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Formation of Carbon−Sulfur and Carbon−Selenium Bonds by Palladium-Catalyzed Decarboxylative Cross-Couplings of Hindered 2,6-Dialkoxybenzoic Acids

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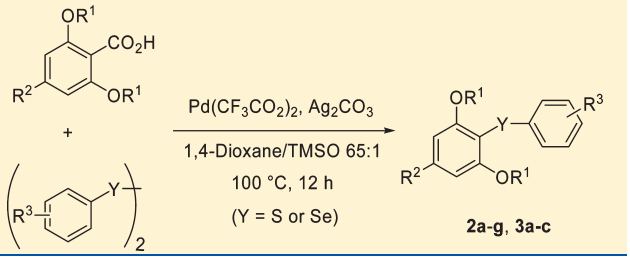
Supporting Information

ABSTRACT: A simple route to diaryl sulfides using a decarboxylative palladium-catalyzed reaction between electron-rich 2,6-dialkoxybenzoic acid derivatives and diaryl disulfides is reported. This coupling proceeds efficiently in the presence of $Pd(CF_3CO_2)_2$ and Ag_2CO_3 in a 65:1 mixture of 1,4-dioxane and tetramethylene sulfoxide (TMSO). We present also the first formation of a carbon−selenium bond via a palladium-catalyzed decarboxylative cross-coupling.



Palladium-catalyzed cross-couplings offer one of the most powerful routes for the formation of bonds between two sp^2 carbons with high yields under mild reaction conditions.[1,2] Extensive work has been devoted during the past decade to develop related methodologies for the creation of bonds between a sp^2 carbon and a nitrogen[3,4] or, very recently, an oxygen atom.[5,6] The formation of a bond between a sp^2 carbon and a sulfur atom has received less attention, despite the important pharmaceutical properties of many aryl sulfides as potent drugs for the treatment of inflammation,[7] cancer,[8] immunodeficiency virus (HIV),[9] and Alzheimer's and Parkinson's diseases.[10,11] These sulfides were traditionally prepared via aromatic nucleophilic substitutions of activated chloroarenes with thiolates.[12] Recently, several groups have reported mild and efficient conditions for the formation of diaryl sulfides by couplings of aryl halides with aryl thiols in the presence of copper,[13] palladium,[14,15] nickel,[16] cobalt,[17] iron,[18] or indium catalysts.[19,20] Diaryl sulfides have also been prepared via copper-catalyzed reactions of unfunctionalized arenes with diaryl disulfides, but only simple target molecules can be obtained by this method.[21]

Very recently, the easily available arenecarboxylic acids have emerged as promising reagents for the formation of a bond between an aryl carbon and a sp^2 carbon via decarboxylative cross-couplings[22,23] but the formation of carbon−sulfur bonds by this method was only very recently reported: the palladium-copper-catalyzed decarboxylative cross-coupling between a 2-substituted arenecarboxylic acid and a thiol or a disulfide[24] afforded good yields only in the presence of an electron-withdrawing group on the arenecarboxylic acid.[25] We have recently published the palladium-catalyzed formation of aryl−aryl bonds from an arenecarboxylic acid and an aryl iodide[26] or a diaryl iodonium triflate.[27] We present here a simple and efficient route to diaryl sulfides from hindered electron-rich 2,6-disubstituted arenecarboxylic acids.

