Synthesis of N-Heterocyclic Carbene Adduct with BCl_3 and its Reactivity with Amines

And

Zn (II) complexes Bearing N, O-Chelate Ligands: Synthesis and Characterization

A Project Report

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By

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Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of **Dr. Tarun K. Panda**.

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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This thesis entitled **"Synthesis of N-Heterocyclic Carbene Adduct with BCl_3 and its Reactivity with Amines and Zn (II) complexes Bearing N, O-Chelate Ligands: Synthesis and Characterization"** by Ria Rana is approved for the degree of Master of Science from IIT Hyderabad.

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Dedicated to

My Beloved Parents

And

Respected Teachers

Contents

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Abstract

In the chapter 1 of my thesis I have described the synthesis of a Lewis adduct of 1, 3-bis (2, 6-diisopropylphenyl) imidazole-2-ylidine (Dipp-NHC) with boron trichloride. The reaction of Dipp-NHC and BCl_3 in equimolar ratio in toluene solution at room temperature for 24 h afforded the Lewis adduct Dipp-NHC•BCl_3 (**1**). The compound **1** was further treated with 2, 4, 6-trimethylaniline to afford *N*,*N*',*N*''-trismesitylboranetriamine [$B(NH(2,4,6\text{-}Me_3C_6H_2))_3$] (**2**) in good yield. The compound **2** was characterized by ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ NMR spectroscopy.

In the last part of my thesis which is in chapter 2, 4-(N-2,4,6-trimethylphenylimino)pentan-2-one ligand (**3**) and 4-(2,6-diiisopropylphenyl)amino-3-penten-2-one ligand AcNac (**4**) [$CH_3C(O)CHC(NAr)CH_3$, Ar = 2,4,6-$Me_3C_6H_2$ = Mes (**3**) and 2, 6-$^iPr_2C_6H_3$ (**4**)] were synthesized by the reaction of acetyl acetone and 2, 4, 6-trimethylaniline and 2, 6-diiisopropylaniline respectively in 1:1 molar ratio in methanol and at a temperature of 60 °C under refluxing condition for 3 days. Then we have synthesized and determined the structure of Zinc complex of molecular formula Zn $[R_1COCHC(NAr)R_2]_2$ [Ar = 2, 4, 6-$Me_3C_6H_2$, and $R_1 = R_2 = CH_3$] (**3**), which was obtained by using **3** and $ZnEt_2$ in toluene solution and at a temperature of 90 °C for 12 h. The complex was characterized by FTIR, ^1H, $^{13}C\{^1H\}$NMR spectroscopy. Also we have synthesized the Zinc complex having formula $ZnBr_2$ $[R_1COCHC(NAr)R_2]$ Ar = 2, 6-$^iPr_2C_6H_3$, and $R_1 = R_2 = CH_3$] by using ligand **4** and $ZnBr_2$ in dichloromethane. These complexes were characterized by FTIR, ^1H, $^{13}C\{^1H\}$NMR spectroscopy.

Chapter-1: Synthesis of N-heterocyclic carbene adduct with BCl_3 and its reactivity with amine:

1. **Introduction:**

At the end of the 19th century, it was found that the nitrogen-donor ligands played an important role ever since the earliest developments in the field of co-ordination chemistry. N-heterocyclic carbenes are the cyclic carbenes which are attached with α-amino substituents.

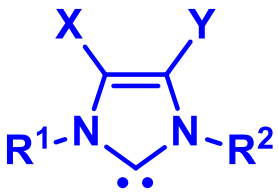
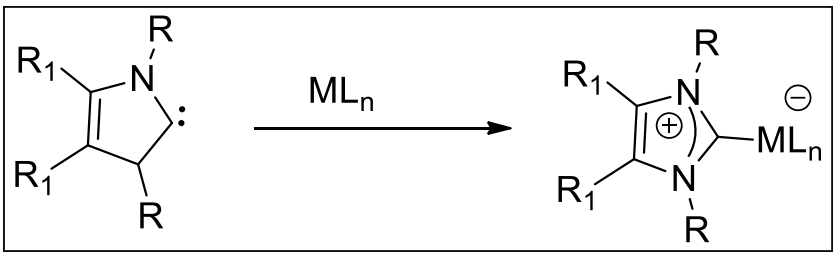


Fig 1: N-heterocyclic carbene where R^1 and R^2 denotes α-amino substituents

Since the first reveal of their evidence, carbene played a crucial role in organic chemistry. In early chemistry of the laboratory interest carbene was established by Skell in the 1950s. [1] In 1964, Fisher et al. first introduced carbene into the inorganic and the organometallic chemistry. [2] In macro molecular chemistry, organic synthesis and catalysis, metal carbenes have become more significant. [3-6] The chemistry of N-heterocyclic carbenes (NHCs) has been limited to metal-coordination compounds which were derived from azolium precursors, which was first introduced by öfele [7] and Wanzlick [8] in 1968. Through the work of A. J. Arduengo (III) in the early 1991s, free carbenes are now available. [9] A seminal report on the structural characterisation of the imidazolin-2-ylidine (Im) and its isolation by Aduengo, had set the ground for another important scientific discovery, since Im and other N-heterocyclic carbenes (NHCs) have immediately become essential to the development of various research areas. [10-12]

N-heterocyclic carbenes (NHCs), as a distinctive type of carbon-based ligand, have been extensively applied in transition metal chemistry. [13]The implementation of N-heterocyclic carbenes (NHCs) as strong σ-donors, but weak π-acceptors has generated interesting reactivity and NHCs have tunable steric properties. [14] For these electronic and structural features of NHCs, the complexes of them show unique reactivity. It was found that N-heterocyclic carbenes are used in early to mid-first-row transition metal Chemistry as supporting ligands for its large number of application from small molecule activation [15] to catalysts [16] and biomimetic chemistry. [17-20] It is due to its strong σ-donating and weak π-accepting properties of NHCs these have generated major advancements in homogeneous catalysts. [21] These carbenes show strong electron-donating capacity and high nucleophilicity. For this reason these carbenes can be ascribed to the capability of the imidazolium ring to effectively stabilise a positive charge. So there is the Imidazolium-type resonance structure upon metal co-ordination and therefore there is a formation of the complexes of type (Im)ML_n (Scheme 1). It is due to the increase of negative charge, basicity and nucleophilicity of the compounds-formed. [22]



Scheme 1. Formation of imidazolin-2-ylidine complexes.

In very few cases, the use of NHCs in supporting group 13 elements for example boron, is limited. [23-25]

Evidently, the structure and reactivity studies in these complexes may have created a new aspect into future catalysis, material, and medicinal applications. The effective concept of frustrated Lewis pairs has spread great interest in the use of bulky NHC-B(C_6F_5)$_3$ for hydrogen activation. [24] Seminal works by Fensterbank, Lacôte, Malacria and Curran have demonstrated NHC boranes which are nontoxic and these are stable radical hydrogen atom donors. [25] It was found that these NHC-boranes are efficient co-initiators for radical acylate photopolymerisation. [26] In particular secondary amino-NHC, examples of the use of functional NHC ligands for boron, appear to be non-existent inspite of the extensive use of these functionalized ligands in transition metals. [27]

In the synthesis and reactivity of various Lewis acids, the intrinsic electron deficiency of boron including others group 13 elements plays a major role. [28]Generally, one of the most encouraging approaches to further increase the Lewis acidic properties of compound was to prepare related cationic or polycationic complexes. Monocationic species are well-developed with respect to boron. These type of species are classified on the basis of the coordination number and named as borinium, borenium and bironium. [29]

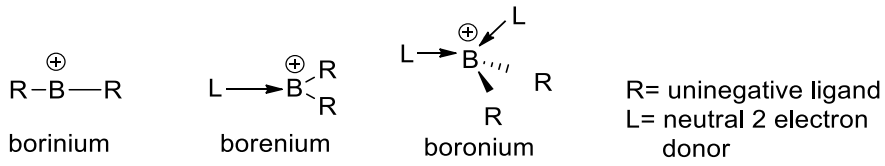
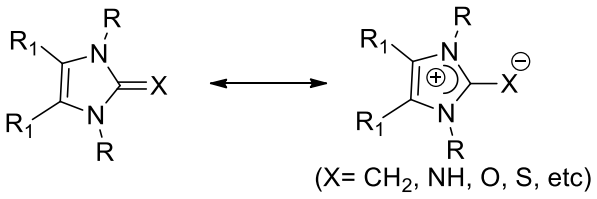


Fig 2: Different borocations

Previously, our group has reported on the metal-borane complexes.[30] These are also termed as "metallaboratranes". Several research groups developed a wide range of structural design.[31-33] Besides this boron chemistry we have curious to develop the [NHC→BCl_3] adduct [NHC = (R'C)$_2$(NR)$_2$C; R = ^{i}Pr, R$^{'}$ = H) and its amine derivative.

2. Scope of work:

In recent study of various kinds of N-heterocyclic carbenes (NHCs) are known to stabilize a positive charge and formation of the complexes of type (Im)ML_n. The strong electron donating capacity and high neucleophilicity of these carbenes was also applied to organic imidazolium derivatives, Imx, containing an exocyclic atom or organic moiety X which is attached at the 2-position of N-heterocycle.



Scheme 2: Resonance structure of imidazole-based ligands

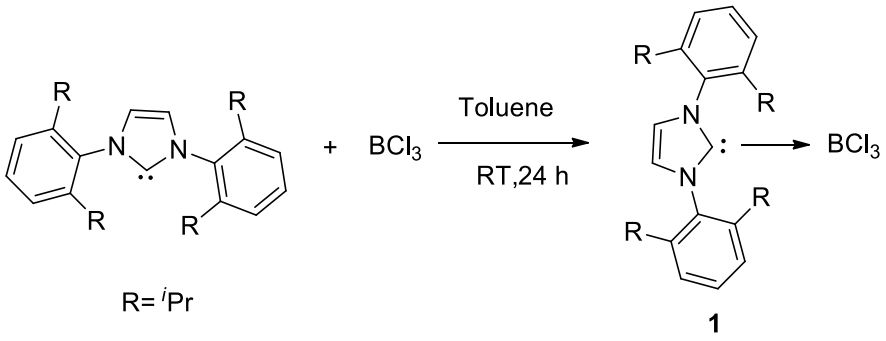
Now a days in inorganic research, transition-metal imido chemistry is one of the essential areas. It is because they play an important role in industrial, numerous biological and catalytic process. Also, metal-imido group has an ability to undergo metathesis, C-H bond activation, cycloaddition, and hyrdroamination reaction.

