FULL PAPER

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A General Procedure for Regioselective Synthesis of Aryl Thioethers and Aryl Selenides Through C-H Activation of Arenes

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A general procedure for the syntheses of aryl thioethers and aryl selenides in one-pot through the sequential iridium-catalyzed *meta* C-H borylation and copper-promoted C-S and C-Se bond formations in one-pot is described. Functional groups including chloro, nitro, fluoro, trifluoromethyl and nitrogen-containing heterocycles are all tolerated by the described reaction conditions. Importantly, not only aryl thiols and selenides but also alkyl analogs are all suitable coupling partners, giving the products with high *meta*-regioselectivity and good yields.

Introduction

Transition-metal-catalyzed direct C-H functionalization is an important strategy for constructing C-C,[1] C-N,[2] and other C-heteroatom bonds[3] from the atom economy point of view.[4] Many elegant studies have reported the synthesis of a C-C bond through C-H activation. Aryl thioethers are important skeletons found in biology,[5] and many methods have been achieved for preparing such molecules,[6-12] Among the reactions leading to carbon-heteroatom bond formation, investigation of C-S bond formation through C-H activation is less studied.[13-17] 2-Phenylpyridine has been reported to couple with thiophenols and methyl disulfide in the presence of copper catalyst to provide the products with high *ortho* selectivity.[13] Dong et al. demonstrated the palladium-catalyzed *ortho*-sulfonylation of 2-phenylpyridine with $ArSO_2Cl$.[14] Although a highly regioselective for *ortho*-C-S bond formation has achieved by these two protocols, pyridine is required as a directing group for this transformation. Recently, Cheng et al. reported the copper-catalyzed direct C-H thioetherification of arenes; however, the starting material is limited to very electron-rich arenes such as 1,3,5-trimethoxybenzene and 1,2,4-trimethoxybenzene, resulting in the corresponding aryl thioethers in low to moderate yields.[15] Very recently, Beller et al. reported the palladium-catalyzed coupling of arylsulfonyl cyanides with simple arenes, giving the diaryl thioethers in moderate yields.[16] However, some drawbacks remain with this system and need to be addressed. First, this system employs trifluoroacetic acid as a solvent and acid sensitive functional groups may not survive under these conditions. Second, the mixtures of *ortho*- and *para*-arythiolated products were observed in most cases. Third, the substrates are limited to electron-rich arenes. Notably, the above-mentioned protocols prefer the *ortho* and *para* rather than *meta* C-S formation. In 2011, Frost reported the first *meta* sulfonation of 2-phenylpyridines with sulfonyl chlorides through ruthenium catalysis. However, this catalytic system again requires pyridine as a directing group.[17] Recently, we communicated the one-pot *meta* C-H thioetherification of simple arenes in the absence of a directing group through iridium-catalyzed C-H borylation[18] followed by copper-catalyzed C-S bond formation.[19] Although good results are obtained by the reactions of aryl disulfides, the alkyl disulfides are not suitable as the coupling partners for the synthesis of aryl alkyl thioethers under these reaction conditions.[19] Therefore, it is necessary to develop a general method to overcome this difficulty. Here we report that the combination of $Cu(OAc)_2$ and pyridine could be applied to promote the step of C-S and C-Se cross-coupling reactions. Thus, the aryl alkyl thioethers and selenides could be prepared through the sequential iridium-catalyzed *meta* C-H borylation and copper-promoted C-S and C-Se bond formations in one-pot.

Results and Discussion

Initially, 3,5-dimethylphenyl boronic ester and 1-dodecanethiol were chosen as substrates to examine in order to determine the optimal reaction conditions. When the reaction was carried out by using DMF as a solvent in the presence of $Cu(OAc)_2$ and three equiv of pyridine at 155 °C for 3 h[20] only trace amounts of product was detected by GC-MS (Table 1, entry 1). The product yield was raised to 45% when the reaction time was extended to 24 h (Table 1, entry 2). A better result was obtained when the reaction was performed without molecular sieves (Table 1, entry 3). To our surprise, a 91% yield was achieved for 24 h at 120 °C (Table 1, entry 4). However, only 27% of product was formed at 110 °C (Table 1, entry 5).

With the optimized reaction conditions for copper-promoted C-S bond formation in hand; we then examined the scope of the tandem iridium-catalyzed borylation and copper-promoted C-S bond coupling reaction through one-pot procedure. 1,3-Disubstituted arenes are reacted smoothly with B_2Pin_2 in the presence of an iridium catalyst to afford the arylboronates. After removing the volatile residues by vacuum, the resulting arylboronates were

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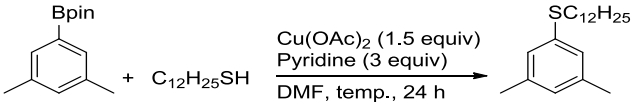
conducted with alkyl thiols including dodecanethiol (Table 2, entries 1, 3, 6, 9 and 14), 2-methy-1-butanethiol (Table 2, entries 2, 4, 7, 10, 12 and 15), cyclohexanethiol (Table 2, entries 5, 11 and 13), benzyl mercaptan (Table 2, entry 8) in the presence of $Cu(OAc)_2$, giving the corresponding aryl alkyl thioethers in moderate to good yields (Table 2, entries 1-15). Meanwhile, this methodology is also applicable to the formation of diaryl thioethers (Table 2, entries 16-26). Functional groups including chloro (Table 2, entries 3-5, 9-13, 18-26), trifluoromethyl (Table 2, entries 6-8, 16 and 17), pyridine (Table 2, entries 14 and 15), fluoro (Table 2, entry 25) and nitro (Table 2, entry 26) are all tolerated by the reaction conditions employed.

