5. Khan, N. H.; Kureshy, R. I.; Abdi, S. H. R.; Agrawal, S.; Jasra, R. V. *Coord. Chem. Rev.* **2008**, *252*, 593–623.
6. Pahar, S.; Kundu, G.; Sen, S. S. *ACS Omega* **2020**, *5*, 25477–25484.
7. a) Yang, Z.; Mingdong Zhong, M.; Xiaoli Ma X.; Susmita De, S.; Anusha, C.; Parameswaran, P. Roesky, H. W.; *Angew. Chem., Int. Ed.* **2015**, *54*, 10225–10229. b) Yang, Z.; Yi; Zhong, M.; De, S.; Mondal, T.; Koley, D.; Ma, X.; Zhang, D.; Roesky, H. W. *Chem. Eur. J.* **2016**, *22*, 6932–6938. c) Sharma, M. K.; Sinhababu, S.; Mukherjee, G.; Rajaraman, G.; Nagendran, S. *Dalton Trans.* **2017**, *46*, 7672–7676; d) Rawat, S.; Bhandari, M.; Prashanth, B.; Singh, S. *ChemCatChem* **2020**, *12*, 2407–2411.
8. Liberman-Martin, A. L.; Bergman, R. G.; Tilley, T. D. *J. Am. Chem. Soc.* **2015**, *137*, 5328–5331.
9. Swamy, V. S. V. S. N.; Bisai, M. K.; Das, T.; Sen, S. S. *Chem. Commun.* **2017**, *53*, 6910–6913.
10. Siwatch, R. K.; Nagendran, S. Germylene Cyanide Complex: *Chem. Eur. J.* **2014**, *20*, 13551–13556.
11. Dasgupta, R.; Das, S.; Hiwase, S.; Pati, S. K.; Khan, S. *Organometallics* **2019**, *38*, 1429–1435.
12. Sen, N.; Gothe, P.; Sarkar, P.; Das, S.; Tothadi, S.; Pati, S. K.; Khan, S. *Chem. Commun.* **2022**, *58*, 10380–10383
13. a) Schwamm, R. J.; Coles, M. P.; Fitchett, C. M. *Dalton Trans.* **2017**, *46*, 4066–4074; b) Baumann, W.; Schulz, A.; Villinger, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 9530 –9532; c) Veith, M.; Bertsch. B.; Huch, V. *Z. anorg. Allg. Chem.* **1988**, *559*, 73-88; d) Olaru, M.; Duvinage, D.; Lork, E.; Mebs, S.; Beckmann, J. *Angew. Chem. Int. Ed.* **2018**, *57*, 10080–10084; d) Kannan, R.; Kumar, S.; Andrews, A. P.; Jemmis, E. D.; Venugopal, A. *Inorg.*

-
- Chem.* **2017**, 56, 9391–9395; e) *Chem. Eur. J.* **2020**, 26, 10250 – 10258; e) Dengel, H.; Lichtenberg, C. *Chem. Eur. J.* **2016**, 22, 18465–18475.
14. Li, Y.; Wang, J.; Wu, Y.; Zhu, H.; Samuel, P. P.; Roesky, H. W. *Dalton Trans.* **2013**, 42, 13715–13722.
15. a) Tschersich, C.; Hoof, S.; Frank, N.; Herwig, C.; Limberg, C. *Inorg. Chem.* **2016**, 55, 1837–1842.; b) Tschersich, C.; Limberg, C.; Roggan, S.; Herwig, C.; Ernsting, N.; Kovalenko, S.; Mebs, S. *Angew. Chem., Int. Ed.* **2012**, 51, 4989–4992.
16. Schwamm, R. J.; Day, B. M.; Coles, M. P.; Fitchett, C. M. *Inorg. Chem.* **2014**, 53, 3778–3787.
17. a) Lehmann, M.; Schulz, A.; Villinger, A. *Angew. Chem., Int. Ed.* **2012**, 51, 8087–8091; b) Lichtenberg, C.; Pan, F.; Spaniol, T. P.; Englert, U.; Okuda, J. *Angew. Chem., Int. Ed.* **2012**, 51, 13011–13015.
18. Walley, J. E.; Warring, L. S.; Wang, G.; Dickie, D. A.; Pan, S.; Frenking, G.; Gilliard, R. J. Jr. *Angew. Chem. Int. Ed.* **2021**, 60, 6682–6690.
19. a) Mayer, U.; Gutmann, V.; Gerger, W., The acceptor number—A quantitative empirical parameter for the electrophilic properties of solvents. *Monatsh. Chem.* **1975**, 106, 1235–1257; b) Beckett, M. A.; Strickland, G. C.; Holland, J. R.; Varma, K. S., A convenient nmr method for the measurement of Lewis acidity at boron centers: correlation of reaction rates of Lewis acid-initiated epoxide polymerizations with Lewis acidity. *Polymer* **1996**, 37, 4629–4631.

Summary

In conclusion, it can be stated that the overall objective of my doctoral research work mainly focuses on the study of low valent main group *p*-block elements. Our aim was to explore the structure and bonding patterns of the heavier congeners of group 14 and 15 elements in their low valent state and also to investigate their catalytic efficiency in the field of homogeneous catalysis. Along with the synthesis of low-valent stannylenes the stabilization of Sn_2E_2 (E – S, Se, Te) is also challenging. Generally the formation of a double bond or the four-membered cyclic depends on the bulky nature of the ligand backbone of the central Sn(II) atom. In our work, since we have employed a less bulky aminopyridinate ligand backbone, we have isolated and characterized a series of four-membered cyclic Sn_2E_2 (E – S, Se) complexes. This thesis also deals with the reactivity of disilene towards various halides of groups 13, 14 and 15 elements. In our work, we have mainly checked whether the disilene we have employed behaves as a disilene or exhibits acyclic silylene character. In doing so we have treated it with the Lewis acids like BCl_3 , $\text{AlCl}_3/\text{AlBr}_3$, GeCl_2 , SnCl_2 , and PPh_2Cl . In each case, we have isolated different types of products due to oxidative addition and rearrangement. From all the reactivities we have concluded that the disilene actually behaves as an acyclic silylene. Due to the presence of lone pair electrons at the Si center, it tends to undergo complexation reaction with different Lewis acids leading to the formation of various types of rearranged products as well as adduct formation. The last part of my thesis mainly includes the stabilization of donor-free stibenium and bismuthenium cations. Although there are few previous reports of donor-free stibenium cation but we have explored for the first-time catalytic efficiency of our synthesized donor-free stibenium cation as a cyanosilylation catalyst. We are well aware of the catalytic potential of bismuthenium ions. In our work low catalyst loading with less time for the cyanosilylation of ketones is the important feature of our synthesized bismuthenium cation. Further, we have also isolated for the first time stibine-manganese carbonyl complex. We have treated our previously reported chlorostibine with $\text{NaMn}(\text{CO})_5$ which resulted in the formation of a dimeric four-membered cyclic Sb_2Mn_2 complex. Eventually, we have also examined the catalytic application of the transition metal-based stibine complex. We have utilized our complex in various catalytic transformation which includes hydroboration of primary amides and also CO_2 . Along with this, we have also employed our complex as a catalyst for hydrosilylation of ketones.

So, this thesis work mainly targets to address the application of the main group *p*-block elements in homogeneous catalysis mimicking the transition metal in a greener and cheaper way.



Appendix

Appendix of Chapter 2

Table 2.A.1. Crystallographic details of compounds 2.3, 2.4 and 2.5.

	2.3	2.4	2.5
Chemical formula	C ₂₂ H ₁₈ N ₄ Sn	C ₁₆ H ₂₆ N ₄ Si ₂ Sn	C ₄₄ H ₃₆ N ₈ S ₂ Sn ₂
Formula weight	457.09 g/mol	449.28 g/mol	978.31 g/mol
Temperature	150(2) K	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> n	<i>P</i> -1	<i>P</i> 21/n
Unit cell dimensions	<i>a</i> = 8.3110(17) Å	<i>a</i> = 8.6112(12) Å	<i>a</i> = 9.1857(7) Å
	<i>b</i> = 11.292(2) Å	<i>b</i> = 9.8494(15) Å	<i>b</i> = 16.6555(11) Å
	<i>c</i> = 20.344(4) Å	<i>c</i> = 13.638(2) Å	<i>c</i> = 13.1143(9) Å
	α = 90°	α = 70.969(4)°	α = 90°
	β = 97.679(5)°	β = 71.965(3)°	β = 98.387(3)°
	γ = 90°	γ = 78.588(4)°	γ = 90°
Volume	1892.2(7) Å ³	1033.7(3) Å ³	1984.9(2) Å ³
Z	4	2	2
Density (calculated)	1.605 g/cm ³	1.443 g/cm ³	1.637 g/cm ³
Absorption coefficient	1.364 mm ⁻¹	1.356 mm ⁻¹	1.408 mm ⁻¹
F(000)	912	456	976
Theta range for data collection	2.54 to 28.37°	2.34 to 27.46°	2.45 to 26.12°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -15 ≤ <i>k</i> ≤ 15, -27 ≤ <i>l</i> ≤ 27	-11 ≤ <i>h</i> ≤ 11, -13 ≤ <i>k</i> ≤ 13, -18 ≤ <i>l</i> ≤ 18	-11 ≤ <i>h</i> ≤ 11, -19 ≤ <i>k</i> ≤ 19, -15 ≤ <i>l</i> ≤ 15
Reflections collected	41001	35884	40921
Independent reflections	9456 [R(int) = 0.0584]	5179 [R(int) = 0.0620]	3584 [R(int) = 0.0930]
Coverage of independent reflections	99.9%	99.8%	100%
Function minimized	$\sum w(\text{Fo}^2 - \text{Fc}^2)^2$	$\sum w(\text{Fo}^2 - \text{Fc}^2)^2$	$\sum w(\text{Fo}^2 - \text{Fc}^2)^2$
Data / restraints / parameters	9456 / 8 / 488	5179 / 0 / 214	3584 / 0 / 253
Goodness-of-fit on F²	1.067	1.056	1.051
Δ/σ max	0.000	0.003	0.001
Final R indices	8858 data; [<i>I</i> > 2σ(<i>I</i>)] R1 = 0.0360, wR2 = 0.0764	4288 data [<i>I</i> > 2σ(<i>I</i>)], R1 = 0.0316, wR2 = 0.0529	2870 data [<i>I</i> > 2σ(<i>I</i>)], R1 = 0.0295, wR2 = 0.0496
	all data, R1 = 0.0405, wR2 = 0.0779	all data, R1 = 0.0499, wR2 = 0.0571	all data, R1 = 0.0478, wR2 = 0.0542
Largest diff. peak and hole	1.590 and -1.318 eÅ ⁻³	0.435 and -0.654 eÅ ⁻³	0.444 and -0.402 eÅ ⁻³
R.M.S. deviation from mean	0.107 eÅ ⁻³	0.103 eÅ ⁻³	0.094 eÅ ⁻³

Table 2.A.2. Crystallographic details of compounds 2.6, 2.8 and 2.9

	2.6	2.8	2.9
Chemical formula	C ₄₄ H ₃₆ N ₈ Se ₂ Sn ₂	C ₃₂ H ₅₂ N ₈ Se ₂ Si ₄ Sn ₂	C ₂₂ H ₁₈ Cl ₂ N ₄ Sn ₂
Formula weight	1072.1 g/mol	1056.47 g/mol	646.68 g/mol
Temperature	150(2) K	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 21/n	<i>P</i> 21/n	<i>P</i> 21
Unit cell dimensions	<i>a</i> = 9.2002(19) Å	<i>a</i> = 14.842(6) Å	<i>a</i> = 9.356(2) Å
	<i>b</i> = 16.760(4) Å	<i>b</i> = 9.932(4) Å	<i>b</i> = 9.653(2) Å
	<i>c</i> = 13.255(3) Å	<i>c</i> = 16.011(7) Å	<i>c</i> = 12.400(3) Å
	α = 90°	α = 90°	α = 90°
	β = 98.321(5)°	β = 110.405(10)°	β = 102.378(7)°
	γ = 90°	γ = 90°	γ = 90°
Volume	2022.3(8) Å ³	2212.0(16) Å ³	1093.7(5) Å ³
Z	2	2	2
Density (calculated)	1.761 g/cm ³	1.586 g/cm ³	1.964 g/cm ³
Absorption coefficient	3.078 mm ⁻¹	2.915 mm ⁻¹	2.545 mm ⁻¹
F(000)	1048	1048	624
Theta range for data collection	2.43 to 25.92°	2.32 to 26.61°	2.23 to 23.82°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -20 ≤ <i>k</i> ≤ 20, -15 ≤ <i>l</i> ≤ 15	-17 ≤ <i>h</i> ≤ 17, -11 ≤ <i>k</i> ≤ 11, -19 ≤ <i>l</i> ≤ 19	-12 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 16, -16 ≤ <i>l</i> ≤ 16
Reflections collected	54136	75808	33737
Independent reflections	3647 [R(int) = 0.1325]	4004 [R(int) = 0.1345]	5423 [R(int) = 0.1579]
Coverage of independent reflections	100%	100%	100%
Function minimized	Σ w(Fo ² - Fc ²) ²	Σ w(Fo ² - Fc ²) ²	Σ w(Fo ² - Fc ²) ²
Data / restraints / parameters	3647 / 0 / 253	4004 / 0 / 223	5423 / 43 / 272
Goodness-of-fit on F²	1.139	1.020	1.030
Δ/σ max	0.000	0.002	0.000
Final R indices	2811 data; [I > 2σ(I)] R1 = 0.0622, wR2 = 0.1499	3153 data [I > 2σ(I)], R1 = 0.0319, wR2 = 0.0469	3826 data [I > 2σ(I)], R1 = 0.0558, wR2 = 0.0604
	all data, R1 = 0.0863, wR2 = 0.1642	all data, R1 = 0.0542, wR2 = 0.0527	all data, R1 = 0.1118, wR2 = 0.0702
Largest diff. peak and hole	2.944 and -1.588 eÅ ⁻³	0.552 and -0.537 eÅ ⁻³	1.250 and -1.317 eÅ ⁻³
R.M.S. deviation from mean	0.229 eÅ ⁻³	0.119 eÅ ⁻³	0.248 eÅ ⁻³

Table 2.A.3. Crystallographic details of compounds **2.10** and **2.11**

	2.10	2.11
Chemical formula	C ₁₆ H ₂₆ Cl ₂ N ₄ Si ₂ Sn ₂	C ₃₆ H ₄₄ Se ₄ Sn
Formula weight	638.87 g/mol	911.24 g/mol
Temperature	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
Space group	<i>P</i> b c n	<i>P</i> 21/ <i>n</i>
Unit cell dimensions	<i>a</i> = 18.850(3) Å	<i>a</i> = 12.684(3) Å
	<i>b</i> = 15.271(3) Å	<i>b</i> = 21.928(5) Å
	<i>c</i> = 8.0566(14) Å	<i>c</i> = 13.181(3) Å
	α = 90°	α = 90°
	β = 90°	β = 105.824(5)°
	γ = 90°	γ = 90°
Volume	2319.1(7) Å ³	3527.1(14) Å ³
Z	4	4
Density (calculated)	1.830 g/cm ³	1.716 g/cm ³
Absorption coefficient	2.497 mm ⁻¹	4.876 mm ⁻¹
F(000)	1248	1784
Theta range for data collection	2.67 to 27.82°	2.46 to 20.18°
Index ranges	-22 ≤ <i>h</i> ≤ 22, -18 ≤ <i>k</i> ≤ 18, -9 ≤ <i>l</i> ≤ 9	-15 ≤ <i>h</i> ≤ 15, -26 ≤ <i>k</i> ≤ 26, -15 ≤ <i>l</i> ≤ 15
Reflections collected	50426	112442
Independent reflections	2104 [R(int) = 0.0876]	6384 [R(int) = 0.3139]
Coverage of independent reflections	99.9%	99.9%
Function minimized	$\Sigma w(\text{Fo}^2 - \text{Fc}^2)^2$	$\Sigma w(\text{Fo}^2 - \text{Fc}^2)^2$
Data / restraints / parameters	2104 / 0 / 121	6384 / 30 / 382
Goodness-of-fit on F²	1.356	1.098
Δ/σ max	0.001	0.006

Final R indices	1770 data; [$I > 2\sigma(I)$] $R1 = 0.0523$, $wR2 = 0.1055$	3927 data[$I > 2\sigma(I)$], $R1 = 0.0891$, $wR2 = 0.2105$
	all data , $R1 = 0.0652$, $wR2 = 0.1097$	all data , $R1 = 0.1563$, $wR2 = 0.2396$
Largest diff. peak and hole	1.835 and -1.275 eÅ ⁻³	2.642 and -1.349 eÅ ⁻³
R.M.S. deviation from mean	0.165 eÅ ⁻³	0.269 eÅ ⁻³

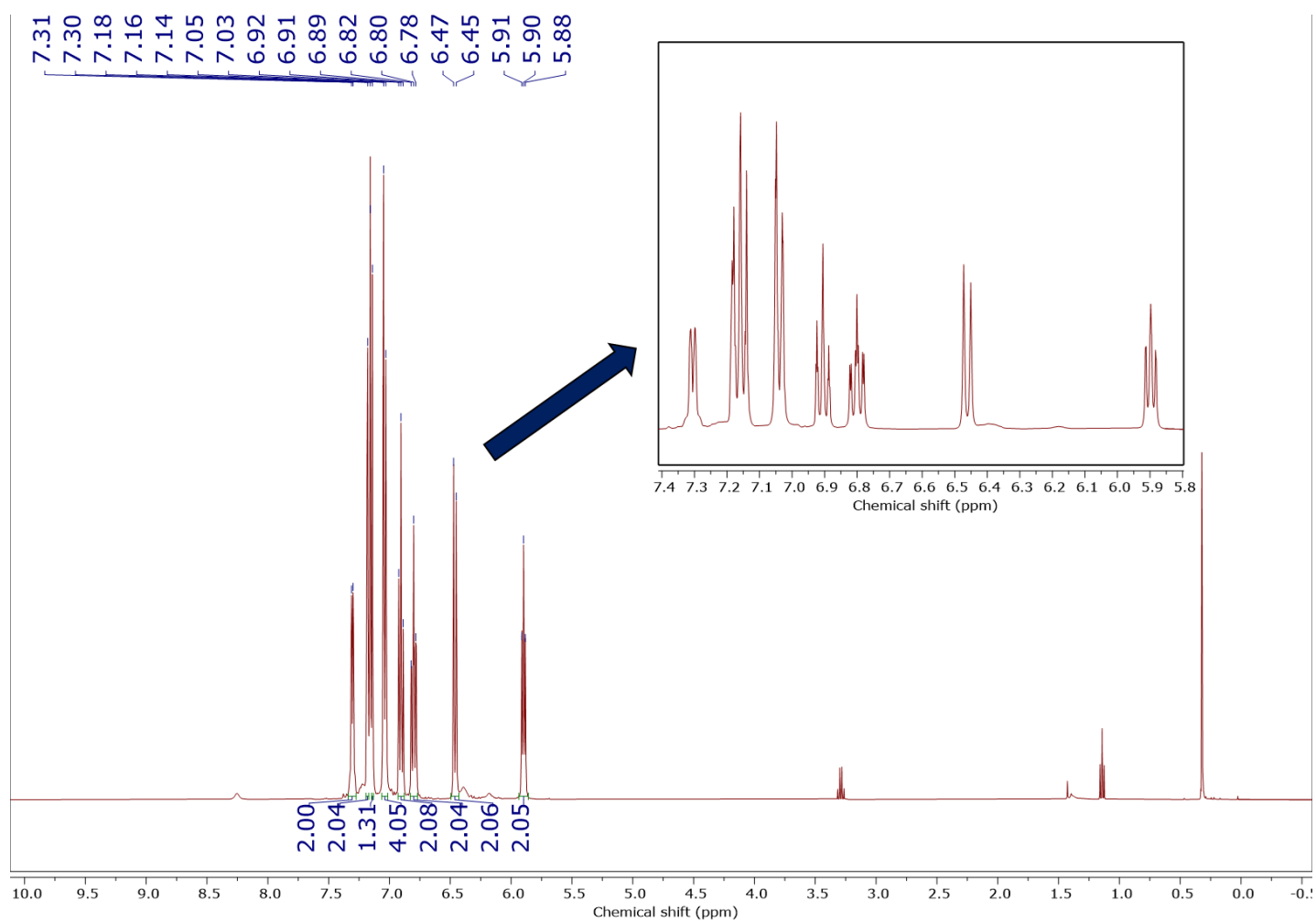


Figure 2.A.1. ^1H NMR spectrum of **2.3** in C_6D_6 (Solvent peak at δ 7.16 ppm), (400 MHz, 298 K).

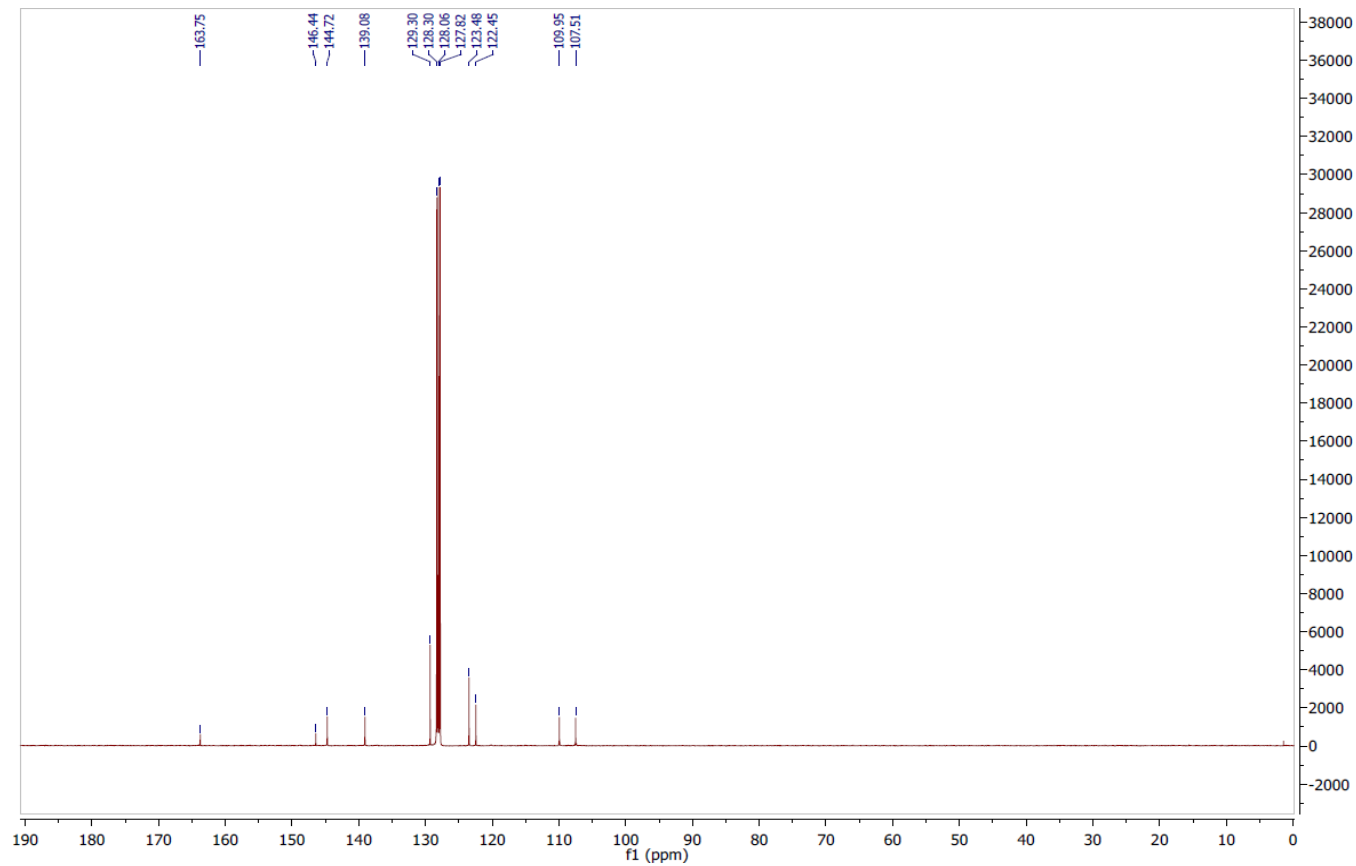


Figure 2.A.2. ^{13}C NMR spectrum of **2.3** in C_6D_6 (Solvent peak at δ 128.06 ppm), (100.613 MHz, 298 K).

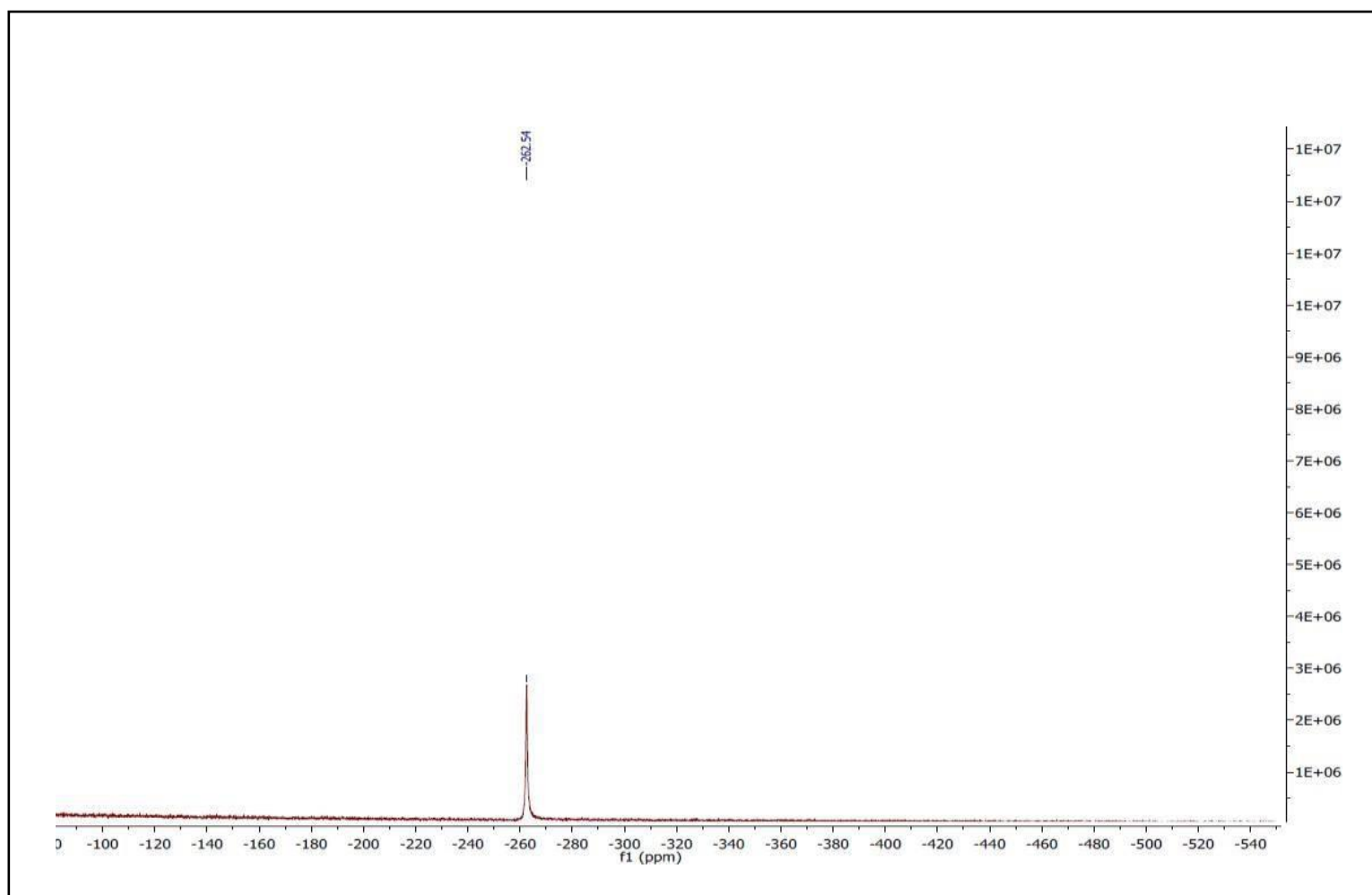


Figure 2.A.3. ^{119}Sn NMR spectrum of **2.3** in C_6D_6 (149.18 MHz, 298K).

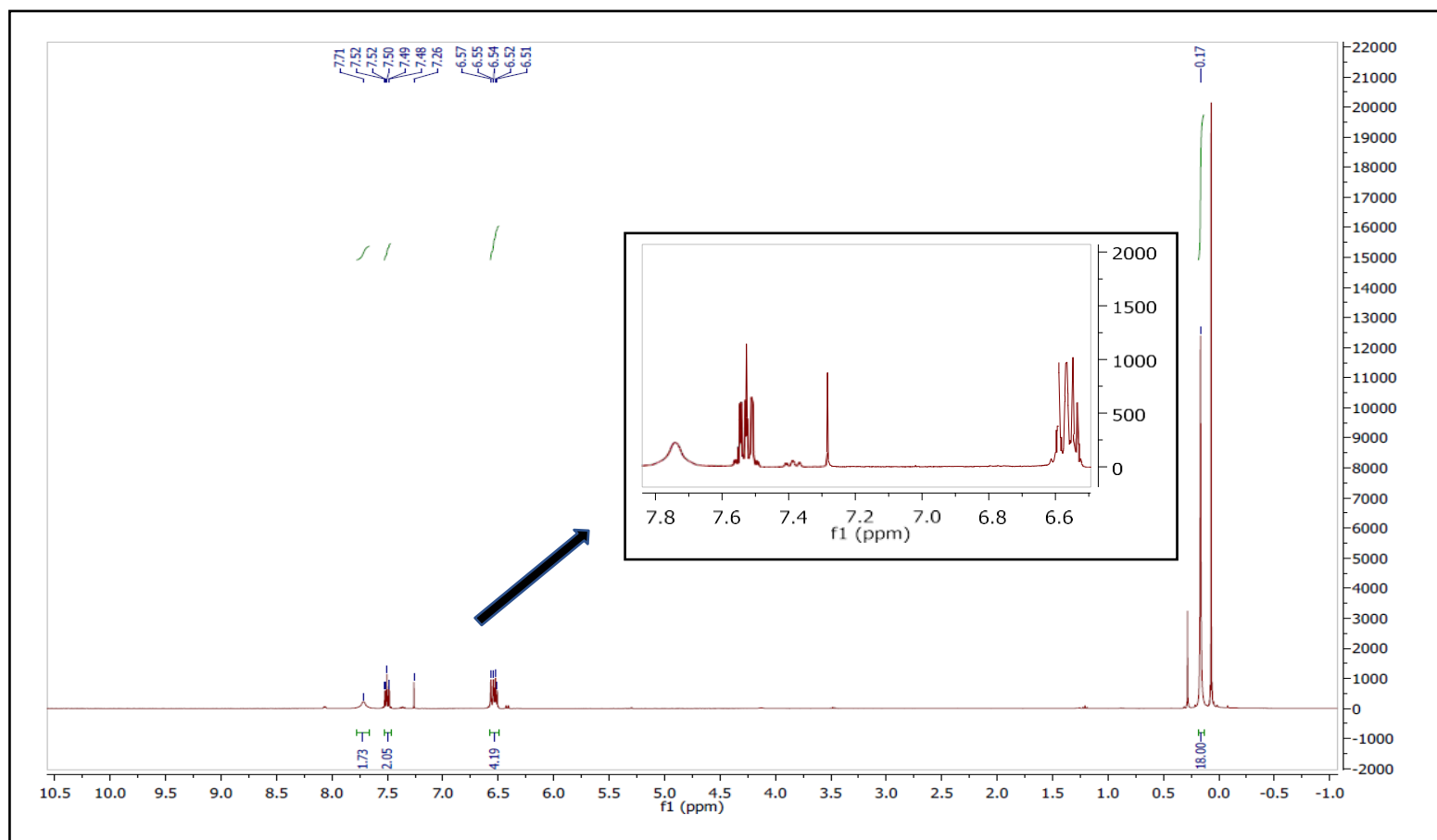


Figure 2.A.4. ^1H NMR spectrum of **2.4** in CDCl_3 (Solvent peak δ 7.26 ppm), (400 MHz, 298 K).

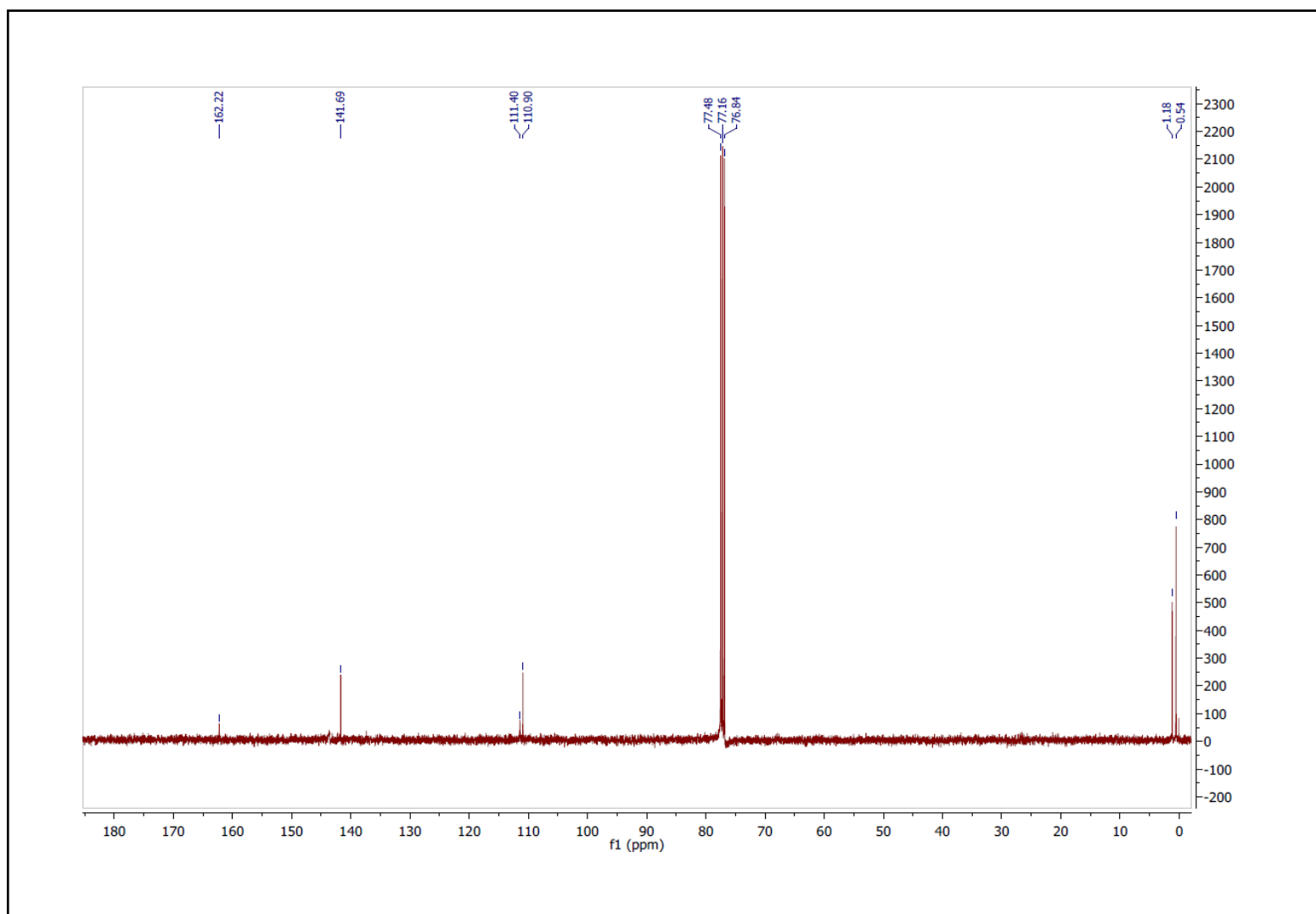


Figure 2.A.5. ^{13}C NMR spectrum of **2.4** in CDCl_3 (Solvent peak δ 77.16 ppm), (100.613 MHz, 298 K).

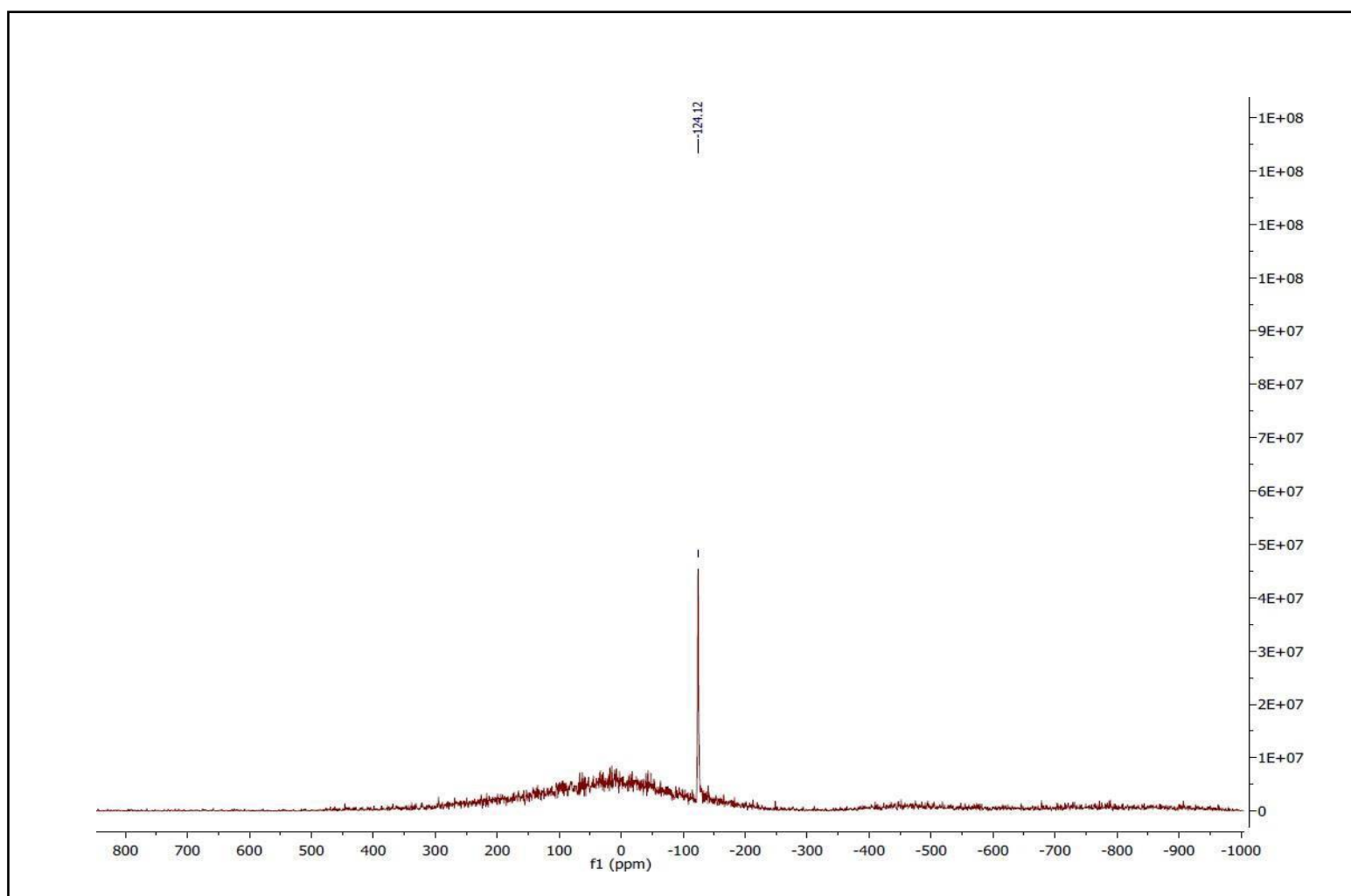


Figure 2.A.6. ^{119}Sn NMR spectrum of **2.4** in CDCl_3 (149.18 MHz, 298K).

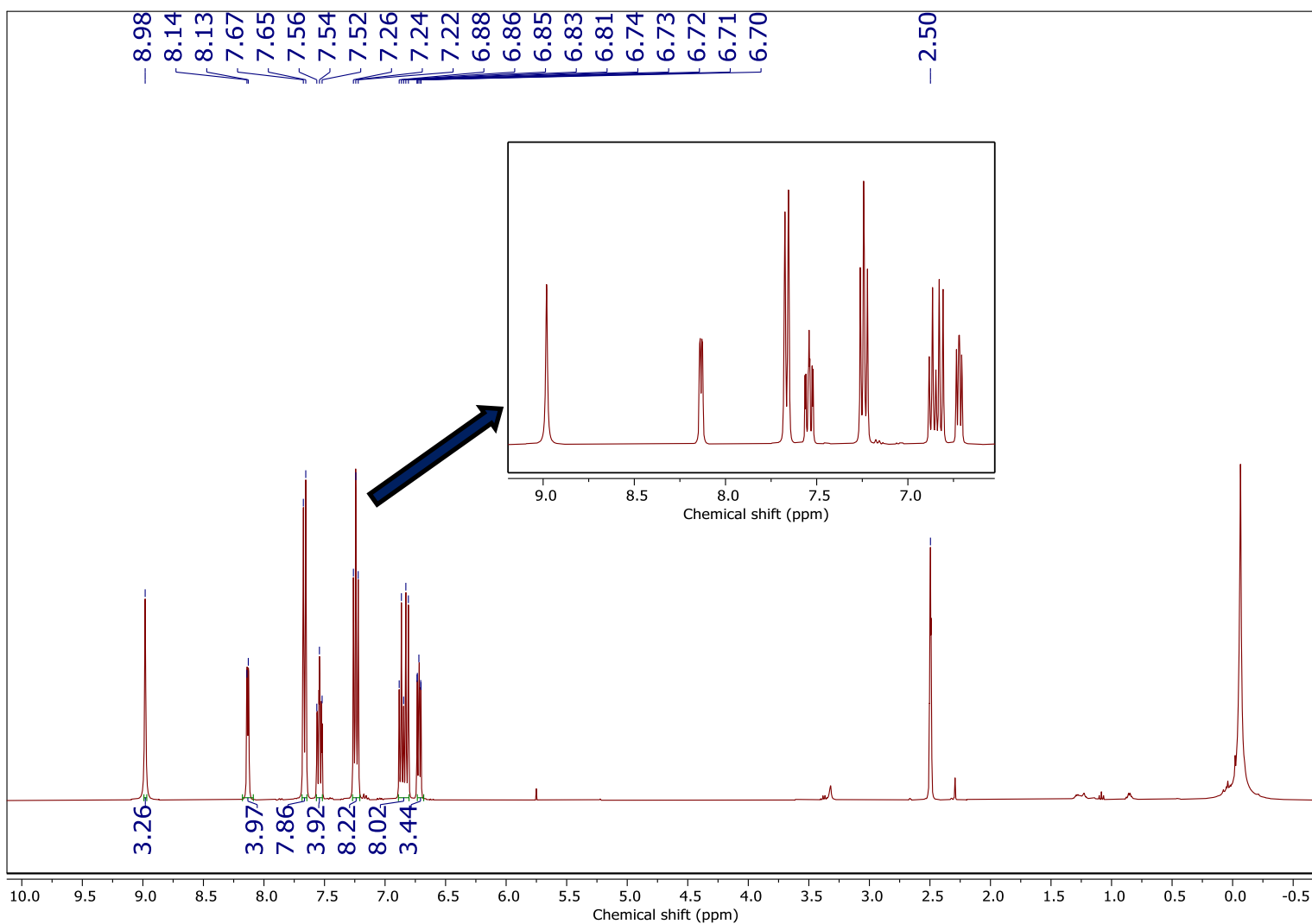


Figure 2.A.7. ^1H NMR spectrum of 2.5 in $\text{DMSO}-d_6$ (Solvent peak δ 2.50 ppm) (400 MHz, 298 K).

