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Synthesis and characterization of 1,2,3-selena/thiadiazoles linked to other heterocyclic units

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Synthesis of novel 1,2,3-selena/thiadiazoles, linked to different benzo-1,3-heteroazole ring by sulfur has been reported. Structural features of the compounds have been analyzed by ^{1}H and ^{13}C NMR, mass and single crystal X-ray studies.

Keywords: Oxidation; Selenium heterocycles; Sulfur heterocycles; Phase transfer catalysis; X-ray diffraction

1. Introduction

Sulfur linked heterocyclic compounds (figure 1) received considerable attention in recent times because of their pharmacological importance [1–3]. Compounds having benzo-1,3-heteroazole moiety (figure 2) have been claimed to have beneficial medicinal and agricultural applications [4–9]. 1,2,3-Selena/thiadiazoles are a class of biologically active compounds and useful intermediates in organic synthesis, whose chemistry has been recently reviewed [10–12]. Hence, it has been planned to synthesize selenadiazole/thiadiazole connected to benzoxazole/benzothiazole/benzimidazole unit via hetero atoms since the target molecule are expected to have enhanced biological activity.

2. Results and discussion

The precursors for the present investigation, 2-(1,3-benzoheteroazol-2-ylsulfanyl)-1-aryl-1-ethanone (**1**), were prepared by nucleophilic substitution of 2-mercaptobenzothia(oxa/imida)zole and ω-brominated arylmethyl ketones. These β-ketosulfides (**1**) have been shown to

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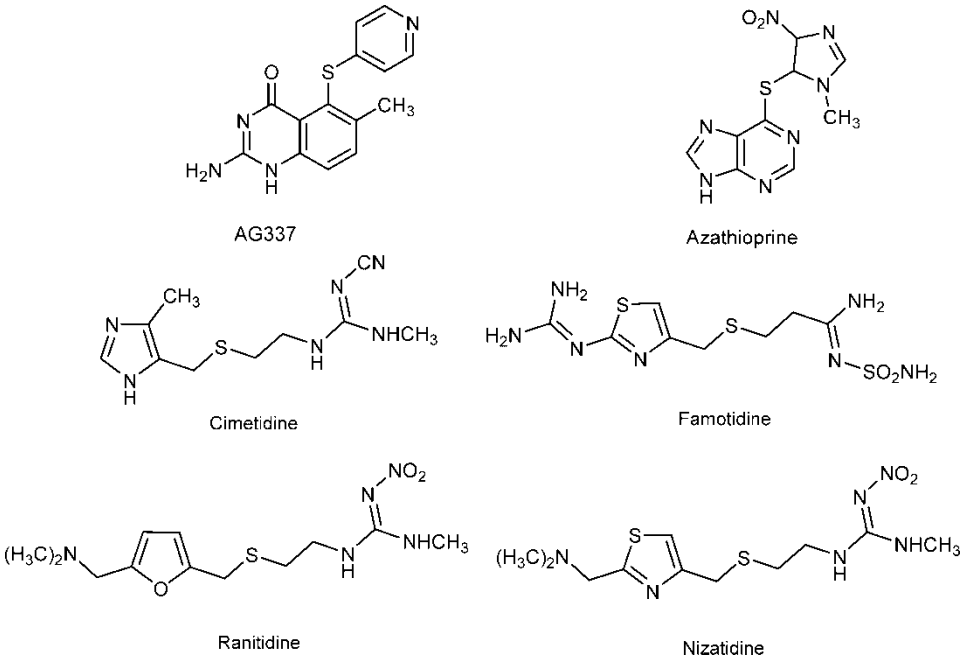

Figure 1. Important sulfur linked heterocyclic compounds.

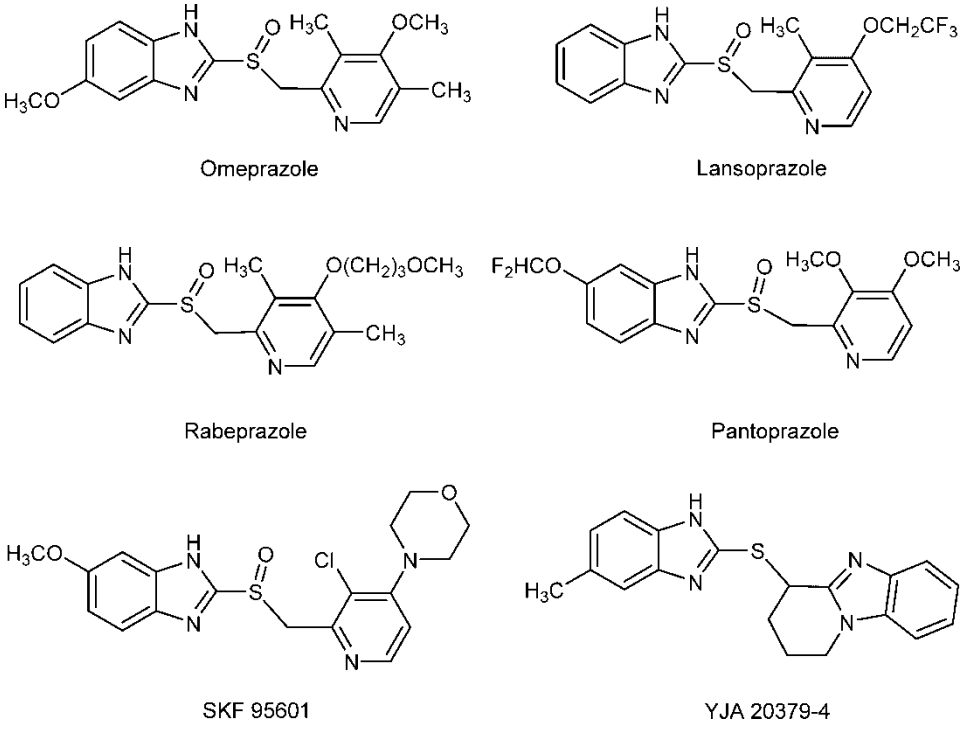

Figure 2. Sulfur linked benzimidazoles as Proton Pump Inhibitors.

undergo cyclization to give fused heterocyclic derivatives [13]. Reactions involving the methylene group of this ketone have also been investigated [14–18].

In the present investigation, 2-(1,3-heteroazol-2-ylsulfanyl)-1-aryl-1-ethanones (**1**) were converted into their semicarbazones (**2**) by phase transfer catalysis using tetrabutylammonium bromide in good yield (figure 3, table 1). When converted to its semicarbazone, the *Z* isomer is obtained as a major product. To ascertain the preferred geometry, X-ray analysis of one of the semicarbazones **2k** [19] was carried out, though what is found in solid state need not be the case in solution. The results are presented in table 2 and the ORTEP and the packing diagram are shown in figure 4. This study clearly confirms the *Z* orientation around C=N bond. The hydrogen on the NH group is involved in intramolecular hydrogen bonding with the nitrogen of the benzothiazole unit (N1 . . . H3A = 2.08 (2) Å, N3−H3 = 0.86 (2) Å, N1 . . . N3 = 2.897 (2) Å and N3−H3A . . . N1 = 159(2)°). It is interesting to notice that in the solid state, one of the hydrogens on the NH_2 group of one molecule is involved in hydrogen bonding with the carbonyl oxygen of a symmetry-related molecule (N4−H4A = 0.88 (3) Å, H4A . . . O1* = 2.10 (3) Å, N4 . . . O1* = 2.901 (2) Å and N4−H4A . . . O1 = 150 (2)°; the * indicates that O1 is at equivalent position (−1/2 + x, 3/2 − y, 1 − z).) thus forming a linear chain as shown in the packing diagram (figure 4), whereas in related semicarbazones [20–22], either the hydrogen on NH or that in NH_2 or both hydrogens on NH and NH_2 group of one molecule is involved in hydrogen bonding with the carbonyl oxygen of the other molecule thus forming a closed dimer.

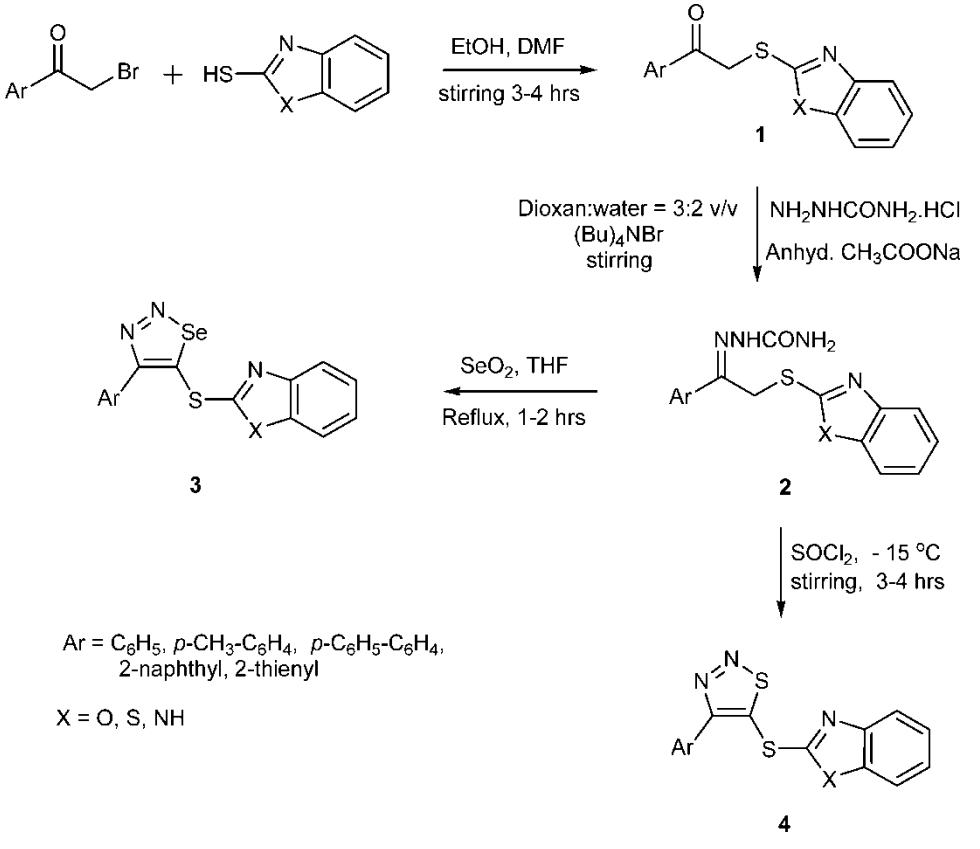

Figure 3. Synthesis of Selenadiazole (**3**) and Thiadiazole (**4**).

