STUDY OF PINCER TYPE N-HETEROCYCLIC CARBENES AND N, N’-DISUBSTITUTED AMIDINES AND THEIR METAL COMPLEXES

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A dissertation submitted for the partial fulfilment of BS-MS dual degree in science

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November 2014

Certificate of Examination

This is to certify that the dissertation titled " **Study of Pincer Type N-Hetrocyclic Carbenes and N,N-Disubstituted Amidines and their Metal Complexes**" submitted by Mr. Aditya Verma (Reg. No. MS09009) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds work done by the candidate satisfactory and recommends that the report be accepted.

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Dated: November 27, 2014

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Sanjay Singh at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledge of collaborative research and discussions. This thesis is a bonafide record of the original work done by me and all sources listed within have been detailed in the bibliography.

Aditya Verma

Dated: November 27, 2014

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Sanjay Singh

(Supervisor)

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Content

List of Figures .... **(i)**

List of Tables... **(ii)**

List of Charts.. **(ii)**

List of Schemes.. **(iii)**

Notations and Abbreviations... **(iv)**

CHAPTER 1: N-Heterocyclic Carbenes

1.1.Introduction.. 1

1.2. Results and Discussion.. 4

1.3. Experimental Section... 10

1.3.1. General remarks.. 10

1.3.2. X-ray crystallography.. 11

1.3.3. Synthetic procedure

1. Synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide (**1**).. 12
2. Synthesis of 1,3-dibenzylbenzimidazolium chloride (**2**)... 12
3. Synthesis of of 1,3-dibenzylbenzimidazol-2-ylidene silver chloride (**3**).. 13
4. Synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene silver bromide) (**4**) 13
5. Synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene mercury) dibromide (**5**)... 14

1.4. Summary and Future Directions 15

1.5. References 16

CHAPTER 2: N-N’-disubstituted amidines

2.1. Introduction.. 18

2.2. Results and Discussion.. 19

2.3. Experimental Section... 23

2.3.1. General remarks 23

2.3.2.Synthetic procedure 24

1. Synthesis of **L_1**$RuCl_3$ complex (**1**).. 24

2. Synthesis of **L_1**$CrCl_2$ complex (**2**).. 24

3. Synthesis of **L_2**$CrCl_2$ complex (**3**).. 25

4. Synthesis of **L_1**$FeBr_2$ complex (**4**)... 25

5. Synthesis of **L_2**$FeBr_2$ complex (**5**).. 25

6. Synthesis of **L_1**Cu[2OTf] complex (**6**).. 26

7. Synthesis of **L_2**Ni[2OTf] complex (**7**).. 26

8. Synthesis of **L_2**Ni[$2BPh_4$] complex (**8**).. 26

2.4. Summary and Future Directions... 27

2.5. References 27

Annexure

Chapter 1

(i) ^{1}H NMR spectrum of **2** in DMSO-d_6.. 28
(ii) ^{13}C NMR spectrum of **2** in DMSO-d_6.. 29
(iii) ^{1}H NMR spectrum of **3** in DMSO-d_6... 30
(iv) ^{13}C NMR spectrum of **3** in DMSO-d_6... 31
(v) ^{1}H NMR spectrum of **4** in $CDCl_3$... 32
(vi) ^{13}C NMR spectrum of **4** in $CDCl_3$... 33
(vii) ^{1}H NMR spectrum of **5** in DMSO-d_6.. 34
(viii) ^{13}C NMR spectrum of **5** in $CDCl_3$.. 35

Chapter 2

(i) IR(KBr pallet) spectrum of **3**... 36

(ii) IR(KBr pallet) spectrum of **5** 37

(iii) IR(KBr pallet) spectrum of **6** 38

(iv) IR(KBr pallet) spectrum of **7**... 39

(v) IR(KBr pallet) spectrum of **8** 40

List of Figures

Chapter 1:

Figure 1. Hermann’s pincer carbene palladium iodide complex....................... 2

Figure 2. Crabtree’s CCC pincer carbene palladium bromide complex............. 3

Figure 3. Crabtree’s CNC pincer carbenes with and without methylene spacers……. 3

Figure 4. Ortep representation of silver chloride complex of 1,3-dibenzylbenzimidazol-2-ylidene **(3)**.. 8

Chapter 2:

Figure 1. Amidine.. 18

List of Tables

Chapter 1.

Table 1. Crystal data and structure refinement details for 1,3-dibenzylbenzimidazol-2-ylidene silver chloride **(3)**.. 7

Table 2. Selected bond lengths and bond angles of 1,3-dibenzylbenzimidazol-2-ylidene silver chloride **(3)**.. 8

Chapter 2.

Table 1. Ligands worked and discussed in this chapter........................... 19

List of Charts

Chapter 1.

Chart 1. Singlet and triplet carbene... 1

List of schemes

Chapter 1.

Scheme 1. Synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide **(1)**. 5

Scheme 2. Synthesis of 1,3-dibenzylbenzimidazolium chloride **(2)**............................ 5

Scheme 3. Synthesis of of 1,3-dibenzylbenzimidazol-2-ylidene silver chloride **(3)**....... 6

Scheme 4. Synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene silver bromide) **(4)**.. 9

Scheme 5. Synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene mercury) dibromide **(5)**.. 10

Chapter 2:

Scheme 1. Synthesis of $\mathbf{L_1}RuCl_3$ complex (**1**)... 19

Scheme 2. Synthesis of Cr (II) complexes $\mathbf{L_1}CrCl_2$ (**2**) and $\mathbf{L_2}CrCl_2$ (**3**) …………… 20

Scheme 3. Synthesis of Fe (II) complexes $\mathbf{L_1}FeBr_2$ (**4**) and $\mathbf{L_2}FeBr_2$ (**5**)……………… 21

Scheme 4. Synthesis of $\mathbf{L_1}$Cu[2OTf] complex (**6**) 22

Scheme 5. Synthesis of $\mathbf{L_2}$Ni[2OTf] complex (**7**)... 22

Scheme 6. Synthesis of $\mathbf{L_2}Ni[2BPh_4]$ complex (**8**).. 23

Notations and Abbreviations

Å	angstrom
μ	bridging
b	broad
C	celcius
δ	chemical shift in ppm
d	doublet
DMSO	dimethylsulfoxide
DCM	dichloromethane
DMF	dimethylformamide
IR	infra-red
K	Kelvin
ppm	parts per million
MeOH	methanol
m	multiplet
M. P.	Melting point
NMR	nuclear magnetic resonance
THF	tetrahydrofuran
s	singlet
t	triplet
v	wave number

CHAPTER 1: N-Hetrocyclic Carbenes (NHC's)

1.1 Introduction

Carbene is a molecule which contains a neutral carbon atom with a valence of two shared and two unshared valance electron. Two types of carbenes are commonly known based on their ground state spin multiplicity as singlet and triplet. Singlet carbenes are spin paired whereas triplet carbenes have two unpaired electrons and may have either linear or bent geometry. Spin state acquired by a carbene depends upon nature of the groups attached to carbene carbon.[1a]

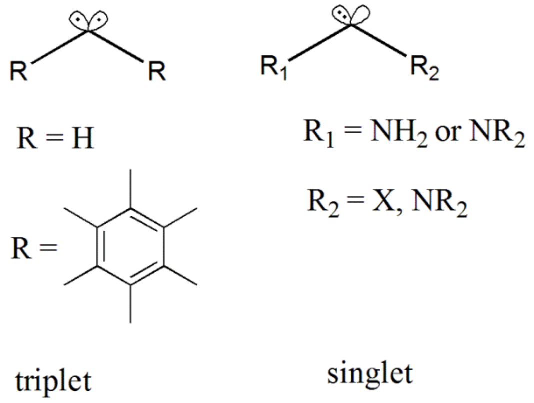


Chart 1. Singlet and triplet carbenes

N-heterocyclic carbenes (NHCs) are molecules among the carbenes that contain nitrogen atom(s) in its ring apart from carbon and are stable compounds of divalent carbon. The N-heterocyclic carbenes are strongly stabilized by π-donating substituents, are good σ-donors but π-bonding with the metal is weak. On the other hand the alkyl carbenes (alkylidene) are relatively strong π-acceptors. NHCs are stable due the resonance property and the LUMOs of free NHCs are quite high in energy, relative to other kinds of carbenes.

Imidazol-2-ylidenes, triazol-5-ylidenes (and less so, diaminocarbenes) have been shown to coordinate to a plethora of elements from main group elements, transition metals and even lanthanides and actinides. Stable carbenes are believed to behave in a fashion similar to organophosphines in their coordination properties to metals. Molecules containing two and three carbene moieties have been prepared as potential bidentate and tridentate carbene ligands.[1b]

N-heterocyclic carbenes based metal complexes have emerged as effective catalyst in a number of reactions such as transfer hydrogenation,[2] Suzuki Miyuara coupling,[3] CO/ethylene copolymerization,[4] hydrosilylation,[5] and olefin metathesis.[6] Carbenes as ligands have been compared to phosphines by the nature of their bonding to metals.[7]

The pincer carbenes are the new emerging molecules containing more than one carbene center, connected by some type of bridging group which could then coordinate to a metal in a multidentate fashion. Various pincer carbenes based on imidazolium salts[8] as well as benzimidazolium salts[11] have been synthesized. In a more recent development the direct metallation of imidazolium salt with $Pd(OAc)_2$ has been proved successful.[8] Pincer carbene complexes have been found as useful catalysts in several organic synthesis reactions. Herrmann and co-workers[8] have recently performed Heck coupling of aryl chlorides with olefin using imidazole based Pd containing complexes (Figure 1).

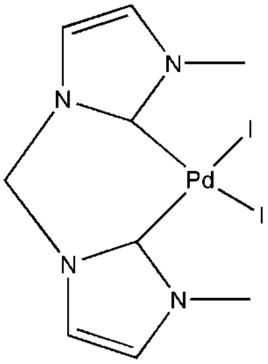


Figure 1. Herrmann's pincer cabene palladium iodide complex.

To induce the hybrid and dual coordinating properties in these pincer systems donor hetroatoms such as nitrogen, phosphorus, oxygen, sulfur donor atoms have been incorporated in the spacers bridged between two crabenes. Such type of pincer systems have been reported by Crabtree and co-workers (Figure 2 and 3) where two NHCs are bridged by aryl groups and pyridyl groups [9,10] representing CCC and CNC pincer ligands, respectively.

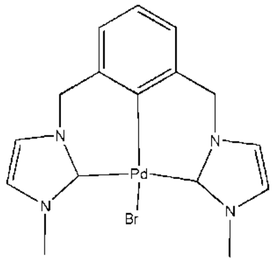


Figure 2. Crabtree's CCC pincer carbene palladium bromide complex.

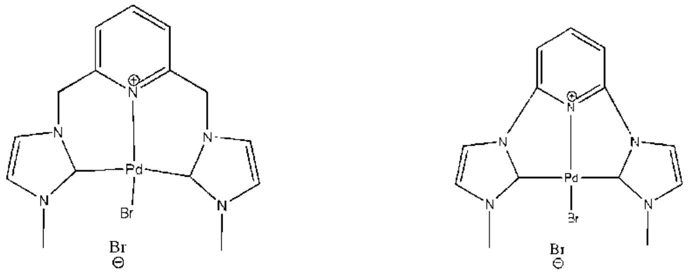


Figure 3. Crabtree's CNC pincer carbenes with and without methylene spacers.

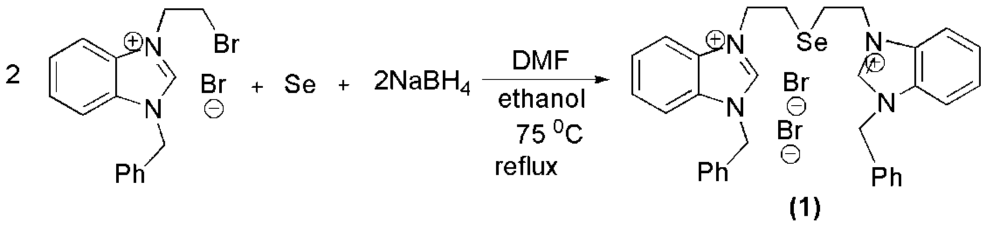
Recently, Huynh *et al.* have reported the pseudo-pincer and CSC pincer-type Pd(II) complexes derived from benzannulated N-hetrocyclic carbenes.[11] NHC pincers thus generated by combining one or two NHC moieties may provide three binding sites that increase the rigidity of such complexes that show good reactivity in catalytic processes such as Mizoroki-Heck coupling reactions due to the thermal stability.[11]

The applicability of the pincer systems inspired us to synthesize the benzimidazole based pseudo pincer or pincer type system bearing Se as a heterodonor atom. Selenium belongs to the chalcogen family (group 16) and is considered as a soft donor therefore it is expected that selenium bridging two NHC moieties should also participate in coordination with metal ion that would give C-Se-C pincer backbone. Following these directions the present work was designed and aimed to synthesize CSeC pincer N-heterocyclic carbene precursors and it's mononuclear and dinuclear complexes.

