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### Magnetically Separable and Reusable Copper Ferrite Nanoparticles for **Cross-Coupling of Aryl Halides with Diphenyl Diselenide**

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A simple and efficient procedure for the synthesis of diaryl selenides has been developed by a copper ferrite nanoparticle catalyzed reaction of aryl iodides/aryl bromides with diphenyl diselenide in the presence of base and solvent at

#### Introduction

Extensive studies have recently been focused on the development of cross-coupling reactions due to their significance in synthetic chemistry.<sup>[1]</sup> During the past decade, organic selenium compounds have attracted considerable attention in organic synthesis as well as in industry.<sup>[2]</sup> Selenium compounds play an important role in organic chemistry, in view of their potential biological activities, such as antiviral, antihypertensive, antioxidant, antitumor, antimicrobial, and anticancer properties.<sup>[3]</sup> In addition, many chiral as well as achiral organoselenium compounds act as catalysts in organic synthesis.<sup>[4]</sup> Earlier approaches for the synthesis of diaryl selenides include the reaction of aryl selenide anions with aryl halides,<sup>[5]</sup> aryl diazonium salts,<sup>[6]</sup> and the reaction of aryl selenides with aryl boronic acids under an oxygen atmosphere (air) by oxidative coupling in the presence of a transition-metal catalyst.<sup>[7]</sup> The reaction between phenyl tributylstannyl selenide and aryl halides is reportedly catalyzed by the palladium complex Pd(PPh)<sub>4</sub> to obtain the corresponding diaryl and arylalkyl selenides in moderate to good yields [8] Diaryl selenides can also be prepared by the reaction of aryl/alkyl metal selenoates with aryl halides,<sup>[9]</sup> the reaction of organometallic compounds like aryllithiums and arylmercurials with selenium dications,<sup>[10]</sup> and the reduction of diselenides by metals to monoselenides.[11]

However, the existing synthetic protocols have limited scope due to lengthy synthetic sequences, often requiring

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120 °C. Using this protocol, a variety of diselenides were obtained in good to excellent yields. The copper ferrite nanoparticles were magnetically separated, recycled, and reused up to three cycles.

photochemical conditions, instability of reagents, use of strong acidic/basic conditions, strong reducing agents like DIBAL-H or LiAlH<sub>4</sub>,<sup>[12]</sup> polar toxic inflammable organic solvents such as quinoline or HMPA, as well as complex reaction conditions,<sup>[13]</sup> In general, to avoid the foul smelling nature of selenium reagents, diphenyl diselenides are used as starting materials in the synthesis of diphenyl selenides.<sup>[15]</sup> Earlier, Cristau and co-workers reported that aryl selenides can be obtained by a cross-coupling reaction of aryl halides and sodium benzeneselenoate in the presence of a Ni<sup>II</sup>based catalytic system.<sup>[9]</sup> Venkataraman<sup>[16]</sup> et al. explored the cross-coupling reaction of aryl iodides and diphenyl diselenide by using CuI (10 mol-%) and neocuprine as a catalyst and ligand and NaOtBu as a base in toluene at 110 °C to obtain diaryl selenides in good to excellent yields. Several metals like palladium,<sup>[17]</sup> copper,<sup>[18]</sup> nickel,<sup>[9,14,19]</sup> indium,<sup>[20]</sup> and lanthanum<sup>[21]</sup> based catalysts in combination with various ligands are employed for the formation of C-Se bonds. However, these metal-catalyzed reactions involve the addition of well-designed ligands and well-defined catalysts, require longer reaction times, and provide lower yields, which may increase the cost and limit the scope of applications. Very recently, Ranu<sup>[22]</sup> and co-workers reported the heterogeneous Al-supported Cu-catalyzed synthesis of unsymmetrical diaryl/alkyl selenides by using phenylselenyl bromide with phenyl boronic acid in the presence of  $K_2CO_3$ in THF at 70 °C, which provided the coupled product in good yields. Recently, several transition-metal catalytic systems were described under ligand-free conditions such as CuO nanoparticles<sup>[23]</sup> or CuO nanoparticles with Zn<sup>[24]</sup> for C-Se cross-coupling reactions in water between arvl halides/vinyl halides and diphenyl diselenides at 110 °C in DMSO. Zhao<sup>[25]</sup> et al. reported a novel and highly efficient CuS/Fe catalytic system for the coupling of aryl halides with diaryl diselenides in the presence of DMSO as solvent at 110 °C.

