An Efficient Copper(I) Iodide Catalyzed Synthesis of Diaryl Selenides through C_{Ar}–Se Bond Formation Using Solvent Acetonitrile as Ligand

Arpan Dandapat, Chiranjeevi Korupalli, D. J. C. Prasad, Rahul Singh, Govindasamy Sekar*

Department of Chemistry, Indian Institute of Technology Madras, Chennai, Tamil Nadu 600 036, India
Fax +91(44)22574202; E-mail: gsekar@iitm.ac.in

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Abstract: A wide range of diaryl selenides can be synthesized through C_{Ar}–Se bond formation using readily available copper(I) iodide as catalyst under mild reaction conditions (82 °C) from aryl iodides and diphenyl diselenide. In this coupling reaction, solvent acetonitrile acts as ligand for copper(I) iodide and no external ligand is required. Less reactive aryl bromides also provide the diaryl selenides in good isolated yields.

Key words: copper catalyst, acetonitrile, C–Se bond formation, selenium

Organoselenium compounds have become very important target molecules for synthetic organic chemists due to their vital biological activities,[1] and because of their application as chiral catalysts.[2] Particularly, diaryl selenides have attracted considerable attention because of their anticancer, antitumor, antiviral, antimicrobial, and antioxidant properties (Figure 1).[3]

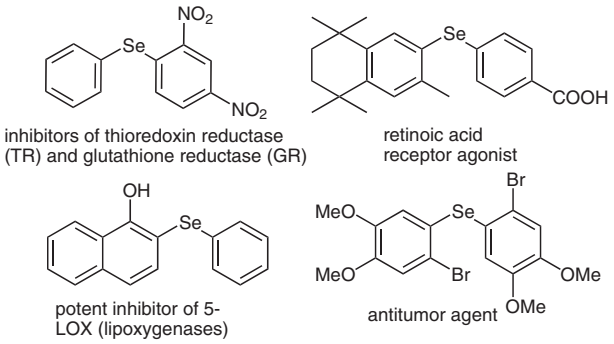
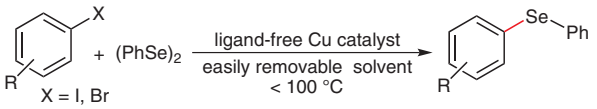


Figure 1 Some biologically important compounds containing the diaryl selenide skeleton

Traditionally, C_{Ar}–Se bond formation requires harsh reaction conditions, such as high reaction temperature, photochemical/UV light, or the use of toxic and polar solvent such as hexamethylphosphoramide.[4] Cross-coupling of aryl halides with aryl selenol in the presence of transition-metal catalysts emerged as an alternative method to the traditional synthesis of diaryl selenides.[5] Further improvement was achieved by replacing unstable, expensive, and foul-smelling aryl selenol with diphenyl diselenide. Nickel-,[6] palladium-,[7] lanthanum-,[8] or copper-based[9] catalysts in combination with appropriate ligands are used for this cross-coupling reaction. It is important to mention that these metal catalysts require external ligands and high reaction temperature (≥100 °C) for the diaryl selenide synthesis. Recently, copper(II) oxide nanoparticles were used as a successful catalyst to synthesize diaryl selenides from aryl boronic acid and diaryl diselenide in dimethylsulfoxide at 100 °C.[10] Very recently, a ligand-free bimetallic catalyst (CuS/Fe) was reported for the synthesis of diaryl selenides in dimethylsulfoxide at 110 °C.[11] Therefore, it is very desirable to develop new catalytic systems that are economical, free of external ligand, and capable of catalyzing the cross-coupling reaction at low reaction temperature (<100 °C) with easily removable organic solvent (Scheme 1).



Scheme 1

As part of our ongoing research towards copper-catalyzed oxidation chemistry,[12] we have recently reported a copper complex as an efficient catalyst for the synthesis of ethers, sulfides, N-arylated indoles, arylated alkynes, benzoxazines, and benzothiazines through C_{Ar}–O, C_{Ar}–S, C_{Ar}–N, and C_{Ar}–C bond forming Ullmann type/Sonogashira coupling reactions.[13] Herein, we report a simple procedure for the synthesis of diaryl selenides from easily available aryl halides and diphenyl diselenide using copper(I) iodide as catalyst in acetonitrile solvent under mild reaction conditions (82 °C).