1.2 Results and Discussion

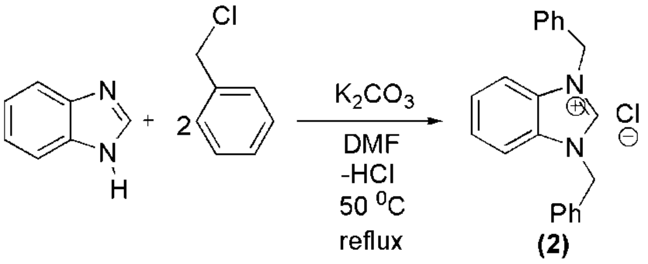
Ligand syntheses

In order to synthesize the selenoether bridged N-heterocyclic carbene complexes mentioned above the selenoether bridged benzimidazolium salt was synthesized as a precursor. In this direction the entry point seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide **(1)** was synthesized by reaction of 1-benzyl-3-(2-bromoethyl)-benzimidazolium bromide (prepared according to literature procedure)[12] with Na_2Se, generated *in situ* with selenium and $NaBH_4$, in presence of DMF and ethanol (Scheme 1). The formation of compound **1** was confirmed by ^1H NMR spectrum showing two triplets at 3.28 ppm (for $–CH_2Se$) and 4.89 ppm (for $–NCH_2$) these triplets are upfield shifted as compared to its precursor 1-benzyl-3-(2-bromoethyl)-benzimidazolium bromide that showed the corresponding signals at 4.08 ppm ($-CH_2Br$) and 5.06 ppm ($-NCH_2$). Additionally, the imidazolium hydrogen (NC*H*N) in **1** was observed at 10.32 ppm that is slightly downfield shifted as compared to the corresponding signal (10.19 ppm) in its precursor 1-benzyl-3-(2-bromoethyl)-benzimidazolium bromide. In ^{13}C NMR spectrum of **1** the signal for carbon due to $-CH_2Se$ and $-NCH_2$ appeared at upfield region at 47.3 and 22.1 ppm due to the replacement of more electronegative bromine with less electronegative selenium. The resonance for N*C*HN was seen at 143.10 ppm that is comparable to its precursor 1-benzyl-3-(2-bromoethyl)-benzimidazolium bromide that showed the same carbon resonating at 143.02 ppm.



Scheme 1. Synthesis of Seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide **(1)**.

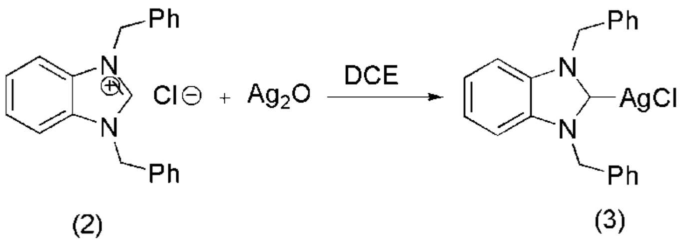
For the synthesis of another carbene precursor, 1,3-dibenzyl benzimidazolium chloride **(2)** a reaction of benzimidazole was carried out with two equivalent of benzyl chloride in DMF using potassium carbonate as a base that yielded 1,3-dibenzyl benzimidazolium chloride (Scheme 2). In the ^{1}HNMR of compound **2** the -CH_2Ph protons resonate at 5.82 ppm as a singlet and –N*C*HN in ^{13}CNMR of compound **2** appeared at 143.24 ppm whereas the signal for *C*H$_2$Ph was seen at 49.94 ppm.



Scheme 2. Synthesis of 1,3-dibenzyl benzimidazolium chloride **(2)**.

Metal complexes of N-heterocyclic carbenes

To synthesize N-heterocyclic carbene complexes, precursor **2** was reacted with Ag_2O in DCE that resulted in the elimination of water that was removed using molecular sieves. Formation of the silver chloride complex of 1,3-dibenzyl benzimidazol-2-ylidene **(3)** was confirmed by disappearance of the imidazolium hydrogen in its ^{1}H NMR spectrum. In ^{13}C NMR spectrum of compound **3** the peak for N*C*N was observed at 165.14 in comparison to 143.24 ppm due to N*C*HN in compound **2**



Scheme 3. Synthesis of silver chloride complex of 1,3-dibenzyl benzimidazol-2-ylidene **(3)**.

Crystals suitable for single crystal X-ray diffraction of compound **3** were obtained from DCM/ether mixture. Compound **3** crystallized in monoclinic system with $P2_1/c$ space group (Table 1). In the solid state the carbene carbon of 1,3-dibenzyl benzimidazol-2-ylidene coordinates with silver in a manner significantly deviated from linearity with the C(1)-Ag(1)-Cl(1) bond angle of 169.19(8)° (Figure 4). The Ag(1)-Cl(1) bond length of 2.385(2) Å is comparable to that reported for 1,3-*bis*(2,6-*bis*(diphenylmethyl)-4-methylphenyl)imidazole-2-ylidene silver chloride 2.381 Å.[13] The C(1)-Ag(1) bond length of 2.099(3) Å is also consistent with that of 2.081(4) Å reported for 1,3-*bis*(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazole-2-ylidene silver chloride.[14]

Table 1. Crystal data and structure refinement details for mononuclear silver chloride complex of 1,3-dibenzyl benzimidazol-2-ylidene **(3)**.

Empirical formula	$C_{42}H_{36}Ag_2Cl_2N_4$
Formula weight	441.71
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.0887(11) Å
	b = 9.4406(14) Å; β = 94.248(2)°
	c = 20.317(2) Å
Volume	1738.4(4) $Å^3$
Z	4
Density (calculated)	1.688 mg/mm^3
Absorption coefficient	1.318 mm^{-1}
$F(000)$	888.0
Crystal size	0.2x0.2x0.2 mm^3
2 θ range for data collection	4.02 to 50.06°
Index ranges	$-10 \le h \le 10$
	$-11 \le k \le 11$
	$-23 \le l \le 24$
Reflections collected	15944
Independent reflections	3178
Data / restrains / parameters	3178/0/225
Goodness-of-fit on F^2	1.050
Final R indices ($I > 2\sigma(I)$)[a]	$R_1 = 0.0189$, $wR_2 = 0.0483$
R indices (all data)[a]	$R_1 = 0.0198$, $wR_2 = 0.0489$
Largest diff. peak and hole	0.41/-0.48

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. $wR2 = [\Sigma w(|Fo^2| - |Fc^2|)^2/\Sigma w|Fo^2|^2]^{1/2}$

Selected bond angles and bond lengths of compound **3** are given in Table 2.

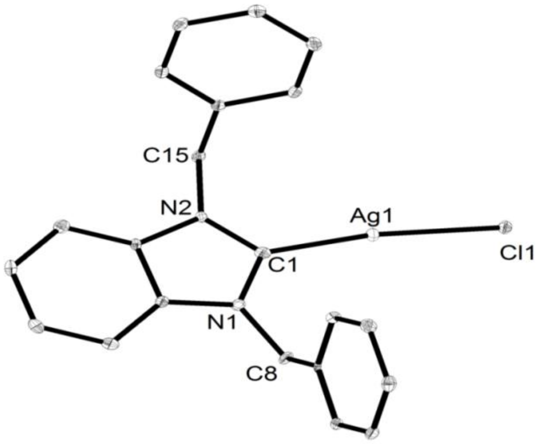
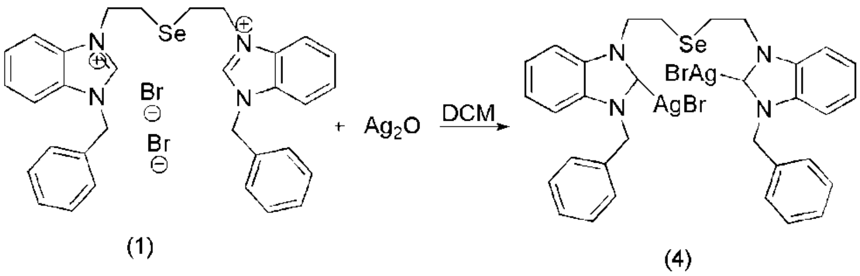


Figure 4. Ortep representation of silver chloride complex of 1,3-dibenzylbenzimidazol-2-ylidene **(3)**. All hydrogen atoms have been deleted for clarity and thermal ellipsoids have been drawn at 30% probability level.

Table 2. Selected bond lengths and bond angles of 1,3-dibenzylbenzimidazol-2-ylidene silver chloride **(3)**

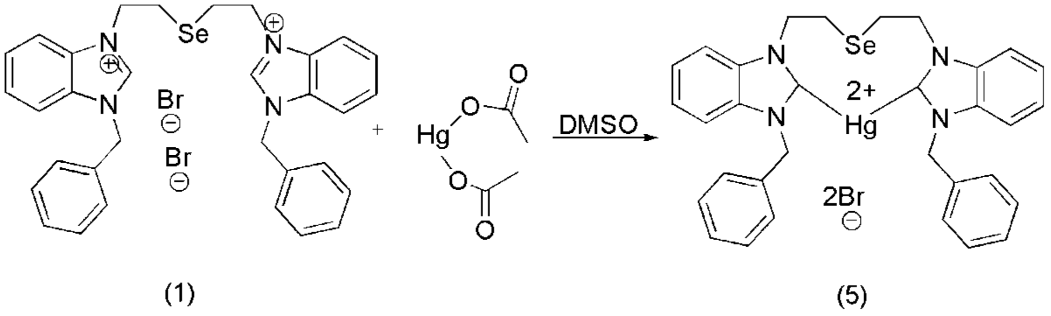
Bond length [Å]		**Bond angle [°]**	
C(1)-N(1)	1.371(3)	C(1)-N(1)-C(7)	111.2(3)
C(1)-N(2)	1.339(4)	C(1)-N(1)-C(8)	124.3(3)
Ag(1)-C(1)	2.099(3)	C(1)-N(2)-C(15)	125.1(2)
Ag(1)-Cl(1)	2.385(2)	C(1)-Ag(1)-Cl(1)	169.19(8)

Reaction of seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide **(1)** with Ag_2O in DCM resulted in the elimination of water, that was removed from the reaction mixture using molecular sieves, and formation of a dinuclear silver chloride complex, seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene silver bromide) **(4)**. Compound **4** was characterized by spectroscopic methods and mass spectrometry. In the ^{1}H NMR spectrum of **1** the signal for imidazolium hydrogen (-NC*H*-N-), that appeared at 10.32 ppm in **1**, was not observed confirming replacement of this imidazolium hydrogen with silver. Other relevant signals in the ^{1}H NMR were observed for CH_2Ph, NCH_2 and CH_2Se at 5.65, 4.86 and 3.23 ppm, respectively. The carbenoid carbon could not be located in ^{13}C NMR spectrum of **4** however, the downfield shift in the resonances for $–CH_2Se$ (29.8 ppm), NCH_2 (49.5 ppm) and CH_2Ph (53.8 ppm) as compared to the corresponding resonances in its precursor **1** at 22.1, 47.3 and 50.28 ppm respectively, were indicative of complex formation. Additionally, formation of complex **4** and its dinuclear nature was confirmed by high resolution mass spectrometry where the peak at *m/z* = 924.2416 corresponds to $[M]^+$ and $[M/2]^+$ peak appeared at *m/z* = 384.2096.



Scheme 4. Synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene silver bromide) **(4)**.

In another reaction when seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide **(1)** was reacted with mercuric acetate in DMSO resulted in the formation of seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene mercury) dibromide **(5)**. Acetic acid formed in this reaction as a side product was removed by water workup after completion of the reaction. Compound **5** was characterized by heteronuclear NMR and mass spectrometry. The signal for imidazolium hydrogen (-NC*H*-N-) that appeared at 10.32 ppm in the ^{1}HNMR of **1** had disappeared for complex **5** confirming the C-Hg bond formation. In the ^{13}C NMR spectrum of **5** the signal for the carbenoid carbon appeared at 181.19 ppm that is downfield shifted in comparison to the corresponding signal for **1** (143.10 ppm) reinforcing the C-Hg bond formation. The exact nuclearity of complex **5** could not be ascertained due to unsuccessful attempts to obtain single crystals for X-ray diffraction analysis. However, high resolution mass spectrometric measurements, in the positive ion mode, indicated towards a mononuclear complex. Measurements in the negative mode were not informative about identity of the anion and the signals observed were too weak to be assigned. Thus, the signal at *m/z* = 910.9690 was assigned to $[M+H]^+$ including two bromides associated with the metal. The peak at *m/z* = 375.0629 was due to $[M-2Br]^{2+}$ in the expected isotopic distribution pattern.



Scheme 5. Synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene mercury) dibromide **(5)**.

1.3. Experimental Section

1.3.1 General remarks

All the moisture and air sensitive reactions were carried out under inert atmosphere using the Schlenk line and Glove box. The solvents used in reaction were dried and distilled using appropriate drying agents and MBraun solvent purification system (SPS).

- Dimethylformamide (DMF): DMF was dried over CaH_2 and distilled under vacuum prior to use in the reaction.
- Ethanol: Ethanol was also dried over CaH_2 and distilled under vacuum for further reaction.

- Chloroform: Chloroform was dried over calcium chloride and distilled under nitrogen.
- Dichloroethane (DCE): DCE was collected from solvent purification system and stored over molecular sieves.
- Dichloromethane (DCM): DCM was dried over P_2O_5 and distilled under nitrogen.

All the prepared compounds were purified by crystallization and characterized using the spectroscopic techniques *i.e.*, ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy.