Our aim is to synthesis the carbene-boron trichloride adduct and also to check the reactivity of this adduct to various kind of amines. Such kind of compounds show different catalytic, material and medicinal applications.

3. Results and Discussion:

3.1. Synthesis of BCl_3 adduct of 1, 3-bis (2, 6-diisopropylphenyl) imidazol-2-ylidine:

As part of our interest in the N-heterocyclic carbene chemistry, we attempted the reaction of equivalent amount of 1, 3-bis (2, 6-diisopropylphenyl) imidazol-2-ylidine with BCl_3. The 1, 3-bis (2, 6-diiisopropylphenyl) imidazol-2-ylidine was prepared according to the published procedure. The synthesis of the BCl_3 adduct of 1, 3-bis (2, 6-diisopropylphenyl) imidazol-2-ylidine can be achieved by the treatment of NHC [NHC= $(HC)_2(NR)_2C$; R=^{i}Pr, R$^{'}$=H] with BCl_3 in toluene at ambient temperature (Scheme-**2**). The compound **1** was characterised by analytical/spectroscopic techniques.



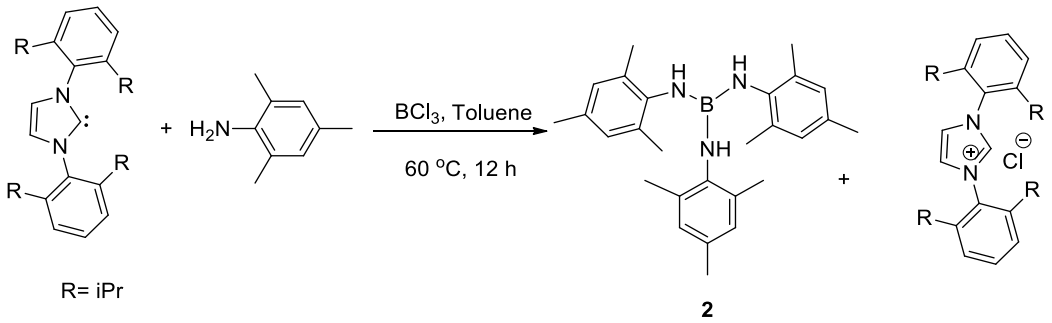
Scheme 3. Preparation of NHC adduct with BCl_3

In ^{1}H NMR spectra, the triplet signal at δ = 7.18-7.22 ppm can be assigned for the two para proton and the doublet signal at δ = 7.04-7.06 ppm can be assigned to the four ortho proton of aromatic ring. Additionally, complex **1** shows one singlet at δ = 6.32 ppm for the resonances of two olefinic protons present in the imidazole backbone. A septet signal is observed at δ = 2.93 ppm for CH

proton of isopropyl group which indicates that the presence of tertiary carbon on the aromatic ring. The two doublets in 1:1 ratio are observed at δ = 0.98 ppm and 1.41 ppm for CH_3 protons of isopropyl moiety in the aromatic ring, but they are slightly at different region due to having different chemical environments. In $^{13}C\{^1H\}$ NMR spectra, the resonance signals observed at δ = 29.5 and 25.5 ppm indicate the carbon atoms of CH_3 group of isopropyl moiety. The signal observed at δ = 124.3 ppm indicates the two olefinic carbon present in the imidazole backbone and the signal at δ = 127 ppm indicates the aromatic carbon with isopropyl moiety. The resonance signal which is observed at δ = 145.4 ppm indicating the aromatic carbon attached with imidazole moiety. In $^{11}B\ \{^1H\}$ NMR spectra, in complex **1**, shows only one signal which is observed at δ = 2.1 ppm representing one Boron atom present in the molecule.

3.2. Synthesis of *N,N′,N″*-trimesitylboranetriamine:

N,N′,N″-trimesitylboranetriamine (**2**) was prepared successfully by the reaction of NHC→BCl_3 adduct with 2, 4, 6-trimethylaniline in toluene at 60 °C (**Scheme 3**).



Scheme 4. Synthesis of *N,N′,N″*-trimesitylboranetriamine (**2**)

In ^{1}H NMR spectra, the multiplet signals at δ = 7.10-7.15 ppm can be assigned for the six meta proton of aromatic ring. Additionally, complex **2** shows one broad singlet at δ = 3.10 ppm which clearly indicate the formation of three NH group in the product. A singlet signal is observed at δ = 2.19 ppm for eighteen *o*-methyl proton which indicates that the presence of methyl carbon on the aromatic ring. Also, in the spectra we get one singlet at δ = 1.91 ppm which can be assigned for the nine proton of the *p*-methyl group. In ^{13}C{^{1}H}NMR spectra, the signal observed at δ = 17.6 ppm and 21.4 ppm indicating the carbon atoms of methyl group present in the ortho and para position of the compound **2** respectively. The resonance signals at δ = 128.5 ppm and 129.3 ppm indicate the *o* and *m*-carbon of aromatic ring respectively. The peak observed at δ = 133.5 ppm indicates the aromatic carbon of *p*-position. The signal at δ = 145.5 ppm indicating the aromatic carbon attached with NH group. In ^{11}B{^{1}H}NMR spectra, in compound **2** shows only one signal which is observed at δ = 2.1 ppm representing one boron atom present in the molecule.

4. Experimental section:

4.1. General Information

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware, either on a dual manifold Schlenk line interfaced with a high vacuum (10^{-4} torr) line or in an argon-filled M. Braun glove box. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$ and stored in the glove box. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H}NMR (100 MHz) spectra were recorded on a BRUKER ADVANCE III-400 spectrometer. A BRUKER ALPHA FT-IR was used for the FT-IR measurements. Elemental analysis were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. Dipp-Carbenes were prepared according to the published

procedure. 2, 6-diisopropylaniline, 2, 4, 6-trimethylaniline, and trimethylsilylchloride were purchased from Alfa Aesar and used as received. The Boron trichloride and the NMR solvents C_6D_6 was purchased from Sigma Aldrich and dried by Na/K alloy prior to use.

4.2. Preparation of the BCl_3 adduct of 1, 3-bis (2, 6-diisopropylphenyl) imidazole- 2-ylidine (1):

In a 25 ml of dry schlenk flask, 1, 3-bis (2, 6-diisopropylphenyl) imidazole-2-ylidine (0.3 g, 0.77 mmol in toluene) was taken and BCl_3 (0.067 mL, 0.77 mmol) were added to it via syringe under N_2. The reaction mixture was stirred for 24 h at room temperature. After filtration the solution was evaporated to afford the Boron adduct as a white solid. Yield: 0.25g (63%).

^{1}H NMR (400 MHz, C_6D_6): δ = 7.04-7.06 (d, 4H, Ar-*H*), 7.18-7.22 (t, 2H, Ar-*H*), 6.32(s, 2H, NC*H*=C*H*N), 2.11(s, 1H, C*H* $(CH_3)_2$), 1.40-1.41(d, 12H, CH $(CH_3)_2$), 0.97-0.98(d, 12H, CH $(CH_3)_2$). ^{13}C{^{1}H}NMR (C_6D_6, 100 MHz): δ = 145.4 (Ar-*C*-N), 134.8 (*o*-phenyl), 130.8 (*m*-phenyl), 127.9 (*p*-phenyl), 124.3 (N*C*H=C*H*N), 29.4 (*C*H $(CH_3)_2$), 25.5 (CH $(CH_3)_2$), 22.6 (CH $(CH_3)_2$) ppm. ^{11}B{^{1}H}NMR (128.4 MHz, C_6D_6): δ = 2.1 ppm.

4.3. Preparation of *N,N′,N″*-trimesitylboranetriamine (2):

In a 25 ml of dry schlenk flask, Dipp carbene (0.3 g, 77 mmol in toluene) was taken. BCl_3 (0.068 mL, 77 mmol) and Mesityl amine (1.16 mL, 77 mmol) were added to the solution via a syringe under inert atmosphere. The reaction mixture was stirred for 12 h at room temperature. Then it was also stirred for 6 h at 40^{o}C. After filtration the solution was evaporated to afford the product as a white solid. Yield: 0.18 g (66%).

^{1}H NMR (400 MHz, C_6D_6): δ = 7.10-7.15 (m, 6H, Ar-*H*), 3.10 (s, 3H, N*H*), 2.19 (s, 18H, Ar-*H*), 1.91 (s, 9H, Ar-*H*); ^{13}C{^{1}H}NMR (C_6D_6, 100 MHz): δ= 145.5 (HN-*C*), 133.5 (*p*-phenyl), 129.3 (*m*-phenyl), 128.5 (*o*-phenyl), 21.4 (*o*-CH_3), 17.6 (*p*-CH_3); ^{11}B{^{1}H}NMR (128.4 MHz, $CDCl_3$): δ = 2.1 ppm.

5. **Conclusion:**

In conclusion, we report the straight forward synthesis of the BCl_3 adduct of 1, 3-bis (2, 6-diisopropylphenyl) imidazol-2-ylidine (**1**). With this adduct we have successfully prepared *N*,*N*′,*N*″-trimesitylboranetriamine (**2**) which was spectroscopically characterised by the NMR.

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Chapter 2: Synthesis and characterisation of Zn (II) and Al (III) complexes supported by N, O-Donor ligands:

7. Introduction:

The Lewis bases that donate its two pair ("bi") of electrons to a metal atom are called bidentate ligands. As these ligands can "grab" a metal atom in two places, they are often referred to as chelating ligands (the word "chelate" is derived from the Greek word "claw").

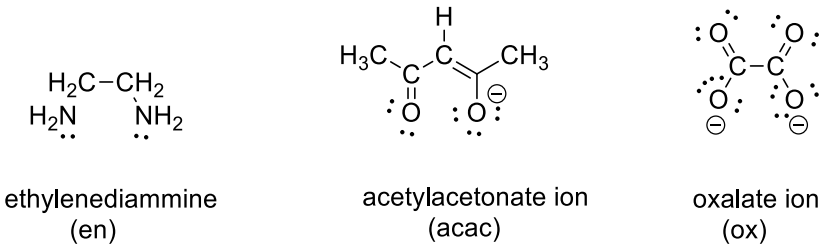


Fig 3: Some bidentate ligands

Acac is an example of bidentate ligand. This can exists in two tautomeric forms and that forms interconvert rapidly. [1-2] For this reason in most of applications, these are treated as a single compound.