Recently, we have reported the use of Cu(II)-BINAM (**L1**) and Cu(I)-(±)-Diol (**L2**) complexes as efficient catalysts for the synthesis of aryl ethers and aryl thioethers through C_{Ar}–O[13a–c] and C_{Ar}–S[13d,j] bond formation, respectively. Hoping that the same catalysts will catalyze the diaryl selenide formation through C_{Ar}–Se bond formation, the cross-coupling reaction of aryl halide with phenyl selenol in the presence of $Cu(OTf)_2$-BINAM (**L1**) complex in *N*,*N*-dimethylformamide at 110 °C was studied. In the preliminary studies, 20 mol% **L1** as ligand with 20 mol% $Cu(OTf)_2$ were used for the synthesis of diaryl selenide **4** using cesium carbonate as base in *N*,*N*-dimethylformamide at 110 °C. After 22 hours, the coupling reaction provided 80% isolated yield of diaryl selenide **4** (Table 1, entry 1). When **L1**–$Cu(OTf)_2$ complex was replaced by

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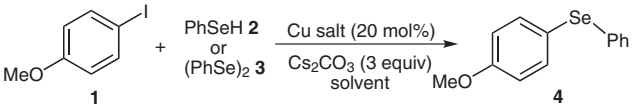
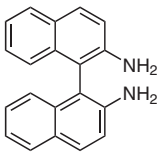
L2–CuBr complex, the reaction took place at a lower temperature of 82 °C in acetonitrile solvent, but the yield was decreased to 70% (entry 2).

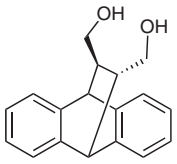
Table 1 Effect of Ligands, Temperature and Solvents for the Synthesis of Diaryl Selenide



Entry	Ligand	Cu salt	Selenide source	Solvent	Temp (°C)	Time (h)	Yield (%)[a]
1	**L1**	$Cu(OTf)_2$	PhSeH	DMF	110	22	80[b]
2	**L2**	CuBr	PhSeH	MeCN	82	32	70[b]
3	**L2**	CuI	$(PhSe)_2$	MeCN	82	21	88[b]
4	–	CuI	$(PhSe)_2$	MeCN	82	22	87
5	–	–	$(PhSe)_2$	MeCN	82	72	–
6	–	CuI	$(PhSe)_2$	DCE	82	28	5
7	–	CuI	$(PhSe)_2$	DMF	82	48	10
8	–	CuI	$(PhSe)_2$	dioxane	82	48	–
9	–	CuI	$(PhSe)_2$	toluene	82	48	–
10	–	CuI	$(PhSe)_2$	DMSO	82	48	40



L1



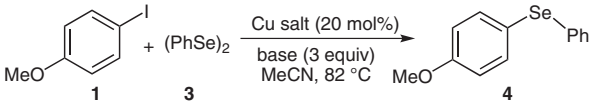
L2

[a] Isolated yield.
[b] 20 mol% ligand was used.

Replacement of unstable, expensive and foul-smelling phenyl selenol by easily available diphenyl diselenide yielded the desired product (88%) of the cross-coupling reaction (entry 3). To our surprise, the cross-coupling reaction provided the same yield when the reaction was carried out without any external ligand (entry 4). However, no product was observed when the cross-coupling reaction was carried out without copper(I) iodide (entry 5), which shows that copper(I) iodide is the real catalytic species for the coupling reaction. The reaction was then carried out with several solvents to increase the efficiency of the coupling reaction; acetonitrile turned out to be the solvent of choice (entry 4 vs 6–10). This result clearly showed that the solvent acetonitrile acted as ligand for copper(I) iodide to increase its catalytic activity towards the coupling reaction.

The reaction was then screened with several copper salts, bases and different amounts of catalyst to increase the efficiency of the coupling reaction (Table 2). Copper(I) iodide turned out to be the best copper salt with respect to isolated yield (entry 1). Use of cesium carbonate as base provided better results than other bases such as potassium phosphate, potassium carbonate and sodium *tert*-butoxide (entry 1 vs. 7–9). Reduction of catalyst loading from 20 mol% to 5 mol% increased the isolated yield for diaryl selenide **4** to 95% without any change in the reaction time (entry 11). However, further reduction of copper(I) iodide to 2.5 mol% reduced the yield to 75% (entry 12).

