

## (2-(Phenylseleninyl)ethene-1,1-diyl)dibenzene derivatives synthesis via a copper-catalyzed tandem reaction of C–Se bond coupling/selenoxidation

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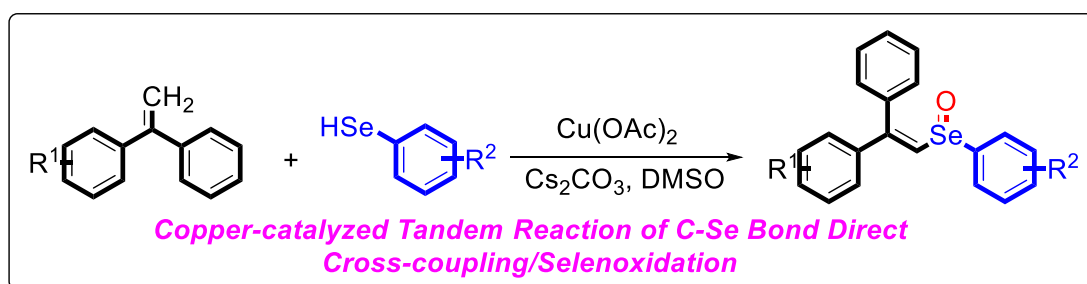
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### Abstract

A copper-catalyzed tandem reaction of C–Se bond direct cross-coupling/selenoxidation has been developed. Starting from substituted ethene-1,1-diyl dibenzene and benzeneselenols, versatile and structurally diverse (2-(phenylseleninyl)ethene-1,1-diyl)dibenzene derivatives were efficiently synthesized under mild reaction conditions. The reaction mechanism was studied using control experiments. These protocols exhibit a wider substrate scope and provide an economical approach toward C–Se bond formation.

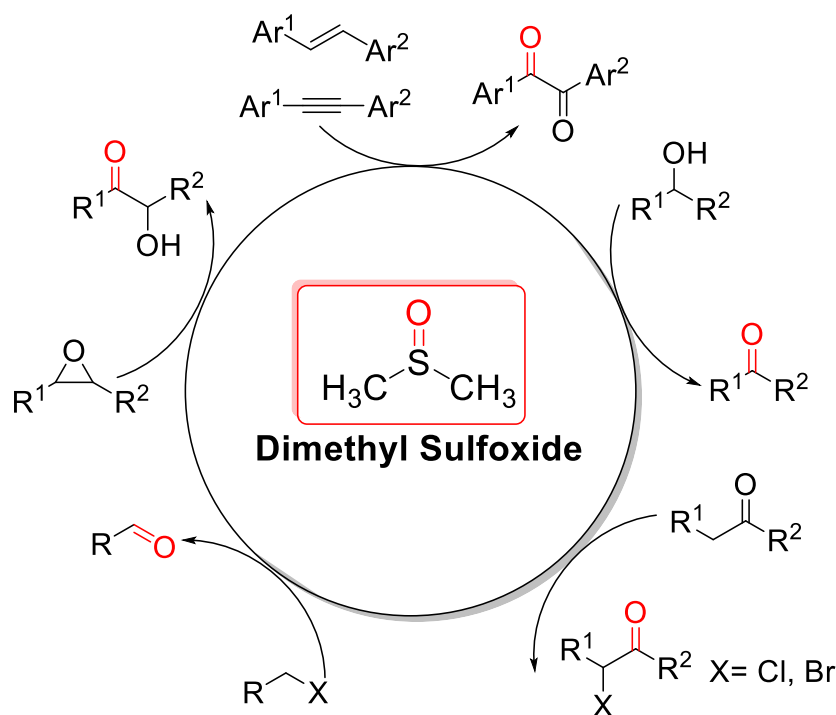


**Keywords:** Ethene-1,1-diyl dibenzene; benzeneselenols; copper catalyst; tandem reaction; C–selenium bond formation

## Introduction

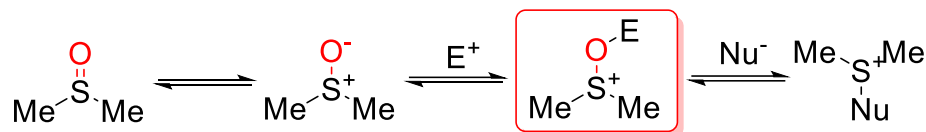
Selenium compounds are widely used in various fields, such as synthetic chemistry, pharmaceuticals, pesticides, and functional materials.<sup>1,2</sup> Furthermore, selenium is one of the most important markers in the human body and has a variety of important functions for human health. First, selenium can enhance the ability of the immune system to identify pathogens in the body. Selenium also helps to maintain the sensitivity of the nervous system.<sup>3,4</sup> Secondly, selenium is an effective antioxidant that can eliminate free radicals in the body, reducing oxidative damage to cells and thereby preventing and reducing the severity of certain chronic diseases. Selenium can reduce cholesterol levels in the blood, prevent the occurrence of arteriosclerosis, inhibit platelet agglomeration, and preserve cardiovascular health.<sup>5-7</sup> Selenium also has a positive impact on male reproductive health, improving sperm quality and enhancing fertility. In terms of the digestive system, selenium can improve and enhance the absorption function of the digestive system, accelerate gastrointestinal motility, promote the decomposition and absorption of gastrointestinal content, and help to reduce the symptoms of indigestion.<sup>8-11</sup> Taninia reported a click reaction of selenols with isocyanates (Scheme 1).<sup>12</sup> In this method, selenols react with isocyanates under mild catalyst-free conditions to generate selenocarbamates in a good yield and with high selectivity over the potentially competing nucleophilic addition reactions. The methodology enables the incorporation of a wide variety of functional groups, providing access to a broad array of densely functionalized selenocarbamates. The synthesis of organic selenium compounds with a variety of functions is of great significance.

Dimethyl sulfoxide (DMSO) is a widely used polar aprotic solvent with the advantages of low toxicity, high polarity, and water miscibility<sup>13-18</sup>, and also serves as a mild oxidant for the oxidation of chalcogen-containing compounds (e.g., selenides to selenoxides) under mild conditions, which avoids the use of strong oxidants and improves the operational simplicity of the reaction.<sup>19-28</sup>



**Scheme 1.** Oxidation reactions involving dimethyl sulfoxide.

The oxidizability of dimethyl sulfoxide depends on its nucleophilic properties.<sup>29,30</sup> As a nucleophilic reagent, oxygen in the molecule has a stronger nucleophilic ability than sulfur. In most reactions, when the under the activation of electrophilic reagents are activated, the nucleophilic reagent attacks the sulfur atom to obtain an intermediate (shown in the red box annotation, Scheme 2) that which further eliminates and loses one molecule of dimethyl sulfide to formobtain a double bond, thus achieving the oxidation process.