IR spectra were recorded as nujol mulls between KBr plates with PerkinElmer lambada35 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded with Bruker 400 MHz spectrometer with TMS as the external reference and chemical shift values are reported in ppm. High resolution mass spectrometry was performed with Waters SYNAPT G2-S.

Caution

Mercuric acetate was handled using all necessary precaustions like gloves, mask. Any unseen residual mercury traces obtained during filtration were treated with sulphur to avoid any toxicity hazards.

1.3.2 X-ray crystallography

Single crystal X-ray diffraction data for compound **3** were collected using Bruker AXS KAPPA APEX-II CCD diffractometer (monochromatic MoKα radiation) equipped with Oxford Cryosystem 700 plus at 100 K. Data collection and unit cell refinement for the data sets were done using the Bruker APEX-II suite, data reduction and integration were performed by SAINTV 7.685A (*Bruker AXS*, 2009) and the absorption corrections and scaling were done using SADABSV2008/1 (*Bruker AXS 2009*). The crystal structure was solved by OLEX2[15] package *SHELXS* 97[16] solution program direct methods and the structure was refined *SHELXL-97* 2008[17] using least square minimization. All non hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at geometrically calculated positions and were refined using riding model.

1.3.3 Synthetic procedure

1. Synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide **(1)**

Selenium (3.91 mmol, 0.31g) was added in a 100 mL Schlenk flask containing $NaBH_4$ (7.83 mmol, 0.30 g) to it was added ethanol (8 mL) slowly over 30 minutes at 0 °C. A gradual change of the initial black color to red was observed during this period. This was followed by addition of 8 mL of DMF and contents of the flask were stirred at 60 °C for 20 minutes under nitrogen to afford a colorless solution. To this solution was added 1-benzyl-3-(2-bromoethyl)-benzimidazolium bromide (7.84 mmol, 3.07 g) at room temperature. The reaction mixture was stirred for 48 hours at 75 °C. All volatiles were removed under vacuum and the resulting solid was extracted in chloroform by filtration to give a yellow filtrate that was evaporated in vacuum to give pale white solid. Yield: 70 %. ^1H NMR (400MHz, DMSO-d_6): δ = 10.32 (s, 2H, NC*H*N), 8.18-8.19 (d, 2H, Ar-H, *J* = 4 Hz), 7.98-7.99 (d, 2H, Ar-H, *J* = 4 Hz), 7.65-7.68 (m, 4H, Ar-H), 7.55-7.57 (d, 4H, Ar-H, *J* = 8 Hz), 7.35-7.40 (m, 6H, Ar-H), 5.86 (s, 4H, -NCH_2Ph), 4.88-4.90 (t, 4H, -NCH_2, *J* = 8 Hz), 3.28-3.30 (t, 4H, -CH_2Se, *J* = 8 Hz) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 143.10, 134.49, 131.51, 13, 131.13, 129.43, 129.19, 128.74, 127.24, 127.17, 114.66, 114.39, 50.28, 47.3, 22.1 ppm. IR (Nujol, KBr): ν = 1506, 1303, 1261, 1167, 1079, 1011, 965, 888, 840, 421 cm^{-1}.

2. Synthesis of 1,3-dibenzylbenzimidazolium chloride **(2)**

Benzimidazole (200 mmol, 23.6 g) and anhydrous K_2CO_3 (436 mmol, 60.16 g) were taken in a 500 mL two neck flask. Freshly distilled DMF (60 mL) was added to this flask under nitrogen followed by slow addition of benzylchloride (400 mmol, 50.4 mL) and the solution was stirred at 50 °C for 5-6 h. After cooling this flask to room temperature the mixture was poured into ice water and yellowish precipitates were collected by filtration and dried. The precipitates were further recrystallized from ethanol. Yield: 75%. Mp: 224℃. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 10.24 (s, 1H, -NC*H*N), 7.97-7.99 (d, 2H, Ar-H, *J* = 8 Hz), 7.38-7.45 (m, 12H, Ph), 5.82 (s, 4H, -C*H*$_2$Ph) ppm. ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 143.24, 134.46, 133.52, 129.49, 129.23, 128.79, 127.27, 114.52, 50.47 ppm.

3. Synthesis of 1,3-dibenzylbenzimidazol-2-ylidene silver chloride **(3)**

Molecular sieves were taken in a 100 mL Schlenk flask and were heated for 30 minutes with hot air gun. After cooling down to room temperature 1,3-dibenzylbenzimidazolium chloride (0.8 mmol, 0.302 g) and Ag_2O (1.2 mmol, 0.28 g) were added to the flask in a glove box. This flask was protected against light by using aluminum foil. Dry DCE (30 mL) was added to the flask and the solution was refluxed at 80 °C for 24 hours. The resulting solution was filtered and the filtrate was evaporated to dryness under vacuum and the residue was washed with hexane and the washings were discarded. The resulting solid was recrystallized from DCM and diethylether. Yield: 48%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 7.28-7.36 (m, 14H, Ph), 5.67 (s, 4H, -CH$_2$Ph) ppm. ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 165.34, 134.66, 133.92, 129.20, 129.16, 128.67, 127.26, 124.46, 112.20, 53.61 ppm.

4. Synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene silver bromide) **(4)**

A 100 mL Schlenk flask was heated for 30 minutes with hot air gun. After cooling it down to room temperature Ag_2O (2.1 mmol, 0.486 g) was added to the flask in a glove box and the flask was covered by aluminum foil. Seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide (1.4 mmol, 1.0 g) was added to the flask. DCM (25 mL) was added to this flask under nitrogen. The solution was stirred for 48 hours. After completion of the reaction, solution was filtered over Celite. The solution was evaporated under vacuum to give white solid. Yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22-7.27 (m, 14H, Ar-H), 7.28-7.35 (dd, 4H, Ar-H), 5.65 (s, 4H, NCH_2Ph), 4.86-4.83 (t, 4H, -NCH_2, J = 12 Hz), 3.23-3.20 (t, 4H, CH_2Se, J = 12 Hz) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 135.34, 133.7, 133.6, 128.9, 128.2, 127.5, 124.1, 124.0, 112.2, 111.2 53.4 (NCH$_2$Ph), 49.5 (NCH$_2$) 29.8 (s, CH$_2$Se) ppm. IR (Nujol, KBr): ν = 2923, 2724, 1692, 1458, 1375, 1261, 1158, 1085, 1019, 800, 725, 617, 432 cm^{-1}. MS (ESI): (+ve ion) *m/z* = 924.2416 [M]$^+$, 384.2096 [M-2Br]$^{2+}$

5. Synthesis of of seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene mercury) dibromide **(5)**

A 100 mL Schlenk flask was heated for 30 minutes with hot air gun. After cooling it down to room temperature seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide (0.85 mmol, 0.6 g) and mercuric acetate (1.275 mmol, 0.407 g) were added to the flask in a glove box. DMSO (6 mL) was added to the flask under nitrogen and the solution was stirred for 72 hour at room temperature. After completion of the reaction the solution was filtered and residue was dissolved in water. The white precipitates were allowed to settle and filtered. This precipitate was dissolved in DCM and dried over MgSO$_4$. The DCM portion was isolated and was removed using rotary evaporator. The white product obtained gave a mixture of the mononuclear complex along with some side products. ^{1}H NMR (400MHz, DMSO-d$_6$): δ = 8.11-8.13 (d, 2H, Ar-H), 7.77-7.80 (d, 2H, Ar-H), 7.55-7.60 (m, 10H, Ar-H), 7.34-7.40 (dd, 2H, Ar-H), 7.20-7.26 (dd, 2H, Ar-H) 6.23 (s, 4H, NCH_2Ph), 5.21 (t, 4H, NCH$_2$, J = 12 Hz), 3.47 (t, 4H, CH$_2$Se, J = 12 Hz) ppm. ^{13}C (100 MHz, DMSO-d$_6$): δ = 181.19 (carbenoid carbon), 153.72, 144.70, 133.35, 133.08, 129.26, 127.75, 126.38, 123.24, 122.15, 113.81, 111.21, 51.49 (NCH$_2$Ph), 49.17 (NCH$_2$), 27.85 (CH$_2$Se) ppm. MS (ESI): (+ve ion) *m/z* = 910.9690 [M+H]$^+$, 831.0494 [M-Br]$^+$, 375.0629 [M-2Br]$^{2+}$. IR (Nujol, KBr) *v* = 2920,2853, 2733, 1694, 1604, 1491, 1405, 1376, 1304, 1152, 1026, 1015, 801, 741, 724, 699, 565, 457, 422 cm^{-1}.

1.4 Summary and Future Directions:

Summary:

The present report covers the synthesis and characterisation of N-heterocyclic carbene precursors and their mononuclear and dinuclear silver chloride adducts. In this direction 1-benzylbenzimidazole was synthesized and was used for making 1-benzyl-3-(2-bromoethyl)-benzimidazolium bromide that was further used for the synthesis of seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide.

Another precursor, 1,3-dibenzylbenzimidazolium chloride was also synthesized by reaction of excess of benzyl chloride with benzimidazole which was further reacted with Ag_2O to give mononuclear complex, 1,3-dibenzylbenzimidazol-2-ylidene silver chloride. Seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide was reacted with Ag_2O which yielded di-nuclear complex seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene silver bromide). Seleno-*bis*(1-benzyl-3-ethyl-benzimidazolium) dibromide was also reacted with mercuric acetate to yield mononuclear mercury complex seleno-*bis*(1-benzyl-3-ethyl-benzimidazol-2-ylidene mercury) dibromide.

Future directions:

The further scope of this chemistry is expected as follows:

(1) The mono- & di-nuclear silver chloride and mercury complexes of selenium bridged bezimidazol-2-ylidene can be used for the transmetallation reactions.

(2) The free carbene can be generated by treatment of the benzimidazolium bromide with potassium *t*-butoxide as base. The free carbene will be used further for the preparation of the metal complexes as an alternative to the transmetallation route.

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CHAPTER 2. N-N’-Disubstituted Amidines

2.1 Introduction:

The present chapter will focus on the *N*-arylimidoyl amidine based supporting ligand that can be fine-tuned to find appropriate balance in terms of its electronic and steric factors by altering substituent’s steric bulk that would simultaneously discourage the formation of aggregates compounds. Gerhardt was a pioneer, to first synthesize amidines (R′NH-CR=NR′) by the reaction of aniline with *N*-phenylbenzimidyl chloride in 1858 and were named after the acid or amide obtained by their hydrolysis. The nomenclature of these compounds have been formulated by using amidine as suffix with respective R group, when R = H, the compound is known as a formamidine; R = CH_3, acetamidine; R = Ph, benzamidine etc. Amidines are dinitrogen analogues of carboxylic acids and esters, with a rich chemistry owing to their unique structure and diverse binding properties.[1,2] These ligands attribute combined properties of an azomethine (like C=N) and an amide (like C-N) and are very useful because of their basicity,[3,4] biological activity,[5] in few hetrocyclic complexes[6] and as intermediate in some metallocyclic complexes[6].

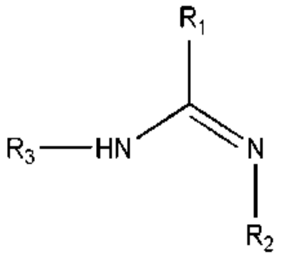
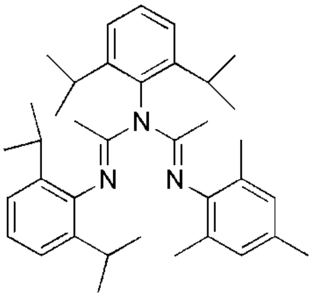
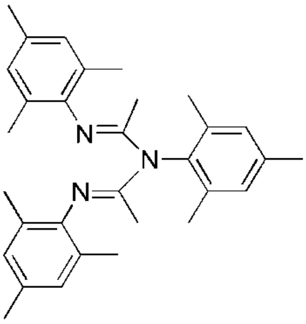


Figure 1. Amidine

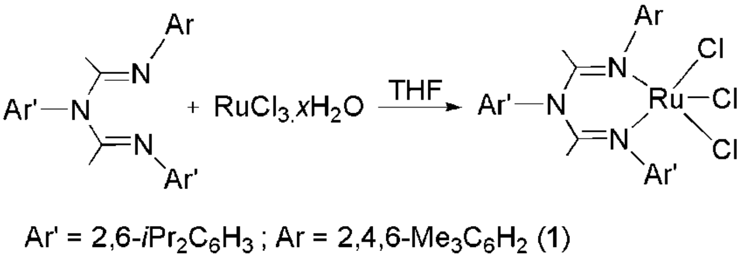
The monoanionic amidinate ligand (Figure 1) act as 2e$^-$ donor *via* more basic and less sterically crowded imino lone pair to form simple adducts such as $CoCl_2(AmH)_2$ and $PdCl_2(AmH)_2$ (AmH = amidine).[7] Variation of the substituent’s on the carbon and nitrogen atoms can alter their steric and electronic property, which makes these ligand highly suitable for complexation. The 1,3,5-triazapentadienes (tap) are less studied compounds, but known for more than a century. Amidines are good precursor to synthesize 1,3,5-triazapentadienes.[7] The main focus of this chapter is to study the coordination behaviour of the tap ligand, where H is altered by methyl group. Currently, a variety of viable synthetic methods are available for the preparation of neutral and anionic forms of imidoylamidines. The neutral quaternary *N*-arylimidoylamidines are prepared by reaction of an amine with an imidoylchloride in a 1:2 stochiometric ratio in presence of base.[8]

Table 1. Ligands worked and discussed in this chapter

	L_1	**L_2**
Molecular formula	$C_{37}H_{51}N_3$	$C_{31}H_{39}N_3$
Structure		

2.2. Results and Discussion

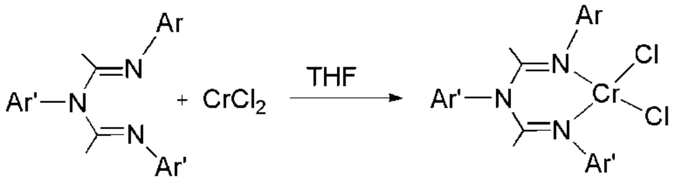
Synthesis of ruthenium complex



Scheme 1. Synthesis of L_1RuCl_3 complex (1).

