

# Bisimidazole Selone Supported Zinc Compound: Synthesis and Characterizations

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भारतीय प्रौद्योगिकी संस्थान हैदराबाद  
Indian Institute of Technology Hyderabad

Department of Chemistry

14<sup>th</sup> April, 2014

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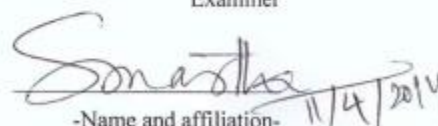
## Approval Sheet

This thesis entitled **Bisimidazole Selone Supported Zinc Compound: Synthesis and Characterizations** by Saswati Gharami is approved for the degree of Master of Science from IIT Hyderabad.


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Dedicated to

My parents, brother and my best friend

## Abstract

Metal-selenides have got vast applications in the field of metallurgy. In particular, the zinc selenide material is one of the most important materials that show excellent optical applications. In general, ZnSe is prepared by hydrothermal methods while the soft approach to prepare this material is limited, whereby Zn:Se ratio can be effectively controlled. Thus, a new 3,3'-methylenebis(1-isopropyl-1H-imidazole-2(3H)-selenone (**3**) ligand has been prepared by the reaction of 3,3'-methylenebis(1-isopropyl-1H-imidazole-3-ium) bromide and methyl bromide. The new zinc selenide complex has been prepared from the reaction of zinc tetrafluoroborate and (**3**), where one Zn is coordinated to four Se centres. The selenone ligand and the ZnSe complex have been characterized thoroughly by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FT-IR, solution UV-vis and single crystal X-ray diffraction techniques. The thermal stability of the zinc selenide is also studied by TGA. In addition, novelbisimidazoselenone ligand with ethyl spacer and imidazoselenone ligand with biphenyl spacer have been prepared and characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FT-IR, solution UV-vis and single crystal X-ray diffraction techniques.

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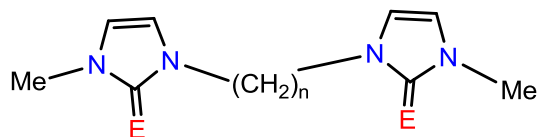


# Chapter 1

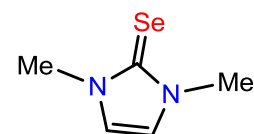
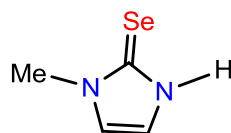
## 1.1. Introduction

The systematic design and exploration of selenium containing ligands<sup>[1]</sup> with metals have been examined for studies in bioinorganic chemistry and for their ability to form diverse coordination network architectures. This selenium is now established as essential trace element for thyroid function. So selenium analogues can show antioxidant activity by reducing H<sub>2</sub>O<sub>2</sub> even in presence of Glutathione (GSH).<sup>[2-7]</sup> Guziec *et al.* was the first to synthesize imidazole based thione ligand (MMI) and its selenium analogues.<sup>[8]</sup> These type of selenium compounds show potent biological significance when coordinated to biologically important transition metals (Cu, Fe, Ni, Zn, Mn, Mo etc.).<sup>[9-11]</sup> In this report, we have synthesized bis-(NHC) imidazo-selenone compounds having methylene, ethylene and 4, 4'-biphenyl spacer.

There are many examples of metal selenides reported in recent years. For instance, Lippolis *et al.* reported coordination chemistry of group-9 complexes with 1,1-methylenebis(3-methylimidazoline-2-selone) [Mbis], 1,1-(1,2-ethanediyl)bis(3-methylimidazoline-2-selone) [Ebis], 1,1-(butane-1,4-diyl)bis(3-methylimidazoline-2-thione) [Bbit] and 1,1-(pentane1,5-diyl)bis(3-methylimid-azoline-2-selone) [Pbis] ligands.<sup>[12]</sup> Then Jin *et al.* reported the first half-sandwich iridium and rhodium complexes of these same Mbis, Ebit and Ebis ligands which are very much used as catalyst precursors.<sup>[13]</sup> Recently Muges *et al.* explored the biological activities of the selenourea compounds along with its synthesis and characterization.<sup>[6]</sup>



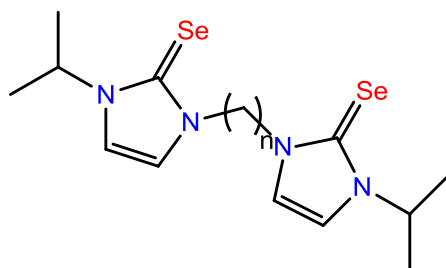
E= S, n= 4, Bbit  
 E= Se, n= 1, Mbis  
 E= Se, n= 2, Ebis  
 E= Se, n= 3, Pbis  
 E= S, n= 1, Mbit  
 E= S, n= 2, Ebit



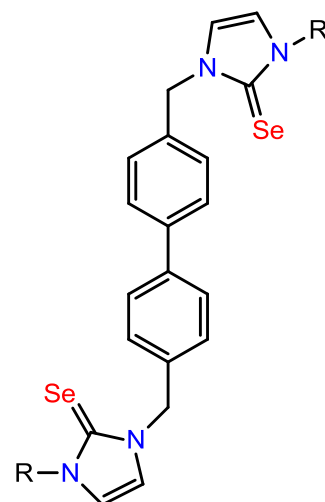
Mugesh et al. 2011

Lippolis et al. 2011

Jin et al. 2008



n= 1 (3)  
 = 2 (5)

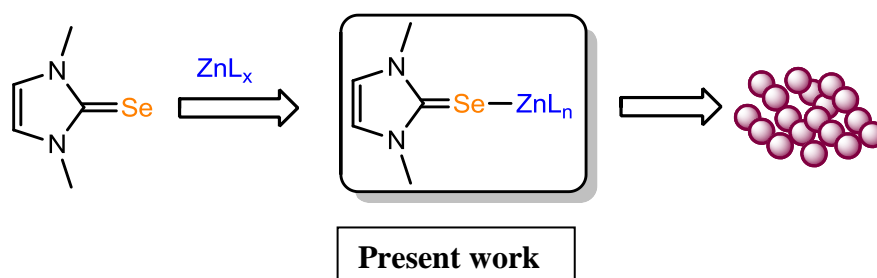


R = -CH<sub>2</sub>-CH=CH<sub>2</sub> (6)

Present work

But the imidazolone supported group 10 derivatives such as ZnSe, CdSe and HgSe are very rare. Zinc selenides have a great application in optical electronics along with laser technology and it also acts as an intrinsic semiconductor.<sup>[14]</sup> and were used to form blue-green light emitted diodes (LED) and diode lasers also.<sup>[15-17]</sup> ZnSe compounds contribute mostly in the material based applications<sup>[14]</sup> and also largely used as nanoparticle semiconductors<sup>[18,19]</sup>, till now only one report is present on zinc selenide with imidazole based ligand<sup>[14]</sup> and this suggests the another way to synthesize ZnSe, X-ray structure of the compound shows expected tetrahedral symmetry of the zinc and no anomaly is found with single crystal and powder XRD and thermo gravimetric analysis (TGA). A powder diffraction pattern collected on the

residue revealed broad peaks which matched perfectly with the ICDD pattern for hexagonal ZnSe.<sup>[14]</sup> And this encouraged us to explore the ZnSe chemistry using imidazoselenones, In this report, we have synthesized the four Selenium coordinated Zn (II) complex from bisimidazoselenone ligand, and the solid-state structure of these newly synthesized Zn (II) complex was unambiguously confirmed by single crystal X-ray diffraction technique, <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT, FT-IR, solution-state UV-vis. In addition the thermal properties of the ZnSe complex were examined using TGA.



## 1.2. Aim of work:

Following the success of their monodentate analogues, chelating bis(N-heterocyclic carbenes) (bis-NHCs) have become popular ligands in transition metal catalysis.<sup>[20]</sup> This (bis)-NHCs form more stable complexes with transition metals than that of monodentate NHCs.<sup>[20]</sup> Selenium compounds with heterocycles are found to show immense potential for antithyroid drugs and other biomedical applications.<sup>[5]</sup> It also has a great application in semiconductor based studies.<sup>[14]</sup>

For this purpose, our aim of work is the synthesis and characterization of bis-(N-heterocyclic carbenes) followed by the reaction of this ligand with zinc precursors to synthesize zinc selenide compound, which we have deliberated in **Chapter 1**, along with characterization.

In **chapter 2**, we report the synthesis of imidazoselenone ligand with biphenyl spacer. The larger spacer is expected to act as single molecule and coordinate with well separated metal sites.

## Part A:

## 2. Experimental section

### 2.1. General remarks

All manipulations were carried out under argon using Schlenk-vacuum line techniques. The solvents were purchased from commercial sources and purified according to standard procedures. Imidazole, isopropyl bromide, potassium hydroxide, 1,2-dibromoethane, acetonitrile, methanol, potassium carbonate and selenium powder were purchased from commercial sources. FT-IR (neat) measurements were carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV- vis spectra were measured on a T90+ UV-visible spectrophotometer. NMR spectra were recorded on Bruker Ultrashield spectrometer at 25 °C, unless otherwise stated. Chemical shifts are given relative to Me<sub>4</sub>Si and were referenced to the solvent resonances as internal standards. The crystal structure of **3** and **4** and **6** were measured on an Oxford Supernova diffractometer. Single crystals were mounted on a Goniometer KM4/Xcalibur equipped with Sapphire2 (large Be window) detector (CuK<sub>α</sub> radiation source, λ = 1.5418 Å). Data were collected at 153 K. Using Olex2, the structure was solved with the olex2.solve. Structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss-Newton minimisation.[1] CCDC 945326 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

### 2.2. Synthesis of 1-isopropyl-1H-imidazole (**1**):

In a round bottom flask containing 1H-imidazole (10 g, 147.06 mmol) and DMSO (250 ml) KOH (12.37 g, 220.5 mmol) was added under argon atmosphere and the RB was closed with septum and a balloon, filled with argon was inserted into it. After stirring for 5 h, isopropyl bromide was added dropwise by syringe technique under vigorous stirring and water-bath cooling. After 2 h, the reaction was stopped and water (500 ml) was added to it and extracted with chloroform (125 ml x 6). Then sodium sulphate was added to it, stirred, water was added and again separated. It was evaporated so that no DMSO is present. To remove excess DMSO work up was done by diethyl ether and water. The product was formed

as yellowish liquid after evaporation. It is confirmed by  $^1\text{H}$  NMR.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.39 (s, 1H, ImH), 7.67-7.65 (d,  $^2J_{\text{HH}} = 8$  Hz, 4H, ImH), 4.22-4.17 (m, 1H,  $^i\text{PrH}$ ), 1.35-1.33 (d,  $^2J_{\text{HH}} = 8$  Hz, 6H,  $^i\text{PrH}$ ) ppm.

### 2.3. Synthesis of 3,3'-methylenebis(1-isopropyl-1H-imidazole-3-ium) bromide (**2**):

$\text{CH}_2\text{Br}_2$  (0.53 g, 3.03 mmol) and **1** (1 g, 9.09 mmol) was taken in a schlenk tube under argon atmosphere and acetonitrile (25 ml) was added to it. The reaction was done at 90 °C for 48 h. After reaction, white precipitate came. White solid was obtained after work up. Yield: 95% (based on **1**).  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 400 MHz):  $\delta$  7.69-7.68 (d,  $^2J_{\text{HH}} = 4$  Hz, 1H, ImH), 7.64-7.63 (d,  $^2J_{\text{HH}} = 4$  Hz, 1H, ImH), 6.57 (s, 2H,  $\text{NCH}_2$ ), 4.70-4.59 (m, 2H, NCH), 1.48-1.35 (dd, 12H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  122.1, 123.02 (Im-CH), 54.09 (N- $\text{CH}_2$ -), 58.89 ( $(\text{CH}_3)_2\text{-CH-}$ ), 21.74 ( $(\text{CH}_3)_2\text{-CH-}$ ) ppm.

### 2.4. Synthesis of 3,3'-methylenebis(1-isopropyl-1H-imidazole-2(3H)-selenone (**3**):

**2** (0.4g, 1.01 mmol) was taken in a schlenk tube containing activated potassium carbonate (0.418 g, 3.03 mmol) and vacuum applied for 20 minutes. After that selenium powder (0.16 g, 2.02 mmol) and methanol (30 ml) was added to it under argon atmosphere and constant stirring. Reaction was started at 65 °C and continued for 24 h. After the completion of the reaction, work up is done with dichloromethane and water and then evaporated. As a result white crystalline solid was obtained. Yield: 80% (based on **2**). M.p., 160-165°C (melted to yellowish liquid).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.12-8.11 (d,  $^2J_{\text{HH}} = 4$  Hz, 2H, ImH), 6.84-6.83 (d,  $^2J_{\text{HH}} = 4$  Hz, 2H, ImH), 6.61 (s, 2H,  $\text{NCH}_2$ ), 5.19-5.13 (m, 2H, NCH), 1.98-1.97 (d,  $^2J_{\text{HH}} = 4$  Hz, 12H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  156.05 (C=Se), 121.23, 114.66 (Im-CH), 58.12 ( $(\text{CH}_3)_2\text{-CH-}$ ), 51.18 (N- $\text{CH}_2$ -), 21.69 ( $(\text{CH}_3)_2\text{-CH-}$ ) ppm. FT-IR (neat,  $\nu$ ): 3130(w), 2958(w), 2921(m), 2851(m), 2349(w), 2149(w), 1665(m), 1564(w), 1496(w), 1459(s), 1392(s), 1360(s), 1260(m), 1228(s), 1186(m), 1116(m), 1083(m), 1018(m), 940(w), 845(m), 801(s), 760(s), 706(s), 669(s)  $\text{cm}^{-1}$ .

### 2.5. Synthesis of Zinc(II)- 3,3'-methylenebis(1-isopropyl-1H-imidazole-2(3H)-selenone (4):

In a schlenk tube, first the **3** (0.15 g, 0.38 mmol) was taken and dissolved in dry methanol (~ 4 ml) while stirring. Then zinc tetrafluoroborate hydrate (0.0454 g, 0.19 mmol) was added in it and kept it in oil-bath and the reaction was started at 70 °C and continued for 10 days. After completion of the reaction, the reaction mixture was turned orange-red in colour. Then it was filtered and orange-red filtrate was kept in freeze for crystallization. After 3 days brick-red coloured crystals came. Yield: 30% (based on **3**). M.p., 117-120 °C (melted), 158-162 °C (decomposed to black). <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400 MHz): δ 7.727-7.721 (d, <sup>2</sup>J<sub>HH</sub> = 2.4 Hz, 4H, ImH), 7.97-7.94 (d, <sup>2</sup>J<sub>HH</sub> = 12 Hz, 4H, ImH), 4.97-4.91 (m, 4H, (CH<sub>3</sub>)<sub>2</sub>-CH-), 1.38-1.31 (d, <sup>2</sup>J<sub>HH</sub> = 28 Hz, 24H, -CH-(CH<sub>3</sub>)<sub>2</sub>), 6.59 (s, 4H, NCH<sub>2</sub>) ppm. <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 400 MHz): δ 187.04 (C=Se), 122.63, 118.86 (Im-CH), 59.04 ((CH<sub>3</sub>)<sub>2</sub>-CH-), 54.86 (N-CH<sub>2</sub>-), 21.48 ((CH<sub>3</sub>)<sub>2</sub>-CH-) ppm. FT-IR (neat,  $\bar{\nu}$ ): 3134 (w), 2975 (w), 2931 (w), 1630 (w), 1564 (m), 1516 (w), 1442 (w), 1404 (s), 1371 (m), 1179 (m), 1053 (s), 881 (m), 775 (m), 724 (s), 667 (m), 520 (w) cm<sup>-1</sup>.

### 2.6. Synthesis of 3,3'-(ethane-1,2-diyl)bis(1-isopropyl-1H-imidazol-3-ium)bromide (5) :

1,2-dibromo ethane (2.27 g, 12.08 mmol) and **1** (4 g, 36.1 mmol) was taken in a schlenk tube under argon atmosphere and dry acetonitrile (30 ml) was added to it. The reaction was done at 90 °C for 48 h. After reaction, white precipitate came. White solid product was obtained after work up with diethyl ether. Yield: 90% (based on **1**). <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz): δ 7.58-7.57 (d, <sup>2</sup>J<sub>HH</sub> = 4 Hz, 1H, ImH), 7.36-7.35 (d, <sup>2</sup>J<sub>HH</sub> = 4 Hz, 1H, ImH), 4.58-4.52 (m, 1H, (CH<sub>3</sub>)<sub>2</sub>-CH-), 1.36-1.34 (d, <sup>2</sup>J<sub>HH</sub> = 8 Hz, 6H, -CH-(CH<sub>3</sub>)<sub>2</sub>), 4.67 (s, 2H, NCH<sub>2</sub>) ppm. The imidazolium proton (N-CH-N) peak is not obtained as it has been exchanged with D<sub>2</sub>O. <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz): δ 122.27, 121.73 (Im-CH), 53.63 ((CH<sub>3</sub>)<sub>2</sub>-CH-), 48.86 (N-CH<sub>2</sub>-), 22.54, 21.97 ((CH<sub>3</sub>)<sub>2</sub>-CH-) ppm.

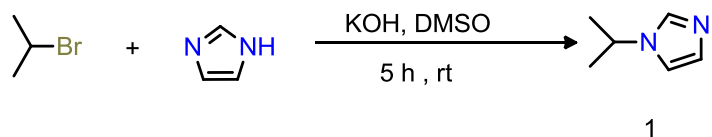
### 2.7. Synthesis of 3,3'-(ethane-1,2-diyl)bis(1-isopropyl-1H-imidazol-2(3H)-selenone) (6) :

**4** (2 g, 4.89 mmol) was taken in a schlenk tube containing activated potassium carbonate (2 g, 14.47 mmol) and vacuum applied for 20 minutes. After that selenium powder (0.77 g, 9.75 mmol) and methanol (30 ml) was added to it under argon atmosphere and constant stirring.

