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A Convenient Approach to 2-Aminobenzo[*b*]chalcogenophenes Based on Copper-Catalyzed Transformation of 4-(2-Bromophenyl)-1,2,3-chalcogenodiazoles in the Presence of a Base and Amines

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Abstract—The reactions of 4-(2-bromophenyl)-1,2,3-thia- and -selenadiazoles with amines in the presence of potassium carbonate and copper(I) iodide afforded 2-aminobenzo[*b*]chalcogenophenes. The corresponding thia- and selenamides, prepared by interaction of 4-(2-bromophenyl)-1,2,3-thia- and -selenadiazoles with amines in the absence of copper salt, were transformed into 2-aminobenzo[*b*]chalcogenophenes by the action of potassium carbonate and copper(I) iodide in DMF in different yields.

Keywords: benzo[*b*]thiophene, benzo[*b*]selenophene, 1,2,3-thiadiazole, 1,2,3-selenadiazole, copper-catalyzed cyclization

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Application of benzo[*b*]thiophene and its derivatives in the prepation of bioactive compounds is of great interest to chemists. As example, they have been used in the development of acetyl-CoA carboxylase inhibitors [1, 2] and tubulin polymerization inhibitors [3–5]. Among others 2-aminobenzo[*b*]thiophenes have been successfully applied to the synthesis of selective estrogen receptor modulator raloxiphene and its analogues [6, 7]. Also, benzo[*b*]thiophene, benzo[*b*]selenophene, and related fused aromatic compounds are key part of structural motif in the development of optoelectronic materials like field-effect transistors, organic semiconductors for optoelectronic devices, etc. [8–14].

Nowadays several methods for the synthesis of 2-aminobenzo[*b*]chalcogenophenes are known. The unsubstituted 2-aminobenzo[*b*]thiophene has been prepared from thiosalicylic acid via five-step synthesis [15]. Also, 2-aminobenzo[b]thiophene has been obtained from 1-benzothiophen-2-ylmagnesium chloride [16]. The reaction between diverse (2-bromophenyl)acetonitriles and $Na_2S_2O_3$ in the presence of palladium catalyst also gave rise to the substituted 2-aminobenzo[*b*]thiophenes [18–20]. There are some another examples of the synthesis of substituted 2-aminobenzo[*b*]thiophenes [18–20]. As for 2-aminobenzo[*b*]selenophene, the only known method for the synthesis of these compounds is based on reduction of 2-nitrobenzo[*b*]selenophene [21]. The reaction of 2-acetyl-3-phenylbenzo[*b*]selenophene oxime with polyphosphoric acid gave 2-acetylamino-3-phenylbenzo[*b*]selenophene [22]. 2-Benzoylamino-3-phenylbenzo[*b*]selenophene has been prepared by reacting benzoyl isoselenocyanate with diphenyldiazomethane [23]. However, up to the present time there is no general method for the synthesis of 2-aminobenzo[*b*]chalcogenophenes.

Recently we reported that 4-(2-halogenaryl)-1,2,3-thia- and -selenadiazoles bearing nitro group in the *para*-position to the halogen gave 2-aminobenzo[*b*]chalcogenophenes when heated in DMF in the presence of amine and potassium carbonate [24, 25]. But only thia- and -selenamides were obtained under similar reaction condition when using the substrates without an acceptor group [25, 26]. Here we report on the catalytic method for the synthesis of unsubstituted 2-aminobenzo[*b*]-chalcogenophenes in up to 87% yields.

The Hurd–Mori reaction was used for the synthesis of 4-(2-halophenyl)-1,2,3-thiadiazoles **3a** and **3b** from

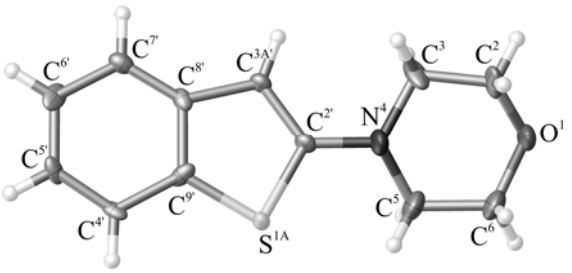


Fig. 1. General view of the molecule of compound **5a** in the crystal.

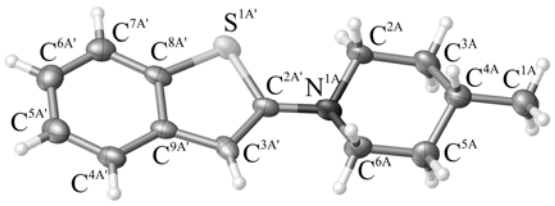
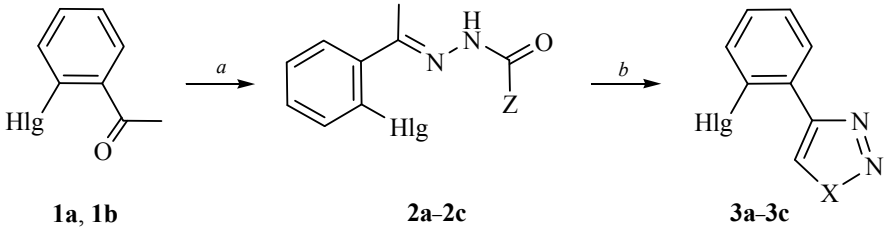


Fig. 2. General view of the molecule of compound **5d** in the crystal.

methyl ketones **1a** and **1b** by reacting thionyl chloride with the corresponding ethoxycarbonylhydrazones **2a** and **2b** [27–29]. The reaction of 2-bromoacetophenone **1b** with semicarbazide hydrochloride gave semicarbazone **2c** which was converted into 4-(2-bromophenyl)-1,2,3-selenadiazole **3c** under the action of selenium dioxide in acetic acid (Scheme 1).

