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Copper-Catalyzed Three Component Coupling Reaction of Azoles, Se Powder, and Aryl Iodides

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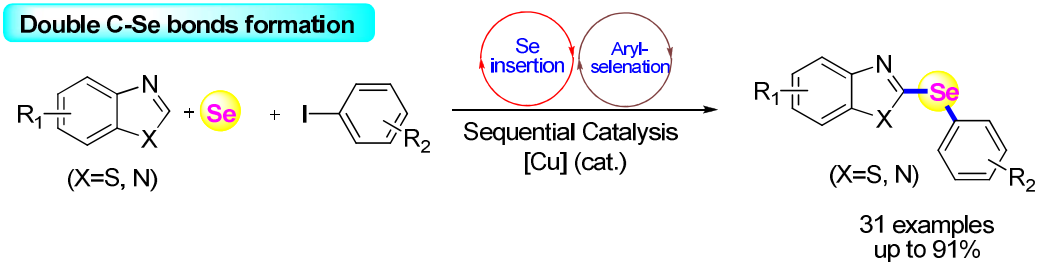


Abstract: A copper-catalyzed three-component coupling reaction of azoles, Se powder and aryl iodide is described for the first time. This transformation provides a straightforward and facile pathway to synthesis 2-arylselenation of azoles via copper-catalyzed double C-Se bonds formation process. This reaction is attractive and practical since the cheap copper catalyst is employed and don't require ligands proceed in generally good yields and a broad range of functional groups tolerance.

Introduction

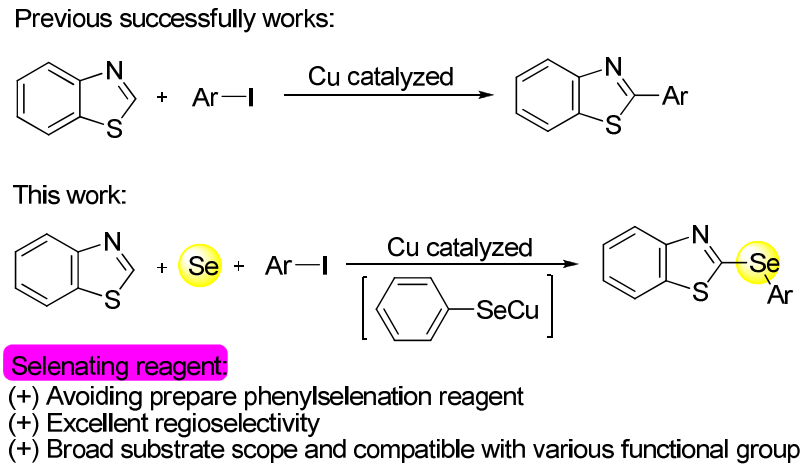
Selenium-containing compounds have aroused the interest of organic chemists over the last few years, due to organoselenium compounds are widely founded in pharmaceutical, agrochemical molecules, fluorescent molecular probes as well as in promising biomaterials.[1] Particularly relevance is the emergence of diary selenides, versatile skeleton are found in drug candidates, for example, human cancer cell growth inhibitor,[2a] antitumor agent,[2a] antioxidant,[2b] RAR agonist,[2c]

even important application to synthesis useful intermediates and catalysts.[3] a large number of approaches to access diaryl selenides including transition-metal catalyzed selenation of aryl halides / boronic acids with diselenides or selenols.[4] However, these methoeds commonly suffer from immense limination and shortcoming. For example, the starting aryl selenium reagents have to be to synthesis and restricted the substrate scope. Therefore, it will be significant synthetic value to provide an efficient and concise pathway to access diverse unsymmetrical diaryl selenides.

The introduction of selenium elemental into organic molecules via transition-metal-catalyzed insertion of selenium powder is attractive and promising in organic synthesis, due to their stable, easily operated, and commercial available. Therefore, in the last decade, it witnessed wonderful achievements have been made in this area. In these cases, selenium elemental is utilized as bridge atom to link two cross-coupling partners. In 2005, Taniguchi[5a] reported a pioneer work of copper-catalyzed selenation of aryl iodides to gain symmetrical diaryl diselenides, using aluminium as reductant and $MgCl_2$ as additive. The same group[5b] also described a copper-catalyzed oxidative coupling diarylation of chalcogen elements, employing aryboronic acids as substrates to generate symmetrical diaryl selenides. During the reaction process, PhSeCu was reasoned as the key intermediate, which was generated via copper-catalyzed insertion of selenium elemental with aryl iodides, consequently, this intermediate proceed through homo-coupling to provide symmetrical diaryl selenides. Copper-catalyzed cascade reactions of Se powder have attracted immensely attetion, rapid progress has been made in the synthesis selenium-containing heterocycles[6], trifluoromethylthiolation[7] and bioactive ebselen[8]. Lately, our group has established the copper-catalyzed double C-Se bonds formation strategy to synthesis

C3-phenylselenation of indoles,[9] this protocol also further exteneded to intramolecular C-H phenylselenation of (hetero)aryl to build benzoselenopheno[3,2-b]indole. We also described that copper-catalyzed ring-opening reaction of epoxides with Se and aryl iodides,[10] this approach provides a concise method to the synthesis of β-hydroxy phenylselenides with highly regioselectivity. In despite of the great advancements, it is still necessary to broaden the substrates to construct diverse selenium-containing compounds in a versatile way remains a significant challenge.