Table 2 Effect of Copper Salts, Bases and Amount of Catalyst on the Cross-Coupling Reaction



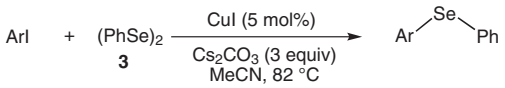
Entry	Cu salt	Base	Time (h)	Yield (%)[a]
1	CuI	Cs_2CO_3	28	87
2	CuCl	Cs_2CO_3	28	69
3	CuBr	Cs_2CO_3	28	71
4	$CuSO_4$	Cs_2CO_3	48	09
5	$Cu(OAc)_2$	Cs_2CO_3	28	52
6	$Cu(OTf)_2$	Cs_2CO_3	28	79
7	CuI	K_3PO_4	48	45
8	CuI	K_2CO_3	48	30
9	CuI	*t*-BuONa	24	55
10	CuI	Cs_2CO_3	30	65[b]
11	CuI	Cs_2CO_3	28	95[c]
12	CuI	Cs_2CO_3	28	75[d]

[a] Isolated yield.
[b] 10 mol% of CuI was used.
[c] 5 mol% of CuI was used.
[d] 2.5 mol% of CuI was used.

Using the optimized reaction conditions mentioned above, investigations were initiated on the scope of the copper(I) iodide catalyzed cross-coupling of various aryl iodides with diphenyl diselenide; the results are summarized in Table 3. Both electron-donating (entries 1, 4, 6, 7, 9, 10 and 14) and electron-withdrawing groups (entries 2, 3, 5, 12 and 13) containing aryl iodides reacted with diphenyl diselenide to produce the corresponding diaryl selenides in good yields under the optimal reaction conditions. Interestingly, sterically hindered *ortho*-substituted aryl iodides also yielded the corresponding diaryl selenides in good yields (entries 6, 7, 9 and 13) and even the heteroatom-containing 2-iodopyridine provided the corresponding product in 95% yield (entry 15).

The new catalytic system was also successfully used for the synthesis of diaryl selenides from less reactive aryl bromides, particularly aryl bromides with electron-withdrawing groups. However, these aryl bromides required slightly higher reaction temperature (Table 4). It has been

Table 3 Synthesis of Diaryl Selenides through Copper(I) Iodide Catalyzed Coupling of Aryl Iodides with Diphenyl Diselenide

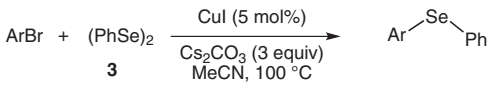


Entry	Ar	Product	Time (h)	Yield (%)[a]
1	4-$MeOC_6H_4$	**4**	28	95
2	4-$F_3CC_6H_4$	**5**	28	48
3	3-$O_2NC_6H_4$	**6**	40	77
4	3-$MeOC_6H_4$	**7**	30	45
5	4-$O_2NC_6H_4$	**8**	24	88
6	2-$MeOC_6H_4$	**9**	28	76
7	2-$H_2NC_6H_4$	**10**	48	46
8	1-naphthyl	**11**	28	81
9	2-MeC_6H_4	**12**	28	60
10	4-MeC_6H_4	**13**	28	73
11	Ph	**14**	20	59
12	4-AcC_6H_4	**15**	24	63
13	2-BrC_6H_4	**16**	24	78
14	3,5-$Me_2C_6H_3$	**17**	23	56
15	2-pyridyl	**18**	36	95

[a] Isolated yield.

observed that these aryl bromides provided the same products even in the absence of the catalyst copper(I) iodide through nucleophilic substitution reactions.[14] However, the reaction became more productive in the presence of a catalytic amount of copper(I) iodide (5 mol%), particularly for aryl bromides containing weak electron-withdrawing groups.