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#### **Results and Discussion**

Catalytic processes induced by a heterogeneous catalytic system are more favored than those performed in a homogeneous system in industry because the former is easier to handle, requires simple workup, and excludes metal contamination. The process can be made more advantageous if it can be high yielding, responsive to mild reaction conditions, and efficient in the presence of multifunctional groups with catalyst recyclability. The use of metal nanoparticles as efficient catalysts in organic synthesis is well established, has attracted considerable interest, and has attained tremendous growth in applications in recent times. Recent reports indicate that magnetic nanoparticles are efficient supports for catalysts in various organic transformations.<sup>[26]</sup> Generally, catalysts in nanoscale quantities afford a more effective process and provide greater advantages over traditional methods in organic reactions, as they have higher surface area, fewer coordination sites, and reactive morphologies, which maximize the reaction rates and minimize consumption of the catalyst.<sup>[27]</sup> As a part of our ongoing research program and continuous interest in the field of cross-coupling reactions aimed at the exploration of new synthetic protocols focused on the development of reusable catalysts for the formation of aryl-selenium bonds, Cu/Febased catalysts were examined for their catalytic efficiency, due to their economic and industrial importance. We herein report a significant finding on the use of magnetically separable copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>) nanoparticles<sup>[28]</sup> as catalysts for C-Se coupling processes. To the best of our knowledge, this is the first report on the copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>) nanoparticle catalyzed coupling of aryl iodides/bromides with diphenyl diselenide to form aryl selenides in a very efficient manner.

In a preliminary reaction, iodobenzene (1, R = H) was treated with diphenyl diselenide (2) in the presence of copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>, 5 mol-%) nanoparticles and KOH (2.0 equiv.) in DMSO (2.0 mL) for 18 h at 120 °C to provide selenide **3a** in 98% yield (Scheme 1). The reaction conditions were optimized by taking into consideration parameters such as solvent, base, and catalyst. During the preliminary studies, the influence of different solvents such as DMSO, DMF, toluene, dioxane, and NMP was examined. In this regard, DMSO was observed to be the most efficient solvent for this reaction, affording the best yields for the diaryl selenides (Table 1, Entries 1–5). The effect of base other than KOH, such as K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, Na-O*t*Bu, and KO*t*Bu, was less encouraging (Table 1, Entries 6–10).



Scheme 1. Nano-CuFe $_2O_4$ -catalyzed cross-coupling of aryl halides with diphenyl diselenide.

Table 1. Nano-CuFe $_2O_4$ -catalyzed cross-coupling of iodobenzene with diphenyl diselenide.<sup>[a]</sup>

Entry	Solvent	Base (2 equiv.)	<i>Т</i> [°С]	Yield [%] <sup>[b]</sup>
1	DMSO	KOH	120	98
2	DMF	KOH	120	78
3	toluene	KOH	120	68
4	dioxane	KOH	120	67
5	NMP	KOH	120	65
6	DMSO	$K_3PO_4$	120	68
7	DMSO	$K_2CO_3$	120	60
8	DMSO	$Cs_2CO_3$	120	61
9	DMSO	NaOtBu	120	58
10	DMSO	KOtBu	120	58
11	DMSO	KOH	80	68
12	DMSO	КОН	100	72

[a] Reaction conditions: iodobenzene (1.0 mmol), 2 (0.5 mmol), CuFe<sub>2</sub>O<sub>4</sub> (5 mol-%, 12 mg). N<sub>2</sub>, 120 °C, 18 h. [b] Isolated yield.