Scheme 1. Strategies for the formation of Double C-Se Bonds

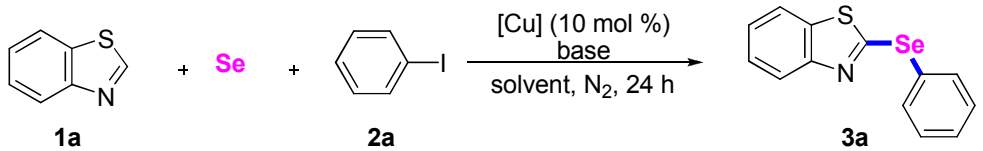


In recent years, Daugulis and Miura reported the copper-catalyzed C-H arylation of azoles derivatives with iodobenzene,[13] this reaction represents one of the most powerful strategies because of their economic advantage. Nonetheless, the electrophile aryl halides and azoles were utilized in this type reactions are limited. One significant reaction remains largely unexplored, namely the insertion of selenium elemental (Scheme 1). Simple copper catalyzed selenation of iodobenze followed by direct C-H arylselenation of azoles in the presence of selenium elemental is under developed albeit of its practical importance and high demand in present context. Herein, we wish to report a copper-catalyzed cascade reaction of aryl iodides, Se and azoles for the first

time. This transformation supplies a concise and convenient route to dissymmetric diaryl selenides under ligand-free condition. Notably, single atom Se links different cross-coupling partner strategy will be widespread in the synthesis of complex pharmaceutical compounds by synthetic chemists.

Results and Discussion

Table 1. Reaction Optimization[a]



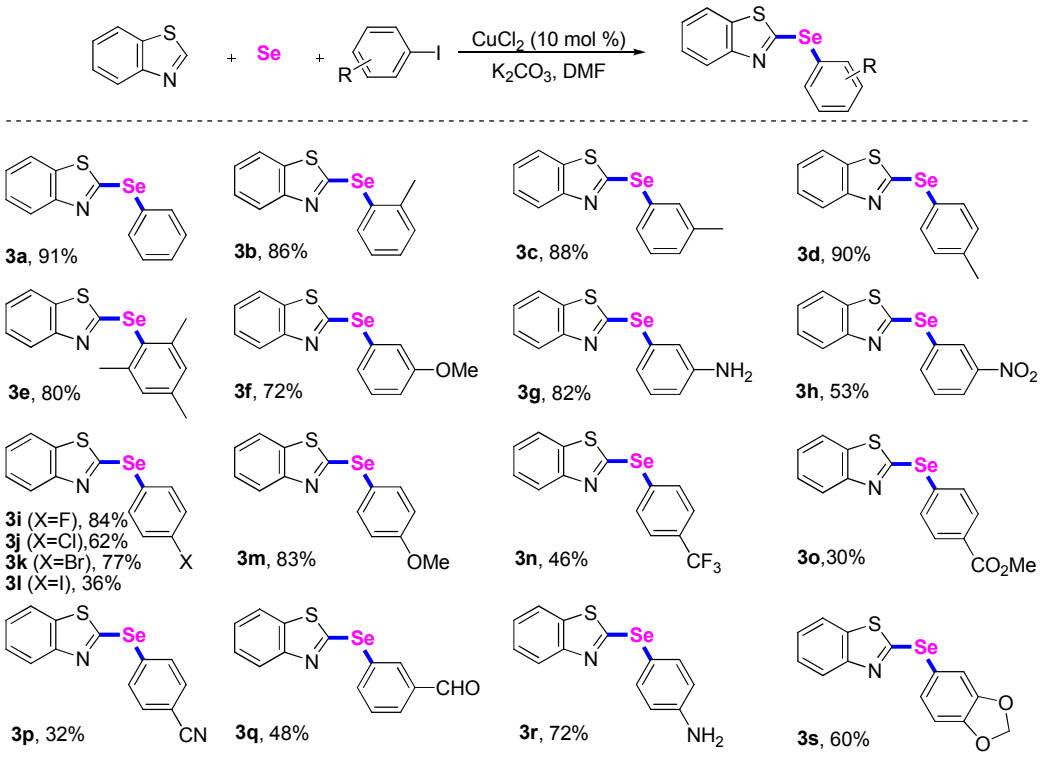
1a **2a** **3a**

entry	[Cat]	base	solvent	yield %[b]
1	$Pd(OAc)_2$	K_3PO_4	DMF	0
2	$Pd(PPh_3)_4$	K_3PO_4	DMF	0
3	$Ni(acac)_2$	K_3PO_4	DMF	0
4	$Ni(PPh_3)_2Cl_2$	K_3PO_4	DMF	0
5	$CuCl_2$	K_3PO_4	DMF	88
6	$CuCl_2$	Li_2CO_3	DMF	trace
7	$CuCl_2$	Na_2CO_3	DMF	63
8	$CuCl_2$	K_2CO_3	DMF	91
9	$CuCl_2$	Cs_2CO_3	DMF	85
10[c]	$CuCl_2$	K_2CO_3	DMF	75
11	CuO	K_2CO_3	DMF	68
12	CuI	K_2CO_3	DMF	30
13	CuBr	K_2CO_3	DMF	35
14	CuCl	K_2CO_3	DMF	27
15	$CuBr_2$	K_2CO_3	DMF	51
16	$Cu(OAc)_2$	K_2CO_3	DMF	47
17	$CuCl_2$	K_2CO_3	DMSO	50
18	$CuCl_2$	K_2CO_3	dioxane	trace
19	$CuCl_2$	K_2CO_3	CH_3CN	trace
20	$CuCl_2$	K_2CO_3	DCE	trace
21	$CuCl_2$	K_2CO_3	toluene	trace
22	$CuCl_2$	K_2CO_3	CH_3CN	trace
23[d]	$CuCl_2$	K_2CO_3	DMF	0
24[e]		K_2CO_3	DMF	0

[a]Reaction conditions unless specified otherwise: 0.4 mmol of Benzothiazole, 1.0 mmol of Iodobenzene, 1.0 mmol of Se, 0.04 mmol of [Cu], 2.0 mmol of base, 1 mL of solvent, under N_2, 150 ℃, 24 h. [b]Isolated yield. [c]At 140 °C. [d]Under O_2. [e]In the absence of copper catalyst.

