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Facile synthesis of benzimidazolin-2-chalcogenones: Nature of the carbon–chalcogen bond

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ABSTRACT

A new method using chalcogen nucleophiles E^{2-}/E_2^{2-} (E = S, Se, Te) for the convenient and high yield synthesis of benzimidazolin-2-chalcogenones has been developed. The reaction of strong nucleophiles E^{2-}/E_2^{2-} with various benzimidazolium salts under mild conditions afforded benzimidazolin-2-chalcogenones (**10a**–**10g**) in better yield compared to the other methods involving E^0 powder. Benzimidazolin-2-tellurones were found to be unstable when pyridyl/phenyl groups were bonded to one of the nitrogens of the benzimidazolium salts and the reaction led to the isolation of the corresponding diamines (**12a** and **12b**). The selenones/tellurones could be easily oxidized to the corresponding dihaloderivatives (**16a**–**16e**) by the reaction of the chalcogenones with bromine/iodine. The nature of the carbon–chalcogen double bond has been investigated with the help of single crystal X-ray, NMR spectroscopy and Density Functional Theory (DFT) calculations.

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1. Introduction

The chemistry of *N*-heterocyclic carbenes (NHCs) and their metal complexes [1,2] is of considerable current interest due to their applications in homogeneous catalysis [3] and medicinal chemistry [4]. The successful applications of *N*-heterocyclic carbene (NHC) based catalysts include; carbon–carbon cross-coupling reactions [5], olefin metathesis [6], hydrosilylation [7], and CO/ethylene copolymerization [8]. The *N*-heterocyclic carbenes play an important role both as reactive intermediates and as ligands in complexes of metal and metalloid centers because of highly nucleophilic character [9].

The chalcogen derivatives of NHC have been studied by several groups. The first chalcogenone, 1,3-dialkylimidazole-2-thione was synthesized by reacting the corresponding iodide salt with sulfur powder in methanol in the presence of potassium carbonate [10]. Arduengo et al. reported synthesis of the thione and tellurium analogs (**1**) [11,12]. The chalcogen(IV) compounds (**2**) have been synthesized by treating chalcogenones with halogens/halogenating agents [13,14]. Devillanova and co-workers have synthesized stable bis(selenones) and their halogen derivatives [15]. The benzimidazolin-2-chalcogenones have been synthesized using other chalcogen sources such as CSe_2, thiophosgene, etc. instead of elemental chalcogens [16,17].

Recently, our group and others have extensively studied the synthesis, structure and reactivity of diaryl diselenide (**3**–**5**) (Fig. 1) [18], stabilized by intramolecular secondary bonding interaction. Some derivatives exhibit excellent glutathione peroxides-like (GPx-like) activities. In view of the interesting reactivity and GPx-like activities shown by intramolecularly coordinated organochalcogen systems, we envisaged to synthesize a new series of organochalcogen compounds stabilized by intramolecular coordination with carbene carbon as the donor atom instead of heteroatoms (N, O). In this paper we report the attempted synthesis of organochalcogen derivatives stabilized by carbene carbon as the donor atom. Various commonly used strategies explored for the synthesis of the desired dichalcogenides stabilized by carbene donors always led to the facile formation of the chalcogenone derivatives in very good yields. In view of the interesting observations, we systematically explored the reaction for developing a facile high yield synthetic route for benzimidazolin-2-chalcogenones and their halogen derivatives.

We have further synthesized a series of benzimidazolin-2-chalcogenones (chalcogen = S, Se, Te) with different substituent groups at the benzimidazolium nitrogen and their halogen derivatives to enable study of the effect of the substituent groups at benzimidazole nitrogen on the stability of *N*-heterocyclic chalcogenones, nature of C=E bond (E = S, Se, Te) and the relative charges

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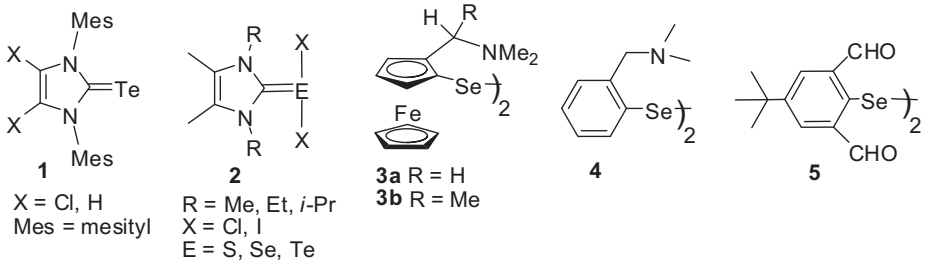


Fig. 1. Chalcogen derivatives.

on the chalcogen atoms. We have also probed in depth the nature of the bond between carbene carbon and chalcogens using DFT calculations.

2. Results and discussion

2.1. Synthesis

The precursor benzimidazolium salts were prepared by two different routes; 1) nucleophilic substitution at the nitrogen atoms of the imidazole, or 2) multi-component reactions for the generation of the *N*,*N*′-substituted heterocycles [19]. Compounds **7a**–**7d** were prepared by alkylation [5] or arylation [20] of benzimidazole (**6**). The *N*,*N*′-substituted benzimidazolium salts **8a**–**8d** were synthesized from the respective *N*-substituted benzimidazoles **7a**–**7d** and 2-bromobenzylbromide (Scheme 1) [21].

The synthesis of carbene stabilized dichalcogenides **9a** and **9b** was attempted by two different methods (Scheme 2). The synthesis of **9a** and **9b** was attempted by the lithiation (method A) of salt **8c** with *n*-BuLi at different concentrations (1 eqv, 2 eqv or 3 eqv) followed by the addition of selenium/tellurium powder in dry THF and oxidative work up. However, the reactions always afforded benzimidazolin-2-chalcogenones **10d** and **10f** (30–40%), instead of the desired compounds. Method B involved the addition of **8c** to an *in situ* generated solution of disodium diselenides/disodium ditellurides (1 eqv) in the presence of potassium *tert*-butoxide in THF. The reaction, again, led to the isolation of same products (**10d** and **10f**) in much better yield (60–80%) when compared to method A. When derivatives **10d** and **10f** were prepared by the conventional method C i.e., by treatment of salt **8c** with potassium *tert*-butoxide in THF followed by selenium/tellurium, the yield of the desired product (**10d** and **10f**) were poor (20–30%).

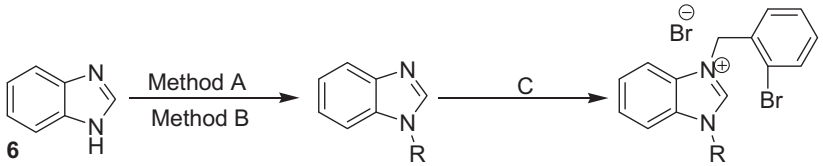
In view of these initial results, we next set out to systematically explore the utility of this method for the synthesis of benzimidazolin-2-chalcogenones using method B.

The *n*-butyl substituted thione **10a** was synthesized by reacting benzimidazolium salt (**8c**) with disodium disulfide [22]. Similarly selenones (**10b**–**10e**) were prepared from the corresponding salts (**8a**–**8d**). The plausible mechanism for the high yield formation of chalcogenones by method B is shown in Scheme 3.

The high yields of the chalcogenones derived from the less reactive benzimidazolium salts compared to the more reactive imidazolium salts, we believe, is due to the more facile attack of the strong nucleophiles, E_2^{2-} (E = S, Se and Te) compared to weaker nucleophiles, E^0 (E = S, Se and Te). When one chalcogen nucleophile E^{2-} (i.e. Na_2Se) rather than two chalcogen nucleophile, (Na_2E_2) was used, the reaction afforded **10d** in excellent yield (more than 98%).

The synthesis of the tellurones derived from benzimidazolium salts having electron-withdrawing groups on the nitrogen turned out to be much more difficult as compared with their sulfur and selenium analogs. The *n*-butyl- and *iso*-propyl substituted tellurones (**10f** and **10g**) could be easily synthesized by treating the corresponding salts (**8c** and **8d**) with an *in situ* generated disodium ditelluride. The tellurones are stable at room temperature in the solid state; however, they slowly decomposed in solution to give a tellurium mirror. Attempted synthesis of compounds **11** from salt **8** using all three methods was unsuccessful. The reaction afforded compounds **12a** [23] and **12b** in moderate yield (Scheme 4). The cleavage of the carbene carbon from benzimidazole ring in **12a** and **12b** may be due to the destabilization of C=Te bond by the electron withdrawing groups present on the benzimidazolium nitrogen and the steric crowding near the carbene carbon.

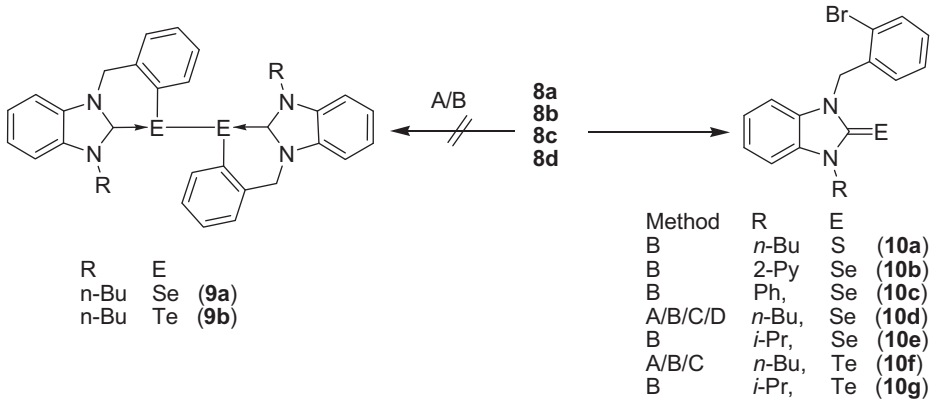
To establish the effect of the electron withdrawing group, the synthesis of 1,3-bis(2-bromobenzyl)-1H-benzo[d]imidazole-2(3H)-



Method	R		R		Yield
A	2-Py	(**7a**)	2-Py	(**8a**)	82%
A	Ph	(**7b**)	Ph	(**8b**)	37%
B	*n*-Bu	(**7c**)	*n*-Bu	(**8c**)	71%
B	*i*-Pr	(**7d**)	*i*-Pr	(**8d**)	68%

Reagents and conditions: A) Benzotriazole, DMSO. *t*-BuOK, arylbromide, CuI; B) 30% aq. NaOH, 1.5% equiv Bu_4NBr, 1.2 equiv bromoalkane, 3 h, 55 °C; C) 2-bromobenzylbromide, 1,4-dioxane, reflux

Scheme 1. Synthesis of benzimidazolium salts.



