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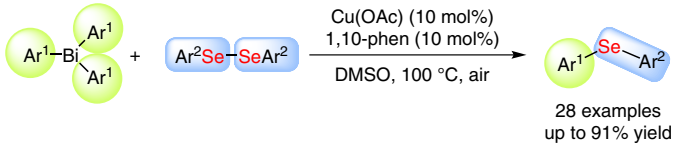
Synthesis of Unsymmetrical Diaryl Selenides: Copper-Catalyzed Se-Arylation of Diaryl Diselenides with Triarylbismuthanes

Mio Matsumura[a]
Kohki Shibata[a]
Sota Ozeki[a]
Mizuki Yamada[a]
Yuki Murata[a]
Naoki Kakusawa[b]
Shuji Yasuike*[a]

[a] School of Pharmaceutical Sciences, Aichi Gakuin University, 1-100 Kusumoto-cho, Chikusa-ku, Nagoya 464-8650, Japan
[b] Faculty of Pharmaceutical Sciences, Hokuriku University, Ho-3 Kanagawa-machi, Kanazawa 920-1181, Japan
s-yasuik@dpc.agu.ac.jp



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Abstract Copper-catalyzed C(aryl)–Se bond formation by the reaction of diaryl diselenides with triarylbismuthanes in the presence of copper(I) acetate (10 mol%) and 1,10-phenanthroline (10 mol%) under aerobic conditions led to the formation of unsymmetric diaryl selenides in moderate to excellent yields. This reaction proceeded efficiently; all three aryl groups in the bismuthane and both the selanyl groups in the diaryl diselenide were transferred to the coupling products.

Key words bismuthanes, diselenides, selenides, copper, catalysis, cross-coupling

Recently, organoselenium compounds have attracted interest because of their use as important reagents in organic synthesis and their potential biological activities.[1,2] Among the various organoselenium compounds, diaryl selenides have been prominent in the last two decades owing to their wide range of biological and pharmaceutical properties, such as anticancer, antitumor, antiviral, antimicrobial, and antioxidant activities.[3] Consequently, many methods have been developed for the synthesis of unsymmetrical diaryl selenides. Transition-metal-catalyzed C–Se bond formation is one of the most popular methods for the synthesis of organoselenides.[1c,4] Many studies have reported on copper-catalyzed Se-arylation reactions. Such reactions are generally conducted by reactions of aryl halides with selenols,[5] diselenides,[6] or alkyltin selenides,[7] reactions of aryl boronic acids with diselenides[4c,8] or selenium bromides,[9] or reactions of arylsilanes or stannanes with selenium bromides.[9] However, except for the reactions of boronic acids with diselenides, most of these reactions require a base and/or an inorganic reagent as an additive. In these reactions, diaryl diselenides are superior to other selenium reagents (selenols, arylselenium bromides, or alkyltin selenides) as sources of selenium for the synthesis of unsymmetrical diaryl selenides, with respect to their odor, stability, and toxicity. However, diphenyl diselenide is the principal reagent used in this type of reaction; only a few examples involving the use of other substituted diselenides are known.

Organobismuth compounds are generally nontoxic, environmentally benign, and useful synthetic reagents.[10] Trivalent organobismuth compounds such as triarylbismuthanes (Ar_3Bi) have been used as arylating agents in copper-mediated N- and O-arylation reactions, even though stoichiometric amounts of the copper reagents were required.[11,12] Moreover, triarylbismuthanes can also be used for C(aryl)–Se bond-formation reactions. Diaryl selenides were obtained by the reaction of diaryl diselenides with triarylbismuthanes on heating to a high temperature (140 °C) for a prolonged reaction time (24–48 h).[13] Photoinduced reactions of diaryl diselenides with triarylbismuthanes also afforded diaryl selenides; however, an excess of the bismuth agent bearing three aryl groups was required for this reaction.[14] We recently reported that a copper-catalyzed C(aryl)–S bond-formation reaction of diaryl disulfides with triarylbismuthanes can be conducted under aerobic conditions.[15] All three aryl groups of the bismuth reagent and both the sulfanyl groups of the diaryl disulfide participated in this reaction. As a continuation of our studies on C(aryl)–heteroatom bond formation, we now report an atom-economic and simple copper-catalyzed method for the synthesis of diaryl selenides from diaryl diselenides and triarylbismuthanes in the absence of additives under aerobic conditions.