We began our investigation with the reaction of benzothiazole **1a** and iodobenzene **2a** in the presence of elemental selenium to study reaction conditions including the optimization of catalyst, base and solvents. As shown in Table 1, at the outset, palladium and nickel were used as catalyst, no desired product was gained when the reaction conducted in the presence of K_3PO_4 as the base in DMF at 150 ^oC under N_2 atmosphere for 24 h (entry 1-4). Gratifyingly, the yield of product **3a** was obtained in 88% when the catalyst changed to $CuCl_2$ (entries 5). By screening different bases for this double C-Se bonds formation reaction, K_2CO_3 was demonstrated to be more suitable base than others such as Li_2CO_3, Na_2CO_3 and Cs_2CO_3, it is worthy that the effect of bases to the reaction was depended on the amounts of bases and their anions (entries 6-9). It is perhaps that base was required to activate the selenium powder to destroy the structure of high polymer catenation, and assist copper-catalyzed C-H activation of azoles to trigger the reaction. The examination of all commercial available copper catalysts including CuO, CuI, CuBr, CuCl, $CuBr_2$ and $Cu(OAc)_2$(entry 8, 11-16), $CuCl_2$ was proved to be the best efficient catalyst species for this transformation. The choice of proper solvent is critical for this reaction, when the reactions were conducted in apolar solvent such as toluene and DCE, or weak coordination solvent dioxane and CH_3CN, trace product was detected(entry 18-22). In addition, replacing DMF with DMSO, gave no better yield. Reducing yield was obtained in the reaction operated in 140 ^oC. Remarkably, no desired product was obtained under O_2 atmosphere (entry 23), indicating that N_2 was essential for present reaction. Additionally, no coupling product was detected by GC in the absence of copper catalyst, this control experiment suggested that the copper is critical for successful for this transformation.

Scheme 2. Aryl Iodides Scope[a]



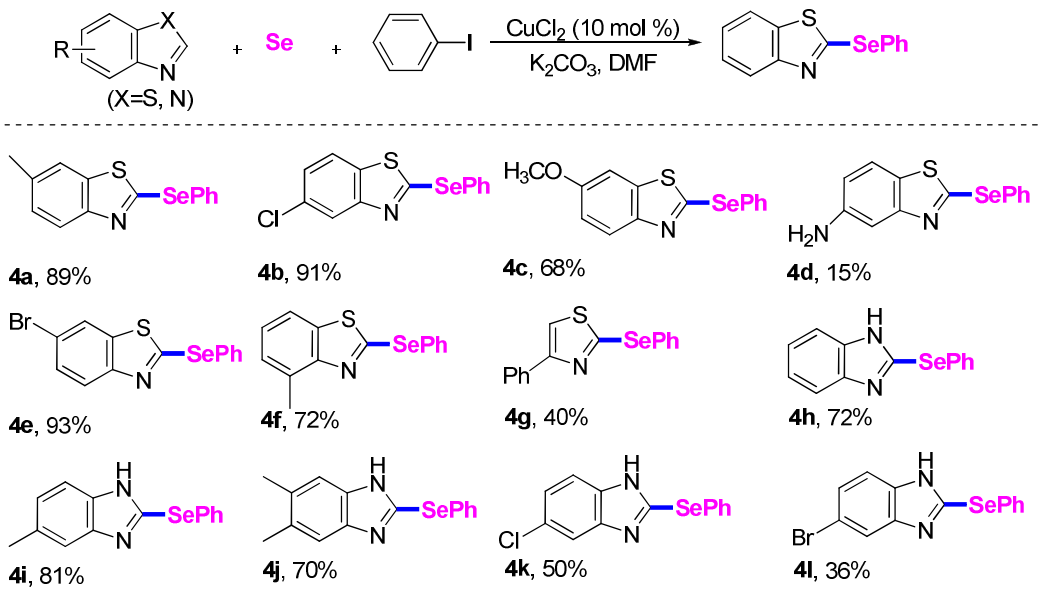
[a]Reaction conditions unless specified otherwise: benzothiazole (0.4 mmol), Se_8 (1.0 mmol), aryl iodides (1.0 mmol), $CuCl_2$ (0.04 mmol), K_2CO_3 (2.0 mmol), DMF (1 mL), 150 °C, 24 h, N_2. Isolated yields are given.

Next, the respect of aryl iodides scope was examined under the optimal conditions, the results were shown in Scheme 2. Generally, aryl iodides bearing both electron-donating and elecetron-withdrawing groups in ortho, meta or para position of the iodide group, smoothly proceeded and afforded the corresponding productins in moderat to good yields, indicated a broad range of functional groups tolerance. Noteworthy, sterically hindered groups on the aromatic ring could afford the desired product (**3e**) showed less effect toward the reaction of transformation. Halogen atoms fluoro (**3i**), chloro (**3j**), bromo (**3k**) are well tolerated, remarkably, when employing the 1, 4-diiodobenzene as substance, just one iodide was substituted to generate the **3l**

product. Moreover, sensitive cyan (**3p**), aldehyde (**3q**), ester (**3o**) and nitro (**3h**) were also compatible under current optimal reaction condition. These transformation groups provide a platform for the further decoration of the complex products. Surprisingly, the free proton containing substrates, aniline underwent the reaction smoothly and provided corresponding products **3g** and **3r** in good yields, which is a big challenge in several coupling reactions.