**Scheme 2.** The oxidation process of dimethyl sulfoxide.

The oxidation reaction involving DMSO generally requires the assistance of an activator ( $\text{E}^+$ ), which can enhance the ability of oxygen atoms in dimethyl sulfoxide to leave, thereby obtaining sulfonium cations. The common activation oxidation reagents include DCC, oxalyl chloride, acetic anhydride, trifluoroacetic anhydride, phosphorus pentoxide, pyridine/sulfur trioxide complex, acetyl chloride, PDCP, etc. These reagents have their own characteristics, and different activators can be selected according to different reaction conditions and requirements to achieve oxidation.

Copper-mediated C–Se bond formation has been well established in Ullmann-type or oxidative selenation reactions, but these methods usually suffer from two major limitations: (1) the selenation and subsequent oxidation of selenides to selenoxides require separate reaction conditions (two-pot process) with strong oxidants (e.g., *m*-CPBA,  $\text{H}_2\text{O}_2$ ); (2) the substrate scope is narrow for substrates with strong electron-withdrawing groups. In this work, we developed a one-pot copper-catalyzed tandem C–Se bond coupling/selenoxidation reaction, in which DMSO (the reaction solvent) acts as the mild terminal oxidant, and the reaction is compatible with a variety of functional groups (including  $\text{CF}_3$ , CN). This tandem method realizes the efficient construction of vinyl selenoxide derivatives under a single set of mild conditions, which is more atom-economical and operationally simple than the reported stepwise methods.

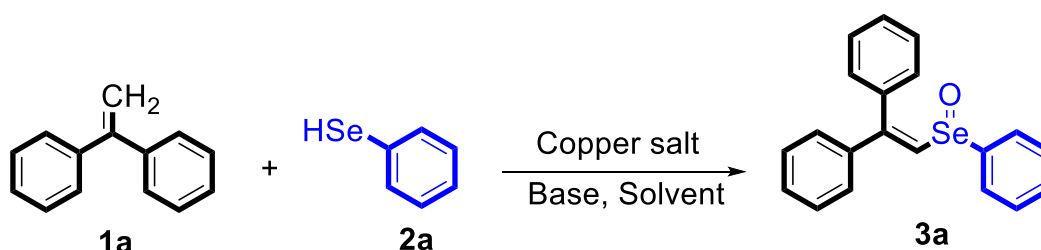
Our interest focuses on the traditional metal-catalyzed C–H bond functionalization. Over the past decade, many reactions involving S–C and Se–C bond formation have been developed by our group.<sup>31–36</sup> Herein, a copper-catalyzed tandem reaction of C–Se bond direct cross-coupling/selenoxidation has been developed. Starting from substituted ethene–1,1–diyl)dibenzene and benzeneselenols, versatile and structurally diverse (2–(phenylseleninyl)ethene–1,1–diyl)dibenzene derivatives were efficiently synthesized under mild reaction conditions. The reaction mechanism was studied using control experiments. These protocols exhibit a wider substrate scope and provide an economical approach toward C–selenium bond formation.

## Results and Discussion

The  $\text{Cu}(\text{OAc})_2$  used in all experiments is analytical grade (99.9% purity, Aladdin Chemical Reagent Co., Ltd.). All reactions were carried out under strictly anhydrous and oxygen-free  $\text{N}_2$  atmosphere to exclude the interference of water and molecular oxygen. At the beginning of our experiments, we investigated the model reaction of ethene–1,1–diyl)dibenzene **1a** and benzeneselenol **2a** to study the reaction conditions, including the optimization of catalysts, bases, and solvents. As shown in Table 1, at the outset, copper salts were used

as the catalyst (entries 1–6), and no desired product was gained when the reaction was conducted in the presence of CuO as the catalyst in DMF (entry 1). These results show that using the proper solvent is critical for this reaction as, when the reactions were conducted in an apolar solvent, the DMSO product was detected in a moderate yield. CuBr<sub>2</sub> was proven to be the most efficient catalyst for this reaction (entry 5). The yield of product **3a** was 62% when the catalyst was changed to Cu(OAc)<sub>2</sub> (entry 6). By screening different bases for the reaction, Cs<sub>2</sub>CO<sub>3</sub> was demonstrated to be a more suitable base than others such as NaOH, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaOEt, K<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>PO<sub>3</sub> (entries 6–12). A reduced yield was obtained in the reactions operated at 100 °C (62% yield, entry 15) and 120 °C (67% yield, entry 16). We also found that the yields of the product decreased when the amount of copper catalyst used was higher or lower than 10 mol % equivalent (entries 17 and 18). Finally, we determined that the optimal reaction conditions were as follows: Cu(OAc)<sub>2</sub> used as the catalyst, Cs<sub>2</sub>CO<sub>3</sub> used as the base, a ratio of **1a**:**2a** of 1:1.5, a N<sub>2</sub> atmosphere, 110 °C, and reaction time of 24 h.

