Synthesis and Characterization of N,N-ligands and their Group 14 Compounds

M.Sc. Thesis

by

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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

May 2022

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A Thesis

Submitted in partial fulfilment of the

requirements for the award of the degree

of

Master of Science

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented here in the thesis entitled as **Synthesis and Characterization of N,N-ligands and their Group 14 Compounds** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted to the **DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from August 2021 to May 2022. Thesis submission under the supervision of Dr. Dipak K. Roy, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Banti

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

27.05.2022
Dr. Dipak K. Roy

Banti has successfully given her M.Sc. Oral Examination held on **May 25, 2022**

Signature of Supervisor of M.Sc. thesis	Convener, DPGC
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Signature of PSPC Member #1	Signature of PSPC Member #2
Date: 25-5-2022	Date: 25-05-2022

ACKNOWLEDGEMENT

I would like to thank my thesis supervisor **Dr. Dipak K. Roy** for valuable guidance, suggestions and supervision, and constant encouragement throughout my research work. I have learned different aspects of Inorganic Chemistry. Further, I would like to thank my PSPC members**, Dr. Selvakumar Sermadurai** and **Dr. Tridib K. Sarma** for their valuable suggestions and support. I am highly obliged in taking the opportunity to sincerely thank all the faculty members, seniors (research scholars), SIC staff of **IIT INDORE** for their help and co-operation during this dissertation work. I wish to express my special thanks to my lab mates (**Mr. Rahul K. Yadav** & **Ms. Darakshan Praveen**). Despite your own project, you never hesitated to answer my questions to help me out with the project's motto. All the things that you were willing to share with me were highly inspiring, not only for this specific project but also for the communication practice in general as well.

I want to extend my thanks to my batch mates who are always there and never let me down during these M.Sc. days. Last but not the least, I would like to pay sincere thanks to my loving parents for their continuous help and moral support.

Banti

M.Sc. 2nd year (2003131006)

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Dedicated to.....

MY BELOVED FAMILY

ABSTRACT

Germylenes or heavier group 14 analogues of carbenes have been found to be reactive species towards small molecule activation or several organic transformations. Based on previous literatures, where N-Heterocyclic Carbenes (NHCs) have shown tremendous applicability in the field of main group chemistry. We focused on using NHC in low valent germanium and silicon chemistry. In this work, several N,N-based ligands have been synthesized, isolated and characterized. Further, using $GeCl_2$·dioxane, NHC-$GeCl_2$, $SiCl_4$ as group 14 precursors, several N,N-based group 14 compounds have been synthesized and characterized. The details will be discussed in following chapters.

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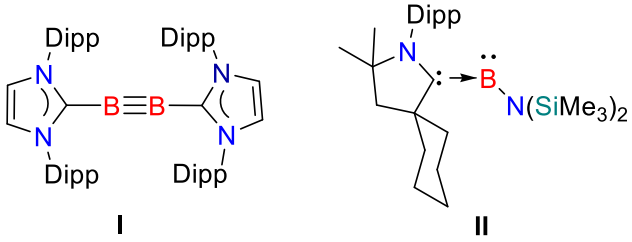
ABBREVIATIONS

AcOH	Acetic Acid
C_6D_6	Benzene-d_6
n-BuLi	Butyl Lithium
$CDCl_3$	Chloroform-d
DAD	Diazadiimine
DCM	Dichloromethane
Dipp	2,6-diisopropylphenyl
DI	Distilled Water
DIPC	Diisopropylcarbodiimide
DMF	DimethylFormamide
DMSO	DimethylSulphoxide
EA/EtOAc	Ethyl Acetate
MeOH	Methanol
LCMS	Liquid Chromatography Mass Spectrometry
$MgSO_4$	Magnesium Sulphate
NBS	N-Bromo Succinamide
NMR	Nuclear Magnetic Resonance
KOH	Potassium Hydroxide
KO^tBu	Potassium tert-Butoxide
PFA	Paraformaldehyde
$POCl_3$	Phosphorous oxychloride
PTSCl	P-Toluene Sulphonyl Chloride
Na_2CO_3	Sodium Carbonate
Na_2SO_4	Sodium Sulphate
NaOH	Sodium Hydroxide
THF	TetrahydroFuran
TMSCl	TrimethylSilyl Chloride
$BF_4.OEt_3$	Tetrafluroborate - Etherate

CHAPTER 1

INTRODUCTION

In recent years, the research on low valent s- and p-block compounds have shown that they possess similar properties as transition metals because they have vacant as well as filled orbital so they can show similar reactivity and bonding nature [1-4]. Hypo- valent main groups elements (E) have amphoteric nature and form highly reactive carbene- E bond [5]. NHCs are more effective for stabilisation of low-coordinated elements in different oxidation state for main group chemistry. For examples, as shown in fig. 1, B-B triple bond compound (**I**) [6], borylenes (**II**) [7], P-P bonded compounds (**III**) [8], cAAC stabilised beryllium complex (**IV**) [9] and digermanium complex (**V**) [10]. NHCs form adducts with non- metals and semi-metallic species. NHCs have many applications in catalytic transformation in chemical industries and their reactivity upon coordination to the main group elements and as an organo-catalyst [11] has opened a new area of research. NHCs also played a role in medicinal chemistry [12].



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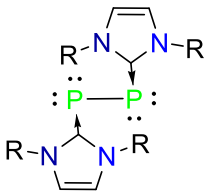

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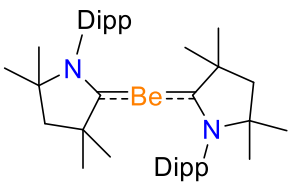

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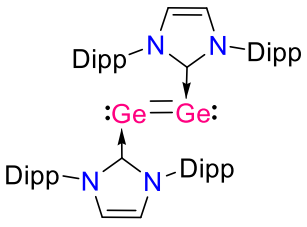


V

Figure 1: A few important low coordinated main group compounds stabilized by NHCs

1.1: N- Heterocyclic Carbenes:

In 1951, Mizuhara found that NHCs nucleophilic part in coenzyme vitamin B_1 play catalytic role in biochemical reaction. After that, Bertrand discovered the first stable carbene that is acyclic phosphino silyl in 1988 and is stabilized by favourable interaction with phosphorous and silicon substituents [13]. After three years, Arduengo discovered an isolable and bottleable imidazoline-2-ylidene. Arduengo in 1991 synthesize the first NHC 1,3-di(adamantyl)imidazol-2-ylidene **IAd** [14] (fig. 2)**.**

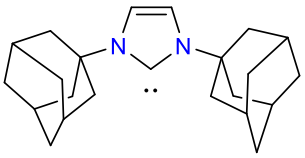


Figure 2: Structure of first NHC

This carbene was colorless crystal whose kinetic and thermodynamic stability easily characterized and was unstable in presence in oxygen and moisture. Carbenes are divalent neutral species having six electrons on carbon atom. Because of their incomplete octet they are not stable and are reactive in nature. N-heterocyclic carbenes (NHCs) are bivalent have six electrons in its valence shell at least one heteroatom must be present the ring skeleton, two electron donor like conventional phosphine donors. [15].

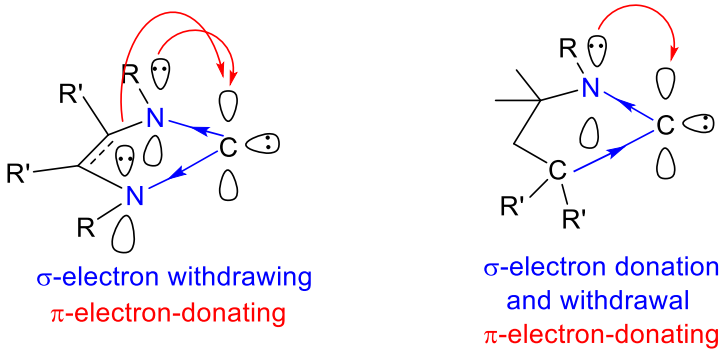
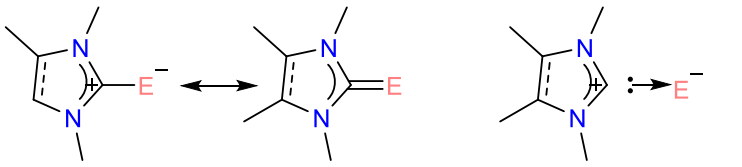


Figure 3: Electronic nature in NHCs and cAACs

The electronic and steric effect describe the stability of carbene centre C (fig.3). The two bulky adamentyl group adjacent to carbene atom kinetically stabilise by disfavouring dimerization to olefins. In NHCs, the backbone substituents affect the carbene electronics and have stabilisation from aromaticity. The cyclic structure favours the bent singlet ground state. In comparison to the normal carbenes, NHCs are having singlet ground state and the energy level of their HOMO has high energy than the classical carbenes. Lowest unoccupied molecular orbital (LUMO) present on that carbon which in flanged between two nitrogen atom and has sp^2 hybrid orbital [15].

The π-electron donating and σ-electron pulling potential of nitrogen atoms lowers the HOMO energy and increases the energy of LUMO. The energy band gap increases between HOMO and LUMO ground state and behaves as strong σ- donor. The lone pair of carbon lies in the plane of heterocyclic ring, so NHCs behaves as nucleophiles. In cAACs, instead of nitrogen atom, presence of carbon atom with a nearby quaternary carbon centre, decreases the HOMO -LUMO gap more, compared to the classical NHCs. That's why cAACs behaves as a tool of better σ-donor, due to low lying LUMO and a better π-acceptor properties. [16] As cAACs have more π-accepting tendency so they have more ability to form double bond $C_{carbene}$ -E. Depending on E, NHC adducts either single bond or double bond [17].



ylide **VI** ylene **VII** donor acceptor complex **VIII**

Figure 4: Ylide (VI) and ylene (VII) resonance structures of NHC adducts with E, and (VIII) shows dative bond of NHC and E

NHC are act as and metal atom act as acceptor so they can form donor acceptor complex which shows that NHC behave as 2 electron conventional donor (L-type) ligand [18-20] and a dative bond as an arrow [21] formed that is not accepted by IUPAC [22]. The behavior of C_{NHC} -E bond changes from singlet dative bond to double dative bond by π-back donation and σ donation. So, electron sharing

C=E bond formed between p- block element and triplet carbene where singlet carbene formed dative bond (fig.4). There are different class of carbene that differ in ring size, degree of heteroatom and substitution pattern (fig. 5).

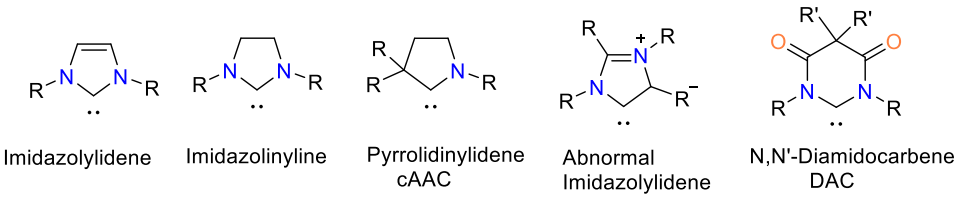


Figure 5: Different types of carbene

NHCs are more effective for stabilisation of low-coordinated compounds in different oxidation state of main group elements. They form adducts with non-metals and semi-metallic species. NHC-metal complexes have σ-donation from carbene to vacant p-orbital of p-block elements. This dative bond is highly stable, non-labile complex and have different properties and reactivities related to other adducts. Applications of NHCs in the main group chemistry are (i) stabilization of main group compounds in their low oxidation states, (ii) formation of multiple bonds in higher congeners of p-block elements. These two applications are tuned due to the special quantification of steric and electronic properties of the carbenes.

In multiple bond chemistry, only the pictures of few molecules came in mind like alkenes, alkynes, dinitrogen, carbon dioxide, carbon monoxide etc. In 2009, Driess applied the NHC stabilization technique to prepare a stable silylene (R_2Si**:**) which on oxidation gave a unique example of a Si=O double bonded compound [25]. **Roesky** synthesized higher analogue of N-heterocylic carbene like NHSi and NHGe and studied the addition reaction of these complexes [26]. Recently Braunschweig and co-workers synthesized and isolate boron-boron triple bond in ambient conditions with the help of NHC [27]. Without the help of NHC, isolation of such novel types of low valent main group compounds would not have been possible. NHCs are the remote-control multi-gamer and it play like main player in different area of chemistry like industrial use, medicinal use, homogeneous-heterogeneous catalysis, and in material science too.

The sustainability in lower oxidation number or low valent main group compounds depends on the electronic or steric crowd protection at the metal

centre. Strong electron donating ligands provides sufficient electron density to the reactive main group element to moderate its reactivity. In multiple bonds chemistry of higher congeners of carbon needs some bulky substituents, because they provide steric bulk around the metal centre and this property prevents the easily attack of any type of nucleophile or electrophiles. The chemistry of alkenes and alkynes are totally different in contrast of metallenes and metallynes because these bonds are easily affected by the any types of influence (electrophiles or nucleophiles). Ligands such as amidinate and guanidinates etc they have bulky substituents, are the boon for the main group low valent complexes. They play an important role in the isolation of low oxidation state and multiple bonded compounds of main group elements. Literature precedence shows that the N,N-, and N,O-donor have the capability to stabilise low valent main group complexes.

N,N-donor ligands:

N,N-coordinating ligand viz: guadinate, boraguadinate phospha-guadinate and *β*-diketiminate ligands can easily be tuned by changing the different substituents on both nitrogen centre like alkyl or aryl substituents resulting in a change in their steric and electronic properties. These are the well-known ligand in stabilizing the low oxidation states of metals either it belongs to d-block or main group elements. In the previous decade, there have been a resurgence in the field of main group chemistry through the isolation of different types of low valent main group complexes with N-N, chelating ligands.

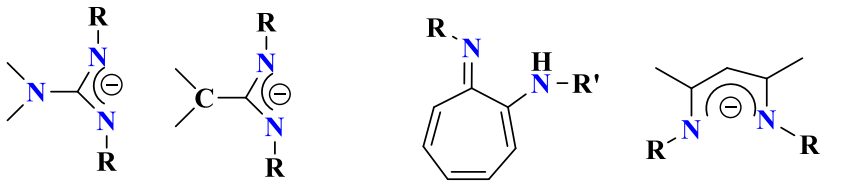


Figure 6: N,N -donor ligands

Amidinate, guanidinate and aminotroponiminate and β-diketiminate (fig. 6) ligands are well known N,N-type donor ligand which stabilize the low valent main group complexes. Amidinate and guadinate complexes form four membered cyclic rings while aminotroponiminate ligand form five- membered

cyclic ring and *β*-diketiminate complexes form six membered rings. Aminotroponiminate features a delocalisation of 10π electron while amidinate and β-diketiminate have delocalisation of 4π and 6π electron [28,29,30] (fig 7).

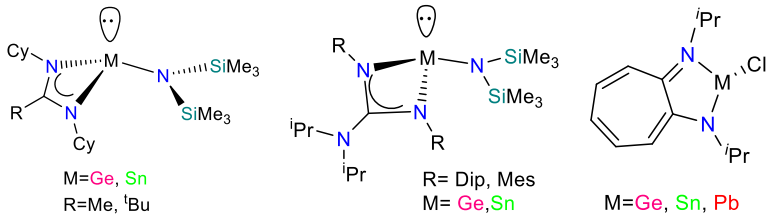


Figure 7: N,N-donor stabilised metal complexes

N,O-donor ligands:

After successful synthesis of N,N-donor based low valent complexes of p-block elements many research group moved to isolate new type of complexes with N,O-donor ligand. N,O-donor ligands have wide range of application in the area of catalysis and medicinal chemistry. A number of transition and rare earth metal complexes were synthesized. By applying similar methodology main group complexes are isolated. N,O-donor ligands have their own unique identity[31]. At o-iminoquinone, the bulkier substituents are able to stabilize di- as well as tetravalent Ge complexes (fig. 8).

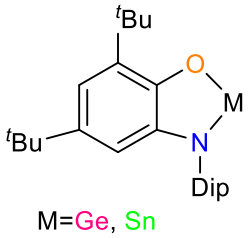


Figure 8: N,O-donor stabilised metal complexes

1.2: Germanium complexes:

Germylene, a germanium analogue of carbene primarily have the singlet ground state due to larger HOMO-LUMO gap than that of carbene. Therefore, lone pair of electrons in germylene present in sp^2 orbital which has much greater s-character and a vacant p-orbital (fig. 9). Germylenes are synthesized by

photolysis reaction (scheme 1) or by treating lithiated ligand with $GeCl_2$ (scheme 2).

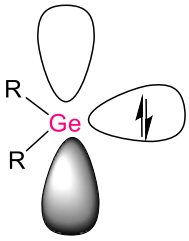
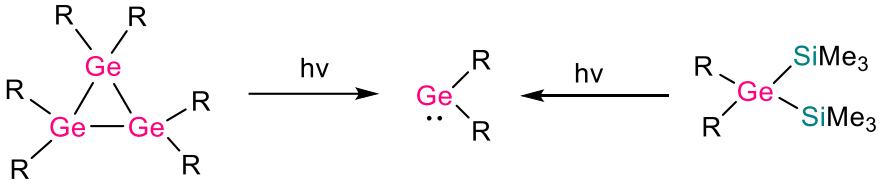
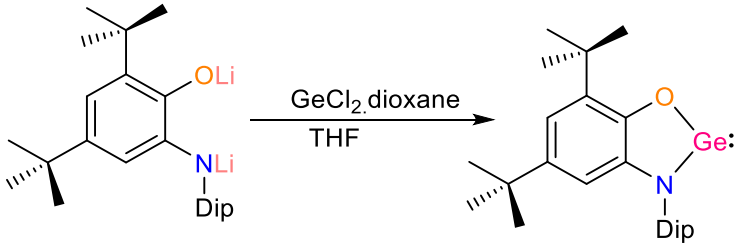


Figure 9: General representation of germylene



Scheme 1: Synthesis of germylene by photolysis



Scheme 2: Synthesis of germylene by $GeCl_2$.dioxane

The reactivity of germylenes can be reduced by making the adduct with Lewis' base, which increase the electron density on Germanium (II). By the donation of electron with the help of Lewis' base it reduces the electrophilicity on Ge (II) make donor acceptor type complex and in this way NHC ligands are the tools which helps in stabilization and isolation of Germanium (II) complexes [32].

The first NHC-Ge adduct was formed by Arduengo and coworkers in 1993 and that is [{HCN(C_6H_2-2,4,6-Me_3)}$_2$C: GeI_2] (fig. 10a) [33]. In 2009, Rivard et al. and Jones et al. prepared [{HCN(C_6H_3-2,6-^{i}Pr)}$_2$C: $GeCl_2$] (fig. 10b) by direct reaction of carbene and $GeCl_2$.dioxane [34,35]. Then Rivard treated this $GeCl_2$ adduct with $LiBH_4$ and [(IDipp)$GeH_2(BH_3)$] (fig.10c) was obtained. The

presence of boron and hydrogen in this complex is confirmed by ^{11}B NMR or ^{1}H NMR respectively and its solid structure shows that it is tetracoordinated [36].

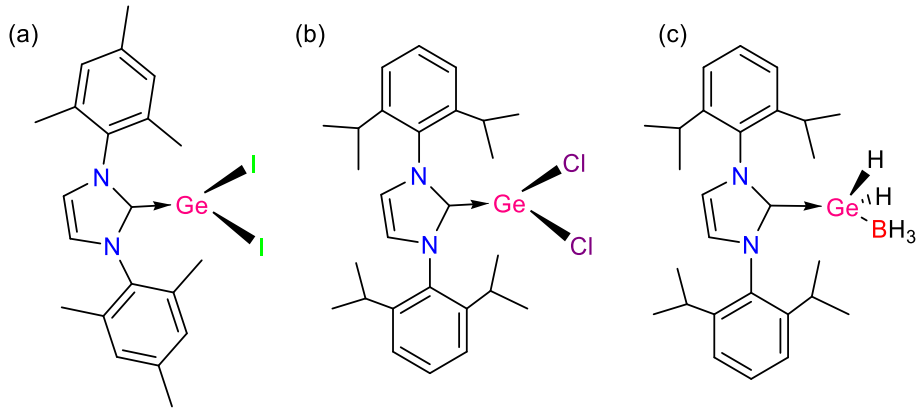


Figure 10: NHC Germanium (II) complexes

In 2012, Röschenthaler and coworkers synthesized NHC coordinated tetrahalide complexes of GeX_4 (X = F, Cl) (fig. 11) in its (+4) oxidation state. The geometry of the complexes is typical TBP which are regular in penta coordinated group 14 complexes [37] Germylenes enabled with a NHCs shows better coordination towards the Lewis' acids and electron deficient species [38].

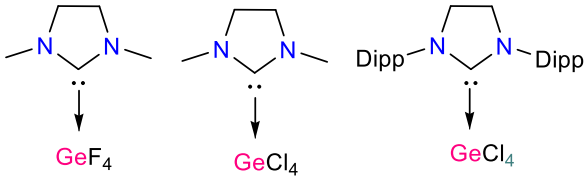
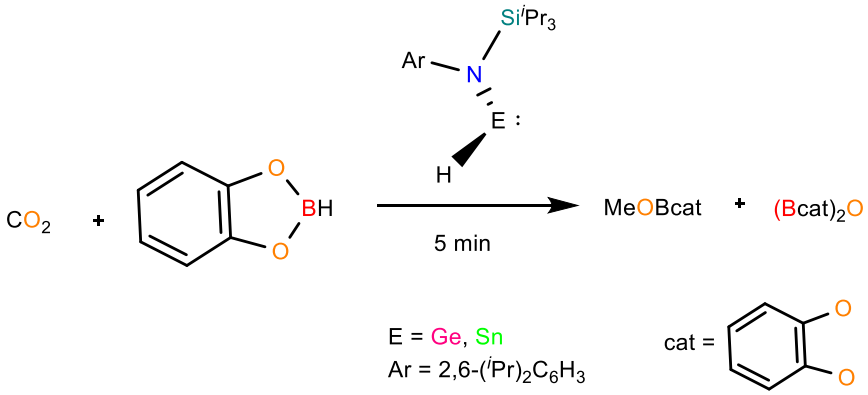


Figure 11: NHC-stabilized Germanium (IV) complexes

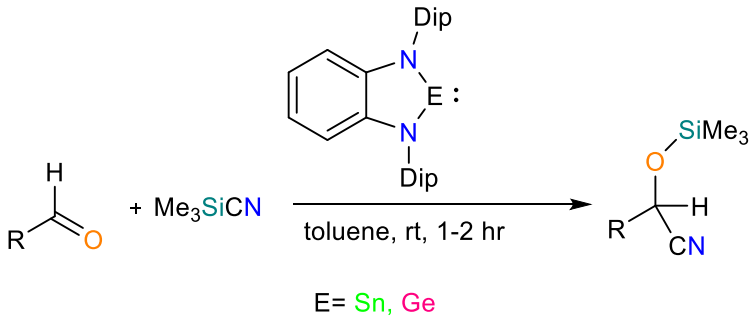
Global warming is a challenge for every living being on the earth and the rise in CO_2 level is contributing to that. Several research groups are working towards the conversion of CO_2 into various valuables products. Traditionally the transition metal-based catalysts are used for this aim. In recent years a few main group metal hydrides showed their reactivity in the activation of CO and CO_2. Catalytic conversion of CO_2 by the main group catalyst is in their infancy compared to the transition metal catalysis. Main group catalysts are abundant and cheaper than transition metal-based catalyst and reports show that main group catalysts reduce CO_2 at lower temperature while TM based catalyst needs high temperature and pressure. Seeing this property, main group compounds take more attention from researchers. Jones et al. synthesized amido ligand-

based substrate of Ge (II) and Sn (II) hydrides for the activation of carbon dioxide [39] (scheme 3).