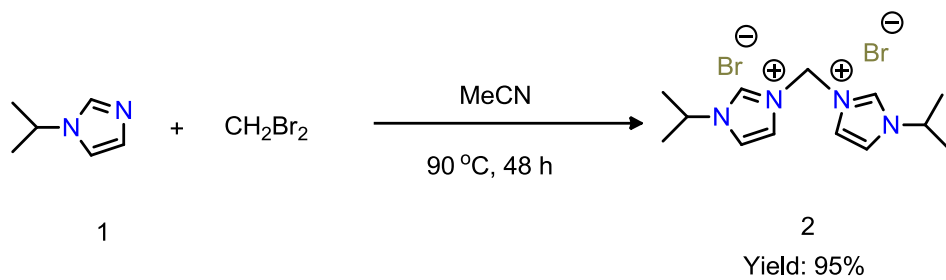
Reaction was started at 65 °C and continued for 48 h. After the reaction, TLC was monitored and the product formation was confirmed. Then the work up with dichloromethane and water was done and white crystalline solid was obtained. Yield: 80% (based on **4**). M.p., 184-188°C (melted to off-white liquid) . <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 6.78-6.77 (d, <sup>2</sup>J<sub>HH</sub> = 4 Hz 1H, ImH), 6.81-6.80 (d, <sup>2</sup>J<sub>HH</sub> = 4 Hz, 1H, ImH), 5.17-5.11 (m, 1H, (CH<sub>3</sub>)<sub>2</sub>-CH-), 1.36-1.34 (d, <sup>2</sup>J<sub>HH</sub> = 8 Hz, 6H, -CH-(CH<sub>3</sub>)<sub>2</sub>), 4.62 (s, 2H, NCH<sub>2</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 154.10 (C=Se), 120.29, 114.66 (Im-CH), 50.87((CH<sub>3</sub>)<sub>2</sub>-CH-), 46.62(N-CH<sub>2</sub>-), 21.86 ((CH<sub>3</sub>)<sub>2</sub>-CH-) ppm. FT-IR (neat, ν): 3153 (w), 3082 (m), 2966 (w), 2935 (w), 1665(w), 1643 (w), 1561 (w), 1447 (m), 1426 (s), 1407 (s), 1371 (s), 1290 (m), 1228 (s), 1162 (m), 881 (w), 708 (s), 665 (s), 625 (w) cm<sup>-1</sup>.

## Part B:

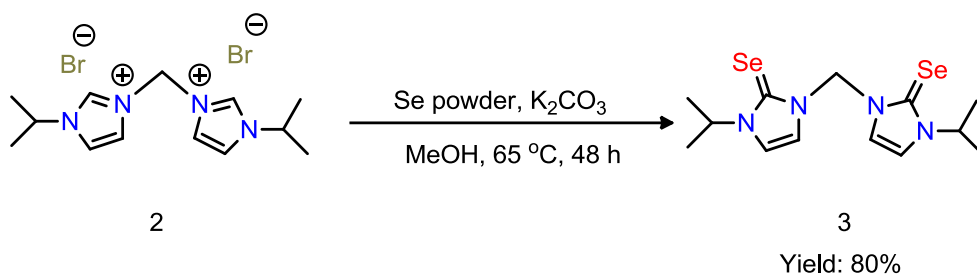
**Scheme 1:** Synthesis of **(1)**, **(2)**, **(3)**, **(4)**, **(5)** and **(6)**



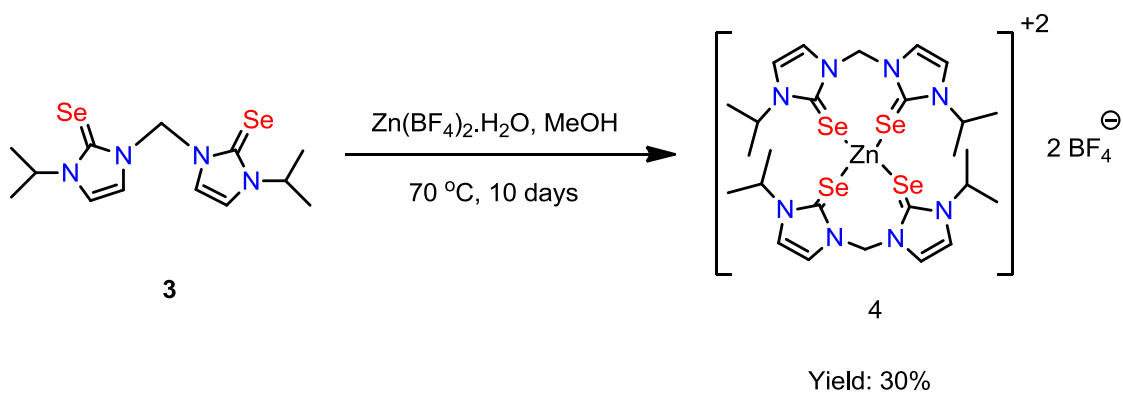
Scheme 1



Scheme 2

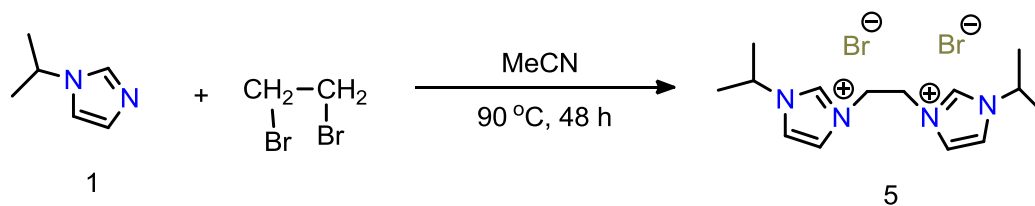


Scheme 3



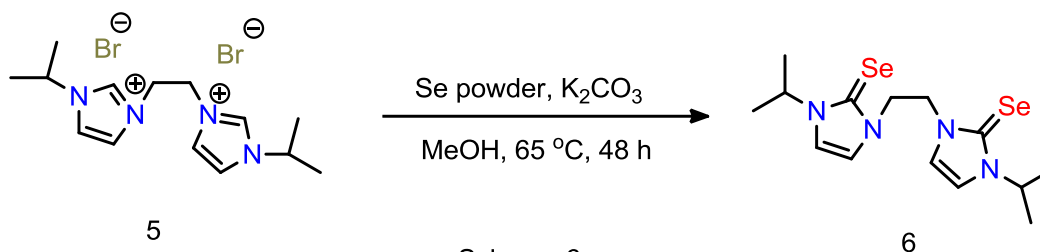
Scheme 4





Scheme 5

Yield: 90%



Scheme 6

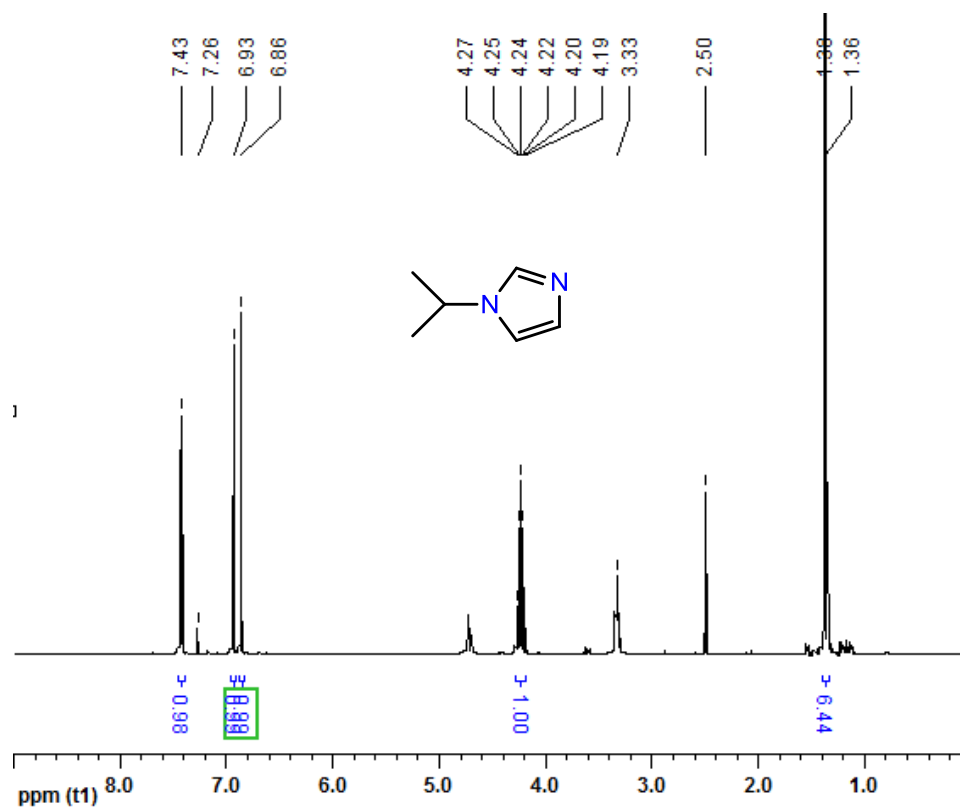
Yield: 80%

## Part C:

### 3. Results and discussion

#### 3.1. Synthesis and characterization of **1**

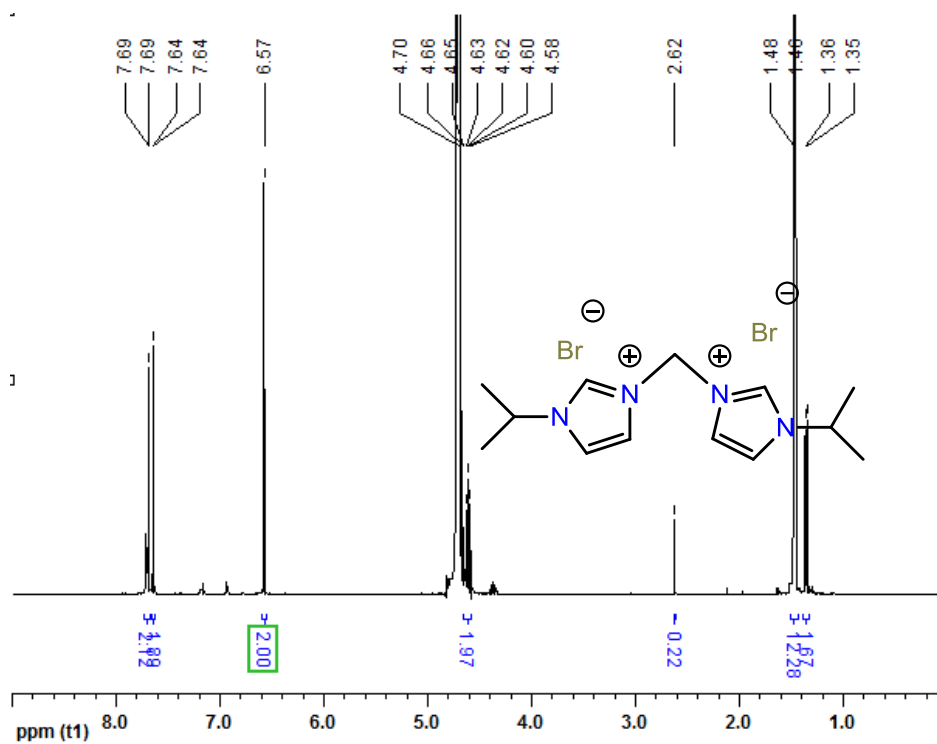
As outlined in scheme 1, compound **1** was obtained in moderate yield by combining 1H-imidazole with potassium hydroxide in DMSO at rt under argon atmosphere in a RB closed with a septum containing balloon. After stirring for 5 h, isopropyl bromide was added dropwise by syringe technique under vigorous stirring and water-bath cooling. After 2 h, the reaction was stopped and water (500 ml) was added to it and extracted with chloroform (125 ml x 6). Then sodium sulphate was added to it, stirred, water was added and again separated. It was evaporated so that no DMSO is present. To remove excess DMSO, work up was done by diethyl ether and water. The product was formed as yellowish liquid product (**1**) after filtration followed by evaporation.<sup>[21-23]</sup> Yield: 25%. Then the compound was characterized by <sup>1</sup>H NMR spectroscopy. The Im-*H* peak arises at 7.39 ppm. The isopropyl protons give doublet at 1.33-1.35 ppm.



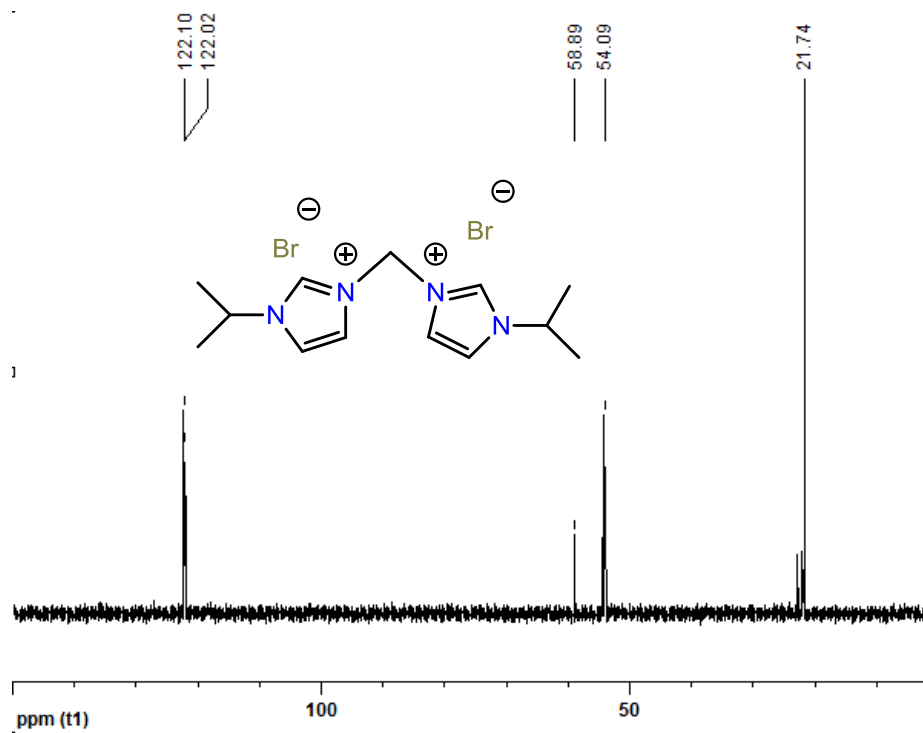
**Figure 1:** <sup>1</sup>H NMR of Compound 1 (400MHz, CDCl<sub>3</sub>, RT)

### 3.2. Synthesis and characterization of 2

CH<sub>2</sub>Br<sub>2</sub> and **1** were taken in a schlenk tube under argon atmosphere and acetonitrile (25 ml) was added to it. The reaction was done at 90 °C for 48 h. After reaction, white precipitate came. Then it was decanted after adding diethyl ether and kept in ice for 5 minutes. Then it was applied vacuum and white crystalline product was obtained (**2**).<sup>[24,25]</sup> Yield: 90% (based on **1**). It is soluble in CDCl<sub>3</sub>. The compound was characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR. The Im-*H* peak appears at downfield region (7.69-7.68 and 7.64-7.63 ppm). The NCH<sub>2</sub> gives a singlet. In <sup>13</sup>C NMR, Im-CH peak appears at 122.1 and 122.02 ppm. The chemical shift value for isopropyl carbon ((CH<sub>3</sub>)<sub>2</sub>-CH) appears at 21.74 ppm and the N-CH<sub>2</sub> peak appears at 58.89 ppm.



**Figure 2:**  $^1\text{H}$  NMR of Compound **2** (400MHz,  $\text{D}_2\text{O}$ , RT)



**Figure 3:**  $^{13}\text{C}$  NMR of Compound **2** (400MHz,  $\text{D}_2\text{O}$ , RT)

### 3.3. Synthesis and characterization of **3** and **4**

Compound **2** was taken in a schlenk tube containing activated potassium carbonate and vacuum was applied for 20 minutes. After that selenium powder and methanol was added to it under argon atmosphere with constant stirring. Reaction was started at 65 °C and continued for 48 h. After completion of the reaction, the solvent was evaporated and dichloromethane was added into it. Then it was filtered and evaporated and white crystalline solid was obtained. Yield: 80% (based on **2**). M.p., 160-165 °C. The ligand was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT, FT-IR, solution UV and single crystal X-ray diffraction technique. Then in a schlenk tube, first ligand **3** was taken and dissolved in dry methanol while stirring. Then zinc tetrafluoroborate hydrate was added in it and kept it in oil-bath and the reaction was started at 70 °C and continued for 10 days. After completion of the reaction, the reaction mixture was turned orange-red in colour. Then it was filtered and orange-red filtrate was kept in freeze for crystallization. After 3 days, brick-red coloured crystals (**4**) came. Yield: 30% (based on **3**). M.p., 117-120°C (melted), 158-162 °C (decomposed to black). This compound is characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, solution UV, FT-IR, single crystal XRD and the thermal stability of the compound is measured by thermogravimetric analysis (TGA). The selected characterization parameters for **3** and **4** are listed in table 1. In **3**, C=Se stretching frequency appeared at 1078 cm<sup>-1</sup> while in **4** it appeared at 1052 cm<sup>-1</sup>. The decrease in stretching frequency is due to the rigidity gained by **4** than that of **3**. The N-C-N stretching frequency of **3** and **4** appears at 1381 and 1371 cm<sup>-1</sup>. In <sup>1</sup>H NMR, the chemical shift values for Im-CH, Im-CH<sub>2</sub> and <sup>i</sup>Pr protons are comparable in **3** and **4**. In **3**, the Im-H gave two doublets at 8.12-8.11 and 6.84-6.83 ppm while in **4**, the doublets appear at 7.721-7.727 and 7.94-7.97 ppm. The NCH<sub>2</sub> peak appears as a singlet at 6.61 ppm in **3** while in **4**, it appears at 6.59 ppm. In <sup>13</sup>C NMR of **3**, the C=Se chemical shift value appears at 156.05 ppm while in **4**, the peak gives a doublet at 187.04 ppm. The Im-CH peak arises at 122.63 and 118.86 ppm in **3** whereas in **4**, it appears at 124.15 and 127.91 ppm. The NCH<sub>2</sub> appears at 51.18 ppm in **3** but in **4**, the chemical shift value appears at 54.86 ppm.

