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

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Dedicated to Professor Teruaki Mukaiyama[‡]

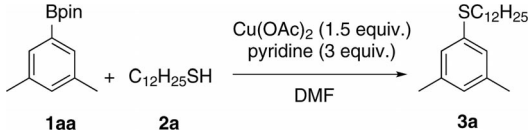
Keywords: Sulfur / Selenide / C–H activation / Arenes / Iridium / Copper

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

Introduction

Transition-metal-catalyzed direct C–H functionalization is an important strategy for the construction of C–C,[1] C–N,[2] and other C–heteroatom bonds[3] from the viewpoint of atom economy.[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 reported for the preparation of such molecules.[6–12] Among the reactions leading to C–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 a 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 high regioselectivity for *ortho* C–S bond formation was 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, which resulted in the formation of 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 to give 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, 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 *ortho* and *para* C–S formation 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-cata-

Table 1. Optimization of the reaction conditions.[a]



1aa 2a 3a

Entry	Temp. [°C]	Time [h]	Yield [%][b]
1	155	3	trace[c]
2	155	24	45[c]
3	155	24	53
4	120	24	91
5	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 DMF (2 mL) under an argon atmosphere; Bpin = pinacolboryl. [b] Isolated yield. [c] Molecular sieves (3 Å) were added.

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[‡] On the occasion of the 40th anniversary of the Mukaiyama aldol reaction

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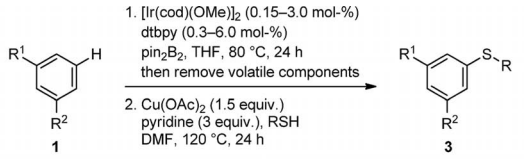
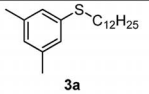
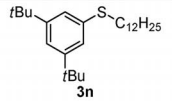
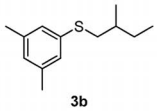
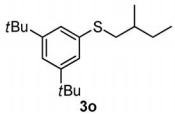
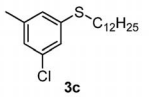
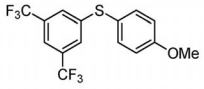
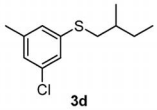
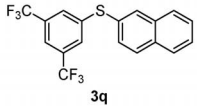
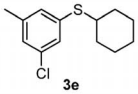
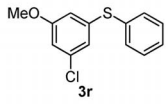
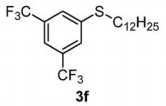
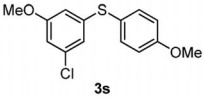
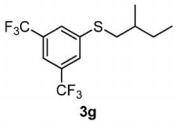
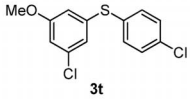
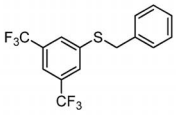
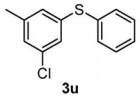
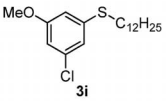
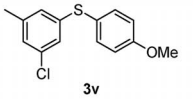
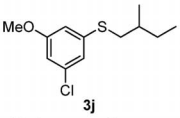
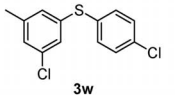
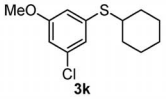
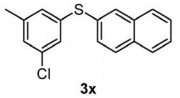
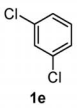
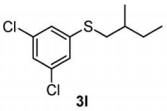
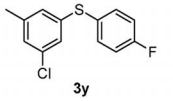
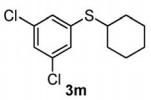
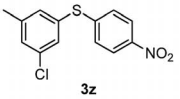
Table 2. Tandem iridium-catalyzed borylation and copper-promoted C–S bond formation.[a]