Scheme 2. Synthesis of benzimidazolin-2-chalcogenones.

selenone was attempted (Scheme 5). The desired benzimidazole **13** was prepared according to the literature method [24]. The addition of *o*-bromobenzyl bromide to (1H-benzo[d]imidazol-1-yl)(phenyl) methanone (**13**) in 1,4-dioxane unexpectedly, afforded compound **14**. The formation of **14** from **13**, presumably, takes place via the hydrolysis of the benzoyl group in **13** with the traces of water [24]. Salt **14** could also be directly synthesized from the reaction of benzimidazole with two equivalents of 2-bromobenzylbromide. The reaction of compound **14** with disodium diselenide gave a white crystalline product, which was characterized as benzimidazolone **15**, instead of the expected 1,3-bis(2-bromobenzyl)-1H-benzo[d]imidazole-2(3H)-selenone. This, probably, results from the hydrolysis of **14**. Similar hydrolysis reactions of carbenes to imidazolones are reported [24]. The substituted benzimidazolones are crucial precursors to many pharmacologically active compounds [25].

Compounds **10a**–**10g** were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR signal for the acidic NCHN proton (around δ 11–12 ppm) present in salts **8a**–**8d** was absent in the chalcogenone derivatives. The significant shift in the ^{13}C NMR signal of carbene carbon from the precursor salt (δ 143 ppm in **8c**) to the chalcogenone compound (δ 167 ppm in **10d**) suggested the deshielding of the carbene carbon. It is further observed that the ^{13}C NMR signal for **10a** was downfield shifted compared with **10d** and **10f** (see Table 1). This was probably due to the decreasing electronegativity and increasing size of the chalcogen atoms.

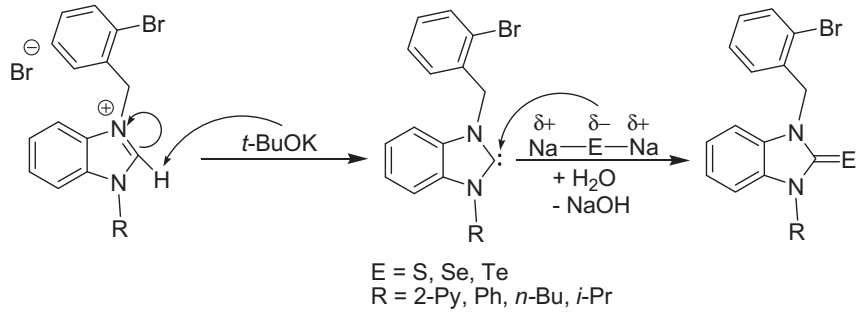
After obtaining the chalcogenones, we next set out to study their oxidation reactions with halogens. Bromination of selenone **10d** with bromine in THF gave a crystalline yellow-colored product **16a** in good yield. Similarly, the oxidative addition products **16b**–**16d** were isolated in excellent yields by the reaction of selenones **10b**–**10f** with iodine. The reaction of iodine with tellurone **10d** afforded a dark red colored compound **16e** in excellent yield (Scheme 6).

Compounds **16a**–**16e** were characterized by ^{1}H, ^{13}C, ^{77}Se and ^{125}Te NMR spectroscopy. As expected, the bromine derivative shows more downfield shifts in ^{77}Se NMR (δ 393 ppm) spectrum compared to the iodine derivatives ($\sim\delta$ 218 ppm). For the iodo-derivatives of selenones, variation of the substituents (2-Py, *n*-Bu, *i*-Pr) at the N of the benzimidazole has no effect on the chemical shift of the ^{77}Se NMR signal. The iodo derivative of the butyl substituted tellurone shows a large downfield shift in the ^{125}Te NMR signal (δ −130 ppm in **10f** to δ 330 ppm in **16e** see in Table 1).

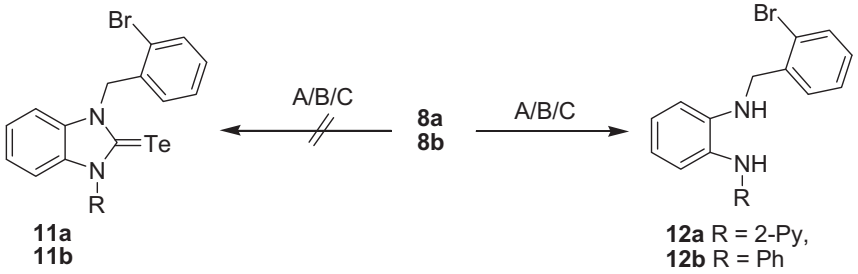
2.2. Single crystal X-ray crystallographic studies

2.2.1. Molecular and crystal structure of compounds *15, 10a, 10d and 10f*

The molecular structures of compounds **15**, **10a**, **10d** and **10f** are depicted in Fig. 2 (for molecular structures of compounds **10b**, **10e** and **10g** see the Supporting information) and selected bond lengths and bond angles are given in Table 2. In compound **15**, the C–O distance (1.226(8) Å) is closer to the C–O double bond distance [26]. Both 2-bromo-benzyl rings are *trans* to each other with respect to the core benzimidazole ring. The benzimidazole core of **10a** is planar and the sulfur atom is also in the same plane. The C–S bond distance (1.674(2) Å) is shorter than the single bond (1.789(1) Å) and longer than the double bond distances (1.635 Å)



Scheme 3. Plausible mechanism for the formation of chalcogenones.



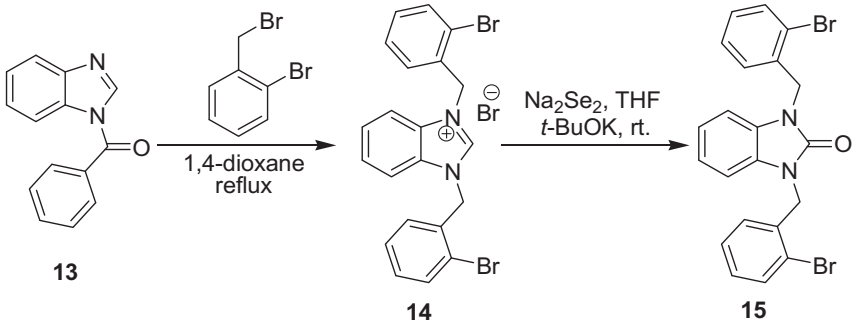
Scheme 4. Attempted synthesis of tellurone with electron withdrawing groups.

[27]. This suggested a partial carbon–sulfur double bond character. The C–Se bond distances in the cases of selenones **10b** (1.825(2) Å), **10d** (1.831(5) Å) and **10e** (1.833(2) Å) are similar and are comparable with the reported value [13]. The C–Te bond distances for **10f** (2.0772(19) Å) and **10g** (2.062(4) Å) are similar. The carbon–chalcogen bond distances, as expected, gradually increase from O to Te. The carbene C–N bond length of the compounds **10a**, **10b**, **10d**, **10e**, **10f** and **10g** are similar. Also the bond angles around the carbene carbon in compound **10a** (N2–C1–S 127.75(14)°, N1–C1–S 125.93(14)° and N2–C1–N1 106.32(16)°) are comparable with compounds **10b**, **10d** and **10f**, while in *iso*-propyl substituted compounds **10e** and **10g**, the angle N1B–C1–N1A (107.30(17)°) is slightly higher than the other compounds.

The intermolecular CH···O distance (2.324 Å) in compound **15** lead to a chain of molecules formed due to two different types of intermolecular CH···O bond interactions (Fig. 3a). In the crystal packing of **10f** (Fig. 3b), the molecules are linked by intermolecular Te···Te* and Te···Br interactions giving rise to a ribbon-like structure. The intermolecular Te···Te* (3.675 Å) and Te···Br (3.724 Å) distances are higher than the sum of covalent radii of two atoms (2.94 Å and 2.51 Å) [28]. These are significantly shorter than the sum of their van der Waals radii (4.12 Å and 4.15 Å) [29] respectively. The intermolecular CH···Te distance (2.944 Å) in crystal packing of **10g** is higher than the sum of covalent radii (1.7 Å), but shorter than the sum of van der Waals radii (3.15 Å). This suggested the existence of intermolecular CH···Te interactions (Fig. 3c). Steiner was the first to report a similar intermolecular CH···Te hydrogen bonding interaction [30].

2.2.2. Molecular and crystal structure of compounds *16a*, *16c* and *16e*

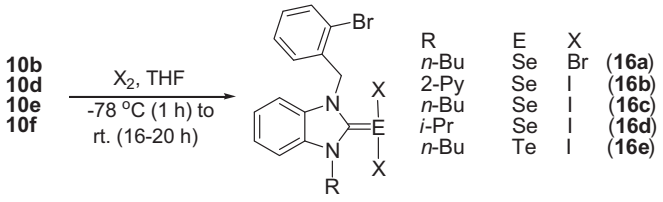
The molecular structures of chalcogen(IV) compounds, **16a**, **16c** and **16e** are shown in Fig. 4. In compound **16a**, the geometry around selenium is T-shaped where selenium bonded two bromides and one carbene carbon. On considering the two equatorial lone pairs of selenium, the geometry can be regarded as distorted trigonal bipyramidal. The geometries around the selenium and tellurium in compounds **16c** and **16e** respectively resemble to that observed for compound **16a**. In compound **16a**, the benzimidazole ring lies in the equatorial plane and the Br2–Se–Br3 unit is almost perpendicular to this plane. The Se1–Br2 (2.4944(3) Å) bond length is shorter than Se1–Br3 (2.6529(3) Å). Also the bond angles C14–Se1–Br2 (89.18(5)°) and C14–Se1–Br3 (86.36(5)°) are not equal. Ragogna and co-workers [14] have reported a related molecular structure with equal Se–Br bond lengths (2.5870(10) Å) and bond angles (87.87(3)°). The Se1–C14 bond length (1.8967(15) Å) and Br2–Se1–Br3 (175.527(8)°) also resemble with the values reported in literature [14]. In compound **16c**, bond distances I1–Se (2.7040(3) Å) and I2–Se (2.8982(3) Å) are significantly unequal with a difference of 0.2 Å and the bond angle C1–Se–I1 (91.91(7)°) is much larger than C1–Se–I2 (84.22(7)°). However, in the crystal structure reported by Kuhn and co-workers [13], only small differences (0.1 Å) in the bond length of Se–I1 (2.854(1) Å) and Se–I2 (2.768(1) Å) and bond angles I1–Se–C1 (87.3(1)°) and I2–Se–C1 (88.2(1)°) were observed. In compound **16e**, the strong Te···I intermolecular interaction gives rise to a dimeric structure placing the two tellurium atoms at the diagonal corners of the distorted square. The two core benzimidazole rings are planar. The two bond lengths Te–I1 (2.8330(3) Å) and Te–I2 (3.0394(3) Å) are significantly different in compound **16e**. Also the bond angle C1–Te–I1 (88.35(8)°) is quite larger than C1–Te–I2 (80.59(8)°). The dimeric molecule reported by Kuhn et al. [13] has two different bond lengths of Te–I1 (2.989(1) Å) and Te–I2 (2.897(1) Å) and the bond angle C1–Te–I1 (83.6(1)°) is significantly smaller than the C1–Te–I2 (89.8(1)°). The monomeric compound reported in the literature [13] have two equal bond lengths of Te–I1 (2.9446(7) Å) and Te–I2 (2.9333(6) Å) and the similar bond angle C1–Te–I1



Scheme 5. Attempted synthesis of 1,3-bis(2-bromobenzyl)-1H-benzo[d]imidazole-2(3H)-selenone.