**Table 1.** Characterization of **3** and **4**.

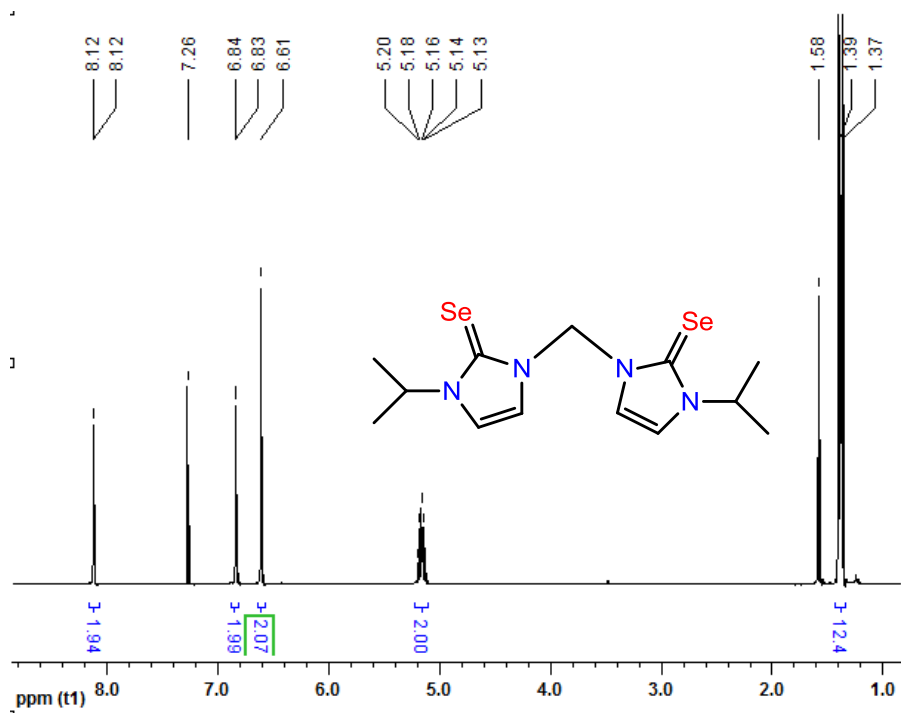
Compound	M.P. (°C)	Yield (%)	<sup>1</sup> H NMR $\delta$ Im-CH (ppm)	<sup>13</sup> C NMR $\delta$ N-C(Se)-N (ppm)	Solution UV-vis abs. (nm)
----------	-----------	-----------	--------------------------------------------	----------------------------------------------------	---------------------------------

<b>3</b>	160-165	80	8.12-8.11, 6.84-6.83	156.05	216, 280
<b>4</b>	117-120	30	7.721-7.727, 7.94-7.97	192.32	215, 281

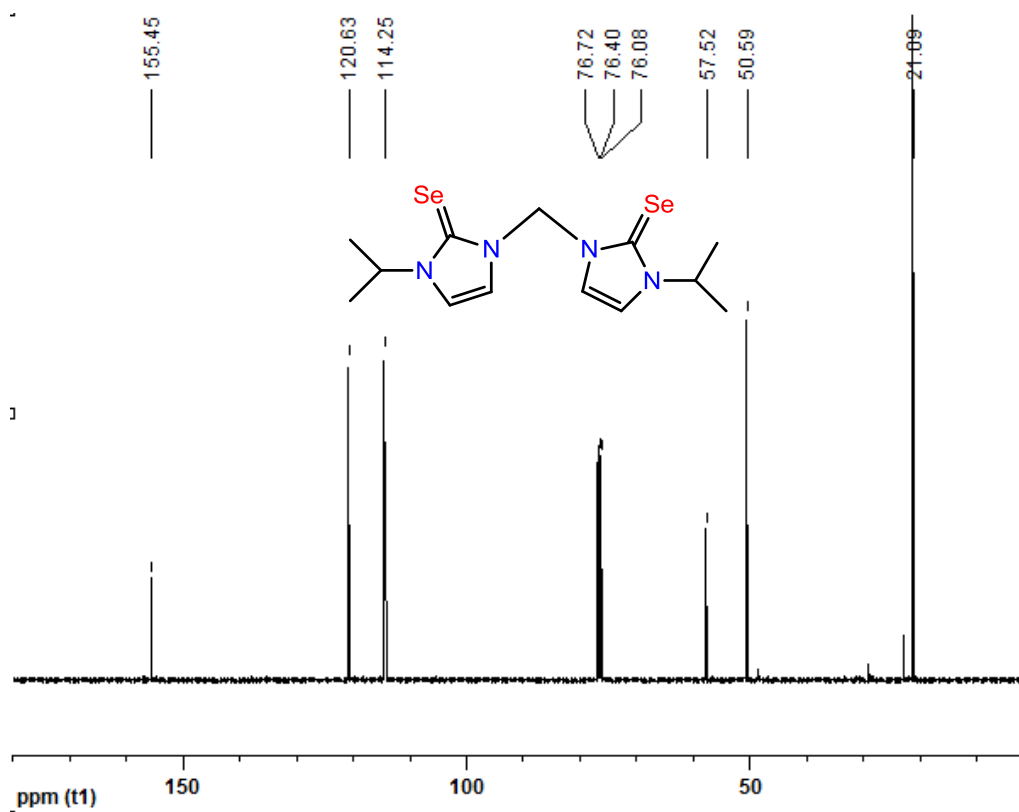
The formation of **3** was further characterized by 2D NMR spectroscopy i.e. DEPT, HMBC and HSQC. Notably the structural exploration for the imidazole selenone using 2D NMR is rare. In DEPT spectrum, **3** clearly gave one CH<sub>2</sub> group, one CH group, two CH<sub>3</sub> groups and three CH groups (vide infra).

HSQC spectrum of **3** showed C-H correlations as follows, the imidazolium CH group showed strong correlation between the carbons and the hydrogens attached to it. The CH group of isopropyl moiety also showed a strong correlation between CH carbon and the only hydrogen atom attached to it and in CH<sub>3</sub> groups, the C-H correlation is also observed. Total five C-H correlations are observed, including NCH<sub>2</sub>N and C-H correlation, which indicates that **3** contain five equivalent carbon which contains hydrogen.

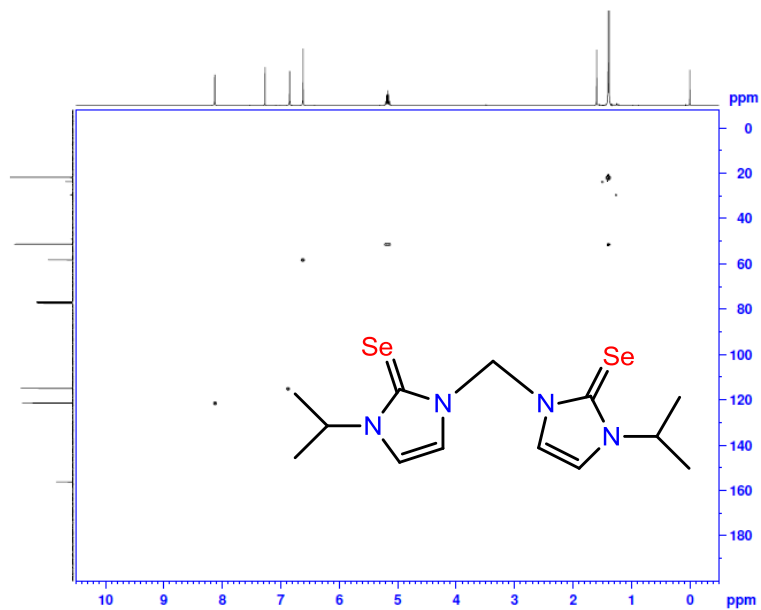
The structure of **3** is further confirmed by HMBC spectrum that showed the mapping carbon coupling with neighbouring protons. The C=Se carbon couples with the nearest CH<sub>2</sub> and CH protons strongly (<sup>3</sup>J) but the coupling is not that much strong with other two imidazolium protons (<sup>3</sup>J). The CH<sub>2</sub> protons couple more strongly with nearest imidazolium proton (<sup>3</sup>J) than that of farthest one (<sup>4</sup>J). On the other hand two couplings of the CH<sub>3</sub> protons with the nearest imidazolium carbon and isopropyl CH carbon are observed (<sup>4</sup>J).



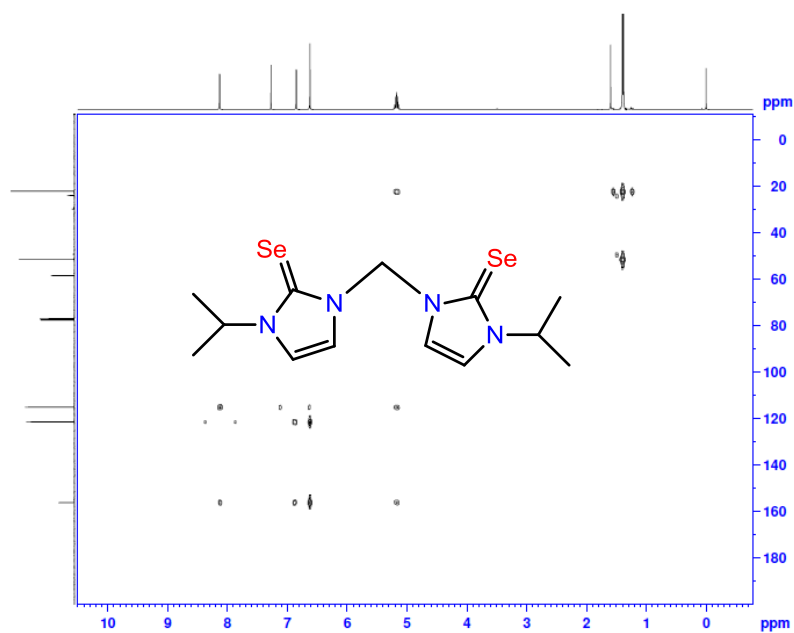
**Figure 4:**  $^1\text{H}$  NMR of Compound **3** (400MHz,  $\text{CDCl}_3$ , RT)



**Figure 5:**  $^{13}\text{C}$  NMR of Compound **3** (400MHz,  $\text{CDCl}_3$ , RT)



**Figure 6:** HSQC of Compound 3 (400MHz, CDCl<sub>3</sub>, RT)



**Figure 7:** HMBC of Compound 3 (400MHz, CDCl<sub>3</sub>, RT)

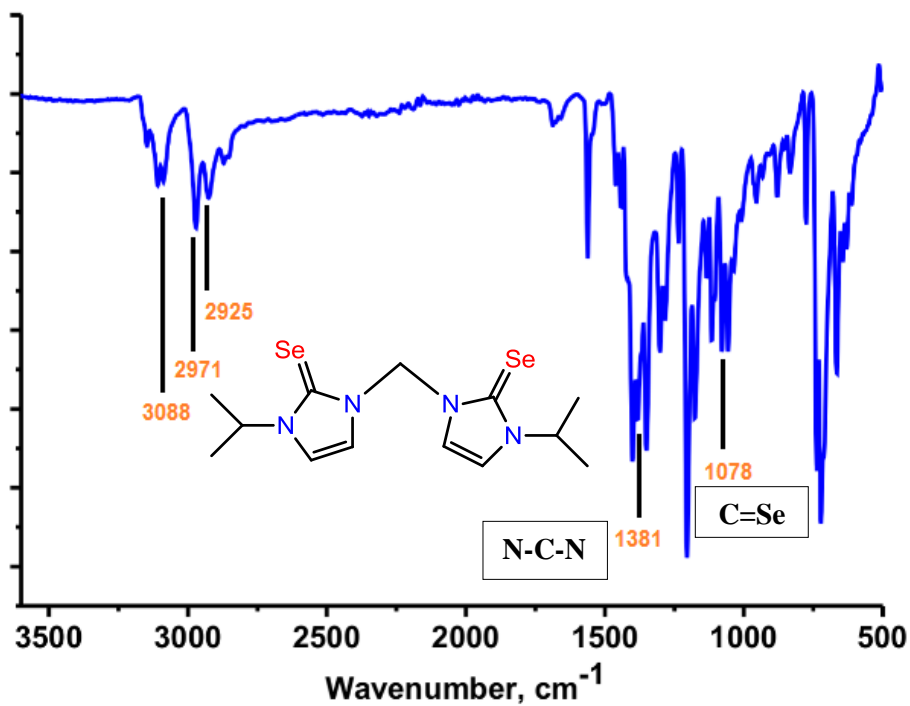


Figure 8: IR spectrum of compound 3

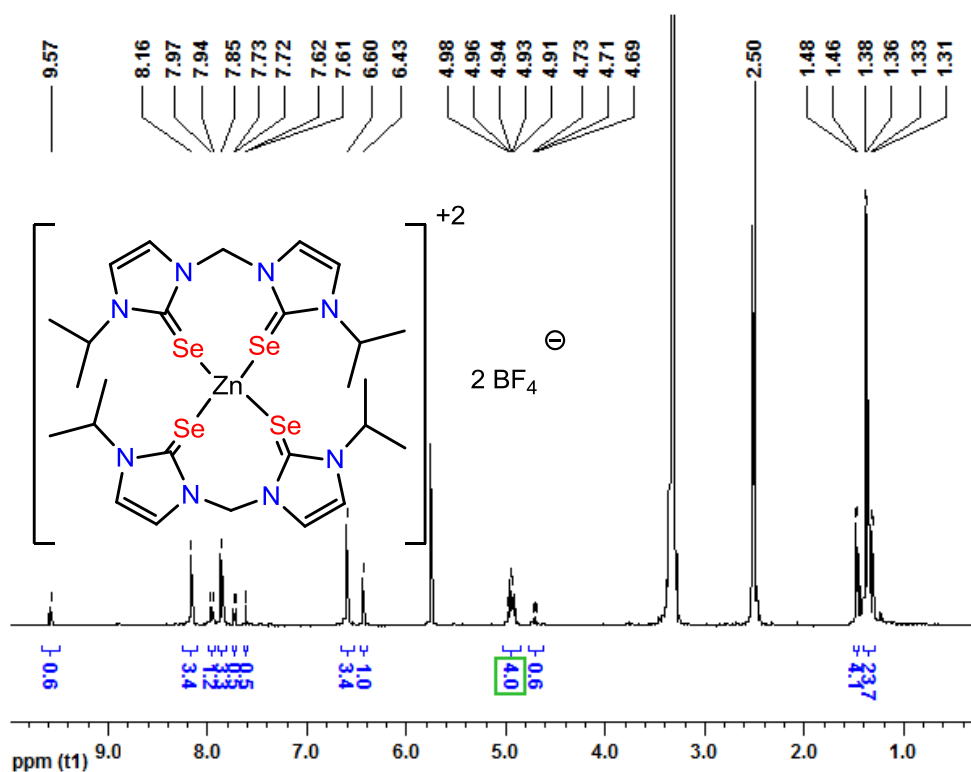


Figure 9:  $^1\text{H}$  NMR of Compound 4 (400MHz,  $\text{DMSO-d}_6$ , RT)



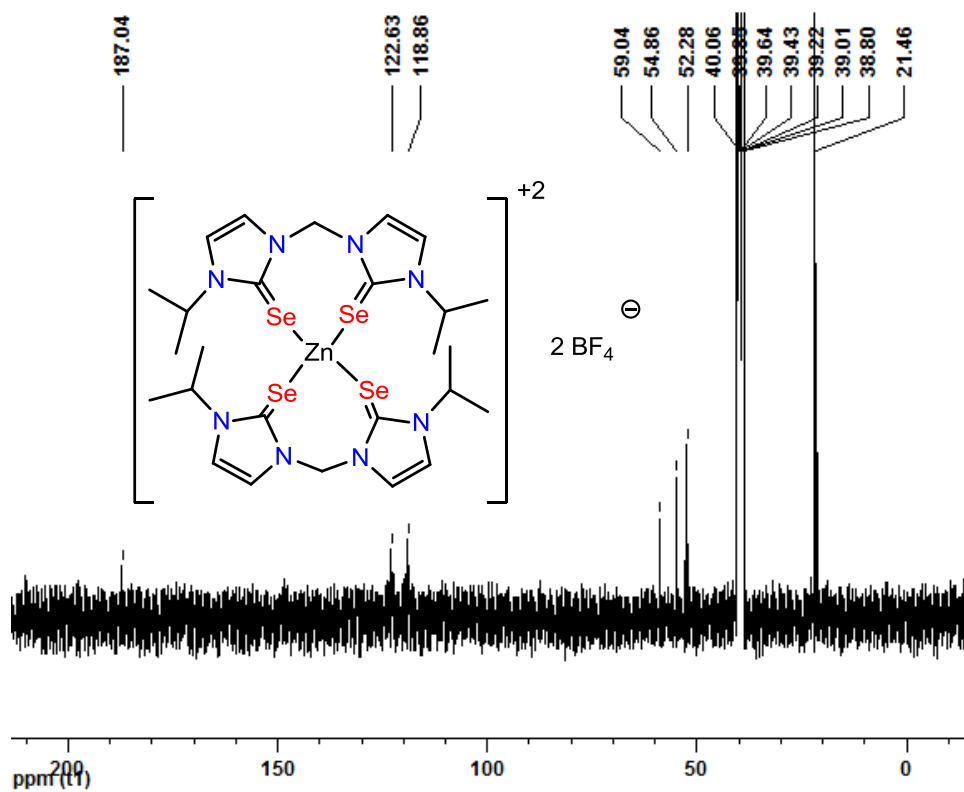
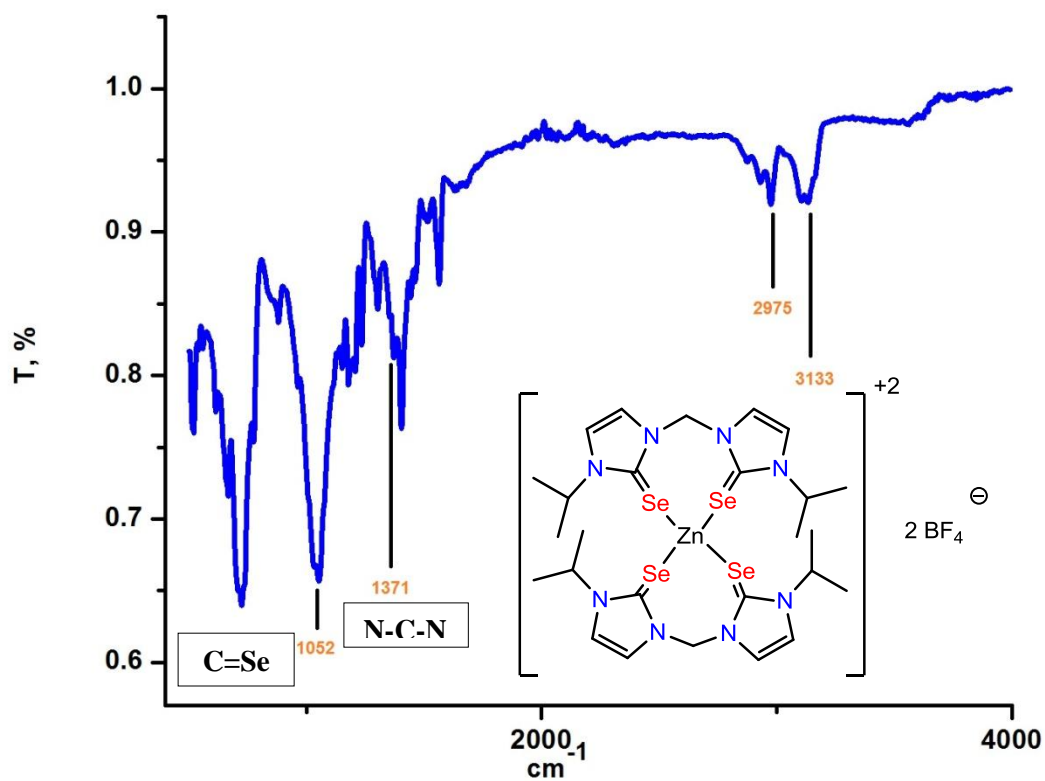


Figure 10: <sup>13</sup>C NMR of Compound 4 (400MHz, DMSO-d<sub>6</sub>, RT)



**Figure 11:** IR spectrum of compound **4**

### 3.4. Single crystal X-ray structure of **3** and **4**

The solid state structures of **3** and **4** were unambiguously determined by single crystal X-ray diffraction techniques. (Fig. 13-16) The structural parameters are listed in table 2. The selected bond distances and bond angles are accumulated in table 3. Molecules **3** and **4** were crystallized in triclinic and monoclinic space group, with P2<sub>1</sub>/n and P-1 respectively. The structural feature of **3** and **4** are discussed in detail. The C-Se bond lengths in **4** (1.86 Å) have increased notably than in **3** (1.82 Å). The C(Se)-N bond lengths in **3** and **4** are comparable (1.35 Å for both **3** and **4**). The N-C(Se)-N bond angles in **4** (107°) have been increased to some extent than that of **3** (104°), whereas the N-CH<sub>2</sub>-N bond angles in **4** (113°) is shorter than that of **3** (111°).

