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Labile Dioxy-Functionalised Zwitterionic Imidazolinium Salt: Access to Zwitterionic and Neutral Imidazolidin-2-ylidene Derivatives and π-Acceptor Properties of Imidazolidine-2-selones

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The dioxy-functionalised zwitterionic imidazolinium salt (**3**) is synthesised by the condensation of *N*,*N*′-dimesitylformamidine with glyoxal in the presence of ammonium tetrafluoroborate. The nucleophilicity of the carbene carbon is ascertained using the in situ generated anionic NHC from **3** with different electrophiles. Further, **3** consists of a labile anionic five membered C_2O_2B at the backbone position of imidazolinium unit which can be tailored to prepare neutral NHC chalcogen compounds, containing symmetrical and unsymmetrical oxy-functionalisation at the backbone. Further, the π-acceptor properties of NHCs were evaluated using ^{77}Se NMR in their respective imidazolidine-2-selones.

Introduction

The widespread use of N-heterocyclic carbenes (NHCs) as ligands for transition-metal ions and its use as catalyst for carrying organic transformation led to the quest for electronically modulated NHCs which culminated interest in synthesis of various N- and C4/5- substituted NHCs and their complexation with several metal ions.[1] In addition, the non-metal containing compounds of NHCs such as borylenes, silylenes, phosphinidines, thiones, selenones, etc. have also been reported, of which the phosphinidenes and selenones derivatives have found application in determining π-acceptor properties of NHCs.[2,3] Besides, imidazole based thio-/seleno-ureas are known for its use in treating hyperthyroidism.[2g] Additionally, these compounds have been used as ligands for the synthesis of different metal complexes.[4]

Among the NHCs, the synthesis of saturated NHCs has received considerable attention owing to their enhanced Lewis basicity which enables them to exhibit higher reactivity in the organometallic catalysis as compared to their unsaturated counterparts.[5,6] It was also observed that ruthenium complex of backbone substituted saturated NHCs showed higher conversion with low catalyst loading with respect to backbone unsubstituted analogues in the ring closing metathesis which highlights the importance of backbone functionalisation in catalysis.[5c] Although the imidazolinium salts containing backbone alkyl or aryl substitution are known, substitution with the heteroatom containing functional group remains rare. Hermann and co-workers reported the osmylation of Mo-NHC complex to afford the backbone oxy functionalized bimetallic complex.[6h] Later, boron containing imidazolium/imidazolinium salts and their metal complexes as well as its utility in the dihydrogen activation and hydrogenation of alkenes were reported.[7] Then after, the synthesis of NHC precursor containing oxo-functionalities at backbone was reported by Ganter's group and others.[8] Among them, the carbene derived from **1** showed a strong electrophilic and greater π-acceptor carbene character.[8h] In addition, the carbene is utilised as halodehydrating reagents, in ammonia activation, [2+1] cycloaddition with alkyne and styrene (chart 1).[8] Even though boron containing pendant groups attached to endocyclic nitrogen or at the backbone position in an imidazolium/imidazolinium salts or as a part of inorganic framework in five/six membered NHC and its precursor are known,[9] imidazolinium salts with backbone functional group containing a substituted boron moiety remain elusive.

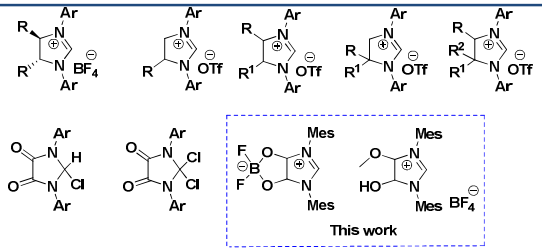

Chart 1. Various known substituted imidazolinium salts and present work.

Recently, we have reported the synthesis and structural characterizations of backbone mono-/bis-functionalised imidazolium salts, containing carboxylic acid/silyl-/phosphino-/thio-substituents, for the synthesis of normal and mesoionic carbenes

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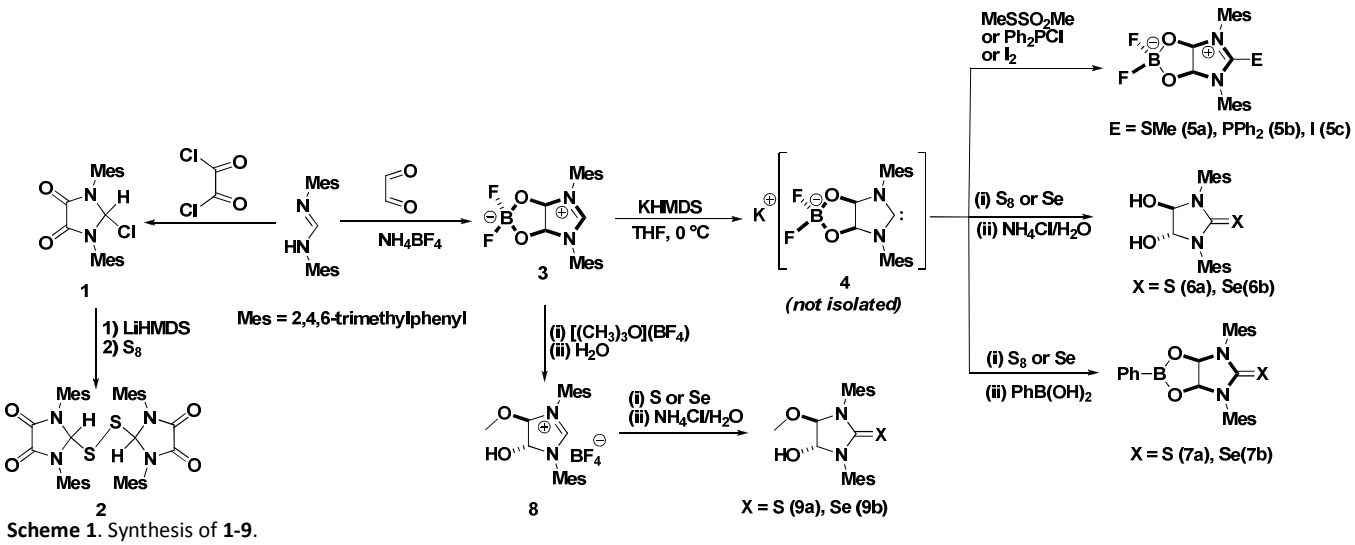
†Electronic Supplementary Information (ESI) available: Additional figures and X-ray crystallographic data in CIF format have been deposited with the Cambridge Structural Database. CCDC 1401392 (**2**), 1063837 (**3**), 1063842 (**5a**), 1407615 (**5b**), 1063838 (**6a**), 1063839 (**6b**), 1063840 (**7a**), 1063841 (**7b**) and 1063843 (**9a**).



Scheme 1. Synthesis of **1-9**.

metal complexes.[10] In continuation, we have extended our studies to synthesize the backbone oxy–substituted imidazol(in)ium salts. In this paper, we describe the synthesis and reactivity of zwitterionic imidazolinium salt (**3**) with backbone dioxy backbone attached to BF_2 moiety. In addition, we also report the π-acceptor characters of various symmetrical (**6**, **7**) and unsymmetrical (**9**) oxy-functionalised imidazolinium compounds.