Table 1. Yields and melting points of **2**, **3** and **4**.

1	Ar	X	Product **2**	Yield (%)	Mp (°C)	Product **3**	Yield (%)	Mp (°C)	Product **4**	Yield (%)	Mp (°C)
a	C_6H_5	O	**2a**	77	129	**3a**	42	118–120	**4a**	16	78–80
b	p-CH_3-C_6H_4	O	**2b**	82	159	**3b**	40	97	**4b**	15	116
c	p-C_6H_5-C_6H_4	O	**2c**	84	179	**3c**	37	145	**4c**	[a]	
d	2-naphthyl	O	**2d**	80	169	**3d**	29	114	**4d**	11	123
e	2-thienyl	O	**2e**	78	154	**3e**	32	115	**4e**	[a]	
f	C_6H_5	NH	**2f**	42	162	**3f**	24	166	**4f**	21	178–180
g	p-CH_3-C_6H_4	NH	**2g**	49	172	**3g**	37	176	**4g**	24	190–191
h	p-C_6H_5-C_6H_4	NH	**2h**	55	146	**3h**	40	169	**4h**	[a]	
i	2-naphthyl	NH	**2i**	52	204–206	**3i**	36	171	**4i**	23	194–195
j	2-thienyl	NH	**2j**	51	178	**3j**	43	162	**4j**	[a]	
k	C_6H_5	S	**2k**	77	204	**3k**	43	141–142	**4k**	40	128
l	p-CH_3-C_6H_4	S	**2l**	86	175	**3l**	58	148	**4l**	71	129
m	p-C_6H_5-C_6H_4	S	**2m**	75	205	**3m**	47	231	**4m**	45	159
n	2-naphthyl	S	**2n**	93	188	**3n**	33	154	**4n**	71	145–147
o	2-thienyl	S	**2o**	89	176–178	**3o**	55	216–218	**4o**	81	154

[a]Hydrolysis takes place instead of cyclisation with thionyl chloride leading to the corresponding ketones.

Table 2. Crystal data and structural refinement for **2k** and **3m**.

Parameters	**2k**	**3m**
Empirical formula	$C_{16}H_{14}N_4OS_2$	$C_{21}H_{13}N_3S_2Se$
Formula weight	342.43	450.42
Temperature	273(2) K	273(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, Space group	Orthorhombic, Pbca	Monoclinic, P2(1)/c

Unit cell dimensions	a = 9.1514(6) Å;
	b = 15.4629(10) Å;
	c = 22.7430(15) Å.
		a = 7.5228(7) Å;
		b = 6.7571(6) Å;
		c = 36.861(3) Å;
		β = 94.394(2) deg.

Z, Volume	8,3218.3(4) Å^3	4, 1868.2(3) Å^3
Density (calculated)	1.413 Mg/m^3	1.601 Mg/m^3
Absorption coefficient	0.340 mm^{-1}	2.244 mm^{-1}
F(000)	1424	904
Crystal size	0.43 × 0.32 × 0.22 mm	0.24 × 0.16 × 0.06 mm
Theta range for data collection	1.79 to 26.01 deg.	2.22 to 25.97 deg.
Index ranges	$-6 \le h \le 11$, $-16 \le k \le 18$, $-28 \le l \le 21$	$-9 \le h \le 9$, $-8 \le k \le 8$, $-44 \le l \le 44$
Reflections collected	13720	18455
Independent reflections	3158 [R(int) = 0.0269]	3656 [R(int) = 0.0334]
Absorption correction	Multi-scan	Multi-scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squareson F^2
Data/restraints/parameters	3158/0/220	3656/0/244
Goodness-of-fit on F^2	1.035	1.025
Final R indices [I > 2sigma(I)]	$R_1 = 0.0430$, $wR_2 = 0.1083$	$R_1 = 0.0341$, $wR_2 = 0.0799$
R indices (all data)	$R_1 = 0.0527$, $wR_2 = 0.1149$	$R_1 = 0.0448$, $wR_2 = 0.0846$
Largest diff. peak and hole	0.300 and −0.248 e. Å^{-3}	0.651 and −0.241 e. Å^{-3}

The semicarbazones **2** upon selenium dioxide treatment in THF gave the 1,2,3-selenadiazoles **3** with benzimidazole/benzoxazole/benzimidazole unit linked by a heteroatom in moderate yield (table 1). Tetrahydrofuran has been found to be the solvent of choice for this conversion. The thionyl chloride treatment of these semicarbazones is found to be very sensitive to the temperature. Hydrolysis of the semicarbazone to its parent ketone was found to be predominant at 0 °C. However, in many cases the targeted thiadiazoles **4** were obtained at −15 °C, in varying yield. When the heterocyclic ring present in the starting semicarbazone is

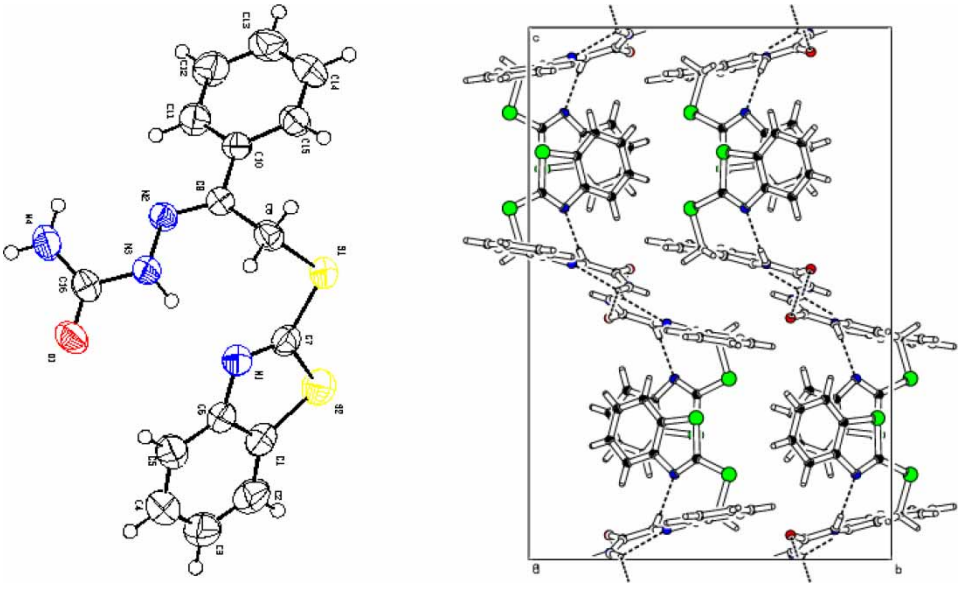

Figure 4. ORTEP (50% probability displacement ellipsoids) and packing diagram (view along a axis) of 2-[(*Z*)-2-(1,3-benzothiazol-2-ylsulfanyl)-1-phenylethylidene]-1-hydrazinecarboxamide (**2k**).

benzoxazole or benzimidazole, the yield of thiadiazole is poor, hydrolysis being the dominating process under this condition. But when benzothiazole unit is present in the parent semicarbazone, very good yield of the resultant thiadiazole is noticed upon thionyl chloride treatment (table 2). The synthesized molecules have all been characterized by NMR spectroscopy.

The complete characterization of a representative selenadiazole, 1,3-benzothiazol-2-yl 4-(4-methylphenyl)-1,2,3-selenadiazol-5-yl sulfide, **3l** (figure 5) is described here. The proton NMR spectrum of **3l** exhibits a singlet at 2.47 ppm accounting for three hydrogens. There are two doublets each accounting for two hydrogens with the coupling constant of 7.8 Hz at 7.39 ppm and 7.78 ppm due to the *p*-methylphenyl ring. There are two triplet of doublet at 7.43 ppm and 7.56 ppm ($J = 8.1$, 0.6 Hz) and two doublets at 7.83 ppm and 8.07 ppm ($J = 8.1$ Hz) each accounting for one hydrogen, all due to the benzothiazole unit.

The methyl singlet at 2.47 ppm, which has a C,H-COSY contour with a signal at 21.4 ppm, shows HMBC contours with the signals at 129.6 ppm and 139.2 ppm. The former signal is assigned to the carbons *ortho* to methyl group (C-8 and C-10) and the latter, which is a

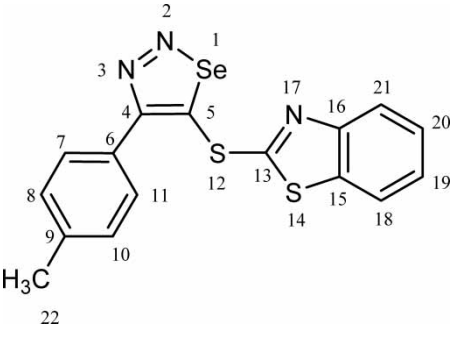

Figure 5. 1,3-benzothiazol-2-yl 4-(4-methylphenyl)-1,2,3-selenadiazol-5-yl sulfide (**3l**).

quaternary carbon, to the C-9. The former makes a C,H-COSY cross peak with the signal at 7.39 ppm which is assigned to hydrogens *ortho* to methyl group (H-8 and H-10). As the signal at 7.78 ppm makes a H,H-COSY contour with that at 7.39 ppm, it is assigned to hydrogens *meta* to methyl group (H-7 and H-11). From C,H-COSY spectrum the signal at 129.0 ppm is found to be due to the carbons *meta* to methyl group (C-7 and C-11). The signal at 7.39 ppm, in addition to the methyl carbon, makes HMBC contour with the signal at 129.3 ppm which is now assigned to C-6. The carbons C-4 and C-5 are assigned to signals at 158.0 ppm and 160.1 ppm, respectively which is confirmed from HMBC contours of H-7/H-11 with the signal at 158.0 ppm. The signals at 136.2 ppm and 150.7 ppm shall be assigned to the carbons C-15 and C-16 respectively based on the additivity rules. As C-15 makes an intense HMBC contour with the signal at 7.43 ppm, the latter is assigned to H-19. H-19 has an intense HMBC contour with the signal at 122.1 ppm, which is assigned to C-21. The signals at 125.7 ppm and 8.07 ppm are assigned to C-19 and H-21 from C,H-COSY spectra. By a similar analysis, the signals at 7.83 ppm and 7.56 ppm are assigned to H-18 and H-20, while the signals at 121.6 ppm and 126.8 ppm to the respective carbons. Finally, the left out carbon signal at 141.4 ppm is assigned to C-13.