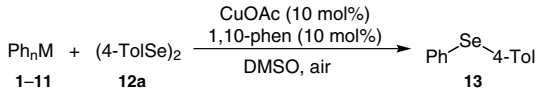
We previously reported that the cross-coupling reaction of diaryl disulfides with triarylbismuthanes in the presence of copper(I) acetate and 1,10-phenanthroline (1,10-phen) as the catalytic system under aerobic conditions in dimethyl sulfoxide afforded the corresponding diaryl sulfides.[15] To

evaluate the efficiency of triarylbismuthanes as aryl donors, we examined the reaction between di-4-tolyl diselenide (**12a**) and the phenyl-substituted compounds **1**–**11**, which contain group 14, 15 or 16 elements, under the optimal conditions determined previously [CuOAc (10 mol%), 1,10-phenanthroline (10 mol%), DMSO, 100 °C]. The progress of the reaction was monitored by gas–liquid chromatography, and the reaction times necessary to obtain products **13** were determined (Table 1). In the case of group 14 compounds, tetraphenyllead (**4**, M = Pb) afforded compound **13** in a moderate yield (60%) after a long reaction time (24 h) (Table 1, entry 4). Among the pnictogen compounds, triphenylbismuthane (**8a**, M = Bi) was efficiently converted into **13**; however, **5** (M = P), **6** (M = As), and **7** (M = Sb) showed no ability to transform (entries 5–8). The chalcogen compounds **9**–**11** provided inferior results (entries 9–11). These results show that triphenylbismuthane (**8a**) is superior to other reagents for this Se-arylation in terms of the reaction time (2 h) and the yield of **13** (87%; entry 8). Notably, all three phenyl groups of the bismuth reagent and both the selanyl groups of the diselenide participated in the reaction. When the reaction was carried out at 60 °C, compound **13** was obtained in 52% yield after 24 hours (entry 12). This shows that is necessary to heat the reaction mixture at 100 °C to complete the reaction. Decreasing the loading of copper(I) acetate from 10 mol% to 5 mol% or 1 mol% gave significantly lower yields of **13** (entries 13 and 14). Screening of solvents showed that the best results were obtained in dimethyl sulfoxide (2 h, 87%), although the reaction proceed effectively in *N*,*N*-dimethylformamide (80%) or *N*-methylpyrrolidin-2-one (71%) after 24 hours, whereas acetonitrile (39%), toluene (9%), 1,4-dioxane (7%), and 1,2-dichloroethane (7%) gave inferior results.

To demonstrate the efficiency and generality of this Se-arylation, we examined the reactions of various triarylbismuthanes (**8**; 0.75 mmol) and diaryl diselenides (**12**; 0.5 mmol) with copper(I) acetate (10 mol%) and 1,10-phenanthroline (10 mol%) as the catalytic system under aerobic conditions in dimethyl sulfoxide at 100 °C. The results are summarized in Table 2. The reactions of triphenylbismuthane (**8a**) with diaryl diselenides **12a**–**e** containing electron-donating or electron-withdrawing groups on the phenyl ring afforded the corresponding coupling products **13**–**17** in good to excellent yields (entries 1–5). The coupling of the sterically hindered *ortho*-substituted diselenides **12f**–**h** with **8a** gave the corresponding selenides **18**–**20** without any difficulty (entries 6–8). Moreover, the reactions of the heterocyclic diselenides **12i** and **12j** afforded the corresponding diaryl selenides **21** and **22** (entries 9 and 10). Next, we treated various triarylbismuthanes **8b**–**k** with diphenyl diselenide (**12k**) under the same reaction conditions. These reactions also afforded the corresponding coupling products **13**–**22** in good to excellent yields (entries 11–20). Furthermore, this reaction gave the polysubstituted diaryl selenides **23**–**26** by using various combinations of **8** and **12** (entries 21–26). All three aryl groups on the bismuth reagent and both the selanyl groups of the diselenide participated in these Se-arylations. Moreover, the electronic nature (electron-rich or electron-deficient) of the substituents in the 4-substituted series of bismuth and selenium reagents did not affect the outcome of this reaction (entries 1–5, 11–15, and 21–26). Additionally, the effect of steric hindrance in the bismuth and selenium reagents was remarkable: the bulkiest mesityl derivatives **8h** and **12g** were superior reagents for this reaction in terms of their reaction times and the yields of the Se-arylation products (entries 7, 17, 27, and 28). However, the reactions of triphenylbismuthane with dialkyl diselenides such as dibenzyl or dibutyl diselenide resulted in complex mixtures, and did not afford the desired coupling products.