Results and discussion

Previously, various groups reported the condensation of urea/thiourea and glyoxal to afford 4,5-dihydroxy imidazolidine-2-one/thione compounds.[11] Our methodology began with the understanding of the cyclisation of formamidine with glyoxal or substituted glyoxal to introduce oxygen-donor functionalisation at the backbone of imidazol(in)ium salts. Earlier, Ganter and co–workers reported the synthesis of the oxalamide backbone containing **1** using oxalyl chloride as precursor and formation of Wanzlick dimer from **1**.[8d,e] However, the reaction of an *in situ* generated carbene from **1** using LiHMDS with elemental sulphur led to the formation of disulphide derivative (**2**) rather than 1,3-dimesityl- 2-thioxoimidazolidine-4,5-dione, a product obtained under similar condition using NaHMDS as base (Scheme 1).[8e] Due to the poor solubility of **2** in common organic solvents the spectroscopic characterization in solution could not be carried out. Hence the structure of **2** was studied by single crystal X-ray diffraction method. The molecular structure of **2** consists of two five membered imidazolinium ring connected through the disulphide bond at C-2 position (Fig. S1 and Table S1 for crystallographic data in the ESI†). The C1-S1 bond distance in **2** (1.844(3) Å) is slightly longer than the C-S single bond distance (1.736 (3) Å) of cationic imidazolium disulphide.[4b] Also, a shorter S-S bond distance (2.031(1) Å) is observed than those of similarly known compounds (2.1015(10) Å).[4c]

In contrast to the above reaction, the condensation of *N*,*N*′-dimesitylformamidine with glyoxal in the presence of ammonium tetrafluoroborate afforded a colourless solid (**3)** (Scheme 1). The identity of **3** was established by ^{1}H NMR spectra, in which the protons attached to C4/5 and NCN carbon centres appear at 5.99 ppm (doublet) and 8.94 ppm (singlet) respectively, which are typical chemical shift values reported for imidazolinium salts. In addition, ^{19}F NMR spectrum shows two peaks at two different chemical shifts (-142.1 ppm and -145.4 ppm) which could be assigned to two non-equivalent fluorine atoms (ABX, X = ^{11}B) and the ^{11}B NMR spectrum consists of a singlet at 5.26 ppm (ESI†). These observations support the chelation of BF_2 moiety with the oxygen atoms appended on the imidazolinium ring which was further unambiguously confirmed through X–ray diffraction analysis. The molecular structure of **3 (**Fig. 1 and Table S1 for crystallographic data ESI†) indicates that average N1–C1 bond distance [1.314 (18) Å] and N–C–N bond angles (114.1(2)°) measured were in accord with those of previously reported imidazolinium salts.[1c] **3** was remarkably stable to air- and moisture and its integrity is also confirmed by ESI-MS analysis (see in the ESI†).

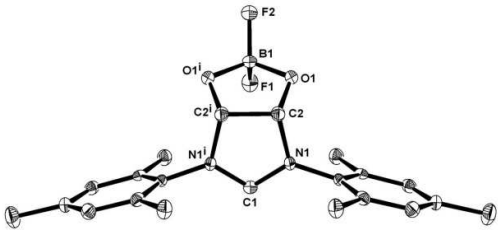
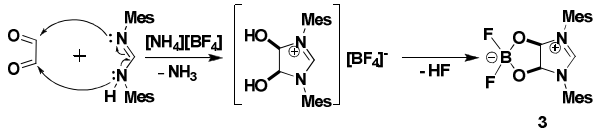


Fig. 1 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B(1)-F(1) 1.395(3), B(1)-F(2) 1.385(3), B(1)-O(1) 1.477(2), C(2)-O(1) 1.369(2), C(2)-N(1) 1.496(2), C(1)-N(1) 1.3119(19), C(2)-C(2)# 1.551(3), F(2) B(1)-F(1) 108.3(2), C(2)-O(1)-B(1) 109.31(14), N(1)-C(2)-C(2)# 102.59(8), N(1)-C(1)-N(1)# 114.2(2).

The formation of **3** can be rationalised with those of 4,5-dihydroxyimidazolidine-2-one/thione containing *cis* or *trans* positioned dihydroxy units at the backbone C-centers.[11b,c] Accordingly, the condensation between formamidine and glyoxal

was envisaged to occur via a concerted route through an intermediate 4,5-dihydroxy substituted imidazolinium cation before the formation of functionalised imidazolinium zwitterionic salt (**3**) (Scheme 2).



Scheme 2. Proposed mechanism for the formation of **3**.

Derivatization of 3 at carbene center with electrophiles: The nucleophilicity of **4** is manifested in its reactivity towards various electrophiles such as *S*-methyl methanethiosulphonate and chlorodiphenylphosphine to afford the respective compounds (**5a–5b**) which was thoroughly characterized. The characteristic disappearance of proton attached to the NCN carbon centre and shielding of the C4/5-*H* of imidazole ring relative to **3** in the ^{1}H NMR spectra are consistent with those observed for similarly known compounds. Further, ^{31}P NMR of **5b** indicates a large shielding effect for the C2 substituted diphenylphosphine (-3.28 ppm) against the starting material Ph_2PCl (80 ppm) and comparable to that of $[SIMesPPh_2][(B(C_6F_5)_4]$ (-1.5 ppm).[2c] However, in both the cases (**5a** and **5b**) the ^{11}B-NMR resonances remain largely unaltered compared to **3**. The base peak corresponding to *m/z* 413.1873 and 551.2432 for adducts **5a** and **5b** respectively in their ESI-MS spectrum further supports their formation. In addition the structure of **5a** and **5b** were crystallographically characterized in which the C-P bond distance (1.865(3) Å) is similar to that of the only other crystallographically characterized compound $[SIMesPPh_2](B(C_6F_5)_4]$ (Fig.2), (Fig.S2; Table S1 and Table S2 for crystallographic data ESI†).[2c] Reaction of **4** with elemental iodine affords zwitterionic adducts **5c**, reveals the electrophilic nature of corresponding carbene. Formation of **5c** was confirmed through the spectroscopic, spectrometric and analytical methods.

The carbenic nature as well as its π-acceptor property was studied using thiones/selenones obtained from **4**. Reaction of **3** with elemental sulfur or selenium in presence of excess of potassium bis(trimethylsilyl)amide followed by stepwise addition of ammonium chloride and water afforded the hydrolyzed product (**6a** or **6b)**, instead of ammonium salt of anionic thiourea of **4** as observed by Lavigne and co-worker for anionic NHC containing malonate backbone,[12] which was ascertained through the spectroscopic, spectrometric studies and by X-ray crystallography. The molecular structure of **6a** or **6b** consists of five membered imidazolinium ring which adopts an 'envelope' conformation and the two hydroxyl groups in the backbone of the ring lie *trans* to each other (Fig. 3), (Fig. S3 and Table 1 for bond lengths and angles; Table S2 for crystallographic data ESI†). Interestingly, when phenylboronic acid was used in place of ammonium chloride/water it results in the formation of **7a** or **7b**. The molecular structure of **7a** and **7b** (Fig. 4 and Fig. S4; Table 2 and Table S3) adopts a bowl

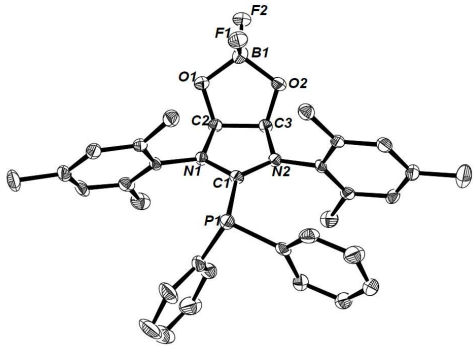


Fig. 2 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **5b**. Hydrogen atoms and one molecule have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-P(1) 1.865(3), C(1)-N(1) 1.326(4), C(1)-N(2) 1.334(3), C(2)-N(1) 1.492(3), C(3)-N(2) 1.500(3), C(2)-C(3) 1.542(4), C(2)-O(1) 1.392(3), C(3)-O(2) 1.390(3), N(1)-C(1)-N(2) 111.7(2).