Scheme 3: Hydroboration of CO_2 using catalyst

Divalent Ge (II) compounds are neutral and iso-valent to the singlet carbenes. Singlet carbenes, have one vacant p-orbital and one lone pair. Similarly, germylene also possess one vacant p-orbital and one lone pair. Due to presence of one filled and one empty orbital at germanium centre, it can donate electron to the Lewis' acid and accept electron from the Lewis' base. Accepting and donating tendency shown by a single site is known as amphoteric nature,



Scheme 4: Cyanosilylation of aldehydes

1.3 Hypervalent Silicon Complexes:

The hypervalent molecules were first coined by Jeremy I. Musher in 1969 [40]in which molecules having central atom from the group 13th to 18th in any valence other than the lowest (3, 2, 1, 0) respectively, based on the Lewis' octet rule. Divalent and tetravalent compounds are more common, but silicon shows different coordination number like penta- and hexa-coordination. In the field

organic synthesis organosilicon complex have tremendous growth by means of the electropositive character of silicon. In organic chemistry intermediates are the game changer like carbocations, carbanions, free radicals, and carbenes. By the similar way silicon forms silicocations, silylanion, silyl radical and silylenes respectively [41]. Here we are going to introduces about the hypervalent silicon compound, their use and reactivity.

In 19th century, the first hypervalent silicon compounds [$(SiF_6)_2$] and [trans-$SiF_4(NH_3)_2$] (fig. 12) were discovered by Lussac [41, 42]. In recent few decades hyper coordinate silicon complex attracted the attention of many researchers in the field of catalysis of various organic reaction and nucleophilic activations. Hyper coordinate species can be achieved mainly by the three types viz, (i) by the substitutions of organosilane, (ii) intra or inter-molecular donation of neutral donor to silicon and at the last (iii) coordination of anions to silicon compounds.

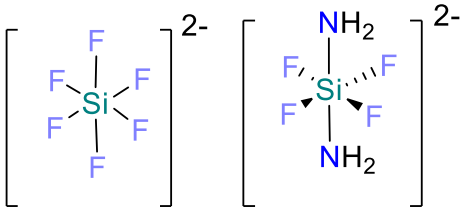


Figure 12: Hexa coordinate silicon complexes

Mainly the hypervalent complex of silicon formed by the silicon halides like fluorine and chlorine due to sufficient electrophilic nature of the silicon atom. Mostly they can be achieved by nitrogen donor, oxygen donor or mixed type donor ligand N-O, N-S donor ligands [43]. Stability of such compounds increases as the number of chelating ligands present in the hypervalent complexes. Pyridine adduct hypervalent complexes of H_2SiCl_2 and $SiCl_4$ are stable in solid state however, it decomposes on treating with polar solvent or heating a little bit while as bipyridine substituted hypervalent complexes are thermodynamically more stable (fig. 13).

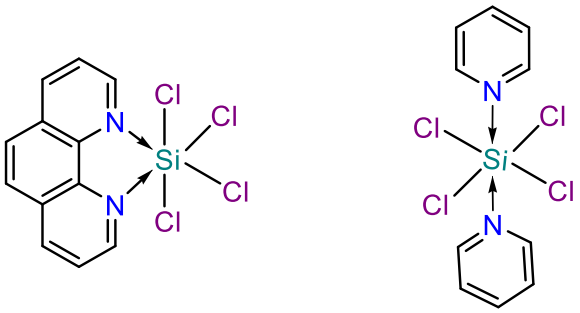


Figure 13: N,N based hexacoordinated silicon complexes

Since the last decades tremendous growth has been seen in the field of hyper coordinate chemistry this is due the special kind of ligand like imine-based N-N donor, amidinato, phthalocyanine, porphyrin and amine ligand have tendency to stabilized the hyper coordinate compounds. Here we are going to introduces amidinato ligands-based silicon complexes (fig. 14).

Amidinato ligands:

Amidinato ligands are bidentate in nature, and they can bind with silicon in hyper coordinate compound in bidentate manners. Amidinato ligands are easily prepared by simply addition of nucleophile on different types of carbodiimides. Here the special features of these ligands are their electronic and stearic properties which can be modified according to the requirement. They play a key role in the stabilization and isolation of hypervalent silicon compounds [44-47].

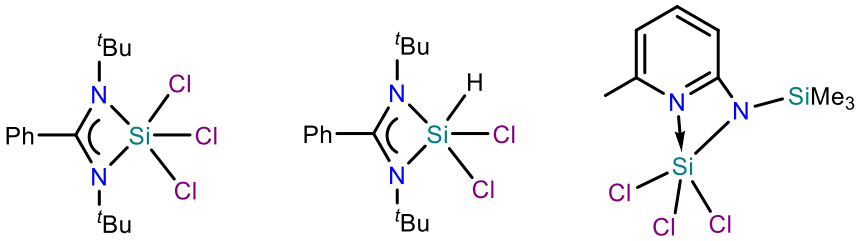


Figure 14: Hypervalent amidinate silicon complexes

Chapter 2

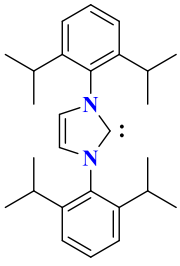
Experimental Section

2.1 Material and Instrumentation:

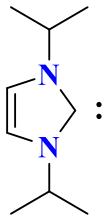
Reagent and chemicals were used as received if not mentioned somewhere. Solvents were purified as standard method and stored under the inert atmosphere on 4Å molecular sieves. Several reactions were performed under the inert environment wherever mentioned and ligands or precursors were prepared in open air and checked by TLC. Mass spectra were obtained through Bruker Daltonik High Performance LCMS spectrometer. All the ^{1}H & ^{13}C NMR spectra were obtained on Bruker 500 spectrometer in $CDCl_3$ or in Benzene-d_6 operating at 500 MHz for ^{1}H NMR. Data for NMR Chemical shifts are mentioned in delta (δ) units, showed in ppm downfield from tetramethyl silane (TMS). $CDCl_3$ and C_6D_6 is used as an internal standard with a residual peak at 7.26 and 7.16 ppm respectively. The ^{1}H NMR multiplet signals have been mentioned as singlet(s), double(d), triplet(t) & multiplet (m). Compounds were named by using Chem draw Ultra 16.0 and NMR data processed by Mestre Nova.

2.2 Synthesis of Carbenes:

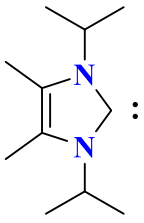
In this chapter we synthesize Dipp free carbene (**1**), IPr carbene (**2**) and IPr^{Me} carbene (**3**).



1



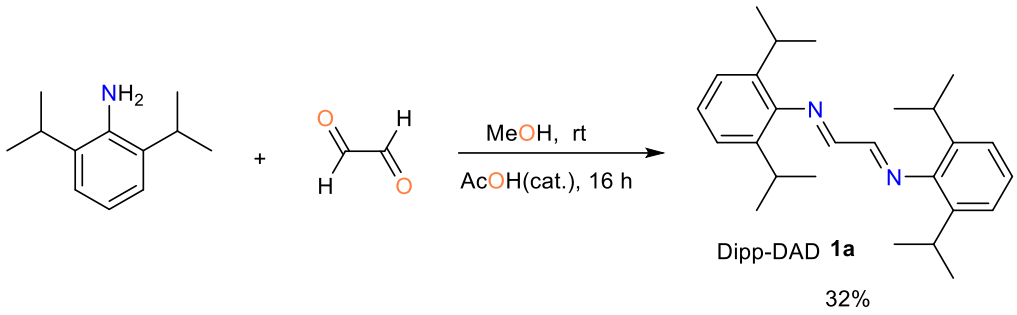
2



3

2.2.1 Synthesis of Dipp free carbene (1)

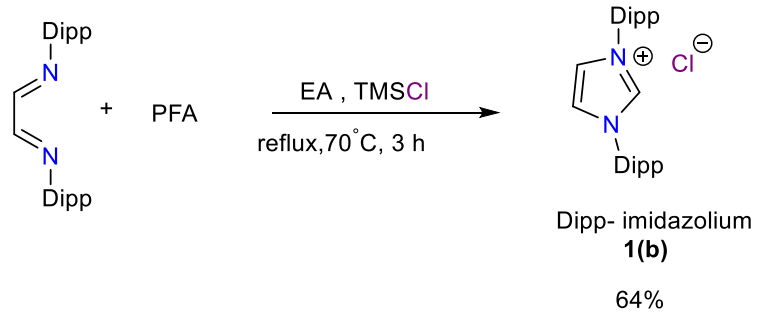
2.2.1a Synthesis of N, N-bis(2,6-diisopropylphenyl) ethane-1,2-diimine 1(a):



Scheme 5: Synthesis of Dipp-DAD (1a)

To synthesize **1(a)** the solution of glyoxal (1.53 g, 26.5 mmol) in MeOH was added to 2,6-diisopropylaniline (9.4 g, 53.1 mmol), a mixture of AcOH (1 mL) and MeOH was poured in reaction pot and then heat it up to 50 ˚C, a stirring continuously for 15 min and product crystallised. Then the mixture further stirred for 16 h at room temp., filtered the suspension and washed with cold MeOH and a yellow-coloured product was obtained in 32% yield.

2.2.1b. Synthesis of 1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-3-ium chloride 1(b):

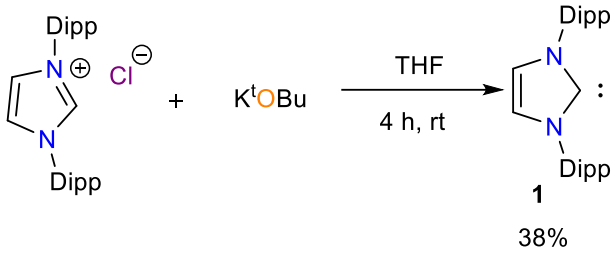


Scheme 6: Synthesis of Dipp Imidazolium Chloride 1(b)

To synthesize **1(b)** Dipp-DAD (5 g, 13.3 mmol) and paraformaldehyde (0.410 g, 13.7 mmol) in ethyl acetate (10 mL) was refluxed at 70 ˚C for 3 h and then the mixture of TMSCl (1.485 g, 13.7 mmol) in EA was added dropwise and further stirred the mixture for 3 h. After cooling down it to rt the reaction mixture was filtered and washed with EA and diethyl ether to get light pink colour solid

in 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.07 (s, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 4H), 2.38 (p, J = 6.8 Hz, 4H), 1.22 (d, J = 6.7 Hz, 12H), 1.18 (d, J = 6.7 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.16, 138.68, 132.33, 130.01, 126.94, 124.88, 29.84, 29.29, 24.90, 23.90.

2.2.1c. Synthesis of Dipp- Carbene (1)

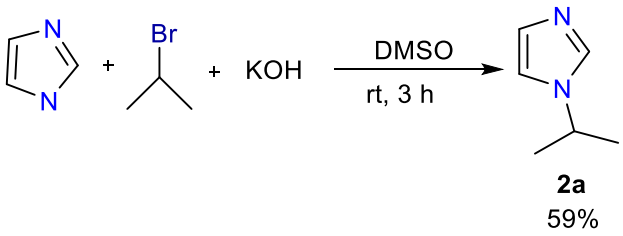


Scheme 7: Synthesis of free carbene (1)

To synthesize (**1**) Dipp-imidazolium (**1(b)**) (4 g, 9.4 mmol) and potassium tert-butoxide (1.267 g, 11.3 mmol) were added in Schlenk tube in inert atmosphere. Dry THF (10 mL) was added and the mixture becomes turbid and stirred it for 5 h at rt. Excess solvent was dried under vacuum and dry toluene was added and filtered the reaction mixture through bed of celite. Excess solvent was dried in vacuum and triturate the product with hexane and then remove the solvent under vacuum and we get off white coloured solid in 38% yield. ^{1}H NMR (500 MHz, C_6D_6) δ 7.26 (dd, J = 8.2, 7.2 Hz, 2H), 7.15 – 7.11 (m, 4H), 6.58 (s, 2H), 2.93 (m, J = 6.9 Hz, 4H), 1.25 (d, J = 6.9 Hz, 12H), 1.15 (d, J = 7.0 Hz, 12H).

2.2.2 Synthesis of IPr carbene (2):

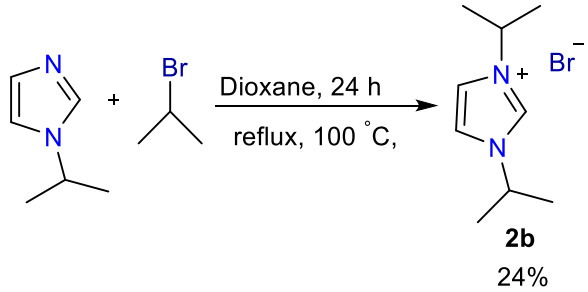
2.2.2a Synthesis of 1-isopropyl-1H-imidazole 2a:



Scheme 8: Synthesis of isopropyl imidazole 2a

To synthesize **2a**, potassium hydroxide (1.236 g, 22.03 mmol), added to a solution of imidazole (1 g, 14.7 mmol) in DMSO (5 mL) & this mixture stirred in open air till 30 minutes. After isopropyl bromide (2.1 g, 16.3 mmol) was mixed in the reaction vessels & further stirred for 3 h. After 3 h, the mixture quenching was done by chilled water and workup with chloroform and organic layer was washed with water and dried it with anhydrous $MgSO_4$. All volatiles dried under vacuum pressure and to get the colourless liquid in 59% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.76 (d, *J* = 11.3 Hz, 2H), 4.13 (m, *J* = 6.7 Hz, 1H), 1.25 (d, *J* = 6.7 Hz, 6H). [49]

2.2.2b. Synthesis of 1,3-diisopropyl-imidazol-3-ium bromide 2b:

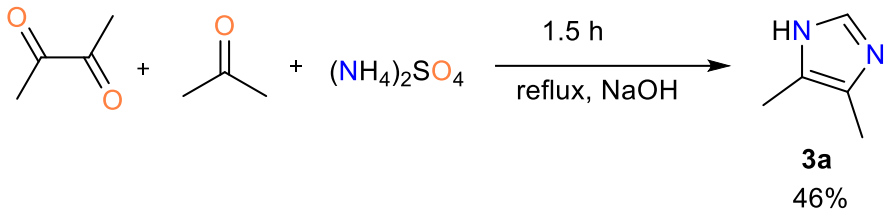


Scheme 9: Synthesis of diisopropyl-imidazol-3-ium bromide 2b

To synthesize **2b**, **2a** (1.5 g, 13.6 mmol) taken in 2N flasks, dioxane (5 mL) used as solvent then isopropyl bromide (1.66 g, 13.6 mmol) poured in the reaction vessels and kept the mixture for stirring with reflux condition at hundred degree celcious for 24 h. Reaction cooled down the slowly up ambient temperature and then dried it under reduced pressure and get the solid in 24% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 10.92 (s, 1H), 7.34 (d, J=0.03H, 2H), 4.9 (m, J=0.1, 2H), 1.6 (d, J=0.01, 12H).

2.2.3: Synthesis of IPr^{Me} carbene (3):

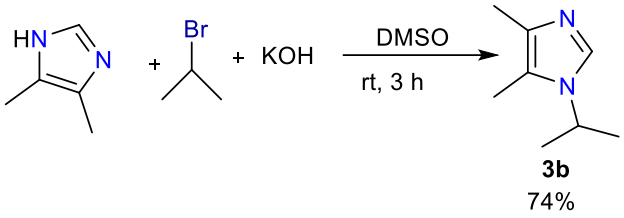
2.2.3a. Synthesis of 4,5-dimethyl-1H-imidazole 3a:



Scheme 10: Synthesis of 4,5 dimethyl imidazole 3a

To synthesize **3a,** ammonium sulphate (7.5 g, 56.9 mmol) was added in water (4 M) & required amount of aldehyde (0.9 g, 30.1 mmol) was added. Diketone (2.5 g, 28.5 mmol) poured to the pot and & kept the for stirring along with refluxed for one and half hour. Then reaction cooled and made basic by adding NaOH (2.3 g, 40 mmol), extracted with EA and extra water was removed by anhydrous MgSO4, dried the liquid and got the product in 46% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.41 (s, 1H), 2.15 (s, 6H).

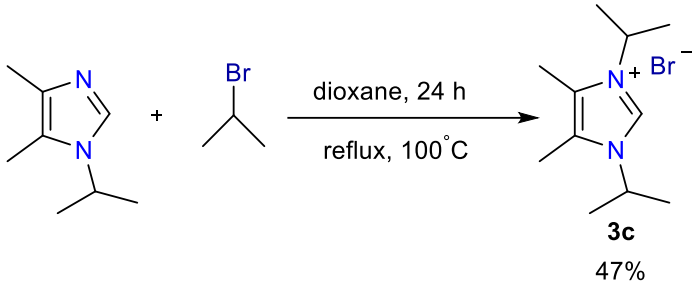
2.2.3b. Synthesis of 1-isopropyl-4,5-dimethyl-1H imidazole 3b:



Scheme 11: Synthesis of isopropyl-4,5-dimethyl-imidazole 3b

To synthesize **3b**, potassium hydroxide (1.05 g, 18.7 mmol) mixed to a solution of 4,5-dimethyl imidazole (1.2 g, 12.5 mmol) in DMSO & reaction mixture was stirred with the help of magnet bar till 30 minutes. After that isopropyl bromide (1.7 g, 13.83 mmol) poured in to the reaction vessels and further kept it for three hours. After 3 h, the mixture was diluted with chilled water & workup with chloroform and aqueous layer washed with chloroform and dried by pouring magnesium sulphate. Excess solvent was dried under vacuum and got colourless liquid of desired compound in 74% yield.

2.2.3c Synthesis of 1,3-diisopropyl-4,5-dimethyl-1H-imidazol-3-ium bromide 3c:



3c

47%

Scheme 12: Synthesis of diisopropyl -4,5 dimethyl imidazolium bromide 3c

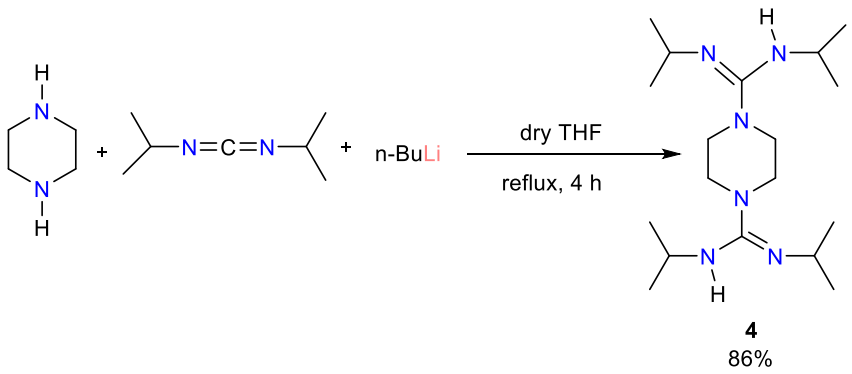
To synthesize **3c**, **3b** (2 g, 14.48 mmol) poured in dioxane (6 mL) and then isopropyl bromide (1.9 g, 14.5 mmol) was dissolved and reaction vessel kept for stirring with reflux condition at 100 ˚C for 24 h. Slowly decrease the reaction vessel temperature up to ambient temperature then dried under high vacuum to get brownish solid in 47% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 4.56 (m, J=0.02, 2H), 2.28 (s, 6H), 1.71 (d, J=0.02, 12H).

2.3 Synthesis of N, N based ligand:

In this chapter we synthesize guanidine, amidinate and thiophene based ligands.

2.3.1 Synthesis of guanidine-based ligands:

2.3.1a Synthesis of tetraisopropylpiperazine-1,4-bis(carboximidamide) 4:



4

86%

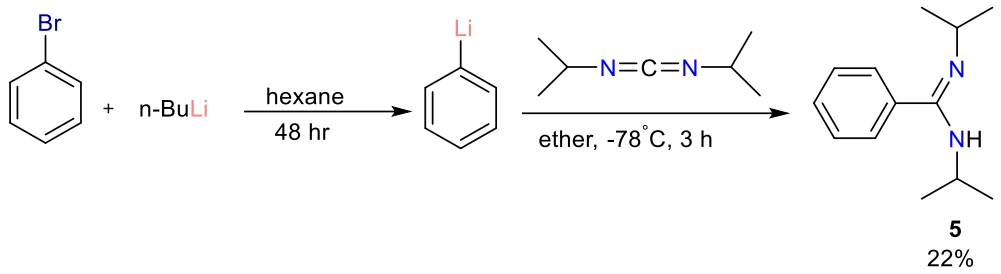
Scheme 13: Synthesis of diisopropyl guanidine ligand 4

To synthesize **4**, THF (5 mL) was added to piperazine (1 g, 11.6 mmol) under inert atmosphere and then n-BuLi (14.5 mL, 23.3 mmol) poured with the help

of sterile syringe and stirred it for 1 h and after that DIPC (2.93 g, 23.2 mmol) was poured and again stirred for 1 h at ambient temperature. Reflux the mixture for 2 h, after that reaction allow to cool to rt, poured water in reaction mixture. All volatiles were removed under vacuum and add more water & DCM and wash the water layer with DCM and extract the product in DCM. Dry it with $MgSO_4$ and filter it to get off white colour product in 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.46 (m, J = 6.7 Hz, 2H), 3.29 (m, J = 6.4 Hz, 2H), 3.06 (s, 8H), 1.08 (d, J = 6.4 Hz, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.79, 48.46, 47.22, 46.28, 25.04, 23.83, 1.16.

2.3.2: Synthesis of amidinate based ligands:

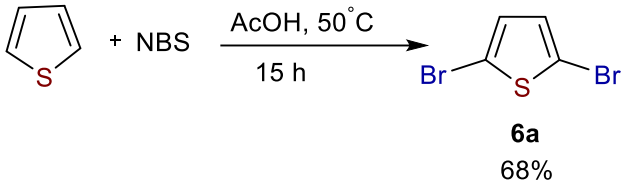
2.3.2.1: Synthesis of N,N'-diisopropylbenzimidamide 5:



Scheme 14: Synthesis of diisopropylbenzimidamide 5

First, we synthesize phenyl lithium in situ. For this, bromobenzene (1.5 g, 9.5 mmol) was dissolved in dry hexane (15 mL) and n-BuLi (5.9 mL, 9.6 mmol) was added to reaction mixture at -80 ˚C and allow the reaction mixture to warm slowly at rt and kept the reaction mixture for stirring for 48 h. After that excess solvent was dried in vacuum to get off white solid as lithiated product. Then DIPC (1.2 g, 9.3 mmol) was added to the solution of phenyl lithium in diethyl ether at negative seventy-eight degree Celsius and allow to slowly increase temperature of the reaction setup warm slowly up to rt and stirred it 3 h. Then DI water was added, DCM was poured in the aqueous layer with DCM and extract the product in DCM. Dry it with $MgSO_4$ and filter it and dried the filtrate to get liquid product in 22% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 6.8 Hz, 3H), 7.25 – 7.20 (m, 2H), 3.55 (sept, J = 6.3 Hz, 2H), 1.08 (d, J = 6.5 Hz, 12H).

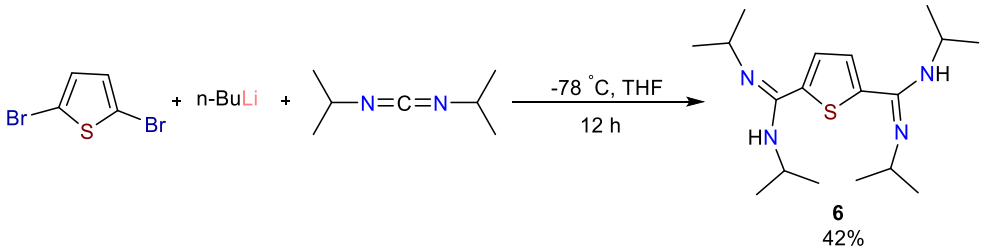
2.3.2.2(a). Synthesis of 2,5-dibromothiophene:



Scheme 15: Synthesis of dibromothiophene

Acetic acid (1 mL) poured to mixture of Thiophene (3.2 g, 37.9 mmol) and NBS (14.2 g,79.6 mmol) in inert atmosphere and stirred the reaction mixture for 15 h with heating at 50 ˚C. After that cool down the reaction mixture and add 10 M NaOH (10 mL) solution in it and the product was extracted in hexane and (aq layer washed with hexane 3 times) and dried it by magnesium sulphate and reduced all volatiles under reduced pressure and get reddish liquid in 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.49, 111.67.