**Table 1.** Optimization of reaction conditions <sup>a</sup>.



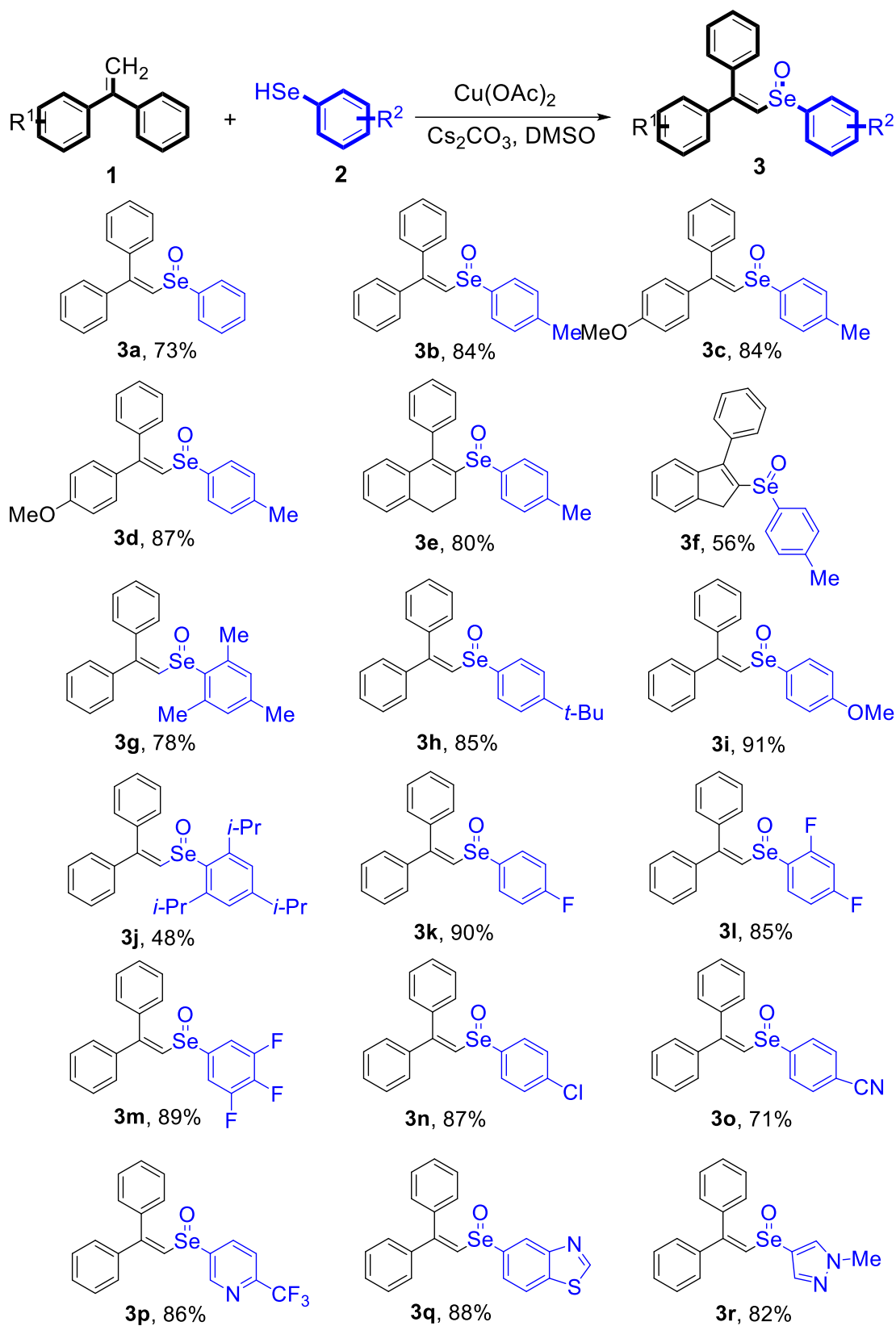
Entry	Copper Salt	Base	Solvent	1a:2a	Yield (%) <sup>b</sup>
1	CuO	Na <sub>2</sub> CO <sub>3</sub>	DMF	1:1	0
2	CuSO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	DMSO	1:1	21
3	CuI	Na <sub>2</sub> CO <sub>3</sub>	DMSO	1:1	28
4	CuCl <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DMSO	1:1	37
5	CuBr <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DMSO	1:1	49
6	Cu(OAc) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DMSO	1:1	62
7	Cu(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	1:1	64
8	Cu(OAc) <sub>2</sub>	NaOH	DMSO	1:1	45
9	Cu(OAc) <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	DMSO	1:1	39
10	Cu(OAc) <sub>2</sub>	NaOEt	DMSO	1:1	67
11	Cu(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	1:1	54
12	Cu(OAc) <sub>2</sub>	K <sub>2</sub> PO <sub>3</sub>	DMSO	1:1	57
13	Cu(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	1:1	5
14	Cu(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	1:1.5	73
15	Cu(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	1:1.5	62 <sup>c</sup>
16	Cu(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	1:1.5	67 <sup>d</sup>
17	Cu(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	1:1.5	73 <sup>e</sup>
18	Cu(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	1:1.5	59 <sup>f</sup>

<sup>a</sup> Unless specified otherwise, reaction conditions were **1a** (10 mmol), **2a** (10 mmol), copper catalyst (10 mol %), base (2 equivalent, under N<sub>2</sub> atmosphere), solvent (10 mL), and 110 °C for 24 h. <sup>b</sup> Isolated yield. <sup>c</sup> 100 °C. <sup>d</sup> 120 °C. <sup>e</sup> Cu(OAc)<sub>2</sub> (15 mol %). <sup>f</sup> Cu(OAc)<sub>2</sub> (5 mol %).

To clarify the role of DMSO and the involvement of molecular oxygen, control experiments were carried out: (1) no target product was obtained when DMF/CH<sub>3</sub>CN was used as the solvent instead of DMSO (even under O<sub>2</sub> atmosphere), confirming DMSO is the sole terminal oxidant; (2) the reaction under air/O<sub>2</sub> atmosphere only gave a 28% yield of **3a**, confirming molecular oxygen is not involved in the reaction and the N<sub>2</sub> atmosphere is optimal for the reaction.

To verify that the tandem C–Se coupling/selenoxidation is not a simple stepwise transformation, the C–Se coupled selenide intermediate was isolated and subjected to the standard reaction conditions. The results showed that the selenide intermediate could only be oxidized to the seleninyl product **3a** in the presence of Cu(OAc)<sub>2</sub> (68% yield), while no oxidation occurred in the absence of the copper catalyst (0% yield). This confirmed that the copper catalyst is essential for both the C–Se coupling and selenoxidation steps, and the two steps are kinetically coupled (tandem catalysis). Kinetic studies further showed no accumulation of the selenide intermediate during the reaction, consistent with a one-pot tandem process.