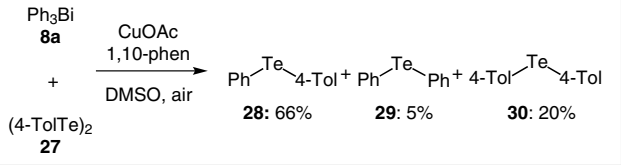
We also examined the reaction between di-4-tolyl ditelluride (**27**) with triphenylbismuthane (**8a**) under the same conditions (Scheme 1). This gave the unsymmetrical diaryl telluride **28** as the main product, along with the two symmetrical diaryl tellurides **29** and **30**. The yields are based on GLC analysis, because products **28**–**30** could not be separat-

Table 1 Copper-Catalyzed Coupling of Di-4-tolyl Diselenide with Group 14, 15 or 16 Reagents



Entry		Ph$_n$M	Temp (°C)	Time (h)	Yield[a] (%)
1[b]	**1**	Ph_4Si	100	24	7
2[b]	**2**	Ph_4Ge	100	24	10
3[b]	**3**	Ph_4Sn	100	24	21
4[b]	**4**	Ph_4Pb	100	24	60
5[c]	**5**	Ph_3P	100	24	8
6[c]	**6**	Ph_3As	100	24	6
7[c]	**7**	Ph_3Sb	100	24	15
8[c]	**8a**	Ph_3Bi	100	2	87
9[d]	**9**	Ph_2S	100	24	5
10[d]	**10**	Ph_2Se	100	24	6
11[d]	**11**	Ph_2Te	100	24	14
12[c]	**8a**	Ph_3Bi	60	24	52
13[c,e]	**8a**	Ph_3Bi	100	24	69
14[c,f]	**8a**	Ph_3Bi	100	24	29

[a] Yield by GLC. A 100% yield corresponds to the formation of 1 mmol (entries 1–4), 1.5 mmol (entries 5–8, 12), or 1 mmol (entries 9–11) of **13**.
[b] **1**–**4** (0.25 mmol), **12** (0.5 mmol).
[c] **5**–**8** (0.5 mmol), **12** (0.75 mmol).
[d] **9**–**11** (0.5 mmol), **12** (0.5 mol).
[e] CuOAc (5 mol%), 1,10-phenanthroline (5 mol%).
[f] CuOAc (1 mol%), 1,10-phenanthroline (1 mol%).

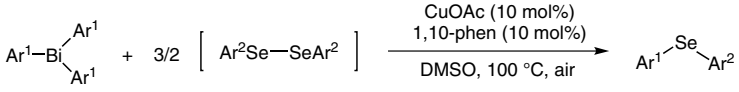


Scheme 1 Copper-catalyzed Te-Arylation of di-4-tolyl ditelluride with triphenylbismuthane

ed by column chromatography on silica gel. Unfortunately, this result shows that the reaction of di-4-tolyl ditelluride (**27**) with triphenylbismuthane (**8a**) is ineffective for Te-arylation.

At present, the mechanism of the Se-arylation reaction is unclear. Scheme 2 shows a possible mechanism for the synthesis of diaryl selenides through C(Ar)–Se bond formation from triarylbismuthanes and diaryl diselenides in the presence of catalytic amounts of the copper(I) reagent. The

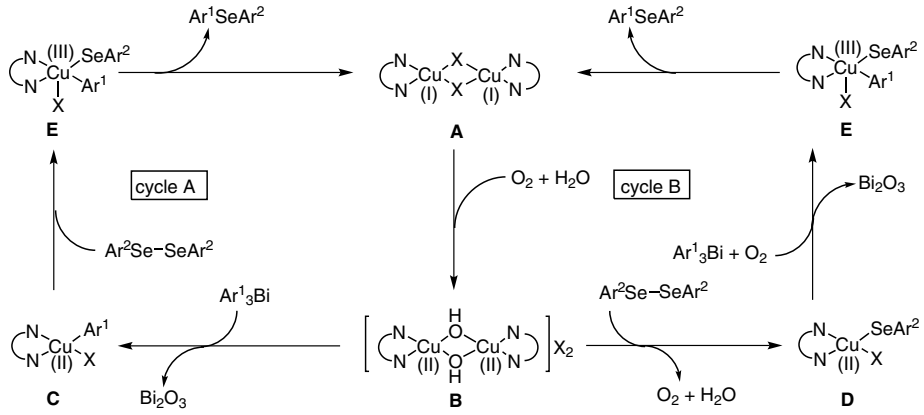
Table 2 Copper-Catalyzed Se-Arylation of Diaryl Diselenides with Triarylbismuthanes[a]