Compounds **3a**–**3c** were further introduced into the reaction with amines in DMF medium in the presence of copper(I) iodide and potassium carbonate in an inert atmosphere; heating up to 80°C for a different time led to the formation of 2-aminobenzo[*b*]chalcogenophenes **5a**–**5h** in 19–83% yields (Scheme 2, Table 1). In the case of **3a** only thioamide **4a** was formed. Structure of compounds **5a**, **5d**, and **5g** was proved by single-crystal X-ray diffraction method (Figs. 1–3). The molecule of **5a** was found to have disordered thiophene ring in the crystal. Such phenomenon is not unique, there are some other compounds (like dibenzothiophene) for which disordered thiophene fragment in crystal is obserwed [30]. The reaction terms were investigated using the reaction of 4-(2-bromophenyl)-1,2,3-thiadiazole **3b** with morpholine as a model

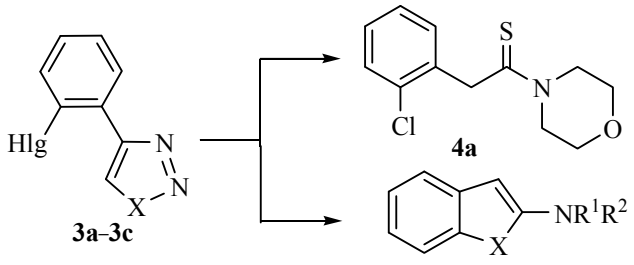
Scheme 1.



1a, **1b** **2a**–**2c** **3a**–**3c**

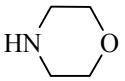
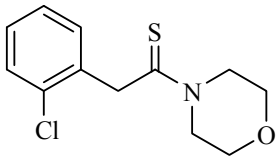
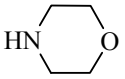
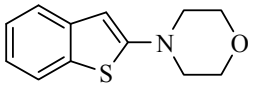
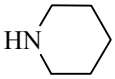
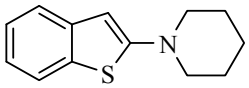
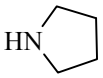
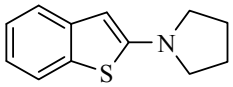
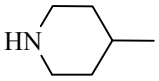
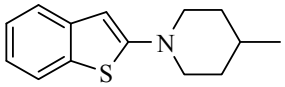
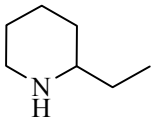
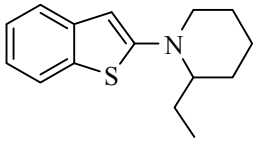
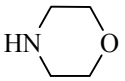
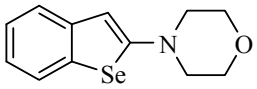
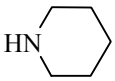
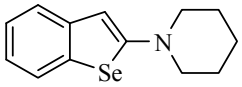
Z = OEt, Hlg = Cl (**2a**); Z = OEt, Hlg = Br (**2b**); Z = NH_2, Hlg = Br (**2c**); X = S, Hlg = Cl (**3a**, 70%); X = S, Hlg = Br (**3b**, 84%); X = Se, Hlg = Br (**3c**, 72%). X = S: *a*, $NH_2NHC(O)OEt$, EtOH, 3 h, 80°C; *b*, $SOCl_2$, 2 h, 80°C; X = Se: *a*, $NH_2NHC(O)NH_2 \cdot HCl$, EtOH, 3 h, 80°C; *b*, SeO_2, 3 h, 65°C.

Scheme 2.



X = S, Hlg = Cl (**4a**); X = S, Hlg = Br (**5a**–**5e**); X = Se, Hlg = Br (**5f**, **5g**). Reaction conditions: X = S, Hlg = Br(Cl), K_2CO_3, CuI (20 mol %), HNR^1R^2, DMF, inert atmosphere, 1–96 h, 80°C; X = Se, Hlg=Br, K_2CO_3, CuI (20 mol %), HNR^1R^2, DMF, inert atmosphere, 8–50 h, 80°C.

Table 1. Reaction conditions and yields of 2-aminobenzo[*b*]chalcogenophenes **5a**–**5g**

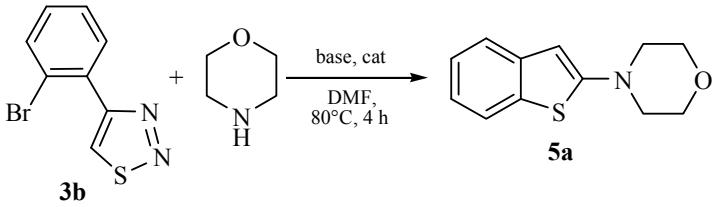
Run no.	Amine	Reaction time, h	Product no.	Reaction product	Yield, %
1		4	**4a**		74
2		4	**5a**		83
3		4	**5b**		49
4		4	**5c**		78
5		4	**5d**		68
6		8	**5e**		46
7		50	**5f**		35
8		8	**5g**		19

(Scheme 3, Table 2). It was found that copper(I) and copper(II) salts can be used in the reaction and the nature of an anion in copper salt does not affect the process course. The use of microwave activation made it possible to reduce the reaction time but it did not influence the yield. As to the nature of a base, potassium carbonate and cesium carbonate were found to be appropriate bases, but not the potassium *tert*-butylate.

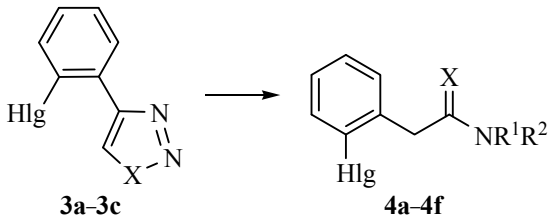
The corresponding thio- and selenamides **4b**–**4f** obtained by reacting 4-(2-bromophenyl)-1,2,3-thia- and -selenadiazole with various amines (Scheme 4) can be transformed into 2-aminobenzo[*b*]chalcogenophenes under the action of potassium carbonate and catalytic amount of copper(I) iodide in DMF (Scheme 5, Table 3). The structure of thioamide **4b** was proved by single-crystal X-ray diffraction method (Fig. 4).

According to the experimental data (see Tables 1 and 3), the transformation of 4-(2-halophenyl)-1,2,3-thia- and -selenadiazoles into 2-aminobenzo[*b*]chalcogenophenes has several limitations and specific features. First of all, only bromo-substituted 4-(2-halophenyl)-1,2,3-thia- and -selenadiazoles (**3b**, **3c**) can be used for the complete transformation to compounds **5**. In the case of **3a** only the product **4a** was obtained under the

Scheme 3.

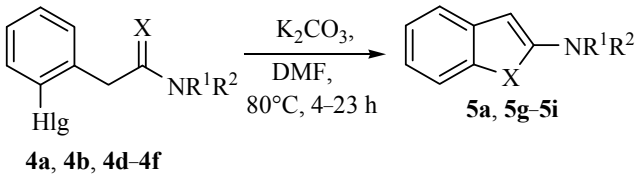


Scheme 4.