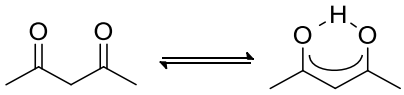


Fig 4: Tautomeric structure of acac

The colourless liquid, acetylacetone, is a precursor of acac (acetylacetonate). For the synthesis of heterocyclic compounds acac can act as building block. When one of oxygen -atom of acac is replaced by Nitrogen atom, then this kind of ligand is called AcNac ligand. Although the compound is formally named as AcNac ligand, they are often called β-ketoiminate ligands.

In the area of coordination and organometallic chemistry, the development of β-diiminate (Nacnac) was a turning point (Figure 3). [3] NacNac ligands are superior to the Acac ligands and it is due to Steric as well as electronic properties which can be readily turned and it is essential for the stabilisation of complexes that shows unexpected photochemical properties, coordination numbers, Oxidation states, bonds, geometry, or reactivity. [4-5]

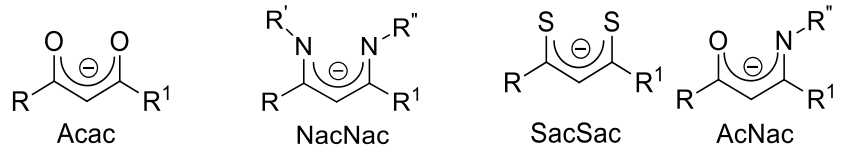


Fig 5: *β*-Diketonate (Acac), *β*-diiminate (NacNac), *β*-ketoiminate (AcNac), *β*-dithioketonate (SacSac), *β*-ketophosphenate (AcPac), and *β*-thioketiiminate (SacNac) ligand.

The organometallics complexes of *β*-dithionate ligands (SacSac) and also its coordination complexes have been revealed in literature. [6] But the attention has been pointed towards the design of hybrid ligands which contained chemical functionalities of 2-different types. The extensive majority of these bidentate ligands containing only hard donor atoms, oxygen and nitrogen. Most of the *β*-ketoiminate ligands (AcNac) supplies thermal and kinetic stability for their application in catalysis. [7] Besides, in this type of single ligands, hard and soft donor atoms are combined and therefore resulting of hybrid ligands which have attracted remarkable interest in this field. [8]

It is very difficult to handle early transition metal complexes and they are conflicting with polar monomers because of their high oxophilicity and they have tendency for functionalities to coordinate with the active species. There are a few examples where polar vinyl monomer shows vinyl polymerisation [9-10]. Though the possibilities are limited but is was shown that some early transition metals polymerised olefins with distant polar groups [11-14]. The oxophilicity of the late

transition metal catalysts are less than their early transition metals and also they are not poisoned potentially by polar functionalities containing O [15-16].

Recently, due to the polymerisation of polar olefins and α-olefins, there is increasing interest in the development of late transition metal based complexes which can be used as catalysts [17-22]. O-R (where R is S or N) types of ligands are particularly interesting and these ligands are also subsequently interesting to the catalytic systems of mixed ligand complex [23-24]. These are the very useful catalysts in polar olefin and α-olefin polymerisation. Nickel-based systems are the examples of it. Different heterodonor ligands stabilised the late transition metals and therefore there is a formation of mono- or dinuclear complexes having various coordination modes [25-27]. Bimetallic systems are of considerable interest as complexes having 2 metal centres catalyses the polar olefins more effectively than the analogous monometallic species [28-32].

Our group's work focused towards the investigation of synthetic methodologies which allow to a facile, clean, high yield production of the molecules and also determination of the molecular structure and function. In our group, we have synthesised some N, O-chelating ligand and some NacNac ligands and their complexes with metals. Besides, we also introduced some more metal complexes of N, O-chelating ligands. These ligands play an important role in coordination chemistry and also in organotransition metal chemistry. We have prepared the Zn (II) and Al (III) complexes of AcNac ligands. These complexes are expected to be interesting for Lewis acid catalysis, Olefin polymerisation, and they have other potential applications. [33]

8. Scope of work:

In recent study of various kinds of *β*-kitoiminate ligands (AcNac) are known to stabilize a large number of transition metal ions by their different coordination modes. These kind of ligands has proven to be flexible ligands both in the coordination chemistry and catalysis. The *β*-ketoiminate ligands has widespread applications in catalysis. Our group have already done some synthesis of *β*-kitoiminates (AcNac) and *β*-diiminate (NacNac) ligand system and the metal complexes of $ZnCl_2$ and ZnI_2 complexes with some AcNac and NacNac ligand systems. Now our aim is to synthesise some different kind of AcNac ligand system. The examples of our target ligands are shown below.

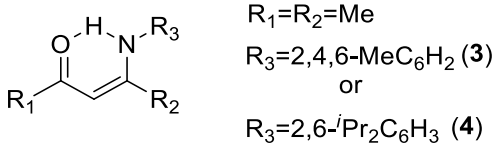


Figure 6. AcNac ligands 4-(N-2, 4, 6-trimethylphenylimino) pentan-2-one (**3**) and 4-(2, 6-diisopropylphenyl) amino-3-penten-2-one (**4**)

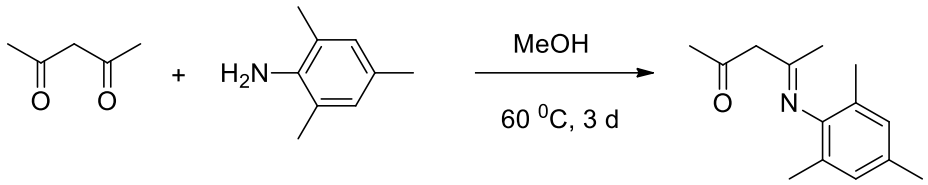
Also our aim is to show that AcNac ligand **3** can form metal complexes of Et_2Zn and ligand **4** can form metal complexes with $ZnBr_2$ and then attempt to isolate these complexes.

These AcNac complexes are interesting compounds in catalytic activity because they contain two different donor atoms (nitrogen and oxygen) with the same chelating ligand.

9. Results and Discussion:

9.1. Synthesis of 4-(N-2, 4, 6-trimethylphenylimino) pentan-2-one ligand (3):

The synthesis of ligand **3** can be achieved by the treatment of 2, 4-pentanedione in methanol with 2, 4, 6-trimethylaniline in presence of acetic acid under refluxing condition at 60 ˚C for 3 days (**Scheme-5**). The ligand **3** was characterised by analytical/spectroscopic techniques.



Scheme 5. Preparation of 4-(N-2, 4, 6-trimethylphenylimino) pentan-2-one.

The structure of the ligand was determined by single crystal X-ray diffraction analysis. In ^{1}H NMR spectrum of ligand **3**, the singlet signal at δ= 1.61 ppm and can be assigned for the three methyl protons adjacent to C=O group and the resonance signal at δ= 2.27 ppm can be assigned for the three methyl protons adjacent to the C-NH group. The methyl protons adjacent to the C=O group is more deshielded than the protons adjacent to the (C-NH) group. For this reason, the chemical shift value of the methyl proton adjacent to C=O group is higher than that of the protons adjacent to the C-NH group. The strong singlets obtained at δ=2.15 ppm and δ=2.09 ppm for *o*-methyl proton and p-methyl protons of Mesityl group present in ligand **3**. The *o*-methyl protons are more deshielded and hence their chemical shift values are higher than the *p*-methyl protons. The medium singlet signal obtained at δ= 5.19 ppm indicating the protons of (CH=CN) group present in the ligand **3**. The absorption at δ= 6.89 ppm indicating the aromatic protons. A broad singlet absorbed at δ= 11.86 ppm is for NH proton which indicates that the NH proton is more deshielded. In ^{13}C{^{1}H} NMR Spectra of ligand **3**, peaks at δ=18.1 ppm and at δ= 20.9 ppm are for *o* and *p*-methyl

carbon of Mesityl group present in the ligand **3** respectively. The *p*-methyl carbon is more deshielded than the ortho one and hence its chemical shift value is higher than the p-methyl carbon. The peaks at δ= 18.8 ppm and δ= 28.3 ppm indicate the carbon atom adjacent to C-N group and C=O respectively. The carbon atom adjacent to C=O group is more deshielded than the latter one. The resonance at δ= 97.8 ppm is for *C*H=CN carbon. The resonance at δ= 128.9 ppm and δ= 133.9 ppm indicating the *o* and *p* carbon of aromatic ring respectively. The peak at δ= 137 ppm is for aromatic carbon attached with NH group. This carbon atom is more deshieled than other ones due to its attachment with NH group. The peaks at δ= 163.2 ppm and δ= 196 ppm indicate for the carbon atoms attached with NH group and C=O group respectively.

The solid-state structure of the ligand **3** is established by single crystal X-ray diffraction analysis. Ligand **3** crystallizes in the monoclinic space group $P2_1/n$ having 3 independent molecules in the unit cell. The C4-N1 bond length is 1.340(4) (Å) which is in the range of reported value of C=N (1.35-1.15 (Å)). The C3- C4- N1 bond angle is 122.0° (3) and C5-C4-N1 bond angle is 117.5° (3). The details of structural parameter is given below in the **Table 1.**

Table 1. Crystallographic data for ligand **3**.

