

Discrete monomeric bismuth(III) triflate trapped by bis-selenone

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भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

Department of Chemistry

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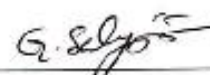
Approval sheet

This thesis entitled **Discrete monomeric bismuth(III) triflate trapped by bis-selenone** by Anindita Mandal is approved for the degree of Master of Science from IIT Hyderabad.

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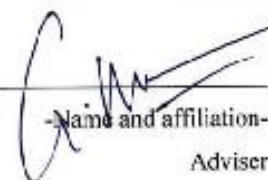


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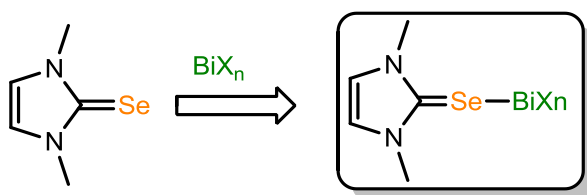
My sincere thanks to my Supervisor Dr. G. Prabusankar for his constant support and encouragement, My seniors and my friends in laboratory for providing me good working and learning experience, Department of Chemistry, IIT Hyderabad.

Dedicated to

My Parent and Sister

Abstract

A series of imidazolium salts were made from the reaction between alkyl or aralkyl dihalide and 1-alkyl imidazole. These were treated with Selenium metal powder in the presence of K_2CO_3 as base to generate insitu carbene to make imidazoselones. The product formation was unambiguously confirmed by NMR (1H NMR, ^{13}C NMR, DEPT and HSQC, HMBC correlations), FTIR and UV-vis studies. In addition the solid-state structure also proved by single crystal X-ray diffraction technique. These newly prepared imidazoselones were subjected towards bismuth(III)triflate to get tetra selenium coordinated bismuth(III)triflate complex which was unambiguously confirmed by single crystal X-ray diffraction technique. Further it was characterized by NMR (1H NMR, ^{13}C NMR, DEPT and ^{19}F NMR), FT-IR, UV-vis and powder X-ray diffraction technique. The thermal stability of the bismuth(III)triflate complex was carried out by TGA.



Theme of project work

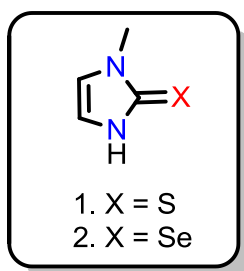
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Introduction

N-Heterocyclic carbenes have become universal ligand in organometallic and inorganic co-ordination chemistry. They not only bind to any transition metal in low or high oxidation states, but also to main group elements such as chalcogens (oxygen, sulfur, selenium, tellurium).^[1] N-heterocyclic carbenes (NHCs) have emerged as extremely powerful and versatile ligands for transition metals in organometallic catalysis, with tremendous applications in organic synthesis.^[2-3] These popularities commonly attributed to an unprecedented set of properties: their electron-rich nature, their tight binding to the metal, their original shape and resulting steric bulk. ^[4-5] NHC can bind to the chalcogens to form chalcogenides, which has versatile applications in catalysis, material science and biological field. ^[6-]

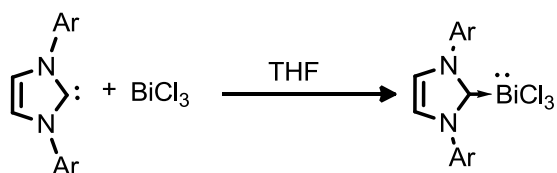
Guziec *et al.* was the first to synthesize imidazole based thione ligand (MMI) and its selenium analogues. ^[11]



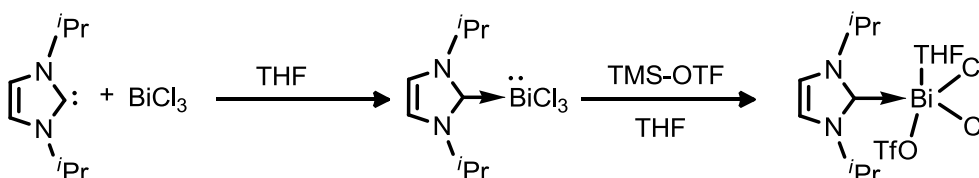
Guziec *et al.* 1994

All of the chalcogens have some role in biological functions, either as a nutrient or a toxin. Selenium is an important nutrient but is also commonly toxic. Organo selenium derivatives have been now established as essential trace element for thyroid functions. ^[12-13] The selenium analogue of imidazole can show antioxidant activity by reducing H₂O₂ even in presence of Glutathione (GSH). ^[13] For this reason it can be useful in hyperthyroidism.

Bismuth selenides are well known for their catalytic activity in organic synthesis. ^[15] There are very few examples of bismuth NHC compounds so far. ^[15-19] The first bismuth NHC compound was reported by Dutton *et al.* in 2014 by direct reaction of BiCl₃ with the NHCs Dipp₂NHC or iPr₂(Me₂)NHC. ^[16]

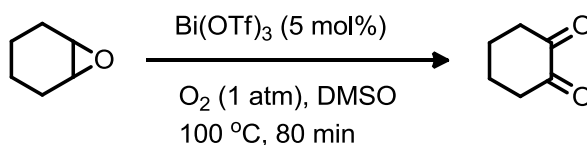


Ar = 2,6-diisopropylphenyl



In spite of its heavy metal status, bismuth is considered to be safe, as it is non-toxic and non-carcinogenic in contrast to its other congeners (arsenic, antimony, lead and tin) which are highly poisonous and hazardous to the environment.^[20-22] Bismuth has been considered to be *green element* for its non toxicity and its compounds are being used in medicinal and cosmetic purposes also.^[15]

Bismuth(III) triflate has received attention for past few years for its powerful lewis acidity. The dawn of the use of Bi(OTf) as a new catalyst has to be attributed to the seminal work of Dubac *et al.* who first established the Lewis acid nature of Bi(OTf)³.^[35] It has vast application in catalysis in wide range of organic synthesis in various catalytic reactions.^[28-34] The first example of bismuth(III) triflate-catalysed oxidation of organic compounds has been reported in the one-pot selective oxidation of internal epoxides to diketones by Antoniotti *et al.* in 2003.^[28]



Though a very few bismuth NHC compounds are reported but to the best of our knowledge bismuth compounds of seleniated ligand of imidazole is not reported so far. In our work, we have tried to trap the bismuth triflate by different seleniated ligands of imidazole to

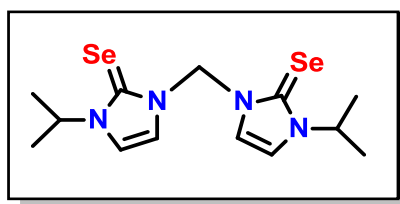
explore the characteristics of trapped bismuth(III) triflate which has not been enlightened so far.

Chapter 1

Aim of work: *Synthesis of monometallic compound*

Bismuth(III) triflate being potential catalyst for organic synthesis, our aim is to trap it by bisimidazolium ligand of selenium derivative. In the first phase of our work we have planned for synthesis of monometallic compound. For this we have to use the ligand in which the active centres (here selenium centre) are not far from each other. So we have planned to use small spacer between the two imidazole moiety.

Target ligand:



3,3'-methylenebis(1-isopropyl-1H-imidazole-2(3H)-selenone) (**3**)

1. Experimental section

General remarks

All manipulations were carried out under argon using Schlenk-vacuum line techniques and argon. The solvents were purchased from commercial sources and purified according to standard procedures. 1,1'-([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(3-methyl-1H-imidazol-3-ium) chloride (**2**) was prepared by the previously reported reaction procedure between 4,4'-bis(chloromethyl)-1,1'-biphenyl (**1**) and 1-methyl-1H-imidazole. Methyl

imidazole, acetonitrile, Methanol, Potassium carbonate, Selenium powder were purchased from commercial sources. IR measurements were carried out on a Bruker Alpha-P Fourier transform spectrometer. NMR spectra were recorded on Bruker Ultrashield spectrometer 25 °C unless otherwise stated. Chemical shifts are given relative to Me₄Si and were referenced to the solvent resonances as internal standards. The crystal structure of **3** was measured on an Oxford Supernova diffractometer. Single crystals were mounted on a Goniometer KM4/Xcalibur equipped with Sapphire2 (large Be window) detector (MoK_α radiation source, $\lambda = 0.71073 \text{ \AA}$). Crystals of **3** were obtained from mixture of Dichloromethane and Methanol solution of **3** at room temperature over a period of 12 hours. The crystal structure of **1** was measured on an Oxford Xcalibur 2 diffractometer. Data were collected at 153 K. The structure was solved by direct methods using the SIR-97 program [31] and refined with a full matrix least-squares method on F2 using the SHELXL-97 program [32-33]. CCDC-886715 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 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.

Part A:

1. Synthesis and characterization of **3** and **4**

1.1 Synthesis of 1-isopropyl-1H-imidazole (**1**):

In a RB containing 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 balloon filled with argon was inserted into it. After stirring for 5 h ipr-I was added dropwise by syringe technique under vigorous stirring and waterbath 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

ether and water. The product was formed as transparent liquid. ^1H NMR (CDCl_3 , 400 MHz): δ 7.39 (s, 1H, ImH), 4.22-4.17(m, 1H, ^iPrH), 1.35-1.33 (d, $^2J_{\text{HH}} = 8\text{Hz}$, 6H, ^iPrH) ppm.

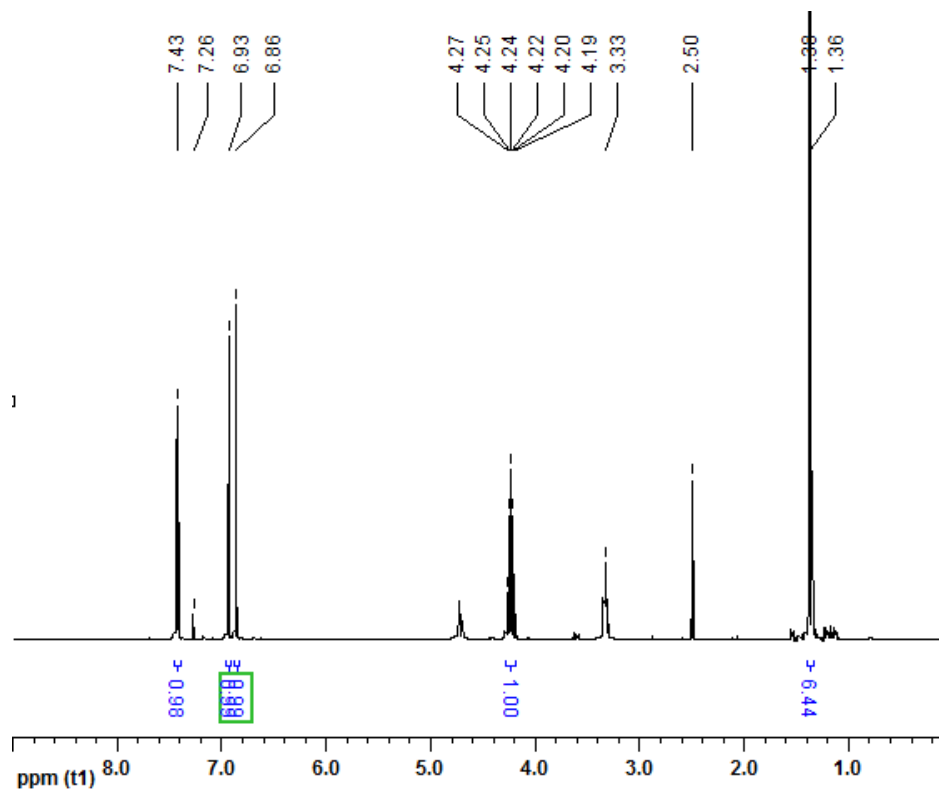


Figure 1: ^1H NMR of compound **1** (400 MHz, D_2O , RT)

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

CH_2Br_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 $^\circ\text{C}$ for 48 h. After reaction white precipitate came. White solid was obtained after work up. Yield: 85% (based on **1**). M.p., 102-104 $^\circ\text{C}$ (melted to transparent liquid). ^1H NMR (D_2O , 400 MHz): δ 7.69-7.68 (d, $^2J_{\text{HH}} = 4\text{ Hz}$, 1H, ImH), 7.64-7.63(d, $^2J_{\text{HH}} = 4\text{ Hz}$, 1H, ImH), 6.57 (s, 2H, NCH_2), 4.70-4.59 (m, 2H, NCH), 1.48-1.35 (dd, 12H, CH_3) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ 122.10, 122.02 (Im-CH), 58.117 (Im-CH), 51.2 (CH), 21.74 (CH_3) ppm.