It should be mentioned that in lower concentration of the benzimidazole (**3f–j** and **4f–j**) in DMSO-d_6 the signals due to H-18 and H-21 appear together along with other aromatic hydrogens around 7.60 ppm but in a higher concentration the signals due to this hydrogens got separated, appearing as broad bands at 7.73 ppm and 7.43 ppm. This can be attributed to the absence and presence of intermolecular hydrogen bonding respectively in the above cases controlling the 1,3-tautomerism of the benzimidazole unit [23]. The tautomerism associated with the benzimidazole ring has much influence in the ^{13}C NMR spectrum of these compounds leading to very poor intensity for some of the aromatic carbon signals of the benzimidazole unit.

Single crystal of **3m** [24] with diffraction quality was grown from chloroform and the X-ray analysis for this compound confirms the above structural assignment (figure 6). In the crystal state, the aryl substituent at the 4th position of the selenadiazole is twisted out of plane with respect to the selenadiazole ring by 39.45° while the two phenyl rings of the biphenyl unit themselves go out of plane by 38.65°.

Though none of the selenadiazoles **3** show the molecular ion peak (table 3), their mass spectral features differ widely depending on the other heterocyclic unit present in the molecule.

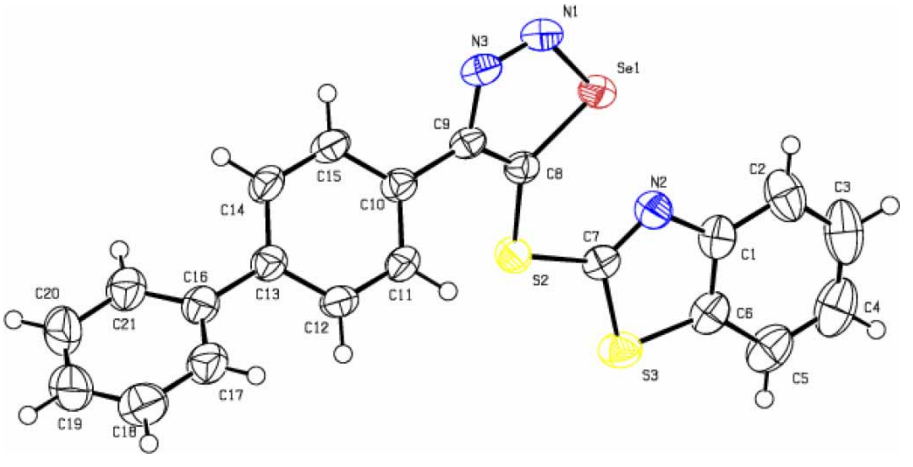

Figure 6. ORTEP diagram of 1,3-benzothiazol-2-yl 4-[1,1'-biphenyl]-4-yl-1,2,3-selenadiazol-5-yl sulfide (**3m**). Displacement ellipsoids are drawn at the 50% probability level.

Table 3. Mass spectral data of compounds 3**b, 3g, 3l, 4b, 4g** and **4l**.

Entry	M	M-N_2	M-[N_2-(S/Se)]	M-[N_2-(S/Se)-S] Ar-C=C-X	C_9H_7S (m/z = 147)	C_8H_7S (m/z = 135)	C_9H_7 (m/z = 115)	C_8H_7 (m/z = 103)	Others
3b	373 (0%)	345 (63%)	265 (39%)	233 (100%)	28%	2%	63%	25%	294 (5%), 283 (6%), 204 (6%), 195 (34%), 193 (16%), 156 (5%), 122 (10%)
3g	372 (0%)	344 (100%)	264 (82%)	232 (70%)	14%	39%	–	45%	312 (84%), 296 (44%), 280 (16%), 249 (41%), 219 (22%), 184 (26%)
3l	389 (0%)	361 (57%)	280 (100%)	249 (38%)	14%	12%	38%	20%	297 (9%), 266 (7%), 236 (11%), 195 (13%)
4b	325 (1%)	297 (100%)	265 (1%)	233 (38%)	36%	44%	–	36%	282 (5%), 122 (15%)
4g	324 (1%)	296 (100%)	264 (6%)	232 (17%)	13%	32%	–	20%	281 (9%), 251 (6%), 219 (5%)
4l	341 (<1%)	313 (100%)	280 (8%)	249 (16%)	13%	36%	–	27%	298 (7%), 236 (6%)

Thus **3 g** gives the base peak at m/e 344 due to the loss of nitrogen molecule from the molecular ion, while **3l** has its base peak at m/e 280 due to the loss of both nitrogen molecule and selenium atom. Interestingly, the base peak for **3b** appears at m/e 233, due to the loss of nitrogen, selenium and sulfur, the latter by a possible extrusion path [25]. In contrast, the thiadiazoles **4** have uniform pattern in their mass spectra. They all have a very weak molecular ion peak and irrespective of the other heterocyclic unit, the base peak is that due to the loss of nitrogen molecule alone (table 3). This subsequently loses sulfur giving another fragment with reasonable intensity. All the compounds **3** and **4** show fragments at m/e 147, 135 and 103 with varying intensities.

Ab initio calculations were carried out on Hyperchem 7.5 by using RHF with a basic function 3-21G to arrive at the minimum energy structure and it is found that the energy minimized structure is consistent with that obtained using X-ray technique. Thus the synthesis of a new set of 1,3-heteroazol-2-yl 4-aryl-1,2,3-selenadiazol/thiadiazol-5-yl sulfides is achieved.

3. Experimental

3.1 *General*

1,3-Benzoxazole-2-thiol, 1,3-benzothiazole-2-thiol were purchased from Aldrich and 1*H*-1,3-benzimidazole-2-thiol was prepared by a reported procedure [26]. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 MHz instrument in $CDCl_3$/DMSO-d_6 using TMS as internal standard. Chemical shifts are given in parts per million (δ-scale) and coupling constants are given in Hertz. IR spectra were recorded on a JASCO FT-IR instrument using KBr pellets. The single crystal X-ray data were collected on a CCD area detector diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å).

3.2 *General procedure for the preparation of 2-(1,3-benzoxazol-2-ylsulfanyl)-1-aryl-1-ethanone (1a–e), 2-(1H-1,3-benzimidazol-2-ylsulfanyl)-1-aryl-1-ethanone (1f–j) and 2-(1,3-benzothiazol-2-ylsulfanyl)-1-aryl-1-ethanone (1k–o)*

3.2.1 Method A. To a solution of 1,3-benzothiazole-2-thiol (1.67 g, 0.01 mole) in ethyl alcohol (20 mL) and dimethyl formamide (5 mL), 0.01 mole of arylacyl bromide in ethyl alcohol (20 mL) and dimethyl formamide (5 mL) was added by portion. It was stirred for two hours and then kept overnight in a refrigerator. The product obtained was filtered and then dried. Compounds **1k-o** were prepared by this method.

3.2.2 Method B. It is essentially the same as method **A** except that in method **B** the reaction was carried out in the presence of triethylamine (0.01 mole). Compounds **1a–e** and **1f–j** were prepared by this method. Ketones **1a, 1b, 1f, 1g, 1h, 1j, 1k** and **1l** have already been reported [27, 28].

3.2.3 2-(1,3-Benzoxazol-2-ylsulfanyl)-1-[1,1'-biphenyl]-4-yl-1-ethanone (1c). M.pt. 134 °C; IR (KBr): 3031, 2962, 2910, 1676, 1599, 1498, 1450, 1381, 1315, 1199, 1178, 1134, 999, 827, 764, 741 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 4.97$ (s, 2H), 7.23 (td, $J = 7.5$, 1.5 Hz, 1H), 7.28 (td, $J = 7.5$, 1.5 Hz, 1H), 7.38–7.51 (m, 4H), 7.58 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 8.14 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 41.1$, 110.0 (CH), 118.4 (CH), 124.1 (CH), 124.4

(CH), 127.3 (2xCH), 127.5 (2xCH), 128.5 (CH), 129.0 (2xCH), 129.2 (2xCH), 133.8, 139.5, 141.8, 146.7, 152.0, 164.1, 192.0; *Anal. Calcd.* for $C_{21}H_{15}NO_2S$: C, 73.02; H, 4.38; N, 4.06. Found: C, 73.18; H, 4.41; N, 4.14.

3.2.4 2-(1,3-Benzoxazol-2-ylsulfanyl)-1-(2-naphthyl)-1-ethanone (1d). M.pt. 141 °C; IR (KBr): 3033, 2962, 2924, 1674, 1628, 1500, 1450, 1388, 1308, 1180, 1132, 1001, 831, 756, 727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 5.10$ (s, 2H), 7.25 (td, $J = 7.5$, 1.5 Hz, 1H), 7.29 (td, $J = 7.5$, 1.5 Hz, 1H), 7.45 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.56–7.67 (m, 3H), 7.90 (d, $J = 7.9$ Hz, 1H), 7.94 (d, $J = 8.7$ Hz, 1H), 8.01 (d, $J = 7.9$ Hz, 1H), 8.09 (dd, $J = 8.7$, 1.8 Hz, 1H), 8.64 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 41.2$, 110.0 (CH), 118.4 (CH), 123.8 (CH), 124.1 (CH), 124.4 (CH), 127.1 (CH), 127.9 (CH), 128.8 (CH), 129.0 (CH), 129.7 (CH), 130.7 (CH), 132.4, 132.5, 135.9, 141.7, 152.0, 164.1, 192.4; *Anal. Calcd.* for $C_{19}H_{13}NO_2S$: C, 71.45; H, 4.10; N, 4.39. Found: C, 71.53; H, 4.16; N, 4.45.

3.2.5 2-(1,3-Benzoxazol-2-ylsulfanyl)-1-(2-thienyl)-1-ethanone (1e). M.pt. 80 °C; IR (KBr): 3109, 3084, 2960, 2918, 1662, 1498, 1452, 1410, 1385, 1350, 1310, 1238, 1198, 1134, 1097, 845, 752, 729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 4.85$ (s, 2H), 7.20 (dd, $J = 5.1$, 3.9 Hz, 1H), 7.25 (td, $J = 7.5$, 1.5 Hz, 1H), 7.29 (td, $J = 7.5$, 1.5 Hz, 1H), 7.45 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.58 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.75 (dd, $J = 5.1$, 1.2 Hz, 1H), 7.95 (dd, $J = 3.9$, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 40.2$, 110.0 (CH), 118.4 (CH), 124.1 (CH), 124.4 (CH), 128.4 (CH), 133.3 (CH), 135.1 (CH), 141.6, 141.8, 152.0, 163.7, 185.2; *Anal. Calcd.* for $C_{13}H_9NO_2S_2$: C, 56.71; H, 3.29; N, 5.09. Found: C, 56.75; H, 3.35; N, 5.15.