**Table 2.** Crystallographic data, details of data collection and structure refinement parameters for **3** and **4**

	<b>3</b>	<b>4</b>
Empirical formula	H <sub>10</sub> C <sub>6.5</sub> N <sub>2</sub> Se	C <sub>26</sub> H <sub>40</sub> N <sub>8</sub> Se <sub>4</sub> Zn <sub>2</sub> .2(BF <sub>4</sub> ).1(CO)
Formula weight	390.25	1075.55
Temperature (K)	150	298
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 <sub>1</sub> /c
<i>a</i> , Å	7.1055	9.0308
<i>b</i> , Å	11.403	22.3292
<i>c</i> , Å	11.4572	11.1512
$\alpha$ , °	69.174	90
$\beta$ , °	80.152	100.845
$\gamma$ , °	74.059	90
Volume, Å <sup>3</sup>	831.5	2208.5

<i>Z</i>	2	2
$\rho_{\text{calc}}$ , mg mm <sup>-3</sup>	1.5586	1.6172
$\mu$ , mm <sup>-1</sup>	5.502	5.152
<i>F</i> (000)	385.5	1049.4
Data collected	8.28 to 142.22°	7.92 to 141.82°
Unique data	2775/0/176	3055/0/235
<i>R</i> <sub>int</sub>	0.0299	0.0305
GOF on <i>F</i> <sup>2</sup>	1.032	1.027
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0653	0.0669
w <i>R</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.2053	0.1764
<i>R</i> <sub>1</sub> values (all data)	0.1013	0.0973
w <i>R</i> <sub>2</sub> values (all data)	0.2053	0.2348

**Table 3.** Selected bond lengths [Å] and angles [°] of **3** and **4**

	Bond lengths [Å]			Bond angles [°]	
	<b>3</b>	<b>4</b>		<b>3</b>	<b>4</b>
C–Se	1.822	1.866	N–C(Se)–N	104.2	106.7
	1.826	1.864		105.2	107.1
C(Se)–N	1.357	1.332	N–CH <sub>2</sub> –N	113.2	111.2
	1.367	1.344			
	1.374	1.338			

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1.358 1.352

1.332

1.470

1.406

1.344

1.391

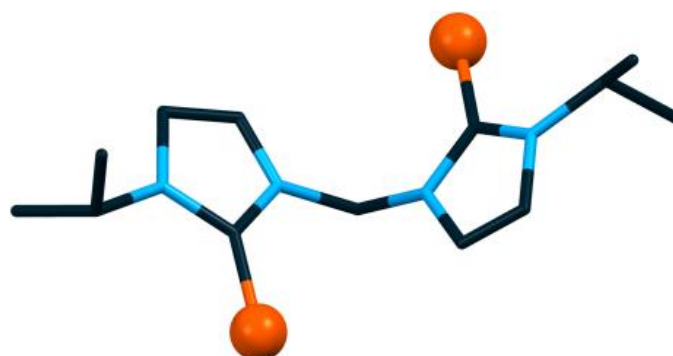
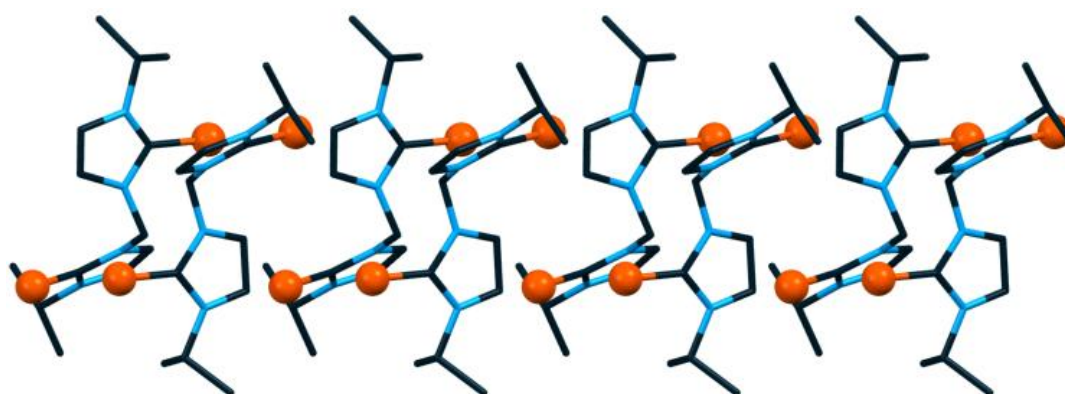
1.463

1.338

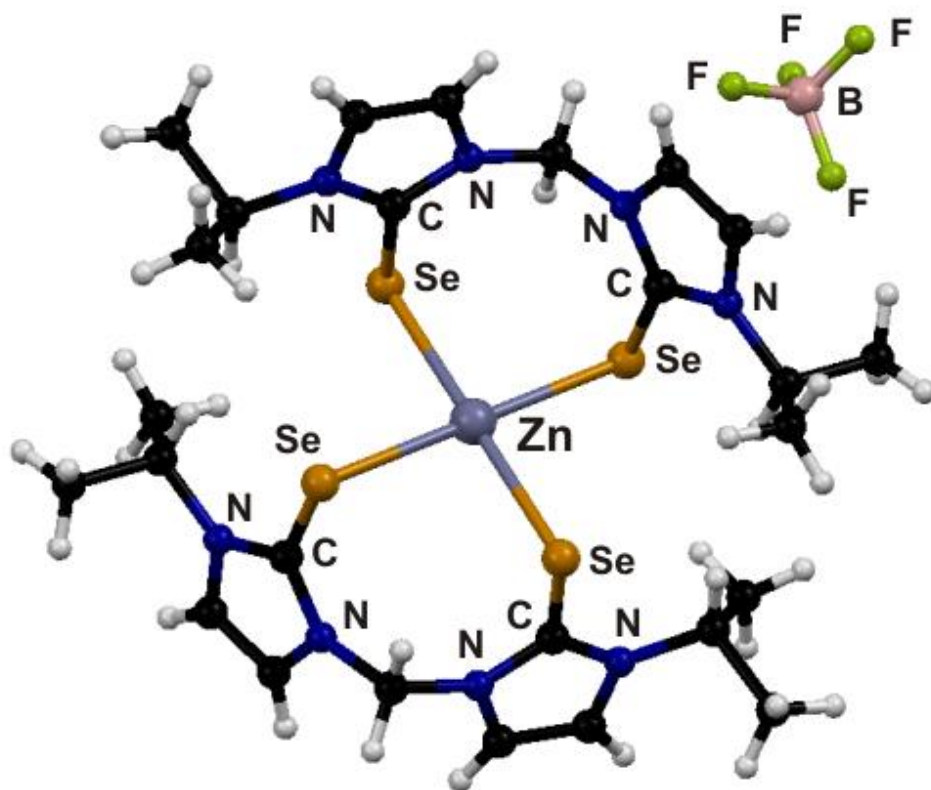
1.455

1.372

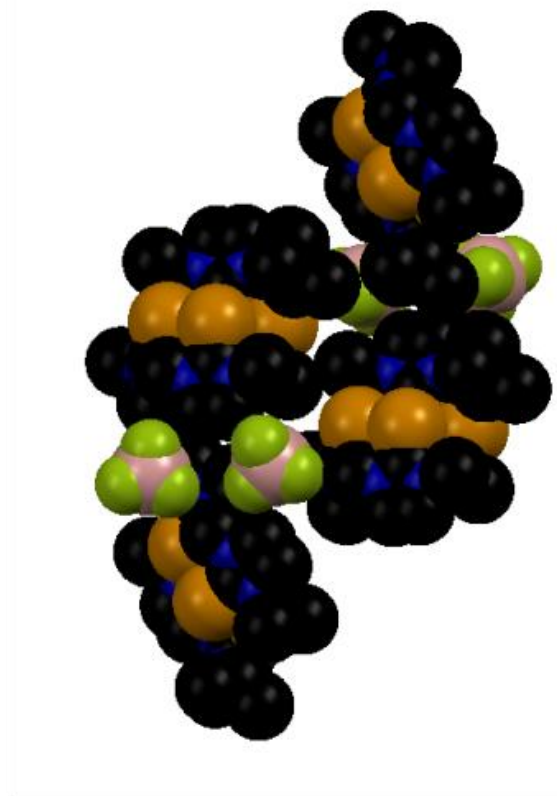
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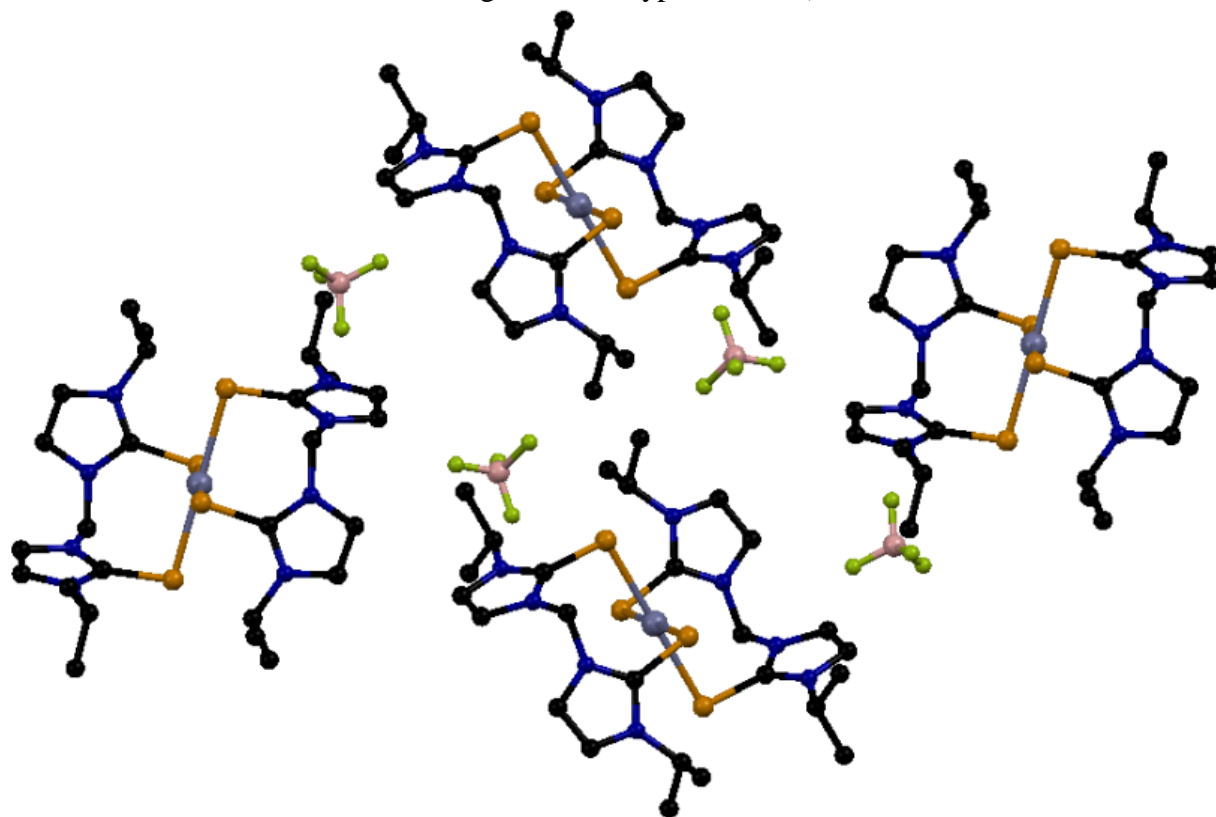
**Figure 12.** Crystal structure of compound 3



**Figure 13.** Crystal structure of compound 4

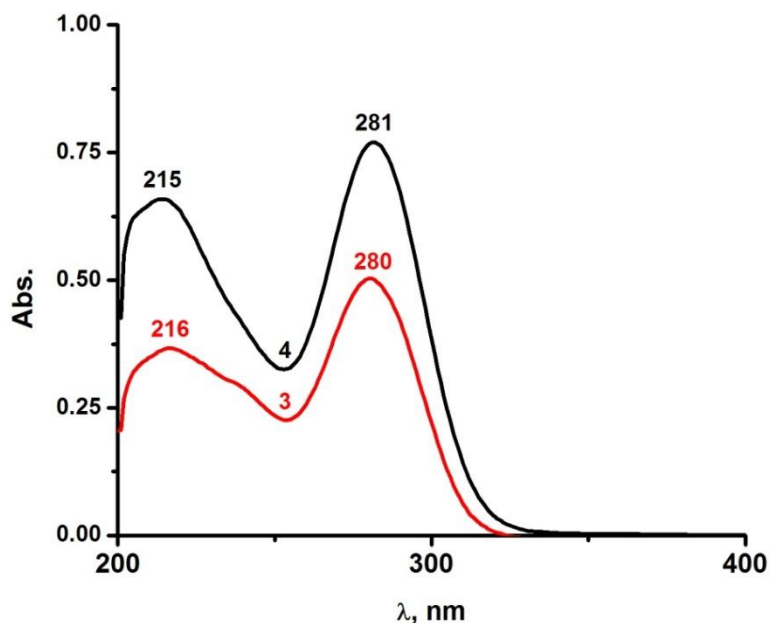


**Figure 14.** Space filled molecular packing of compound **4** (Se is in between two imidazole moieties forming sandwich type structure)



**Figure 15.** Packing of compound **4**

### 3.5. UV-vis solid and solution state absorption spectra of **3** and **4**



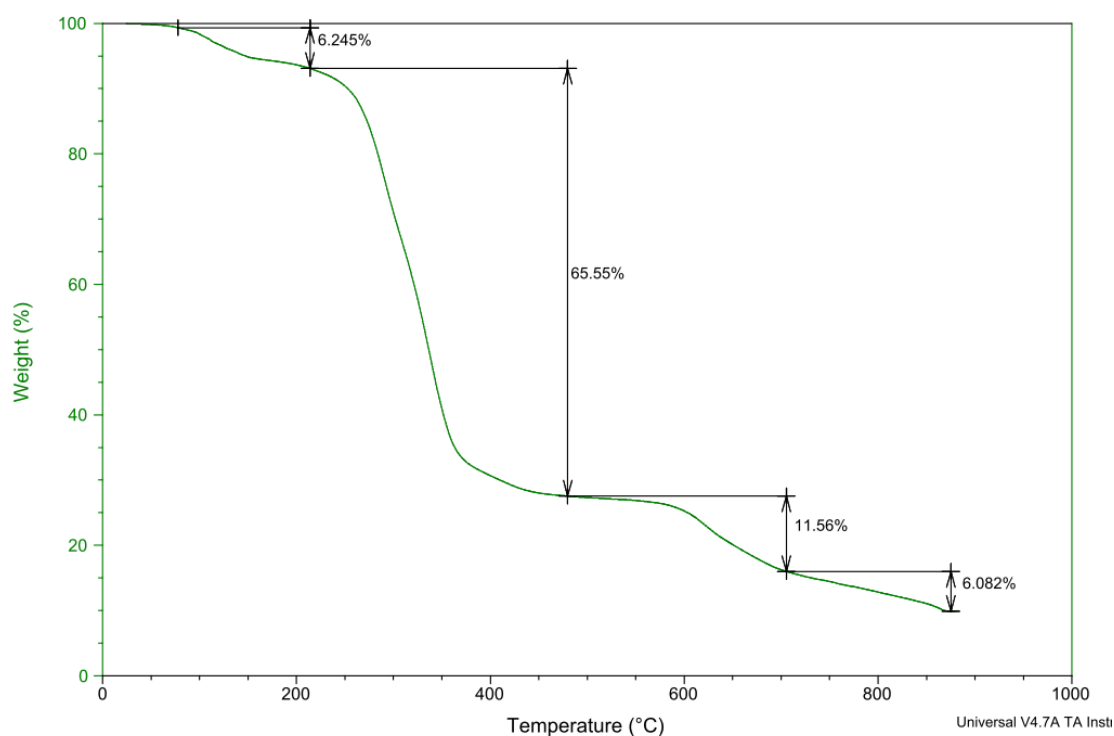
**Figure 16:** The solution state UV-vis spectra of **3** and **4** in MeOH at RT ( $4.91 \times 10^{-6}$  M)

Solution state UV-vis absorption spectra of **3** and **6** were measured in methanol (Fig. 17). The solution state UV of the methylene ligand and the metal compounds are comparable. In the metal compound **6** absorption appears at 215 nm whereas the absorption for **5** appears at 216 nm due to  $\pi$ - $\pi^*$  transition with molar extinction coefficient of  $138634 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $75433 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Other transitions of **3** and **4** are due to  $n$ - $\pi^*$  transition (281 nm for **3** and 282 nm for **6**).

### 3.6. Thermogravimetric analysis of compound **4**:

In order to understand the thermal decomposition pathway of **6**, thermogravimetric analysis (TGA) ( $10 \text{ }^\circ\text{C min}^{-1}$ , 30–1000  $^\circ\text{C}$ , under  $\text{N}_2$  atmosphere) was carried out on **6** (Fig. 18). It shows enough stability upto 215  $^\circ\text{C}$  (with 6% weight loss) then the sharp weight loss occurred with starting at 215  $^\circ\text{C}$  and ending at 475  $^\circ\text{C}$  (with 66% weight loss), attributable to decomposition of ligand and solvent molecules. The TGA profile of **6** reveals the gradual

weight loss from the beginning to 700 °C (12%). After 710 °C, weight loss occurred upto 875 °C with 6% weight loss.



**Figure 17:** The TGA curve of 4

### 3.7. Synthesis and characterization of 5

1,2-dibromoethane and **1** were taken in a schlenk tube under argon atmosphere and acetonitrile (25 ml) was added to it. The reaction was done at 90 °C for 48 h. After reaction, white precipitate came. Then it was decanted after adding diethyl ether and kept in ice for 5 minutes. Then it was applied vacuum and white crystalline product was obtained (**5**). Yield: 90% (based on **1**). It is soluble in  $\text{CDCl}_3$ . The compound was characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. In  $^1\text{H}$  NMR, the two  $\text{ImH}$  peaks appear at 7.58-7.57 and 7.36-7.35 ppm. The  $\text{NCH}_2$  peak appeared at 4.67 ppm. In  $^{13}\text{C}$  NMR, the  $\text{Im-CH}$  peak appears at 122.27 and 121.73 ppm. The  $\text{N-CH}_2$  chemical shift value arises at 48.86 ppm.