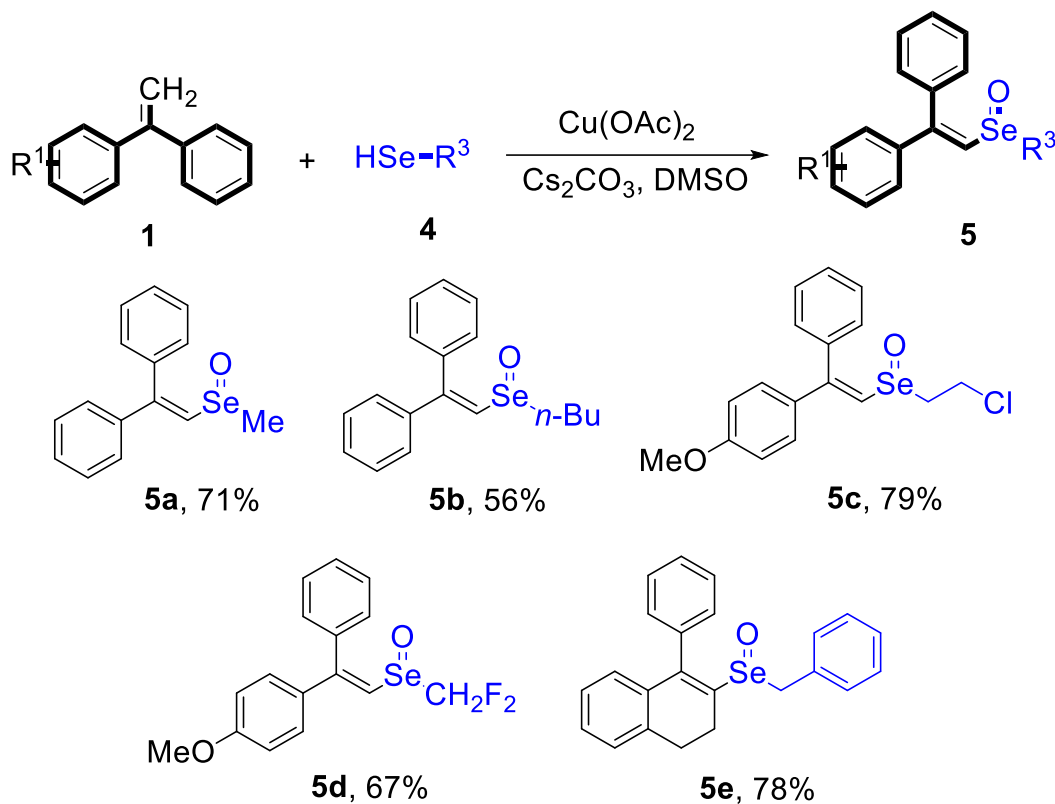
Next, the substrate scope was examined under the optimal conditions, and the results are shown in Table 2. Ethene–1,1–diylidibenzenes **1** and benzeneselenols **2** were subjected to the reaction, and the products were produced in good to excellent yields (48–91%). A variety of functional groups, including methyl, methoxy, halogen, and cyano groups were compatible with benzeneselenols **2**. It was found that both the electron-donating and electron-withdrawing ethene–1,1–diylidibenzenes **1** reacted smoothly with benzeneselenols **2**. Ethene–1,1–diylidibenzenes **1** bearing electron-donating groups showed better activity than those bearing electron-withdrawing groups. On the contrary, benzeneselenols **2** bearing electron-withdrawing groups showed better activity than those bearing electron-donating groups. This suggests that the conjugated structure could strongly coordinate with the copper catalyst, providing good yields (**3m**, 85% yield; **3l**, 89% yield). Despite the strong electron-withdrawing effect of trifluoromethyl, the yield of the corresponding product **3p** was still 86%.

**Table 2.** Copper-catalyzed tandem reaction of C–Se bond direct cross-coupling/selenoxidation<sup>a</sup>

<sup>a</sup> Unless specified otherwise, the reaction conditions were as follows: **1** (10 mmol), **2** (15 mmol),  $\text{Cu}(\text{OAc})_2$  (10 mol%),  $\text{Cs}_2\text{CO}_3$  (2 equivalent), a  $\text{N}_2$  atmosphere, DMSO (10 mL), and  $110^\circ\text{C}$  for 24 h. <sup>b</sup> Isolated yield.

After the group tolerance of ethene-1,1-diylidibenzenes **1** was demonstrated, the diversity of alkylselenol derivative **4** partners was further investigated under the optimized reaction conditions. A wide array of alkylselenol derivatives **4** were subjected to this reaction, and the products were produced in moderate to good yields (56–79%). A variety of functional groups, including methyl, *n*-butyl, ethyl chloroethoxyacetate, and difluoromethyl groups, were compatible. The results are shown in Table 3. We also attempted to use strong electron-withdrawing groups such as trifluoromethyl and nitro under the current reaction conditions; however, this only led to the decomposition of the starting material without the expected product.

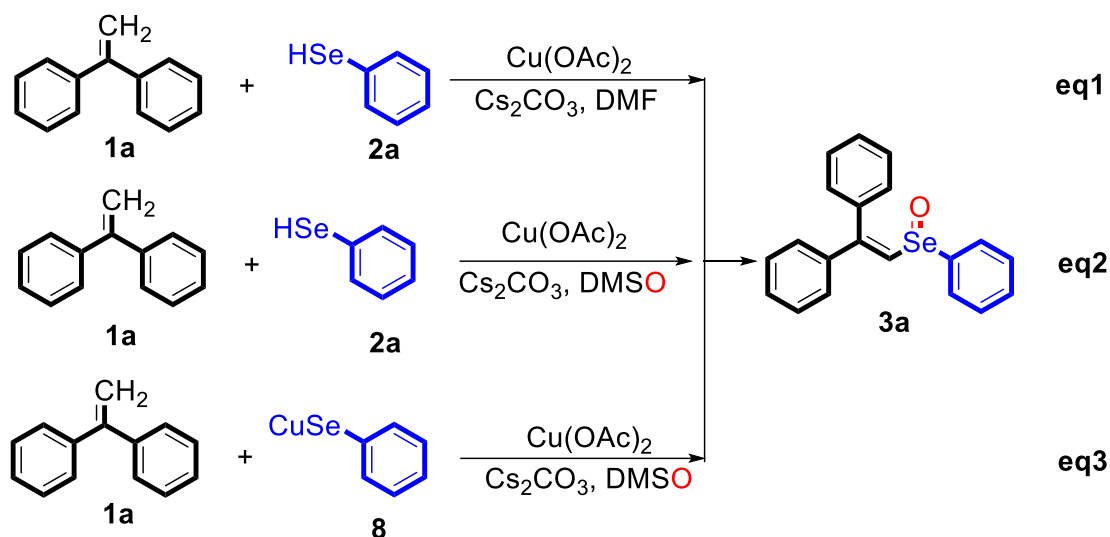
**Table 3.** Copper-catalyzed tandem reaction of C–Se bond direct cross-coupling/selenoxidation<sup>a</sup>