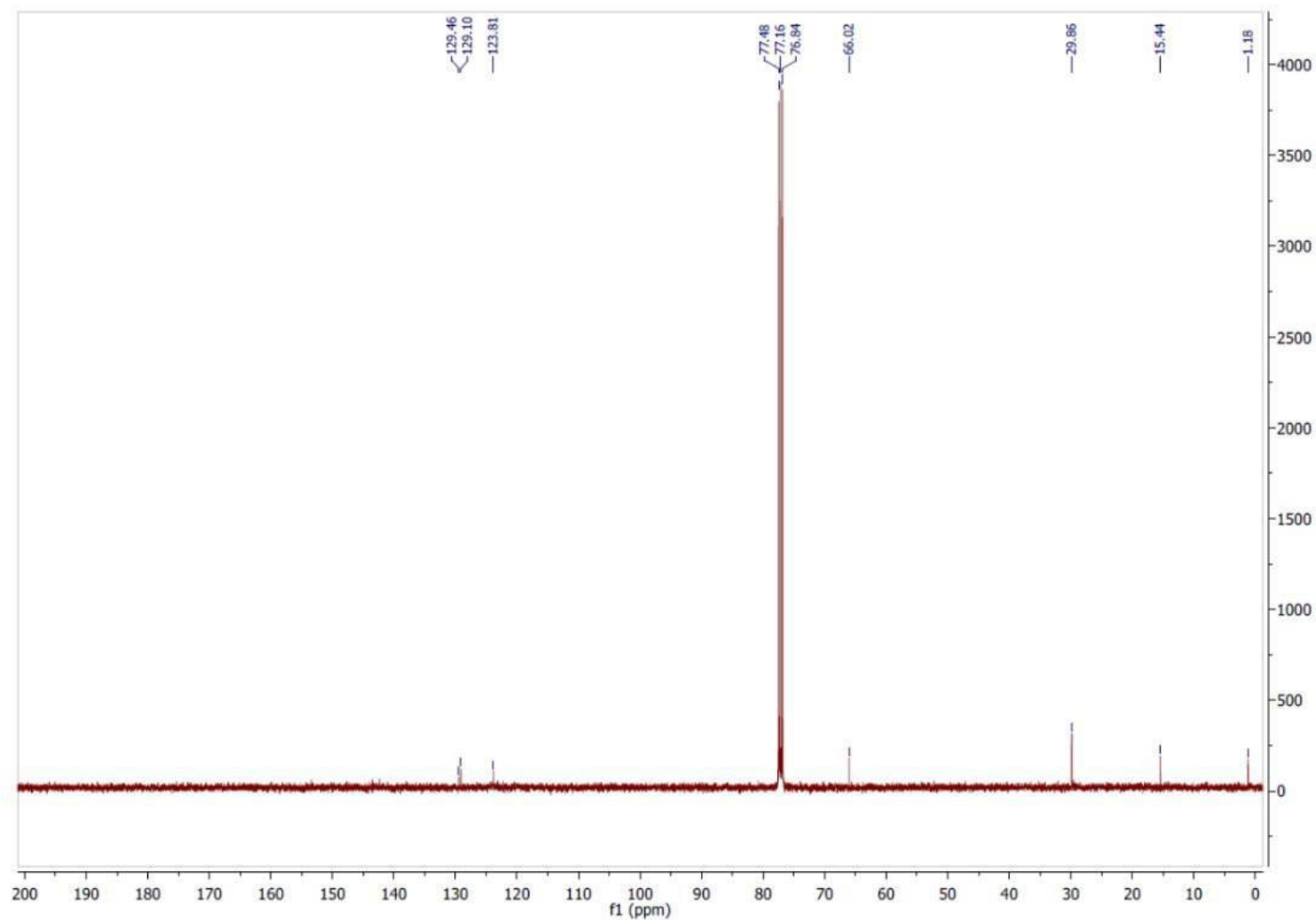


Figure 2.A.8. ^{13}C NMR spectrum of 2.5 in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

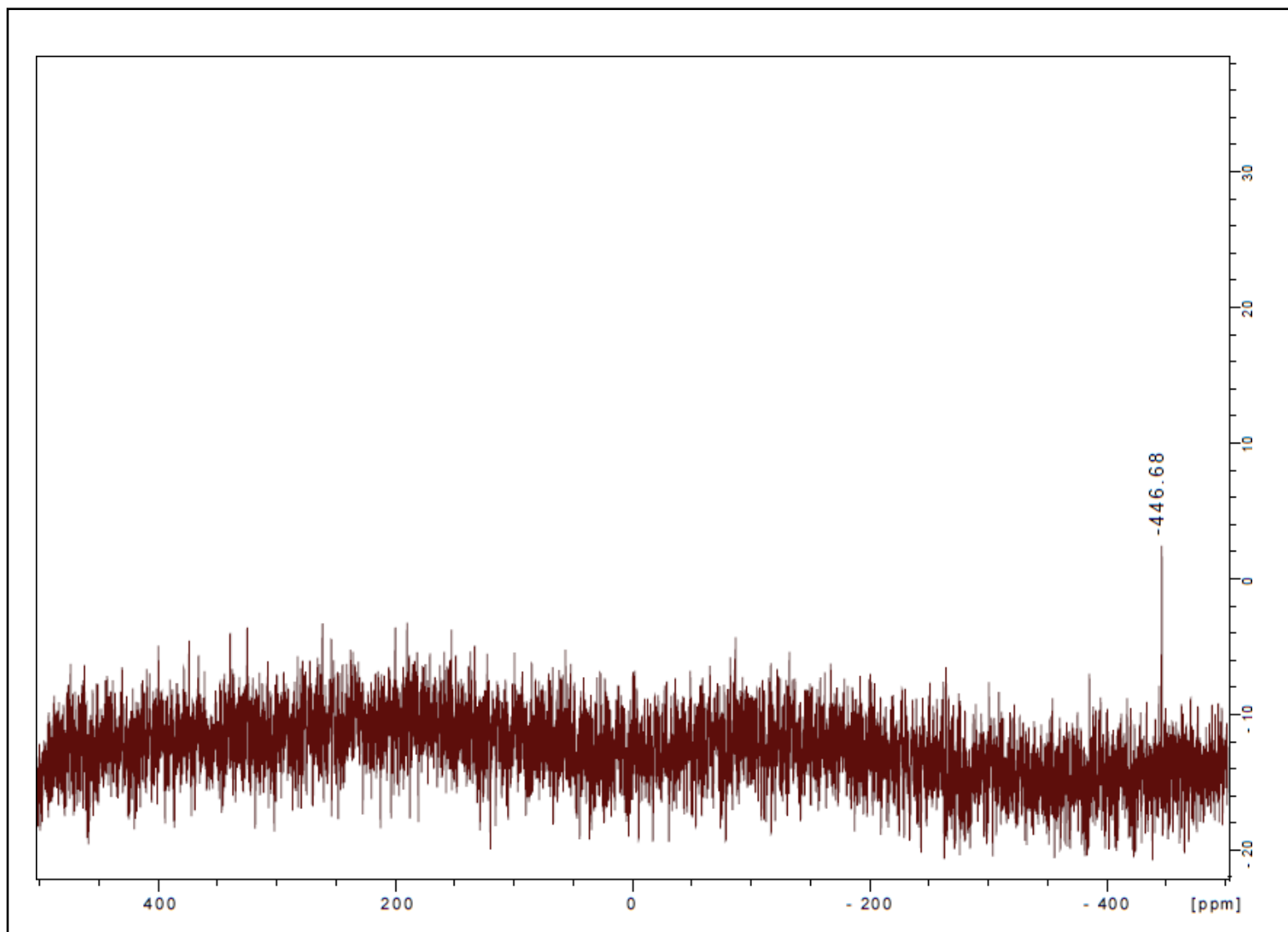


Figure 2.A.9. ^{119}Sn NMR spectrum of **2.5** in CDCl_3 (149.18 MHz, 298K).

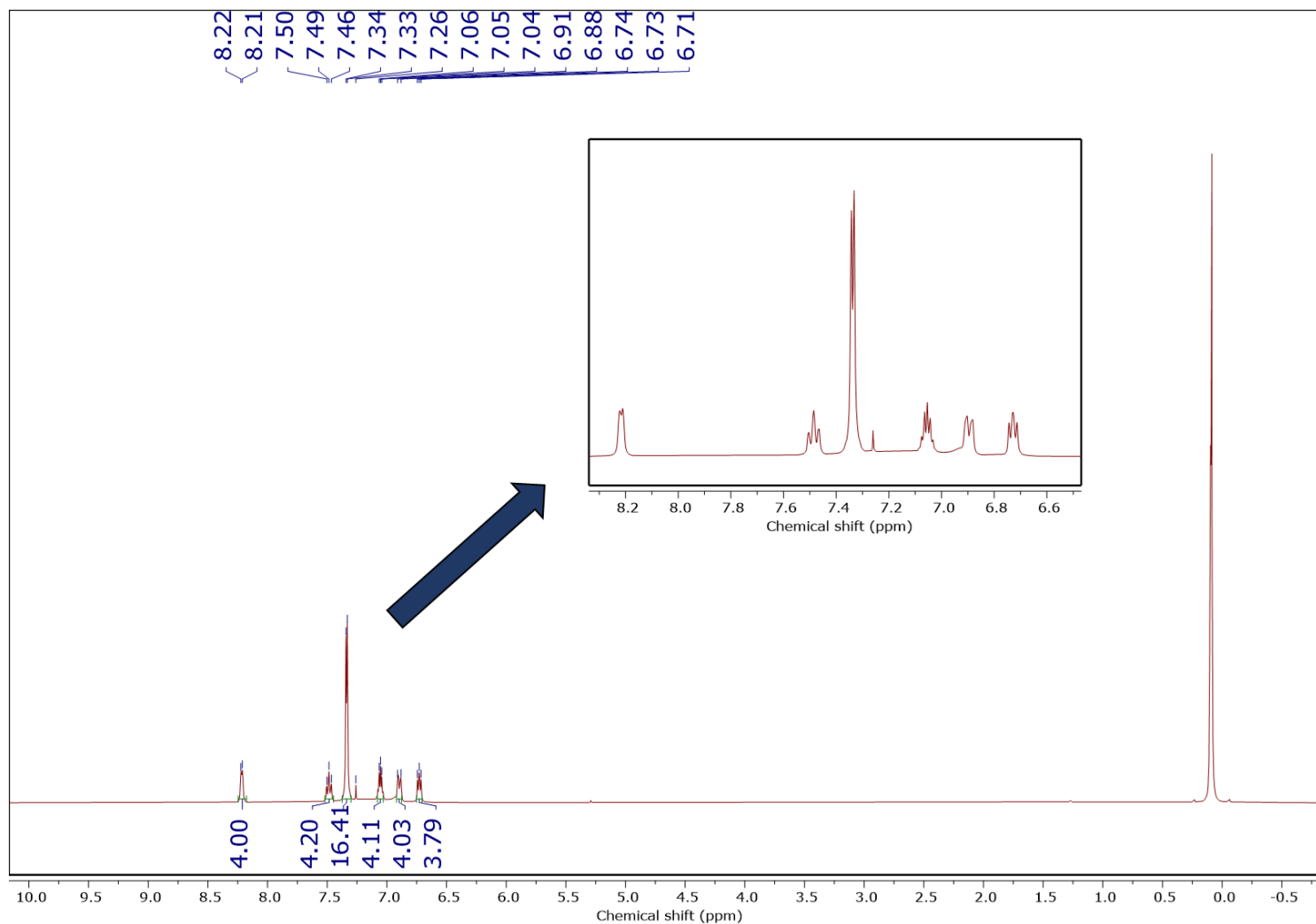


Figure 2.A.10. ^1H NMR spectrum of **2.6** in CDCl_3 (Solvent peak δ 7.26 ppm), (400 MHz, 298 K).

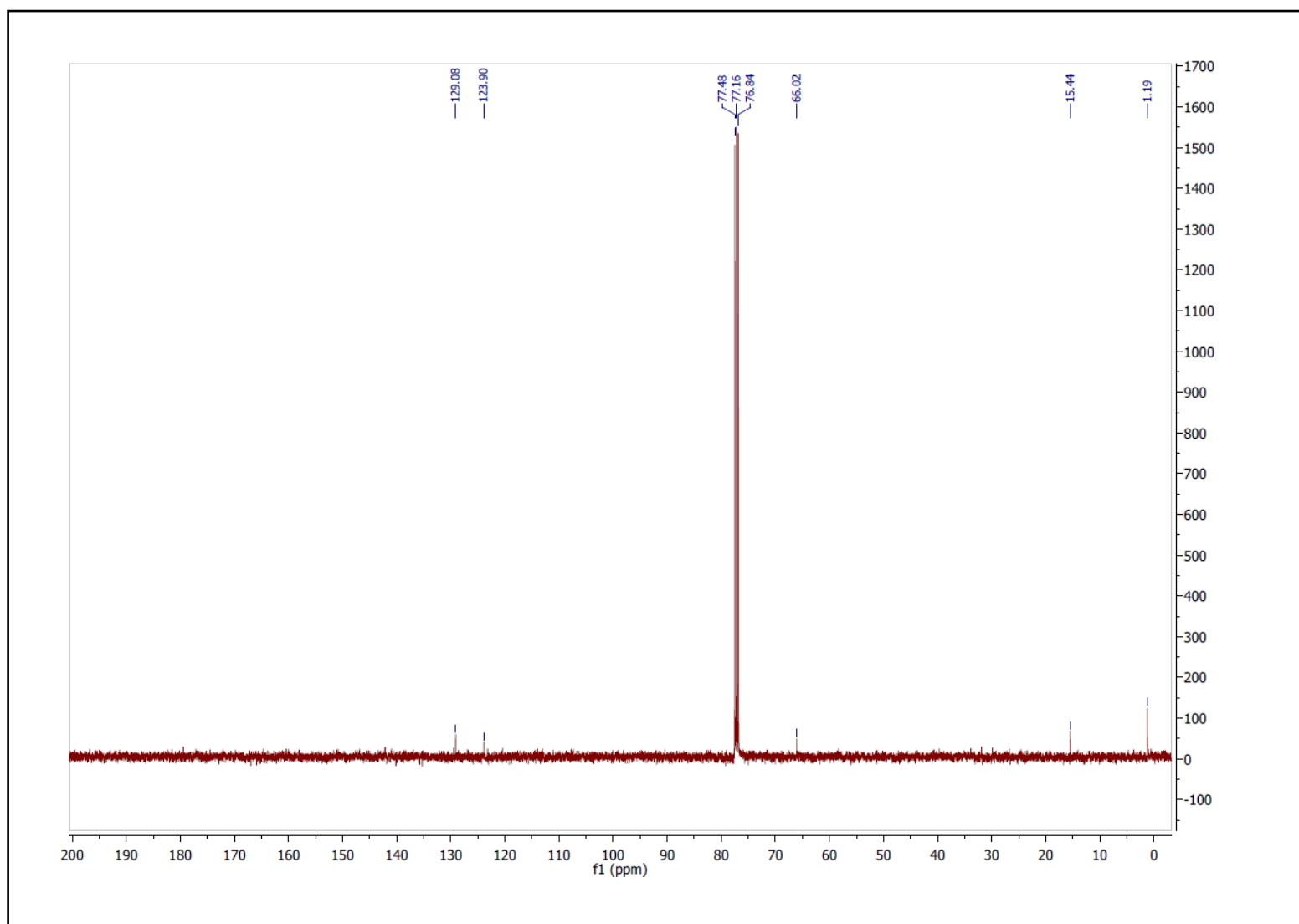


Figure 2.A.11. ^{13}C NMR spectrum of **2.6** in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

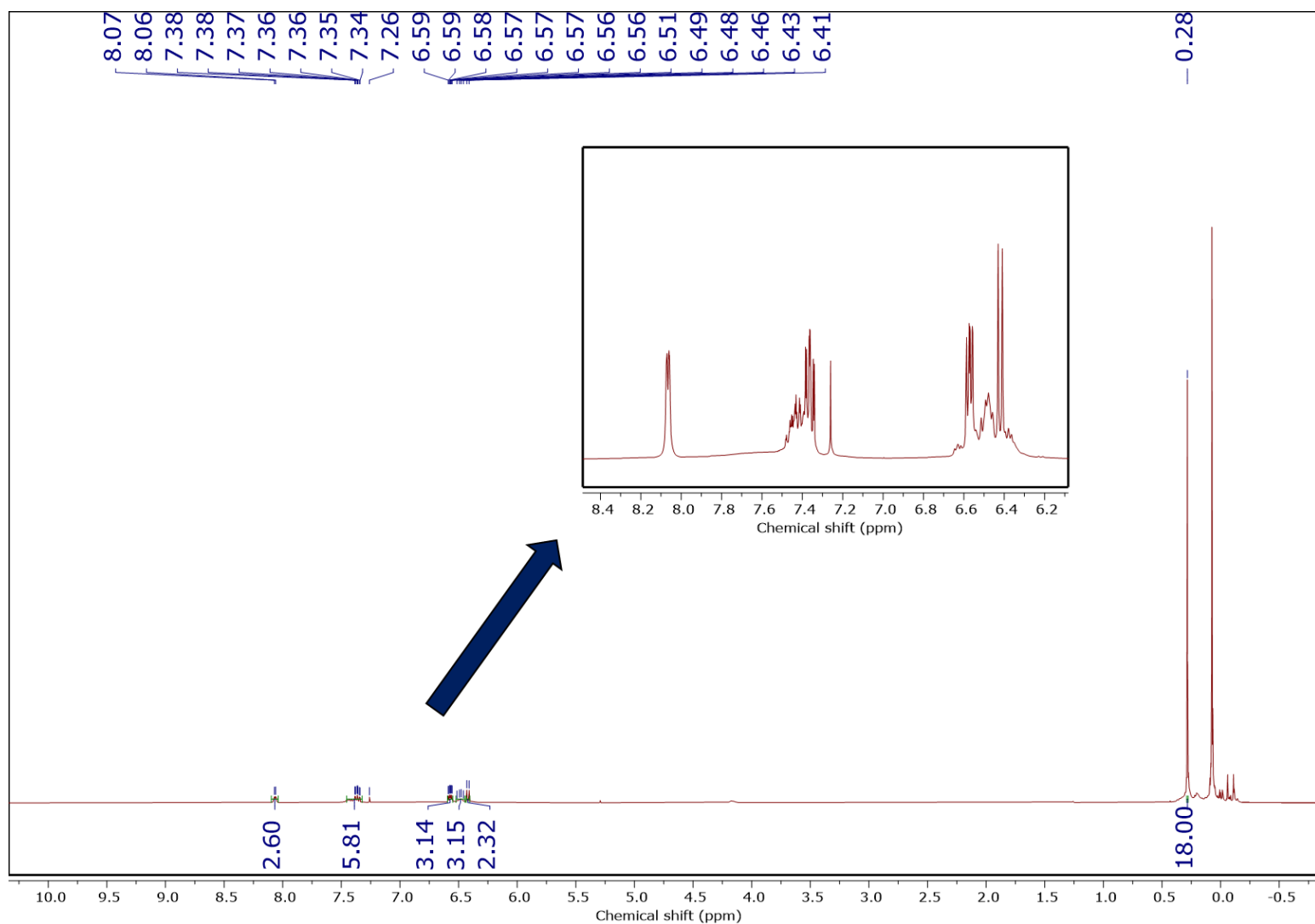


Figure 2.A.12. ^1H NMR spectrum of **2.7** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

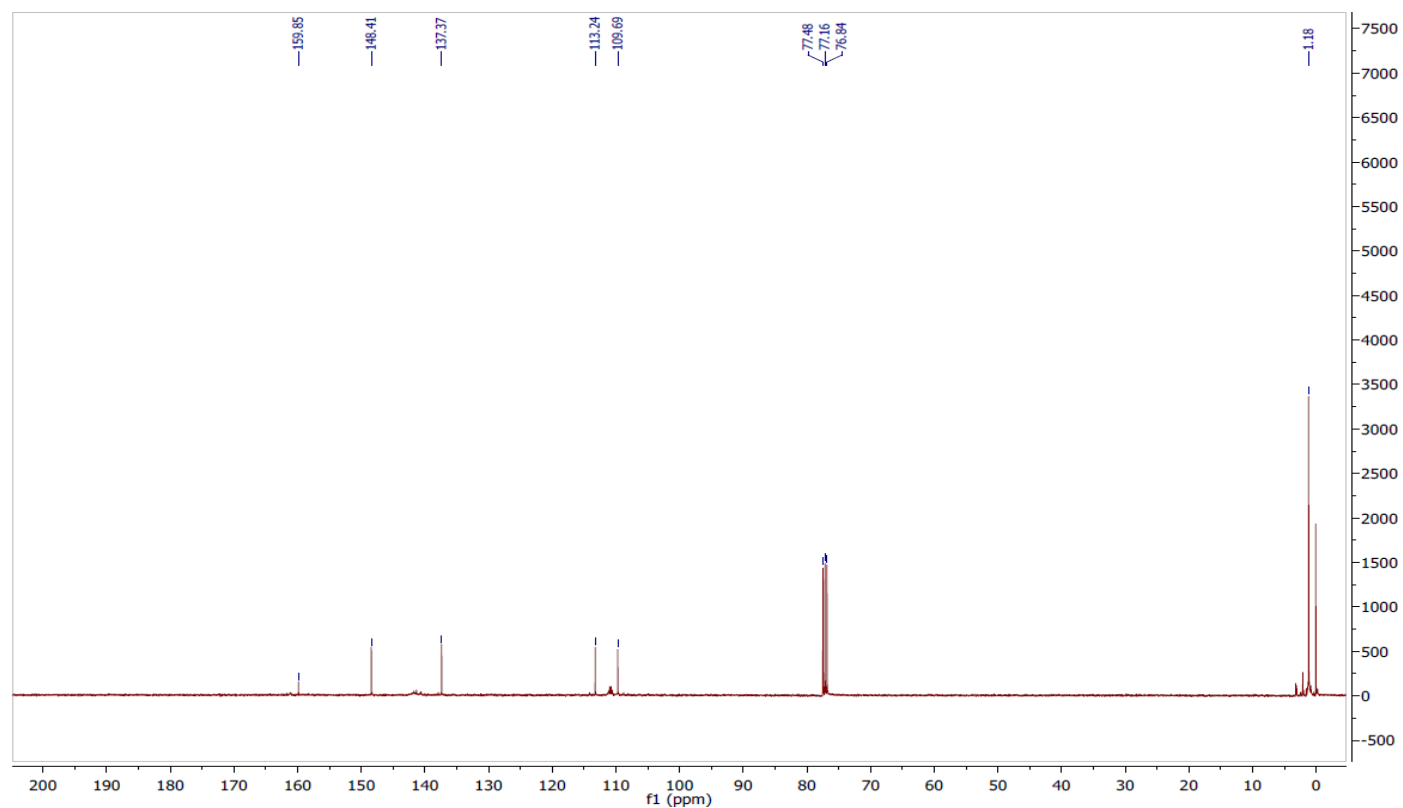


Figure 2.A.13. ^{13}C NMR spectrum of **2.7** in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

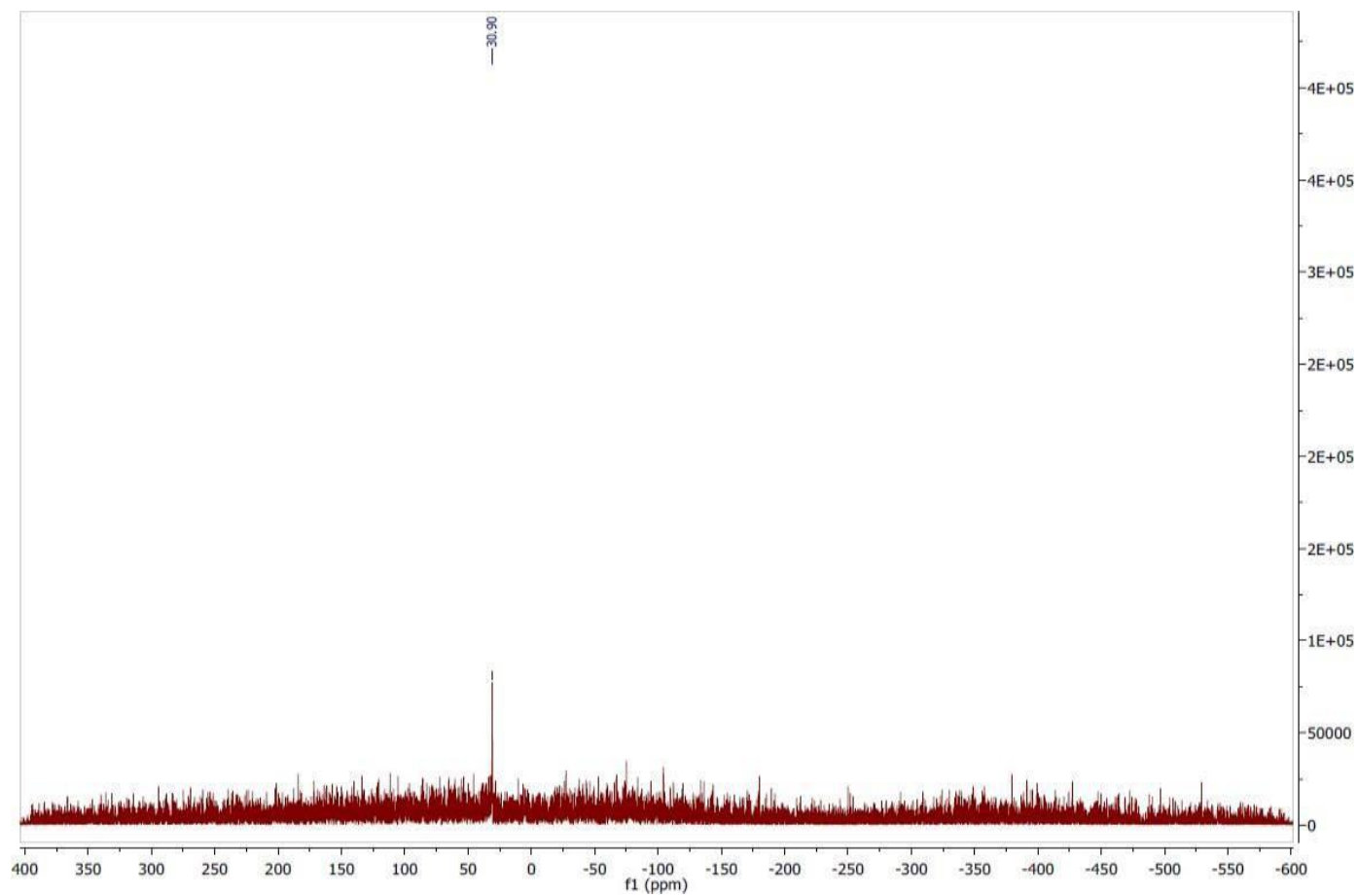


Figure 2.A.14. ^{119}Sn NMR spectrum of 2.7 in CDCl_3 (149.18 MHz, 298K).

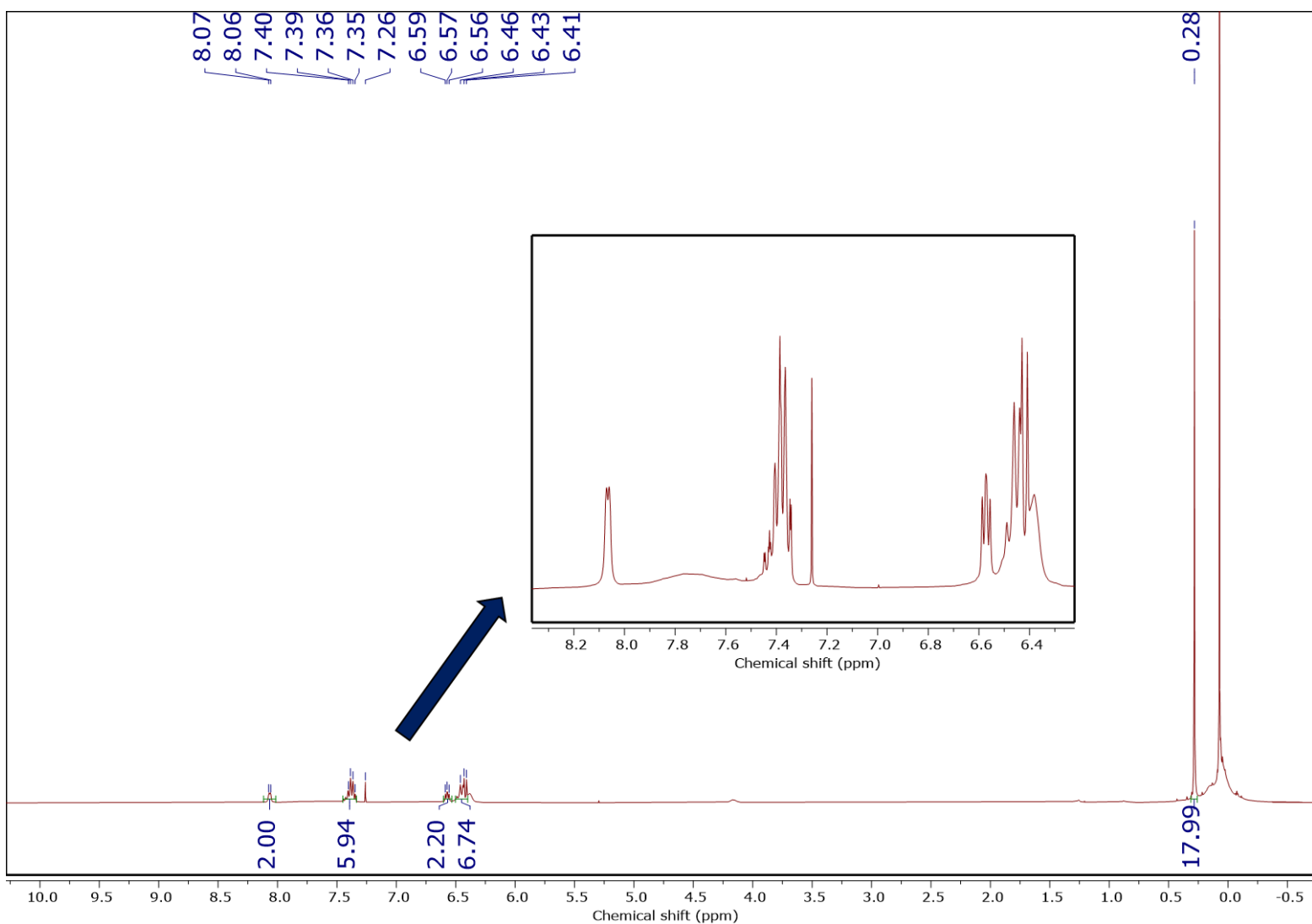


Figure 2.A.15. ¹H NMR spectrum of **2.8** in CDCl₃ (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

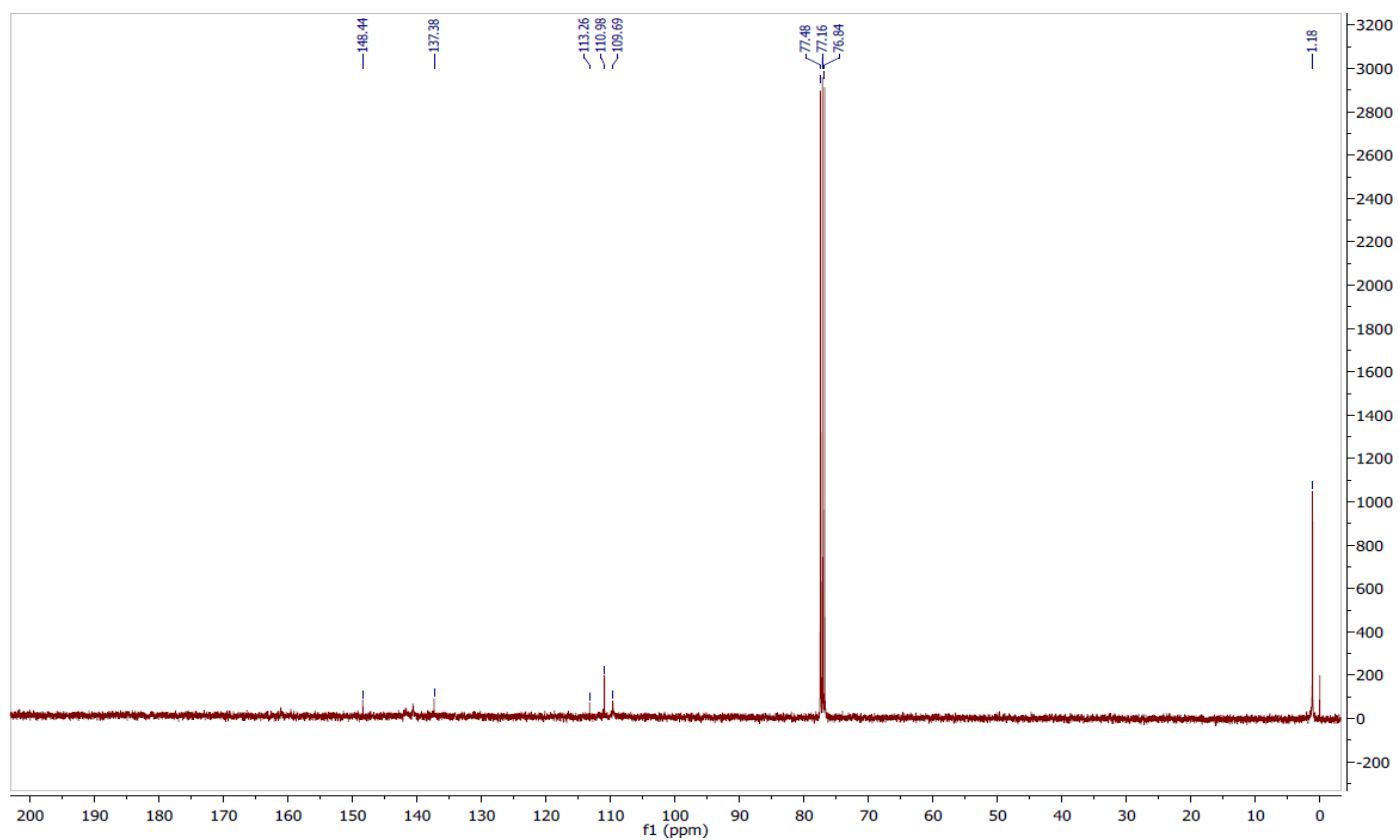


Figure 2.A.16. ^{13}C NMR spectrum of **2.8** in CDCl_3 (Solvent peak δ 7.26 ppm) (100.613 MHz, 298 K).

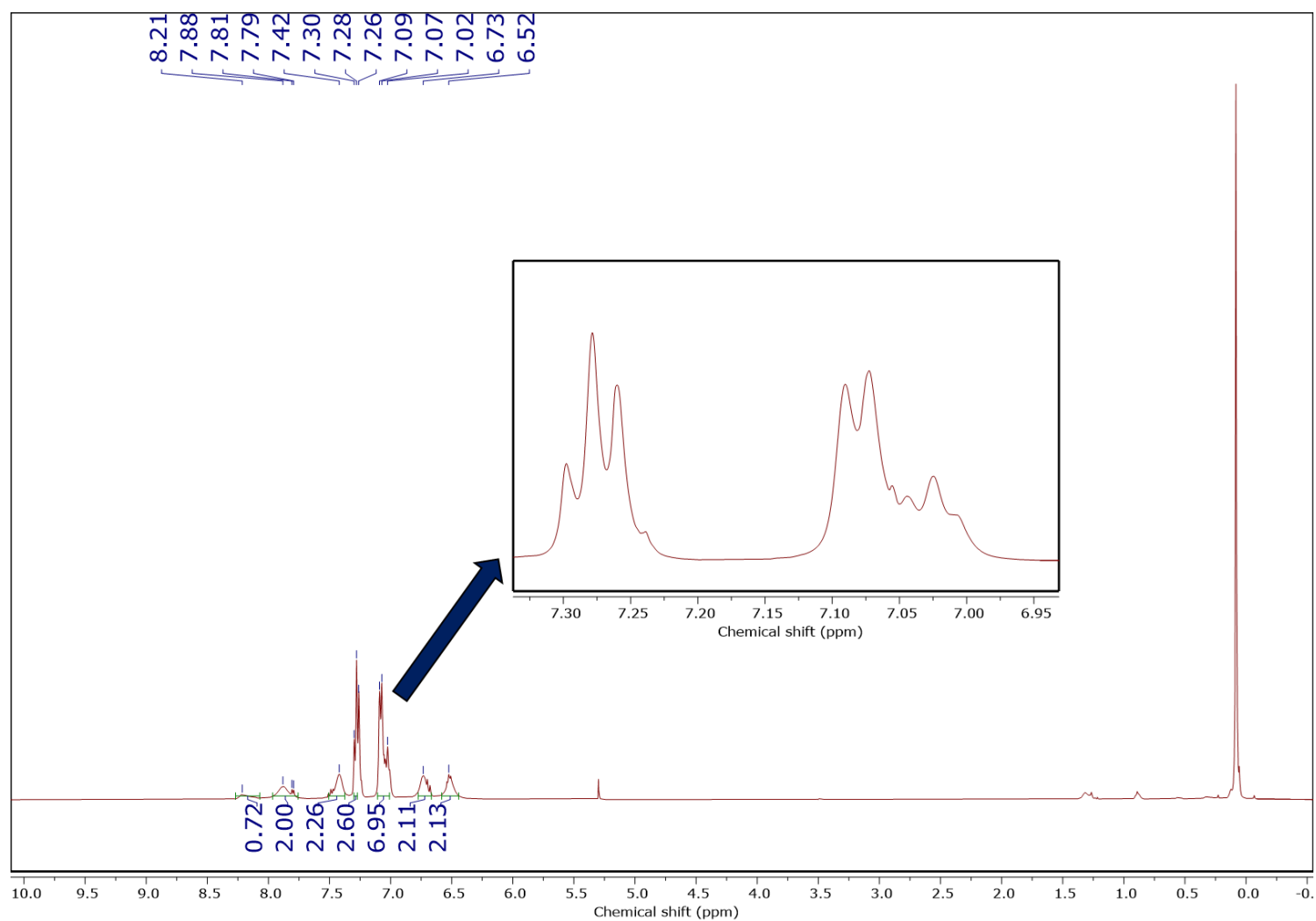


Figure 2.A.17. ¹H NMR spectrum of **2.9** in CDCl₃ (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

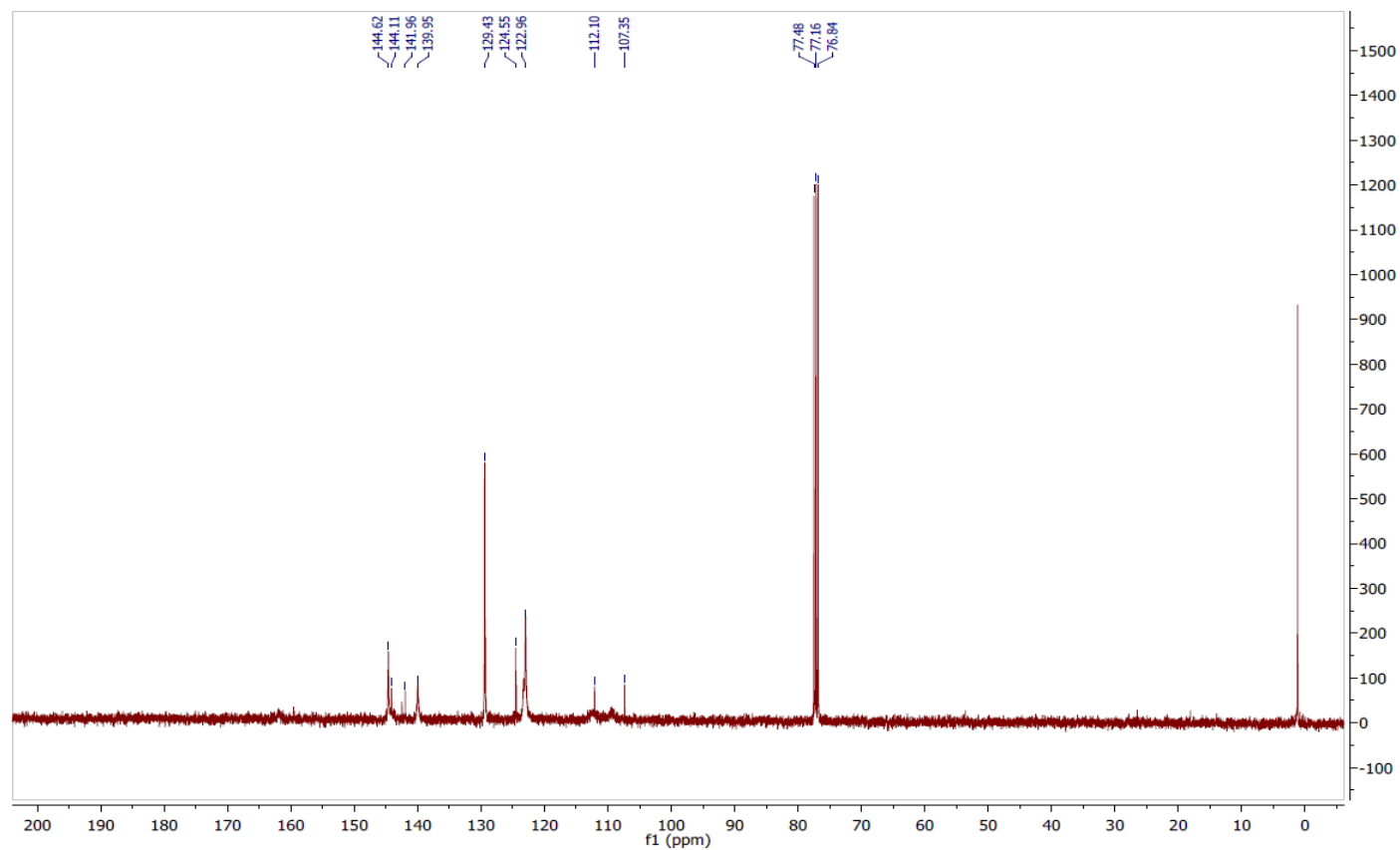


Figure 2.A.18. ¹³C NMR spectrum of **2.9** in CDCl₃ (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

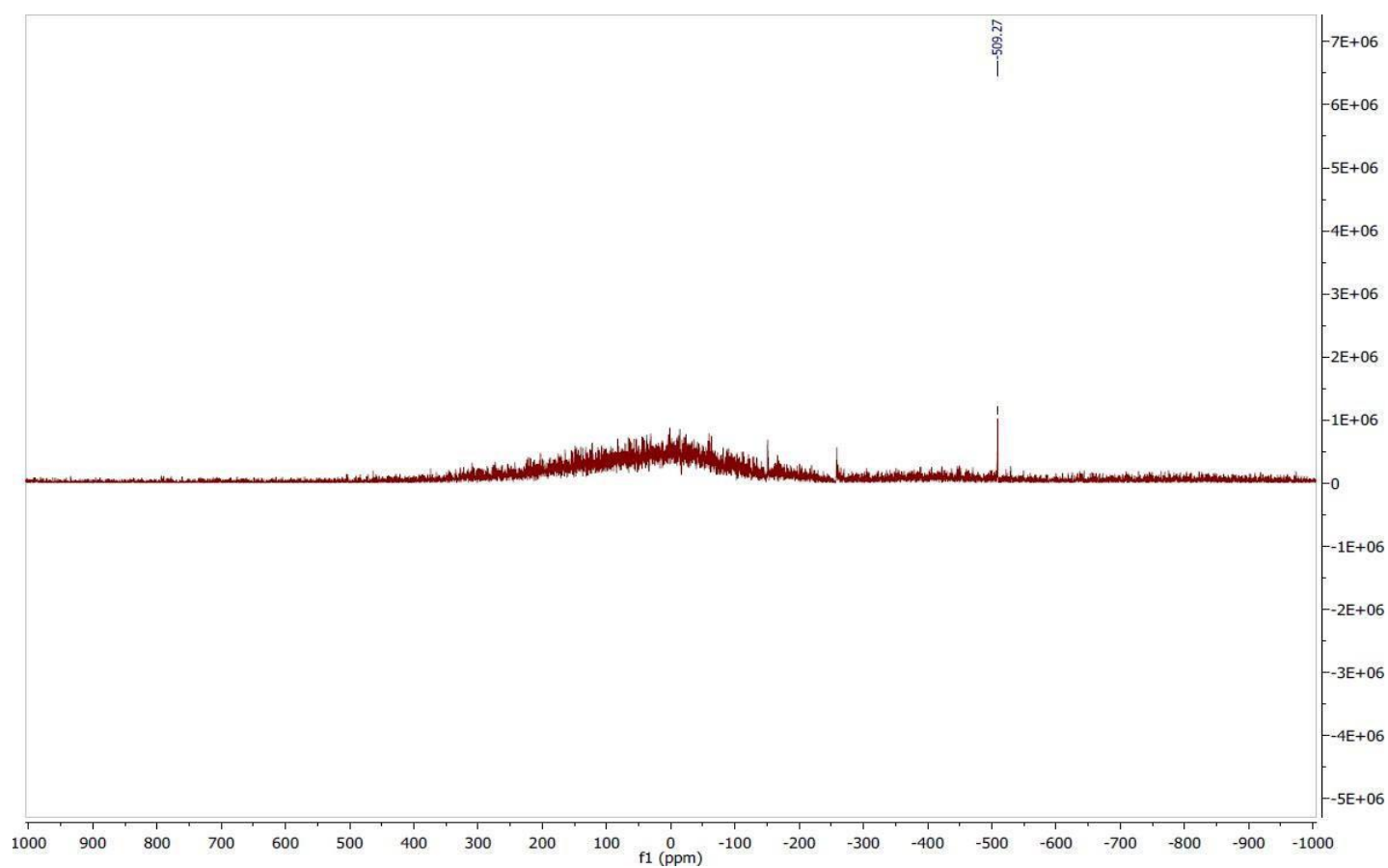


Figure 2.A.19. ^{119}Sn NMR spectrum of **2.9** in CDCl_3 (149.18 MHz, 298K).