After the group tolerance of aryl iodides derivatives were demonstrated, the diversity of 1,3-azoles partners were further investigated under the optimized reaction conditions. The results were shown in Scheme 3, overall, moderate to good yields of **4** were obtained, and various substituents on the benzene ring of azoles showed little effect on the efficiency of the reaction except the product **4d**. It perhaps that free proton amine group could strongly coordinate with copper catalyst, which attenuates the reactivity of transition-metal. A variety of functional groups including methyl (**4a**, **4f**, **4i** and **4j**), methoxy (**4c**), chloride (**4b**, **4k**), bromide (**4e**, **4l**) were compatible. Next, we attempted the direct arylselenation of benzoxazole under the current reaction condition, however, only decomposition of the starting material without the expected product.

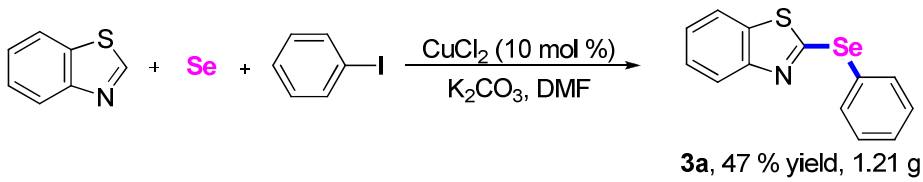
Scheme 3. 1,3-Azoles Scope



[a]Reaction conditions unless specified otherwise: Iodobenzene (1.0 mmol), Se_8 (1.0 mmol), azoles (0.4 mmol), $CuCl_2$ (0.04 mmol), K_2CO_3 (2.0 mmol), DMF (1 mL), 150 °C, 24 h, N_2. Isolated yields are given.

Base on previous literature [12], it's perhaps that the relative more C-H acidic (p*K*a < 16) of C2 benzoxzaole, liable to occur the ring-opening reaction under the strong base condition.

Scheme 4. A gram-scale cross-coupling reaction

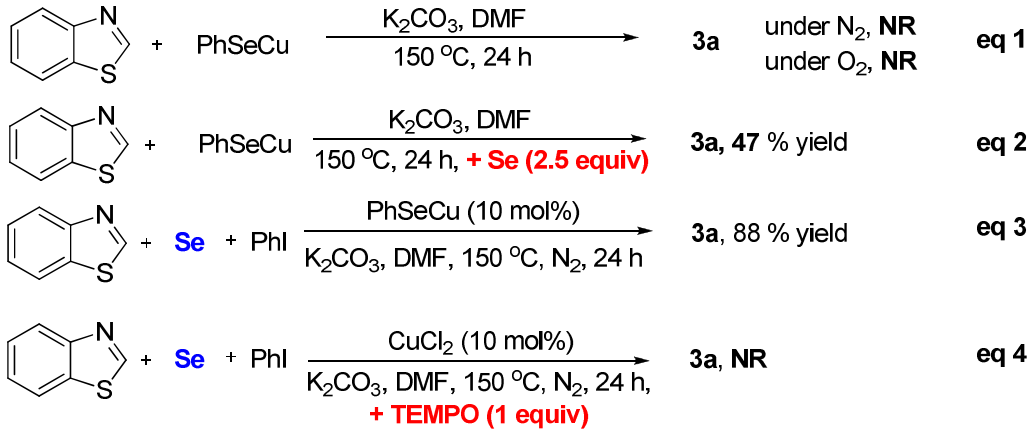


The utility of this new method was further demonstrated by an efficient gram-scale synthesis (Scheme 4), the copper-catalyzed double C-Se bond formation produced the product 3a in 47% yield as 1.21 gram under standard reaction conditions.

To gain more insights into the reaction mechanism, some selective and control experiments were performed (Scheme 5). we have examined the chemical conpetence of PhSeCu[5a] under our optimal condtion in the presence of benzothizaole under N_2 and O_2 atmosphere (Scheme 5, **eq 1**).,

however, no desired product was detected by GC. An amusing phenomenon was also observed, when 2.5 equiv of selenium powder was added into the standard reaction condition, the desired product **3a** was obtained in 47 % isolated yield, (Scheme 5, **eq 2**); These data for stoichiometric reactions of PhSeCu suggested that selenium elemental perhaps play a key role in the process of double C-Se formation and also reason this transformation waste excess amount of Se powder.

Scheme 5. Preliminary Mechanism Investigation



As shown in **eq 3**, which is consistent with our envision that PhSeCu may be a chemically competent intermediate, which first through Ullman-type selenation between aryl iodides and selenium in situ during the catalytic cycle. Finally, by the addition of radical inhibitor TEMPO under the optimized reaction conditions(Scheme 5, **eq 4**), the desired transformation was shut down, this result indicated that the arylselenation of azoles might go through the radical pathway.

In conclusion, a novel and concise route to gain the unsymmetrical diaryl selenides via copper-catalyzed three-component coupling reaction of azoles, Se powder, and aryl iodides has been developed. This reaction proceeds through activation of commercially available elemental selenium and the formation of double C-Se bonds. Importantly, copper-catalyzed azole C-H arylselenation enrich the functionalized reaction of oxazoles, which will drive the development of

rapid, and cost effective methods for their elaboration. This reaction is attractive and practical since the cheap copper catalyst is employed and don't require ligands proceed in generally good yields and a broad range of functional groups tolerance. Further studies on the reaction mechanism, the development of new strategies of selective selenation transformation, broaden the reaction new types of insertion of selenium elemental are underway in our laboratory.