Crystal	**3**
Empirical formula	$C_{20}H_{20}NO$
Formula weight	290.37
T (K)	293(2)
λ (Å)	1.54184
Crystal system	monoclinic
Space group	$P2_1/n$

a (Å)	10.1929(5)
b (Å)	10.0202(7)
c (Å)	12.8216(9)
α (^{o})	90.00
β(◦)	98.691(5)
γ(^{o})	90.00
V (Å^3)	1294.50(14)
Z	3
D_{calc} g cm^{-3}	1.117
μ (mm^{-1})	0.530
F (000)	465.0
Theta range for data Collection	10.36 to 141.52°
Limiting indices	-12 ≤ h ≤ 12, -10 ≤ k ≤ 12, -15 ≤ l ≤ 14
Reflections collected / unique	5536/2430[R(int) = 0.0386]
Refinement method	Full matrix Least square on F^2
Data / restraints / Parameters	2430/0/158
Goodness-of-fit on F2	1.329
Final R indices [I>2sigma(I)] R indices (all data)	R_1 = 0.0798, wR_2 = 0.2075 R_1 = 0.1125, wR_2 = 0.2530

The solid-state structure of ligand **3** is given in **Figure 7.**

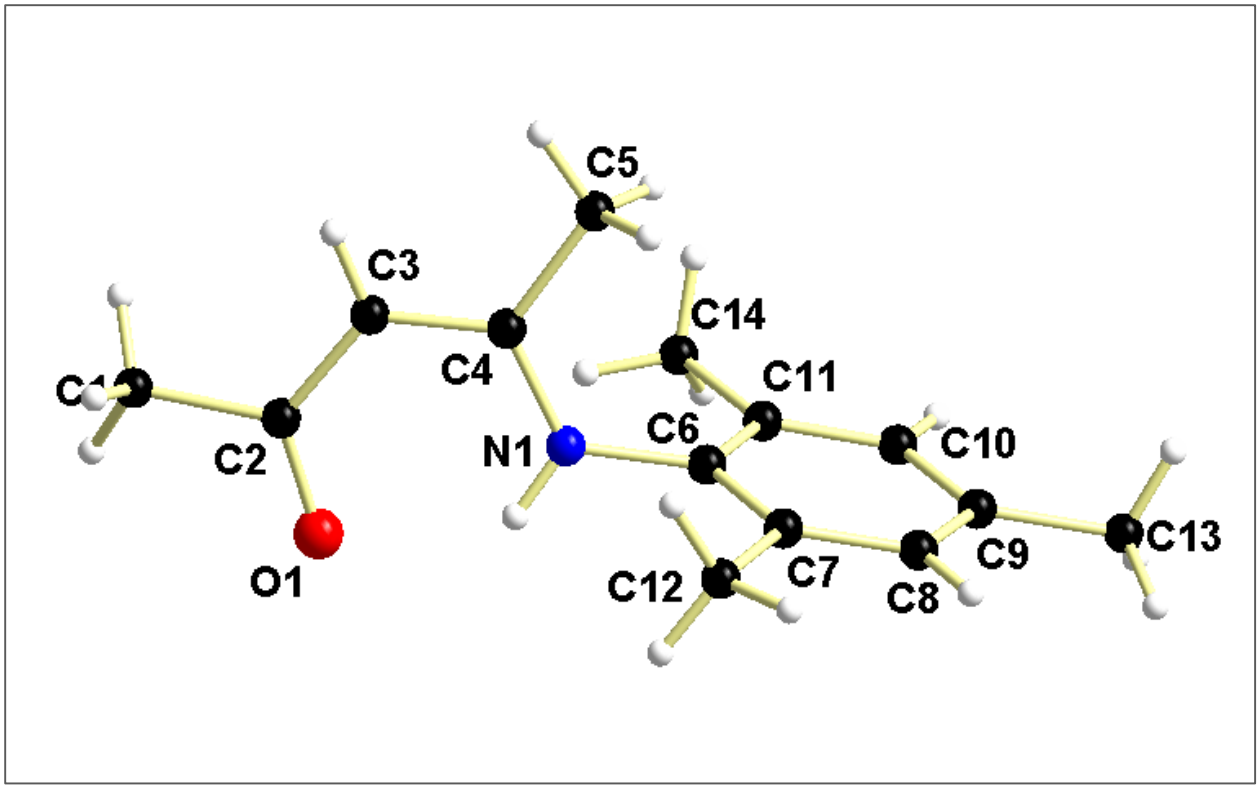
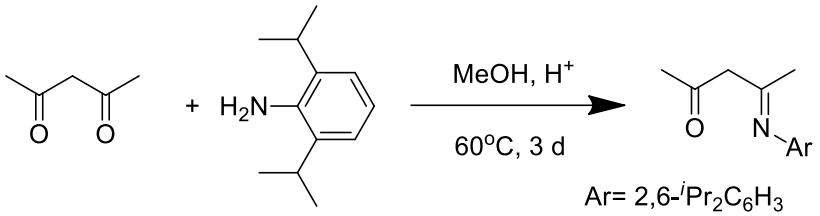


Figure 7. DIAMOND drawing of ligand **3** with thermal displacement parameters drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): C1-C2=1.512 (4), C2-01=1.244(4), C2-C3=1.416(4), C3-C4=1.377(4), C4-C5=1.504(4), C4-N1=1.340(4), N1-C6=1.432(4); C1-C2-O1=117.5, C1-C2-C3=119.1(3), O1-C2-C3=123.4, C2-C3-C4=123.4(3), C3-C4-C5=120.5(3), C3-C4-N1=122.0(3), C5-C4-N1=117.5(3), C4-N1-C6=125.7(2).

9.2. Synthesis of 4-(2, 6-diisopropylphenyl) amino-3-penten-2-one ligand (4):

Ligand **4** was synthesised by the reaction of 2, 4-pentanedione in methanol with 2, 6-diisopropylaniline in presence of acetic acid under refluxing condition at 60 ˚C for 3 days (Scheme-6). The ligand **4** was characterised by analytical/spectroscopic techniques.

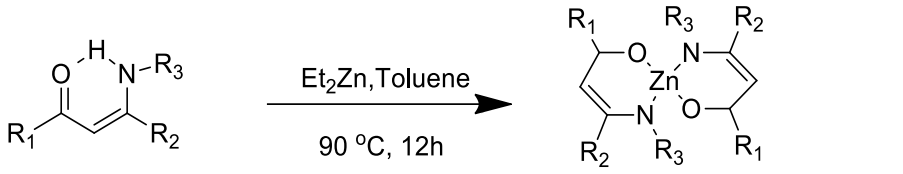


Scheme 6. Preparation of 4-(2, 6-diisopropyl) amino-3-penten-2-one

In the ^{1}H NMR spectrum of ligand **4**, two doublet at δ=1.16 ppm and 1.22 ppm in 1:1 ratio are obtained, which can be assigned as methyl protons attached to isopropyl groups on the aromatic rings. The septet obtained at δ= 2.99-3.08 ppm for methyl protons attached with tertiary carbon atoms for ligand **4**. The multiplet resonance at δ= 7.16 – 7.31 ppm indicating the three aromatic protons. A broad singlet at δ= 12.06 ppm is for NH proton indicating that the NH proton is deshielded. The singlet peak at δ= 5.21 ppm can be assigned for the one proton of CH=C (NH) group. The singlet signals obtained at δ= 1.63 ppm and 2.12 ppm indicating the methyl protons adjacent to C=O group and δ= 2.12 ppm indicates the methyl proton adjacent to CN group. The protons adjacent to C=O group is more shielded than protons attached with N-atom. In $^{13}C\{^{1}H\}$NMR Spectra of ligand **4**, peaks at δ= 19.2 ppm and 28.5 ppm are for carbon atom adjacent to CNH-CH_3 group and C=O group respectively. Carbon adjacent to C=O is more deshielded. The resonance at δ= 29.1 ppm and 22.7 ppm are for tertiary carbon of isopropyl group and methyl carbon of isopropyl group the aromatic ring. The peaks obtained at δ=146.3 ppm and 123.3 ppm indicating the ortho and meta phenyl carbon respectively. The signals at δ= 163.3 ppm and 196 ppm can be assigned for the carbon atom adjacent to the NH group and C=O group respectively. The carbonyl carbon is more deshielded and for this reason its chemical shift value is high.

9.3. Zinc complex with 4-(N-2, 4, 6-trimethylphenylimino) pentan-2-one ligand (**3**):

The formation of Zinc (II)-complex takes place in presence of toluene on constant stirring and kept overnight at 90 ˚C. Then evaporate the solvent under high vacuum. And then washed with n-hexane and dried in vacuum. The white colored solid was recrystallized from toluene (**Scheme 7**). The complex was characterized by analytical/spectroscopic techniques.



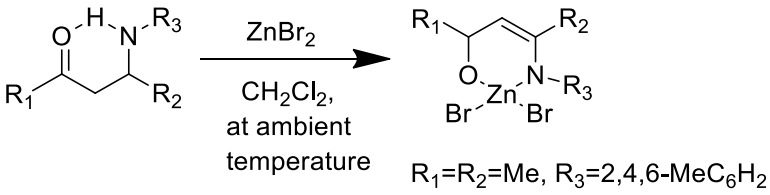
Scheme 7. Zinc complex of ligand (**3**)

In ^{1}H NMR spectrum of the Zinc complex of ligand **3** in $CDCl_3$ shows singlet at δ= 6.66 ppm for two aromatic protons. The peak at δ= 4.92 ppm indicates singlet signal for two protons of (CH=CN) group. This value of chemical shift is less than the ligand value. That is these protons are more shielded than the corresponding ligand. The two singlet signals at δ= 2.41 ppm and 2.00 ppm can be assigned for the *p*-methyl and *o*-methyl protons of the mesityl group. In this ^{1}H NMR spectra, the amino proton of the ligand **3** which was present at δ= 11.86 ppm is absent. The two singlet obtained at δ= 2.16 ppm and 1.30 ppm for six methyl protons adjacent to the (C-NH) group and C=O group respectively. In ^{13}C{^{1}H}NMR Spectra of ligand **3**, peaks at δ= 17.2 ppm and at 20.9 ppm are for *o* and *p*-methyl carbon of mesityl group present in the ligand **3** respectively. The *p*-methyl carbon is more deshielded than the *o*- one and hence its chemical shift value is higher than the *p*-methyl carbon. The peaks at δ= 18.5 ppm and 27.9 ppm indicate the carbon atom adjacent to C-N group and C=O respectively. The carbon atom adjacent to C=O group is more

deshielded than the latter one. The resonance at δ= 96.4 ppm is for *C*H=CN carbon. The resonance at δ= 128.1 ppm and 133.9 ppm indicating the ortho and para carbon of aromatic ring respectively. There is no peak at δ= 137 ppm indicated that there is no NH group present in the complex. This carbon atom is more deshieled than other ones due to its attachment with NH group. The peaks at δ= 144.4 ppm and δ= 186.2 ppm indicate for the carbon atom attached with NH group and C=O group respectively. The chemical shift values of this Zinc Complex is less than that of the corresponding ligand which indicates that the carbons are more shielded than the corresponding ligand.