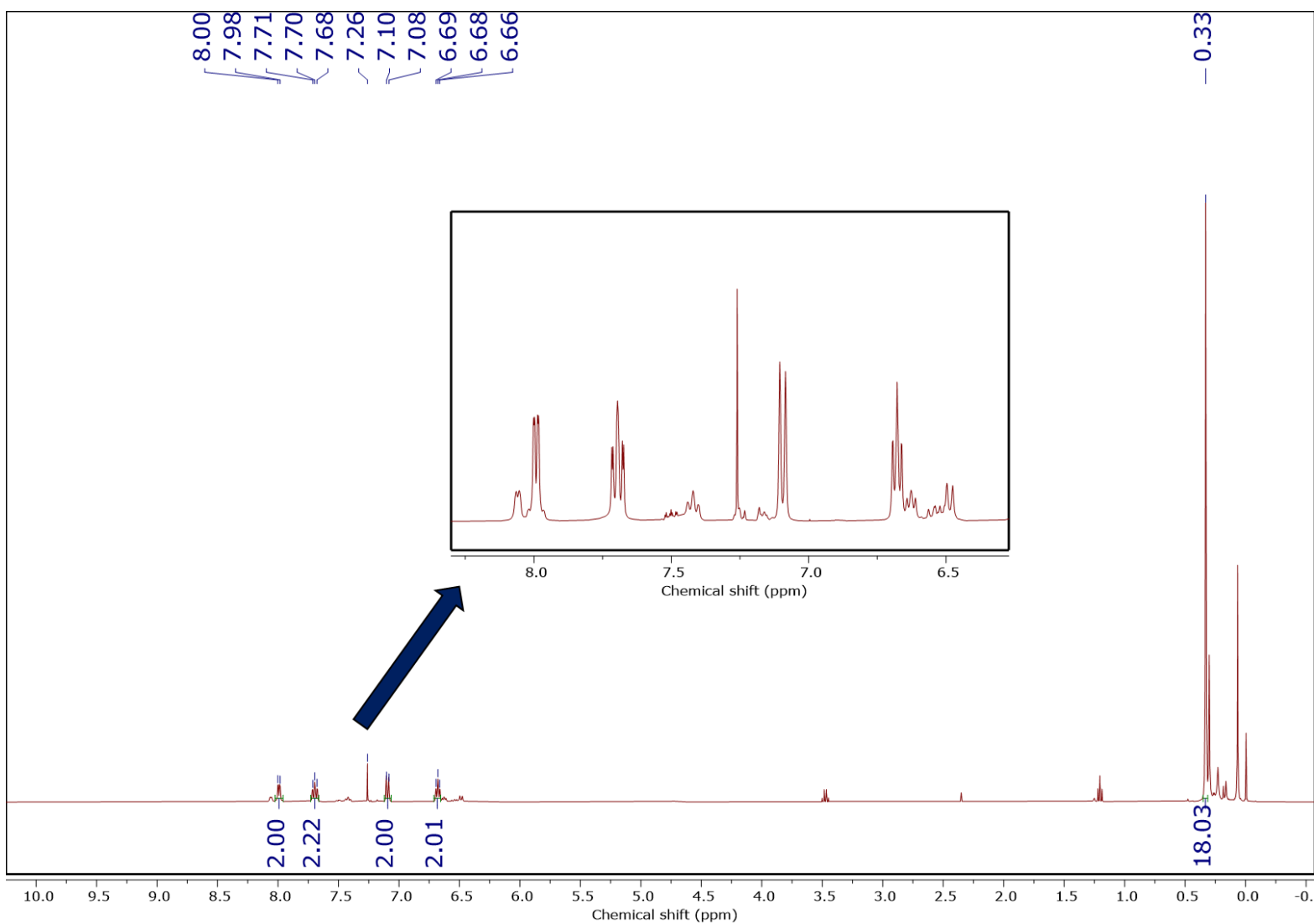


Figure 2.A.20. ^1H NMR spectrum of **2.10** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

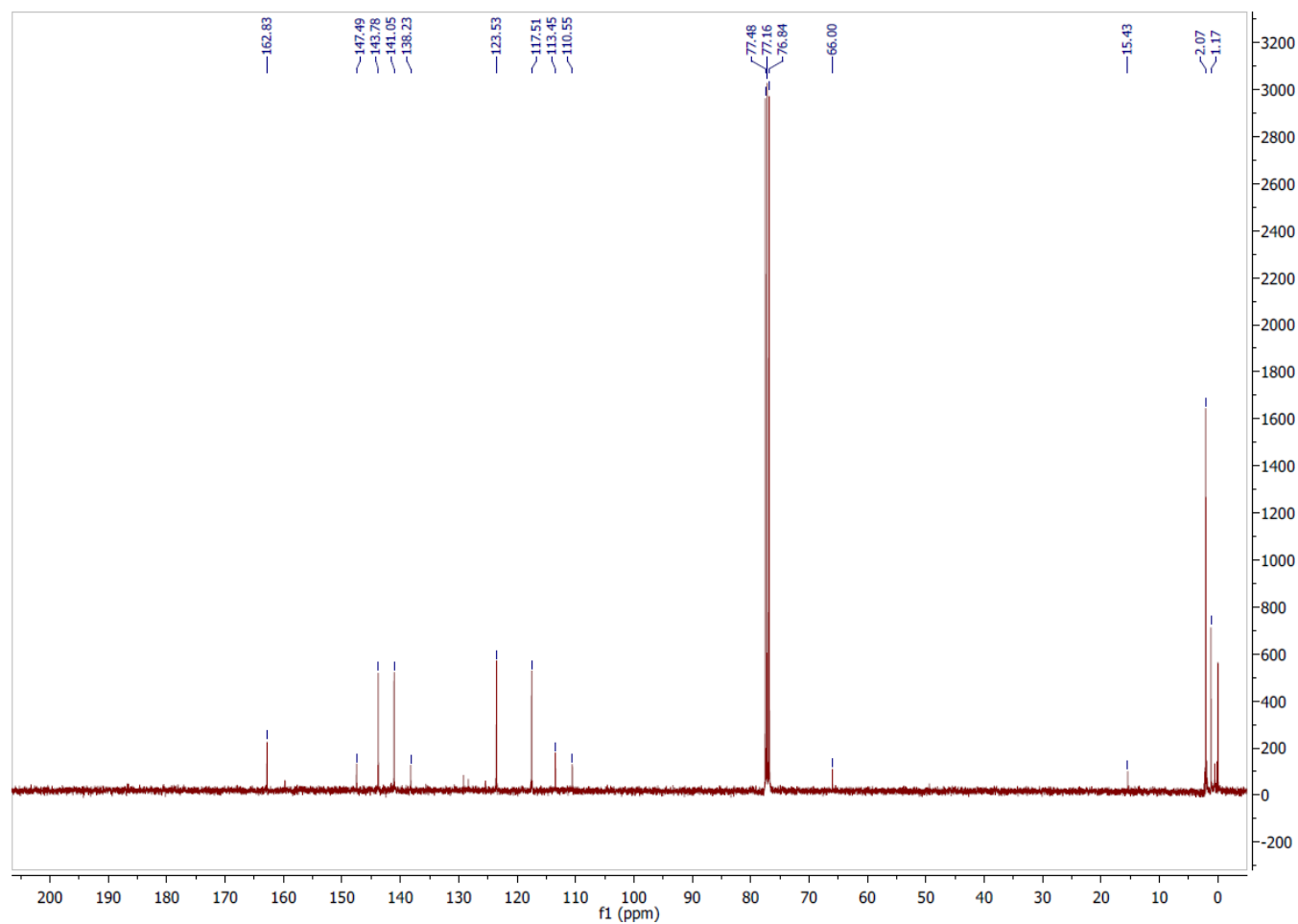


Figure 2.A.21. ¹³C NMR spectrum of **2.10** in CDCl₃ (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

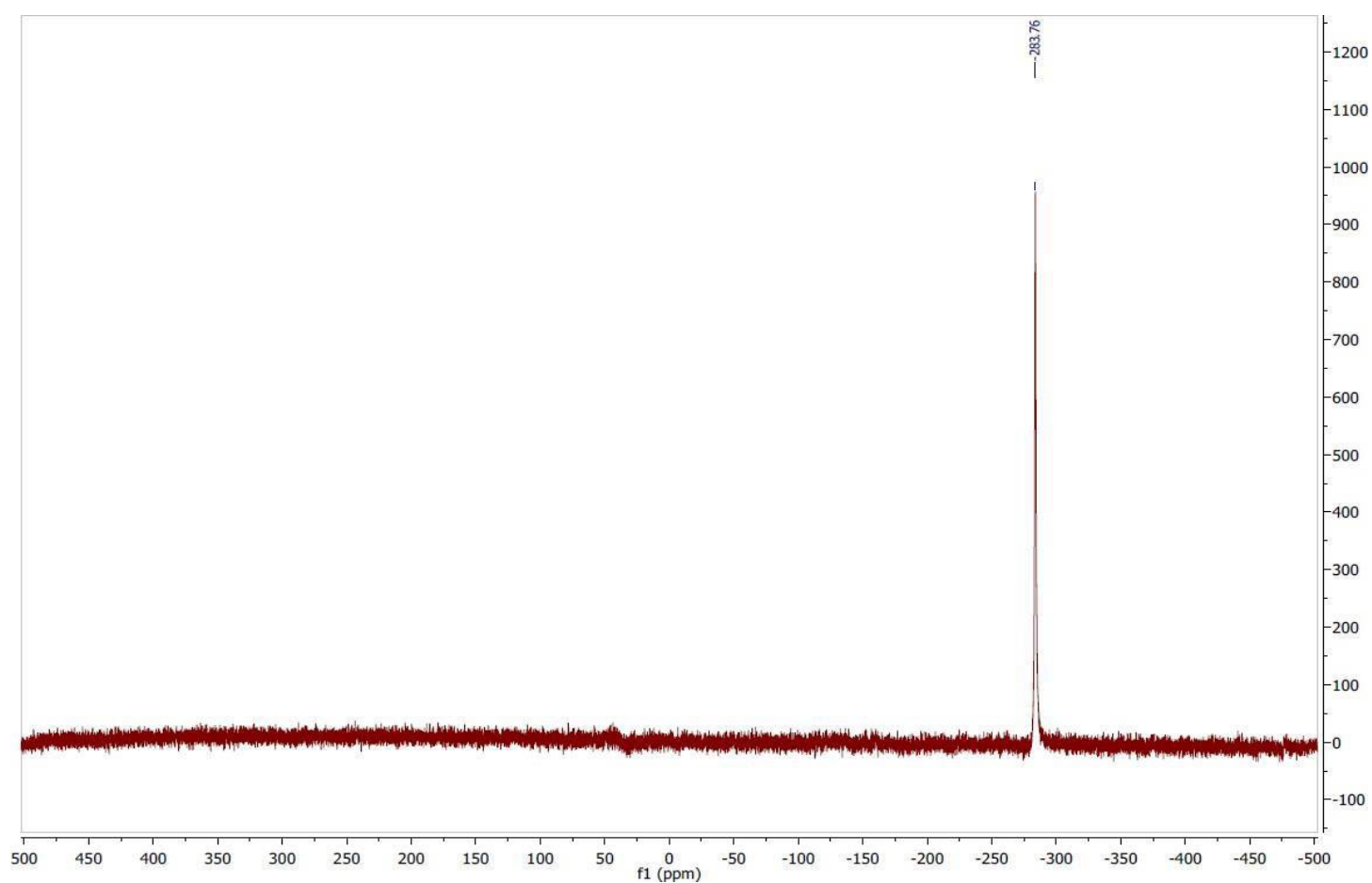


Figure 2.A.22. ^{119}Sn NMR spectrum of **2.10** in CDCl_3 (149.18 MHz, 298K).

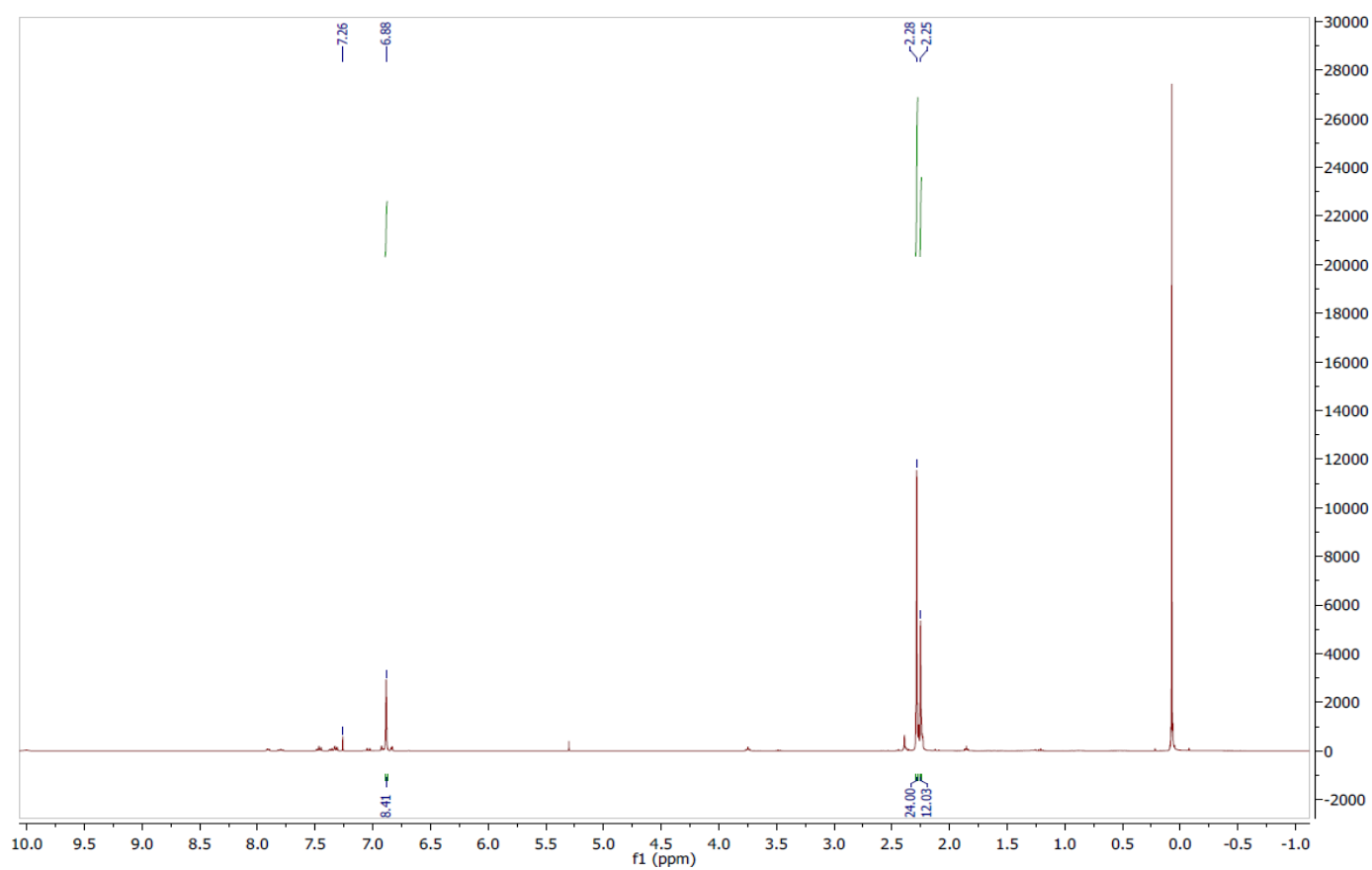


Figure 2.A.23. ^1H NMR spectrum of **2.11** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

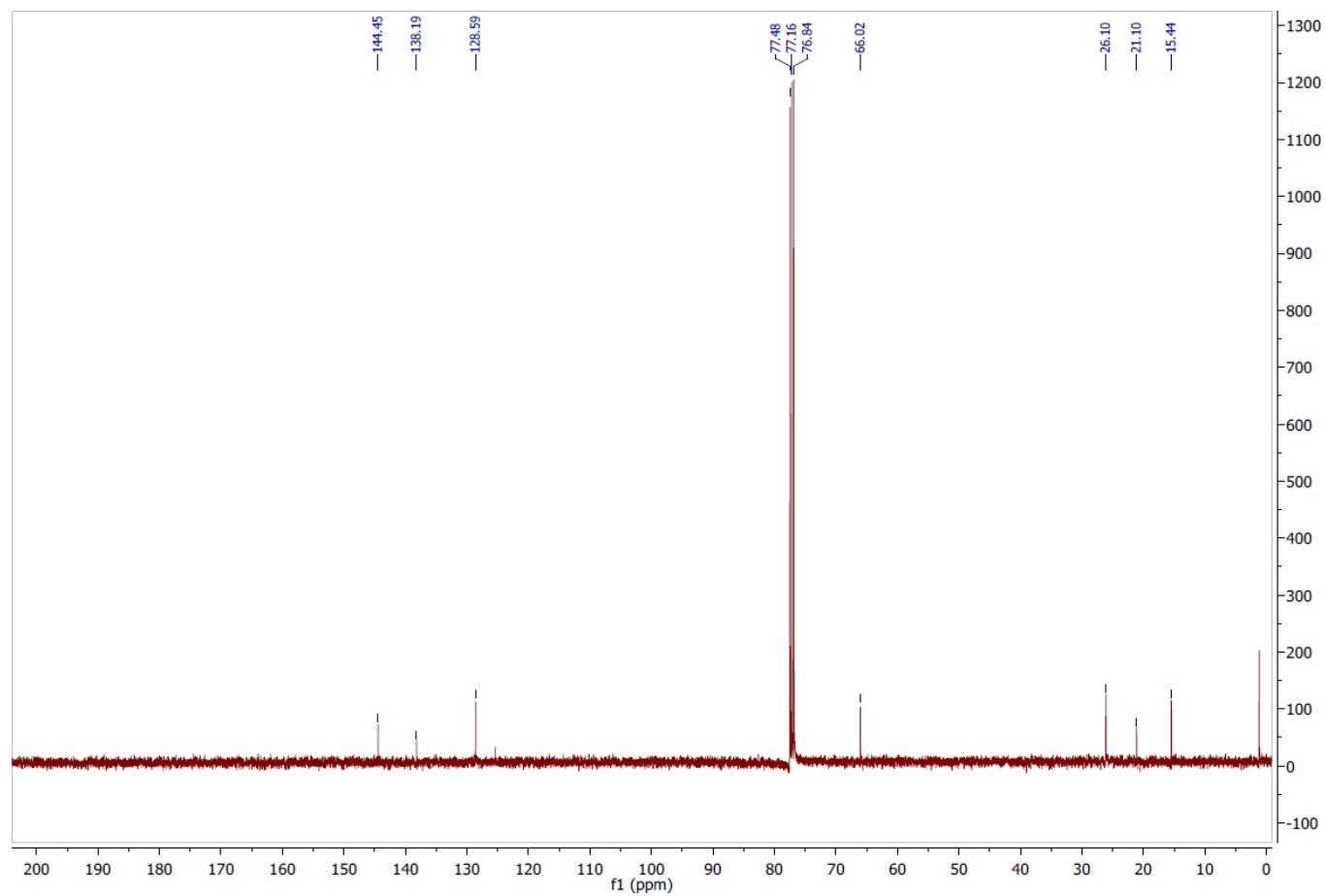


Figure 2.A.24. ¹³C NMR spectrum of **2.11** in CDCl₃ (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

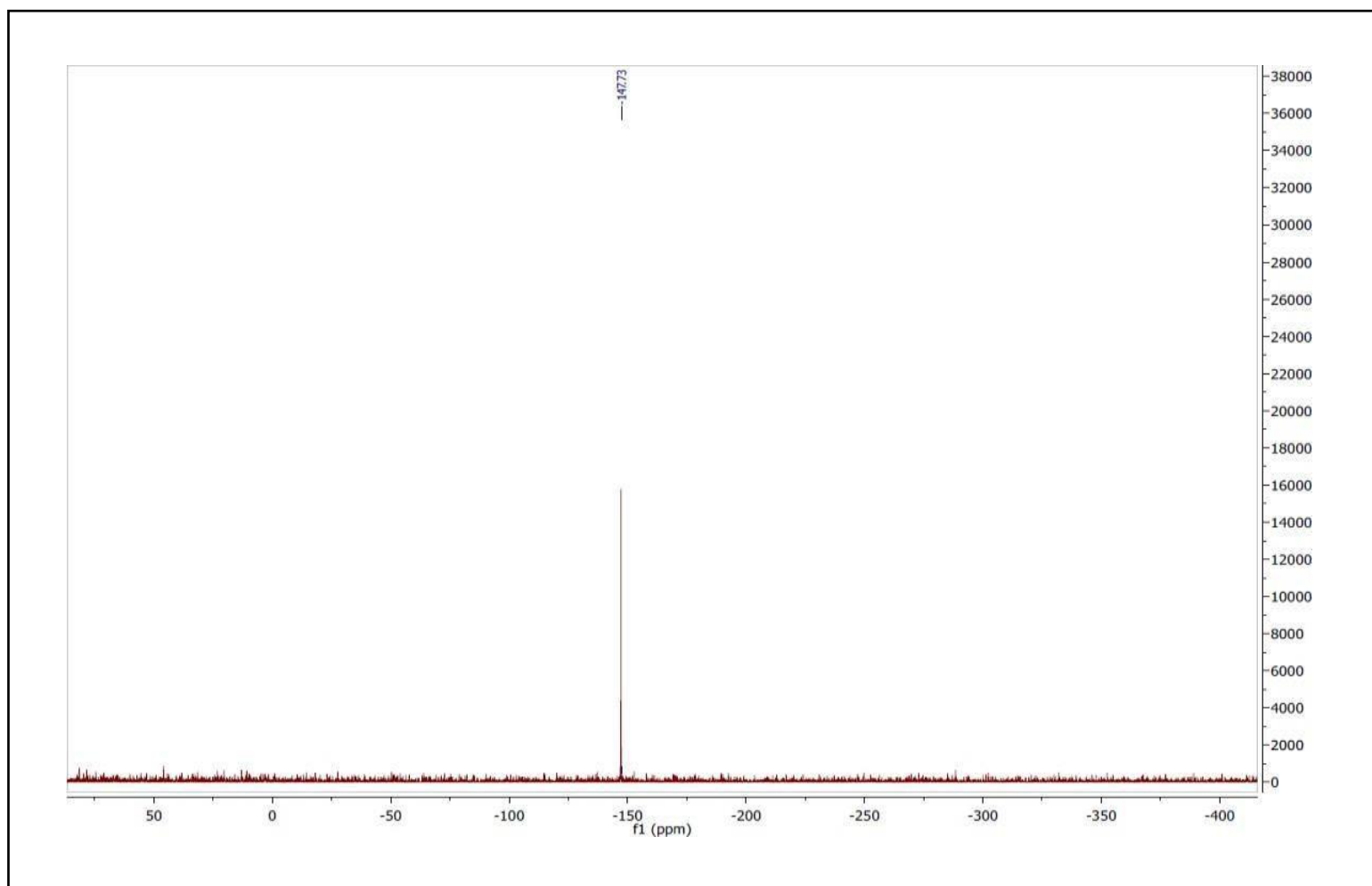


Figure 2.A.25. ^{119}Sn NMR spectrum of **11** in CDCl_3 (149.18 MHz, 298K).

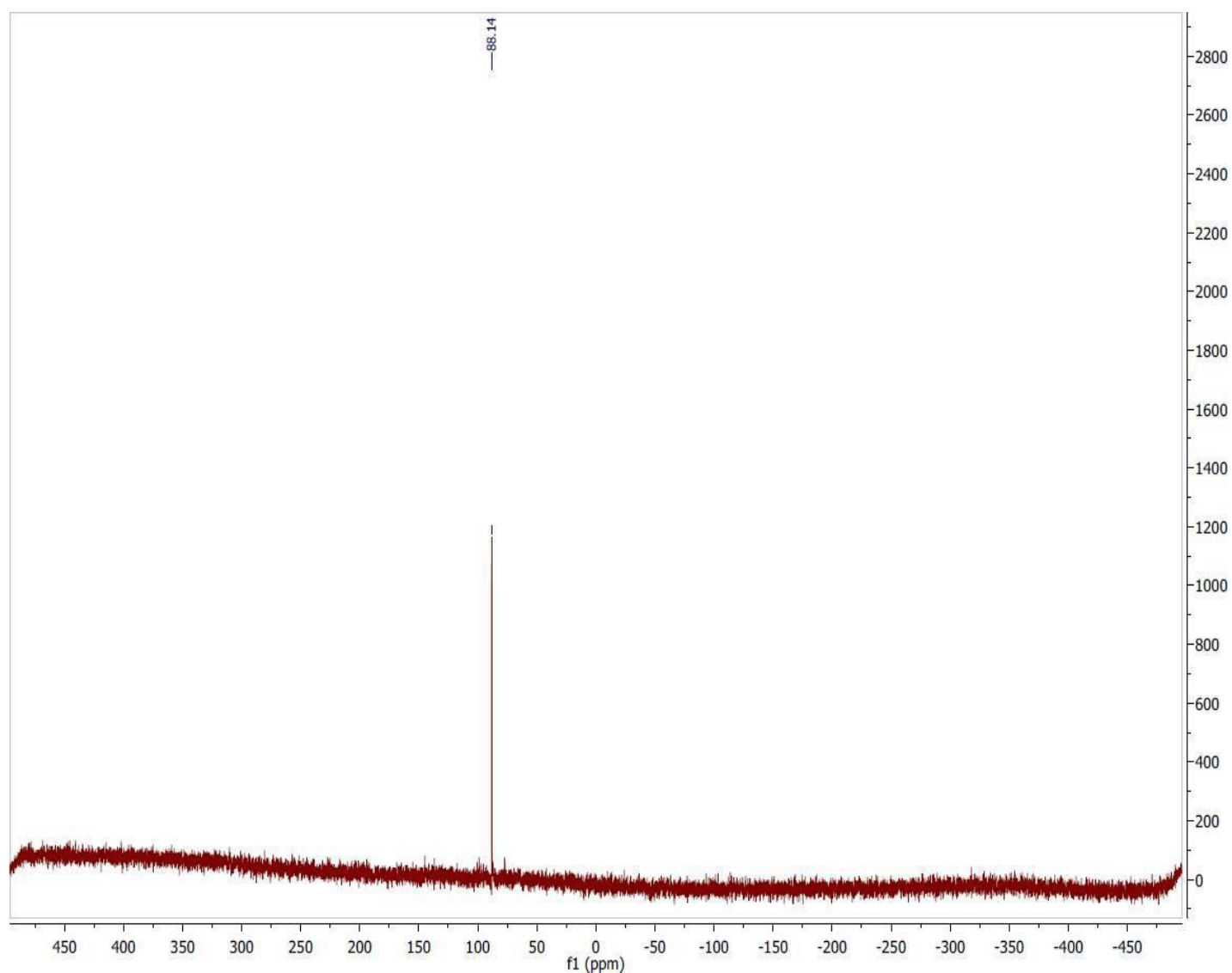


Figure 2.A.26. ^{77}Se NMR of **2.11** in CDCl_3

Appendix of Chapter 3

Table 3.A.1. Crystallographic details of compounds **3.2**, **3.3** and **3.4**

	3.2	3.3	3.4
Chemical formula	C ₁₆ H ₃₃ B ₂ Cl ₈ NSi ₄	C ₂₈ H ₅₅ BClNSi ₃	C ₁₆ H ₃₃ AlCl ₃ NSi ₃
Formula weight	657.01 g/mol	536.26 g/mol	457.03 g/mol
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 21/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 21/ <i>n</i>
Unit cell dimensions	<i>a</i> = 8.5462(12) Å	<i>a</i> = 40.184(4) Å	<i>a</i> = 8.6938(16) Å
	<i>b</i> = 29.100(5) Å	<i>b</i> = 9.0153(11) Å	<i>b</i> = 35.813(7) Å
	<i>c</i> = 12.0798(19) Å	<i>c</i> = 17.4609(16) Å	<i>c</i> = 8.7868(18) Å
	α = 90°	α = 90°	α = 90°
	β = 94.993(4) °	β = 93.345(4)°	β = 116.889(5)°
	γ = 90°	γ = 90°	γ = 90°
Volume	2992.8(8) Å ³	6314.8(12) Å ³	2440.0(8) Å ³
Z	4	8	4
Density (calculated)	1.458 g/cm ³	1.128 g/cm ³	1.244 g/cm ³
Absorption coefficient	0.922 mm ⁻¹	0.252 mm ⁻¹	0.560 mm ⁻¹
F(000)	1352	2352	968
Theta range for data collection	2.49 to 24.22°	2.32 to 28.27°	2.27 to 28.15°
Index ranges	-10 ≤ <i>h</i> ≤ 10, -34 ≤ <i>k</i> ≤ 34, -14 ≤ <i>l</i> ≤ 14	-48 ≤ <i>h</i> ≤ 48, -10 ≤ <i>k</i> ≤ 10, -20 ≤ <i>l</i> ≤ 20	-11 ≤ <i>h</i> ≤ 11, -47 ≤ <i>k</i> ≤ 47, -11 ≤ <i>l</i> ≤ 11
Reflections collected	72111	75331	92721
Independent reflections	5417 [R(int) = 0.1863]	5709 [R(int) = 0.0865]	6073 [R(int) = 0.1116]
Coverage of independent reflections	99.9%	99.8%	100%
Function minimized	Σ w(Fo ² - Fc ²) ²	Σ w(Fo ² - Fc ²) ²	Σ w(Fo ² - Fc ²) ²
Data / restraints / parameters	5417 / 0 / 291	5709 / 0 / 318	6073 / 0 / 228
Goodness-of-fit on F²	1.059	1.185	1.117
Δ/σ max	0.007	0.001	0.000
Final R indices	3613 data; [I > 2σ(I)] R1 = 0.0639, wR2 = 0.0924	4770 data; [I > 2σ(I)], R1 = 0.0627, wR2 = 0.1355	4665 data; [I > 2σ(I)], R1 = 0.0533, wR2 = 0.0939
	all data, R1 = 0.1171, wR2 = 0.1066	all data, R1 = 0.0782, wR2 = 0.1414	all data, R1 = 0.0833, wR2 = 0.1017
Largest diff. peak and hole	0.571 and -0.511 eÅ ⁻³	0.506 and -0.311 eÅ ⁻³	0.422 and -0.399 eÅ ⁻³

R.M.S. deviation from mean	0.119 eÅ-3	0.074 eÅ-3	0.094 eÅ-3
----------------------------	------------	------------	------------

Crystallographic details of compounds 3.5, 3.6 and 3.7

	3.5	3.6	3.7
Chemical formula	C ₁₆ H ₃₃ AlBr ₃ NSi ₃	C ₁₈ H ₅₅ Cl ₆ GeN ₃ Si ₉	C ₁₀ H ₁₅ ClSn
Formula weight	590.41 g/mol	851.75 g/mol	289.36 g/mol
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Trigonal	Monoclinic
Space group	<i>P</i> 21/ <i>n</i>	<i>R</i> -3	<i>C</i> 2/ <i>c</i>
Unit cell dimensions	<i>a</i> = 8.8529(9) Å	<i>a</i> = 12.685 Å	<i>a</i> = 16.770(6) Å
	<i>b</i> = 35.584(3) Å	<i>b</i> = 12.685 Å	<i>b</i> = 12.188(5) Å
	<i>c</i> = 8.9606(8) Å	<i>c</i> = 45.584 Å	<i>c</i> = 11.706(4) Å
	α = 90°	α = 90°	α = 90°
	β = 116.920(3) °	β = 90°	β = 109.555(9)°
	γ = 90°	γ = 120°	γ = 90°
Volume	2516.9(4) Å ³	6351.9 Å ³	2254.7(15) Å ³
Z	4	6	8
Density (calculated)	1.558 g/cm ³	1.336 g/cm ³	1.705 g/cm ³
Absorption coefficient	4.988 mm ⁻¹	1.373 mm ⁻¹	2.453 mm ⁻¹
F(000)	1184	2664	1136
Theta range for data collection	2.61 to 26.07°	2.57 to 27.65°	2.50 to 28.39°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -47 ≤ <i>k</i> ≤ 47, -11 ≤ <i>l</i> ≤ 11	-15 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 15, -54 ≤ <i>l</i> ≤ 54	-20 ≤ <i>h</i> ≤ 20, -14 ≤ <i>k</i> ≤ 14, -14 ≤ <i>l</i> ≤ 14
Reflections collected	58371	53299	13832
Independent reflections	6255 [R(int) = 0.1550]	2575 [R(int) = 0.0976]	2043 [R(int) = 0.1085]
Coverage of independent reflections	100%	100%	99.9%
Function minimized	Σ w(Fo ² - Fc ²) ²	Σ w(Fo ² - Fc ²) ²	Σ w(Fo ² - Fc ²) ²
Data / restraints / parameters	6255 / 210 / 228	2575 / 0 / 118	2043 / 0 / 114
Goodness-of-fit on F²	1.131	1.197	2.092
Δ/σ max	0.000	0.000	0.017
Final R indices	4053 data; [I > 2σ(I)] R1 = 0.1114, wR2 =	2023 data [I > 2σ(I)], R1 = 0.0382, wR2 =	1526 data [I > 2σ(I)], R1 = 0.0690, wR2 =

	= 0.2420	0.0771	0.1108
	all data , R1 = 0.1737, wR2 = 0.2650	all data , R1 = 0.0600, wR2 = 0.0858	all data, R1 = 0.1010, wR2 = 0.1152
Largest diff. peak and hole	2.088 and -2.184 eÅ ⁻³	0.947 and -0.610 eÅ ⁻³	1.549 and -0.954 eÅ ⁻³
R.M.S. deviation from mean	0.279 eÅ ⁻³	0.093 eÅ ⁻³	0.234 eÅ ⁻³

Crystallographic details of compounds 3.8, 3.9 and 3.10

	3.8	3.9	3.10
Chemical formula	C ₁₀ H ₁₅ AlCl ₄ Ge	C ₂₈ H ₄₃ ClNPSi ₃	C ₃₂ H ₆₆ N ₂ Si ₆ Cl ₂
Formula weight	376.59 g/mol	544.32 g/mol	653.04 g/mol
Temperature	100(2) K	100(2) K	100(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>P b c a</i>	<i>P -1</i>	<i>P -1</i>
Unit cell dimensions	<i>a</i> = 9.2944(7) Å	<i>a</i> = 9.3619(7) Å	<i>a</i> = 9.460(5) Å
	<i>b</i> = 14.8331(9) Å	<i>b</i> = 9.7615(6) Å	<i>b</i> = 9.470(5) Å
	<i>c</i> = 22.8652(17) Å	<i>c</i> = 17.6509(12) Å	<i>c</i> = 13.081(7) Å
	α = 90°	α = 90.876(2)°	α = 94.59(3)°
	β = 90°	β = 105.291(2)°	β = 107.804(16)°
	γ = 90°	γ = 105.151(2)°	γ = 116.76(3)°
Volume	3152.3(4) Å ³	1495.70(18) Å ³	963.0(9) Å ³
Z	8	2	1
Density (calculated)	1.587 g/cm ³	1.209 g/cm ³	1.126 g/cm ³
Absorption coefficient	2.651 mm ⁻¹	0.319 mm ⁻¹	0.274 mm ⁻¹
F(000)	1504	584	352
Theta range for data collection	2.59 to 28.42°	2.32 to 28.29°	2.49 to 29.38°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -17 ≤ <i>k</i> ≤ 17, -27 ≤ <i>l</i> ≤ 27	-11 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 11, -21 ≤ <i>l</i> ≤ 21	-13 ≤ <i>h</i> ≤ 13, 13 ≤ <i>k</i> ≤ -13, 17 ≤ <i>l</i> ≤ -18
Reflections collected	70772	49679	39085
Independent reflections	2852 [R(int) = 0.0764]	5419 [R(int) = 0.0479]	5317 [R(int) = 0.0759]
Coverage of independent reflections	100%	100%	99.9%
Function minimized	$\Sigma w(\text{Fo}^2 - \text{Fc}^2)^2$	$\Sigma w(\text{Fo}^2 - \text{Fc}^2)^2$	$\Sigma w(\text{Fo}^2 - \text{Fc}^2)^2$
Data / restraints / parameters	2852 / 0 / 150	5419 / 0 / 318	5317 / 0 / 218
Goodness-of-fit on F²	1.254	1.009	1.088
Δ/σ max	0.000	0.001	0.000
Final R indices	2475 data; [I > 2σ(I)] R1 = 0.0419, wR2 =	4624 data [I > 2σ(I)], R1 = 0.0314, wR2 =	3602 data [I > 2σ(I)], R1 = 0.1026, wR2 =

	= 0.0964	0.0679	0.2008
	all data , R1 = 0.0519, wR2 = 0.1004	all data , R1 = 0.0420, wR2 = 0.0730	all data , R1 = 0.1558, wR2 = 0.2235
Largest diff. peak and hole	0.827 and -0.721 eÅ ⁻³	0.319 and -0.278 eÅ ⁻³	0.688 and -0.526 eÅ ⁻³
R.M.S. deviation from mean	0.112 eÅ ⁻³	0.052 eÅ ⁻³	0.087 eÅ ⁻³

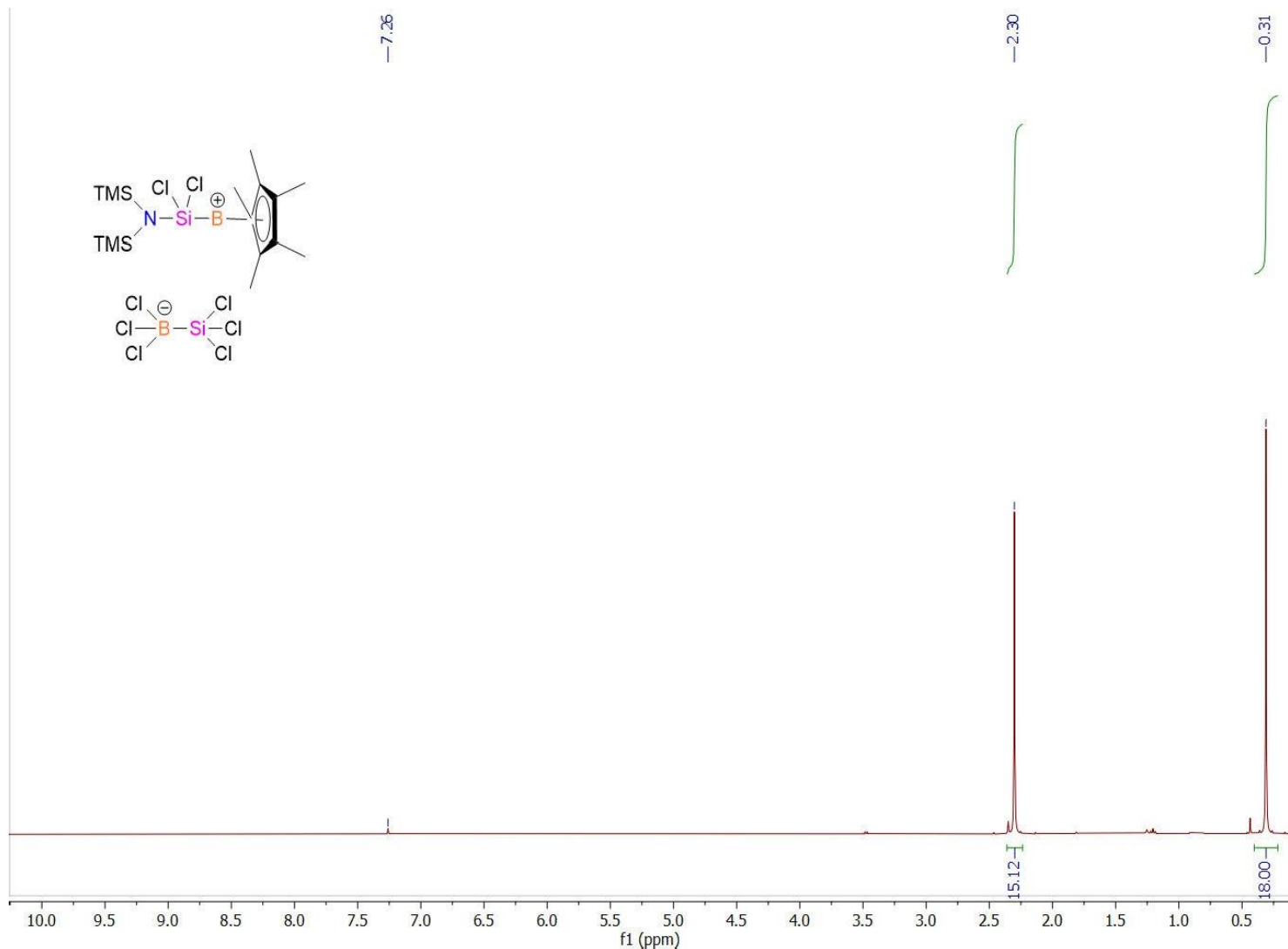


Figure 3.A.1. ^1H NMR spectrum of compound **3.2** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

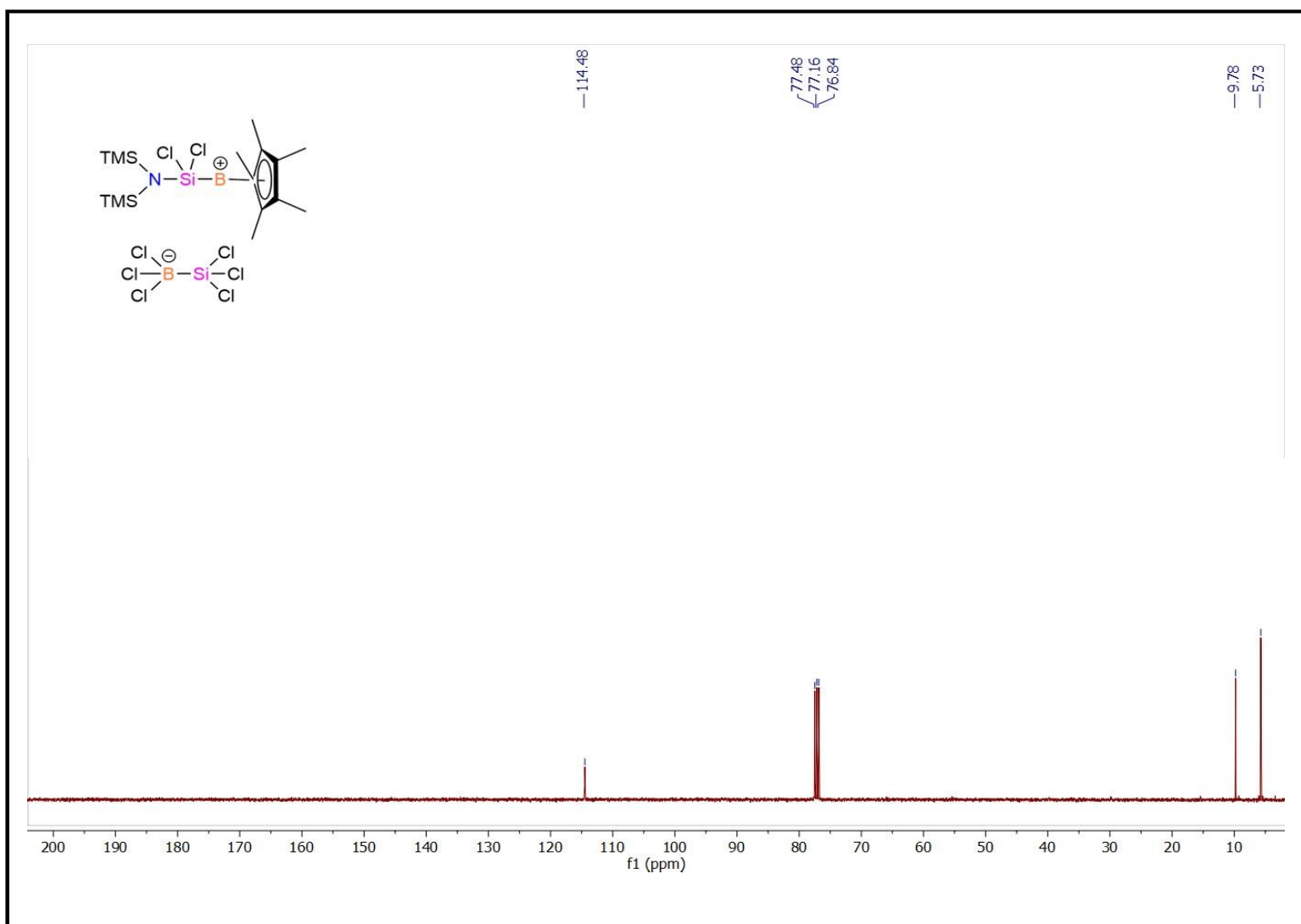


Figure 3.A.2. ^{13}C NMR spectrum of compound **3.2** in CDCl_3 (Solvent peak δ 77.26 ppm) (100.613 MHz, 298 K).