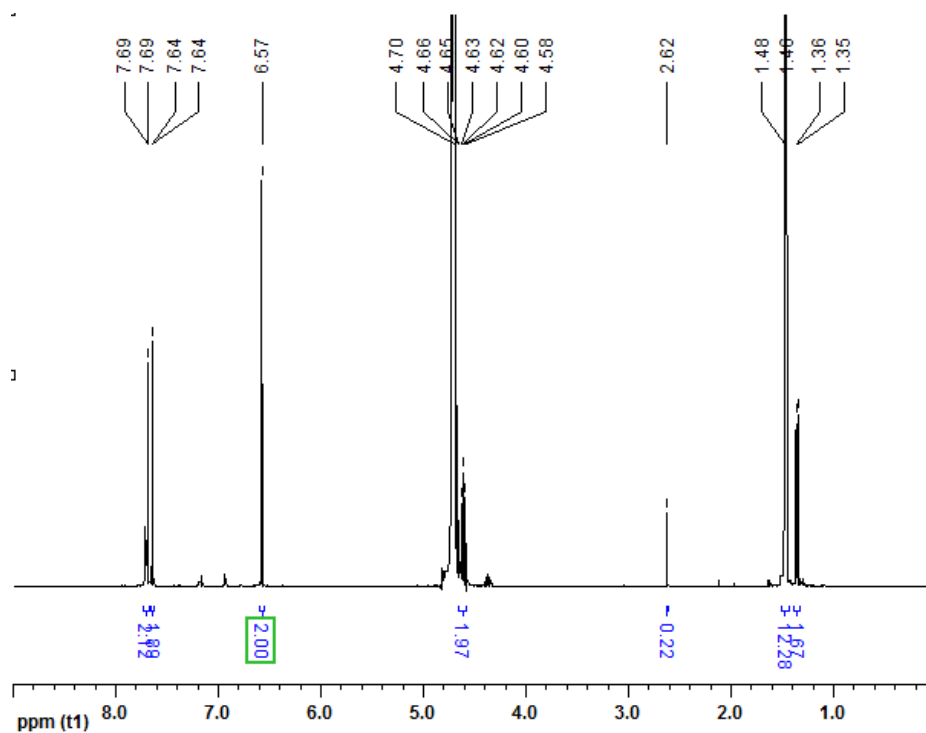


Figure 2: ^1H NMR of compound **2** (400 MHz, D_2O , RT)

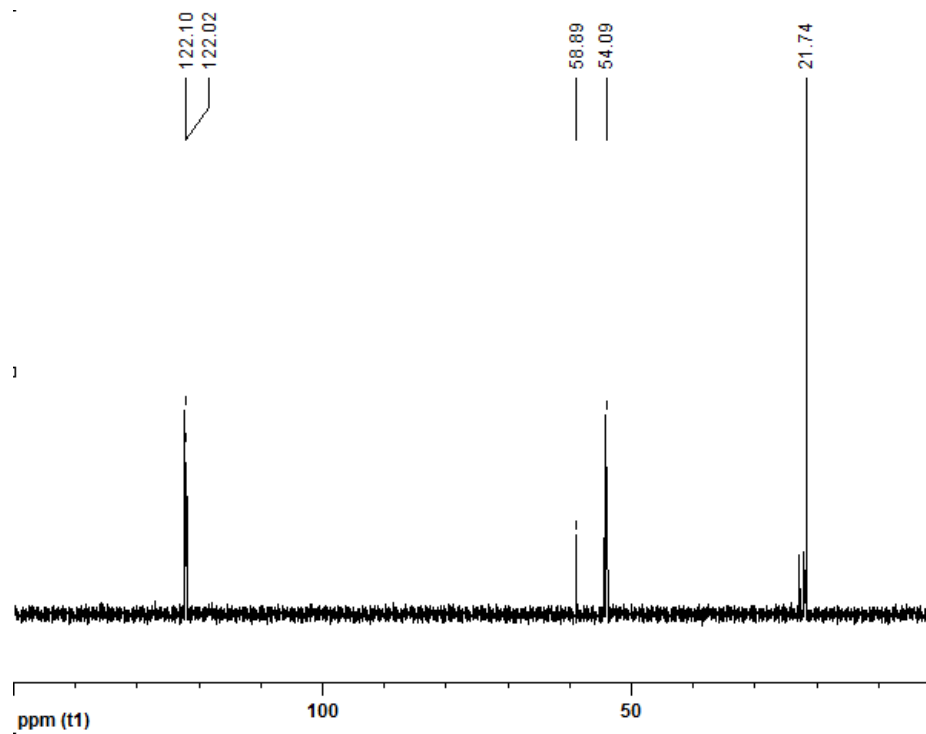


Figure 3: ^{13}C NMR of compound **2** (400 MHz, D_2O , RT)

1.3 synthesis of 3,3'-methylenebis(1-isopropyl-1H-imidazole-2(3H)-selenone (3) :

2 (0.4 g, 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. White crystalline solid was obtained after work up. Yield: 85% (based on **2**). M.p., 120 °C -124 °C (melted to transparent liquid). ¹H NMR (CDCl₃, 400 MHz): δ 8.12-8.11 (d, ²J_{HH} = 4 Hz, 2H, ImH), 6.84-6.83 (d, ²J_{HH} = 4 Hz, 2H, ImH), 6.61 (s, 2H, NCH₂), 5.19-5.13 (m, 2H, NCH), 1.98-1.37 (d, ²J_{HH} = 4 Hz, 12H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ 156.05 (C=Se), 121.23 (Im-CH), 114.85 (Im-CH), 58.12 (N-CH₂), 51.18 (N-CH), 21.09 (CH₃) ppm. FT-IR (neat, ν): 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) cm⁻¹.

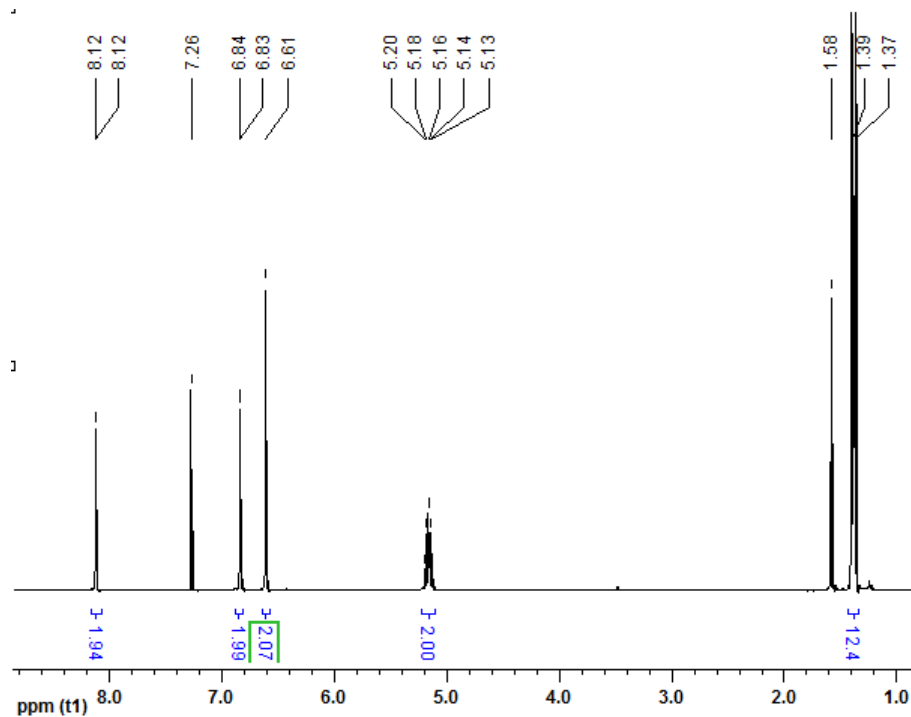


Figure 4: ¹H NMR of compound **3** (400 MHz, D₂O, RT)

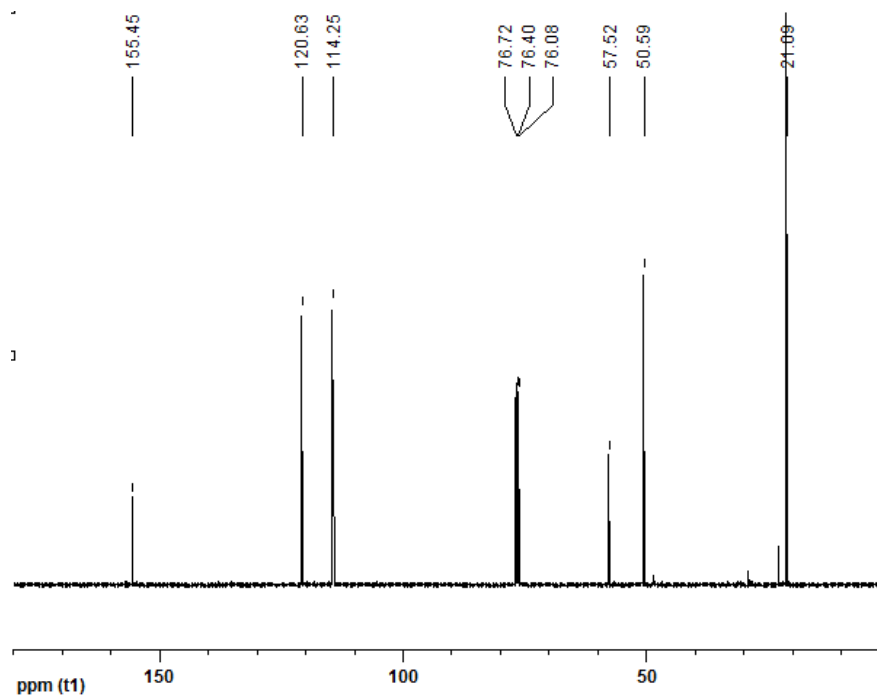


Figure 5: ^{13}C NMR of compound **3** (400 MHz, D_2O , RT)

1.4 Synthesis of bismuth compound of **3** (**4**):

To the solution of **3** (0.05 g, 0.24 mmol) in toluene (2 ml) bismuth(III) triflate (0.114 g, 0.24 mmol) was added in argon atmosphere under vigorous stirring. The reaction was started at 100 °C and continued for 24 h. The reaction mixture appeared as yellow solution with orange precipitate. The precipitate was collected by filtration and dissolved in methanol leading to a deep red solution. It was kept for crystallisation after cannula filtration. After 20 h it gave deep orange crystals of bismuth triflate compound of **3**. Yield: 77%. M.p., 158-160 °C (decomposes to black). ^1H NMR (DMSO, 400 MHz): δ 7.84-7.83 (d, $^2J_{\text{HH}} = 4$ Hz, 2H, ImH), 7.49-7.48 (d, $^2J_{\text{HH}} = 4$ Hz, 2H, ImH), 6.39 (s, 2H, NCH₂), 4.98-4.91 (m, 2H, NCH₂), 1.31-1.29 (d, $^2J_{\text{HH}} = 8$ Hz, 12H, CH₃) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 154.45 (C=Se), 119.91 (Im-CH), 116.55 (Im-CH), 57.67 (N-CH₂), 50.18 (N-CH), 20.17 (CH₃) ppm. ^{19}F NMR (DMSO, 400 MHz): δ -77.74 (CF₃) ppm. FT-IR (neat, ν): 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) cm^{-1} .