Entry	1	3	Yield [%]	Entry	1	3	Yield [%]
1	 1a	 3a	66[b]	14	 1f	 3n	53[d]
2	1a	 3b	67[b]	15	1f	 3o	72[d]
3	 1b	 3c	78	16	1c	 3p	55[c,e]
4	1b	 3d	82	17	1c	 3q	55[c,e]
5	1b	 3e	80	18	 1d	 3r	62[e]
6	 1c	 3f	59[c]	19	1d	 3s	56[e]
7	1c	 3g	53[c]	20	1d	 3t	60[e]
8	1c	 3h	47[c]	21	1b	 3u	67[e]
9	 1d	 3i	90	22	1b	 3v	56[e]
10	1d	 3j	76	23	1b	 3w	65[e]
11	1d	 3k	71	24	1b	 3x	71[e]
12	 1e	 3l	57	25	1b	 3y	51[e]
13	1e	 3m	52	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-%; cod = 1,5-cyclooctadiene), di-*tert*-butyl bipyridine (dtbpy; 0.003 mmol, 0.3 mol-%) in THF (1.5 mL) for the first step; $Cu(OAc)_2$ (0.75 mmol, 1.5 equiv.), pyridine (1.5 mmol, 3 equiv.), thiol (0.5 mmol) in DMF (2 mL) under an argon atmosphere for the second step. [b] Borylation with $[Ir(cod)OMe]_2$ (1.5 mol-%) and dtbpy (3.0 mol-%). [c] Borylation with $[Ir(cod)OMe]_2$ (0.1 mol-%) and dtbpy (0.2 mol-%). [d] Borylation with $[Ir(cod)OMe]_2$ (3.0 mol-%) and dtbpy (6.0 mol-%). [e] 135 °C.

lyzed C–H borylation[18] followed by copper-catalyzed C–S bond formation.[19] Although good results were obtained for reactions of aryl disulfides, alkyl disulfides were not suitable as coupling partners for the synthesis of aryl alkyl thioethers under the reaction conditions.[19] Therefore, it is necessary to develop a general method to overcome this difficulty. Herein, we report that the combination of $Cu(OAc)_2$ and pyridine could be applied to promote the C–S and C–Se cross-coupling reaction step. Thus, the aryl alkyl thioethers and selenides could be prepared through sequential iridium-catalyzed *meta* C–H borylation and copper-promoted C–S and C–Se bond formations in one pot.

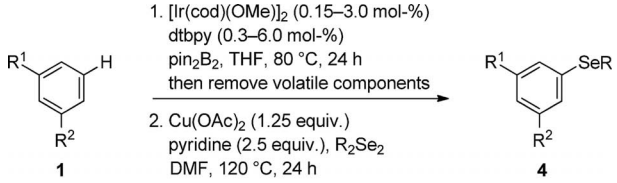
Results and Discussion

Initially, (3,5-dimethylphenyl)boronic ester and 1-dodecanethiol were chosen as substrates to determine the optimal reaction conditions. When the reaction was carried out with DMF as the solvent in the presence of $Cu(OAc)_2$ and pyridine (3 equiv.) at 155 °C for 3 h,[20] only a trace amount of the product was detected by GC–MS (Table 1, entry 1). The product yield could be raised to 45% if 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 after 24 h at 120 °C (Table 1, entry 4). However, only 27% of the product was formed at 110 °C (Table 1, entry 5).

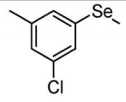
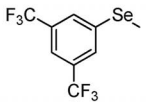
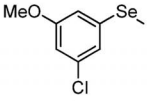
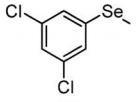
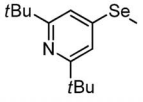
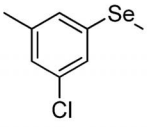
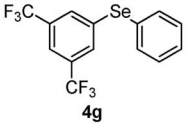
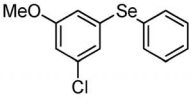
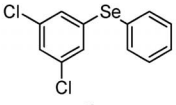
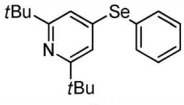
With the optimized reaction conditions for the copper-promoted C–S bond-formation reaction in hand, we then examined the scope of the tandem iridium-catalyzed borylation and copper-promoted C–S bond-coupling reaction through a one-pot procedure. 1,3-Disubstituted arenes reacted smoothly with pin_2B_2 [bis(pinacolato)diboron] in the presence of an iridium catalyst to afford the arylboronates. After removing the volatile residues by vacuum, the resulting arylboronates were treated 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), and benzyl mercaptan (Table 2, entry 8) in the presence of $Cu(OAc)_2$ to give the corresponding aryl alkyl thioethers in moderate to good yields (Table 2, entries 1–15). Moreover, this methodology could be applied 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) were all tolerated under the reaction conditions.