At the outset, we used experimental conditions analogous to those of our previous work,[26,27] and Table 1 presents the optimization experiments. It turned out that $PdCl_2$ was the most active catalyst and afforded **2a** in 53% yield (entry 2). No improvement was achieved by increasing the reaction time or the amounts of catalyst or Ag_2CO_3[23a] or by performing the reaction in anhydrous conditions under an oxygen atmosphere or in the presence of molecular sieves. The replacement of diphenyl disulfide by thiophenol (1.1 equiv) gave **2a** in <30% yield. Apart from $Pd(CF_3CO_2)_2$, which gave results similar to those obtained with $PdCl_2$, other Pd(II) or Pd(0) catalysts gave **2a** in poor yields (entries 3−9). Performing the coupling with $PdCl_2$ in the presence of various ligands,[28] or in a 9:1 mixture of DMF/DMSO,[23e] afforded **2a** in <50% yield (entries 10−17). Replacing $PdCl_2$ with $Ni(acac)_2$, $NiCl_2(PPh_3)_2$, or CuI gave 1,3-dimethoxybenzene as the major product and only traces of **2a**. Modification of the order of addition of the reagents or replacement of Ag_2CO_3 by other silver salts (Ag_3PO_4, AgOTf, AgOAc) by other bases (Li_2CO_3, Cs_2CO_3, Et_4NHCO_3, CsF, or TMSOK) afforded **2a** in only much lower yields. In all cases of Table 1, even entry 1, it should be noted that no starting material was present at the end of the reaction and the only byproduct that could be isolated was 1,3-dimethoxybenzene. While our work was in progress, the group of Su[29] has reported an efficient direct arylation of indoles with arenecarboxylic acids using $Pd(CF_3CO_2)_2$, Ag_2CO_3, and TMSO in refluxing 1,4-dioxane. Inspired by this report, the coupling of **1a** and diphenyl disulfide was performed with $Pd(CF_3CO_2)_2$ in a 65:1 mixture either of 1,4-dioxane/DMSO or of 1,4-dioxane/TMSO. It turned out that **2a** was obtained, respectively, in improved 68% and 70% yields (entries 19 and 20). Use of 0.15 equiv of $Pd(CF_3CO_2)_2$ gave **2a** in a still good

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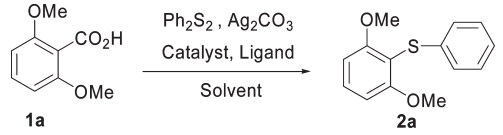
Table 1. Determination of the Reaction Conditions



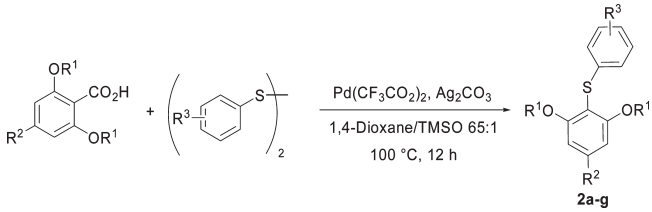
entry	catalyst	ligand	solvent	yield[a] (%)
1[b]			DMSO	no reaction
2[b,c]	$PdCl_2$		DMSO	53
3[b,c]	$PdCl_2(PPh_3)_2$		DMSO	<10
4[b,c]	$PdCl_2(PCy_3)_2$		DMSO	25
5[b,c]	$PdCl_2(MeCN)_2$		DMSO	49
6[b,c]	$Pd(OAc)_2$		DMSO	34
7[b,c]	$Pd(CF_3CO_2)_2$		DMSO	49
8[b,c]	$Pd_2(dba)_3$		DMSO	35
9[b,c]	$Pd(PPh_3)_4$		DMSO	<10
10[b−d]	$PdCl_2$	$AsPh_3$	DMSO	25
11[b−d]	$PdCl_2$	P(*o*-tolyl)$_3$	DMSO	17
12[b−d]	$PdCl_2$	JohnPhos	DMSO	47
13[b−d]	$PdCl_2$	DavePhos	DMSO	27
14[b−d]	$PdCl_2$	tBu XPhos	DMSO	40
15[b,c,e]	$PdCl_2$	DPEphos	DMSO	30
16[b,c,e]	$PdCl_2$	DPPE	DMSO	15
17[b,c]	$PdCl_2$		DMF/DMSO 9:1	40
18[f]	$Pd(CF_3CO_2)_2$		1,4-dioxane	64
19[f]	$Pd(CF_3CO_2)_2$		1,4-dioxane/DMSO 65:1	68
20[f]	$Pd(CF_3CO_2)_2$		1,4-dioxane/TMSO 65:1	70[g,h] (60)[i]
21[f]	$Pd(OAc)_2$		1,4-dioxane/TMSO 65:1	22
22[f]	$PdCl_2$		1,4-dioxane/TMSO 65:1	31