X = S, Hlg = Cl, NR^1R^2 = morpholine (**4a**, 68%); X = S, Hlg = Br, NR^1R^2 = morpholine (**4b**, 83%); X = Se, Hlg = Br, NR^1R^2 = morpholine (**4c**, 32%); X = S, Hlg = Br, NR^1R^2 = piperidinyl (**4d**, 92%); X = Se, Hlg = Br, NR^1R^2 = diethylamino (**4e**, 76%); X = Se, Hlg = Br, NR^1R^2 = pirrolidinyl (**4f**, 76%). Reaction conditions: K_2CO_3, amine, DMF, inert atmosphere, 70–85°C, 1–96 h (**4a–4d**); $HNEt_2$, KOH, 3 h, 55°C (**4e**); pirrolidin, room temperature, 40 min (**4f**).

Scheme 5.



reaction condition (with the presence of CuI in the reaction mixture or without it). There is one more limitation for this method related to the amine nature. Secondary amines reacted actively to form the corresponding 2-aminobenzo[*b*]chalcogenophenes with various yields. Yet at the use of *n*-butilamine and benzylamine the tarring of the reaction mixture occurred. The yields of 2-aminobenzo[*b*]selenophenes are a little lower than the yields of the same 2-aminobenzo[*b*]thiophenes (Table 1). It may be explained by the fact that under heating the initial selenadiazoles are less stable then thiadiazoles and decompose actively at 80°C without future interaction.

Table 2. Optimization of the reaction conditions of 4-(2-bromophenyl)-1,2,3-thiadiazole **3b** with morpholine

Run no.	Base	Catalyst	Yield, %
1	K_2CO_3	CuI	83
2	K_2CO_3	CuCl	83
3	K_2CO_3	CuBr	82
4	K_2CO_3	$CuCl_2$	87
5	K_2CO_3	$Cu(OAc)_2$	92
6	Cs_2CO_3	CuI	77
7	*t*-BuOK–DMF	CuI	22
8	*t*-BuOK–THF	CuI	31
9[a]	K_2CO_3	CuI	82

[a] The reaction mixture was subjected to microwave irradiation (600 W) at 80°C for 90 min.

The structure of the target compounds was confirmed by NMR spectra. In the ^1H NMR spectrum of compound **5d** six signals related to the protons of piperidine ring and to the protons of methyl group were observed in the range of 0.8–6.6 ppm. Such spectral pattern indicates that the pyrrolidine ring is present in a definite conformation and the conformations interconvertin time exceeds the time if the spectrum recording (otherwise, we would expect the appearance of four signals: one for each methylene group as they are symmetric, one for the single proton, and one for the methyl group). The COSY and HSQC spectra proved that 2.88 and 3.58 ppm signals belong

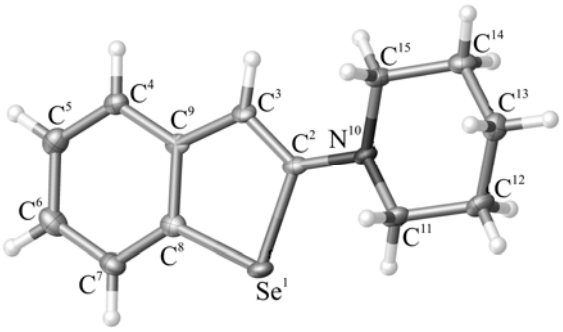


Fig. 3. General view of the molecule of compound **5g** in the crystal.

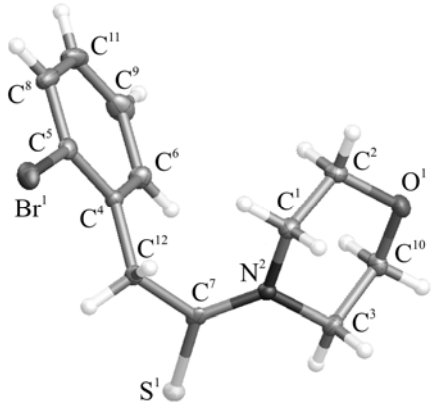
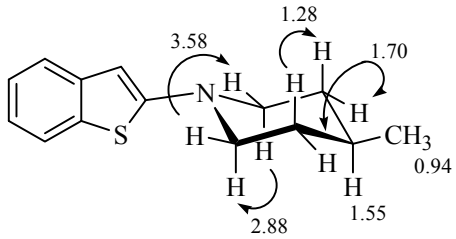


Fig. 4. General view of the molecule of compound **4b** in the crystal.

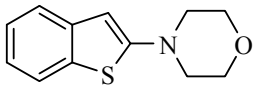
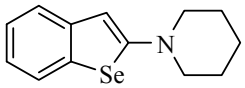
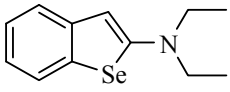
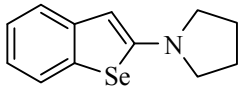
to H_{ax} and H_{eq} at the C^2 and C^6 atoms of the piperidine ring, respectively. The signals at 1.28 and 1.70 ppm correspond to H_{ax} and H_{eq} at the C^3 and C^5 atoms, respectively. In this case the spin-spin coupling constants J_{gem} for the protons $H_{ax}^{2(6)}$–$H_{eq}^{2(6)}$ and $H_{ax}^{3(5)}$–$H_{eq}^{3(5)}$ equal 13.1 and 12.1 Hz, respectively.