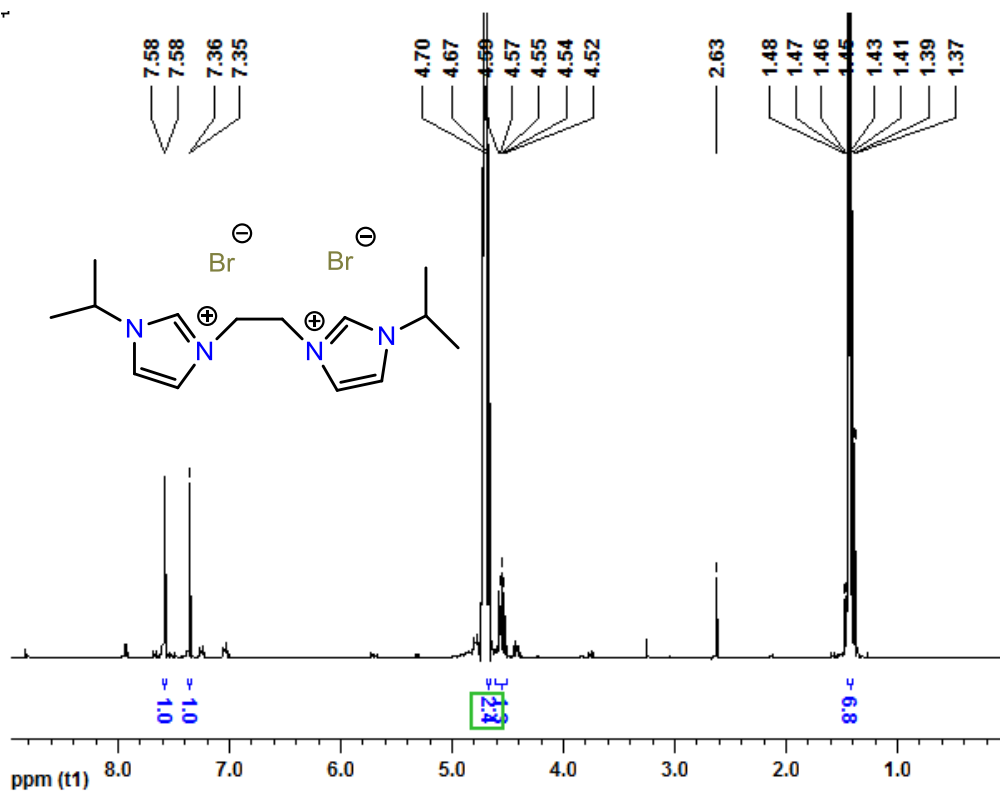


Figure 18: <sup>1</sup>H NMR of Compound 5 (400MHz, D<sub>2</sub>O, RT)

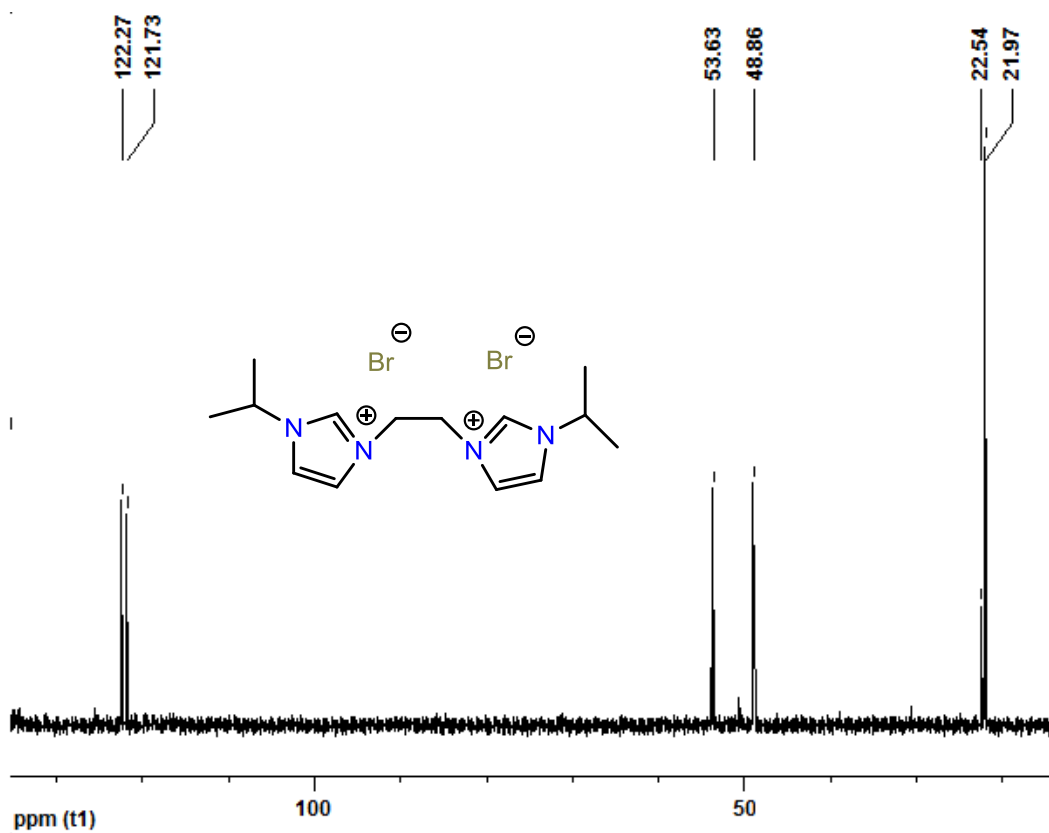
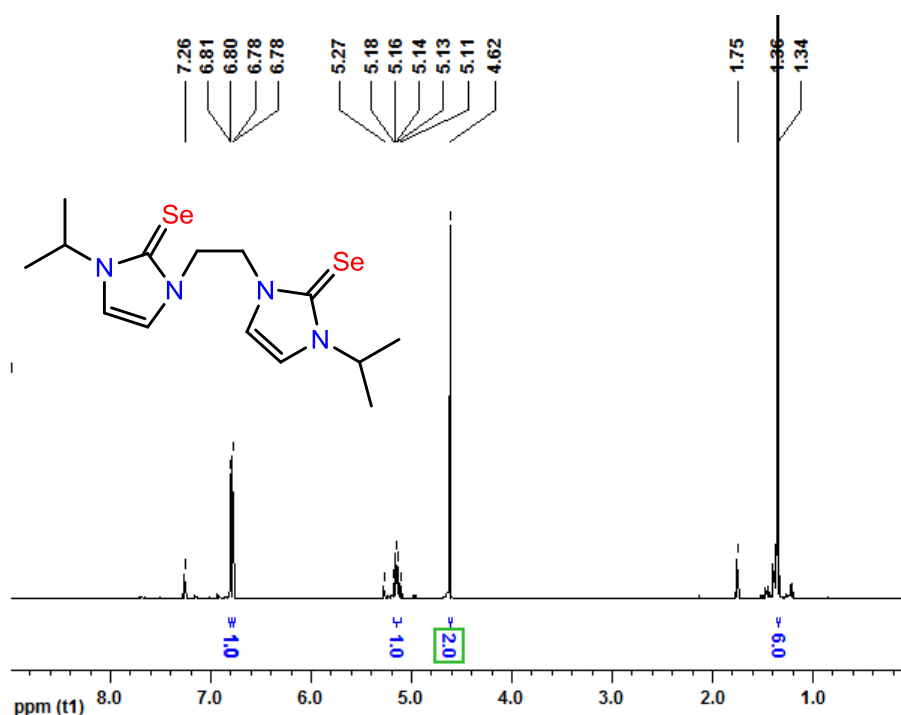


Figure 19: <sup>13</sup>C NMR of Compound 5 (400MHz, D<sub>2</sub>O, RT)

### 3.8. Synthesis and characterization of **6**

**5** was taken in a schlenk tube containing activated potassium carbonate and vacuum applied for 20 minutes. After that selenium powder and methanol (30 ml) was added to it under argon atmosphere and constant stirring. Reaction was started at 65 °C and continued for 48 h. After the reaction, TLC was monitored and the product formation was confirmed. Then the work up with dichloromethane and water was done and white crystalline solid was obtained. Yield: 80% (based on **5**). It is soluble in CDCl<sub>3</sub>. The compound is characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT, FT-IR and single crystal XRD. The C=Se stretching frequency comes at 1070 cm<sup>-1</sup> and the N-C-N stretching frequency appears at 1370 cm<sup>-1</sup>. In <sup>1</sup>H NMR, the Im-CH peaks appear at 6.77-6.78 and 6.80-6.81 ppm. The N-CH<sub>2</sub> peak appears at 4.62 ppm. In <sup>13</sup>C NMR, the chemical shift value appears at 154.10 ppm. Similarly the chemical shift values for Im-CH<sub>2</sub> and N-CH<sub>2</sub> appear at 120.29, 114.66 and at 46.62 ppm respectively.



**Figure 20:** <sup>1</sup>H NMR of Compound **6** (400MHz, CDCl<sub>3</sub>, RT)

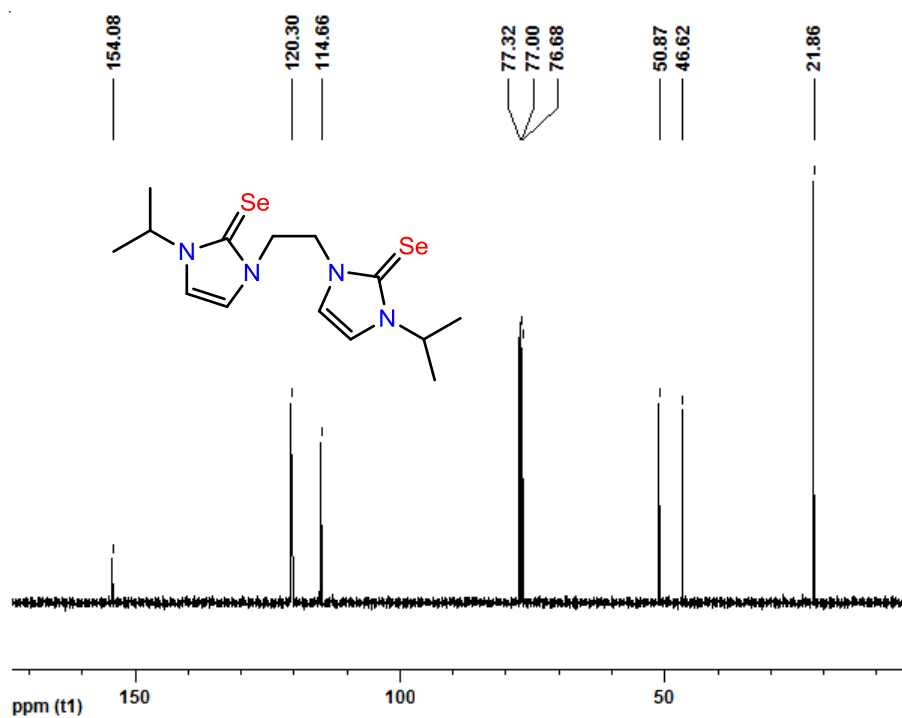


Figure 21:  $^{13}\text{C}$  NMR of Compound 6 (400MHz,  $\text{CDCl}_3$ , RT)

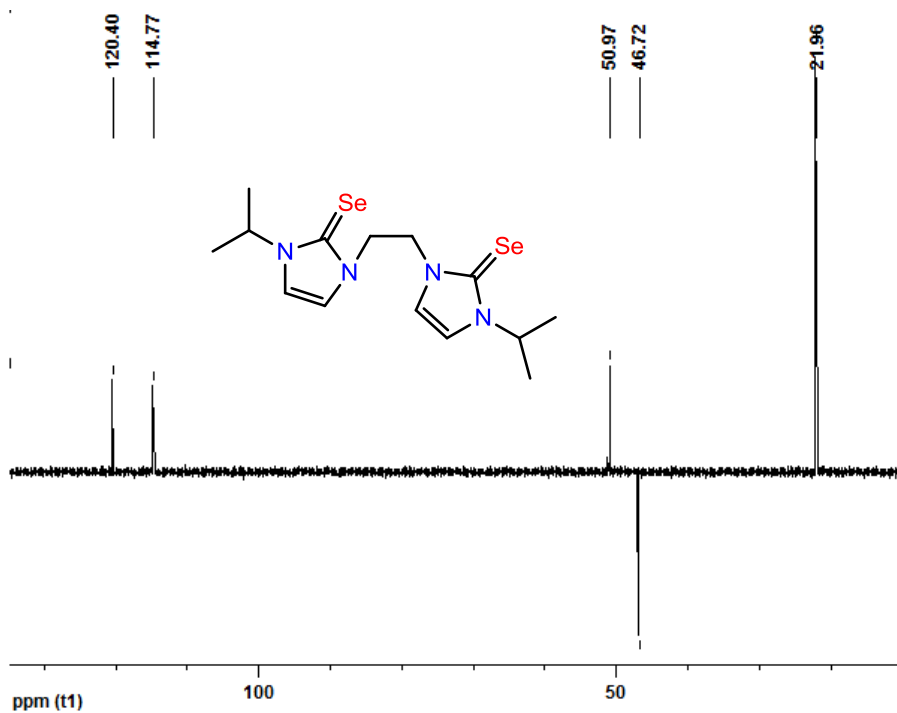
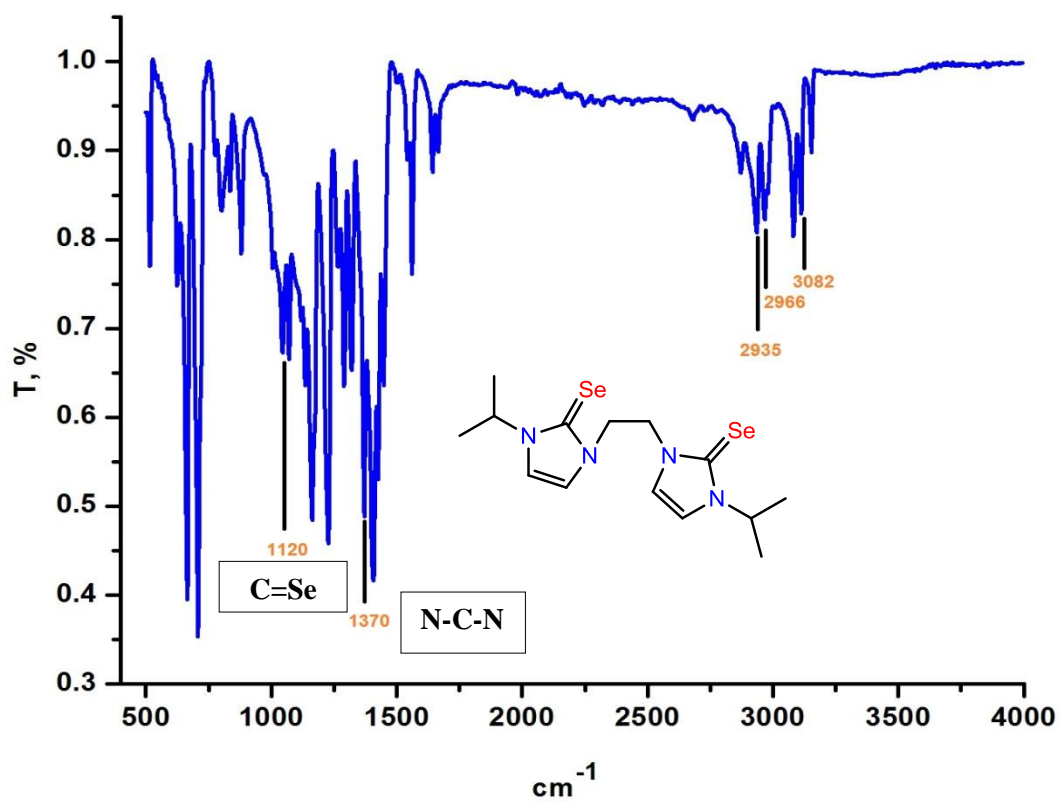
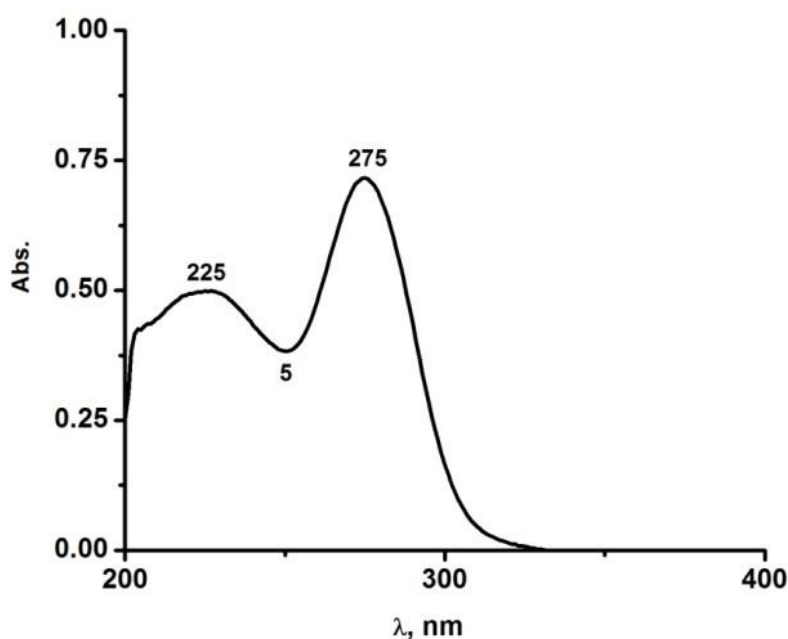


Figure 22: DEPT of Compound 6 (400MHz,  $\text{CDCl}_3$ , RT)



**Figure 23:** FT-IR spectrum of compound 6

### 3.9. UV-vis solid and solution state absorption spectra of 6



**Figure 24:** The solution state UV-vis spectra of **6** in MeOH at RT ( $9.81 \times 10^{-6}$  M)

The solution state UV spectrum of **6** is measured in methanol (Fig. 24). The ligand shows absorption at 225 and 275 nm due to  $\pi$ - $\pi^*$  transition with molar extinction coefficient of  $50765 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $73394 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

### 3.10. Single crystal X-ray structure of compound (**6**):

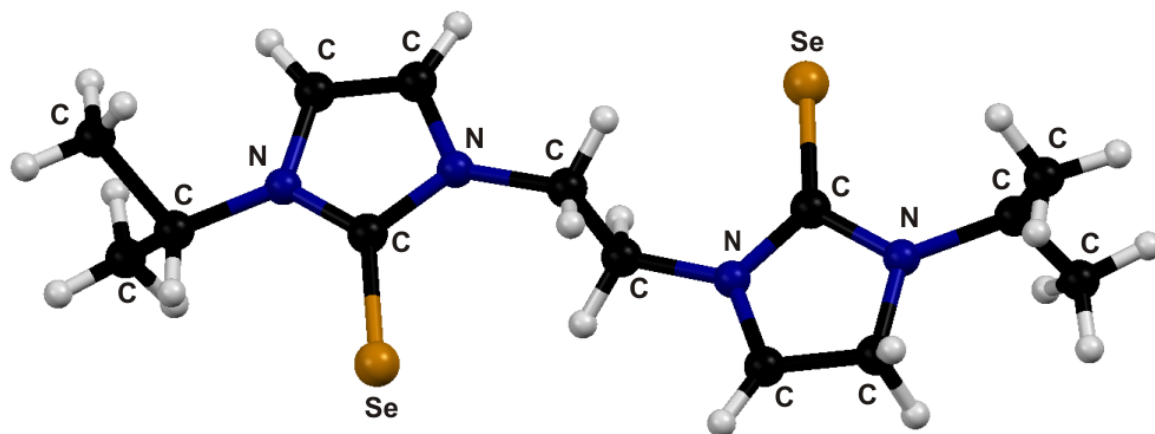
The solid state structure of **6** was unambiguously determined by single crystal X-ray diffraction techniques (Fig. 26 & 27). The structural parameters are listed in table 4. The selected bond distances and bond angles are accumulated in table 4. Molecule **6** was crystallized in triclinic and space group with P-1 respectively. The structural feature of **6** is discussed in detail. The C-Se bond lengths in **6** are 1.80 and 1.86 Å. The C(Se)-N bond lengths in **6** are also mentioned in table 5. The N-C(Se)-N bond angles in **6** appears at  $107.2^\circ$  and  $103.2^\circ$ .