[a] Calculated yields by ^{1}H NMR of the crude reaction mixture. [b] Reaction conditions: 2,6-dimethoxybenzoic acid (0.50 mmol, 1.0 equiv), diphenyl disulfide (1.1 equiv), and Ag_2CO_3 (1.1 equiv) at 150 °C for 6 h. [c] Reaction performed in the presence of a Pd catalyst (0.2 equiv). [d] Reaction performed in the presence of 0.4 equiv of ligand. [e] Reaction performed in the presence of 0.2 equiv of ligand. [f] Reaction conditions: 2,6-dimethoxybenzoic acid (0.50 mmol, 1.0 equiv), diphenyl disulfide (1.1 equiv), Ag_2CO_3 (2.2 equiv), and Pd catalyst (0.2 equiv) at 100 °C for 12 h. [g] Using only 0.5 equiv of diphenyl disulfide gave **2a** in ca. 40% yield. [h] Performing the coupling with 1.1 equiv of Ag_2CO_3 afforded **2a** in a lower 53% yield. [i] Coupling performed in the presence of 0.15 equiv of Pd catalyst. Using 0.1 equiv of Pd catalyst afforded **2a** in <30% yield. Using 0.3 equiv or 0.4 equiv of Pd catalyst gave 74−75% yields (vide infra).

60% yield (entry 20). No improvement was achieved by replacement of $Pd(CF_3CO_2)_2$ with $Pd(OAc)_2$ or $PdCl_2$ in these conditions (entries 21 and 22). Finally, performing the coupling in the presence of only 0.05 equiv of Ag_2CO_3 and 2.1 equiv of Na_2CO_3 afforded **2a** in a much lower yield of 36%. This shows that a catalytic amount of the silver salt is not sufficient for the reaction to proceed satisfactorily.

The scope and limitations of the reaction were then evaluated (Table 2). The use of electron-rich 2,6-dimethoxybenzoic acid and 2,4,6-trimethoxybenzoic acid afforded the desired diaryl sulfides, respectively, in 75% and 71% yields using 0.3 equiv of $Pd(CF_3CO_2)_2$ (entries 1 and 2). Interestingly, the sterically more hindered 2,6-diisopropoxybenzoic acid gave the corresponding diaryl sulfide in a good 68% yield (entry 3). The reaction of **1a** with various diaryl disulfides bearing electron-donating

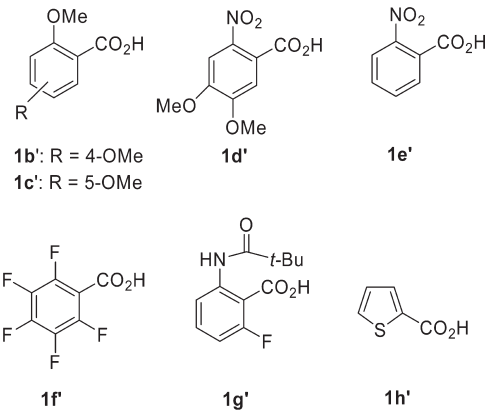
Table 2. Synthesis of Diaryl Sulfides



entry[a]	R^1	R^2	R^3	product	yield[b] (%)
1	Me	H	H	**2a**	75 (60)[c]
2	Me	OMe	H	**2b**	71 (65)[c]
3[d]	iPr	H	H	**2c**	68 (40)[c]
4	Me	H	4-Me	**2d**	64 (51)[c]
5	Me	H	4-OMe	**2e**	58 (47)[c]
6	Me	H	4-Cl	**2f**	50 (39)[c]
7	Me	H	4-NO_2	**2g**	51 (30)[c]

[a] Reaction conditions: arenecarboxylic acid (0.50 mmol, 1.0 equiv), diaryl disulfide (1.1 equiv), Ag_2CO_3 (2.2 equiv), and $Pd(CF_3CO_2)_2$ (0.3 equiv). [b] Isolated yields after flash chromatography of the crude reaction mixture on silica gel. [c] Yield obtained in the presence of only 0.15 equiv of $Pd(CF_3CO_2)_2$. [d] Reaction performed in the presence of 1.6 equiv of diphenyl disulfide.

Scheme 1. Structures of Arenecarboxylic Acids Used



or electron-withdrawing groups gave the corresponding products in 50−64% yields (entries 4−7).[30] It is noteworthy that the use of only 0.15 equiv of the palladium catalyst gave the desired compounds in still acceptable yields (Table 2). As has already been noted during the optimization studies, no starting material was ever found at the end of the reaction, the only byproduct being the decarboxylated arenes. The cross-couplings between **1a** and 2,4-dimethoxybenzoic acid **1b′**, 2,5-dimethoxybenzoic acid **1c′**, 2-nitro-4,5-dimethoxybenzoic acid **1d′**, 2-nitrobenzoic acid **1e′**, pentafluorobenzoic acid **1f′**, 2-fluoro-6-(pivalamido)-benzoic acid **1g′**, and 2-thiophenecarboxylic acid **1h** were unsuccessful (Scheme 1).