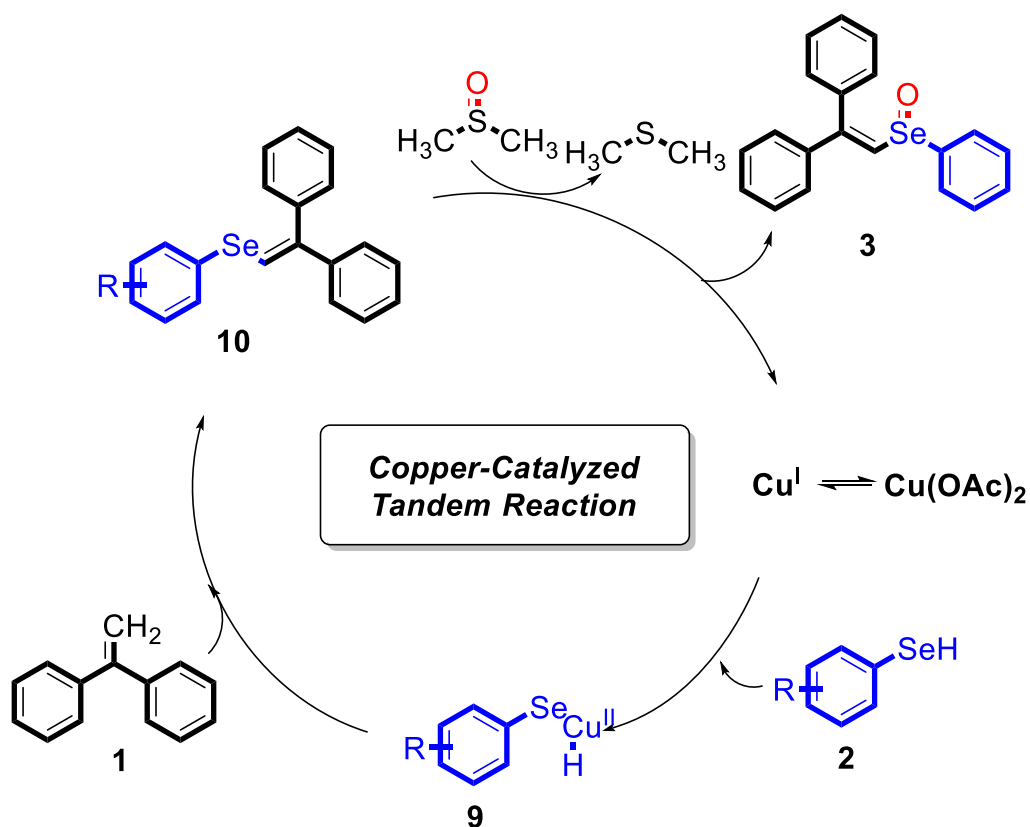
<sup>a</sup> Unless specified otherwise, the reaction conditions were as follows: **1** (10 mmol), **4** (15 mmol),  $\text{Cu}(\text{OAc})_2$  (10 mol %),  $\text{Cs}_2\text{CO}_3$  (2 equivalent), a  $\text{N}_2$  atmosphere, DMSO (10 mL), and  $110^\circ\text{C}$  for 24 h. <sup>b</sup> Isolated yield.

After the group tolerance of ethene-1,1-diylidibenzenes **1** was demonstrated, the diversity of heteroatom selenol derivative **6** ( $\text{X} = \text{N}, \text{O}$ ) partners was further investigated under the optimized reaction conditions. A wide array of heteroatom selenol derivatives **6** were subjected to this reaction, and the products were produced in moderate to good yields (66–85%). A variety of functional groups, including tetrahydropyrrole and hexahydropyridyl groups, were compatible. The results are shown in Table 4.





**Scheme 3.** Investigation of preliminary mechanism.



**Scheme 4.** Proposed mechanism for copper-catalyzed tandem reaction of C–Se bond direct cross-coupling/selenoxidation.

Based on the above results and classic Ullmann-type selenation chemistry, a possible Cu(I)/Cu(II) redox reaction mechanism is proposed (Scheme 4)<sup>37–41</sup>. At the beginning of the reaction, the Cu(II) catalyst ( $\text{Cu}(\text{OAc})_2$ ) is reduced to the active Cu(I) species by substituted benzeneselenols **2** under the basic conditions of  $\text{Cs}_2\text{CO}_3$ . Then, the Cu(I) species coordinates with substituted benzeneselenols **2** to form a Cu(I)-selenolate complex,

which undergoes an addition reaction with the C=C double bond of substituted ethene-1,1-diyl dibenzene **1** to generate a Cu(II)-alkyl intermediate. Next, reductive elimination of the Cu(II)-alkyl intermediate forms the C–Se bond coupled selenide intermediate. Finally, the selenide intermediate is oxidized to the desired vinyl selenoxide products **3** by DMSO (the sole terminal oxidant), and the Cu(II) species is regenerated to re-enter the catalytic cycle. Notably, the copper catalyst is essential for the efficient progress of the selenoxidation step.

## Conclusions

In summary, a copper-catalyzed tandem C–Se bond cross-coupling/selenoxidation reaction has been developed, which efficiently synthesizes structurally diverse (2-(phenylseleninyl)ethene-1,1-diyl)dibenzene derivatives from substituted ethene-1,1-diyl dibenzene and selenols under mild reaction conditions. The reaction mechanism was studied by means of control experiments, and a reasonable Cu(I)/Cu(II) redox catalytic cycle was proposed, which is chemically consistent with the reaction conditions and classic Ullmann-type selenation chemistry. This method features a wide substrate scope (compatible with various electron-donating and strong electron-withdrawing groups), one-pot tandem catalysis, and the use of DMSO as both the reaction solvent and mild terminal oxidant (avoiding the use of strong oxidants such as m-CPBA and H<sub>2</sub>O<sub>2</sub>). Compared with the reported stepwise copper-catalyzed selenation/oxidation methods, this tandem approach is more atom-economical, operationally simple and has better functional group tolerance, providing a new and efficient strategy for the construction of vinyl selenoxide derivatives.

## Experimental Section

**Materials.** All reagents used in experiment were obtained from commercial sources and used without further purification. Solvents for chromatography were technical grade and distilled prior to use. Solvent mixtures were measured as volume/volume. Chemical yields refer to pure isolated substances. Analytical-grade catalysts were purchased. Thin-layer chromatography employed 0.25 mm silica gel-coated glass plates with the F<sub>254</sub> indicator, visualized by irradiation with UV light. Reactions were carried out under argon in flame-dried or oven-dried glassware unless otherwise specified. Dichloroethane, dichloromethane, acetonitrile, toluene (after distilling from sodium), dimethyl sulfoxide, and tetrahydrofuran (after distilling from sodium) were dried using 4Å molecular sieves. Synthesis-grade solvents were used as-purchased. The chromatographic purification of products was accomplished using silica gel (300–400 mesh). For thin-layer chromatography (TLC) analysis, Merck pre-coated TLC plates (silica gel 60 GF<sub>254</sub>, 0.25 mm) were employed, using UV light as the visualizing agent. The compounds were isolated using Biotage flash column chromatography.