Table 1
^{13}C, ^{77}Se and ^{125}Te NMR chemical shift in ppm.

Compound	$^{77}Se/^{125}Te$	^{13}C (only NCN)
8a	–	149.1
8b	–	142.3
8c	–	143.4
8d	–	141.9
10a	–	170.4
10b	101	168.4
10c	95	169.1
10d	60	167.8
10e	58	167.4
10f	−130	147.5
10g	−126	147.5
16a	293	150.0
16b	220	153.1
16c	218	148.3
16d	219	151.4
16e	330	133.4



Scheme 6. Oxidative addition reactions of chalcogenone compounds.

(84.79(11)°) and C1–Te–I2 (84.74(11)°). This molecule showed very weak intermolecular Te–I interactions.

The crystal packing of molecule **16a** shows two types of secondary interactions C–H5A···Br3 (2.925(2) Å) and Br3···Br1 (3.618(5) Å). In the crystal packing diagram of molecule **16c**, two different types of intermolecular secondary interactions C–H17B···I2 (3.062(1) Å) and Se···I2* (3.528(2) Å) have been observed. The other two secondary interactions observed in the crystal packing diagram are CH13B···I2 (3.040(9) Å) and Te···Te* (4.021(7) Å) (Fig. 5a–c).

It is clear from the Table 3 that there is not much effect of the alkyl/aryl substituents at nitrogen atoms on the C–E bond lengths. Expectedly, there is significant increase in the C–E bond distances as we move down the chalcogen group from oxygen to tellurium. Also it is observed that the two Se–X/Te–X bond distances and two C–Se–X/C–Te–X bond angles in compounds **16a**, **16c** and **16e** are significantly different.

2.3. Computational studies

In order to get a better understanding of the bonding mode of synthesized chalcogenones and the variation in their property with the change in the chalcogen atoms, density functional calculations (DFT) were carried out with the Gaussian 03 program [31]. All the structures were optimized at MPW1PW91 method by using Lanl2dz(dp) basis set for S, Se, Te, Br and 6-311g(d,p) for the rest of the atoms. The gas phase optimized geometries obtained on performing DFT calculations were well in conformity with the crystal structures of the respective compounds. In particular the C–E bond (E = S, Se, Te) is very much in agreement with the crystal structure bond lengths. For instance, the C–E bond lengths for **10a**, **10d** and **10f** from the crystal structure are 1.674(2), 1.831(5) and 2.0772(19) Å respectively and are close to the C–E bond lengths of 1.679 Å (**10a**), 1.833 Å (**10d**) and 2.058 Å (**10f**) in the optimized geometries. In case of dihaloderivatives **16c** and **16e** the calculated C–Se and C–Te bond lengths for the optimized structure were found to be 1.901 and 2.118 Å respectively. These values are also close to that obtained from the molecular structures of **16c** and **16e** (1.902 and 2.128 Å for C–Se and C–Te bond lengths respectively).

On analysis of the molecular orbitals (MO's) of the chalcogenones, it becomes apparent that HOMO's of these molecules have significant p-character of chalcogen while the LUMO's have antibonding π^* character associated with C–E bond. The MO's responsible for σ character of C–E bond are buried deep inside the energy levels while high lying MO's contribute to the π character of C–E bond. The frontier orbitals as well as the orbitals that contribute to the σ character of C–Se bond of representative compound **10d** are shown in Fig. 6a–f. The MO responsible for σ character of C–Se bond are the inner MO's such as HOMO-44 and

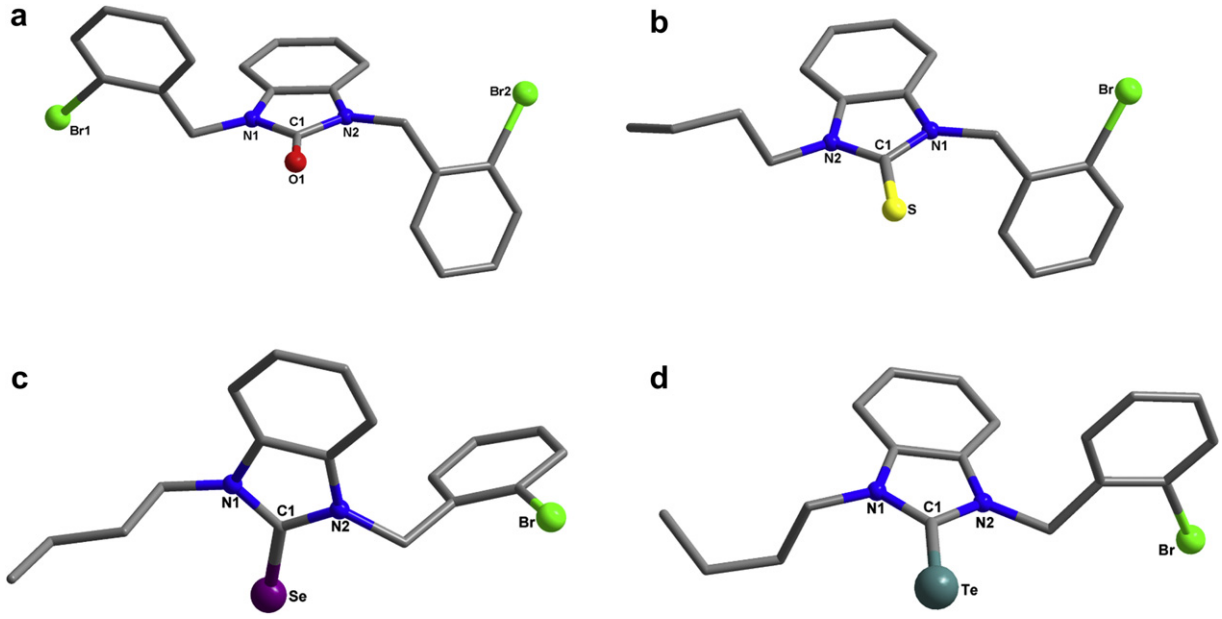


Fig. 2. (a) The molecular structure of compound **15**. (b) The molecular structure of compound **10a**. (c) The molecular structure of compound **10d**. (d) The molecular structure of compound **10f**. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths and bond angles for compounds **10a**, **10b**, **10d**–**10g**, **15**, **16a**, **16c** and **16e**.

Bond lengths [Å]		Bond angles [°]	
15			
O1–C1 1.226(8)	N1–C1 1.376(8)	O1–C1–N1 127.7(6)	O1–C1–N2 126.8(6)
N2–C1 1.377(8)		N1–C1–N2 105.5(6)	
10a			
S–C1 1.674(2)	N1–C1 1.376(2)	N2–C1–S 127.75(14)	N1–C1–S 125.93(14)
N2–C1 1.369(2)		N2–C1–N1 106.32(16)	
10b			
Se–C1 1.825(2)	N1–C1 1.363(3)	N1–C1–Se 126.51(15)	N2–C1–Se 127.47(17)
N2–C1 1.383(3)		N1–C1–N2 106.01(19)	
10d			
Se–C1 1.831(5)	N1–C1 1.364(6)	N1–C1–Se 126.7(4)	N2–C1–Se 126.5(4)
N2–C1 1.367(6)		N1–C1–N(2) 106.8(4)	
10e			
Se–C1 1.833(2)	N1A–C1 1.360(2)	N1B–C1–Se 127.42(15)	N1A–C1–Se 125.29(15)
N1B–C1 1.354(2)		N1B–C1–N1A 107.30(17)	
10f			
Te–C1 2.0772(19)	N1–C1 1.360(2)	N1–C1–Te 127.13(14)	N2–C1–Te 126.05(13)
N2–C1 1.362(2)		N1–C1–N2 106.71(16)	
10g			
Te–C1 2.062(4)	N1–C1 1.342(5)	N1–C1–Te 125.0(3)	N2–C1–Te 127.7(3)
N2–C1 1.368(5)		N1–C1–N2 107.3(3)	
16a			
Se1–C14 1.8967(15)	Se1–Br2 2.4944(3)	C14–Se1–Br2 89.18(5)	C14–Se1–Br3 86.36(5)
Se1–Br3 2.6529(3)		Br2–Se1–Br3 175.527(8)	
16c			
I1–Se 2.7040(3)	I2–Se 2.8982(3)	C1–Se–I1 91.91(7)	C1–Se–I2 84.22(7)
Se–C1 1.902(2)		I1–Se–I2 176.109(9)	
16e			
Te–C1 2.128(3)	Te–I1 2.8330(3)	I1–Te–I2 168.938(9)	C1–Te–I1 88.35(8)
Te–I2 3.0394(3)	Te–I2* 3.5627(3)	C1–Te–I2 80.59(8)	I1–Te–I2* 85.486(7)

HOMO-49 while the MO's such as HOMO-4, HOMO-5 which are higher in energy are responsible for π character of C–Se bond.

Natural bond orbital (NBO) analyses [32] on the optimized geometries of the molecules were performed for the evaluation of Natural Population Analysis (NPA) charges and Wiberg bond indices [33] and it revealed some of the expected trends. NPA results reveal that the net charges on the chalcogen atoms are negative in chalcogenones whereas it is positive for the carbon attached to the chalcogen (see Table 4). In case of thiones, the NPA charge on sulfur atom varies from −0.318 (**19**) to −0.218 (**20a**) depending on the substituent attached to the nitrogen of benzimidazole ring. Similarly, in cases of selenones and tellurones the charges on Se and Te are in the range of −0.212 (**10d**) to −0.177 (**10c**) for Se and −0.160 (**10f**) to −0.129 (**20b**) for Te respectively. It is to be noted that +I effect of alkyl groups (Me, Et, *i*-Pr, *n*-Bu) attached to nitrogen leads to a higher negative charge on chalcogens when compared with chalcogenones having aryl substituents. The model compounds (Fig. 7) were optimized for comparison and we observed that the negative charge on chalcogen decreases from S to Te due to gradual decrease in electronegativity from S to Te. In the case of dihaloderivatives **16c**, **16e** and the model compound **22**, the NPA charges follow a similar pattern as that of chalcogenones. The NPA charge on Te, Se and S in **16e**, **16c** and **22** are 0.455, 0.25 and 0.09 respectively. These high values of NPA charge are in accordance with the high oxidation state of chalcogens as well as delocalization of electronic charge to halides in these compounds.