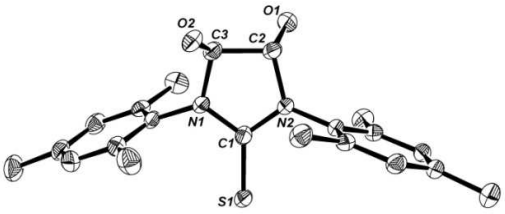


Fig. 3 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **6a**. Hydrogen atoms and one ethyl acetate molecule have been omitted for clarity.

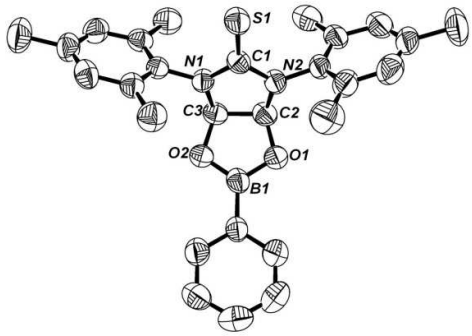


Fig. 4 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **7a**. Hydrogen atoms and one ethyl acetate molecule have been omitted for clarity.

shape structures with both the oxygen atoms attached to the boron are on the same plane. In ^{1}H NMR spectra, the C-4/5 protons in **6** or **7** appear as singlet that is consistent with the molecular structures.

Determination of the π-acceptor property of NHCs using ^{77}Se NMR of imidazole-2-selenone/imidazolidine-2-selenone compound was determined first reported by Ganter and co-workers.[3b,c] Subsequently, Nolan and co-workers studied the π-acceptor properties of wide range of NHCs using PhSeSePh as standard.[3a] Utilizing the latter method, the ^{77}Se NMR of **7b** shows a deshielded signal at 194 ppm as against 169 ppm observed for **6b** which indicates greater π- accepting nature of **7b**. Unlike in the other

reported structures of thiones and selenones of NHCs, the effect of π-acceptor character of carbene and the effect of backbone functionalisation is clearly noticed in these structures.[3a-c] The Bond lengths of these compounds indicate a shorter C=X (X=S (**7a**); Se (**7b**)) and a slightly longer C(2/3)-N(1/2) (backbone) relative to **6a** or **6b** was observed (Table 1 and 2). Comparison of these values indicates that the C=X bond distances in **7a** and **7b** are slightly shorter than those of 1,3-dimesitylimidazolidine-2-thiones/selenone and it is longer as compared to those of 1,3-dimesityl-2-thioxo(/selenoxo)imidazolidine-4,5-dione. Similar comparison with **6a** and **6b** reveals that the C=X bond distance in these compounds are slightly longer (in **6b** the value is negligible) than in the case of 1,3-dimesitylimidazolidine-2-thione/selenone.[2j, 3a] These comparisons and correlation with the ^{77}Se NMR of these compounds suggest that the carbene center in **6** and **7** have appreciable π-acceptor character and between the two, the greater π-acceptor character is observed for **7**. Compound **7a** and **7b** have the potential to form adducts with a variety of donors (4-dimethylaminopyridine, diazabicyclo-(2.2.2)-octane etc.) and show interesting photophysical properties and can act as synthons for supramolecular compounds besides being used as optical sensors for Lewis bases.[13] Also aryl boronic esters are important starting materials for cross coupling reactions and imidazole containing boronic esters still remain elusive.[13b]

Table 1 Selected bond lengths [Å] and angles (°) for compound **6a**, **7a** and **9a**.

6a	**7a**	**9a**
C(1)-S(1) 1.682(2)	C(1)-S(1) 1.644(4)	C(1)-S(1) 1.669(4)
C(1)-N(1) 1.357(3)	C(1)-N(1) 1.363(4)	C(1)-N(1) 1.337(4)
C(1)-N(2) 1.352(3)	C(1)-N(2) 1.363(4)	C(1)-N(2) 1.355(4)
C(2)-N(2) 1.467(3)	C(2)-N(2) 1.438(4)	C(2)-N(2) 1.461(4)
C(3)-N(1) 1.471(3)	C(3)-N(1) 1.440(4)	C(3)-N(1) 1.460(4)
C(2)-C(3) 1.531(3)	C(2)-C(3) 1.529(5)	C(2)-C(3) 1.535(5)
C(2)-O(1) 1.404(3)	C(2)-O(1) 1.427(4)	C(2)-O(1) 1.399(4)
C(3)-O(2) 1.402(3)	C(3)-O(2) 1.419(4)	C(3)-O(2) 1.390(4)
N(2)-C(1)-N(1) 108.8(2)	B(1)-O(1) 1.376(5)	N(2)-C(1)-N(1) 109.1(3)
	B(1)-O(2) 1.367(5)	
	N(2)-C(1)-N(1) 107.5(3)	

Table 2 Selected bond lengths [Å] and angles (°) for compound **6b** and **7b**

6b	**7b**
C(1)-Se(1) 1.834(3)	C(1)-Se(1) 1.812(3)
C(1)-N(1) 1.335(3)	C(1)-N(1) 1.354(4)
C(1)-N(2) 1.345(3)	C(1)-N(2) 1.353(4)
C(2)-N(2) 1.464(3)	C(2)-N(2) 1.451(4)
C(3)-N(1) 1.459(3)	C(3)-N(1) 1.444(4)
C(2)-C(3) 1.528(4)	C(2)-C(3) 1.546(4)
C(2)-O(1) 1.401(3)	C(2)-O(1) 1.423(4)
C(3)-O(2) 1.387(3)	C(3)-O(2) 1.426(4)
N(2)-C(1)-N(1) 109.4(2)	B(1)-O(1) 1.373(4)
	B(1)-O(2) 1.376(4)
	N(2)-C(1)-N(1) 108.5(3)

Synthesis of unsymmetrically substituted oxy-imidazolinium salt and their derivatives with chalcogens: Finally, the reaction to introduce unsymmetric *O*-substitution at the backbone centre was attempted. Accordingly, the reaction of **3** with trimethyloxonium tetrafluoroborate followed by addition of water afforded the unsymmetrical functionalised imidazolinium salt (**8**) in high yield (80%). Due to unsymmetrical substitution, the C4/5-*H* of imidazole ring appears as two different doublets at 5.72 ppm (C4-*H*) and 6.23 ppm (C5-*H*) respectively in ^{1}H NMR spectrum. The carbenic and π-acceptor character of **8** was discerned using the thione and selenone derivatives (**9a** and **9b**). The ^{77}Se NMR of **9b** (167 ppm) shows a larger downfield shift compared to 1,3-dimesitylimidazolidine-2-selenone (110 ppm) which suggests the stronger π-acceptor character of carbene in **9b** but it is slightly upfielded with respect to **6b** (169 ppm) hence having comparable π-acceptor properties. Also, **9a** was crystallographically characterized (Fig. 5 and Table 1 for bond lengths and angles; and Table S3 for crystallographic data ESI†). Comparison of bonding parameters with **6a** indicates a slightly shorter bond distance of C=S in **9a**, but the value is comparable with 1,3-dimesitylimidazolidine-2-thione.[2j]