Table 1. Optimization of the Reaction Conditions.[a]

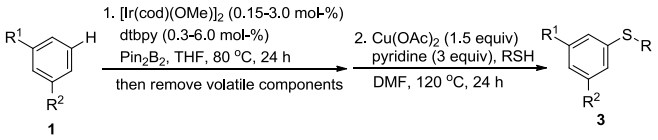


1aa **2a** **3a**

Entry	Solvent	Temp. (°C)	Time (h)	Yield(%)[b]
1	DMF	155	3	trace[c]
2	DMF	155	24	45[c]
3	DMF	155	24	53
4	**DMF**	**120**	**24**	**91**
5	DMF	110	24	27

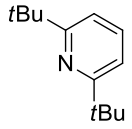
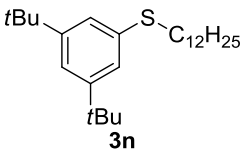
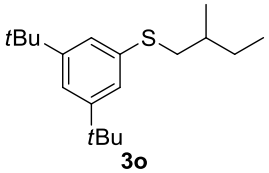
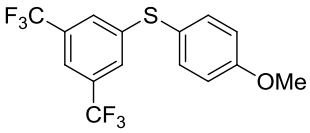
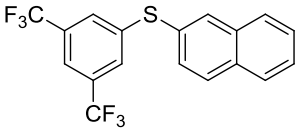
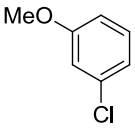
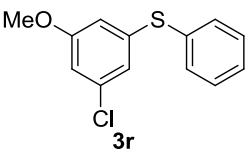
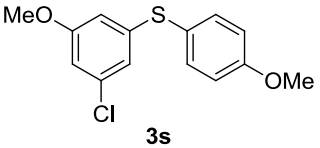
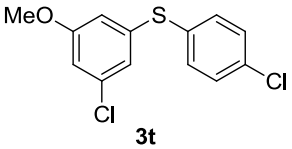
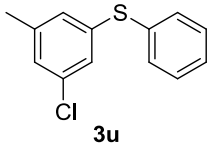
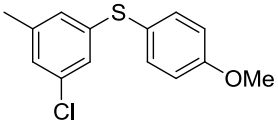
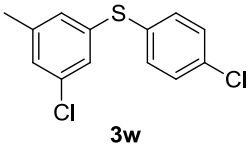
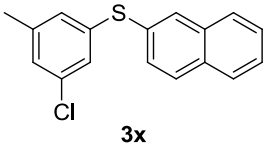
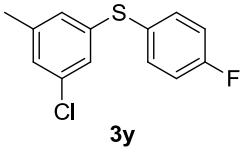
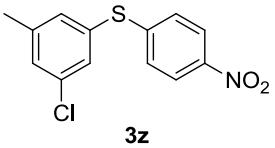
[a] Reaction conditions: $Cu(OAc)_2$ (0.75 mmol), pyridine (1.5 mmol), 3,5-dimethylphenyl boronic ester (1 mmol) and 1-dodecanethiol (0.5 mmol) in 2 mL DMF under argon atmosphere. [b] Isolated yield. [c] 3 Å molecular sieves were added.

Table 2. Tandem Iridium-Catalyzed Borylation and Copper-Promoted C-S Bond Formation.[a]



1 **3**

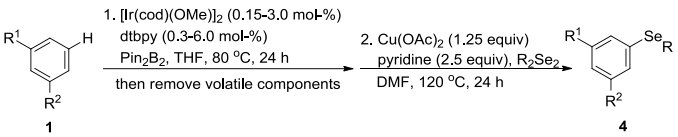
Entry	**1**	**3**	Yield (%)
1	**1a**	**3a**	66[b]
2	**1a**	**3b**	67[b]
3	**1b**	**3c**	78
4	**1b**	**3d**	82
5	**1b**	**3e**	80
6	**1c**	**3f**	59[c]
7	**1c**	**3g**	53[c]
8	**1c**	**3h**	47[c]
9	**1d**	**3i**	90
10	**1d**	**3j**	76
11	**1d**	**3k**	71
12	**1e**	**3l**	57
13	**1e**	**3m**	52

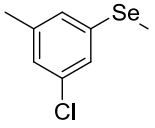
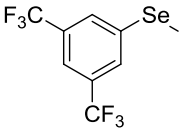
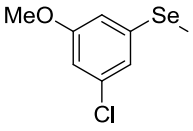
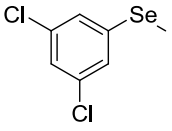
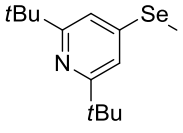
14	 **1f**	 **3n**	53[d]
15	**1f**	 **3o**	72[d]
16	**1c**	 **3p**	55[c,e]
17	**1c**	 **3q**	55[c,e]
18	 **1d**	 **3r**	62[e]
19	**1d**	 **3s**	56[e]
20	**1d**	 **3t**	60[e]
21	**1b**	 **3u**	67[e]
22	**1b**	 **3v**	56[e]
23	**1b**	 **3w**	65[e]
24	**1b**	 **3x**	71[e]
25	**1b**	 **3y**	51[e]
26	**1b**	 **3z**	46[e]

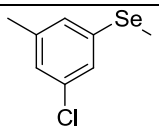
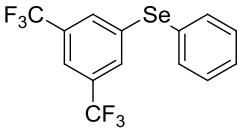
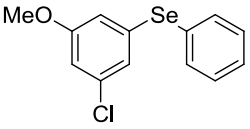
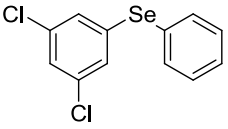
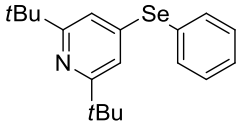
[a] Reaction conditions unless otherwise stated: arene (1.0 mmol), $[Ir(cod)OMe]_2$ (0.0015 mol, 0.15 mol-%), dtbpy (0.003 mmol, 0.3 mol-%) in 1.5 mL THF for the first step; $Cu(OAc)_2$ (0.75 mmol, 1.5 equiv), pyridine (1.5 mmol, 3 equiv), thiol (0.5 mmol) in 2 mL under argon atmosphere for the second step. [b] Borylation with 1.5 mol-% $[Ir(cod)OMe]_2$ and 3.0 mol-% dtbpy. [c] Borylation with 0.1 mol-% $[Ir(cod)OMe]_2$ and 0.2 mol-% dtbpy. [d] Borylation with 3.0 mol-% $[Ir(cod)OMe]_2$ and 6.0 mol-% dtbpy. [e] 135 °C.