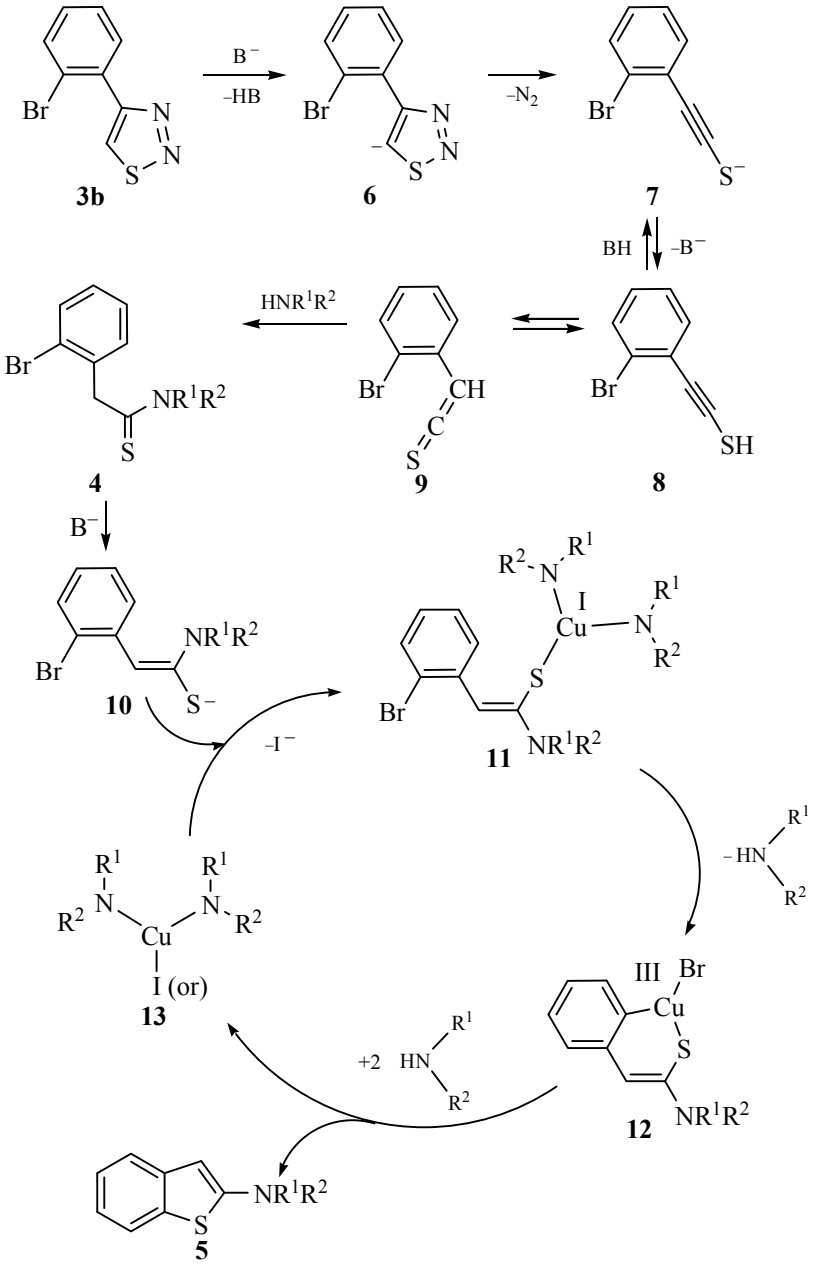
In the ^{1}H NMR spectra of compound **5e** there were three separate signals of the protons which are located two bonds away from the nitrogen atom, ppm: 3.07–3.20 (1H), 3.47 br.d (1H, J = = 12.05 Hz), 3.54–3.64 m (1H) (these signals correspond to C^2H_{ax}, C^6H_{ax} and C^6H_{eq} of the piperidine ring). The presence of such signals in the spectrum indicates the staggered conformation of the piperidine ring with the ethyl substituent playing an anchor role. However, an unambiguous correlation of the signals was possible due to the COSY spectral method. The COSY spectra contained the following cross-peaks, ppm: 3.63↔1.73 (1.60–1.90 ppm, C^3, C^4, C^5 methylene groups and $\underline{CH_2}CH_3$), 3.47↔1.76 (1.60–1.90 ppm), 3.47↔3.16 (3.09–3.23 ppm, 1H). Due to the presence of the corresponding cross-peaks and the fact that the signal at 3.47 ppm was registered as a broad doublet (J = 12.05 Hz) and the signal at 3.07–3.20 ppm was recorded as a multiplet with several spin-spin coupling constants of more than 10 Hz (it is typical for axial-axial and geminal interaction between the protons in ring systems), it may be stated that the signal at 3.07–3.20 ppm belongs to C^6H_{ax} of the piperidine ring, the signal at 3.47 ppm belongs to C^6H_{eq} (J^{gem}_{HH} = 12.05 Hz), and the signal at 3.54–3.64 ppm belongs to C^2H_{ax}.

The presumable reaction mechanism was proposed and outlined in Scheme 6 by the example of 4-(2-bromophenyl)-1,2,3-thiadiazole. We made the conclusion that **3→5** transformation in the presence of copper(I) iodide includes the decomposition of compound **3**

Table 3. The reaction conditions and yields of 2-aminobenzo[*b*]chalcogenophenes **5a**, **5g**–**5i**

Run no.	Amide	Reaction time, h	Reaction product	Yield, %
1	**4a**	12	–	–
2	**4b**	4	 **5a**	88
3	**4d**	33	 **5g**	39
4	**4e**	43	 **5h**	50
5	**4f**	28	 **5i**	32

Scheme 6.



under the action of a base followed by transformation in thioketene **9**. Further addition of amine to thioketene followed by cyclization under the action of copper(I) salt gives the desired 2-aminobenzo[*b*]thiophene. The possibility of using copper(I) and copper(II) salts suggests that the process includes catalytic cycle with one-electron transfer. As the reaction rate decreases twice when using 2-ethylpiperidine instead of piperidine (8 h vs 4 h), it means that amine nature plays an important role in the rate-determining step. If the nucleophilic substitution of the halogen in aromatic ring is the rate-determining step, then the decrease in the reaction rate, when using sterically hindered amine, can prove that copper is not only electron-carrier in the reaction course but forms directly a complex with amine. The presence of a substituent near the reaction site in amine makes the complex formation difficult.

In summary, we developed a catalytic method of the synthesis of unsubstituted 2-aminobenzo[*b*]chalcogenophenes from 4-(2-bromophenyl)-1,2,3-thia- and -selenadiazoles as well as the corresponding thio- and selenamides.

EXPERIMENTAL

Melting points were measured on a Boetius melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13 and 100.16 MHz, respectively. High-resolution mass spectra (electrospray ionization) were taken on a Micromass 70-VSE instrument. The reaction progress was monitored by TLC on Silica gel 60 F254 plates; spots were visualized under UV light or by treatment with iodine vapor. Single-crystal X-ray diffraction analysis was performed on a Xcalibur Agilent Technologies instrument (Oxford Diffraction). X-ray diffraction data were deposited at the Cambridge Crystallographic Data Centre [CCDC 1449609 (**5a**), 1449608 (**5d**), 1047330 (**5g**), 1433686 (**4b**)].

