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

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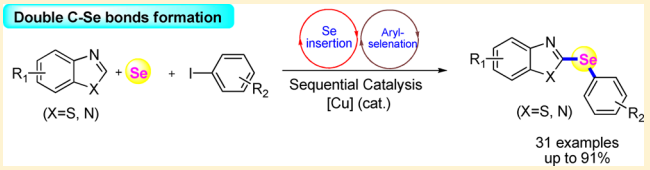
Supporting Information

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-arylselanyl-azoles via a copper-catalyzed double C−Se bonds formation process. This reaction is attractive and practical since the cheap copper catalyst is employed and it does not require ligands, proceeds in generally good yields, and has a broad range of functional groups tolerance.



INTRODUCTION

Selenium-containing compounds have aroused the interest of organic chemists over the past few years, due to that organoselenium compounds are widely found in pharmaceutical, agrochemical molecules, fluorescent molecular probes as well as in promising biomaterials.[1] Particularly relevant is the emergence of diary selenides, whose versatile skeletons are found in drug candidates, for example, human cancer cell growth inhibitor,[2a] antitumor agent,[2a] antioxidant,[2b] RAR agonist,[2c] and even important application to the synthesis of useful intermediates and catalysts.[3] The exist 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 limitations and shortcomings. For example, the starting aryl selenium reagents have to be synthesized and restricted the substrate scope. Therefore, it will be of significant synthetic value to provide an efficient and concise pathway to access diverse unsymmetrical diaryl selenides.

The introduction of elemental selenium into organic molecules via transition-metal-catalyzed insertion of selenium powder is attractive and promising in organic synthesis, due to that it is stable, easily operated, and commercial available. Therefore, in the past decade, wonderful achievements have been made in this area. In these cases, elemental selenium is utilized as a bridge atom to link two cross-coupling partners. In 2005, Taniguchi[5a] reported a pioneering work of copper-catalyzed selenation of aryl iodides to gain symmetrical diaryl diselenides, using aluminum as reductant and $MgCl_2$ as additive. The same group[5b] also described a copper-catalyzed oxidative coupling diarylation of chalcogen elements, employing arylboronic 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 elemental selenium with aryl iodides; consequently, this intermediate proceeded through homocoupling to provide symmetrical diaryl selenides. Copper-catalyzed cascade reactions of Se powder have attracted immense attetion, and 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 was also further extended to intramolecular C−H phenylselenation of (hetero)aryl to build benzoselenopheno-[3,2-*b*]indole. We also described the 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 high regioselectivity. Despite the great advancements, it is still necessary to broaden the substrates to construct diverse selenium-containing compounds in a versatile way, which remains a significant challenge.

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 its economic advantage. Nonetheless, the electrophile aryl halides and azoles that were utilized in this type of reaction are limited. One significant reaction remains largely unexplored, namely, the insertion of elemental selenium (Scheme 1). Simple copper-catalyzed selenation of iodobenze, followed by direct C−H arylselenation of azoles in the presence of elemental selenium, is underdeveloped, albeit of its practical importance and high demand in the 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

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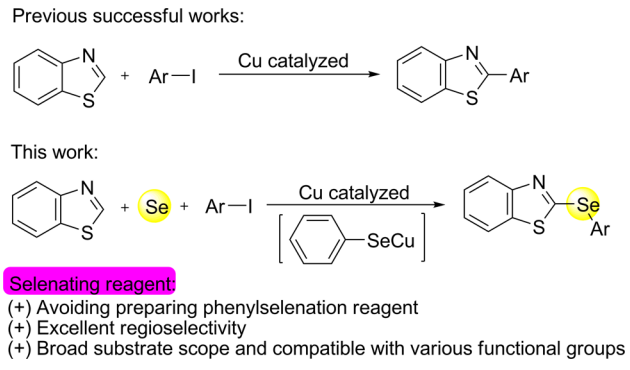
Scheme 1. Strategies for the Formation of Double C−Se Bonds



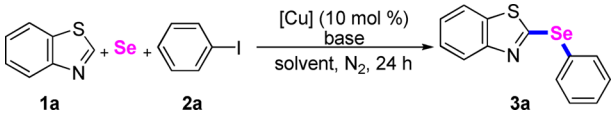
selenides under ligand-free condition. Notably, the single atom Se links different cross-coupling partners strategy will be widespread in the synthesis of complex pharmaceutical compounds by synthetic chemists.