Further, we standardized the temperature conditions, as the temperature also had an influence on the product yields. When the reaction temperature was increased to 80, 100, and 120 °C, the product yield increased to 68, 72, and 98%, respectively (Table 1, Entries 11 and 12). Notably, KOH gave the best result with DMSO as solvent at 120 °C. To optimize the protocol, the impact of the catalyst on the reaction efficiency was investigated. We examined the best magnetically separable catalyst for diaryl selenide formation with KOH in DMSO at 120 °C by using different metal nanoparticles with different aryl iodides. However, Cu-Fe<sub>2</sub>O<sub>4</sub> nanoparticles produced diphenyl selenide **3a** in an

Table 2. Optimization studies for the C–Se cross-coupling reaction with different nanocatalysts.<sup>[a]</sup>

Entry	Aryl iodide 1	Selenide	Nanocatalyst	Yield [%] <sup>[b]</sup>
1			Co <sub>3</sub> O <sub>4</sub>	58
2		Se	Fe <sub>3</sub> O <sub>4</sub>	75
3			Sb <sub>2</sub> O <sub>3</sub>	70
4			SnO <sub>2</sub>	60
5			CuFe <sub>2</sub> O <sub>4</sub>	98
6			CoFe <sub>2</sub> O <sub>4</sub>	45
7			Co <sub>3</sub> O <sub>4</sub>	54
8	MeO MeO		Fe <sub>3</sub> O <sub>4</sub>	75
9		Se	$Sb_2O_3$	60
10		MeO	SnO <sub>2</sub>	55
11			CuFe <sub>2</sub> O <sub>4</sub>	89
12			CoFe <sub>2</sub> O <sub>4</sub>	43
13			Co <sub>3</sub> O <sub>4</sub>	45
14	A 5 6 7 8 8	50	Fe <sub>3</sub> O <sub>4</sub>	55
15		J Se	Sb <sub>2</sub> O <sub>3</sub>	46
16		онс	SnO <sub>2</sub>	40
17			CuFe <sub>2</sub> O <sub>4</sub>	85
18			CoFe <sub>2</sub> O <sub>4</sub>	35

[a] Reaction conditions: aryl iodide (1.0 mmol), 2 (0.5 mmol), KOH (2.0 equiv.), DMSO (2.0 mL), N<sub>2</sub>, 120 °C, 18 h. [b] Isolated yield.

impressive yield compared to that obtained with  $Co_3O_4$ ,  $Fe_3O_4$ ,  $Sb_2O_3$ ,  $SnO_2$ , and  $CoFe_2O_4$  (Table 2). Eventually, the catalytic system consisting of  $CuFe_2O_4$  (5 mol-%) nanoparticles was chosen to study the coupling reaction between diphenyl diselenide and aryl/alkyl iodides and aryl bromides in the presence of KOH as a base and DMSO as solvent at 120 °C under a nitrogen atmosphere. An electron-withdrawing group at the *para* or *meta* position and an electrondonating group at the *para* position afforded very clean reactions, and the corresponding product was obtained in high yields under the established reaction conditions. Sterically demanding 2-methyl- and 2-methoxyphenyl iodides (Table 3, Entries 3 and 7) and 1,2-diiodobenzene (Table 3, Entry 17) also afforded good yields. The C–Se coupling reaction conducted with alkyl iodides also gave good yields under the same reaction conditions (Table 3, Entries 24 and 25).

It is significant to note that aryl iodides were more reactive than aryl bromides (Table 3, Entries 26–29) and chlorobenzene did not react under the present reaction conditions (Table 3, Entry 30). The issue of recyclability of the nano-CuFe<sub>2</sub>O<sub>4</sub> catalyst was examined, and the results are summa-

Entry Product Yield [%]<sup>[b]</sup> Entry Product Yield [%]<sup>[b]</sup> Aryl halide 1 Aryl halide 1 3a 98 1 3 78 18 3b 90 2 19 3 84 80 3s 3c Λe 4 86 3d Et Ft 20 3t Me 70 Me 5 3e 90 ŃΟ Мe Me 6 87 3f 21 3u 75 MeC MeC EtO 7 80 3g 22 3v 85 8 85 Me<sub>\_C</sub> 3h Me Me Me Me Мe 9 78 23 80 3i 3w OMe MeC MeC 10 3j 89 E 24 3x 3k 88 78 C<sub>12</sub>H<sub>25</sub>I 11 CI Ċ<sub>12</sub>H<sub>25</sub> 31 89 12 25 C<sub>16</sub>H<sub>33</sub>I 75 3γ F<sub>3</sub>C Ċ<sub>16</sub>Н<sub>33</sub> 3m 74 13 B 3a 26 78 3n 80 Br 14 3b 27 78 3d 85 28 77 30 15 F онс OHC F 3p 86 30 29 60 16 OHC NC NC OHC С 30 3a 3q 85 17 HO но

Table 3. Nano-CuFe<sub>2</sub>O<sub>4</sub>-catalyzed cross-couplig of aryl halides with diphenyl diselenide.<sup>[a]</sup>



rized in Table 4. The yields of the selenides were almost the same up to three consecutive cycles of the same reaction.

