Bidentate Selones Supported Bismuth(III) Catalysts for *O*-Acylative Cleavage of Cyclic Ethers

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By

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Declaration

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

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

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This thesis entitled "**Bidentate Selones Supported Bismuth(III) Catalysts for *O*-Acylative Cleavage of Cyclic Ethers**" by *Argha Bhattacharjee* is approved for the degree of Master of Science from IIT Hyderabad.

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I may not be in the place where I am today if a boundless support and encouragement has been sprinkled on me over the years by my family. They are always with me in my every step of life, fighting with me and being amazingly patient and cooperative. My parents have exhilarated me to study and follow whatever I required ever since I was a kid. Their continuous faith and confidence has definitely helped me become better.

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Thanks to all for helping me discover my way.

Argha Bhattacharjee

Dedicated

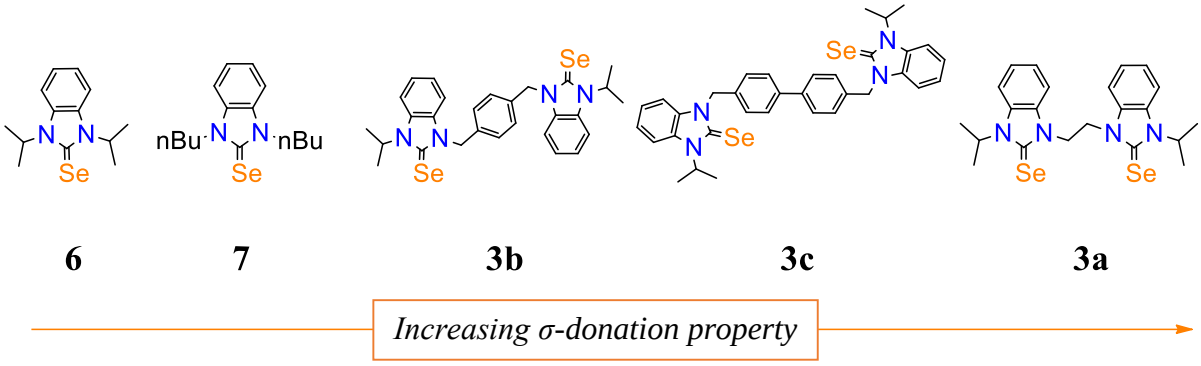
to

My parents

Contents

1. Abstract

An efficient noble methodology, to synthesise a series of novel dibenzimidazole based selone compounds with high yield has been demonstrated here by using NaH route at room temperature. On the basis of experimental data here a method has been adopted for the evaluation of a series of selone compounds by which σ-donor and π-acceptor components of NHC moieties has been investigated.



Moreover, a mild, quantitative, regioselective *O*-acylative cleavage of cyclic ethers was established by in situ generation of bidentate selones supported bismuth(III) catalysts. In particular, with increasing σ-donation property as well as increasing chelation capability of selone ligands towards bismuth(III) activity of catalyst towards O-acylative cleavage of 2-methyl tetrahydrofuran also increases.

2. INTRODUCTION:

Benzimidazoles are the example of class of heterocyclic, aromatic chemical compounds having a fundamental structural characteristic of six-membered Benzene fused to the 4 and 5 positions of five-membered Imidazole (Figure 1). Benzimidazoles are also known as 1,3-benzodiazoles.

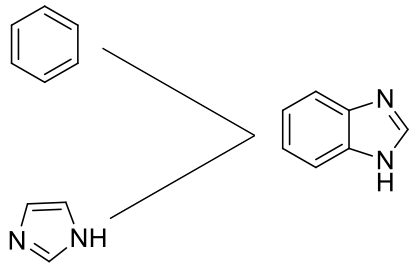
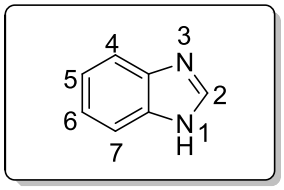


Figure 1: The skeleton of Benzimidazole is the fusion of Benzene ring and Imidazole moiety.

This important group of substances has originate many practical applications in a number of fields. Recently the awareness in benzimidazole chemistry has been re-energized somewhat by the discovery that the 5,6-dimethylbenzimidazole moiety is part of the chemical structure of vitamin B_{12}. Historically, the first benzimidazole was synthesised in 1872 by Hoebrecker who obtained 2,5(or 2, 6)dimethylbenzimidazole by the reduction of 2-nitro-4-methylacetanilide. Several years later Ladenburg obtained the same compound by refluxing 3,4-diaminotoluene with acetic acid.

The numbering of the benzimidazole system is as follows:



Occasionally the 2-position is designated as the μ-position.

Most interestingly, it possess both acidic and basic characteristics. The existent of NH group in a benzimidazole moiety possess relatively strongly acidic and also weakly basic. The capacity of formation of salts from benzimidazoles or benzimidazole derivatives is a significant characteristics of this moiety. Benzimidazoles with unsubstituted NH groups exhibit fast prototropic tautomerism, which leads to equilibrium mixtures of asymmetrically substituted compounds (Figure 2).

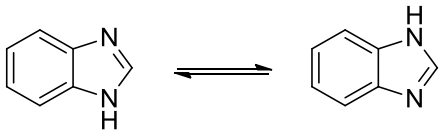


Figure 2: Prototropic tautomerism

Purines are the well-known example of basic '6+5' heterocyclic structure is shared by another class of chemical compounds (Figure 3). Many important biomolecules such as adenine, guanine, uric acid, and caffeine[1] are belongs to this group. For this similarity in fundamental structures, it is believed that benzimidazole containing molecules and benzimidazole derivatives have some biological activity in some small molecules such as vitamin B_{12} and a variety of antimicrobial, antiulcer, antihypertensive, anti-HIV, anti-inflammatory, antioxidant, anxiolytics and even antitumor agents[1-2].

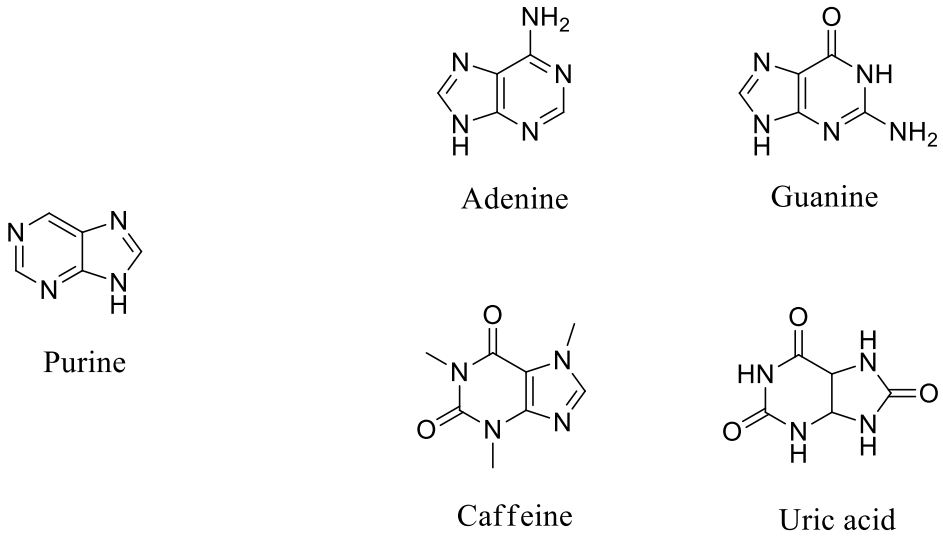


Figure 3: The most important biomolecules belong to the class of Purines having '6+5' heterocyclic structure with benzimidazole.

Benzimidazole having a great importance in biomedical research, it also have a prominent field in organocatalysis, organometallic[3], and materials chemistry[4] because of two reasons stemming from their molecular architecture: 1) an imidazole moiety is a precursor to N-heterocyclic carbenes; 2) the benzene ring offers a convenient skeleton to which additional functionality may be easily added to revise the spatial and electronic characteristics of a benzimidazole derivative. One of the motives for the topical rise in study and use of benzimidazoles and their N-heterocyclic carbene derivatives, is, no doubt, this combination of a reactive carbene centre with a modifiable backbone.

NHCs or N-heterocyclic carbenes are a unique class of the carbene family. The divalent carbon atoms of carbenes with two nonbinding electrons that are covalently bonded to two adjacent groups, are well-known to be extremely reactive species due to their electron deficiency. Typically, in both synthetic organic and organometallic chemistry, these highly reactive species are recognised mostly as important reaction intermediates[5]. But Interest in isolable carbenes extends in the early part of the 1800s. However, surprisingly the first isolable NHC, 1,3-di-1-adamntyl-imidazol-2-ylidene, is obtained by Arduengo et al. in 1991[6]. In 1960s, by several studies on saturated imidazoline rings, Wanzlick first recognised that NHCs would be stable and isolable due to the carbene centre, situated at the 2-position of the imidazole ring, being stabilized by the electron-donating effects of the neighbouring nitrogen atoms(Figure 4)[7].

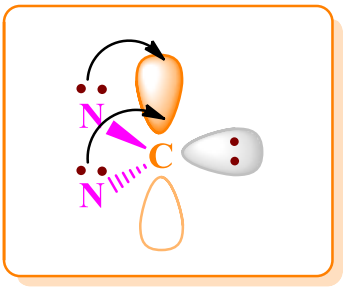


Figure 4: The singlet ground state of NHC, at the 2 position, has a vacant p orbital, into which neighbouring substituents may donate electrons to stabilize the carbene centre.

It is worth mentioning that the stability of such NHC fragments depends on two factors: 1) the steric demand of the substituents on the nitrogen atoms of the heterocyclic ring, which helps to prevent the carbene from dimerising; and, 2) more importantly, electronic factors such as the beneficial overlap of the lone pair on the nitrogen atoms with the empty p orbital of the carbene carbon centre[7].

From the above discussions it can be concluded that NHCs are electron-rich and neutral σ-donor ligands. Compared to phosphine ligands, electron donating ability of NHCs span a very narrow range. But order of electron donating power can be improved by changing the nature of the azole ring: ***benzimidazole<imidazole<imidazoline***.

The great development in NHC chemistry is due to its mainly Chemical stability as well as coordination versatility which is reflected all the introductions of the publications regarding NHCs that have appeared for the past few past decades. NHCs establish a well-known class of ligands for transition-metal complexes that have been progressively applied in homogeneous catalysis, thus surpassing the abundant phosphorus ligands in organometallic chemistry[8]. Not only that, the easy preparation of NHC-precursors has allowed an almost endless access to novel organometallic topologies, in which the only restriction seems to be the imagination of the researchers, i.e. A detailed understanding of the electronic nature of a ligand is essential for the design of a suitable catalyst. Basically, NHCs were initially considered as *pure σ-donors* until some recent literatures, on both theoretical and experimental, has exposed that *π- back-donation* may actually contribute significantly to the metal–carbene bonding and a couple of strongly π-acidic NHCs have been prepared[9].

At first, Bertrand reported Phosphinidene adducts of NHCs with a proper explanation of π-accepting properties of NHCs[10]. Later, Ganter clarified the ^{77}Se resonances of NHC–Se adducts which are also correlate with the π-accepting character of the particular NHC having two analogues canonical structures[11], given below (Figure 5).

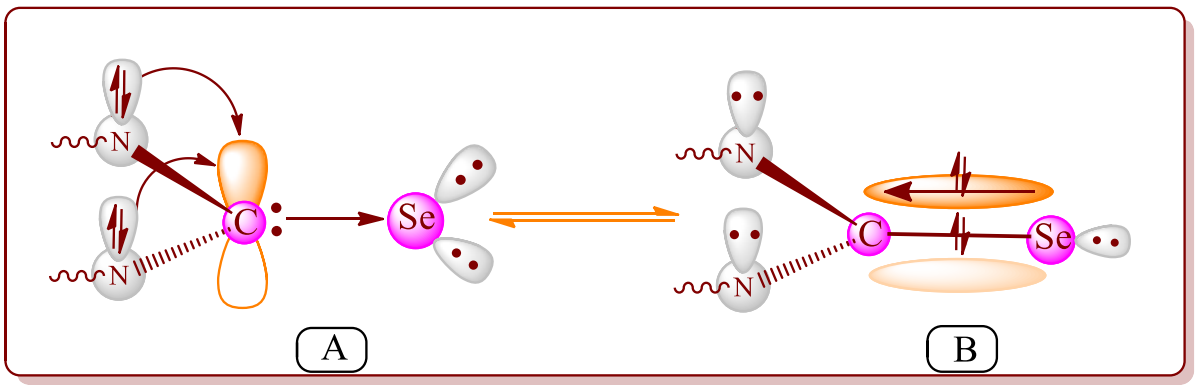


Figure 5: Two canonical structures of Selenium–NHC Adducts: A) having *σ-donating* property of NHC; B) having *π- accepting* property of NHC.

Ganter first demonstrated that increasing π-acceptor character of the NHC leads to a stronger contribution of formula B, shifting the ^{77}Se resonance to lower field. According to our literature survey it is already well-known that ^{77}Se NMR chemical shifts appear over a wide range of 320 ppm[11]. In case of *purely σ-donating* NHCs, selenium atom become highly shielded with a high-field resonance, which leads mainly towards Lewis structure A. In contrast, due to π-acidic nature of NHCs, selenium atom become less shielded which results into a low-field resonance, having a double bond character between carbon and selenium, resembles with Lewis structure B. It is worth to mentioning that, In comparison to the phosphinidene adducts the benefit is that the selenium compounds can be directly obtained in one step by deprotonation of a suitable NHC precursor in the presence of elemental selenium with NaH/CH_3CN at ambient temperature. Anyhow, it is true that the stabilisation of the free carbene under ambient conditions is not an easy task. That's why, preparation of these type of soft ligands form NHCs, which exist only as intermediate species of limited lifetime at low temperature, is very useful to design a suitable catalyst. More interestingly, for selenium−NHC adducts, the σ-donation property as well as π-acidity can be controlled for carbenes by altering the electron-donating substituents and electron withdrawing substituents respectively in nitrogen centre or by changing the cyclic nature of the carbene moiety. The former one, depends upon the interaction of the nitrogen lone pair with the vacant p orbital on the carbene C atom as discussed earlier whereas, latter one deals with conformational flexibility of the carbene system[11]. Here it is worth to mentioning that we prepared a range of poly N-heterocyclic-carbene (NHC)-derived selones, in order to quantify the π-back bonding ability of NHCs.

According to their coordination capabilities of poly-NHC ligands may be classified as bis-NHCs, tris-NHCs, and tetra-NHC. Among the all poly NHC, bis-NHCs are by far the most lavish ones. The easy preparation of this type of ligand has permitted a skilful study of their coordination to metals by revising the length of the aliphatic linker, and some important effects on the structural properties and reactivity of the resultant products have been widely researched. Structural Properties of Coordinated Bis-NHC Ligands are given schematically in figure 6. The common moralities governing the steric properties of NHCs ascend from their fan-shaped profile. When there is some probability of free rotation about the M-C bond, the azole ring is expected to orientate its slim axis to the bulky plane of the complex, minimizing the steric repulsions. Several structural factors have to be taken into account in case of chelating coordination form, such as *the coordination bite angle, the angle between the azole ring and the coordination plane of the complex, and the "in-plane" distortion of the NHC*[12].