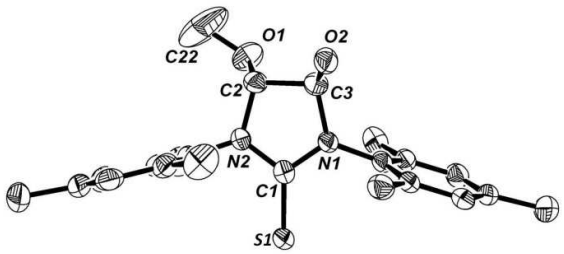


Fig. 5 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **9a**. Hydrogen atoms and one ethyl acetate molecule have been omitted for clarity.

Conclusions

In conclusion, a zwitterionic 4,5-dioxy functionalised imidazolinium salt (**3**) was synthesised using simple and readily available starting reagents which involves intramolecular cyclisation between glyoxal and formamidine in presence of ammonium tetraflouroborate. The nucleophilicity of anionic 4,5-dioxy functionalised NHC (**4**) was evaluated with various electrophiles. The lability of the backbone dixoy-functionalised C_2O_2B ring in **3** was utilised to prepare dihydroxy/hydroxymethoxy functionalized imidazolidine-2-thione/selenone. Besides a synthetically important boronic ester at the backbone positions were synthesised with an in situ generated carbene **4**. Further, the π-acceptor properties of NHCs in **6b**, **7b** and **9b** were evaluated using ^{77}Se NMR of which **7b** shows a greater π-acceptor character. Also, a first example of unsymmetrically substituted *O*-functionalised imidazolinium salt and corresponding chalcogen NHC derivatives is reported. Moreover the current study offers a possible tailoring of the backbone oxy-functioanlization with different organic subtitutents which can significantly alter the electronic properties of NHCs and hence its influence in catalysis.

Experimental Sections

General Procedures

All of the reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques unless otherwise mentioned. Solvents were dried according to the standard literature procedures, and they were freshly distilled under nitrogen prior to use. All other reagents were used as received. Glasswares were dried in an oven maintained at 140 °C overnight prior to use. Chemicals such as potassium bis(trimethylsilyl)amide, (KHMDS, 0.5 M in toluene), ammonium tetraflouroborate, trimethyloxonium tetrafluoroborate, 2,4,6-trimethylaniline, *S*-methyl methanethiosulfonate and diphenylphosphine chloride were purchased from Sigma-Aldrich or iodine and HMDS from sd fine-chem Limited and used as received. *N*,*N*'-dimesitylformamidine[14a] and lithium bis(trimethylsilyl)amide (LiHMDS)[14b] was prepared according to the literature procedures.

Instrumentation

^{1}H NMR, ^{13}C NMR, ^{11}B NMR, ^{19}F NMR and ^{77}Se NMR spectra were obtained on a JEOL-DELTA 400 MHz and 500 MHz spectrometers. The spectra were recorded $CDCl_3$, CD_3CN and DMSO-d_6 as solvents. ^{1}H and ^{13}C NMR Chemical shifts were referenced with respect to tetramethylsilane (TMS). ^{77}Se NMR spectra are reported relative to $SeMe_2$ and are referenced to external PhSeSePh (δ_{Se} 463 ppm). Infrared spectra were recorded as KBr pellets on a Perkin Elmer-Spectrum Two. The mass spectra of all the compounds were obtained using Electrospray ionisation (ESI) method using Waters-Q-Tof Premier-HAB213 spectrometer. Elemental analyses were performed with a Perkin Elmer Series-II CHNS/O analyzer 2400. Melting points reported are uncorrected.

X-ray Crystallography

The crystal data were collected on a Bruker SMART APEX CCD diffractometer (for compound **2** and **6a**) and Bruker D8-quest-Photon diffractometer (for compound **3**, **5a**, **5b**, **6b**, **7a**, **7b** and **9a**). Data were collected using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 100 K. All of the structures were solved by direct methods using SHELXTL-97[15] and refined by full matrix least-squares on F^2. All of the hydrogen atoms were included in idealized positions and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. Disordered solvent molecules in compound **5a** and **6b** were treated by PLATON/ SQUEEZE procedure.[15c]

Synthesis of Compound 1. This title compound was prepared by a slight modification of previously reported procedure of Ganter and co-workers.[8e] Accordingly, a stirred solution of *N,N'*-bis(2,4,6-trimethylphenyl)formamidine (1.64 g, 5.85 mmol) in THF (40 mL), oxalyl chloride (0.61 mL, 7.02 mmol) was added at 0 °C. The mixture was warmed to room temperature and the stirring was continued for 4 h. Removal of volatiles under vacuum and washing the residue with dry hexane afforded the title compound as a colourless solid. Yield: 1.94 g (90%).

Synthesis of Compound 2. To a mixture **1** (0.370 g, 1 mmol) and LiHMDS (0.201 g, 1.2 mmol) in Schlenk flask was added THF (40 mL) and cooled to -78 °C. After 5 min of stirring, elemental sulphur (0.068 g, 2.1 mmol) was added to it and the solution was stirred for 1 h at this temperature. The resulting mixture was slowly allowed to warm to room temperature and the stirring was continued further for 2 h. Removal of all volatiles under vacuum gave a residue which was purified by column chromatography (SiO_2, hexane/ dichloromethane: 1/1 to 1/2) to afford the title compound as yellow solid. Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of methanol/acetonitrile/DMSO (2/2/1) solvent mixture of **2** at room temperature. Yield: 0.12 g (32 %). Mp: >250 °C. Anal. Calcd for $C_{42}H_{46}N_4O_4S_2$: C, 68.64; H, 6.31; N, 7.62. Found: C, 67.43; H, 7.21; N, 7.41. IR (KBr, cm^{-1}): 2917 (w), 1758 (vs), 1608 (m), 1484 (s), 1366 (s), 1304 (w), 1225 (m), 1201 (s), 1167 (m), 1084 (w), 1034 (w), 895 (w), 857 (m), 760 (w), 735 (w), 564 (w) cm^{-1}. Due to its poor solubility in common organic solvent ($CHCl_3$, CH_3CN and DMSO), it could not be spectroscopically characterized.