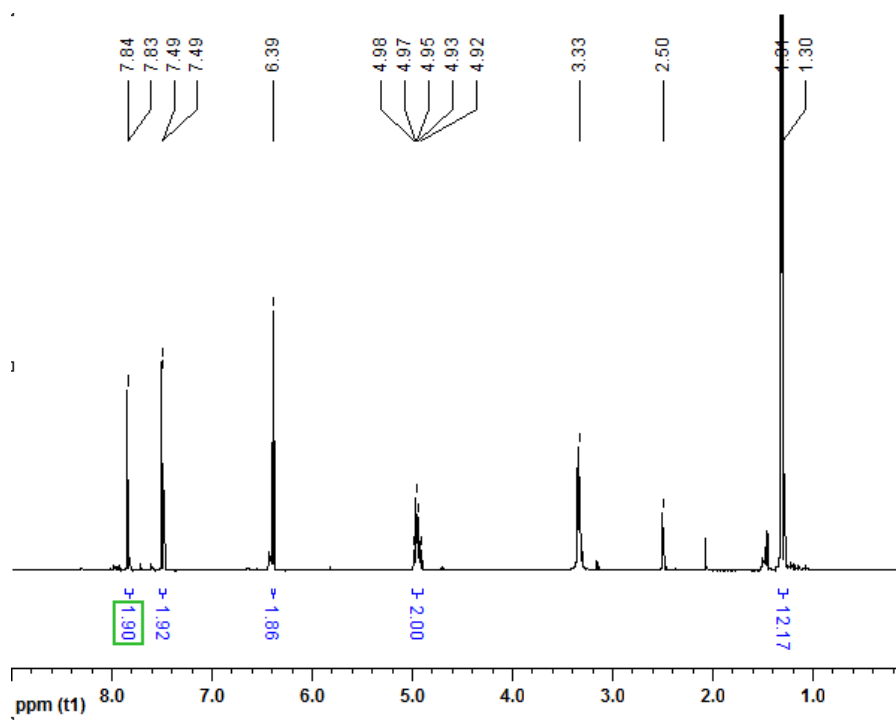


Figure 6: ^1H NMR of compound **4** (400 MHz, DMSO, RT)

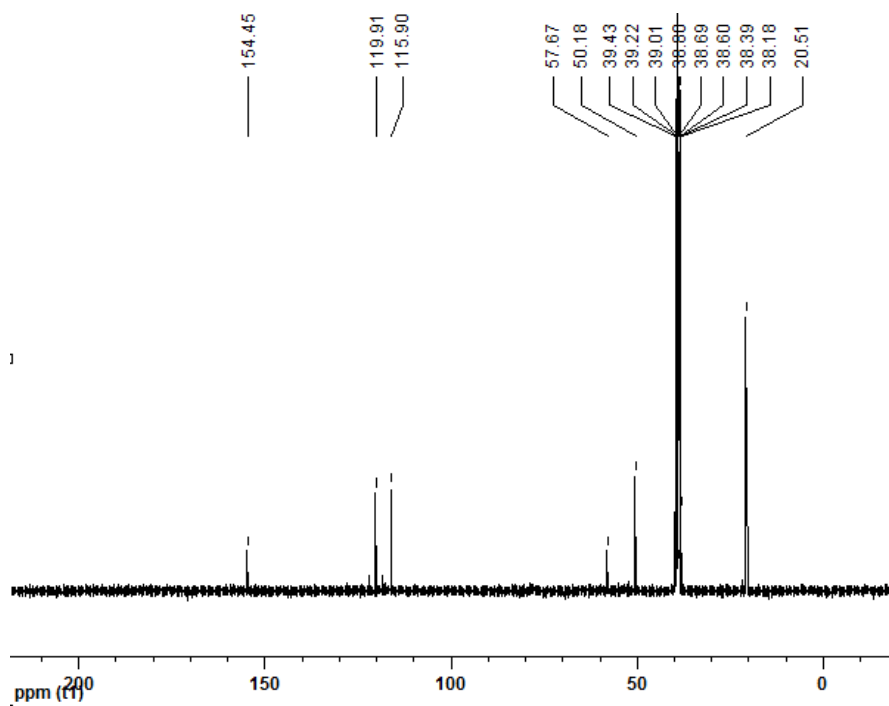


Figure 7: ^{13}C NMR of compound **4** (400 MHz, DMSO, RT)

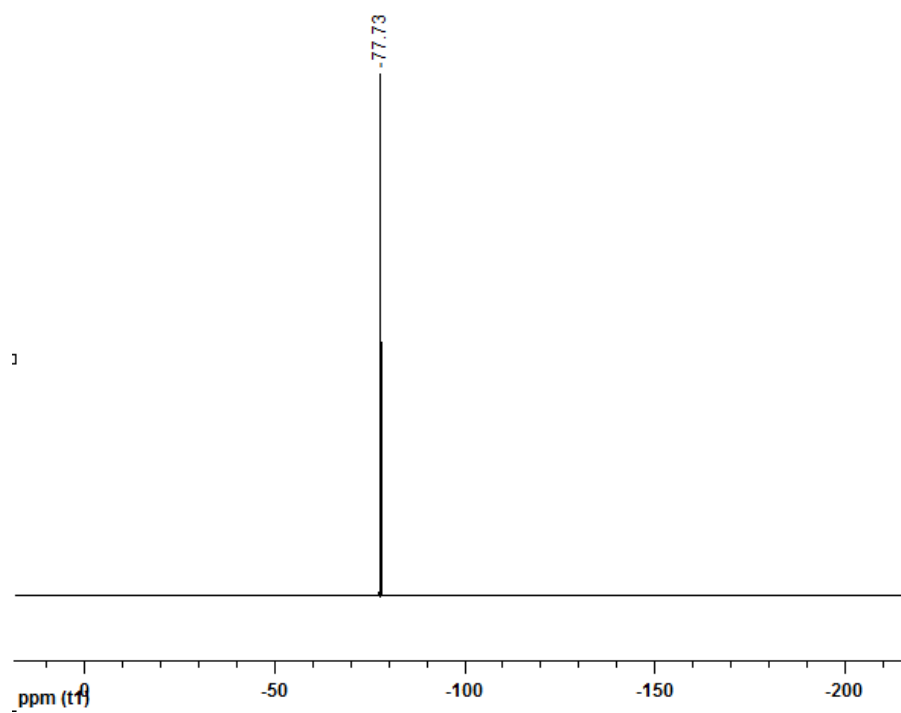
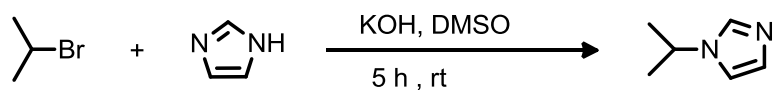


Figure 8: ^{19}F NMR of compound **4** (400 MHz, DMSO, RT)

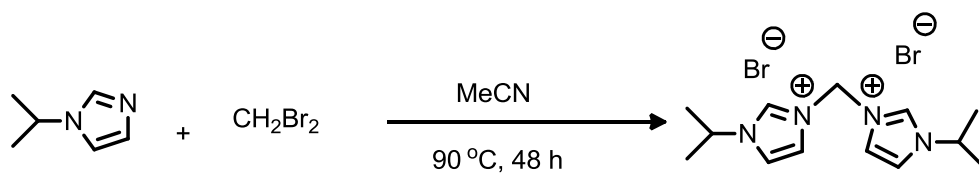
Part B:

2. Scheme of synthesis of 3 and 4



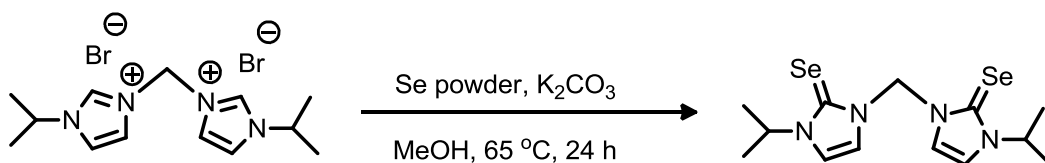
Scheme 1

1



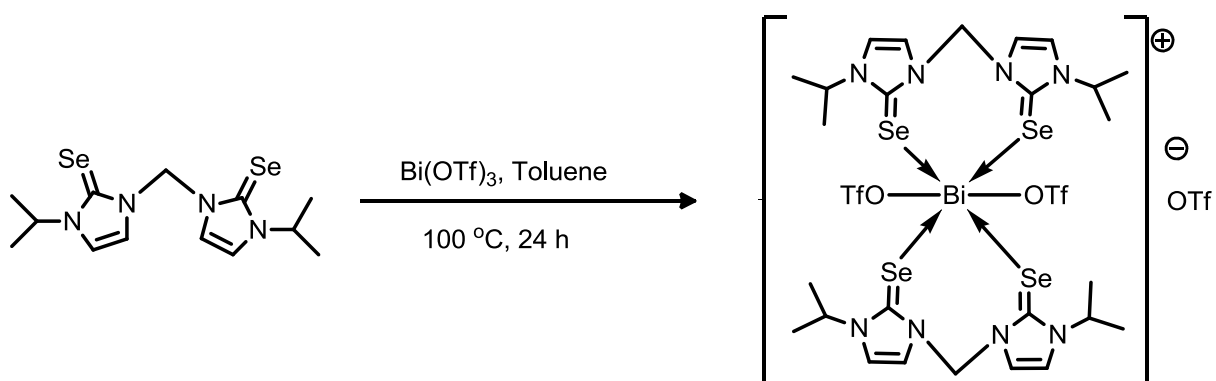
Scheme 2

2



Scheme 3

3



Scheme 4

4

Part C:

3. Results and Discussions

3.1. Synthesis and characterisation of **3** and **4**

In a schlenk tube **2** was heated with 2 equivalent of activated potassium carbonate and 2 equivalent of Se powder in presence of methanol at 65 °C to result **3** (Scheme 3). The white solid compound **3** is soluble in methanol-dichloromethane mixture. The compound **3** was characterized by FT-IR, ¹H NMR, ¹³C NMR, 2D NMR, UV-vis and single crystal X-ray diffraction techniques. **3** was further treated with 1 equivalent of bismuth(III) triflate in toluene to yield **4** at 100 °C. **4** was characterised by FT-IR, ¹H NMR, ¹³C NMR, ¹⁹F NMR, UV-vis, TGA, powder and single crystal X-ray diffraction techniques. The selected characterization parameters for **3** and **4** are listed in table 1. In **3**, C=Se stretching frequency appeared at 1078 cm⁻¹ while in **4** it appeared at 1018 cm⁻¹.^[5, 29] 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** appeared at 1561 and 1568 cm⁻¹.^[5] In ¹H NMR, the chemical shift values for Im-CH, Im-CH₂ and ⁱPr protons are comparable in **3** and **4**. In ¹³C NMR, the C=Se chemical shift value for **3** is greater than that of **4** (δ 156.05 ppm for **3** and δ 154.45 ppm for **4**). Similarly, the ¹³C NMR chemical shift values of Im-CH₂ for **3** (δ 57.67 ppm) and **4** (δ 58.12 ppm) are comparable. The only one ¹⁹F NMR peak (-77.74 ppm) indicates that there is only one type of triflate group is present in the coordination sphere.