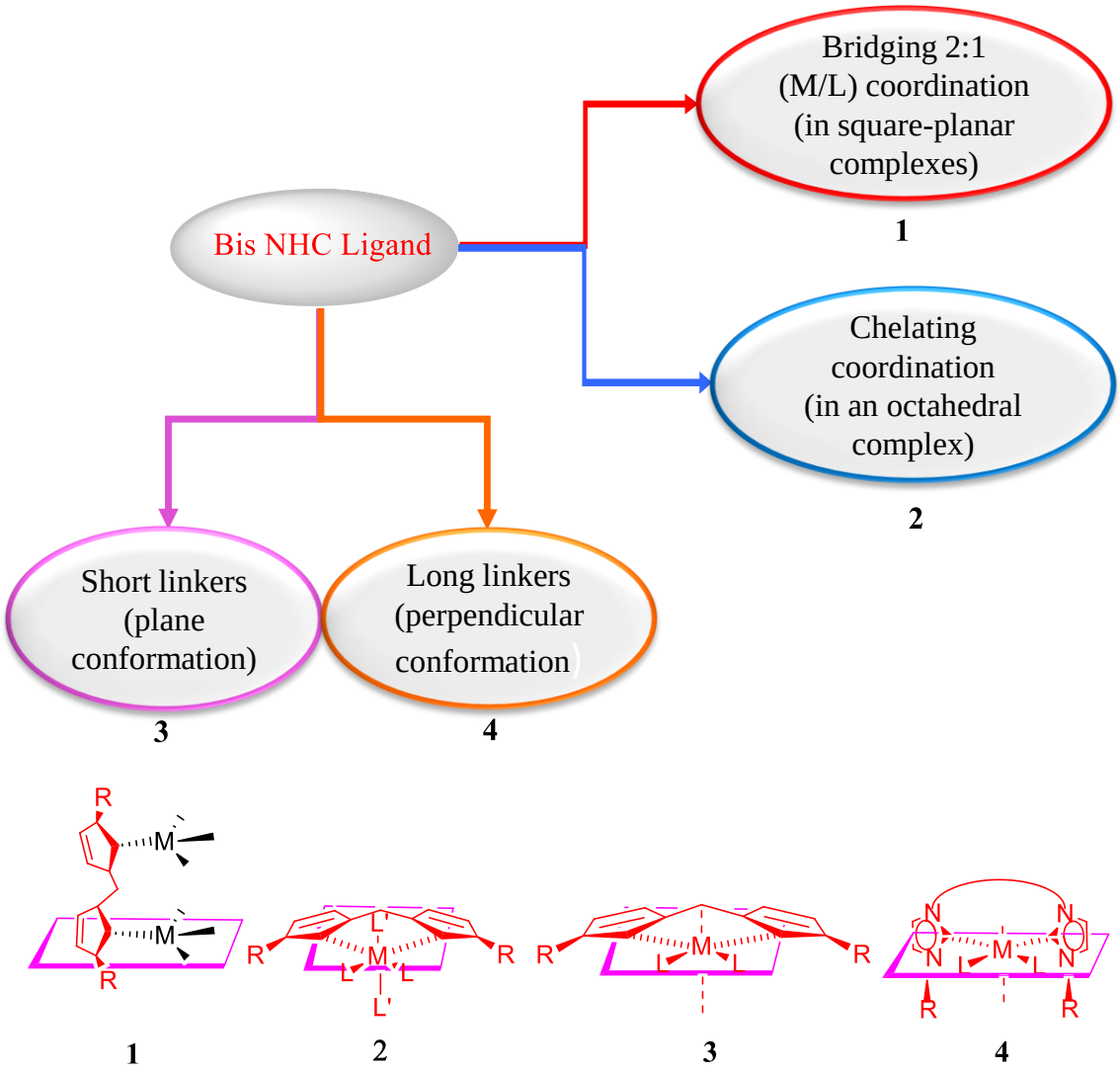
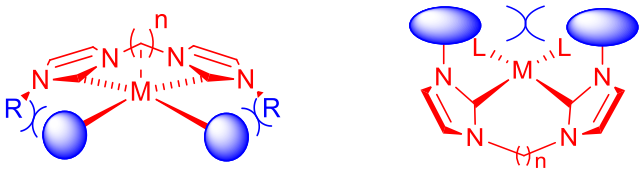


Figure 6: Structural Properties of Coordinated Bis-NHC Ligands[12]

First Crabtree and co-workers has given a more detailed study on Chelating and Bridging Coordination of bis-NHC Ligands such as the steric size of the N-substituents (R) and the nature of the counter ion[13]. In case of small R substituents, the longer linkers support chelation due to their capability to avoid the steric clash between R and the other ligands (L). But for bulkier R groups are used, longer linkers are expected to bring the two bulky substituents too close to each other. So chelation is avoided in principle when long linkers and bulky steric R groups are used, whereas for short linkers and bulky R groups, they can then form chelates. Actually, two steric considerations must be considered to guess the chelation ability of a bis-NHC ligand: (1) the length of the linker between the azole rings and (2) the steric size of the N-substituents (R). The possibility of chelation depends on steric consideration, in principle

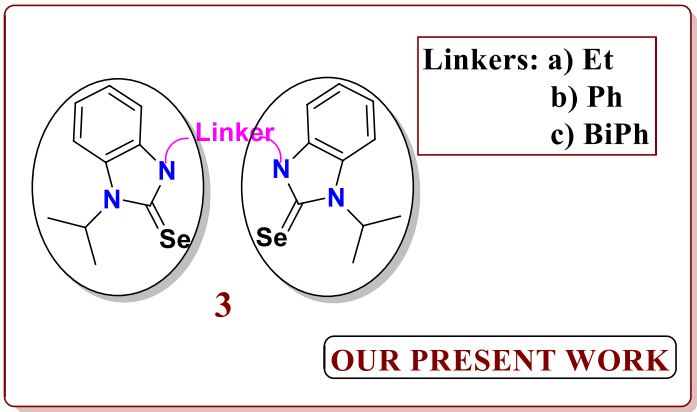
both the steric clash between the R groups and the L ligand (R · · · L), and that between the two R groups (R · · · R) must be avoided[12] (figure 7).



1 **2**

Figure 7: 1) Wingtip-ligand (R · · · L) 2) wingtip-wingtip (R · · · R) steric interactions.

It is worth to mentioning that for our present work we have chosen our ligand in such way that contains from short linkers with some flexibility to large linkers with a high a rigidity. Our actual motivation is to synthesise bidendate selones having benzimidazole moiety for first time and to investigate *O*-acylative cleavage of cyclic ethers by bidendate selones supported bismuth (III) catalysts.[14] It is known that cyclic ethers undergo cleavage in the presence Lewis acids to give 4-halobutanes. But the actual problem to choose a perfect Lewis acid to afford regioselectivity for that type of acylative cleavage. Not only that sometimes it needs long periods of heating for reaction to complete and sometimes Lewis acids are air sensitive, environmentally toxic or expensive which are an additional drawbacks for that reaction. Here we describe a mild a mild and regioselective catalytic applications for the acylative cleavage of cyclic ethers by in-situ generation of bismuth mediated catalyst using 3a-3c ligand. As we know there are very few examples of the coordination chemistry of main group metalthiones, selones and tellones known in the literature. Especially, the heavy main group p-block atoms have a known propensity to form supramolecular or polynuclear aggregates with or without metal···metal interactions[15]. Basically a normal concept says that, a heavier metal centre with high charge can be stabilised by a ligand with a high σ-donating property. Bismuth (III) is belongs to heavier main group metal having +3 charge and as our work is on selone, it is worth to mentioning that selone ligands have a pure σ-donation property basically.



3. Experimental Section:

3.1. General consideration:

All manipulations were carried out under nitrogen using Schlenk vacuum line techniques. The solvents were purchased from commercial sources and purified according to standard procedures. N-isopropylbenzimidazole was prepared as previously reported in literature[16]. Starting materials were purchased from commercial sources and used without further purification. FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV−Vis spectra were measured on a T90+ UV-Visble spectrophotometer. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF. NMR spectra were recorded on Bruker Ultrashield-400 MHz spectrometers at 25ºC unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. Thermo gravimetric analysis (TGA) was performed using a TASDT Q600, Tzero-press. Elemental analyses were performed by the Euro EA-300 elemental analyzer.

3.2. Synthesis of dibenzimidazolium salts:

3.2a. Synthesis for 1,1'-diisopropyl-3,3'-ethylenedibenzimidazolium dibromide:

To a stirred solution of the N-isopropylbenzimidazole (20 mmol, 2 eq) in 5 mL of acetonitrile dibromoethane (10 mmol, 1 eq) was added drop wise under inert atmosphere, then the reaction mixture was stirred at 90ºC for 2 days. The solution was filtered off, and the precipitate was washed with 2x5 mL of THF and dried high vacuum to yield a white powder.

White solid. Yield 83% (based on 1). M.P., 284-286ºC. FT-IR (neat, $\bar{\upsilon}$): 3127 (w), 3065 (w), 3016 (w), 2968 (w), 1607 (w), 1556 (m), 1435 (m), 1209 (m), 1097 (w), 837 (m), 751 (s) cm^{-1}. ^{1}H NMR (D_2O, 400 MHz): δ 9.39 (s, 2H, Benzim-H), 7.80-7.78 (d, 2H, Ar-H), 7.54-7.50 (t, 2H, Ar-H), 7.40-7.36 (t, 2H, Ar-H), 7.13-7.11 (d, 2H, Ar-H), 5.07 (m, 6H, ^{i}Pr-CH & Et-H), 1.44-1.43 (d, 12H, CH_3) ppm. ^{13}C NMR (D_2O, 100 MHz): δ 139.45 (Benzim-C), 131.14, 130.49, 127.68, 127.36, 114.07, 111.23 (Ar-C), 51.51 (^{i}Pr-C), 46.37 (Et-C), 21.01 (Me-C) ppm.

3.2b. Synthesis for 3,3'-(1,4-phenylenebis(methylene))bis(1-isopropylbenzimidazolium) dichloride:

To a stirred solution of the N-isopropylbenzimidazole (20 mmol, 2 eq) in 5 mL of acetonitrile α,α'-Dichloro-p-xylene (10 mmol, 1 eq) was added under inert atmosphere, then the reaction mixture was stirred at 90^{o}C for 2 days. The solvent was removed under vacuum, and the residue was washed with n-hexane and THF (2x5 ml), dried under high vacuum for several hours to yield a white powder.

White solid. Yield 76% (based on 1). M.P., 284-286oC. FT-IR (neat, ῡ): 3415 (m), 3115 (w), 3018 (w), 2977 (w), 1612 (w), 1555 (m), 1433 (m), 1266 (w), 1196 (m), 754 (s) cm^{-1}. ^{1}H NMR (D_2O, 400 MHz): δ 9.39 (s, 2H, Benzim-H), 7.62-7.60 (d, 2H, Ar-H), 7.46-7.28 (t, 6H, Ar-H), 7.24-7.22 (q, 2H, Ar-H), 5.58 (m, 6H, ^{i}Pr-CH & Benzyl-H), 1.51-1.49 (d, 12H, CH_3) ppm. ^{13}C NMR (D_2O, 100 MHz): δ 139.09 (Benzim-C), 134.28, 131.11, 130.93, 128.88, 126.78, 126.57, 113.54, 113.32 (Ar-C), 51.24 (^{i}Pr-C), 50.13 (Benzyl-C), 21.01 (Me-C) ppm.

3.2c. Synthesis for 3,3'-([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(1-isopropylbenzimidazolium) dichloride:

To a stirred solution of the N-isopropylbenzimidazole (20 mmol, 2 eq) in 5 mL of acetonitrile 4,4'-bis(chloromethyl)-1,1'-biphenyl (10 mmol, 1 eq) was added under inert atmosphere, then the reaction mixture was stirred at 90^{o}C for 2 days. The solvent was removed under vacuum, and the residue was washed with n-hexane and THF (2x5 ml), dried under high vacuum for several hours to yield a white powder.

White solid. Yield 81% (based on 1). M.P., 294-296^{o}C. FT-IR (neat, ῡ): 3018 (w), 2873 (w), 2762 (w), 1611 (w), 1555 (m), 1438 (m), 1267 (w), 1227 (w), 1093 (w), 1004 (w), 796 (m), 765 (s) cm^{-1}. ^{1}H NMR (D_2O, 400 MHz): δ 9.42 (s, 2H, Benzim-H), 7.67-7.65 (d, 4H, Ar-H), 7.38-7.24 (m, 16H, Ar-H), 5.43 (s, 4H, Benzyl-H), 1.53-1.51 (d, 12H, CH_3) ppm. ^{13}C NMR (D_2O, 100 MHz): δ 139.09 (Benzim-C), 134.28, 131.11, 130.93, 128.88, 126.78, 126.57, 113.54, 113.32 (Ar-C), 51.24 (^{i}Pr-C), 50.13 (Benzyl-C), 21.01 (Me-C) ppm.

3.3. General procedure for synthesis of bis(benzimidazoline-2-selone) derivatives:

NaH (3 eq) was dissolved in dry acetonitrile (5 mL) in an oven-dried Schlenk tube, under inert atmosphere and dibenzimidazolium Salts (1 eq), followed by Selenium (3 eq) was added slowly maintaining a complete inert atmosphere. The reaction mixture was stirred overnight at room temperature. The solution was removed under vacuum, the residue was quenched in water (50 mL), extracted with dichloromethane, dried over sodium sulphate and evaporated. The residue was washed with n-hexane and methanol (2-3 drops), dried under high vacuum for several hours to yield an analytically pure form of product.

3.3a. 1,1'-diisopropyl-3,3'-ethylenebis(benzimidazoline-2-selone):

Brown solid. Yield 82% (based on 2a). M.P., 252-254^{o}C. FT-IR (neat, $\bar{\upsilon}$): 3207 (w), 2971 (w), 2931 (w), 2185 (w), 1601 (w), 1439 (w), 1402 (m), 1329 (s), 1292 (w), 1249 (w), 1084 (w), 793 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.41 (q, 2H, Ar-H), 7.29-7.27 (m, 2H, Ar-H), 7.04-7.01 (m, 4H, Ar-H), 5.87-5.80 (q, 2H, ^{i}Pr-CH), 4.97 (s, 4H, Et-H), 1.57-1.55 (d, 12H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.72 (C=Se), 133.91, 130.62, 123.07, 122.72, 110.79, 109.92 (Ar-C), 51.52 (^{i}Pr-C), 43.93 (Et-C), 19.99 (Me-C) ppm.

3.3b. 3,3'-(1,4-phenylenebis(methylene))bis(1-isopropylbenzoimidazole-2-selenone):

Off white solid. Yield 85% (based on 2b). M.P., 264-266^{o}C. FT-IR (neat, $\bar{\upsilon}$): 3022 (w), 2969 (w), 2928 (w), 1604 (w), 1513 (s), 1477 (m), 1406 (s), 1380 (s), 1337 (s), 1299 (m) 1257 (m), 1088 (m), 787 (w), 748 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51-7.49 (d, 2H, Ar-H), 7.31-7.26 (t, 4H, Ar-H), 7.20-7.15 (m, 2H, Ar-H), 7.13-7.08 (m, 4H, Ar-H), 5.94-85 (q, 2H, ^{i}Pr-CH), 5.68 (s, 4H, Benzyl-H), 1.63-1.61 (d, 12H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.60 (C=Se), 135.07, 133.30, 131.44, 127.87, 123.11, 122.96, 111.29, 110.52 (Ar-C), 52.10 (^{i}Pr-C), 50.06 (Benzyl-C), 20.11 (Me-C) ppm.