In order to explore the scope of this method to the synthesis of aryl selenides, we then investigated diaryl diselendies as the coupling partners. The results are summarized in Table 3. Aryl alkyl selenides (Table 3, entries 1-5) and diaryl selenides (Table 3, entries 6-10) are formed with moderate to good yields. The functional groups such as chloro (Table 3, entries 1, 3, 4, 6, 8 and 9), trifluoromethyl (Table 3, entries 2 and 7) and pyridine (Table 3, entries 5 and 10) are also tolerated by these reaction conditions.

Table 3. Synthesis of Aryl Alkyl- and Diaryl Selenides Through Tandem Iridium-Catalyzed Borylation and Copper-Promoted C-Se Bond Formation.[a]



Entry	**1**	**4**	Yield (%)
1	**1b**	 **4a**	61
2	**1c**	 **4b**	52[b]
3	**1d**	 **4c**	64
4	**1e**	 **4d**	52
5	**1f**	 **4e**	53[c]

6	**1b**	 **4f**	65
7	**1c**	 **4g**	63[b]
8	**1d**	 **4h**	66
9	**1e**	 **4i**	75
10	**1f**	 **4j**	66[c]

[a] Reaction conditions unless otherwise stated: arene (1.0 mmol), $[Ir(cod)OMe]_2$ (0.0015 mol, 0.15 mol-%), dtbpy (0.003 mmol, 0.3 mol-%) in 1.5 mL THF for the first step; $Cu(OAc)_2$ (0.75 mmol, 1.25 equiv), pyridine (1.5 mmol, 2.5 equiv), diselenide (0.6 mmol) in 2 mL under argon atmosphere for the second step. [b] Borylation with 0.1 mol-% $[Ir(cod)OMe]_2$ and 0.2 mol-% dtbpy. [c] Borylation with 3.0 mol-% $[Ir(cod)OMe]_2$ and 6.0 mol-% dtbpy.

Conclusions

In conclusion, we have reported a general and convenient procedure for the syntheses of aryl alkyl- and diaryl thioethers and selenides through iridium-catalyzed *meta* borylation followed by copper-promoted C-S and C-Se bond cross-coupling reactions from simple arenes in one-pot. Functional groups including chloro, trifluoromethyl, pyridine, fluoro and nitro are all tolerated by the reaction conditions employed. Screening the biological activities of these molecules is under progress in our laboratory.

Experimental Section

General information: All chemicals were purchased from commercial suppliers and used without further purification. DMF was dried over CaH_2 and stored in the presence of activated molecular sieves. All reactions were carried out under an inert atmosphere. Flash chromatography was performed on silica gel 60 (230-400 mesh).

Analysis: NMR spectra were recorded using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, b = broad. Melting points (m.p.) were determined using an apparatus and are reported uncorrected. High resolution mass spectra (HRMS) were performed on an electron ionization time-of-flight (EI-TOF) mass spectrometer.

General procedure for Table 1: A Schlenk tube equipped with a magnetic stirrer bar was charged with 3,5-dimethylphenyl boronic ester (1.0 mmol), copper salt (0.75 mmol), thiol (0.5 mmole) in a nitrogen-filled glove box. The Schlenk tube was then covered with a rubber septum and removed from the glove box. Under an argon atmosphere, solvent (2.0 mL) was added via syringe, and the Schlenk tube was connected to an argon-filled balloon and heated at 120 °C in an oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of silica gel then washed with ethyl acetate (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO_2, hexane) to yield **3a**.

Representative example of Table 1: 3,5-Dimethylphenyl dodecyl sulfide 3a (Table 1, entry 4): Following the general procedure for Table 1, using $Cu(OAc)_2$ (0.136 g, 0.75 mmol) and 1-dodecanethiol (0.123 mL, 0.5 mmol) in DMF (2.0 mL), then purified by column chromatography (SiO_2, hexane) to provide **3a** as a colorless oil (0.139 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.26-1.43 (m, 18 H), 1.60-1.67 (m, *J* = 7.5 Hz, 2 H), 2.28 (s, 6 H), 2.89 (t, *J* = 7.4 Hz, 2 H), 6.78 (s, 1 H), 6.94 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.2, 22.7, 28.8, 29.1, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 33.5, 126.4, 127.5, 136.5, 138.3 ppm. HREI-MS calcd. for $C_{20}H_{34}S$: 306.2381, found: 306.2391.

General procedure for Table 2: A Schlenk tube equipped with a magnetic stirrer bar was charged with $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol) and B_2pin_2 (0.189 g, 0.73 mmol) in a nitrogen-filled glove box. The Schlenk tube was then covered with a rubber septum and removed from the glove box. Under a nitrogen atmosphere, arene (1.0 mmol) and THF (1.5 mL) were added via syringe, and the Schlenk tube was heated at 80 °C in an oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature, after removed the volatile components under vacuum. This Schlenk tube was returned to the glove box, $Cu(OAc)_2$ (0.136 g, 0.75 mmol) was added, the Schlenk tube was then covered with a rubber septum and removed from the glove box. Under an argon atmosphere, thiol (0.5 mmol), pyridine (0.123 mL, 1.5 mmol) and DMF (2.0 mL) were added via syringe, and the Schlenk tube was connected to an argon-filled balloon and heated at 120 °C in an oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of silica gel then washed with ethyl acetate (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO_2, hexane) to yield **3**.