9.4. Zinc complex with 4-(2, 6-diisopropylphenyl) amino-3-penten-2-one ligand (4):

Zinc complexes with N, O-donor ligands are the important precursors for catalytic reactions. The treatment of ligand **4** with $ZnBr_2$ in 1:1 molar ratio in dichloromethane at ambient temperature afforded a white solid and it was kept for crystallisation at -40 ˚C. The complex was characterised by analytical/ spectroscopic techniques.



Scheme 8. Zinc Complex of ligand **4**

In ^{1}H NMR spectrum of Zinc complex of ligand **4**, two doublet at δ= 1.14 ppm and 1.19 ppm in 1:1 ratio are obtained, which can be assigned as methyl protons attached to isopropyl groups on the aromatic rings. Here the value is slightly lower from its ligand's chemical shift value. That is

the protons are more shielded than the corresponding ligand **4**. The septet obtained at δ= 2.84-2.94 ppm for methyl proton attached with tertiary carbon atoms of ligand **4**. The multiplet observed at δ= 7.18-7.4 ppm indicating the three aromatic protons. A broad singlet absorbed at δ= 11.86 ppm is for NH proton indicting that the NH proton is deshielded. The singlet peak at δ= 5.30 ppm can be assigned for the one proton of CH=C (NH) group. The singlet signals at δ= 1.72 ppm and 2.30 ppm indicating the methyl protons adjacent to C=O group and CN group respectively. The protons adjacent to C=O group is more shielded than the protons attached with nitrogen. In $^{13}C\{^{1}H\}$NMR Spectra of ligand **4**, peak at δ= 19.9 ppm is for carbon atom adjacent to CNH-CH_3 group. The peak at δ= 28.3 ppm is for C=O group. It is because the carbon adjacent to C=O is more deshielded than the other one. The resonance peak at δ= 28.7 ppm and 22.6 ppm are for tertiary carbon of isopropyl group and methyl carbon of isopropyl group of the aromatic ring. The peaks obtained at δ=145.5 ppm and 123.9 ppm indicating the ortho and meta phenyl carbon respectively. The signals at δ= 169.5 ppm and δ= 195.1 ppm can be assigned for the carbon atom adjacent to the NH group and C=O group respectively. The carbonyl carbon is more deshielded and hence its chemical shift value is high.

10. Experimental section:

10.1. General Information

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware, either on a dual manifold Schlenk line interfaced with a high vacuum (10^{-4} torr) line or in an argon-filled M. Braun glove box. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$ and

stored in the glove box. ^{1}H NMR (400 MHz) and ^{13}C {^{1}H} NMR (100 MHz) spectra were recorded on a BRUKER ADVANCE III-400 spectrometer. A BRUKER -ALPHA FT-IR was used for the FT-IR measurements. Elemental analysis were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. 2, 6-diisopropylaniline, 2, 4, 6-trimethylaniline, and acetyl acetone were purchased from Alfa Aesar and used as received. The NMR solvents $CDCl_3$ was purchased from Sigma Aldrich and dried by Na/K alloy prior to use. Et_2Zn and $ZnBr_2$ were purchased from Sigma Aldrich and used without any purification.

10.2. Preparation of 4-[N-2, 4, 6-trimethylphenylimino] pentan-2-one ligand:

In a dry 100 mL round bottomed flask, 4 mL of 2, 4-pentanedione (4 g, 40 mmol) was taken and 5.6 mL of (40 mmol) 2,4,6-trimethylaniline was added with 40 mL of methanol followed by the addition of 1 mL of acetic acid. The reaction mixture was kept for refluxing for 3 days with constant stirring at 60 ° C. After this the solvent was evaporated through rotatory evaporator and washed with *n*-hexane which after filtration gave an orange yellow solution. Then the orange coloured solution was kept at -40°C for 2 days. The yellowish colour crystals were observed, **3**. (Yield: 4.5 g, 51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ= 11.86 (s, 1H, N*H*), 6.89 (s, 2H, Ar-*H*), 5.19 (s, 3H, C*H*=CN), 2.09 (s, 3H, *p*-C*H*$_3$), 2.27 (s, 3H, (C*H*$_3$) C=O), 2.15 (s, 6H, *o*-C*H*$_3$), 1.61 (s, 3H, NHC (C*H*$_3$); ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ= 196 (*C*=O), 163.2 (*C*(CH$_3$)N-Ar), 137.0 (Ar), 133.9 (*p*-phenyl), 128.9 (*o*-phenyl), 97.8 (*C*H=C(CH$_3$)), 29 (*C*H$_3$CO), 20.9 (*p*-*C*H$_3$), 18.3 (HN*C*-CH$_3$), 18.1 (o-*C*H$_3$) ppm.

10.3. Preparation of 4-(2, 6-diisopropylphenyl) amino-3-penten-2-one ligand (4):

In a dry 100 mL round bottomed flask, 4 mL of 2, 4-pentanedione (4 g, 40 mmol) was taken and 7.35 mL of (40 mmol) 2,6-diisopropylaniline was added with 40 mL of methanol followed by the addition of 1 mL of acetic acid. The reaction mixture was kept for refluxing for 3 days with constant stirring at 60 ˚C. After this the solvent was evaporated through rotatory evaporator and washed with *n*-hexane which after evaporation gave a whitish solution. Then the solution was kept at -40 ˚C for 2 days. The whitish colour crystals were observed, **4**. (Yield: 7.1 g, 69%).

^{1}H NMR (400 MHz, C_6D_6): δ= 12.06 (s, 1H, N*H*), 7.16-7.31 (m, 3H, Ar-*H*), 5.21 (s, 1H, C*H*=C (NH)), 2.99-3.08 (sept, 2H, C*H* $(CH_3)_2$), 2.12 (s, 3H, CH_3-CN), 1.63 (s, 3H, CO (CH_3)), 1.22 (d, 6H, CH(CH_3)$_2$), 1.16 (D, 6H, CH(CH_3)$_2$); ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ= 196 ((CH$_3$)*C*O), 163.3 (*C*(CH$_3$)NH), 146.3 (*o*-phenyl), 133.5 (Ar-*C*NH), 123.6 (*m*-phenyl), 95.6 (*C*H=CNH), 29.1 (*C*H(CH$_3$)$_2$), 19.2 (NH*C*-CH$_3$) ppm.

10.4. Preparation of Zinc-metal complex with ligand 3:

In a flame dried 25 mL of Schlenk flask ligand **3** (100mg, 0.46mmol) and toluene (5mL) was taken. To this solution 0.26 mL of Et_2Zn (0.23 mmol) was added. After 12 hours of stirring at 90 ˚C, the solvent was evaporated. The compound was extracted from *n*-hexane and dried in vacuum. The complex was re-crystallised from C_6D_6 at room temperature. (Yield: 50 mg, 70%).

^{1}H NMR (400 MHz, C_6D_6): δ= 6.66 (s 4H, Ar-*H*), 4.92 (s, 2H, C*H*=CN (CH$_3$)), 2.41 (s, 6H, *p*-CH_3), 2.16 (s, 6H, CN (CH_3)), 2.00 (s, 12H, *o*-CH_3), 1.30 (s, 6H, (OC (CH_3)); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 17.2 (o-*C*H$_3$), 18.5 (p-*C*H$_3$), 21.8 (NHC-*C*H$_3$), 27.9 (*C*H$_3$CO), 96.4 (*C*H=C(CH$_3$)), 128.1 (*m*-phenyl), 133.9 (*p*-phenyl), 144.4 (Ar *C*-N), 173 ((CH$_3$)*C*-N), 186.2 (C=O) ppm.

10.5.Preparation of Zinc-metal complex with ligand 4:

In a flame dried 25 mL of Schlenk flask ligand **4** (200 mg, 0.77 mmol) and dichloromethane was taken. To this solution $ZnBr_2$ (173 mg, 0.77 mmol) in dichloromethane was added. The reaction mixture was stirred at ambient temperature for 12 h. Filtration and evaporation of dichloromethane in vacuum gives a white coloured solid. This solid was kept for crystallisation in dichloromethane at -40 ˚C. (Yield: 110 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ= 11.86 (s, 1H, N*H*), 7.18-7.40 (m, 3H, Ar-*H*), 5.30 (s, 1H, C*H*=C(NH)), 2.84-2.94 (sept, 2H, C*H*$(CH_3)_2$), 2.30 (s, 3H, C*H*$_3$CN), 1.72 (s, 3H, C*H*$_3$CO), 1.19 (d, 6H, CH(C*H*$_3)_2$), 1.14 (d, 6H, CH(C*H*$_3)_2$); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ= 195.1 (*C*=O), 169.5 (CH_3*C*N), 145.5 (*o*-phenyl), 132.1 (Ar*C*-N), 129.3 (*p*-phenyl), 123.9 (*m*-phenyl), 97.3 (*C*H=C(NH)), 28.7 (*C*H$(CH_3)_2$), 28.3 (*C*H_3CO), 24.7 (CH(*C*$H_3)_2$), 22.6 (CH(*C*$H_3)_2$), 19.9 (*C*H_3CN) ppm.

11. Conclusion:

In conclusion, we have successfully synthesised and structurally characterised the ligand **3** and ligand **4** by usual procedure. With ligand **3,** we have successfully prepared the dimeric Zinc complex which was spectroscopically characterised by the IR, NMR and also with ligand **4**, we have successfully prepared the complex of Zinc Bromide.