3.3c. 3,3'-([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(1-isopropylbenzimidazole-2-selone):

Brown solid. Yield 80% (based on 2c). M.P., 280-282^{o}C. FT-IR (neat, $\bar{\upsilon}$): 2973 (w), 2929 (w), 1699 (w), 1606 (w), 1476 (w), 1399 (m), 1334 (m), 1296 (m), 1256 (m), 1086 (w), 787 (w), 745 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53-7.39 (m, 10H, Ar-H), 7.26-7.13 (m, 6H, Ar-H), 5.97-5.90 (q, 2H, ^{i}Pr-H), 5.77 (s, 4H, Benzyl-H), 1.65-1.63 (d, 12H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.61 (C=Se), 140.18, 134.57, 133.61, 131.49, 128.00, 127.47, 127.42, 123.32, 122.98, 111.35, 1110.56 (Ar-C), 52.14 (^{i}Pr-C), 50.22 (Benzyl-C), 20.16 (Me-C) ppm.

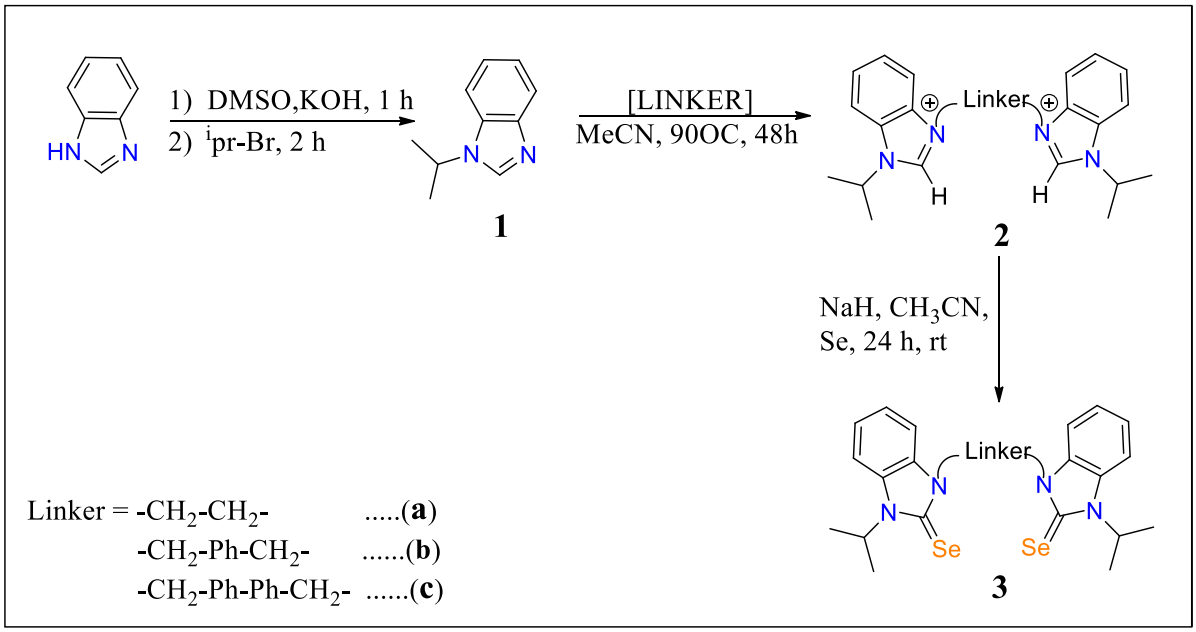
3.4. Catalyzed *O*-acylative cleavage of cyclic ethers (Table 1, Entry 1-5):

Under very mild conditions the catalytic reactions were performed using acetyl chlorides in dichloromethane, to which 2-MTHF was added after few minutes. Then ligand (1-3) (1.5 mol %), followed by $BiCl_3$ was added and kept under stirring at room temperature for 2hr. The reaction progress was monitored by TLC. After the completion of reaction, water (30 mL) was added to the reaction mixture which affords a suspension. It was extracted by chloroform (3 x 25 mL). These combined extracts were dried (Na_2SO_4) and concentrated under vacuum to produce an oily liquids. The vanishing of the starting materials and appearance of products were conveniently analysed by ^{1}H NMR spectroscopy.

4. Results and Discussions:

4.1. Synthesis and characterization of 2-3:

N-isopropylbenzimidazole is prepared in a conventional method as reported earlier from benzimidazole[16] using 2-Bromopropane in presence of potassium hydroxide as a base with DMSO a solvent. Isopropylbenzimidazole was distilled at 106°C at high vacuum to yield a colourless oil. Instead of a conventional route[17], for the preparation of dibenzimidazole salts (2a-2c) first time here a straight forward methodology has been used where acetonitrile used as solvent at 80°C for two days which afford white precipitates (scheme 1). The precipitates are washed with THF as well as hexane and diethyl ether to remove the starting material which is actually more non polar in nature than product one, to obtain analytical pure compounds with 83%, 76%, 81% yield respectively. An attempt to synthesize 3a by mixing with selenium powder with 2a in presence of potassium carbonate in methanol[14b] was failed. Therefore, 2a was treated with selenium in the presence of NaH in acetonitrile at room temperature over a period of one day to result 3a in fairly good yields (82%) (Scheme 1). Here, an efficient methodology has been established for first time to synthesise a selone compounds having benzimidazole moiety which affords high yields for every compounds (3b-85%, 3c-80%). The formation of selone compounds were confirmed by ^{1}H and ^{13}C NMR.

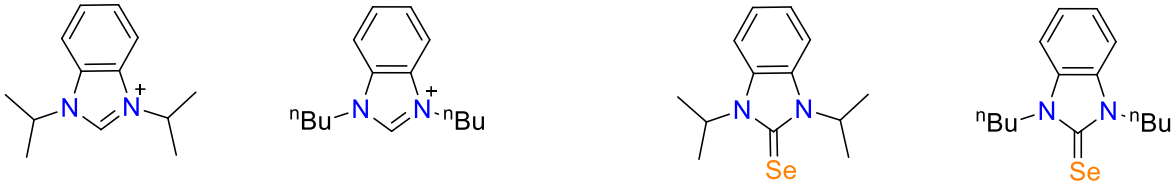


Scheme 1: Synthesis of 3

Initially for dibenzimidazole salt 3a, most desheilded C-H peak has been appeared at δ=9.39, whereas that peak is missing for selone compound in ^{1}H NMR which approves the formation of carbene. In ^{13}C NMR also the most desheilded peak is appeared at δ=139.45 for dibenzimidazole salt 3a, whereas for dibenzimidazole-selone the most desheilded peak has been shifted by about 25 ppm downfield compared to chemical shift value of the salt one, which confirms the C=Se bond in 3a compound. Basically according to our general concept we can conclude that, as the pure σ-donation property of carbene carbon increases, amount desheilding for carbene carbon also increases compared to salt one. In figure 5, Lewis structure A describes the pure σ-donation property of carbene toward selenium and Lewis structure B describes the π-acceptance property of carbene from selenium. Usually in case of N-heterocyclic-carbene, nitrogen having one lone pair, attached to carbene carbon, is liable to donate its lone pair towards the vacant p-orbital of the carbene carbon which the main driving force to stabilise a single state carbene in its ground state. So as long as a carbene is in singlet state by stabilisation through the adjacent nitrogen atom lone pair, it is likely to show mainly pure σ-donation property rather than π-acceptance property which leads to more downfield shift of carbene carbon attached to selenium. In our case we investigate the amount of desheilding to give a detail description about the pure σ-donation property our ligand through ^{13}C NMR.

Table 1: Amount of desheilding:

Entry	Compound	^{13}C-NMR Peak (in ppm)	Compound	^{13}C-NMR Peak (in ppm)	Amount of desheilding (in ppm)
1	**4**	133.65	**6**	164.90	31.25
2	**5**	136.47	**7**	165.37	28.90
3	**2a**	139.45	**3a**	164.72	25.27
4	**2b**	139.09	**3b**	166.60	27.51
5	**2c**	139.87	**3c**	166.61	26.74



4 **5** **6** **7**

As compound 4, 5, 6 and 7 are reported in literature already[11, 18], these four has taken as a reference to investigate the amount of desheilding with respect to our selone compounds. Amount of desheilding is measured by the amount of downfield shift of C=Se peak in ^{13}C NMR for dibenzimidazole selone compared to C-H peak in 13C NMR for benzimidazolium salt.

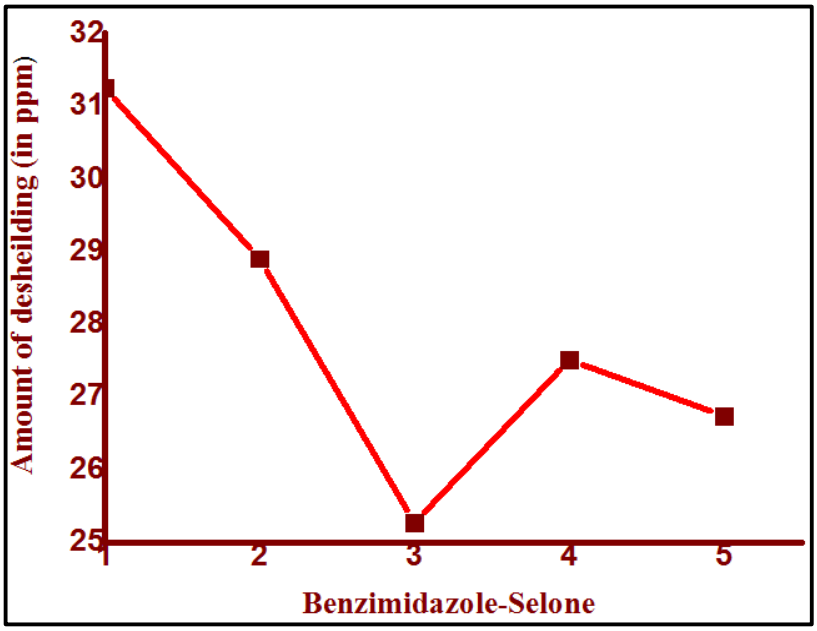


Figure 8: Amount of desheilding with respect to selone compounds

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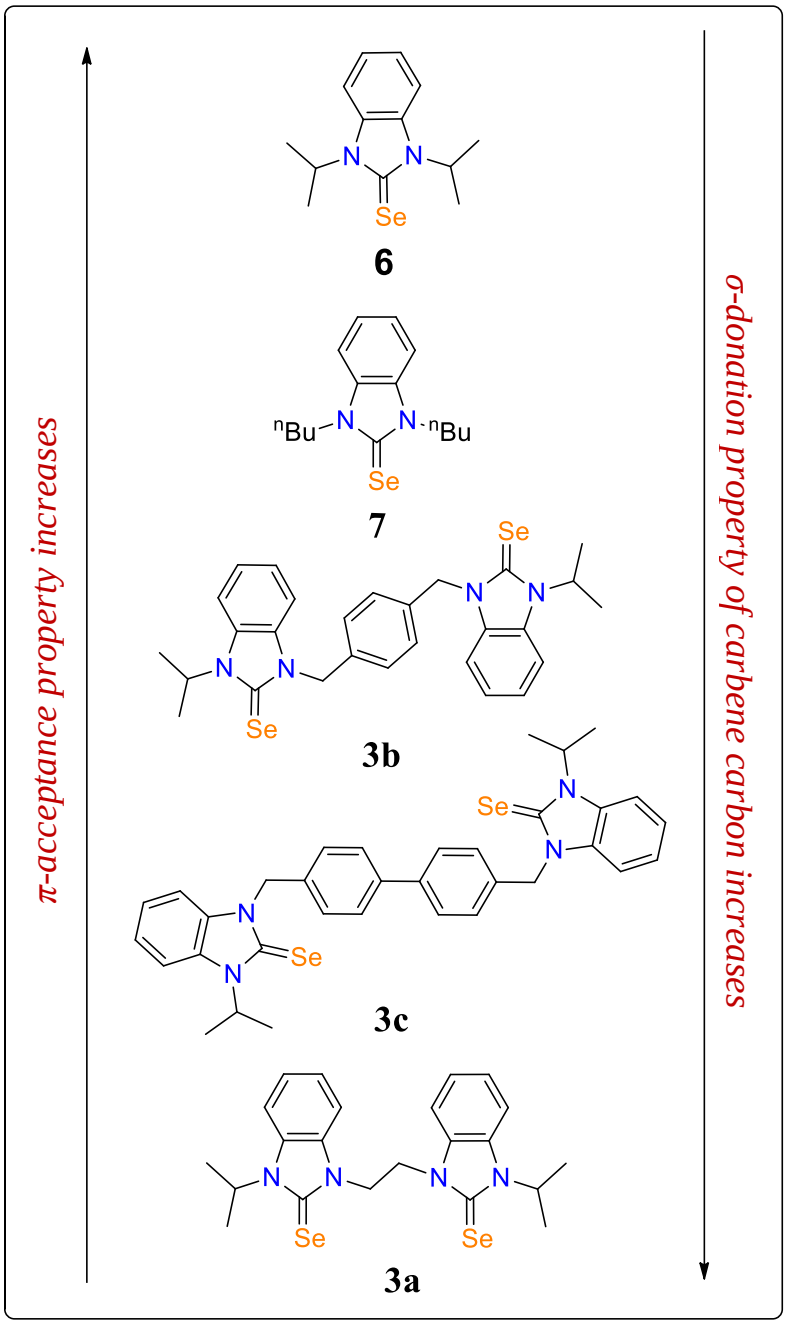
In figure 8, it is cleared that the amount of desheilding is less for ethyl bridged dibenzimidazole salt whereas for entry 1 in table 1 more amount of desheilding is observed for selone compound compared to benzimidazole salt. So it is obvious that as the +I effect of N-substituent of benzimidazole increases, form isopropyl to n-butyl, amount of desheilding is decreasing and it is worth to mentioning the amount desheilding is more in case of ethyl bridge N-isopropyl-dibenzimidazole selone due to influence of another benzimidazole moiety.

For dibenzimidazole selone complexes entry 3 is also exhibit less amount of desheilding rather than entry 5 and 6. Due to –I effect of phenyl linkages the phenyl bridged and biphenyl bridged dibenzimidazole salt exhibit more amount of desheilding compared to entry 3. As a conclusion it can predict that as carbene carbon resides in more upfield region, i.e., for an electron rich carbene carbon σ-donation property will be more towards selenium atom. This σ-donation property can be regulate by altering the N-substituents adjacent to the carbene atom. It is already discussed that with increasing σ-donation property of ligand, stabilisation of heavier main group metals should be easier.



4.2. TGA analysis:

In order to understand the thermal decomposition pathway of 3a-3c, thermogravimetric analysis (TGA) (10 °C min−1, 30-1000°C, under N_2 atmosphere) was carried out on 3a-3c (Figure 9). 3b show enough stability up to 300°C, and 3c is also thermally stable up to 280°C and then shows loss of weight up to about 98% in three steps. But, Compared to 3b and 3c, 3a is less air stable selone compound decomposes only at about 110°C.