3,5-Dimethylphenyl dodecyl sulfide 3a (Table 2, entry 1): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (9.9 mg, 0.015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (8.2 mg, 0.03 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-dimethylbenzene (0.125 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.1362 g, 0.75 mmol), 1-dodecanethiol (0.123 mL, 0.5 mmol), pyridine (0.123 mL, 1.5 mmol) and DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3a** as a colorless oil (0.101 g, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.26-1.43 (m, 18 H), 1.60-1.67 (m, *J* = 7.5 Hz, 2 H), 2.28 (s, 6 H), 2.89 (t, *J* = 7.4 Hz, 2 H), 6.78 (s, 1 H), 6.94 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 21.2, 22.7, 28.8, 29.1, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 33.5, 126.4, 127.5, 136.5, 138.3 ppm. HREI-MS calcd. for $C_{20}H_{34}S$: 306.2381, found: 306.2391.

3,5-Dimethylphenyl 2-methyl-1-butyl sulfide 3b (Table 2, entry 2): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (9.9 mg, 0.015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (8.2 mg, 0.03 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-dimethylbenzene (0.125 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3b** as a colorless oil (0.070 g, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.4 Hz, 3 H), 1.02 (d, *J* = 6.8 Hz, 3 H), 1.23-1.30 (m, 1 H), 1.50-1.57 (m, 1 H), 1.63-1.68 (m, 1 H), 2.27 (s, 6 H), 2.73 (dd, *J* = 7.2, 12.4 Hz, 1 H), 2.93 (dd, *J* = 5.8, 12.2 Hz, 1 H), 6.78 (s, 1 H), 6.94 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2, 19.0, 21.2, 28.8, 34.5, 40.6, 126.3, 127.4, 137.0, 138.3 ppm. HREI-MS calcd. for $C_{13}H_{20}S$: 208.1286, found: 208.1288.

3-Chloro-5-methylphenyl dodecyl sulfide 3c (Table 2, entry 3): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 1-dodecanethiol (0.123 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3c** as a colorless oil (0.128 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.26-1.43 (m, 18 H), 1.60-1.67 (m, *J* = 7.3 Hz, 2 H), 2.28 (s, 3 H), 2.89 (t, *J* = 7.2 Hz, 2 H), 6.94 (s, 1 H), 6.97 (s, 1 H), 7.07 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.1, 22.7, 28.8, 28.9, 29.1, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 33.2, 124.8, 126.3, 127.1, 134.3, 138.9, 140.0 ppm. HREI-MS calcd. for $C_{19}H_{31}ClS$: 326.1835, found: 326.1843.

3-Chloro-5-methylphenyl 2-methyl-1-butyl sulfide 3d (Table 2, entry 4): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3d** as a colorless oil (0.094 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.4 Hz, 3 H), 1.02 (d, *J* = 6.8 Hz, 3 H), 1.24-1.31 (m, 1 H), 1.49-1.56 (m, 1 H), 1.64-1.69 (m, 1 H), 2.28 (s, 3 H), 2.73 (dd, *J* = 7.6, 12.4 Hz, 1 H), 2.92 (dd, *J* = 6.0, 12.4 Hz, 1 H), 6.93 (s, 1 H), 6.98 (s, 1 H), 7.07 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2, 18.9, 21.1, 28.8, 34.4, 40.2, 124.8, 126.2, 127.1, 134.2, 139.4, 135.0 ppm. HREI-MS calcd. for $C_{12}H_{17}ClS$: 228.0739, found: 228.0735.

3-Chloro-5-methylphenyl cyclohexyl sulfide 3e (Table 2, entry 5): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), cyclohexanethiol (0.065 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3e** as a colorless oil (0.096 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24-1.38 (m, 5 H), 1.60-1.63 (m, 1 H), 1.76-1.79 (m, 2 H), 1.96-1.99 (m, 2 H), 2.29 (s, 3 H), 3.09-3.14 (m, 1 H), 6.99 (s, 1 H), 7.06 (s, 1 H), 7.16 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 25.7, 25.9, 33.2, 46.4, 127.3, 127.8, 130.1, 134.1, 137.0, 140.0 ppm. HREI-MS calcd. for $C_{13}H_{17}ClS$: 240.0739, found: 240.0737.

3,5-Bis(trifluoromethyl)phenyl dodecyl sulfide 3f (Table 2, entry 6): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 1-dodecanethiol (0.123 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3f** as a colorless oil (0.1224 g, 59% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.26-1.48 (m, 18 H), 1.67-1.72 (m, 2 H), 3.00 (t, *J* = 7.2 Hz, 2 H), 7.61 (s, 1 H), 7.65 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.5, 28.8, 29.1, 29.3, 29.4, 29.5, 29.6, 31.9, 32.8, 118.7, 123.1 (q, *J* = 226.0 Hz), 127.1, 132.0 (q, *J* = 27.5 Hz), 141.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.7 (s) ppm. HREI-MS calcd. for $C_{20}H_{28}F_6S$: 414.1816, found: 414.1812.

3,5-Bis(trifluoromethyl)phenyl 2-methyl-l-butyl sulfide 3g (Table 2, entry 7): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3g** as a colorless oil (0.083 g, 53% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.5 Hz, 3 H), 1.06 (d, *J* = 6.6 Hz, 3 H), 1.31-1.35 (m, 1 H), 1.53-1.57 (m, 1 H), 1.70-1.73 (m, 1 H), 2.83 (dd, *J* = 7.8, 12.6 Hz, 1 H), 3.04 (dd, *J* = 5.7, 12.3 Hz, 1 H), 7.60 (s, 1 H), 7.66 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.2, 19.0, 28.8, 34.3, 39.7, 118.6, 123.1 (q, *J* = 226.0 Hz), 127.0, 132.0 (q, *J* = 27.7 Hz), 141.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.7 (s) ppm. HREI-MS calcd. for $C_{13}H_{14}F_6S$: 316.0720, found: 316.0725.