Computation of the total Wiberg bond index on chalcogen revealed that it is highest for S (1.89–1.92) and lowest for Te (1.56–1.59). For selenones the values of total Wiberg bond index on Se were found in the range of 1.76–1.79. Thus C–E bond has more double bond character for thiones followed by selenones and tellurones. It can be well explained by the proper overlap of similar energy orbitals of carbon and sulfur atoms. The lowest Wiberg bond index of tellurium in tellurone is due to the mismatch of the overlapping carbon and Te orbitals. This also renders C–Te bond relatively weak as compared to C–S or C–Se bond. Also, it is reported in the literature that the donor–acceptor bonding mode not only comprises of a σ donation from the carbene, but also significant π back-bonding from the main group elements [34]. The benzimidazolium systems are considered to be more robust in comparison to the imidazolium as they can provide more stability by further enhancing conjugation in the system. A comparison of Wiberg bond index of chalcogen on model imidazolium derivatives **23a**–**23c** reveals that total bond indices of chalcogen is higher for benzimidazolium systems. As compared to bond indices of 1.89, 1.77 and 1.56 for S, Se and Te in **17a**–**17c** respectively, the corresponding Wiberg bond indices for chalcogens in the imidazolium systems were 1.81, 1.68 and 1.47 respectively, thus pointing towards stronger C–E bond in benzimidazolium systems.

3. Conclusions

In summary, the use of stronger nucleophiles E_2^{2-}/E^{2-} in place of E, in the reaction with benzimidazolium salts afforded a high yield of the desired benzimidazolin-2-chalcogenones. The plausible mechanism for the formation of chalcogenone suggested the favorable attack of E_2^{2-}/E^{2-} nucleophile at the carbene carbon. It is observed that, as the substitution at nitrogen of benzimidazole varies from electron donating groups to electron withdrawing groups, the stability of the chalcogenone compounds decreases. It showed good stability with electron donating groups. The ^{13}C NMR signal of carbene carbons and the chalcogens (^{77}Se, ^{125}Te) showed a partial negative charge on the chalcogen atoms. This is well supported by the DFT calculations. The DFT calculations also reveal the carbon–chalcogen double bond character and this carbon–chalcogen bond in benzimidazolin-2-chalcogenone system is stronger compared to the simple imidazole-2-chalcogenone systems. The oxidative addition reactions of chalcogenone compounds with halogens afforded the halide derivatives chalcogenones.

4. Experimental section

4.1. General considerations

All the manipulations were carried out under nitrogen or argon atmosphere using standard Schlenk techniques unless otherwise noted. Solvents were purified and dried by standard procedures and were distilled prior to use. Melting points were recorded on a Veego VMP-I melting point apparatus in capillary tubes and were uncorrected. ^1H (400 MHz) and ^{13}C (100.56 MHz) nuclear magnetic resonance spectra were recorded on Varian VXR 400S and Bruker AV 400 spectrometers at 25 °C. The ^{77}Se (57.22 MHz and 76.3 MHz)

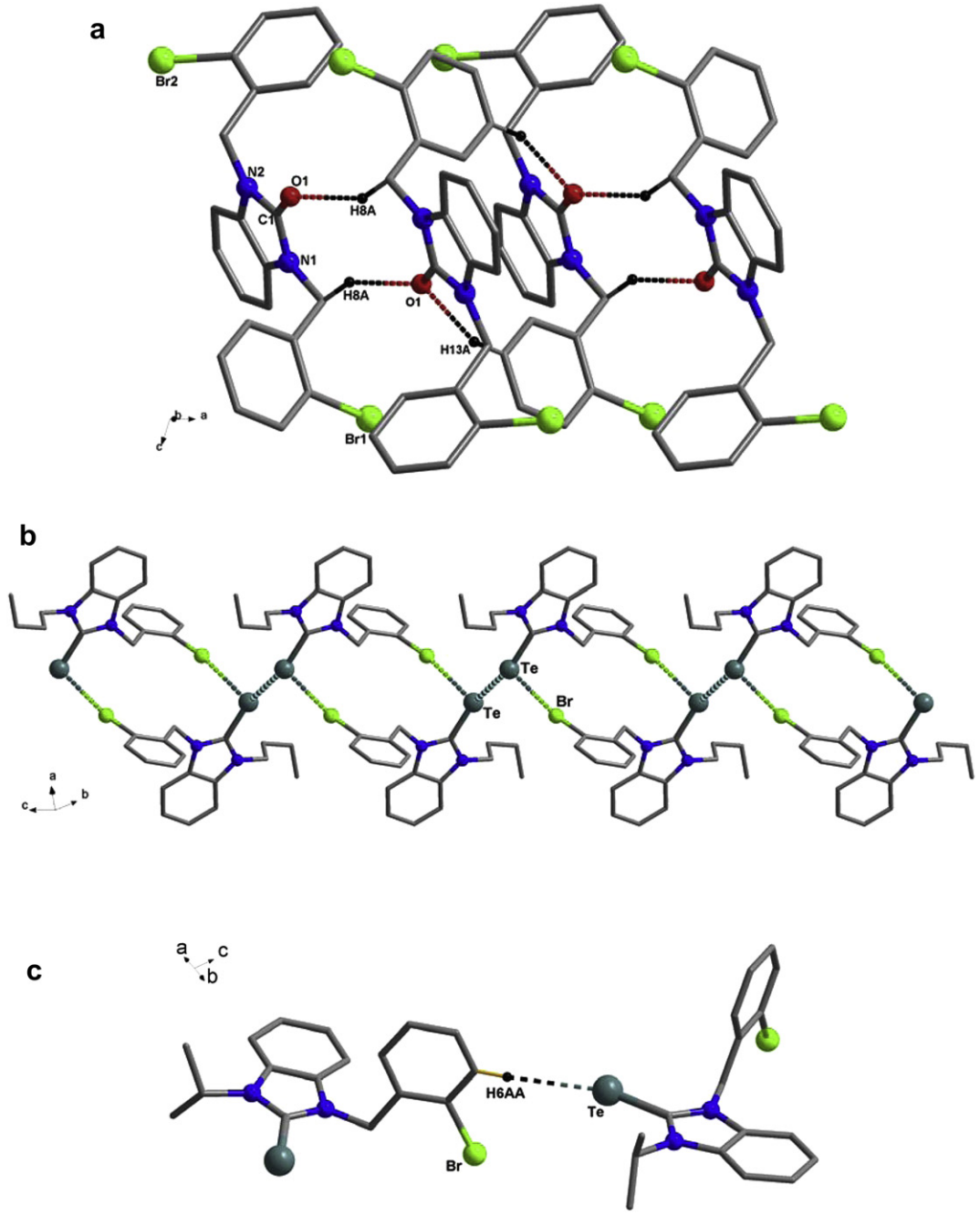


Fig. 3. (a) The crystal packing diagram of compound **15** showing two different types of intermolecular hydrogen bonds. (b) The crystal packing diagram of compound **10f** showing the intermolecular Te···Te* and Te···Br interactions. (c) The crystal packing diagram of compound **10g** showing the intermolecular hydrogen bond interactions. Hydrogen atoms (except those are involved in interactions) are omitted for clarity.

and ^{125}Te (94.79 MHz and 157.97 MHz) spectra were recorded on a Varian VXR 300S and Bruker AV 400 spectrometers. Chemical shifts are cited with respect to Me_4Si as internal standard (^{1}H and ^{13}C) and Me_2Se (^{77}Se) and Me_2Te (^{125}Te) as external standards. Elemental analyses were performed on a Carlo Erba Model 1106 elemental analyzer. The ESI mass spectra were recorded on a Q-Tof micro (YA-105) mass spectrometer.

4.2. Synthesis of compounds **7a**–**7d**

Precursor salts **7a**–**7d** were synthesized by the reported procedures and their purity was confirmed by ^{1}H NMR spectroscopy prior to use [19–21].

4.3. General procedure for the synthesis of salts (**8a**–**8d**)

A solution of 2-bromobenzylbromide and *N*-alkylated/arylated benzimidazole derivative in 1,4-dioxane (40 mL) was refluxed under nitrogen atmosphere for 16 h. Then the solvent was removed and the solid residue was washed with THF (10 mL X 2). The white solid obtained was dried in vacuum.

4.3.1. Synthesis of compound **8a**

The reagents used are *N*-pyridyl benzimidazole (0.86 g, 4.40 mmol) and 2-bromobenzylbromide (1.01 g, 4.40 mmol). Yield: 1.61 g (82%). Mp. 199–201 °C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.02 (s, 1H), 8.76 (dd, $J = 8.2$ Hz, $J = 0.8$ Hz, 1H),

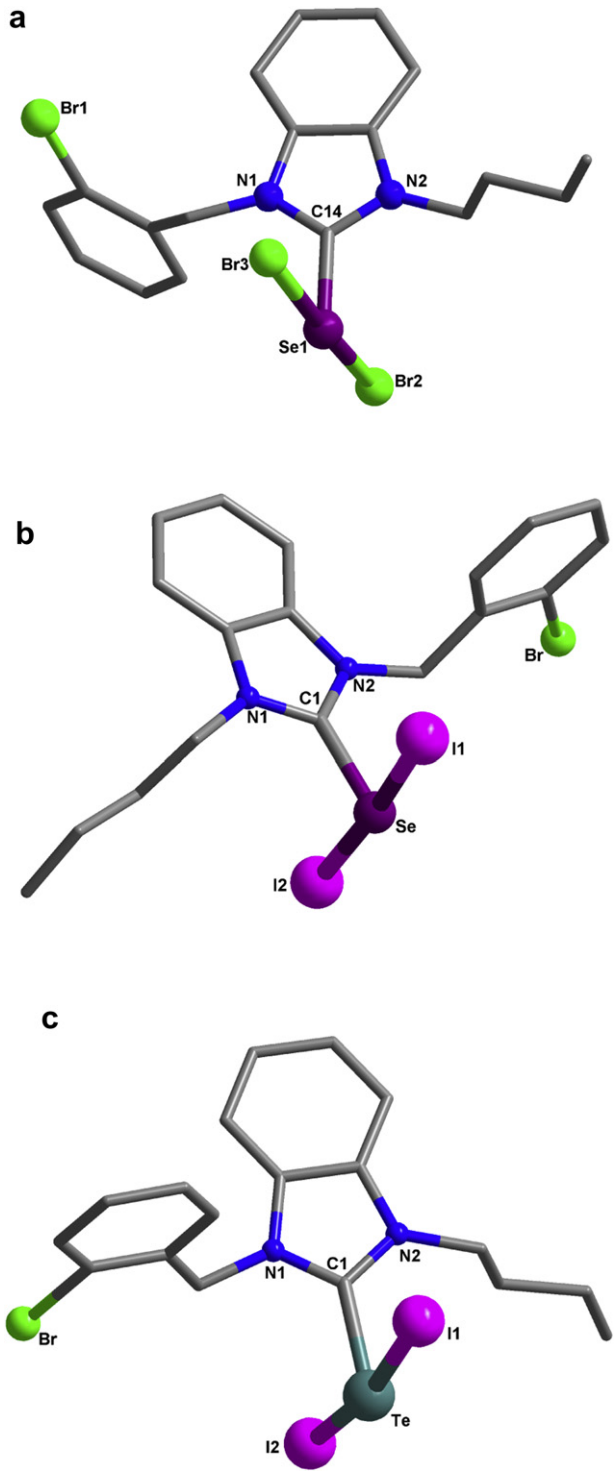


Fig. 4. (a) The molecular structure of compound **16a**. (b) The molecular structure of compound **16c**. (c) The molecular structure of compound **16e**. Hydrogen atoms are omitted for clarity.

