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Silver-Catalyzed Synthesis of Diaryl Selenides by Reaction of Diaryl Diselenides with Aryl Boronic Acids

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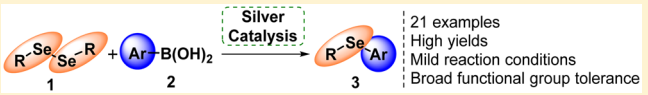
Supporting Information

ABSTRACT: We described herein our results on the silver-catalyzed synthesis of diaryl selenides via a cross-coupling reaction of diaryl diselenides with aryl boronic acids. The methodology is tolerant to electron-donor and electron-withdrawing groups at the substrates and the desired products were obtained in good to excellent yields.



Organoselenium compounds have been known for many years merely as precursor to introduce unsaturated carbon−carbon bonds to organic molecules by an intramolecular *syn* elimination of selenoxides.[1] Although, it is still a widely used method, since the 80s, with the success of ebselen (Figure 1) as the first synthetic organoselenium compound considered as a promising antioxidant[2] and a neuroprotective agent,[3] many other applications into chemistry, biochemistry, and materials sciences have been found for this class of compounds.[4]

In this context, diaryl selenides have attracted considerable attention because of their biological activities (e.g., anticancer, antitumor, antiviral, antimicrobial, and antioxidant) and some biologically important molecules containing the diaryl selenide skeleton are shown in Figure 1.[5]

This point has motivated the report of different methodologies to synthesize these compounds, and the use of diorganyl dichalcogenides combined to aryl boronic acids are one of the most studied.[6−8] In this sense, many transition metals, such as indium,[6] iron,[7] and mainly copper salts,[8] have been used as catalysts for this purpose. Alternatively, our research group recently published the reaction of nucleophilic arylselenium species, generated *in situ* by the reaction of diorganyl diselenides with hypophosphorous acid (H_3PO_2), with arenediazonium salts.[9]

On the other hand, silver has emerged in the last years as an efficient transition metal-catalyst used for many organic transformations, such as aza-Diels−Alder,[10] asymmetric aldol,[11] and cyclization[12] reactions. The selective interaction of silver(I) salts with the C−C π-bond of alkynes appeared to be the more explored property for the construction of new C−C and C-heteroatom bonds through C−H activation reaction.[13] Regarding to the chalcogen chemistry, silver has become an interesting building block for the construction of supramolecular assemblies and semiconductor devices.[14] However, to the best of our knowledge, the use of silver catalyst in the synthesis of diorganyl chalcogenides have not been reported before.

In view of the explained above and due to our interest in the development of versatile protocols to the synthesis of organochalcogenides, we report here our results on the silver-catalyzed cross-coupling reaction of aryl boronic acids with diaryl diselenides (Scheme 1).

Initially, our efforts were devoted to select a suitable catalytic system for an efficient coupling. In this way, diphenyl diselenide **1a** and 4-methoxy-phenyl boronic acid **2a** were considered as standard substrates to the silver-catalyzed cross-coupling reaction. Thus, diphenyl diselenide **1a** (0.15 mmol) and commercially available 4-methoxy-phenyl boronic acid **2a** (0.30 mmol) were reacted in the presence of different silver(I) salts and a variety of solvents and the results are showed in Table 1.