Synthesis of Compound 3. To a mixture of *N*,*N*'-dimesitylformamidine (0.561 g, 2 mmol) and ammonium tetraflouroborate (0.252 g, 2.4 mmol) in toluene (30 mL), glyoxal (0.60 mL, 4 mmol, 40% glyoxal in water) was added in drop wise at room temperature. The reaction mixture was heated at 80 °C for 24 h which resulted in the formation of a brown coloured precipitate. The precipitate was filtered through frit, washed twice with diethyl ether (20 mL) and followed by washing with a solvent mixture of TH /diethyl ether (3 mL/17 mL) to afford colourless solid which was purified by column chromatography (SiO_2, hexane/ethylacetate: 1/1 followed by methanol/dichloromethane: 2/98) to yield **3** as a colourless solid. Single crystals of **3** suitable for X-ray diffraction were obtained by slow evaporation of saturated solution of **3** in DMSO. Yield: 0.54 g, (70 %). Mp: 274-278 °C (decomp.). Anal. Calcd for $C_{21}H_{25}BF_2N_2O_2$: C, 65.30; H, 6.52; N, 7.25. Found: C, 65.68; H, 6.63; N, 7.44. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 2.29 (s, 12H, C$H_{3\ o\text{-}Mes}$), 2.37 (s, 6H, C$H_{3\ p\text{-}Mes}$), 6.0 (d, J = 3 Hz, 2H, C$H_{\text{im-4,5}}$), 7.02 (s, 4H, CH_{Mes}), 8.95 (s, 1H, C_2–H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 18.1 (C$H_{3\ \text{Mes}}$), 18.4 (C$H_{3\ \text{Mes}}$), 21.0 (C$H_{3\ \text{Mes}}$), 92.1 (C$H_{\text{im-4,5}}$), 129.7, 129.8, 130.8, 135.8, 137.5, 139.6, 159.2 (NCN). ^{11}B NMR (DMSO-d_6, 128 MHz): δ 5.26 (s, 1B, BF_2). ^{19}F NMR (DMSO-d_6, 376 MHz): δ -142.14 (dd, $^{2}J_{FF}$ = 84 Hz, $^{1}J_{FB}$ = 27 Hz, 1F, BF_2), -145.45 (dd, $^{2}J_{FF}$ = 84 Hz, $^{1}J_{FB}$ = 27 Hz, 1F, BF_2). ^{1}H NMR (CD_3CN, 500 MHz): δ 2.26 (s, 6H, C$H_{3\ \text{Mes}}$), 2.28 (s, 6H, C$H_{3\ \text{Mes}}$), 2.42 (s, 6H, C$H_{3\ \text{Mes}}$), 6.01 (s, 2H, C$H_{\text{im-4,5}}$), 7.02 (s, 4H, CH_{Mes}), 8.04 (s, 1H, C_2–H). ^{13}C NMR (CD_3CN, 100 MHz): δ 18.2 (C$H_{3\ \text{Mes}}$), 18.5 (C$H_{3\ \text{Mes}}$), 21.0 (C$H_{3\ \text{Mes}}$), 93.3 (C$H_{\text{Im-4,5}}$), 130.4, 130.6, 130.7, 136.5, 138.2, 141.1, 158.8 (NCN). IR (KBr, cm^{-1}): 2922 (vs), 2853 (s), 1627 (w), 1459 (w), 1376 (vw), 1290 (vw), 1248 (vw), 1086 (w), 1014 (w), 886 (vw), 852 (w), 659 (w), 600 (w), 570 (vw), 547 (vw), 427 (vw), 406 (w) cm^{-1}. ESI-MS: calcd 367.1988, found 367.1992 $(M\text{-}F^-)^+$.

Synthesis of compound 5a. To a stirred solution of **3** (0.154 g, 0.4 mmol) in THF (20 mL) at 0 °C was added KHMDS (0.8 mL, 0.4 mmol) and stirred for 15 min. During this period, a yellow–orange coloured

mixture was formed, to which *S*-methyl methanethiosulfonate (~0.06 mL, 0.6 mmol) was added at 0 °C and allowed to warm to room temperature and further stirred for 3 h. The volatiles were removed and the resulting residue was washed with diethyl ether to afford an orange coloured residue which was dissolved in acetonitrile (10 mL) and filtered through a small pad of celite. The filtrate was concentrated and the resulting crude product was purified by column chromatography (SiO_2, dichloromethane followed by methanol/dichloromethane: 2/98) to yield **5a** as an off white solid. Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of ethylacetate/DMSO (10/1) solvent mixture of **5a** at room temperature. Yield: 0.09 g, (54 %). Mp: 112-116 ˚C (decomp.). Anal. Calcd for [$C_{22}H_{27}BF_2N_2O_2S$+$(CH_3)_2SO$]: C, 56.47; H, 6.52; N, 5.49. Found: C, 57.65; H, 6.26; N, 5.13. ^{1}H NMR (CD_3CN, 500 MHz): δ 1.73 (s, 3H, SCH_3), 2.27-2.44 (m, 18H, $CH_{3\ Mes}$) 5.88 (s, 2H, $CH_{\ im\text{-}4,5}$), 7.04 (s, 4H, CH_{Mes}). ^{13}C NMR (CD_3CN, 125 MHz): δ 13.2, 17.2 ($CH_{3\ Mes}$), 17.7 ($CH_{3\ Mes}$), 20.1 ($CH_{3\ Mes}$), 92.5 ($CH_{\ Im\text{-}4,5}$), 129.7, 135.8, 138.6, 140.7, 167.4 (N2*C*-SCH$_3$). ^{11}B NMR (CD_3CN, 128 MHz): δ 5.18 (m, 1B, BF_2). ^{19}F NMR (CD_3CN, 376 MHz) δ -144.09 (m, 1F, BF_2), -146.99 (m, 1F, BF_2). IR (KBr, cm^{-1}): 2921 (m), 1610 (m), 1558 (s), 1531 (vs), 1480 (m), 1358 (w), 1308 (w), 1267 (w), 1211 (w), 1173 (s), 1082 (vs), 880 (w), 852 (w), 579 (w), 550 (w) cm^{-1}. ESI-MS: calcd 413.1865, found 413.1873 $(M\text{-}F^-)^+$.

Synthesis of compound 5b. Compound **5b** was prepared by using a procedure similar to that for compound **5a**. Compound **3** (0.154 g, 0.4 mmol), KHMDS (0.8 mL, 0.4 mmol), diphenylphosphine chloride (~0.12 mL, 0.6 mmol) and THF (20 mL) were used. The volatiles were removed under vacuum and the residue was washed with diethyl ether to afford a pale yellow residue which was dissolved in acetonitrile (10 mL) and filtered through celite. The filtrate was dried under vacuum to afford the title compound. Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of acetonitrile/DMSO (5/1) solvent mixture of **5b** at room temperature. Yield: 0.17 g, (75%). Mp: 172-176 ˚C (decomp.). Anal. Calcd for $C_{33}H_{34}BF_2N_2O_2P$: C, 69.48; H, 6.01; N, 4.91. Found: C, 68.93; H, 5.99; N, 4.50. ^{1}H NMR (CD_3CN, 500 MHz): δ 2.08 (s, 6H, $CH_{3\ Mes}$), 2.13 (s, 6H, $CH_{3\ Mes}$), 2.44 (s, 6H, $CH_{3\ Mes}$), 5.86 (s, 2H, $CH_{\ im\text{-}4,5}$), 6.51 (s, 2H, CH_{Mes}), 6.63 (s, 2H, CH_{Mes}), 7.08 (m, 4H, CH_{Ph}), 7.22-7.33 (m, 6H, CH_{Ph}). ^{13}C NMR (CD_3CN, 125 MHz): δ 18.3 ($CH_{3\ Mes}$), 18.9 ($CH_{3\ Mes}$), 19.9 ($CH_{3\ Mes}$), 92.6 ($CH_{\ im\text{-}4,5}$), 126.8, 128.5, 129.5, 129.7, 130.1, 130.8, 135.1, 135.3, 137.7, 139.8, 171.2 (N_2CPPh_2). ^{11}B-NMR (CD_3CN, 128 MHz): δ 5.15 (br, 1B, BF_2). ^{19}F-NMR (CD_3CN, 376 MHz): δ -145.30 (m, 1F, BF_2), -147.45 (m, 1F, BF_2). ^{31}P NMR (CD_3CN, 162 MHz): δ -3.28 (s, 1P, *P*Ph2). IR (KBr, cm^{-1}): 2954 (w), 2922 (w), 1609 (w), 1511 (vs), 1479 (m), 1437 (m), 1377 (w), 1308 (w), 1277 (w), 1173 (s), 1162 (s), 1108 (m), 1069 (s), 1045 (s), 1007 (m), 954 (w), 918 (w), 878 (m), 861 (m), 745 (s), 698 (s), 579 (w), 500 (w) 486 (w), 435 (w) cm^{-1}. ESI-MS: calcd 551.2429, found 551.2432 $(M\text{-}F^-)^+$.