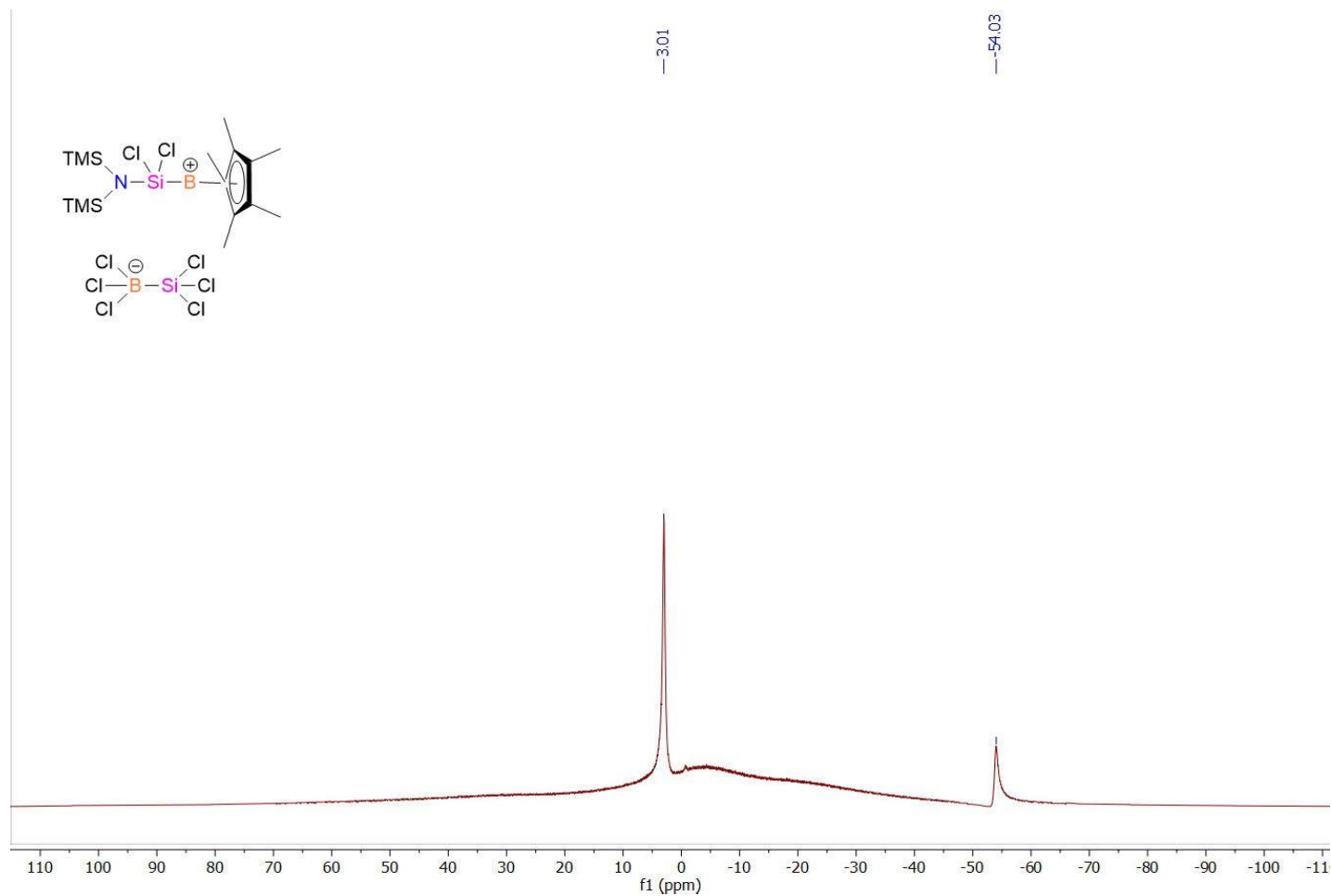


Figure 3.A.3. ^{11}B NMR spectrum of compound **3.2** in CDCl_3 (128.387 MHz, 298 K).

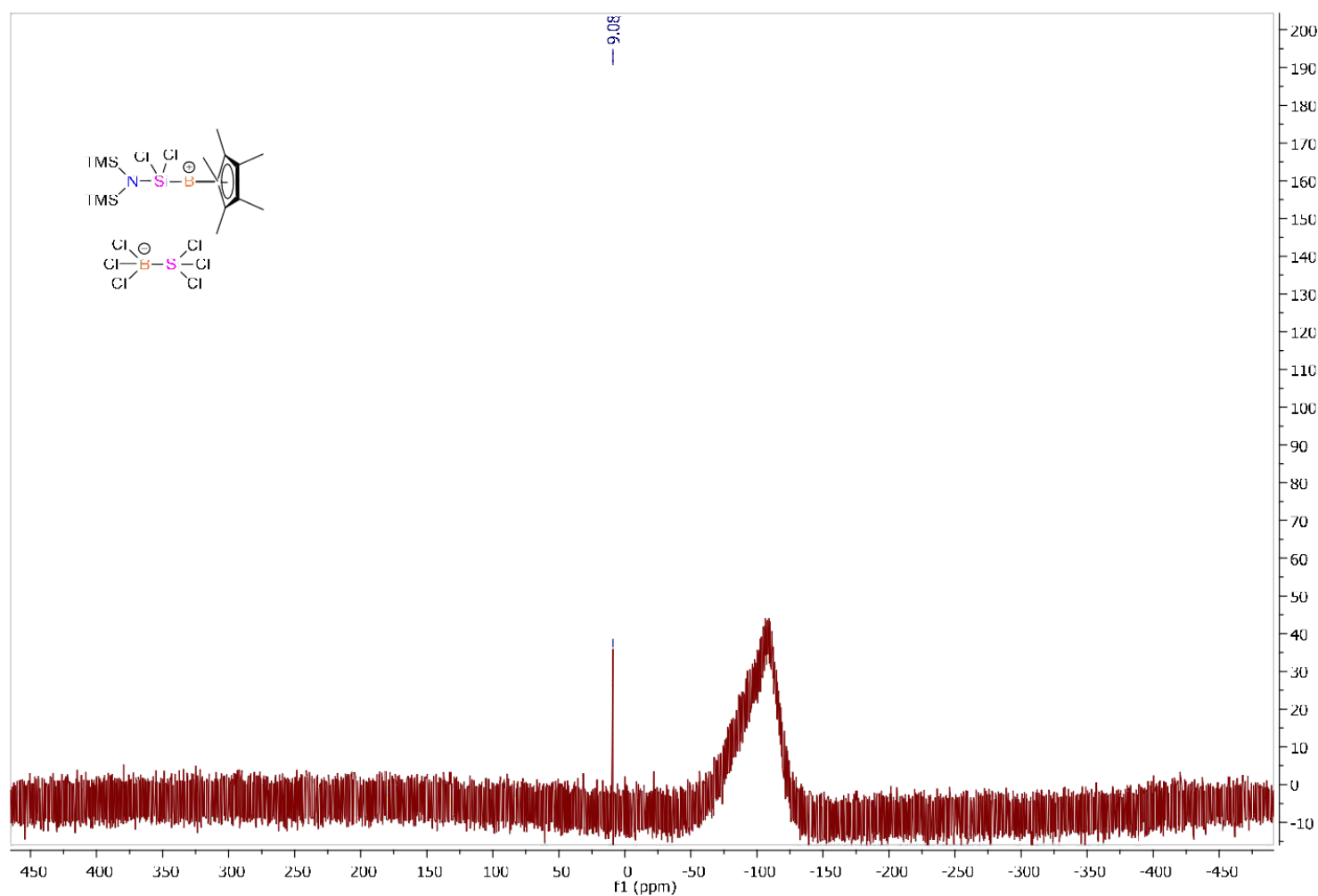


Figure 3.A.4. ^{29}Si NMR spectrum of compound **3.2** in CDCl_3 (79.495 MHz, 298 K).

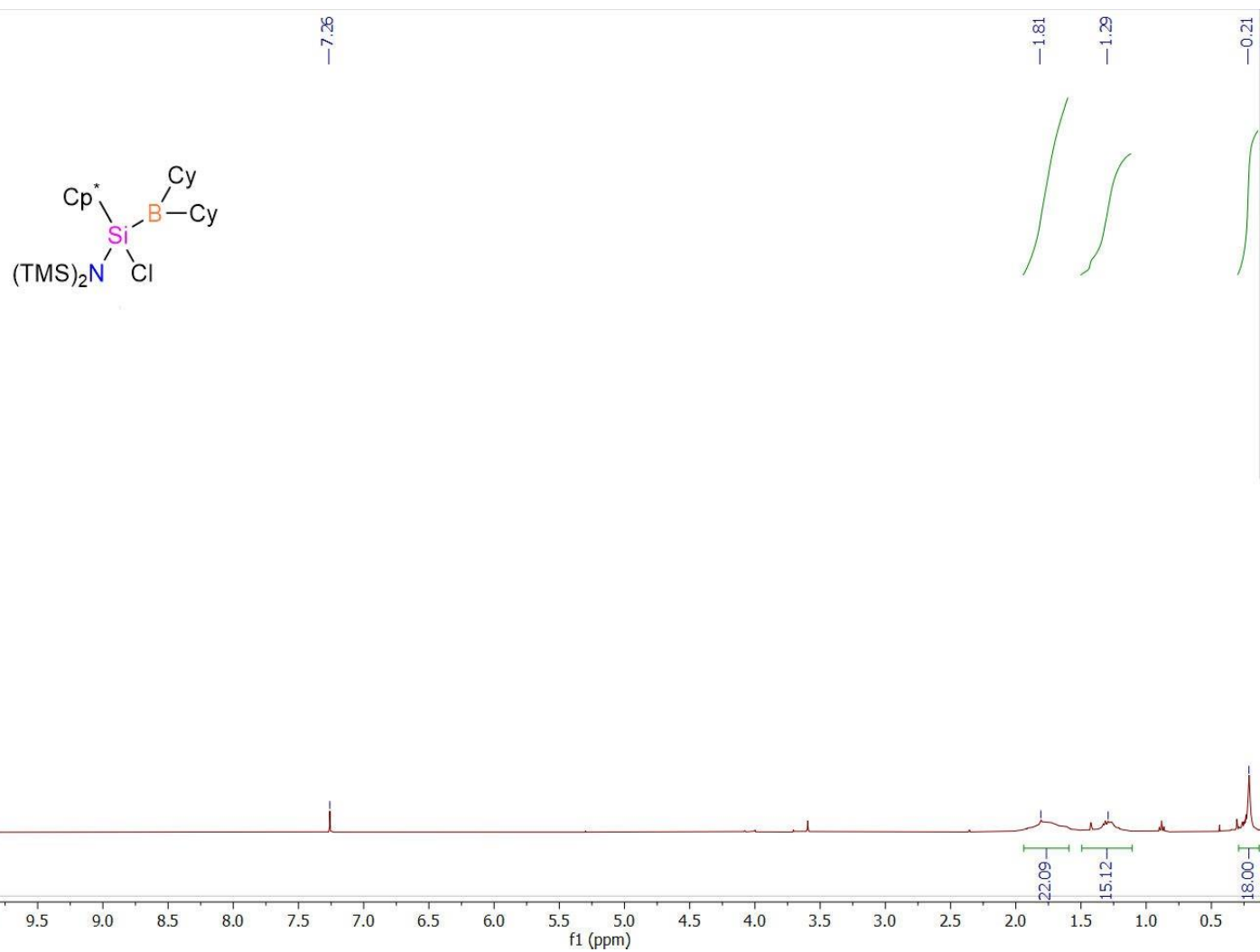


Figure 3.A.5. ^1H NMR of compound **3.3** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

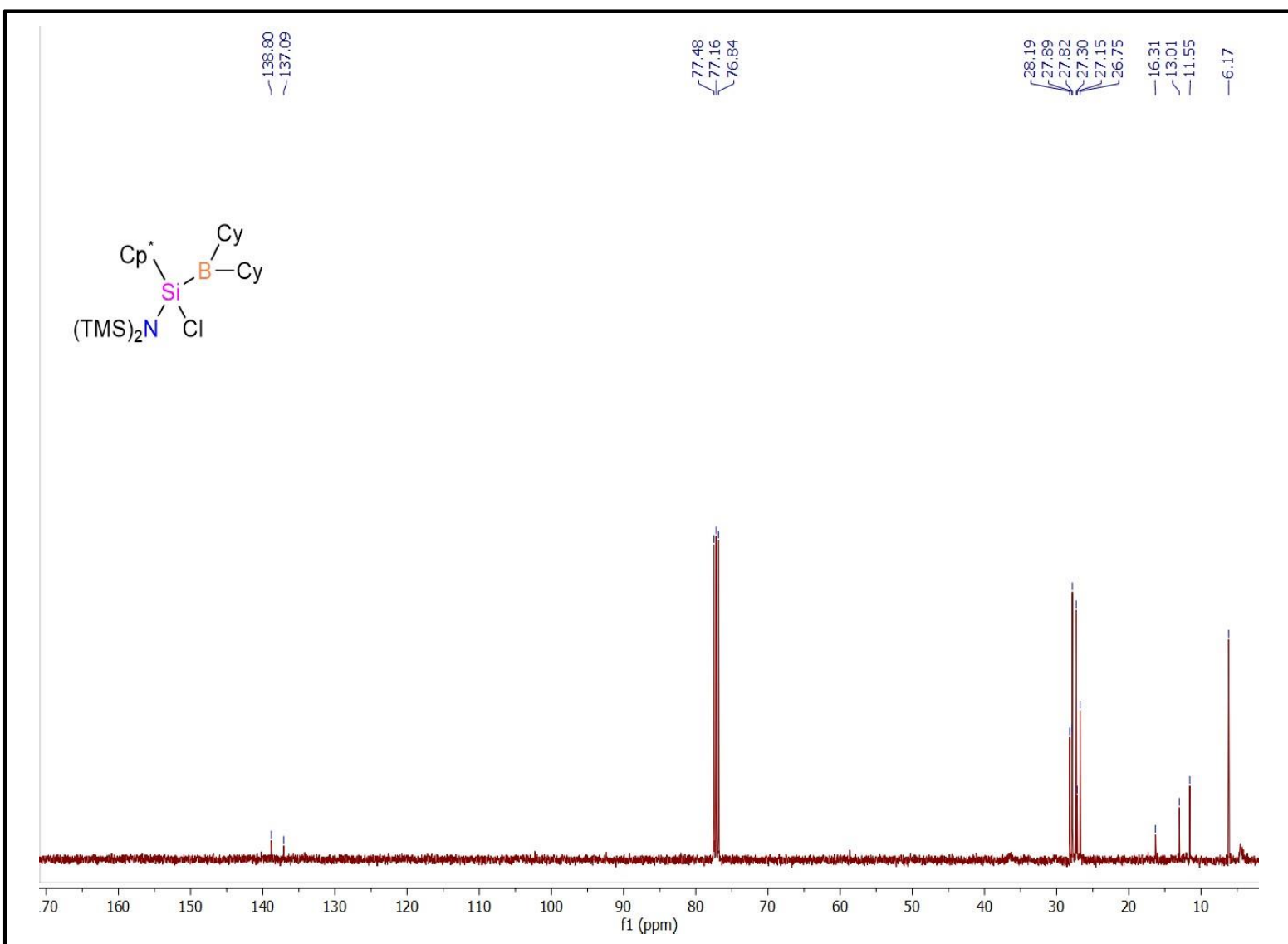


Figure 3.A.6. ^{13}C NMR spectrum of compound **3.3** in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

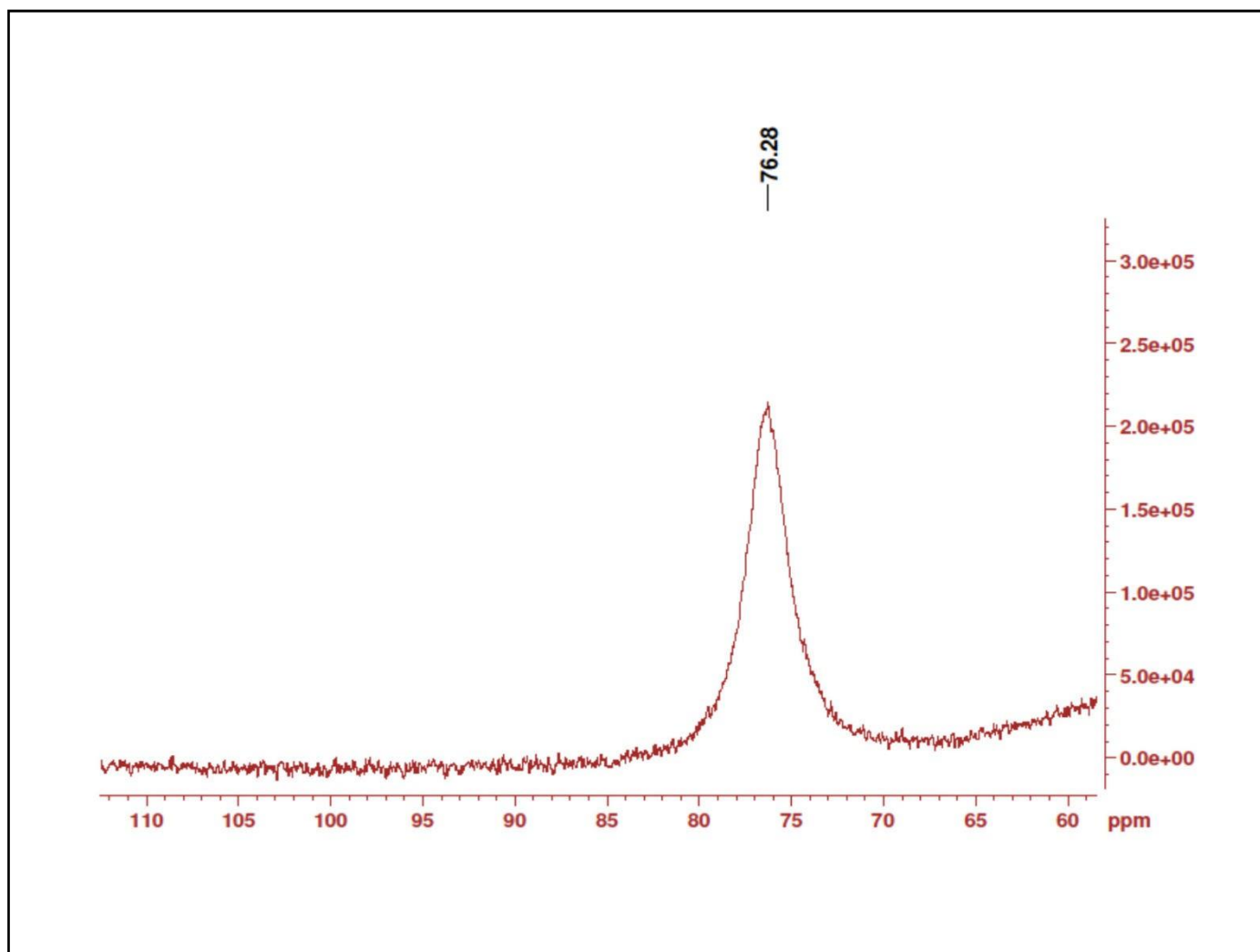


Figure 3.A.7. ^{11}B NMR spectrum of compound **3.3** in CDCl_3 (128.387 MHz, 298 K).

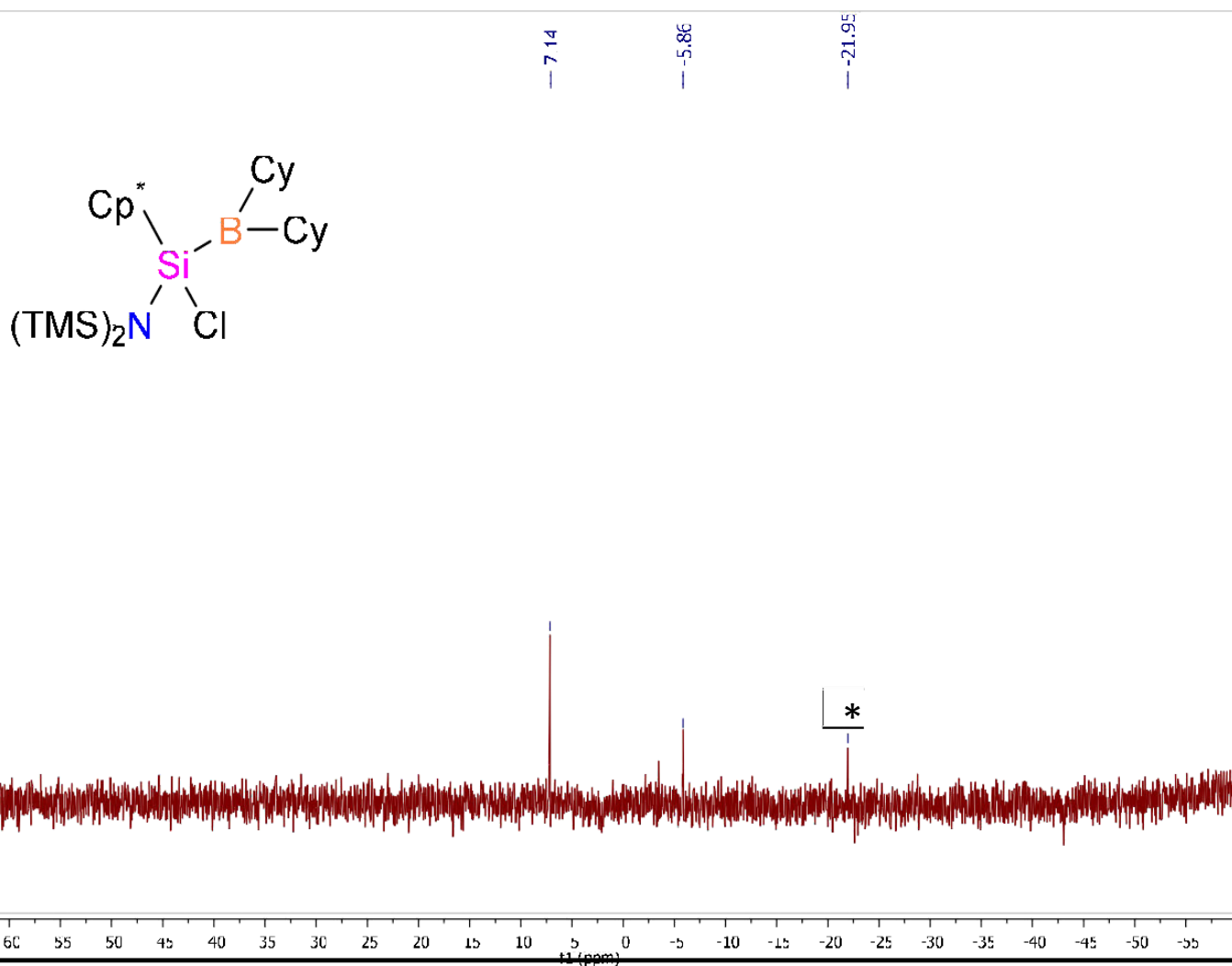


Figure 3.A.8. ^{29}Si NMR spectrum of compound **3.3** in CDCl₃; * = Grease peak (79.495 MHz, 298 K).

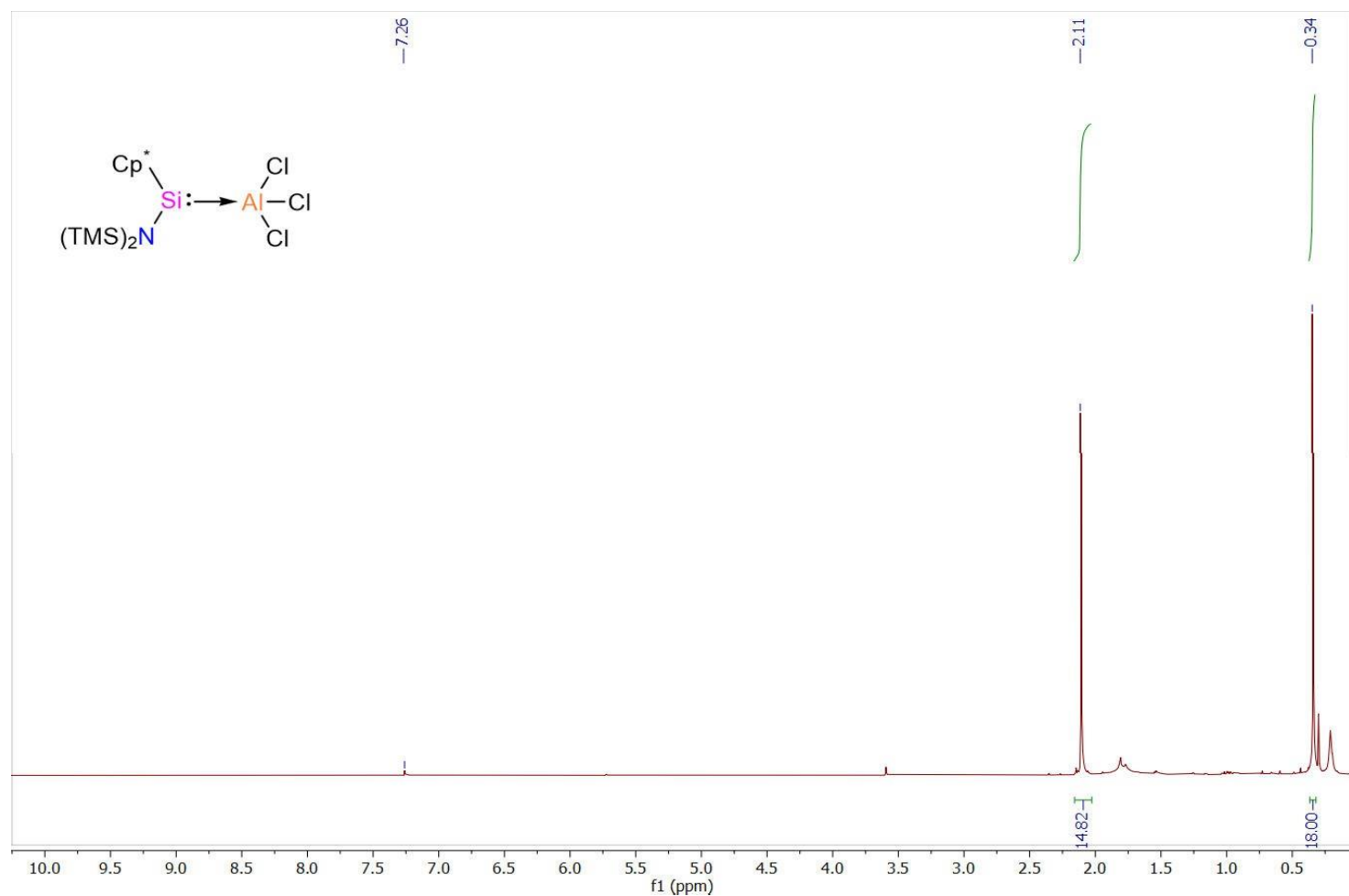


Figure 3.A.9. ^1H NMR spectrum of compound **3.4** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz 298 K).

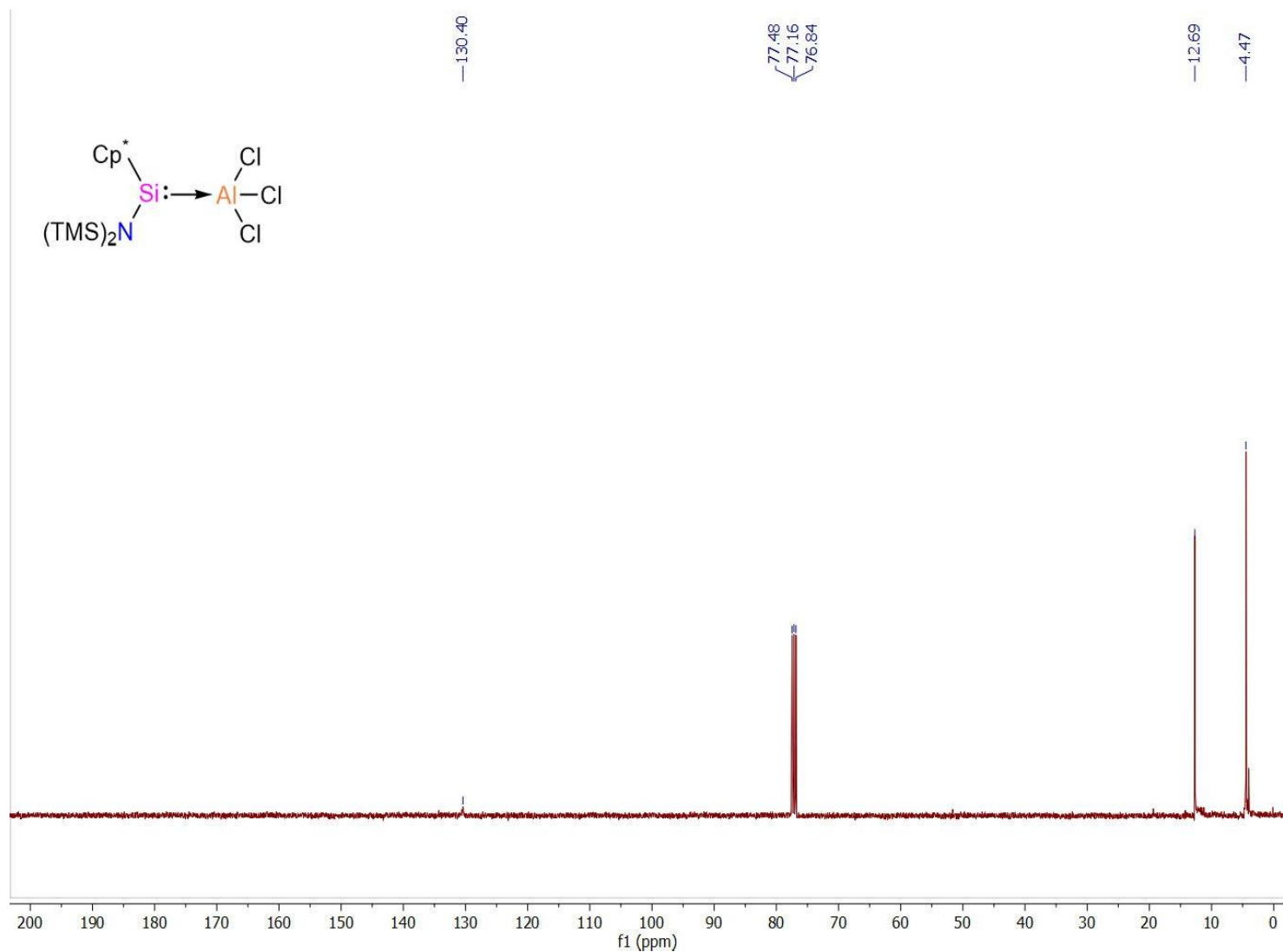


Figure 3.A.10. ^{13}C NMR spectrum of compound **3.4** in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

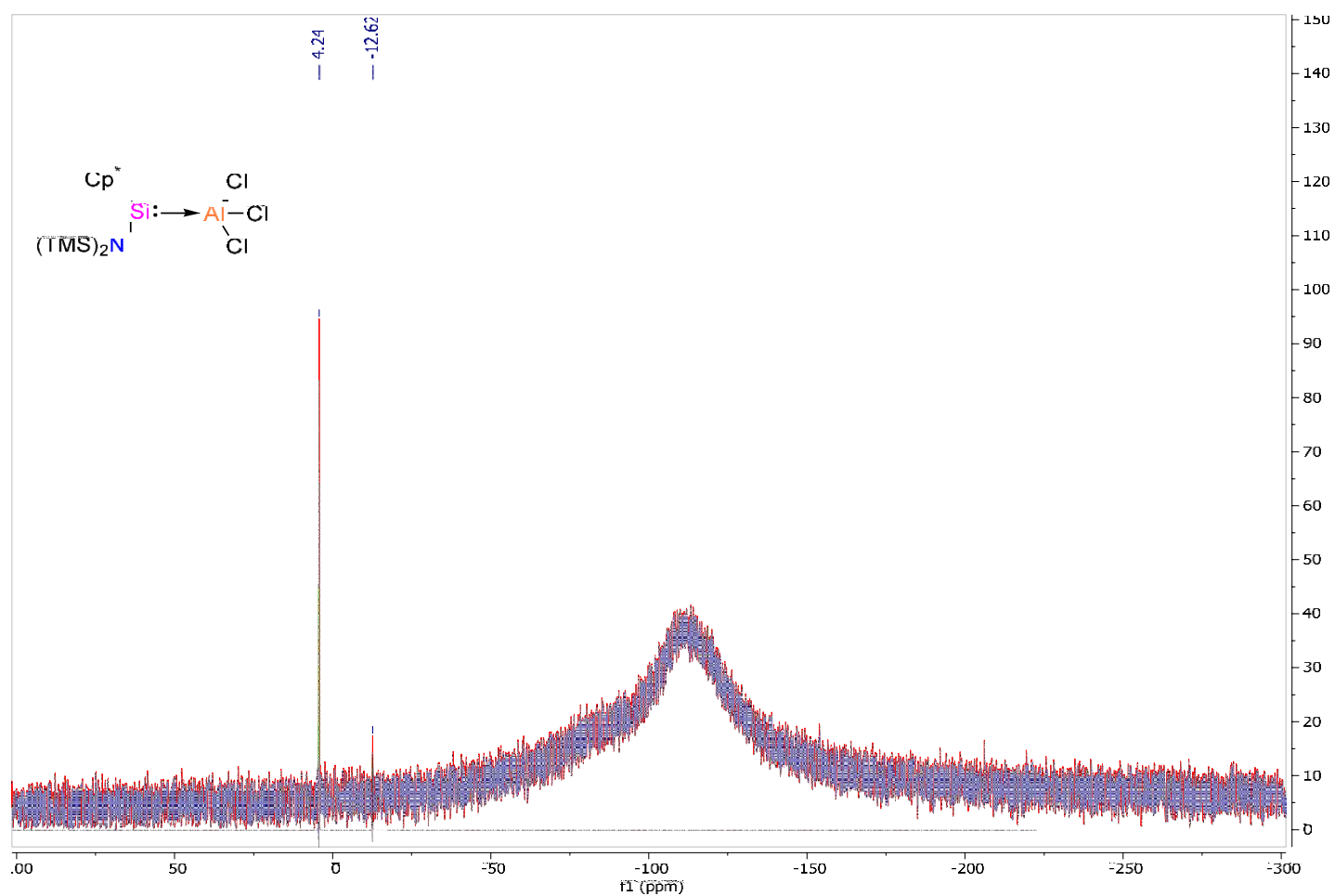


Figure 3.A.11. ^{29}Si NMR spectrum of compound **3.4** in CDCl_3 (79.495 MHz, 298 K).