As a preliminary experiment 10 mol% of silver(I) acetate was used as catalyst in 1,4-dioxane (0.5 mL) at 100 °C and under this condition, the desired (4-methoxyphenyl) (phenyl)selenide **3a** was obtained in 30% yield after 12 h (Table 1, entry 1). With this result in hand, as shown in Table 1, entries 2−5, several silver(I) catalysts were tested in the same catalytic amount (10 mol%). The best result was obtained when $AgNO_3$ was used, giving the desired product **3a** in 93% yield (Table 1, entry 3). Next, we planned to verify the influence of the solvent in the reaction and diverse solvents with different characteristics, such as toluene, DMF, DMSO, H_2O, glycerol, and PEG-400 were used (Table 1, entries 6−11). However, no chemical or environmental benefits were achieved in these experiments. It is important to mention that when the cross-coupling reaction was performed at room temperature, only 48% yield of the expected selenide **3a** was obtained (Table 1, entry 12) and even a slight decrease in the temperature from 100 to 80 °C considerably affects the reaction yield (Table 1, entry 13). Moreover, it is worth noting that when the amount of $AgNO_3$ was reduced from 10 to 5 mol% or 2 mol%, a consecutive decrease in the yields of the coupling products was observed (Table 1, entries 14 and 15).

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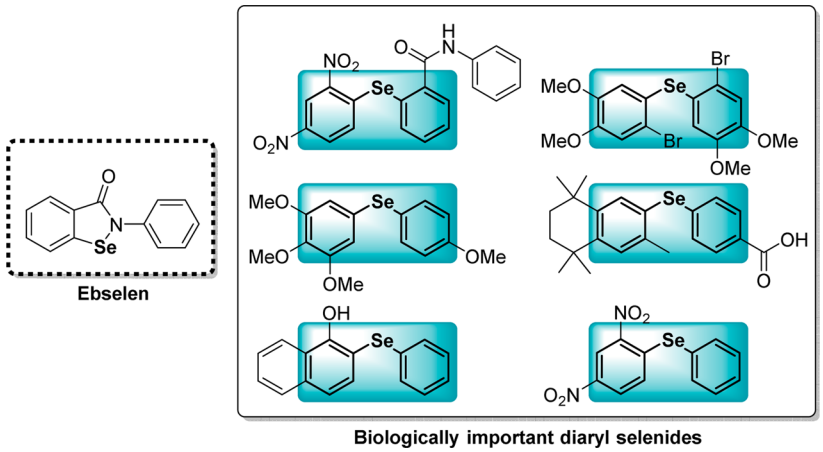


Figure 1. Biologically important selenium compounds.

Scheme 1

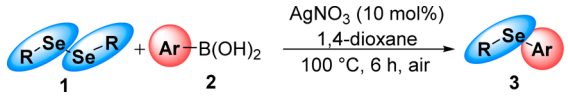
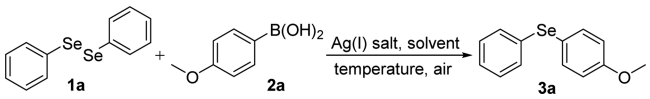


Table 1. Optimization of the Reaction Conditions[a]



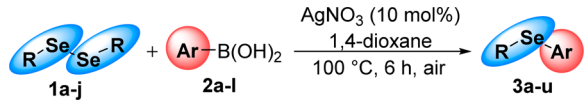
entry	silver(I) salt (mol%)	solvent	temp. (°C)	yield (%)
1	AgOAc (10)	1,4-dioxane	100	35
2	Ag_2SO_4 (10)	1,4-dioxane	100	40
3	$AgNO_3$ (10)	1,4-dioxane	100	93
4	AgOTf (10)	1,4-dioxane	100	NR
5	Ag_2CO_3(10)	1,4-dioxane	100	30
6	$AgNO_3$ (10)	DMF	110	20
7	$AgNO_3$ (10)	DMSO	110	70
8	$AgNO_3$ (10)	toluene	100	50
9	$AgNO_3$ (10)	H_2O	90	30
10	$AgNO_3$ (10)	glycerol	90	20
11	$AgNO_3$ (10)	PEG-400	90	traces
12[b]	$AgNO_3$ (10)	1,4-dioxane	r.t.	48
13	$AgNO_3$ (10)	1,4-dioxane	80	75
14[c]	$AgNO_3$ (5)	1,4-dioxane	100	75
15[c]	$AgNO_3$ (2)	1,4-dioxane	100	60
16[d]	**$AgNO_3$ (10)**	**1,4-dioxane**	**100**	**91**

[a]The reactions were performed using diphenyl diselenide **1a** (0.15 mmol), 4-methoxy-phenyl boronic acid **2a** (0.30 mmol), silver salt, and solvent (0.5 mL) during 12 h under air. [b]Reaction time of 48 h. [c]Reaction time of 24 h. [d]Reaction time of 6 h. NR = no reaction.