Table 4. Recyclability of the nano-CuFe<sub>2</sub>O<sub>4</sub> catalyst.

Entry	Isolated yield [%]	Catalyst recovery [%]
1	98	_
2	91	95
3	89	89

After each cycle, the nanoparticles were magnetically concentrated, washed with ethyl acetate and acetone, air dried, and used directly for the next cycles without further purification. No significant loss of activity in case of Cu-Fe<sub>2</sub>O<sub>4</sub> was observed up to three cycles in the C–Se coupling reaction between aryl iodides and diphenyl diselenide.

AAS (atomic absorption spectroscopy) was employed to determine the copper content of the CuFe<sub>2</sub>O<sub>4</sub> nanoparticles, and it was found to be 27.32%. The leaching of the metal after the second cycle was determined and found to be 0.004% from AAS. From SEM, XRD, and FTIR spectral studies, it was revealed that the CuFe<sub>2</sub>O<sub>4</sub> nanoparticles remained in the same state, even after the three cycles. Figure S1a,b (Supporting Information) shows the SEM image of the CuFe<sub>2</sub>O<sub>4</sub> catalyst before and after the cycle, and it was observed that the morphology and size of the nanoparticle did not change considerably, even after the third cycle. The XRD<sup>[28]</sup> pattern of the CuFe<sub>2</sub>O<sub>4</sub> nanoparticles is presented in Figure S2a,b (Supporting Information) before and after use. It was observed that the diffraction signals of Cu- $Fe_2O_4$  appeared at  $2\theta$  values, which were compared with those reported in the literature. The XRD pattern of the CuFe<sub>2</sub>O<sub>4</sub> nanoparticles showed that identical peaks appeared in the fresh catalyst and the used catalyst. FTIR<sup>[28]</sup> spectra are presented in Figure S3a,b (Supporting Information), and significant bands in the range  $600-400 \text{ cm}^{-1}$ prove the presence of  $CuFe_2O_4$  peaks. These peaks appeared both in the fresh and reused catalyst. From the entire experimental data presented it can be conclusively proven that there was no significant change in the catalytic activity of nano-CuFe<sub>2</sub>O<sub>4</sub> before and after the utilization in the reaction (Table 4).

A plausible mechanism for the  $CuFe_2O_4$  nanoparticle catalyzed coupling reaction involves a heterogeneous process, which may occur on the surface of the catalyst. Evi-



Scheme 2. Plausible mechanistic pathway.

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dently, the results obtained in our studies support an oxidative addition/reductive elimination mechanism for the  $CuFe_2O_4$  nanoparticle catalyzed C–Se cross-coupling of aryl halides with diphenyl diselenide as illustrated in Scheme 2.

#### Conclusions

In conclusion, we have developed a facile copper ferrite nanoparticle catalyzed cross-coupling of aryl halides with diphenyl diselenide to afford diaryl selenides under ligandfree conditions. This method also offers significant improvements with regard to operational simplicity, reaction time, and general applicability to the synthesis of both aryl and alkyl selenides, with high yields of the corresponding products, involving an inexpensive, efficient, and recyclable catalytic system. To the best of our knowledge, this is the first report on the use of magnetically separable recyclable  $CuFe_2O_4$  nanoparticles for a cross-coupling process to afford alkyl and aryl selenides.

### **Experimental Section**

**General:** Iodobenzene (99%), diphenyl diselenide (99.5%), and other aryl halides were purchased from Sigma Aldrich and used without purification. All experiments were carried out under a nitrogen atmosphere. Column chromatography was carried out with 60–120 mesh silica gel using hexane as eluent. Analytical TLC was performed with Merck silica gel 60  $F_{254}$  plates, and the products were visualized by UV detection. <sup>1</sup>H NMR and <sup>13</sup>C NMR (Avance 300, Innova 400 MHz and Bruker Gemini 200 MHz) spectra were recorded in CDCl<sub>3</sub> using TMS as internal standard. Melting points were determined with a Fischer-Johns melting-point apparatus. IR and MS were recorded with a Thermo Nicolet Nexus 670 FTIR spectrometer and Finnegan MAT 1020 mass spectrometer operating at 70 eV.