**Table 4.** Crystallographic data, details of data collection and structure refinement parameters for **6**

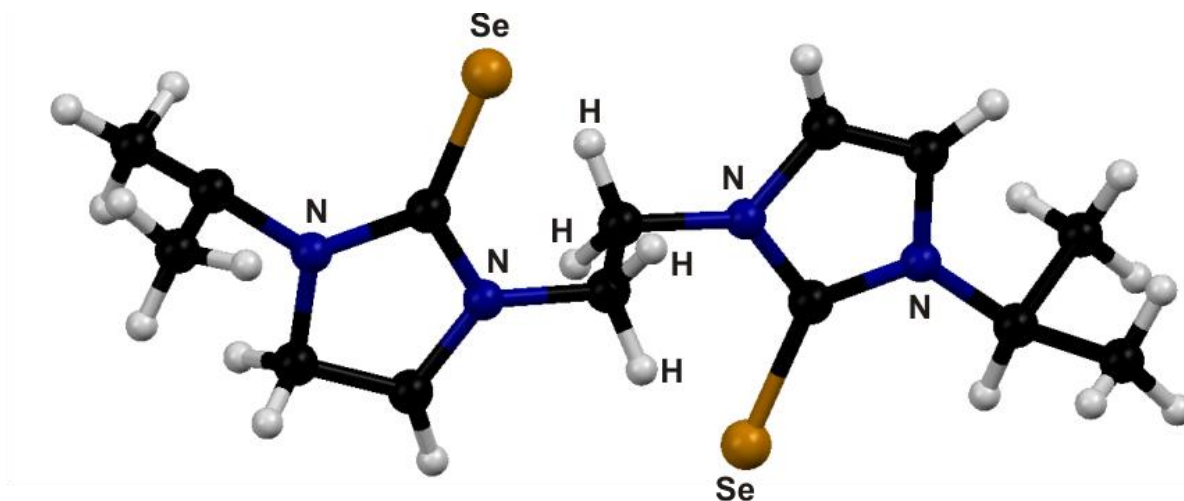
	<b>Compound 6</b>
Empirical formula	C <sub>14</sub> H <sub>22</sub> N <sub>4</sub> Se <sub>2</sub>
Formula weight	404.27
Temperature (K)	298
Crystal system	Triclinic
Space group	P1
<i>a</i> , Å	5.7360
<i>b</i> , Å	7.4671
<i>c</i> , Å	10.3513
$\alpha$ , °	81.162
$\beta$ , °	80.397
$\gamma$ , °	81.772
Volume, Å <sup>3</sup>	428.80
<i>Z</i>	1
$\rho_{\text{calc}}$ , mg mm <sup>-3</sup>	1.873
$\mu$ , mm <sup>-1</sup>	7.326
<i>F</i> (000)	242.0
Data collected	8.74 to 141.2°
Unique data	1821/3/185
<i>R</i> <sub>int</sub>	0.0168
GOF on <i>F</i> <sup>2</sup>	1.368
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0558
w <i>R</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.1489
<i>R</i> <sub>1</sub> values (all data)	0.0572
w <i>R</i> <sub>2</sub> values (all data)	0.1512

**Table 5.** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] of **6**

Bond lengths [ $\text{\AA}$ ]		Bond angles [ $^\circ$ ]	
C–Se	1.801	N–C(Se)–N	107.2
	1.866		103.2
C(Se)–N	1.397	N–CH <sub>2</sub> –CH <sub>2</sub>	110.5
	1.342		109.9
	1.382		
	1.320		



**Figure 25.** Crystal structure of compound **6**



**Figure 26.** Staggered form of compound **6**

## Chapter 2

The synthesis and characterization is reported here in both solid and solution state of new compounds, methyl and allyl imidazolone ligands. In our study imidazolone compounds were prepared by treating imidazolium salt having biphenyl spacer with Se powder in presence of a base.

## 4. Experimental section

### 4.1. General remarks

All manipulations were carried out under argon using Schlenk-vacuum line techniques. The solvents were purchased from commercial sources and purified according to standard procedures. Allyl imidazole, acetonitrile, methanol, potassium carbonate, selenium powder and 4,4'-bis(chloromethyl)-1,1'-biphenyl (**6**) were purchased from commercial sources. FT-IR measurements were carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV- vis spectra were measured on a T90+ UV-visible spectrophotometer. NMR spectra were recorded on Bruker Ultrashield spectrometer at 25 °C, unless otherwise stated. Chemical shifts are given relative to Me<sub>4</sub>Si and were referenced to the solvent



resonances as internal standards. The crystal structure of **9** were measured on an Oxford Supernova diffractometer. Single crystals were mounted on a Goniometer KM4/Xcalibur equipped with Sapphire2 (large Be window) detector (CuK $\alpha$  radiation source,  $\lambda = 1.5418$  Å). Crystals of **6** were obtained from mixture of dichloromethane and methanol solution of **6** at room temperature over a period of 12 hours. Data were collected at 153 K. Using Olex2, the structure was solved with the olex2.solve.Structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss-Newton minimisation. [2CCDC 945326 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

#### 4.2. Synthesis of **8**

Acetonitrile (25 mL) was added to **7** (5 g, 19.9 mmol) under argon atmosphere with stirring then allyl imidazole (6.43 mL, mmol) was added to the reaction mixture and stirred for 16 hr at 90 °C, reaction progress was monitored by TLC. After completion of the reaction, work up with diethyl ether was done and sticky off-white compound was appeared and dried under high vacuum to obtain off-white solid, **8**.<sup>[26]</sup> Yield: 95% (based on **7**). M.p., 74-76°C (melted to transparent liquid). <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz):  $\delta$  7.50 (s, 4H, ImH), 7.42-7.40 (d, <sup>2</sup>J<sub>HH</sub> = 8 Hz, 8H, ArH), 5.93-5.87 (m, 2H, CH<sub>2</sub>=CH-), 5.37-5.34 (d, <sup>2</sup>J<sub>HH</sub> = 12 Hz, 6H, CH<sub>2</sub>=CH-), 5.30-5.26 (d, <sup>2</sup>J<sub>HH</sub> = 16 Hz, 2H, CH<sub>2</sub>=CH-), 4.70 (s, 4H, NCH<sub>2</sub>) ppm. The imidazolium proton (N-CH-N) peak is not obtained as it has been exchanged with D<sub>2</sub>O. <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz):  $\delta$  122.74, 122.33 (Im-CH), 130.18, 140.31 (Ph-C) 121.23 (CH<sub>2</sub>=CH-), 133.23 (CH<sub>2</sub>=CH-), 51.61 (CH<sub>2</sub>=CH-CH<sub>2</sub>-), 129.23, 127.66 (Ar-C), 52.48 (N-CH<sub>2</sub>-) ppm. FT-IR (neat,  $\nu$ ): 3358(s), 3242(w), 3121(m), 3058(m), 2845(w), 1643(w), 1621(w), 1555(s), 1397(m), 1207(w), 1192(w), 1141(s), 995(m), 961(s), 849(s), 804(s), 754(s) cm<sup>-1</sup>.

#### 4.3. Synthesis of **9**

Potassium carbonate (2.1 g, 8.03 mmol) was heated for about 10 min. by an airgun and after cooling it for sometimes, **8** (2 g, 4.02 mmol) and Se powder (0.634 g, 8.04 mmol) were added under argon atmosphere and then methanol (25 mL) was added to the reaction mixture. Then the reaction mixture was stirred for 36 h at 70 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, water was added to the reaction mixture and extracted with dichloromethane (3 x 15 mL). The organic extract was washed with brine solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Organic solvent was evaporated under reduced pressure. As a result crude amorphous yellowish product was obtained (**8**). <sup>[14]</sup> Yield: 70% (based on **7**). M.p., 214-218 °C (melted to black). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.53-7.51 (d, <sup>2</sup>J<sub>HH</sub> = 8 Hz, 4H, ArH), 7.39-7.37 (d, <sup>2</sup>J<sub>HH</sub> = 8 Hz, 4H, ArH), 6.85-6.84 (d, <sup>2</sup>J<sub>HH</sub> = 4 Hz, 2H, ImH), 6.79-6.78 (d, <sup>2</sup>J<sub>HH</sub> = 4 Hz, 2H, ImH), 6.0-5.90 (m, 2H, CH-), 5.39 (s, 4H, Ar-CH<sub>2</sub>-Im), 5.32-5.29 (d, <sup>2</sup>J<sub>HH</sub> = 12 Hz, 2H, CH<sub>2</sub>=CH-), 5.27-5.23 (d, <sup>2</sup>J<sub>HH</sub> = 16 Hz, 2H, CH<sub>2</sub>=CH-), 4.81-4.80 (d, <sup>2</sup>J<sub>HH</sub> = 4 Hz, 4H, Im-CH<sub>2</sub>-CH=) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 156.63 (C=Se), 140.38 (Ph-C), 134.70 (CH<sub>2</sub>-C), 131.58 (Im-CH), 129.76 (Ph-CH), 127.46 (CH<sub>2</sub>-Ph-C), 119.56 (CH<sub>2</sub>=CH), 118.72 (CH<sub>2</sub>=CH), 118.61 (Im-CH), 52.75 (=CH-CH<sub>2</sub>), 52.23 (N-CH) ppm. FT-IR (neat, ν) 2922(w), 2850(w), 2342 (w), 2148(w), 1665(m), 1566(m), 1496(m), 1447(m), 1397(s), 1220(m), 1170(m), 1103 (w), 1044 (w), 990 (m), 935 (m), 730 (s), 619 (m) cm<sup>-1</sup>.

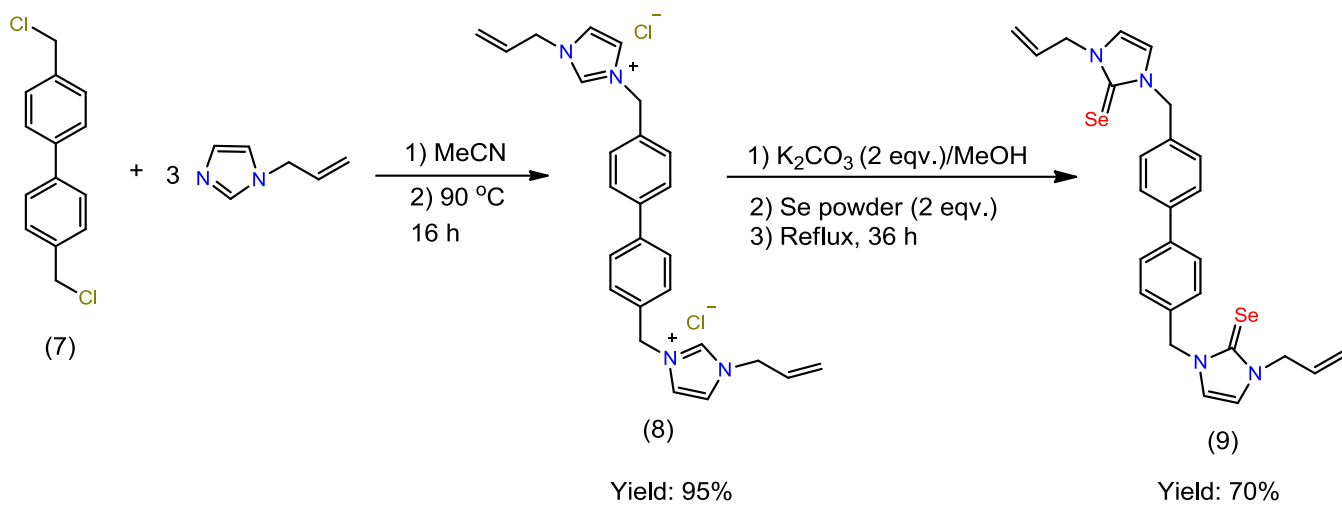
## 5. Results and discussion

### General synthesis of selenone

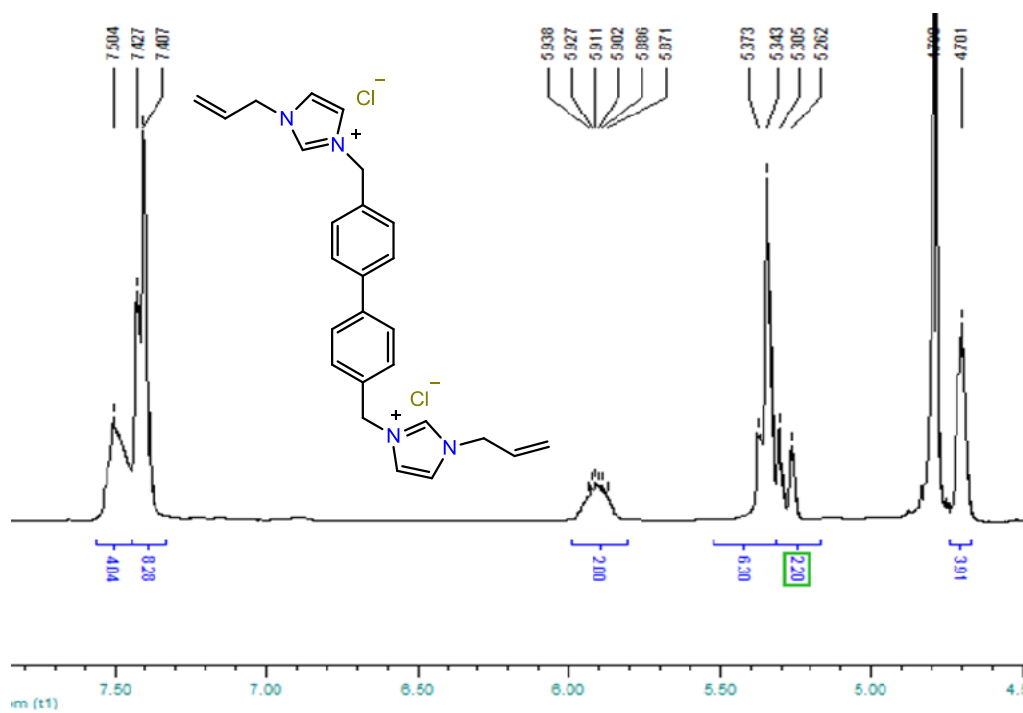
The selenone was prepared by the reaction of imidazolium salt and selenium powder in presence of activated potassium carbonate and methanol solvent.

#### 5.1. Synthesis and characterization of **8**

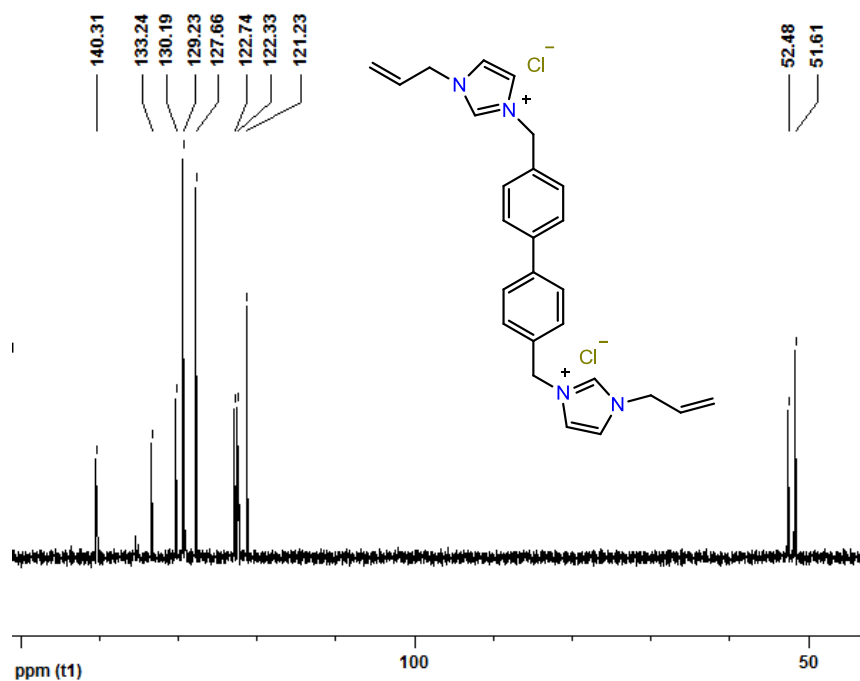
As outlined in scheme 1, compound **8** was obtained in excellent yield by combining N-allyl imidazole with 4,4'-bis(chloromethyl)-1,1'-biphenyl (**7**) in acetonitrile at 90 °C under argon atmosphere. Compound (**8**) was soluble in water and hygroscopic in nature. (**8**) was characterized by FT-IR, UV-vis, <sup>1</sup>H NMR and <sup>13</sup>C NMR techniques. In (**8**), the N<sub>2</sub>CH peak is absent due to fast proton exchange of N<sub>2</sub>C H by deuterium.