3.2.6 2-(1H-1,3-Benzimidazol-2-ylsulfanyl)-1-(2-naphthyl)-1-ethanone (1i). M.pt. 237°C; IR (KBr): 3140, 3030, 2924, 2846, 1670, 1628, 1516, 1462, 1431, 1375, 1190, 1120, 1003, 813, 769, 743 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 5.60$ (s, 2H), 7.49 (dd, $J = 6.0$, 3.0 Hz, 2H), 7.66–7.76 (m, 4H), 8.04–8.12 (m, 3H), 8.18 (d, $J = 7.8$ Hz, 1H), 8.90 (s, 1H), 12.78 (bs, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 39.7$, 111.1 (2xCH), 121.6 (CH), 123.2 (2xCH), 125.3 (CH), 125.8 (CH), 126.6 (CH), 127.2 (CH), 127.6 (CH), 129.1 (CH), 130.0, 130.1, 130.6 (2xC), 133.4, 148.5, 190.0; *Anal. Calcd.* for $C_{19}H_{14}N_2OS$: C, 71.67; H, 4.43; N, 8.80. Found: C, 71.73; H, 4.51; N, 8.91.

3.2.7 2-(1,3-Benzothiazol-2-ylsulfanyl)-1-[1,1'-biphenyl]-4-yl-1-ethanone (1m). M.pt. 109 °C; IR (KBr): 3059, 2954, 2908, 1689, 1601, 1452, 1425, 1358, 1294, 1186, 991, 758, 721 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 4.99$ (s, 2H), 7.30 (td, $J = 7.5$, 1.2 Hz, 1H), 7.37–7.50 (m, 4H), 7.64 (d, $J = 7.8$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 7.5$ Hz, 1H), 7.83 (d, $J = 7.5$ Hz, 1H), 8.15 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 40.9$, 121.1 (CH), 121.5 (CH), 124.4 (CH), 126.0 (CH), 127.3 (2xCH), 127.4 (2xCH), 128.4 (CH), 129.0 (2xCH), 129.2 (2xCH), 134.1, 135.5, 139.6, 146.5, 152.8, 165.3, 192.5; *Anal. Calcd.* for $C_{21}H_{15}NOS_2$: C, 69.78; H, 4.18; N, 3.87. Found: C, 69.84; H, 4.23; N, 3.95.

3.2.8 2-(1,3-Benzothiazol-2-ylsulfanyl)-1-(2-naphthyl)-1-ethanone (1n). M.pt. 137 °C; IR (KBr): 3057, 2958, 2916, 1689, 1460, 1425, 1352, 1294, 1176, 1120, 997, 854, 814, 754, 727 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 5.17$ (s, 2H), 7.30 (td, $J = 7.5$, 1.5 Hz, 1H), 7.39 (td, $J = 7.5$, 1.5 Hz, 1H), 7.60 (td, $J = 7.5$, 1.5 Hz, 1H), 7.66 (td, $J = 7.5$, 1.5 Hz,

1H), 7.75 (dd, $J = 7.8, 0.9$ Hz, 1H), 7.82 (dd, $J = 7.8, 0.9$ Hz, 1H), 7.92–7.98 (m, 2H), 8.04–8.07 (m, 2H), 8.74 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 39.3$, 119.7 (CH), 119.8 (CH), 122.3 (CH), 122.9 (CH), 124.6 (CH), 125.5 (CH), 126.3 (CH), 127.1 (CH), 127.4 (CH), 128.2 (CH), 129.2 (CH), 130.8, 131.3, 133.6, 134.1, 151.2, 163.9, 191.2; *Anal. Calcd.* for $C_{19}H_{13}NOS_2$: C, 68.03; H, 3.91; N, 4.18. Found: C, 68.05; H, 3.89; N, 4.21.

3.2.9 2-(1,3-Benzothiazol-2-ylsulfanyl)-1-(2-thienyl)-1-ethanone (1o). M.pt. 118 °C; IR (KBr): 3074, 2962, 2904, 1670, 1464, 1427, 1406, 1356, 1294, 1232, 1198, 995, 767, 733 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 4.86$ (s, 2H), 7.18 (dd, $J = 5.1$, 3.9 Hz, 1H), 7.30 (td, $J = 7.5$, 1.5 Hz, 1H), 7.41 (td, $J = 7.5$, 1.5 Hz, 1H), 7.73 (dd, $J = 5.1$, 0.9 Hz, 1H), 7.75 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.82 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.96 (dd, $J = 3.9$, 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 40.3$, 121.1 (CH), 121.5 (CH), 124.4 (CH), 126.0 (CH), 128.3 (CH), 133.3 (CH), 134.9 (CH), 135.5, 142.2, 152.7, 165.0, 185.8; *Anal. Calcd.* for $C_{13}H_9NOS_3$: C, 53.58; H, 3.11; N, 4.81. Found: C, 53.61; H, 3.15; N, 4.87.

3.3 *General procedure for the preparation of 2-[(Z)-2-(1,3-benzoxazol-2-yl-sulfanyl)-1-arylethylidene]-1-hydrazinecarboxamide (2a–e), 2-[(Z)-2-(1H-1,3-benzimidazol-2-ylsulfanyl)-1-arylethylidene]-1-hydrazinecarboxamide (2f–j) and 2-[(Z)-2-(1,3-benzothiazol-2-ylsulfanyl)-1-arylethylidene]-1-hydrazinecarboxamide (2k–o)*

3.3.1 Method A. To a solution of appropriate ketone (0.005 mole), semicarbazide hydrochloride (3.90 g, 0.035 mole) and sodium acetate (2.87 g, 0.035 mole) in a dioxane-water mixture (50 mL, 3:2 v/v), a catalytic amount of phase transfer catalyst (tetrabutylammonium bromide) was added. The reaction mixture was stirred at room temperature for three days, poured onto crushed ice, extracted with chloroform, and evaporated to dryness. The ethyl acetate insoluble portion was recrystallized from ethanol to give the respective semicarbazones. Compounds **2a–e** and **2k–o** were prepared by this method.

3.3.2 Method B. To a warm solution of 0.005 mole of the appropriate ketone in a ethanol-dimethyl sulphoxide mixture (40 mL, 3:1 v/v), a solution of equimolar amount of semicarbazide hydrochloride (3.90 g, 0.035 mole) and anhydrous sodium acetate (2.87 g, 0.035 mole) in 20 mL of water was added and refluxed for 4 hr. The solution was cooled and poured onto crushed ice and filtered and washed with cold alcohol. Compounds **2f–j** were prepared by this method. Compound **2k** has already been reported [29].

3.3.3 2-[(Z)-2-(1,3-Benzoxazol-2-ylsulfanyl)-1-phenylethylidene]-1-hydrazinecarboxamide (2a). IR (KBr): 3467, 3284, 3186, 3128, 2935, 1709, 1589, 1498, 1450, 1433, 1236, 1141, 1097, 736 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 4.49$ (s, 2H), 5.45 (bs, 1H), 6.14 (bs, 1H), 7.21–7.33 (m, 3H), 7.38–7.41 (m, 3H), 7.66–7.69 (m, 2H), 7.78 (d, $J = 7.5$ Hz, 1H), 11.72 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 26.4$, 110.0 (CH), 118.9 (CH), 124.4 (CH), 124.9 (CH), 126.0 (2xCH), 128.7 (2xCH), 129.5 (CH), 135.8, 140.6, 143.2, 152.3, 158.2, 164.5; *Anal. Calcd.* for $C_{16}H_{14}N_4O_2S$: C, 58.88; H, 4.32; N, 17.17. Found: C, 58.94; H, 4.44; N, 17.24.

3.3.4 2-[(Z)-2-(1,3-Benzoxazol-2-ylsulfanyl)-1-(4-methylphenyl)ethylidene]-1-hydrazinecarboxamide (2b). IR (KBr): 3477, 3282, 3203, 3145, 2924, 1710, 1587, 1494, 1450,

1430, 1238, 1138, 1099, 812, 746 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 2.36$ (s, 3H), 4.58 (s, 2H), 6.20 (bs, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 7.26 (td, $J = 7.5$, 1.5 Hz, 1H), 7.31 (td, $J = 7.5$, 1.5 Hz, 1H), 7.43 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 2H), 7.71 (dd, $J = 7.5$, 1.5 Hz, 1H), 10.73 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 21.1$, 26.2, 110.0 (CH), 118.5 (CH), 124.3 (CH), 124.6 (CH), 125.9 (2xCH), 129.2 (2xCH), 132.9, 139.2, 140.7, 142.4, 152.0, 158.0, 164.4; *Anal. Calcd.* for $C_{17}H_{16}N_4O_2S$: C, 59.98; H, 4.74; N, 16.46. Found: C, 59.87; H, 4.68; N, 16.50.

3.3.5 2-[(Z)-2-(1,3-Benzoxazol-2-ylsulfanyl)-1-[1,1'-biphenyl]-4-ylethylidene]-1 -hydr azinecarboxamide (2c). IR (KBr): 3469, 3284, 3203, 3145, 2935, 1712, 1589, 1498, 1450, 1429, 1240, 1240, 1138, 1099, 739 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 4.78$ (s, 2H), 6.64 (bs, 2H), 7.31–7.38 (m, 3H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.58 (d, $J = 7.2$ Hz, 1H), 7.63–7.66 (m, 5H), 7.99 (d, $J = 8.4$ Hz, 2H), 10.34 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25°C): $\delta = 24.0$, 108.3 (CH), 116.4 (CH), 122.5 (CH), 122.8 (CH), 124.6 (2xCH), 124.7 (2xCH), 124.9 (2xCH), 125.7 (CH), 127.0 (2xCH), 133.0, 137.6, 138.0, 138.6, 139.0, 149.6, 155.2, 161.6; *Anal. Calcd.* for $C_{22}H_{18}N_4O_2S$: C, 65.65; H, 4.51; N, 13.92. Found: C, 65.58; H, 4.54; N, 13.97.