Representative Experimental Procedure for the Synthesis of Diphenyl Selenides by Using CuFe<sub>2</sub>O<sub>4</sub> as a Catalyst: To stirred solution of iodobenzene (1.0 mmol) and diphenyl diselenide (0.5 mmol) in dry DMSO (2.0 mL) was added nano-CuFe<sub>2</sub>O<sub>4</sub> powder (5 mol-%, 12 mg) and KOH (2.0 equiv.), and the reaction mixture was heated at 120 °C under a nitrogen atmosphere for 18 h; the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under vacuum to give the crude product, which was purified by column chromatography (hexane) to yield expected product **3a** (228 mg, 98%) as a yellowish oil. The purity of the product was confirmed by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy and mass spectrometry.

**Recycling Experiment for CuFe<sub>2</sub>O<sub>4</sub> Nanoparticle Recovery:** After completion of the reaction, the catalyst was recovered magnetically with the aid of a magnet, washed with ethyl acetate followed by acetone, and then air dried. The recovered catalyst was used directly in the next runs and no substantial loss of activity was observed up to three cycles.

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**Diphenyl Selane (3a):**<sup>[187]</sup> Yellowish oil (98%, 228 mg; Table 3, Entry 1). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.43–7.41 (m, 4 H), 7.31–7.19 (m, 6 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 132.9, 131.1, 129.2, 127.2 ppm. MS (ESI): *m/z* = 256 [M + Na].

**Phenyl(***p***-tolyl)selane (3b):**<sup>[18f]</sup> Yellowish oil (90%, 197 mg; Table 3, Entry 2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.39–7.32 (m, 4 H), 7.24–7.15 (m, 3 H), 7.03 (d, *J* = 8.49 Hz, 2 H), 2.34 (s, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 137.9, 133.5, 132.3, 130.1, 129.2, 126.9, 21.3 ppm. IR (neat):  $\hat{v}$ 3070, 2858, 1570, 1508, 1055, 915, 842, 730 cm<sup>-1</sup>. MS (ESI): *m/z* = 270 [M + Na].

**Phenyl**(*o*-tolyl)selane (3c):<sup>[18f]</sup> Yellowish oil (80%, 197 mg; Table 3, Entry 3). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.38–7.31 (m, 2 H), 7.26 (d, *J* = 7.65 Hz, 1 H), 7.25–7.11 (m, 5 H), 7.01 (t, *J* = 6.8 Hz, 1 H), 2.32 (s, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.9, 133.4, 132.8, 131.9, 130.5, 129.9, 129.3, 127.5, 127.0, 126.5, 22.8 ppm. IR (neat):  $\tilde{v}3069$ , 2925, 1575, 1450, 930, 840, 710 cm<sup>-1</sup>. MS (ESI): *m*/*z* = 270 [M + Na].

**(4-Ethylphenyl)(phenyl)selane (3d):**<sup>[23a]</sup> Yellowish oil (86%, 223 mg; Table 3, Entry 4). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.42–7.32 (m, 4 H), 7.25–7.16 (m, 3 H), 7.08 (d, *J* = 8.12 Hz, 2 H), 2.62 (q, *J* = 7.5, 7.5 Hz, 2 H), 1.24 (t, *J* = 7.5 Hz, 1 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.9, 133.4, 132.8, 131.9, 130.5, 129.9, 129.3, 127.5, 127.0, 126.5, 22.8 ppm. IR (neat):  $\tilde{v}$ 3054, 2933, 2842, 1561, 917, 810, 741 cm<sup>-1</sup>. MS (ESI): *m*/*z* = 284 [M + Na].

(3,5-Dimethylphenyl)(phenyl)selane (3e):<sup>[22]</sup> Yellowish oil (90%, 234 mg; Table 3, Entry 5). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.41–7.37 (m, 2 H), 7.25–7.17 (m, 3 H), 7.07 (br. s, 2 H), 6.85 (br. s, 1 H), 2.27 (s, 6 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.7, 132.4, 131.0, 130.3, 129.2, 129.1, 126.8, 124.3, 21.1 ppm. IR (neat):  $\tilde{v}$ 3050, 2918, 1570, 809, 727 cm<sup>-1</sup>. MS (ESI): m/z = 284 [M + Na].