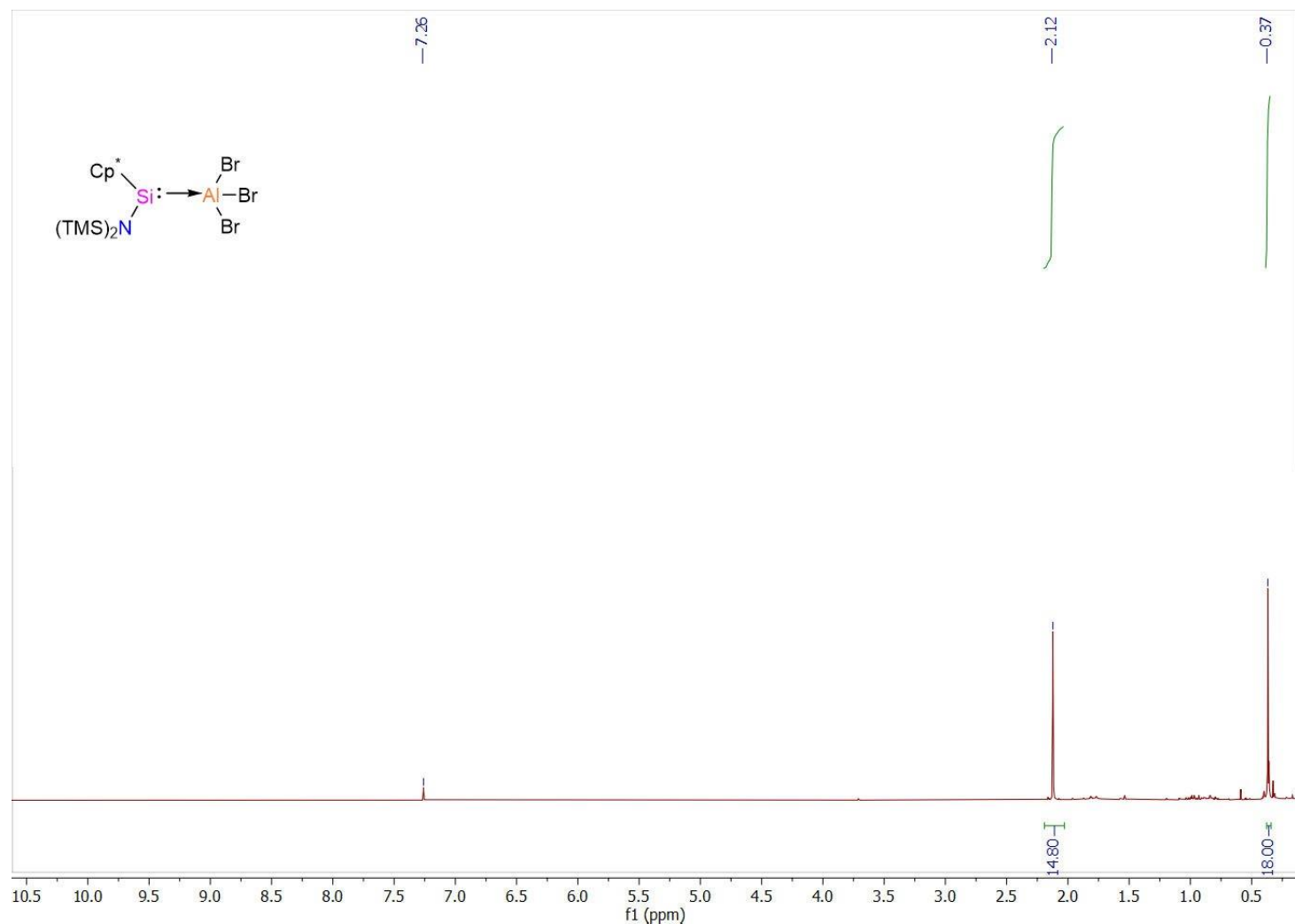


Figure 3.A.12. ^1H NMR spectrum of compound **3.5** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

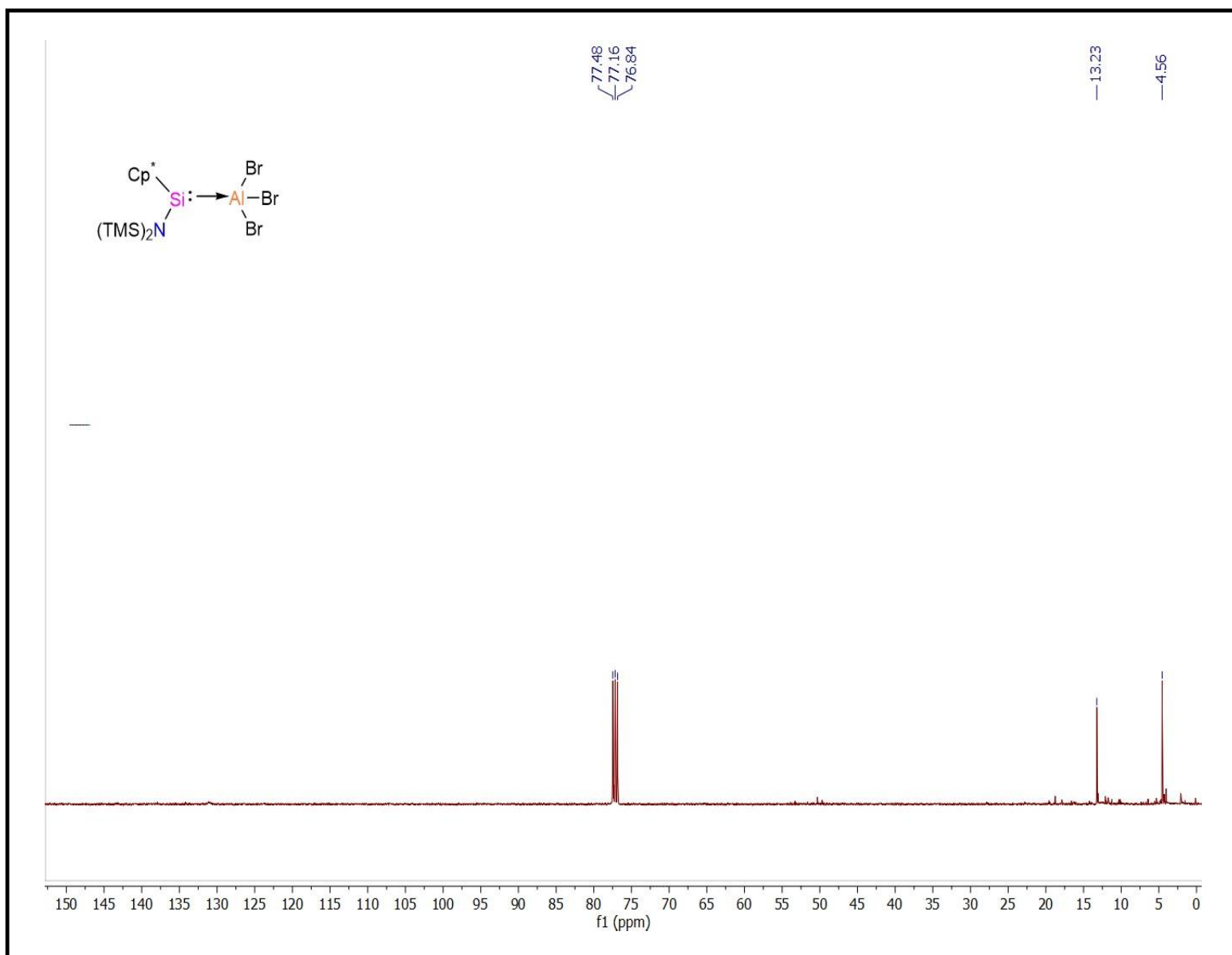


Figure 3.A.13. ^{13}C NMR spectrum of compound **3.5** in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

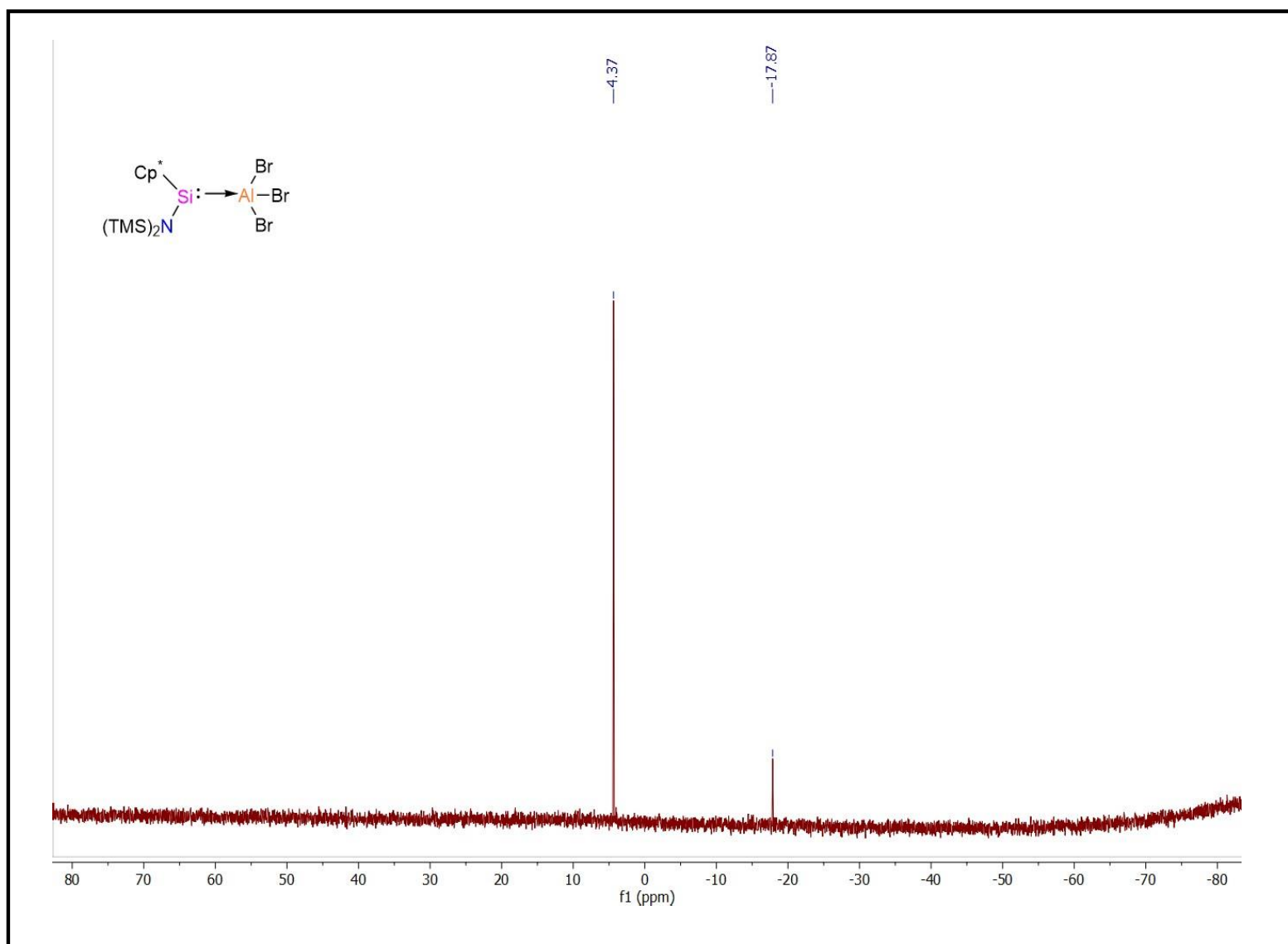


Figure 3.A.14. ^{29}Si NMR spectrum of compound **3.5** in CDCl_3 (79.495 MHz, 298 K).

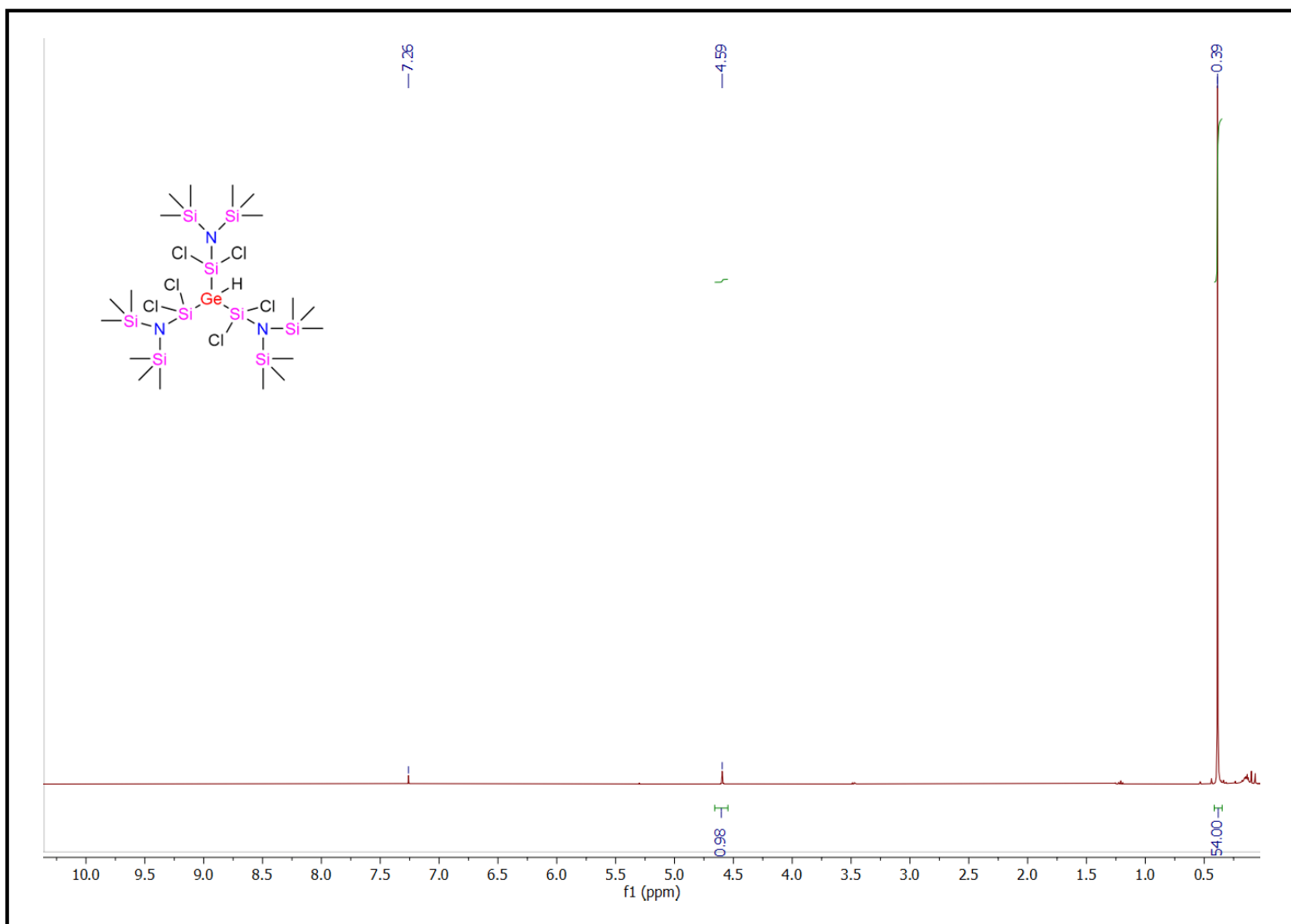


Figure 3.A.15. ^1H NMR spectrum of compound **3.6** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

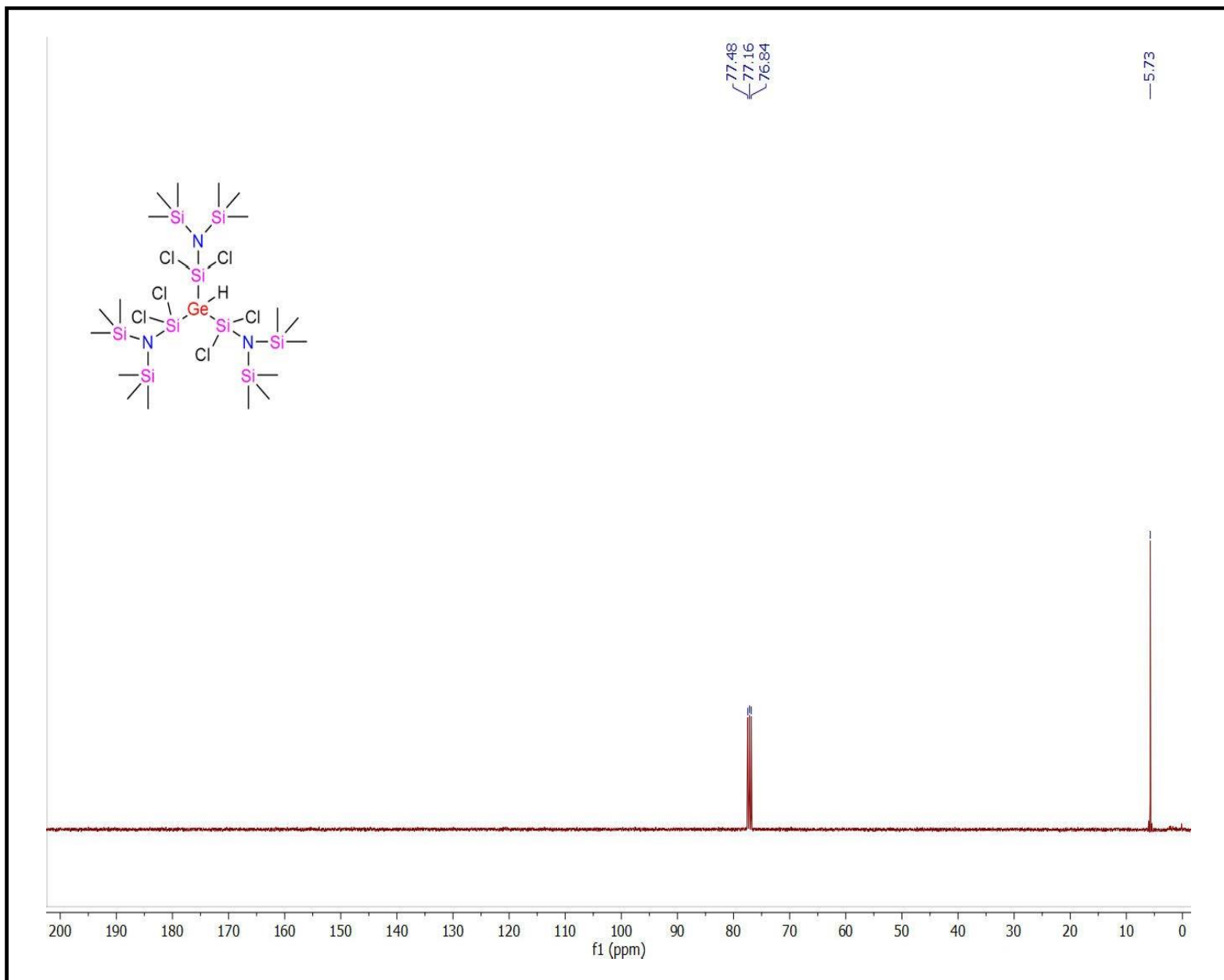


Figure 3.A.16. ^{13}C NMR spectrum of compound **3.6** in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

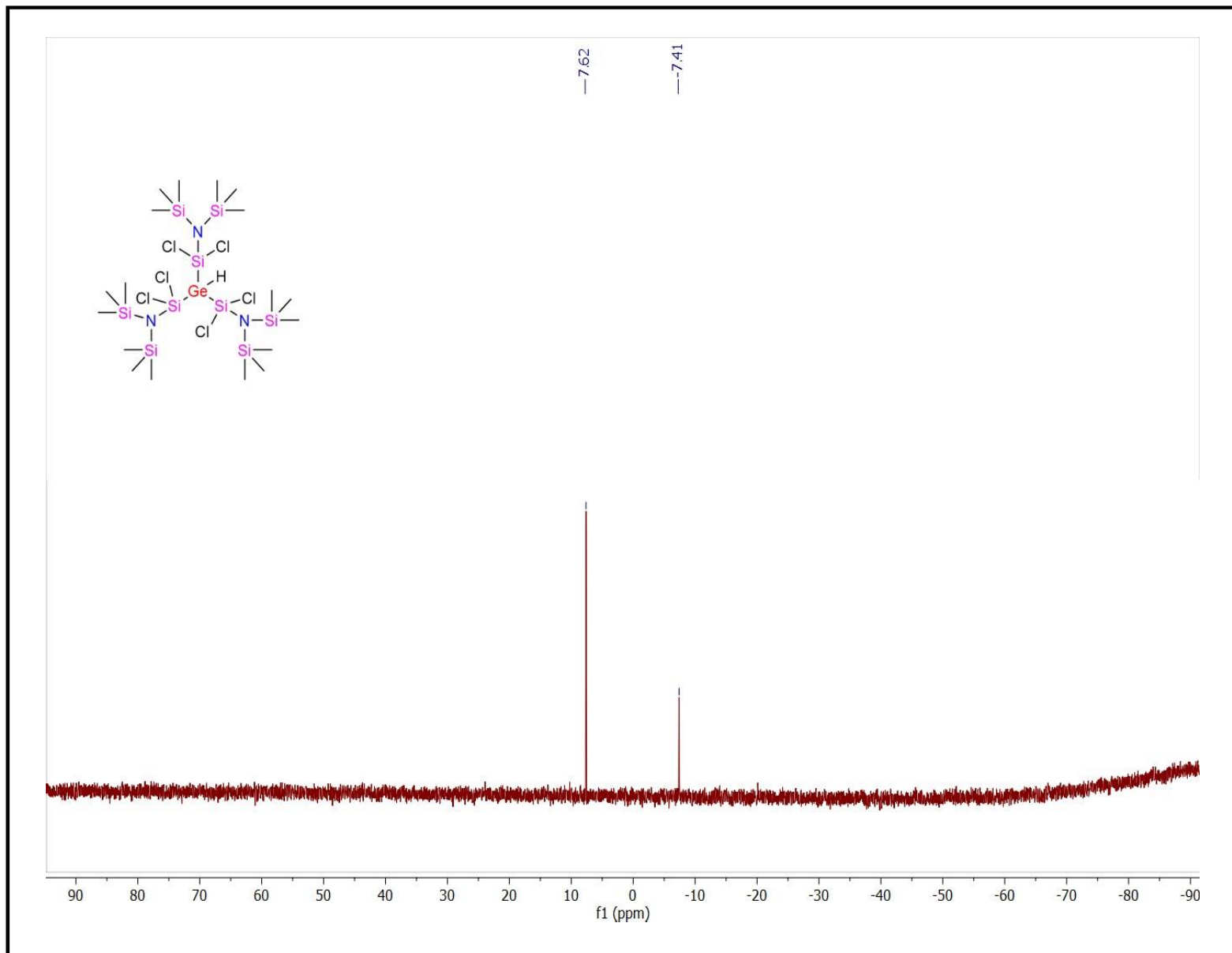


Figure 3.A.17. ^{29}Si NMR spectrum of compound **3.6** in CDCl_3 (79.495 MHz, 298 K).

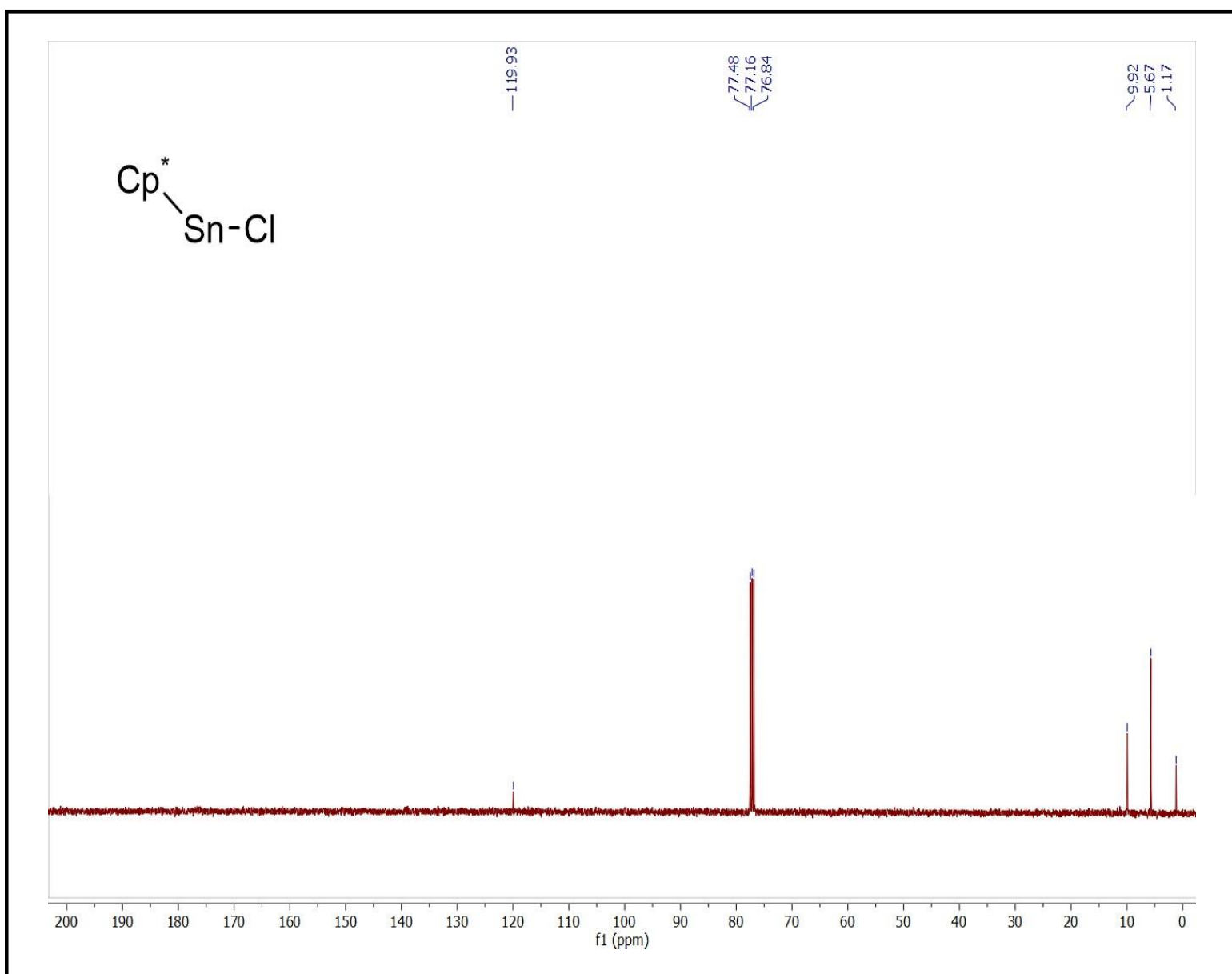


Figure 3.A.18. ^{13}C NMR spectrum of compound **3.7** in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

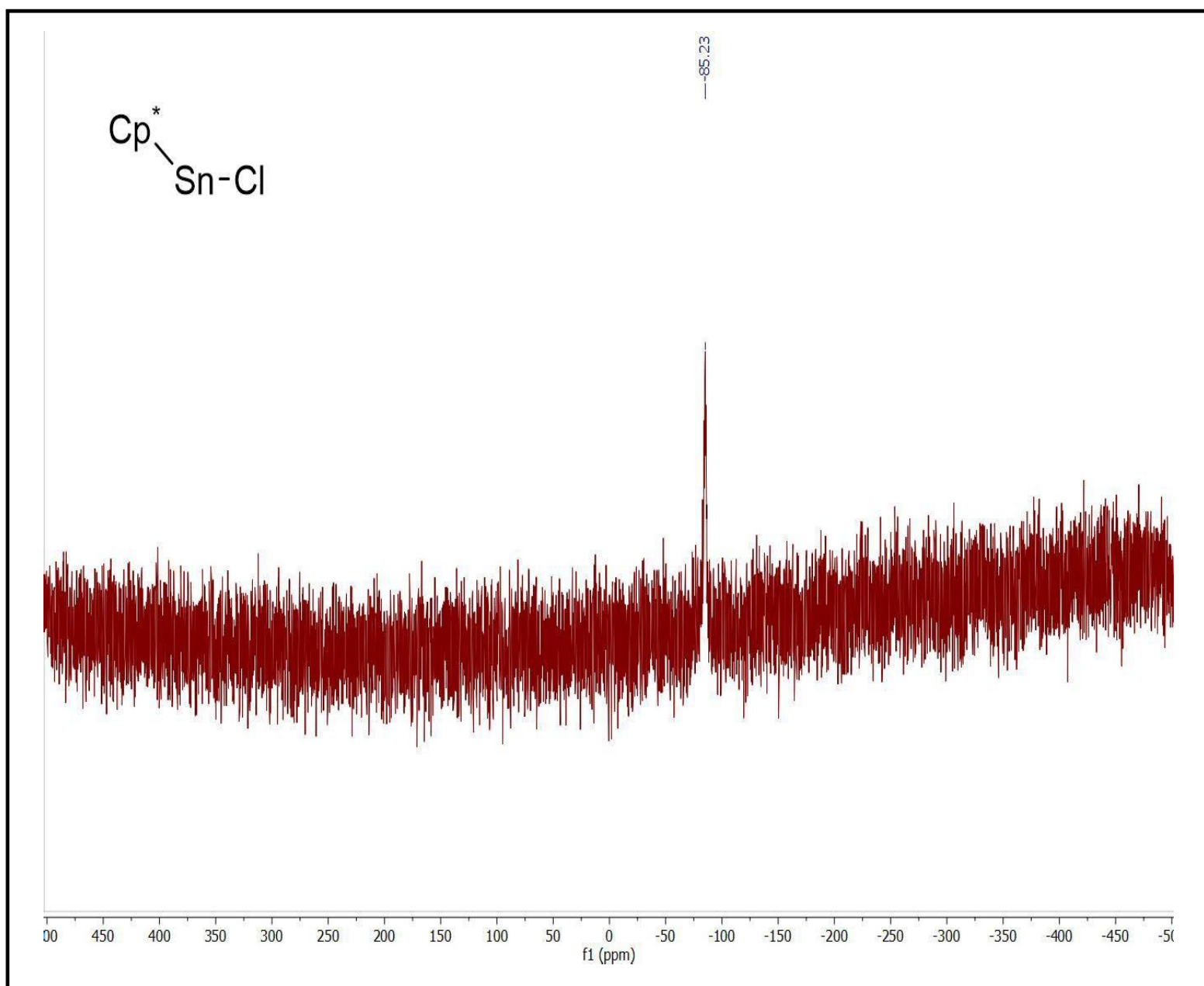


Figure 3.A.19. ^{119}Sn NMR spectrum of compound **3.7** in CDCl_3 (149.18 MHz, 298K).

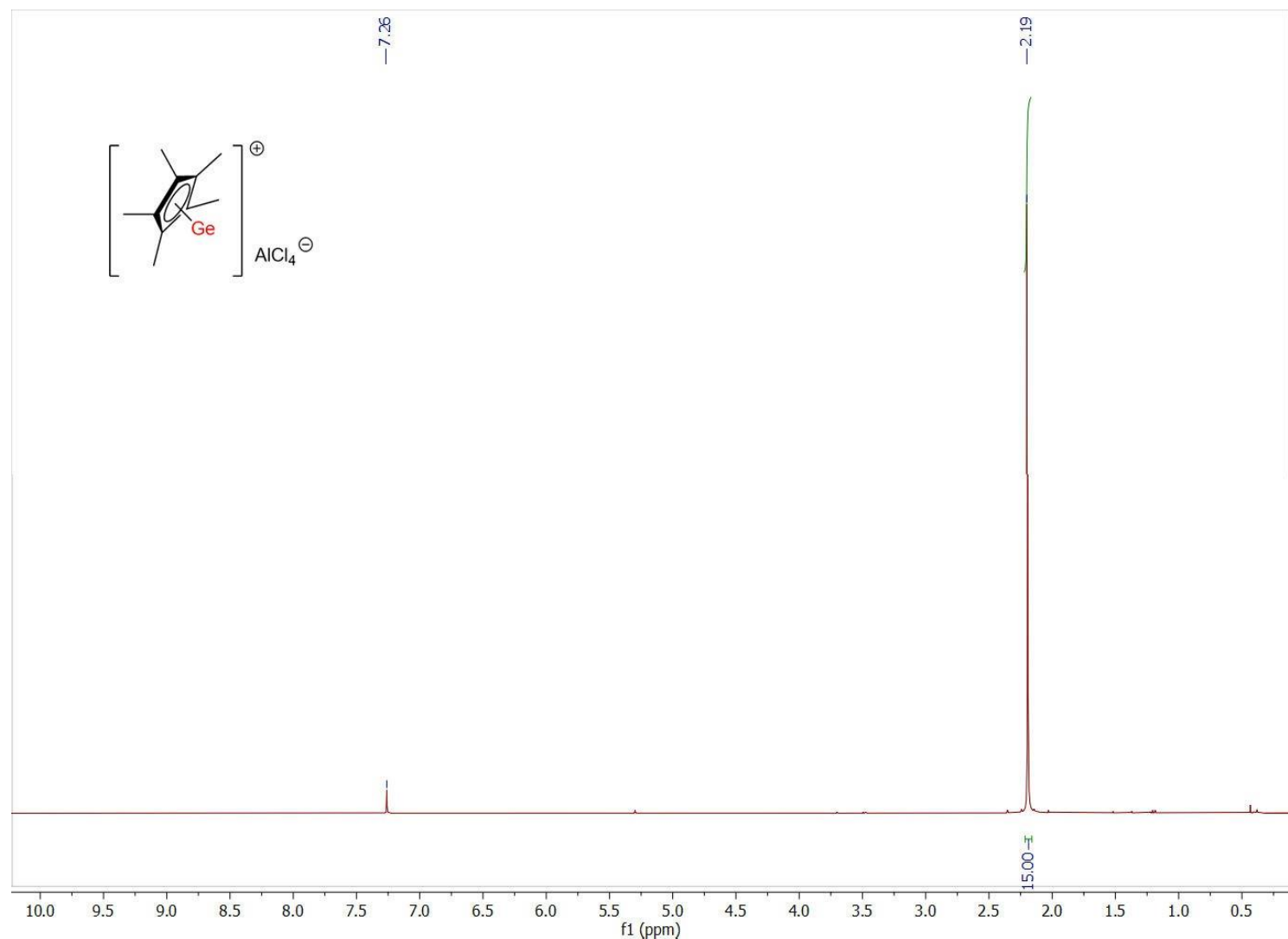


Figure 3.A.20. ^1H NMR spectrum of compound **3.8** in CDCl_3 (400 MHz, 298 K).

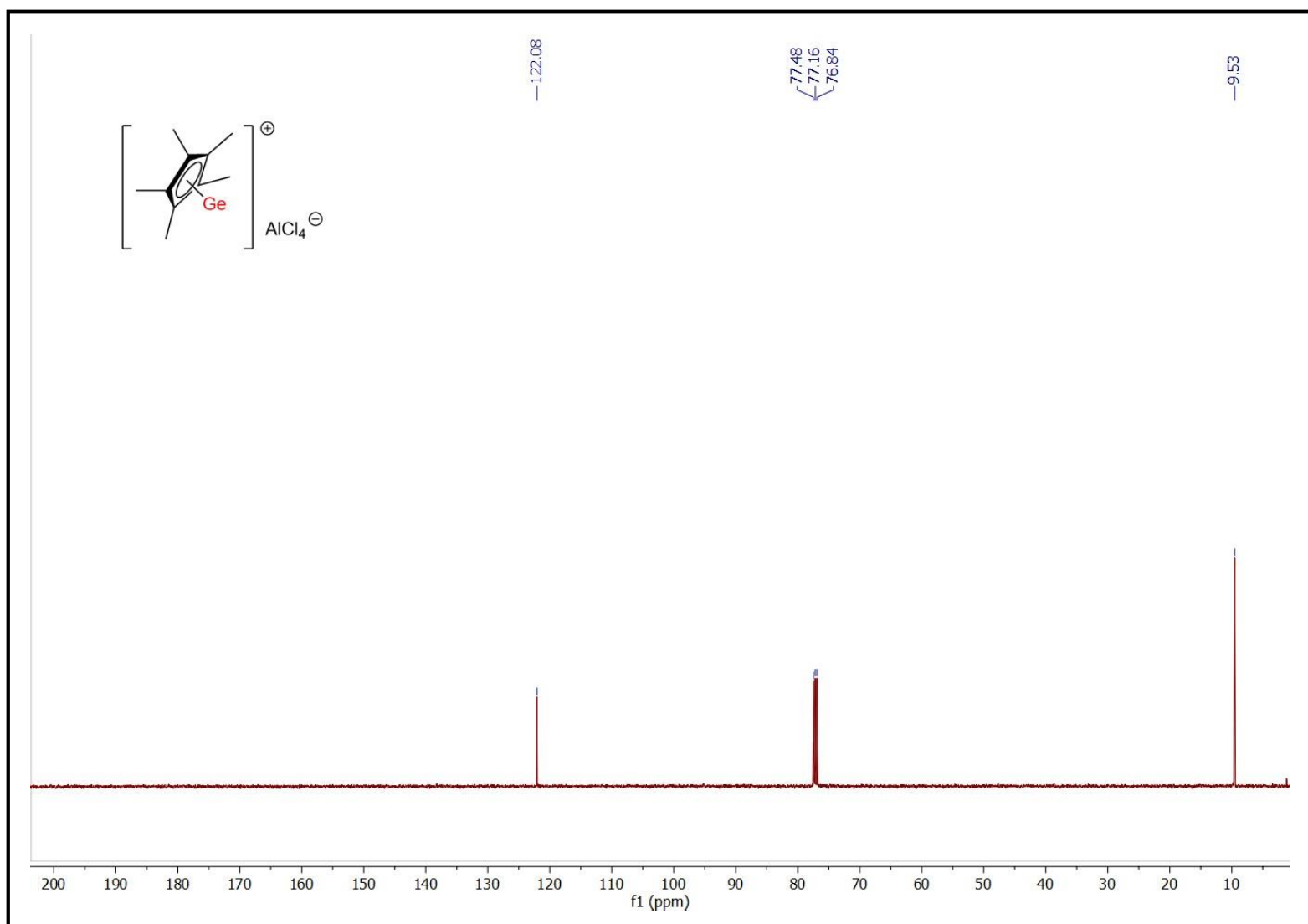


Figure 3.A.21. ^{13}C NMR spectrum of compound **3.8** in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

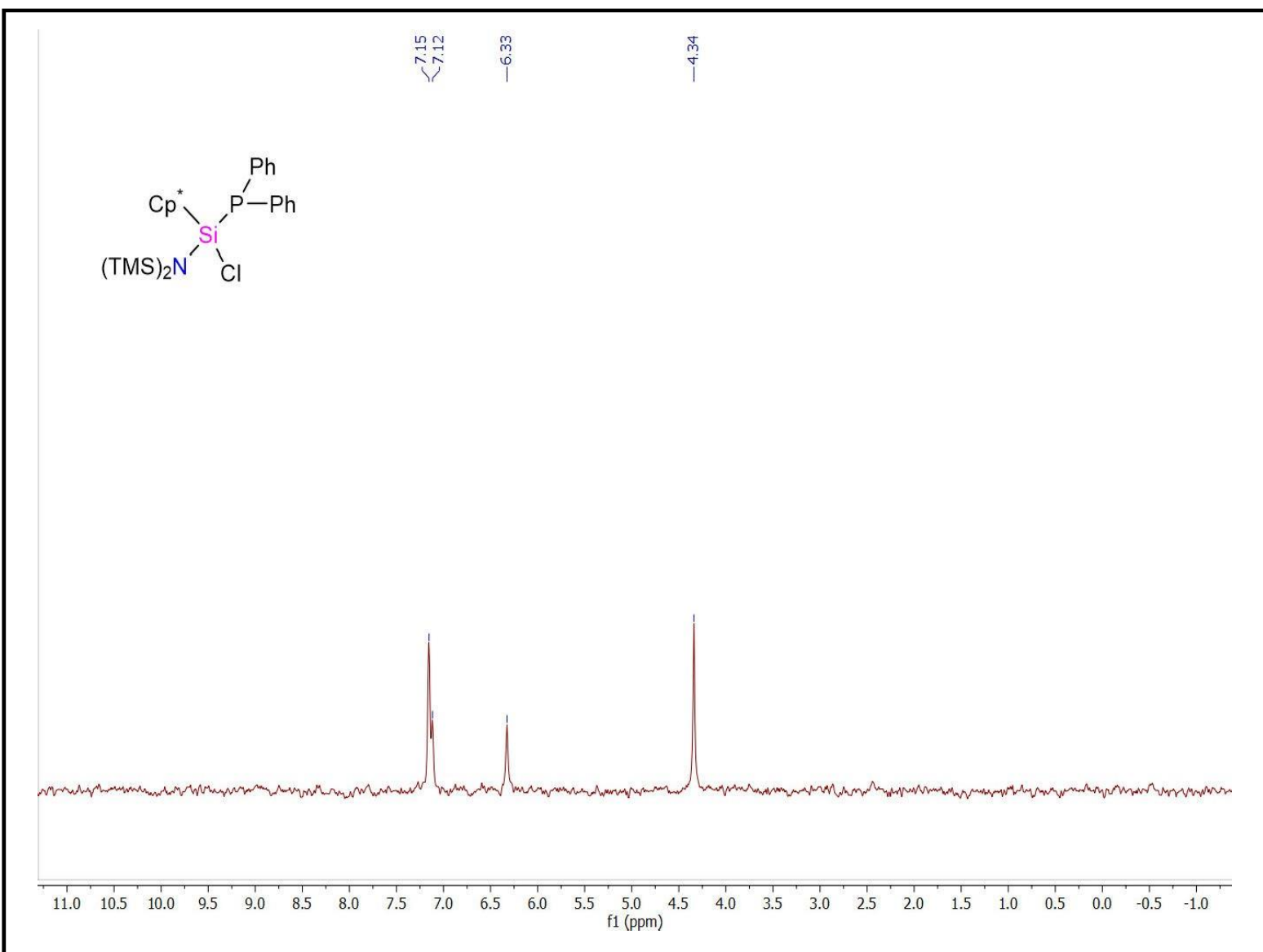


Figure 3.A.22. ^{29}Si NMR spectrum of compound **3.9** in CDCl_3 (79.495 MHz, 298 K).

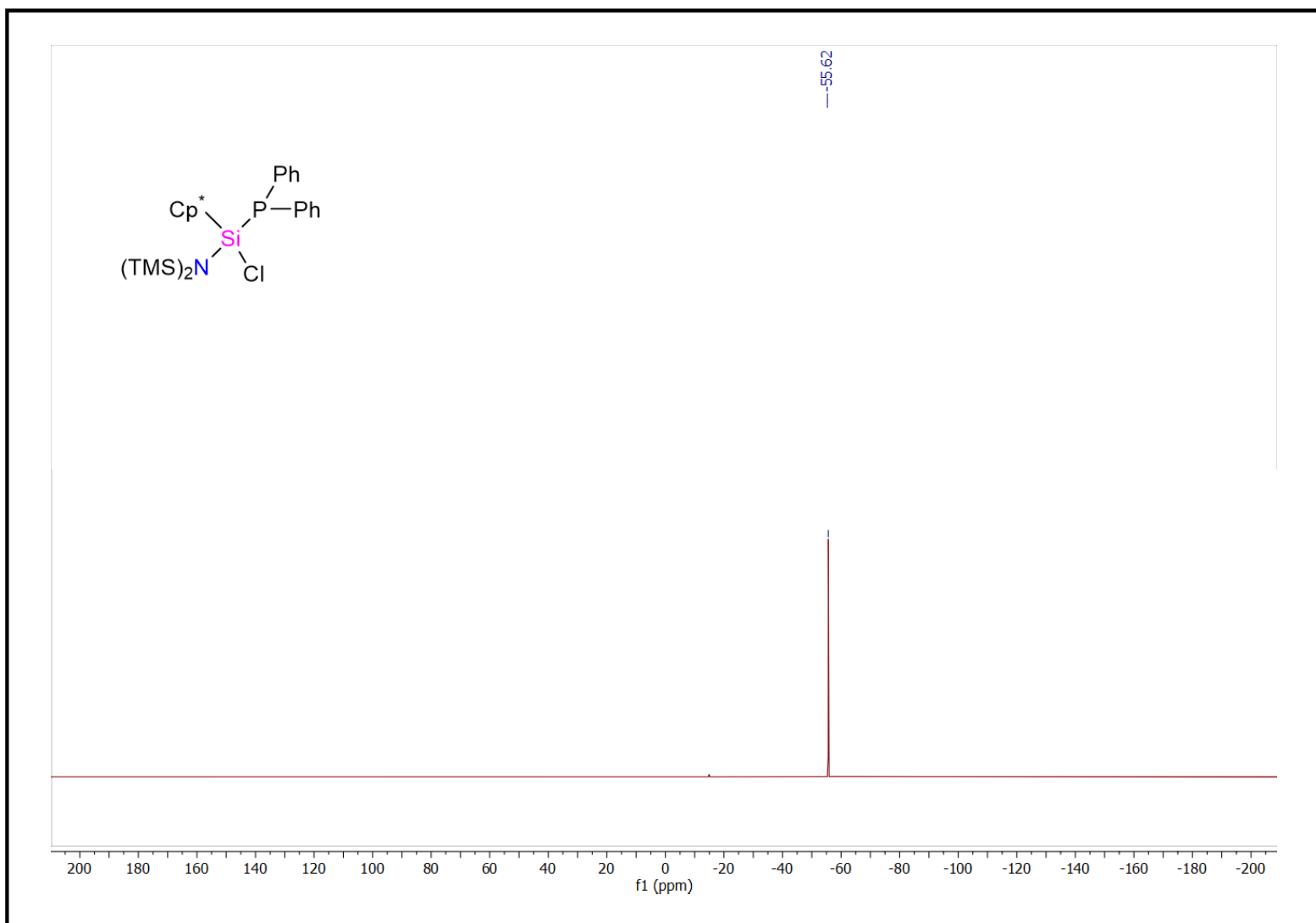


Figure 3.A.23. ^{31}P NMR spectrum of compound **3.9** in CDCl_3 (161.976 MHz, 298 K).