8 **12** **13–26**

Entry	Ar_3Bi	Ar^1	$(Ar^2Se)_2$	Ar^2	Time[b] (h)	Product	Yield[c] (%)
1	**8a**	Ph	**12b**	4-$MeOC_6H_4$	2	**14**	80
2	**8a**	Ph	**12a**	4-Tol	2	**13**	87
3	**8a**	Ph	**12c**	4-ClC_6H_4	1	**15**	85
4	**8a**	Ph	**12d**	4-$EtO_2CC_6H_4$	1.5	**16**	78
5	**8a**	Ph	**12e**	4-$F_3CC_6H_4$	1	**17**	89
6	**8a**	Ph	**12f**	2-Tol	2	**18**	88
7	**8a**	Ph	**12g**	Mes	2	**19**	82
8	**8a**	Ph	**12h**	1-naphthyl	2	**20**	90
9	**8a**	Ph	**12i**	2-thienyl	2	**21**	82
10	**8a**	Ph	**12j**	2-benzo[*b*]thienyl	2	**22**	85
11	**8b**	4-$MeOC_6H_4$	**12k**	Ph	1.5	**14**	83
12	**8c**	4-Tol	**12k**	Ph	1.5	**13**	86
13	**8d**	4-ClC_6H_4	**12k**	Ph	1	**15**	86
14	**8e**	4-$EtO_2CC_6H_4$	**12k**	Ph	1	**16**	81
15	**8f**	4-$F_3CC_6H_4$	**12k**	Ph	1	**17**	85
16	**8g**	2-Tol	**12k**	Ph	1.5	**18**	84
17	**8h**	Mes	**12k**	Ph	1	**19**	86
18	**8i**	1-naphthyl	**12k**	Ph	1	**20**	85
19	**8j**	2-thienyl	**12k**	Ph	1	**21**	72
20	**8k**	2-benzo[*b*]thienyl	**12k**	Ph	1.5	**22**	74
21	**8b**	4-$MeOC_6H_4$	**12a**	4-Tol	2	**23**	85
22	**8c**	4-Tol	**12b**	4-$MeOC_6H_4$	3	**23**	82
23	**8e**	4-$EtO_2CC_6H_4$	**12e**	4-$F_3CC_6H_4$	1.5	**24**	91
24	**8f**	4-$F_3CC_6H_4$	**12d**	4-$EtO_2CC_6H_4$	1.5	**24**	90
25	**8b**	4-$MeOC_6H_4$	**12e**	4-$F_3CC_6H_4$	1.5	**25**	88
26	**8f**	4-$F_3CC_6H_4$	**12b**	4-$MeOC_6H_4$	2	**25**	85
27	**8g**	2-Tol	**12g**	Mes	2	**26**	84
28	**8h**	Mes	**12f**	2-Tol	1	**26**	85

[a] Reaction conditions: **8** (0.5 mmol), **12** (0.75 mmol), CuOAc (0.05 mmol), 1,10-phenanthroline (0.05 mmol), DMSO, 100 °C, air.
[b] Heating was continued until the spot for the bismuth reagent on a TLC plate disappeared.
[c] Isolated yield.



Scheme 2 Possible mechanisms

catalytic cycle of this reaction should be similar to that of the Cu-catalyzed S-arylation of diaryl disulfides with triarylbismuthanes that we reported previously.[15] The first step of the reaction involves the generation of a bimetallic intermediate $[(Phen)_2Cu^{I}{}_2X_2]$ (**A**) from copper(I) acetate and 1,10-phenanthroline. Molecular oxygen and the moisture present in the air and/or solvent bind efficiently to intermediate **A**, which is then oxidized to produce the catalytically active (μ-hydroxide)copper(II) complex **B**.[16] In cycle A, the triarylbismuthane undergoes transmetalation with complex **B**, affording intermediate **C**; subsequently, oxidative addition of the diselenide (Ar^2–Se–Se–Ar^2) affords the copper(III) intermediate **E**. Intermediate **E** undergoes reductive elimination to give the product, with regeneration of the bimetallic intermediate **A**. An alternative cycle B is also possible: in this, the ligand-exchange reaction of **B** with the diaryl diselenide forms the copper(II) complex **D**; subsequent oxidative addition of triarylbismuthane gives the copper(III) intermediate **E**, which presumably undergoes reductive elimination to afford the diaryl selenide.