3,5-Bis(trifluoromethyl)phenyl benzyl sulfide 3h (Table 2, entry 8): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), phenylmethanethiol (0.060 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3h** as a colorless oil (0.079 g, 47% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.19 (s, 2 H), 7.27-2.31 (m, 5 H), 7.63-7.64 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 38.3, 119.6, 119.6, 119.6, 123.0 (q, *J* = 226.3 Hz), 127.8, 128.6, 128.8, 128.8, 131.9 (q, *J* = 27.6 Hz),135.6, 140.1 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.6 (s) ppm. HREI-MS calcd. for $C_{15}H_{10}F_6S$: 336.0407, found: 336.0414.

3-Chloro-5-methoxyphenyl dodecyl sulfide 3i (Table 2, entry 9): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 1-dodecanethiol (0.123 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3i** as a colorless oil (0.154 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.25-1.44 (m, 18 H), 1.57-1.67 (m, 2 H), 2.90 (t, *J* = 7.4 Hz, 2 H), 3.77 (s, 3 H), 6.67 (t, *J* = 2.0 Hz, 1 H), 6.71 (t, *J* = 2.0 Hz, 1 H), 6.85 (t, *J* = 1.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.8, 28.8, 29.1, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 33.0, 111.4, 112.1, 119.9, 135.0, 140.2, 160.2 ppm. HREI-MS calcd. for $C_{19}H_{31}ClOS$: 342.1784, found: 342.1780.

3-Chloro-5-methoxyphenyl 2-methyl-1-butyl sulfide 3j (Table 2, entry 10): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3j** as a colorless oil (0.093 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.4 Hz, 3 H), 1.02 (d, *J* = 6.8 Hz, 3 H), 1.23-1.31 (m, 1 H), 1.49-1.57 (m, 1 H), 1.64-1.70 (m, 1 H), 2.73 (dd, *J* = 7.2, 12.4 Hz, 1 H), 2.93 (dd, *J* = 6.0, 12.4 Hz, 1 H), 3.77 (s, 3 H), 6.66 (t, *J* = 2.0 Hz, 1 H), 6.71 (t, *J* = 1.0 Hz, 1 H), 6.85 (t, *J* = 1.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2, 18.9, 28.8 34.4, 40.0, 55.5, 111.3, 112.0, 119.9, 135.0, 140.6, 160.2 ppm. HREI-MS calcd. for $C_{12}H_{17}ClOS$: 244.0689, found: 244.0684.

3-Chloro-5-methoxyphenyl cyclohexyl sulfide 3k (Table 2, entry 11): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), cyclohexanethiol (0.065 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3k** as a colorless oil (0.091 g, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23-1.25 (m, 5 H), 1.60-1.64 (m, 1 H), 1.76-1.79 (m, 2 H), 1.98-2.01 (m, 2 H), 3.13-3.17 (m, 1 H), 3.77 (s, 3 H), 6.72 (t, *J* = 2.0 Hz, 1 H), 6.79 (t, *J* = 1.8 Hz, 1 H), 6.94 (t, *J* = 1.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 25.9, 33.1, 46.2, 55.5, 112.2, 114.8, 122.6, 134.8, 138.3, 160.1 ppm. HREI-MS salcd. for $C_{13}H_{17}ClOS$: 256.0689, found: 256.0681.

3,5-Dichlorophenyl 2-methyl-1-butyl sulfide 3l (Table 2, entry 12): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-dichlorobenzene (0.115 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3l** as a colorless oil (0.071 g, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.4 Hz, 3 H), 1.01 (d, *J* =

4.4 Hz, 3 H), 1.24-1.32 (m, 1 H), 1.47-1.56 (m, 1 H), 1.63-1.70 (m, 1 H), 2.74 (dd, *J* = 7.6, 12.4 Hz, 1 H), 2.93 (dd, *J* = 5.8, 12.4 Hz, 1 H), 7.09-7.13 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2, 18.9, 28.8, 34.3, 40.0, 125.2, 125.6, 135.1, 141.7 ppm. HREI-MS salcd. for $C_{11}H_{14}Cl_2S$: 248.0193, found: 248.0186.

3,5-Dichlorophenyl cyclohexyl sulfide 3m (Table 2, entry 13): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-dichlorobenzene (0.115 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), cyclohexanethiol (0.065 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3m** as a colorless oil (0.068 g, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20-1.43 (m, 5 H), 1.59-1.64 (m, 1 H), 1.74-1.86 (m, 2 H), 1.92-2.04 (m, 2 H), 3.10-3.22 (m, 1 H), 7.17 (t, *J* = 2.0 Hz, 1 H), 7.21 (d, *J* = 2.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 25.9, 33.1, 46.3, 126.3, 128.4, 134.9, 139.4 ppm. HREI-MS salcd. for $C_{12}H_{14}Cl_2S$: 260.0193, found: 260.0190.

2,6-Di-*tert*-butyl-4-pyridyl dodecyl sulfide 3n (Table 2, entry 14): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (19.9 mg, 0.03 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.4 mg, 0.06 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 2,6-di-*tert*-butylpyridine (0.232 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.1362 g, 0.75 mmol), 1-dodecanethiol (0.123 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3n** as a colorless oil (0.103 g, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.0 Hz, 3 H), 1.26-1.32 (m, 34 H), 1.42-1.47 (m, 2 H), 1.69-1.72 (m, 2 H), 2.95 (t, *J* = 7.2 Hz, 2 H), 6.93 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.8, 29.0, 29.2, 29.3, 29.5, 29.6, 29.6, 30.0, 30.8, 31.9, 37.6, 112.7, 148.1, 167.4 ppm. HREI-MS salcd. for $C_{25}H_{45}NS$: 391.3273, found: 391.3279.