Finally, we used analogous conditions to obtain diaryl selenides. These studies are still underway. The coupling of **1a** with diphenyl diselenide (Scheme 2) gave us the desired diaryl selenide **3a** in 62% isolated yield, whereas performing the reaction with 1,2-bis(4-methylphenyl)diselenide or 1,2-bis(4-chlorophenyl) diselenide[31] afforded the corresponding diaryl selenides **3b** and **3c**,

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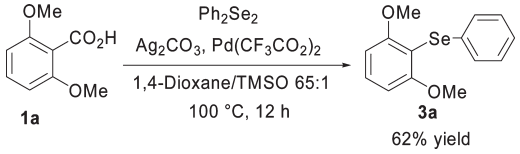
Scheme 2. Synthesis of a Diaryl Selenide



respectively, in 29% and 25% yields, whereas no reaction was observed with dimethyl diselenide. To the best of our knowledge, this cross-coupling represents the first reaction of formation of a carbon−selenium bond from an arenecarboxylic acid.[20,32]

In conclusion, it should be noted that this carbon−sulfur bond-forming reaction constitutes for arenecarboxylic acids bearing electron-donating substituents a useful addition to the method previously published by Liu and co-workers[24] which seems reserved to acids possessing electron-withdrawing substituents.

EXPERIMENTAL SECTION

General Remarks. The reagents were obtained from commercial sources and were used without further purification. 1,4-Dioxane was purified by distillation under vacuum before use. Purifications of compounds **2a**−**g** and **3a**−**c** were performed by flash chromatography on silica gel (40−63 μm). ^{1}H and ^{13}C NMR spectra were recorded using a 400 MHz instrument in $CDCl_3$. Chemical shifts are reported in parts per million (δ) downfield from TMS. Spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), hept (heptuplet) and m (multiplet). 2,6-Diisopropoxybenzoic acid, 1,2-bis(4-methylphenyl)diselenide, and 1,2-bis(4-chlorophenyl)diselenide were prepared according to previous literature reports.[31,33] HRMS spectra were obtained by positive ESI ionization.

General Procedure for the Syntheses of Compounds 2a−b,d−g and 3a−c. 1,4-Dioxane (8 mL) and TMSO (0.12 mL) were added to a mixture of the diaryl disulfide or diaryl diselenide (0.55 mmol, 1.1 equiv), the arenecarboxylic acid (0.50 mmol, 1.0 equiv), Ag_2CO_3 (1.1 mmol, 303 mg, 2.2 equiv), and $Pd(CF_3CO_2)_2$ (0.15 mmol, 50 mg, 0.3 equiv). The reaction mixture was directly refluxed for 12 h. After being cooled to rt, the reaction mixture was filtered with Celite and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography on silica gel to afford pure reaction products after drying under vacuum (0.1 mbar).

1,3-Dimethoxy-2-(phenylthio)benzene (***2a***). Elution with AcOEt/cyclohexane 5:95 afforded 92 mg (75% yield) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.82 (s, 6H), 6.65 (d, ^3J = 8.6 Hz, 2H), 7.06 (m, 3H), 7.17 (m, 2H), 7.38 (t, ^3J = 8.6 Hz, 1H). ^{13}C NMR (80 MHz, $CDCl_3$) δ (ppm): 56.3, 104.3, 107.4, 124.6, 126.1, 128.5, 131.2, 137.8, 161.5. IR ($CHCl_3$) ν (cm^{-1}) 3069, 3003, 2940, 1582, 1471, 1430, 1291, 1252, 1086, 1024. HRMS: m/z calcd for $C_{14}H_{15}O_2S$ $[M + H]^+$ 247.0787, found $[M + H]^+$ 247.0777.

1,3,5-Trimethoxy-2-(phenylthio)benzene (***2b***). Elution with AcOEt/cyclohexane 15:85 afforded 98 mg (71% yield) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.82 (s, 6H), 3.88 (s, 3H), 6.23 (s, 2H), 7.04 (m, 3H), 7.16 (m, 2H). ^{13}C NMR (80 MHz, $CDCl_3$) δ (ppm): 55.4, 56.3, 91.2, 124.3, 125.6, 128.5, 138.6, 162.5, 162.9. IR ($CHCl_3$) ν (cm^{-1}) 3059, 3004, 2964, 2939, 1580, 1467, 1456, 1339, 1227, 1205, 1124, 1094. HRMS: m/z calcd for $C_{15}H_{17}O_3S$ $[M + H]^+$ 277.0893, found $[M + H]^+$ 277.0895.