In conclusion, we have developed a simple copper-catalyzed Se-arylation of diaryl diselenides with triarylbismuthane under aerobic conditions in the absence of any additive. All three aryl groups of the bismuth reagent and both the selanyl groups on the diaryl diselenide participated in the reaction. Bismuthanes and diselenides with various functional groups afforded the corresponding cross-coupling products in satisfactory yields. Studies on reactions of triarylbismuthanes with other coupling partners in the presence of the catalytic system are in progress.

Melting points were determined on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and are uncorrected. ^{1}H NMR (internal standard TMS; δ = 0.00) and ^{13}C NMR (internal standard $CDCl_3$; δ = 77.00) spectra were recorded on JEOL JNM-AL400 (400 MHz and 100 MHz) spectrometers in $CDCl_3$ unless otherwise stated. Mass spectra (MS) were obtained on a JEOL JMP-DX300 instrument (70 eV, 300 μA). Elemental analysis was performed on MT-6 elemental analyzer (Yanagimoto). IR spectra were recorded on an FTIR-8400S system (Shimadzu); only selected IR bands are reported. All chromatographic separations were performed on Silica Gel 60N (Kanto Chemical Co., Inc.). TLC was performed with Macherey–Nagel precoated TLC plates (Sil G25 UV_{254}). Ph_3Bi (**8a**), tri(2-tolyl)bismuthane (**8g**), and PhSeSePh (**12k**) were purchased from TCI Fine Chemicals, Japan. **8b–d**,[17] **8e**,[18] **8f**,[13] **8h**,[19] **8i**,[17] **8j**,[20] **12a**,[21] **12b–c**,[21] **12d**,[22] **12e**,[13] **12f**,[21] **12g**,[23] **12h**,[21] **12i**,[24] and **12j**[25] were prepared according to the reported procedures. Diaryl selenides **13**–**21** and **23** are known compounds (unless otherwise shown below), and their spectroscopic data were identical to those reported in the literature.[6g,26,27]

Tris(2-benzo[*b*]thienyl)bismuthane (8k)

A solution of 1-benzothiophene (4.02 g, 30 mmol) in dry Et_2O (50 mL) was cooled to –80 °C, and a 1.6 M solution of BuLi in hexane (20.6 mL, 33 mmol) was added dropwise under argon. The mixture was stirred for 3 h, warmed to –10 °C, and a solution of $BiCl_3$ (3.15 g, 10 mmol) in dry THF was added dropwise at –10 °C. The mixture was then stirred for a further 20 h at r.t. and then diluted with $CHCl_3$ (70 mL). The reaction was quenched with H_2O (1 mL), and anhyd $MgSO_4$ was added to the mixture, which was refluxed for 5 min. The supernatant was removed by decantation. This treatment was repeated three times, and then the separated supernatant solution was concentrated under reduced pressure. The residue was recrystallized ($CHCl_3$) to give colorless needles; yield: 2.8 g (46%); mp >280 °C ($CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.3 Hz, 3 H, Ar-H), 7.79 (d, *J* = 6.8 Hz, 3 H, Ar-H), 7.77 (s, 3 H, Ar-H), 7.33 (td, *J* = 7.3, 1.5 Hz, 6 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1 (s), 141.8 (s), 135.1 (d), 124.3 (d), 124.2 (d), 123.2 (d), 122.1 (d), 96.1 (s).

MS (EI): *m/z* (%) = 266 (100) $[M - C_8H_5BiS]^+$, 134 (58).

Anal. Calcd for $C_{24}H_{15}BiS_3$: C, 47.37; H, 2.48. Found: C, 47.41; H, 2.50.

Asymmetric Diaryl Selenides 13–26: General Procedure

A solution of the appropriate triarylbismuthane **8** (0.5 mmol), diselenide **12** (0.75 mmol), CuOAc (0.05 mmol), and 1,10-phenanthroline (0.05 mmol) in DMSO (5 mL) was heated at 100 °C under air for the appropriate time (see Table 2) until the starting material was completely consumed (TLC). After dilution with CH_2Cl_2 (50 mL) and H_2O (30 mL), the mixture was separated and the aqueous layer was ex-

tracted with CH_2Cl_2 (2 × 30 mL). The organic layers were combined, washed with 5% aq NH_3 (30 mL) and H_2O (30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude residue was purified by column chromatograph (silica gel) to give diaryl selenides **26** (hexane), **22** (hexane–CH_2Cl_2, 10:1), **19**, **23** (hexane–CH_2Cl_2, 5:1), **13**–**18**, **20**, **21**, **24**, and **25** (hexane–CH_2Cl_2, 3:1).