2,6-Di-*tert*-butyl-4-pyridyl 2-methyl-1-butyl sulfide 3o (Table 2, entry 15): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (19.9 mg, 0.03 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.4 mg, 0.06 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 2,6-di-*tert*-butylpyridine (0.232 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3o** as a colorless oil (0.106 g, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 67.4 Hz, 3 H), 1.05 (d, *J* = 6.8 Hz , 3 H), 1.26-1.37 (m, 19 H), 1.48-1.58 (m, 1 H), 1.71-1.76 (m, 1 H), 2.75 (dd, *J* = 7.6, 12.4 Hz, 1 H), 3.01 (dd, *J* = 5.8, 12.6 Hz, 1 H), 6.93 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4, 19.1, 29.0, 30.3, 34.5, 37.7, 37.7, 112.7, 148.4, 167.4 ppm. HREI-MS salcd. for $C_{18}H_{31}NS$: 293.2177, found: 293.2170.

3,5-Bis(trifluoromethyl)phenyl 4-methoxyphenyl sulfide 3p (Table 2, entry 16):[19] Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-methoxythiophenol (0.063 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3p** as a white solid (0.097 g, 55% yield). m.p. 54-55 °C (lit.[19] 54-55 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.76 (s, 3 H), 6.88 (dd, *J* = 1.8, 6.6 Hz, 2 H) , 7.36 (s, 2 H), 7.38 (dd, *J* = 2.4, 6.6 Hz, 2 H), 7.47 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.4, 115.7, 118.7, 118.7, 118.7, 118.8, 118.8, 120.3, 123.1 (q, *J* = 226.1 Hz), 126.1, 126.1, 132.0 (q, *J* = 27.6 Hz), 136.8, 143.6, 161.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.6 (s) ppm.

3,5-Bis(trifluoromethyl)phenyl 2-naphthyl sulfide 3q (Table 2, entry 17): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-naphthalenethiol (0.081 g, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3q** as a colorless oil (0.101 g, 55% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 1.8, 8.4 Hz, 1 H), 7.52-7.55 (m, 2 H), 7.62 (s, 2 H), 7.65 (s, 1 H), 7.80-7.81 (m, 1 H), 7.84-7.86 (m, 2 H), 8.04 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 119.7, 119.7, 119.7, 123.0 (q, *J* = 226.3 Hz), 127.1, 127.3, 128.0, 128.0, 128.0, 128.3, 129.8, 129.9, 132.3 (q, *J* = 27.8 Hz), 133.2, 133.5, 133.9, 141.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.6 (s) ppm. HREI-MS calcd. for $C_{18}H_{10}F_6S$: 372.0407, found: 372.0399.

3-Chloro-5-methoxyphenyl phenyl sulfide 3r (Table 2, entry 18):[19] Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), thiophenol (0.053 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3r** as a colorless oil (0.078 g, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 3 H), 6.68 (t, *J* = 2 Hz, 1 H), 6.72 (t, *J* = 2.2 Hz, 1 H), 6.81 (t, *J* = 1.6 Hz, 1 H), 7.30-7.39 (m, 3 H), 7.40-7.46 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 112.5, 113.4, 121.4, 128.1, 129.5, 132.6, 133.4, 135.3, 139.7, 160.4 ppm.

3-Chloro-5-methoxyphenyl 4-methoxyphenyl sulfide 3s (Table 2, entry 19): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-methoxythiophenol (0.063 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3s** as a yellow oil (0.079 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3 H), 3.84 (s, 3 H), 6.53 (t, *J* = 1.8 Hz, 1 H), 6.64 (t, *J* = 1.4 Hz, 2 H), 6.92 (dd, *J* = 2.2, 6.6 Hz, 2 H), 7.44 (dd, *J* = 2.2, 7.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 55.5, 111.2, 111.4, 115.2, 119.2, 122.3, 135.2, 136.3, 142.2, 160.3, 160.4 ppm. HREI-MS calcd. for $C_{14}H_{13}ClO_2S$: 280.0325, found: 280.0335.

3-Chloro-5-methoxyphenyl 4-chlorophenyl sulfide 3t (Table 2, entry 20):[19] Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-chlorothiophenol (0.074 g, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3t** as a colorless oil (0.086 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 3 H), 6.67 (t, *J* = 1.8 Hz, 1 H), 6.73 (t, *J* = 2.0 Hz, 1 H), 6.80 (t, *J* = 1.6 Hz, 1 H), 7.30-7.32 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 112.9, 113.8, 121.7, 129.6, 132.3, 133.6, 134.2, 135.4, 138.9, 160.5 ppm.

3-Chloro-5-methylphenyl phenyl sulfide 3u (Table 2, entry 21):[19] Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), thiophenol (0.053 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3u** as a colorless oil (0.078 g, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 6.99 (s, 2 H), 7.04 (s, 1 H), 7,28-7.39 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 126.8, 127.6, 127.7, 128.8, 129.4, 132.0, 134.2, 134.5, 138.1, 140.4 ppm.

3-Chloro-5-methylphenyl 4-methoxyphenyl sulfide 3v (Table 2, entry 22):[19\ Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-methoxythiophenol (0.063 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **4h** as a colorless oil (0.075 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3 H), 3.82 (s, 3 H), 6.85 (d, *J* = 7.6 Hz, 2 H), 6.91 (dd, *J* = 2.0, 6.8 Hz, 3 H), 7.42 (dd, *J* = 2.0, 6.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1,

55.3, 115.1, 122.9, 124.3, 126.3, 126.4, 134.4, 135.9, 140.2, 140.7, 160.2 ppm.