12. References :

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Appendix:

Supporting Information:

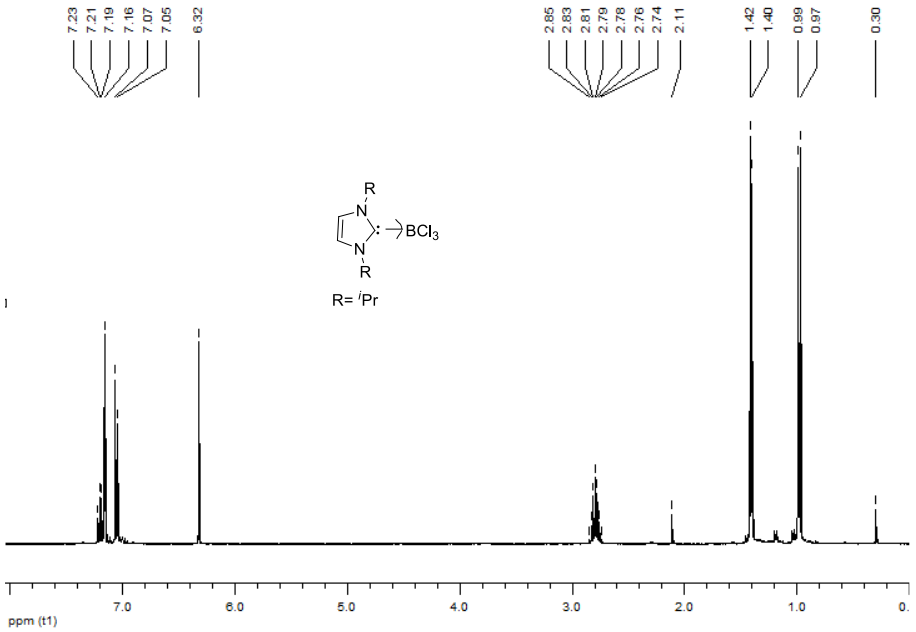

Figure 8. ^{1}H NMR (C_6D_6, 400 MHz) of compound **1**

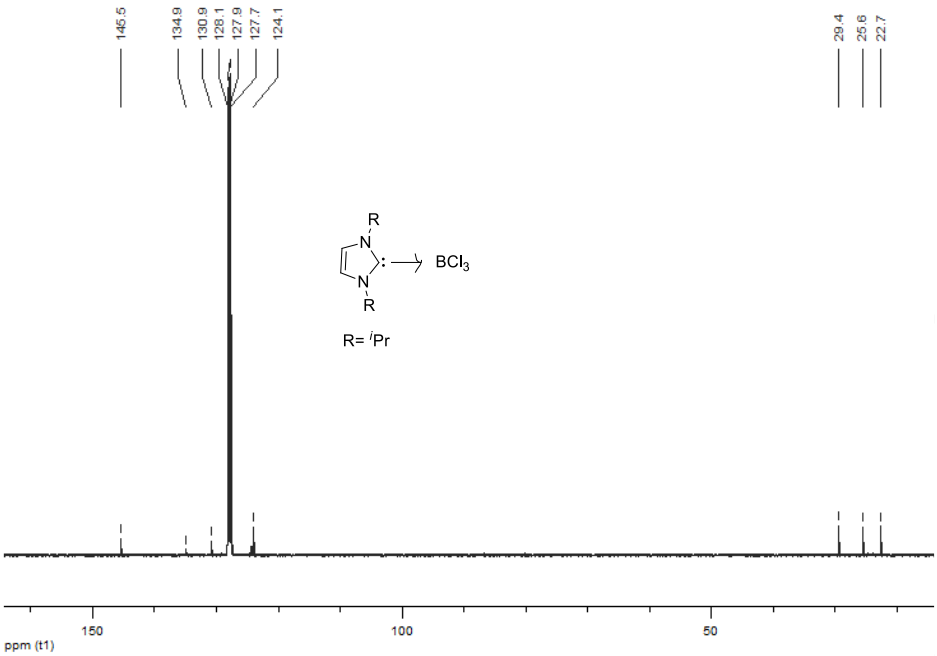

Figure 9. ^{13}C {^{1}H} NMR of compound **1**

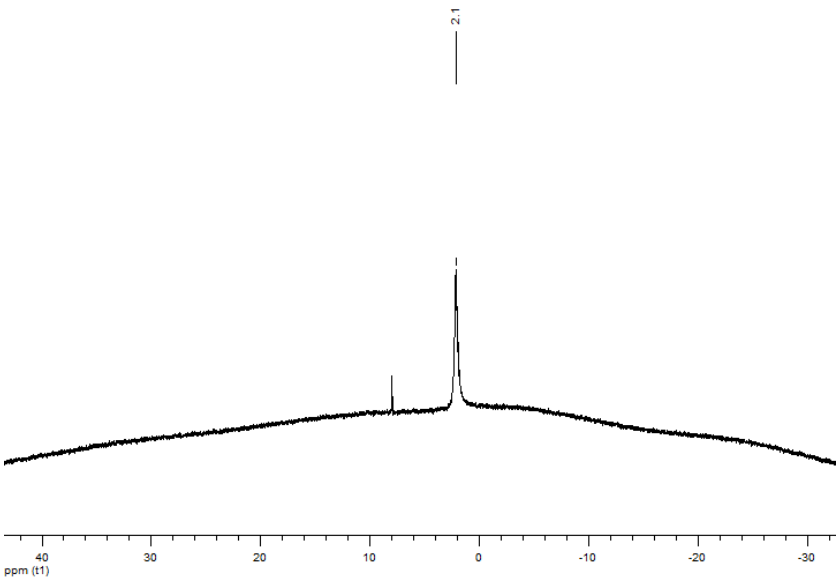

Figure 10. ^{11}B {^{1}H} NMR of compound **1**

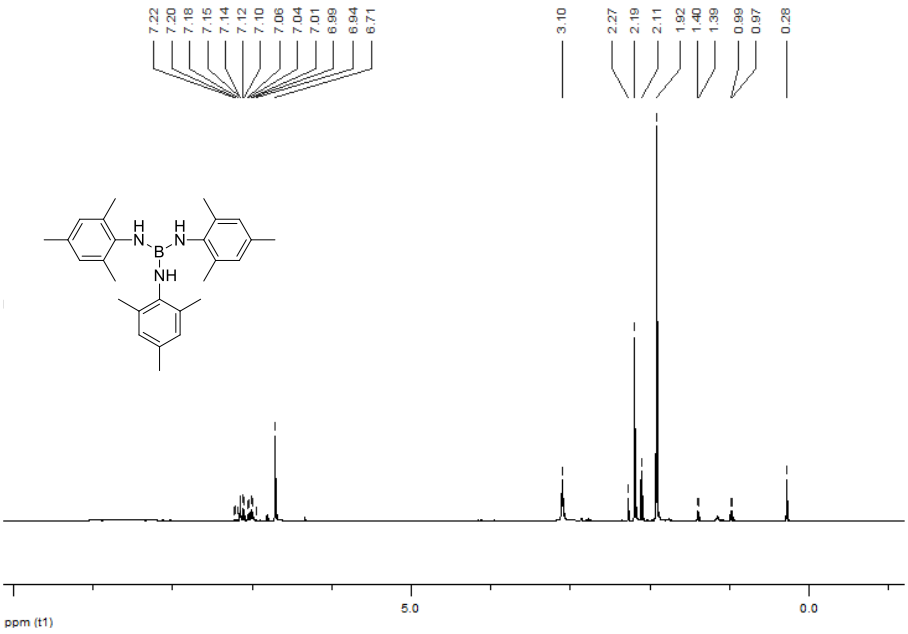

Figure 11. ^{1}H NMR Spectra of compound **2**

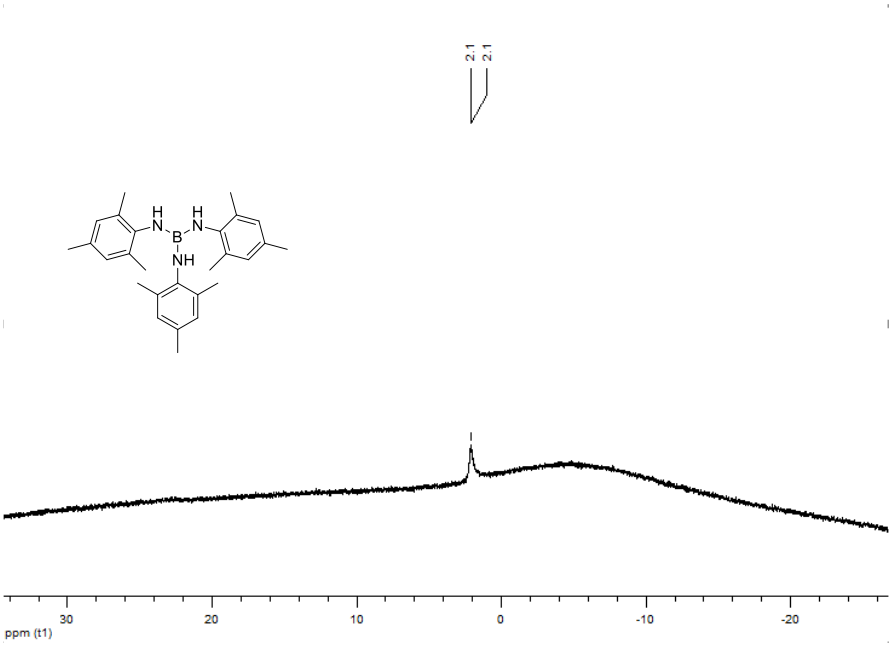