RESULTS AND DISCUSSION

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, and no desired product was gained when the reaction was conducted in the presence of K_3PO_4 as the base in DMF at 150 °C under a N_2 atmosphere for 24 h (entries 1−4). Gratifyingly, the yield of product **3a** was obtained in 88% when the catalyst was changed to $CuCl_2$ (entry 5). By screening different bases for this double C−Se bonds formation reaction, K_2CO_3 was demonstrated to be a more suitable base than others such as Li_2CO_3, Na_2CO_3, and Cs_2CO_3; it is worthy to note that the effect of bases to the reaction was dependent 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. After the examination of all commercially available copper catalysts including CuO, CuI, CuBr, CuCl, $CuBr_2$, and $Cu(OAc)_2$ (entries 8, 11−16), $CuCl_2$ was proved to be the best efficient catalyst species for this transformation. The choice of the 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 (entries 18−22). In addition, replacing DMF with DMSO gave no better yield. A reduced yield was obtained in the reaction operated in 140 °C. Remarkably, no desired product was obtained under an O_2 atmosphere (entry 23), indicating that N_2 was essential for the 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 the success of this transformation.

Next, the respect of aryl iodides scope was examined under the optimal conditions, and the results are shown in Scheme 2.

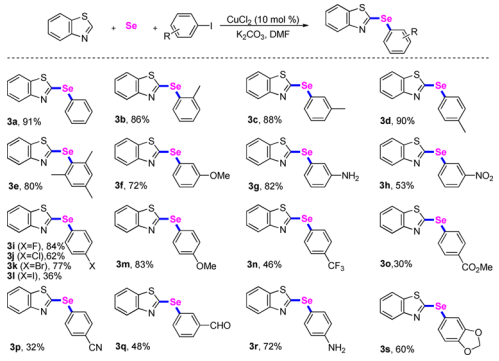
Table 1. Reaction Optimization[a]



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 °C, 24 h. [b]Isolated yield. [c]At 140 °C. [d]Under O_2. [e]In the absence of copper catalyst.

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.

Generally, aryl iodides bearing both electron-donating and elecetron-withdrawing groups in the ortho, meta, or para position of the iodide group smoothly proceeded and afforded the corresponding products in moderate to good yields, which indicated a broad range of functional groups tolerance. Noteworthy, sterically hindered groups on the aromatic ring could afford the desired product (**3e**), which showed less effect toward the reaction of transformation. Halogen atoms fluoro (**3i**), chloro (**3j**), and 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

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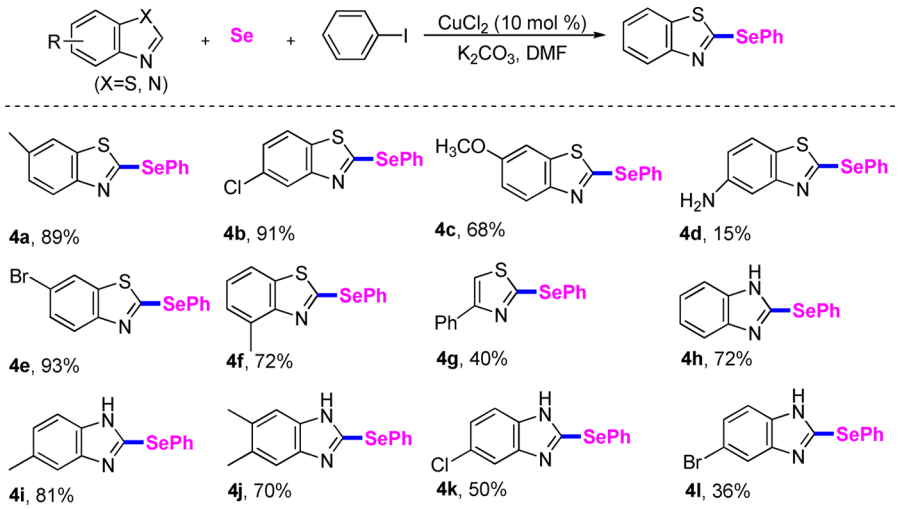
Scheme 3. 1,3-Azoles Scope[a]



[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.

(**3o**), and nitro (**3h**) were also compatible under the current optimal reaction conditions. These transformation groups provide a platform for the further decoration of the complex products. Surprisingly, substrates containing active hydrogen proton aniline underwent the reaction smoothly and provided corresponding products **3g** and **3r** in good yields, which is a big challenge in several coupling reactions.