The solvents used were purified and dried according to standard procedures. All chemicals were used as purchased.

Ethyl 2-(1-(2-chlorophenyl)ethylidene)hydrazinocarboxylate (2a). A mixture of 1-(2-chlorophenyl)ethanone **1a** (15.45 g, 0.1 mol), ethyl carbazate (10.4 g, 0.1 mol), and three drops of H_2SO_4 in 50 mL of EtOH was refluxed for 3 h and left overnight at room temperature. The precipitate was filtered off, washed with EtOH–H_2O (1 : 1), and dried. Yield 21.90 g (89%), white crystals, mp 131–132°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 t (3H, J = 7.1 Hz), 2.22 s (3H), 4.33 q (2H, J = 7.1 Hz), 7.26–7.30 m (2H), 7.35–7.38 m (1H), 7.41–7.44 m (1H), 7.93 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.6, 16.8, 62.2, 126.9, 129.7, 129.9, 130.5, 132.3, 138.8, 149.5. The spectral data correspond to those described in [24].

Ethyl 2-(1-(2-bromophenyl)ethylidene)hydrazinocarboxylate (2b) was prepared similarly from 29.4 g (0.15 mol) of 1-(2-bromophenyl)ethanone **1b** and 15.35 g (0.15 mol) of ethyl carbazate; the reaction time 2 h. Yield 36.23 g (86%), white crystals, mp 139–140°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t (3H, J = 6.8 Hz), 4.34 q (2H, J = 6.8 Hz), 2.24 s (3H), 7.17–7.26 m (1H), 7.29–7.36 m (1H), 7.39 d (1H, J = 7.1 Hz), 7.57 d (1H, J = 8.2 Hz), 7.94 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.6, 17.1, 62.2, 121.6, 127.5, 130.0, 130.6, 132.9, 140.8, 150.5, 154.0. Mass spectrum (HRMS-EI), m/z: 285.0233 $[M + H]^+$ (calculated for $C_{11}H_{13}BrN_2O_2$: 285.0239).

2-[1-(2-Bromophenyl)ethylidene]hydrazinocarboxamide (2c) was prepared as described in [31]. Yield 88%, white crystals, mp 175–177°C (mp 175–177°C [32].

Table 4. ^{1}H, ^{1}H–^{1}H COSY and ^{1}H–^{13}C HSQC NMR spectral data for compound **5d**

δ, ppm		δ_C, ppm
^{1}H	^{1}H–^{1}H COSY	^{1}H–^{13}C HSQC
0.94	1.55 (1.48–1.62)	22.08
1.28 (1.20–1.36)	1.70, 2.88, 3.58	33.32
1.55 (1.48–1.62)	0.94, 1.28	30.19
1.70	1.28 (1.20–1.36), 2.88, 3.58	33.32
2.88	1.28 (1.20–1.36), 1.70, 3.58	51.14
3.58	1.28 (1.20–1.36), 1.70, 2.88	51.14
6.25	–	98.51
7.02 (6.98–7.06)	7.19 (7.15–7.24), 7.64	121.16
7.19 (7.15–7.24)	7.02 (6.98–7.06), 7.42	124.90
7.42	7.19 (7.15–7.24)	120.78
7.64	7.02 (6.98–7.06)	121.93

4-(2-Chlorophenyl)-1,2,3-thiadiazole (3a). A solution of 3.05 g (12.7 mmol) of compound **2a** in 7 mL of $SOCl_2$ was refluxed within 2 h, then cooled, and poured into water. The precipitate was filtered off, washed thoroughly with water, and crystallized from $CHCl_3$–MeOH. Yield 1.72 g (70%), white crystals, mp 34–35°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.37–7.47 m (2H), 7.53–7.57 m (1H), 8.12–8.16 m (1H), 9.05 s (1H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 127.4, 129.6, 130.4, 130.6, 131.9, 132.3, 134.6, 159.1. Mass spectrum (HRMS-EI), m/z: 195.9935 $[M + H]^+$ (calculated for $C_8H_5ClN_2S$: 196.9940). The spectral data correspond to those described in [24].

4-(2-Bromophenyl)-1,2,3-thiadiazole (3b) was prepared similarly. Yield 3.58 g (84%), pale yellow crystals, mp 41.5–42.5°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.27–7.35 m (1H), 7.42–7.50 m (1H), 7.73 d (1H, J = 8.1 Hz), 7.94 d (1H, J = 8.0 Hz), 9.01 s ($1H_{Het}$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 122.3, 127.9, 130.6, 131.7, 132.2, 133.9, 134.7, 160.5. Mass spectrum (HRMS-EI), m/z: 240.9430 $[M + H]^+$ (calculated for $C_8H_5BrN_2S$: 240.9435). The spectral data correspond to those described in [33].

4-(2-Bromophenyl)-1,2,3-selenadiazole (3c). Selenium dioxide (0.31 g, 2.80 mmol) was added with stirring to a suspension of semicarbazone **2c** (0.64 g, 2.5 mmol) in glacial acetic acid (6 mL). The mixture was stirred at 30°C for 4 h and then at 47°C for 22 h, cooled to room temperature, poured into water (50 mL), and extracted with chloroform (3×15 mL).

The extract was washed with an aqueous solution of sodium carbonate (3×10 mL), brine (3×10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed at a reduced pressure to yield the crude product. Purification of the crude product by column chromatography using ethyl acetate–petroleum ether (1 : 10) as the eluent gave **3c** (0.52 g, 72%) as pale orange crystals, mp 37–38°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.31 t (1H, *J* = 8.0 Hz), 7.45 t (1H, *J* = 7.5 Hz), 7.74 d (1H, *J* = 8.0 Hz), 7.88 d (1H, *J* = 7.5 Hz), 9.65 s (1H + HSe satellite, *J* = 41.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 122.4, 127.6, 130.2, 132.4, 132.7, 133.7, 142.1, 160.3. Mass spectrum (EI), *m*/*z* (*I*, %): 260 (34) $[M - N_2]^+$, 181 (60) $[M - N_2 - Se]^+$, 101 (63) $[M - N_2 - Se - Br]^+$, 89 (65), 75 (100), 50 (66). Mass spectrum (HRMS-ESI), *m*/*z*: 310.8700 $[M + Na]^+$ (calculated for $C_8H_5BrN_2NaSe$: 310.8699).