Phenyl 4-Tolyl Selenide (13)[6g]

Pale-yellow oil; yield: 323 mg (87%; Table 2, entry 2) or 319 mg (86%; Table 2, entry 12); R_f = 0.3 (hexane–CH_2Cl_2, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.42 (m, 4 H, Ar-H), 7.25–7.24 (m, 3 H, Ar-H), 7.11 (d, *J* = 8.2 Hz, 2 H, Ar-H), 2.34 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.6 (s), 133.8 (d), 132.1 (s), 132.0 (d), 130.1 (d), 129.2 (d), 126.8 (d), 126.7 (s), 21.1 (q).

MS (EI): *m/z* (%) = 248 (80) [M$^+$], 232 (55), 168 (62), 83 (100).

HRMS: *m/z* [M$^+$] calcd for $C_{13}H_{12}Se$: 248.0104; found: 248.0132.

4-Methoxyphenyl Phenyl Selenide (14)[6g]

Colorless oil; yield: 316 mg (80%; Table 2, entry 1) or 327 mg (83%, entry 11); R_f = 0.3 (hexane–CH_2Cl_2, 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.32 (d, *J* = 6.3 Hz, 2 H, Ar-H), 7.22–7.16 (m, 3 H, Ar-H), 6.85 (d, *J* = 8.3 Hz, 2 H, Ar-H), 3.79 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7 (s), 136.5 (d), 133.2 (s), 130.9 (d), 129.1 (d), 126.4 (d), 119.9 (s), 115.1 (d), 55.2 (q).

MS (EI): *m/z* (%) = 264 (92) [M$^+$], 221 (10), 184 (100), 169 (52).

HRMS: *m/z* [M$^+$] calcd for $C_{13}H_{12}OSe$: 264.0053; found: 264.0061.

4-Chlorophenyl Phenyl Selenide (15)[6g]

Colorless oil; yield: 342 mg (85%; Table 2, entry 3) or 347 mg (86%, entry 13); R_f = 0.3 (hexane–CH_2Cl_2, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.44 (m, 2 H, Ar-H), 7.36 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.28–7.26 (m, 3 H, Ar-H), 7.21 (d, *J* = 8.2 Hz, 2 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.1 (d), 134.0 (d), 133.5 (s), 133.2 (d), 130.6 (s), 129.5 (s), 129.4 (d), 127.6 (d).

MS (EI): *m/z* (%) = 268 (60) [M$^+$], 188 (80), 152 (46).

HRMS: *m/z* [M$^+$] calcd for $C_{12}H_9ClSe$: 267.9558; found: 267.9574.

Ethyl 4-(Phenylselanyl)benzoate (16)[6g]

Colorless oil; yield: 357 mg (78%; Table 2, entry 4) or 372 mg (81%, entry 14); R_f = 0.3 (hexane–CH_2Cl_2, 1:1).

IR (neat): 2980, 1717, 1271, 1105 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.58–7.55 (m, 2 H, Ar-H), 7.37–7.25 (m, 5 H, Ar-H), 4.35 (q, *J* = 7.3 Hz, 2 H, OEt), 1.37 (t, *J* = 7.3 Hz, 3 H, OEt).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2 (s), 139.4 (s), 134.8 (d), 130.4 (d), 130.1 (d), 129.6 (d), 128.8 (s), 128.6 (s), 128.4 (d), 60.9 (t), 14.3 (q).

MS (EI): *m/z* (%) = 306 (95) [M$^+$], 261 (38), 232 (24), 83 (100).

HRMS: *m/z* [M$^+$] calcd for $C_{15}H_{14}O_2Se$: 306.0159; found: 306.0151.

Phenyl 4-(Trifluoromethyl)phenyl Selenide (17)[6g]

Colorless oil; yield: 403 mg (89%; Table 2, entry 5) or 384 mg (85%, entry 15); R_f = 0.4 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.55 (m, 2 H, Ar-H), 7.46–7.40 (m, 4 H, Ar-H), 7.37–7.32 (m, 3 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8 (s), 134.8 (d), 131.0 (d), 129.7 (d), 128.7 (q, ^2J_F = 21 Hz), 128.6 (s), 128.5 (d), 125.9 (q, ^3J_F = 4.1 Hz), 124.1 (q, ^1J_F = 272 Hz).

MS (EI): *m/z* (%) = 302 (100) [M$^+$], 281 (14), 222 (100).

HRMS: *m/z* [M$^+$] calcd for $C_{13}H_9F_3Se$: 301.9822; found: 301.9844.