Synthesis of compound 5c. Compound **5c** was prepared by using a procedure similar to that for compound **5a**. Compound **3** (0.154 g, 0.4 mmol), KHMDS (0.8 mL, 0.4 mmol), iodine (0.152 g, 0.6 mmol) and THF (20 mL) were used. After evaporation of all volatiles, the crude product was purified by column chromatography (SiO_2, dichloromethane followed by methanol/dichloromethane: 2/98) to yield **5c** as a pale yellow solid. Yield: 0.13 g, (64%). Mp: 198-202 ˚C (decomp.). Anal. Calcd for $C_{21}H_{24}BF_2IN_2O_2$: C, 49.25; H, 4.72; N, 5.47. Found: C, 49.58; H, 5.15; N, 4.45. ^{1}H NMR (CD_3CN, 500 MHz): δ 2.20 (s, 6H, $CH_{3\ Mes}$), 2.32 (s, 6H, $CH_{3\ Mes}$), 2.39 (s, 6H, $CH_{3\ Mes}$), 5.87 (s, 2H, $CH_{\ im\text{-}4,5}$), 7.07 (s, 4H, CH_{Mes}). ^{13}C NMR (CD_3CN, 100 MHz): δ 17.2 ($CH_{3\ Mes}$), 17.8 ($CH_{3\ Mes}$), 20.3 ($CH_{3\ Mes}$), 92.7 ($CH_{\ im\text{-}4,5}$), 129.6, 129.9, 132.8, 135.7, 138.1, 140.3, 146.3. ^{11}B NMR (CD_3CN, 128 MHz; δ, ppm): 5.23 (br, 1B, BF_2). ^{19}F NMR (CD_3CN, 376 MHz): δ -144.69 (m, 1F, BF_2), -147.99 (m, 1F, BF_2). IR (KBr, cm^{-1}): 2920 (m), 1609 (m), 1538 (vs), 1531 (vs), 1479 (m), 1452 (m), 1362 (m), 1308 (w), 1285 (w), 1262 (m), 1149 (s), 1082 (vs), 1007 (vs), 951 (m), 890 (m), 865 (m), 768 (w), 726 (w), 677 (w), 573 (w), 549 (w), 408 (w) cm^{-1}. ESI-MS: calcd 493.0954, found 493.0953 $(M\text{-}F^-)^+$.

Synthesis of Compound 6a. To a mixture of **3** (0.154 g, 0.4 mmol) and elemental sulfur (0.019 g, 0.6 mmol) in Schlenk flask was added THF (20 mL) and cooled to 0 °C. To it, KHMDS (3 mL, 1.44 mmol) was added at 0 °C and stirred for 15 min. During this period a yellow–orange coloured mixture was obtained which was allowed to warm to room temperature with continuous stirring for 3 h. Ammonium chloride (0.043 g, 0.8 mmol) was added as solid to the reaction mixture followed by addition of water (0.4 mL) and stirred for 30 min. All volatiles were removed under vacuum, the residue was extracted with dichloromethane and filtered through celite. The filtrate was concentrated to dryness and the crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate: 1/1) to yield **6a** as a pale yellow coloured solid. Single crystals suitable for X-ray diffraction were grown by slow evaporation of ethyl acetate/hexane (1/1) mixture of compound **6a** at room temperature. Yield: 0.11g (74 %). Mp: 190-194 ˚C (decomp.). Anal. Calcd for $C_{21}H_{26}N_2O_2S$: C, 68.08; H, 7.07; N, 7.56. Found: C, 67.79; H, 6.92; N, 7.22. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.17 (s, 6H, $CH_{3\ Mes}$), 2.26 (s, 6H, $CH_{3\ Mes}$), 2.33 (s, 6H, $CH_{3\ Mes}$), 5.42 (s, 2H, $CH_{\ im\text{-}4,5}$), 6.92 (m, 4H, $CH_{\ Mes}$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 17.9 ($CH_{3\ Mes}$), 18.6 ($CH_{3\ Mes}$), 21.2 ($CH_{3\ Mes}$), 81.7 ($CH_{\ im\text{-}4,5}$), 129.4, 132.1, 136.0, 138.5, 180.1 (*C*=S). IR (KBr, cm^{-1}): 3140 (br, m), 2919 (m), 2855 (w), 1655(w), 1610 (w), 1484 (vs), 1455 (vs), 1397 (s), 1373 (w), 1300 (vs), 1253 (s), 1122 (vs), 1091 (s), 1051 (m), 1032 (m), 883 (w), 850 (s), 734 (w), 678 (w), 621 (w), 579 (w), 520 (w), 439(w) cm^{-1}. ESI-MS: calcd 371.1788, found 371.1790 $(M+H^+)^+$.

Synthesis of compound 6b. Compound **6b** was prepared by using a procedure similar to that for compound **6a**. Compound **3** (0.154 g, 0.4 mmol), selenium (0.047 g, 0.6 mmol) and dry THF (20 mL) were used. After evaporation of all volatiles, the crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate: 5/1 to 1/1) to yield **6b** as a pale yellow coloured solid. Single crystals suitable for X-ray diffraction were grown by slow evaporation of ethyl acetate/hexane (1/1) mixture of compound **6b** at room temperature. Yield: 0.10 g (60 %). Mp: 206-210 ˚C (decomp.). Anal. Calcd for $C_{21}H_{26}N_2O_2Se$: C, 60.43; H, 6.28; N, 6.71. Found: C, 60.32;

H, 6.19; N, 6.57. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.25 (s, 6H, C$H_{3\ Mes}$), 2.30 (s, 6H, C$H_{3\ Mes}$), 2.40 (s, 6H, C$H_{3\ Mes}$), 5.35 (s, 2H, C$H_{\text{im-4,5}}$), 6.97 (m, 4H, C$H_{\ Mes}$) . ^{13}C NMR ($CDCl_3$, 125 MHz): δ 17.7, 19.0, 21.2, 82.3, 129.7, 132.5, 135.8, 139.2, 181.8 (*C*=Se). ^{77}Se NMR ($CDCl_3$, 76 MHz): δ 169.4 (C=*Se*). IR (KBr, cm^{-1}): 3219(br, s), 2919 (m), 2856 (w), 1742 (w), 1609 (w), 1485 (s), 1457(s), 1394 (m), 1376 (m), 1290 (vs), 1202 (w), 1167 (w), 1077 (vs), 1058 (s), 1036 (s), 979 (w), 865 (w), 850 (w), 732 (w), 665 (w), 578 (w), 433 (w) cm^{-1}. ESI-MS: calcd 419.1232, found 419.1231 $(M+H^+)^+$.