8.69–8.64 (m, 2H), 8.16–8.11 (m, 1H), 7.87 (dd, $J = 8.3$, $J = 1.5$ Hz, 1H), 7.74 (dd, $J = 8.5$, $J = 0.9$ Hz, 1H), 7.71–7.61 (m, 3H), 7.55–7.52 (m, 1H), 7.41–7.36 (m, 1H), 7.29–7.25 (m, 1H), 6.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 149.1 (NCHN), 148.0, 142.1, 140.7, 133.5, 131.7, 131.6, 131.2, 130.1, 128.7, 128.2, 127.9, 125.0, 123.9, 117.7, 117.5, 113.7, 51.4. ESI-MS: (m/z) 366 $[M - Br]^+$. Anal. Calcd. for $C_{19}H_{15}Br_2N_3$ (%): C, 51.26; H, 3.40; N, 9.44. Found: C, 49.84; H, 3.02; N, 9.26.

4.3.2. Synthesis of compound **8b**

The reagents used are *N*-phenyl benzimidazole (1.01 g, 5.19 mmol) and 2-bromobenzylbromide (1.29 g, 5.19 mmol). Yield: 0.84 g (37%). Mp. 202–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 11.04 (s, 1H), 8.01 (d, $J = 7.6$ Hz, 1H), 7.95–7.92 (m, 1H), 7.85–7.80 (m, 1H), 7.73–7.61 (m, 7H), 7.41 (t, $J = 7.2$, 1H), 7.30–7.25 (m, 2H), 6.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.3 (NCHN), 133.3, 132.7, 132.0, 131.7, 131.2, 131.0, 130.6, 130.5, 128.5, 127.7, 127.6, 124.8, 123.9, 114.1, 113.5, 51.3. ESI-MS: (m/z) 363 $[M - Br]^+$. Anal. Calcd. for $C_{20}H_{16}Br_2N_2$ (%): C, 54.08; H, 3.63; N, 6.31. Found: C, 53.68; H, 3.30; N, 6.42.

4.3.3. Synthesis of compound **8c**

The reagents used are *N*-butyl benzimidazole (2.74 g, 15.73 mmol) and 2-bromobenzylbromide in (3.93 g, 15.73 mmol). Yield: 4.73 g (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 11.54 (s, 1H), 7.71–7.56 (m, 6H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.32–7.25 (m, 1H), 6.01 (s, 2H). 4.65 (t, $J = 7.6$ Hz, 1H), 2.11–2.04 (m, 2H), 1.53–1.44 (m, 2H), 1.01 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.4 (NCHN), 133.6, 132.0, 131.5, 131.4, 131.2, 128.8, 127.5, 127.4, 123.9, 114.1, 113.4, 51.4, 47.8, 31.4, 19.9, 13.7. ESI-MS: (m/z) 344 $[M - Br]^+$. Anal. Calcd. for $C_{18}H_{20}Br_2N_2$ (%): C, 50.97; H, 4.75; N, 6.60. Found: C, 50.62; H, 4.80; N 6.39.

4.3.4. Synthesis of compound **8d**

The reagents used are *N-iso*-propyl benzimidazole (1.50 g, 9.37 mmol) and 2-bromobenzylbromide (2.34 g, 9.37 mmol). Yield: 2.61 g (68%). Mp. 169–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 11.38 (s, 1H), 7.88–7.85 (m, 1H), 7.67–7.53 (m, 5H), 7.35 (td, $J = 7.3$, $J = 1.2$ Hz, 1H), 7.24 (td, $J = 7.9$, $J = 1.8$ Hz, 1H), 6.10 (s, 2H), 5.12 (m, 1H), 1.86 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 141.9 (NCHN), 133.5, 132.0, 131.5, 131.3, 130.9, 130.7, 128.6, 127.3, 127.2, 123.7, 114.1, 113.7, 52.1, 51.1, 22.4. ESI-MS: (m/z) 329 $[M - Br]^+$. Anal. Calcd. for $C_{18}H_{20}Br_2N_2$ (%): C, 49.78; H, 4.42; N, 6.83. Found: C, 48.29; H, 4.45; N, 6.24.

4.4. General procedure for the synthesis of chalcogenone compounds (**10a**–**10g** and **12b**)

The chalcogenone compounds were synthesized using four different methods.

Method (A): In a round bottom flask, salt (**8c**) was taken in dry THF (40 mL) under nitrogen atmosphere. *n*-BuLi (at different concentrations 1 eqv/2 eqv/3 eqv) was added at −78 °C and the reaction mixture was stirred for 1–2 h. Then elemental powder (Se or Te) was added to the reaction mixture at room temperature and stirred for 8–10 h. The reaction mixture was quenched in water (30 mL) and extracted with dichloromethane, dried over anhydrous sodium sulfate and evaporated. The residue obtained was dissolved in toluene (5 mL) and petroleum ether (15 mL) to separate the impurity from the solution. The solution was filtered, evaporated and the residue was recrystallized from slow evaporation of diethyl ether and petroleum ether (3:1) to afford the product in moderate yield.

Method (B): The salt (**8a**–**8d**, 1 eqv) was added into the brown solution of Na_2E_2 (E = S, Se, Te: prepared *in situ*; 1 eqv) [31] in THF (30 mL) under nitrogen atmosphere and stirred for 6–10 h at room temperature. Then potassium *tert*-butoxide (1 eqv) was added to the above reaction mixture and stirred for further 5–7 h. The reaction mixture was quenched in water (50 mL) and extracted with diethyl ether, dried over sodium sulfate and evaporated. The residue was recrystallized from slow evaporation of diethyl ether and petroleum ether (3:1) to afford the crystalline product in good yield.

Method (C): In a round bottom flask containing salt (**8c**, 1 eqv) was taken in THF (40 mL) under nitrogen atmosphere and chalcogen powder (S, Se or Te; 1 eqv) followed by addition potassium *tert*-butoxide (1 eqv). The reaction mixture was stirred for 5–6 h at room temperature. The reaction mixture was quenched in water (50 mL) and extracted with dichloromethane, dried over sodium

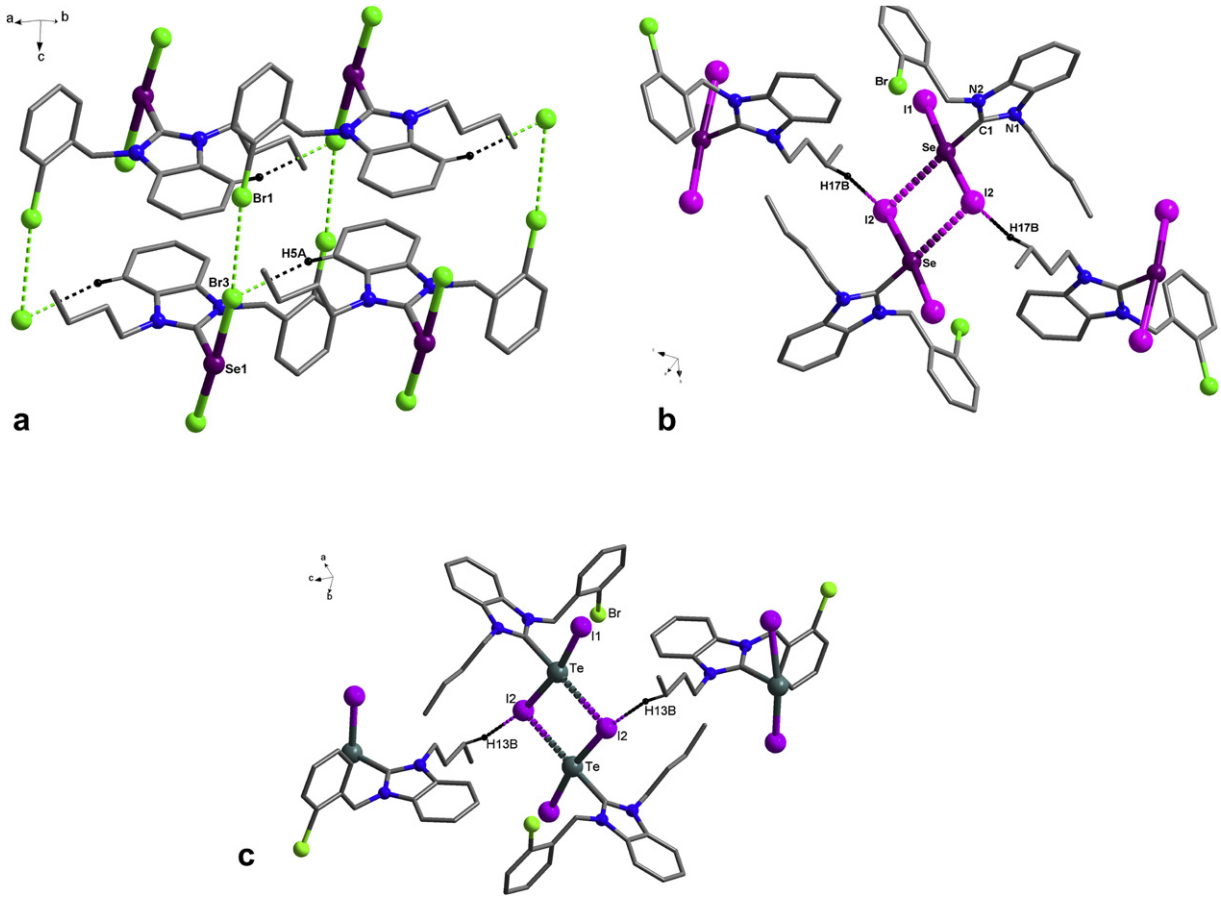


Fig. 5. (a) The crystal packing diagram of compound **16a** showing CH5A···Br3 and Br1···Br3 intermolecular interactions. (b) The crystal packing diagram of compound **16c** showing CH17B···I2 and Se···I2* intermolecular interactions. (c) The crystal packing diagram of compound **16e**. Hydrogen atoms (except those are involved in interactions) are omitted for clarity.

sulfate and evaporated. The residue obtained was purified as given in method A to afford the product.

Method (D): The salt **8c** (1 eqv) was added into the solution of Na_2Se (prepared *in situ*; 1 eqv) [31] in THF (30 mL) under nitrogen atmosphere and stirred for 6–10 h at room temperature. Then potassium *tert*-butoxide (1 eqv) was added to the above reaction mixture and stirred for further 5–7 h. The reaction mixture was quenched in water (50 mL) and extracted with diethyl ether, dried over sodium sulfate and evaporated. The residue was recrystallized from slow evaporation of diethyl ether and petroleum ether (3:1) to afford the crystalline product in excellent yield.

The yields reported for the compounds are by method B.

Table 3
C–E, E–X bond lengths and C–E–X, X–E–X bond angles.