Phenyl 2-Tolyl Selenide (18)[6g]

Pale-yellow oil; yield: 325 mg (88%; Table 2, entry 6) or 312 mg (84%, entry 16); R_f = 0.3 (hexane–CH_2Cl_2, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.38 (m, 2 H, Ar-H), 7.35 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.27–7.21 (m, 4 H, Ar-H), 7.18 (dt, *J* = 7.2, 1.4 Hz, 1 H, Ar-H), 7.05 (dt, *J* = 7.2, 1.4 Hz, 1 H, Ar-H), 2.39 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8 (s), 133.7 (d), 132.7 (d), 131.7 (s), 130.8 (s), 130.2 (d), 129.3 (d), 127.7 (d), 127.1 (d), 126.7 (d), 22.3 (q).

MS (EI): *m/z* (%) = 248 (100) [M$^+$], 168 (44), 91 (44).

HRMS: *m/z* [M$^+$] calcd for $C_{13}H_{12}Se$: 248.0104; found: 248.0112.

Mesityl Phenyl Selenide (19)[26]

Yellow oil; yield: 339 mg (82%; Table 2, entry 7) or 355 mg (86%, entry 17); R_f = 0.5 (hexane–CH_2Cl_2, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.04 (m, 5 H, Ar-H), 6.99 (s, 2 H, Ar-H), 2.44 (s, 6 H, Me), 2.28 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6 (s), 139.0 (s), 133.4 (s), 129.0 (d), 128.8 (d), 128.4 (d), 126.8 (s), 125.3 (d), 24.1 (q), 21.1 (q).

MS (EI): *m/z* (%) = 276 (100) [M$^+$], 248 (38), 204 (42).

HRMS: *m/z* [M$^+$] calcd for $C_{15}H_{16}Se$: 276.0417; found: 276.0409.

1-Naphthyl Phenyl Selenide (20)[6g]

Colorless oil; yield: 383 mg (90%; Table 2, entry 8) or 361 mg (85%, entry 18); R_f = 0.3 (hexane–CH_2Cl_2, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34–8.33 (m, 1 H, Ar-H), 7.84–7.82 (m, 2 H, Ar-H), 7.75 (d, *J* = 7.3 Hz, 1 H, Ar-H), 7.51–7.46 (m, 2 H, Ar-H), 7.37–7.32 (m, 3 H, Ar-H), 7.21–7.13 (m, 3 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.1 (s), 134.1 (s), 133.8 (d), 131.7 (d), 131.6 (s), 129.4 (s), 129.3 (d), 129.2 (d), 128.5 (d), 127.6 (d), 126.9 (d), 126.8 (d), 126.3 (d), 126.0 (d).

MS (EI): *m/z* (%) = 276 (38) [M$^+$], 204 (40), 83 (100).

HRMS: *m/z* [M$^+$] calcd for $C_{16}H_{12}Se$: 284.0104; found: 284.0110.

2-(Phenylselanyl)thiophene (21)[6g]

Colorless oil; yield: 294 mg (82%; Table 2, entry 9) or 256 mg (72%, entry 19); R_f = 0.6 (hexane–EtOAc, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 5.4, 0.9 Hz, 1 H, Ar-H), 7.34–7.30 (m, 3 H, Ar-H), 7.24–7.16 (m, 3 H, Ar-H), 7.04 (dd, *J* = 5.4, 3.9 Hz, 1 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0 (s), 133.5 (s), 132.0 (d), 129.9 (d), 129.2 (d), 128.3 (d), 126.7 (d), 123.1 (s).

MS (EI): *m/z* (%) = 240 (100) [M$^+$], 160 (90).

HRMS: *m/z* [M$^+$] calcd for $C_{10}H_8SSe$: 239.9512; found: 239.9519.

2-(Phenylselanyl)benzo[*b*]thiophene (22)

Colorless oil; yield: 368 mg (85%; Table 2, entry 10) or 322 mg (74%, entry 20); R_f = 0.6 (hexane–CH_2Cl_2, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.74 (m, 2 H, Ar-H), 7.51 (s, 1 H, Ar-H), 7.49–7.46 (m, 2 H, Ar-H), 7.36–7.30 (m, 2 H, Ar-H), 7.28–7.24 (m, 3 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8 (s), 140.2 (s), 132.2 (d), 131.7 (s), 131.4 (d), 129.3 (d), 127.3 (d), 126.9 (s), 124.7 (d), 124.4 (d), 123.3 (d), 121.8 (d).