**Scheme 2.** Synthesis of **8** and **9**



**Figure 27:**  $^1\text{H}$  NMR of compound **8** (400 MHz,  $\text{D}_2\text{O}$ )



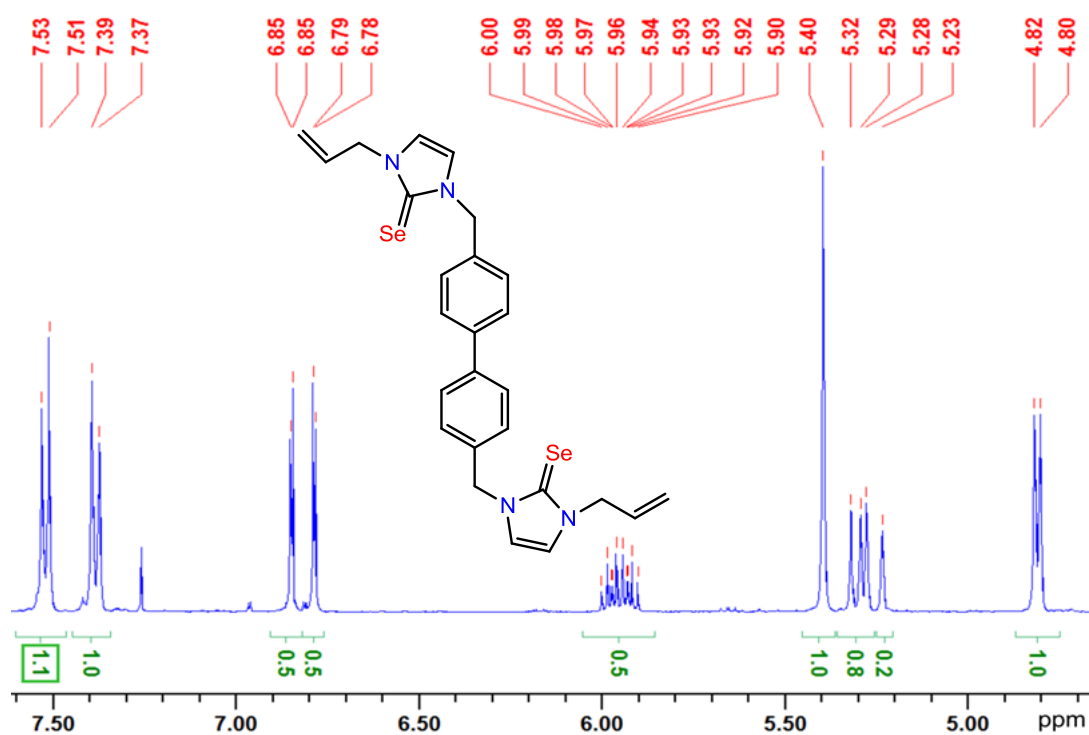
**Figure 28:**  $^{13}\text{C}$  NMR of compound **8** (400 MHz,  $\text{D}_2\text{O}$ )

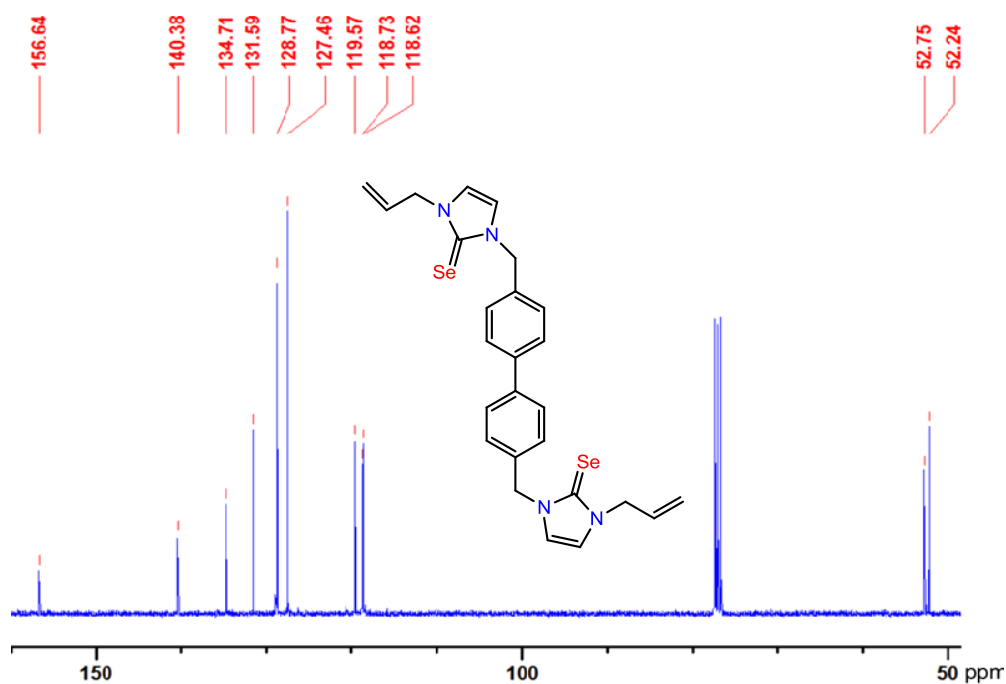
### 5.2. Synthesis and characterization of **9**

In a schlenk tube (**8**) was further heated with 2 equivalent of activated potassium carbonate and 2 equivalent of Se powder in presence of methanol at 70 °C to result (**9**) (Scheme 2).<sup>[29,30]</sup> Compound (**9**) is soluble only in dichloromethane. It is yellowish in colour. The compound is characterized by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, UV-vis and single crystal X-ray diffraction techniques. In this ligand, the C=Se stretching frequency appeared at 1103  $\text{cm}^{-1}$  and the N-C-N stretching frequency appeared at 1566  $\text{cm}^{-1}$ .<sup>[26]</sup> The Im-CH peak of this allyl ligand appeared at 6.85-6.84 and 6.79-6.78 ppm and the allyl protons at  $\delta$  5.32-5.23 ppm. The N-CH<sub>2</sub> peak is upfield shifted ( $\delta$  4.70 ppm) for (**9**). In  $^{13}\text{C}$  NMR, the C=Se chemical shift value appeared at 156.6 ppm. Similarly, the  $^{13}\text{C}$  NMR chemical shift value of Im-CH<sub>2</sub> appeared at 52.75 ppm.

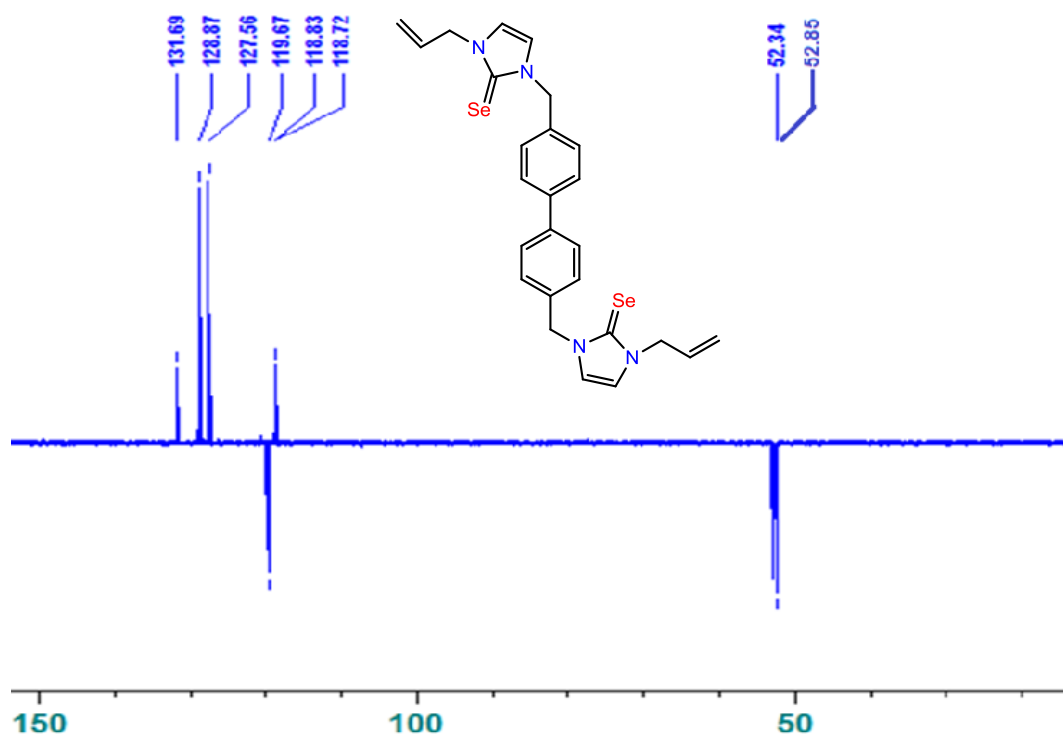
**Table 6.**Characterization of **8** and **9**

Compound	M.P. (°C)	Yield (%)	<sup>1</sup> H NMR δIm-CH (ppm)	<sup>13</sup> C NMR δ N-C (ppm)	Solution UV-vis abs. (nm)	Solid state UV- vis abs. (nm)
<b>8</b>	74-76	95	7.5	51.61	262	267
<b>9</b>	214-218	70	6.85-6.84 6.79-6.78	52.24	273	322

**Figure 29:** <sup>1</sup>H NMR of compound **9** (400 MHz, CDCl<sub>3</sub>, RT)



**Figure 30:**  $^{13}\text{C}$ NMR of compound **9** (400 MHz,  $\text{CDCl}_3$ , RT)



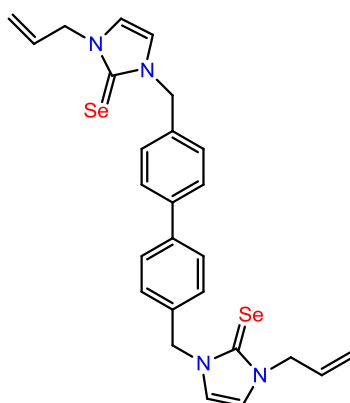
**Figure 31:** DEPT of compound **9** (400 MHz,  $\text{CDCl}_3$ , RT)

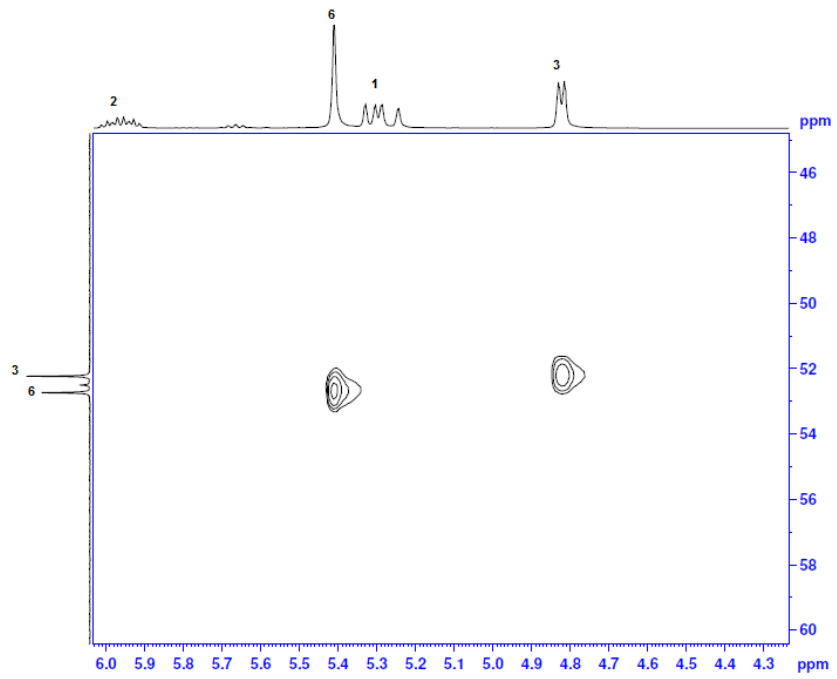
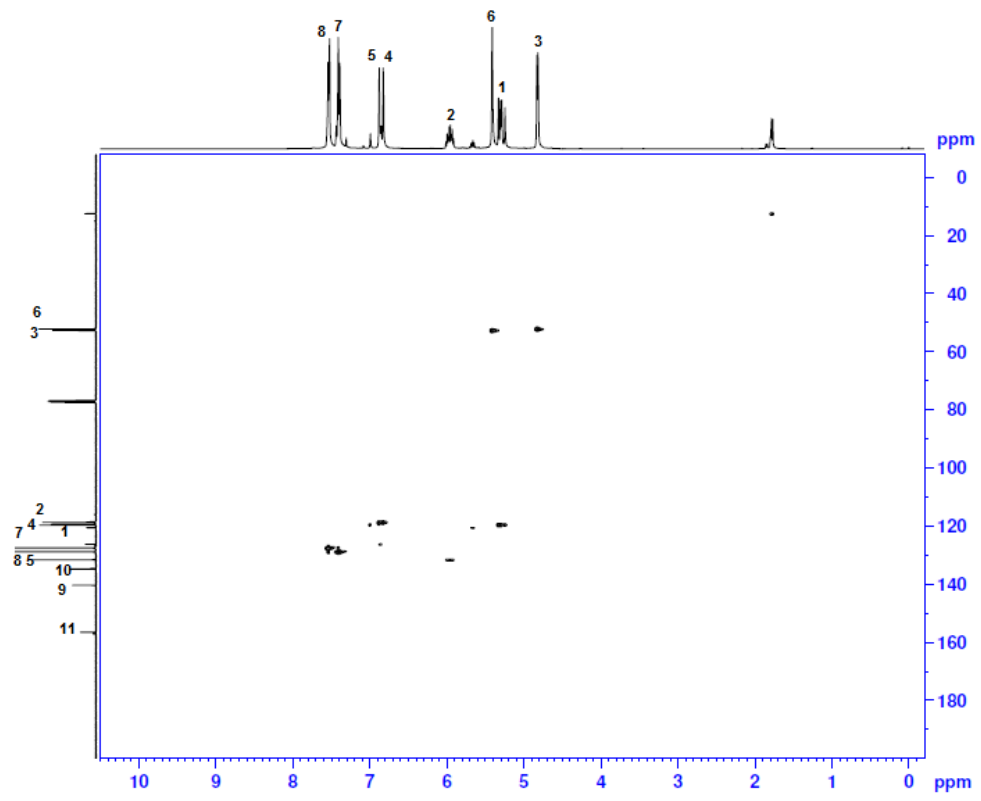
The formation of (**9**) was further characterized by 2D NMR spectroscopy i.e. DEPT, HMBC and HSQC. Notably the structural exploration for the imidazole selenone using 2D

NMR is rare. In DEPT spectrum, (9) gave three CH<sub>2</sub> groups and five CH groups which are in accordance with the structures of (9) (vide infra).

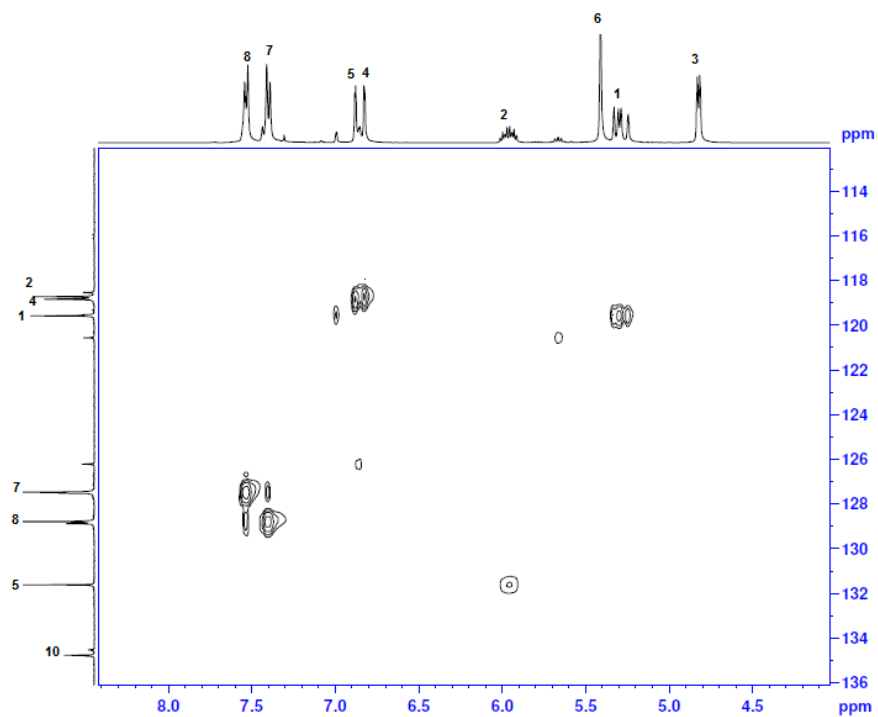
HSQC spectrum of (9) showed C-H correlations as follows, the imidazolium CH group showed strong correlation between the carbons and hydrogen attached to corresponding moieties. The CH group of benzene ring also showed a strong correlation between CH carbon and hydrogen atom attached and in CH<sub>2</sub> group, the C-H correlation is also observed. In (9), the C-H correlation of allyl group is also observed. From this, the complete CH correlations are confirmed.

The structure of (9) is further confirmed by HMBC spectrum that showed the mapping carbon coupling with neighbouring protons. In (9), the CH<sub>2</sub> carbon couples with the nearest proton of the benzene ring (<sup>3</sup>J). CH<sub>2</sub> carbon of the allyl group attached to nitrogen atom couples with the CH-proton (<sup>2</sup>J) of allyl moiety and CH<sub>2</sub>-proton (<sup>3</sup>J) of allyl moiety. CH carbon of allyl moiety shows correlation with the imidazole proton (<sup>4</sup>J, <sup>3</sup>J). CH<sub>2</sub> proton of allyl moiety attached to nitrogen shows correlation with nearest CH-carbon (<sup>3</sup>J) of imidazolium moiety. Protons of the CH<sub>2</sub> group, nearest to the benzene ring show correlation to the neighbouring carbon atom (<sup>4</sup>J) of that benzene ring. Imidazolium CH-carbon couples with the CH<sub>2</sub>-proton (<sup>4</sup>J) of the allyl moiety. Quarternary carbon of benzene ring shows correlation with the neighbouring CH<sub>2</sub> proton (<sup>2</sup>J). The carbon containing selenium correlates with the imidazolium protons (<sup>3</sup>J, <sup>3</sup>J) and it also correlates with protons of both the neighbouring CH<sub>2</sub> moieties (<sup>3</sup>J, <sup>3</sup>J).