To explore the scope of this method for the synthesis of aryl selenides, we then investigated diaryl diselenides as the coupling partners (Table 3). Aryl alkyl selenides (Table 3, entries 1–5) and diaryl selenides (Table 3, entries 6–10) were formed in moderate to good yields. 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, en-

Table 3. Synthesis of aryl alkyl and diaryl selenides through tandem iridium-catalyzed borylation and copper-promoted C–Se bond formation.[a]



1 **4**

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 THF (1.5 mL) 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 DMF (2 mL) under an argon atmosphere for the second step. [b] Borylation with $[Ir(cod)OMe]_2$ (0.1 mol-%) and dtbpy (0.2 mol-%). [c] Borylation with $[Ir(cod)OMe]_2$ (3.0 mol-%) and dtbpy (6.0 mol-%).

tries 5 and 10) were also tolerated under these reaction conditions.

Conclusions

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

Experimental Section

General Information: All chemicals were purchased from commercial suppliers and used without further purification. DMF was dried with 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). NMR spectra were recorded by using $CDCl_3$ as the solvent. Chemical shifts are referenced to the residual solvent resonance. Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, q = quartet, m = multiplet, br. = broad. Melting points (m.p.) were determined by using a Büchi 535 apparatus and are reported uncorrected. High-resolution mass spectra (HRMS) were performed with an electron ionization time-of-flight (EI-TOF) mass spectrometer.

General Procedure for Reaction in Table 1: A Schlenk tube equipped with a magnetic stirring bar was charged with (3,5-dimethylphenyl)boronic ester (1.0 mmol), copper salt (0.75 mmol), and thiol (0.5 mmol) 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 by 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**.

3,5-Dimethylphenyl Dodecyl Sulfide (3a): Following the general procedure for Table 1, $Cu(OAc)_2$ (0.136 g, 0.75 mmol) and 1-dodecanethiol (0.123 mL, 0.5 mmol) in DMF (2.0 mL). Purification provided **3a** (Table 1, entry 4) 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. HRMS (EI): calcd. for $C_{20}H_{34}S$ 306.2381; found 306.2391.

General Procedure for Reactions in Table 2: A Schlenk tube equipped with a magnetic stirring bar was charged with $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), and pin_2B_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 by 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 removal of 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, and the Schlenk tube was 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 by 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 and 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): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (9.9 mg, 0.015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (8.2 mg, 0.03 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-dimethylbenzene (0.125 mL, 1.0 mmol) in THF (1.5 mL). After removal of 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). Purification provided **3a** (Table 2, entry 1) 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. HRMS (EI): calcd. for $C_{20}H_{34}S$ 306.2381; found 306.2391.

3,5-Dimethylphenyl 2-Methyl-1-butyl Sulfide (3b): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (9.9 mg, 0.015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (8.2 mg, 0.03 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-dimethylbenzene (0.125 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3b** (Table 2, entry 2) 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. HRMS (EI): calcd. for $C_{13}H_{20}S$: 208.1286; found 208.1288.

3-Chloro-5-methylphenyl Dodecyl Sulfide (3c): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 1-dodecanethiol (0.123 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3c** (Table 2, entry 3) 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. HRMS (EI): calcd. for $C_{19}H_{31}ClS$ 326.1835; found 326.1843.

3-Chloro-5-methylphenyl 2-Methyl-1-butyl Sulfide (3d): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3d** (Table 2, entry 4) 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. HRMS (EI): calcd. for $C_{12}H_{17}ClS$ 228.0739; found 228.0735.

3-Chloro-5-methylphenyl Cyclohexyl Sulfide (3e): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), cyclohexanethiol (0.065 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3e** (Table 2, entry 5) 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. HRMS (EI): calcd. for $C_{13}H_{17}ClS$ 240.0739; found 240.0737.

3,5-Bis(trifluoromethyl)phenyl Dodecyl Sulfide (3f): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.5 mg, 0.002 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 1-dodecanethiol (0.123 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3f** (Table 2, entry 6) 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. HRMS (EI): calcd. for $C_{20}H_{28}F_6S$ 414.1816; found 414.1812.

3,5-Bis(trifluoromethyl)phenyl 2-Methyl-l-butyl Sulfide (3g): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.5 mg, 0.002 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3g** (Table 2, entry 7) 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. HRMS (EI): calcd. for $C_{13}H_{14}F_6S$ 316.0720; found 316.0725.