Figure 12. ^{11}B {^{1}H} NMR Spectra of compound **2**

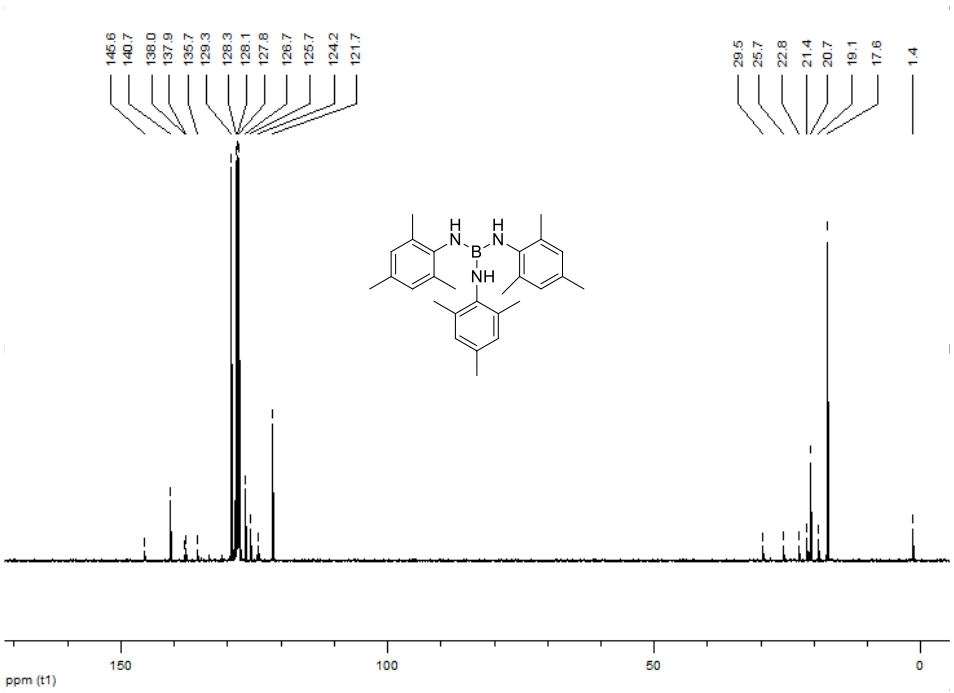

Figure 13. ^{13}C {^{1}H} NMR Spectra of compound **2**

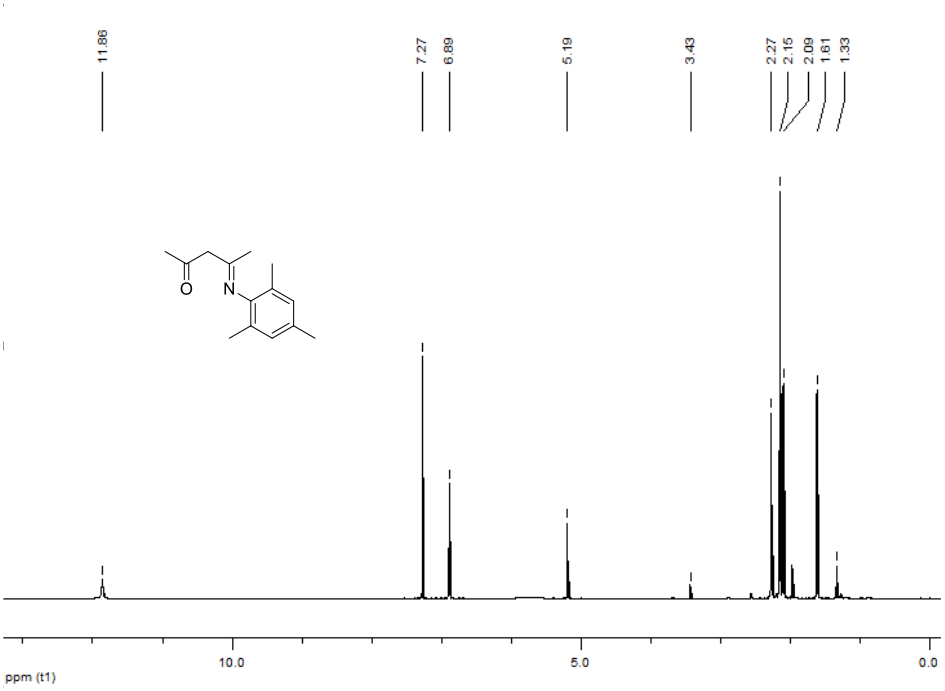

Figure 14. ^{1}H NMR Spectra of ligand **3**

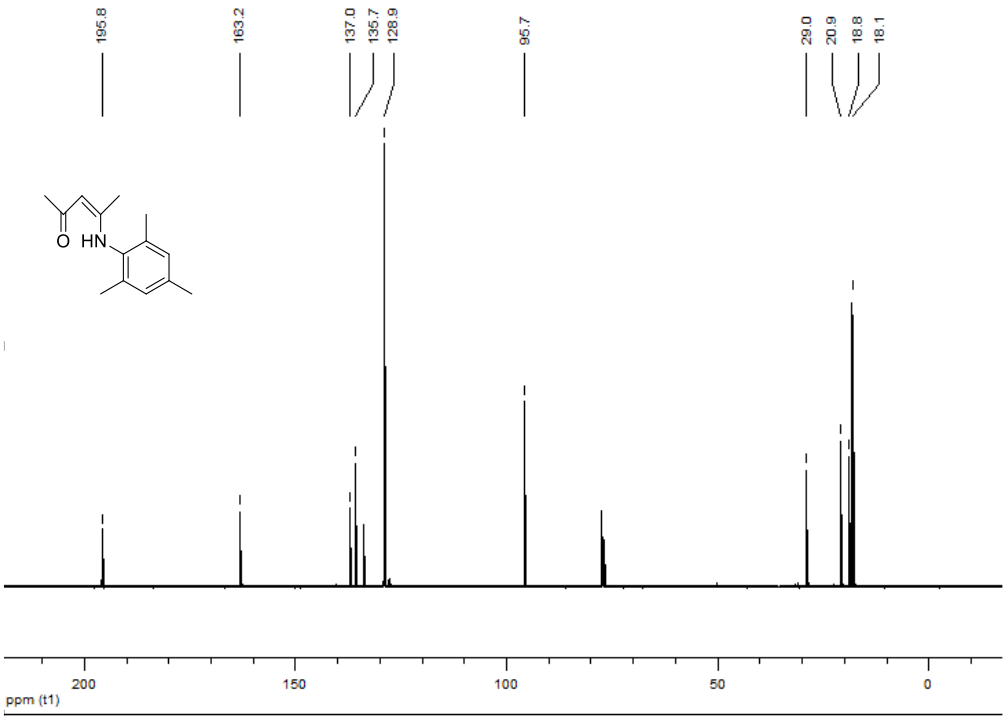

Figure 15. ^{13}C {^{1}H} NMR Spectra of ligand **3**

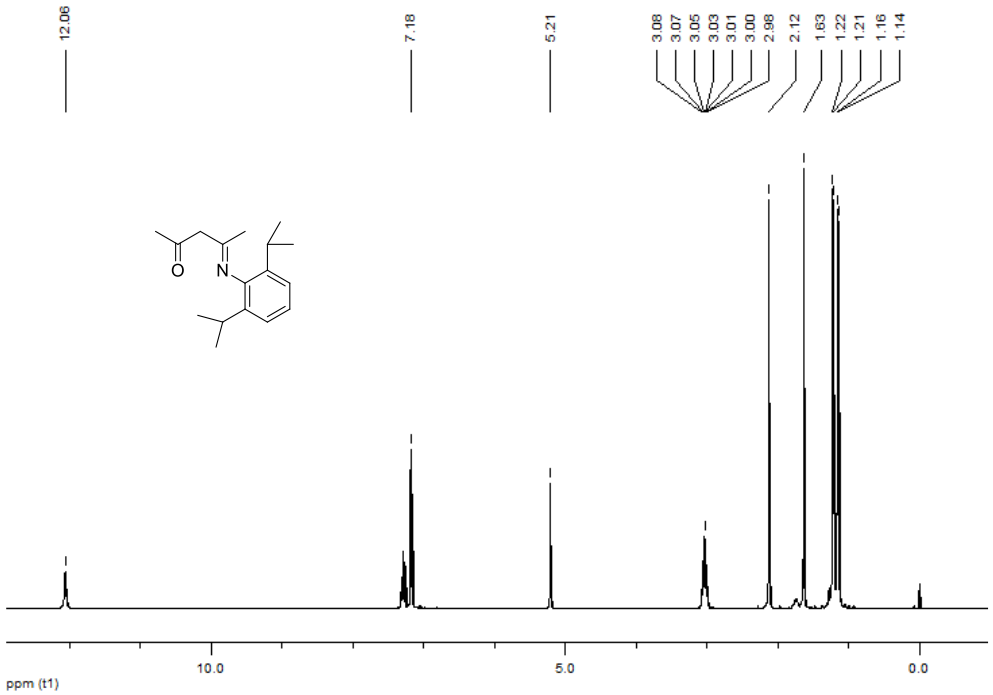

Figure 16. ^{1}H NMR Spectra of ligand **4**

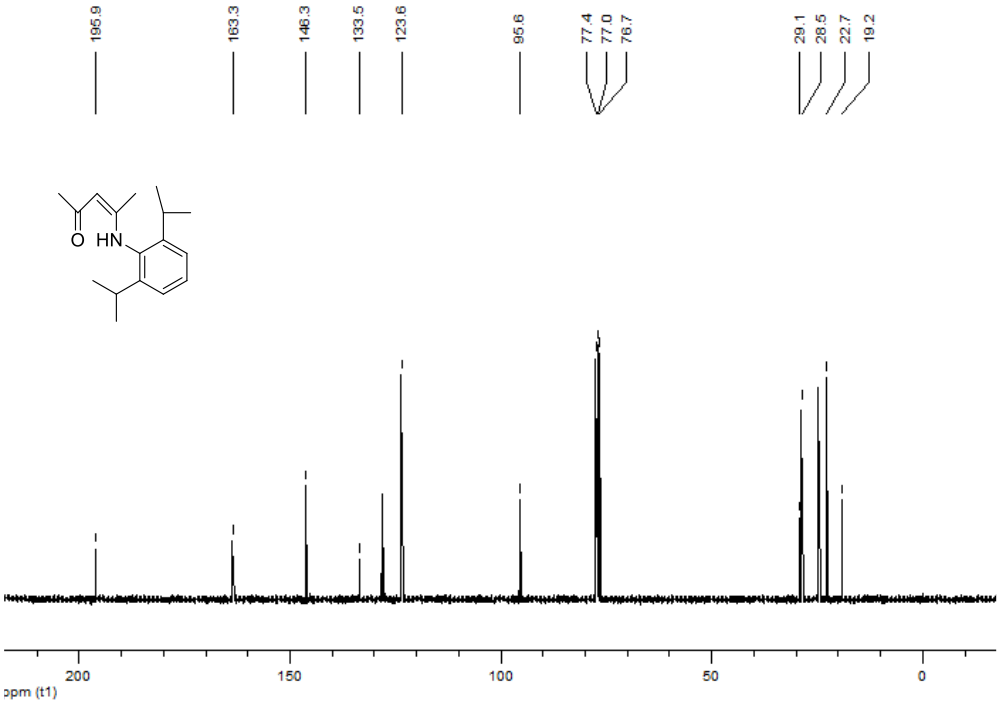