3.3.6 2-[(Z)-2-(1,3-Benzoxazol-2-ylsulfanyl)-1-(2-naphthyl)ethylidene]-1-hydrazineca rboxamide (2d). IR (KBr): 3471, 3288, 3201, 3139, 2933, 1722, 1593, 1500, 1450, 1429, 1240, 1142, 760, 739 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25°C): $\delta = 4.76$ (s, 2H), 6.30 (bs, 2H), 7.26 (t, $J = 6.0$ Hz, 1H), 7.32 (t, $J = 6.0$ Hz, 1H), 7.45 (d, $J = 7.5$ Hz, 1H), 7.50 (dd, $J = 6.0$, 3.3 Hz, 2H), 7.72 (d, $J = 7.5$ Hz, 1H), 7.83 (d, $J = 8.7$ Hz, 2H), 7.88–7.91 (m, 1H), 8.04 (dd, $J = 8.7$, 1.5 Hz, 1H), 8.14 (s, 1H), 10.79 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 25.0$, 108.9 (CH), 117.5 (CH), 122.5 (CH), 123.3 (CH), 123.6 (CH), 124.6 (CH), 125.4 (CH), 125.7 (CH), 126.4 (CH), 127.0 (CH), 127.4 (CH), 131.8, 132.2, 132.3, 139.7, 140.7, 150.9, 156.7, 163.3; *Anal. Calcd.* for $C_{20}H_{16}N_4O_2S$: C, 63.81; H, 4.28; N, 14.88. Found: C, 63.69; H, 4.14; N, 14.74.

3.3.7 2-[(E)-2-(1,3-Benzoxazol-2-ylsulfanyl)-1-(2-thienyl)ethylidene]-1-hydrazinecarb oxamide (2e). IR (KBr): 3469, 3286, 3197, 3141, 2956, 1707, 1589, 1494, 1450, 1425, 1236, 1136, 1099, 748, 702 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 4.57$ (s, 2H), 6.12 (bs, 2H), 7.04 (t, $J = 4.5$ Hz, 1H), 7.27–7.34 (m, 4H), 7.45 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.73 (dd, $J = 7.5$, 1.5 Hz, 1H), 10.94 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 25.9$, 109.2 (CH), 117.7 (CH), 123.6 (CH), 123.9 (CH), 125.3 (CH), 126.5 (CH), 126.6 (CH), 138.4, 139.7, 140.7, 151.2, 156.8, 163.5; *Anal. Calcd.* for $C_{14}H_{12}N_4O_2S_2$: C, 50.59; H, 3.64; N, 16.86. Found: C, 50.62; H, 3.71; N, 16.90.

3.3.8 2-[(Z)-2-(1H-1,3-Benzimidazol-2-ylsulfanyl)-1-phenylethylidene]-1-hydrazineca rboxamide (2f). IR (KBr): 3479, 3375, 3338, 3099, 2983, 1676, 1570, 1439, 1414, 1306, 1267, 1230, 1093, 1005, 972, 744 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 4.55$ (s, 2H), 6.19 (bs, 2H), 7.13 (dd, $J = 6.0$, 3.0 Hz, 2H), 7.36–7.39 (m, 3H), 7.55 (bs, 2H), 7.73–7.76 (m, 2H), 12.09 (s, 1H), 12.38 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 24.7$, 112.9* (2xCH), 120.8 (2xCH), 124.9 (2xCH), 127.4 (2xCH), 127.9 (CH), 134.9, 138.4* (2xC), 142.8, 148.7, 157.4; *Anal. Calcd.* for $C_{16}H_{15}N_5OS$: C, 59.06; H, 4.65; N, 21.52. Found: C, 58.94; H, 4.53; N, 21.48.

3.3.9 2-[(Z)-2-(1H-1,3-Benzimidazol-2-ylsulfanyl)-1-(4-methylphenyl)ethylidene]-1-hydrazinecarboxamide (2 g). IR (KBr): 3479, 3305, 3136, 3051, 2974, 1687, 1573, 1456, 1444, 1269, 1232, 1043, 741 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 2.36$ (s, 3H), 4.52 (s, 2H), 6.17 (bs, 2H), 7.12 (dd, $J = 6.0, 3.0$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 7.34 (bs, 1H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.46 (bs, 1H), 12.05 (s, 1H), 12.41 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 20.0$, 24.5, 109.4* (CH), 116.8* (CH), 120.8* (2xCH), 124.8 (2xCH), 128.0 (2xCH), 132.1, 132.9*, 134.7*, 137.9, 141.6*, 143.0, 148.8, 157.4; *Anal. Calcd.* for $C_{17}H_{17}N_5OS$: C, 60.16; H, 5.05; N, 20.63. Found: C, 60.21; H, 5.09; N, 20.59.

3.3.10 2-[(Z)-2-(1H-1,3-Benzimidazol-2-ylsulfanyl)-1-[1,1'-biphenyl]-4-ylethylidene]-1-hydrazinecarboxamide (2 h). IR (KBr): 3473, 3399, 2985, 1679, 1568, 1442, 1423, 1358, 1267, 1232, 1091, 1005, 737 cm^{-1}; ^1H NMR$^{\$}$ (300 MHz, DMSO-d_6, 25 °C): $\delta = 4.57$ (s, 2H), 6.10 (bs, 2H), 7.15 (dd, $J = 6.0, 3.0$ Hz, 2H), 7.37 (tt, $J = 7.5, 2.1$ Hz, 1H), 7.44–7.49 (m, 3H), 7.58–7.65 (m, 5H), 7.82 (d, $J = 8.4$ Hz, 2H), 12.12 (s, 1H); ^{13}C NMR$^{\#}$ (75 MHz, DMSO-d_6, 25 °C): $\delta = 30.9$, 127.2* (2xCH), 131.7 (2xCH), 132.0 (2xCH), 132.1 (2xCH), 132.9 (CH), 134.1 (2xCH), 140.1, 145.1, 146.7, 149.0, 154.9, 163.7; *Anal. Calcd.* for $C_{22}H_{19}N_5OS$: C, 65.81; H, 4.77; N, 17.44. Found: C, 65.73; H, 4.84; N, 17.41.

3.3.11 2-[(Z)-2-(1H-1,3-Benzimidazol-2-ylsulfanyl)-1-(2-naphthyl)ethylidene]-1-hydrazinecarboxamide (2i). IR (KBr): 3475, 3303, 3132, 3049, 2979, 1161, 1572, 1443, 1414, 1348, 1269, 1232, 1117, 741 cm^{-1}; ^1H NMR$^{\$}$ (300 MHz, DMSO-d_6, 25 °C): $\delta = 4.65$ (s, 2H), 6.17 (bs, 2H), 7.14 (dd, $J = 6.0, 3.0$ Hz, 2H), 7.49 (dd, $J = 6.0, 3.0$ Hz, 2H), 7.59–7.62 (bs, 1H), 7.80–7.89 (m, 4H), 7.83 (d, $J = 8.4$ Hz, 2H), 12.25 (s, 1H); ^{13}C NMR$^{\#}$ (75 MHz, DMSO-d_6, 25 °C): $\delta = 24.8$, 121.1 (2xCH), 122.7 (CH), 124.7 (CH), 125.6 (CH), 125.9 (CH), 126.7 (CH), 127.2 (CH), 127.6 (CH), 132.1, 132.5, 132.6, 143.2, 148.9, 157.7; *Anal. Calcd.* for $C_{20}H_{17}N_5OS$: C, 63.98; H, 4.56; N, 18.65. Found: C, 63.87; H, 4.51; N, 18.59.

3.3.12 2-[(E)-2-(1H-1,3-Benzimidazol-2-ylsulfanyl)-1-(2-thienyl)ethylidene]-1-hydrazinecarboxamide (2j). IR (KBr): 3475, 3327, 3134, 3087, 2979, 1674, 1566, 1495, 1431, 1412, 1350, 1267, 1232, 1132, 742 cm^{-1}; ^1H NMR$^{\$}$ (300 MHz, DMSO-d_6, 25 °C): $\delta = 4.48$ (s, 2H), 6.04 (bs, 2H), 7.04 (dd, $J = 4.8, 3.6$ Hz, 1H), 7.14 (dd, $J = 6.0, 3.3$ Hz, 2H), 7.24 (dd, $J = 3.6, 0.6$ Hz, 1H), 7.31 (dd, $J = 4.8, 0.6$ Hz, 1H), 7.58 (bs, 2H), 12.31 (s, 1H); ^{13}C NMR$^{\#}$ (75 MHz, DMSO-d_6, 25 °C): $\delta = 26.2$, 121.9 (2xCH), 125.7 (CH), 127.2 (CH), 127.2 (CH), 141.2, 141.8, 149.6, 158.2; *Anal. Calcd.* for $C_{14}H_{13}N_5OS_2$: C, 50.74; H, 3.95; N, 21.13. Found: C, 50.69; H, 3.90; N, 21.08.

3.3.13 2-[(Z)-2-(1,3-Benzothiazol-2-ylsulfanyl)-1-phenylethylidene]-1-hydrazinecarboxamide (2 k). IR (KBr): 3502, 3305, 3059, 2929, 1687, 1562, 1488, 1425, 1306, 1238, 1149, 1074, 1024, 1005, 752 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 4.63$ (s, 2H), 6.17 (bs, 2H), 7.31–7.48 (m, 5H), 7.74–7.79 (m, 3H), 8.25 (d, $J = 8.1$ Hz, 1H), 11.03 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 25.4$, 119.9 (CH), 120.4 (CH), 123.5 (CH), 124.8 (2xCH), 125.1 (CH), 127.2 (2xCH), 127.8 (CH), 133.6, 134.4, 141.5, 150.4, 156.6, 164.8.

3.3.14 2-[(Z)-2-(1,3-Benzothiazol-2-ylsulfanyl)-1-(4-methylphenyl)ethylidene]-1-hydrazinecarboxamide (2l). IR (KBr): 3462, 3280, 3058, 2927, 1705, 1591, 1423, 1311, 1240, 1167, 1101, 1039, 1003, 764 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 2.36$ (s, 3H), 4.60 (s, 2H), 6.28 (bs, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 7.32 (td, $J = 7.5, 1.2$ Hz, 1H), 7.45 (td,

$J = 7.5, 1.2$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 7.5$ Hz, 1H), 8.23 (d, $J = 7.5$ Hz, 1H), 10.98 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 20.0, 25.6, 120.0$ (CH), 120.7 (CH), 123.6 (CH), 124.9 (2xCH), 125.3 (CH), 128.0 (2xCH), 131.8, 133.8, 138.1, 142.0, 150.6, 156.9, 165.0; *Anal. Calcd.* for $C_{17}H_{16}N_4OS_2$: C, 57.28; H, 4.52; N, 15.72. Found: C, 57.21; H, 4.45; N, 15.64.