(4-Methoxyphenyl)(phenyl)selane (3f):<sup>[187]</sup> Yellowish oil (87%, 228 mg; Table 3, Entry 6). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.48 (d, *J* = 8.0 Hz, 2 H), 7.30–7.25 (m, 2 H), 7.23–7.16 (m, 3 H), 6.80 (d, *J* = 8.0 Hz, 2 H), 3.76 (s, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.5, 136.2, 133.5, 131.0, 129.2, 126.5, 119.8, 115.4, 55.5 ppm. IR (neat):  $\hat{v}$ 1575, 1490, 1045, 853, 747 cm<sup>-1</sup>. MS (ESI): *m*/*z* = 286 [M + Na].

(2-Methoxyphenyl)(phenyl)selane (3g):<sup>[23a]</sup> Yellowish oil (80%, 210 mg; Table 3, Entry 7). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.45 (d, J = 8.5 Hz, 2 H), 7.23–7.18 (m, 5 H), 6.82 (d, J = 8.49 Hz, 2 H), 3.79 (s, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 156.4, 135.3, 130.9, 129.3, 128.5, 128.0, 127.6, 121.9, 121.4, 109.9, 55.8 ppm. IR (neat):  $\tilde{v}$  = 1577, 1473 cm<sup>-1</sup>. MS (ESI): m/z = 286 [M + Na].

(4-*tert*-Butylphenyl)(phenyl)selane (3h):<sup>[23a]</sup> Yellowish oil (85%, 245 mg; Table 3, Entry 8). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.42–7.35 (m, 4 H), 7.28–7.19 (m, 5 H), 1.31 (s, 9 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.5, 133.2, 132.4, 131.7, 129.1, 127.2, 126.9, 126.4, 34.6, 31.3 ppm. IR (neat):  $\hat{v}$ 3055, 2915, 2854, 1022, 842, 736 cm<sup>-1</sup>. MS (ESI): *m*/*z* = 312 [M + Na].

(2,4-Dimethoxyphenyl)(phenyl)selane (3i):<sup>[23a]</sup> Yellowish oil (78%, 228 mg; Table 3, Entry 9). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.41–7.35 (m, 2 H), 7.26–7.15 (m, 4 H), 6.52–6.40 (m, 2 H), 3.82 (s, 3 H), 3.81 (s, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 161.2, 159.4, 135.6, 132.5, 131.1, 129.1, 126.5, 110.2, 105.5, 98.9, 55.8, 55.3 ppm. IR (neat):  $\hat{v}$ 3058, 2930, 1579, 1061, 917, 827, 735 cm<sup>-1</sup>. MS (ESI): = 317 [M + Na].

**(4-Fluorophenyl)(phenyl)selane (3j):**<sup>[23a]</sup> Yellowish oil (89%, 223 mg; Table 3, Entry 10). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): *δ* = 7.54–7.51 (m, 2 H), 7.41–7.04 (m, 6 H), 6.98–6.85 (m, 1 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 134.4, 130.2, 129.8, 129.1, 128.0, 127.3, 118.5, 118.3, 114.0, 113.1 ppm. IR (neat):  $\tilde{v}$ 1599, 1576, 1060, 827, 730 cm<sup>-1</sup>. MS (ESI): *m/z* = 274 [M + Na].

(4-Chlorophenyl)(phenyl)selane (3k):<sup>[23a]</sup> Yellowish oil (88%, 234 mg; Table 3, Entry 11). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47–7.39 (m, 2 H), 7.33 (d, J = 8.0 Hz, 2 H), 7.27–7.19 (m, 5 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 134.1, 133.3, 129.6, 127.5 ppm. IR (neat):  $\tilde{v}1595$ , 1570, 1050 cm<sup>-1</sup>. MS (ESI): m/z = 290 [M + Na].

**Phenyl[4-(trifluoromethyl)phenyl]selane (31)**:<sup>[21a]</sup> Yellowish oil (89%, 267 mg; Table 3, Entry 12). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.58–7.50 (m, 2 H), 7.49–7.36 (m, 4 H), 7.35–7.23 (m, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 133.6, 133.4, 132.7, 132.1, 130.2, 129.3, 129.2, 128.4, 127.1, 126.5 ppm. IR (neat):  $\hat{v}$ 1599, 1576, 1060, 827, 730 cm<sup>-1</sup>. MS (ESI): m/z = 324 [M + Na].