**General procedure for preparation of **3**, **5**, and **7**.** A mixture of ethene-1,1-diyl dibenzene **1a** (1.80 g, 10 mmol), benzeneselenol **2a** (1.57 g, 15 mmol), Cu(OAc)<sub>2</sub> (182 mg, 10 mol %), Cs<sub>2</sub>CO<sub>3</sub> (6.52 g, 2 equiv), and DMSO (10 mL) was used. The tube was evacuated and refilled with N<sub>2</sub> three times. The reaction was carried out under a nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 24 h. After it was cooled, the reaction mixture was diluted 3 times with 20 mL of ethyl ether. The filtrate was washed with water (3×15 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure and filtered through a pad of silica gel, followed by the washing of the pad of silica gel with water (20 mL). The residue was then purified using flash chromatography on silica gel to provide the corresponding product. The obtained

yield of pure product (R)-(2-(phenylseleninyl)ethene-1,1-diyl)dibenzene **3a** was 2.56 g (73%). More experimental details about this procedure can be found in the Supplementary Materials.

**(2-(Phenylseleninyl)ethene-1,1-diyl)dibenzene (3a)**. Purified with a 1:4 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 73%.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.61–7.57 (m, 2H), 7.55–7.51 (m, 1H), 7.42–7.36 (m, 5H), 7.34–7.29 (m, 5H), 7.24–7.20 (m, 2H), 7.10–7.07 (m, 2H), 6.99 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  155.4, 142.0, 139.6, 136.1, 133.3, 130.6, 130.1, 129.2, 129.2, 129.0, 128.9, 128.6, 128.2, 127.9. HRMS (ESI+): Calculated for 353.0445 (M+H) found 353.0449.

**(2-(*p*-Tolylseleninyl)ethene-1,1-diyl)dibenzene (3b)**. Purified with a 1:4 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 84%.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  7.52–7.49 (m, 2H), 7.42–7.38 (m, 2H), 7.36–7.31 (m, 4H), 7.28–7.25 (m, 2H), 7.24–7.20 (m, 2H), 7.09–7.05 (m, 3H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  155.4, 145.2, 140.2, 139.8, 136.9, 131.1, 130.5, 130.4, 129.6, 129.6, 129.5, 129.1, 128.7, 128.3, 21.5. HRMS (ESI+): Calculated for 367.0601 (M+H) found 367.0605.

**(*E*)-1-Methoxy-4-((2-phenyl-2-(*p*-tolyl)vinyl)seleninyl)benzene (3c)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 84%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J=8.1$  Hz, 2H), 7.36 (t, 1H), 7.28 (t, 2H), 7.16–7.12 (m, 4H), 7.07 (d,  $J=7.3$  Hz, 2H), 6.94 (s, 1H), 6.8 (d,  $J=8.8$  Hz, 2H), 3.79 (s, 3H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  160.4, 154.8, 143.8, 139.9, 138.9, 131.7, 130.2, 129.8, 129.4, 128.6, 128.5, 128.4, 127.7, 113.3, 55.4, 21.6. HRMS (ESI+): Calculated for 397.0707 (M+H) found 397.0712.

**(*E*)-1-Methoxy-4-(1-phenyl-2-(*p*-tolylseleninyl)vinyl)benzene (3d)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 87%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J=6.0$  Hz, 2H), 7.36 (t, 1H), 7.30 (t, 2H), 7.22–7.15 (m, 4H), 7.09–7.06 (d,  $J=8.9$  Hz, 2H), 6.89 (s, 1H), 6.82 (d,  $J=8.5$  Hz, 2H), 3.85 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.5, 154.4, 143.6, 139.0, 135.8, 131.5, 129.8, 129.4, 129.3, 128.8, 127.8, 127.7, 126.8, 114.0, 55.5, 21.6. HRMS (ESI+): Calculated for 419.0526 (M+Na) found 419.0530.

**4-Phenyl-3-(*p*-tolylseleninyl)-1,2-dihydronaphthalene (3e)**. Purified with a 1:4 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 80%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J=8.4$  Hz, 2H), 7.38–7.29 (m, 3H), 7.22 (t, 1H), 7.19–7.13 (m, 3H), 7.06–7.00 (m, 3H), 6.63 (d,  $J=9.3$  Hz, 1H), 2.94 (m, 4H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.2, 143.6, 138.9, 136.9, 136.4, 135.8, 135.2, 129.8, 129.7, 129.4, 128.5, 127.8, 127.8, 127.6, 127.5, 126.8, 28.4, 24.3, 21.6. HRMS (ESI+): Calculated for 393.0578 (M+H) found 393.0582.

**3-Phenyl-2-(*p*-tolylseleninyl)-1*H*-indene (3f)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 56%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J=8.4$  Hz, 2H), 7.48 (d,  $J=8.7$  Hz, 1H), 7.43 (d,  $J=6.2$  Hz, 1H), 7.39–7.34 (m, 2H), 7.31 (d,  $J=8.5$  Hz, 2H), 3.68 (d,  $J=2.6$  Hz, 2H), 2.59 (t, 3H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.9, 144.1, 142.7, 139.3, 137.4, 130.0, 128.4, 127.3, 127.2, 124.1, 121.7, 39.2, 21.7, 11.7. HRMS (ESI+): Calculated for 379.0601 (M+H) found 379.0605.

**(2-(Mesitylseleninyl)ethene-1,1-diyl)dibenzene (3g)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 78%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (s, 1H), 7.31 (s, 2H), 7.27 (s, 1H), 7.20 (d,  $J=9.0$  Hz, 4H), 7.06 (s, 1H), 6.99 (s, 2H), 6.76 (s, 2H), 2.44 (s, 6H), 2.24 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.2, 142.6, 139.5, 139.3, 135.6, 135.5, 131.8, 131.3, 130.2, 129.2, 128.7, 128.6, 128.1, 127.9, 22.6, 21.0. HRMS (ESI+): Calculated for 395.0941 (M+H) found 395.0945.

**(2-((4-*tert*-butyl)phenyl)seleninyl)ethene-1,1-diyl)dibenzene (3h)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 85%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d, 2H), 7.39 (m, 4H), 7.33 (m, 4H), 7.22 (d,  $J=9.0$  Hz, 2H), 7.07 (d, 2H), 6.99 (s, 1H), 1.31 (s, 9H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  157.2, 154.8, 139.7, 138.8, 136.2, 130.5, 130.1, 129.5, 129.0, 128.9, 128.5, 128.1, 127.7, 126.2, 35.4, 31.1. HRMS (ESI+): Calculated for 409.1071 (M+H) found 409.1075.

**(2-((4-Methoxyphenyl)seleninyl)ethene-1,1-diyl)dibenzene (3i)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 91%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (s, 2H), 7.36 (s, 2H), 7.30 (s, 4H),

7.21 (s, 2H), 7.11 (d,  $J=1.2$  Hz, 2H), 7.01 (s, 1H), 6.81 (s, 2H), 3.83 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 154.6, 139.6, 135.9, 133.5, 130.5, 130.2, 130.1, 129.7, 129.1, 128.9, 128.5, 128.2, 114.2, 56.0. HRMS (ESI+): Calculated for 405.0370 (M+H) found 405.0374.