Finally, considering the reaction time, we believe that the best performance for this reaction of diphenyl diselenide **1a** with boronic acid **2a** catalyzed by silver(I) nitrate in 1,4-dioxane at 100 °C was obtained after a period of 6 h, when the product **3a** was isolated in 91% yield (Table 1, entry 16).

Once the best experimental conditions to the synthesis of **3a** was established (Table 1, entry 16), we envisioned to extend the methodology to a variety of diorganyl diselenides **1a−j**, as well as, differently substituted aryl boronic acids **2a−l**. Fortunately, the method proved robust and general, with the respective diorganyl selenides **3a−u** being obtained efficiently in good to excellent yields and the results are presented in Table 2.

Table 2. $AgNO_3$-Catalyzed Synthesis of Differently Substituted Diorganyl Selenides[a]



entry	R (**1**)	Ar (**2**)	product **3** (Yield)
1	Ph (**1a**)	4-$OMeC_6H_4$ (**2a**)	**3a** (91%)
2	Ph (**1a**)	4-MeC_6H_4 (**2b**)	**3b** (96%)
3	Ph (**1a**)	Ph (**2c**)	**3c** (96%)
4	Ph (**1a**)	4-BrC_6H_4 (**2d**)	**3d** (85%)
5	Ph (**1a**)	4-ClC_6H_4 (**2e**)	**3e** (83%)
6	Ph (**1a**)	3-$CF_3C_6H_4$ (**2f**)	**3f** (75%)
7	Ph (**1a**)	2-$OMeC_6H_4$ (**2g**)	**3g** (90%)
8	Ph (**1a**)	2-MeC_6H_4 (**2h**)	**3h** (92%)
9	Ph (**1a**)	2-ClC_6H_4 (**2i**)	**3i** (82%)
10	Ph (**1a**)	2-BrC_6H_4 (**2j**)	**3j** (60%)
11	Ph (**1a**)	2-Naph (**2k**)	**3k** (90%)
12	Ph (**1a**)	3-Th (**2l**)	**3l** (77%)
13	4-ClC_6H_4 (**1b**)	4-$OMeC_6H_4$ (**2a**)	**3m** (86%)
14	4-FC_6H_4 (**1c**)	4-$OMeC_6H_4$ (**2a**)	**3n** (83%)
15	3-$CF_3C_6H_4$ (**1d**)	4-$OMeC_6H_4$ (**2a**)	**3o** (80%)
16	4-$OMeC_6H_4$ (**1e**)	4-$OMeC_6H_4$ (**2a**)	**3p** (93%)
17	4-MeC_6H_4 (**1f**)	4-$OMeC_6H_4$ (**2a**)	**3q** (72%)
18	2-MeC_6H_4 (**1g**)	4-$OMeC_6H_4$ (**2a**)	**3r** (70%)
19	Mes (**1h**)	4-$OMeC_6H_4$ (**2a**)	**3s** (55%)
20	2-Py (**1i**)	4-$OMeC_6H_4$ (**2a**)	**3t** (80%)
21	*n*-Bu (**1j**)	4-$OMeC_6H_4$ (**2a**)	**3u** (75%)

[a]The reactions were performed using diorganyl diselenide **1** (0.15 mmol), aryl boronic acid **2** (0.30 mmol), $AgNO_3$ (10 mol%, 0.005 g) at 100 °C in 1,4-dioxane (0.5 mL) under air during 6 h.