MS (EI): *m/z* (%) = 290 (38) [M$^+$], 210 (100).

HRMS: *m/z* [M$^+$] calcd for $C_{14}H_{10}SSe$: 289.9668; found: 289.9659.

1-Methoxy-4-[(4-tolyl)selanyl]benzene (23)[27]

Colorless prisms (hexane); yield: 355 mg (85%; Table 2, entry 21) or 342 mg (82%, entry 22); mp 57–59 °C; R_f = 0.6 (hexane–CH_2Cl_2, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.28 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.04 (d, *J* = 8.3 Hz, 2 H, Ar-H), 6.83 (d, *J* = 8.8 Hz, 2 H, Ar-H), 3.80 (s, 3 H, OMe), 2.30 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5 (s), 136.6 (s), 135.7 (d), 131.8 (d), 130.0 (d), 128.9 (s), 120.9 (s), 115.0 (d), 55.2 (q), 21.08 (q).

MS (EI): *m/z* (%) = 278 (90) [M$^+$], 276 (50), 198 (100).

HRMS: *m/z* [M$^+$] calcd for $C_{14}H_{14}OSe$: 278.0210; found: 278.0218.

Ethyl 4-{[4-(Trifluoromethyl)phenyl]selanyl}benzoate (24)

Colorless oil; yield: 510 mg (91%; Table 2, entry 23) or 503 mg (90%, entry 24); R_f = 0.4 (hexane–CH_2Cl_2, 1:1).

IR (neat): 2983, 1717, 1396, 1325, 1124 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.57–7.45 (m, 6 H), 4.38 (q, *J* = 7.3 Hz, 2 H, Et), 1.39 (t, *J* = 7.3 Hz, 3 H, Et).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0 (s), 136.5 (s), 135.3 (s), 133.0 (d), 132.5 (d), 130.5 (d), 129.9 (s), 129.9 (q, ^2J_F = 33.1 Hz), 126.2 (q, ^3J_F = 3.3 Hz), 123.9 (q, ^1J_F = 272.3 Hz), 61.1 (t), 14.3 (q).

MS (EI): *m/z* (%) = 374 (10) [M$^+$], 372 (50), 329 (55).

HRMS: *m/z* [M$^+$] calcd for $C_{16}H_{13}F_3O_2Se$: 374.0033; found: 374.0028.

1-Methoxy-4-{[4-(trifluoromethyl)phenyl]selanyl}benzene (25)

Colorless plates (hexane–CH_2Cl_2); yield: 436 mg (88%; Table 2, entry 25) or 424 mg (85%, entry 26); mp 81–83 °C; R_f = 0.5 (hexane–CH_2Cl_2, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.41 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.31 (d, *J* = 8.3 Hz, 2 H, Ar-H), 6.91 (d, *J* = 8.8 Hz, 2 H, Ar-H), 3.83 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4 (s), 139.5 (s), 137.7 (d), 129.5 (d), 128.1 (q, ^2J_F = 32.3 Hz), 125.7 (q, ^3J_F = 4.1 Hz), 124.2 (q, ^1J_F = 271.5 Hz), 118.0 (s), 115.5 (d), 55.3 (q).

MS (EI): *m/z* (%) = 332 (95) [M$^+$], 330 (55), 252 (100).

HRMS: *m/z* [M$^+$] calcd for $C_{14}H_{11}F_3OSe$: 331.9927; found: 331.9930.

Mesityl 2-Tolyl Selenide (26)

Colorless plates (hexane); yield: 364 mg (84%; Table 2, entry 27) or 367 mg (85%, entry 28); mp 59–61 °C; R_f = 0.5 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, *J* = 6.8 Hz, 1 H, Ar-H), 7.01 (t, *J* = 6.8 Hz, 1 H, Ar-H), 7.00 (s, 2 H, Ar-H), 6.88 (t, *J* = 7.8 Hz, 1 H, Ar-H), 3.57 (d, *J* = 7.8 Hz, 1 H, Ar-H), 2.41 (s, 9 H, Me), 2.31 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9 (s), 139.1 (s), 136.5 (s), 134.0 (s), 129.9 (d), 128.9 (d), 126.4 (s), 125.2 (d), 24.1 (q), 21.4 (q), 21.1 (q).

MS (EI): *m/z* (%) = 290 (100) [M$^+$], 288 (50).

HRMS: *m/z* [M$^+$] calcd for $C_{16}H_{18}Se$: 290.0574; found: 290.0582.

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Supporting Information

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