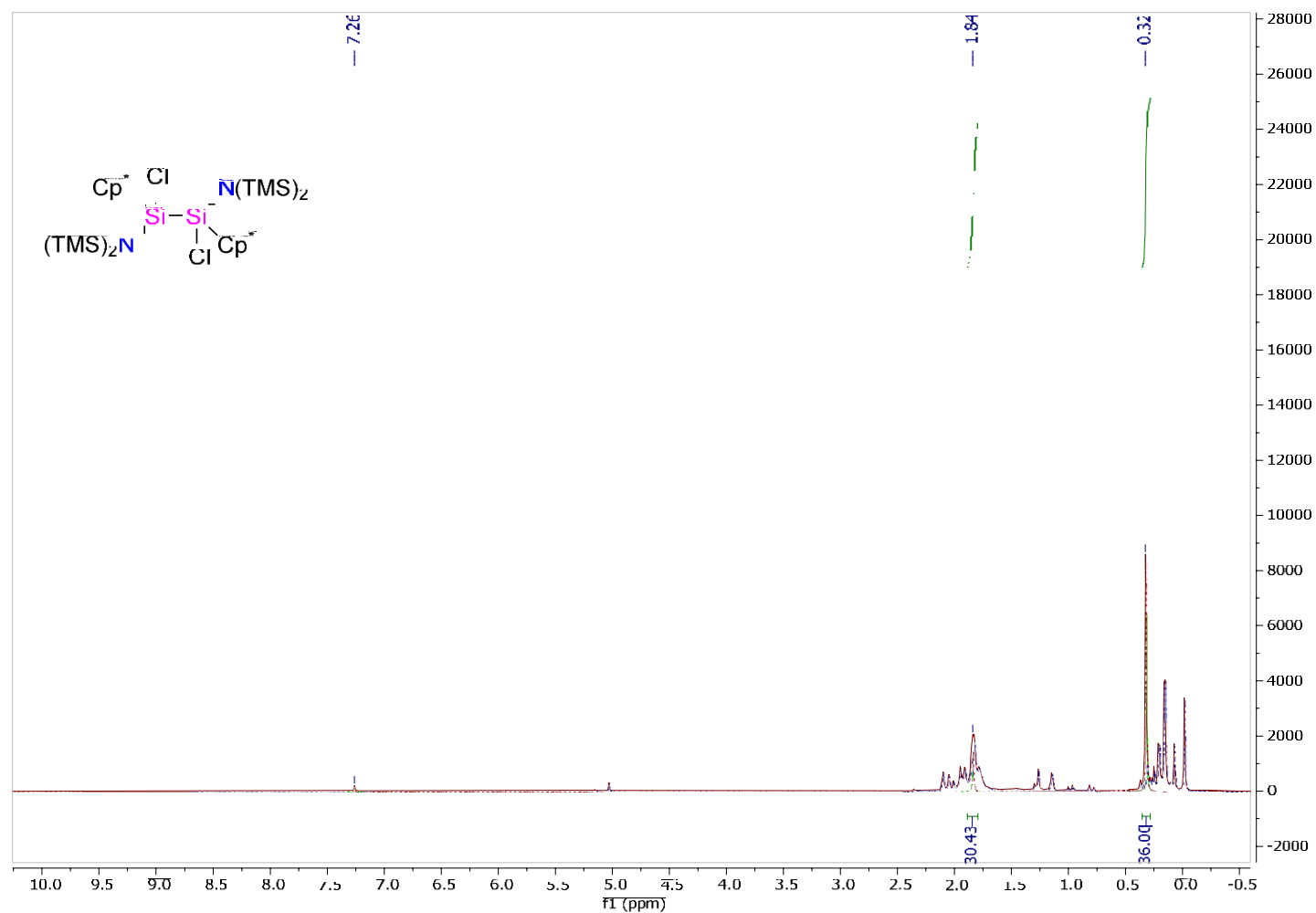


Figure 3.A.24. ^1H NMR spectrum of compound **3.10** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

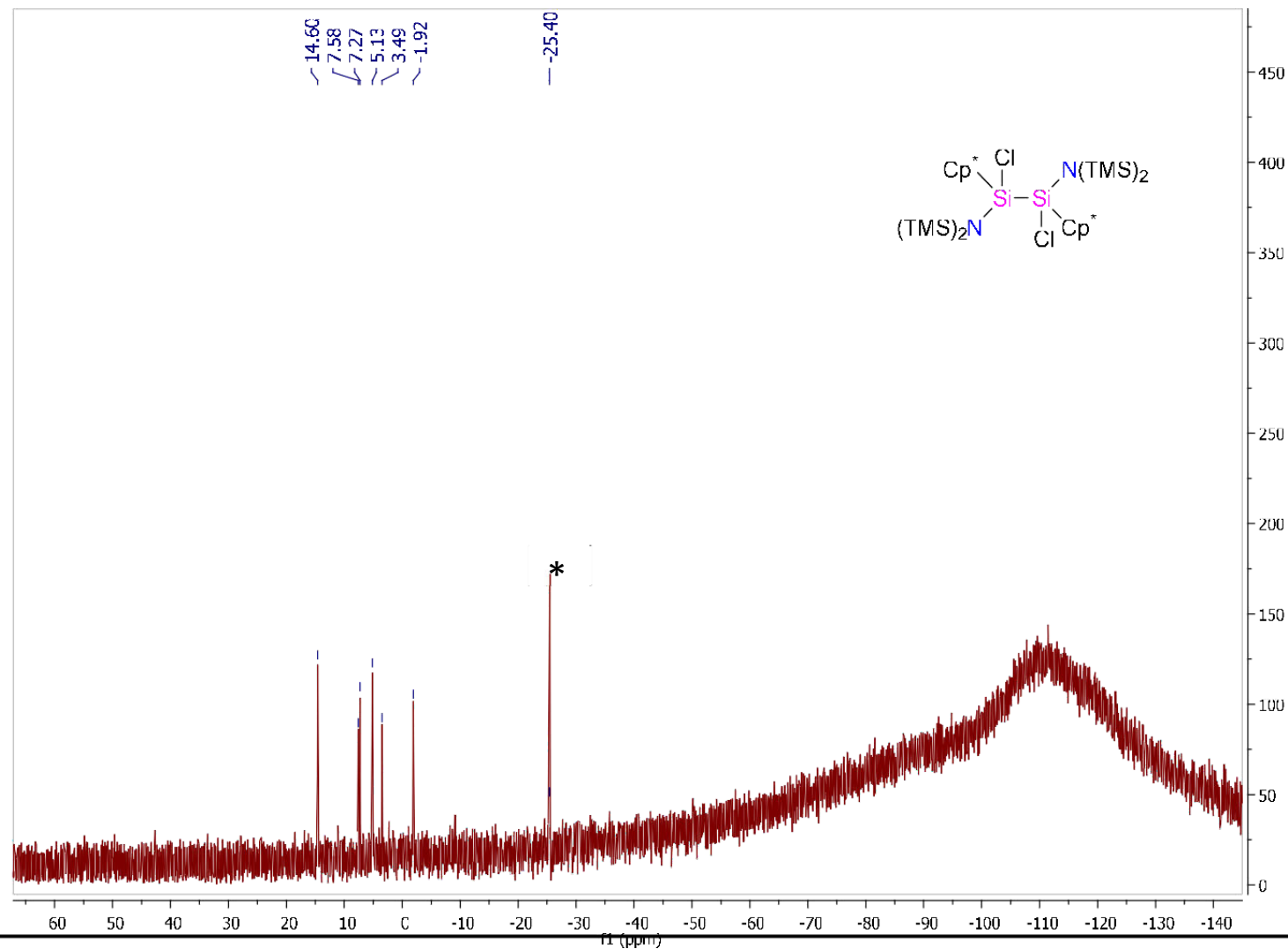


Figure 3.A.25. ^{29}Si NMR spectrum of compound **3.10** in CDCl_3 . * = Grease peak (79.495 MHz, 298 K).

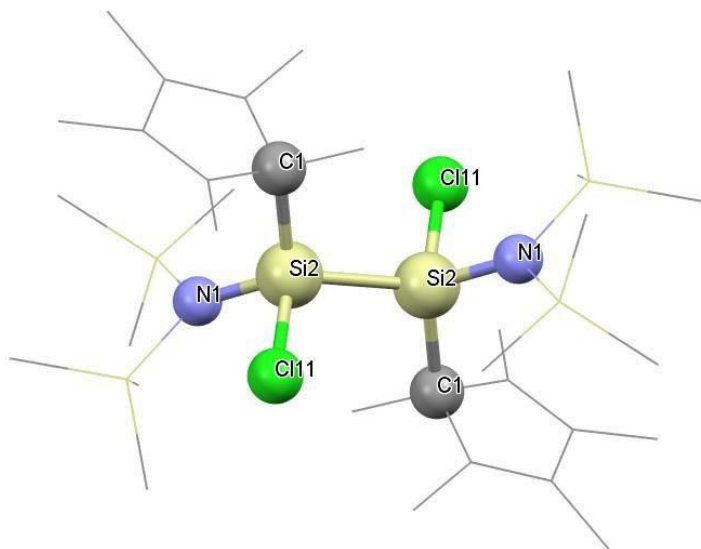


Figure 3.A.26. Molecular structure of **3.10** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) for **3.10**: Si2-Cl11 2.118(8), Si2-Si2 2.433(2).

Appendix of Chapter 4A

Table 4A.A.1. Crystallographic data of compounds **4A.2**, **4A.3** and **4A.4**.

	4A.2	4A.3	4A.4
Chemical formula	C ₁₉₂ H ₃₁₂ Cl ₁₂ N ₂₄ Sb ₁₂	C ₁₇ H ₂₆ F ₃ N ₂ O ₃ SSb	C ₁₆ H ₂₆ F ₆ N ₂ Sb ₂
Formula weight	4843.04 g/mol	517.22 g/mol	603.89 g/mol
Temperature	150(2) K	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 21/ <i>c</i>	<i>P</i> 21	<i>P</i> 21/ <i>n</i>
Unit cell dimensions	<i>a</i> = 28.428(3) Å	<i>a</i> = 8.8486(6) Å	<i>a</i> = 11.2599(14) Å
	<i>b</i> = 11.5247(12) Å	<i>b</i> = 11.4722(9) Å	<i>b</i> = 11.4547(15) Å
	<i>c</i> = 16.1500(18) Å	<i>c</i> = 9.9293(8) Å	<i>c</i> = 16.001(2) Å
	α = 90°	α = 90°	α = 90°
	β = 98.154(3) °	β = 95.050(3) °	β = 92.702(3) °
	γ = 90°	γ = 90°	γ = 90°
Volume	5237.6(10) Å ³	1004.04(13) Å ³	2061.5(5) Å ³
Z	1	1	4
Density (calculated)	1.535 g/cm ³	1.711 g/cm ³	1.946 g/cm ³
Absorption coefficient	1.727 mm ⁻¹	1.525 mm ⁻¹	2.675 mm ⁻¹
F(000)	2448	520	1168
Theta range for data collection	2.24 to 28.31°	2.72 to 28.35°	2.55 to 28.37°
Index ranges	-34 ≤ <i>h</i> ≤ 34, -13 ≤ <i>k</i> ≤ 13, -19 ≤ <i>l</i> ≤ 19	-11 ≤ <i>h</i> ≤ 11, -15 ≤ <i>k</i> ≤ 15, -13 ≤ <i>l</i> ≤ 13	-13 ≤ <i>h</i> ≤ 13, -13 ≤ <i>k</i> ≤ 13, -19 ≤ <i>l</i> ≤ 19
Reflections collected	196163	38327	76882
Independent reflections	9483 [R(int) = 0.0596]	5003 [R(int) = 0.0428]	3736 [R(int) = 0.0288]
Coverage of independent reflections	100%	99.9%	99.8%
Function minimized	Σ w (Fo2 - Fc2)2	Σ w (Fo2 - Fc2)2	Σ w (Fo2 - Fc2)2
Data / restraints / parameters	9483 / 0 / 560	5003 / 1 / 250	3736 / 0 / 242
Goodness-of-fit on F2	1.331	0.694	1.283
Δ/σ max	0.001	0.000	0.002
Final R indices	8523 data; [I > 2σ(I)] R1 0 = 0.0302, wR2 = 0.0795	4655 data; [I > 2σ(I)], R1 = 0.0240, wR2 = 0.0754	3530 data; [I > 2σ(I)], R1 = 0.0173, wR2 = 0.0570
	all data, R1 = 0.0375, wR2 = 0.0881	all data, R1 = 0.0295, wR2 = 0.0841	all data, R1 = 0.0189, wR2 = 0.0583
Largest diff. peak and hole	1.012 and -0.612 eÅ ⁻³	0.626 and -0.724 eÅ ⁻³	0.670 and -0.684 eÅ ⁻³

R.M.S. deviation from mean	0.223 eÅ-3	0.126 eÅ-3	0.118 eÅ-3
----------------------------	------------	------------	------------

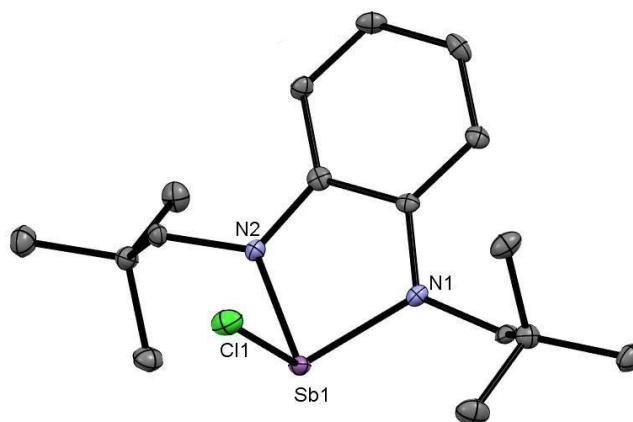


Figure 4A.A.1. Molecular structure of **4A.2** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) for **4A.2**: Sb1-Cl1 2.565(1), Sb1-N1 1.985(3), Sb1-N2 1.990(3). Selected bond angles (°) for **2**: Cl1-Sb1-N1 102.2(1), Cl1-Sb1-N2 92.3(1), N1-Sb1-N2 81.6(1).

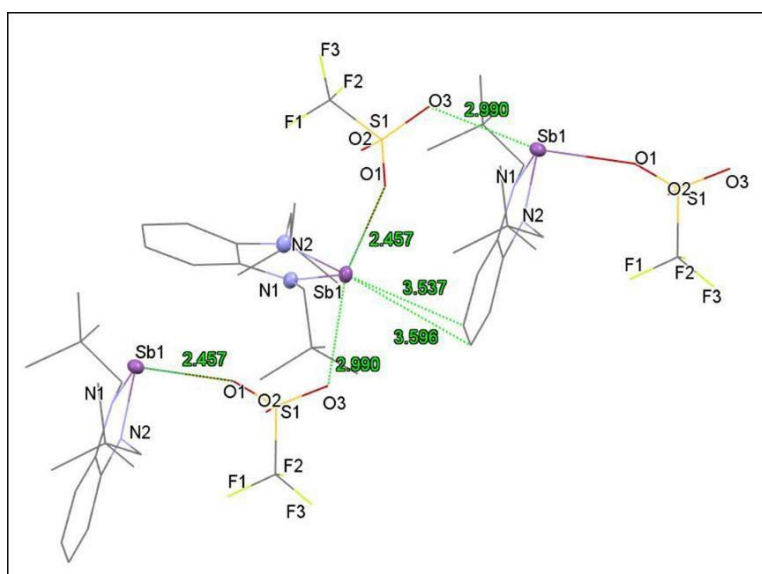


Figure 4A.A.2. Representation of the extended head-to-tail cation chains observed for compound **4A.3**. Hydrogen atoms are not shown for clarity. Short contacts are shown in green dotted lines.

Compound **4A.3** exhibits a different pattern of cation-cation interaction in the solid-state where an extended form of zigzag chains is visible from the molecular structure (Figure 4.A.A.3). In this case, the cations are arranged in a head-to-tail chain-like fashion where the cations are oriented in a perpendicular direction with the antimony centre in one moiety

directed towards the adjacent arene ring resulting in $\text{Sb} \cdots \pi$ interaction which is in η^2 coordination mode. Here the Sb-centroid of the arene ring separation is 3.537-3.596 Å which is slightly shorter than the sum of the van der Waals radii of both antimony and carbon. It is also observed that the antimony centre exhibits two long contacts with oxygen atoms of the triflate anions. This type of similar π interaction has been reported in the case of diamidonaphthalene stabilized phosphonium and arsenium cations where the P-arene contact is 3.426(7) Å and the As-arene distance is 3.228(6) Å.¹ Here the antimony center is in close contact with two oxygen atoms for two triflate moieties (2.457 and 2.990 Å) which much shorter than that reported by Gudat and coworkers where a four membered cyclic structure is observed and Sb-O length is much greater (3.349 and 3.170 Å).²

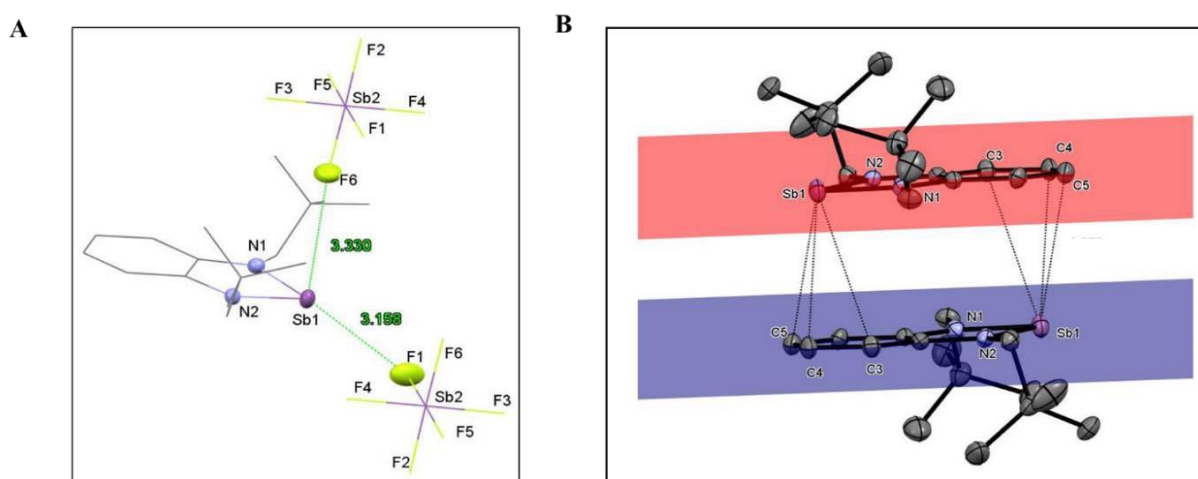


Figure 4A.A.3. A) Representation of the interactions with the central cationic antimony with the adjacent fluorine atoms of compound **4A.4**. B) Representation of π -stacked cation-cation interactions (antiparallel dimers) of compound **4A.4**. Hydrogen atoms are not shown for clarity.

The molecular structure also reveals that the stibonium cation comprises π -stacked dimers which are antiparallel to each other in orientation (Figure 4.A.A.3) and the antimony centre displays an intermolecular π interaction with the arene ring of the adjacent moiety in η^3 fashion ($\text{Sb} \cdots \text{C5}$ is 3.654 Å, $\text{Sb} \cdots \text{C4}$ is 3.370 Å and $\text{Sb} \cdots \text{C3}$ is 3.532 Å). It is also observed that the antimony centre displays two long contacts with two fluorine atoms located on two different hexafluoroantimonate anions with Sb-F distances being 3.158 and 3.330 Å respectively which is shorter than that reported compound $[(\text{CH})_2(\text{NtBu})_2\text{Sb}^+(\text{OTf})^-]$ (3.459 Å) by Gudat and co-workers.² The π -stacking cation-cation contact is 3.512 Å which is somewhat longer than that reported for $[\text{P}(\text{iPrN})_2\text{C}_{10}\text{H}_6]\text{GaCl}_4$ (3.47(1) Å) and $[\text{As}(\text{iPrN})_2\text{C}_{10}\text{H}_6]\text{GaCl}_4$ (3.35(1) Å).¹

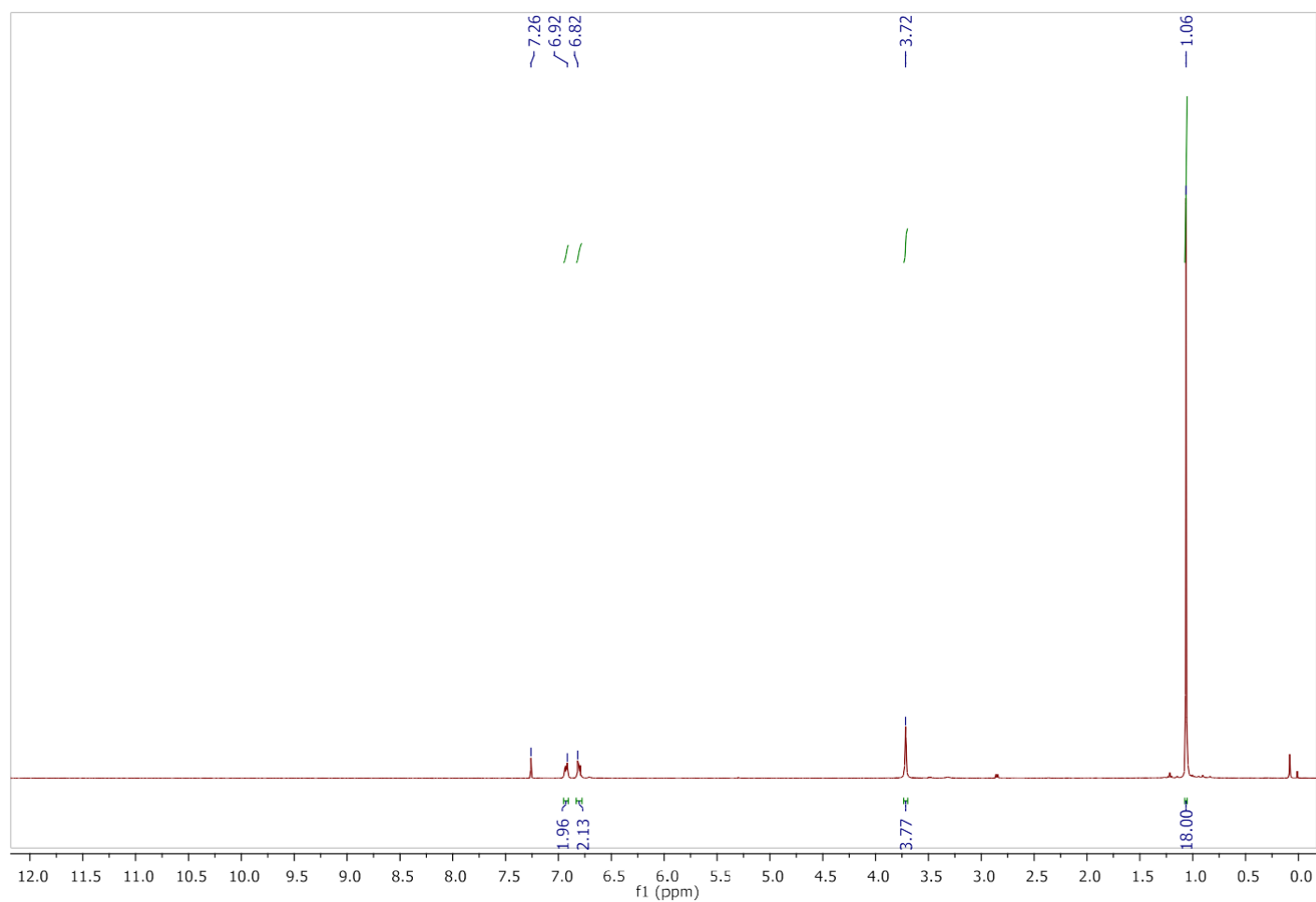


Figure 4A.A.6. ^1H NMR spectrum of compound 4A.2 in CDCl_3 (400 MHz, 298 K).

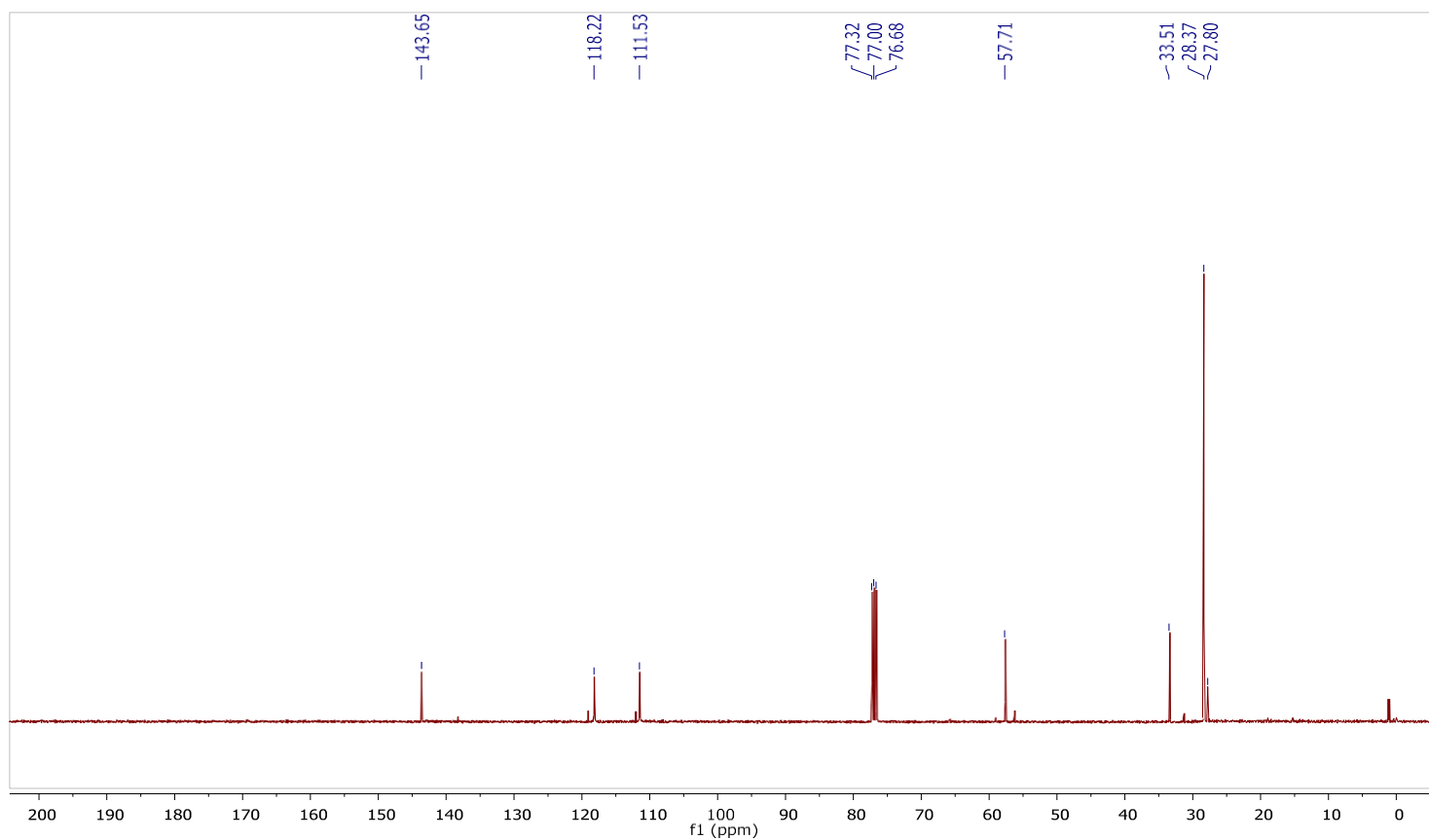


Figure 4A.A.7. ¹³C NMR spectrum of compound **4A.2** in CDCl₃ (100.613 MHz, 298 K).

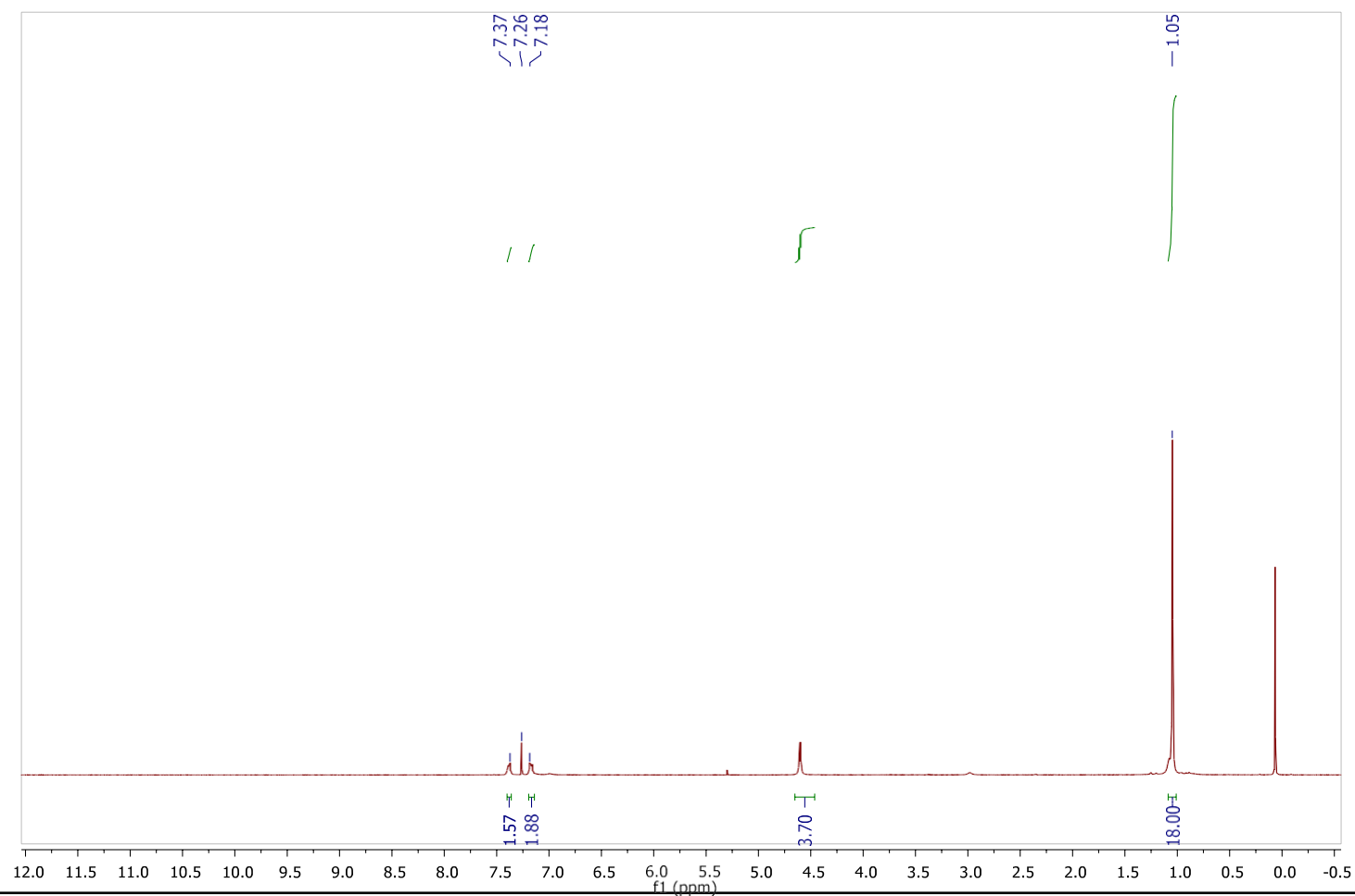


Figure 4A.A.8. ^1H NMR spectrum of compound **4A.3** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

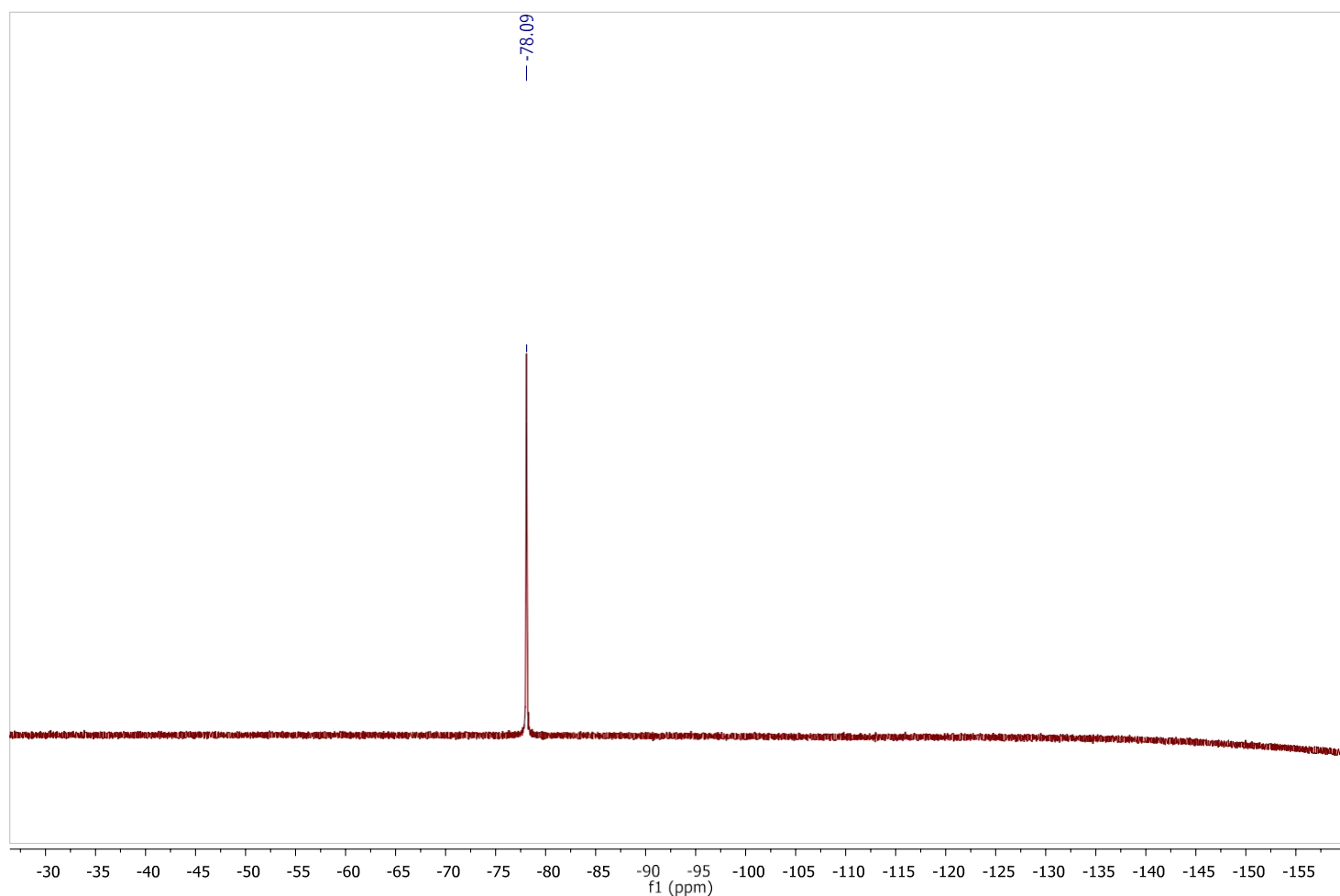


Figure 4A.A.9. ^{19}F NMR spectrum of compound **4A.3** in CDCl_3 (376.49 MHz, 298 K).

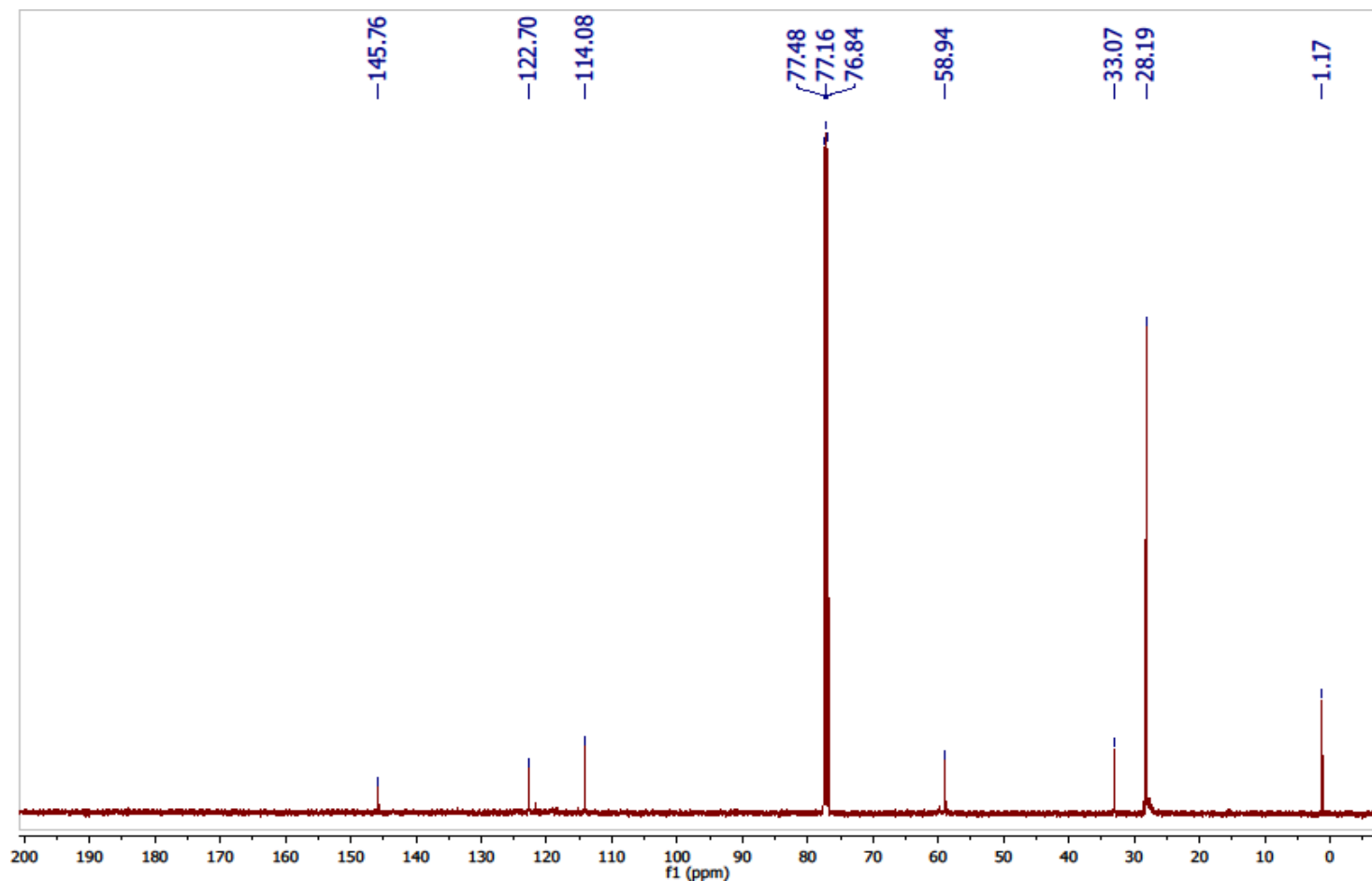


Figure 4A.A.10. ^{13}C NMR spectrum of compound 4A.3 in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

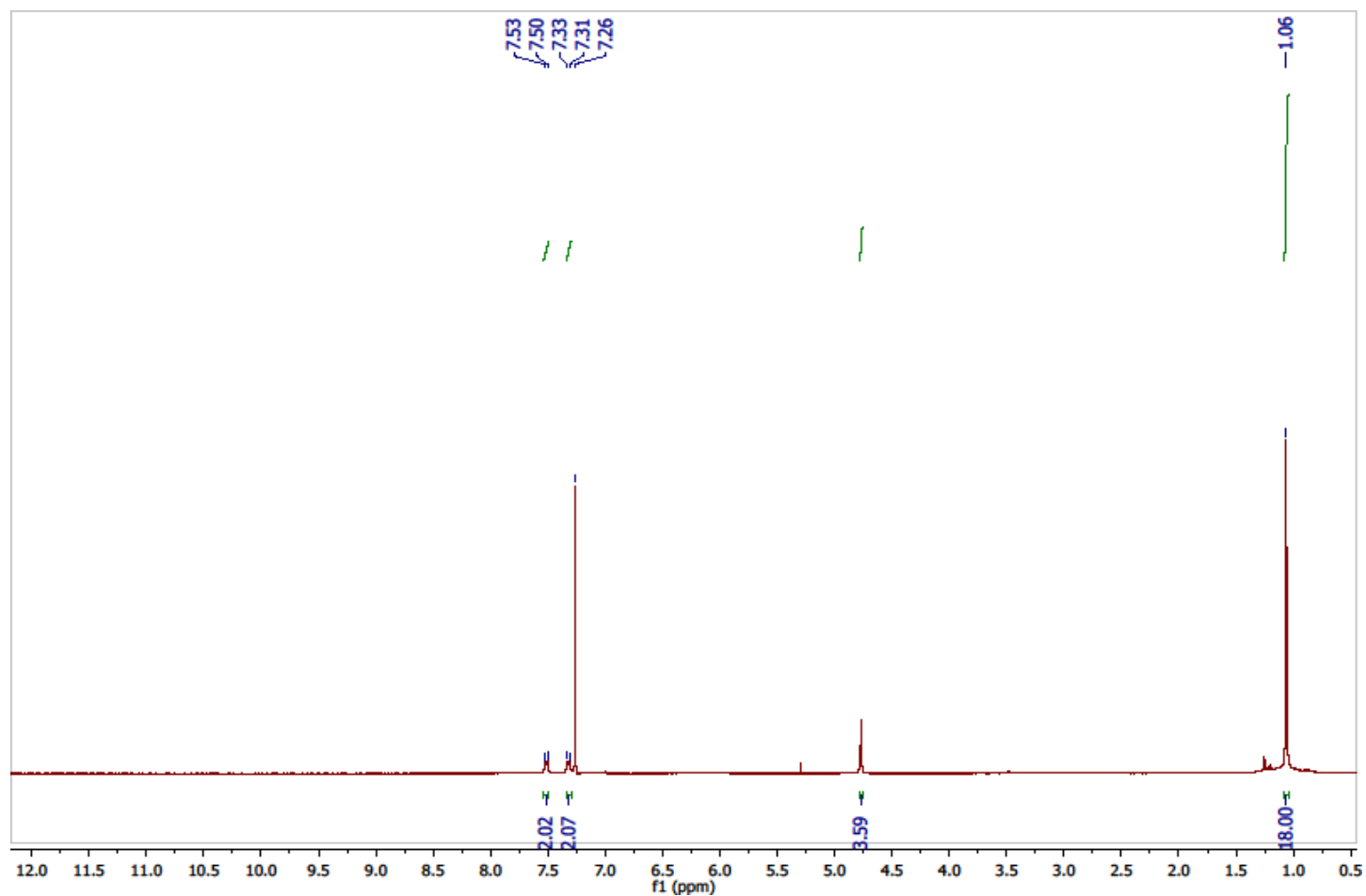


Figure 4A.A.11. ^1H NMR spectrum of compound **4A.4** in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

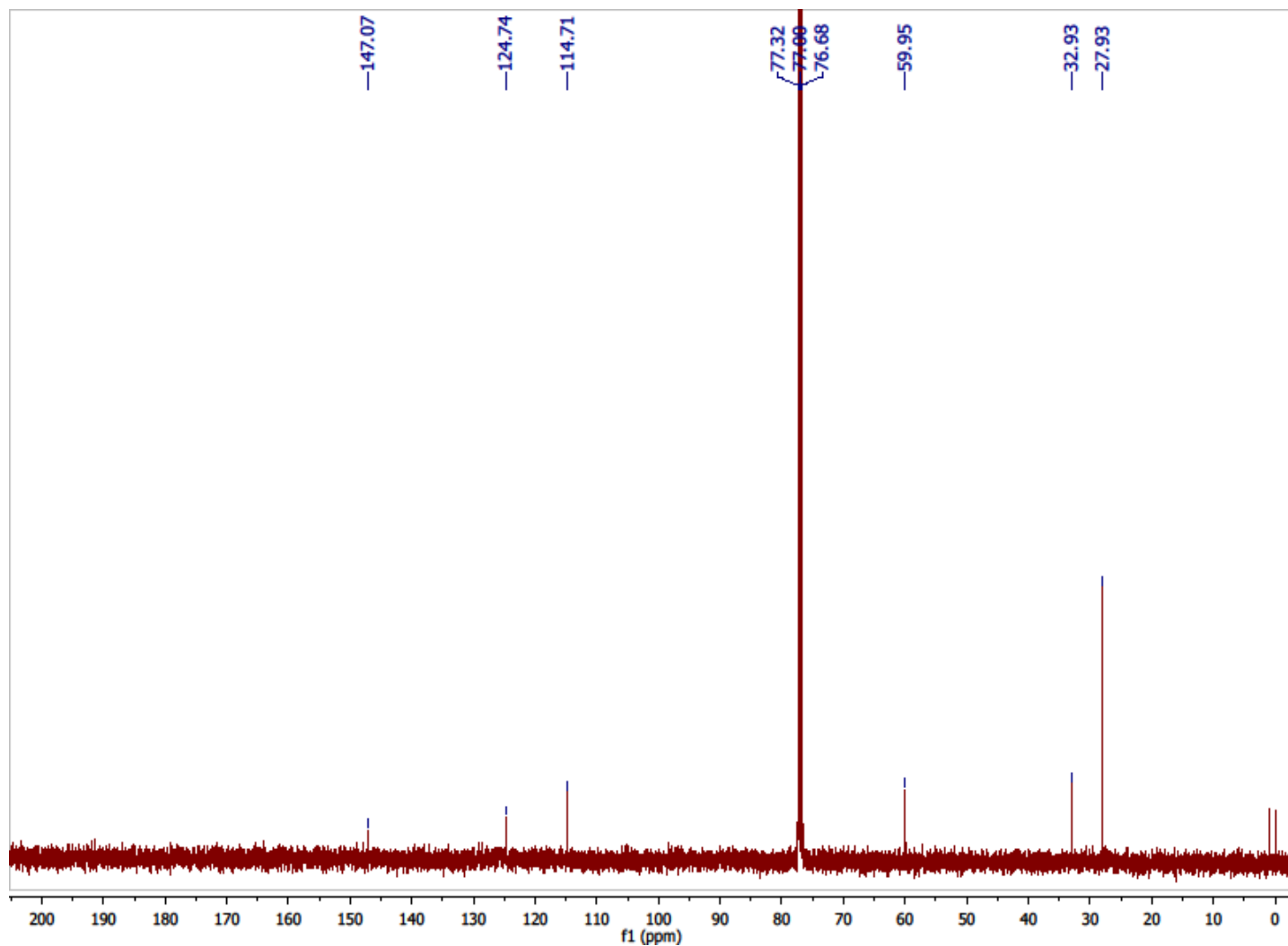


Figure 4A.A.12. ^{13}C NMR spectrum of compound **4A.4** in CDCl_3 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K)