Figure 17. ^{13}C {^{11}H} NMR Spectra of ligand **4**

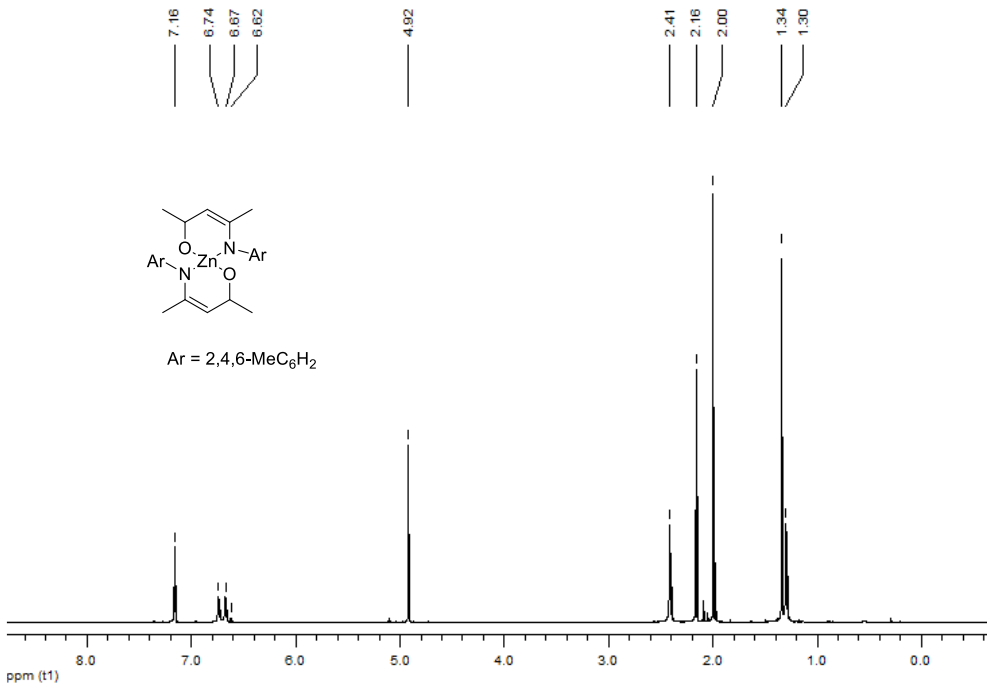

Figure 18. ^{1}H NMR Spectra of $ZnEt_2$ complex of ligand **3**

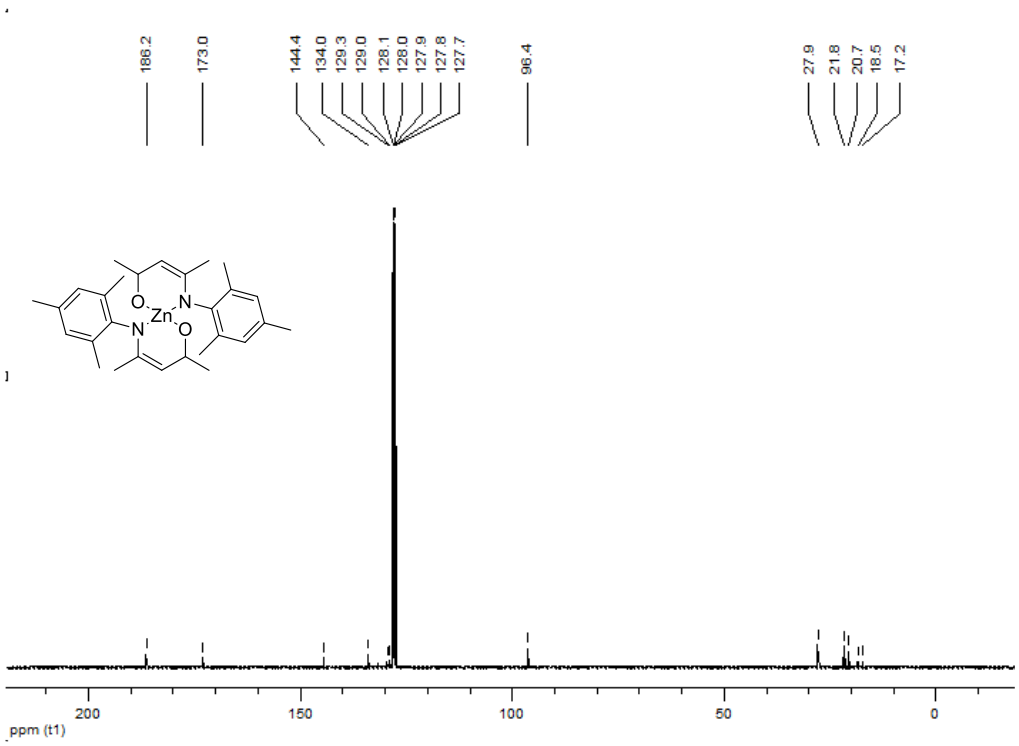

Figure 19. ^{13}C {^{1}H} NMR Spectra $ZnEt_2$ complex of ligand **3**

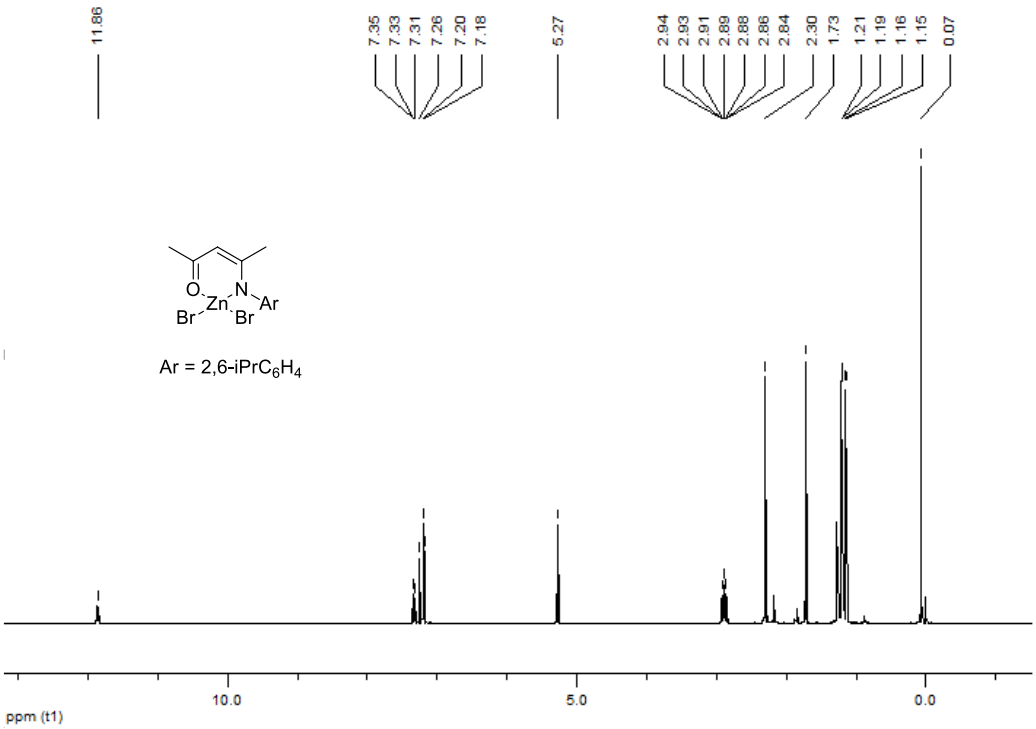

Figure 20. ^{1}H NMR Spectra of Zinc Bromide complex of ligand **4**

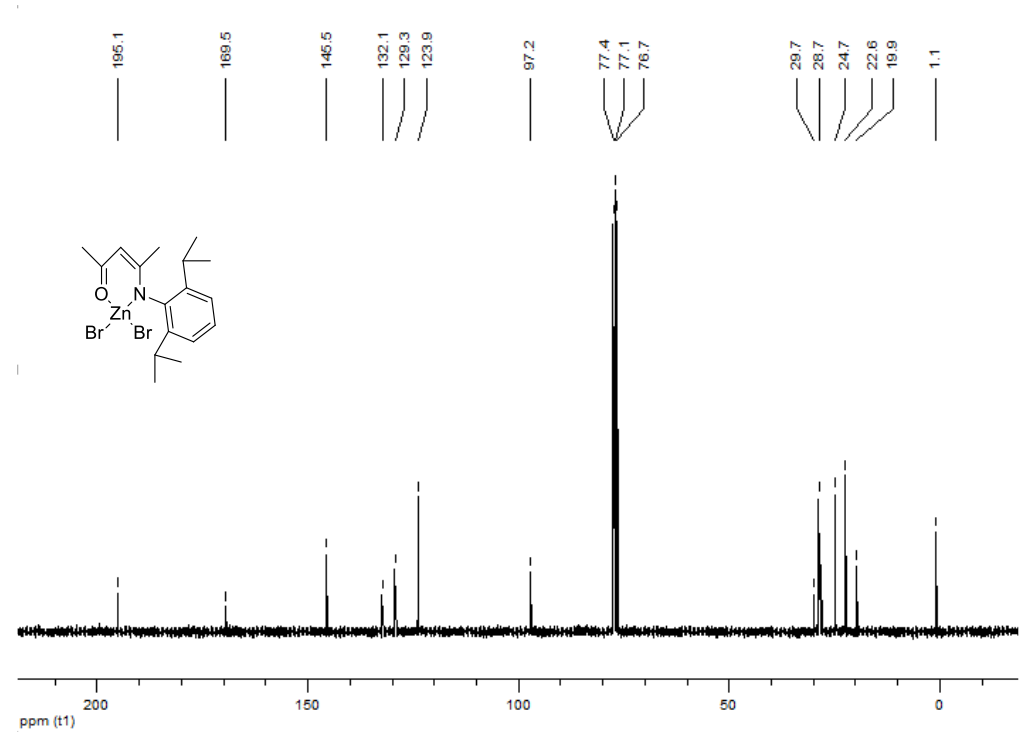

Figure 21. ^{13}C {^{1}H} NMR Spectra of the Zinc Bromide complex of ligand **4**