Experimental Section

General Remarks. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 MHz) spectra were recorded in DMSO-d_6 solutions using a 500 MHz spectrometer. High-resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. All reactions were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300−400 mesh). ^{1}H NMR and ^{13}C NMR spectra are provided as Supporting Information. 6-methylbenzothiazole,[13] 5-chlorobenzothiazole,[13] 6-methoxybenzothiazole,[13] 5-aminobenzothiazole,[13] 6-bromobenzothiazole,[13] 4-methylbenzothiazole,[13] 4-phenylthiazole [13] were prepared according to the reported procedures. ^{1}H and ^{13}C spectra of known compounds were in accordance with those described in the literature.

Procedure for C-H Phenylselenation of Azoles Reactions. In a 25 mL Schlenk tube equipped with a stir bar were placed benzothiazole **1** (0.4 mmol), iodobenzene **2** (1.0 mmol), Se (1.0 mmol), $CuCl_2$ (10 mol %), and K_2CO_3 (2.0 mmol) in DMF (1 mL). The tube was evacuated and refilled with N_2 three times. The reaction mixture was stirred at 150 ^{o}C for 24 h. After it was cooled, the reaction mixture was diluted with 10 mL of ethyl ether, and filtered through a pad of silica gel, followed by washing the pad of silica gel with the same solvent (20 mL). The filtrate was washed with water (3×15 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated under

reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

Preliminary Mechanism Investigation. In Two 10 mL of Schlenk tubes equipped with a stir bar were placed with PhSeCu (1.0 mmol), benzothiazole (0.4 mmol), and K_2CO_3 (2.0 mmol) in DMf (1 mL). The first tube, was evacuated and refilled N_2 three times. The other tube, was fitted with a rubber septum, and then it was evacuated and refilled with O_2 three times. These reaction mixtures were stirred at 150 ^oC for 24 h (see Scheme 5, eq 1). To a 10 mL Schlenk tube equipped with a stir bar were placed PhSeCu (1.0 mmol), Se (1.0 mmol), benzothiazole (0.4 mmol), and K_2CO_3 (2.0 mmol) in DMF (1 mL). The tube was evacuated and refilled with N_2 three times. The reaction mixture was stirred at 150 ^oC for 24 h (see Scheme 5, eq 2). In a 10 mL Schlenk tube equipped with a stir bar were placed benzothiazole (0.4 mmol), iodobenzene (1.0 mmol), Se (1.0 mmol), PhSeCu (10 mol %), and K_2CO_3 (2.0 mmol) in DMF (1 mL). The tube was evacuated and refilled with N_2 three times. The reaction mixture was stirred at 150 ^oC for 24 h (see Scheme 5, eq 3). In a 10 mL Schlenk tube equipped with a stir bar were placed benzothiazole **1** (0.4 mmol), iodobenzene **2** (1.0 mmol), Se (1.0 mmol), TEMPO (0.4 mmol), $CuCl_2$ (10 mol %), and K_2CO_3 (2.0 mmol) in DMF (1 mL). The tube was evacuated and refilled with N_2 three times (see Scheme 5, eq 4). After it was cooled, the reaction mixture was diluted with 10 mL of ethyl ether, and filtered through a pad of silica gel, followed by washing the pad of silica gel with the same solvent (20 mL). The filtrate was washed with water (3×15 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

Characterization Data of Compounds 3 and 4:

2-phenylselenobenzothiazole (**3a**). Following the general procedure, using 20 / 1 petroleum ether / EtOAc as the eluant afforded a yellow solid (105.6 mg, 91 % yield), mp 41-42 °C. The 1 H and 13 C NMR spectra were in accordance with those described in the literature.[14]

2-(2-methylphenylseleno)benzothiazole (**3b**). Following the general procedure, using 20 / 1 petroleum ether / EtOAc as the eluant afforded a yellow viscous oil liqid (105 mg, 86 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.91 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.27 – 7.22 (m, 2H), 2.55 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) : δ 162.9, 154.8, 143.0, 138.3, 136.6, 130.9, 130.9, 127.7, 127.3, 125.9, 124.2, 121.9, 120.7, 23.2. HRMS (TIC): calcd for $C_{14}H_{12}NSSe$ $[M + H]^+$ 305.9850, found 305.9823. The ^{1} H and ^{13} C NMR spectra were in accordance with those described in the literature.[14]

2-(3-methylphenylseleno)benzothiazole (**3c**). Following the general procedure, using 20 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (107.6mg, 88 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.95 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.69 (s, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.47 – 7.33 (m, 4H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.5, 154.1, 139.8, 136.6, 135.9, 133.3, 131.0, 130.0, 126.2, 125.7, 124.4, 121.6, 121.4, 20.7. HRMS (TIC): calcd for $C_{14}H_{12}NSSe$ $[M + H]^+$ 305.9850, found 305.9823.