The reaction of ligand (**L_1**) with one equivalent of $RuCl_3$ in THF at room temperature afforded dark green colored crystalline solid complex **1** (Scheme 1). It has been characterized by IR and mass spectrometry. The complex is highly soluble in THF, $CHCl_3$, dichloromethane but not soluble in hydrocarbon solvents. The IR spectrum of this complex showed the C=N stretch at 1641 cm^{-1} (2 cm^{-1} lower than the free ligand). The mass spectrometric measurement showed a positive ion peak at *m/z* = 769.6088 corresponding to $[M+Na]^+$.

Synthesis of chromium complexes



Ar' = 2,6-*i*$Pr_2C_6H_3$; Ar = 2,4,6-$Me_3C_6H_2$ (**2**)
Ar' = Ar = 2,4,6-$Me_3C_6H_2$ (**3**)

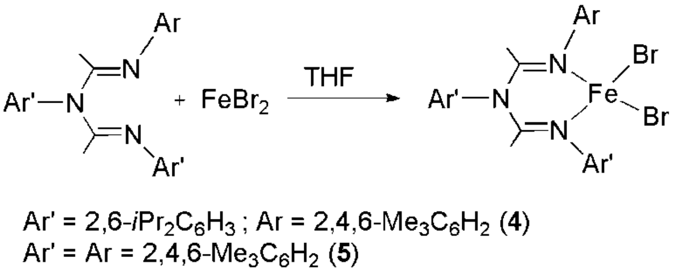
Scheme 2. Synthesis of Cr (II) complexes **L_1**$CrCl_2$ (**2**) and **L_2**$CrCl_2$ (**3**)

L_1 $CrCl_2$ (**2**) was synthesized by reaction of **L_1** with $CrCl_2$ in THF at room temperature (Scheme 2). The reaction mixture changes to light green colour. The melting point of compound **2** is 177℃. Complex **2** is highly soluble in THF, DCM, $CHCl_3$. The IR spectrum of this complex showed the C=N stretch at 1641 cm^{-1} (2 cm^{-1} lower than the free ligand). The mass spectrometric measurement showed a positive ion peak at *m/z* = 684.3490 corresponding to $[M+Na]^+$.

The reaction of **L_2** with one equivalent of anhydrous $CrCl_2$ was carried out in THF at room temperature to easily afford **L_2**·$CrCl_2$ **(3)** in quantitative yield (Scheme 2). Compound **3** is a light-green solid and melts at 172 °C. The IR spectrum of **3** shows the C=N vibrations at 1638

cm^{-1} (about 6 cm^{-1} lower than the free ligand). The complex is highly soluble in THF, DCM, $CHCl_3$. The signal at *m/z* = 574.5444 in the EI mass spectrum of **3** corresponds to the $[M+H]^+$

Synthesis of iron complexes

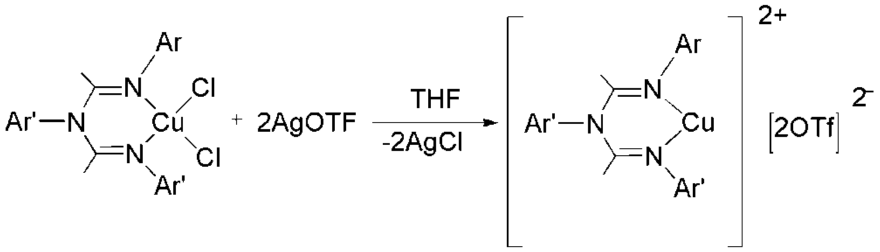


Scheme 3. Synthesis of Fe(II) complexes $\mathbf{L_1}FeBr_2$ (**4**) and $\mathbf{L_2}FeBr_2$ **(5).**

$\mathbf{L_1}FeBr_2$ **(4)** was synthesized by reaction of $\mathbf{L_1}$ with $FeBr_2$ in THF at room temperature. The reaction mixture was monitored by change in color from red to reddish brown. Complex **4** is soluble in THF, DCM, $CHCl_3$ but not soluble in hydrocarbon solvents. The IR spectrum of compound **4** showed the C=N stretch at 1641 cm^{-1} (2 cm^{-1} lower than the free ligand). The mass spectrometric measurements showed a positive ion peak at *m/z* = 776.1650 corresponding to $[M+Na]^+$.

$\mathbf{L_2}FeBr_2$ (**5**) was synthesized by reaction of $\mathbf{L_2}$ with $FeBr_2$ in THF at room temperature. The reaction was monitored by change in color to Brick red color. The complex is soluble in THF, DCM, $CHCl_3$ but not soluble in hydrocarbon solvents. The IR spectrum of compound **5** showed the C=N stretch at 1636 cm^{-1} (about 8 cm^{-1} lower than the free ligand). Mass spectrometric measurements showed a positive ion peak at *m/z* = 669.3594 corresponding to $[M+H]^+$.

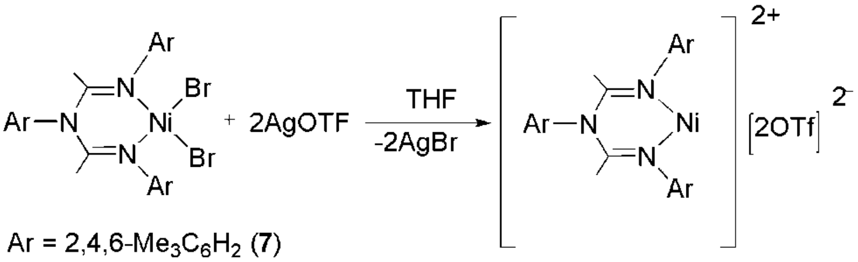
Reaction chemistry of N-arylimidoylamidine complexes of Cu(II) and Ni(II) with AgOTf and $NaBPh_4$



Ar' = 2,6-$i$$Pr_2C_6H_3$; Ar = 2,4,6-$Me_3C_6H_2$ (**6**)

Scheme 4. Synthesis of $\mathbf{L_1}$Cu[2OTf] complex **(6).**

A copper triflate complex L_1Cu[2OTf] **(6)** was prepared by reacting $\mathbf{L_1}CuCl_2$ with two equivalents of AgOTf. The reaction was monitored by change in colour from dark brown to greenish yellow and the insoluble AgCl was removed by filtration. The complex was characterized by IR, EI mass spectrometry. Compound **6** melts at 160 °C. The mass spectrum of compound **6** showed a peak at *m/z* = 897.6551 that corresponds to [M-H]. The IR spectrum of compound **6** showed the C=N stretch at 1636 cm^{-1} (4 cm^{-1} lower than $\mathbf{L_1}CuCl_2$).

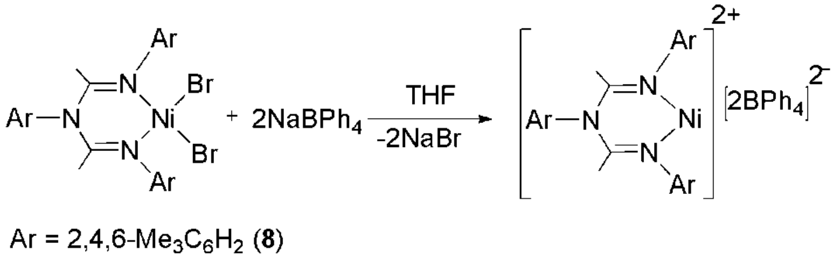


Ar = 2,4,6-$Me_3C_6H_2$ (**7**)

Scheme 5. Synthesis of $\mathbf{L_2}$Ni[2OTf] complex **(7).**

$\mathbf{L_2}$Ni[2OTf] **(7)** was synthesized by reaction of $\mathbf{L_2}NiBr_2$ with AgOTf in 1:2 ratio. The color changes progressively to light yellow and the insoluble AgCl was removed by filtration. The complex was characterized by IR, EI mass spectrometry. Compound **7** melts 183 °C. The mass spectrum of compound **7** showed a signal at *m/z* = 811.7714 that corresponds to

$[M+H]^+$. The IR spectrum of complex showed the C=N stretch at 1647 cm^{-1} (about to 10 cm^{-1} shift from **L**$_2$NiBr$_2$ complex).



Scheme 6. Synthesis of **L**$_2$Ni[2BPh$_4$] complex **(8).**

L$_2$Ni^{2+}[2BPh$_4$]$^{2-}$ **(8)** was synthesized by reaction of **L**$_2$NiBr$_2$ with two equivalents of NaBPh$_4$. The color changes progressively to light yellow and the insoluble NaBr was removed by filtration. Complex **8** was characterized by IR. Compound **8** melts at 167 ºC. The IR spectrum of complex showed the C=N stretch at 1630 cm^{-1} (about to 5 cm^{-1} shift from **L**$_2$NiBr$_2$ complex (1635 cm^{-1}).

2.3. Experimental Section

2.3.1. General remarks

The solvents used in reactions were distilled using appropriate drying agents and solvent purification system (SPS). Ethanol was dried over CaH$_2$ and distilled under nitrogen for further reaction. Rotary evaporator was used for removing some of solvents after reaction. All the manipulations and handling of reagents were done under nitrogen. All glassware were dried at 130 °C for at least 10 hour and assembled hot and cooled in vacuum prior to use.

Physical measurements

IR spectra of the complexes were recorded in the range 4500-400 cm^{-1} using a Perkin-Elmer lambda 35-spectrophotometer. Melting points were determined on buchi B-540 melting point apparatus. Mass spectrometry was performed with Thermo Scientific LTQ XL instrument.

Starting materials

All starting materials were purchased from Aldrich Chemical Co. and were used as received. The ligands $\mathbf{L_1}$ = [2,6-*i*$Pr_2C_6H_3NC(Me)N(2,6$-*i*$Pr_2C_6H_3)C(Me)N$-2,4,6-$Me_3C_6H_2$] and $\mathbf{L_2}$ = [2,4,6-$Me_3C_6H_2N\{C(Me)N(2,4,6\text{-}Me_3C_6H_2)\}_2$] were prepared as per the adopted procedure.[8]

2.3.2 Synthetic procedure

1. Synthesis of $\mathbf{L_1}RuCl_3$ complex **(1)**

A suspension of $RuCl_3$ (0.5 mmol, 0.11 g) in THF (20 mL) was prepared. To it was added drop wise a solution of $\mathbf{L_1}$ (0.5 mmol, 0.27 g) in dry THF (20 mL) at room temperature. Color of the solution changed to dark green color. The solution was stirred overnight. After complete reaction the volatiles were removed under *vacuum* afforded dark green solid. Yield: (0.305 g, 68 %). M.p.: 198 °C. MS (ESI) (+ve ion): *m/z* = 769.6088 $[M+Na]^+$. IR (KBr): ν = 2962, 2870, 2729, 1941, 1641, 1588, 1459, 1311, 1266, 1221, 1178, 1096, 1027, 934, 803 cm^{-1}

2. Synthesis of $\mathbf{L_1}CrCl_2$ complex **(2)**

A suspension of $CrCl_2$ (0.5 mmol, 0.09 g) in THF (20 mL) was prepared. To it was added drop wise a solution of L_1 in 20 mL dry THF (0.7 mmol, 0.37 g) at room temperature. Color of the solution changed to light green color. The solution was stirred overnight. After complete reaction the volatiles were removed under *vacuum* afforded light green solid. Yield:

(0.431 g, 65.5 %). Mp: 177 ºC. MS (ESI): (+ve ion) *m/z* = 684.3490 $[M+Na]^+$. IR (KBr): ν = 2963, 2874, 1759, 1641, 1460, 1374, 1261, 1182, 1097, 1038, 932, 804, 704 cm^{-1}

3. Synthesis of **L_2**$CrCl_2$ complex **(3)**

A suspension of $CrCl_2$ (0.7 mmol, 0.1 g) in THF (20 mL) was prepared. To it was added drop wise a solution of **L_2** in 20 mL dry THF (0.8 mmol, 0.36 g) at room temperature. Color of the solution changed to light green color and further stirred overnight. After complete reaction the volatiles were removed under *vacuum* afforded light green solid. Yield: (0.323 g, 56.3 %). Mp: 198 ºC. MS (ESI): (−ve ion) *m/z* = 574.5444 $[M-H]^-$. IR (KBr): ν = 2963, 1638, 1482, 1441, 1380, 1261, 1216, 1034, 945, 854, 801 cm^{-1} .