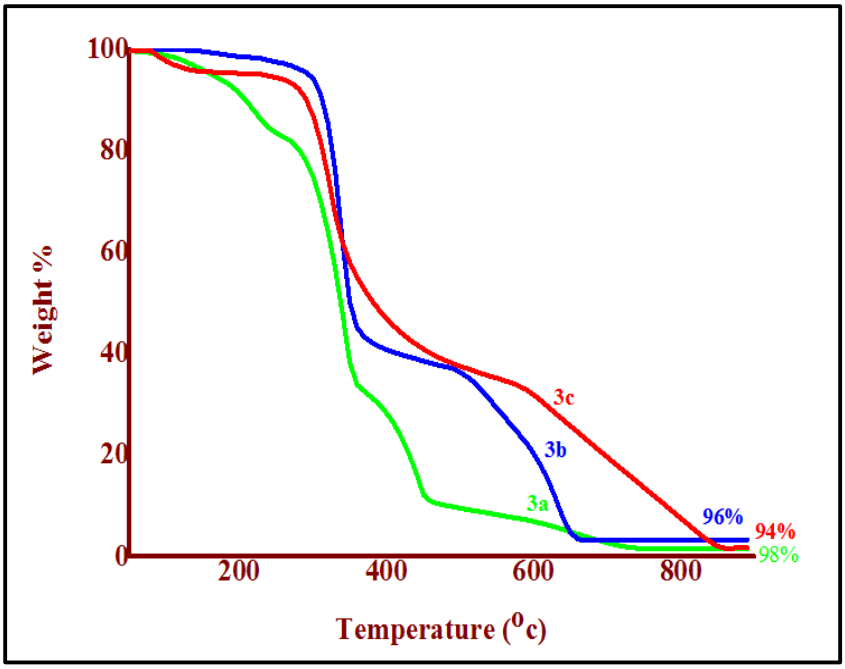


Figure 9: TGA curves for 3a-3c 10 °C min^{-1} under N_2 atmosphere

4.3. UV-visible absorption study:

Solid state UV-visible absorption spectra of 2a-2c is measured at room temperature and displayed a bathochromic shift from 2a (270 nm), 2b (272 nm) to 2c (277 nm) (figure 10).

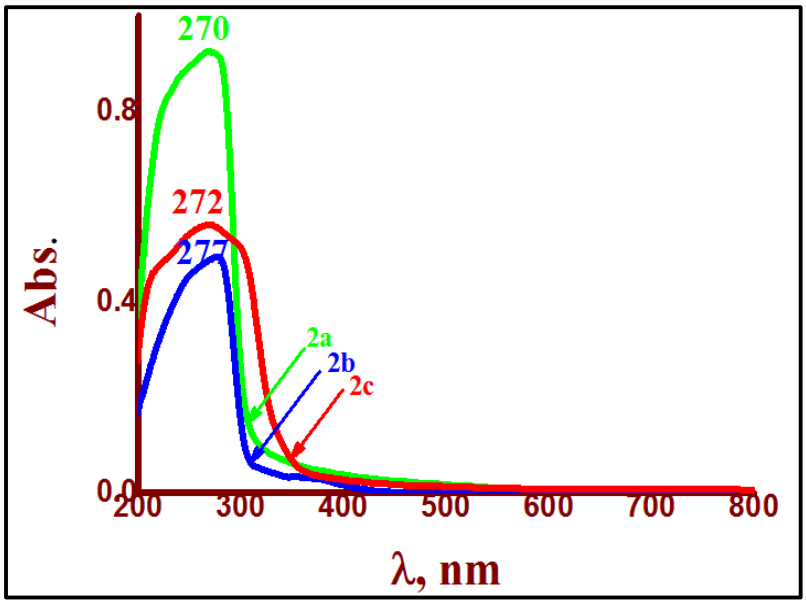


Figure 10: Dibenzimidazole salts: Solid state UV

These are characteristics of aromatic structures of benzimidazole moiety. Due to substituent effect these type of transition shifts the UV-visible absorption spectra towards higher wavelength region, i.e., bathochromic shifts is observed. In the solid state UV-visible spectra of 3a-3c are nearly comparable with solution state absorption spectra. Thus, the molecular association and stability of 3a-3c are comparable. In solid state UV-visible absorption spectra 1st transition for 3a-3c is observed at 250 nm, 246 nm and 242 nm respectively (figure 11).

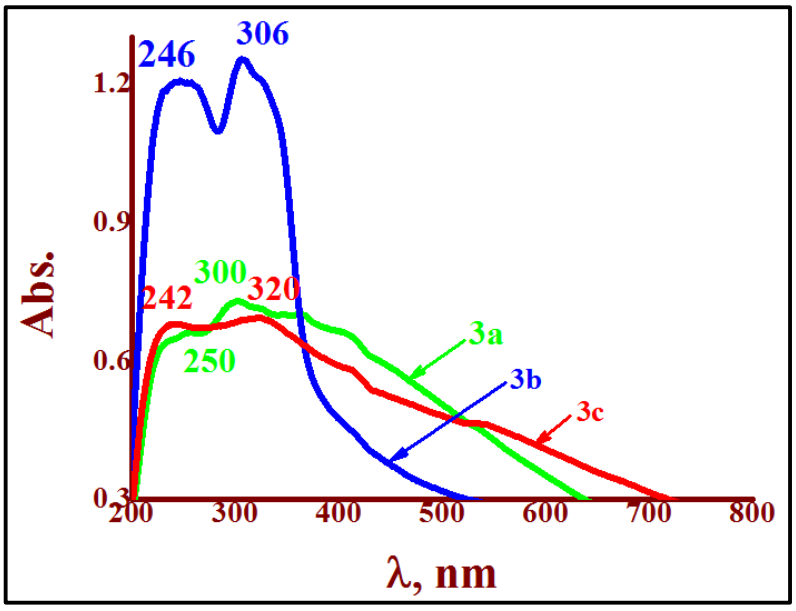


Figure 11: Dibenzimidazole Selone: Solid state UV

These are characteristics of aromatic structures of dibenzimidazole-selone moiety. The additional absorption is observed for dibenzimidazole selones (3a-3c) at 300 nm, 306 nm and 320 nm respectively. This additional absorption for 3a-3c can be attributed to the benzimidazole carbene carbon to selenium charge transfer. The pattern of solution state UV-visible absorption spectra for dibenzimidazole selone derivatives is mostly similar to the solid state UV-visible absorption having a double humped nature in both cases. But a bathochromic shift is observed for 2nd transition for solution UV-spectra compared to solvent UV-spectra, whereas a hypsochromic shift is observed for 1st transition (expect 3c) for solution UV-spectra. The solution state absorption spectra is observed for 3a at 320 nm, 3b at 325 nm and 3c at 327 nm can be attributed to the benzimidazole carbene carbon to selenium charge transfer (Figure 12).

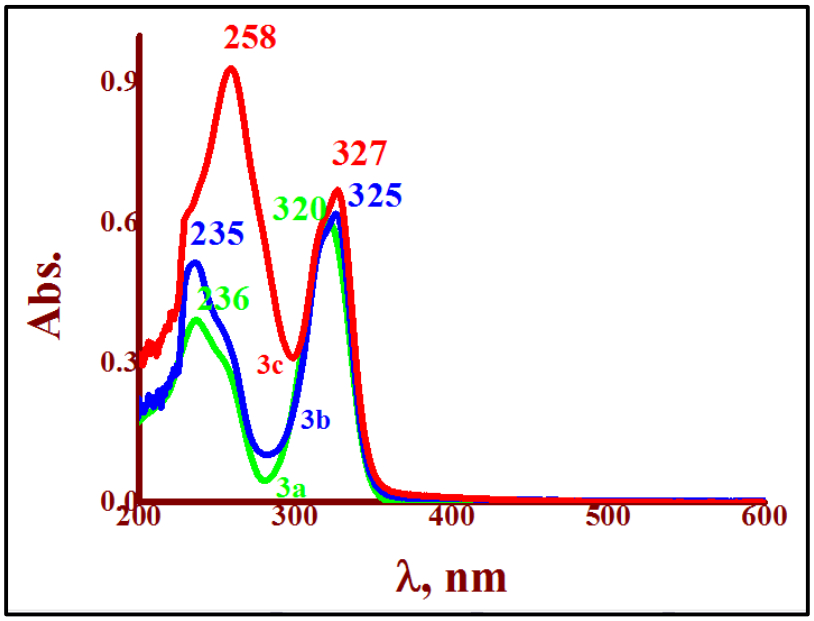
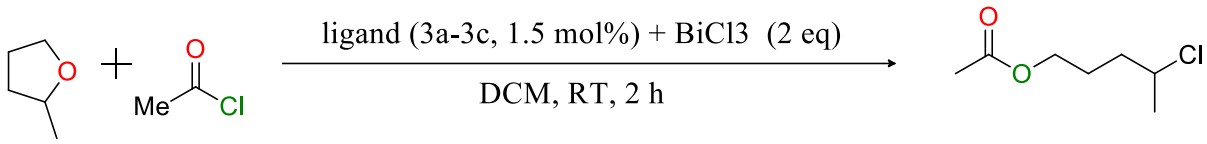


Figure 12: Solution state UV-visible spectra of dibenzimidazole selone in DCM at 25^{o}C (2.5 X 10^{-2} M)

4.4. Bismuth(III) catalyzed *O*-acylative cleavage of cyclic ethers:

We already established a mild and regioselective catalytic applications for the *O*-acylative cleavage of cyclic ethers using monodentate selone supported bismuth(III) catalyst[14b]. Our present work is to create the same catalyst applications using bidentate selone supported bismuth(III) catalyst (scheme 2). Our main motivation for that work is establish a mild as well as regioselective *O*-acylative cleavage using a catalyst in such a way that needs low catalyst loadings.



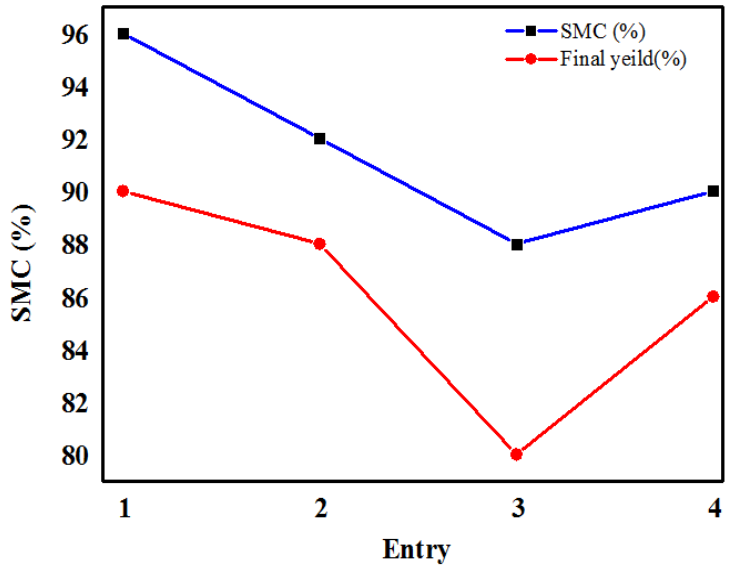
Scheme 2: 4-Chloropentylacetate from acylative cleavage of 2-methyl tetrahydrofuran.

The selective *O*-acylative cleavage and successive intramolecular trapping of cations generated from cyclic ethers using bismuth(III) halides as catalyst shows much potential in organic synthesis[14a]. Despite the popularity and versatility of metal mediated C–O bond cleavages of cyclic ethers like THF/2-MTHF/THP to deliver 4-haloalkyl alkanoates, there are very limited examples of bismuth mediated C–O bond cleavage reactions known in the literature[19]. Here we have demonstrated a regioselective *O*-acylative cleavage of cyclic ethers, by in-situ generation of bismuth(III) mediated catalyst using 3a-3c ligand. The reaction progress was frequently monitored using TLC (Table 2). After completion of the reaction, the routine workup gave 4-Chloropentylacetate in excellent yield (Table 2, Entries 1-14, Yield 80-90%). Besides, the catalytic performance of $BiCl_3$ with entry 4 has given below to demonstrate the efficiency of ligand 3a for the *O*-acylative cleavage of cyclic ether.

Table 2: 4-Chloropentylacetate from acylative cleavage of 2-methyl tetrahydrofuran.

Entry	Ligand	Metal halide	Time (h)	SMC (%)	Yield (%)[a]
1	**3a**	$BiCl_3$	**2**	96	90
2	**3b**	$BiCl_3$	**2**	92	88
3	**3c**	$BiCl_3$	**2**	88	80
4	-	$BiCl_3$	**4**	90	86
5	-	-	**4**	0	0

[a] %Yields were calculated based on the weight of products and the starting material conversion.



As expected, the catalytic efficiency of 1-4 can be recognised to their solubility and electronic nature and generation of an efficient catalyst in-situ. Among entries 1-4, entry 1 depicted 96% conversion (Table 2) in the least time (2h) with outstanding yield although with low loadings of ligands compared to previously reported catalysts[14b]. While entry 3 showed less starting material conversion (88%) and lower yield (80%) in 2h. So, it should be concluded that the conversion of starting materials decreases from 3a to 3c due the due to decreasing stability of NHC=Se-Bi metal. It is worth to mentioning that stability of a bidentate ligand metal complexes is depends on chelation capability of ligands along with electronic nature of that ligands.

5. Conclusion:

In summary, here we have established an efficient methodology for first time to synthesise a selone compounds with high yields. A series of dibenzimidazole salts has prepared by a straight forward route as well as dibenzimidazole based selone compounds has been synthesised for the first time by NaH route at room temperature. A combined spectroscopic study like ^{1}H NMR, ^{13}C NMR, FT-IR, UV-Visible absorption spectroscopy has been done for the recognition of the structures of the 3a-3c selone compounds. By a clear investigation of ^{13}C NMR of selone compounds it is observed that among the three ligands, ethyl bridged dibenzimidazole selone compound exhibits least amount of desheilding which affords most σ-donation property among the three bidentate selone compounds. It is true that the stabilisation of the free carbene under ambient conditions is not an easy task. That's why, preparation of these type of soft ligands form NHCs, which exist only as intermediate species of limited lifetime at low temperature, is very useful to design a suitable catalyst and to design a suitable catalyst a detailed understanding of the electronic nature of a ligand is crucial. Here a method has been adopted for the evaluation of a series of selone compounds by which σ-donor and π-acceptor components of NHC moieties has been separated on the basis of experimental data. The efficient catalytic property of the bismuth(III) supported by bidentate Selone ligands were verified in the regioselective *O*-acylative cleavage of cyclic ethers like 2-methyl tetrahydrofuran. From above catalytic work it can be predicated that as a consequence of increasing σ-donation property as well as increasing chelation capability of selone ligands the efficiency of catalyst is also increased. Synthesis and isolation of well-defined benzimidazole based bidentate selone based bismuth catalyst is currently an on-going tasks in our laboratories and this will successively be extended for the preparation of other bidentate ligands having excellent chelation capabilities.

6. References

1. Kamal, A.; Praveen Kumar, P.; Sreekanth, K.; Seshadri, B. N.; Ramulu, P., Synthesis of new benzimidazole linked pyrrolo[2,1-c][1,4]benzodiazepine conjugates with efficient DNA-binding affinity and potent cytotoxicity. *Bioorganic & Medicinal Chemistry Letters* **2008,** *18* (8), 2594-2598.