General procedure for the synthesis of amides 4a–4d. A mixture of **3** (1 equiv), K_2CO_3 (2.5–3 equiv), and amine (4.4–27 equiv) in DMF (3–10 mL) was stirred at 70–85°C for 4–96 h under argon atmosphere. After cooling to room temperature, the solvent was evaporated in a vacuum. The residue was dissolved in chloroform and thoroughly washed with water, dried over anhydrous Na_2SO_4. The solvent was evaporated at a reduced pressure. The crude product was purified by recrystallization or column chromatography.

2-(2-Chlorophenyl)-1-(morpholin-1-yl)ethanethione (4a). Yield 0.88 g (68%), white crystals, mp 119–120°C (hexane–petroleum ether–chloroform, 50 : 5 : 3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.45 m (2H), 3.53 m (2H), 3.75 m (2H), 4.37 m (2H), 4.35 s (2H), 7.18–7.26 m (2H), 7.36 d (1H, *J* = 8.0 Hz), 7.41 d (1H, *J* = 6.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 47.1, 50.0, 50.7, 66.1, 66.3, 127.2, 128.5, 129.1, 129.5, 133.1, 133.7, 199.4. Mass spectrum (HRMS-EI), *m*/*z*: 256.0557 $[M + H]^+$ (calculated for $C_{12}H_{14}ClNOS$: 256.0563). The spectral data correspond to those described in [34].

2-(2-Bromophenyl)-1-(morpholin-1-yl)ethanethione (4b). Yield 1.03 g (83%), white crystals, mp 115–117°C (Et_2O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.53 t (2H, *J* = 4.5 Hz), 3.66–3.76 m (4H), 4.23 s (2H), 4.28 t (4H, *J* = 5.0 Hz), 7.18–7.24 m (1H), 7.26 d (1H, *J* = 7.0 Hz), 7.34–7.41 m (1H), 7.62 d (1H, *J* = 8.0 Hz). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.49 t (2H, *J* = 4.5 Hz), 3.56 t (2H, *J* = 4.5 Hz), 3.79 t (2H, *J* = 4.5 Hz), 4.34–4.44 m (4H), 7.12–7.20 m (1H), 7.29–7.36 m (1H), 7.44 d (1H, *J* = 7.5 Hz), 7.59 d (1H, *J* = 8.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 49.2, 50.2, 50.9, 66.2, 66.2, 124.6, 128.3, 129.2, 130.6, 132.9, 136.9, 198.3. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 50.0, 50.1, 50.9, 66.2, 66.2, 66.4, 124.0, 128.0, 128.8, 129.2, 132.9, 135.5, 199.5. Mass spectrum (HRMS-ESI), *m*/*z*: 323.9859 $[M + Na]^+$ (calculated for $C_{12}H_{14}BrNNaOS$: 323.9857).

2-(2-Bromophenyl)-1-(morpholin-1-yl)ethaneselenone (4c). Yield 0.05 s (32%), pale orange crystals, mp 135–136°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.46 br.s (4H), 3.82 t (2H, *J* = 5.2 Hz), 4.46–4.55 m (2H), 4.51 s (2H), 7.15 t (1H, *J* = 7.9 Hz), 7.31 t (1H, *J* = 7.9 Hz), 7.52 d (1H, *J* = 7.9 Hz), 7.56 d.d (1H, *J* = 7.9, 0.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 51.9, 53.8, 54.7, 65.8, 66.3, 123.8, 128.0, 128.8, 128.9, 132.9, 134.6, 203.7. Mass spectrum (HRMS-ESI), *m*/*z*: 369.9358 $[M + Na]^+$ (calculated for $C_{12}H_{14}BrNOSe$: 369.9322).

2-(2-Bromophenyl)-1-(piperidin-1-yl)ethaneselenone (4d). Yield 0.22 g (92%), orange crystals, mp 75–77°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 br.s (2H), 1.47–1.90 m (5H), 3.43 br.s (2H), 4.19–4.77 m (4H), 7.13 br.s (1H), 7.27 br.s (1H), 7.41–7.76 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.8, 25.5, 26.2, 52.7, 54.3, 56.5, 124.0, 128.0, 128.7, 129.2, 132.9, 135.1, 201.5. Mass spectrum (HRMS-ESI), *m*/*z*: 383.9273 $[M + K]^+$ (calculated for $C_{13}H_{16}BrKNSe$: 383.9268).

***N*,*N*-Diethyl-2-(2-bromophenyl)ethaneselenoamide (4e).** A mixture of compound **3c** (0.3 g, 1.05 mmol), KOH (0.12 g, 2.1 mmol) and diethylamine (1.5 mL, 1.07 g, 1.5 mmol) was stirred at 55°C until nitrogen evolution ceased. The mixture was cooled to room temperature, poured into water (75 mL), neutralized with dilute acetic acid, and extracted with chloroform (3×10 mL). The extract was dried over anhydrous Na_2SO_4; the solvent was evaporated at a reduced pressure. The residue was chromatographed using ethyl acetate–petroleum ether (1 : 10) as the eluent. Yield 0.26 g (76%), bright yellow crystals, mp 69–70°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 t (3H, *J* = 7.1 Hz), 1.34 t (3H, *J* = 7.1 Hz), 3.37 q (2H, *J* = 7.1 Hz), 4.12 q (2H, *J* = 7.1 Hz), 4.39 s (2H), 7.11 t (1H, *J* = 7.5 Hz), 7.25 t (1H, *J* = 7.5 Hz), 7.47 d (1H, *J* = 7.5 Hz), 7.52 d (1H, *J* = 7.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 10.9, 12.6, 47.4, 51.6, 53.6, 124.2, 127.8, 128.5, 129.1, 132.6, 135.3, 201.9. Mass spectrum (EI), *m*/*z* (*I*, %): 254 (42) $[M - Br]^+$, 183 (16), 169 (24), 158 (13), 89

(18), 72 (26), 29 (100). Mass spectrum (HRMS-ESI), *m*/*z*: 333.9712 $[M + H]^+$ (calculated for $C_{12}H_{16}BrNSe$: 333.9710), 355.9532 $[M + Na]^+$ (calculated for $C_{12}H_{16}BrNNaSe$: 355.9529).