4. Synthesis of **L_1**$FeBr_2$ complex **(4)**

A solution of $FeBr_2$ (0.7 mmol, 0.15 g) in THF (20 mL) was prepared. To it was added drop wise a solution of **L_1** in 20 mL dry THF (0.7 mmol, 0.37 g) at room temperature. Color of the solution turned to dark reddish color and the reaction mixture was stirred overnight. After complete reaction the volatiles were removed under *vacuum* afforded dark red solid solid. Yield: (0.457 g, 74.1 %). Mp: 185 ºC. MS (ESI): (+ve ion) *m/z* = 776.1650 $[M+Na]^+$. IR (KBr): ν = 2961, 2871, 1949, 1764, 1641, 1457, 1373, 1260, 1189, 1096, 1031, 932, 802 cm^{-1}.

5. Synthesis of **L_2** $FeBr_2$ complex **(5)**

A solution of $FeBr_2$ (0.8 mmol, 0.17 g) in THF (20 mL) was prepared. To it was added drop wise a solution of **L_2** (0.8 mmol, 0.36 g) in 20 mL dry THF at room temperature. Color of the solution turned to dark reddish color and the reaction mixture was stirred overnight. After complete reaction the volatiles were removed under *vacuum* afforded dark red solid solid. Yield: (0.408 g, 73.2 %). Mp: 185 ºC. MS (ESI): (+ve ion): *m/z* = 669.3594 $[M+H]^+$. IR (KBr) ν = 3231, 2965, 1758, 1636, 1483, 1377, 1262, 1216, 1034, 857, 803, 703 cm^{-1}

6. Synthesis of **L_1**Cu[2OTf] complex **(6)**

A solution of **L_1**$CuCl_2$ (0.33 mmol, 0.22 g) in dry THF (20 mL) was added to a stirred suspension of $AgSO_3CF_3$ (0.65 mmol, 0.17 g) in THF (20 mL) at room temperature and was stirred for 12 h. The precipitate was filtered off, and the solvent was partially removed (ca. 15 mL) under*vacuum*. Storage of the remaining solution at −20 ºC gave greenish yellow colored solid. Yield: (62.8 %). Mp: 160 ºC. MS (ESI): (−ve ion) *m/z* = 897.6155 $[M-H]^-$. IR (KBr) ν = 2965, 1748, 1636, 1464, 1385, 1261, 1163, 1161, 1096, 1030, 803 cm^{-1}.

7. Synthesis of **L_2**Ni[2OTf] complex **(7)**

A solution of **L_2**$NiBr_2$ (0.6 mmol, 0.42 g) in dry THF (20 mL) was added to a stirred suspension of $AgSO_3CF_3$ (1.23 mmol, 0.32 g) in THF (20 mL) at room temperature and was stirred for 12 h. The precipitate was filtered off, and the solvent was partially removed (*ca.* 15 mL) under *vacuum*. Storage of the remaining solution at −20 ºC gave light pink solid precipitated. Yield: (59.7 %). Mp: 160 ºC. MS (ESI): (+ve ion) *m/z* = 811.7714 $[M+H]^+$. IR (KBr): *ν* = 2964, 1743, 1646, 1465, 1388, 1262, 1165, 1062, 805.

8. Synthesis of **L_2**Ni[2BPh$_{4]}$ complex **(8)**

In a 100mL schlenk flask $NaBPh_4$ (2mmol, 0.684g) was taken using glove box. Ni complex (1mmol, 0.671g) was added under nitrogen. 50mL dry THF were added under nitrogen. The solution stirred for 15 hour at room temperature. The solution filtered under vacuum. THF evaporated under vacuum to 20% and solution kept for crystallization. Yield: (0.43 g, 38 %). Mp: 167 ºC. IR (KBr) ν = 3265, 2967, 2364, 1630, 1604, 1479, 1438, 1427, 1373, 1261, 1215, 1183, 1150, 1095, 1031, 855, 801, 743, 704, 612 cm^{-1}

2.4 Summary and Future Directions

Summary

In this chapter ligand **L_1** and **L_2** were reacted with metal halides like $CrCl_2$, $RuCl_3$, $FeBr_2$ for formation of metal complexes. Some preformed metal complexes of Ni, Cu were reacted further with AgOTf and $NaBPh_4$ for anion exchange.

Future directions

The further scope of this chemistry is expected as follows:

(1) To synthesize different kind of metal complex with **L_1** and **L_2** ligands.

(2) Use of metal complex for anion exchange.

2.6 References:

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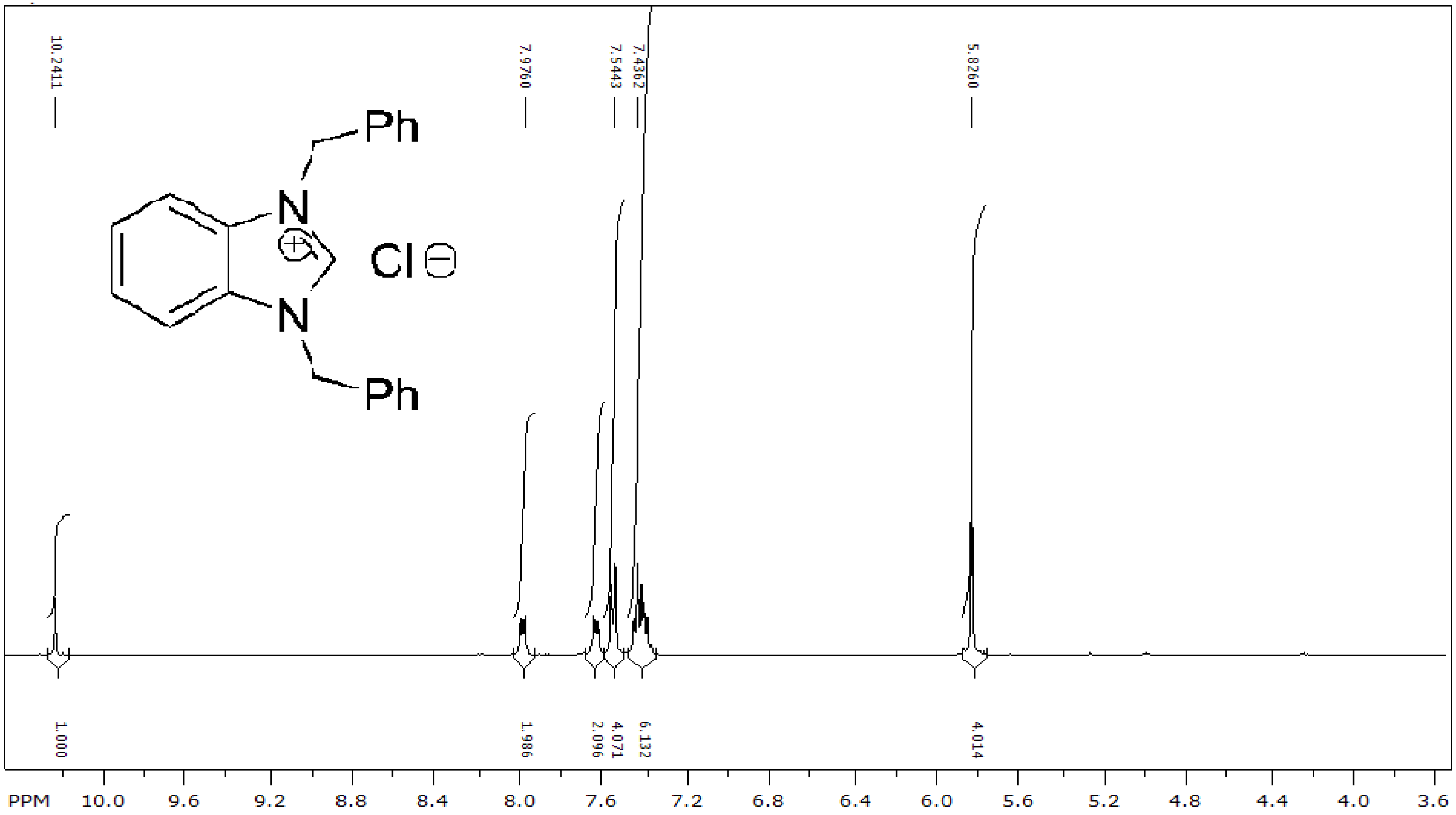
[7]. Kopylovich, M. N., Pombeiro, A.J.L. *Coord. Chem. Rev.,* **2011**, *255*, 339-355.

[8]. Prashanth, B., Singh, S., Verma, A. *Unpublished result*

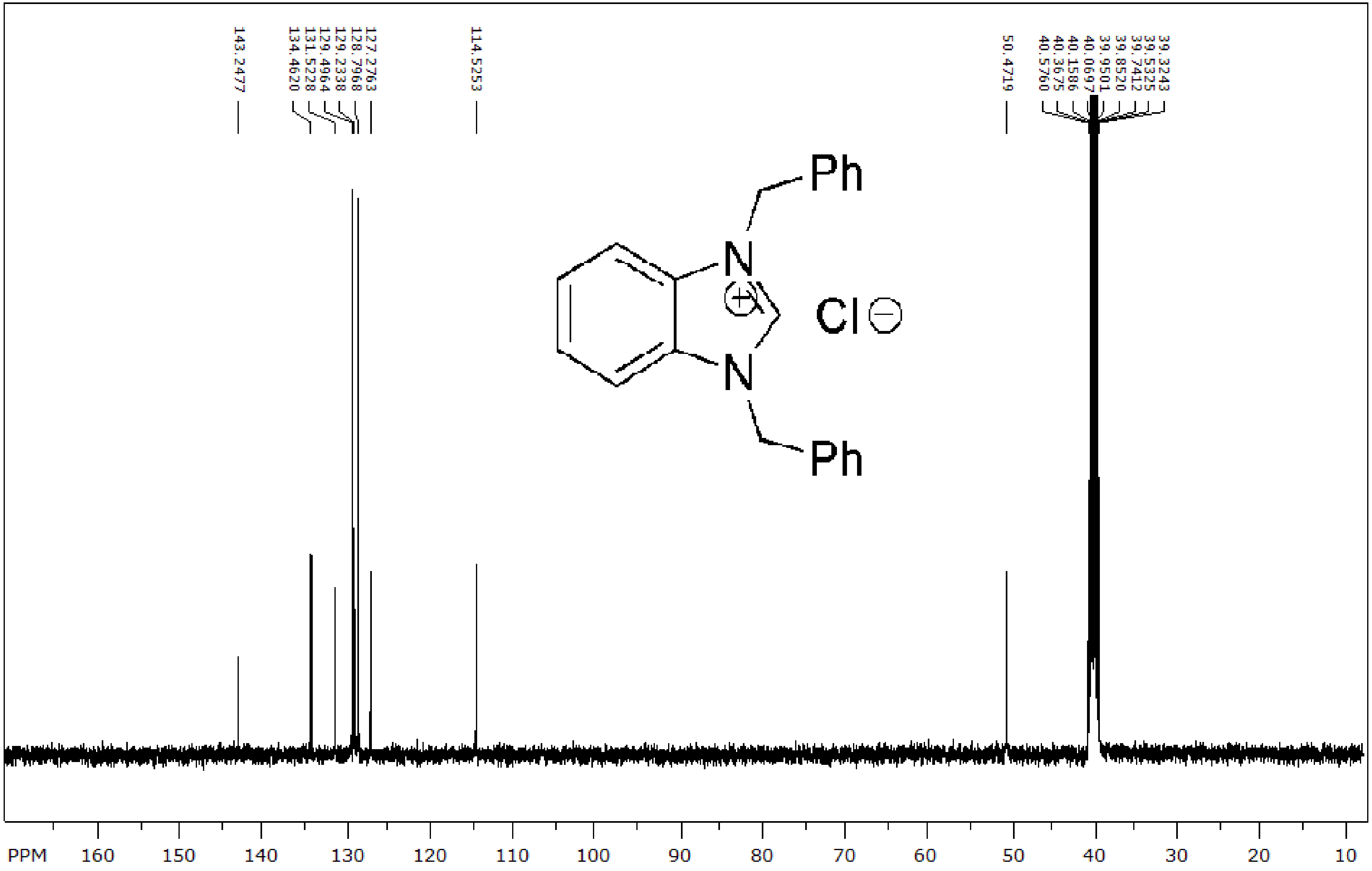
Annexure

Chapter 1.