1,3-Dimethoxy-2-((4-methylphenyl)thio)benzene (***2d***). Elution with AcOEt/cyclohexane 5:95 afforded 83 mg (64% yield) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.26 (s, 3H), 3.83 (s, 6H), 6.64 (d, ^3J = 8.5 Hz, 2H), 6.98 (m, 4H), 7.36 (t, ^3J = 8.5 Hz, 1H). ^{13}C NMR (80 MHz, $CDCl_3$) δ (ppm): 20.9, 56.3, 104.3, 126.6, 129.3, 131.0, 134.4, 161.5. IR ($CHCl_3$) ν (cm^{-1}) 3004, 2924, 1580, 1492, 1431, 1252, 1106. HRMS: m/z calcd for $C_{15}H_{17}O_2S$ $[M + H]^+$ 261.0944, found $[M + H]^+$ 261.0929.

1,3-Dimethoxy-2-((4-methoxyphenyl)thio)benzene (***2e***). Elution with AcOEt/cyclohexane 15:85 afforded 93 mg (67% yield) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.75 (s, 3H), 3.83 (s, 6H), 6.62 (d, ^3J = 8.3 Hz, 2H), 6.75 (d, ^3J = 6.9 Hz, 2H), 7.12 (d, ^3J = 6.9 Hz, 2H), 7.33 (t, ^3J = 8.3 Hz, 1H). ^{13}C NMR (80 MHz, $CDCl_3$) δ (ppm): 55.3, 56.3, 104.3, 114.2, 128.3, 129.4, 130.7, 157.7, 161.2. IR ($CHCl_3$) ν (cm^{-1}) 3001, 2961, 2938, 1579, 1492, 1470, 1430, 1285, 1251, 1173, 1104, 1030. HRMS: m/z calcd for $C_{15}H_{17}O_3S$ $[M + H]^+$ 277.0893, found $[M + H]^+$ 277.0891.

1,3-Dimethoxy-2-((4-chlorophenyl)thio)benzene (***2f***). Elution with AcOEt/cyclohexane 5:95 afforded 70 mg (50% yield) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.83 (s, 6H), 6.65 (d, ^3J = 8.6 Hz, 2H), 6.98 (d, ^3J = 8.6 Hz, 2H), 7.13 (d, ^3J = 8.6 Hz, 2H), 7.39 (t, ^3J = 8.6 Hz, 1H). ^{13}C NMR (80 MHz, $CDCl_3$) δ (ppm): 56.3, 104.3, 107.0, 127.5, 128.6, 130.3, 131.3, 136.5, 161.4. IR ($CHCl_3$) ν (cm^{-1}) 3006, 2938, 1577, 1472, 1427, 1292, 1251, 1106, 1089, 1007. HRMS: m/z calcd for $C_{14}H_{14}ClO_2S$ $[M + H]^+$ 281.0403, found $[M + H]^+$ 281.0410.

1,3-Dimethoxy-2-((4-nitrophenyl)thio)benzene (***2g***). Elution with AcOEt/cyclohexane 1:9 afforded 74 mg (51% yield) of a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.84 (s, 6H), 6.69 (d, ^3J = 8.3 Hz, 2H), 7.07 (d, ^3J = 8.8 Hz, 2H), 7.47 (t, ^3J = 8.3 Hz, 1H), 8.02 (d, ^3J = 8.8 Hz, 2H). ^{13}C NMR (80 MHz, $CDCl_3$) δ (ppm): 56.3, 104.4, 123.7, 124.5, 126.3, 128.6, 132.4, 137.1, 144.7, 148.4, 161.4. IR ($CHCl_3$) ν (cm^{-1}) 3009, 2942, 1582, 1512, 1473, 1432, 1337, 1216, 1107, 1084. HRMS: m/z calcd for $C_{14}H_{14}NO_4S$ $[M + H]^+$ 292.0638, found $[M + H]^+$ 292.0634.