2-(4-methylphenylseleno)benzothiazole (**3d**). Following the general procedure, using 20 / 1 petroleum ether / EtOAc as the eluant afforded a yellow solid (109.4 mg, 90 % yield)，mp 72-74 °C.. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.90 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.5 Hz, 2H), 7.65 (d, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5Hz, 1H), 7.26 – 7.13 (m, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.7, 154.7, 140.6, 136.8, 136.6, 130.8, 126.0, 124.2, 122.9, 121.9, 120.7, 21.4. HRMS (TIC): calcd for $C_{14}H_{12}NSSe$ $[M + H]^+$ 305.9850, found 305.9823. The ^{1} H and ^{13} C

NMR spectra were in accordance with those described in the literature.[14]

2-(2,4,6-trimethylphenylseleno)benzothiazole (**3e**). Following the general procedure, using 20 / 1 petroleum ether / EtOAc as the eluant afforded a pale yellow solid (106.2 mg, 80 % yield), mp 70-71 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.89 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.15 (s, 2H), 2.46 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.4, 154.5, 143.3, 140.7, 135.6, 129.3, 126.1, 125.4, 124.0, 121.6, 121.0, 23.8, 20.7. HRMS (TIC): calcd for $C_{16}H_{16}NSSe$ $[M + H]^+$ 334.0163, found 334.0132. The ^{1}H and ^{13}C NMR spectra were in accordance with those described in the literature.[14]

2-(3-methoxyphenylseleno)benzothiazole (**3f**). Following the general procedure, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a yellow viscous oil liquid (92.4 mg, 72 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.97 – 7.89 (m, 2H), 7.46 – 7.34 (m, 5H), 7.14 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.2, 159.9, 154.0, 135.9, 131.1, 128.2, 126.7, 126.3,124.5, 121.7, 121.4, 121.2, 116.1, 55.4. HRMS (TIC): calcd for $C_{14}H_{12}NOSSe$ $[M + H]^+$ 321.9800, found 321.9801.

3-(benzothiazol-2-ylseleno)aniline (**3g**). Following the general procedure, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a yellow viscous oil liquid (105 mg, 86 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.95 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 8.5 Hz, 1H), 7.07 (s, 1H), 6.94 (d, J = 7.5 Hz, 1H), 6.75 (d, J = 9.0Hz, 1H), 5.46 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.1, 154.1, 150.3, 135.9, 130.5, 126.2, 125.9, 124.4, 122.8, 121.6, 121.3, 120.8, 115.6. HRMS (TIC): calcd for $C_{13}H_{11}N_2SSe$ $[M + H]^+$ 306.9803, found 306.9815.

2-(3-nitrophenylseleno)benzothiazole (**3h**). Following the general procedure, using 5 / 1 petroleum

ether / EtOAc as the eluant afforded a yellow viscous oil liquid (71.2 mg, 53 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.27 – 8.19 (m, 2H), 8.08 – 7.98 (m, 4H), 7.52 (t, J = 7.0 Hz, 1H), 7.44 (d, J = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.9, 153.6, 147.7, 136.6, 136.5, 135.0, 133.4, 126. 6,125.3, 124.5, 122.0, 121. 9, 121.9. HRMS (TIC): calcd for $C_{13}H_9N_2O_2SSe$ $[M + H]^+$ 336.9545, found 336.9564.

2-(4-fluorophenylseleno)benzothiazole (**3i**). Following the general procedure, using 20 / 1 petroleum ether / EtOAc as the eluant afforded a yellow viscous oil liquid (105.4 mg, 84 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.98 – 7.89 (m, 4H), 7.46 (t, J = 7.5 Hz, 1H), 7.40 – 7.34 (m, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.5 (d, J_F = 224.4 Hz), 162.4, 154.1, 139.1 (d, J_F = 8.6 Hz), 135.8, 126.3, 124.5, 121.7, 121.4, 121.3 (d, J_F = 3.2 Hz), 117.4 (d, J_F = 21.8 Hz). ^{19}F NMR (470 MHz, DMSO-d_6): δ -110.15(s, 1F). HRMS (TIC): calcd for $C_{13}H_9FNSSe$ $[M + H]^+$ 309.9600, found 309.9603. The ^{1} H and ^{13} C NMR spectra were in accordance with those described in the literature.[14]

2-(4-chlorophenylseleno)benzothiazole (**3j**). Following the general procedure, using 20 / 1 petroleum ether / EtOAc as the eluant afforded a yellow viscous oil liquid (82.9 mg, 62 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.98 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.6, 153.9, 137.9, 135.9, 135.4, 130.2, 126.3, 124.9, 124.6, 121.7, 121.5. HRMS (TIC): calcd for $C_{13}H_9ClNSSe$ $[M + H]^+$ 325.9304, found 325.9329. The ^{1} H and ^{13} C NMR spectra were in accordance with those described in the literature.[14]

2-(4-bromophenylseleno)benzothiazole (**3k**). Following the general procedure, 0.04 mmol $CuCl_2$, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liquid (116.4mg, 77 % yield).

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.96 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.77 – 7.68 (m, 4H), 7.45(t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.4, 153.9, 138.0, 135.9, 133.0, 126.1, 125.4, 124.6, 124.1, 121.6, 121.4. HRMS (TIC): calcd for $C_{13}H_9BrNSSe$ $[M + H]^+$ 369.8799, found 369.8795.

2-(4-iodophenylseleno)benzothiazole (**3l**). Following the general procedure, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a white solid (59.8mg, 36 % yield), mp 46-47 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.96 (d, J = 7.5 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.75 (t, J = 6.5 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.37 – 7.32 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.3, 153.9, 138.9, 138.6, 137.9, 137.0, 135.8, 132.8, 126.3, 124.6, 121.5. HRMS (TIC): calcd for $C_{13}H_9INSSe$ $[M + H]^+$ 417.8660, found 417.8662.