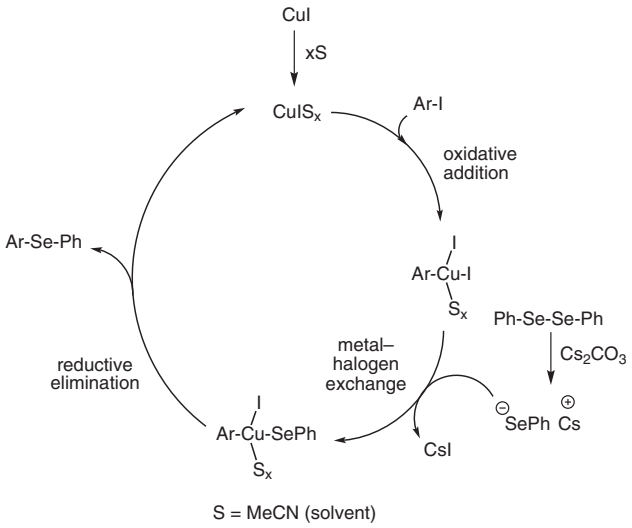
Table 4 Synthesis of Diaryl Selenides from Aryl Bromides



Entry	Ar	Product	Time (h)	Yield (%)[a]
1	4-$O_2NC_6H_4$	**8**	30	85
2			40	80[b]
3	4-NCC_6H_4	**19**	48	75
4			48	25[b]
5	4-AcC_6H_4	**15**	48	51
6			48	32[b]
7	2-pyridyl	**18**	50	58
8			50	50[b]

[a] Isolated yield; all the reactions were carried out in sealed tubes.
[b] Isolated yield without CuI.

A possible mechanism for the synthesis of diaryl selenides through C_{Ar}–Se bond formation from aryl iodides and diphenyl diselenide in the presence of catalytic quantities of copper(I) iodide is shown in Scheme 2.



Scheme 2 Possible mechanism for the external ligand-free copper(I) iodide catalyzed synthesis of diaryl selenides in acetonitrile, using cesium carbonate as base

In summary, for the first time, a copper(I) iodide catalyzed diaryl selenide synthesis has been demonstrated. The reaction proceeds through C_{Ar}–Se bond formation at 82 °C starting from readily available aryl iodides and diphenyl diselenides. In this reaction, the solvent acetonitrile acts as ligand for copper(I) iodide and there is no need for any external ligand. Aryl iodides containing both electron-withdrawing and electron-donating groups and even sterically hindered *ortho*-substituted groups are well tolerated. Less reactive aryl bromides also provide the diaryl selenides in good isolated yields. This synthetic method is expected to have applications in various areas because the reaction is carried out under additive and external-ligand-free conditions at temperatures as low as 82 °C.

All reactions were carried out in reaction tubes under a nitrogen atmosphere. CuI, Cs_2CO_3, and diphenyl diselenide were purchased from Sigma Aldrich chemical company. 4-Iodoanisole was purchased from Avra Chemicals, India. MeCN was dried over calcium hydride and freshly distilled. Reaction temperatures were controlled by a Varivolt temperature modulator, thin-layer chromatography (TLC) was performed using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and visualized by UV fluorescence quenching. Silica gel (particle size 100–200 mesh) purchased from SRL India was used for chromatography. ^1H and ^{13}C NMR spectra were recorded with a Bruker 400 MHz instrument. ^1H NMR spectra are reported relative to TMS (δ = 0.0 ppm) or residual $CHCl_3$ (δ = 7.26 ppm). ^{13}C NMR are reported relative to $CDCl_3$ (δ = 77.16 ppm). FTIR spectra were recorded with a Nicolet 6700 spectrometer and are reported in frequency of absorption (cm^{-1}). High-resolution mass spectra (HRMS) were recorded with a Q-Tof Micro mass spectrometer. GC-MS were recorded with a JEOL GCMATE II mass spectrometer.

(4-Methoxyphenyl)(phenyl)selane (4);[7c] Typical Procedure
Diphenyl diselenide (**2**; 109.3 mg, 0.35 mmol), 4-iodoanisole (**1**; 117 mg, 0.5 mmol), CuI (4.8 mg, 0.025 mmol), and Cs_2CO_3 (488.7 mg, 1.5 mmol) were taken in a 10 mL reaction tube equipped with a septum. The reaction tube was evacuated and then back-filled with nitrogen. Acetonitrile (2.5 mL) was added at r.t. and the resulting reaction mixture was heated at 82 °C for 28 h. After complete disappearance of 4-iodoanisole (the progress of the reaction was followed by TLC), the reaction mixture was allowed to cool to r.t. and the solvent was evaporated under reduced pressure. The crude residue was directly purified by column chromatography on silica gel (EtOAc–hexanes) to afford (4-methoxyphenyl)(phenyl)selane **4**.

Yield: 125.0 mg (95%); slightly yellow oil; R_f = 0.50 (EtOAc–hexanes, 1:49).