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

Compound	M.P. (°C)	Yield (%)	¹ H NMR δ Im-CH (ppm)	¹³ C NMR δ N-C(Se)-N (ppm)	¹⁹ F NMR δ CF ₃ (ppm)	Solution UV-vis abs. (nm)
3	102-104	85	8.12-8.11, 6.84-6.83	156.05	---	204,279
4	158-160	77	7.84-7.83, 7.49-7.48	154.45	-77.74	205,280

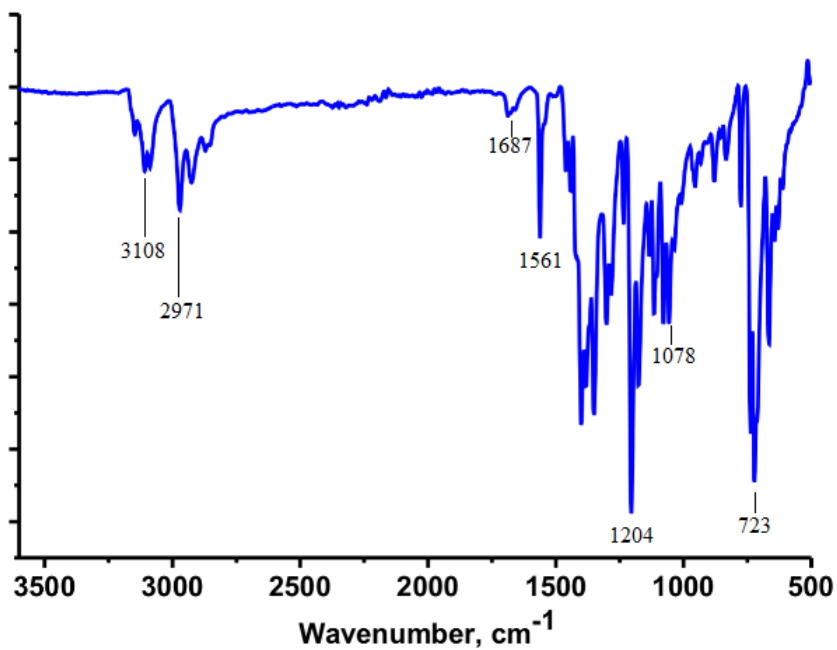


Figure 9: FTIR data of compound 3

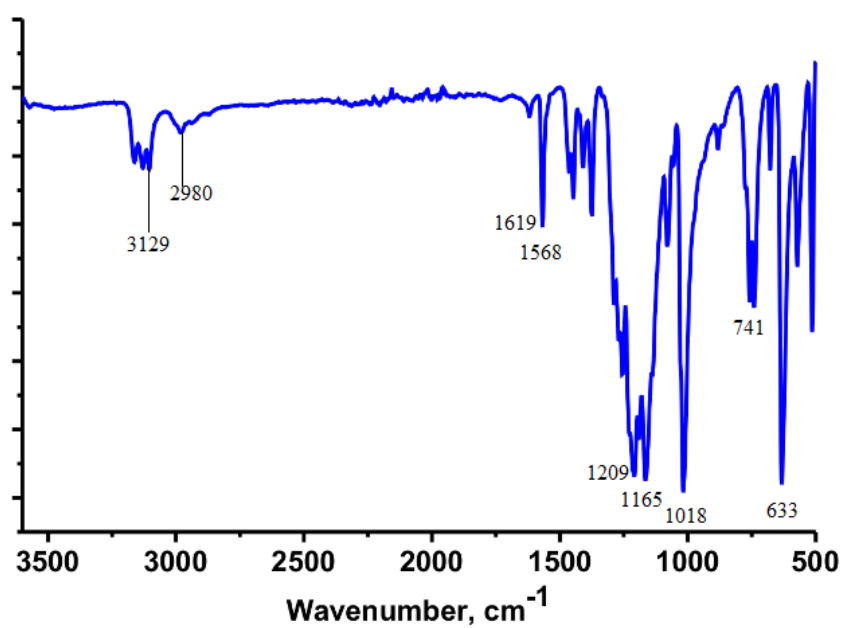


Figure 10: FTIR data of compound 4

3.1 2D NMR data interpretation

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 CH₂ group, one CH group, two CH₃ 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 CH₃ groups, the C-H correlation is also observed. Total five C-H correlations are observed, including NCH₂N C-H correlation, which indicates that **3** contains 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 CSe carbon couples with the nearest CH₂ and CH protons strongly (³J) but the coupling is not that much strong with other two imidazolium protons (³J). the CH₂ protons couple more strongly with nearest imidazolium proton (³J) than that of farthest one (⁴J). On the other hand two couplings of the CH₃ protons with the nearest imidazolium carbon and isopropyl CH carbon are observed (⁴J).

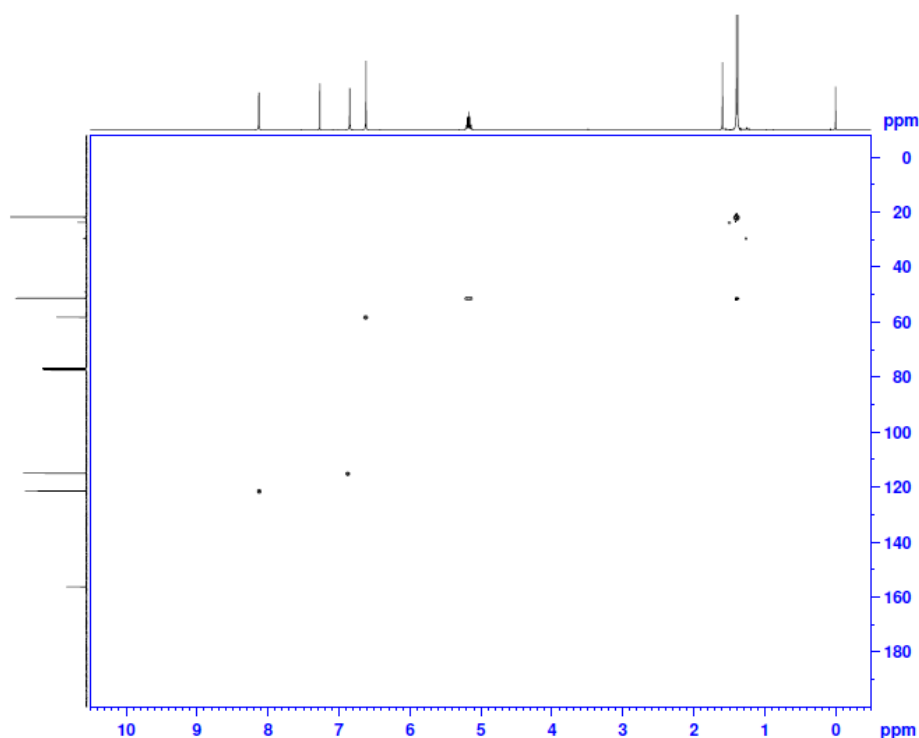


Figure 11: HSQC of compound **3** (400 MHz, CDCl₃, RT).

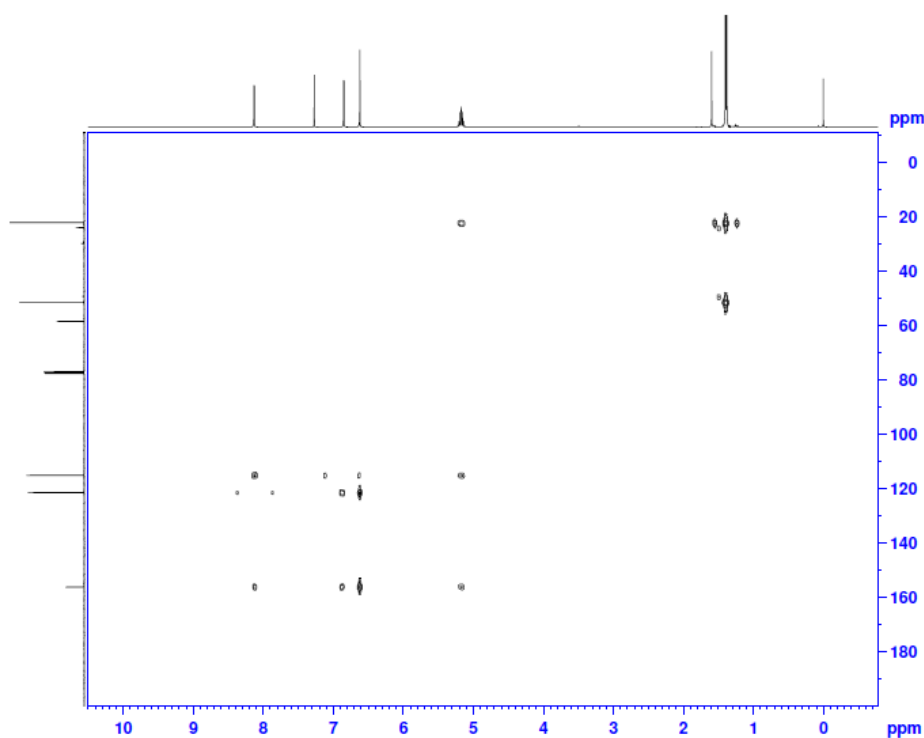


Figure 12: HMBC of compound **3** (400 MHz, CDCl₃, RT).

3.2 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. 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 P2₁/n and P-1 respectively. The structural feature of **3** and **4** are discussed in detail. The C-Se bond lengths in **4** (1.88 Å) have increased notably than in **3** (1.82 Å). The C(Se)-N bond lengths in **3** and **4** are comparable, although for **4** it has decreased slightly (1.35 Å for **3** and 1.34 Å for **4**).^[5] The N-C(Se)-N bond angles in **4** (107 °) have been increased to some extent than that of **3** (104 °), whereas, the N-CH₂-N bond angles in **4** (113 °) is shorter than that of **3** (112 °).