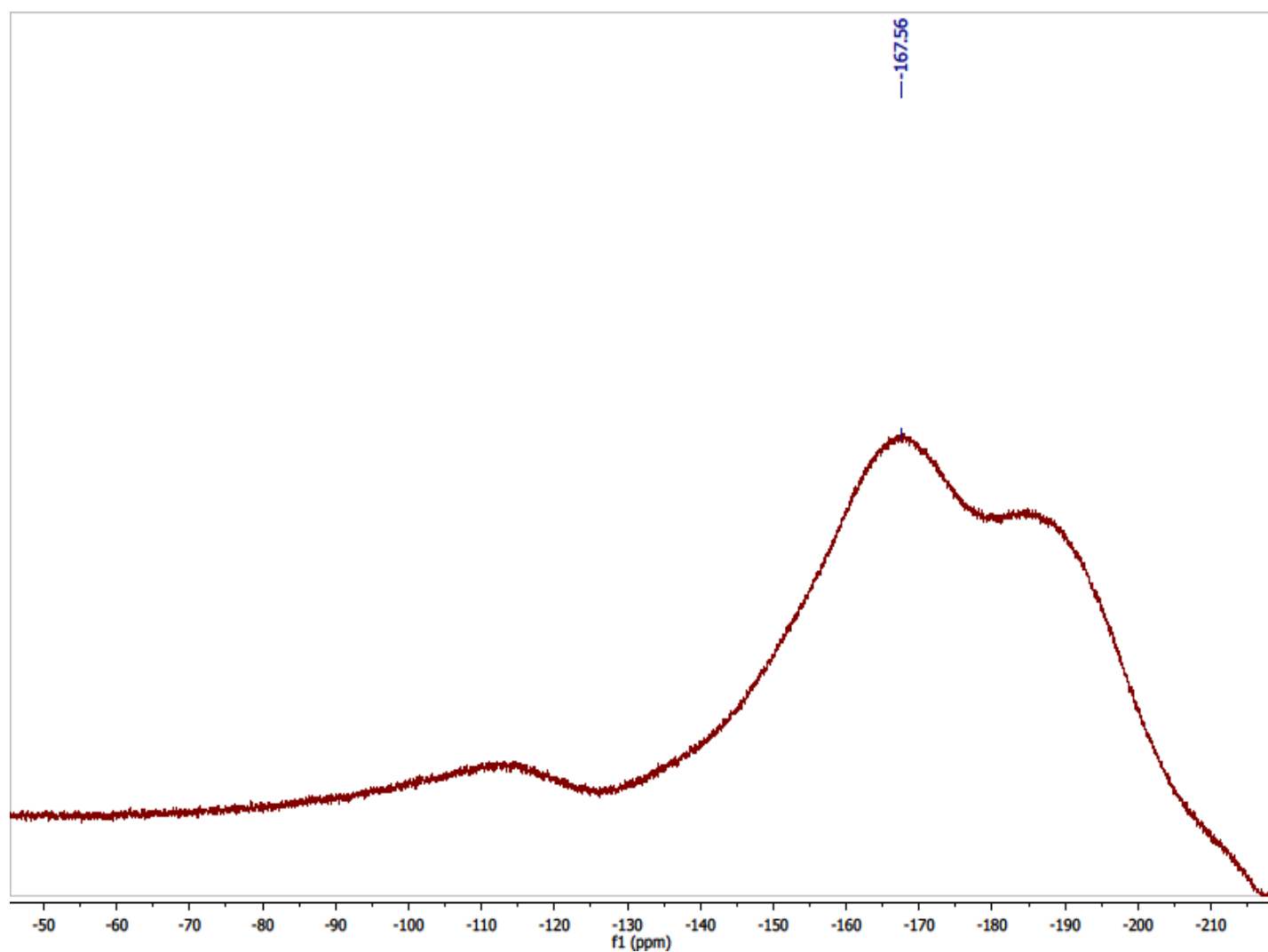


Figure 4A.A.13. ^{19}F NMR spectrum of compound **4A.4** in CDCl_3 (376.49 MHz, 298 K)

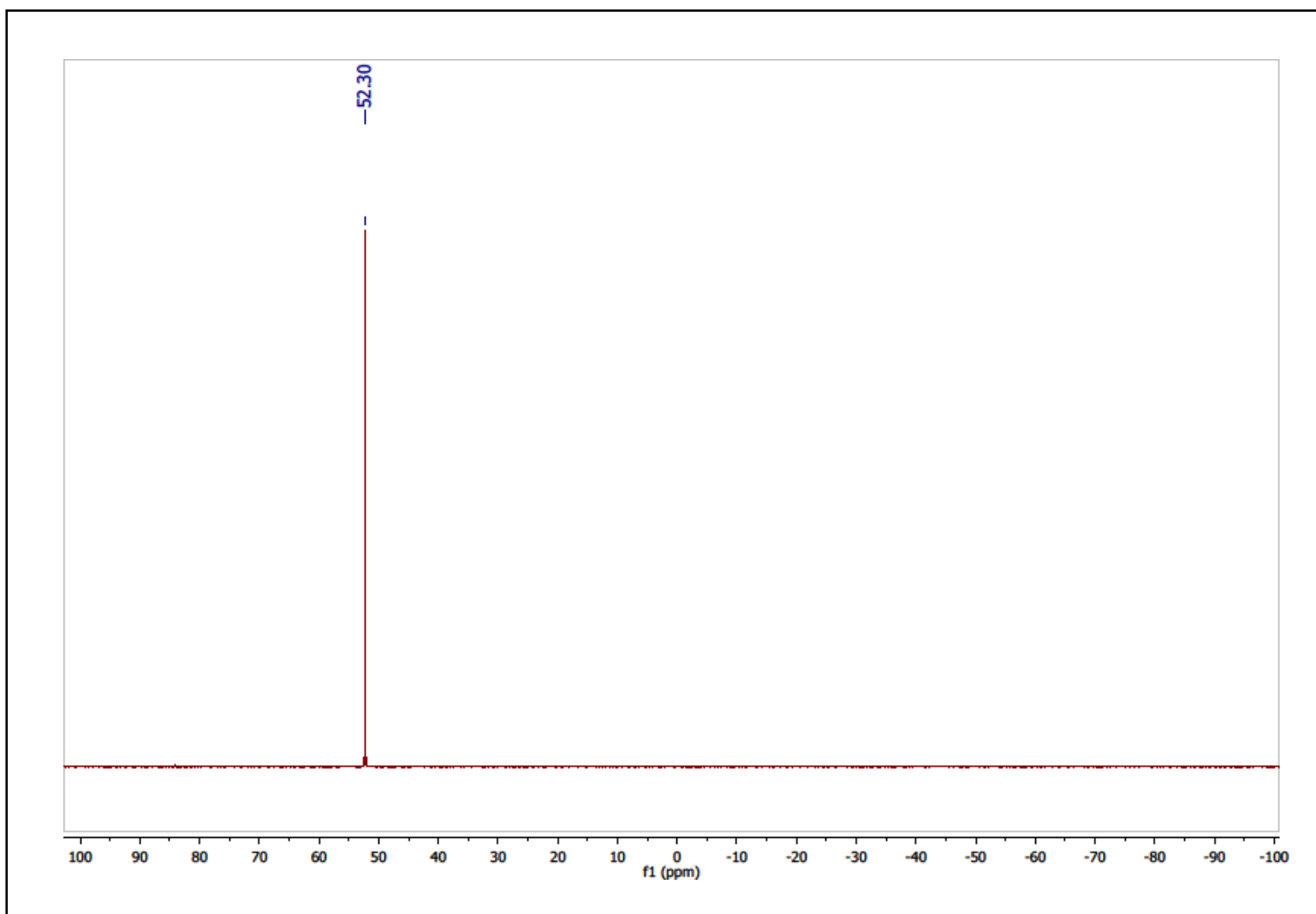


Figure 4A.A.14. ^{31}P NMR spectrum of compound **4A.2** and OPEt_3 in CDCl_3 (161.976 MHz, 298 K).

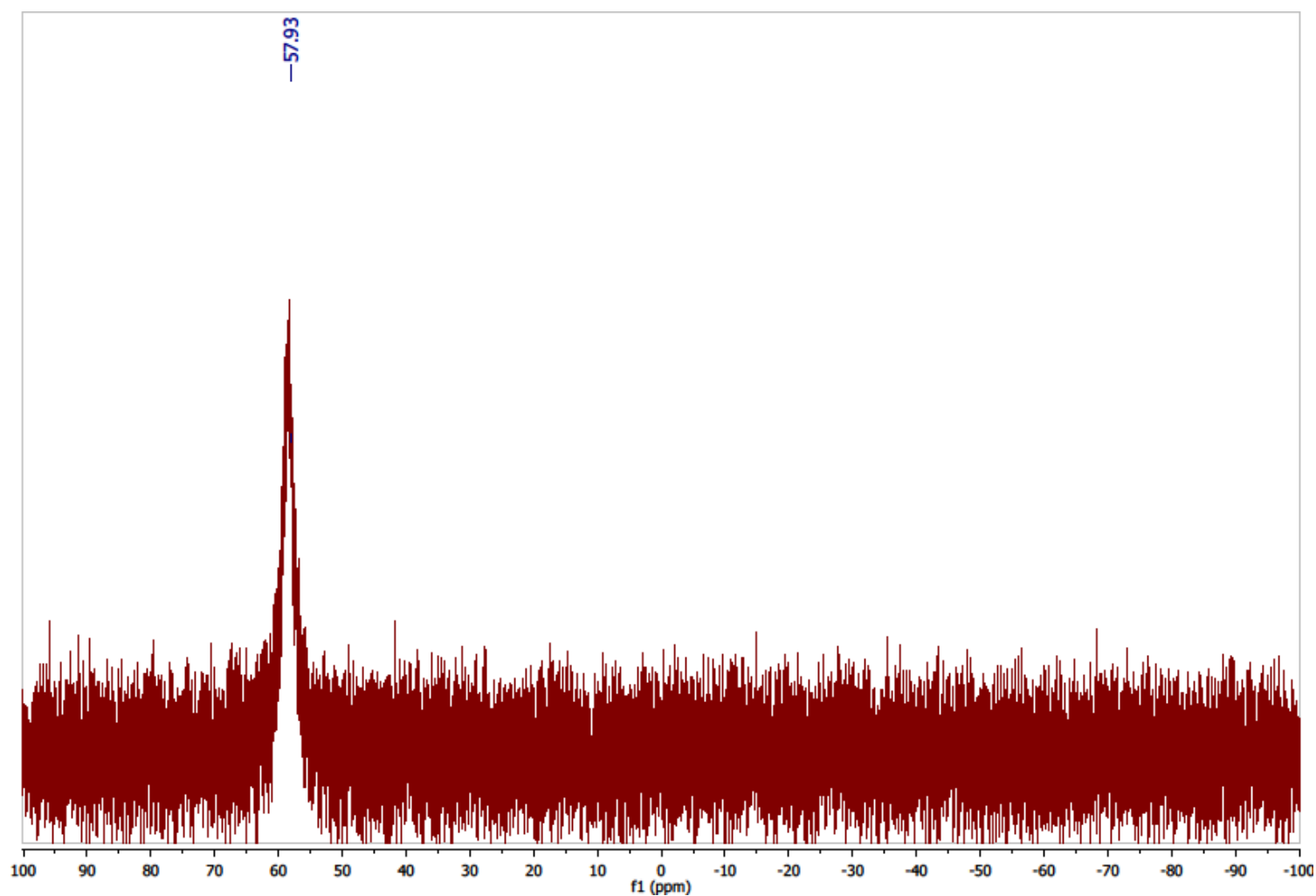


Figure 4A.A.15. ^{31}P NMR spectrum of compound **4A.3** and OPET_3 in CDCl_3 (161.976 MHz, 298 K).

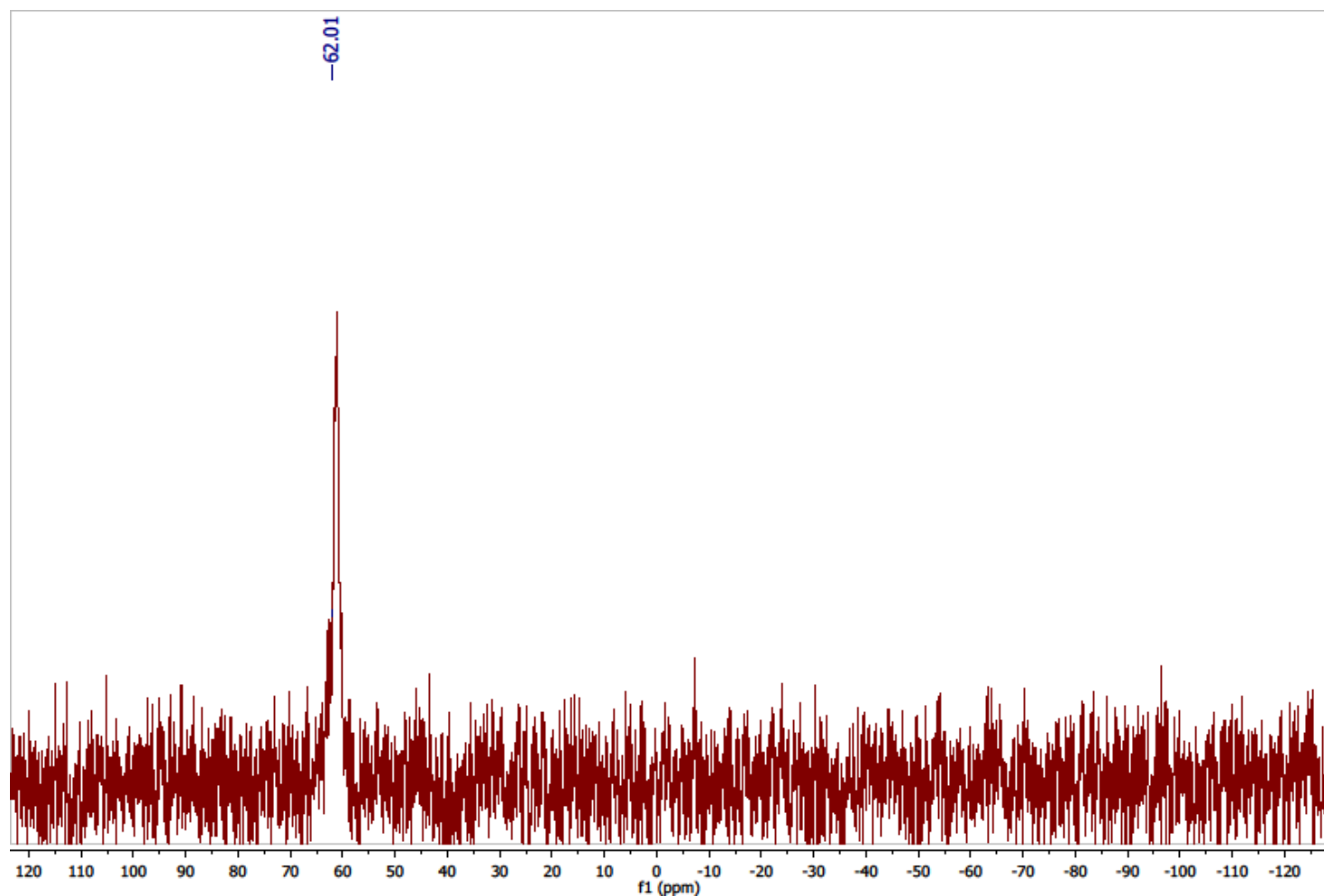


Figure 4A.A.15. ^{31}P NMR spectrum of compound **4A.4** and OPET_3 in CDCl_3 (161.976 MHz, 298 K).

Representative procedure for reaction rate determination: The order of the cyanosilylation reaction catalyzed by compound **4A.4** for aldehydes was determined by the method of initial rates.⁵⁻⁶ The rate of the reaction k_{obs} was calculated from the slope of the graph that is plotted as the concentration of the product formation with respect to time while the concentration of one of the starting reactants was varied keeping the concentration of another reactant as well as the catalyst constant. The k_{obs} value for each reaction was determined using ^1H NMR experiment using mesitylene as the internal standard. ^1H NMR spectra were collected at every 5 min interval starting from $t = 0$ to $t = 30$ min. The value of k_{obs} was determined from the slope of each linear best fit plot of [Product] vs. time. The plot of rate k_{obs} vs concentration of benzaldehyde indicates the order of the reaction with respect to benzaldehyde.

Firstly, the catalyst (0.0025 mmoles) was taken in the NMR tube inside the glove box and then benzaldehyde (0.25 mmoles) along with mesitylene (0.25 mmoles) was added followed by the addition of TMSCN (in different mmoles) and CDCl_3 (0.5 ml) was added to the NMR tube under argon. ^1H NMR spectra were recorded at various time intervals. The varying TMSCN concentration and concentration of catalyst and benzaldehyde are provided in Table 4.A.A.2 and represented graphically. The plot of k_{obs} vs concentration of TMSCN indicates that upon increasing the concentration of TMSCN it follows a linear co-relation with k_{obs} .

SI. NO.	Catalyst (mmoles)	Benzaldehyde (mmoles)	TMSCN (mmoles)	Kobs values (10^{-3})
1	0.0025	0.25	0.150	4.4
2	0.0025	0.25	0.200	6.4
3	0.0025	0.25	0.250	8.4
4	0.0025	0.25	0.300	10.0

Table 4A.A.2. Initial rates (k_{obs}) for the cyanosilylation of aldehydes with TMSCN catalyzed by catalyst **4A.4**, carried out under varying concentrations of TMSCN.

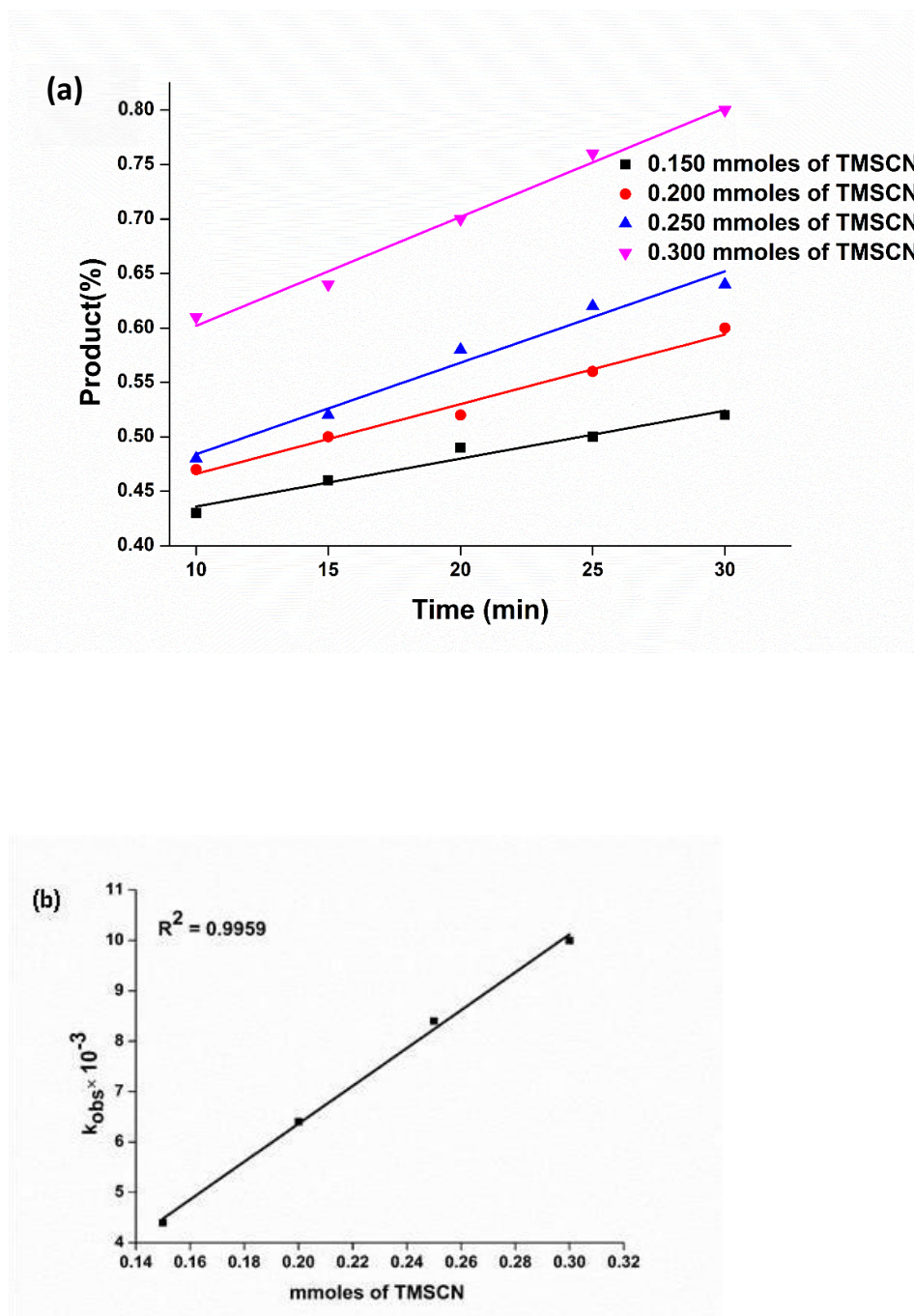


Figure 4A.A.16. (a) Plot of Product (%) vs Time for the determination of the initial rate (k_{obs}) values. (b) Plot of k_{obs} vs mmol of TMSCN for the determination of order of the reaction.

After this, the kinetic experiment was performed varying the concentration of benzaldehyde and keeping the concentrations of both catalyst and TMSCN constant. Catalyst (0.0025 mmoles) was taken in an NMR tube inside the glove box and benzaldehyde (in different concentrations, i.e., 0.150 mmol, 0.200 mmoles, 0.300 mmoles and 0.400 mmoles), TMSCN (0.25 mmoles) and mesitylene (0.25 mmoles) and CDCl_3 (0.5 ml) were added to the NMR tube under inert atmosphere. After this ^1H NMR spectra were recorded at 5 min time interval. The concentration of the catalyst, varying concentration of benzaldehyde and concentration of TMSCN for each set of experiments along with the rate of each reaction kobs have been given in Table 4A.A.3. The plot of rate (kobs) vs concentration benzaldehyde indicates that upon increase in the concentration of benzaldehyde it follows a linear co-relation with rate.

SI. NO.	Catalyst (mmoles)	Benzaldehyde (mmoles)	TMSCN (mmoles)	Kobs values (10^{-3})
1	0.0025	0.150	0.25	3.6
2	0.0025	0.25	0.25	5.6
3	0.0025	0.300	0.25	6.4
4	0.0025	0.400	0.25	7.4

Table 4A.A.3. Initial rates (kobs) for the cyanosilylation of aldehydes with TMSCN catalysed by catalyst **4A.4**, carried out under varying concentrations of benzaldehyde.

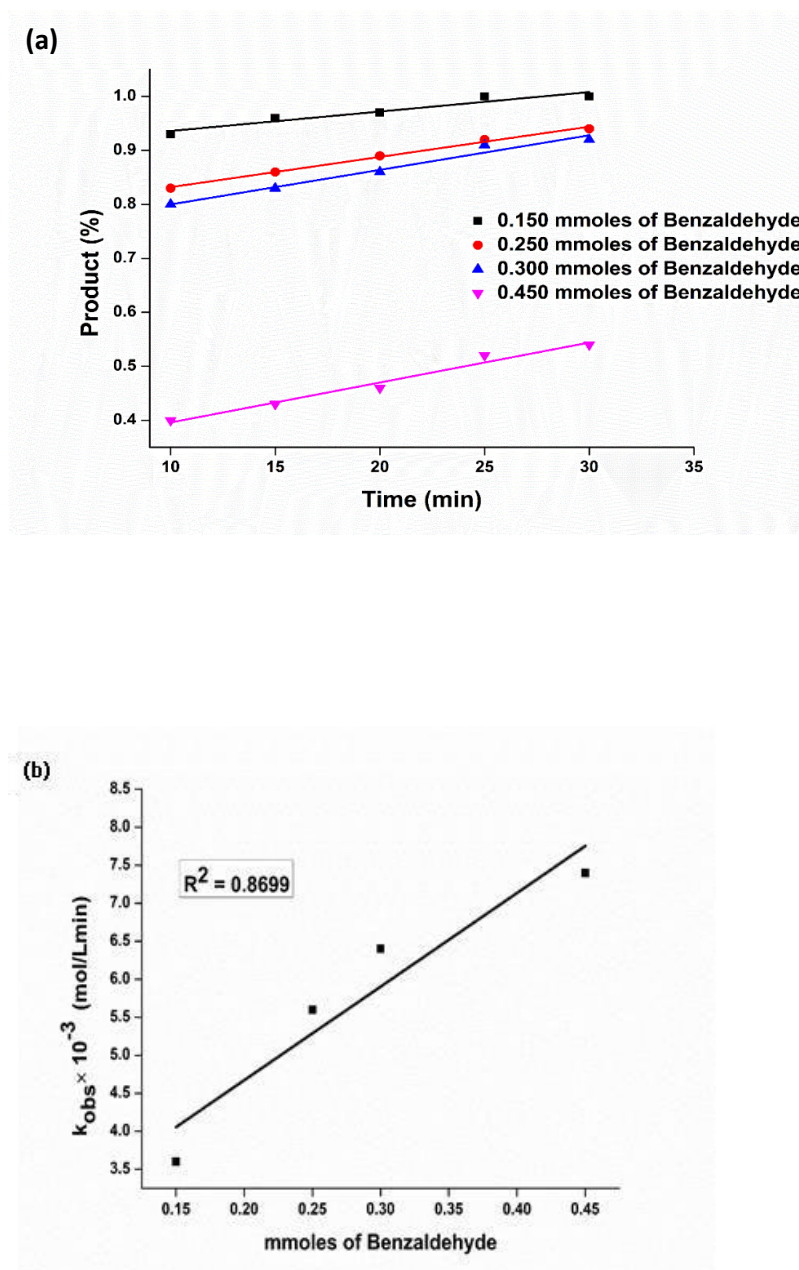


Figure 4A.A.17. (a) Plot of Product (%) vs Time for the determination of the initial rate (k_{obs}) values. (b) Plot of k_{obs} vs mmoles of benzaldehyde for the determination of order of the reaction.

Appendix of Chapter 5

Table 5.A.1. Crystallographic data of compound **5.1**.

	5.1
Chemical formula	C ₃₂ H ₅₂ Bi ₂ F ₁₂ N ₄ Sb ₂
Formula weight	1382.23g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>C</i> 2/c
Unit cell dimensions	<i>a</i> = 36.971(6) Å
	<i>b</i> = 11.0199(18) Å
	<i>c</i> = 21.471(4) Å
	α = 90°
	β = 101.205(5) °
	γ = 90°
Volume	8581(2) Å ³
Z	8
Density (calculated)	2.140 g/cm ³
Absorption coefficient	9.504 mm ⁻¹
F(000)	5184
Theta range for datacollection	2.21 to 28.18°
Index ranges	-48 ≤ <i>h</i> ≤ 44, -14 ≤ <i>k</i> ≤ 14, -27 ≤ <i>l</i> ≤ 27
Reflections collected	64711
Independent reflections	9829 [R(int) = 0.0766]
Coverage of independent reflections	99.9%
Function minimized	Σ w(Fo ² - Fc ²) ²
Data / restraints / parameters	9829 / 0 / 483
Goodness-of-fit on F²	2.557
Δ/σ max	0.012
Final R indices	8398 data; [I > 2σ(I)] R1 = 0.1193, wR2 = 0.3342
	all data , R1 = 0.1317, wR2 = 0.3399
Largest diff. peak and hole	0.282 and -0.045 eÅ ⁻³
R.M.S. deviation from mean	0.007 eÅ ⁻³

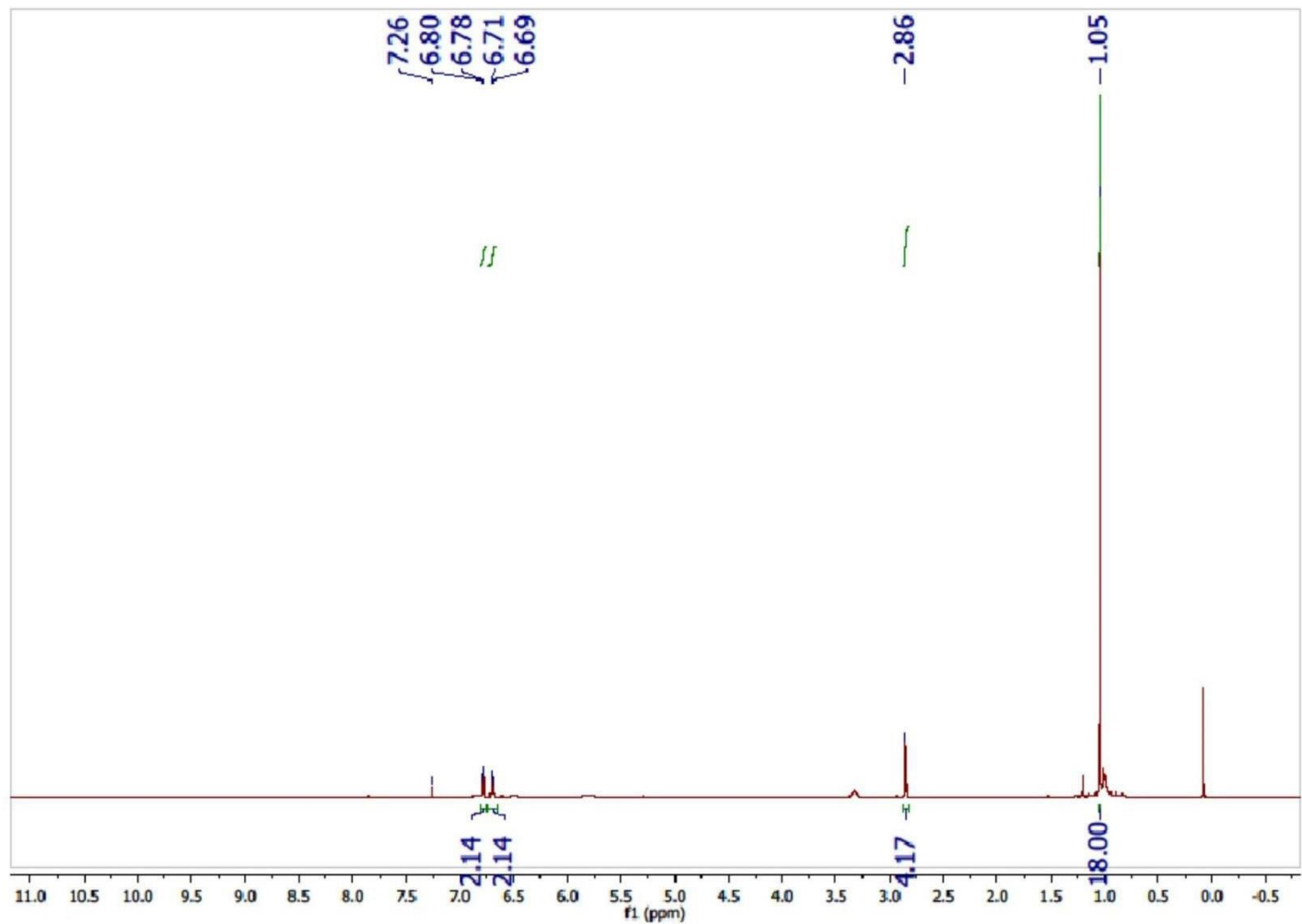


Figure 5.A.1. ^1H NMR spectrum of compound 5.1 in CDCl_3 (400 MHz, 298 K).

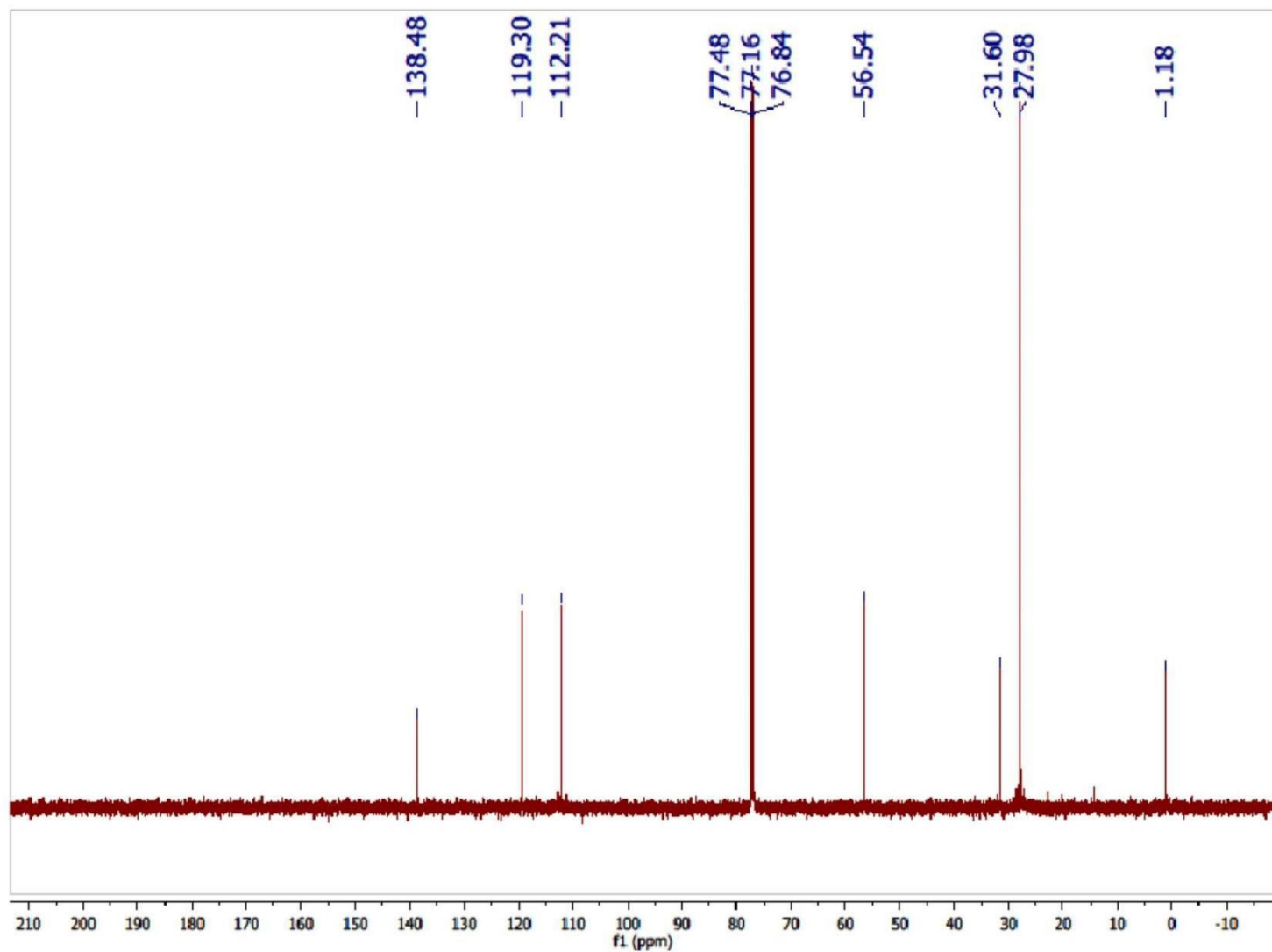


Figure 5.A.2. ^{13}C NMR spectrum of compound 5.1 (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K)

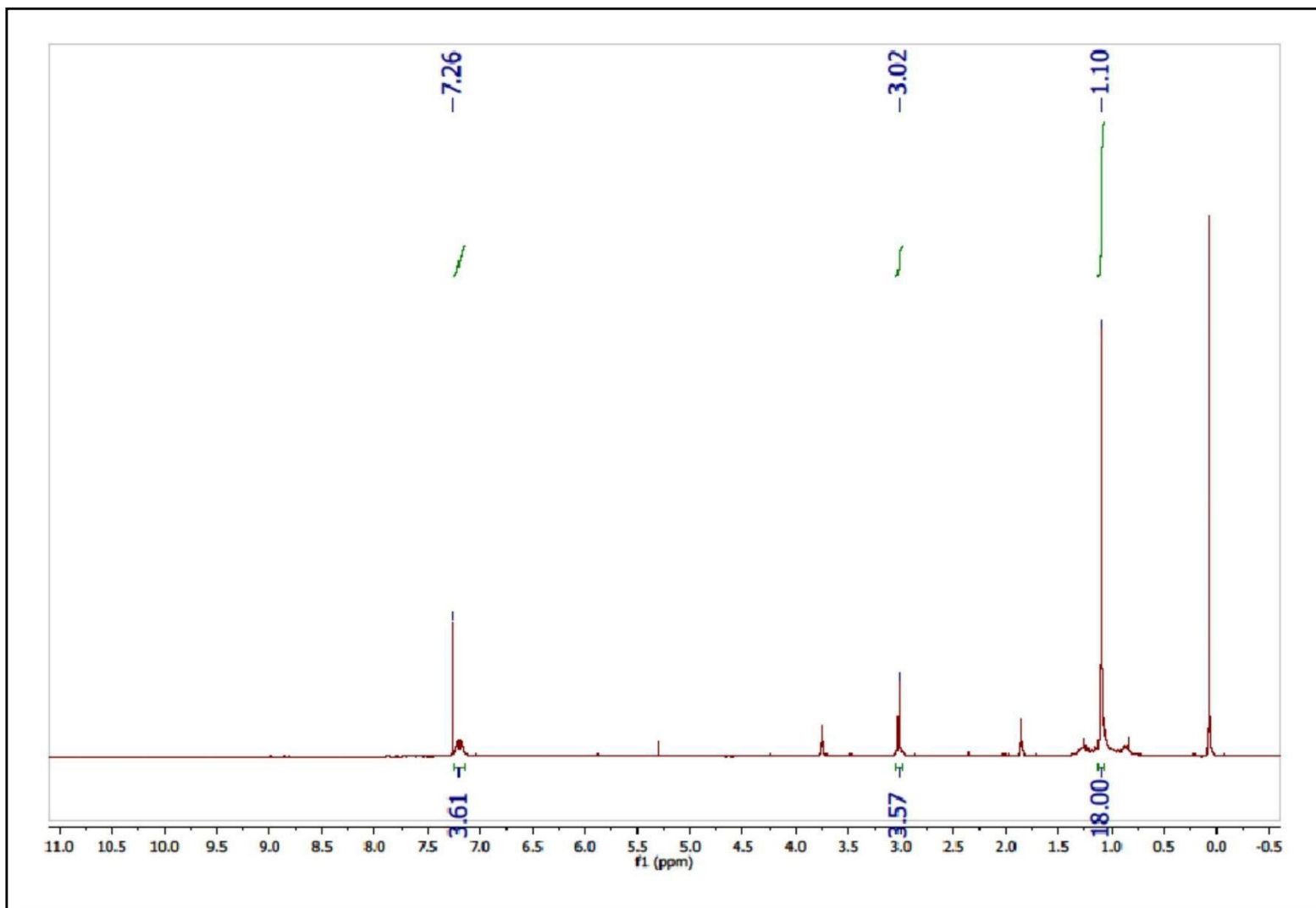


Figure 5.A.3. ^1H NMR spectrum of compound 5.2 in CDCl_3 (Solvent peak δ 7.26 ppm) (400 MHz, 298 K).

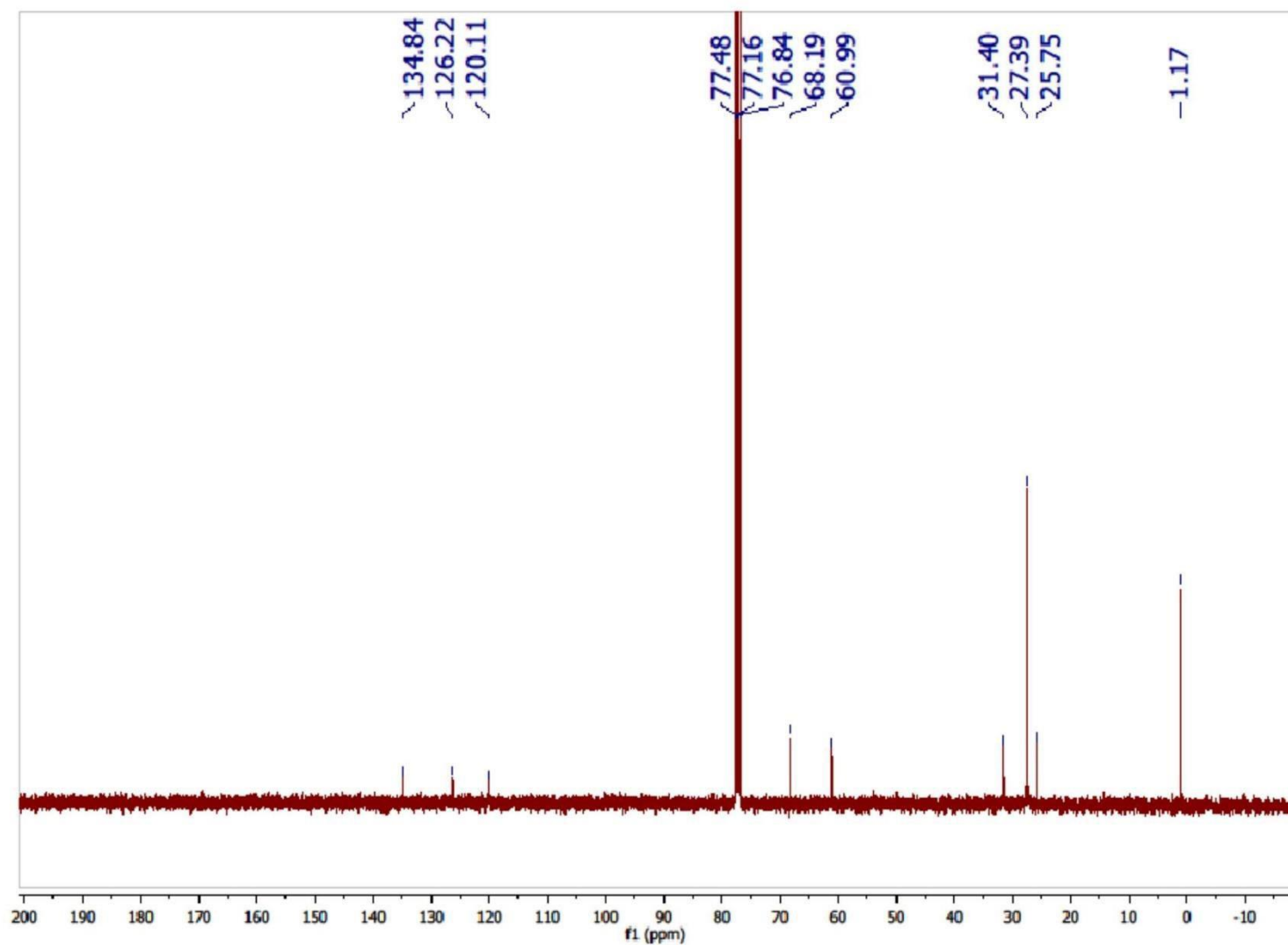


Figure 5.A.4. ¹³C NMR spectrum of compound 5.2 CDCl₃ (Solvent peak δ 77.16 ppm) (100.613 MHz, 298 K).