3-Chloro-5-methylphenyl 4-chlorophenyl sulfide 3w (Table 2, entry 23):[19] Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-chlorothiophenol (0.074 g, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3w** as a colorless oil (0.087 g, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 6.98 (s, 1 H), 7.03 (s, 1 H), 7.05 (s, 1 H), 7.29 (s, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 127.0, 128.0, 129.1, 129.5, 133.0, 133.1, 133.8, 134.6, 137.3, 140.7 ppm.

3-Chloro-5-methylphenyl 2-naphthyl sulfide 3x (Table 2, entry 24):[19] Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.1362 g, 0.75 mmol), 2-naphthalenethiol (0.081 g, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3x** as a colorless oil (0.101 g, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3 H), 7.0-7.01 (m, 2 H), 7.08 (s, 1 H), 7.39 (d, *J* = 2.0 Hz, 1 H), 7.41-7.48 (m, 2 H), 7.73-7.81 (m, 3 H), 7.89 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 126.5, 126.7, 126.7, 127.5, 127.6, 127.7, 128.7, 129.1, 129.3, 131.2, 131.4, 132.5, 133.7, 134.6, 138.1, 140.5 ppm.

3-Chloro-5-methylphenyl 4-fluorophenyl sulfide 3y (Table 2, entry 25): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.1362 g, 0.75 mmol), 4-fluorothiophenol (0.055 mL, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3y** as a colorless oil (0.064 g, 51% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 6.91 (s, 1 H), 6.95 (s, 1 H), 6.98 (s, 1 H), 7.04-7.07 (m, 2 H), 7.40- 7.42 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.1, 116.6, 116.7, 125.7, 127.3, 127.8, 128.7, 128.7, 134.6, 135.0, 135.0, 138.8, 140.5, 161.9, 163.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -114.3 (s) ppm. HREI-MS calcd. for $C_{13}H_{10}ClFS$: 252.0176, found: 252.0171.

3-Chloro-5-methylphenyl 4-nitrophenyl sulfide 3z (Table 2, entry 26): Following the general procedure for Table 2, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.1891 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-nitrothiophenol (0.097 g, 0.5 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3z** as a yellow oil (0.064 g, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 7.22-7.24 (m, 4 H), 7.32 (s, 1 H), 8.10 (d, *J* = 9.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 124.1, 127.4, 130.4, 130.8, 132.3, 132.9, 135.2, 141.6, 145.7, 147.1 ppm. HREI-MS calcd. for $C_{13}H_{10}ClNO_2S$: 279.0121, found: 279.0114.

General procedure for Table 3: A Schlenk tube equipped with a magnetic stirrer bar was charged with $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol) and B_2pin_2 (0.189 g, 0.73 mmol) in a nitrogen-filled glove box. The Schlenk tube was then covered with a rubber septum and removed from the glove box. Under a nitrogen atmosphere, arene (1.0 mmol) and THF (1.5 mL) were added via syringe, and the Schlenk tube was heated at 80 °C in an oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature, after removed the volatile components under vacuum. This Schlenk tube was returned to the glove box, $Cu(OAc)_2$ (0.136 g, 0.75 mmol) was added, the Schlenk tube was then covered with a rubber septum and removed from the glove box. Under an argon atmosphere, diselenide (0.6 mmol), pyridine (0.123 mL, 1.5 mmol) and DMF (2.0 mL) were added via syringe, and the Schlenk tube was connected to an argon-filled balloon and heated at 120 °C in an oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of silica gel then washed with ethyl acetate (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO_2, hexane) to yield **4**.

3-Chloro-5-methylphenyl methyl selenide 4a (Table 3, entry 1): Following the general procedure for Table 3, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), dimethyl diselenide (0.060 mL, 0.6 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **4a** as a yellow oil (0.135 g, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 2.34 (s, 3 H), 6.98 (s, 1 H), 7.09 (s, 1 H), 7.17 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.1, 21.0, 126.5, 126.9, 128.8, 133.3, 134.4, 140.2 ppm. HREI-MS calcd. for C_8H_9ClSe: 219.9558, found: 219.9563.

3,5-Bis(trifluoromethyl)phenyl methyl selenide 4b (Table 3, entry 2): Following the general procedure for Table 3, using $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), dimethyl diselenide (0.060 mL, 0.6 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **4b** as a colorless oil (0.161 g, 52% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 7.65 (s, 1 H), 7.77 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.2, 119.6, 119.7, 119.7, 123.0 (q, *J* = 226.3 Hz), 129.3, 132.0 (q, *J* = 27.6 Hz), 135.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.7 (s) ppm. HREI-MS calcd. for $C_9H_6F_6Se$: 307.9539, found: 307.9544.

3-Chloro-5-methoxyphenyl methyl selenide 4c (Table 3, entry 3): Following the general procedure for Table 3, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), dimethyl diselenide (0.060 mL, 0.6 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **4c** as a colorless oil (0.151 g, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 3.78 (s, 3 H), 6.72 (s, 1 H), 6.82 (s, 1 H), 6.95 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.1, 55.5, 112.0, 114.0, 121.7, 134.3, 135.1, 160.2 ppm. HREI-MS calcd. for C_8H_9ClOSe: 235.9507, found: 235.9500.

3,5-Dichlorophenyl methyl selenide 4d (Table 3, entry 4): Following the general procedure for Table 3, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-dichlorobenzene (0.115 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), dimethyl diselenide (0.060 mL, 0.6 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **4d** as a colorless oil (0.123 g, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 7.17 (s, 1 H), 7.24 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.2, 126.0, 127.6, 135.2 ppm. HREI-MS calcd. for $C_7H_6Cl_2Se$: 239.9012, found: 239.9014.