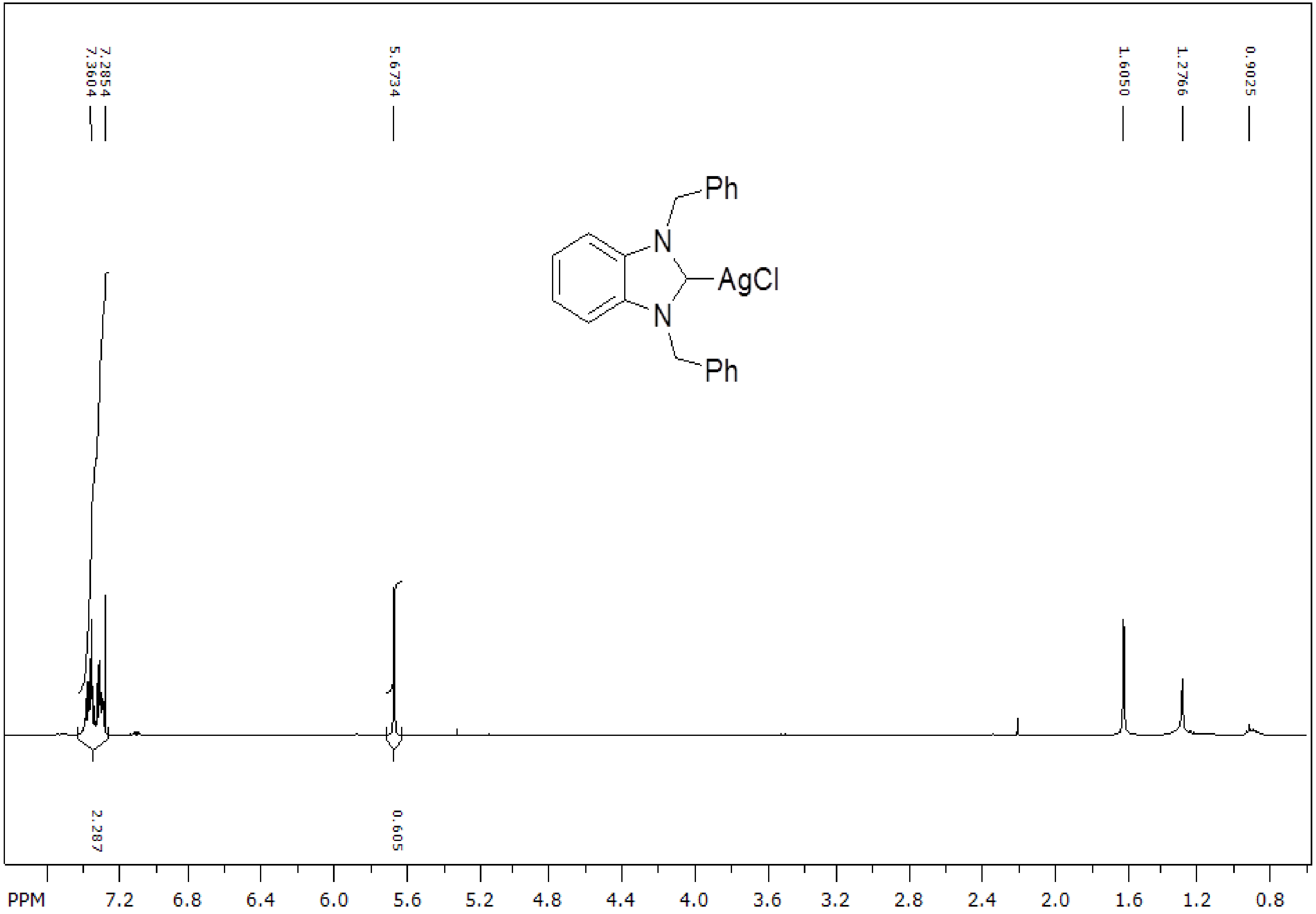
, ^{1}H NMR of **2** in DMSO-D$_6$



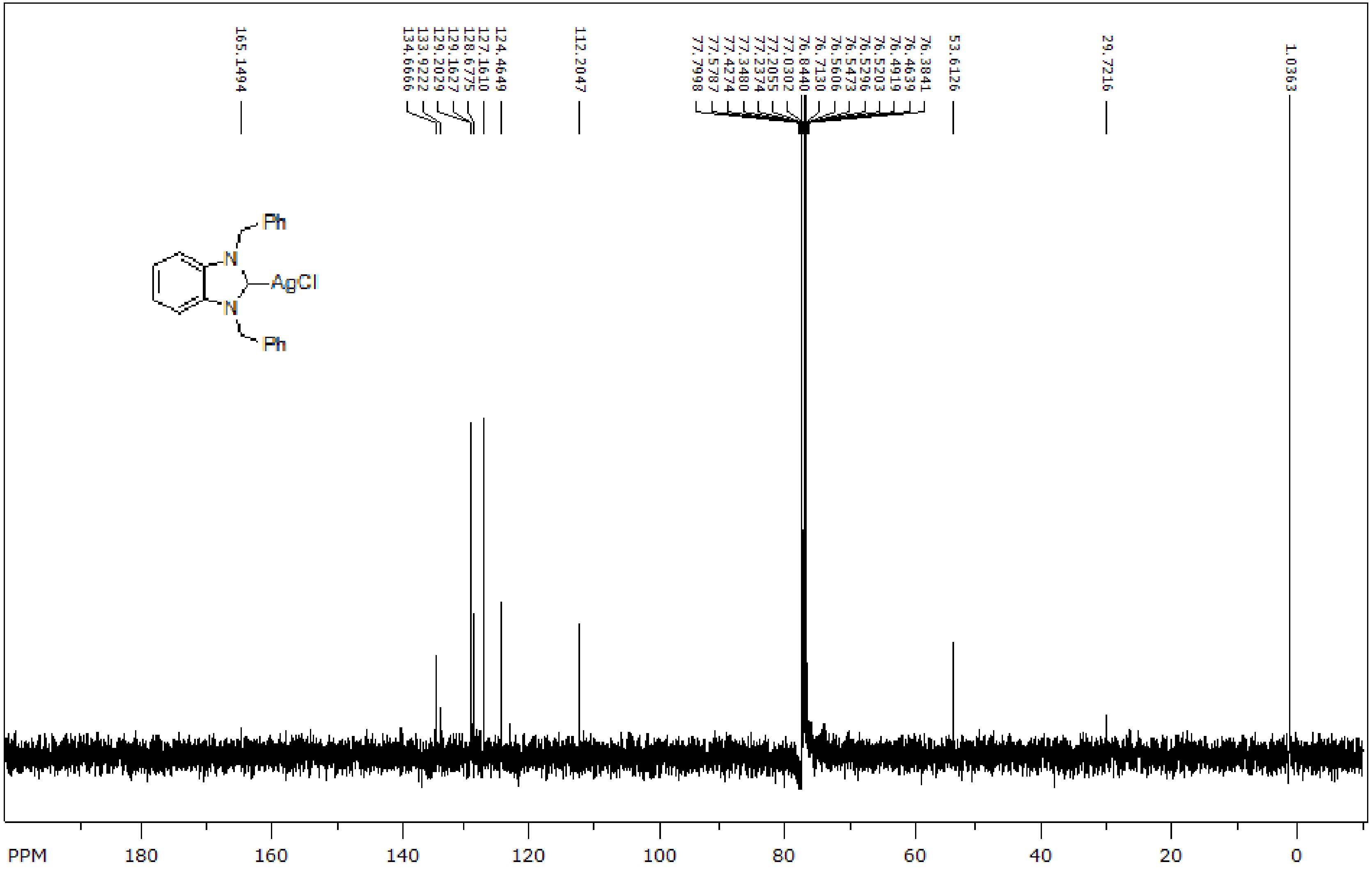
^{13}C NMR of **2** in DMSO-D$_6$



^{1}H-NMR of **3** in DMSO-D$_6$



^{13}C NMR of **3** in DMSO-D_6



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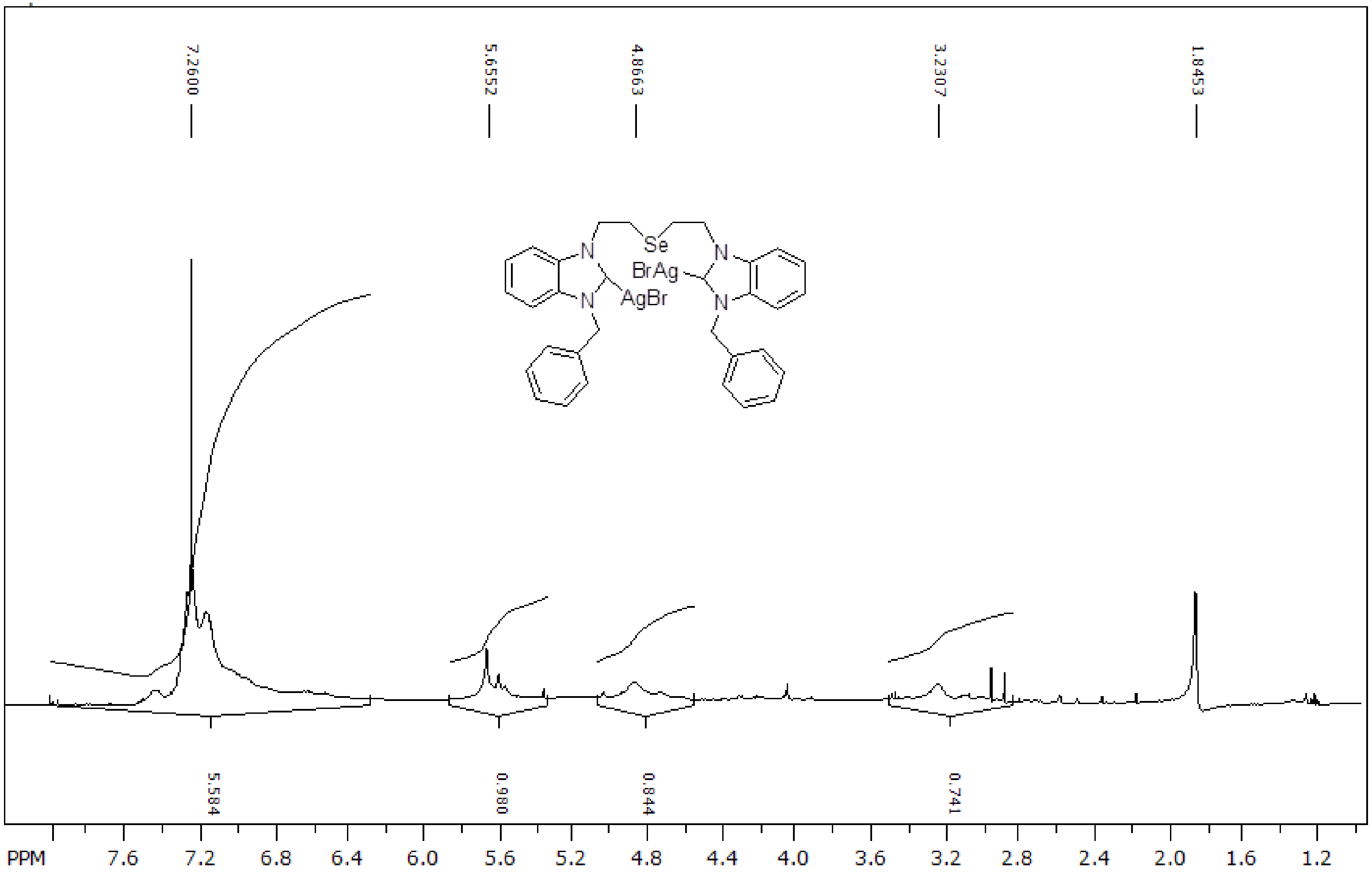

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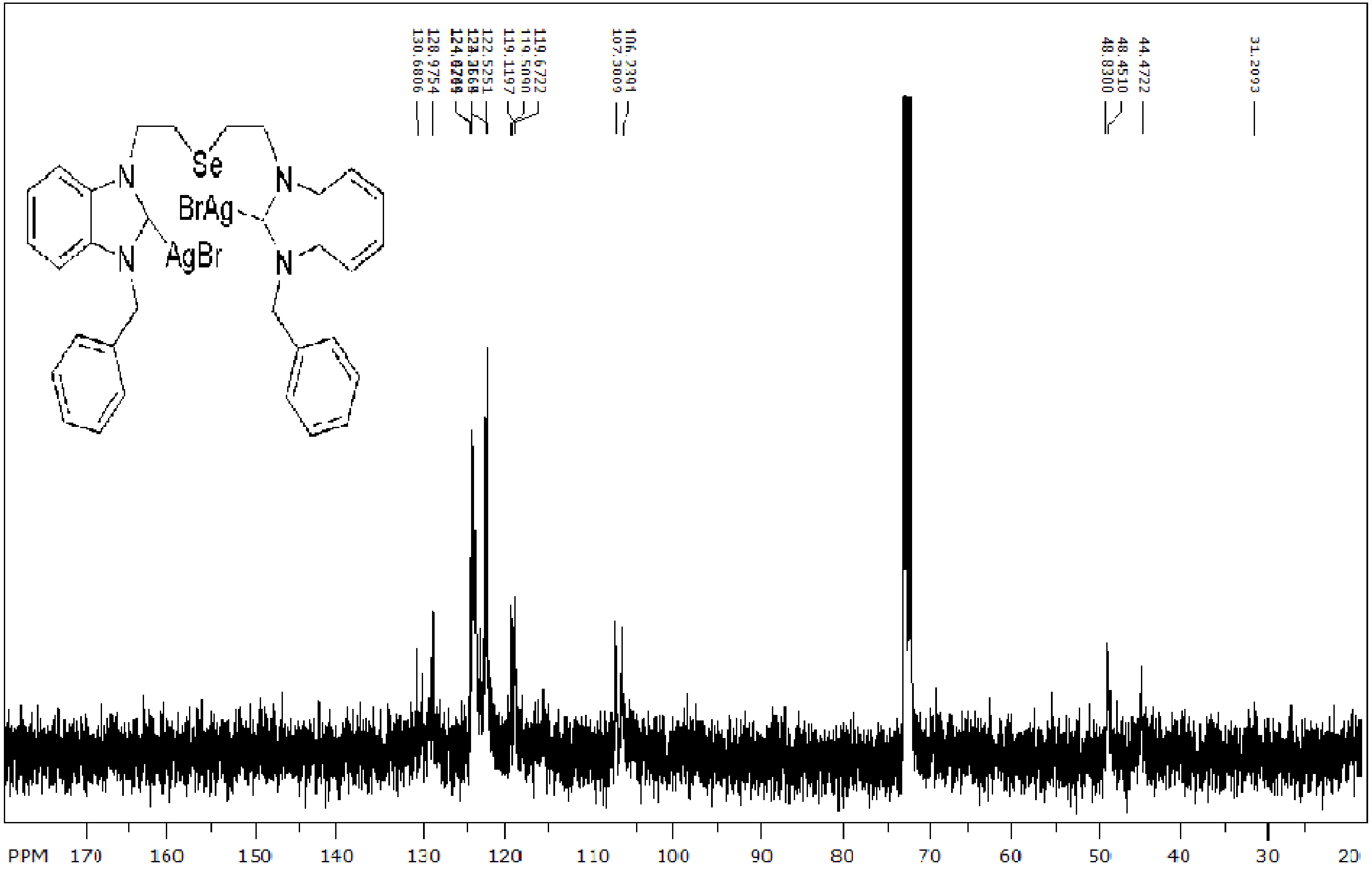