3,5-Bis(trifluoromethyl)phenyl Benzyl Sulfide (3h): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.5 mg, 0.002 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), phenylmethanethiol (0.060 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3h** (Table 2, entry 8) 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. HRMS (EI): calcd. for $C_{15}H_{10}F_6S$ 336.0407; found 336.0414.

3-Chloro-5-methoxyphenyl Dodecyl Sulfide (3i): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 1-dodecanethiol (0.123 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3i** (Table 2, entry 9) 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. HRMS (EI): calcd. for $C_{19}H_{31}ClOS$ 342.1784; found 342.1780.

3-Chloro-5-methoxyphenyl 2-Methyl-1-butyl Sulfide (3j): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3j** (Table 2, entry 10) 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. HRMS (EI): calcd. for $C_{12}H_{17}ClOS$ 244.0689; found 244.0684.

3-Chloro-5-methoxyphenyl Cyclohexyl Sulfide (3k): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), cyclohexanethiol (0.065 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3k** (Table 2, entry 11) 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. HRMS (EI): calcd. for $C_{13}H_{17}ClOS$ 256.0689; found 256.0681.

3,5-Dichlorophenyl 2-Methyl-1-butyl Sulfide (3l): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg,

0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-dichlorobenzene (0.115 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3l** (Table 2, entry 12) 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. HRMS (EI): calcd. for $C_{11}H_{14}Cl_2S$ 248.0193; found 248.0186.

3,5-Dichlorophenyl Cyclohexyl Sulfide (3m): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-dichlorobenzene (0.115 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), cyclohexanethiol (0.065 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3m** (Table 2, entry 13) 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. HRMS (EI): calcd. for $C_{12}H_{14}Cl_2S$ 260.0193; found 260.0190.

2,6-Di-*tert*-butyl-4-pyridyl Dodecyl Sulfide (3n): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (19.9 mg, 0.03 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.4 mg, 0.06 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 2,6-di-*tert*-butylpyridine (0.232 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.1362 g, 0.75 mmol), 1-dodecanethiol (0.123 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3n** (Table 2, entry 14) 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. HRMS (EI): calcd. for $C_{25}H_{45}NS$ 391.3273; found 391.3279.

2,6-Di-*tert*-butyl-4-pyridyl 2-Methyl-1-butyl Sulfide (3o): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (19.9 mg, 0.03 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.4 mg, 0.06 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 2,6-di-*tert*-butylpyridine (0.232 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3o** (Table 2, entry 15) 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. HRMS (EI): calcd. for $C_{18}H_{31}NS$ 293.2177; found 293.2170.

3,5-Bis(trifluoromethyl)phenyl 4-Methoxyphenyl Sulfide (3p):[19] Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.5 mg, 0.002 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-methoxythiophenol (0.063 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3p** (Table 2, entry 16) as a white solid (0.097 g, 55% yield), m.p. 54–55 °C (ref.[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): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.5 mg, 0.002 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 2-naphthalenethiol (0.081 g, 0.5 mmol), and DMF (2.0 mL). Purification provided **3q** (Table 2, entry 17) 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. HRMS (EI): calcd. for $C_{18}H_{10}F_6S$ 372.0407; found 372.0399.

3-Chloro-5-methoxyphenyl Phenyl Sulfide (3r):[19] Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), thiophenol (0.053 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3r** (Table 2, entry 18) 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): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-methoxythiophenol (0.063 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3s** (Table 2, entry 19) 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. HRMS (EI): calcd. for $C_{14}H_{13}ClO_2S$ 280.0325; found 280.0335.

3-Chloro-5-methoxyphenyl 4-Chlorophenyl Sulfide (3t):[19] Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-chlorothiophenol (0.074 g, 0.5 mmol), and DMF (2.0 mL). Purification provided **3t** (Table 2, entry 20) 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):[19] Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), thiophenol (0.053 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3u** (Table 2, entry 21) 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):[19] Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-methoxythiophenol (0.063 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **4h** (Table 2, entry 22) 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):[19] Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-chlorothiophenol (0.074 g, 0.5 mmol), and DMF (2.0 mL). Purification provided **3w** (Table 2, entry 23) 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):[19] Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.1362 g, 0.75 mmol), 2-naphthalenethiol (0.081 g, 0.5 mmol), and DMF (2.0 mL). Purification provided **3x** (Table 2, entry 24) 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): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.1362 g, 0.75 mmol), 4-fluorothiophenol (0.055 mL, 0.5 mmol), and DMF (2.0 mL). Purification provided **3y** (Table 2, entry 25) 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. HRMS (EI): calcd. for $C_{13}H_{10}ClFS$ 252.0176; found 252.0171.