Synthesis of compound 7a. To a mixture of **3** (0.154 g, 0.4 mmol) and elemental sulfur (0.019 g, 0.6 mmol) in Schlenk flask was added THF (20 mL) and cooled to 0 °C. To it, KHMDS (3 mL, 1.44 mmol) was added at 0 °C and stirred for 15 min. During this period a yellow–orange coloured mixture was obtained which was allowed to warm to room temperature and further stirred for 3 h. To this reaction mixture, phenyl boronic acid (0.059 g, 0.48 mmol) was added, stirred for 1 h and the volatiles were removed. The residue was extracted with dichloromethane and filtered through celite. The filtrate was concentrated to dryness, to obtained the crude product which was purified by column chromatography (SiO_2, hexane /ethyl acetate: 5/1) to yield **7a** as a colourless solid. Single crystals suitable for X-ray diffraction were grown by slow evaporation of ethyl acetate/hexane (1/2) solvent mixture of compound **7a** at room temperature. Yield: 0.12 g, (66%). Mp: 260-262 ˚C (decomp.). Anal. Calcd for $C_{27}H_{29}BN_2O_2S$: C, 71.05; H, 6.40; N, 6.14. Found: C, 70.69; H, 6.23; N, 5.92. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.31 (m, 18H, C$H_{3\ Mes}$), 6.21 (s, 2H, C$H_{\text{im-4,5}}$), 7.02 (m, 4H, C$H_{\ Mes}$), 7.42 (t, 2H, C$H_{\ m\text{-Ph}}$), 7.55 (t, 1H, C$H_{\ p\text{-Ph}}$), 7.84 (d, 2H, C$H_{\ o\text{-Ph}}$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 17.9 (*C*$H_{3\ Mes}$), 18.6 (*C*$H_{3\ Mes}$), 21.2 (*C*$H_{3\ Mes}$), 91.3 (*C*$H_{\text{im-4,5}}$), 128.2, 129.6, 129.9, 132.3, 135.4, 135.6, 138.8, 139.1, 181.2 (*C*=S). IR (KBr, cm^{-1}): 2964 (w), 2918 (w), 2854 (w), 1603(m), 1485 (s), 1442 (s), 1421 (s), 1396 (s), 1365 (m), 1346 (m), 1310 (vs), 1299 (vs), 1259 (s), 1236 (m), 1183 (w), 1149 (w), 1086 (vs), 1028 (s), 1011 (w), 900 (w), 849 (w), 801 (w), 758 (w), 736 (w), 696 (vs), 657 (w), 640 (m), 618 (w), 579 (w), 569 (w), 552 (w), 465(w) cm^{-1}. ESI-MS: calcd 457.2116, found 457.2120 $(M+H^+)^+$.

Synthesis of compound 7b. Compound **7b** was prepared by using a procedure similar to that for compound **7a**. Compound **3** (0.154 g, 0.4 mmol), selenium (0.047 g, 0.6 mmol), phenyl boronic acid (0.059 g, 0.48 mmol) and dry THF (20 mL) were used. After evaporation of all volatiles, the crude product was purified by column chromatography (SiO_2, hexane /ethyl acetate: 3/1) to yield **7b** as an off white solid. Single crystals suitable for X-ray diffraction were grown by slow evaporation of chloroform solution of **7b** at room temperature. Yield: 0.05 g, (25%). Mp: 198-200 ˚C (decomp.). Anal. Calcd for $C_{27}H_{29}BN_2O_2Se$: C, 64.43; H, 5.81; N, 5.57. Found: C, 63.85; H, 5.69; N, 5.48. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.33 (m, 18H, C$H_{3\ Mes}$), 6.17 (s, 2H, C$H_{\text{im-4,5}}$), 7.02 (m, 4H, C$H_{\ Mes}$), 7.42 (t, 2H, C$H_{\ m\text{-Ph}}$), 7.56 (t, 1H, C$H_{\ p\text{-Ph}}$), 7.84 (d, 2H, C$H_{\ o\text{-Ph}}$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 18.0 (*C*$H_{3\ Mes}$), 18.8 (*C*$H_{3\ Mes}$), 21.3 (*C*$H_{3\ Mes}$), 92.2 (*C*$H_{\text{im-4,5}}$), 128.0, 128.3, 129.7, 130.0, 132.8, 135.4, 138.5, 139.3, 182.9 (*C*=Se). ^{77}Se NMR ($CDCl_3$, 76 MHz): δ 194.4 (C=*Se*). IR (KBr, cm^{-1}): 3079 (w), 2959 (s), 2923 (vs), 2853 (s), 1712 (w), 1603 (m), 1610 (w), 1486 (s), 1449 (s), 1408 (s), 1393 (s), 1375 (vs), 1363 (vs), 1338 (m), 1306 (s), 1291 (vs), 1260 (s), 1250 (s), 1183 (w), 1091 (vs), 1091 (s), 1064 (s), 1030 (s), 1012 (m), 997 (w), 900 (w), 847 (m), 801 (w), 759 (w), 728 (w), 692 (vs), 687 (vs), 650 (m), 634 (m), 596 (w), 576 (m), 551 (w), 531 (w), 429 (w), 410 (w) cm^{-1}. ESI-MS: calcd 505.1660, found 505.1604 $(M+H^+)^+$.

Synthesis of compound 8. To a mixture of **3** (0.386 g, 1 mmol) and trimethyloxonium tetrafluoroborate (0.178 g, 1.2 mmol) in Schlenk flask was added dichloromethane (40 mL) and refluxed for 10 h. After cooling to room temperature, water (0.02 mL) was added and stirred for 15 min. The reaction mixture was filtered through a pad of celite and filtrate was concentrated to dryness under vacuum and the resulting residue was washed with diethyl ether to afford a colourless solid. Yield: 0.40 g, (80 %). Mp: 78-82 ˚C. Due to the hygroscopic nature of **8**, elemental analysis could not be carried out. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.25 (m, 18H, C$H_{3\ Mes}$), 3.40 (s, 3H, OCH_3), 5.72 (d, J = 5.15 Hz, 1H, C$H_{\text{im-4-OMe}}$), 6.23 (d, J = 5.15 Hz, 1H, C$H_{\text{Im-5-OH}}$), 6.94 (m, 4H, C$H_{\ Mes}$), 7.87 (s, 1H, N_2CH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 17.7 (*C*$H_{3\ Mes}$), 17.8 (*C*$H_{3\ Mes}$), 18.5 (*C*$H_{3\ Mes}$), 21.1 (*C*$H_{3,Mes}$), 61.1 (O*C*H_3), 85.3, 92.1, 127.8, 128.8, 129.9, 130.1, 130.3, 135.9, 136.7, 141.1, 157.1 (N_2*C*H). ^{11}B NMR ($CDCl_3$, 128 MHz; δ, ppm): -2.13 (s, 1B, (*B*F_4)$^-$). ^{19}F NMR ($CDCl_3$, 376 MHz): δ -152.19 (s, 4F, (B*F*$_4$)$^-$). IR (KBr, cm^{-1}): 3426 (br), 2923 (w), 1626 (vs), 1483 (w), 1464 (w), 1376 (w), 1249 (m), 1110 (s), 1083 (s), 1037 (s), 854 (w), 624 (w), 572 (w), 533 (w), 521 (w), 412 (w) cm^{-1}. ESI-MS: calcd 353.2224, found 353.2228 $(M-(BF_4)^-)^+$.