Regarding to the aryl boronic acids **2**, various functional groups directly attached to the benzene ring at *ortho*- or *para*-position were tolerated, but it is important to point out that electronic effects of the substituents have somewhat of an influence in the reaction yield of the corresponding diaryl selenides **3**. For example, electron-rich aryl boronic acids, having a *p*-methoxy (**2a**) or a *p*-methyl group (**2b**), gave better yields if compared to those containing slightly electron-withdrawing groups as bromo (**2d**) and chloro (**2e**). This

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influence becomes still more evident when the boronic acid **2f**, having a trifluoromethane group at the *meta*-position, was used (Table 2, compare entries 1−2 with 4−6). In this way, it is interesting to note that electronic effects are also observed when substituents at the *ortho*-position are evaluated in the aryl boronic acids **2g−j** (Table 2, entries 7−10). In contrast, the reaction appears not to be sensible to steric effects, and comparable yields were obtained for the *para*- and *ortho*-substituted boronic acids where the same functional group is present (Table 2, entries 1 vs 7 and 5 vs 9). 3-Thienylboronic acid **2l** was efficiently reacted with diphenyl diselenide **1a** giving the product **3l** in good yield (Table 2, entry 12).

The possibility to extend the methodology to differently substituted diaryl diselenides **1b−i** was also explored in the reaction with 4-methoxy-phenyl boronic acid **2a**. The reaction worked well, affording the respective diaryl selenides **3m−t** in good to excellent yields under the same reaction conditions (Table 2, entries 13−20). It was observed that the presence of electron-withdrawing groups at the aromatic ring of the diselenide adversely affects the reaction compared to electron-donating ones (Table 2, entries 13−17). Different than that observed for the boronic acids counterpart, when hindered diaryl diselenides **1g−h** were used as substrates in the cross-coupling reaction, lower yields of the respective products **3r-s** were obtained (Table 2, entries 18 and 19).

The methodology was successfully extended to dipyridyl diselenide **1i**, which furnished the expected selenide **3t** in 80% yield, showing the versatility of this reaction also to diheteroaryl diselenides (Table 2, entry 20). Not only aromatic diselenides are suitable substrates to the reaction; dibutyl diselenide **1j** reacted with 4-methoxy-phenyl boronic acid **2a** in the presence of $AgNO_3$ (10 mol%) to produce, after 6 h, (4-methoxy-phenyl) (butyl) selenide **3u** in 75% yield (Table 2, entry 21). This is a valuable result which reinforces the versatility of our protocol. Considering the previously described protocols to access diorganyl selenides from arylboronic acids and diorganyl diselenides, which use indium, iron, and copper catalysts,[6−8] our methodology can be considered an efficient and attractive alternative, once $AgNO_3$ is not expensive and is easily handled.

Based on recent publications involving silver-catalyzed reactions[15] and our experiments, a plausible mechanism proposed for this Ag(I)-catalyzed C−Se coupling reaction of aryl boronic acids **2** with diorganyl diselenides **1** is depicted in Figure 2. We believe that, at first, the reaction of $AgNO_3$ with diorganyl diselenide **1** leads to the Ag(III) intermediate **A**. After that, aryl boronic acid **2** would attack the intermediate **A** to form the corresponding product **3** and the intermediate **B**. Then, the obtained $(RSe)[B(OH)_2]Ag^{III}$ **B** reacts with other equivalent of aryl boronic acid **2** leading to the intermediate **C** and tetrahydroxydiboron **D**. Finally, intermediate **C** can undergo a reductive elimination to form the desired product **3** regenerating the Ag(I) catalyst in the catalytic cycle. The proposed mechanism indicates that this Ag(I)-catalyzed C−Se coupling reaction is able to use both groups on diorganyl dichalcogenide **1**.