**(2-((2,4,6-Triisopropylphenyl)seleninyl)ethene-1,1-diyl)dibenzene (3j)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 48%.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.39–7.35 (m, 1H), 7.31 (s, 3H), 7.23–7.18 (m, 4H), 7.09 (s, 1H), 7.03 (d,  $J=2.6$  Hz, 4H), 3.98 (s, 2H), 2.86 (s, 1H), 1.23 (s, 6H), 1.17 (s, 11H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  153.7, 152.2, 150.5, 139.9, 136.0, 134.8, 133.0, 130.2, 129.8, 128.9, 128.8, 128.3, 128.1, 123.6, 34.7, 30.0, 24.8, 23.7. HRMS (ESI+): Calculated for 479.1853 (M+H) found 479.1858.

**(2-((4-Fluorophenyl)seleninyl)ethene-1,1-diyl)dibenzene (3k)**. Purified with a 1:4 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 90%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (dd,  $J=8.9$  2.1, 5.1 Hz, 2H), 7.40–7.36 (m, 2H), 7.31 (q,  $J=7.5$  Hz, 4H), 7.21 (d,  $J=7.0$  Hz, 2H), 7.07 (d,  $J=7.0$  Hz, 2H), 7.03 (s, 1H), 6.99 (t,  $J=8.6$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3 (d,  $J=255.4$  Hz), 155.5, 139.0, 137.5 (d,  $J=3.2$  Hz), 135.5, 130.6, 130.6 (d,  $J=4.2$  Hz), 129.9, 129.1, 128.9, 128.7, 128.3, 128.0, 115.9 (d,  $J=22.5$  Hz).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.7. HRMS (ESI+): Calculated for 371.0350 (M+H) found 371.0354.

**(2-((2,4-Difluorophenyl)seleninyl)ethene-1,1-diyl)dibenzene (3l)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 85%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (t, 1H), 7.38–7.30 (m, 3H), 7.28–7.20 (m, 3H), 7.13 (d,  $J=1.8$  Hz, 2H), 7.04 (d,  $J=6.9$  Hz, 2H), 6.87–6.79 (m, 1H), 6.72–6.65 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1 (dd,  $J=257.8$ , 11.3 Hz), 160.0 (dd,  $J=258.4$ , 13.0 Hz), 156.3, 138.9, 135.3, 131.9 (d,  $J=10.5$  Hz), 130.7, 129.74, 129.2, 128.8, 128.5, 128.3, 127.9, 126.0 (dd,  $J=11.2$ , 3.7 Hz), 111.5 (d,  $J=3.6$  Hz), 111.4 (d,  $J=3.8$  Hz), 105.5–104.9 (m). HRMS (ESI+): Calculated for 389.0256 (M+H) found 389.0261.

**(2-((3,4,5-Trifluorophenyl)seleninyl)ethene-1,1-diyl)dibenzene (3m)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 89%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50–7.39 (m, 1H), 7.34 (q,  $J=7.6$  Hz, 3H), 7.23 (d,  $J=8.4$  Hz, 1H), 7.13 (t, 1H), 7.08 (d,  $J=6.9$  Hz, 1H), 7.02 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9, 150.7 (dd,  $J=253.7$ , 10.6 Hz), 144.2–140.8 (dt, 260.8, 15.1 Hz), 138.4, 137.3 (d,  $J=5.4$  Hz), 135.1, 131.0, 129.8, 129.6, 128.9, 128.3, 128.1, 127.9, 113.1 (dd,  $J=17.7$ , 6.2 Hz).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -130.4, -130.4, -130.5, -130.5. HRMS (ESI+): Calculated for 407.0162 (M+H) found 407.0166.

**(2-((4-Chlorophenyl)seleninyl)ethene-1,1-diyl)dibenzene (3n)**. Purified with a 1:4 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 87%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J=8.7$  Hz, 2H), 7.39 (t,  $J=7.4$  Hz, 2H), 7.34–7.27 (m, 6H), 7.21 (d,  $J=7.0$  Hz, 2H), 7.06 (d,  $J=8.2$  Hz, 2H), 7.02 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 140.0, 139.6, 138.9, 135.4, 130.6, 129.9, 129.2, 129.2, 129.0, 128.8, 128.7, 128.3, 128.0. HRMS (ESI+): Calculated for 387.0055 (M+H) found 387.0059.

**4-((2,2-Diphenylvinyl)seleninyl)benzotrile (3o)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 71%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J=8.4$  Hz, 2H), 7.59 (d,  $J=8.9$  Hz, 2H), 7.44–7.36 (m, 2H), 7.33 (t,  $J=7.7$  Hz, 2H), 7.29 (t,  $J=7.7$  Hz, 2H), 7.21 (d,  $J=7.0$  Hz, 2H), 7.05 (s, 1H), 7.02 (d,  $J=7.9$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 145.6, 138.5, 135.2, 132.4, 131.0, 129.9, 129.4, 128.9, 128.4, 128.4, 128.1, 127.9, 117.4, 116.4. HRMS (ESI+): Calculated for 400.0217 (M+Na) found 400.0221.

**5-((2,2-Diphenylvinyl)seleninyl)-2-(trifluoromethyl)pyridine (3p)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 86%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78 (d,  $J=2.3$  Hz, 1H), 7.86 (dd,  $J=8.2$ , 2.7 Hz, 2H), 7.55 (d,  $J=8.2$  Hz, 1H), 7.45–7.37 (m, 2H), 7.34 (t, 2H), 7.27 (t,  $J=7.8$  Hz, 2H), 7.23 (d,  $J=8.4$  Hz, 2H), 7.12 (s, 1H), 7.01 (d,  $J=8.2$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.3, 150.9 (q,  $J=35.2$  Hz), 148.9, 140.4, 138.1, 136.9, 134.9, 131.1, 129.8, 129.6, 128.8, 128.3, 128.2, 127.9, 120.6 (q,  $J=275.1$  Hz), 119.9 (q,  $J=2.3$  Hz).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.3. HRMS (ESI+): Calculated for 444.0090 (M+Na) found 444.0094.

**5-((2,2-Diphenylvinyl)seleninyl)benzo[d]thiazole (3q)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 88%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.17 (s, 1H), 8.10 (d,  $J=8.6$  Hz, 1H), 8.01 (d,  $J=1.8$

Hz, 1H), 7.76 (dd,  $J=8.7, 1.8$  Hz, 1H), 7.39–7.35 (m, 1H), 7.30 (ddt,  $J=7.6, 6.7, 1.3$  Hz, 3H), 7.23–7.16 (m, 5H), 7.12 (s, 1H), 7.02–6.99 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 156.0, 155.9, 139.1, 138.7, 135.5, 134.0, 130.9, 130.1, 129.4, 129.3, 129.0, 128.5, 128.1, 125.5, 124.3, 123.5. HRMS (ESI+): Calculated for 410.0118 (M+H) found 410.0122.