Synthesis of compound 9a. To a mixture of **8** (0.285 g, 0.65 mmol) and elemental sulfur (0.032 g, 0.975 mmol) in Schlenk flask was added THF (30 mL) and cooled to 0° C. To it, KHMDS (3.2 mL, 1.56 mmol) was added at 0 °C and stirred for 15 min. During this period a yellow–orange coloured mixture was obtained which was allowed to warm to room temperature and further stirred for 3 h. Ammonium chloride (0.035 g, 0.65 mmol) was added as solid to the reaction mixture followed by addition of water (1 mL) and stirred for 30 min. All volatiles were removed under vacuum, the residue was extracted with dichloromethane and filtered through a pad of celite. The filtrate was concentrated to dryness and the crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate: 5/1) to yield **9a** as a colourless solid. Single crystals suitable for X-ray diffraction were grown by slow evaporation of ethyl acetate/hexane (1/1) mixture of compound **9a** at room temperature. Yield: 0.20 g (81 %). Mp: 172-176 ˚C (decomp.). Anal. Calcd for $C_{22}H_{28}N_2O_2S$: C, 68.72; H, 7.34; N, 7.29. Found: C, 68.97; H, 7.48; N, 7.48. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.26 (m, 18H, C$H_{3\ Mes}$), 3.31 (s, 3H, OCH_3), 4.94 (d, J = 1 Hz, 1H, C$H_{\text{im-4-OMe}}$), 5.32 (d, 1H, J = 1 Hz, C$H_{\text{im-5-OH}}$), 6.94 (m, 4H, C$H_{\ Mes}$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 17.7 (*C*$H_{3\ Mes}$), 18.6 (*C*$H_{3\ Mes}$), 18.9 (*C*$H_{3\ Mes}$), 21.2 (*C*$H_{3\ Mes}$), 57.6 (O*C*H_3), 88.9, 98.4, 129.6, 132.1, 133.3, 135.8, 136.5, 138.5, 138.8, 139.3, 181.3 (*C*=S). IR (KBr, cm^{-1}): 3319 (m), 2921 (m), 2856 (w), 1645 (w), 1609 (w), 1484 (vs), 1450 (s), 1393 (m), 1377 (m), 1323 (vs), 1242 (s), 1193 (w), 1075 (s), 972 (w), 850 (w), 739

(w), 682 (w), 581 (w) cm^{-1}. ESI-MS: calcd 385.1944, found 385.1952 $(M+H^+)^+$.

Synthesis of compound 9b. Compound **9b** was prepared by using a procedure similar to that for compound **9a**. Compound **8** (0.817 g, 1.86 mmol), KHMDS (9 mL, 4.5 mmol), selenium (0.220 g, 2.79 mmol) and dry THF (80 mL) were used. After evaporation of all volatiles, the crude product was purified by column chromatography (SiO_2, hexane /ethyl acetate: 5/1) to yield **9b** as a pale yellow coloured solid. Yield: 0.54 g (67%). Mp: 156-158 ˚C (decomp.). Anal. Calcd for $C_{22}H_{28}N_2O_2Se$: C, 61.25; H, 6.54; N, 6.49. Found: C, 62.78; H, 6.86; N, 6.58. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.21 (m, 18H, C$H_{3\ Mes}$), 3.30 (s, 3H, OCH_3), 4.91 (d, J = 1.5 Hz, 1H, C$H_{\text{im-4-OMe}}$), 5.29 (d, J = 1.5 Hz, 1H, C$H_{\text{im-5-OH}}$), 6.93 (m, 4H, CH_{Mes}). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 17.7 (C$H_{3\ Mes}$), 18.7 (C$H_{3\ Mes}$), 19.0 (C$H_{3\ Mes}$), 21.3 (C$H_{3\ Mes}$), 57.9 (OCH_3), 89.8, 99.4, 129.6, 132.7, 133.9, 135.6, 136.3, 138.7, 138.9, 139.1, 182.2 (*C*=Se). ^{77}Se NMR ($CDCl_3$, 76 MHz): δ 167.3 (C=*Se*). IR (KBr, cm^{-1}): 3285 (w), 2922 (s), 2854 (w), 1644 (w), 1609 (w), 1483 (vs), 1456 (vs), 1376 (m), 1312 (vs), 1292 (vs), 1239 (s), 1192 (w), 1073 (vs), 850 (w), 733 (w), 655 (w), 577 (w) cm^{-1}. ESI-MS: calcd 433.1389, found 433.1397 $(M+H^+)^+$.

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Graphical Abstract

Labile Dioxy-Functionalised Zwitterionic Imidazolinium Salt: Access to Zwitterionic and Neutral Imidazolidin-2-ylidene Derivatives and π-Acceptor Properties of Imidazolidine-2-selones

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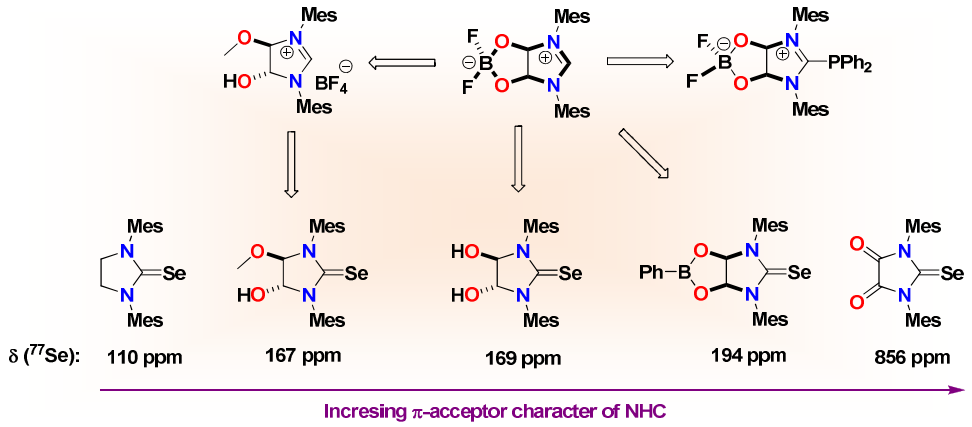
A new method for the synthesis of symmetrical and unsymmetrical oxy-functionalised imidazolinium salt (**3** and **8**) and their derivatives with different electrophiles, and chalcogens are reported. Further, the effect of backbone functional group derivatization on the π-acceptor property of NHCs is evaluated using ^{77}Se NMR in their respective imidazolin-2-selones.



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