Analysis of ^{77}Se NMR spectroscopy and HRMS spectrometry were performed to prove the formation of the intermediate **A**. Diphenyl diselenide **1a** and $AgNO_3$ were mixed in $CDCl_3$ in a NMR tube and after 20 min at room temperature the mixture was analyzed by ^{77}Se NMR and the HRMS was measured in ESI(+)-MS mode (please see the Supporting Information for the spectra images). A peak with m/z of 420.4080 in the HRMS spectrum and the presence of two signals in the ^{77}Se NMR, one

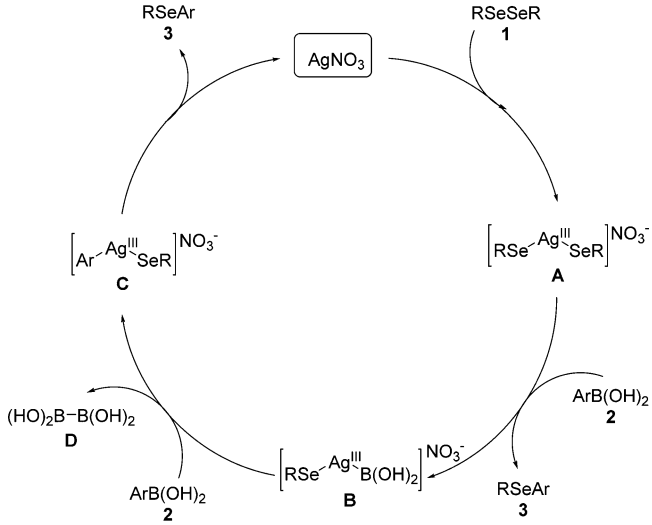

Figure 2. A plausible mechanism of the reaction.

at 462.93 ppm (PhSeSePh **1a**) and another at 382.56 ppm (due to $Ph_2Se_2Ag^{III}$ **A**) are strong indications that support such mechanism, at least in the first step.

In summary, we developed an alternative method for the synthesis of diaryl selenides through the silver-catalyzed cross-coupling reaction of diaryl diselenides with aryl boronic acids. Using a catalytic amount of silver(I) nitrate in 1,4-dioxane at 100 °C under air atmosphere, a range of diaryl selenides were obtained from substituted diaryl diselenides and arylboronic acids bearing electron-withdrawing and electron-donating groups in good to excellent yields. Studies on the determination of the identity of the $AgNO_3$/diorganyl diselenides intermediates are on course in our laboratory.

EXPERIMENTAL SECTION

General Information. The reactions were monitored by TLC carried out on Merck silica gel (60 F_{254}) by using UV light as visualizing agent and 5% vanillin in 10% H_2SO_4 and heat as developing agents. Baker silica gel (particle size 0.040−0.063 mm) was used for flash chromatography. Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 400 MHz and were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the external reference. Coupling constants (J) are reported in Hertz. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), dd (double doublet), ddd (double double doublet), t (triplet), q (quartet), quint. (quintet), sex (sextet), and m (multiplet). Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHz. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Low-resolution mass spectra were obtained with a mass spectrometer using electron ionization (EI) as an ionization method and positive charge ion detector. The starting materials (aryl- or heteroarylboronic acids **2a−v**) were purchased from a commercial supplier. Diorganyl diselenides were synthesized according to the literature.[16]

General Procedure for Silver(I)-Catalyzed Synthesis of Diaryl Selenides (3). To a 5 mL round-bottomed flask equipped with a small magnetic stirring bar and under air atmosphere containing the catalyst $AgNO_3$ (0.005 g, 10 mol%), a solution of 0.15 mmol of the appropriate diorganyl diselenide **1** in 0.5 mL of 1,4-dioxane was added. To this solution, the appropriate aryl boronic acid **2** (0.30 mmol) was added and the reaction mixture was allowed to stir at 100 °C for 6 h. After that, the reaction mixture was cooled to the room temperature, and was quenched using water (5 mL). The mixture was then extracted by ethyl acetate (10 mL) and washed with water (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$

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and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel using hexane (for **3b−k**) or a mixture of hexane/ethyl acetate (for **3a**, **3l−r** and **3t**: 95/5; for **3s**: 80/20) as eluent. All the compounds were characterized and the spectral data of compounds **3a−u** are in agreement with those from literature.