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

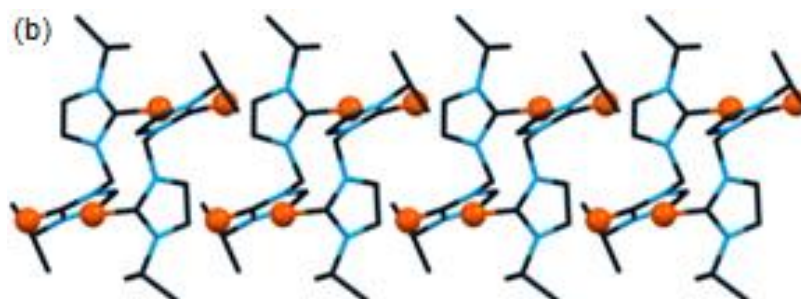
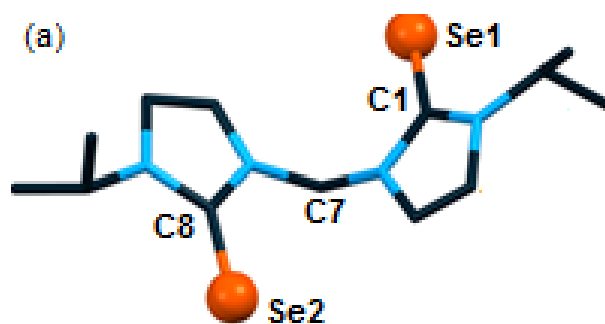
	3	4

Empirical formula	H ₁₀ C _{6.5} N ₂ Se	C ₄₄ H ₄₈ N ₈ O ₆ F ₆ S ₂ Se ₂ Bi ₂
Formula weight	390.25	1436.69
Temperature (K)	150	150.01(10)
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 ₁ /n
<i>a</i> , Å	7.1055(12)	15.3075(6)
<i>b</i> , Å	11.403(2)	13.2282(6)
<i>c</i> , Å	11.4572(19)	23.4813(9)
α , °	69.174(16)	90
β , °	80.152(14)	94.758(4)
γ , °	74.059(16)	90
Volume, Å ³	831.5(3)	4738.4(3)
<i>Z</i>	2	4
ρ_{calc} , mg mm ⁻³	1.5586	2.0138
μ , mm ⁻¹	5.502	12.868
<i>F</i> (000)	385.5	2744.6
Data collected	8.28 to 142.22°	5.8 to 141.58°
Unique data	2775/0/176	8961/0/262
<i>R</i> _{int}	0.0299	0.0477
GOF on <i>F</i> ²	1.032	1.011
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0653	0.0594
w <i>R</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.2053	0.1764
<i>R</i> ₁ values (all data)	0.1013	0.0713
w <i>R</i> ₂ values (all data)	0.2053	0.1764

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

Bond lengths [Å]		Bond angles [°]		
	3	4	3	4

C–Se	1.822(10)	1.880(10)	N–C(Se)–N	104.2(9)	107.4(8)
	1.826(10)	1.879(10)		105.2(9)	107.4(9)
		1.882(10)			107.5(8)
		1.872(10)			107.7(8)
C(Se)–N	1.357(13)	1.339(12)	N–CH ₂ –N	113.2(9)	112.5(8)
	1.367(12)	1.353(12)			112.9(8)
	1.374(12)	1.356(13)			
	1.358(13)	1.341(13)			
		1.348(12)			
		1.335(13)			
		1.336(13)			
	1.350(13)				



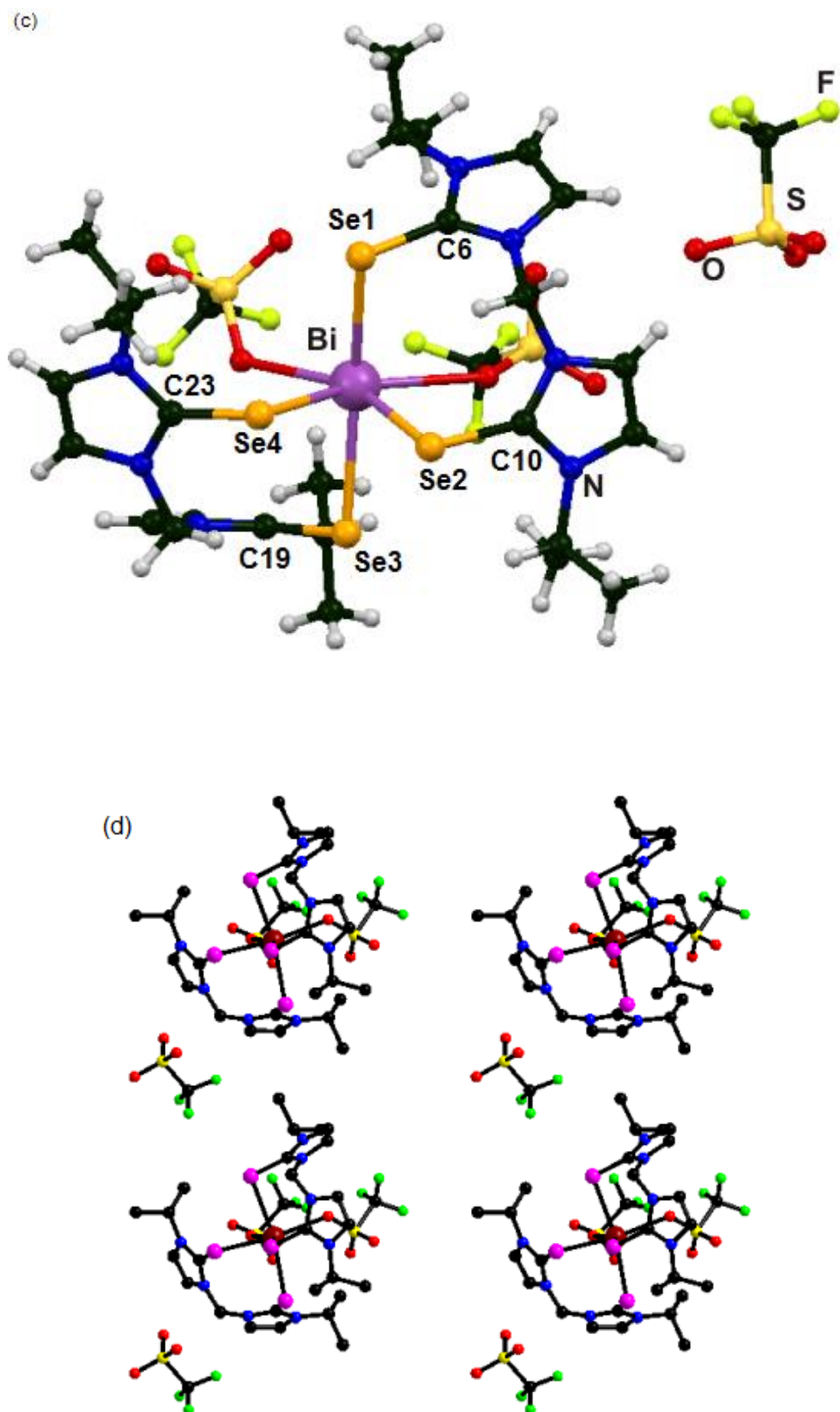


Figure 14: (a) the crystal structure of **3**, (b) the packing pattern of **3**, (c) the crystal structure of **4**, (d) the packing pattern of **4**

3.3 UV-vis solution state absorption spectra of **3** and **4**

Solution state UV-vis absorption spectrum of **3** and **4** were measured in MeOH (Fig. 6 & 7). The solution state UV-vis absorption properties of **3**, **4** are comparable. **3** and **4** both shows an absorption band at 204 and 205 nm due to π - π^* transition with molar extension coefficient of $34706 \text{ L mol}^{-1} \text{ cm}^{-1}$ for **3** and $47353 \text{ L mol}^{-1} \text{ cm}^{-1}$ for **4**. Other transitions of **3** and **4** are due to n- π^* transition (279 nm for **3** and 280 nm for **4**).

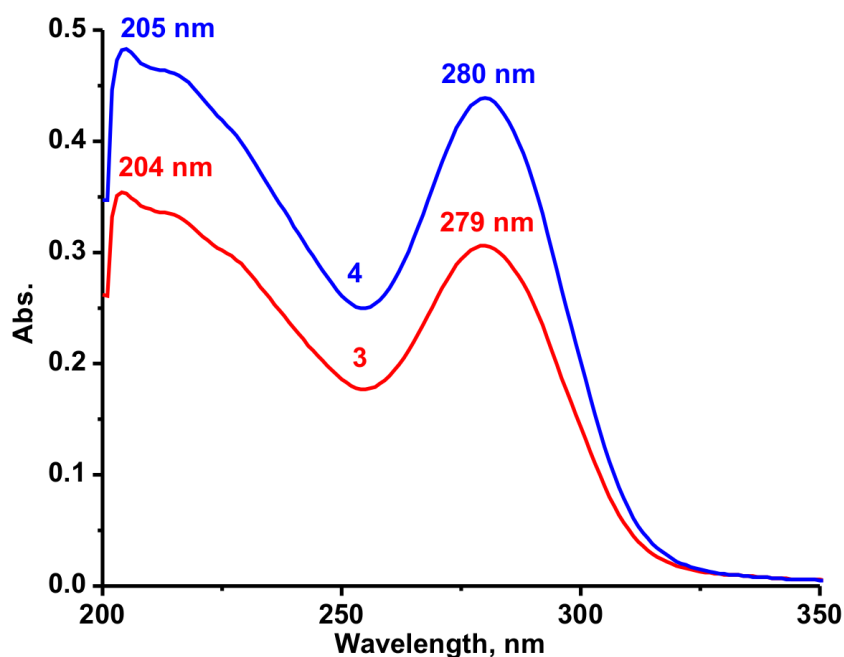


Figure 15: The solution state UV-vis spectra of **3** and **4** in MeOH at RT (1.02×10^{-5} M).

3.4. TGA analysis of **4**

In order to understand the thermal decomposition pathway of **6**, thermogravimetric analysis (TGA) ($10 \text{ }^\circ\text{C min}^{-1}$, 30 – $1000 \text{ }^\circ\text{C}$, under N_2 atmosphere) was carried out on **6**. It shows enough stability upto $265 \text{ }^\circ\text{C}$ then sharp weight loss was detected from $265 \text{ }^\circ\text{C}$ to $451 \text{ }^\circ\text{C}$ (with 56% weight loss). Then gradual weight loss occurs from $451 \text{ }^\circ\text{C}$ to $559 \text{ }^\circ\text{C}$ (with 21% weight loss). After $559 \text{ }^\circ\text{C}$, **6** dissociates completely.

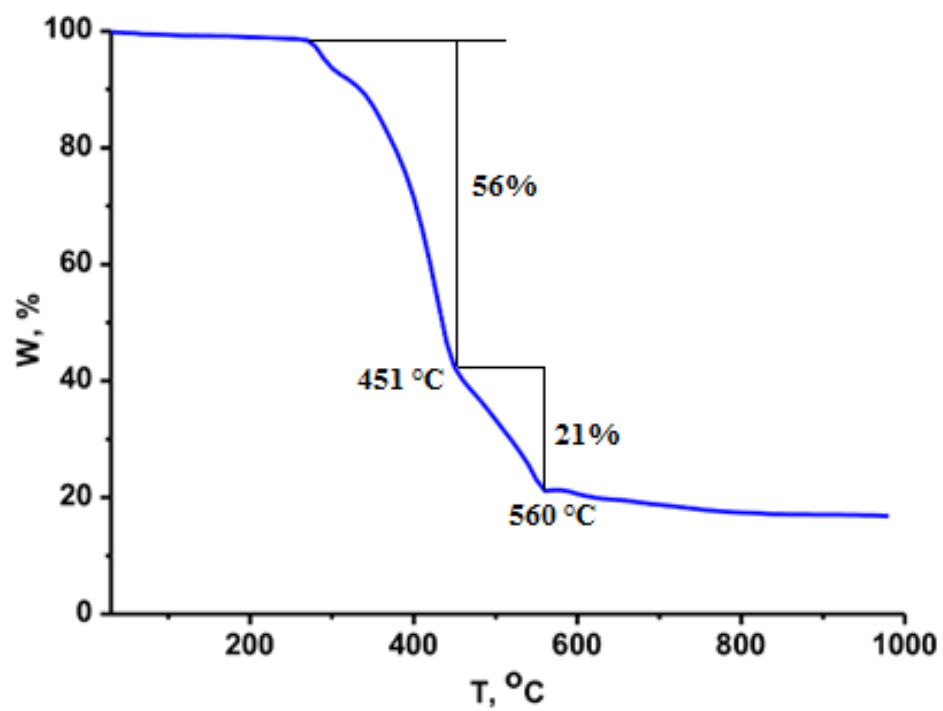


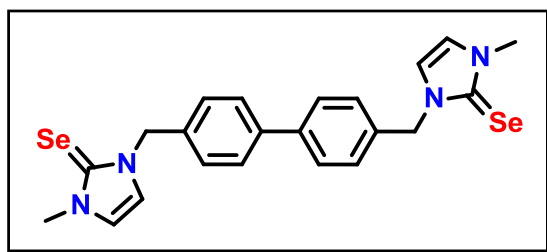
Figure 16: TGA curve of 4

Chapter 2

Aim of work: Synthesis of bimetallic compound

For trapping two metal centres in one compound we should use rigid long spacer so that the active sites (selenium centre) remain far from each other. For this we have designed the following molecule.