2. (a) Graf-Christophe, S.; Kuehm-Caubère, C.; Renard, P.; Pfeiffer, B.; Pierré, A.; Léonce, S.; Caubère, P., Synthesis and antiproliferative activity of Benzocyclobutacarbazol derivatives. A new class of potential antitumor agents. *Bioorganic & Medicinal Chemistry Letters* **2000,** *10* (23), 2589-2591; (b) Güven, Ö. Ö.; Erdoğan, T.; Göker, H.; Yıldız, S., Synthesis and antimicrobial activity of some novel phenyl and benzimidazole substituted benzyl ethers. *Bioorganic & Medicinal Chemistry Letters* **2007,** *17* (8), 2233-2236; (c) Nobilis, M.; Jira, T.; Lísa, M.; Holčapek, M.; Szotáková, B.; Lamka, J.; Skálová, L., Achiral and chiral high-performance liquid chromatographic determination of flubendazole and its metabolites in biomatrices using UV photodiode-array and mass spectrometric detection. *Journal of Chromatography A* **2007,** *1149* (1), 112-120; (d) Denny, W. A.; Rewcastle, G. W.; Baguley, B. C., Potential antitumor agents. 59. Structure-activity relationships for 2-phenylbenzimidazole-4-carboxamides, a new class of minimal DNA-intercalating agents which may not act via topoisomerase II. *Journal of Medicinal Chemistry* **1990,** *33* (2), 814-819.

3. (a) Enders, D.; Balensiefer, T., Nucleophilic Carbenes in Asymmetric Organocatalysis. *Accounts of Chemical Research* **2004,** *37* (8), 534-541; (b) Nair, V.; Bindu, S.; Sreekumar, V., N-Heterocyclic Carbenes: Reagents, Not Just Ligands! *Angewandte Chemie International Edition* **2004,** *43* (39), 5130-5135.

4. Boydston, A. J.; Williams, K. A.; Bielawski, C. W., A Modular Approach to Main-Chain Organometallic Polymers. *Journal of the American Chemical Society* **2005,** *127* (36), 12496-12497.

5. (a) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G., Stable Carbenes. *Chemical Reviews* **2000,** *100* (1), 39-92; (b) von E. Doering, W.; Hoffmann, A. K., The Addition of Dichlorocarbene to Olefins. *Journal of the American Chemical Society* **1954,** *76* (23), 6162-6165; (c) Fischer, E. O.; Maasböl, A., On the Existence of a Tungsten Carbonyl Carbene Complex. *Angewandte Chemie International Edition in English* **1964,** *3* (8), 580-581.

6. Arduengo, A. J., Looking for Stable Carbenes: The Difficulty in Starting Anew. *Accounts of Chemical Research* **1999,** *32* (11), 913-921.

7. Wanzlick, H. W., Nucleophile Carben-Chemie. *Angewandte Chemie* **1962,** *74* (4), 129-134.

8. (a) Herrmann, W. A., N-Heterocyclic Carbenes: A New Concept in Organometallic Catalysis. *Angewandte Chemie International Edition* **2002,** *41* (8), 1290-1309; (b) Díez-González, S.; Marion, N.; Nolan, S. P., N-Heterocyclic Carbenes in Late Transition Metal Catalysis. *Chemical Reviews* **2009,** *109* (8), 3612-3676; (c) Marion, N.; Díez-González, S.; Nolan, S. P., N-heterocyclische Carbene als Organokatalysatoren. *Angewandte Chemie* **2007,** *119* (17), 3046-3058.

9. Khramov, D. M.; Lynch, V. M.; Bielawski, C. W., N-Heterocyclic Carbene−Transition Metal Complexes: Spectroscopic and Crystallographic Analyses of π-Back-bonding Interactions. *Organometallics* **2007,** *26* (24), 6042-6049.

10. (a) Back, O.; Henry-Ellinger, M.; Martin, C. D.; Martin, D.; Bertrand, G., 31P NMR Chemical Shifts of Carbene–Phosphinidene Adducts as an Indicator of the π-Accepting Properties of Carbenes. *Angewandte Chemie* **2013,** *125* (10), 3011-3015; (b) Back, O.; Henry-Ellinger, M.; Martin, C. D.; Martin, D.; Bertrand, G., 31P NMR Chemical Shifts of Carbene–Phosphinidene Adducts as an Indicator of the π-Accepting Properties of Carbenes. *Angewandte Chemie International Edition* **2013,** *52* (10), 2939-2943.

11. Liske, A.; Verlinden, K.; Buhl, H.; Schaper, K.; Ganter, C., Determining the π-Acceptor Properties of N-Heterocyclic Carbenes by Measuring the77Se NMR Chemical Shifts of Their Selenium Adducts. *Organometallics* **2013,** *32* (19), 5269-5272.

12. Poyatos, M.; Mata, J. A.; Peris, E., Complexes with Poly(N-heterocyclic carbene) Ligands: Structural Features and Catalytic Applications. *Chemical Reviews* **2009,** *109* (8), 3677-3707.

13. Leung, C. H.; Incarvito, C. D.; Crabtree, R. H., Interplay of Linker, N-Substituent, and Counterion Effects in the Formation and Geometrical Distortion of N-Heterocyclic Biscarbene Complexes of Rhodium(I). *Organometallics* **2006,** *25* (26), 6099-6107.

14. (a) Coles, S. J.; Costello, J. F.; Draffin, W. N.; Hursthouse, M. B.; Paver, S. P., Bi(III) halides as efficient catalysts for the O-acylative cleavage of tetrahydrofurans: an expeditious entry to tetralins. *Tetrahedron* **2005,** *61* (18), 4447-4452; (b) Srinivas, K.; Suresh, P.; Babu, C. N.; Sathyanarayana, A.; Prabusankar, G., Heavier chalcogenone complexes of bismuth(iii)trihalides: potential catalysts for acylative cleavage of cyclic ethers. *RSC Advances* **2015,** *5* (20), 15579-15590.

15. Arca, M.; Aroz, T.; Concepción Gimeno, M.; Kulcsar, M.; Laguna, A.; Lasanta, T.; Lippolis, V.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E., Homopolynuclear TlI and

Heteropolynuclear AuI–TlI Complexes with Organodiselone Ligands: Activation of Luminescence by Intermetallic Interactions. *European Journal of Inorganic Chemistry* **2011,** *2011* (14), 2288-2297.

16. Shi, Z.; Thummel, R. P., Bridged dibenzimidazolinylidenes as new derivatives of tetraaminoethylene. *Tetrahedron Letters* **1995,** *36* (16), 2741-2744.

17. Riederer, S. K. U.; Gigler, P.; Högerl, M. P.; Herdtweck, E.; Bechlars, B.; Herrmann, W. A.; Kühn, F. E., Impact of Ligand Modification on Structures and Catalytic Activities of Chelating Bis-Carbene Rhodium(I) Complexes†. *Organometallics* **2010,** *29* (21), 5681-5692.

18. Manjare, S. T.; Yadav, S.; Singh, H. B.; Butcher, R. J., Redox Reaction between Main-Group Elements (Te, Sn, Bi) and N-Heterocyclic-Carbene-Derived Selenium Halides: A Facile Method for the Preparation of Monomeric Halides. *European Journal of Inorganic Chemistry* **2013,** *2013* (30), 5344-5357.

19. (a) Fitch, J. W.; Payne, W. G.; Westmoreland, D., Platinum-catalyzed acylative cleavage of cyclic ethers. *The Journal of Organic Chemistry* **1983,** *48* (5), 751-753; (b) Guo, Q.; Miyaji, T.; Hara, R.; Shen, B.; Takahashi, T., *Tetrahedron* **2002,** *58* (36), 7327-7334; (c) Mimero, P.; Saluzzo, C.; Amouroux, R., Regiocontrolled ring opening of 2-methyltetrahydrofuran with acid chlorides and iodides. *Tetrahedron Letters* **1994,** *35* (10), 1553-1556; (d) Bothwell, J. M.; Krabbe, S. W.; Mohan, R. S., Applications of bismuth(iii) compounds in organic synthesis. *Chemical Society Reviews* **2011,** *40* (9), 4649-4707; (e) Bhar, S.; Ranu, B. C., Zinc-Promoted Selective Cleavage of Ethers in Presence of Acyl Chloride. *The Journal of Organic Chemistry* **1995,** *60* (3), 745-747.