3.3.15 2-[(Z)-2-(1,3-Benzothiazol-2-ylsulfanyl)-1-[1,1'-biphenyl]-4-ylethylidene]-1-hydrazinecarboxamide (2 m). IR (KBr): 3465, 3280, 3207, 3145, 3058, 2927, 1710, 1587, 1427, 1309, 1236, 1157, 1120, 1041, 1003, 752 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 4.78$ (s, 2H), 6.64 (bs, 2H), 7.33–7.38 (m, 2H), 7.45 (d, $J = 7.5$ Hz, 2H), 7.48 (td, $J = 6.3$, 0.9 Hz, 1H), 7.64–7.67 (m, 4H), 7.93 (d, $J = 8.1$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 2H), 8.11 (d, $J = 8.1$ Hz, 1H), 10.63 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 24.7$, 119.5 (CH), 119.7 (CH), 122.8 (CH), 124.5 (CH), 124.6 (2xCH), 124.7 (2xCH), 124.8, 125.0 (2xCH), 125.7 (CH), 127.0 (2xCH), 133.0, 137.7, 138.7, 139.4, 149.9, 155.5, 164.1; *Anal. Calcd.* for $C_{22}H_{18}N_4OS_2$: C, 63.13; H, 4.33; N, 13.39. Found: C, 63.19; H, 4.36; N, 13.44.

3.3.16 2-[(Z)-2-(1,3-Benzothiazol-2-ylsulfanyl)-1-(2-naphthyl)ethylidene]-1-hydrazinecarboxamide (2n). IR (KBr): 3469, 3284, 3193, 3136, 3060, 2925, 1716, 1589, 1429, 1305, 1238, 1157, 1101, 1005, 754 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 4.85$ (s, 2H), 6.60 (bs, 2H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.44–7.51 (m, 3H), 7.82–7.93 (m, 4H), 8.16 (d, $J = 8.1$ Hz, 2H), 8.24 (s, 1H), 10.79 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 24.7$, 119.7 (CH), 119.8 (CH), 122.1 (CH), 122.9 (CH), 124.0 (CH), 124.6 (CH), 124.7 (CH), 124.9 (CH), 125.7 (CH), 126.1 (CH), 126.7 (CH), 131.1, 131.4, 131.6, 133.2, 140.1, 150.1, 155.8, 164.3; *Anal. Calcd.* for $C_{20}H_{16}N_4OS_2$: C, 61.20; H, 4.11; N, 14.27. Found: C, 61.09; H, 4.24; N, 14.35.

3.3.17 2-[(E)-2-(1,3-Benzothiazol-2-ylsulfanyl)-1-(2-thienyl)ethylidene]-1-hydrazinecarboxamide (2o). IR (KBr): 3487, 3294, 3095, 2981, 2935, 1668, 1566, 1487, 1429, 1302, 1242, 1078, 1005, 752 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 4.60$ (s, 2H), 6.24 (bs, 2H), 7.05 (t, $J = 4.5$ Hz, 1H), 7.31–7.36 (m, 3H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.79 (d, $J = 7.5$ Hz, 1H), 8.23 (d, $J = 7.5$ Hz, 1H), 10.88 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 26.1$, 120.0 (CH), 120.5 (CH), 123.6 (CH), 125.1 (CH), 125.2 (CH), 126.2 (CH), 126.3 (CH), 133.7, 138.9, 140.3, 150.4, 156.4, 164.8; *Anal. Calcd.* for $C_{14}H_{12}N_4OS_3$: C, 48.25; H, 3.47; N, 16.08. Found: C, 48.31; H, 3.55; N, 16.14.

3.4 *General procedure for the synthesis of 1,3-benzoxa(thia/imida)zol-2-yl 4-aryl-1,2,3-selenadiazol-5-yl sulfides (3a–o)*

A solution of 0.001 mole of the appropriate semicarbazone was dissolved in dry THF by gentle warming and 0.01 mole (1.10 g) of powdered selenium dioxide was added by portion. The reaction mixture was heated to reflux on a water bath for one-two hours. The selenium deposited on cooling was removed by filtration, and the filtrate was poured into crushed ice, extracted with chloroform. The product was purified by column chromatography using silica gel (60–120 mesh) with 97:3 petroleum ether: ethyl acetate (50:50 when X=NH) as eluent.

3.4.1 1,3-Benzoxazol-2-yl 4-phenyl-1,2,3-selenadiazol-5-yl sulfide (3a). IR (KBr): 3055, 1628, 1508, 1450, 1433, 1232, 1213, 1138, 1016, 741, 698 cm^{-1}; ^{1}H NMR (300 MHz,

$CDCl_3$, 25 °C): $\delta = 7.36$ (td, $J = 7.5$, 1.8 Hz, 1H), 7.40 (td, $J = 7.5$, 1.8 Hz, 1H), 7.50–7.62 (m, 4H), 7.75 (dd, $J = 7.5$, 1.8 Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 110.6$ (CH), 119.1 (CH), 125.1 (CH), 125.4 (CH), 129.0 (2xCH), 129.2 (2xCH), 129.3 (CH), 131.6, 140.1, 141.2, 153.0, 158.7, 160.2; *Anal. Calcd.* for $C_{15}H_9N_3OSSe$: C, 50.29; H, 2.53; N, 11.73. Found: C, 50.32; H, 2.61; N, 11.78.

3.4.2 1,3-Benzoxazol-2-yl 4-(4-methylphenyl)-1,2,3-selenadiazol-5-yl sulfide (3b). IR (KBr): 3016, 1651, 1502, 1444, 1232, 1213, 1138, 1095, 816, 737 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 2.47$ (s, 3H), 7.31 (m, 1H), 6.36–7.42 (m, 3H), 7.51 (d, $J = 8.1$ Hz, 1H), 7.73–7.77 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 21.4$, 110.6 (CH), 119.2 (CH), 125.1 (CH), 125.4 (CH), 128.7 (CH), 129.1 (2xCH), 129.7 (2xCH), 139.5, 140.2, 140.6, 153.0, 158.9, 160.4; *Anal. Calcd.* for $C_{16}H_{11}N_3OSSe$: C, 51.62; H, 2.98; N, 11.29. Found: C, 51.68; H, 2.94; N, 11.34.

3.4.3 1,3-Benzoxazol-2-yl 4-[1,1'-biphenyl]-4-yl-1,2,3-selenadiazol-5-yl sulfide (3c). IR (KBr): 3051, 1633, 1508, 1446, 1230, 1140, 1007, 739, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.34$–7.43 (m, 3H), 7.48–7.54 (m, 3H), 7.70 (d, $J = 8.7$ Hz, 2H), 7.76 (dd, $J = 7.5$, 1.8 Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.97 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 110.6$ (CH), 119.2 (CH), 125.2 (CH), 125.4 (CH), 127.2 (2xCH), 127.7 (2xCH), 127.8 (CH), 128.9 (2xCH), 129.6 (2xCH), 130.5, 140.1, 140.2, 141.0, 142.1, 153.0, 158.4, 160.3; *Anal. Calcd.* for $C_{21}H_{13}N_3OSSe$: C, 58.07; H, 3.02; N, 9.67. Found: C, 58.12; H, 2.98; N, 9.71.

3.4.4 1,3-Benzoxazol-2-yl 4-(2-naphthyl)-1,2,3-selenadiazol-5-yl sulfide (3d). IR (KBr): 3051, 1624, 1504, 1448, 1217, 1138, 1097, 1020, 744 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.37$ (td, $J = 7.5$, 1.5 Hz, 1H), 7.41 (td, $J = 7.5$, 1.5 Hz, 1H), 7.53 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.56–7.63 (m, 2H), 7.77 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.93–8.01 (m, 3H), 8.06 (d, $J = 8.4$ Hz, 1H), 8.35 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 110.6$ (CH), 119.2 (CH), 125.2 (CH), 125.4 (CH), 126.5 (CH), 126.8 (CH), 127.1 (CH), 127.9 (CH), 128.4 (CH), 128.8 (CH), 128.9 (CH), 129.1, 133.2, 133.4, 140.1, 141.5, 153.0, 158.7, 160.3; *Anal. Calcd.* for $C_{19}H_{11}N_3OSSe$: C, 55.89; H, 2.72; N, 10.29. Found: C, 55.94; H, 2.79; N, 10.35.

3.4.5 1,3-Benzoxazol-2-yl 4-(2-thienyl)-1,2,3-selenadiazol-5-yl sulfide (3e). IR (KBr): 3101, 1631, 1510, 1448, 1305, 1238, 1214, 1134, 836, 802, 742, 710 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.24$ (dd, $J = 5.1$, 3.9 Hz, 1H), 7.37 (td, $J = 7.5$, 1.8 Hz, 1H), 7.41 (td, $J = 7.5$, 1.8 Hz, 1H), 7.51 (dd, $J = 5.1$, 1.2 Hz, 1H), 7.54 (dd, $J = 7.5$, 1.8 Hz, 1H), 7.74–7.76 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 110.7$ (CH), 119.2 (CH), 125.3 (CH), 125.5 (CH), 127.3 (CH), 127.4 (CH), 127.7 (CH), 134.1, 138.2, 140.0, 153.0, 153.1, 159.9; *Anal. Calcd.* for $C_{13}H_7N_3OS_2Se$: C, 42.86; H, 1.94; N, 11.53. Found: C, 42.91; H, 2.01; N, 11.47.

3.4.6 1H-1,3-Benzimidazol-2-yl 4-phenyl-1,2,3-selenadiazol-5-yl sulfide (3f). IR (KBr): 3139, 3089, 3068, 1618, 1502, 1421, 1355, 1267, 1230, 1010, 968, 760, 731, 690 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 7.25$ (dd, $J = 6.0$, 3.3 Hz, 2H), 7.44 (bs, 1H), 7.51 (tt, $J = 7.2$, 2.1 Hz, 1H), 7.58 (t, $J = 7.2$ Hz, 2H), 7.73 (bs, 1H), 7.88 (d, $J = 7.2$ Hz, 2H),

12.86 (bs, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): δ = 111.3*, 118.0*, 122.3*, 123.0*, 128.7 (2xCH), 128.8 (CH), 128.9 (2xCH), 132.4, 136.5*, 141.9*, 143.8, 144.7, 157.1; *Anal. Calcd.* for $C_{15}H_{10}N_4SSe$: C, 50.42; H, 2.82; N, 15.68. Found: C, 50.48; H, 2.89; N, 15.72.