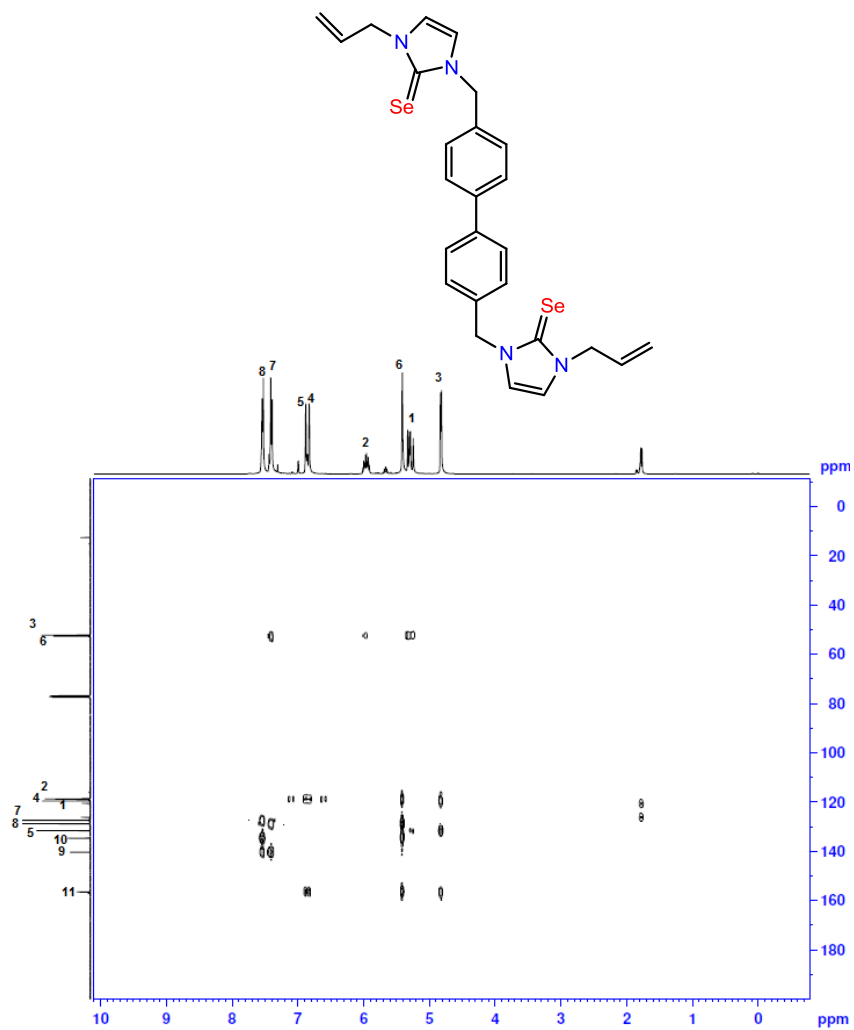


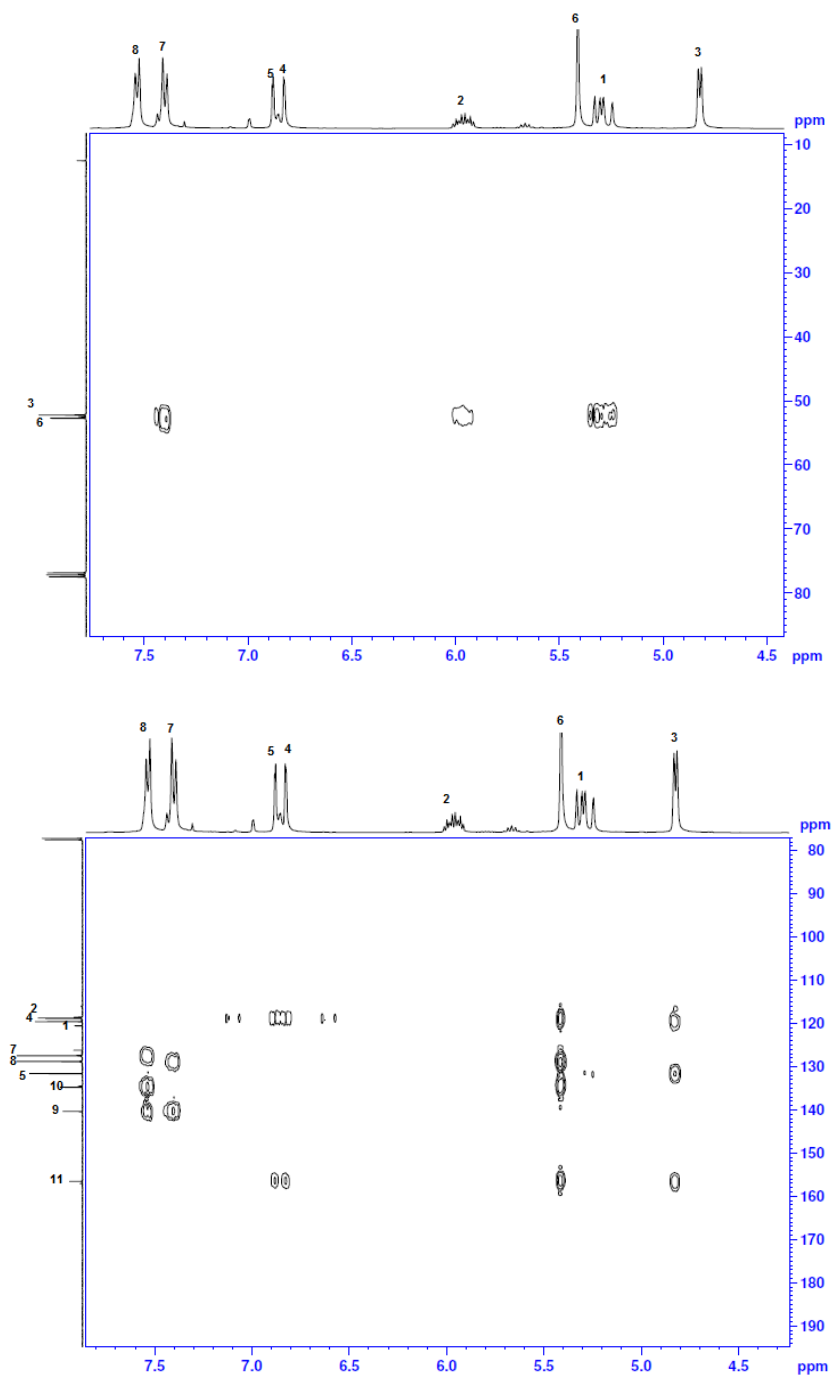




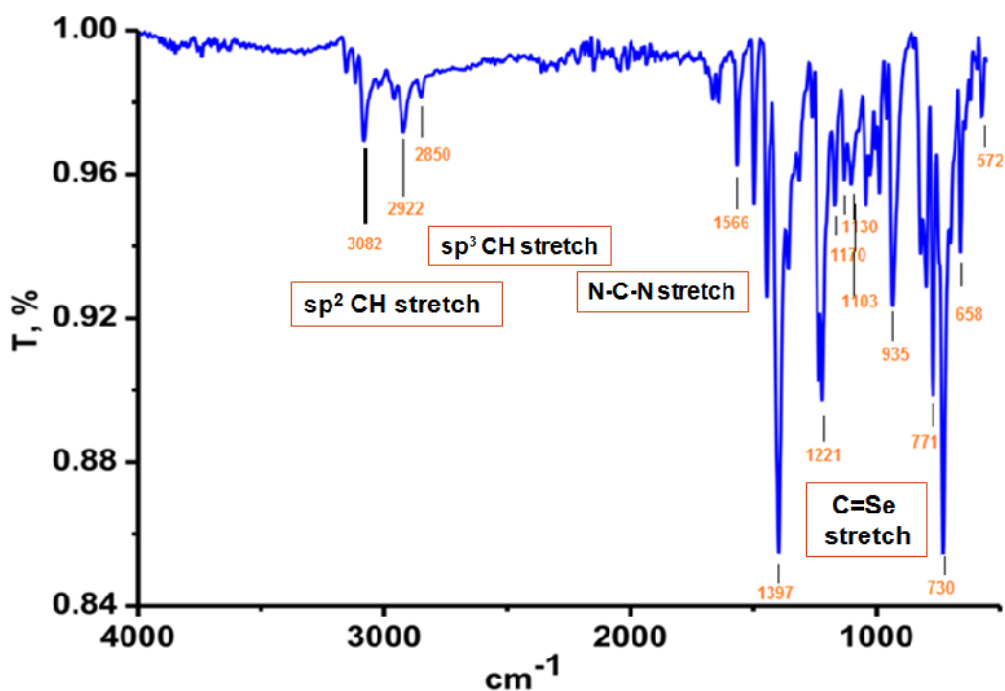


**Figure 32:** HSQC spectra of compound **9** (400 MHz, CDCl<sub>3</sub>)





**Figure 33:** HMBC spectra of compound **9** (400 MHz, CDCl<sub>3</sub>)



**Figure 34:** IR spectrum of compound **9**

### 5.3. Single crystal X-ray structure of (**9**)

The solid state structure of (**9**) was unambiguously determined by single crystal X-ray diffraction techniques. The structural parameters are listed in table 6. The selected bond distance and bond angles are accumulated in table 7. Molecule (**9**) was crystallized in monoclinic structure with  $P2_1/c$  and  $C2/c$  space group respectively. Interestingly the biphenyl rings are in same plane. The [(HCN)<sub>2</sub>C(Se)] heterocyclic rings are oriented in the trans position with respect to biphenyl plane. The (Ph)C-CH<sub>2</sub>-N(Imidazole) angle is close to 111.86° for (**9**). The N-C(Se)-N angle observed in (**9**) is 105.3° which is comparable with that of C<sub>11</sub>H<sub>16</sub>N<sub>4</sub>Se<sub>2</sub> (105.3°).<sup>[27]</sup> The C=Se bond length of (**8**) (1.850 Å) are comparable with that of (1.842 Å).<sup>[28]</sup> Thus, the C=Se bond distance can be described as double bond in nature. The N-C (Se) bond distance in (**9**) is 1.357 Å and 1.342 Å.

**Table 6.** Crystallographic data, details of data collection and structure refinement parameters for **9**

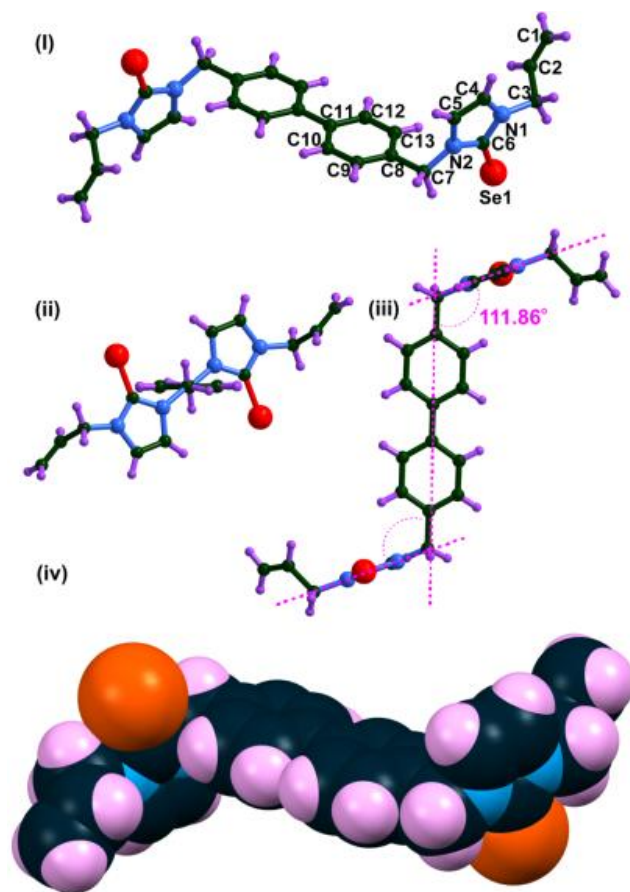
	<b>9</b>
Empirical formula	C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> Se <sub>2</sub>
Formula weight	500.37
Temperature (K)	150.00
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
<i>a</i> , Å	13.3310
<i>b</i> , Å	10.0589
<i>c</i> , Å	7.7456
$\alpha$ , °	90
$\beta$ , °	96.485
$\gamma$ , °	90
Volume, Å <sup>3</sup>	1031.99
<i>Z</i>	2
$\rho_{\text{calc}}$ , mg mm <sup>-3</sup>	1.6101
$\mu$ , mm <sup>-1</sup>	4.590
<i>F</i> (000)	497.8
Data collected	6.68 to 141.48°
Unique data	1859/0/128
<i>R</i> <sub>int</sub>	0.0151
GOF on <i>F</i> <sup>2</sup>	0.881
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0286
<i>R</i> <sub>1</sub> values (all data)	0.0304
w <i>R</i> <sub>2</sub> values (all data)	0.1045

**Table 7.** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] of **9**

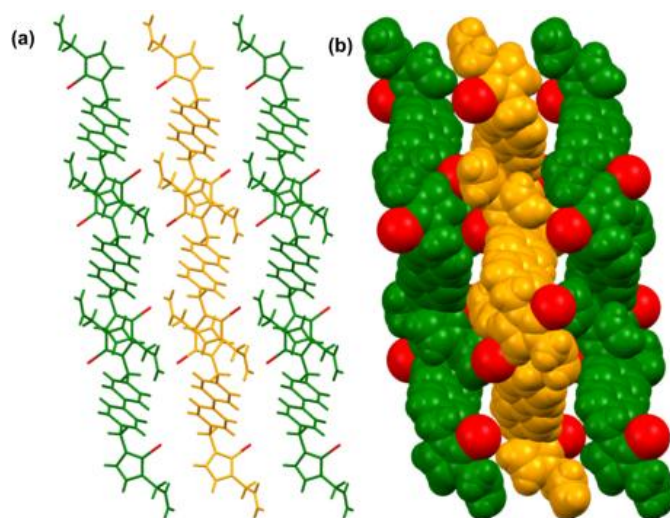
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Bond lengths [ $\text{\AA}$ ]		Bond angles [ $^\circ$ ]	
C–Se	1.847	N–C(Se)–N	105.68
C(Se)–N	1.356		
	1.356		

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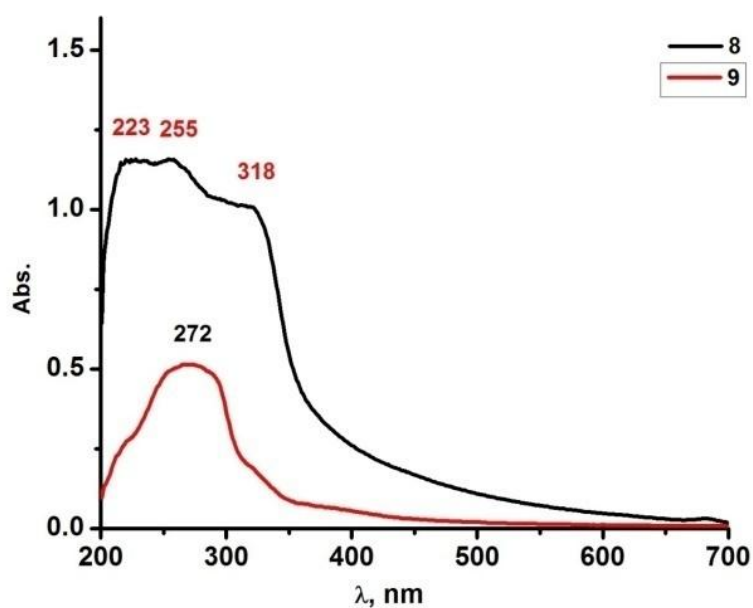
**Figure 35.** (i) Molecular structure of **9**; (ii) Non planar orientation of selenone with respect to biphenyl plane; (iii) Trans orientation of selenone with respect to biphenyl plane; (iv) Space filling model of **9**.



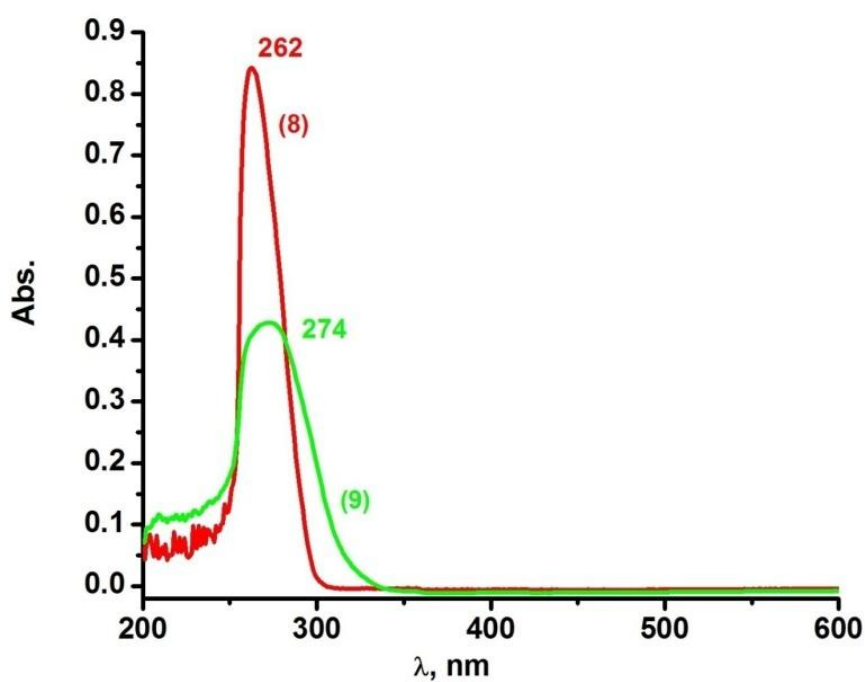
**Figure 36.**(a)Molecular packing of **9**; view along b axis; (b) Space filling model of molecular packing of **9**.

Molecules (**9**) is arranged in a zig-zag one dimensional polymeric structure without inter molecular interaction (Figure **35** and **36**). As shown in figure **36b**, the similar such one dimensional polymeric arrangements are packed as close as possible through *b* axis for **9**.

#### 5.4. UV-vis solid and solution state absorption spectra of **8** and **9**



**Figure 37.** The solution state UV-vis spectra of **8** and **9** in DMSO at RT ( $9.95 \times 10^{-6}$  M)



**Figure 38.** The solid state UV-vis spectra of **8** and **9**

Solution state UV-vis absorption spectrum of **8** and **9** were measured in DMSO (Fig. 37). **8** shows an absorption band at 262 nm due to  $\pi$ - $\pi^*$  transition with molar extension coefficient of  $84623 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Similarly, **9** shows an absorption band at 274 nm due to  $\pi$ - $\pi^*$  transition with molar extension coefficient of  $43015 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The solid state UV-vis absorption spectra of **8** and **9** are different from respective solution state spectra, which clearly indicates that the solid state molecular packing is different from that of solution state molecular packing as proved by single crystal X-ray diffraction technique (*vide supra*) (Fig. 38). In solid state, the strong absorption was observed with bathochromic shift. In **8**, an absorption band arises at 270 nm, while in **9**, the absorption band appears at 223, 259 and 315 nm.

Then compound (**9**) can be easily prepared in one step by adding activated potassium carbonate and Se powder to (**8**) respectively, in presence of methanol as solvent to get an excellent yield.

## 6. Conclusion

In chapter 1, new bisimidazolium ligand salts with methylene (**2**) and ethyl (**5**) spacer along with their corresponding selenone ligands (**3**) and (**6**) respectively were reported and characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT, solution state UV-vis, FT-IR and single crystal X-ray diffraction techniques. The complexation of **5** with zinc precursor results in Zinc(II)-3,3'-methylenebis(1-isopropyl-1H-imidazole-2(3H)-selenone(**4**)). This zinc selenide is also characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT, solution state UV-vis and FT-IR. The compound is confirmed by single crystal X-ray diffraction technique. The thermal stability is also measured by TGA.



In chapter 2, allyl imidazolium salt (**8**) and its corresponding di-seleniated compound **9** are synthesized successfully in good yields which are separated by aromatic spacer. The smooth formation of compounds (**8**) and (**9**) were proved by multinuclear NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ), UV-vis (solid and solution state), FT-IR and single crystal X-ray diffraction techniques. To the best of our knowledge, it is the first report that detailed characterization along with thorough crystallographic study has been reported for these types of di-seleniated ligands with biphenyl spacer. We have used large biphenyl spacer which will keep the reactive centres (C—Se bond mainly) far apart from each other. As reported for monoselenone, the di-selenone compounds expected to be more efficient in biological activities as more than one C=Se moieties are there, in which the Se centre acts as nucleophile towards some harmful moieties which is generated in biological systems.

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