3-Chloro-5-methylphenyl 4-Nitrophenyl Sulfide (3z): Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.1891 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), 4-nitrothiophenol (0.097 g, 0.5 mmol), and DMF (2.0 mL). Purification provided **3z** (Table 2, entry 26) 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. HRMS (EI): calcd. for $C_{13}H_{10}ClNO_2S$ 279.0121; found 279.0114.

General Procedure for Reactions in Table 3: A Schlenk tube equipped with a magnetic stirring bar was charged with $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), and pin_2B_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 by 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 removal of 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, and 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 by 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): Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), dimethyl diselenide (0.060 mL, 0.6 mmol), and DMF (2.0 mL). Purification provided **4a** (Table 3, entry 1) 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. HRMS (EI): calcd. for C_8H_9ClSe 219.9558; found 219.9563.

3,5-Bis(trifluoromethyl)phenyl Methyl Selenide (4b): Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.5 mg, 0.002 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$

(0.136 g, 0.75 mmol), dimethyl diselenide (0.060 mL, 0.6 mmol), and DMF (2.0 mL). Purification provided **4b** (Table 3, entry 2) 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. HRMS (EI): calcd. for $C_9H_6F_6Se$ 307.9539; found 307.9544.

3-Chloro-5-methoxyphenyl Methyl Selenide (4c): Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), dimethyl diselenide (0.060 mL, 0.6 mmol), and DMF (2.0 mL). Purification provided **4c** (Table 3, entry 3) 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. HRMS (EI): calcd. for C_8H_9ClOSe 235.9507; found 235.9500.

3,5-Dichlorophenyl Methyl Selenide (4d): Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-dichlorobenzene (0.115 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), dimethyl diselenide (0.060 mL, 0.6 mmol), and DMF (2.0 mL). Purification provided **4d** (Table 3, entry 4) 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. HRMS (EI): calcd. for $C_7H_6Cl_2Se$ 239.9012; found 239.9014.

2,6-Di-*tert*-butyl-4-pyridyl Methyl Selenide (3e): Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (19.9 mg, 0.03 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.4 mg, 0.06 mmol), pin_2B_2 (0.1891 g, 0.73 mmol), and 2,6-di-*tert*-butylpyridine (0.232 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), dimethyl diselenide (0.060 mL, 0.6 mmol), and DMF (2.0 mL). Purification provided **3e** (Table 3, entry 5) 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. HRMS (EI): calcd. for $C_{14}H_{23}NSe$ 285.0996; found 285.1001.

3-Chloro-5-methylphenyl Phenyl Selenide (4f):[19] Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chlorotoluene (0.123 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), diphenyl diselenide (0.189 g, 0.6 mmol), and DMF (2.0 mL). Purification provided **4f** (Table 3, entry 6) 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 Phenyl Selenide (4g):[19] Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.5 mg, 0.002 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-bis(trifluoromethyl)benzene (0.160 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.1362 g, 0.75 mmol), diphenyl diselenide (0.1893 g, 0.6 mmol), and DMF (2.0 mL). Purification provided **4g** (Table 3, entry 7) 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):[19] Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 3-chloroanisole (0.125 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), diphenyl diselenide (0.189 g, 0.6 mmol), and DMF (2.0 mL). Purification provided **4h** (Table 3, entry 8) 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):[19] Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.0 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 0.003 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 1,3-dichlorobenzene (0.115 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), diphenyl diselenide (0.1893 g, 0.6 mmol), and DMF (2.0 mL). Purification provided **4i** (Table 3, entry 9) 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): Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (19.9 mg, 0.03 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.4 mg, 0.06 mmol), pin_2B_2 (0.189 g, 0.73 mmol), and 2,6-di-*tert*-butylpyridine (0.232 mL, 1.0 mmol) in THF (1.5 mL). After removal of the volatile components under vacuum, $Cu(OAc)_2$ (0.136 g, 0.75 mmol), diphenyl diselenide (0.189 g, 0.6 mmol), and DMF (2.0 mL). Purification provided **4j** (Table 3, entry 10) 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. HRMS (EI): calcd. for $C_{19}H_{25}NSe$ 347.1152; found 347.1144.

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

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