Target ligand:



1,1'-([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(3-methyl-1H-imidazol-3-ium) chloride (**6**)

Part A

4. Experimental section

General remarks

All manipulations were carried out under argon using Schlenk-vacuum line techniques and argon. The solvents were purchased from commercial sources and purified according to standard procedures. 1,1'-([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(3-methyl-1H-imidazol-3-ium) chloride (**2**) was prepared by the previously reported reaction procedure between 4,4'-bis(chloromethyl)-1,1'-biphenyl (**1**) and 1-methyl-1H-imidazole. Methyl imidazole, acetonitrile, Methanol, Potassium carbonate, Selenium powder were purchased from commercial sources. IR measurements were carried out on a Bruker Alpha-P Fourier transform spectrometer. NMR spectra were recorded on Bruker Ultrashield spectrometer 25 °C unless otherwise stated. Chemical shifts are given relative to Me₄Si and were referenced to

the solvent resonances as internal standards. The crystal structure of **3** was measured on an Oxford Supernova diffractometer. Single crystals were mounted on a Goniometer KM4/Xcalibur equipped with Sapphire2 (large Be window) detector (MoK α radiation source, $\lambda = 0.71073 \text{ \AA}$). Crystals of **3** were obtained from mixture of Dichloromethane and Methanol solution of **3** at room temperature over a period of 12 hours. The crystal structure of **1** was measured on an Oxford Xcalibur 2 diffractometer. Data were collected at 153 K. The structure was solved by direct methods using the SIR-97 program [31] and refined with a full matrix least-squares method on F2 using the SHELXL-97 program [32-33]. CCDC-886715 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 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

4.1 Synthesis of **5**

Acetonitrile (35 ml) was added to **a** (5 g, 19.9 mmol) under argon atmosphere then N-methyl imidazole (4.7 ml, 59.7 mmol) was added to it at 92 °C temperature and stirred for 46 h. The reaction progress was monitored by TLC. After completion of the reaction, the product, **5** was formed as white precipitate. Yield: 98% (based on **a**). M.p., 102-104 °C (melted to transparent liquid). ^1H NMR (D $_2$ O, 400 MHz): δ 8.75 (s, 1H, ImH), 7.67-7.65 (d, $^2J_{\text{HH}} = 6.8 \text{ Hz}$, 4H, ImH), 7.46-7.44 (d, $^2J_{\text{HH}} = 8 \text{ Hz}$, 4H, ArH), 7.41-7.40 (d, $^2J_{\text{HH}} = 4 \text{ Hz}$, 6.6 Hz, 4H, ArH), 5.37 (s, 4H, NCH $_2$), 3.84 (s, 6H, CH $_3$) ppm. ^{13}C NMR (CDCl $_3$, 100 MHz): δ 122.09, 123.83 (Im-CH), 133.23, 140.27 (Ph-C), 35.72 (CH $_3$), 129.21, 127.61 (Ar-C), 52.34 (N-CH $_2$ -) ppm. FT-IR (neat, ν): 3367(s), 3296(m), 3138(m), 3118(m), 3077(m), 2984(m), 2845(w), 1652(w), 1569(s), 1560(s), 1501(m), 1453(m), 1186(m), 1159(s), 801(m), 753(s) cm $^{-1}$.

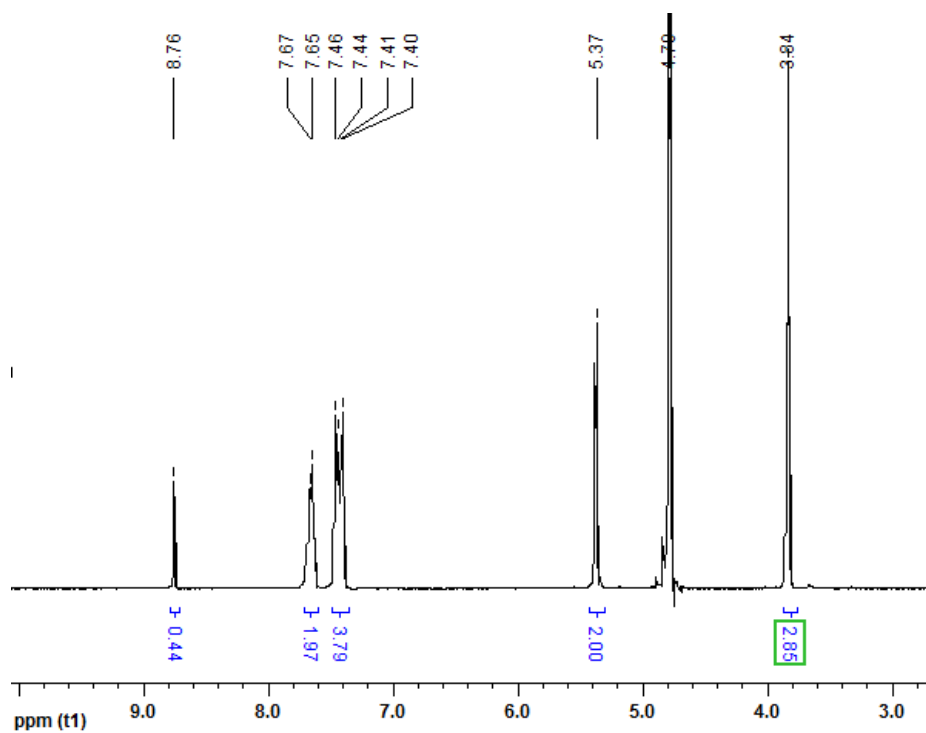


Figure 17: ^1H NMR of compound **5** (400 MHz, D_2O , RT)

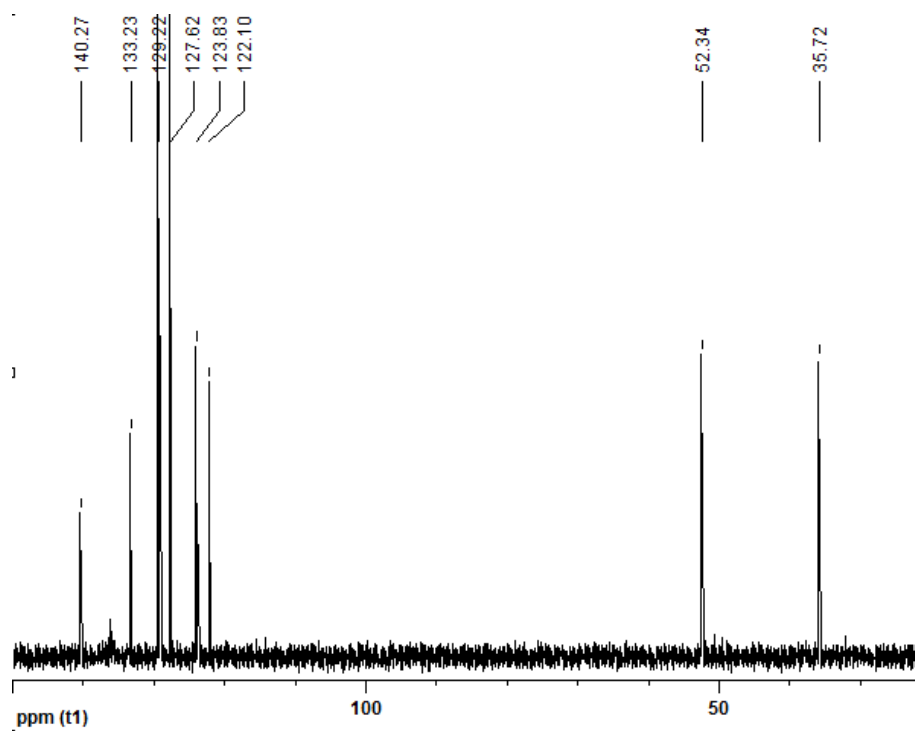


Figure 18: ^{13}C NMR of compound **5** (400 MHz, D_2O , RT)

4.2 Synthesis of **6**

In a schlenk tube, **5** (4 g, 9.63 mmol) was added to activated potassium carbonate (2.6 g, 19.26 mmol). To which, MeOH (10 mL) was added then Se powder (1.5 g, 19.26 mmol) was added under argon atmosphere. The temperature was set at 70 °C and the reaction mixture was stirred for 24 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was transferred to a flask and the solvent was evaporated. Then water was added to it and extracted with dichloromethane (3 x 15 mL). The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄. Organic solvent was evaporated under reduced pressure to result crude amorphous off-white product, **6**. Yield: 55% (based on **5**). M.p., 168-170 °C (decomposed to brown), 260-262 °C (melted to black). ¹H NMR (CDCl₃, 400 MHz): δ 7.54-7.52 (d, ²J_{HH} = 8 Hz, 4H, ArH), 7.40-7.38 (d, ²J_{HH} = 4 Hz, 4H, ArH), 6.86-6.85 (d, ²J_{HH} = 4 Hz, 2H, ImH), 6.78-6.77 (d, ²J_{HH} = 4 Hz, 2H, ImH), 5.38 (s, 4H, CH₂) 3.75 (s, 6H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ 155.40 (C=Se), 139.06 (Ph-C), 135.95 (CH₂-C), 128.31 (Im-CH), 126.68 (Ph-CH), 120.95 (Im-CH), 119.29 (Im-CH), 51.1 (N-CH₂), 36.53 (N-CH₃) ppm. FT-IR (neat, ν): 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) cm⁻¹.