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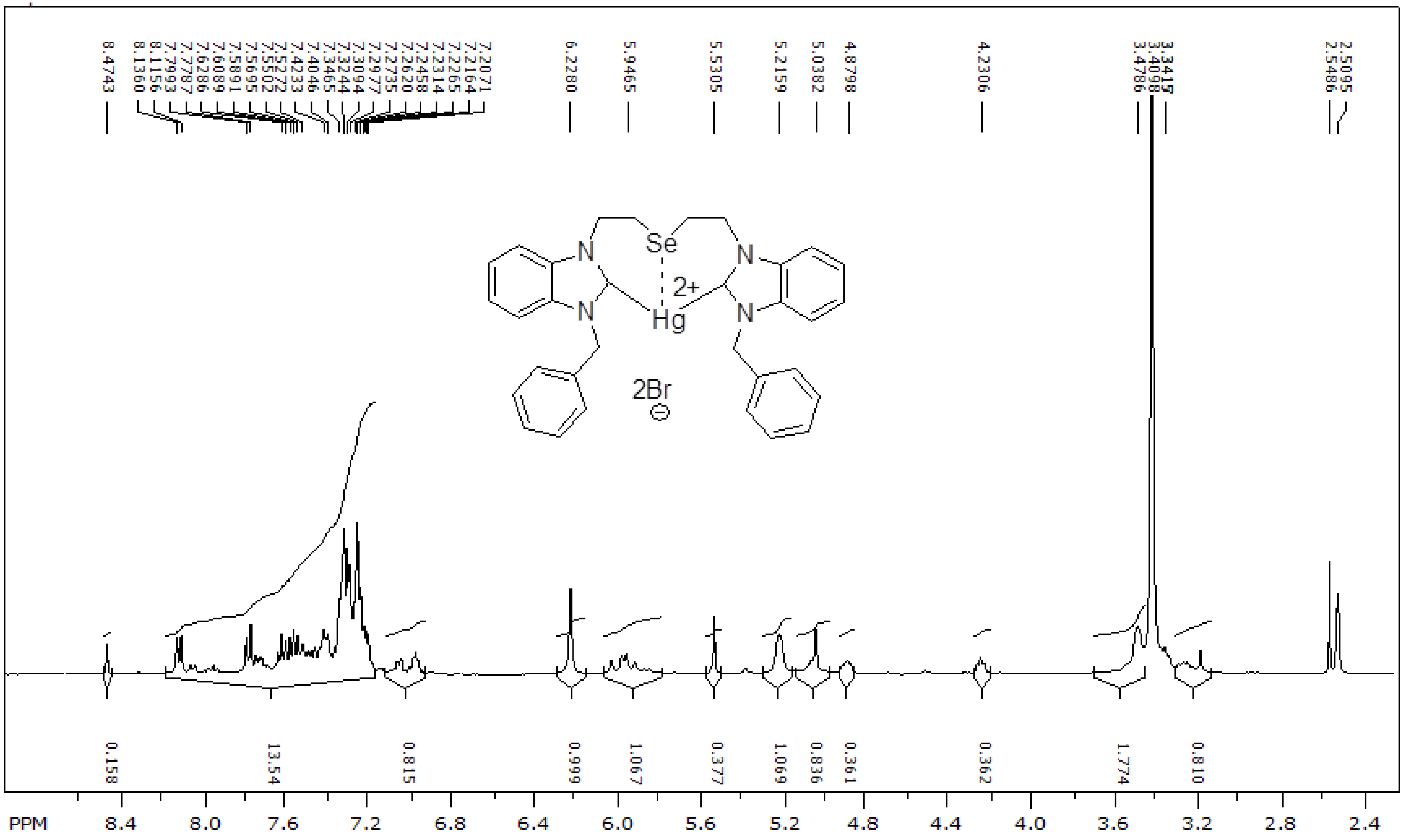
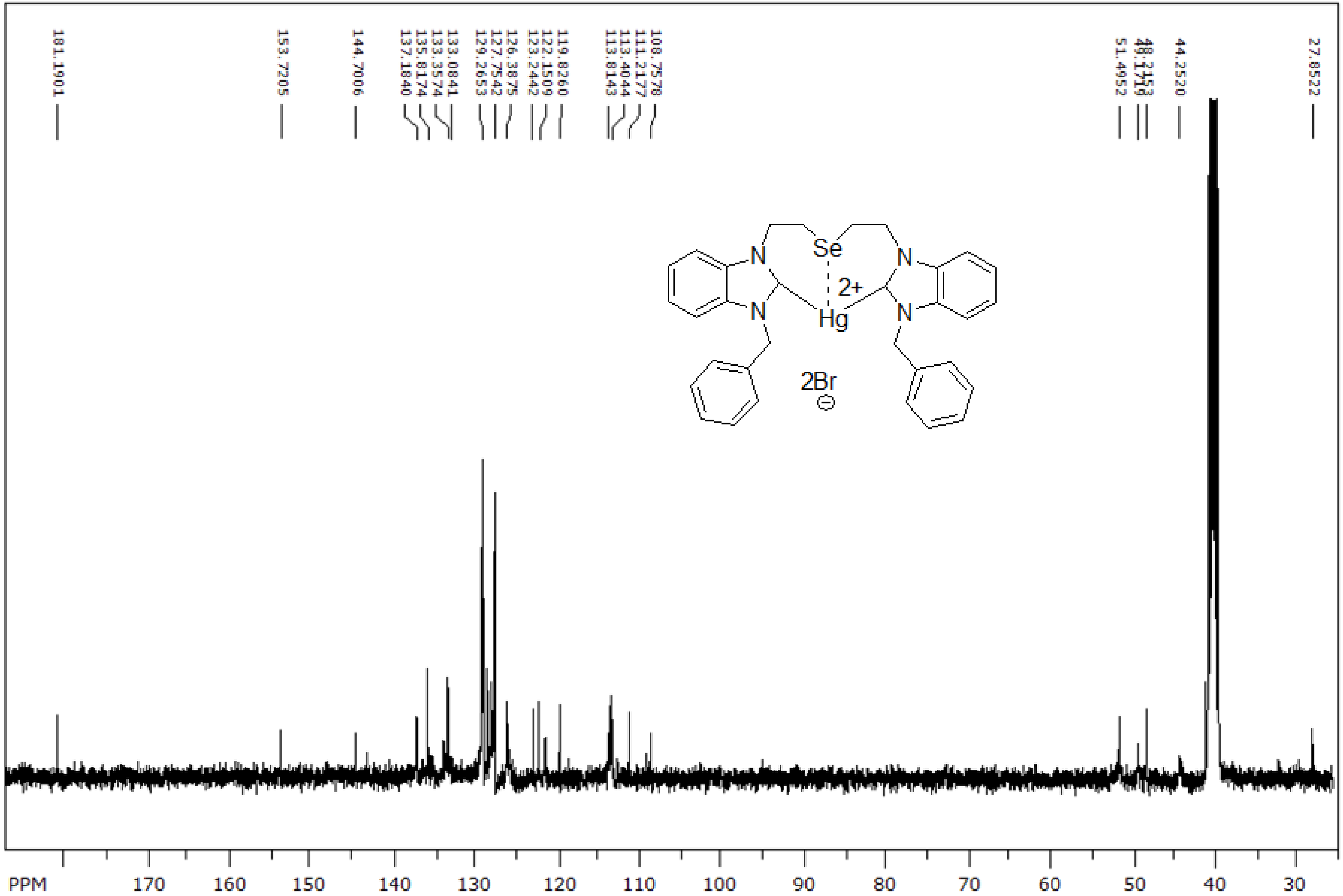
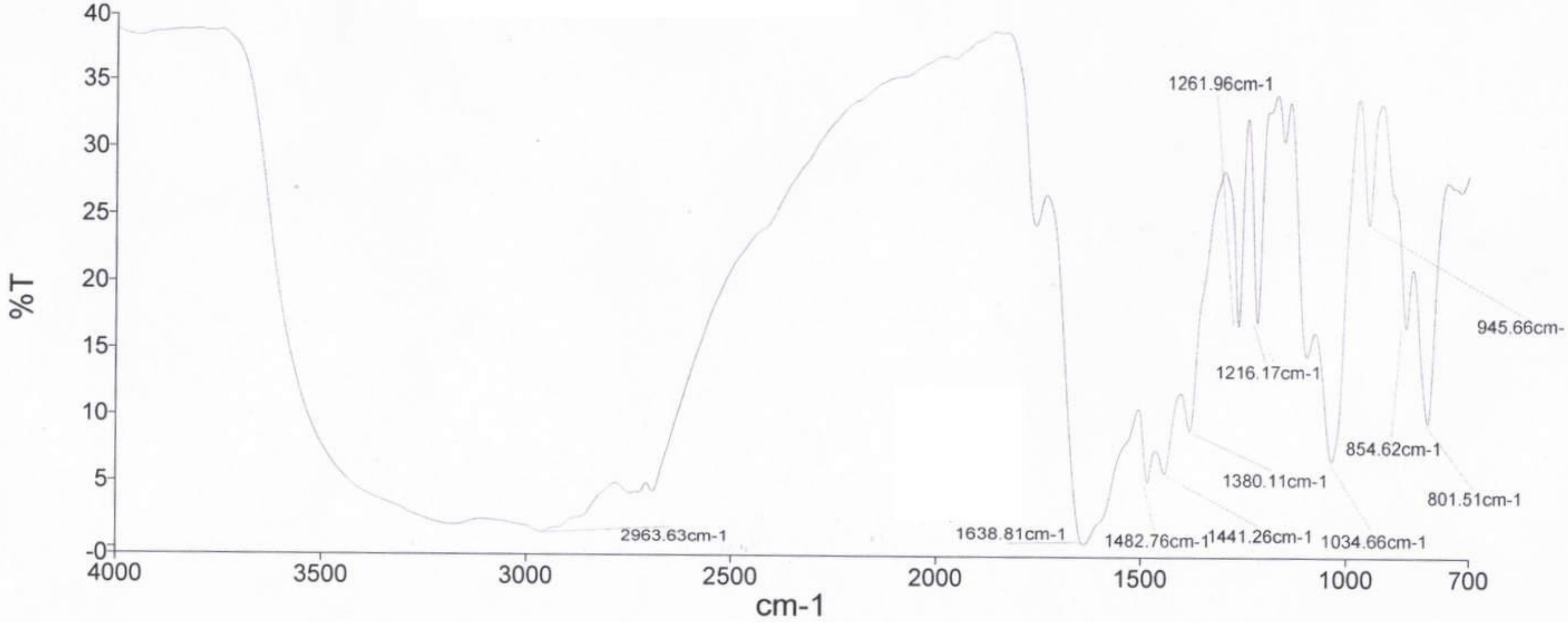