2-(2-Bromophenyl)-1-(pirrolidin-1-yl)ethaneselenone (4f). A solution of selenadiazole **3c** (0.3 g, 1.04 mmol) in pyrrolidine (3 mL, 2.58 g, 36 mmol) was stirred at room temperature for 40 min and then poured into water (75 mL). The solution was extracted with chloroform (3×10 mL), the extract was washed with the diluted solution of acetic acid and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography using ethyl acetate–petroleum ether (1 : 10) as the eluent. Yield 0.26 g (76%), orange crystals, mp 70–71°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.05 sextet (4H, *J* = 6.7 Hz), 3.34 t (2H, *J* = 6.7 Hz), 3.91 t (2H, *J* = 6.7 Hz), 4.32 s (2H), 7.13 t (1H, *J* = 7.5 Hz), 7.29 t (1H, *J* = 7.5 Hz), 7.47 d (1H, *J* = 7.5 Hz), 7.56 d (1H, *J* = 7.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 24.3, 26.6, 51.9, 54.2, 58.0, 124.7, 127.8, 128.6, 129.6, 132.7, 134.9, 199.0. Mass spectrum (HRMS-ESI), *m*/*z*: 331.9533 $[M + H]^+$ (calculated for $C_{12}H_{15}BrNSe$: 331.9553).

General procedures for the synthesis of 2-amino-benzo[*b*]thiophenes and 2-amino-benzo[*b*]selenophenes (5a–5j). *a*. A suspension of **3b** or **3c** (1 equiv), K_2CO_3 (3 equiv) in amine (2 equiv) and DMF (3 mL) was flushed with argon and degassed for three times, then CuI (0.2 equiv) was added. The reaction flask was evacuated, flushed with argon, degassed once more and the reaction mixture was stirred at 70–85°C for 4–50 h. After cooling the reaction mixture was poured into a saturated aqueous solution of NH_4Cl (50 mL) and extracted with ethyl acetate (2×20 mL). The extract was filtered, washed with saturated aqueous solution of NH_4Cl (2×20 mL), brine (2×20 mL), water (2×20 mL), dried over anhydrous Na_2SO_4, and concentrated at a reduced pressure. The crude product was purified by column chromatography [SiO_2, ethyl acetate–hexane (1 : 4, 1 : 5), or ethyl acetate–petroleum ether (1 : 8, 1 : 25)] affording the corresponding 2-amino-benzo[*b*]thiophenes and 2-amino-benzo[*b*]selenophenes with yields of 19–93%.

b. A suspension of **4** (1 equiv) and K_2CO_3 (1.5 equiv) in DMF (3 mL) was flushed with argon and degassed for three times, then CuI (0.2 equiv) was added. The reaction flask was evacuated and flushed with argon, degassed once more and the reaction mixture was stirred at 80°C for 4–23 h. In the case of compounds **5g–5i** an additional amount of CuI (0.2–0.3 equiv) was added and the reaction flask was evacuated, flushed with argon again, and stirred at 80–85°C for 13–24 h. After cooling, the reaction mixture was poured into a saturated aqueous solution of NH_4Cl (50 mL), extracted with chloroform (3×10 mL). The extract was filtered, washed with saturated aqueous solution of NH_4Cl (2×20 mL), brine (2×20 mL), water (2×20 mL), dried over anhydrous Na_2SO_4, and concentrated at a reduced pressure. The crude product was purified by column chromatography [SiO_2, eluent ethyl acetate–hexane (1 : 4), or ethyl acetate–petroleum ether (1 : 25)] affording the target compounds **5a, 5g–5i** with 32–88% yields.

4-(Benzo[*b*]thiophen-2-yl)morpholine (5a). Yield 0.075 g (82%, method *a*), 0.052 g (71%, method *b*), white crystals, mp 179–181°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.27 t (4H, *J* = 5.0 Hz), 3.89 t (4H, *J* = 5.0 Hz), 6.25 s (1H), 7.09–7.17 m (1H), 7.23–7.32 m (1H), 7.50 d (1H, *J* = 8.0 Hz), 7.64 d (1H, *J* = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 51.0, 66.3, 99.5, 121.0, 121.6, 121.7, 124.6, 132.7, 140.3, 157.8. Mass spectrum (HRMS-ESI), *m*/*z*: 204.0841 $[M + H]^+$ (calculated for $C_{12}H_{13}NS$: 204.0841). 1449609. The spectral data correspond to those described in [35].

1-(Benzo[*b*]thiophen-2-yl)piperidine (5b). Yield 0.088 g (49%, method *a*), white crystals, mp 98.5–100°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.53–1.61 m (2H), 1.61–1.71 m (4H), 3.17–3.27 m (2H), 6.26 s (1H), 6.98–7.07 m (1H), 7.15–7.24 m (1H), 7.43 d (1H, *J* = 7.0 Hz), 7.65 d (1H, *J* = 8.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 23.9, 25.1, 51.7, 98.4, 120.8, 121.2, 122.0, 124.9, 132.1, 141.3, 158.3. Mass spectrum (HRMS-ESI), *m*/*z*: 218.0997 $[M + H]^+$ (calculated for $C_{13}H_{15}NS$: 218.0998). The spectral data correspond to those described in [35].

1-(Benzo[*b*]thiophen-2-yl)pyrrolidine (5c). Yield 0.135 g (78%, method *a*), white crystals, mp 87–89°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.90–2.19 m (4H), 3.30–3.55 m (4H), 5.87 s (1H), 6.98–7.06 m (1H), 7.19–7.27 m (1H), 7.44 d (1H, *J* = 8.0 Hz), 7.60 d (1H, *J* = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.8, 50.5, 94.0, 119.7, 121.4, 124.5, 131.8, 141.8, 153.9. Mass spectrum (EI), *m*/*z* (*I*, %): 204 (16) $[M + 1]^+$, 203 (100) $[M]^+$, 202 (54), 175 (6), 160 (30), 147 (35), 134 (14), 121 (10), 89 (28), 41 (28), 27 (23). Mass spectrum (HRMS-ESI), *m*/*z*: 204.0841 $[M + H]^+$

(calculated for $C_{12}H_{13}NS$: 204.0841). The spectral data correspond to those described in [36].