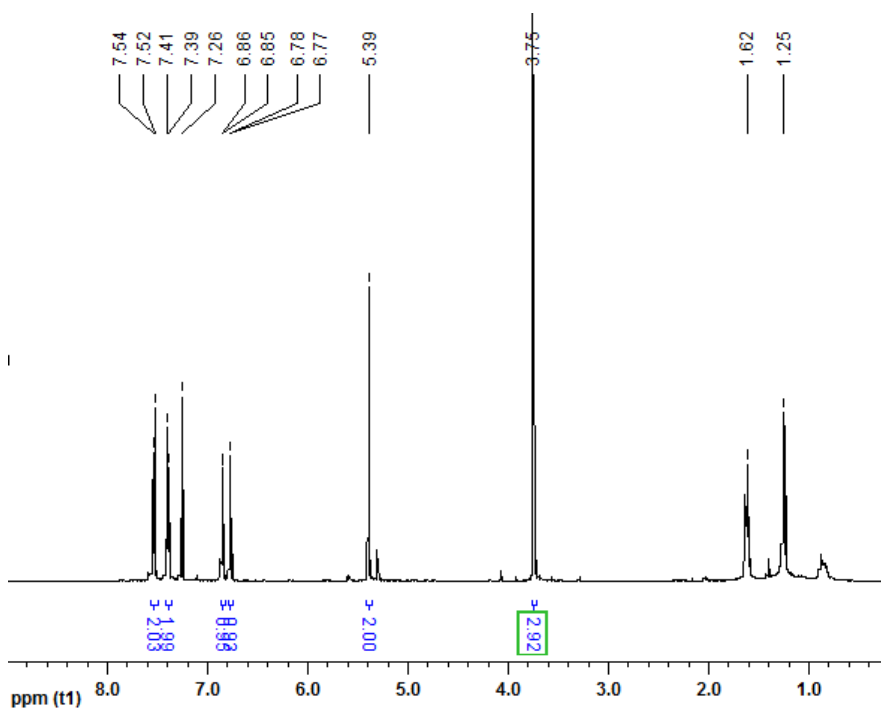


Figure 19: ¹H NMR of compound **6** (400 MHz, CDCl₃, RT)

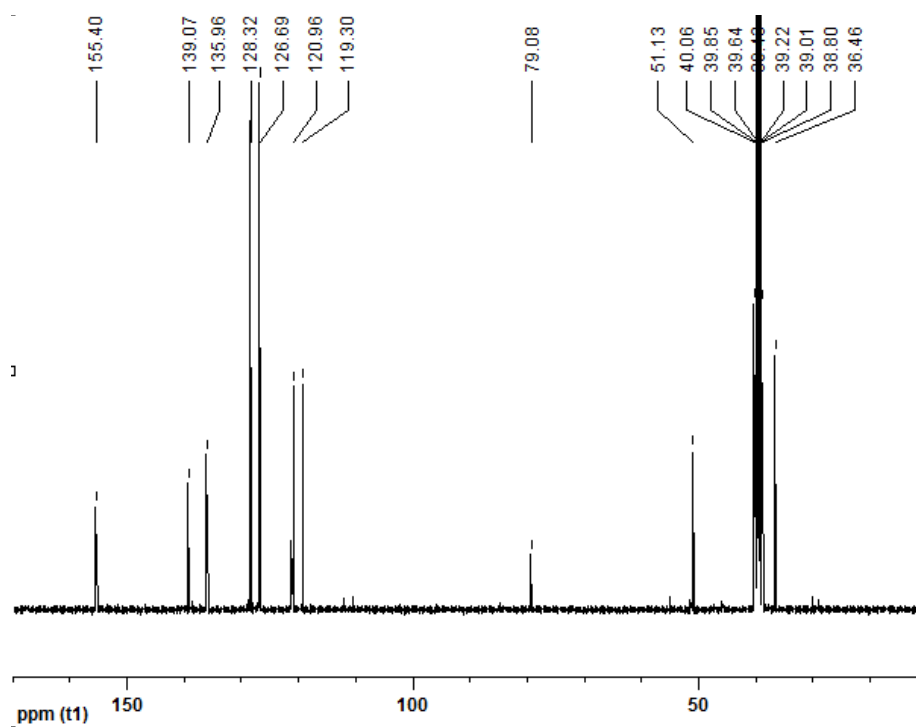
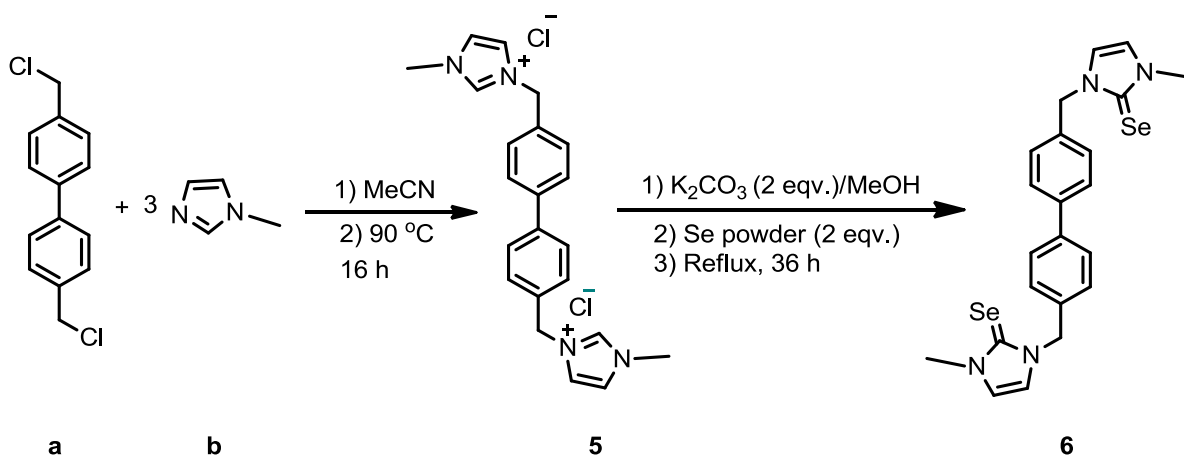


Figure 20: ^{13}C NMR of compound **6** (400 MHz, CDCl_3 , RT)

Part B

5. Scheme of synthesis of **5** and **6**



Scheme 5. Synthesis of **5** and **6**.

Part C

6. Results and discussion

6.1. Synthesis and characterization of **5** and **6**

As outlined in scheme 1, compound **5** were obtained in excellent yield by combining N-methyl or allyl imidazole with 4,4'-bis(chloromethyl)-1,1'-biphenyl (**a**) in acetonitrile at 90 °C under argon atmosphere. Compound **5** was soluble in water and hygroscopic in nature. **5** was characterized by FT-IR, UV-vis, ¹H NMR and ¹³C NMR techniques. In **5** the N₂CH peak appeared at δ 8.75 ppm though fast proton exchange of N₂CH can occur by deuterium. The N-CH₂ peak appeared at δ 5.37 ppm for **6**.

Table 4. Analytical and spectral data of **5** and **6**.

Compound	M.P. (°C)	Yield (%)	¹ H NMR δ Im-CH (ppm)	¹³ C NMR δ N-C (ppm)	Solution UV-vis abs. (nm)	Solid state UV-vis abs. (nm)
	102-104	98	7.67	35.72	263	286
	260-262	55	6.86-6.85 6.78-6.77	36.53	272	341

6.2. Synthesis and characterization of **6**

In a schlenk tube **5** 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 **6** (Scheme 1). Compound **6** is soluble in methanol-dichloromethane mixture. It is off-white solid. The compound **6** were characterized by FT-IR, ¹H NMR, ¹³C NMR, UV-vis and single crystal X-ray diffraction techniques. In **6**, C=Se stretching frequency appeared at 1116 cm⁻¹. The N-C-N stretching frequency of **6** appeared at 1666 cm⁻¹. In ¹³C NMR, the C=Se chemical

shift value for **6** appears at δ 155.4 ppm. Similarly, the ^{13}C NMR chemical shift value of Im- CH_2 for **6** is δ 51.1 ppm.

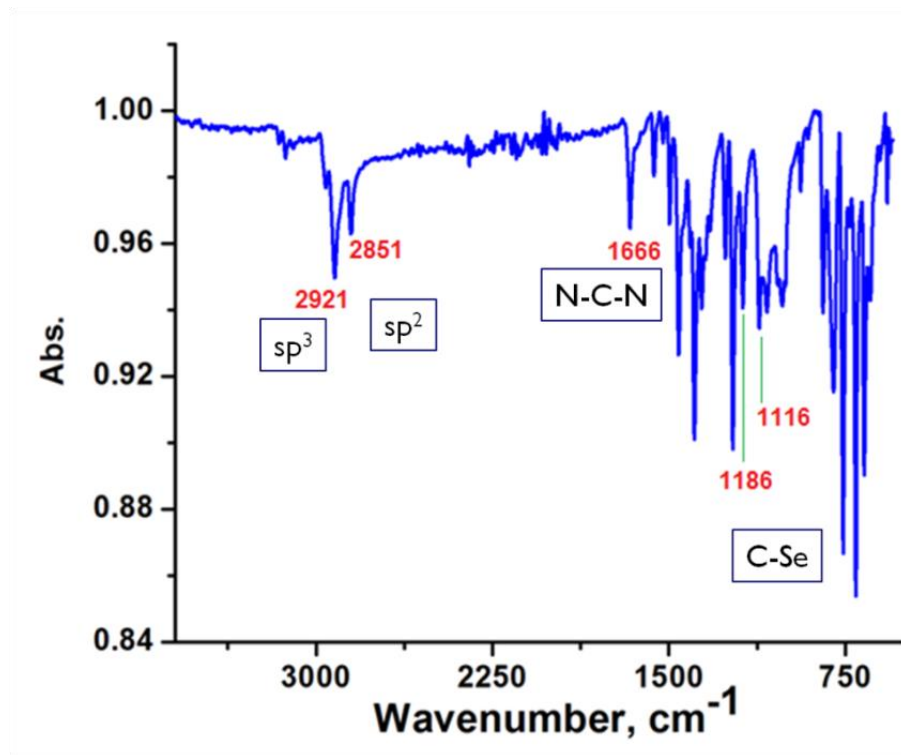


Figure 21: IR spectrum of compound **6**

6.3. 2D NMR data interpretation

The formation of **6** was further characterized by 2D NMR spectroscopy (DEPT, HMBC and HSQC). Notably the structural exploration for the imidazole selenone using 2D NMR is rare. The structures of **6** is confirmed by 2D NMR studies, which are further verified by single crystal X-ray diffraction study (*vide infra*). The present investigation can help to assign the unknown structures of similar class of compounds in biological system. In DEPT spectrum, **6** clearly gave one CH_2 group, one CH_3 group and four CH groups, which are in accordance with the structures of **6** (*vide infra*).

HSQC spectrum of **6** showed CH 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 CH₂ group, the CH correlation is also observed.

The structures of **6** is further confirmed by HMBC spectrum that showed the mapping carbon coupling with neighboring protons. The CH₂ proton couples strongly with the nearest imidazolium carbons (³J), it also couples with the nearest carbon atom (³J) of CH group in benzene ring but does not couple with farthest one. Coupling between the mentioned CH₂ carbon and the quaternary carbon of benzene ring is quite strong (²J). The proton of CH₃ group strongly couples with the nearest Imidazolium carbons (³J). The CH₃ carbon couples with the nearest Imidazolium proton (³J). Another strong correlation is observed between CH₂ carbon and nearest aromatic proton (³J). thus from 2D NMR spectrum the complete structural elucidation of **6** is done.