4-Methoxyphenyl−phenyl-selenide[8g] ***(3a)***. Yield: 0.073 g (91%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, J = 8.8 Hz, 2H); 7.33−7.31 (m, 2H); 7.21−7.16 (m, 3H); 6.84 (d, J = 8.4 Hz, 2H); 3.79 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.7, 136.5, 133.2, 130.9, 129.1, 126.4, 119.9, 115.1, 55.2. MS (relative intensity) m/z: 264 (65), 262 (34), 184 (100), 153 (32), 65 (14).

4-Tolyl-phenyl-selenide[8g] ***(3b)***. Yield: 0.071 g (96%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38−7.32 (m, 4H); 7.23−7.16 (m, 3H); 7.04 (d, J = 8.5 Hz, 2H); 2.33 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 137.6, 133.8, 132.0, 130.1, 129.1, 126.8, 21.1. MS (relative intensity) m/z: 248 (70), 246 (39), 168 (100), 153 (25), 91 (63), 65 (30).

Diphenyl-selenide[8g] ***(3c)***. Yield: 0.067 g (96%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46−7.44 (m, 4H); 7.24−7.21 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 132.9, 131.1, 129.3, 127.2. MS (relative intensity) m/z: 234 (30), 154 (100), 77 (20), 51 (17).

4-Bromophenyl−phenyl-selenide[8g] ***(3d)***. Yield: 0.079 g (85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46−7.44 (m, 2H); 7.34 (d, J = 8.4 Hz, 2H); 7.28−7.25 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 134.1, 133.2, 133.0, 130.4, 130.3, 129.4, 127.6, 121.41. MS (relative intensity) m/z: 314 (68), 312 (86), 234 (84), 232 (99), 152 (100), 116 (27), 77 (58), 51 (41).

4-Chlorophenyl−phenyl-selenide[8g] ***(3e)***. Yield: 0.066 g (83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46−7.44 (m, 2H); 7.36 (d, J = 8.0 Hz, 2H); 7.28−7.26 (m, 3H); 7.21 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 134.1, 133.5, 133.1, 130.6, 129.5, 129.4, 127.6. MS (relative intensity) m/z: 270 (15), 268 (36), 188 (100), 152 (27), 77 (22), 51 (18).

3-(Trifluoromethyl)phenyl−phenyl-selenide[17] ***(3f)***. Yield: 0.067 g (75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (s, 1H); 7.53−7.44 (m, 4H); 7.31−7.26 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 135.1, 134.0, 133.2, 131.5 (q, J = 32.2 Hz), 129.6, 129.5, 129.4, 128.4 (q, J = 3.8 Hz), 128.2, 123.7 (q, J = 272.8 Hz), 123.6 (q, J = 3.8 Hz). MS (relative intensity) m/z: 302 (55), 222 (100), 153 (16), 77 (35), 51 (24).

2-Methoxyphenyl−phenyl-selenide[8g] ***(3g)***. Yield: 0.071 g (90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61−7.56 (m, 2H), 7.35−7.31 (m, 3H), 7.24−7.14 (m, 1H), 6.97−7.74 (m, 3H), 3.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$); δ (ppm): 156.9, 135.2, 131.2, 129.4, 128.6, 127.9, 127.8, 122.0, 121.6, 110.6, 55.9. MS (relative intensity) m/z: 264 (65), 262 (33), 184 (100), 169 (40), 141 (33), 77 (32).

2-Tolyl-phenyl-selenide[8g] ***(3h)***. Yield: 0.068 g (92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40−7.38 (m, 2H); 7.35−7.32 (m, 1H); 7.27−7.17 (m, 5H); 7.08−7.04 (m, 1H); 2.40 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 139.8, 133.6, 132.7, 131.7, 130.7, 130.2, 129.3, 127.7, 127.1, 126.7, 22.3. MS (relative intensity) m/z: 248 (72), 246 (37), 168 (100), 153 (20), 91 (57), 65 (32).