2-(4-methoxyphenylseleno)benzothiazole (**3m**). Following the general procedure, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (106.6 mg, 83 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.94 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.79 (t, J = 8.5 Hz, 2H), 7.44 (t, J = 7.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.09 (d, J =9.0 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.5, 161.1, 154.3, 138.6, 135.7, 126.2, 124.3, 121.3, 121.2, 115.9, 115. 9, 55.4. HRMS (TIC): calcd for $C_{14}H_{12}NOSSe$ $[M + H]^+$ 321.9800, found 321.9803. The ^{1} H and ^{13} C NMR spectra were in accordance with those described in the literature.[14]

2-(4-trifluoromethylphenylseleno)benzothiazole (**3n**). Following the general procedure, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a yellow solid (66.0mg, 46 % yield), mp 75-76 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.03 (t, J = 8.5 Hz, 3H), 7.95 (d, J = 8.5 Hz, 1H), 7.85(d, J = 8.0 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.6, 153.7, 136.1, 135.9, 132.2, 129.9 (q, J_F = 32.5 Hz), 126.6 (q, J_F = 3.8Hz),

126.4, 124.9 122.8, 121.8, 121.7. ^{19}F NMR (470 MHz, DMSO-d_6): δ -61.40(s, 3F). HRMS (TIC): calcd for $C_{14}H_9F_3NSSe$ $[M + H]^+$ 359.9568, found 359.9566.

3-(benzothiazol-2-ylseleno)benzoate (**3o**). Following the general procedure, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a pale yellow solid (41.6mg, 30 % yield), mp 83-85 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.06 (t, J = 8.0 Hz, 3H), 8.00 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.6, 159.8, 153.7, 135.3, 132.5, 130.4, 130.2, 126.4, 124.9, 121.8, 121.7, 52.4. HRMS (TIC): calcd for $C_{15}H_{12}NO_2SSe$ $[M + H]^+$ 349.9749, found 349.9752.

2-(4-cyanophenylseleno)benzothiazole (**3p**). Following the general procedure, using 10 / 1 petroleum ether / EtOAc as the eluant afforded a yellow solid (40.0mg, 32 % yield), mp 75-76 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.97 – 7.90 (m, 4H), 7.80 (d, J = 8.5 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.50(t, J = 7.5 Hz, 1H), 7.41(t, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 158.6, 153.6, 136.3, 135.1, 134.0, 133.3, 133.1, 126.5, 125.1, 121.9, 111.9, 110.5. HRMS (TIC): calcd for $C_{14}H_9N_2SSe$ $[M + H]^+$ 316.9646, found 316.9664..

3-(benzothiazol-2-ylseleno)benzaldehyde (**3q**). Following the general procedure, using 10 / 1 petroleum ether / EtOAc as the eluant afforded a yellow viscous oil liqid (61.3 mg, 48 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.08 (s, 1H), 8.36 (s, 1H), 8.17 (d, J = 7.5 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.98(d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 7.0Hz, 1H), 7.38 (t, J = 8.0Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 192.4, 160.9, 153.9, 141.6, 137.5, 136.7, 136.0, 130.6, 127.6, 126.4, 124.7, 121.7. HRMS (TIC): calcd for $C_{14}H_{10}NOSSe$ $[M + H]^+$ 319.9643, found 319.9648.

4-(benzothiazol-2-ylseleno)aniline (**3r**). Following the general procedure, using 15 / 1 petroleum

ether / EtOAc as the eluant afforded a yellow viscous oil liquid (101.6 mg, 83 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.91 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 6.67 (d, J = 8.0Hz, 2H), 5.73 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.9, 154.6, 151.2, 138.3, 135.7, 126.0, 124.0, 121.5, 121.0, 115.1, 108.8. HRMS (TIC): calcd for $C_{13}H_{11}N_2SSe$ [M + H]+ 306.9803, found 306.9815.

2-(benzo[1,3]dioxol-5-ylseleno)benzothiazole (**3s**). Following the general procedure, using 30 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (80.3mg, 60% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.96 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.46 – 7.43 (m, 2H), , 7.38 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.16 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.9, 154.2, 149.5, 148.4, 135.8, 131.5, 126.2, 124.3, 121.6, 121.2, 116.8, 116.4, 109.9, 101.9. HRMS (TIC): calcd for $C_{14}H_{10}NO_2SSe$ $[M + H]^+$ 335.9592, found 335.9598.

6-methyl-2-phenylselenobenzothiazole (**4a**). Following the general procedure, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (109.1mg, 89% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.84 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 1H), 7.72 (s, 1H), 7.58 – 7.50 (m, 3H), 7.26 (d, J = 8.5 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.6, 157.4, 141.4, 141.3, 139.5, 135.4, 132.9, 132.8, 131.5, 126.4, 126.2, 26.1. HRMS (TIC): calcd for $C_{14}H_{12}NSSe$ $[M + H]^+$ 305.9850, found 305.9823.

5-chloro-2-phenylselenobenzothiazole (**4b**). Following the general procedure, using 10 / 1 petroleum ether / EtOAc as the eluant afforded a white solid (115.4 mg, 91 % yield), mp 40-41 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.97 – 7.94 (m, 2H), 7.86 (d, J = 7.5 Hz, 2H), 7.61 – 7.52 (m, 3H), 7.37 (d, J = 9.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.9 154.8, 136.5, 134.5, 131.0, 130.5, 130.3, 125.7, 124.4, 123.0, 120.7. HRMS (TIC): calcd for $C_{13}H_9ClNSSe$ $[M + H]^+$

325.9304, found 325.9329. The ^{1}H and ^{13}C NMR spectra were in accordance with those described in the literature.[14]

6-methoxy-2-phenylselenobenzothiazole (**4c**). Following the general procedure, using 10 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (87.7 mg, 68 % yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.83 – 7.80 (m, 3H), 7.55 – 7.48 (m, 4H), 7.06 (d, J = 8.5 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6)**:** δ 157.5 156.8, 148.5, 137.6, 135.7, 130.1, 129.9, 126.6, 122.0, 115.2, 104.7, 55.6. HRMS (TIC): calcd for $C_{14}H_{12}NOSSe$ $[M + H]^+$ 321.9800, found 321.9802.