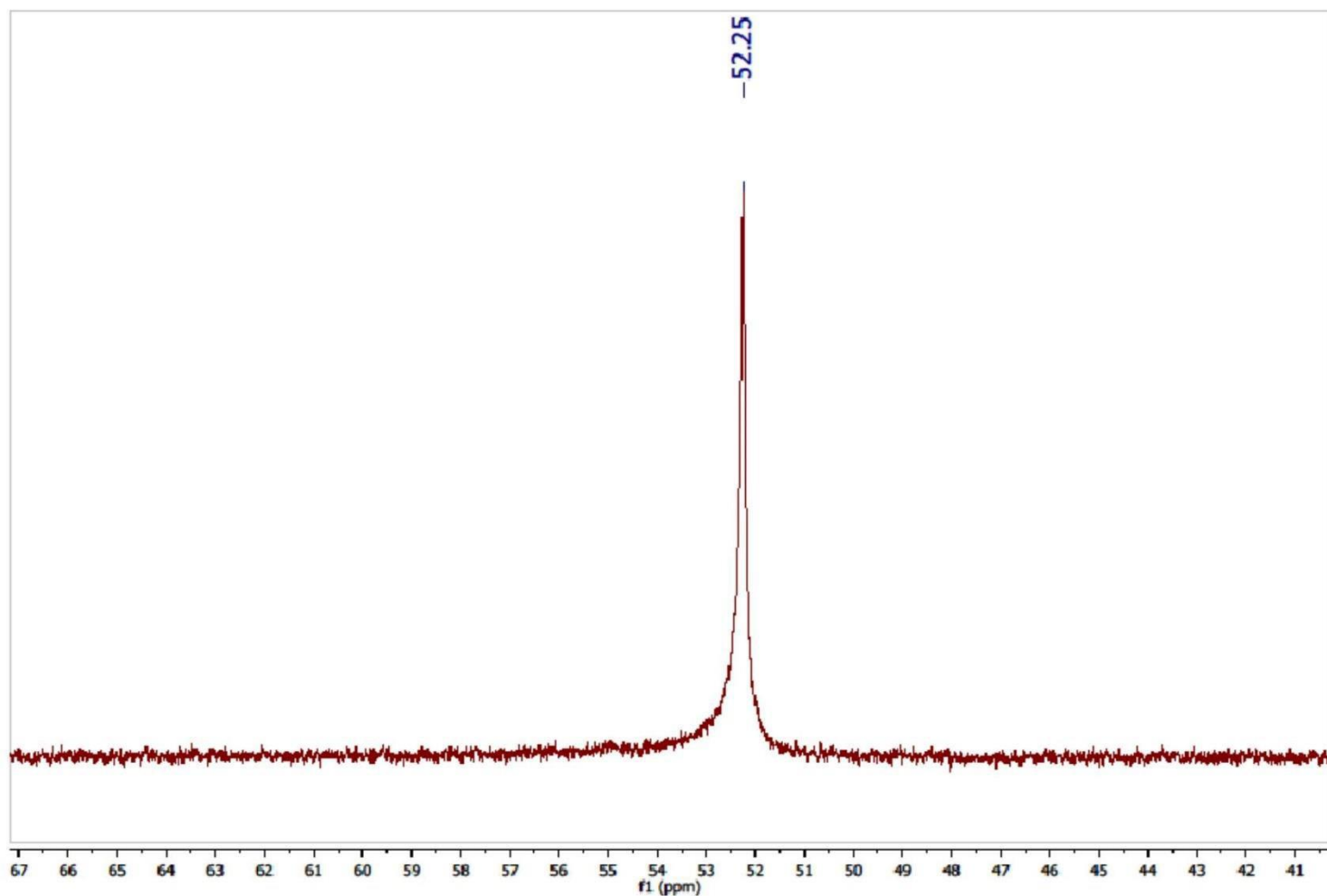


Figure 5A.5. ^{31}P NMR spectrum of compound **5.1** with OPET_3 in CDCl_3 (161.976 MHz, 298 K).

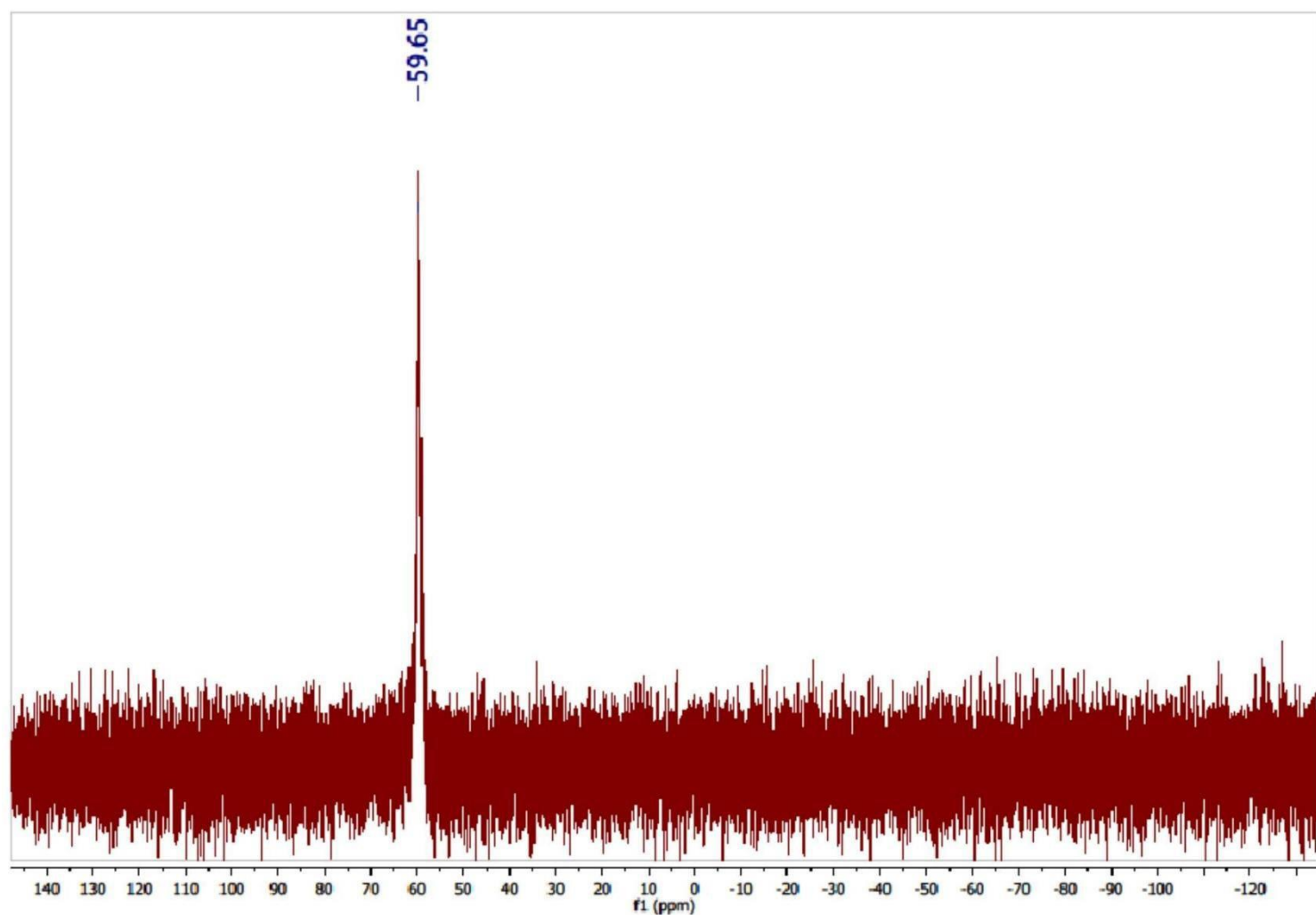


Figure 5.A.6. ^{31}P NMR spectrum of compound 5.2 with OPet_3 in CDCl_3 (161.976 MHz, 298 K).

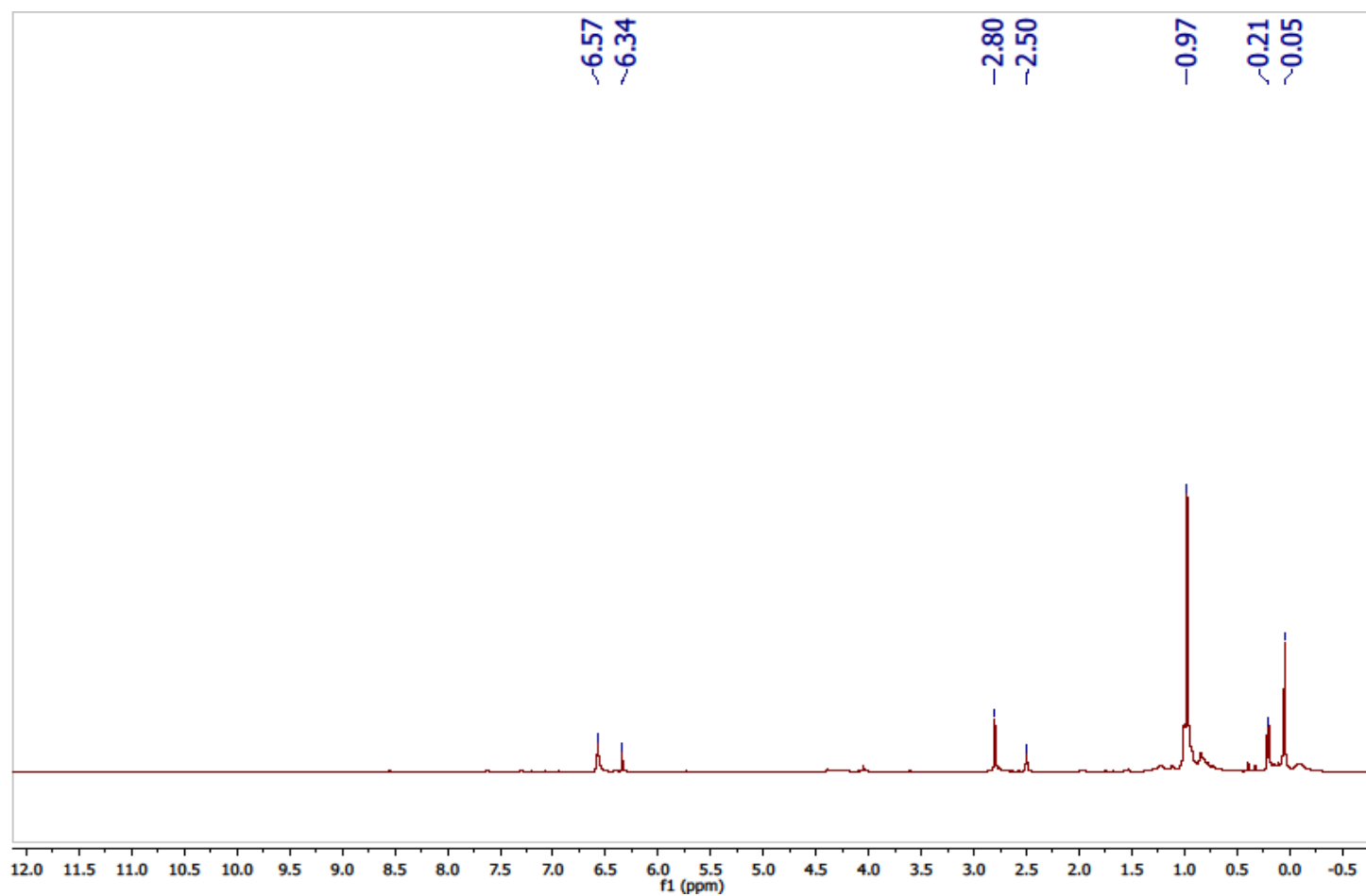


Figure 5.A.7. ^1H NMR of 1:1 reaction of catalyst **5.2** and TMSCN in DMSO- d_6 (Solvent peak δ 2.5 ppm) (400 MHz, 298 K).

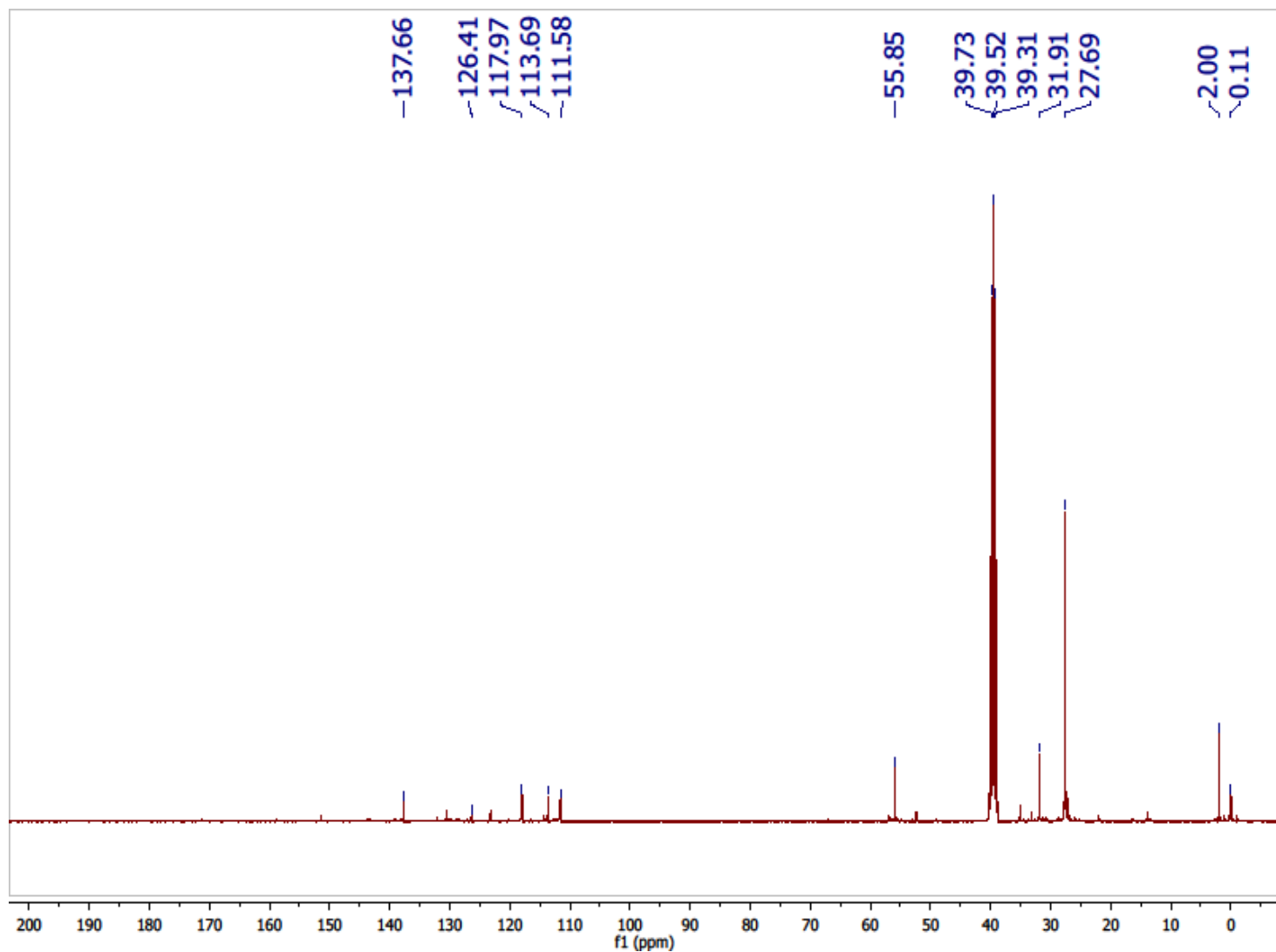


Figure 5.A.8. ¹³C NMR of 1:1 reaction of catalyst 5.2 and TMSCN in DMSO-d₆ (100.613 MHz, 298 K).

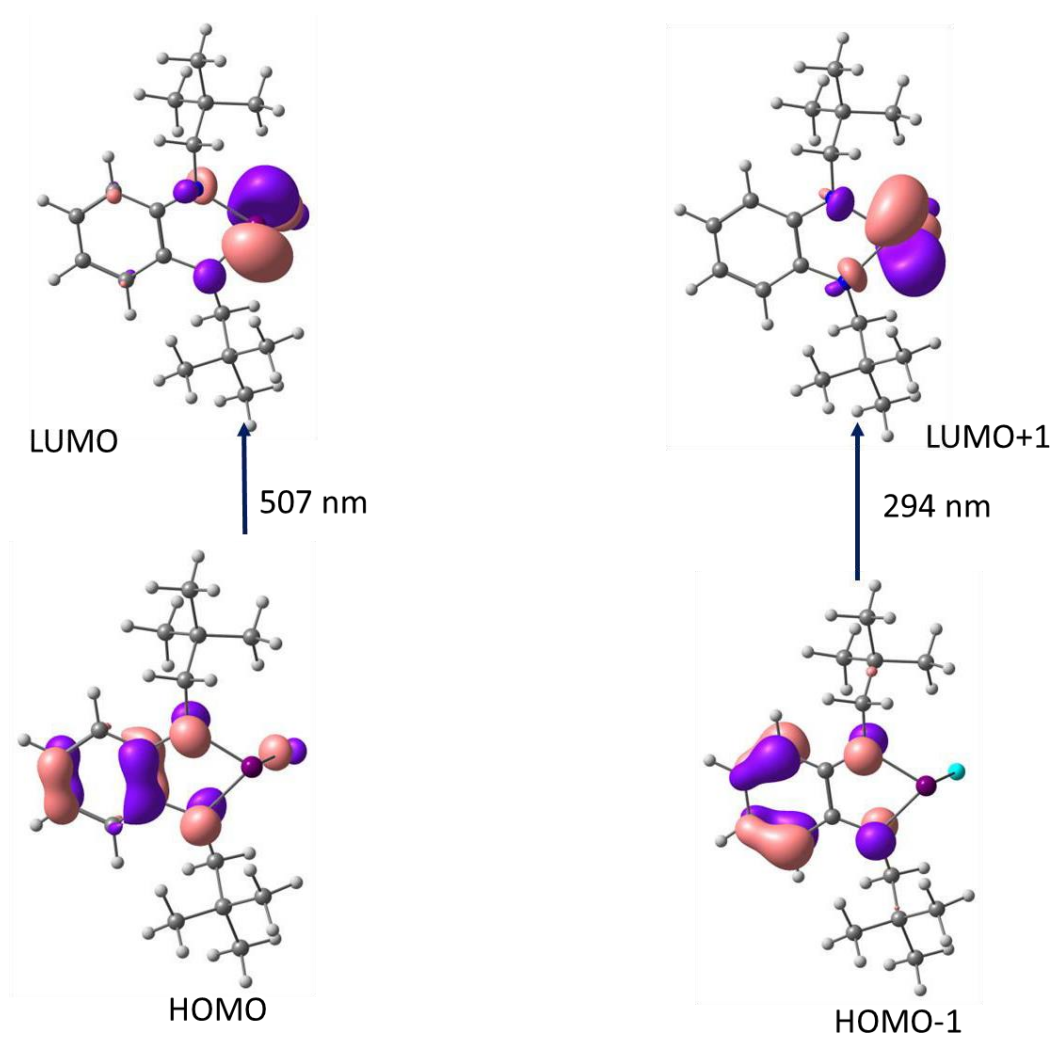


Figure 5.A.9. Calculated transitions for the main absorption of compound 5.1.

	THF (nm)	DCM (nm)	ACN (nm)
Computed Absorption values	294, 507.7	293, 506	289, 498.3

Table 5.A.2. UV-visible spectroscopic data of compound 5.1

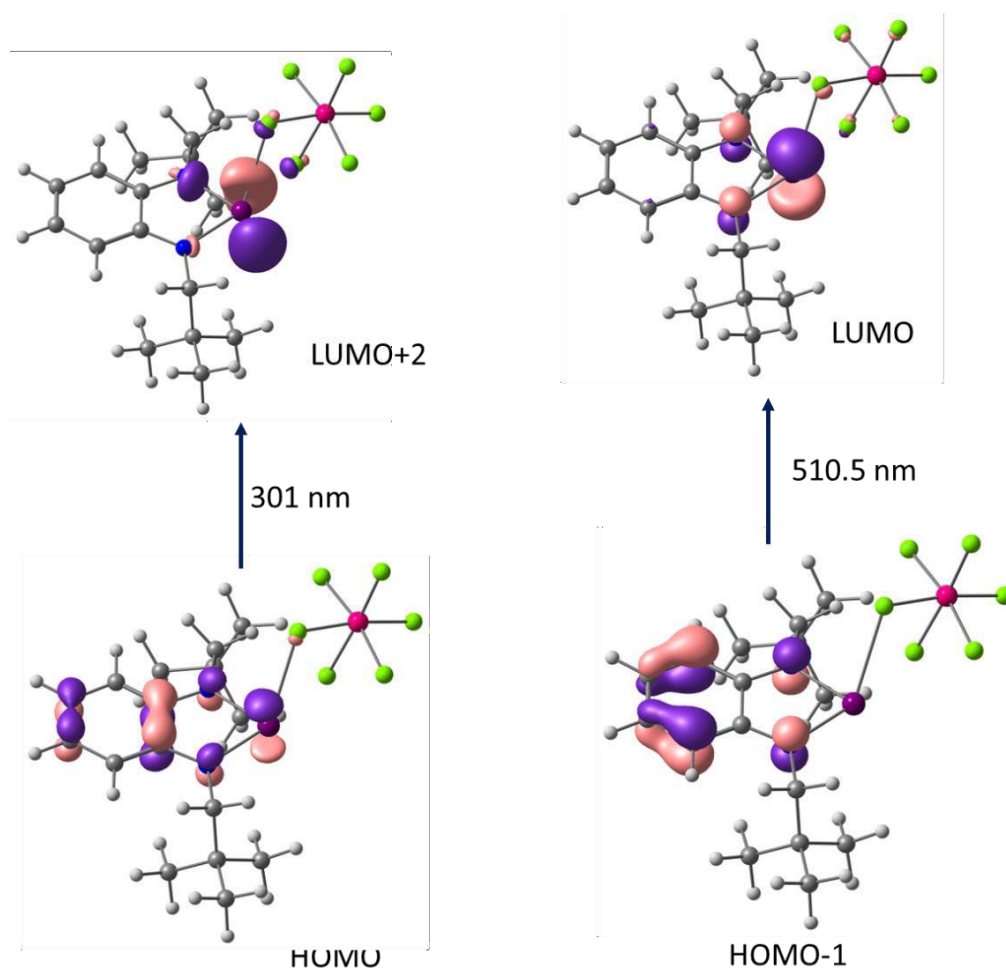


Figure 5.A.10. Calculated transitions for the main absorptions of compound 5.2

	THF (nm)	DCM (nm)	ACN (nm)
Computed Absorption values	301, 510.5	300.8, 509.7	299.8, 506

Table 5.A.3. UV-visible spectroscopic data of compound 5.2

Kinetic study

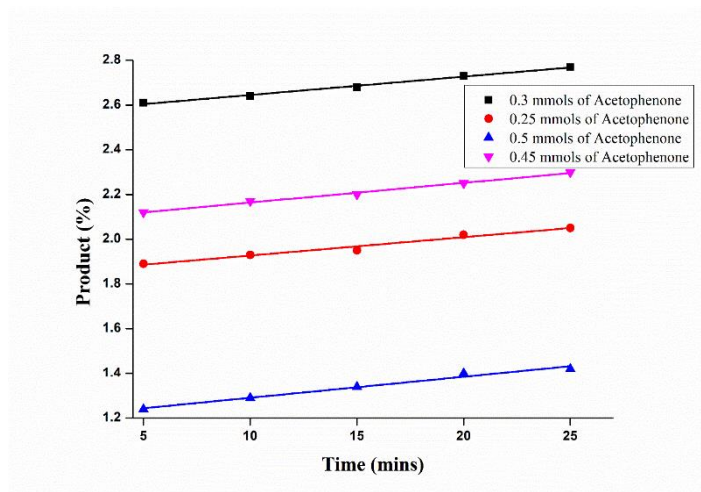
Representative procedure for reaction rate determination: The order of the cyanosilylation reaction of ketones catalyzed by catalyst **5.1** has been determined by using the initial rates method. The rate of the reaction k_{obs} is mainly calculated from the slope of the graph, plotted as the concentration of the product formation versus time. Here the concentration of one of the substrates is varied while the other and the catalyst are kept constant. Mesitylene was used as the internal standard in each experiment. The rate k_{obs} has been determined from the ^1H NMR of each experiment. ^1H NMR spectra were collected at every 5 min starting from $t=5$ to $t=25$ min. The value of the slope of each linear best-fit plot of [Product] vs Time is the value of k_{obs} . The order of the reaction with respect to acetophenone is determined from the plot of k_{obs} vs concentration of acetophenone.

Initially, the catalyst (0.0025 mmoles) was taken in NMR tube inside the glove box followed by the addition of TMSCN (0.25 mmoles) along with mesitylene and then acetophenone (in different mmoles) and CDCl_3 (0.5 ml) were added under argon. ^1H NMR spectra were recorded for each set up at various time intervals. All the concentrations of acetophenone along with concentration of catalyst and TMSCN are provided in the table below. From the k_{obs} and concentration of acetophenone plot it is observed that with the increase in concentration of acetophenone it follows the linear correlation with k_{obs} .

SI. NO.	Catalyst (mmoles)	Acetophenone (mmoles)	TMSCN (mmoles)	k_{obs} values(10^{-3})
1	0.0025	0.25	0.25	8.2
2	0.0025	0.30	0.25	8.2
3	0.0025	0.45	0.25	8.8
4	0.0025	0.50	0.25	9.4

Table 5.A.4. Initial rates (k_{obs}) for the cyanosilylation of aldehydes with TMSCN catalyzed by catalyst **5.2**, carried out under varying concentrations of acetophenone

a)



b)

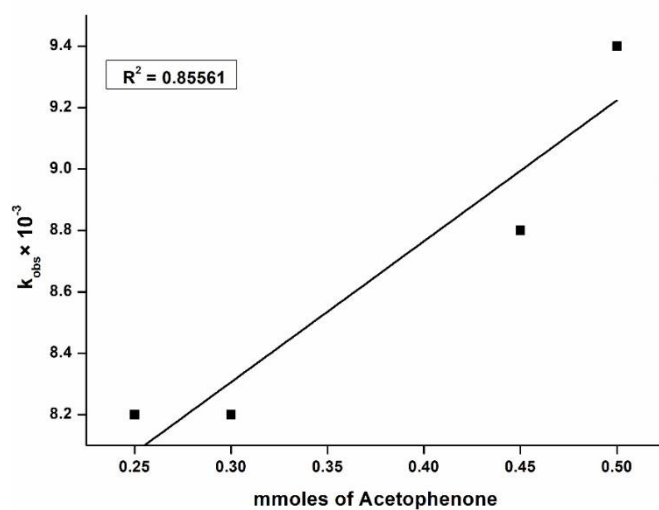


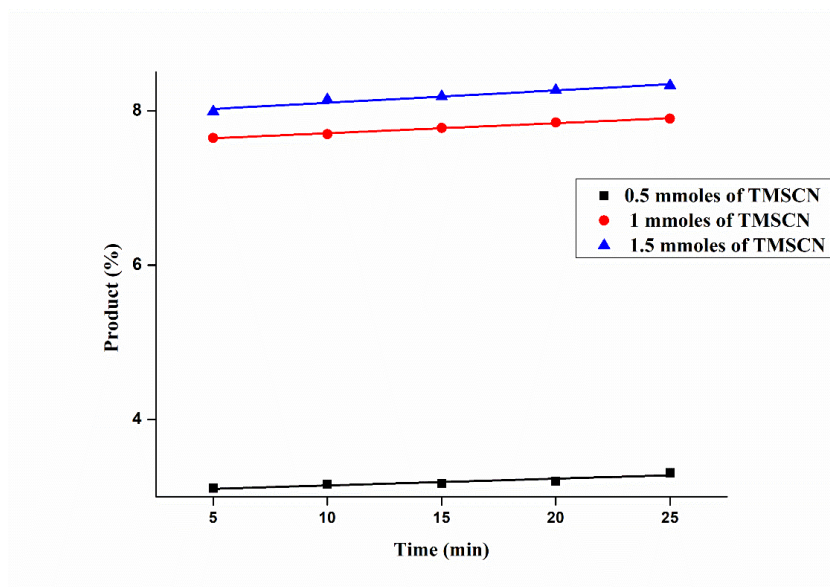
Figure 5.A.11. (a) Plot of Product (%) vs Time for the determination of the initial rate (k_{obs}) values. (b) Plot of k_{obs} vs mmoles of acetophenone for the determination of order of the reaction.

The same experiment was done with varying the concentration of TMSiCN and keeping the concentration of catalyst and acetophenone constant. Here also the catalyst (0.0025 mmoles) was taken in the NMR tube in glove box and TMSiCN (in different concentrations like 0.5 mmol, 1 mmol, 1.5 mmol), TMSiCN (0.25 mmoles), mesitylene (0.25 mmoles) CDCl₃ (0.5 ml) were added to that NMR tube under argon atmosphere. ¹H NMR spectra were recorded after 5 min interval for each set up starting from t=5 to t=25 min. In table (5.A.5) varying concentration of acetophenone and the concentration of catalyst and TMSiCN as well as the value of k_{obs} are given. The plot of k_{obs} vs concentration of acetophenone indicates that there is a linear correlation between the rate with the increase in the concentration of acetophenone.

SI. NO.	Catalyst (mmoles)	Acetophenone (mmoles)	TMSiCN (mmoles)	K_{obs} value (10^{-3})
1	0.0025	0.25	0.5	8.8
2	0.0025	0.25	1.0	13
3	0.0025	0.25	1.5	16

Table 5.A.5. Initial rates (k_{obs}) for the cyanosilylation of aldehydes with TMSiCN catalyzed by catalyst 5.2, carried out under varying concentrations of TMSiCN

a)



b)

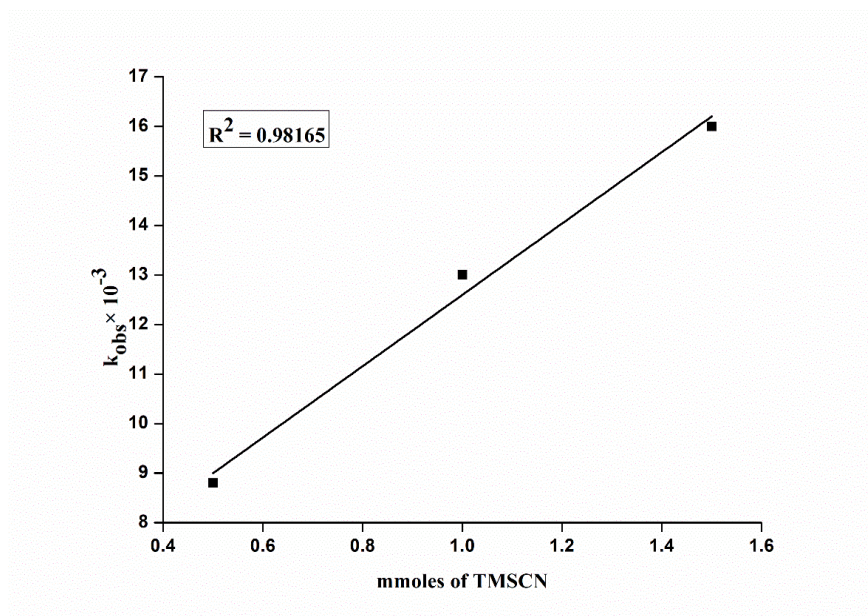
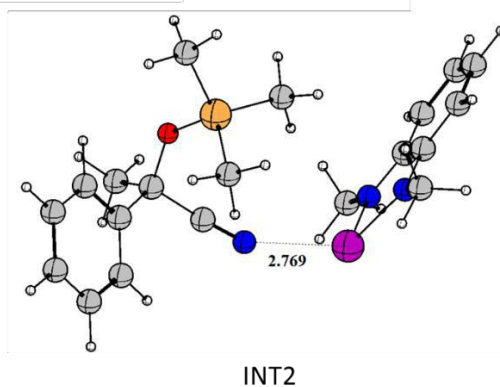
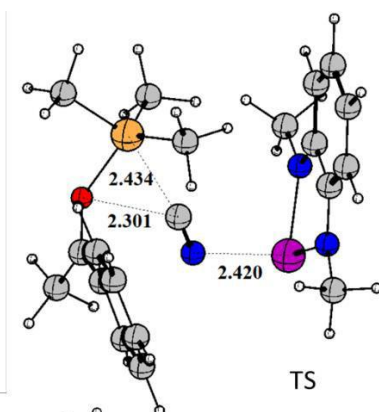
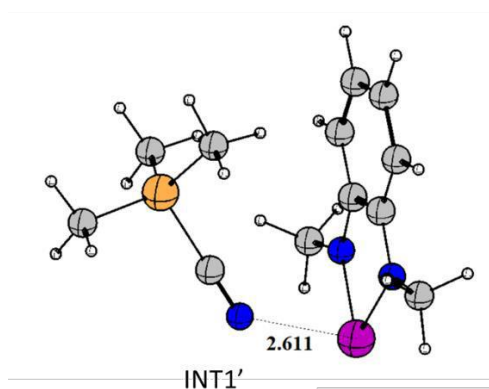
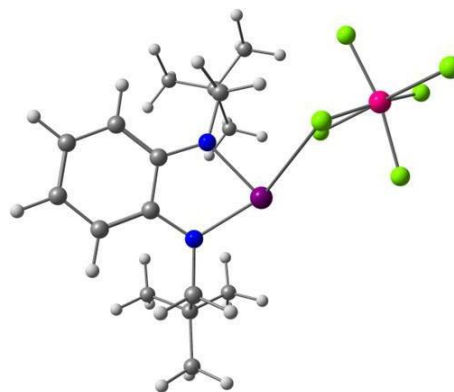
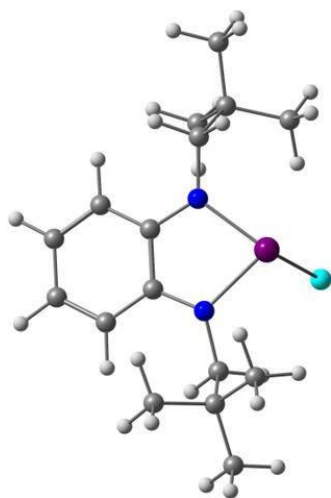


Figure 5.A.12. (a) Plot of Product (%) vs Time for the determination of the initial rate (k_{obs}) values. (b) Plot of k_{obs} vs mmol of TMSCN for the determination of order of the reaction.

Computational Details:

Geometry optimized structures of compounds 5.1, 5.2, reaction intermediates and the transition state



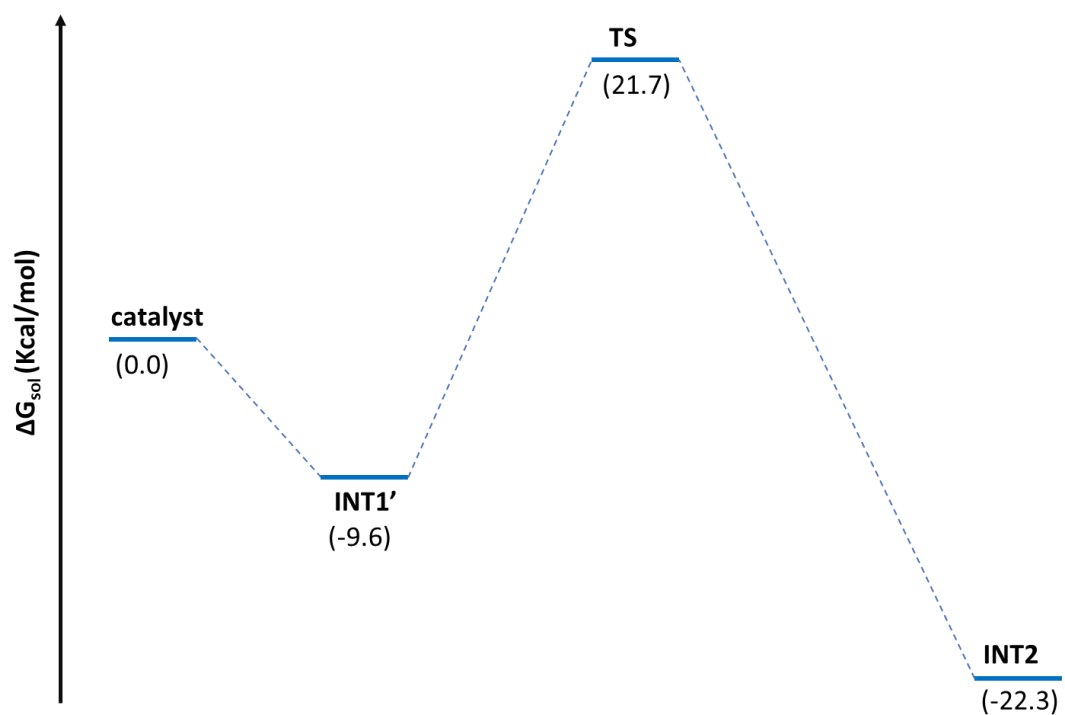


Figure 5.A.13. Relative solvent-corrected Gibbs free energy profiles for the cyanosilylation of acetophenone catalyzed by **5.2m**.

Rights and Permissions

1. Chapter 2:

Reprint of **Sen, N.**; Pal, S.; Khade, V., V.; Khan, S.* Cyclic Four-Membered Stanna Thio and Seleno Compounds from 2-Aminopyridinato Stannylenes, *Eur. J. Inorg. Chem.*, **2019**, 4450–4454.

Copyright 2019: Wiley VCH.

The dissertation author is the main author for this article.

2. Chapter 3:

Reprint of **Sen, N.**; Parvin, N.; Tothadi, S.; Khan, S.* Reactivity of $(\text{TMS})_2\text{N}(\eta^1\text{-Cp}^*)\text{Si}=\text{Si}(\eta^1\text{-Cp}^*)\text{N}(\text{TMS})_2$ toward the Halides of Groups 13–15, *Organometallics*, **2021**, 40, 1874–1883.

Copyright 2021: American Chemical Society

The dissertation author is the main author for this article.

3. Chapter 4:

Reprint of **Sen, N.**; Gothe, P.; Sarkar, P.; Das, S.; Tothadi, S.; Pati, S, K.*; Hotha, S.*; Khan, S.* Donor free stibenium cation as an efficient cyanosilylation catalyst, *Chem. Comm.* **2022**, 58, 10380-10383.

Copyright 2022: Royal Society of Chemistry

The dissertation author is the main author for this article.

JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS

Oct 05, 2023

This Agreement between Indian Institute of Science Education and Research, Pune -- Nilanjana Sen ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number 5642600151169

License date Oct 05, 2023

Licensed Content
Publisher John Wiley and Sons

Licensed Content
Publication European Journal of Inorganic Chemistry

Licensed Content Title Cyclic Four-Membered Stanna Thio and Seleno Compounds from 2-Aminopyridinato Stannylenes

Licensed Content Author Shabana Khan, Vikas Vilas Khade, Shiv Pal, et al

Licensed Content Date Oct 23, 2019

Licensed Content Volume 2019

Licensed Content Issue 41

Licensed Content Pages 5

Type of use Dissertation/Thesis

Requestor type Author of this Wiley article

Format Print and electronic

Portion	Full article
Will you be translating?	No
Title	Syntheses, reactivity and catalytic applications of low-valent compounds with p-block elements
Institution name	Indian Institute of Science Education and Research
Expected presentation date	Dec 2023
Requestor Location	Indian Institute of Science Education and Research, Pune Dr Homi Bhabha Road, Ward No.8 NCL Colony, Pashan, Pune Maharastra - 411008 Pune, Maharashtra 411008 India Attn: Indian Institute of Science Education and Research, Pune
Publisher Tax ID	EU826007151
Total	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

- ♦ The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.
- ♦ You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order**, is for a one-time

use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.

- ♦ With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner.**For STM Signatory Publishers clearing permission under the terms of the [STM Permissions Guidelines](#) only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts,** You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.
- ♦ The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto
- ♦ NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.
- ♦ WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.
- ♦ You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.
- ♦ IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY

SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.

- ♦ Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.
- ♦ The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.
- ♦ This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.
- ♦ Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.
- ♦ These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.
- ♦ In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.
- ♦ WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
- ♦ This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.
- ♦ This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party

hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The [Creative Commons Attribution License \(CC-BY\)](#) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The [Creative Commons Attribution Non-Commercial \(CC-BY-NC\)License](#) permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The [Creative Commons Attribution Non-Commercial-NoDerivs License](#) (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.

Further details can be found on Wiley Online Library
<http://olabout.wiley.com/WileyCDA/Section/id-410895.html>

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customercare@copyright.com.



RightsLink



Home



Help ▾



Live Chat



Sign in



Create Account

Reactivity of (TMS)₂N(η¹-Cp*)Si=Si(η¹-Cp*)N(TMS)₂ toward the Halides of Groups 13–15



Author: Nilanjana Sen, Nasrina Parvin, Srinu Tothadi, et al

Publication: Organometallics

Publisher: American Chemical Society

Date: Jun 1, 2021

Copyright © 2021, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

[BACK](#)[CLOSE WINDOW](#)

© 2023 Copyright - All Rights Reserved | [Copyright Clearance Center, Inc.](#) | [Privacy statement](#) | [Data Security and Privacy](#)
| [For California Residents](#) | [Terms and Conditions](#) Comments? We would like to hear from you. E-mail us at customercare@copyright.com

Issue 74, 2022

[Previous Article](#)

[Next Article](#)



From the journal:
Chemical Communications

Donor free stibenium cation as an efficient cyanosilylation catalyst†‡



Nilanjana Sen,^a Prachi Gothe,^a Pallavi Sarkar,^b Shubhajit Das,^b Srinu Tothadi,^{†b,c} Swapan K. Pati,^{†b} and Shabana Khan



Author affiliations

Abstract

The synthesis of novel stibenium cations and their catalytic application in cyanosilylation of carbonyl compounds have been described. Treatment of chlorostibine L_1SbCl [$L_1 = 1,2-C_6H_4\{N(CH_2^tBu)\}_2$] (**2**) with 1 equiv. of $AgOTf$ and $AgSbF_6$ resulted in the formation of donor free L_1SbOTf (**3**) and $[L_1Sb]^+ [SbF_6]^-$ (**4**), respectively. Among these three compounds, **4** exhibits excellent catalytic activity towards the cyanosilylation of aldehydes and ketones.

About

Cited by

Related

Donor free stibenium cation as an efficient cyanosilylation catalyst

N. Sen, P. Gothe, P. Sarkar, S. Das, S. Tothadi, S. K. Pati and S. Khan, *Chem. Commun.*, 2022, **58**, 10380 DOI: 10.1039/D2CC03158B

To request permission to reproduce material from this article, please go to the [Copyright Clearance Center request page](#).

If you are an author contributing to an RSC publication, you do not need to request permission provided correct acknowledgement is given.

If you are the author of this article, you do not need to request permission to reproduce figures and diagrams provided correct acknowledgement is given. If you want to reproduce the whole article in a third-party publication (excluding your thesis/dissertation for which permission is not required) please go to the [Copyright Clearance Center request page](#).

Read more about [how to correctly acknowledge RSC content](#).