**4-((2,2-Diphenylvinyl)seleninyl)-1-methyl-1H-pyrazole (3r)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 82% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (s, 1H), 7.43 (d,  $J=7.6$  Hz, 1H), 7.37 (t, 3H), 7.32 (t, 2H), 7.22 (d,  $J=5.8$  Hz, 2H), 7.18 (d,  $J=8.2$  Hz, 2H), 7.07 (d,  $J=1.4$  Hz, 2H), 3.75 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  154.0, 139.0, 135.7, 132.9, 130.4, 130.3, 130.0, 128.8, 128.6, 128.1, 127.9, 123.7, 39.2. HRMS (ESI+): Calculated for 357.0506 (M+H) found 357.0510.

**(2-(Methylseleninyl)ethene-1,1-diyl)dibenzene (5a)**. Purified with a 1:4 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 71%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48–7.42 (m, 3H), 7.43–7.33 (m, 5H), 7.28 (d,  $J=7.0$  Hz, 2H), 6.86 (s, 1H), 2.68 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.0, 139.1, 135.7, 130.5, 129.9, 129.7, 128.8, 128.4, 128.4, 128.2, 43.4. HRMS (ESI+): Calculated for 313.0108 (M+Na) found 313.0112.

**(2-(Butylseleninyl)ethene-1,1-diyl)dibenzene (5b)**. Purified with a 1:4 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 56%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47–7.39 (m, 4H), 7.39–7.33 (m, 4H), 7.30–7.25 (m, 2H), 6.76 (s, 1H), 2.72–2.65 (m, 2H), 1.75–1.65 (m, 2H), 1.31 (h,  $J=7.4$  Hz, 2H), 0.85 (t,  $J=7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 139.4, 135.8, 130.5, 129.9, 129.6, 128.8, 128.4, 128.3, 126.6, 54.6, 24.5, 21.6, 13.6. HRMS (ESI+): Calculated for 333.0758 (M+H) found 333.0762.

**(E)-1-(2-((2-Chloroethyl)seleninyl)-1-phenylvinyl)-4-methoxybenzene (5c)**. Purified with a 1:4 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 79%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51–7.41 (m, 4H), 7.37 (m, 4H), 7.31–7.27 (m, 2H), 6.80 (s, 1H), 3.77 (t, 2H), 3.15 (t, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 139.1, 135.4, 130.8, 129.9, 129.8, 128.9, 128.5, 128.4, 126.1, 56.8, 36.1. HRMS (ESI+): Calculated for 369.0161 (M+H) found 369.0165.

**(E)-1-(2-((Difluoro-15-methyl)seleninyl)-1-phenylvinyl)-4-methoxybenzene (5d)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 67%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52–7.42 (m, 2H), 7.39 (t, 1H), 7.35–7.28 (m, 2H), 6.72 (s, 1H), 5.92 (t, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 138.9, 135.1, 131.6, 130.0, 129.8, 128.9, 128.1, 117.0, 114.9 (t,  $J=285.6$  Hz).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.1. HRMS (ESI+): Calculated for 358.0284 (M+H) found 358.0289.

**3-(Benzylseleninyl)-4-phenyl-1,2-dihydronaphthalene (5e)**. Purified with a 1:4 EtOAc/Hexanes gradient over silica. Pale yellow solid. Yield: 78%. Melting point: 99.6–101.8 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.50–7.25 (m, 11H), 7.17 (m, 4H), 6.64 (s, 1H), 4.10 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  157.0, 139.9, 136.2, 131.4, 130.7, 130.1, 129.5, 129.1, 129.1, 129.0, 128.7, 128.2, 125.4, 61.9. HRMS (ESI+): Calculated for 415.0577 (M+Na) found 415.0582.

**1-((2,2-Diphenylvinyl)seleninyl)pyrrolidine (7a)**. Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 74%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.37 (m, 4H), 7.36–7.31 (m, 4H), 7.25–7.21 (m, 2H), 6.70 (s, 1H), 3.18–3.09 (m, 4H), 1.80–1.70 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 140.1, 136.8, 130.0, 129.7, 129.0, 128.7, 128.4, 128.0, 123.8, 47.4, 25.8. HRMS (ESI+): Calculated for 346.0710 (M+H) found 346.0715.

**1-((2,2-Diphenylvinyl)seleninyl)piperidine (7b)**. Purified with a 1:4 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 85%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41–7.36 (m, 4H), 7.36–7.30 (m, 4H), 7.24 (d,  $J=7.0$  Hz, 2H), 6.63 (s, 1H), 3.08–3.02 (m, 4H), 1.55 (t,  $J=6.4$  Hz, 4H), 1.49 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 140.2, 136.7, 130.0, 129.9, 128.9, 128.7, 128.4, 127.9, 123.1, 46.4, 25.6, 23.9. HRMS (ESI+): Calculated for 360.0867 (M+H) found 360.0871.

**(E)-1-((2-(4-Methoxyphenyl)-2-phenylvinyl)seleninyl)azepane (7c).** Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 71%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.43–7.35 (m, 4H), 7.34–7.29 (m, 4H), 7.23 (d, *J*=7.2 Hz, 2H), 6.72 (s, 1H), 3.04 (t, 4H), 1.64 (m, 4H), 1.56 (m, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 152.7, 139.9, 136.8, 129.8, 129.7, 128.9, 128.6, 128.2, 128.1, 125.6, 47.9, 29.6, 27.0. HRMS (ESI+): Calculated for 426.0948 (M+Na) found 426.0952.

**(E)-1-Methoxy-4-(1-phenyl-2-(*p*-tolylseleninyl)vinyl)benzene (7d).** Purified with a 1:3 EtOAc/Hexanes gradient over silica. Pale yellow oil liquid. Yield: 66%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.48–7.42 (m, 4H), 7.41–7.34 (m, 4H), 7.30–7.27 (d, *J*=7.5 Hz, 2H), 6.82 (s, 1H), 5.71 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.7, 138.9, 135.8, 130.9, 129.8, 129.6, 128.9, 128.8, 128.3, 122.1, 74.2. HRMS (ESI+): Calculated for 419.0526 (M+H) found 419.0530.

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## Supplementary Material

Spectroscopic data of synthesized compounds are available in the Supplementary material file associated with this manuscript.

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