5-amino-2-phenylselenobenzothiazole (**4d**). Following the general procedure, using 10 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (18.3 mg, 15% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.81 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 7.5 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.51 – 7.48 (m, 2H), 7.06 (d, J = 9.0 Hz, 1H), 6.91 (d, J =8.0 Hz, 1H), 5.61 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.9 155.6, 135.9, 130.1, 129.2, 128.8, 125.8, 124.0, 123.3, 114.9, 113.4. HRMS (TIC): calcd for $C_{13}H_{11}N_2SSe$ $[M + H]^+$ 306.9803, found 306.9815.

6-bromo-2-phenylselenobenzothiazole (**4e**). Following the general procedure, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (137.2 mg, 93% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.22 (d, J = 2.0 Hz, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 7.5 Hz, 1H), 7.62 – 7.53 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.2, 153.1, 137.7, 136.5, 130.5, 130.3, 129.3, 125.7, 124.2, 122.7, 117.2. HRMS (TIC): calcd for $C_{13}H_9BrNSSe$ $[M + H]^+$ 369.8799, found 369.8795.

4-methyl-2-phenylselenobenzothiazole (**4f**). Following the general procedure, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (88.0mg, 72% yield). ^{1}H NMR (500

MHz, DMSO-d_6): δ 7.86 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.27 – 7.22 (m, 2H), 2.62 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.7, 153.3, 136.1, 135.7, 130.9, 130.1, 126.6, 126.3, 124.5, 118.9, 17.9. HRMS (TIC): calcd for $C_{14}H_{12}NSSe$ $[M + H]^+$ 305.9850, found 305.9823.

4-phenyl-2-phenylselenothiazole (**4g**). Following the general procedure, using 10 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (148.7mg, 40% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.11 (s, 1H), 7.92 (d, J = 7.0 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.53 – 7.43(m, 5H), 7.35 (t, J = 7.5 Hz, 1H), 7.28 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.8, 134.6, 130.2, 130.0, 129.7, 129.5, 128.8, 128.6, 125.9, 117.4. HRMS (TIC): calcd for $C_{15}H_{12}NSSe$ $[M + H]^+$ 317.9850, found 317.9830.

2-phenylselenobenzimidazole (**4h**). Following the general procedure, using 5 / 1 petroleum ether / EtOAc as the eluant afforded a light yellow solid (78.9 mg, 23% yield), mp 180-181 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.63 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.52 – 7.51 (m, 2H), 7.35 – 7.34 (m, 3H), 7.28 (t, J = 7.0 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d6): δ 143.9, 143.4, 136.4, 132.2, 129.7, 128.2, 127.9, 122.7, 121.8, 118.7, 110.4, 31.5. HRMS (TIC): calcd for $C_{13}H_{11}N_2Se$ $[M + H]^+$ 275.0082, found 275.0085. The ^{1} H and ^{13} C NMR spectra were in accordance with those described in the literature.[15]

5-methyl-2-phenylselenobenzimidazole (**4i**). Following the general procedure, using 15 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (89.4 mg, 81% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.70 (s, 1H), 7.57 – 7.56 (m, 2H), 7.35 – 7.34 (m, 5H), 7.00 (d, J = 8.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 173.1, 169.9, 139.9, 134.7, 132.4, 129.6, 128.3, 127.8, 123.1, 117.7, 110.6, 21.2. HRMS (TIC): calcd for $C_{14}H_{13}N_2Se$ $[M + H]^+$ 289.0239,

found 289.0243.

5,6-dimethyl-2-phenylselenobenzimidazole (**4j**). Following the general procedure, using 5 / 1 petroleum ether / EtOAc as the eluant afforded a light yellow solid (80.8mg, 70% yield), mp 166-167 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.59 (s, 1H), 7.52 (d, J = 7.0 Hz, 2H), 7.38 – 7.33 (m, 4H), 7.22 (s, 1H), 2.30 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.9, 139.1, 132.0, 129.8, 129.5, 128.7, 127.7, 118.4, 111.0, 99.5, 19.8. HRMS (TIC): calcd for $C_{15}H_{15}N_2Se$ $[M + H]^+$ 303.0395, found 303.0366.

5-chloro-2-phenylselenobenzimidazole (**4k**). Following the general procedure, using 10 / 1 petroleum ether / EtOAc as the eluant afforded a yellow solid (58.2mg, 50% yield), mp 39-40 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.91 (s, 1H), 7.62 (s, 3H), 7.39 – 7.38 (m, 4H), 7.19 (d, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 133.2, 130.1, 130.0 129.6, 128.3, 127.3, 123.8, 123.7, 117.6, 112.2, 110.6. HRMS (TIC): calcd for $C_{13}H_{10}ClN_2Se$ $[M + H]^+$ 308.9692, found 308.9693.

5-bromo-2-phenylselenobenzimidazole (**4l**) Following the general procedure, using 10 / 1 petroleum ether / EtOAc as the eluant afforded a yellow liqid (51.0mg, 36% yield). ^{1}H NMR (500 MHz, DMSO-d6): δ 12.91 (s, 1H), 7.62 (s, 3H), 7.39 – 7.38 (m, 4H), 7.30 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 133.2, 130.1, 130.1 130.0, 129.6, 129.4, 129.3, 128.3, 127.3, 123.9, 123.7. HRMS (TIC): calcd for $C_{13}H_{10}BrN_2Se$ $[M + H]^+$ 352.9187, found 352.9209.

ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C and ^{19}F NMR spectral data of all compounds reported. Supporting Information is available free of charge the ACS Publications website at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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