IR (neat): 3061, 3002, 2930, 2837, 1243, 823, 736, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3 H), 6.80–6.86 (m, 2 H), 7.14–7.22 (m, 3 H), 7.28–7.34 (m, 2 H), 7.46–7.51 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 115.2, 120.0, 126.5, 129.2, 130.9, 133.3, 136.6, 159.8.

GC-MS (EI+): *m*/*z* = 263.

Phenyl[4-(trifluoromethyl)phenyl]selane (5)[15]
Colorless oil; R_f = 0.78 (EtOAc–hexanes, 1:9).

IR (neat): 3064, 1321, 827, 735, 689 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.30 (m, 3 H), 7.31–7.40 (m, 4 H), 7.45–7.51 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.9, 125.6, 126.0, 126.1, 128.8 (q, *J* = 22.7 Hz), 129.9, 131.2, 135.0, 137.9.

GC-MS (EI+): *m*/*z* = 301.

(3-Nitrophenyl)(phenyl)selane (6)[15]
Yellowish oil; R_f = 0.42 (EtOAc–hexanes, 1:9).

IR (neat): 3062, 1521, 1340, 868, 800, 728, 687 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.31 (m, 4 H), 7.45–7.50 (m, 2 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 8.10 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.7, 125.9, 128.5, 128.9, 129.9, 130.0, 130.8, 134.9, 137.0, 148.7.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{10}NO_2Se$: 279.9877; found: 279.9873.

(3-Methoxyphenyl)(phenyl)selane (7)[16]
Colorless oil; R_f = 0.52 (hexanes).

IR (neat): 3060, 2987, 1234, 1128, 830, 776, 734, 683 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.64 (s, 3 H), 6.70 (dd, *J* = 8.0, 2.0 Hz, 1 H), 6.89–6.96 (m, 2 H), 7.08 (t, *J* = 8.0 Hz, 1 H), 7.15 (t, *J* = 3.6 Hz, 3 H), 7.36 (q, *J* = 3.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.2, 118.2, 125.1, 127.6, 129.4, 130.1, 130.9, 132.3, 133.4, 160.1.

GC-MS (EI+): *m*/*z* = 263.

(4-Nitrophenyl)(phenyl)selane (8)[7c]
Yellowish oil; R_f = 0.65 (EtOAc–hexanes, 1:9).

IR (neat): 3059, 1510, 1334, 839, 736, 684 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.8 Hz, 2 H), 7.37–7.45 (m, 3 H), 7.60–7.66 (m, 2 H), 8.01 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.0, 127.3, 129.4, 129.8, 130.1, 135.9, 144.0, 146.2.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{10}NO_2Se$: 279.9877; found: 279.9879.

(2-Methoxyphenyl)(phenyl)selane (9)[7c]
Colorless oil; R_f = 0.38 (EtOAc–hexanes, 2:98).

IR (neat): 3061, 3002, 2930, 2834, 1237, 741, 692 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 6.73 (t, *J* = 7.6 Hz, 1 H), 6.79 (d, *J* = 8.4 Hz, 1 H), 6.88–6.94 (m, 1 H), 7.09–7.16 (m, 1 H), 7.23–7.32 (m, 3 H), 7.50–7.57 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.9, 110.5, 121.7, 122.0, 127.8, 128.2, 128.3, 129.5, 130.9, 135.5, 156.7.

GC-MS (EI+): *m*/*z* = 263.

2-(Phenylselanyl)aniline (10)[7c]
Brown oil; R_f = 0.22 (EtOAc–hexanes, 2:98).

IR (neat): 3460, 3358, 3058, 1604, 1304, 740, 689 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.17 (s, 2 H), 6.56–6.64 (m, 1 H), 6.67 (dd, *J* = 6.8, 1.2 Hz, 1 H), 7.02–7.22 (m, 6 H), 7.45–7.51 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.7, 115.1, 118.9, 126.2, 129.3, 129.4, 131.1, 131.7, 138.6, 148.7.

HRMS: *m*/*z* [M+ H]$^+$ calcd for $C_{12}H_{12}NSe$: 250.0135; found: 250.0132.

Naphthalen-1-yl(phenyl)selane (11)[7c]
Colorless oil; R_f = 0.63 (hexanes).