7. Annexure

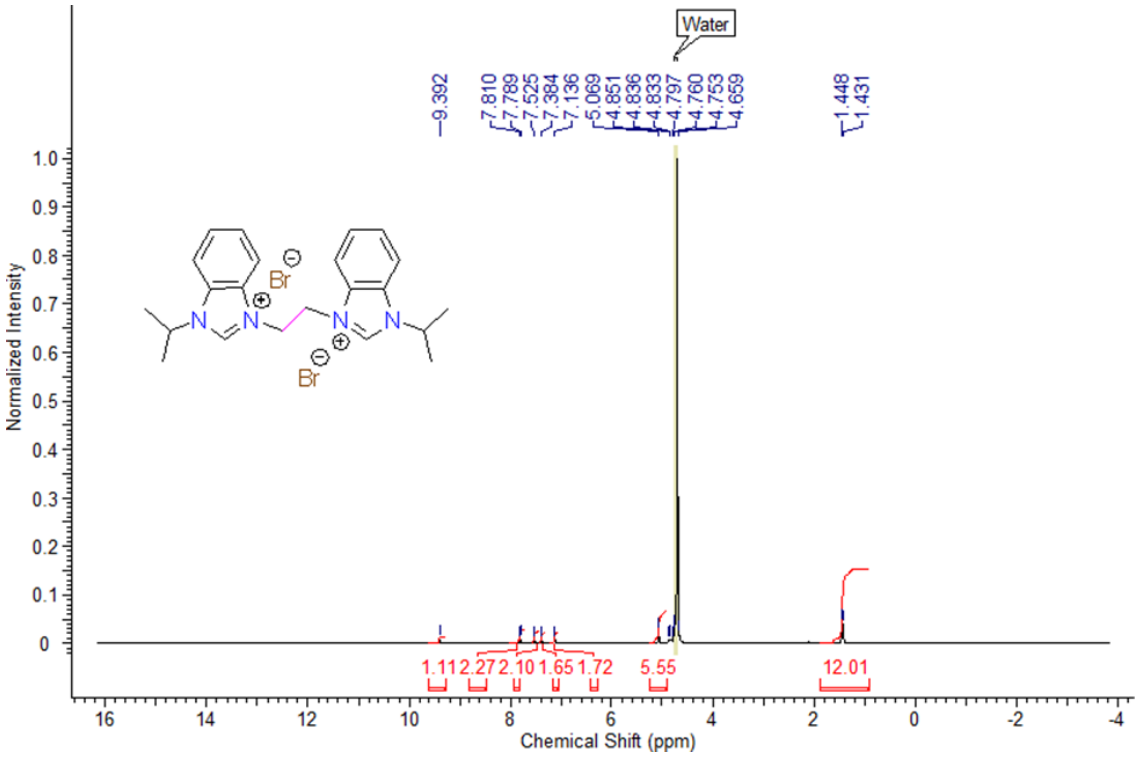


Figure S1: ^{1}H NMR spectrum of **2a**

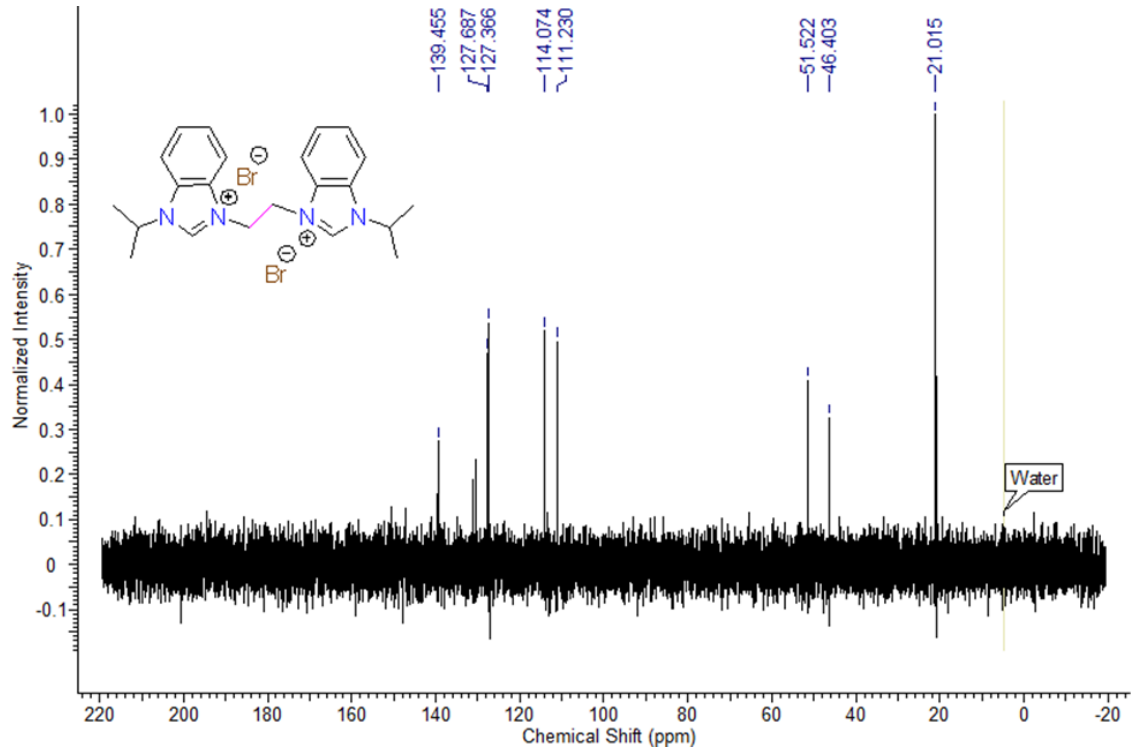


Figure S2: ^{13}C NMR spectrum of **2a**

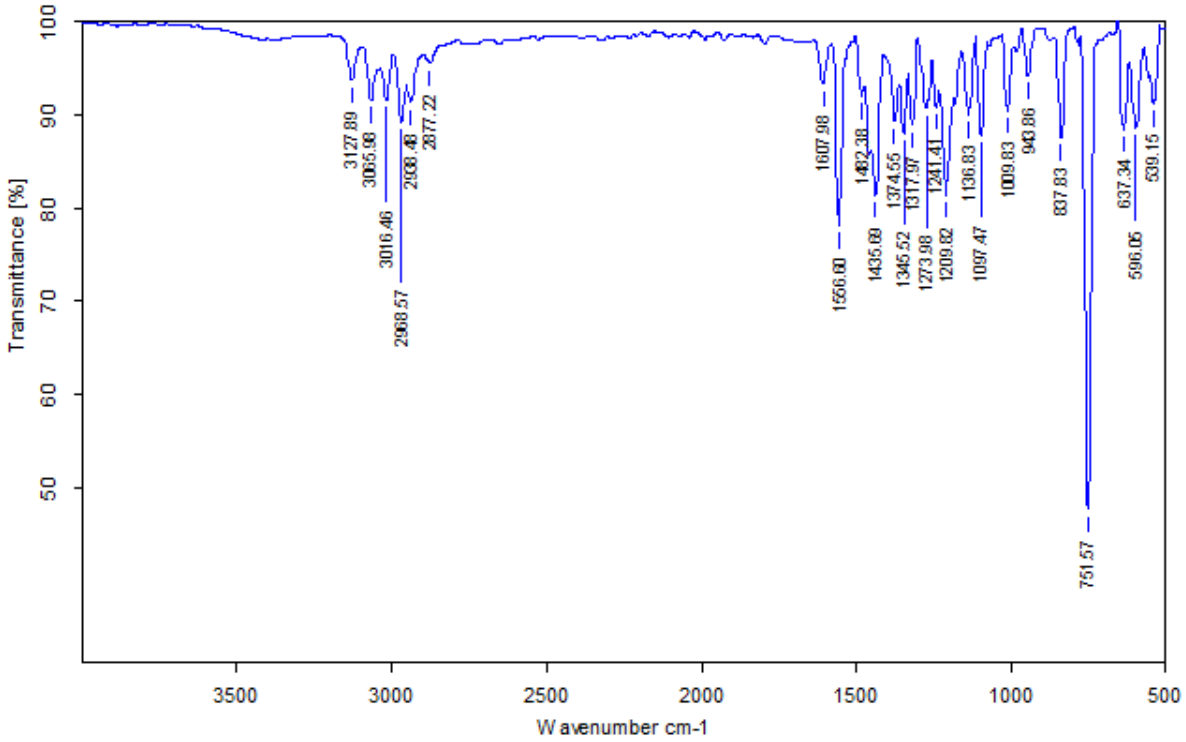


Figure S3: FT-IR (neat) spectrum of **2a**

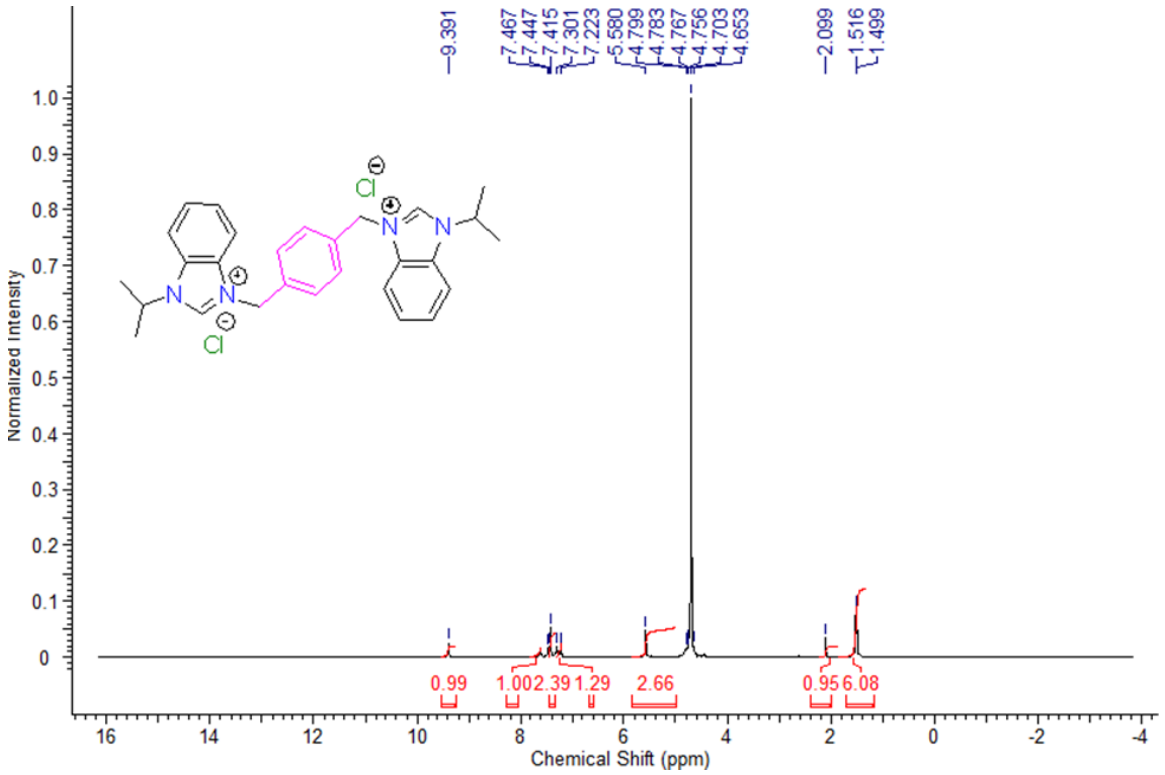


Figure S4: ^{1}H NMR spectrum of **2b**

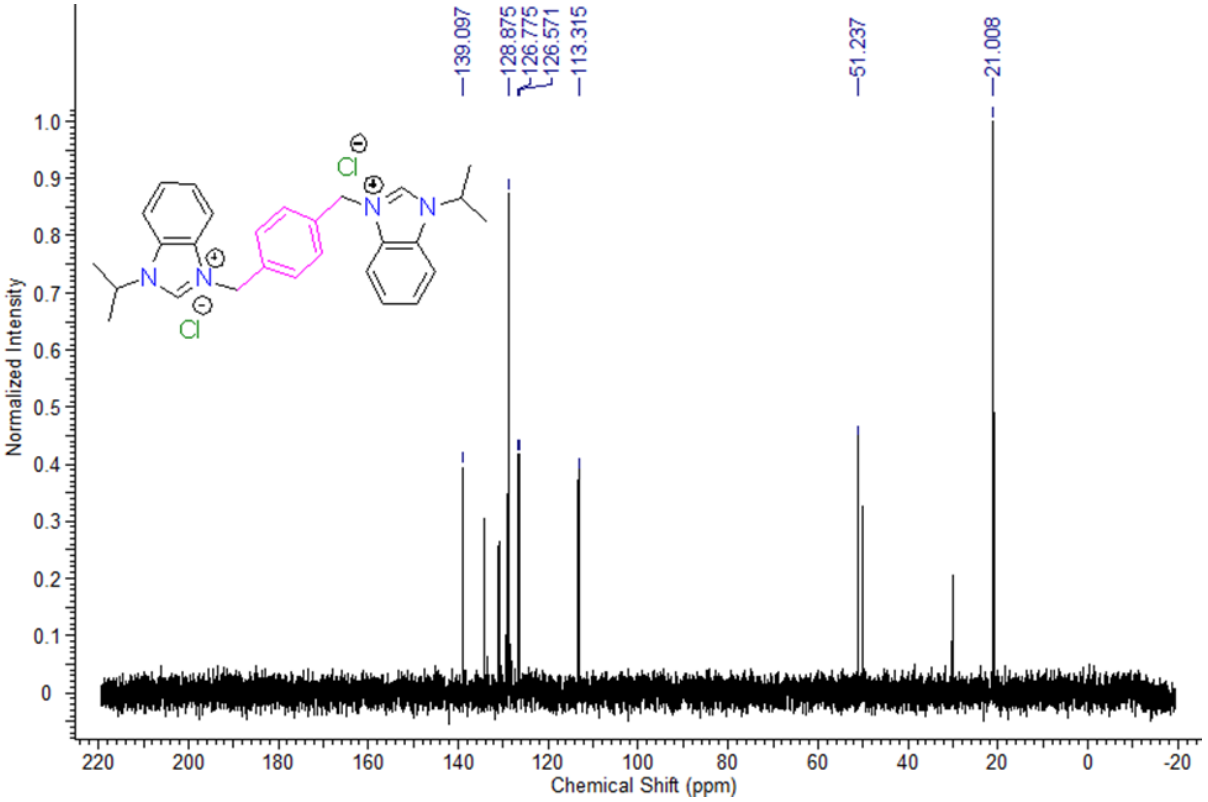


Figure S5: ^{13}C NMR spectrum of **2b**

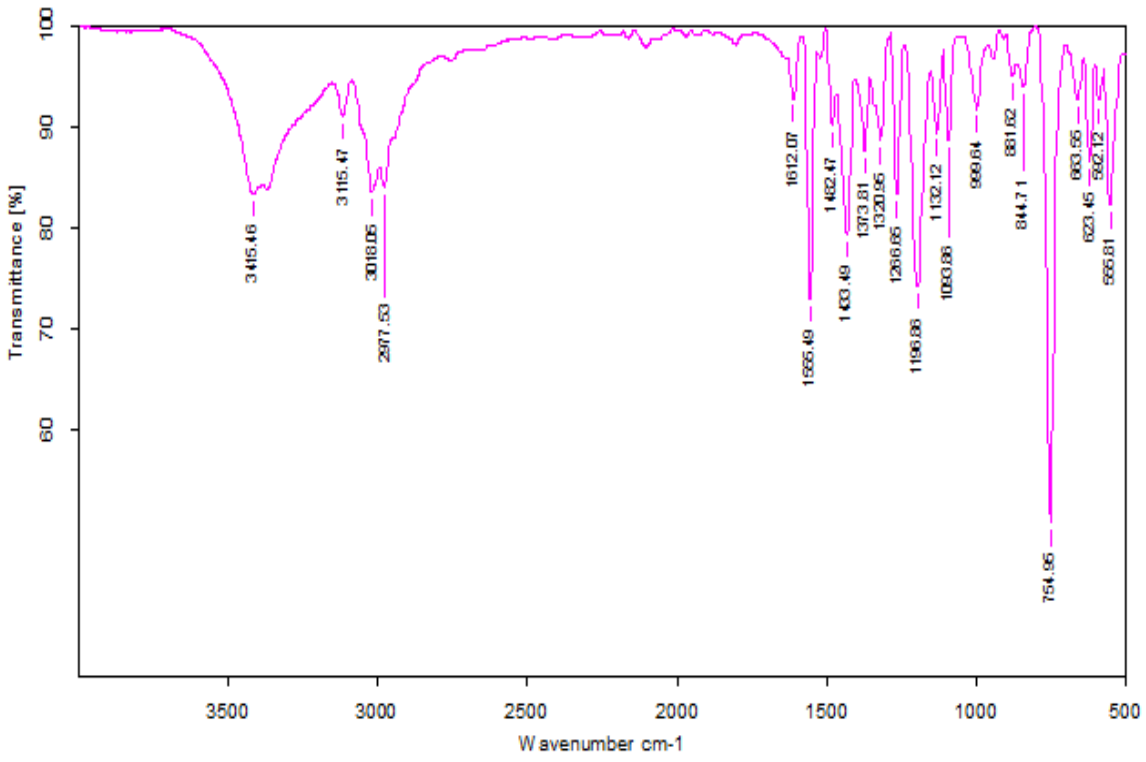


Figure S6: FT-IR (neat) spectrum of **2b**