Compound	C=E bond	Distance/angle
15	C=O	1.226(8)
10a	C=S	1.674(2)
10b	C=Se	1.825(2)
10d	C=Se	1.831(5)
10e	C=Se	1.833(2)
10f	C=Te	2.0772(19)
10g	C=Te	2.062(4)
16a	C–Se	1.8967(15)
	Se–Br(2)	2.4944(3)
	Se–Br(3)	2.6529(3)
	C14–Se–Br2	89.18(5)
	C14–Se–Br3	86.36(5)
	Br2–Se–Br3	175.527(8)
16c	C–Se	1.902(2)
	Se–I1	2.7040(3)
	Se–I2	2.8982(3)
	C1–Se–I1	91.91(7)
	C1–Se–I2	84.22(7)
	I1–Se–I2	176.109(9)
16e	C–Te	2.128(3)
	Te–I1	2.8330(3)
	Te–I2	3.0394(3)
	C1–Te–I1	88.35(8)
	C1–Te–I2	80.59(8)
	I1–Te–I2	168.938(9)

4.4.1. Synthesis of compound ***10a***

The reagents used are salt **8c** (0.46 g, 1.08 mmol), Na_2S_2 (*in situ* prepared, 1.08 mmol), potassium *tert*-butoxide (0.12 g, 1.08 mmol) in dry THF (30 mL). Yield: 0.19 g (43%). Mp. 84–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (dd, $J = 7.2$ Hz, $J = 1.6$ Hz, 1H), 7.23 (d, $J = 4$ Hz, 2H), 7.13 (m, 3H), 7.00 (d, $J = 8$ Hz, 1H), 6.85 (dd, $J = 7.2$ Hz, $J = 2.4$ Hz, 1H), 5.69 (s, 2H), 4.4 (t, $J = 7.6$ Hz, 2H), 1.89–1.84 (m, 2H), 1.51–1.45 (m, 2H), 1.01 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.4 (NCN), 134.6, 132.9, 132.2, 131.9, 129.2, 128.0, 127.9, 123.3, 123.2, 122.6, 109.8, 109.3, 48.1, 45.2, 30.1, 20.3, 13.9. ESI-MS: (m/z) 377 $[M]^+$, 342 $[M - S]^+$. Anal. Calcd. for $C_{18}H_{19}BrN_2S$ (%): C, 57.60; H, 5.10; N, 7.46. Found: C, 57.80; H, 4.91; N, 7.76.

4.4.2. Synthesis of compound ***10b***

Reagents used are salt **8a** (0.96 g, 2.17 mmol), Na_2Se_2 (*in situ* prepared, 2.17 mmol), potassium *tert*-butoxide (0.24 g, 2.17 mmol), in dry THF. Yield: 0.55 g (57%). Mp. 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.73 (td, $J = 4.9$ $J = 0.6$ Hz, 1H), 8.16 (d, $J = 8$ Hz, 1H), 8.01 (dt, $J = 7.7$ Hz, $J = 1.8$ Hz, 1H), 7.64 (dd, $J = 8$ Hz, $J = 1.6$ Hz, 1H), 7.50–7.47 (m, 1H), 7.42–7.39 (m, 1H), 7.23–7.11 (m, 5H), 7.01 (dd, $J = 7.2$ Hz, $J = 2.4$ Hz,

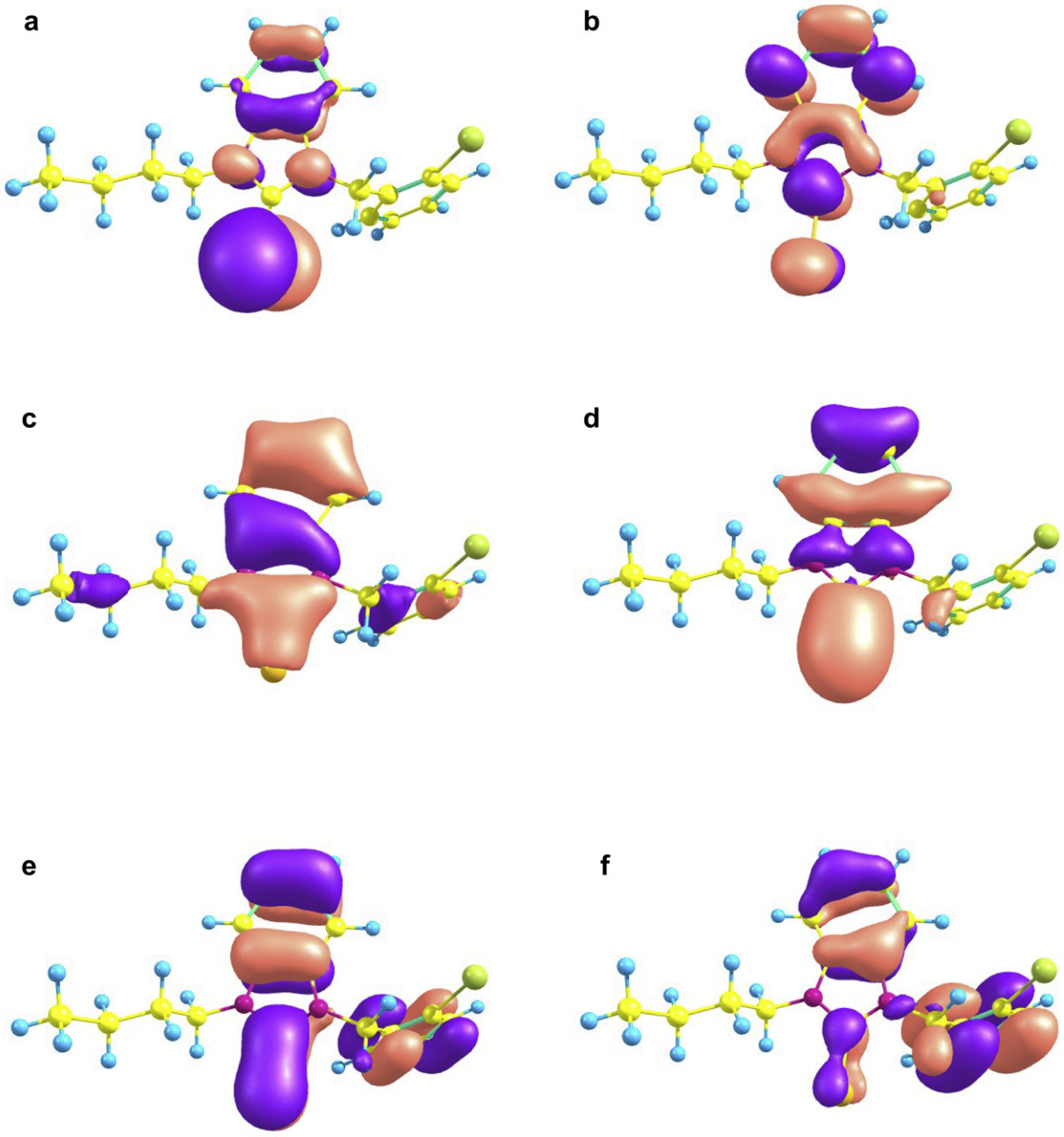


Fig. 6. MO's of compound **10d**. a) HOMO. b) LUMO. c) HOMO-49. d) HOMO-44. e) HOMO-5. f) HOMO-4.

1H), 5.91 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.4 (NCN), 150.4, 149.3, 138.3, 134.0, 133.6, 133.1, 129.4, 128.4, 128.0, 124.5, 124.3, 124.2, 123.9, 122.6, 111.9, 110.3, 50.1. ^{77}Se NMR (57 MHz, $CDCl_3$): δ (ppm) 101. ESI-MS: (m/z) 444 $[M - Br]^+$. Anal. Calcd. for $C_{19}H_{14}BrN_3Se$ (%): C, 51.49; H, 3.18; N, 9.48. Found: C, 52.60; H, 2.60; N, 9.87.

*4.4.3. Synthesis of compound **10c***

Reagents used are salt **8b** (0.24 g, 0.54 mmol), Na_2Se_2 (*in situ* prepared, 0.54 mmol) and potassium *tert*-butoxide (0.06 g, 0.54 mmol) in dry THF. Yield: 0.15 g (63%). Mp. 161–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66–7.57 (m, 6H), 7.23–7.13 (m, 5H), 7.08–7.05 (m, 2H), 5.92 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.1 (NCN), 136.7, 134.6, 134.1, 133.0, 132.9, 129.8, 129.5, 129.4, 128.4, 128.3, 128.0, 124.2, 124.1, 122.6, 110.6, 110.3, 50.2. ^{77}Se NMR (57 MHz, $CDCl_3$): δ (ppm) 95. ESI-MS: (m/z) 443 $[M]^+$. Anal. Calcd. for $C_{20}H_{15}BrN_2Se$ (%): C, 54.32; H, 3.42; N, 6.33. Found: C, 54.11; H, 3.29; N, 6.45.

*4.4.4. Synthesis of compound **10d***

The reagents used are salt **8c** (0.96 g, 2.28 mmol), Na_2Se_2 (*in situ* prepared, 2.28 mmol) and potassium *tert*-butoxide (0.26 g, 2.28 mmol) in dry THF. Yield: 0.71 g (74%). Mp. 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.62 (dd, J = 7.2 Hz, J = 1.6 Hz, 1H), 7.32 (d, J = 8 Hz, 1H), 7.27 (dd, J = 12 Hz, J = 0.8 Hz, 2H), 7.19–7.11 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 6.86 (dd, J = 6.4 Hz, J = 2.4 Hz, 1H), 5.83 (s, 2H), 4.51 (t, J = 8 Hz, 2H), 1.93–1.89 (m, 2H), 1.57–1.47 (m, 2H), 1.02 (t, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.8 (NCN), 134.4, 133.3, 133.0, 129.3, 128.3, 127.9, 123.7, 123.6, 122.6, 110.4, 109.8, 50.0, 47.0, 30.3, 20.3, 13.9. ^{77}Se NMR (57 MHz, $CDCl_3$): δ (ppm) 60. ESI-MS: (m/z) 422 $[M]^+$, 342 $[M - Br]^+$. Anal. Calcd. for

$C_{18}H_{19}BrN_2Se$ (%): C, 51.20; H, 4.54; N, 6.63. Found: C, 51.98; H, 4.59; N, 6.82.

4.4.5. Synthesis of compound **10e**

The reagents used are salt **8d** (0.58 g, 1.43 mmol), Na_2Se_2 (*in situ* prepared, 1.43 mmol) and potassium *tert*-butoxide (0.16 g, 1.43 mmol) in THF. Yield: 462 g (79%). Mp. 178–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (dd, $J = 8$ Hz, $J = 1.6$ Hz, 1H), 7.55 (d, $J = 8$ Hz, 1H), 7.25–7.08 (m, 5H), 6.84 (dd, $J = 7.2$ Hz, $J = 2.4$ Hz, 1H), 5.96–5.91 (m, 1H), 5.84 (s, 2H), 1.67 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.4 (NCN), 134.4, 133.6, 133.0, 131.6, 129.3, 128.2, 128.0, 123.4, 123.2, 122.6, 111.4, 110.6, 52.3, 50.4, 20.3. ^{77}Se NMR (57 MHz, $CDCl_3$): δ (ppm) 58. ESI-MS: (m/z) 408 $[M]^+$. Anal. Calcd. for $C_{17}H_{17}BrN_2Se$ (%): C, 50.02; H, 4.20; N, 6.86. Found: C, 49.91; H, 3.89; N, 7.28.