IR (neat): 3049, 737, 686 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.17 (m, 3 H), 7.24–7.32 (m, 3 H), 7.40–7.49 (m, 2 H), 7.66–7.72 (m, 1 H), 7.73–7.82 (m, 2 H), 8.22–8.30 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.1, 126.5, 126.9, 127.1, 127.8, 128.7, 128.9, 129.3, 129.4, 131.8, 133.0, 134.0, 134.2, 134.3.

GC-MS (EI+): *m*/*z* = 283.

Phenyl(*o*-tolyl)selane (12)[7c]
Colorless oil; R_f = 0.69 (hexanes).

IR (neat): 3053, 2917, 2856, 738, 692 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.54 (s, 3 H), 7.15–7.22 (m, 1 H), 7.29–7.41 (m, 5 H), 7.46–7.62 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.5, 126.8, 127.2, 127.9, 129.4, 129.5, 130.3, 132.8, 133.0, 133.7, 139.9.

GC-MS (EI+): *m*/*z* = 247.

Phenyl(*p*-tolyl)selane (13)[7c]
Colorless oil; R_f = 0.73 (hexanes).

IR (neat): 2930, 2861, 805, 739, 651 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 7.03 (d, *J* = 8 Hz, 2 H), 7.13–7.21 (m, 3 H), 7.30–7.37 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 126.9, 127.0, 129.4, 130.3, 132.2, 133.1, 134.0, 137.8.

GC-MS (EI+): *m*/*z* = 247.

Diphenylselane (14)[7c]
Colorless oil; R_f = 0.81 (hexanes).

IR (neat): 3690, 730, 684 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.45 (m, 6 H), 7.59–7.65 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.4, 129.4, 131.2, 133.0.

GC-MS (EI+): *m*/*z* = 233.

1-[4-(Phenylselanyl)phenyl]ethanone (15)[7c]
Orange solid; mp 55–57 °C (Lit.[17] 57 °C); R_f = 0.53 (EtOAc–hexanes, 1:19).

IR (neat): 3063, 2990, 1675, 821, 737, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.55 (s, 3 H), 7.33–7.45 (m, 5 H), 7.57–7.63 (m, 2 H), 7.76–7.84 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.6, 128.6, 128.8, 129.1, 129.9, 130.5, 135.2, 135.3, 140.4, 197.5.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{13}OSe$: 277.0132; found: 277.0139.

(2-Bromophenyl)(phenyl)selane (16)[6a]
Slightly brown oil; R_f = 0.63 (hexanes).

IR (neat): 3053, 2956, 2922, 2850, 735, 688, 478 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.87–7.20 (m, 3 H), 7.35–7.62 (m, 4 H), 7.63–7.82 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.6, 127.4, 127.9, 128.6, 129.0, 1129.9, 130.6, 132.8, 136.3, 136.5.

GC-MS (EI+): *m*/*z* = 312.

(3,5-Dimethylphenyl)(phenyl)selane (17)[9g]
Colorless oil; R_f = 0.66 (hexanes).

IR (neat): 2921, 2852, 1573, 733, 684 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 6 H), 6.81 (s, 1 H), 7.04 (s, 2 H), 7.12–7.21 (m, 3 H), 7.31–7.39 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.1, 129.3, 129.5, 130.4, 131.1, 131.7, 132.6, 139.1.

GC-MS (EI+): *m*/*z* = 261.

2-(Phenylselanyl)pyridine (18)[9a]
Colorless oil; R_f = 0.54 (EtOAc–hexanes, 1:9).

IR (neat): 3045, 2922, 2852, 1570, 1414, 1083, 741 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.97–7.05 (m, 2 H), 7.33–7.46 (m, 4 H), 7.64–7.76 (m, 2 H), 8.43 (d, *J* = 4.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.5, 124.3, 128.0, 129.0, 129.8, 136.3, 136.8, 150.0, 158.9.

GC-MS (EI+): *m*/*z* = 234.

4-(Phenylselanyl)benzonitrile (19)[6a]
Colorless oil; R_f = 0.65 (EtOAc–hexanes, 1:19).

IR (neat): 3071, 2226, 823, 737, 644 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.49 (m, 7 H), 7.58–7.65 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.6, 118.9, 127.5, 129.2, 130.0, 130.3, 132.5, 135.7, 141.1.

GC-MS (EI+): *m*/*z* = 258.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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