1-(Benzo[*b*]thiophen-2-yl)-4-methylpiperidine (5d). Yield 0.195 g (68%, method *a*), yellow crystals, mp 101–102.5°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.02 d (3H, *J* = 7.0 Hz), 1.34–1.50 m (2H), 1.51–1.63 m (1H), 1.76 d (2H, *J* = 13.1 Hz), 2.92 m (2H), 3.66 br.d (2H, *J* = 12.1 Hz), 6.18 s (1H), 7.03–7.14 m (1H), 7.20–7.27 m (1H), 7.46 d (1H, *J* = 8.0 Hz), 7.61 d (1H, *J* = 8.0 Hz). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.94 d (3H, *J* = 7.0 Hz), 1.20–1.36 m (2H), 1.48–1.62 m (1H), 1.70 br.d (2H, *J* = 13.1 Hz), 2.88 m (2H), 3.58 br.d (2H, *J* = 12.1 Hz), 6.25 s (1H), 6.98–7.06 m (1H), 7.15–7.24 m (1H), 7.42 d (1H, *J* = 8.0 Hz), 7.64 d (1H, *J* = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.8, 30.4, 33.4, 51.5, 98.5, 120.5, 120.9, 121.5, 124.4, 132.6, 140.9, 158.3. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 22.0, 30.2, 33.3, 51.1, 98.5, 120.8, 121.2, 121.9, 124.9, 132.2, 141.3, 158.0. Mass spectrum (HRMS-ESI), *m*/*z*: 232.1157 $[M + H]^+$ (calculated for $C_{14}H_{17}NS$: 232.1154).

1-(Benzo[*b*]thiophen-2-yl)-2-ethylpiperidine (5e). Yield 0.122 g (60%, method *a*), yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.97 t (3H, *J* = 7.0 Hz), 1.60–1.91 m (8H), 3.07–3.20 m (1H), 3.47 br.d (1H, *J* = 12.1 Hz), 3.54–3.64 m (1H), 6.10 br.s (1H), 7.00–7.11 m (1H), 7.19–7.27 m (1H), 7.43 d (1H, *J* = 8.0 Hz), 7.59 d (1H, *J* = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.5, 18.9, 20.6, 25.0, 26.6, 45.9, 60.4, 97.6, 120.1, 120.5, 121.4, 124.4, 132.3, 141.3, 158.0. Mass spectrum (HRMS-ESI), *m*/*z*: 246.1299 $[M + H]^+$ (calculated for: $C_{15}H_{19}NS$ 246.1311).

1-(Benzo[*b*]selenophen-2-yl)morpholine (5f). Yield 0.060 g (35%, method *a*), pale orange crystals, mp 174–176°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.23 t (4H, *J* = 4.5 Hz), 3.86 t (4H, *J* = 4.5 Hz), 6.33 br.s (1H), 7.04 t (1H, *J* = 7.4 Hz), 7.25 t (1H, *J* = 8.2 Hz), 7.47 d (1H, *J* = 7.8 Hz), 7.66 d (1H, *J* = 7.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 52.0, 66.3, 102.4, 121.8, 122.8, 124.7, 125.0, 134.2, 142.8, 159.9. Mass spectrum (HRMS-ESI), *m*/*z*: 268.0252 $[M + H]^+$ (calculated for $C_{12}H_{14}NOSe$: 268.0241).

1-(Benzo[*b*]selenophen-2-yl)piperidine (5g). In the case of the synthesis by method *b* CuI was added trice: 0.022 g (0.116 mmol) at the beginning of the reaction, 0.022 g (0.116 mmol) after 7 h, and 0.011 g (0.058 mmol) after 13 h. The mixture was stirred at 80°C for another 13 h. Yield 0.030 g (19%, method *a*), 0.077 g (50%, method *b*), white crystals, mp 97–98°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.61 sextet (2H, *J* = 5.7 Hz), 1.74 quintet (4H, *J* = 5.7 Hz), 3.24 t (4H, *J* = 5.7 Hz), 6.24 s (1H), 7.00 t (1H, *J* = 7.1 Hz), 7.23 t (1H, *J* = 7.1 Hz), 7.43 d (1H, *J* = 7.7 Hz), 7.64 d (1H, *J* = 7.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.8, 25.2, 53.0, 101.0, 121.1, 122.1, 124.6, 124.7, 134.0, 143.5, 160.6. Mass spectrum (HRMS-ESI), *m*/*z*: 266.0456 $[M + H]^+$ (calculated for $C_{13}H_{16}NSe$: 266.0448).

***N*,*N*-Diethylbenzo[*b*]selenophene-2-amine (5h)** was prepared by method *b*. CuI was added to the reaction mixture twice: 0.012 g (0.064 mmol) at the beginning of the reaction, 0.012 g (0.064 mmol) after 23 h. The mixture was stirred at 85°C for another 20 h. Yield 0.032 g (39%), yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.26 t (6H, *J* = 7.1 Hz), 3.36 q (4H, *J* = 7.1 Hz), 6.13 br.s (1H), 6.96 t (1H, *J* = 7.5 Hz), 7.21 t (1H, *J* = 7.5 Hz), 7.39 d (1H, *J* = 7.8 Hz), 7.61 d (1H, *J* = 7.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.7, 48.4, 98.4, 120.4, 121.5, 124.6, 125.0, 133.4, 144.4, 157.3. Mass spectrum (HRMS-ESI), *m*/*z*: 254.0444 $[M + H]^+$ (calculated for $C_{12}H_{16}NSe$: 254.0442).

1-(Benzo[*b*]seleniphen-2-yl)pyrrolidine (5i) was prepared by method *b*. CuI was added to the reaction mixture twice: 0.015 g (0.08 mmol) at the beginning of the reaction, 0.015 g (0.08 mmol) after 4 h. The mixture was stirred at 85°C for another 24 h. Yield 0.032 g (32%), beige crystals, mp 89–90°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.99 quintet (4H, *J* = 3.5 Hz), 3.26 q (4H, *J* = 7.1 Hz), 5.87 s (1H), 6.85 t (1H, *J* = 7.4 Hz), 7.15 t (1H, *J* = 7.4 Hz), 7.34 d (1H, *J* = 7.7 Hz), 7.68 d (1H, *J* = 7.7 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 25.5, 51.2, 95.7, 119.4, 120.9, 124.8 (2C), 132.7, 144.3, 154.8. Mass spectrum (HRMS-ESI), *m*/*z*: 252.0296 $[M + H]^+$ (calculated for $C_{12}H_{14}NSe$: 252.0291).

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