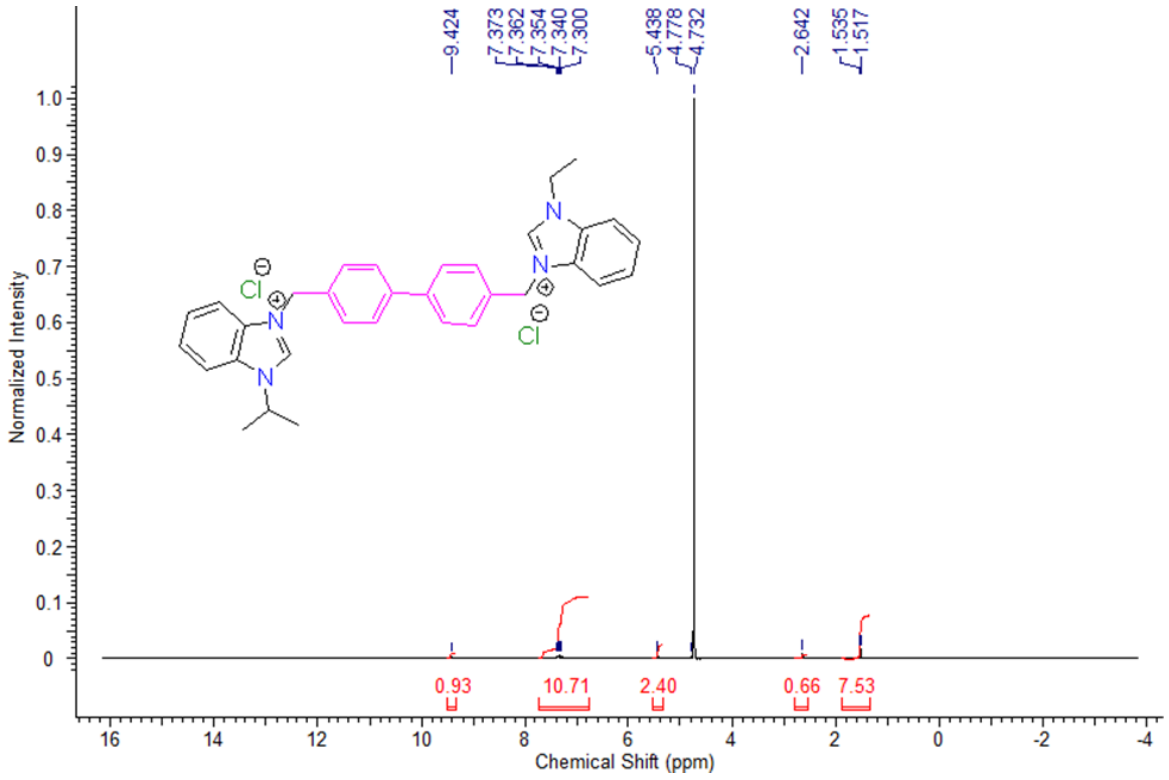


Figure S7: ^{1}H NMR spectrum of **2c**

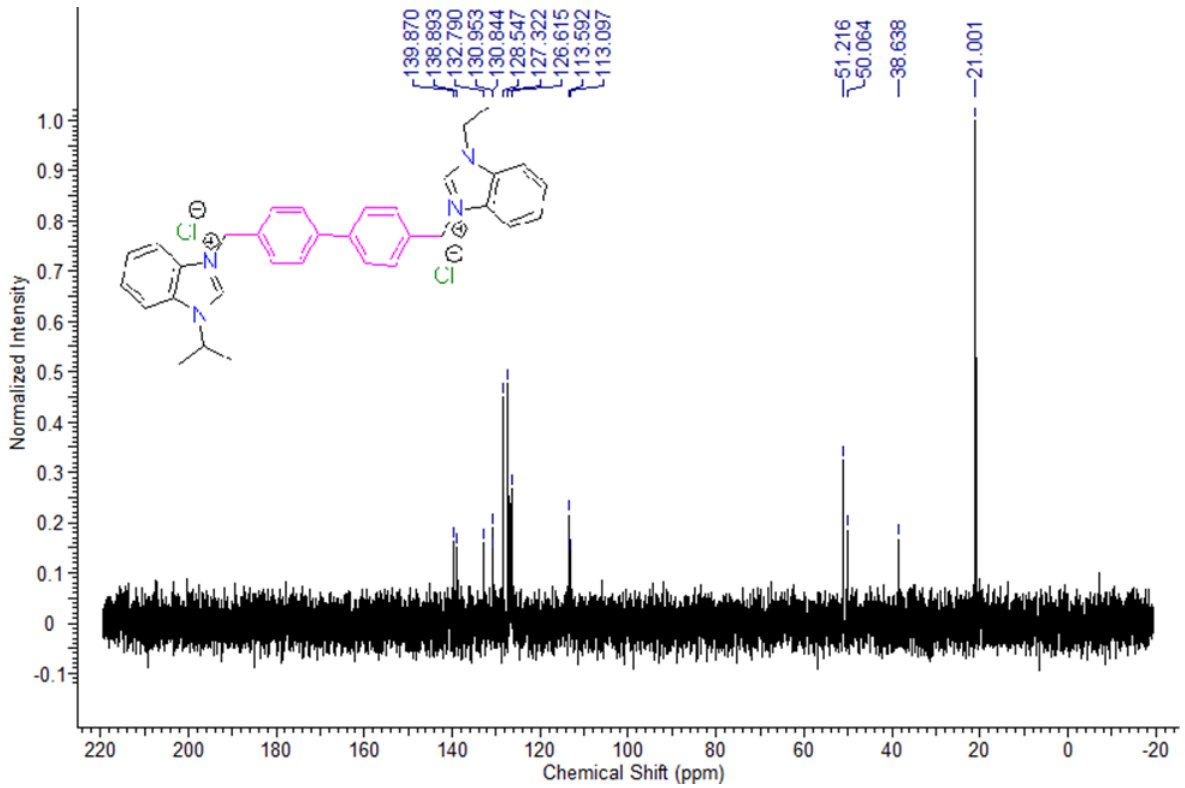


Figure S8: ^{13}C NMR spectrum of **2c**

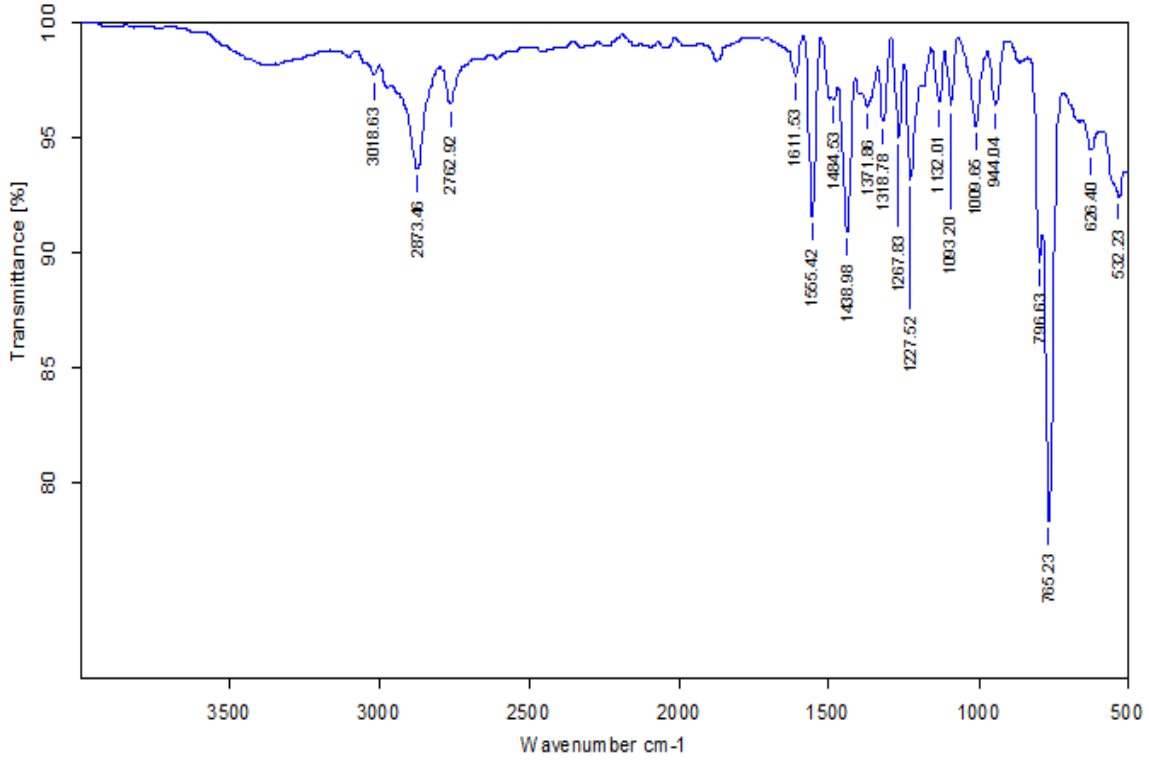


Figure S9: FT-IR (neat) spectrum of **2C**

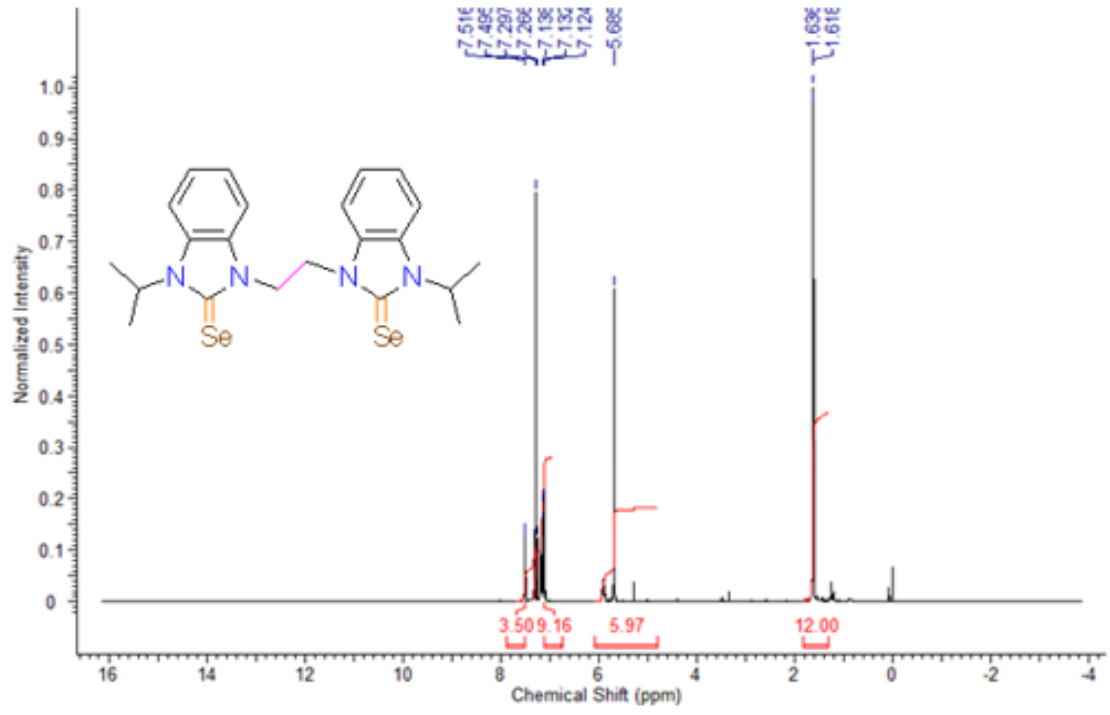


Figure S10: ^{1}H NMR spectrum of **3a**

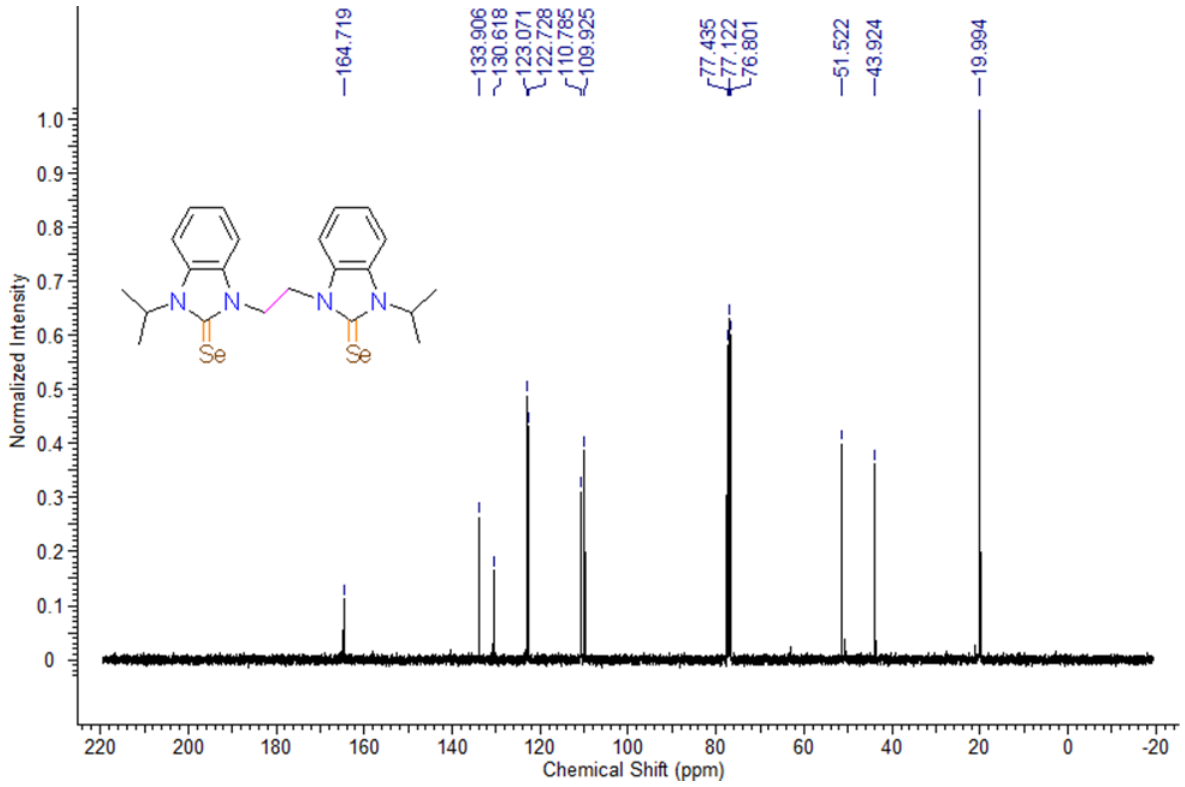


Figure S11: ^{13}C NMR spectrum of **3a**

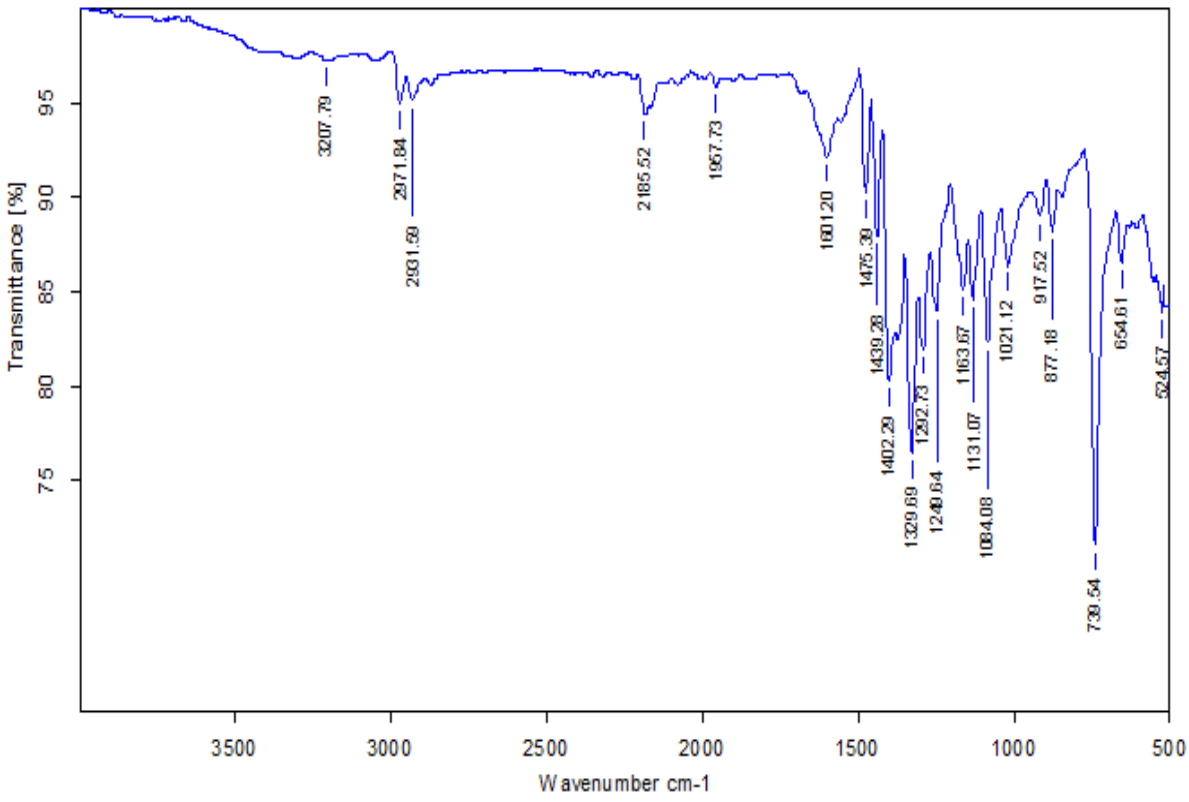


Figure S12: FT-IR (neat) spectrum of **3a**