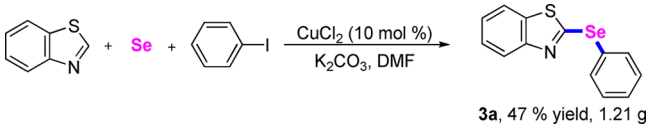
After the group tolerance of aryl iodides derivatives was demonstrated, the diversity of 1,3-azoles partners was further investigated under the optimized reaction conditions. The results are shown in Scheme 3. Overall, moderate to good yields of **4** were obtained, and various substituents on the benzene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

On the basis of previous literature,[11,12] it is perhaps that the relatively more C−H acidic (pK_a < 16) of C2 benzoxzaole makes the ring-opening reaction liable to occur under the strong base conditions.

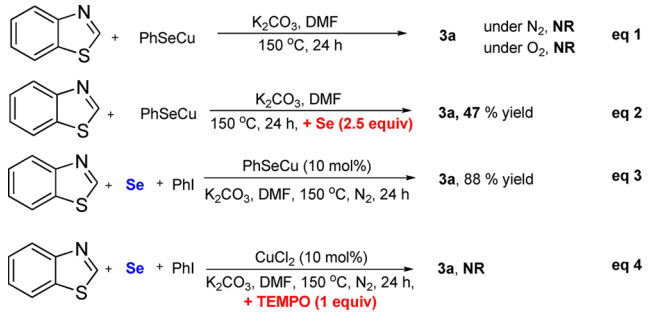
The utility of this new method was further demonstrated by an efficient gram-scale synthesis (Scheme 4); the copper-catalyzed double C−Se bond formation produced the product **3a** in 47% yield as 1.21 g under standard reaction conditions.

To gain more insights into the reaction mechanism, some selective and control experiments were performed (Scheme 5). We have examined the chemical competence of PhSeCu[5a]

Scheme 4. A Gram-Scale Cross-Coupling Reaction



Scheme 5. Preliminary Mechanism Investigation



under our optimal condtions in the presence of benzothizaole under N_2 and O_2 atmospheres (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 conditions, the desired product **3a** was obtained in 47% isolated yield (Scheme 5, eq 2). These data for stoichiometric reactions of PhSeCu suggested that elemental selenium perhaps plays a key role in the process of double C−Se formation and it is also the reason why this transformation wasted an excess amount of Se powder.

As shown in eq 3 (Scheme 5), which is consistent with our vision that PhSeCu may be a chemically competent intermediate, it first went 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 enriches the functionalized reaction of oxazoles, which will drive the development of rapid

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and cost-effective methods for their elaboration. This reaction is attractive and practical since the cheap copper catalyst is employed and it does not require ligands, proceeds in generally good yields, and has a broad range of functional groups tolerance. Further studies on the reaction mechanism, the development of new strategies of selective selenation transformation, and broadening the reaction of new types of insertion of elemental selenium 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] and 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 °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 Schlenk tubes equipped with a stir bar were placed 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 with 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 °C 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 °C 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 °C 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 liquid (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 liquid (107.6 mg, 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 = 7.5 Hz, 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 = 9.0 Hz, 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

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$C_{13}H_9FNSSe$ $[M + H]^+$ 309.9600, found 309.9603. The ^1H 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). ^1H 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 = 7.5 Hz, 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 ^1H 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 of $CuCl_2$, using 15/1 petroleum ether/EtOAc as the eluant afforded a yellow liquid (116.4 mg, 77% yield). ^1H 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 (59.8 mg, 36% yield), mp 46−47 °C. ^1H 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 liquid (106.6 mg, 83% yield). ^1H 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 ^1H 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 (66.0 mg, 46% yield), mp 75−76 °C. ^1H 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 = 3.8 Hz), 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 (41.6 mg, 30% yield), mp 83−85 °C. ^1H 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 (40.0 mg, 32% yield), mp 75−76 °C. ^1H 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 liquid (61.3 mg, 48% yield). ^1H 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 = 7.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 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). ^1H 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 = 8.0 Hz, 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 liquid (80.3 mg, 60% yield). ^1H 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 liquid (109.1 mg, 89% yield). ^1H 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. ^1H 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 ^1H 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 liquid (87.7 mg, 68% yield). ^1H 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 liquid (18.3 mg, 15% yield). ^1H 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 liquid (137.2 mg, 93% yield). ^1H 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 liquid (88.0 mg, 72% yield). ^1H 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,

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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 liquid (148.7 mg, 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 liquid (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 (80.8 mg, 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 (58.2 mg, 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 liquid (51.0 mg, 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02388.

^{1}H, ^{13}C, and ^{19}F NMR spectral data of all compounds reported (PDF)

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Notes

The authors declare no competing financial interest.

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