2.3.2.2. Synthesis of tetraisopropylthiophene-2,5-bis(carboximidamide) 6:

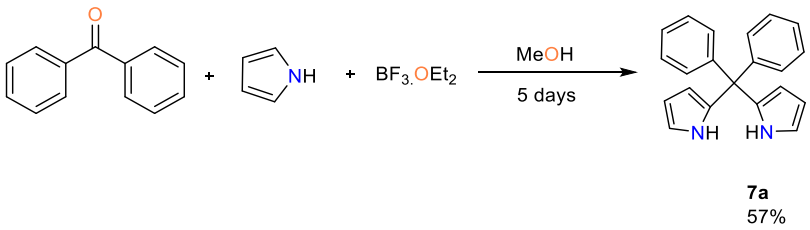


Scheme 16: Synthesis of tetraisopropylthiophene-2,5-bis(carboximidamide) 6

Dry THF was added to 2,5-dibromothiophene (1 g, 4.2 mmol) and n-BuLi (5.7 mL, 9.1 mmol) was added to the mixture at -78 ˚C & kept mixture stirring for 2 h. After 2 h DIPC (1.2 g, 8.3 mmol) dissolved in to reaction setup and allow to stirred it up to 15 h at reflux. DI water was poured and add DCM and wash the water layer with DCM and extract the product in DCM. Dry it with $MgSO_4$ and filter it and dried the filtrate to get liquid product in 42% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (s, 2H), 3.93 – 3.72 (m, J = 6.7 Hz, 4H), 1.13 (d, J = 6.5 Hz, 24H).

2.3.3 Synthesis of Schiffs base ligand 7:

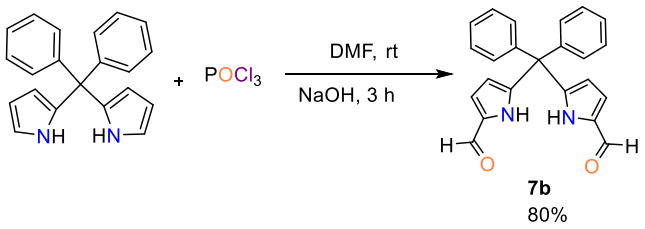
2.3.3.1a Synthesis of diphenyldi(1H-pyrrol-2-yl) methane 7a:



Scheme 17: Synthesis of diphenyldipyrrolemethane 7a

Pyrrole (9.2 g, 137.2 mmol) was dissolved to the solution of benzophenone (10 g, 54.9 mmol) in MeOH (20 mL) at room temperature with continuous stirring. After that Boron Trifluoride etherate (10.3 g, 76.3 mmol) was dissolved and stirred the reaction mixture for 5 days and then filter the mixture and dried the residue with cold MeOH and dried it in vacuum to get creamish solid in 57% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.27 (s, 1H), 7.25 – 7.20 (m, 5H), 7.13 – 7.06 (m, 5H), 6.72 (q, J = 2.6 Hz, 2H), 6.16 (q, J = 2.9 Hz, 2H), 5.95 (d, J = 1.5 Hz, 2H). ^{13}C NMR 125 MHz, $CDCl_3$) δ 146.11, 135.48, 129.39, 128.03, 126.93, 117.52, 109.72, 108.13, 56.01.

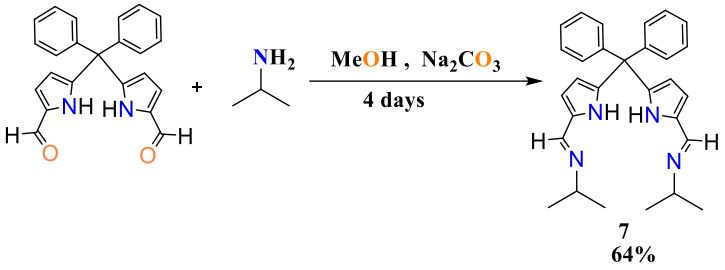
2.3.3.1b: Synthesis of 5,5'-(diphenylmethylene)bis(1H-pyrrole-2-carbaldehyde):



Scheme 18: Synthesis of diphenylmethylene dipyrrolecarbaldehyde

$POCl_3$ (3.1 g, 20.1 mmol) poured to diphenyldipyrrole (3 g, 10.1 mmol) and DMF solution and stirred the mixture for 1 h then DI water was added and then 25 wt% solution of NaOH (15 mL) reaction was added at 0 ˚C and stirred the reaction mixture for 30 min and precipitate formed in the mixture and filter it and made slurry in ethanol then recrystallise the mixture with hot ethanol to get product in 80% yield.

2.3.3.1c: Synthesis of (diphenylmethylene)bis(1H-pyrrole-5,2-diyl))bis(N-isopropylmethanimine) 7:

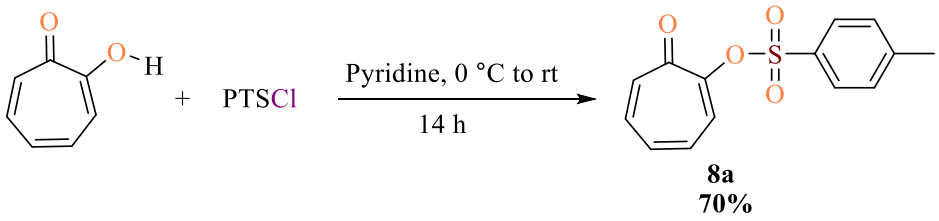


Scheme 19: Synthesis of diphenylmethylene dipyrrolemethaneimine 7

Dry MeOH (15 mL) was added in **7b** (2.8 g, 7.9 mmol) and then Na_2CO_3 (15 g) was added to the reaction mixture and stirred it for 30 min. Then iso-propylamine (excess, 15 mL) was added in excess amount at 0 ˚C and the mixture kept the mixture for stirring for 4 days. After that decand the liquid and dried it to get solid product to get product in 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.16 – 6.86 (m, 5H), 6.37 (d, J = 3.6 Hz, 2H), 5.84 (d, J = 3.6 Hz, 2H), 3.41 (h, J = 6.3 Hz, 2H), 1.18 (d, J = 6.3 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.37, 144.30, 140.63, 130.03, 129.58, 127.69, 127.03, 114.31, 112.14, 60.28, 56.41, 49.88, 24.12.

2.3.4: Aminotroponiminate based ligands:

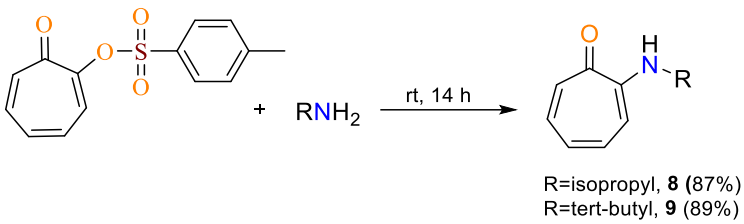
2.3.4.1: Synthesis of 2-(p-tolyloxy)cyclohepta-2,4,6-trien-1-one 8a:



Scheme 20: Synthesis of p-tolyloxycycloheptatrienone 8a

Pyridine (6 mL) was added to PTSCl (1.6 g, 8.2 mmol) at 0 ˚C and stirred the reaction mixture for 15 min. In the mixture tropolone (1 g, 8.2 mmol) was added and kept it stirring for overnight. Then DI water was added and cloudy precipitate was formed. Filter the reaction mixture and wash it with cold water or dried it in vacuum to get product off white solid in 70% yield.

2.3.4.2a Synthesis of 2-(amino)cyclohepta-2,4,6-trien-1-one:



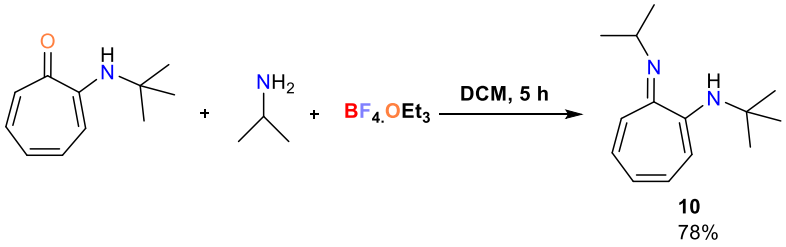
Scheme 21: Synthesis of 2-(tert-butylamino)cycloheptatrienone

Respective amine was added to precooled (**8a**) compound up to 0 ˚C, additionally the mixtures allowed to stir up to 14 h and after that dry the excess solvent and add 2N NaOH solution. Extracted the product with DCM and brine solution and wash the aqueous layer with DCM. Dry it with $MgSO_4$ and filter it and dried the filtrate to get solid in 87% yield.

For **8**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.10 (m, 4H), 6.64 (t, J = 9.5 Hz, 1H), 6.55 (d, J = 10.5 Hz, 1H), 3.83 (h, J = 6.6 Hz, 1H), 1.32 (d, J = 6.4 Hz, 6H).

For **9**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.24 – 7.12 (m, 3H), 6.91 (d, J = 10.6 Hz, 1H), 6.64 (t, J = 9.4 Hz, 1H), 1.51 (s, 9H).

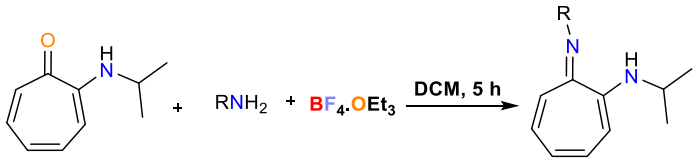
2.3.4.2b: Synthesis of (E)-N-(tert-butyl)-7-(isopropylimino)cyclohepta-1,3,5-trien-1-amine 10:



Scheme 22: Synthesis of (tert-butyl)(isopropylimino)cycloheptatrienamine

$BF_4.OEt_3$ (0.19 g, 0.99 mmol) was added in DCM solution of **9** (0.15 g ,0.9 mmol) and stirred it for 5 h. Then iso-propylamine (5 mL) was added in excess amount and stirred the reaction mixture for 5 h. All volatiles were removed by applying high vacuum in reaction tube and get yellowish product in 78% yield.

2.3.4.3b: Synthesis of N-isopropyl-7-(imino)cyclohepta-1,3,5-trien-1-amine:



R=isopropyl, **11, 73%**
R=*tert*-butyl,**12, 62%**

Scheme 23: Synthesis of N-isopropyl-7-(isopropylimino)cyclohepta-1,3,5-trienamine

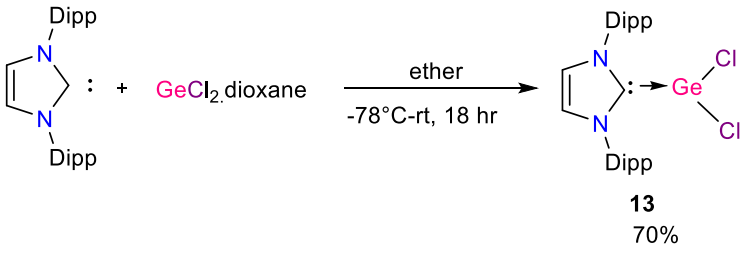
$BF_4.OEt_3$ (2.53 g, 13.4 mmol) salt was added in the DCM and solution of **8** (2 g, 12.3 mmol) and stirred the reaction mixture till 5 h. Then, amine (16 mL) slowly added in excess amount and stirred the reaction mixture till complete dissolution of the 2-aminotropolone (for 5 h.). Then dry the excess solvent and add 2 N NaOH solution extract the product with DCM and brine solution and wash the aqueous layer with DCM. Dry it with $MgSO_4$ and filter it and dried the filtrate to get solid product.

For **11**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.71 (t, J = 10.1 Hz, 2H), 6.28 (d, J = 11.0 Hz, 2H), 6.08 (t, J = 9.3 Hz, 1H), 3.82 (p, J = 6.3 Hz, 2H), 1.25 (d, J = 6.5 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.84, 137.54, 132.92, 122.18, 117.40, 110.21, 46.19, 23.29, 22.38.

For **12**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 6.54 (m, 5H), 3.84 (m, J = 13.0, 6.5 Hz, 1H), 1.42 (s, 15H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.40, 136.50, 128.38, 122.05, 109.14, 53.09, 27.66, 22.14.

2.4. Metalation of carbene and ligands:

2.4.1: Metalation of Dipp-free carbene with Germanium 13:

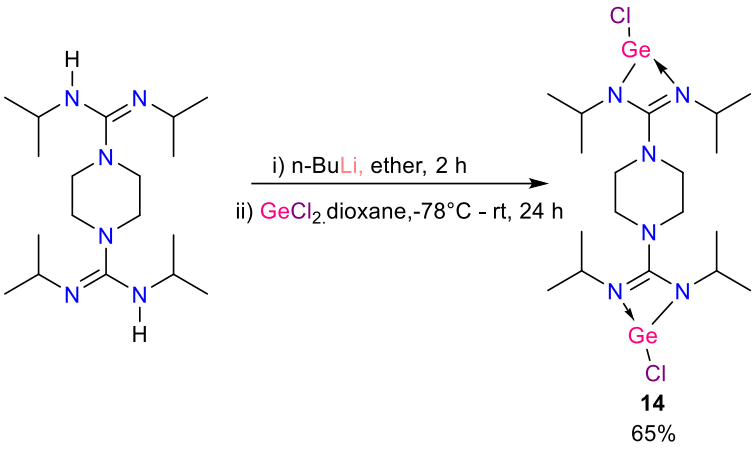


13
70%

Scheme 24: Synthesis of NHC- Germanium (II) complex

In an inert atmosphere, Dipp-carbene (0.8 g, 2.1 mmol) and germanium dichloride (0.300 g, 2.1 mmol) was taken in a Schlenk tube and to it distilled diethyl ether (5 mL) was added at -78 ˚C and stirred the reaction up to 14 h. All volatiles were removed in vacuum and triturated the mixture with hexane to get white solid product in 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, J = 7.7 Hz, 6H), 2.81 (hept, J = 6.8 Hz, 4H), 1.42 (d, J = 6.8 Hz, 12H), 1.00 (d, J = 6.9 Hz, 12H). ^{13}C NMR (125 MHz, C_6D_6) δ 174.80, 145.66, 145.21, 133.04, 124.20, 29.12, 25.53, 22.98.

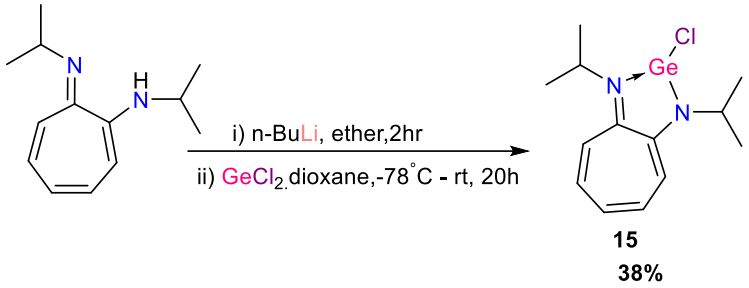
2.4.2: Metalation of tetraisopropylpiperazine-1,4-bis(carboximidamide) 14:



Scheme 25: Synthesis of diisopropyl guanidine Ge (II) complex

Isopropyl guanidine ligand (0.4 g, 1.18 mmol) was taken in a schlenck tube and dry THF was added in it (5 mL). Then, n-BuLi (1.8 mL, 2.3 mmol) poured in the reaction tube in presence of continuous flow of argon at 0 ˚C and stirred it vigorously for 2 hours. Then, solution of $GeCl_2$.dioxane (0.341 g, 2.37 mmol) dissolved in the THF and added it through cannula into lithiated solution at negative -78 ˚C. and stirred the reaction mixture for 24 hours. The excess solvent was removed in vacuum and extraction did with dry THF filtered it through inert filtration tube and dried it and got solid product in 65% in ratio. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58 (d, J = 6.0 Hz, 8H), 3.32 – 3.27 (m, 4H), 1.24 (d, J = 6.1 Hz, 12H), 0.87 (d, J = 6.3 Hz, 12H).

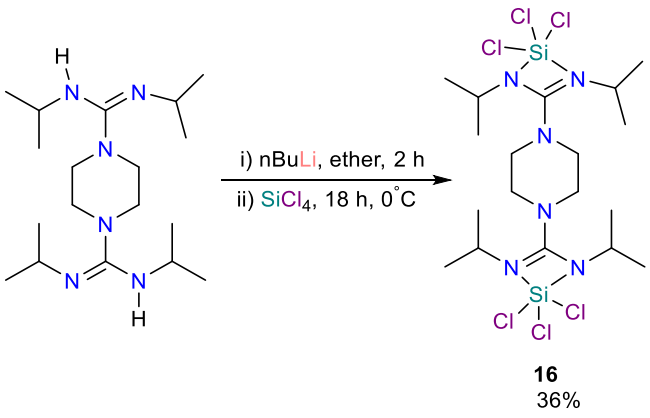
2.4.3: Synthesis of ATI based Ge (II) complex:



Scheme 26: Synthesis of ATI based ligand

Isopropyl-7-(isopropylimino)cyclohepta-1,3,5-trienamine(0.2 g, 0.97mmol) was taken in a Schlenk tube and dry ether was added in it. Then, n-BuLi (0.8 mL, 1.3 mmol) was added at 0 ˚C and kept the reaction stirring for 2 hours. Afterthat, solution of $GeCl_2$.dioxane (0.14 g, 0.97 mmol) in ether was added to lithiated solution at -78 ˚C & kept the mixture stirring for 20 hours. Then, filter the mixture through celite bed and concentrate the filtrate to get yellow solid product. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, J = 5.7, 3.3 Hz, 1H), 6.93 (dd, J = 5.7, 3.3 Hz, 1H), 6.69 – 6.59 (m, 1H), 6.29 – 6.06 (m, 2H), 3.61 (sept, J = 6.2 Hz, 1H), 1.10 (d, J = 6.3 Hz, 6H), 0.86 (d, J = 7.6 Hz, 5H).

2.4.4: Synthesis of Hypervalent Silicon complex:

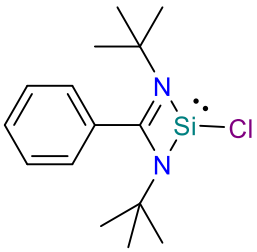


Scheme 27: Synthesis of hypervalent complex

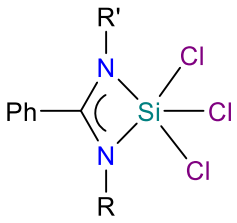
Isopropyl guanidine ligand (0.7 g ,2.2 mmol) taken in a Schlenk and dry ether was added in it. Then, n-BuLi (3.9 mL, 6.3 mmol) was added in the mixture and

stirred it for 2 h and solution of $SiCl_4$ (0.7 g, 4.4 mmol) in ether was added to lithiated solution at 0 ˚C and kept the reaction for stirring for 14 hours, and excess solvent in vacuum and dry DCM was added & filter the reaction mixture through celite bed. Dry the filtrate in vacuum to get cream coloured solid as product in 36% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 – 3.63 (m, 4H), 3.51 (s, 8H), 1.41 (d, J = 6.8 Hz, 12H), 0.88 (d, J = 6.0 Hz, 12H). ^{29}Si NMR (99 MHz, $CDCl_3$) δ (-72 and -74). ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.47, 65.99, 53.56, 47.68, 25.30, 22.26.

Previous literature shows that penta-coordinated complex formed with respect to ^{29}Si NMR.[51].



δ = 14.6 ppm



R'=^{t}Bu R=Cy, δ= -89.16
R'=Mes R=Cy, δ= -98.57
R=R'=^{t}Bu, δ= -98.6

Scheme 28: Penta coordinated Si complexes

After looking into literature reports, we can say that our silicon guadinate compound is pentavalent silicon species whose ^{29}Si NMR comes around -80 to -90 ppm comparable to given pentavalent Si complexes in scheme 28.

Chapter 3

Result And Discussion

3.1. Characterization of ligands

Mass Spectrum of 1a:

LCMS m/z calculated for $C_{26}N_2H_{36}$, [M+H] is 377.2951, found 377.2973

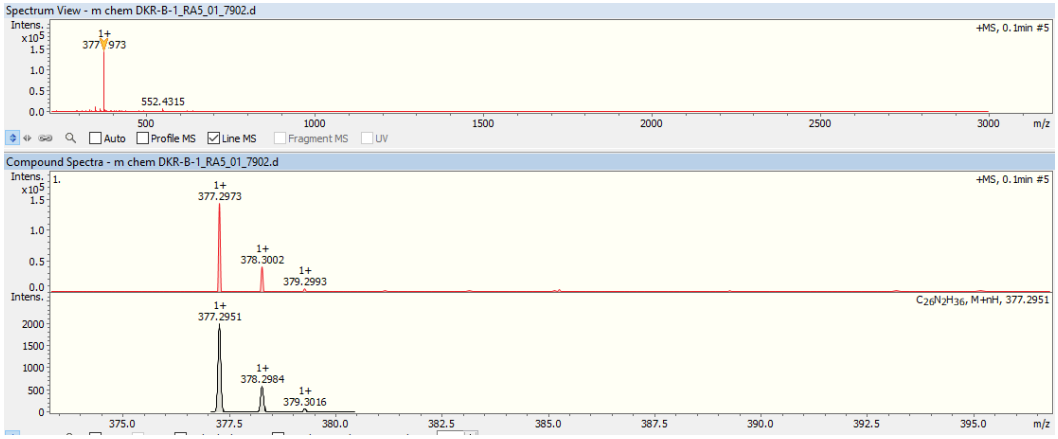


Figure 15: Mass Spectrum of 1a

Mass Spectrum of 1b:

LCMS m/z calculated for $C_{27}H_{37}N_2$, $[M]^+$ is 389.2998, found 389.3006

Figure 16: Mass Spectrum of 1b

^{1}H NMR Spectrum of 1b:

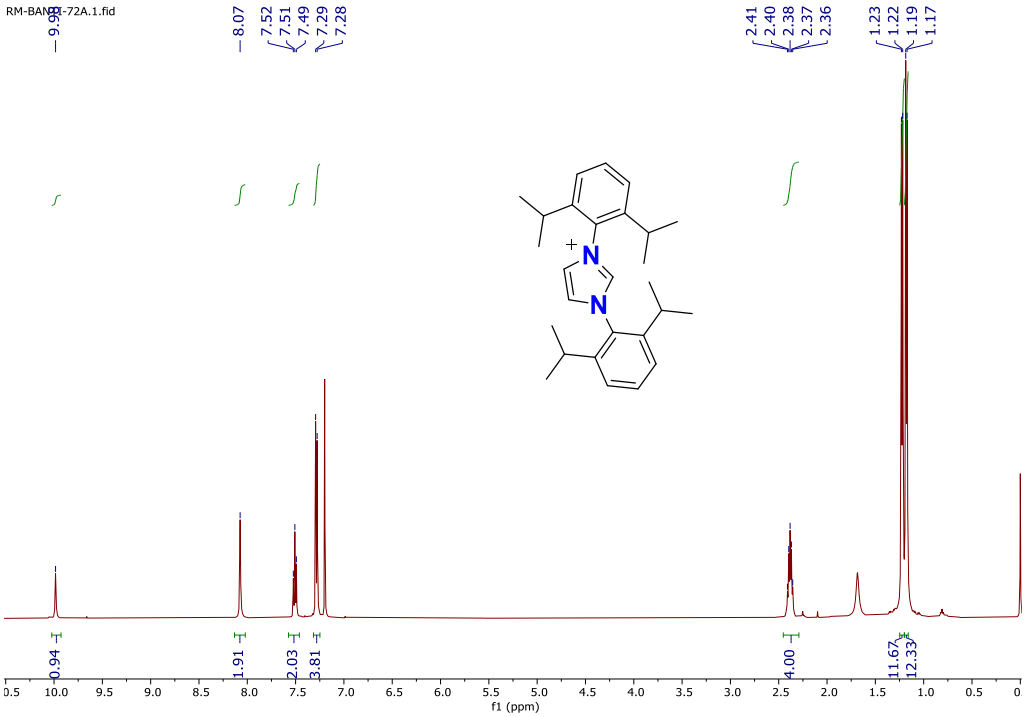


Figure 17: ^{1}H NMR Spectrum of 1b

^{13}C NMR Spectrum of 1b:

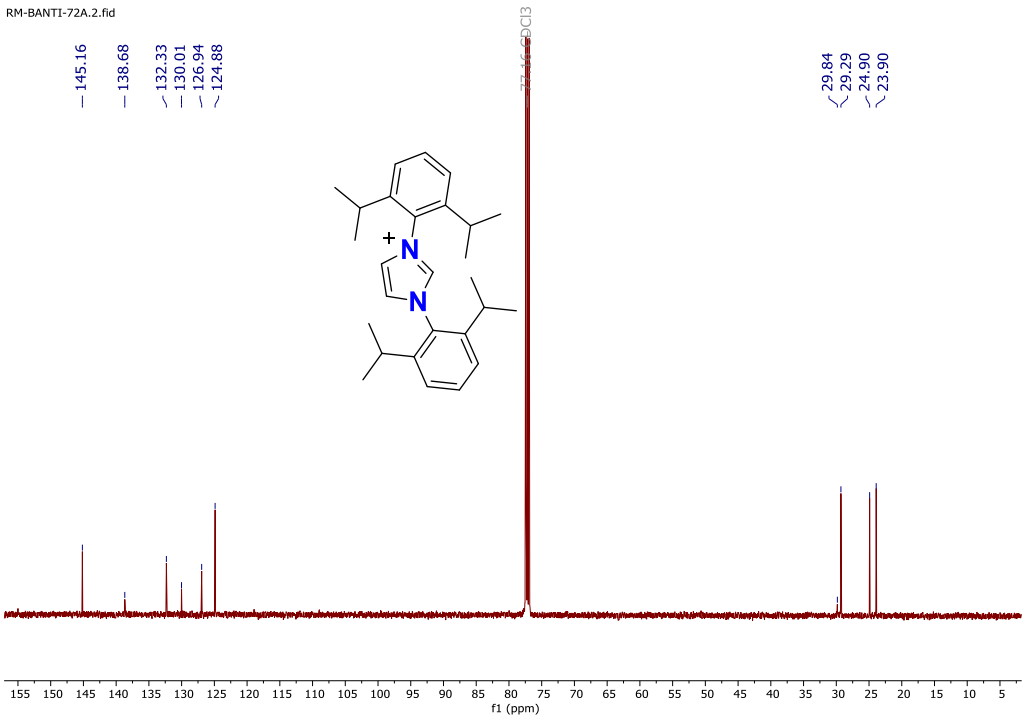


Figure 18: ^{13}C NMR Spectrum of 1b

^{1}H NMR Spectrum of 1:

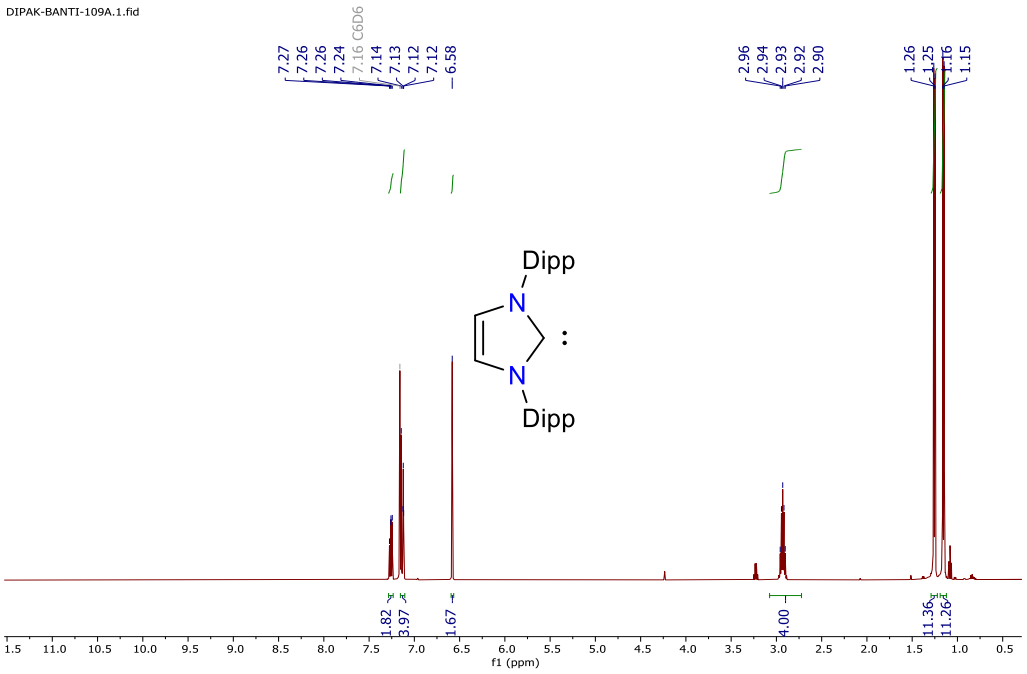


Figure 19: ^{1}H NMR Spectrum of 1

Mass Spectrum of 2a:

LCMS m/z calculated for $C_6H_{10}N_2$, [M+H] is 111.0917, found 111.0949

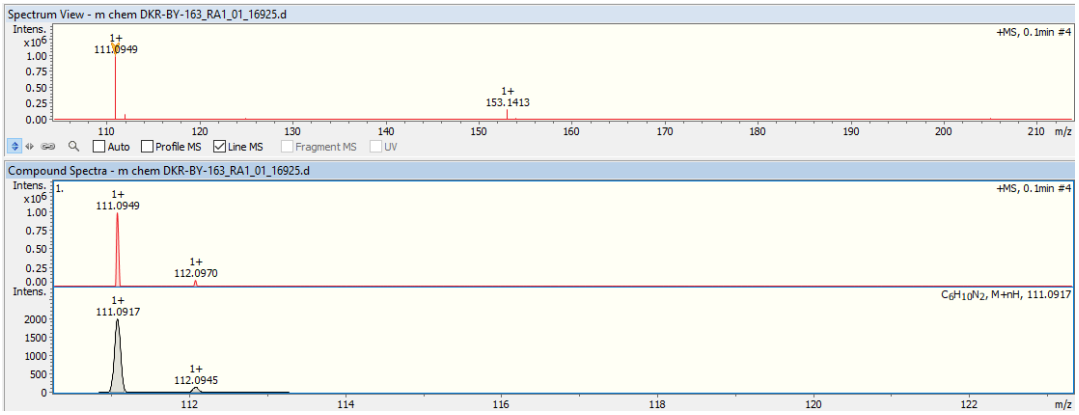


Figure 20: Mass Spectrum of 2a

^{1}H NMR Spectrum of 2a:

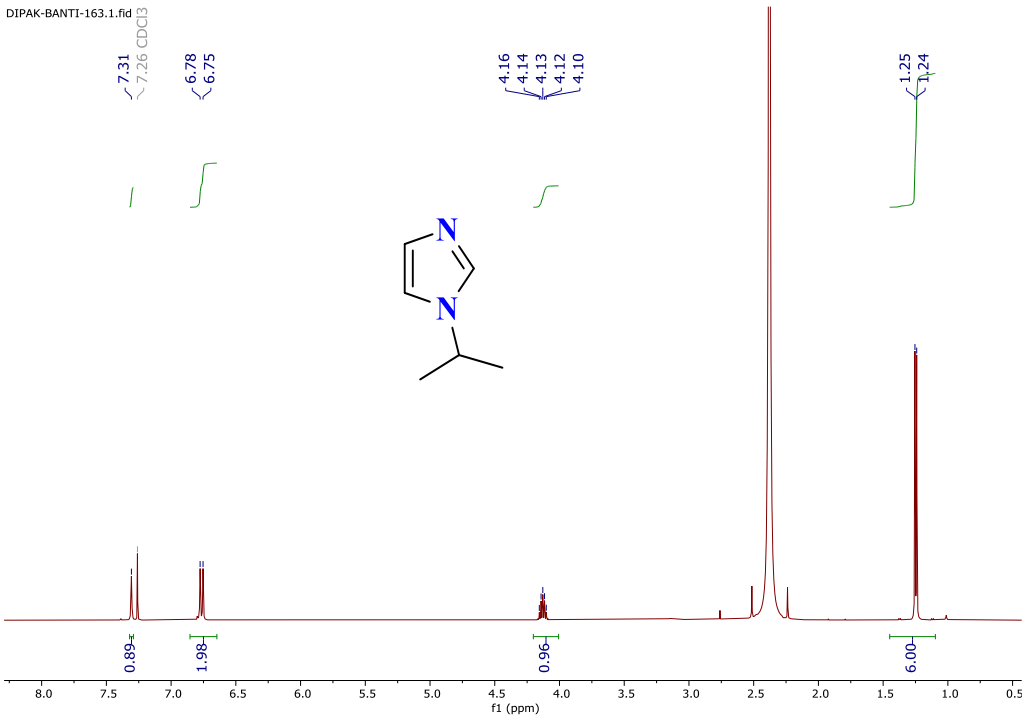


Figure 21: ^{1}H NMR Spectrum of 2a

^{13}C NMR Spectrum of 2a:

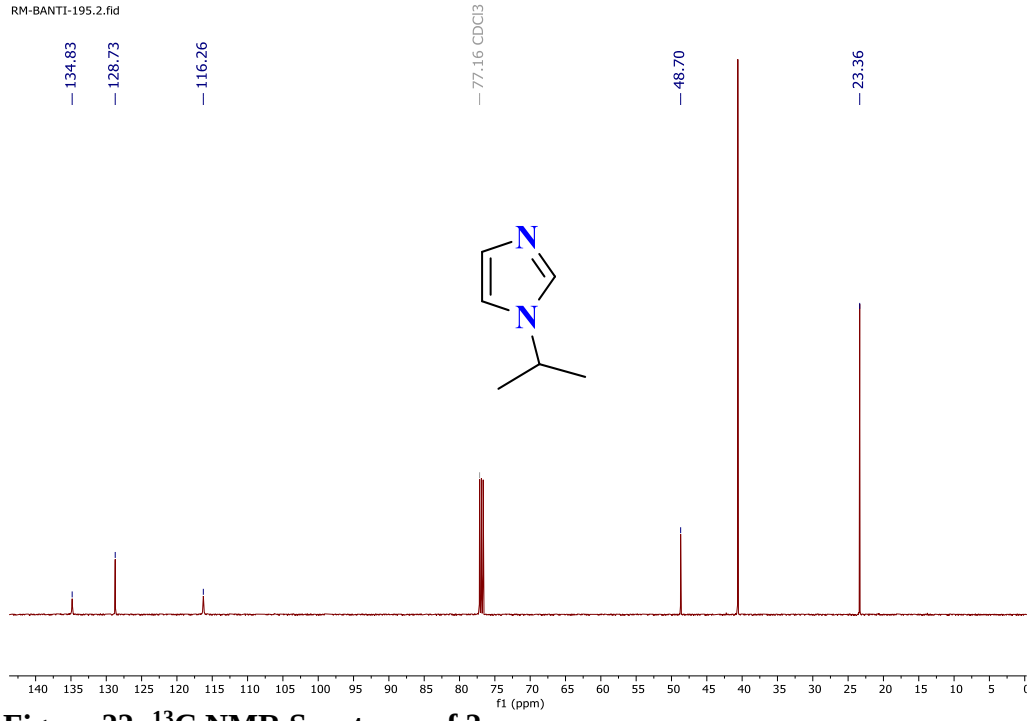


Figure 22: ^{13}C NMR Spectrum of 2a

Mass Spectrum of 2b:

LCMS m/z calculated for $C_9H_{17}N_2$, $[M]^+$ is 153.1386, found 153.1380

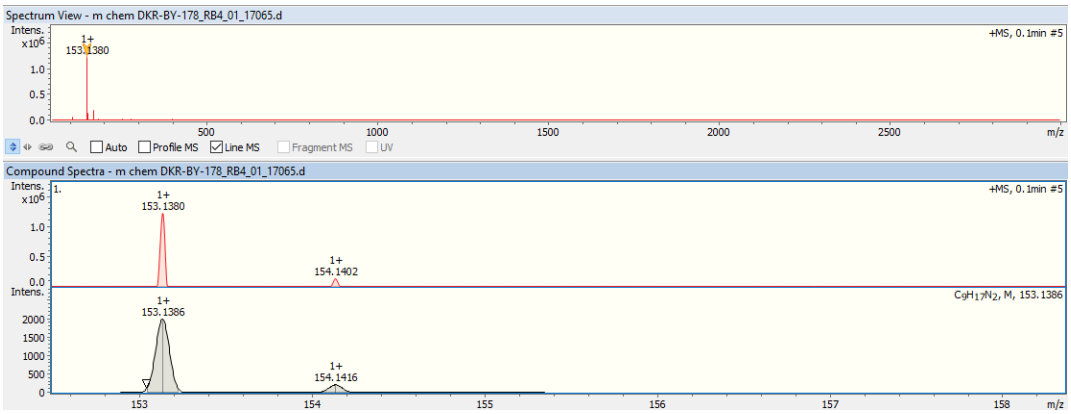


Figure 23: Mass Spectrum of 2b

^{1}H NMR Spectrum of 2b:

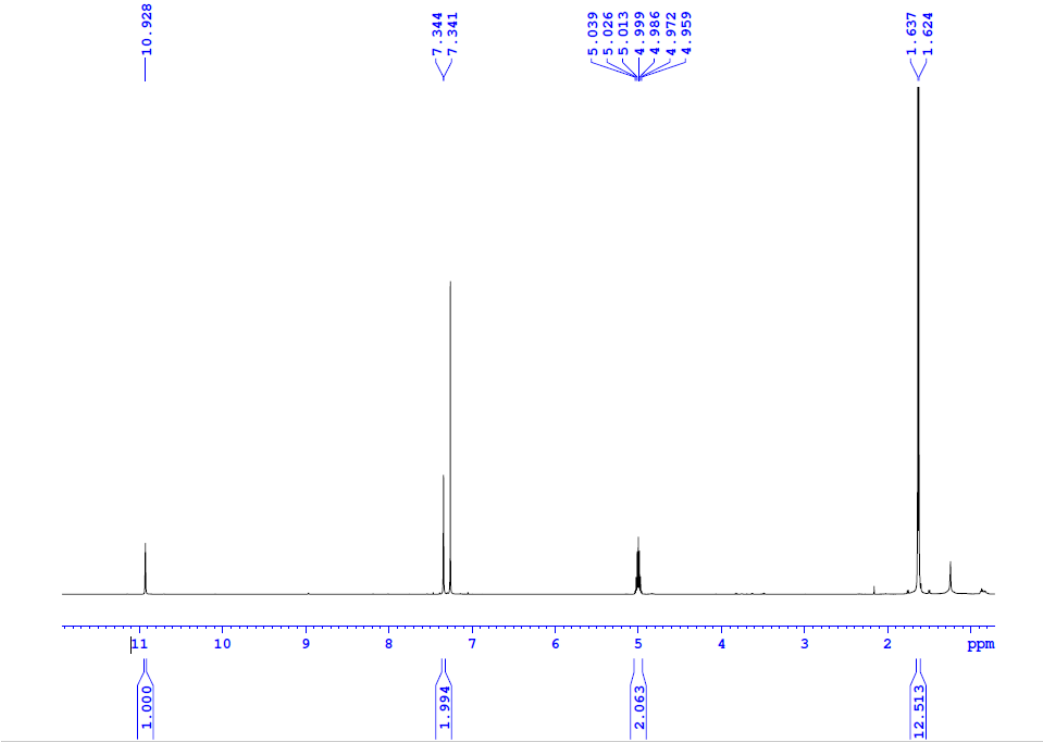


Figure 24: ^{1}H NMR spectrum of 2b

Mass Spectrum of 3a:

LCMS m/z calculated for $C_5H_8N_2$, [M+H] is 97.0760, found 97.084

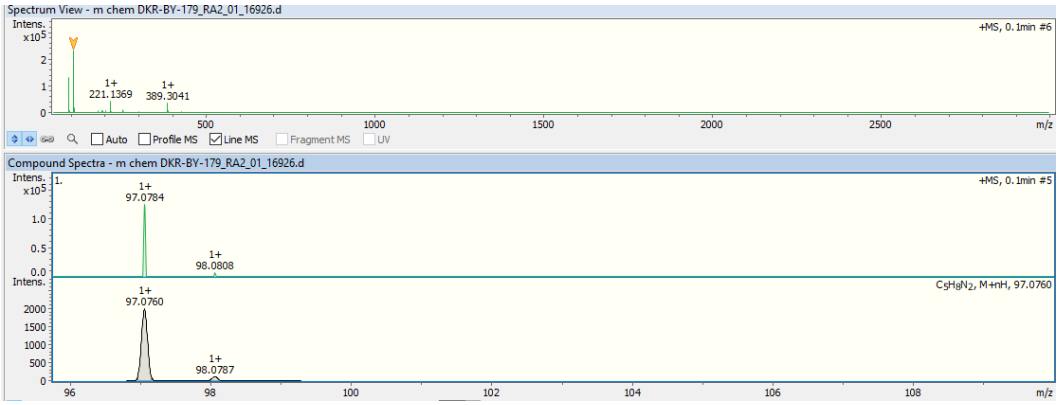


Figure 25: Mass Spectrum of 3a

^{1}H NMR Spectrum of 3a:

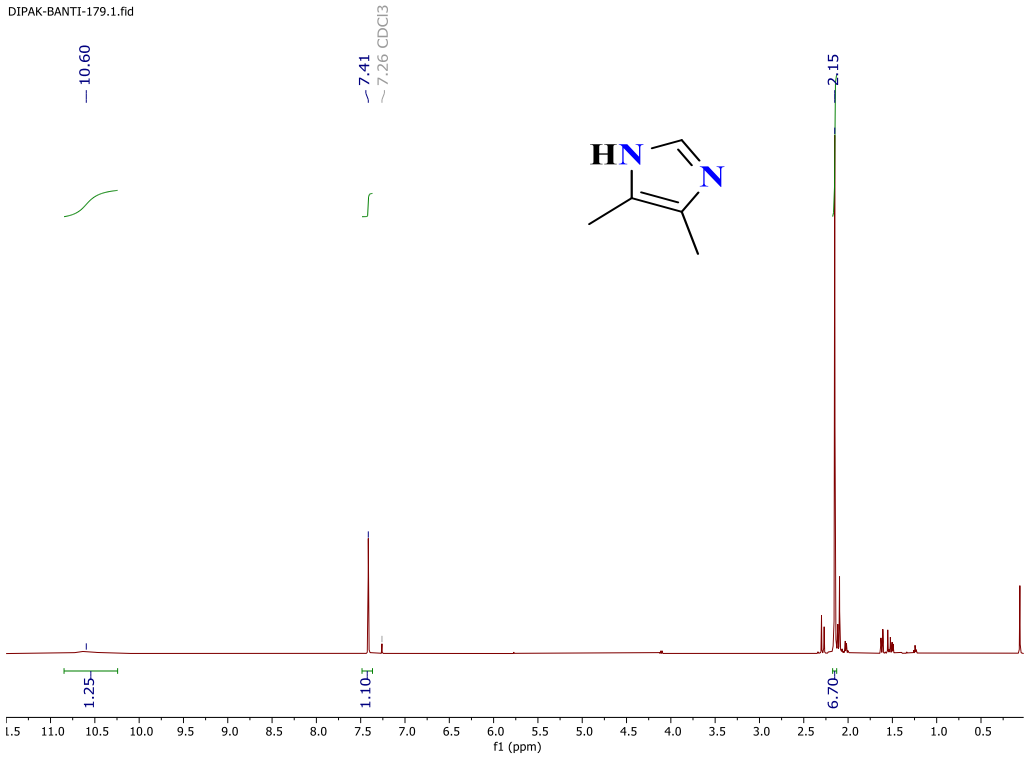


Figure 26: ^{1}H NMR Spectrum of 3a

Mass Spectrum of 3b:

LCMS m/z calculated for $C_8H_{14}N_2$, [M+H] is 139.1230, found 139.1358

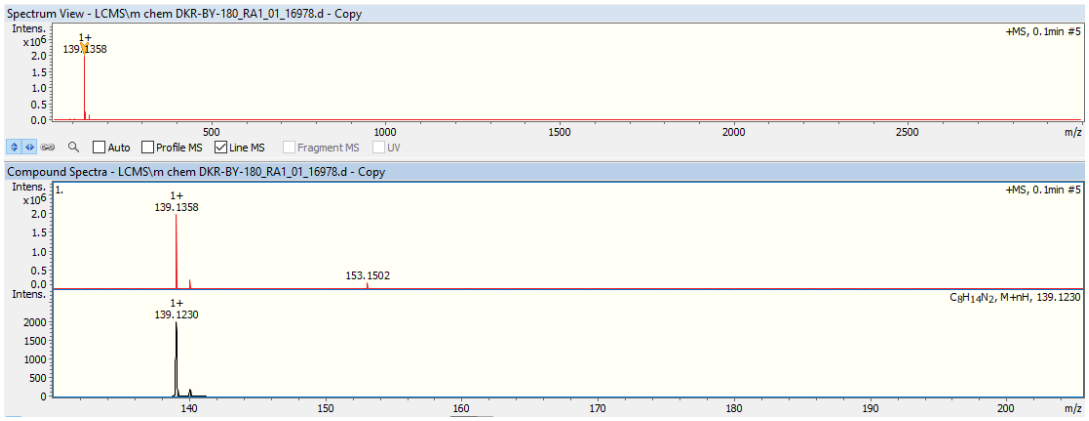


Figure 27: Mass Spectrum of 3b

^{1}H NMR Spectrum of 3b:

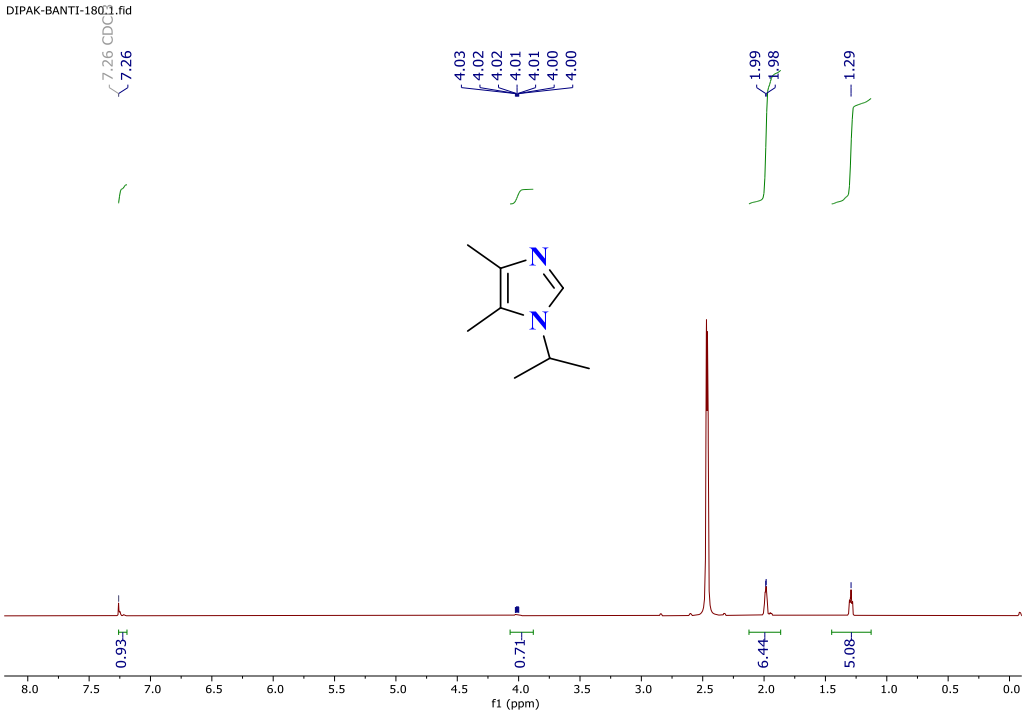


Figure 28: ^{1}H NMR Spectrum of 3b

Mass Spectrum of 3c:

LCMS m/z calculated for $C_{11}H_{21}N_2$, $[M]^+$ is 181.1699, found 181.1690

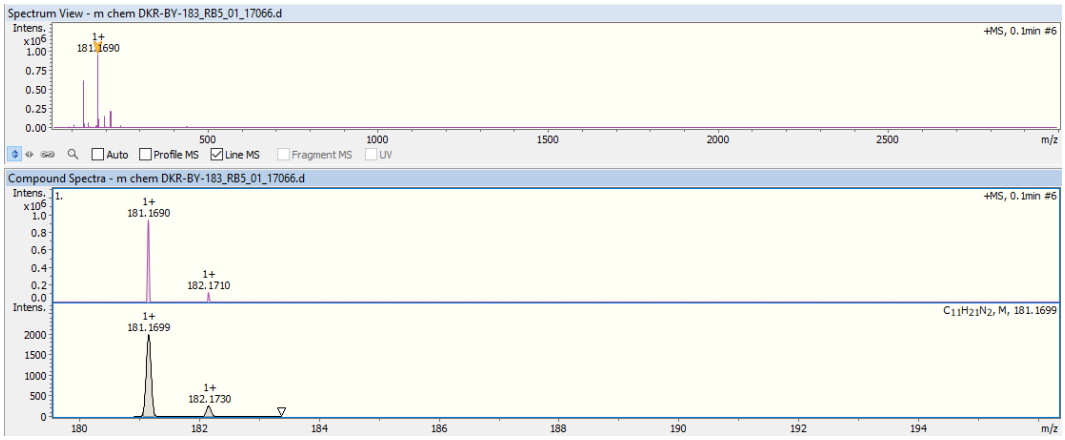


Figure 29: Mass Spectrum of 3c

^{1}H NMR Spectrum of 3c:

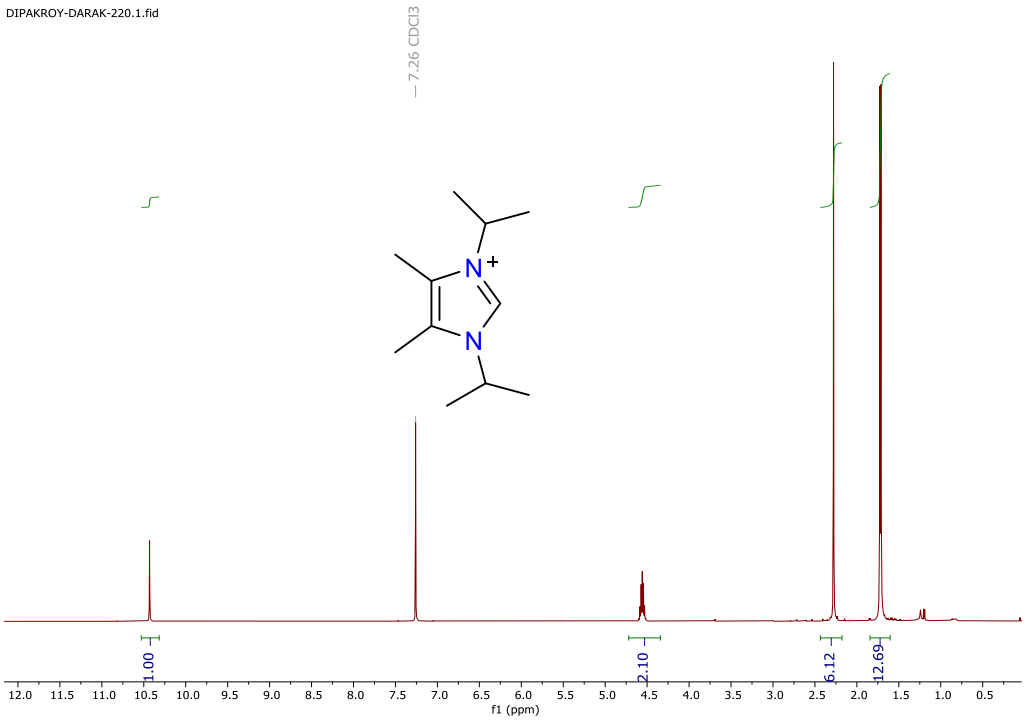


Figure 30: ^{1}H NMR Spectrum of 3c

Mass Spectrum of 4:

LCMS m/z calculated for $C_{18}H_{38}N_6$, [M+H] is 339.3231, found 339.3252

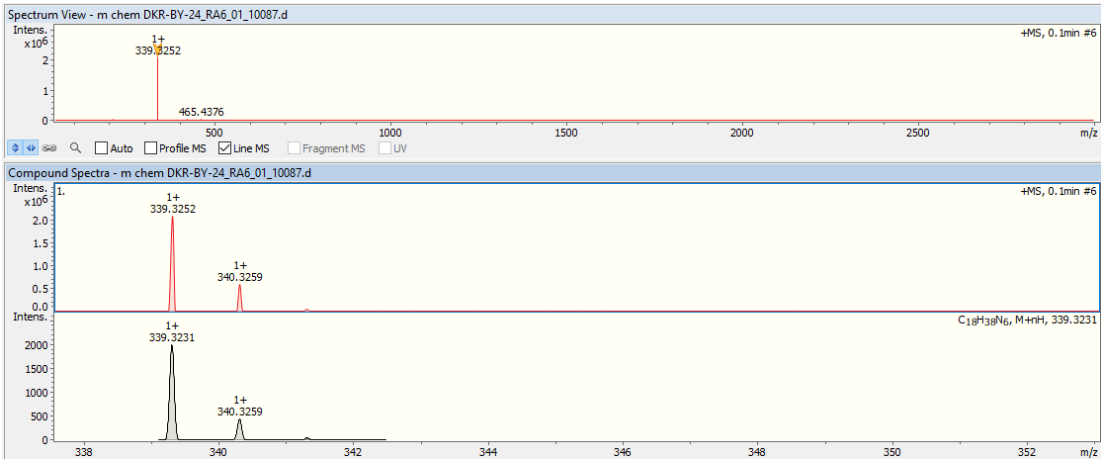


Figure 31: Mass Spectrum of 4

^{1}H NMR Spectrum of 4:

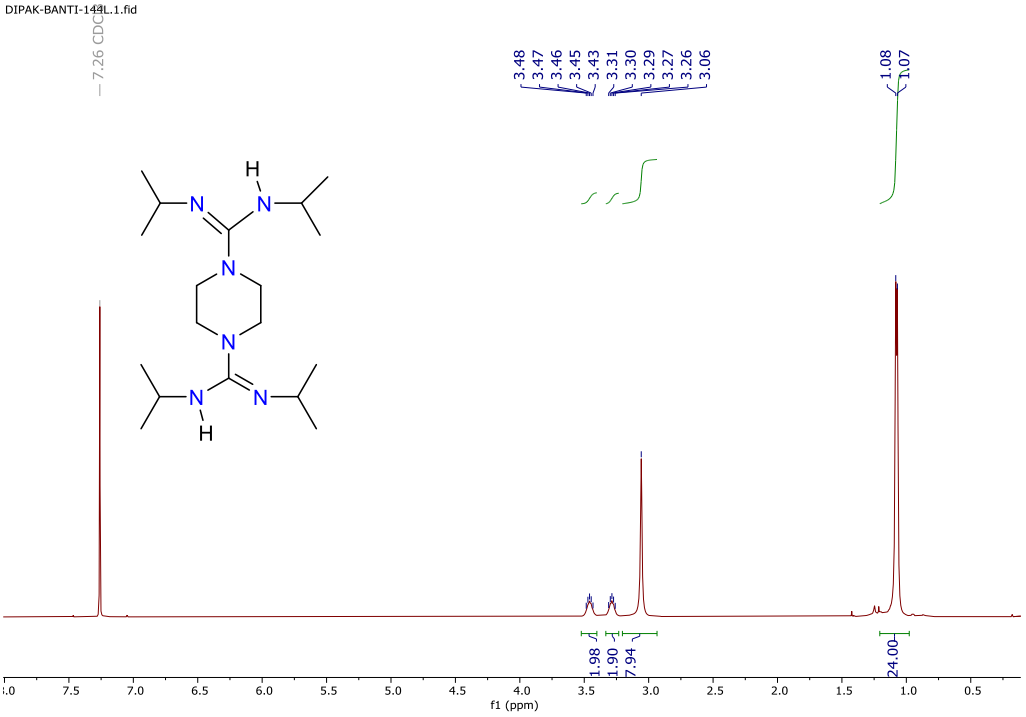


Figure 32: ^{1}H NMR Spectrum of 4

^{13}C NMR Spectrum of 4:

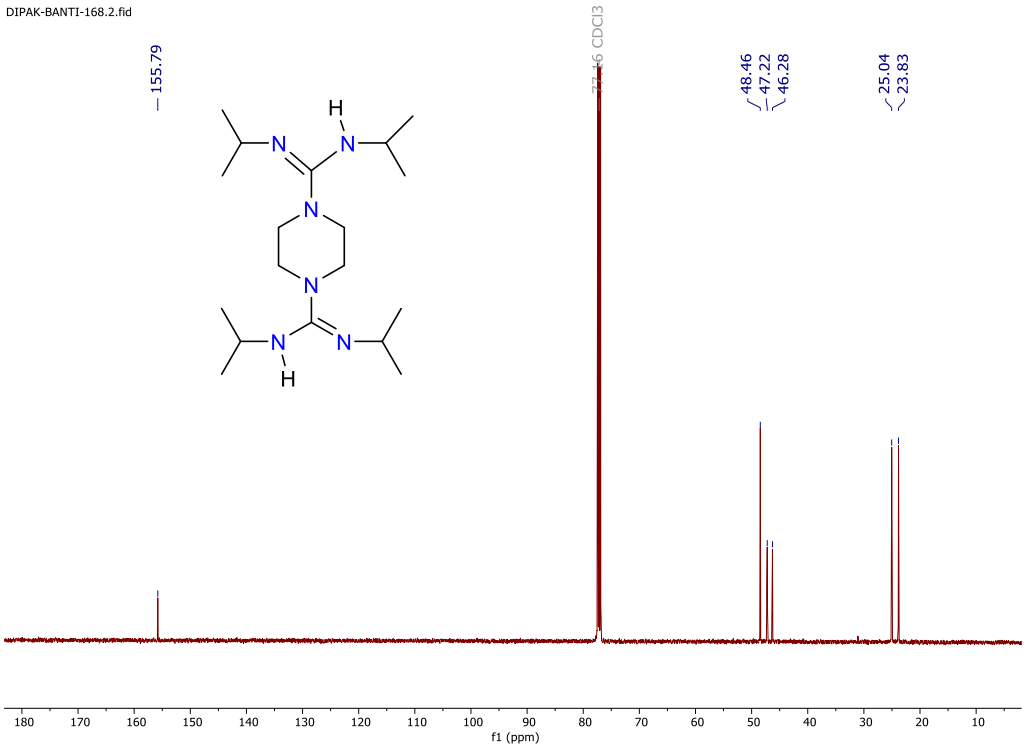


Figure 33: ^{13}C NMR Spectrum of 4

Mass Spectrum of 5:

LCMS m/z calculated for $C_{13}H_{20}N_2$, [M+H] is 205.1699, found 205.1904

Figure 34: Mass Spectrum of 5

^{1}H NMR Spectrum of 5:

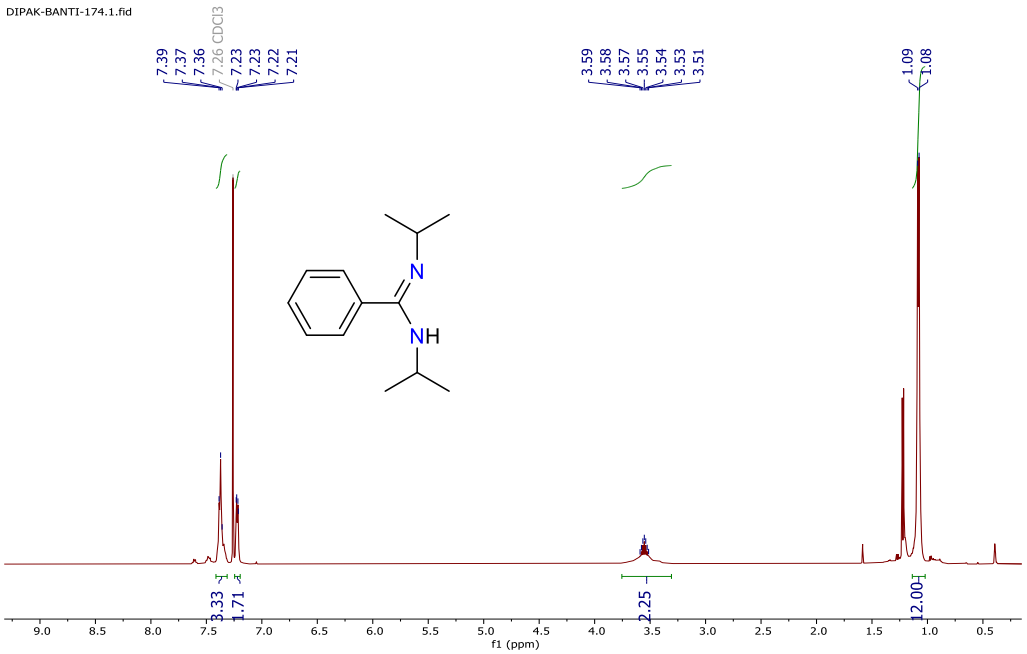


Figure 35: ^{1}H NMR Spectrum of 5

^{1}H NMR Spectrum of 6a:

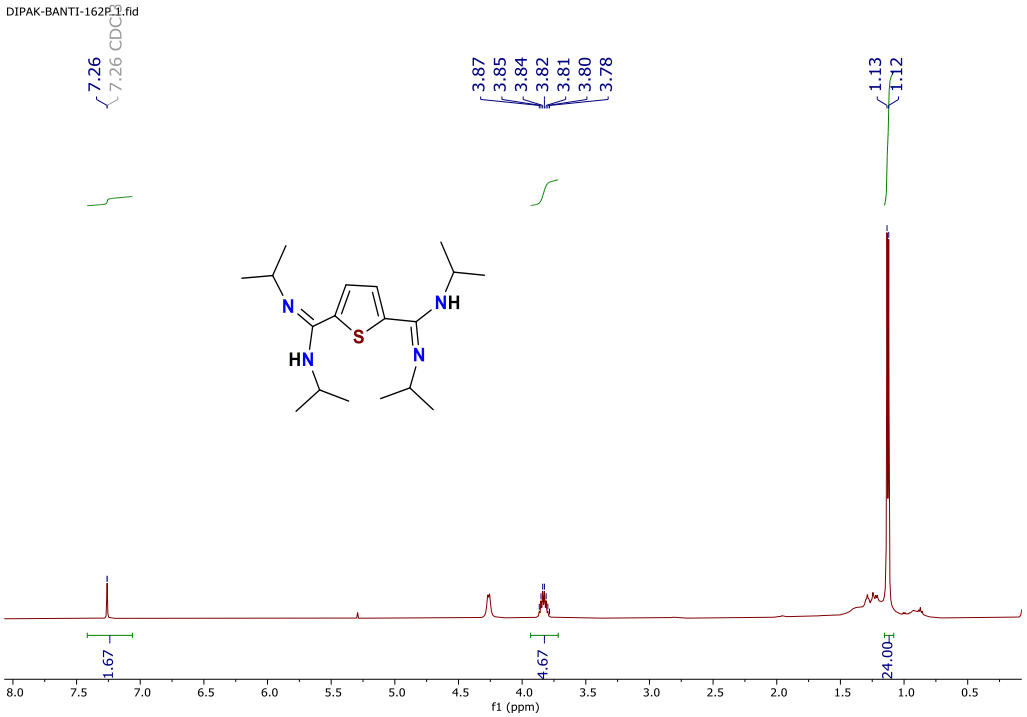


Figure 36: ^{1}H NMR Spectrum of 6a

^{13}C NMR Spectrum of 6a:

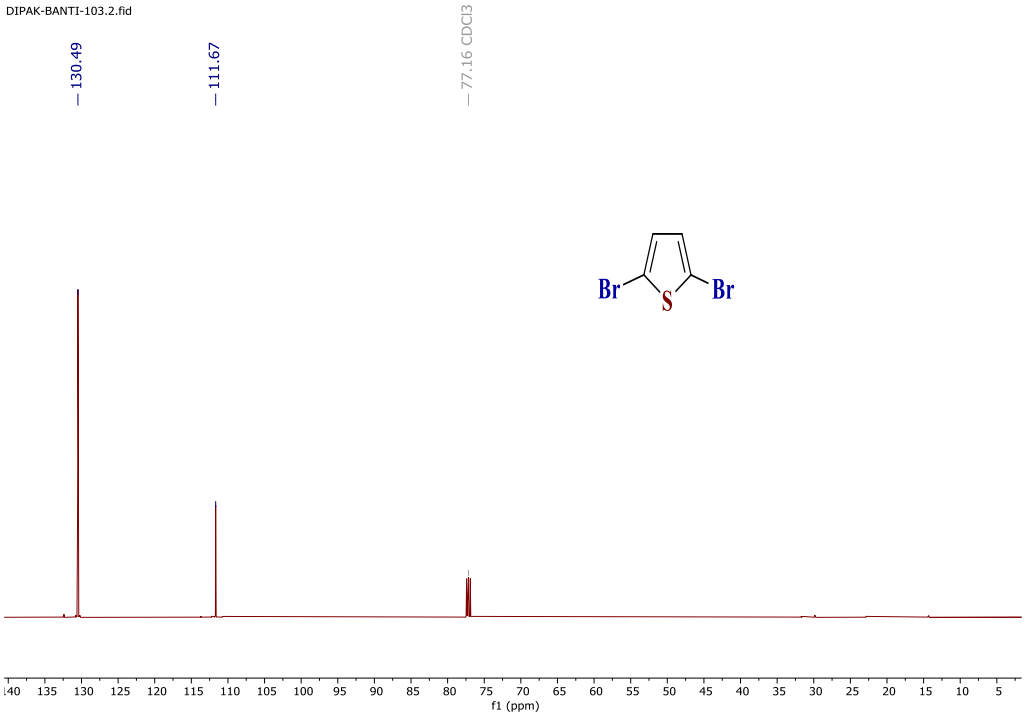


Figure 37: ^{13}C NMR Spectrum of 6a

Mass Spectrum of 6:

LCMS m/z calculated for $C_{18}H_{32}N_4S$, [M+H] is 337.2420, found 337.2328

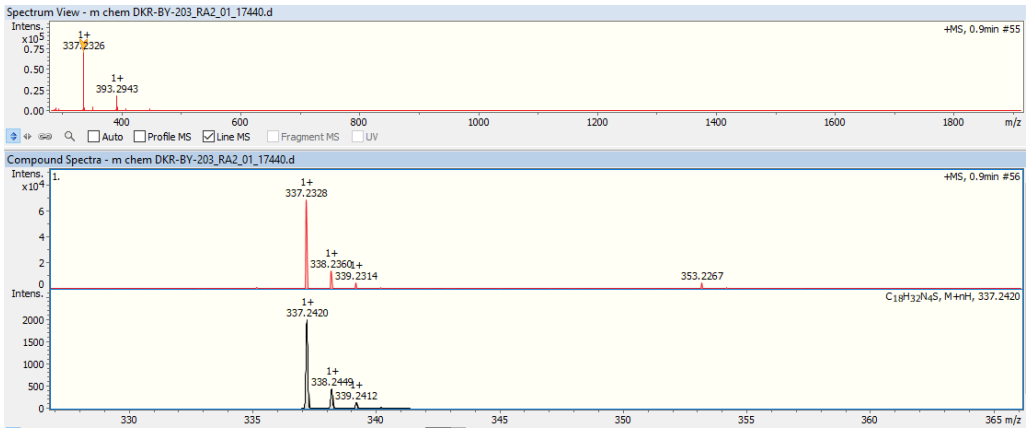


Figure 38: Mass Spectrum 6

^{1}H NMR Spectrum of 6:

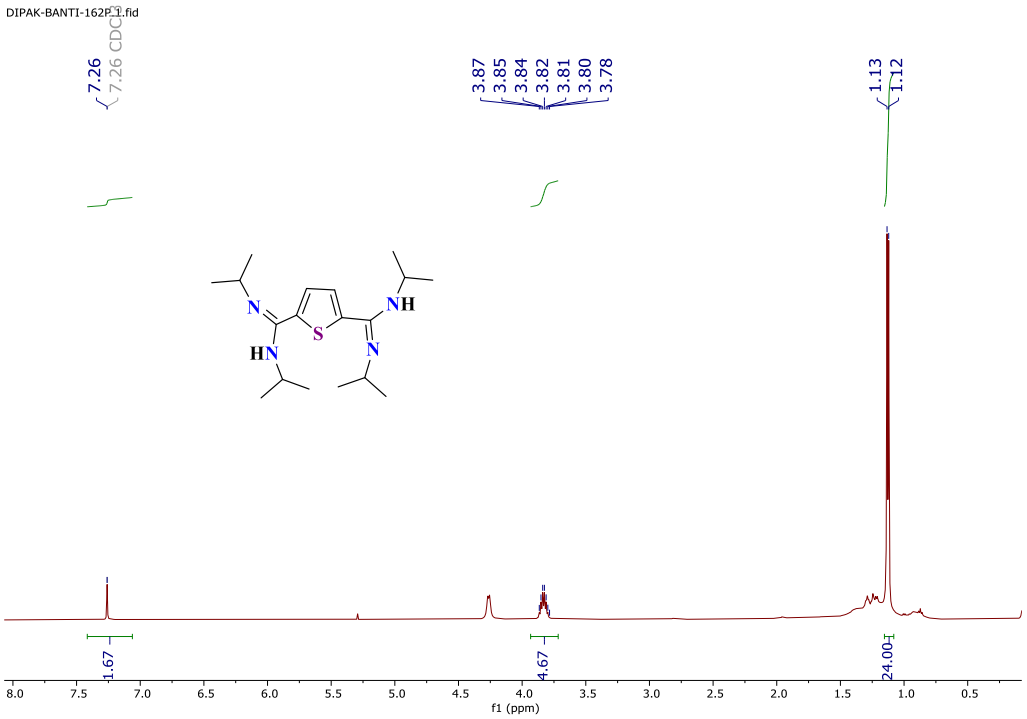


Figure 39: ^{1}H NMR Spectrum 6

^{1}H NMR Spectrum of 7a:

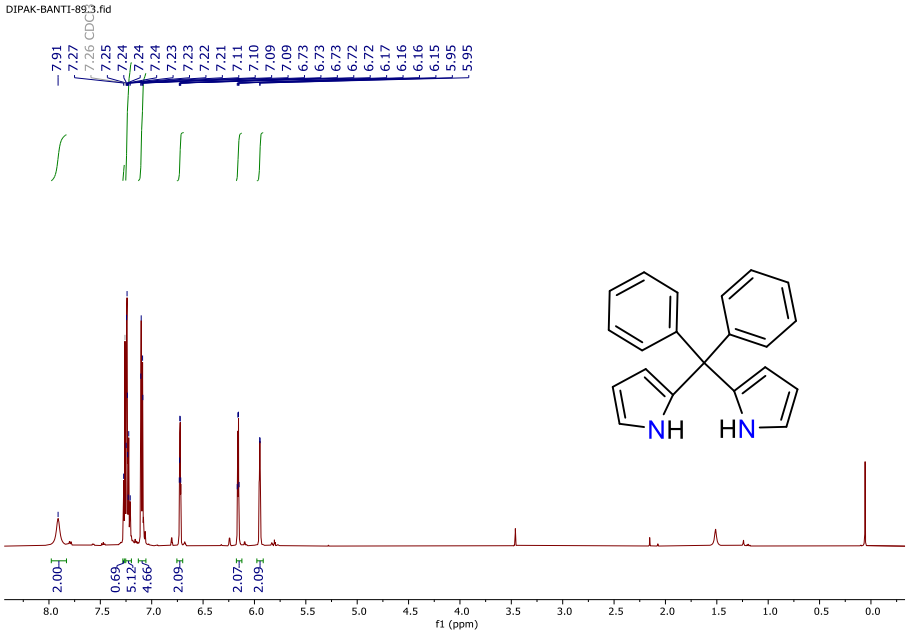


Figure 40: ^{1}H NMR Spectrum of 7a

^{13}C NMR Spectrum of 7a:

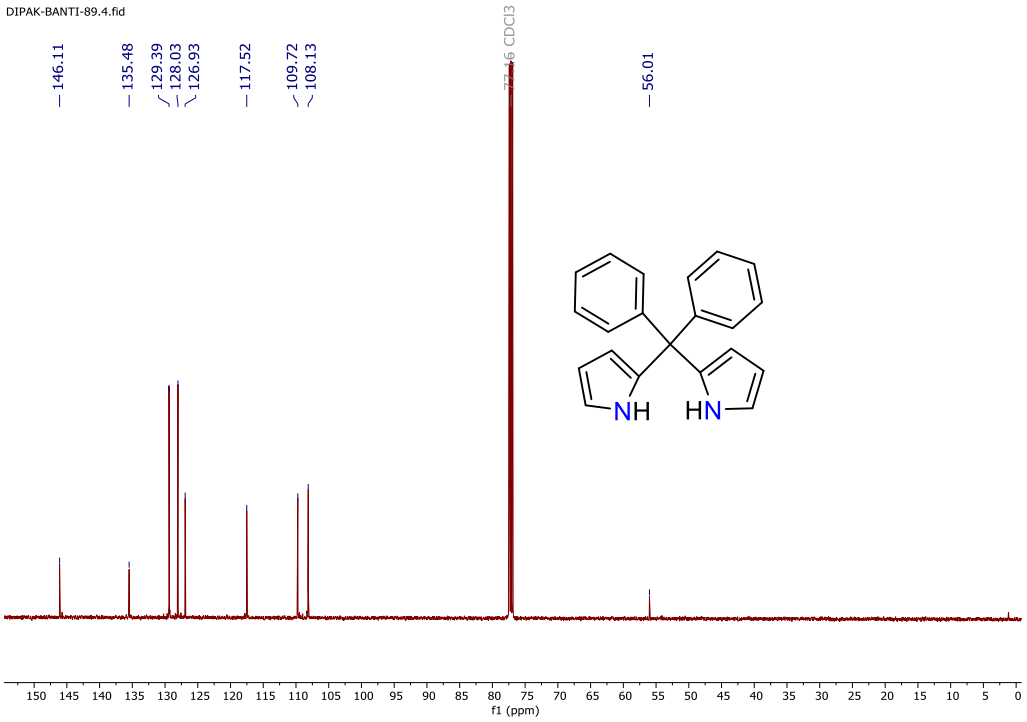


Figure 41: ^{13}C NMR Spectrum of 7a

^{1}H NMR Spectrum of 7b:

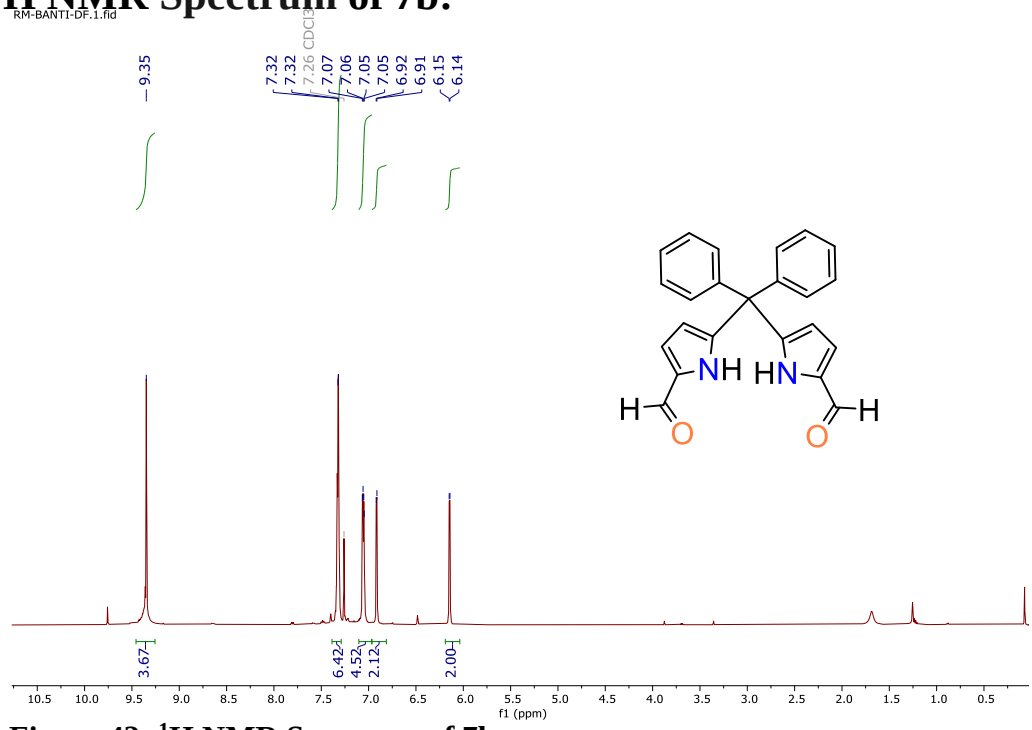


Figure 42: ^{1}H NMR Spectrum of 7b

^{13}C NMR Spectrum of 7b:

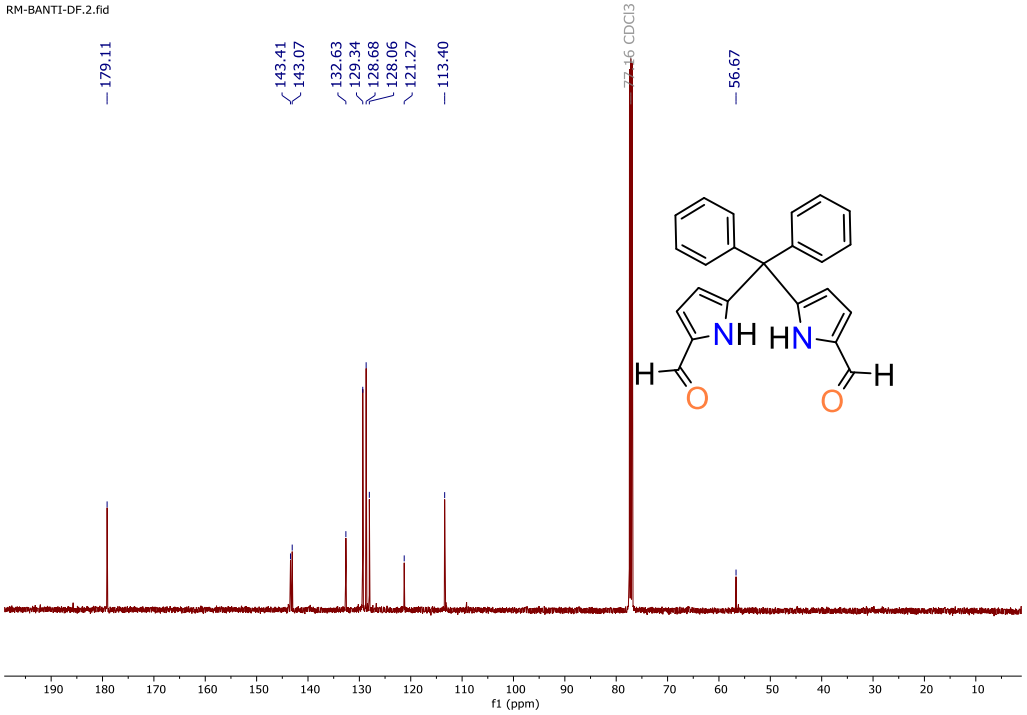


Figure 43: ^{13}C NMR Spectrum of 7b

Mass Spectrum of 7:

LCMS m/z calculated for $C_{29}H_{32}N_4$, [M+H] is 437.2700, found 437.2771

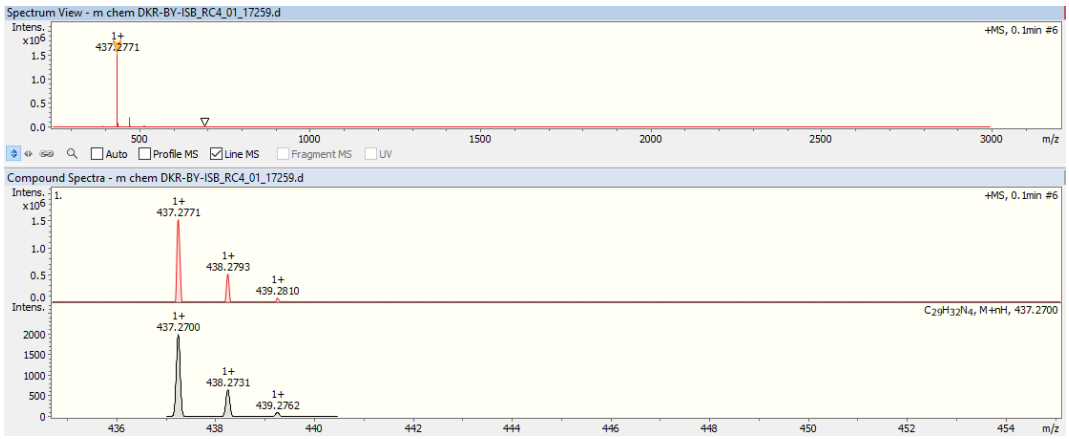


Figure 44: Mass Spectrum of 7

^{1}H NMR Spectrum of 7:

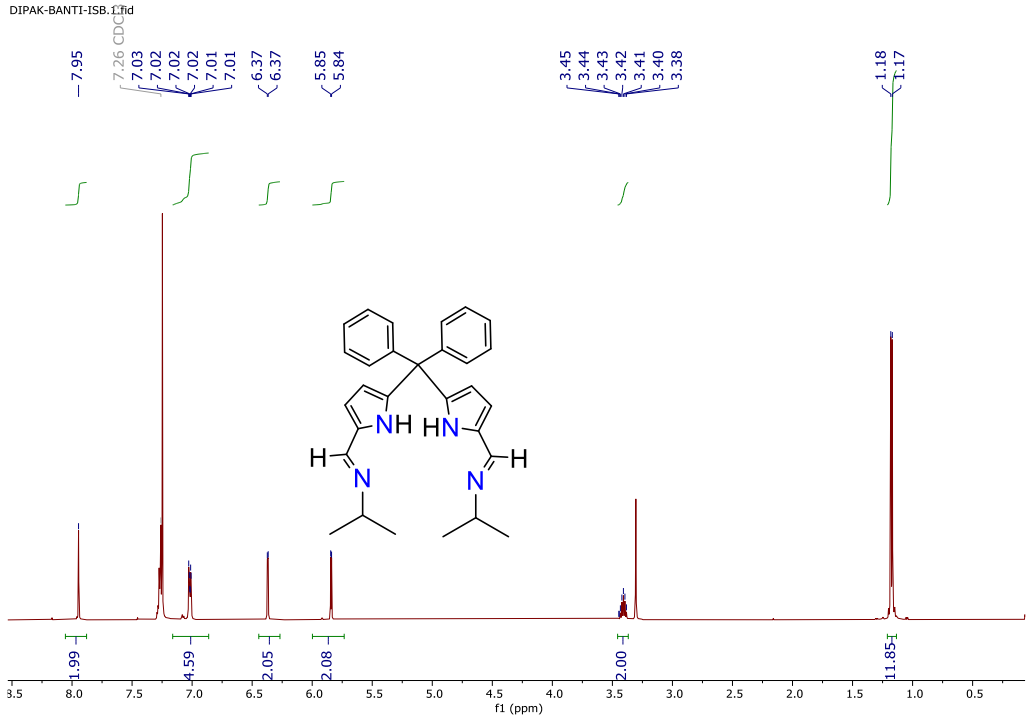


Figure 45: ^{1}H NMR Spectrum of 7

^{13}C NMR Spectrum of 7:

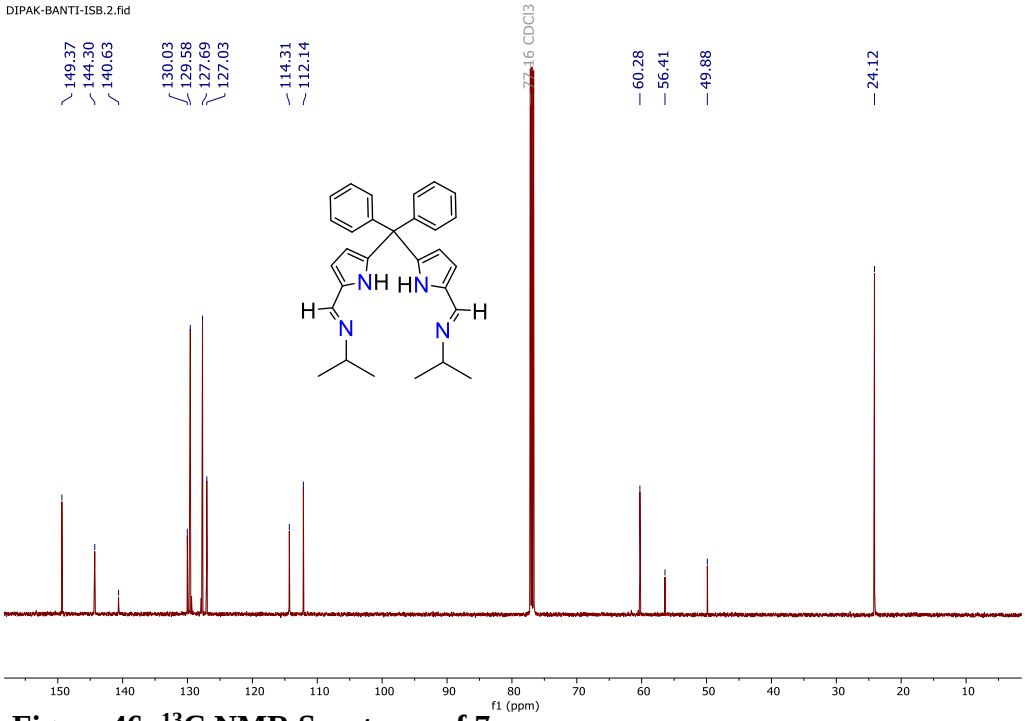


Figure 46: ^{13}C NMR Spectrum of 7

Mass Spectrum of 8a:

LCMS m/z calculated for $C_{14}H_{12}O_4S$, [M+Na] is 299.0349, found 299.0526

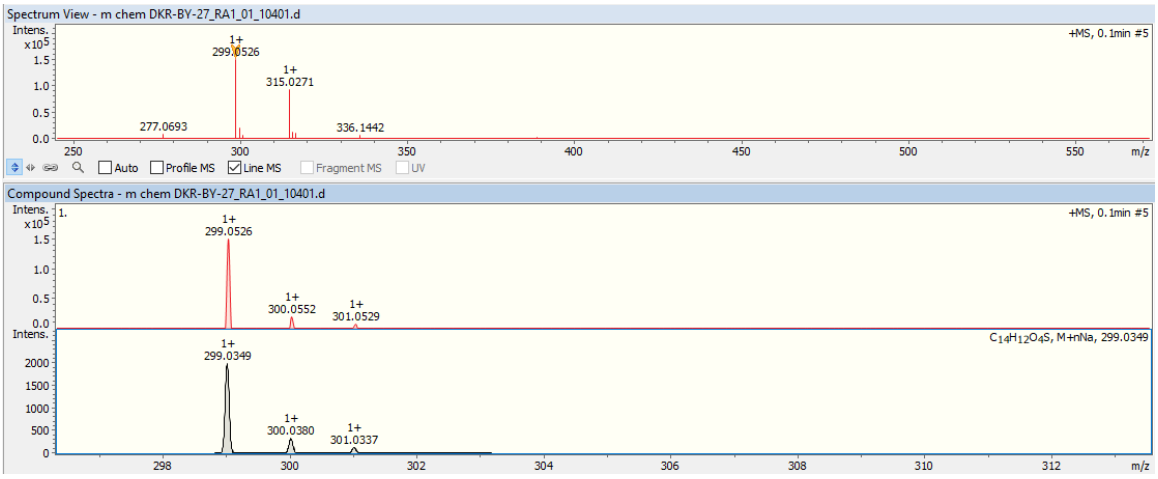


Figure 47: Mass Spectrum of 8a

^{1}H NMR Spectrum of 8a:

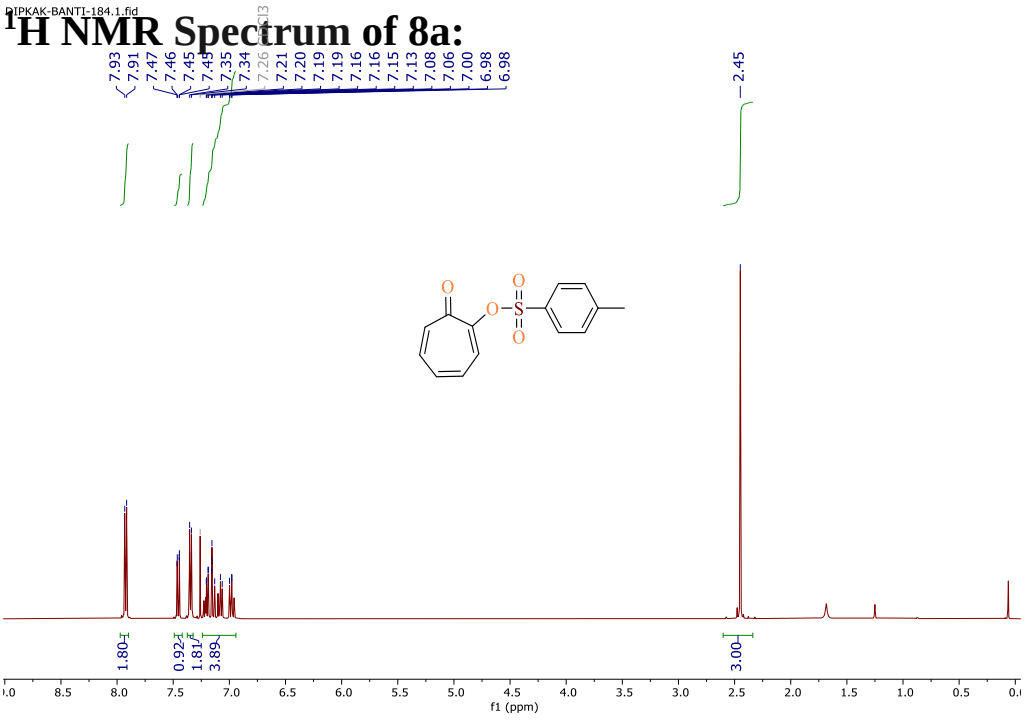


Figure 48: ^{1}H NMR Spectrum of 8a

^{13}C NMR Spectrum of 8a:

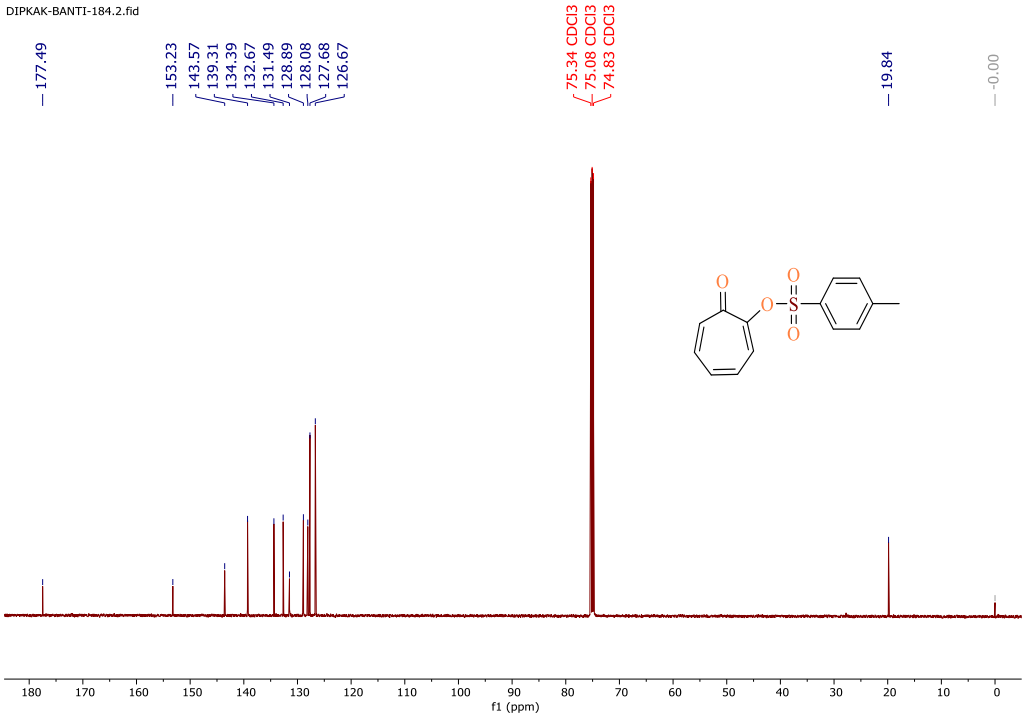


Figure 49: ^{13}C NMR Spectrum of 8a

Mass Spectrum of 8:

LCMS m/z calculated for $C_{10}H_{13}N_1O$, [M+H] is 164.1071, found 164.1032

Figure 50: Mass Spectrum of 8

^{1}H NMR Spectrum of 8:

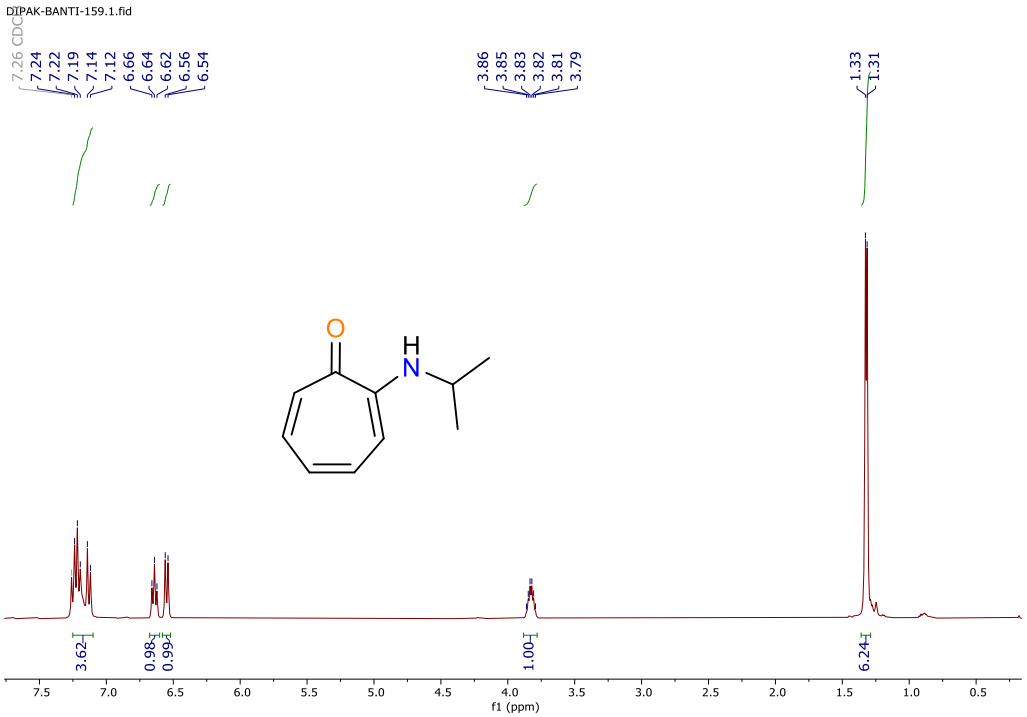


Figure 51: ^{1}H NMR Spectrum of 8

Mass Spectrum of 9:

LCMS m/z calculated for $C_{11}H_{15}NO$, [M+H] is 178.1226, found 178.1294

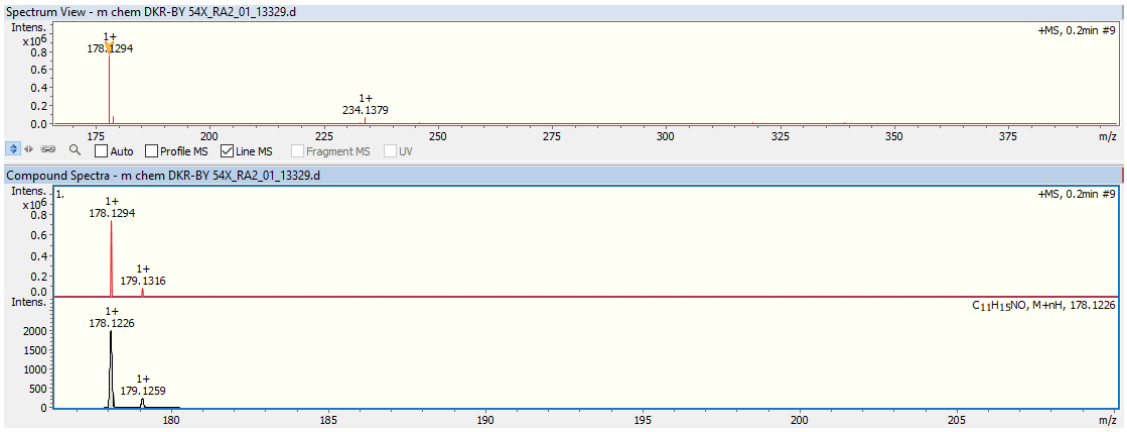


Figure 52: Mass Spectrum of 9

^{1}H NMR Spectrum of 9:

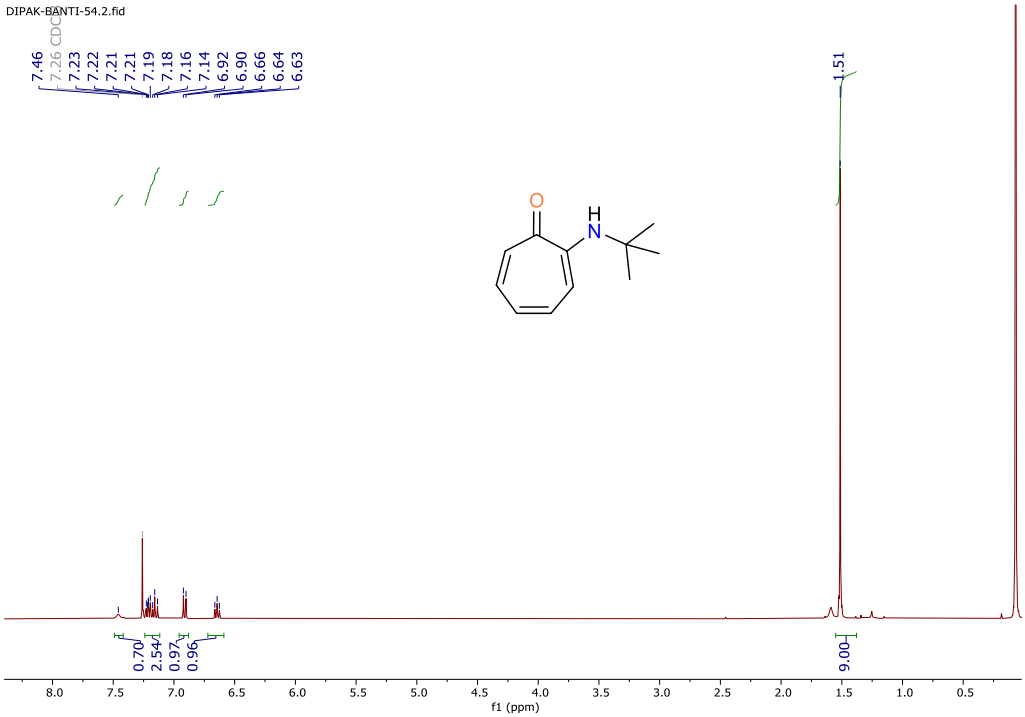


Figure 53: ^{1}H NMR Spectrum of 9

Mass Spectrum of 10:

LCMS m/z calculated for $C_{14}H_{22}N_2$, [M+H] is 219.18456, found 219.1852

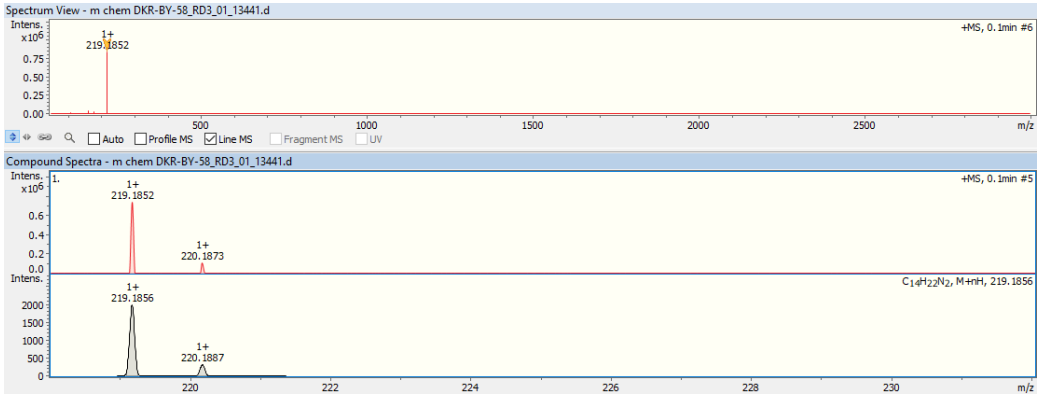


Figure 54: Mass Spectrum of 10

^{1}H NMR Spectrum of 10:

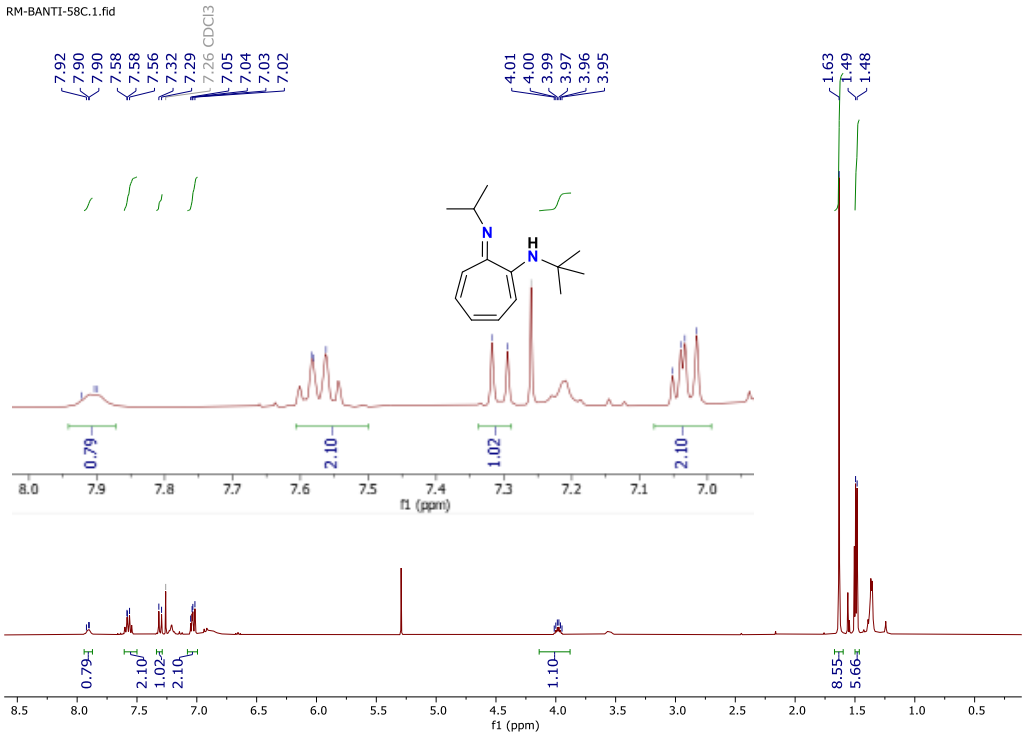


Figure 55: ^{1}H NMR Spectrum of 10

^{13}C NMR Spectrum of 10:

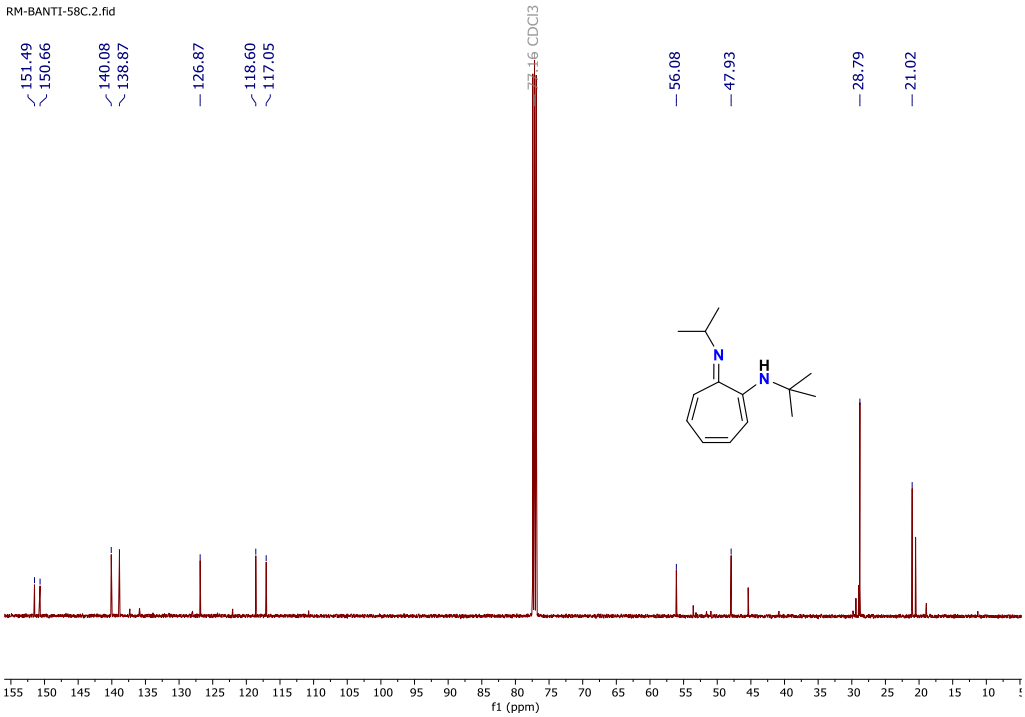


Figure 56: ^{13}C NMR Spectra Spectrum of 10

Mass Spectrum of 11:

LCMS m/z calculated for $C_{13}H_{20}N_2$, [M+H] is 205.1699, found 205.1787

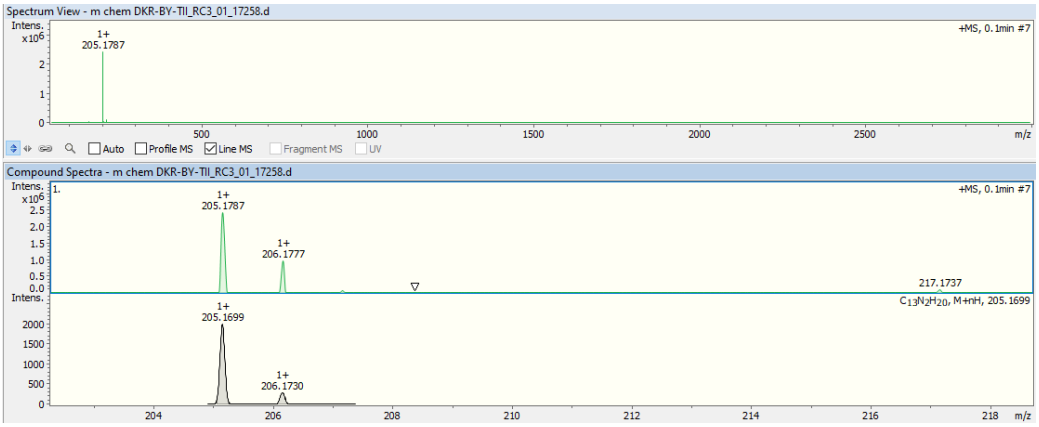


Figure 57: Mass Spectrum of 11

^{1}H NMR Spectrum of 11:

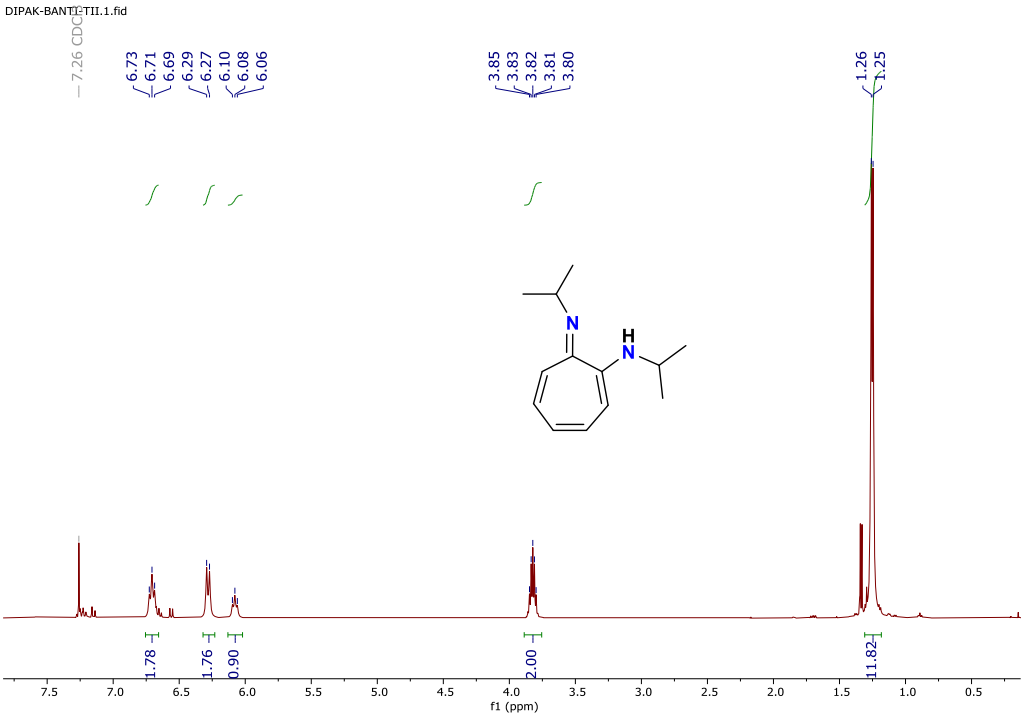


Figure 58: ^{1}H NMR Spectrum of 11

^{13}C NMR Spectrum of 11:

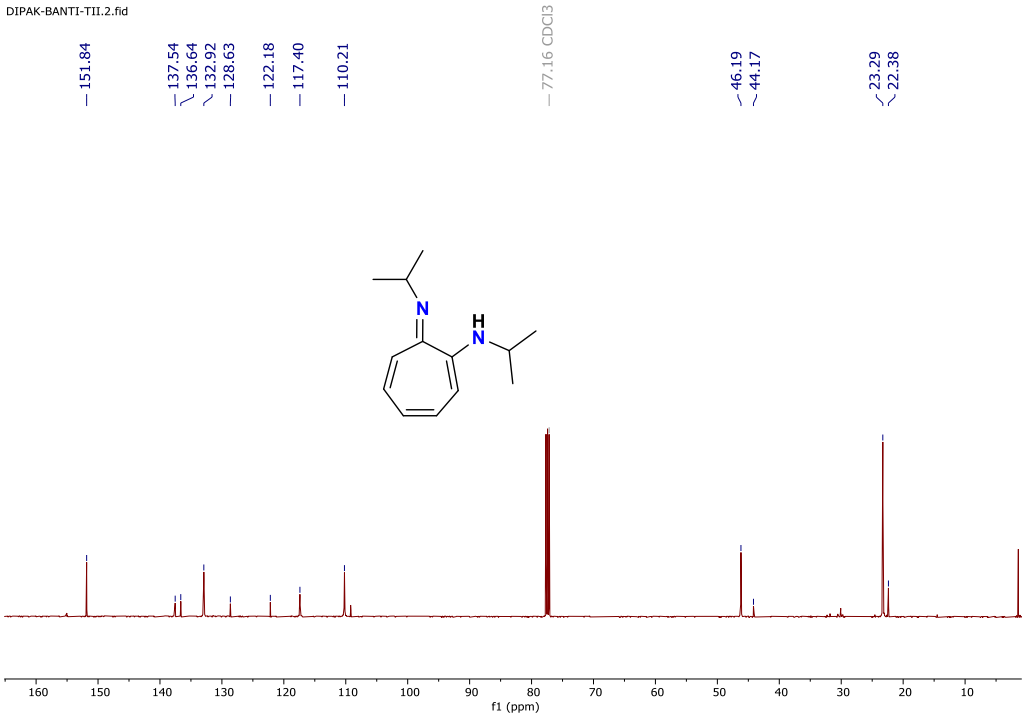


Figure 59: ^{13}C NMR Spectrum of 11

Mass spectra of 12:

LCMS m/z calculated for $C_{14}H_{22}N_2$, [M+H] is 219.1856, found 219.1987

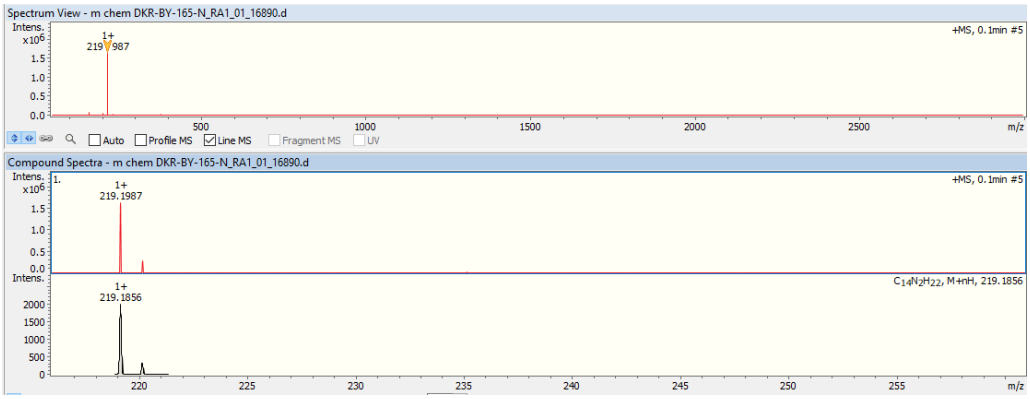


Figure 60: Mass Spectrum of 12

^{1}H NMR Spectrum of 12:

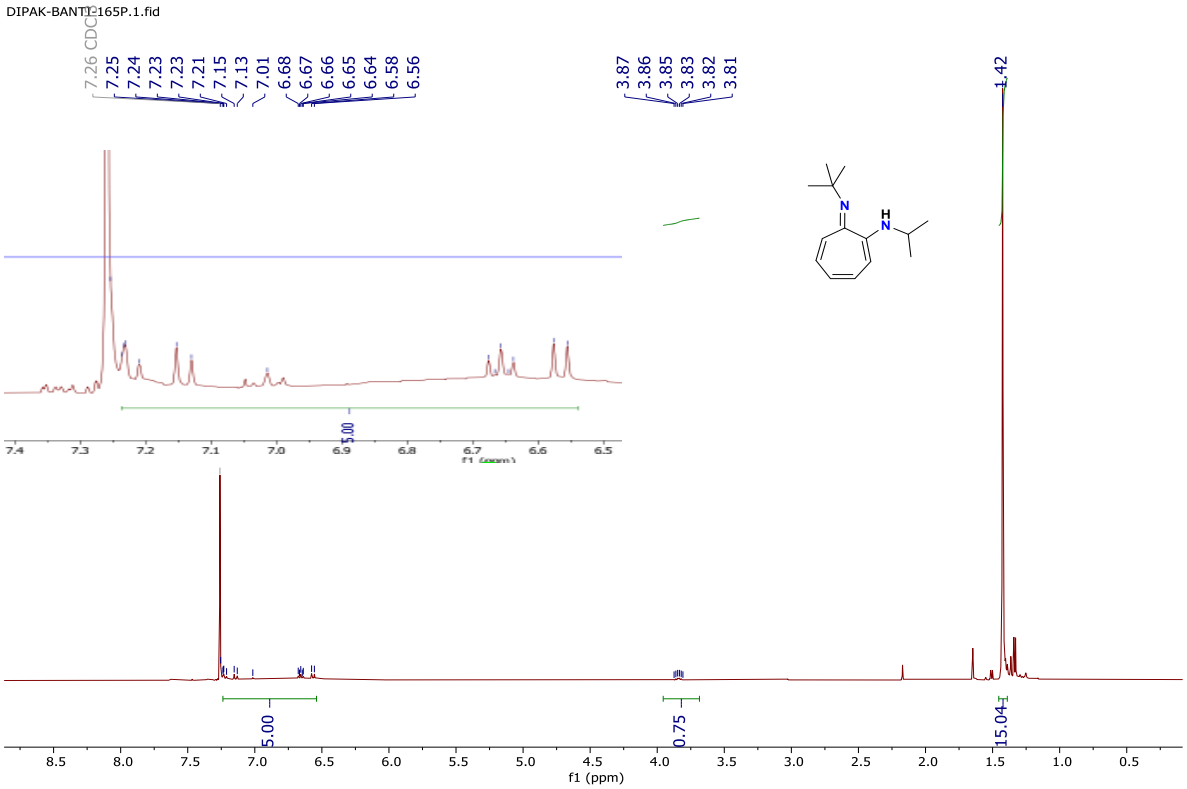


Figure 61: ^{1}H NMR Spectrum of 12

^{13}C NMR Spectrum of 12:

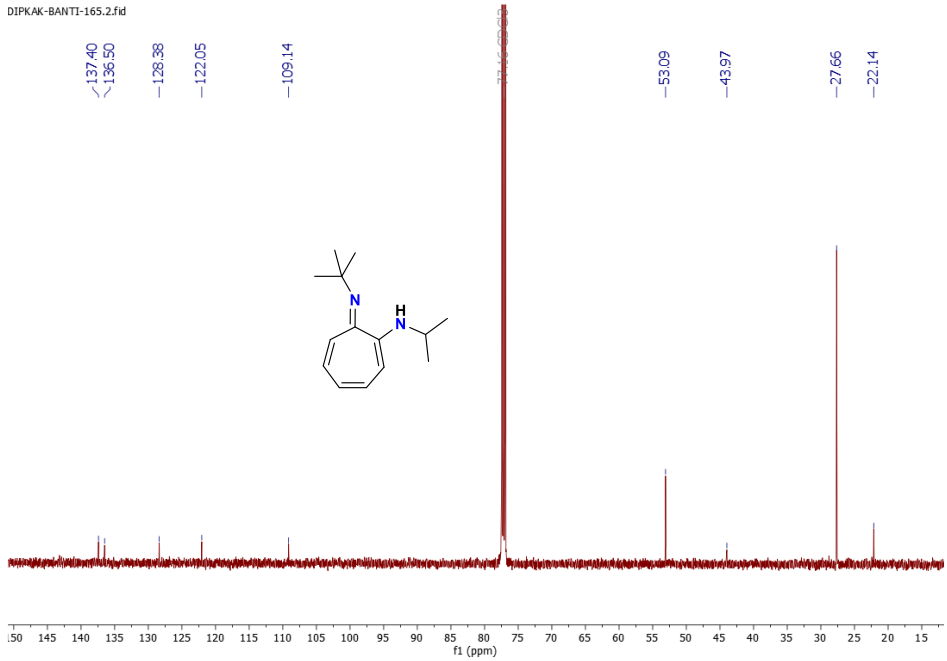


Figure 62: ^{13}C NMR Spectrum of 12

Mass Spectrum of 13:

LCMS m/z calculated for $C_{27}H_{36}N_2Cl_2Ge$, [M+H] is 533.1537, found 533.1273

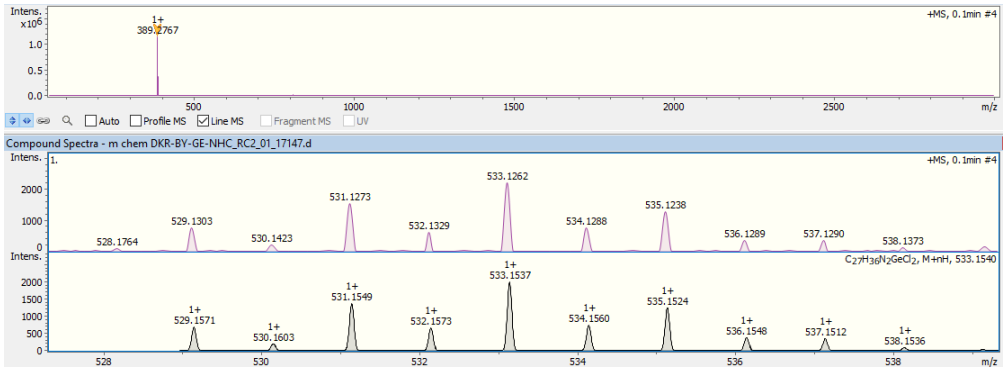


Figure 63: Mass Spectrum of 13

^{1}H NMR Spectrum of 13:

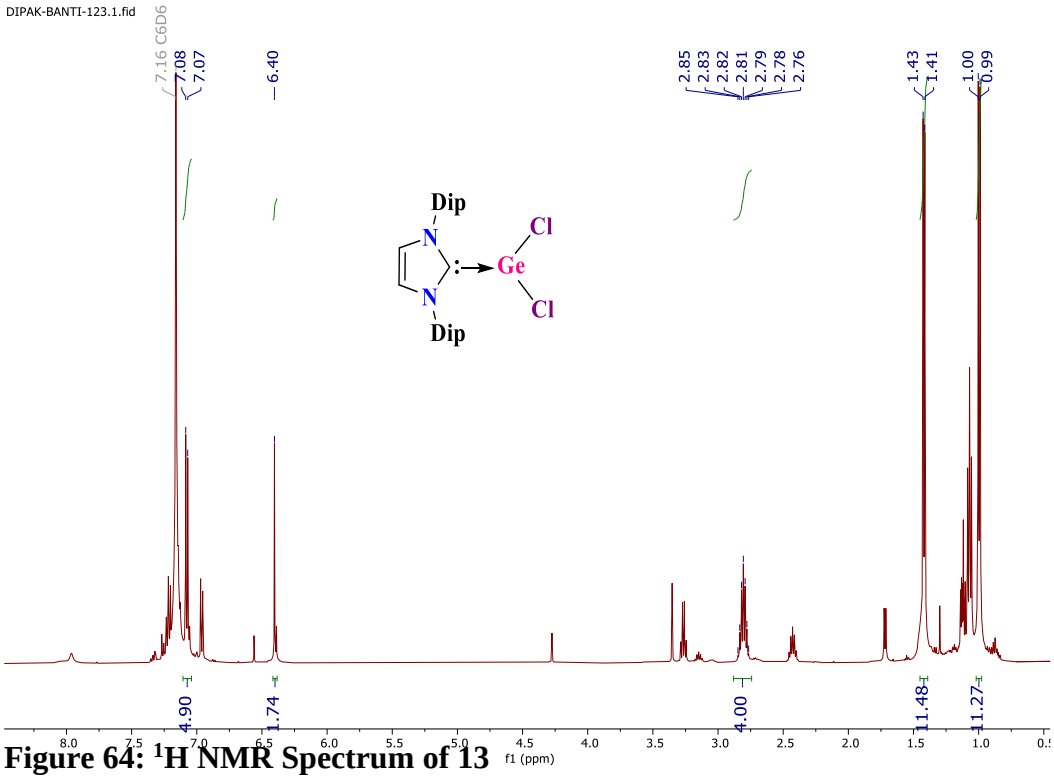


Figure 64: ^{1}H NMR Spectrum of 13

^{13}C NMR Spectrum of 13:

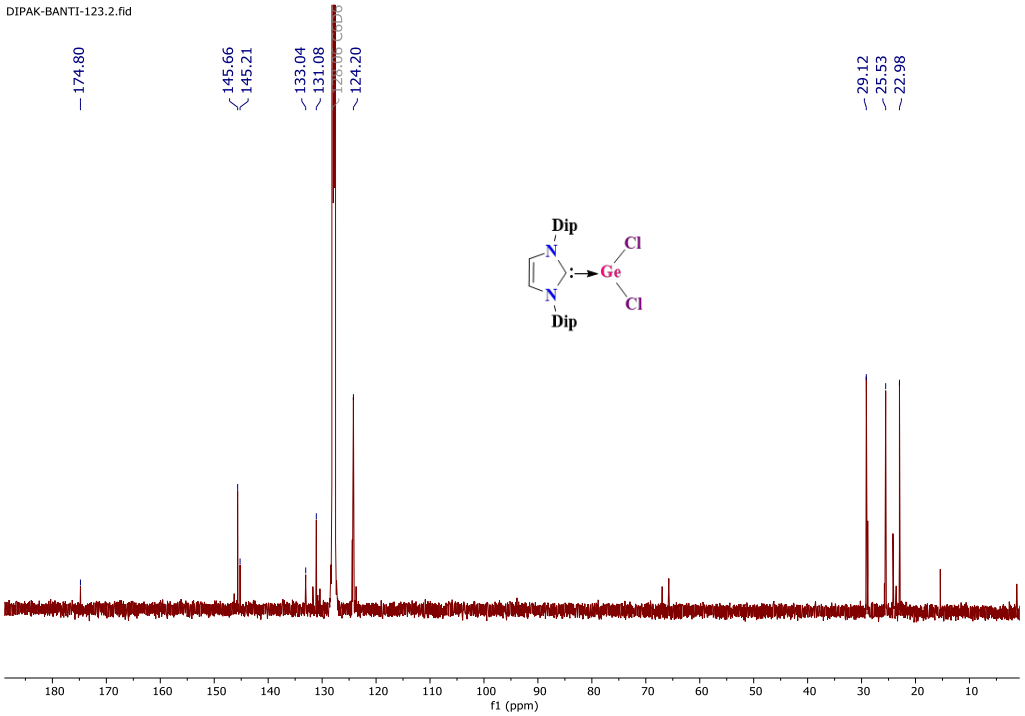


Figure 65: ^{13}C NMR Spectrum of 13

Mass Spectrum of 14:

LCMS m/z calculated for $C_{18}H_{36}N_6Cl_2Ge$, [M+Cl] is found 587.0491, found 587.5012

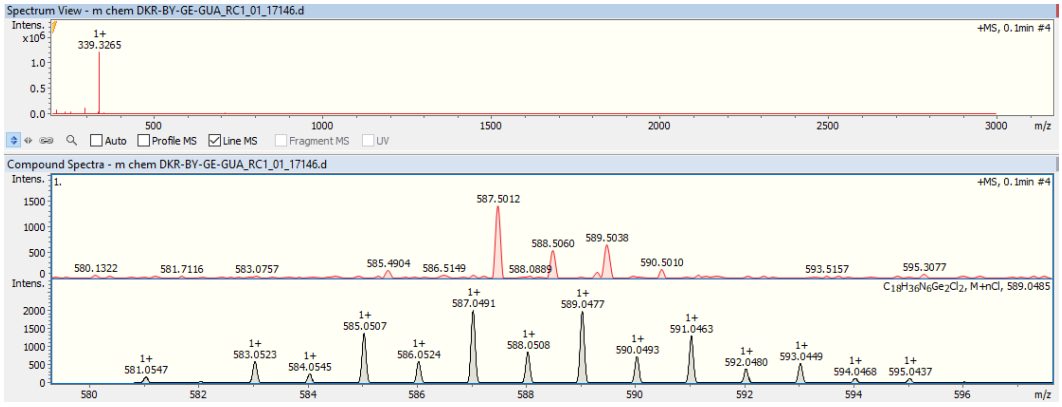


Figure 66: Mass Spectrum of 14

^{1}H NMR Spectrum of 14:

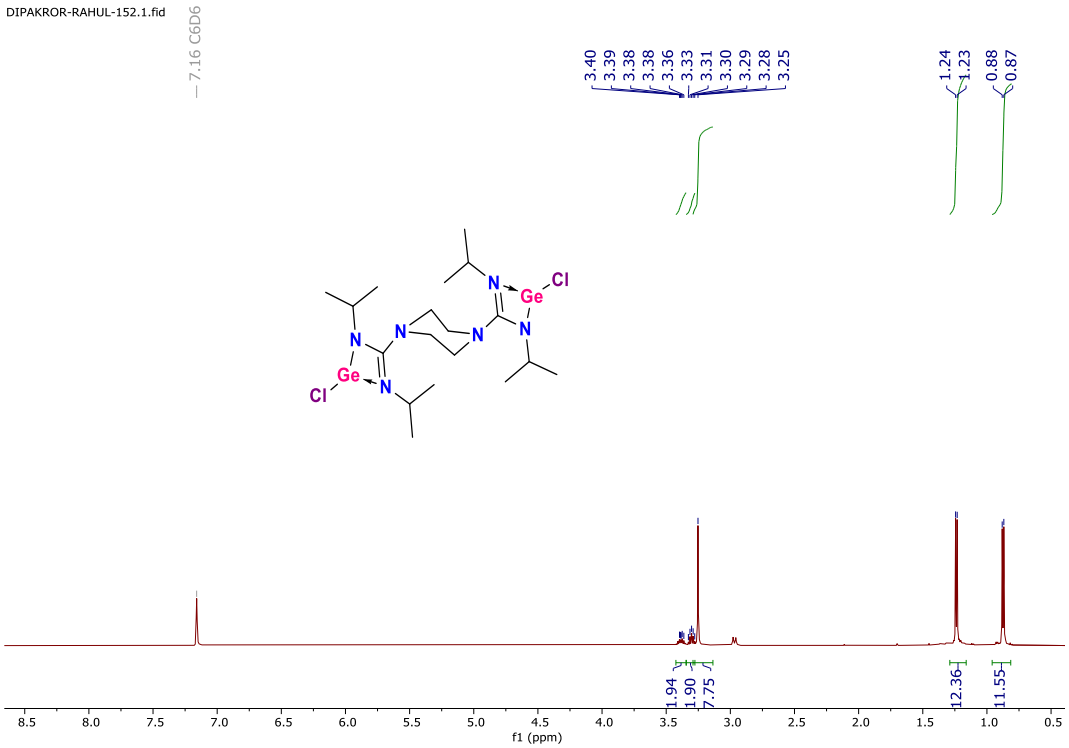


Figure 67: ^{1}H NMR Spectrum of 14

Mass Spectrum of 15:

LCMS m/z calculated for $C_{13}H_{19}N_2ClGe$, [M+H] is 311.0363, found 311.0781

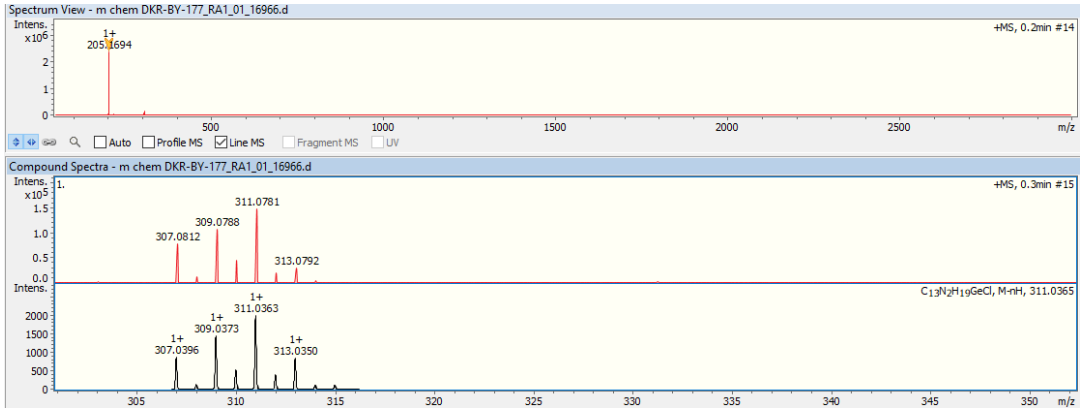


Figure 68: Mass Spectrum of 15

^{1}H NMR Spectrum of 15:

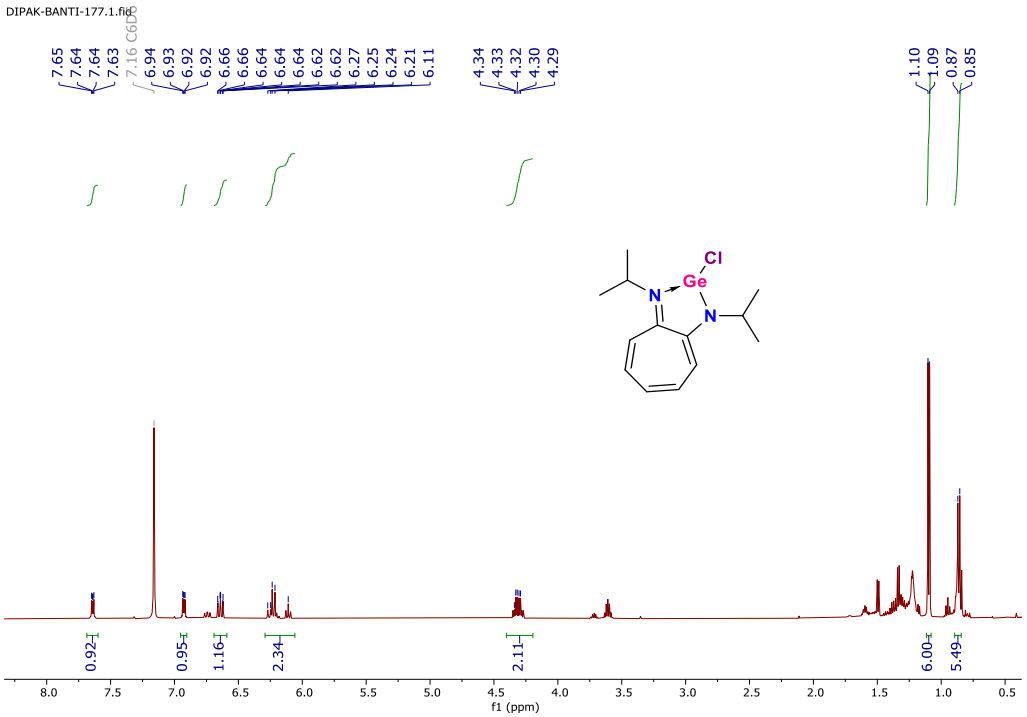


Figure 69: ^{1}H NMR Spectrum of 15

^{13}C NMR Spectrum of 15:

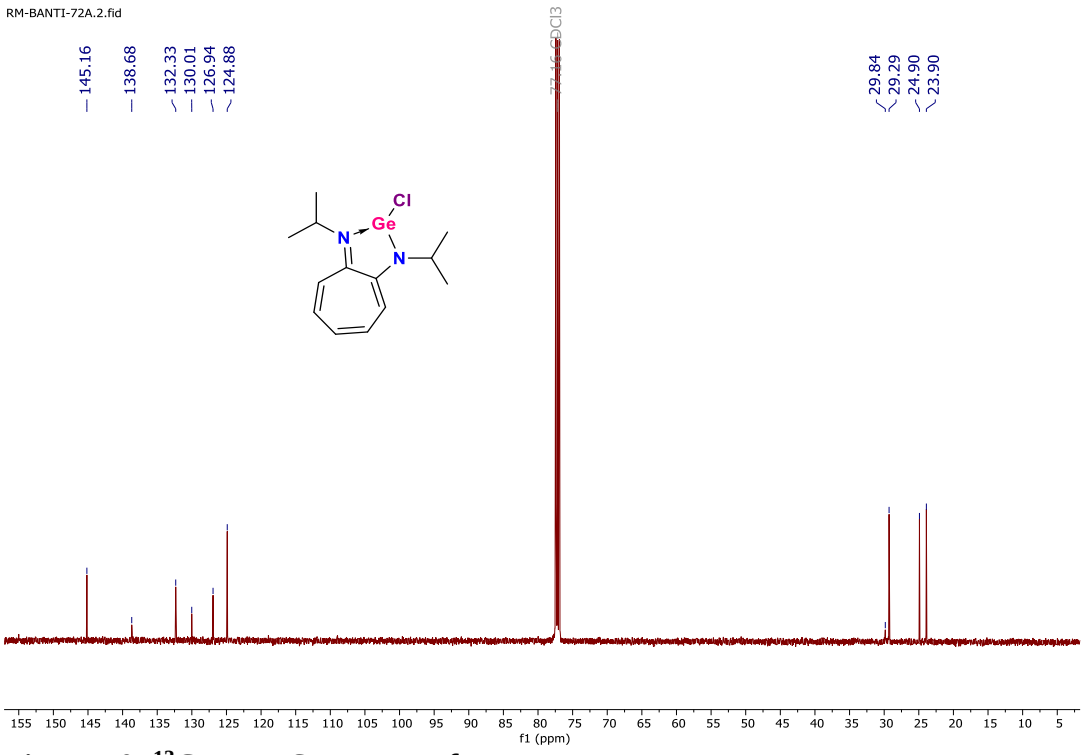


Figure 70: ^{13}C NMR Spectrum of 15

^{1}H NMR Spectrum of 16:

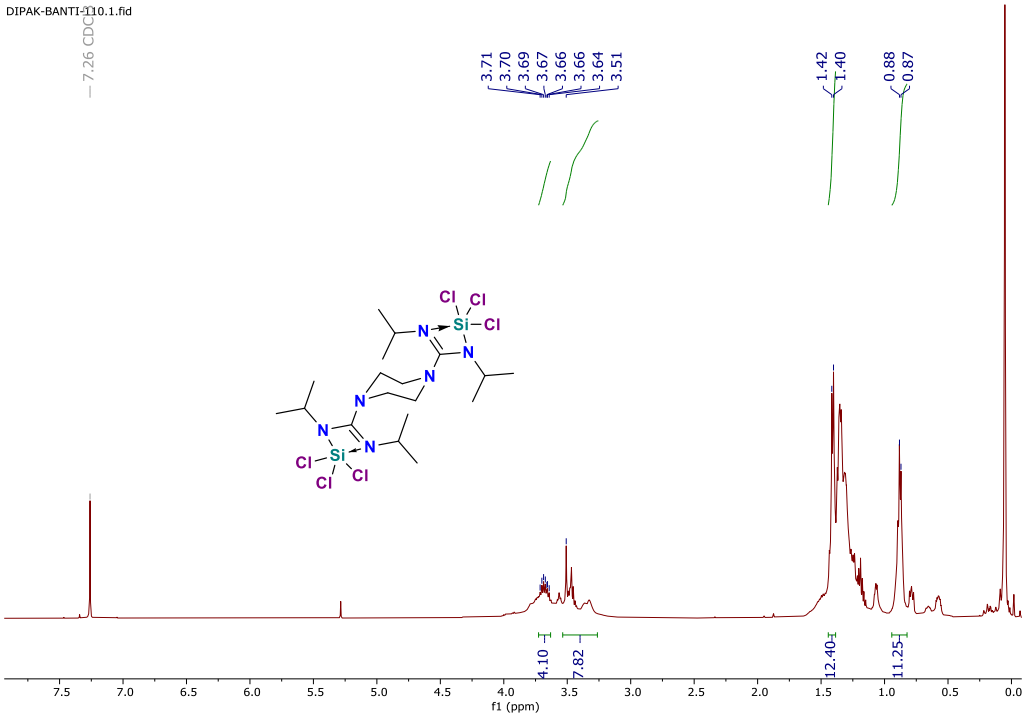


Figure 71: ^{1}H NMR Spectrum of 16

^{29}Si NMR Spectrum of 16:

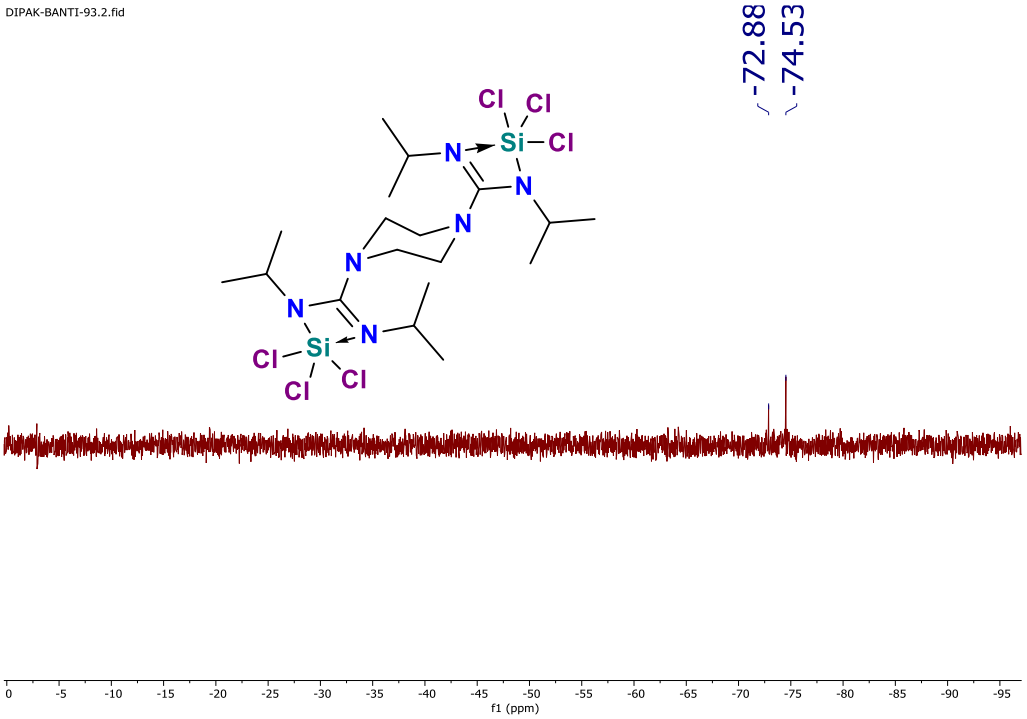


Figure 72: ^{29}Si NMR Spectrum of 16

^{13}C NMR Spectrum of 16:

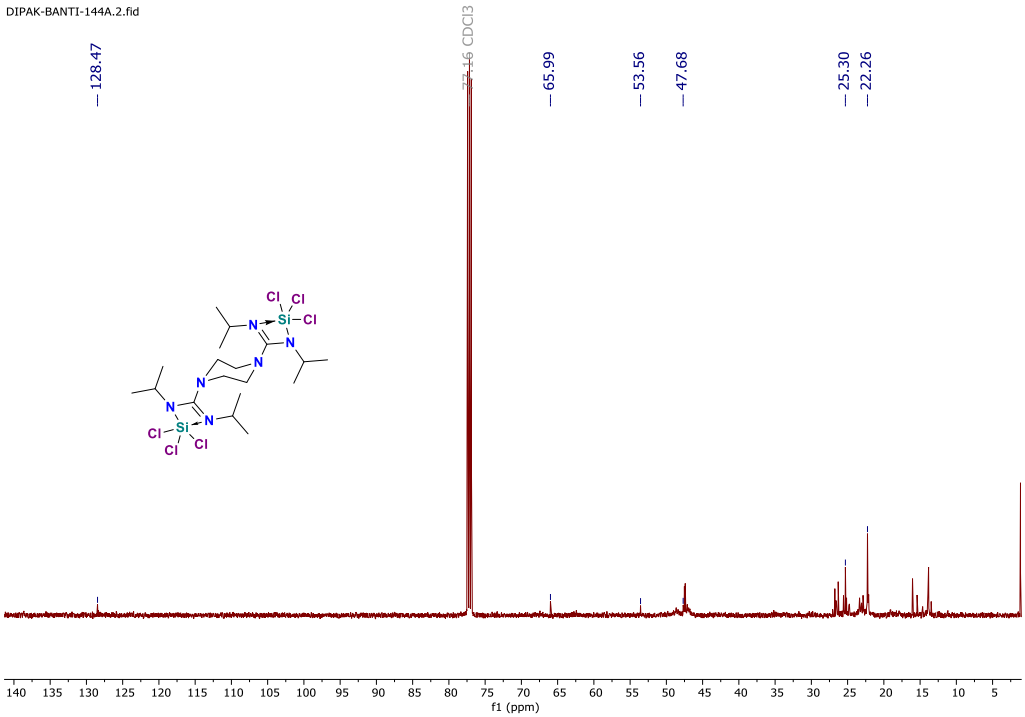


Figure 73: ^{13}C NMR Spectrum of 16

Chapter 4

Conclusion

We have synthesized different type of amidinates, guadinates and ATI based ligand which are well characterised by LCMS, NMR. These are monoanionic ligands inspite of these we have also synthesized some neutral ligands. We successfully synthesized NHCs, guadinate and ATI based group 14 complexes and well characterised by Mass, NMR techniques. Low valent group 14 complexes have wide range of application in activation of small molecules, catalytic hydroboation, cynosilylation and many more.

Outlook

In present time main group chemistry is the most fascinating filed of research in purpose of catalysis and small molecule activations. We are succeeded in synthesizing mono as well as bimetallic complexes of group 14 elements. Mono-metallic low valent complex has potential to catalyse the hydroboration, cynosilylation, silylation of alkene and aldehydes. We will study the cooperative effect of bisguadinate germylene in the activation of small molecules similarly transition metal complex. Low valent complexes show better coordination behaviour so we will also check binding potential of our synthesized complexes and its application in industrial and academic research prolific research.

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