1,3-Dimethoxy-2-(phenylseleno)benzene (***3a***). Elution with AcOEt/cyclohexane 5:95 afforded 91 mg (62% yield) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.80 (s, 6H), 6.63 (d, ^3J = 8.3 Hz, 2H), 7.14 (m, 3H), 7.17 (m, 2H), 7.36 (t, ^3J = 8.3 Hz, 1H). ^{13}C NMR (80 MHz, $CDCl_3$) δ (ppm): 56.3, 104.3, 125.5, 128.6, 129.5, 131.0, 132.8, 145.8, 160.9. IR ($CHCl_3$) ν (cm^{-1}) 3000, 2959, 2931, 1724, 1581, 1469, 1430, 1249, 1105. HRMS: m/z calcd for $C_{14}H_{15}O_2Se$ $[M + H]^+$ 295.0237, found $[M + H]^+$ 295.0240.

1,3-Dimethoxy-2-((4-methylphenyl)seleno)benzene (***3b***). Elution with AcOEt/cyclohexane 5:95 afforded 44 mg (29% yield) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.27 (s, 3H), 3.79 (s, 6H), 6.61 (d, ^3J = 8.6 Hz, 2H), 6.96 (d, ^3J = 7.8 Hz, 2H), 7.17 (d, ^3J = 7.8 Hz, 2H), 7.33 (t, ^3J = 8.6 Hz, 1H). ^{13}C NMR (80 MHz, $CDCl_3$) δ (ppm): 21.0, 56.3, 104.3, 129.5, 130.1, 130.8, 135.4, 160.8. IR ($CHCl_3$) ν (cm^{-1}) 3001, 2919, 1583, 1489, 1439, 1242, 1101. HRMS: m/z calcd for $C_{15}H_{17}O_2Se$ $[M + H]^+$ 309.0394, found $[M + H]^+$ 309.0391.

1,3-Dimethoxy-2-((4-chlorophenyl)seleno)benzene (***3c***). Elution with AcOEt/cyclohexane 5:95 afforded 41 mg (25% yield) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.80 (s, 6H), 6.62 (d, ^3J = 8.3 Hz, 2H), 7.14 (m, 4H), 7.37 (t, ^3J = 8.3 Hz, 1H). ^{13}C NMR (80 MHz, $CDCl_3$) δ (ppm): 56.3, 104.3, 105.9, 128.7, 130.9, 131.1, 131.2, 131.5, 160.7. IR ($CHCl_3$) ν (cm^{-1}) 3004, 2935, 1580, 1478, 1427, 1290, 1251, 1101, 1094, 1009. HRMS: m/z calcd for $C_{14}H_{14}ClO_2Se$ $[M + H]^+$ 328.9848, found $[M + H]^+$ 328.9851.

Synthesis of 1,3-Diisopropoxy-2-(phenylthio)benzene (***2c***). 1,4-Dioxane (8 mL) and TMSO (0.12 mL) were added to a mixture of the diphenyl disulfide (0.8 mmol, 175 mg, 1.6 equiv), 2,6-diisopropoxybenzoic acid (0.50 mmol, 119 mg, 1.0 equiv), Ag_2CO_3 (1.1 mmol, 303 mg, 2.2 equiv), and $Pd(CF_3CO_2)_2$ (0.15 mmol, 50 mg, 0.3 equiv). The reaction mixture was directly refluxed for 12 h. After being cooled to rt, the reaction mixture was filtered with Celite, and the filtrate was concentrated under vacuum. The residue was purified by flash

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chromatography on silica gel (elution with AcOEt/cyclohexane 5:95) to afford **2c** as a yellowish oil (103 mg, 68% yield) after drying under vacuum
(0.1 mbar). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.20 (d, ^3J = 6.0 Hz, 12H), 4.49 (hept, ^3J = 6.0 Hz, 2H), 6.58 (d, ^3J = 8.3 Hz, 2H), 7.05 (m, 1H), 7.14 (m, 4H), 7.23 (t, ^3J = 8.3 Hz, 1H). ^{13}C NMR (80 MHz, $CDCl_3$) δ (ppm): 21.9, 71.3, 107.1, 124.6, 127.5, 128.2, 129.9, 138.8, 159.8. IR ($CHCl_3$) ν (cm^{-1}) 3072, 2977, 2930, 1582, 1457, 1250, 1115, 1059. HRMS: m/z calcd for $C_{18}H_{23}O_2S$ $[M + H]^+$ 303.1419, found $[M + H]^+$ 303.1409.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra for products **2a**−**g** and **3a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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