**Phenyl[3-(trifluoromethyl)phenyl]selane (3m)**:<sup>[24]</sup> Yellowish oil (74%, 222 mg; Table 3, Entry 13). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.68–7.62 (m, 1 H), 7.56–7.41 (m, 4 H), 7.38–7.19 (m, 4 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 135.1, 134.0, 133.2, 129.6, 129.5, 129.4, 128.4, 128.2, 125.4, 123.6, 121.7 ppm. IR (neat):  $\tilde{v}$ 2930, 1577, 1475, 1421, 1320, 1166 cm<sup>-1</sup>. MS (ESI): *m*/*z* = 324 [M + Na].

**Phenyl(***m***-tolyl)selane (3n):**<sup>[23a]</sup> Yellowish oil (80%, 197 mg; Table 3, Entry 14). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.42–7.37 (m, 2 H), 7.28–7.19 (m, 5 H), 7.11 (t, *J* = 7.5 Hz, 1 H), 7.02 (d, *J* = 7.5 Hz, 1 H), 2.31 (s, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.2, 133.8, 132.7, 131.2, 130.5, 130.2, 129.3, 129.2, 128.4, 127.3, 21.3 ppm. IR (neat):  $\tilde{v}$ 3060, 2925, 2854, 1571, 1508, 1455, 921, 842, 717 cm<sup>-1</sup>. MS (ESI): *m/z* = 270 [M + Na].

**4-(Phenylselanyl)benzaldehyde (30):**<sup>[7a]</sup> Yellowish oil (85%, 221 mg; Table 3, Entry 15). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.84 (s, 1 H), 7.91–7.31 (m, 4 H), 7.30–7.16 (m, 3 H), 7.09 (d, *J* = 8.12 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 192.0, 148.2, 134.2, 133.3, 131.2, 130.1, 129.2, 129.0, 126.9 ppm. IR (neat):  $\tilde{v}$  = 3060, 1697, 1597, 1560, 1475, 1403 cm<sup>-1</sup>. MS (ESI): *m*/*z* = 284 [M + Na].

**4-(Phenylselanyl)benzonitrile (3p):**<sup>[25]</sup> Yellowish oil (86%, 221 mg; Table 3, Entry 16). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.55–7.49 (m, 4 H), 7.30–7.23 (m, 5 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 134.0, 132.9, 129.1, 127.5, 120.2, 116.5 ppm. IR (neat):  $\tilde{v}$  = 2924, 2250, 1567, 1577, 1403 cm<sup>-1</sup>. MS (ESI): *m/z* = 281 [M + Na].

**4-(Phenylselanyl)phenol** (**3q**):<sup>[18c]</sup> Yellowish oil (85%, 211 mg; Table 3, Entry 17). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.44 (d, *J* = 8.30 Hz, 2 H), 7.34–7.23 (m, 2 H), 7.20–7.11 (m, 3 H), 6.74 (d, *J* = 8.30 Hz, 2 H), 6.50 (br. s, 1 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 156.1, 136.8, 133.2, 130.5, 129.1, 126.4, 119.8, 116.5 ppm. IR (neat):  $\tilde{v}3400$ , 1599, 1130 cm<sup>-1</sup>. MS (ESI): *m/z* = 272 [M + Na].

**1,2-Bis(phenylselanyl)benzene (3r):**<sup>[16]</sup> Yellowish oil (78%, 302 mg; Table 3, Entry 18). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.49–7.32 (m, 6 H), 7.30–7.10 (m, 8 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 133.0, 131.2, 129.2, 128.9, 127.2 ppm. MS (ESI): *m*/*z* = 411 [M + Na].

**1,4-Bis(phenylselanyl)benzene (3s):**<sup>[23a]</sup> White solid; m.p 101–102 °C (84%, 325 mg; Table 3, Entry 19). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.48–7.42 (m, 4 H), 7.29–7.22 (m, 10 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 133.5, 133.2, 130.7, 130.5, 129.4, 127.5 ppm. MS (ESI): m/z = 411 [M + Na].