^{13}C NMR of **5** in DMSO-d_6

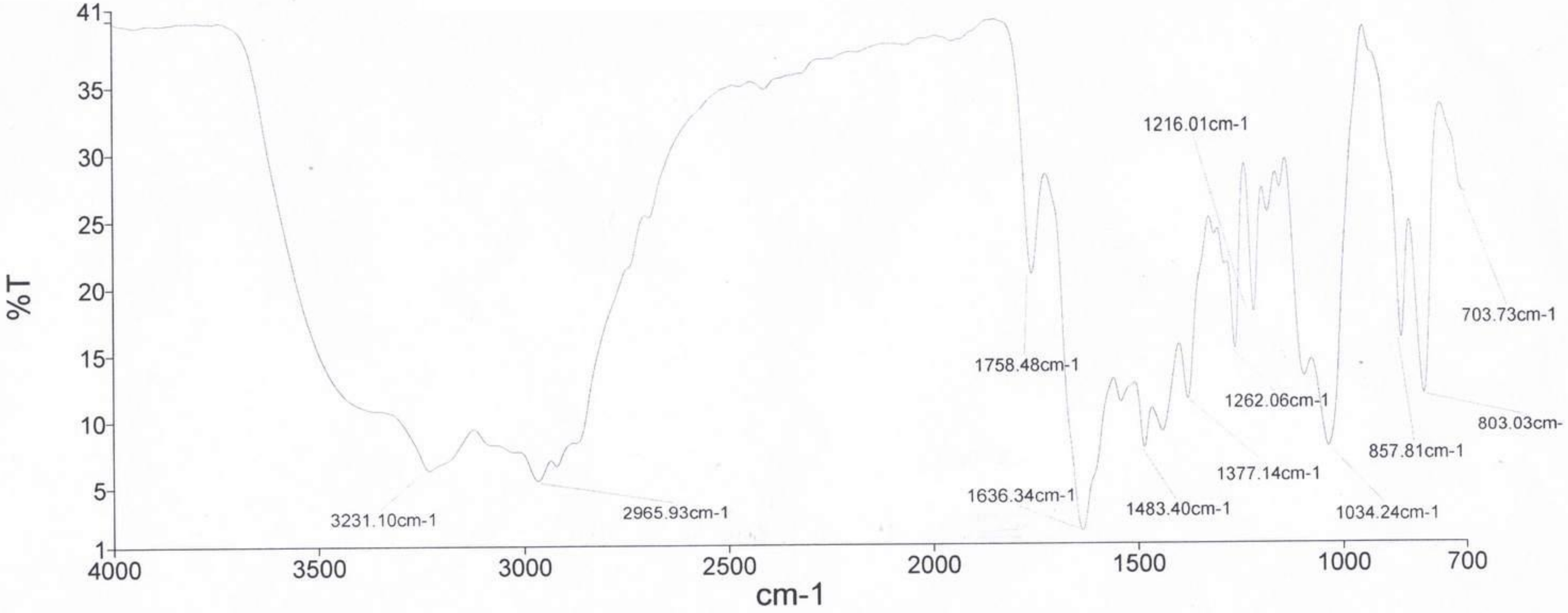


Chapter 2:

IR(KBr) of **3**



IR (KBr) of **5**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2000
1500
1000
700
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2965.93cm-1
1758.48cm-1
1636.34cm-1
1483.40cm-1
1377.14cm-1
1262.06cm-1
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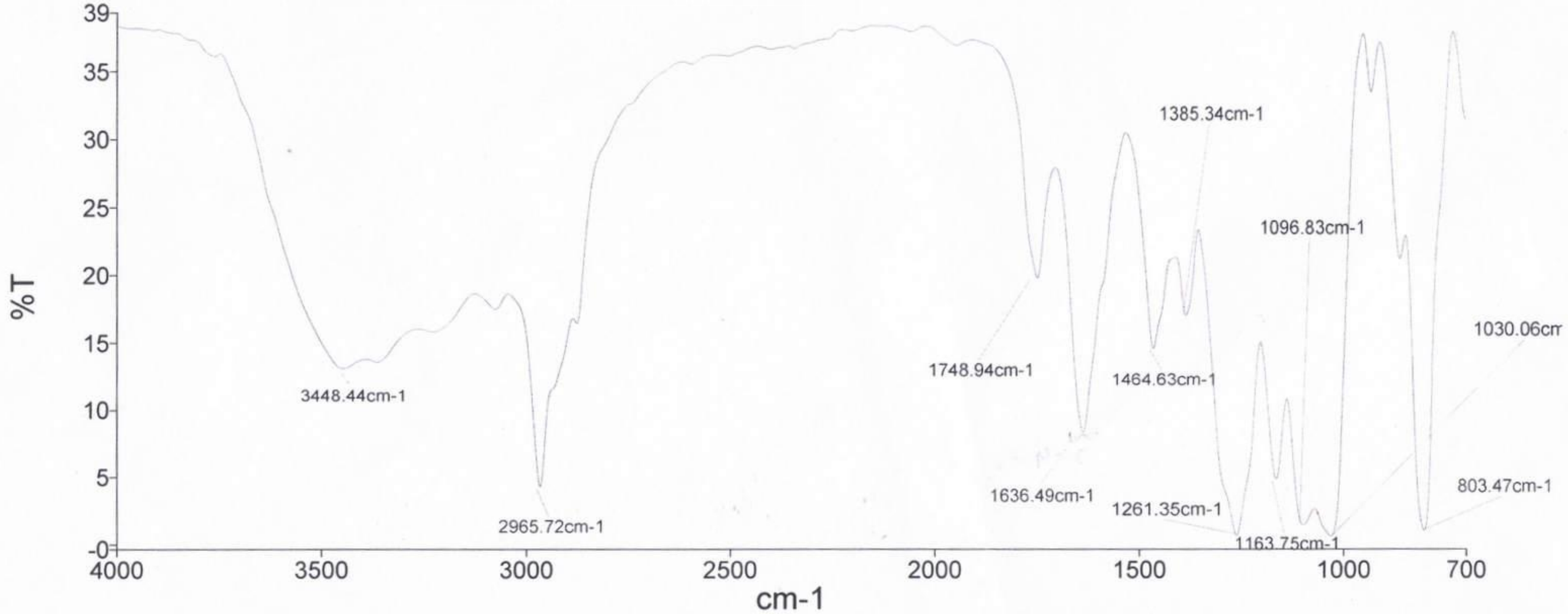
803.03cm-
703.73cm-1

IR(KBr) of **6**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700
cm-1
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1636.49cm-1
1464.63cm-1
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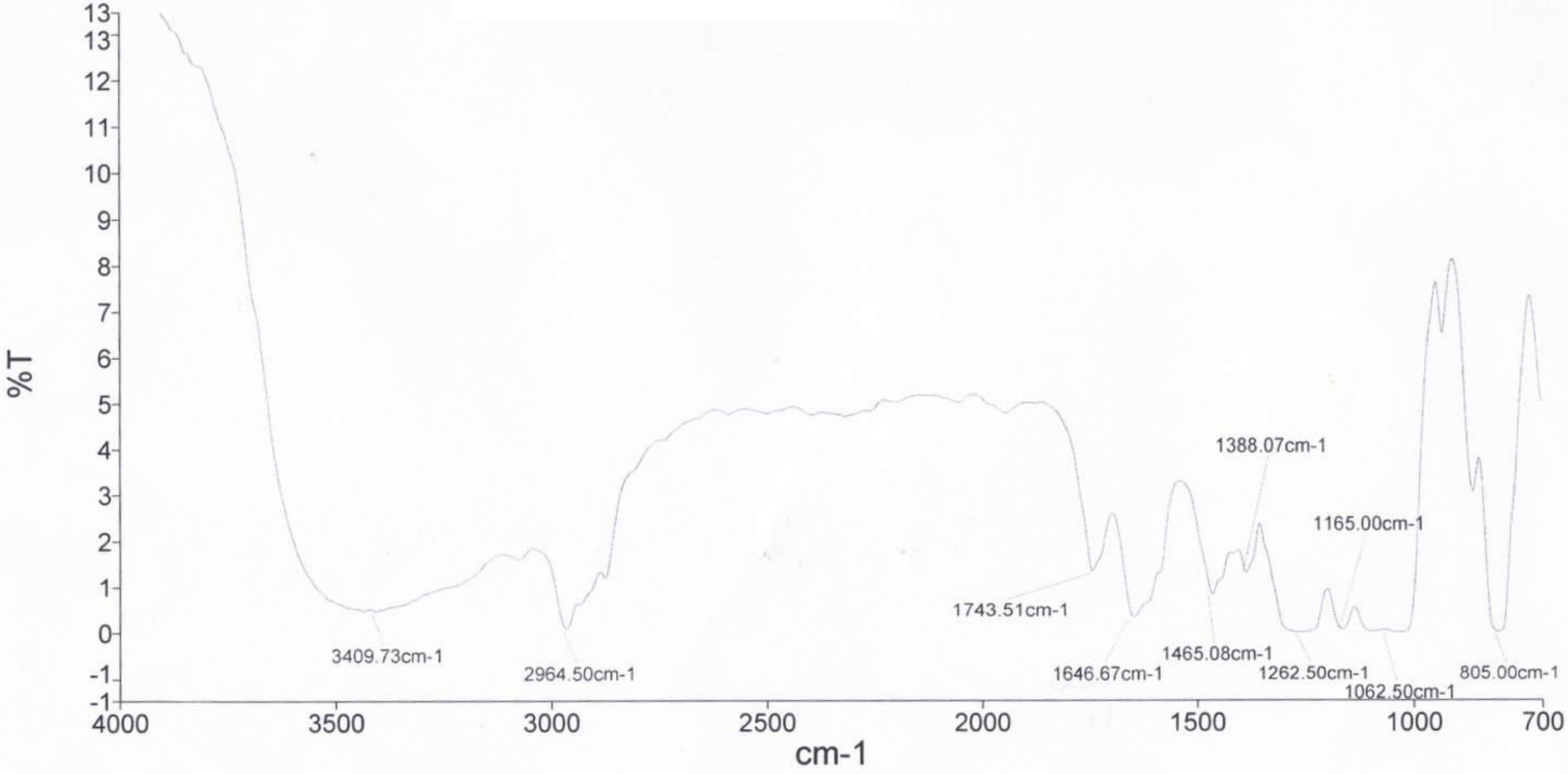
IR (KBr) of **7**



%T
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-1
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3000
2500
2000
1500
1000
700
cm-1
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2964.50cm-1
1743.51cm-1
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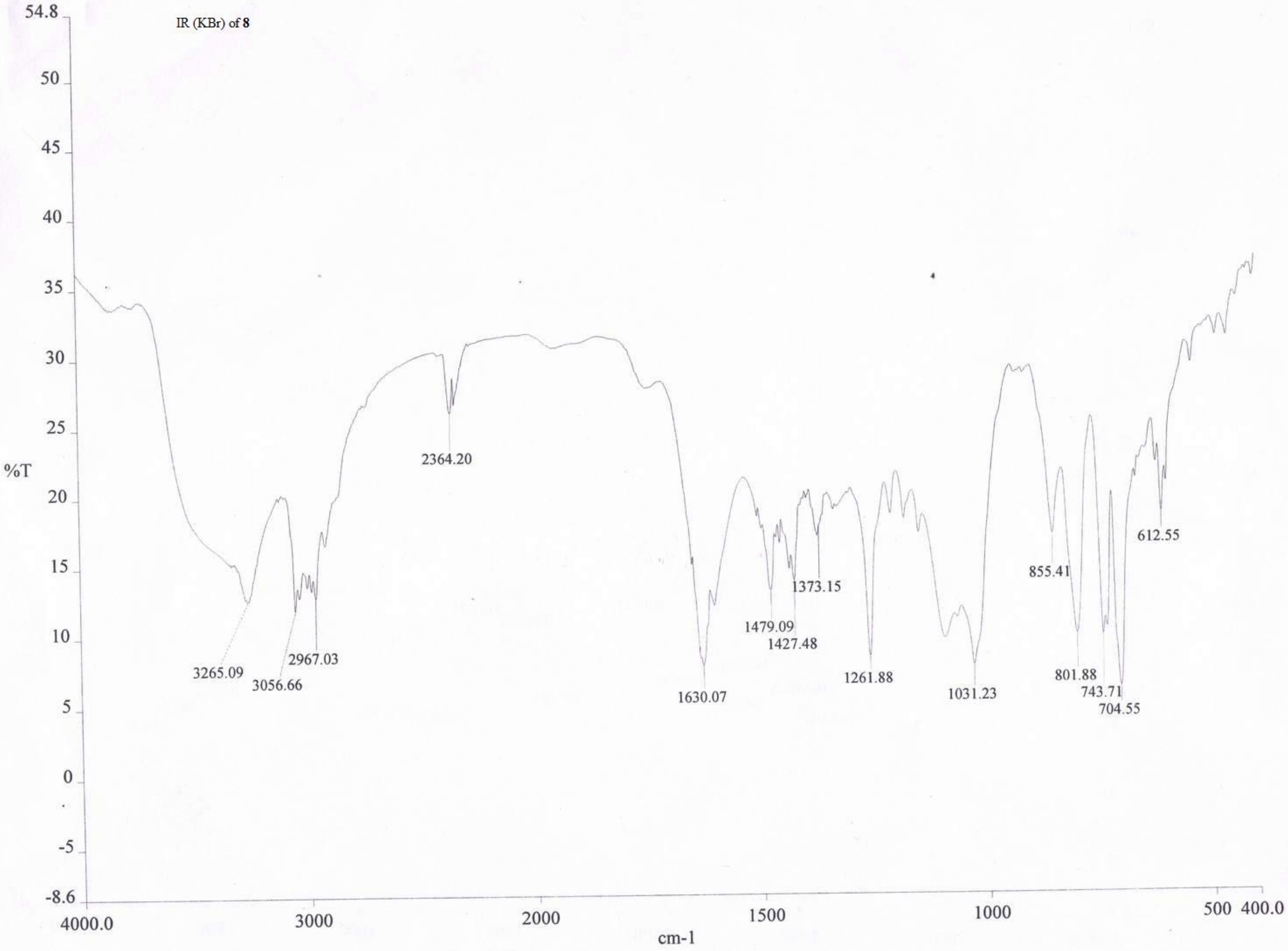
IR (KBr) of **8**
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35
30
25
%T
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10
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-8.6
4000.0
3000
2000
1500
1000
500
400.0
cm-1
3265.09
3056.66
2967.03
2364.20
1630.07
1479.09
1427.48
1373.15
1261.88
1031.23
855.41
801.88
743.71
704.55
612.55