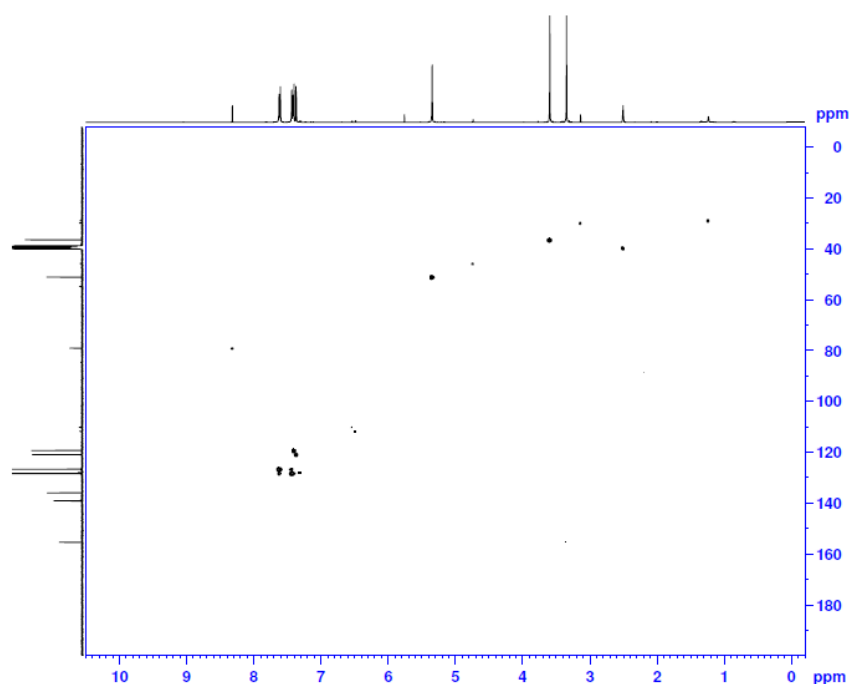


Figure 22: HSQC of compound **6** (400 MHz, DMSO-*d*₆, RT)

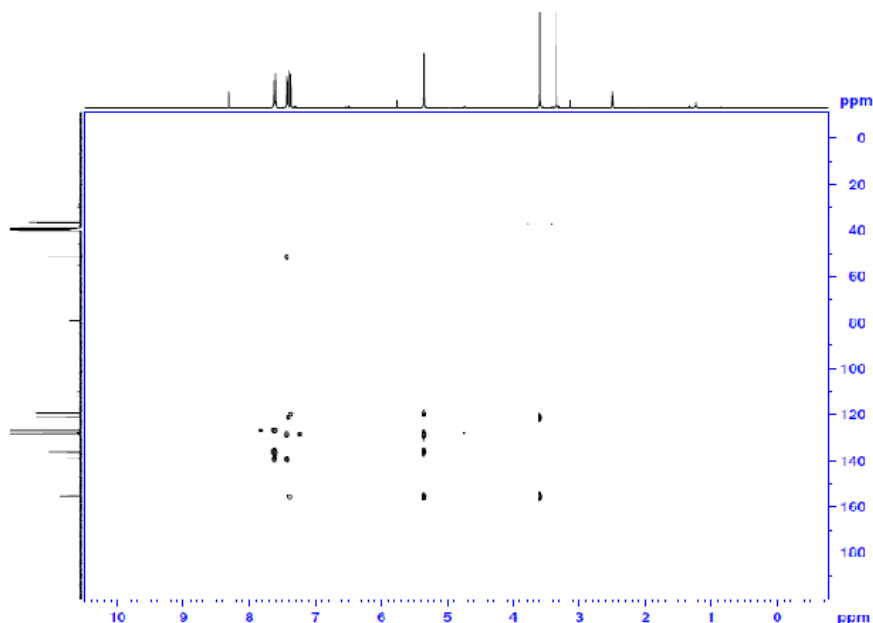


Figure 23: HMBC of compound **6** (400 MHz, DMSO-d₆, RT)

6.4. Single crystal X-ray structure of **6**

The solid state structure of **6** was unambiguously determined by single crystal X-ray diffraction techniques. The structural parameters are listed in table 4. The selected bond distance and bond angles are accumulated in table 5. Molecule **6** was crystallized in monoclinic space group, $P2_1/c$. The structural feature of **6** is discussed in detail. Interestingly the biphenyl rings are in same plane. The [(HCN)₂C(Se)] heterocyclic rings are oriented in the trans position with respect to biphenyl plane. The (Ph)CC(H₂N(Imidazole)) angle is close to 112° (112.96° for **6**). The NC(Se)N angle observed in **3a** (105.7°) is comparable with that of reported selenone, C₁₁H₁₆N₄Se₂ (105.3°).^[5] The C=Se bond length in **6** (1.874 Å) is also comparable with that of C₁₁H₁₆N₄Se₂ (1.842 Å).^[5] Thus, the C=Se bond distance can be described as double bond in nature. The NC (Se) bond distance in **6** are same (1.355 Å and 1.356 Å).

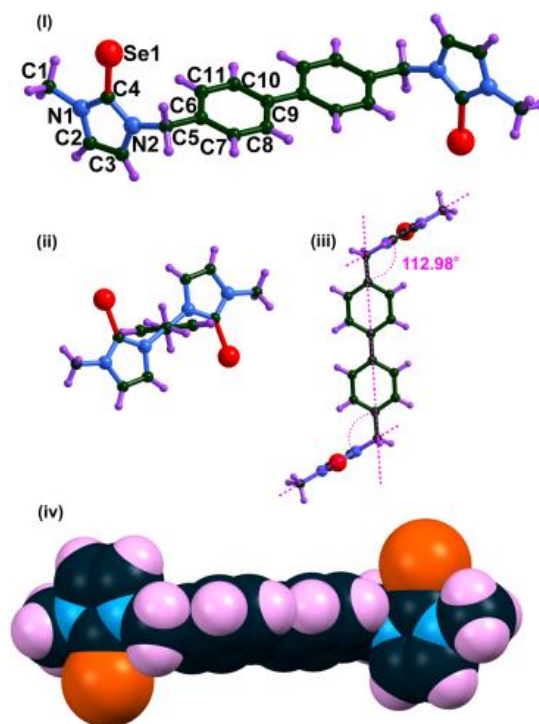


Figure 24. (i) Molecular packing of **6**; (ii) Non-planar orientation of selenone with respect to biphenyl planes; (iii) Trans orientation of selenone with respect to biphenyl planes; (iv) Space filling model of **6**.

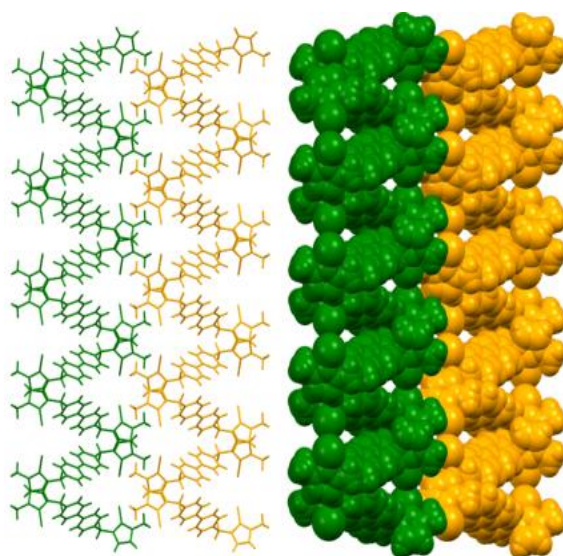


Figure 25. Molecular packing of **6** view along a axis

Table 5. Crystallographic data, details of data collection and structure refinement parameters for **6**

	6
Empirical formula	C ₁₈ H ₂₀ N ₄ SeBr
Formula weight	500.37
Temperature (K)	150.00(10)
Crystal system	Monoclinic
Space group	P21/c
a, Å	13.3310(5)
b, Å	10.0589(3)
c, Å	7.7456(3)
α, °	90
β, °	96.485(3)
γ, °	90
Volume, Å ³	1031.99(6)
Z	2
ρ _{calc} , mg mm ⁻³	1.6101
μ, mm ⁻¹	4.590
F(000)	497.8
Data collected	6.68 to 141.48°
Unique data	
R _{int}	0.0279
GOF on F ²	1.040
R ₁ (I > 2σ(I))	0.0449
wR ₂ (I > 2σ(I))	0.1345

R1 values (all data)	0.0300
wR2 values (all data)	0.0772

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

Bond lengths [\AA]		Bond angles [$^{\circ}$]	
	6		6
C–Se	1.874	N–C(Se)–N	105.7
C(Se)–N	1.355	N–C–C(Ph)	112.96

5.5. UV-vis solid and solution state absorption spectra of **6**

Solution state UV-vis absorption spectrum of **6** was measured in DMSO (Figure 24). The absorption properties of **6** shows an absorption band at 272 nm due to π - π^* transition ($\epsilon = 50552 \text{ L mol}^{-1} \text{ cm}^{-1}$). The solid state UV-vis absorption spectra of **6** is different from that of solution state spectra (Figure 24). In solid state, the strong absorption was observed with bathochromic shift. In solid state the molecules are in compact form leading to more number of transition which in turn leads to the broadness of solid state UV visible peak. In solution state the number of molecule are very less and uniformly distributed in the solution. For this reason the solution state UV peak is much sharper than solid state.

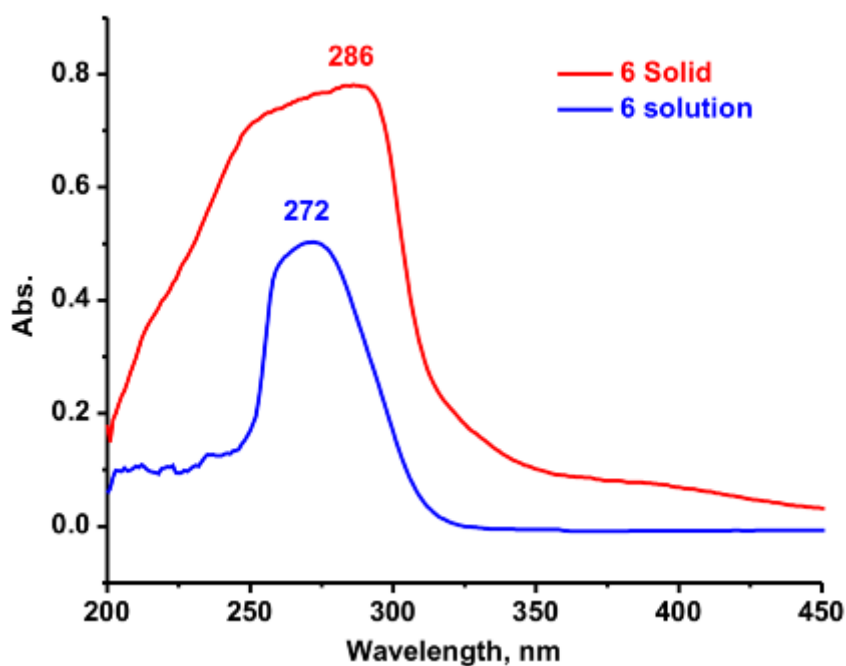


Figure 26: The solution state UV-vis spectra of **6** in DMSO at RT (1.002×10^{-5} M).

Conclusion

The bis-selenium ligands of imidazolium salts were prepared with different types of spacer and characterised thoghoully. The methyl bridged selenium ligand of imidazolium ligand (**3**) was treated with bismuth(III) triflate to obtain the monometallic bismuth selenide in excellent yield. The bismuth compound (**4**) was characterised by multinuclear NMR (^1H , ^{13}C and ^{19}F), UV-vis (solution state), FT-IR and single crystal x-ray diffraction techniques. The thermal stability of **4** was analysed by TGA. In addition, biphenyl spacer was synthesized with the aim of keeping the reactive centres far apart from each other, so that it can accomodate two independent metal centers.

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