2-Chlorophenyl−phenyl-selenide[8g] ***(3i)***. Yield: 0.065 g (82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65−7.58 (m, 2H); 7.41−7.23 (m, 4H); 7.15−6.98 (m, 2H), 6.91 (dd, J = 7.6, 1.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 135.9, 133.9, 131.6, 131.0, 129.7, 129.4, 128.7, 128.2, 127.4, 127.3. MS (relative intensity) m/z: 270 (19), 268 (41), 188 (100), 152 (32), 77 (19), 51 (19).

2-Bromophenyl−phenyl-selenide[18] ***(3j)***. Yield: 0.056 g (60%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66−7.62 (m, 2 H), 7.52−7.38 (m, 4 H), 7.07−7.00 (m, 2 H), 6.88−6.83 (m, 1 H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 136.4, 136.2, 132.7, 130.4, 129.8, 128.9, 128.4, 127.8, 127.3, 123.4. MS (relative intensity) m/z: 312 (61), 232 (58), 207 (27), 156 (22), 152 (100), 77 (50).

2-Naphthyl-phenyl-selenide[19] ***(3k)***. Yield: 0.076 g (90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98−7.97 (m, 1 H), 7.80−7.69 (m, 3 H), 7.53−7.43 (m, 5 H), 7.27−7.24 (m, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$); δ (ppm): 133.9, 132.8, 132.3, 132.0, 131.2, 130.4, 129.3, 128.7, 128.4, 127.7, 127.4, 127.3, 126.5, 126.2. MS (relative intensity) m/z: 284 (24), 204 (100), 126 (11), 115 (19), 77 (11).

3-Thienyl-phenyl-selenide[20] ***(3l)***. Yield: 0.056 g (77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (dd, J = 3.0, 1.0 Hz, 1H), 7.28−7.23 (m, 3H), 7.16−7.10 (m, 3H), 7.01 (dd, J = 4.9, 1.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 132.7, 132.2, 131.0, 129.2 (2C), 126.8, 126.7, 122.7. MS (relative intensity) m/z: 240 (45), 236 (11), 160 (100), 128 (12), 115 (22), 77 (22), 51 (22).

4-Chlorophenyl-4-methoxylphenyl-selenide[8g] ***(3m)***. Yield: 0.076 g (86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 8.8 Hz, 2H); 7.21 (d, J = 8.8 Hz, 2H); 7.14 (d, J = 8.8 Hz, 2H); 6.83 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.9, 136.6, 132.4, 132.0, 131.5, 129.1, 119.4, 115.2, 55.2. MS (relative intensity) m/z: 298 (35), 296 (17), 218 (100), 203 (40), 175 (27), 63 (12).

4-Fluorophenyl-4-methoxylphenyl-selenide[9] ***(3n)***. Yield: 0.069 g (83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, J = 8.9 Hz, 2H), 7.36−7.33 (m, 2H), 6.92 (t, J = 8.8 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm):162.1 (d, J = 246 Hz), 159.7, 135.8, 133.6 (d, J = 7.7 Hz), 127.2 (d, J = 3 Hz), 120.6, 116.3 (d, J = 21 Hz), 115.2, 55.3. MS (relative intensity) m/z: 281 (28), 202 (100), 187 (50), 155 (33), 77 (4).

3-(Trifluoromethyl)phenyl-4-methoxylphenyl-selenide[21] ***(3o)***. Yield: 0.079 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55−7.50 (m, 3H), 7.42−7.23 (m, 3H), 6.88 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 160.3, 137.3, 135.1, 133.4, 131.4 (q, J = 32.2 Hz), 129.4, 126.7 (q, J = 3.8 Hz), 123.8 (q, J = 272.8 Hz), 123.0 (q, J = 3.8 Hz), 118.5, 115.5, 55.3. MS (relative intensity) m/z: 332 (39), 252 (100), 237 (30), 209 (23), 63 (10).