4.4.6. Synthesis of compound **10f**

The reagents used are salt **8c** (0.48 g, 1.13 mmol), Na_2Te_2 (*in situ* prepared, 1.13 mmol) and potassium *tert*-butoxide (0.13 g, 1.13 mmol) in THF. Yield: 0.33 g (62%). Mp. 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.64–7.60 (m, 1H), 7.41 (d, $J = 8$ Hz, 1H), 7.29–7.25 (m, 1H), 7.20–7.11 (m, 4H), 6.81 (dd, $J = 5.6$ Hz, $J = 3.6$ Hz, 1H), 5.91 (s, 1H), 4.57 (t, $J = 8$ Hz, 2H), 1.97–1.89 (m, 2H), 1.55–1.50 (m, 2H), 1.04 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.5 (NCN), 134.4, 134.1, 133.1, 129.4, 128.5, 128.0, 124.1, 122.6, 111.2, 110.6, 53.4, 50.4, 30.8, 20.3, 14.0. ^{125}Te NMR (95 MHz, $CDCl_3$): δ (ppm) −130. ESI-MS: (m/z) 393 $[M - Br]^+$, 343 $[M - Te]^+$. Anal. Calcd. for $C_{18}H_{19}BrN_2Te$ (%): C, 45.91; H, 4.07; N, 5.95. Found: C, 46.25; H, 3.89; N, 6.16.

4.4.7. Synthesis of compound **10g**

The reagents used are salt **8d** (0.26 g, 0.65 mmol), Na_2Te_2 (*in situ* prepared, 0.65 mmol) and potassium *tert*-butoxide (0.07 g, 0.65 mmol) in THF. Yield: 0.17 g (59%). Mp. 185 °C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67–7.61 (m, 2H), 7.27–7.12 (m, 5H), 6.82–6.79 (m, 1H), 5.94 (s, 2H), 5.98–5.89 (m, 1H), 1.70 (d, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.5 (NCN), 134.9, 134.0, 133.0, 132.4, 129.4, 128.4, 127.9, 123.9, 123.5, 122.5, 111.9, 111.5, 56.8, 53.9, 20.3. ^{125}Te NMR (95 MHz, $CDCl_3$): δ (ppm) −126. ESI-MS: (m/z) 457 $[M]^+$, 379 $[M - Br]^+$, 328 $[M - Te]^+$. Anal. Calcd. for $C_{17}H_{17}BrN_2Te$ (%): C, 44.69; H, 3.75; N, 6.13. Found: C, 44.81; H, 3.58; N, 6.05.

4.4.8. Synthesis of compound **12b**

The reagents used are salt **8b** (0.34 g, 0.76 mmol), Na_2Te_2 (*in situ* prepared, 0.76 mmol) and potassium *tert*-butoxide (0.08 g, 0.76 mmol) in THF. The reaction, after work up led to the formation of hydrolyzed diamine product **12b**, instead of the desired tellurone **11b**. Yield: 0.05 g (19%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 (m, 1H), 7.54 (dd, $J = 7.6$ Hz, $J = 1.2$ Hz, 1H), 7.43 (m, 1H), 7.32 (m, 1H), 7.23 (m, 2H), 7.11 (m, 2H), 6.71 (m, 2H), 6.61 (dd, $J = 8$ Hz, $J = 1.2$ Hz, 1H), 6.40 (m, 1H), 6.15 (s, 1H), 4.83 (d, $J = 5.6$ Hz, 1H), 4.41 (d, $J = 6$ Hz, 2H).

4.5. Synthesis of compound **14**

The synthesis of compound **13** was attempted by treating (1H-benzo[d]imidazol-1-yl)(phenyl)methanone (1.00 g, 4.50 mmol) with 1-bromo-2-(bromomethyl)benzene (1.13 g, 4.50 mmol) in 1,4-dioxane (30 mL) under nitrogen atmosphere. The reaction mixture was refluxed with stirring for 24 h, no formation of 1-benzoyl-3-(2-bromobenzyl)-1H-benzo[d]imidazol-3-ium bromide was observed. Thereafter, additional 1-bromo-2-(bromomethyl)benzene (1.13 g, 4.50 mmol) was added to the reaction mixture and continued reflux for 12 h. The reaction mixture when kept aside for 15 days, afforded a white precipitate. The precipitate was collected, washed with THF and characterized as **14**. Yield: 1.20 g (50%). The compound **14** was also synthesized in a direct reaction between two equivalent of 1-bromo-2-(bromomethyl)benzene and benzimidazole. Mp. 191 °C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 11.29 (s, 1H), 7.70 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 2H), 7.64–7.59 (m, 4H), 7.51 (dd, $J = 6.4$ Hz, $J = 3.2$ Hz, 2H), 7.36 (td, $J = 7.6$ Hz, $J = 1.2$ Hz, 2H), 7.24 (td, $J = 8$ Hz, $J = 1.6$ Hz, 2H), 6.01 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5 (NCN), 133.6, 131.8, 131.6, 131.4, 131.2, 128.8, 127.4, 123.9, 113.9, 51.6. ESI-MS: (m/z) 456 $[M - Br]^+$. Anal. Calcd. for $C_{21}H_{17}Br_3N_2$ (%): C, 46.96; H, 3.19; N, 5.22. Found: C, 47.47; H, 2.88; N, 5.74.

4.6. Synthesis of compound **15**

Compound **14** (0.51 g, 1.1 mmol) was added to a brown solution of Na_2Se_2 (*in situ* prepared, 1.1 mmol) in THF (25 mL) at room temperature under nitrogen atmosphere and the reaction mixture was stirred for 7 h. Then potassium *tert*-butoxide (0.12 g, 1.1 mmol) was added to the above reaction mixture and stirred further 5 h. The reaction mixture was quenched with water (50 mL), extracted with dichloromethane and dried over anhydrous Na_2SO_4. The solvent was evaporated to give a semi-solid, which was dissolved in toluene and small amount of petroleum ether was added. The solution was evaporated to afford the solid. Recrystallization of the solid from diethyl ether and petroleum ether (4:1) afforded pure crystalline product of **15** instead of the desired compound 1,3-bis(2-bromobenzyl)-1H-benzo[d]imidazole-2(3H)-selenone.
Yield: 0.19 g (43%). Mp. 137–139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (dd, $J = 8$ Hz, $J = 1.2$ Hz, 2H), 7.22 (dt, $J = 7.2$ Hz, $J = 0.8$ Hz, 2H), 7.14 (dt, $J = 7.6$ Hz, $J = 1.6$ Hz, 2H), 7.07 (d, $J = 7.6$ Hz, 2H), 7.01 (dd, $J = 5.6$ Hz, $J = 3.2$ Hz, 2H), 6.88 (dd, $J = 5.6$ Hz, $J = 3.2$ Hz, 2H), 5.25 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.9 (NCN), 135.6, 133.2, 129.7, 129.5, 128.8, 127.9, 123.0, 121.9, 108.7, 45.3. ESI-MS: (m/z) 473 $[M]^+$, 457 $[M - O]^+$. Anal. Calcd. for $C_{21}H_{16}Br_2N_2O$ (%): C, 53.42; H, 3.42; N, 5.93. Found: C, 53.19; H, 3.00; N, 6.48.

4.7. General procedure for the synthesis of compounds **16a–16e**

In a round bottomed flask containing the solution of selenone or tellurone (**10b** or **10d–10f**; 1 eqv) in THF (40 mL), halogen (Br_2, I_2; 1 eqv) in dry THF (15 mL) was added dropwise at −78 °C under nitrogen atmosphere. The reaction mixture was stirred for 16–20 h at room temperature. The solvent was evaporated to one third of original volume and *n*-pentane (15–20 mL) was added and kept in fridge at −23 °C for overnight to afford the crystalline product.

4.7.1. Synthesis of compound **16a**

The reagents used are bromine (0.11 g, 0.71 mmol) and **10d** (0.30 g, 0.71 mmol). Yield: 0.37 g (89%). Mp. 210–212 °C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (dd, $J = 6.7$ Hz, $J = 1.2$ Hz, 2H), 7.59 (t, $J = 7.9$ Hz, 1H), 7.48 (t, $J = 8.4$ Hz, 1H), 7.40 (dd, $J = 7.3$ Hz, $J = 2.4$ Hz 1H), 7.34 (d, $J = 8.2$ Hz 1H), 7.26–7.20 (m, 2H), 6.09 (s, 2H), 4.78 (t, $J = 7.9$ Hz 2H), 2.25–2.17 (m, 2H), 1.62–1.57 (m, 2H), 1.09 (t, $J = 7.6$ Hz 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.0 (NCN), 133.3, 132.3, 131.9, 130.5, 130.3, 128.6, 127.5, 127.4, 122.9, 114.2, 113.2, 52.8, 49.7, 30.7, 20.5, 13.9. ^{77}Se NMR (57 MHz, $CDCl_3$): δ (ppm) 293. ESI-MS: (m/z) 571 $[M - CH_3]^+$, 448 $[M - C_4H_9Br]^+$, 423 $[M - Br_2]^+$. Anal. Calcd. for $C_{18}H_{19}Br_3N_2Se$ (%): C, 37.14; H, 3.29; N, 4.81. Found: C, 36.76; H, 2.94; N, 4.73.

4.7.2. Synthesis of compound **16b**

The reagents used are **10b** (0.08 g, 0.18 mmol) and iodine (0.05 g, 0.18 mmol). Yield: 0.11 g (87%). Mp. 150–152 °C (decomposed). ^{1}H

Table 4
Charge and Wiberg bond index of chalcogenone compounds.

Compound	Charge on C atom	Charge on chalcogen atom	Total Wiberg bond index on E
17a	0.247	−0.244	1.8921
17b	0.198	−0.204	1.768
17c	0.129	−0.149	1.564
18a	0.248	−0.248	1.888
18b	0.199	−0.208	1.763
18c	0.129	−0.154	1.560
19	0.295	−0.318	1.886
10e	0.205	−0.211	1.764
10g	0.137	−0.156	1.561
10a	0.249	−0.248	1.887
10d	0.202	−0.212	1.762
10f	0.133	−0.160	1.559
20a	0.250	−0.218	1.919
10c	0.196	−0.177	1.794
20b	0.138	−0.129	1.582
21a	0.250	−0.222	1.918
10b	0.203	−0.187	1.790
21b	0.133	−0.133	1.585
22	0.164 I1 −0.419, −0.395	0.210	
16c	0.275 I1 −0.400, −0.363	0.250	2.159
16e	0.195 I1 −0.454, −0.428	0.455	2.077
23a	0.100	−0.216	1.81
23b	0.136	−0.344	1.68
23c	0.120	−0.378	1.47

NMR (400 MHz, $CDCl_3$): δ (ppm) 8.79 (d, J = 4.4 Hz, 1H), 8.16–8.14 (m, 2H), 7.68 (dd, J = 6.9 Hz, J = 1.4 Hz, 1H), 7.65–7.62 (m, 1H), 7.56–7.53 (dd, J = 7.0 Hz, J = 1.3 Hz, 1H), 7.49–7.42 (m, 2H), 7.35–7.32 (dd, J = 7.3 Hz, J = 2.5 Hz, 1H), 7.27–7.22 (m, 2H), 7.08–7.05 (dd, J = 7.3 Hz, J = 2.6 Hz, 1H), 5.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.1 (NCN), 149.9, 148.4, 139.5, 133.5, 132.6, 132.2, 130.3, 128.9, 128.4, 126.9, 125.7, 123.6, 126.9, 125.7, 123.6, 122.8, 113.8, 112.5, 52.2. ^{77}Se NMR (57 MHz, $CDCl_3$): δ (ppm) 219. ESI-MS: (m/z) 570 $[M - I]^+$, 444 $[M - I_2]^+$, 364 $[M - SeI_2]^+$. Anal. Calcd. for $C_{19}H_{14}BrI_2N_3Se$ (%): C, 32.74; H, 2.02; N, 6.03. Found: C, 32.86; H, 1.55; N, 7.06.