3.4.7 1H-1,3-Benzimidazol-2-yl 4-(4-methylphenyl)-1,2,3-selenadiazol-5-yl sulfide (3g). IR (KBr): 3139, 3091, 3062, 1618, 1502, 1439, 1419, 1267, 1234, 1108, 814, 731 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 2.47 (s, 3H), 7.25 (dd, J = 6.0, 3.0 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.45 (bs, 1H), 7.73 (bs, 1H), 7.77 (d, J = 8.1 Hz, 2H), 12.92 (bs, 1H); ^{13}C NMR$^{\#}$ (75 MHz, DMSO-d_6, 25 °C): δ = 21.3, 122.6, 128.8 (2xCH), 129.5 (2xCH), 138.8, 143.2, 144.8, 157.2; *Anal. Calcd.* for $C_{16}H_{12}N_4SSe$: C, 51.75; H, 3.26; N, 15.09. Found: C, 51.68; H, 2.94; N, 11.34.

3.4.8 1H-1,3-Benzimidazol-2-yl 4-[1,1'-biphenyl]-4-yl-1,2,3-selenadiazol-5-yl sulfide (3h). IR (KBr): 3136, 3068, 1618, 1491, 1436, 1267, 1232, 837, 729 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 25°C): δ = 7.26 (dd, J = 6.0, 3.0 Hz, 2H), 7.41 (tt, J = 7.2, 2.1 Hz, 1H), 7.43 (bs, 1H), 7.51 (t, J = 7.2 Hz, 2H), 7.70 (d, J = 7.2 Hz, 2H), 7.74 (bs, 1H), 7.82 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 12.78 (bs, 1H); ^{13}C NMR$^{\#}$ (75 MHz, DMSO-d_6, 25 °C): δ = 126.3 (2xCH), 126.6 (2xCH), 127.1 (CH), 128.3 (2xCH), 128.8 (2xCH), 130.8, 139.4, 140.7, 143.1, 144.1, 156.2; *Anal. Calcd.* for $C_{21}H_{14}N_4SSe$: C, 58.20; H, 3.26; N, 12.93. Found: C, 58.33; H, 3.31; N, 12.99.

3.4.9 1H-1,3-Benzimidazol-2-yl 4-(2-naphthyl)-1,2,3-selenadiazol-5-yl sulfide (3i). IR (KBr): 3141, 2983, 1741, 1629, 1483, 1419, 1357, 1298, 1269, 1022, 737 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 25°C): δ = 6.92–6.94 (m, 1H), 7.25 (dd, J = 6.0, 3.3 Hz, 2H), 7.49 (bs, 1H), 7.61 (dd, J = 6.3, 3.3 Hz, 2H), 7.71 (bs, 1H), 7.97–8.05 (m, 2H), 8.10 (d, J = 8.4 Hz, 1H), 8.38 (s, 1H), 13.14 (bs, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): δ = 109.7*, 116.3*, 118.8 (CH), 120.5*, 121.6*, 124.9 (CH), 125.2 (CH), 125.3 (CH), 126.1 (CH), 126.6 (2xCH), 127.0 (CH), 128.0, 128.3, 135.1, 140.2, 142.1, 142.9, 155.4; *Anal. Calcd.* for $C_{19}H_{12}N_4SSe$: C, 56.02; H, 2.97; N, 13.75. Found: C, 55.89; H, 2.90; N, 13.68.

3.4.10 1H-1,3-Benzimidazol-2-yl 4-(2-thienyl)-1,2,3-selenadiazol-5-yl sulfide (3j). IR (KBr): 3154, 3072, 1618, 1492, 1442, 1415, 1250, 1176, 1005, 838, 741 cm^{-1}; ^{1}H NMR$^{\$}$ (300 MHz, DMSO-d_6, 25 °C): δ = 7.24–7.28 (m, 3H), 7.56 (dd, J = 5.1, 1.2 Hz, 1H), 7.60 (dd, J = 6.0, 3.0 Hz, 2H), 7.75 (dd, J = 3.9, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): δ = 115.3 (2xCH), 123.3 (2xCH), 127.0 (CH), 127.3 (CH), 128.3 (CH), 135.4, 139.8 (2xC), 141.1, 144.8, 152.0; *Anal. Calcd.* for $C_{13}H_8N_4S_2Se$: C, 42.98; H, 2.22; N, 15.42. Found: C, 41.23; H, 1.94; N, 11.17.

3.4.11 1,3-Benzothiazol-2-yl 4-phenyl-1,2,3-selenadiazol-5-yl sulfide (3k). IR (KBr): 3060, 1635, 1467, 1454, 1425, 1384, 1223, 1016, 1003, 754, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 7.40 (td, J = 7.5, 1.8 Hz, 1H), 7.47–7.60 (m, 4H), 7.80 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 121.6 (CH), 122.1 (CH), 125.7 (CH), 126.9 (CH), 128.9 (2xCH), 129.1, 129.2 (2xCH), 132.2, 136.3, 142.0, 150.7, 157.9, 160.0; *Anal. Calcd.* for $C_{15}H_9N_3S_2Se$: C, 48.13; H, 2.42; N, 11.23. Found: C, 48.24; H, 2.37; N, 11.18.

3.4.12 1,3-Benzothiazol-2-yl 4-(4-methylphenyl)-1,2,3-selenadiazol-5-yl sulfide (3l). IR (KBr): 3058, 3024, 1653, 1452, 1428, 1226, 1128, 1074, 1007, 820, 752 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 2.47$ (s, 3H), 7.39 (d, $J = 7.8$ Hz, 2H), 7.43 (td, $J = 8.1$, 0.6 Hz, 1H), 7.56 (td, $J = 8.1$, 0.6 Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 2H), 7.83 (d, $J = 8.1$ Hz, 1H), 8.07 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 21.4$, 121.6 (CH), 122.1 (CH), 125.7 (CH), 126.8 (CH), 129.0 (2xCH), 129.3, 129.6 (2xCH), 136.2, 139.2, 141.4, 150.7, 158.0, 160.1; *Anal. Calcd.* for $C_{16}H_{11}N_3S_2Se$: C, 49.48; H, 2.85; N, 10.82. Found: C, 49.52; H, 2.91; N, 10.75.

3.4.13 1,3-Benzothiazol-2-yl 4-[1,1'-biphenyl]-4-yl-1,2,3-selenadiazol-5-yl sulfide (3m). IR (KBr): 3051, 1628, 1487, 1468, 1452, 1431, 1219, 1076, 1016, 1003, 768, 752, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.37$–7.57 (m, 5H), 7.69 (d, $J = 7.8$ Hz, 2H), 7.79–7.84 (m, 3H), 7.98 (d, $J = 7.8$ Hz, 2H), 8.06 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 121.6$ (CH), 122.1 (CH), 125.7 (CH), 126.9 (CH), 127.2 (2xCH), 127.6 (2xCH), 127.7 (CH), 128.9 (2xCH), 129.6 (2xCH), 131.1, 136.3, 140.3, 141.9, 142.0, 150.7, 157.6, 160.0; *Anal. Calcd.* for $C_{21}H_{13}N_3S_2Se$: C, 56.00; H, 2.91; N, 9.33. Found: C, 56.13; H, 2.97; N, 9.45.

3.4.14 1,3-Benzothiazol-2-yl 4-(2-naphthyl)-1,2,3-selenadiazol-5-yl sulfide (3n). IR (KBr): 3047, 1631, 1427, 1306, 1238, 1207, 1130, 1003, 748, 721 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.41$ (td, $J = 7.2$, 1.0 Hz, 1H), 7.51–7.59 (m, 3H), 7.81 (d, $J = 7.8$ Hz, 1H), 7.91–7.98 (m, 2H), 8.02 (s, 2H), 8.06 (d, $J = 8.1$ Hz, 1H), 8.35 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 121.6$ (CH), 122.0 (CH), 125.7 (CH), 126.5 (CH), 126.7 (CH), 126.9 (CH), 127.0 (CH), 127.8 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 129.7, 133.2, 133.3, 136.3, 142.3, 150.7, 157.9, 160.0; *Anal. Calcd.* for $C_{19}H_{11}N_3S_2Se$: C, 53.77; H, 2.61; N, 9.90. Found: C, 53.83; H, 2.55; N, 9.79.

3.4.15 1,3-Benzothiazol-2-yl 4-(2-thienyl)-1,2,3-selenadiazol-5-yl sulfide (3o). IR (KBr): 3097, 1662, 1458, 1427, 1307, 1242, 1072, 1003, 836, 752, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.25$ (dd, $J = 5.1$, 3.9 Hz, 1H), 7.45 (td, $J = 8.1$, 1.2 Hz, 1H), 7.51 (dd, $J = 5.1$, 1.2 Hz, 1H), 7.57 (td, $J = 8.1$, 1.2 Hz, 1H), 7.79 (dd, $J = 3.9$, 1.2 Hz, 1H), 7.86 (dd, $J = 8.1$, 1.2 Hz, 1H), 8.07 (dd, $J = 8.1$, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 121.7$ (CH), 122.2 (CH), 125.8 (CH), 126.9 (CH), 127.0 (CH), 127.1 (CH), 127.6 (CH), 134.7, 136.3, 138.9, 150.6, 152.3, 159.6; *Anal. Calcd.* for $C_{13}H_7N_3S_3Se$: C, 41.05; H, 1.85; N, 11.05. Found: C, 41.23; H, 1.94; N, 11.17.

3.5 *General procedure for the synthesis of 1,3-benzoxa(thia/imida)zol-2-yl 4-aryl-1,2,3-thiadiazol-5-yl sulfides (4a–o).*

0.001 mole of appropriate semicarbazone was added by portion to 10 mL of thionyl chloride while cooling to –5°C with a freezing mixture. The reaction mixture was allowed to stir for about 3–4 hrs. The excess of thionyl chloride was decomposed using aqueous solution of sodium carbonate and extracted with chloroform. The product was purified by column chromatography using silica gel (60–120 mesh) with 97:3 (50:50 when X=NH) petroleum ether: ethyl acetate as eluent.

3.5.1 1,3-Benzoxazol-2-yl 4-phenyl-1,2,3-thiadiazol-5-yl sulfide (4a). IR (KBr): 3045, 1635, 1508, 1473, 1448, 1431, 1215, 1138, 1026, 748, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,

25 °C): $\delta = 7.31$–7.39 (m, 2H), 7.47–7.58 (m, 4H), 7.71 (dd, $J = 7.5$, 1.8 Hz, 1H), 7.89 (dd, $J = 7.5$, 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 110.4$ (CH), 119.4 (CH), 125.1 (CH), 125.4 (CH), 128.9 (2xCH), 129.0 (2xCH), 129.7 (CH), 130.0, 135.9, 140.9, 152.2, 158.8, 160.0; *Anal. Calcd.* for $C_{15}H_9N_3OS_2$: C, 57.86; H, 2.91; N, 13.49. Found: C, 57.94; H, 2.88; N, 13.53.