Bis-4-methoxylphenyl-selenide[22] ***(3p)***. Yield: 0.081 g (93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (d, J = 8.9 Hz, 4H), 6.65 (d, J = 8.9 Hz, 2H), 3.59 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.1, 134.4, 121.9, 114.8, 55.1. MS (relative intensity) m/z: 294 (71), 214 (100), 186 (42), 65 (17).

4-Tolyl-4-methoxylphenyl-selenide[8g] ***(3q)***. Yield: 0.059 g (72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (d, J = 8.8 Hz, 2H); 7.26 (d, J = 8.0 Hz, 2H); 7.00 (d, J = 8.0 Hz, 2H); 6.79 (d, J = 8.8 Hz, 2H); 3.72 (s, 3H); 2.25 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.4, 136.5, 135.6, 131.7, 129.9, 128.8, 120.8, 114.9, 55.1, 20.9. MS (relative intensity) m/z: 278 (65), 198 (100), 183 (43), 170 (33), 91 (32), 65 (22).

2-Tolyl-4-methoxylphenyl-selenide[8g] ***(3r)***. Yield: 0.058 g (70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, J = 8.8 Hz, 2H), 7.14−7.06 (m, 3H), 6.99−6.95 (m, 1H), 6.83 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.7, 137.8, 136.5, 133.8, 130.7, 129.9, 126.5, 119.2, 115.2, 55.2, 21.8. MS (relative intensity) m/z: 278 (71), 198 (100), 183 (37), 170 (30), 91 (26), 65 (24).

2,4,6-(Trimethyl)phenyl-4-methoxylphenyl-selenide[23] ***(3s)***. Yield: 0.050 g (55%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.95 (d, J = 8.8 Hz, 2H), 6.83 (s, 2H), 6.59 (d, J = 8.8 Hz, 2H), 3.58 (s, 3H), 2.33 (s, 6H), 2.16 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 158.0, 143.2, 138.6, 130.6, 128.7, 127.8, 123.1, 114.8, 55.1, 24.2, 20.9. MS (relative intensity) m/z: 306 (100), 226 (54), 211 (22), 197 (78), 183 (18), 119 (25), 105 (12), 91 (40), 77 (25), 63 (8).

2-Pyridine-4-methoxylphenyl-selenide[23] ***(3t)***. Yield: 0.063 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.41 (ddd, J = 4.9, 1.9, 0.8 Hz, 1H); 7.63 (d, J = 8.9 Hz, 2H); 7.36 (ddd, J = 7.5, 4.9, 1.9 Hz, 1H); 7.01−6.88 (m, 4H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz); δ (ppm): 160.3, 159.8, 149.6, 138.2, 136.5, 123.3, 120.0, 117.6, 115.3, 55.2. MS (relative intensity) m/z: 265 (68), 264 (100), 262 (63), 249 (21), 185 (25), 142 (15), 78 (59), 51 (32).

Butyl-4-methoxylphenyl-selenide[6a] ***(3u)***. Yield: 0.054 g (75%). ^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.45 (d, J = 8.8 Hz, 2H); 6.80 (d, J = 8.8 Hz, 2H); 3.78 (s, 3H); 2.81 (t, J = 7.6 Hz, 2H); 1.63 (quint, J = 7.6 Hz, 2H); 1.40 (sex, J = 7.6 Hz, 2H); 0.89 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz): δ 159.1, 135.4, 120.2, 114.6, 55.2, 32.3, 28.7, 22.8, 13.5. MS (relative intensity) m/z: 244 (32), 188 (39), 108 (100), 77 (6), 57 (7).

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■ ASSOCIATED CONTENT

Supporting Information

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Copy of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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