(3-Nitrophenyl)(phenyl)selane (3t):<sup>[21a]</sup> Yellowish oil (70%, 194 mg; Table 3, Entry 20). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.15 (s, 1 H), 8.03 (d, J = 8.40 Hz, 1 H), 7.61–7.50 (m, 3 H), 7.41–7.24 (m, 4 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.9, 147.8, 137.6, 133.5, 133.1, 131.9, 129.1, 127.7, 123.5 ppm. IR (neat):  $\tilde{v}$ 3040, 3100,



3090, 2950, 2854, 1570, 930, 845, 725 cm<sup>-1</sup>. MS (ESI): m/z = 301 [M + Na].

**Ethyl 4-(Phenylselanyl)benzoate (3u):**<sup>[25]</sup> Yellowish oil (75%, 228 mg; Table 3, Entry 21). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.57–7.48 (m, 4 H), 7.31–7.24 (m, 5 H), 4.32 (q, *J* = 7.6 Hz, 2 H), 1.32 (t, *J* = 7.59 Hz, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.2, 139.5, 135.1, 130.5, 130.2, 129.8, 128.7, 128.5, 127.9, 61.0, 14.5 ppm. IR (neat):  $\tilde{v}$ 3065, 1667, 1635, 1594, 1420 cm<sup>-1</sup>. MS (ESI): *m*/*z* = 329 [M + Na].

**2-(Phenylselanyl)thiophene (3v):**<sup>[16]</sup> Yellowish oil (85%, 203 mg; Table 3, Entry 22). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.54–7.46 (m, 3 H), 7.28–7.20 (m, 5 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 133.0, 130.9, 129.1, 127.5 ppm. IR (neat):  $\tilde{v}$ 3070, 1515, 1470, 1435, 1395 cm<sup>-1</sup>. MS (ESI): m/z = 362 [M + Na].

(Naphthalene-5-yl)(phenyl)selane (3w):<sup>[25]</sup> Yellowish oil (80%, 227 mg; Table 3, Entry 23). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.30 (m, 1 H), 7.80–7.72 (m, 2 H), 7.68 (d, *J* = 7.5 Hz, 1 H), 7.46–7.37 (m, 2 H), 7.33–7.10 (m, 6 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 134.4, 133.9, 131.5, 129.6, 129.2, 129.1, 128.4, 127.8, 126.8, 126.5, 126.3, 126.1 ppm. IR (neat):  $\tilde{v}$ 3054, 1560, 1510 cm<sup>-1</sup>. MS (ESI): *m*/*z* = 306 [M + Na].

**Dodecyl(phenyl)selane** (**3x**):<sup>[20a]</sup> Yellowish oil (78%, 254 mg; Table 3, Entry 24). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.49–7.30 (m, 2 H), 7.28–7.15 (m, 3 H), 2.92–2.82 (m, 2 H), 1.76–1.61 (m, 2 H), 1.46–1.34 (m, 2 H), 1.33–1.18 (m, 16 H), 0.89 (t, *J* = 6.04 Hz, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 132.5, 130.8, 128.9, 126.5, 32.0, 30.2, 29.9, 29.7, 29.4, 29.2, 27.9, 22.7, 14.2 ppm. IR (neat):  $\tilde{v}$  = 3400, 3010, 2850, 1678 cm<sup>-1</sup>. MS (ESI): *m/z* = 348 [M + Na].

**Hexadecyl(phenyl)selane (3y):**<sup>[20b]</sup> White solid; m.p 89–90 °C (75%, 286 mg; Table 3, Entry 25). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.48–7.40 (m, 2 H), 7.28–7.14 (m, 3 H), 2.91–2.81 (m, 2 H), 1.75–1.62 (m, 2 H), 1.47–1.18 (m, 26 H), 0.88 (t, *J* = 6.98 Hz, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 132.5, 130.8, 128.9, 126.5, 32.1, 30.2, 29.9, 29.8, 29.6, 29.5, 29.2, 29.1, 28.0, 22.8, 14.3 ppm. IR (neat): v3400, 3359, 3010, 2850 cm<sup>-1</sup>. MS (ESI): m/z = 404 [M + Na].

**Supporting Information** (see footnote on the first page of this article): Copies of the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all the compounds.

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