3.5.2 1,3-Benzoxazol-2-yl 4-(4-methylphenyl)-1,2,3-thiadiazol-5-yl sulfide (4b). IR (KBr): 3026, 1641, 1512, 1446, 1225, 1130, 1097, 810, 741 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 2.44$ (s, 3H), 7.32–7.39 (m, 4H), 7.49 (dd, $J = 6.6$, 2.4 Hz, 1H), 7.72 (dd, $J = 6.6$, 2.4 Hz, 1H), 7.80 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 21.5$, 110.5 (CH), 119.5 (CH), 125.1 (CH), 125.4 (CH), 127.1, 128.8 (2xCH), 129.7 (2xCH), 135.3, 139.9, 141.0, 152.3, 158.9, 160.3; *Anal. Calcd.* for $CH_{11}N_3OS_2$: C, 59.06; H, 3.41; N, 12.91. Found: C, 58.94; H, 3.38; N, 12.98.

3.5.3 1,3-Benzoxazol-2-yl 4-(2-naphthyl)-1,2,3-thiadiazol-5-yl sulfide (4d). IR (KBr): 3047, 1597, 1516, 1487, 1446, 1226, 1130, 1095, 804, 739 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.35$–7.39 (m, 2H), 7.50 (dd, $J = 6.3$, 2.4 Hz, 1H), 7.56–7.59 (m, 2H), 7.74 (dd, $J = 6.3$, 2.4 Hz, 1H), 7.91–7.97 (m, 2H), 8.02 (s, 2H), 8.38 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 110.5$ (CH), 119.5 (CH), 125.1 (CH), 125.5 (CH), 126.0 (CH), 126.8 (CH), 127.3 (CH), 127.4, 127.9 (CH), 128.5 (CH), 128.8 (CH), 128.9 (CH), 133.1, 133.6, 136.2, 141.0, 152.3, 158.8, 160.0; *Anal. Calcd.* for $C_{19}H_{11}N_3OS_2$: C, 63.14; H, 3.07; N, 11.63. Found: C, 63.19; H, 3.12; N, 11.65.

3.5.4 1H-1,3-Benzimidazol-2-yl 4-phenyl-1,2,3-thiadiazol-5-yl sulfide (4f). IR (KBr): 3151, 3064, 1620, 1427, 1354, 1265, 1225, 730 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 7.25$ (dd, $J = 6.0$, 3.0 Hz, 2H), 7.50–7.62 (m, 5H), 7.89 (dd, $J = 7.5$, 1.5 Hz, 2H), 12.88 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C): $\delta = 116.6$, 118.9, 122.7 (CH), 125.0 (CH), 127.9 (CH), 128.5 (2xCH), 128.9 (2xCH), 129.4 (CH), 130.4, 139.9 (CH), 140.6, 143.8, 157.6; *Anal. Calcd.* for $C_{15}H_{10}N_4S_2$: C, 58.04; H, 3.25; N, 18.05. Found: C, 58.09; H, 3.27; N, 18.11.

3.5.5 1H-1,3-Benzimidazol-2-yl 4-(4-methylphenyl)-1,2,3-thiadiazol-5-yl sulfide (4 g). IR (KBr): 3143, 3105, 1620, 1435, 1354, 1267, 1224, 731 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 2.46$ (s, 3H), 7.25 (dd, $J = 6.0$, 3.0 Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.58 (bs, 2H), 7.79 (d, $J = 8.1$ Hz, 2H), 12.81 (bs, 1H); ^{13}C NMR$^{\#}$ (75 MHz, DMSO-d_6, 25 °C): $\delta = 21.3$, 122.7* (2xCH), 127.7, 128.5 (2xCH), 129.5 (2xCH), 139.3, 140.2, 144.0, 157.9; *Anal. Calcd.* for $C_{16}H_{12}N_4S_2$: C, 59.23; H, 3.73; N, 17.27. Found: C, 59.26; H, 3.80; N, 17.23.

3.5.6 1H-1,3-Benzimidazol-2-yl 4-(2-naphthyl)-1,2,3-thiadiazol-5-yl sulfide (4i). IR (KBr): 3141, 3093, 1618, 1419, 1348, 1267, 1226, 736 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): $\delta = 7.27$ (dd, $J = 6.0$, 3.0 Hz, 2H), 7.54–7.61 (m, 4H), 7.93–7.99 (m, 2H), 8.04 (s, 2H), 8.37 (s, 1H), 12.52 (bs, 1H); ^{13}C NMR$^{\#}$ (75 MHz, DMSO-d_6, 25 °C): $\delta = 122.2$ (CH), 125.4 (CH), 126.2 (CH), 126.5 (CH), 127.1 (CH), 127.5 (CH), 127.7 (CH), 128.0, 132.4, 132.6, 140.8, 143.3, 157.2; *Anal. Calcd.* for $C_{19}H_{12}N_4S_2$: C, 63.31; H, 3.36; N, 15.54. Found: C, 63.37; H, 3.38; N, 15.53.

3.5.7 1,3-Benzothiazol-2-yl 4-phenyl-1,2,3-thiadiazol-5-yl sulfide (4k). IR (KBr): 3052, 1630, 1471, 1454, 1427, 1308, 1225, 1014, 1002, 756, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$,

25 °C): $\delta = 7.41$ (td, $J = 8.1, 0.9$ Hz, 1H), 7.48–7.59 (m, 4H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.94 (dd, $J = 7.8$, 1.5 Hz, 2H), 8.05 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 121.8$ (CH), 122.9 (CH), 126.1 (CH), 127.3 (CH), 129.3 (2xCH), 129.4 (2xCH), 130.1 (CH), 130.9, 136.4, 138.8, 152.5, 159.5, 160.5; *Anal. Calcd.* for $C_{15}H_9N_3S_3$: C, 55.02; H, 2.77; N, 12.83. Found: C, 55.13; H, 2.81; N, 12.86.

3.5.8 1,3-Benzothiazol-2-yl 4-(4-methylphenyl)-1,2,3-thiadiazol-5-yl sulfide (4l). IR (KBr): 3056, 3020, 1642, 1431, 1309, 1221, 1115, 1074, 1001, 816, 750, 719 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 2.45$ (s, 3H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.41 (td, $J = 7.8$, 1.2 Hz, 1H), 7.53 (td, $J = 7.8$, 1.2 Hz, 1H), 7.81 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 2H), 8.04 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 21.5$, 121.4 (CH), 122.5 (CH), 125.6 (CH), 126.8 (CH), 127.5, 128.8 (2xCH), 129.7 (2xCH), 135.9, 137.7, 139.8, 152.2, 159.4, 160.4; *Anal. Calcd.* for $C_{16}H_{11}N_3S_3$: C, 56.28; H, 3.25; N, 12.31. Found: C, 56.24; H, 3.28; N, 12.36.

3.5.9 1,3-Benzothiazol-2-yl 4-[1,1'-biphenyl]-4-yl-1,2,3-thiadiazol-5-yl sulfide (4m). IR (KBr): 3055, 1601, 1450, 1429, 1223, 1003, 762, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.38$–7.45 (m, 2H), 7.48 (d, $J = 7.5$ Hz, 2H), 7.54 (td, $J = 7.2, 0.9$ Hz, 1H), 7.68 (d, $J = 7.5$ Hz, 2H), 7.79 (d, $J = 8.1$ Hz, 2H), 7.83 (d, $J = 7.2$ Hz, 1H), 8.04 (d, $J = 8.1$ Hz, 2H), 8.06 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 121.4$ (CH), 122.5 (CH), 125.7 (CH), 126.9 (CH), 127.2 (2xCH), 127.6 (2xCH), 127.8 (CH), 128.9 (2xCH), 129.2, 129.3 (2xCH), 135.9, 138.2, 140.2, 142.4, 152.1, 158.8, 160.2; *Anal. Calcd.* for $C_{21}H_{13}N_3S_3$: C, 62.50; H, 3.25; N, 10.41. Found: C, 62.63; H, 3.31; N, 10.46.

3.5.10 1,3-Benzothiazol-2-yl 4-(2-naphthyl)-1,2,3-thiadiazol-5-yl sulfide (4n). IR (KBr): 3053, 1629, 1467, 1427, 1221, 1076, 1001, 748, 721 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.41$ (t, $J = 7.8$ Hz, 1H), 7.54 (t, $J = 7.8$ Hz, 1H), 7.56–7.59 (m, 2H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.91–8.00 (m, 3H), 8.03–8.07 (m, 2H), 8.41 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 121.4$ (CH), 122.5 (CH), 123.9, 125.7 (CH), 126.0 (CH), 126.7 (CH), 126.9 (CH), 127.2 (CH), 127.8 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 133.1, 133.5, 136.0, 138.6, 152.1, 159.0, 160.0; *Anal. Calcd.* for $C_{19}H_{11}N_3S_3$: C, 60.45; H, 2.94; N, 11.13. Found: C, 60.51; H, 3.02; N, 11.16.

3.5.11 1,3-Benzothiazol-2-yl 4-(2-thienyl)-1,2,3-thiadiazol-5-yl sulfide (4o). IR (KBr): 3101, 1631, 1458, 1427, 1240, 1074, 1001, 752, 710 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.21$ (dd, $J = 5.1$, 3.9 Hz, 1H), 7.41 (td, $J = 7.8$, 0.9 Hz, 1H), 7.51–7.55 (m, 2H), 7.82 (dd, $J = 7.8$, 0.9 Hz, 1H), 7.88 (dd, $J = 3.9$, 1.2 Hz, 1H), 8.04 (dd, $J = 7.8$, 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 121.4$ (CH), 122.5 (CH), 125.6 (CH), 126.8 (CH), 127.8 (CH), 128.0, 128.1 (CH), 132.3, 135.1, 135.9, 152.4, 154.1, 160.0; *Anal. Calcd.* for $C_{13}H_7N_3S_4$: C, 46.82; H, 2.12; N, 12.60. Found: C, 46.79; H, 2.10; N, 12.65.

*Less intense signal
#All the carbons of benzene ring of benzimidazole ring are not visible
$NH proton of the benzimidazole ring is invisible due to fast tautomerism

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