2,6-Di-*tert*-butyl-4-pyridyl methyl selenide 3e (Table 3, entry 5): Following the general procedure for Table 3, using $[Ir(OCH_3)(C_8H_{12})]_2$ (19.9 mg, 0.03 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.4 mg, 0.06 mmol), B_2pin_2 (0.1891 g, 0.73 mmol) and 2,6-di-*tert*-butylpyridine (0.232 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), dimethyl diselenide (0.060 mL, 0.6 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **3e** as a yellow oil (0.150 g, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, 18 H), 2.37 (s, 3 H), 7.07 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.5, 30.0, 37.7, 115.4, 143.2, 167.5 ppm. HREI-MS calcd. for $C_{14}H_{23}NSe$: 285.0996, found: 285.1001.

3-Chloro-5-methylphenyl phenyl selenide 4f (Table 3, entry 6):[19] Following the general procedure for Table 3, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), diphenyl diselenide (0.189 g, 0.6 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **4f** as a colorless oil (0.183 g, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 7.03 (s, 1 H), 7.13 (s, 1 H), 7.19 (s, 1 H), 7.28-7.30 (m, 3 H), 7.48-7.50 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 127.8, 128.0, 129.0, 129.5, 130.0, 131.1, 132.8, 133.6, 134.5, 140.6 ppm.

3,5-Bis(trifluoromethyl)phenyl pheyl selenide 4g (Table 3, entry 7):[19] Following the general procedure for Table 3, using $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.1362 g, 0.75 mmol), diphenyl diselenide (0.1893 g, 0.6 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **4g** as a yellow oil (0.232 g, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40-7.44 (m, 3 H), 7.59-7.61 (m, 2 H), 7.69 (s, 1 H), 7.74 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 120.4, 120.4, 120.4, 122.9 (q, *J* = 227.9 Hz), 129.2, 130.0, 130.6, 130.6, 132.2 (q, *J* = 27.7 Hz), 135.0, 135.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.6 (s) ppm.

3-Chloro-5-methoxyphenyl phenyl selenide 4h (Table 3, entry 8):[19] Following the general procedure for Table 3, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), diphenyl diselenide (0.189 g, 0.6 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **4h** as a yellow oil (0.195 g, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 3 H), 6.76 (t, *J* = 2.2 Hz, 1 H), 6.82 (dd, *J* = 1.4, 2.2 Hz, 1 H), 6.96 (t, *J* = 1.4 Hz, 1 H), 7.31-7.33 (m, 3 H), 7.52-7.54 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 113.1, 115.8, 123.7, 128.1, 129.4, 129.5, 134.0, 134.1, 135.3, 160.4 ppm.

3,5-Dichlorophenyl phenyl selenide 4i (Table 3, entry 9):[19] Following the general procedure for Table 3, using $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.8 mg, 0.003 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 1,3-dichlorobenzene (0.115 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), diphenyl diselenide (0.1893 g, 0.6 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **4i** as a yellow oil (0.227 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18-7.21 (m, 3 H), 7.33-7.38 (m, 3 H), 7.54-7.56 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.9, 128.4, 128.7, 129.1, 129.8, 134.7, 135.4 ppm.

2,6-Di-*tert*-butyl-4-pyridyl phenyl selenide 4j (Table 3, entry 10): Following the general procedure for Table 3, using $[Ir(OCH_3)(C_8H_{12})]_2$ (19.9 mg, 0.03 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16.4 mg, 0.06 mmol), B_2pin_2 (0.189 g, 0.73 mmol) and 2,6-di-*tert*-butylpyridine (0.232 mL, 1.0 mmol) in THF (1.5 mL) for the first step. After removed the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), diphenyl diselenide (0.189 g, 0.6 mmol), DMF (2.0 mL) were used, then purified by column chromatography (SiO_2, hexane) to provide **4j** as a yellow oil (0.230 g, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 18 H), 6.97 (s, 2 H), 7.36-7.38 (m, 3 H), 7.60-7.62 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.0, 37.6, 116.3, 127.5, 128.6, 129.6, 135.5, 143.9, 167.8 ppm. HREI-MS calcd. for $C_{19}H_{25}NSe$: 347.1152, found: 347.1144.

Supporting Information (see footnote on the first page of this article): NMR spectra for products.

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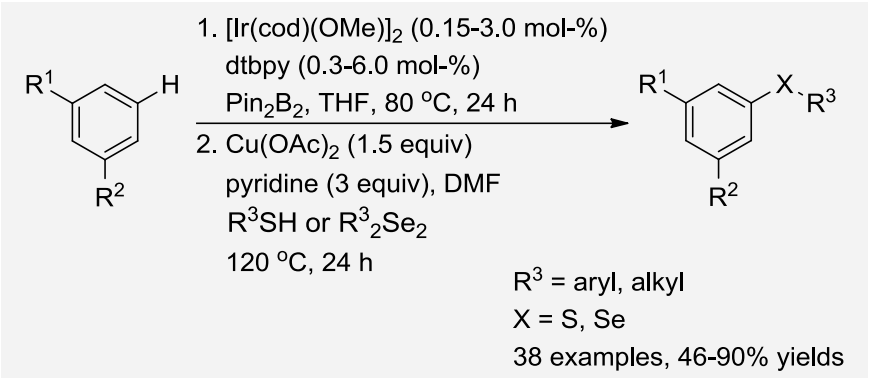
C-H Functionalization

A General Procedure for Regioselective Synthesis of Aryl Thioethers and Aryl Selenides Through C-H Activation of Arenes



A general procedure for the syntheses of aryl thioethers and aryl selenides in one-pot through the sequential iridium-catalyzed *meta* C-H borylation and copper-promoted C-S and C-Se bond formations in one-pot is described. Functional groups including chloro, nitro, fluoro, trifluoromethyl and nitrogen-containing heterocycles are all tolerated by the described reaction conditions. Importantly, not only aryl thiols and selenides but also alkyl analogs are all suitable coupling partners, giving the products with high *meta*-regioselectivity and good yields.