*4.7.3. Synthesis of compound **16c***

The reagents used are iodine (0.03 g, 0.12 mmol) and **10d** (0.05 g, 0.12 mmol). Yield: 0.07 g (87%). Mp. 170–172 °C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67 (dd, J = 7.1 Hz, J = 1.6 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.25–7.20 (m, 2H), 7.04 (d, J = 5.6 Hz, 1H), 5.90 (s, 2H), 4.63 (t, J = 8 Hz, 2H), 2.11–2.03 (m, 2H), 1.60–1.49 (m, 2H), 1.07 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.3 (NCN), 132.9, 132.5, 129.7, 127.6, 125.6, 121.8, 112.1, 109.4, 50.6, 47.4, 30.0, 19.4, 13.5. ^{77}Se NMR (57 MHz, $CDCl_3$): δ (ppm) 217. MS: m/z 423 $[M - I_2]^+$, 343 $[M - SeI_2]^+$, 345 $[(M+2) - SeI_2]^+$. Anal. Calcd. for $C_{18}H_{19}BrI_2N_2Se$ (%): C, 31.98; H, 2.83; N, 4.14. Found: C, 32.52; H, 2.59; N, 4.45.

*4.7.4. Synthesis of compound **16d***

The reagents used are **10e** (0.10 g, 0.25 mmol) and iodine (0.06 g, 0.25 mmol). Yield: 0.11 g (70%). ^{1}H NMR (400 MHz, DMSO-d^6): δ (ppm) 7.81 (d, J = 8.1 Hz, 1H), 7.72–7.60 (m, 2H), 7.57–7.50 (m, 2H), 7.32–7.17 (m, 2H), 6.64 (d, J = 7.0 Hz, 1H), 5.83 (s, 2H), 5.57–5.50 (m, 1H), 1.71 (d, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d^6): δ (ppm) 151.4 (NCN), 133.2, 132.7, 130.5, 129.9, 128.2, 127.8, 126.8, 126.1, 125.9, 121.8, 114.1, 112.9, 54.4, 51.2, 19.8. ^{77}Se NMR (76.3 MHz, DMSO-d^6): δ (ppm) 214. ESI-MS: (m/z) 408 $[M - I_2]^+$, 328 $[M - SeI_2]^+$, 331 $[M - SeI_2]^+$.

*4.7.5. Synthesis of compound **16e***

The reagents used are **10f** (0.10 g, 0.21 mmol) and iodine (0.05 g, 0.21 mmol). Yield: 0.14 g (91%). Mp. 224–226 °C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 8 Hz, 1H), 7.46 (t, J = 8 Hz, 1H), 7.35 (d, J = 8 Hz, 1H), 7.31–7.22 (m, 3H), 6.08 (s, 2H), 4.80 (t, J = 8 Hz, 2H), 2.25–2.19 (m, 2H), 1.65–1.58 (m, 2H), 1.11 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 133.4, 132.8, 132.4, 132.3, 131.7, 130.7, 130.5, 128.6, 127.4, 127.3, 122.8, 114.2, 113.4, 56.3, 52.8, 31.1, 20.6, 13.9. ^{125}Te NMR (126.2 MHz, $CDCl_3$): δ (ppm) 330. ESI-MS: (m/z) 598 $[M - I]^+$, 392 $[M - BrI_2]^+$, 343 $[M - TeI_2]^+$. Anal. Calcd. for $C_{18}H_{19}BrI_2N_2Te$ (%): C, 29.83; H, 2.64; N, 3.87. Found: C, 30.20; H, 2.26; N, 4.12.

5. Single crystal X-ray crystallographic data

The single crystal X-ray diffraction measurements were performed on an Oxford Diffraction Gemini diffractometer. The data were corrected for Lorentz, polarization, and absorption effects. The structures were determined by routine heavy-atom methods using SHELXS 97 [35] and Fourier methods and refined by full-matrix least squares with the non-hydrogen atoms anisotropic and hydrogen with fixed isotropic thermal parameters of 0.07 Å^2 using the SHELXL 97 [36] program. The hydrogens were partially located from difference electron density maps, and the rest were fixed at predetermined positions. Scattering factors were from common sources [37]. Details of the X-ray data collection parameters are given in Tables 5 and 6.

The solvents for growing the crystals are listed below.

Compound **10a**: diethyl ether and petroleum ether (4:1) slow evaporation, **10b**: dichloromethane and petroleum ether (2:1) slow evaporation, **10d**: diethyl ether and petroleum ether (4:1) slow evaporation, **10e**: diethyl ether and petroleum ether (4:1) slow evaporation, **10f**: diethyl ether and petroleum ether (5:1), **10g**: diethyl ether and petroleum ether (5:1), **12a**: diethyl ether and petroleum ether (3:1) slow evaporation, **15**: chloroform-d, **16a**:

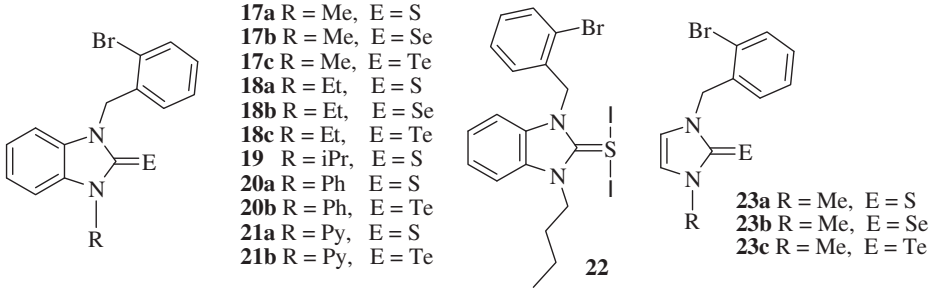


Fig. 7. Optimized model compounds.

Table 5
Details of the X-ray data collection parameters.

Compound	**10a**	**10b**	**10d**	**10e**	**10f**
Formula	$C_{18}H_{19}BrN_2S$	$C_{19}H_{14}BrN_3Se$	$C_{18}H_{19}BrN_2Se$	$C_{17}H_{17\cdot25}BrN_2\ O_{0.13}\ Se$	$C_{18}H_{19}BrN_2Te$
Mr	375.32	443.20	422.22	410.45	470.86
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\ 2_1/n$	$C2/c$	P-1
a[Å]	10.0157(5)	13.0639(6)	11.2184(7)	19.9209(18)	8.943(2)
b[Å]	16.2939(9)	9.7597(4)	10.1733(6)	9.6353(6)	10.518(2)
c[Å]	11.1665(6)	14.0421(5)	16.2720(9)	18.3953(16)	10.978(2)
α[°]	90	90	90	90	118.43(2)
β[°]	114.245(6)	109.427(5)	109.599(6)	110.262(10)	94.420(17)
γ[°]	90	90	90	90	97.033(18)
V[Å^3]	1661.57(16)	1688.43(12)	1749.50(18)	3312.4(5)	890.4(3)
Z	4	4	4	8	2
Crystal size [mm^3]	0.51 × 0.38 × 0.32	0.44 × 0.38 × 0.29	0.51 × 0.35 × 0.30	0.47 × 0.41 × 0.32	0.49 × 0.34 × 0.29
ρ_{calcd} [Mg/m^3]	1.500	1.744	1.603	1.646	1.756
μ [mm^{-1}]	2.598	4.595	4.428	4.676	3.912
Refls. collected	12,894	13,522	12,537	13,719	14,536
Observed reflns [$I > 2\sigma(I)$]	5475	5428	5257	5407	5891
R_1 observed reflns	0.0719	0.0880	0.1549	0.1080	0.0494
wR_2, all	0.0648	0.0780	0.1855	0.0597	0.0509

Table 6
Details of the X-ray data collection parameters.

Compound	**10g**	**15**	**16a**	**16c**	**16e**
Formula	$C_{17}H_{17}BrN_2Te$	$C_{21}H_{16}Br_2N_2O$	$C_{18}H_{19}Br_3N_2Se$	$C_{18}H_{19}BrI_2N_2Se$	$C_{18}H_{19}BrI_2N_2Te$
Mr	456.84	472.18	582.04	676.02	724.66
System	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$C2/c$	P-1	P-1	$P2_1/n$	$P2_1/n$
a[Å]	21.162(6)	7.5360(5)	8.3025(6)	12.2722(2)	12.3800(3)
b[Å]	9.556(8)	9.3672(10)	10.9155(8)	11.8520(2)	11.9892(3)
c[Å]	18.413(6)	13.6128(10)	11.1023(8)	14.5483(2)	14.5863(4)
α[°]	90	98.940(7)	84.187(4)	90	90
β[°]	112.18(4)	105.933(6)	79.706(4)	95.6851(15)	95.313(2)
γ[°]	90	96.726(7)	89.314(4)	90	90
V[Å^3]	3448(3)	899.80(13)	984.85(12)	2105.64(6)	2155.69(10)
Z	8	2	2	4	4
Size [mm^3]	0.47 × 0.38 × 0.31	0.55 × 0.21 × 0.15	0.42 × 0.33 × 0.27	0.53 × 0.47 × 0.36	0.53 × 0.42 × 0.37
ρ_{calcd} [Mg/m^3]	1.760	1.743	1.963	2.132	2.233
μ [mm^{-1}]	4.038	4.517	7.995	6.616	6.101
Refls. collected	17,305	8601	30,208	32,446	17,583
Observed reflns [$I > 2\sigma(I)$]	6882	8604	8351	8595	7203
R_1 observed reflns	0.1327	0.1391	0.0437	0.0625	0.0414
wR_2, all	0.1691	0.2416	0.0601	0.0560	0.0550

chloroform and diethyl ether (3:1), **16c**: THF and *n*-pentane (2:3) at −23 °C, **16e**: chloroform-d slow evaporation.

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Appendix A. Supplementary material

CCDC 878413, 878414, 878415, 878416, 878417, 878418, 759105, 878419, 878420 and 878421 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary Information associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2012.07.025.

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