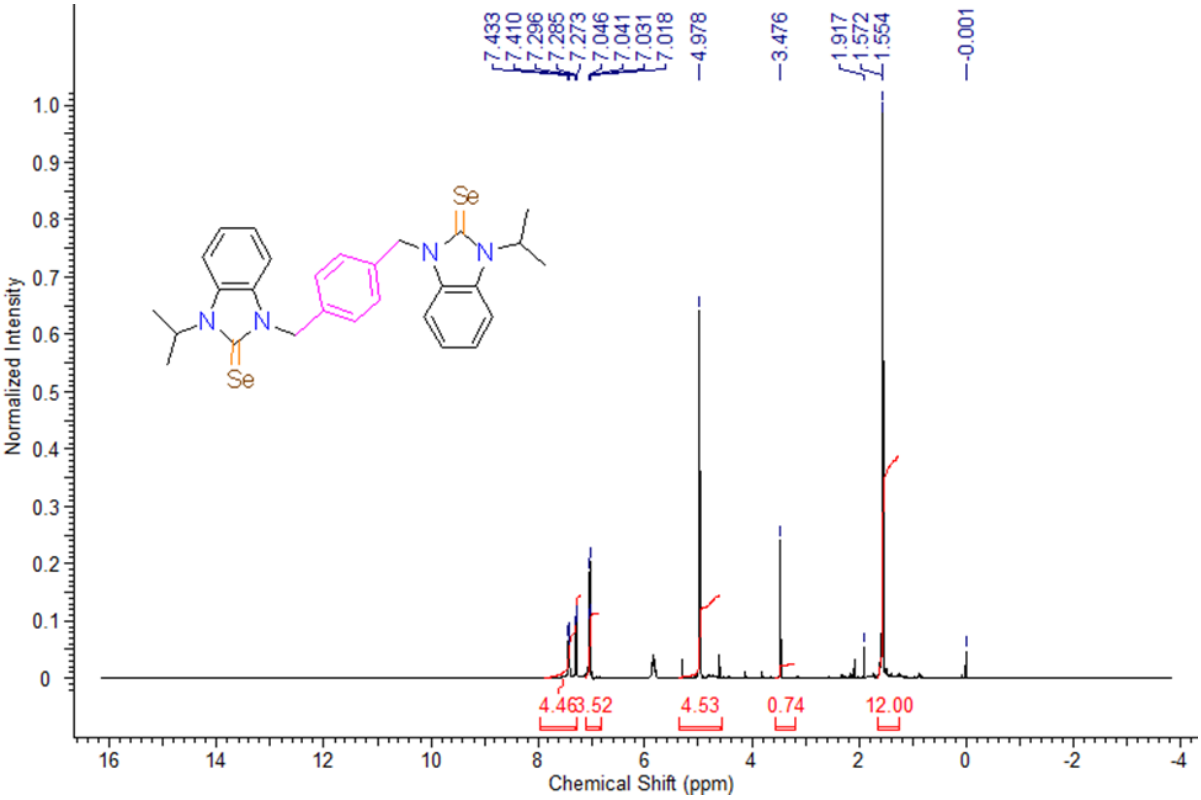


Figure S13: ^{1}H NMR spectrum of **3b**

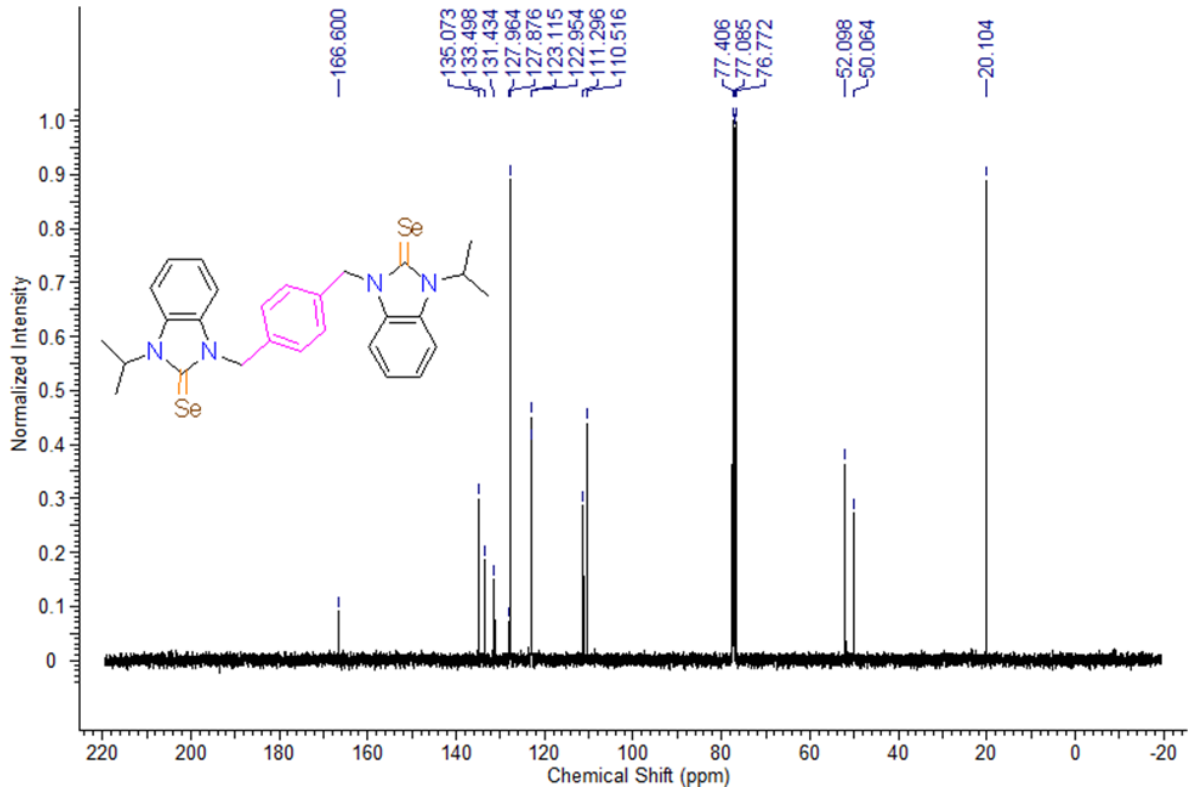


Figure S14: ^{13}C NMR spectrum of **3b**

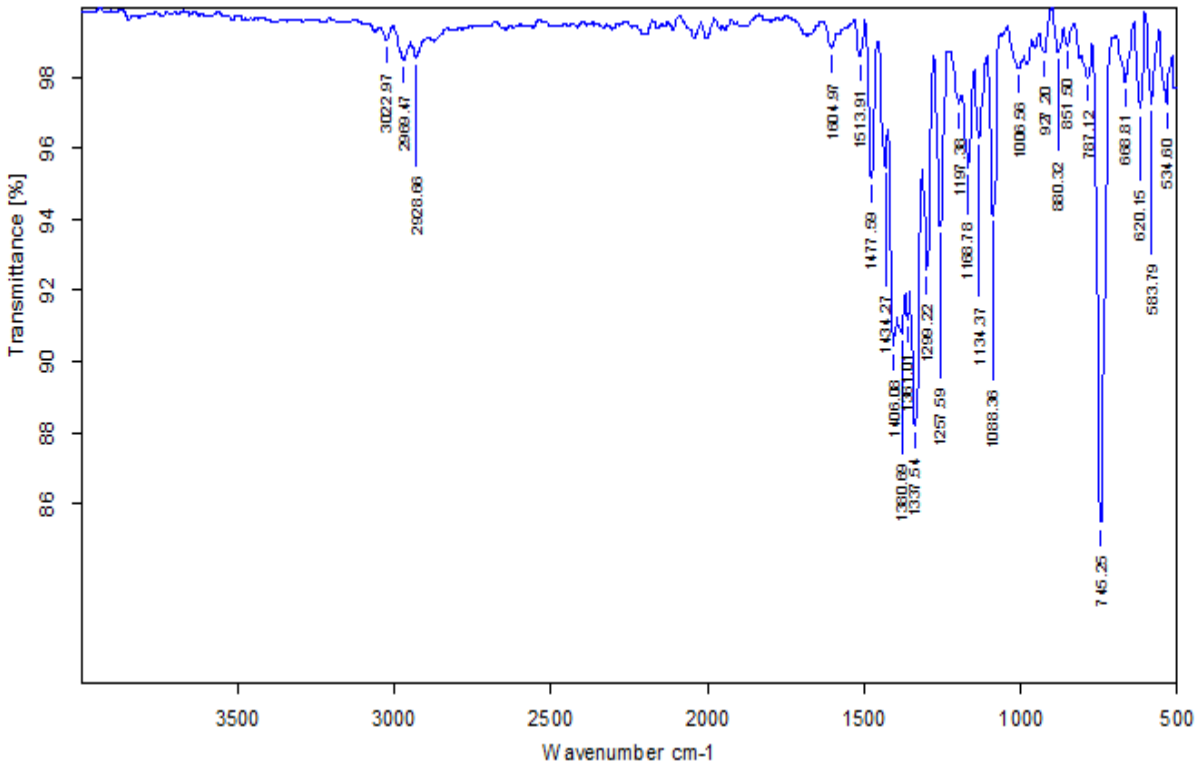


Figure S15: FT-IR (neat) spectrum of **3b**

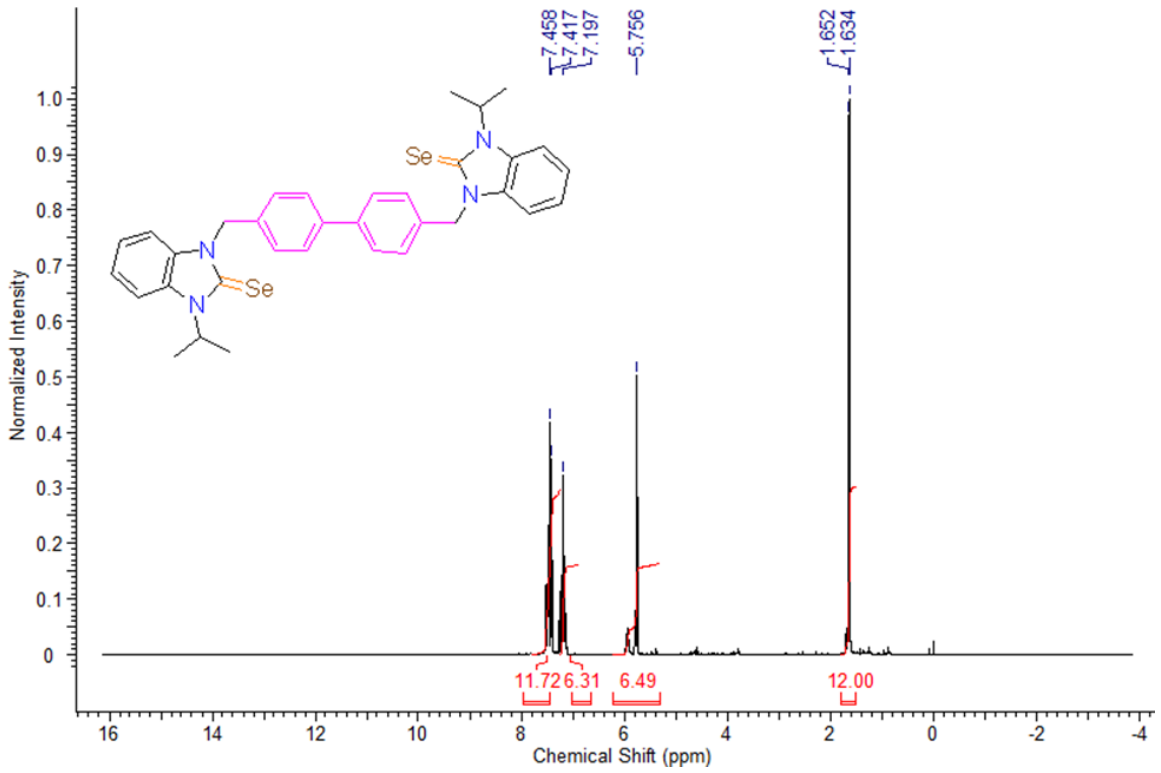


Figure S16: ^{1}H NMR spectrum of **3c**

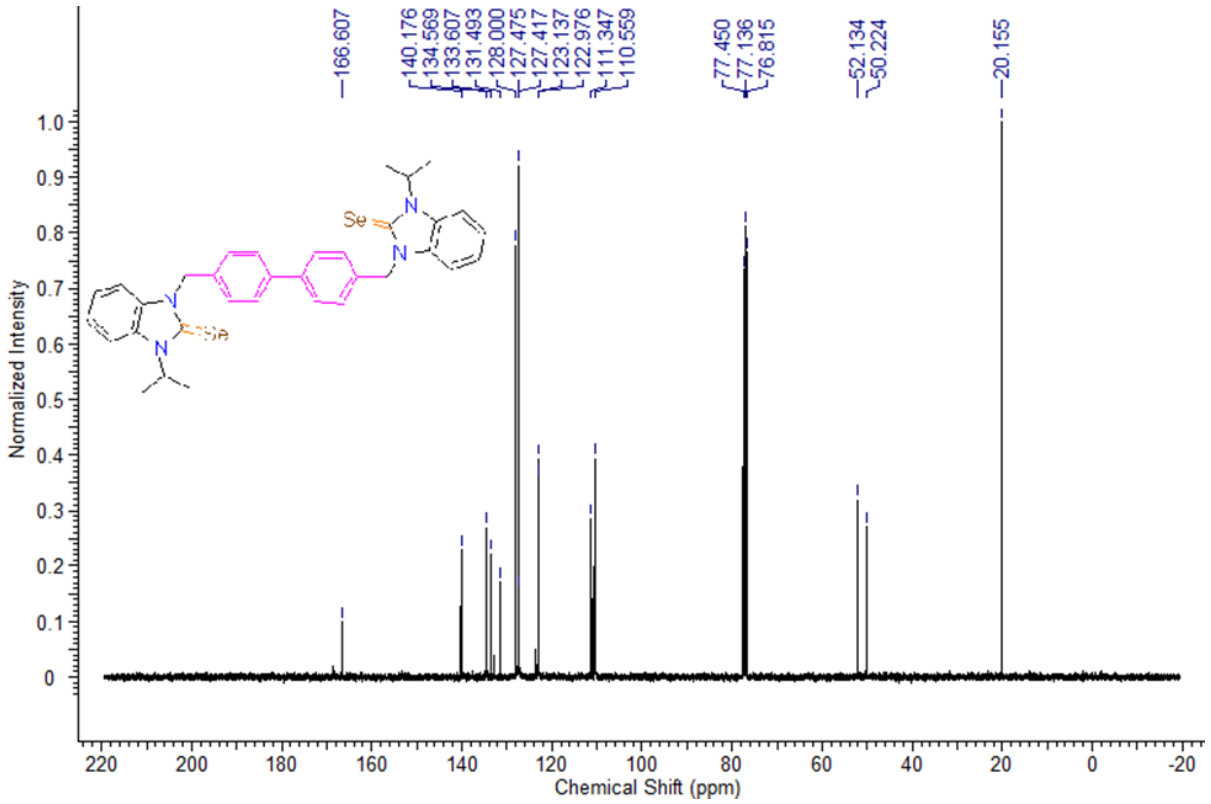


Figure S17: ^{13}C NMR spectrum of **3c**

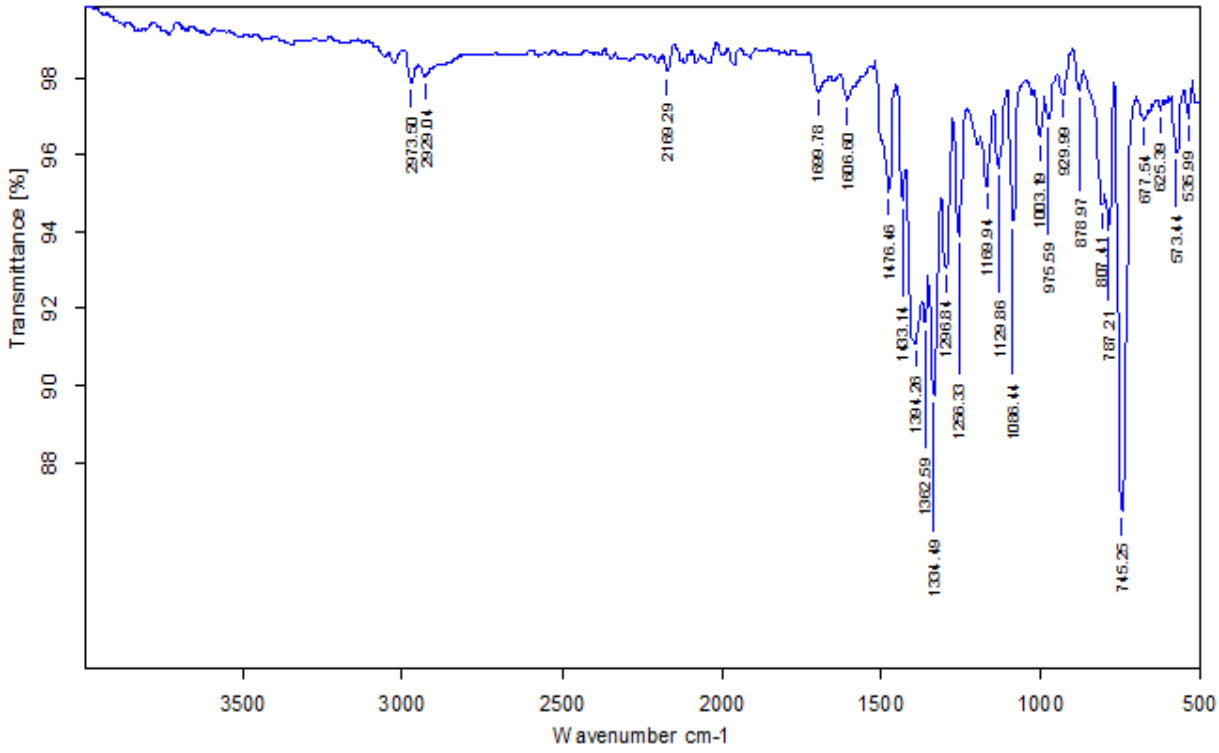


Figure S18: FT-IR (neat) spectrum of **3c**