Supplementary Information

Highly regioselective synthesis of aryl chalcogenides through C-H functionalization of arenes

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1. General information: All chemicals were purchased from commercial suppliers and used without further purification. Toluene was dried over sodium; dioxane, DME, DMSO and DMF were dried over CaH₂ and stored in the presence of activated molecular sieves.

Analysis: NMR spectra were recorded on a Varian Unity Inova-600 or a Varian Mercury-400 instrument using CDCl₃ 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, tt = triplet triplet, q = quartet, m = multiplet, b = broad. Melting points (m.p.) were determined using a Büchi 535 apparatus and are reported uncorrected. GC-MS analyses were performed on a GC-MS analysis on HP 5890 GC equipped with HP 5972 MS. High-resolution mass spectra were carried out on a Jeol JMS-HX 110 spectrometer by the services at the National Chung Hsing University.

2. General procedure for Table 2: A Schrock tube equipped with a magnetic stirrer bar was charged with 3,5-dimethylphenyl boronic ester (1.0 mmol), copper salt (0.05 mmol), ligand (0.05 mmol), disulfide (0.55 mmole) in a nitrogen-filled glove box. The Schrock tube was then covered with a rubber septum and removed from the glove box. Under an air atmosphere, solvent (0.6 mL) was added via syringe, and the Schrock tube was connected to an air-filled balloon and heated at 80 °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 Celite then washed with ethyl acetate (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO₂, hexane) to yield 3a.

2.1 The representative example of Table 1 (entry 14)

Following the general procedure for Table 1, using CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol) in DMSO (0.4 mL) and H₂O (0.2 mL), then purified by column chromatography (SiO₂, hexane) to provide 3a as a colorless oil (188 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.26 (s, 6 H), 6.88 (s, 1 H), 6.99 (s, 2 H), 7.20-7.32 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.1, 126.6, 129.0, 129.1, 130.4, 134.7, 136.3, 138.8.

3. General procedure for Table 2: A Schrock tube equipped with a magnetic stirrer bar was charged with [Ir(OCH₃)(C₆H₅)₂]₂ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol) and B₂pin₂ (186 mg, 0.73 mmol) in a nitrogen-filled glove box. The Schrock 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 Schrock 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 and the solution was concentrated under vacuum. This Schrock tube was returned to the glove box, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), disulfide (0.55 mmol) were added, the Schrock tube was then covered with a rubber septum and removed from the glove box. Under an air atmosphere, DMSO (0.4 mL) and H₂O (0.2 mL) were added, and the Schrock tube was connected to an air-filled balloon and heated at 80 °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 Celite then washed with ethyl acetate (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO₂, hexane) to yield 3.
3,5-Dimethylphenyl phenyl sulfide (3a)

Following the general procedure for Table 2, [Ir(OCH₃)(C₆H₅)]₂ (3.3 mg, 0.05 mmol), 4,4'-di-tert-butyl-2,2'-dipyridyl (2.7 mg, 0.1 mmol), B₃pin₂ (186 mg, 0.73 mmol) and 1,3-dimethylbenzene (125 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), diphenyl disulfide (121.3 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂; hexane) to provide 3a as a colorless oil (118 mg, 55% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.26 (s, 6 H), 6.88 (s, 1 H), 6.99 (s, 2 H), 7.20-7.32 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.1, 126.6, 129.0, 129.1, 130.4, 134.7, 136.3, 138.8; HREI-MS calcd. for C₁₄H₁₃S: 214.0816, Found: 214.0809.

3-Chloro-5-methylphenyl phenyl sulfide (3b)

Following the general procedure for Table 2, [Ir(OCH₃)(C₆H₅)]₂ (1.1 mg, 0.0015 mmol), 4,4'-di-tert-butyl-2,2'-dipyridyl (0.9 mg, 0.003 mmol), B₃pin₂ (186 mg, 0.73 mmol) and 3-chlorotoluene (120 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), diphenyl disulfide (121.3 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂; hexane) to provide 3b as a colorless oil (176 mg, 75% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.24 (s, 3 H), 6.99 (s, 2 H), 7.04 (s, 1 H), 7.27-7.38 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.0, 126.7, 127.5, 127.7, 128.8, 129.3, 132.0, 134.2, 134.5, 138.0, 140.4; HREI-MS calcd. for C₁₃H₁₂ClS: 234.0270, Found: 234.0264.

3-Chloro-5-methylphenyl 4-methoxyphenyl sulfide (3c)

Following the general procedure for Table 2, [Ir(OCH₃)(C₆H₅)]₂ (1.1 mg, 0.0015 mmol), 4,4'-di-tert-butyl-2,2'-dipyridyl (0.9 mg, 0.003 mmol), B₃pin₂ (186 mg, 0.73 mmol) and 3-chlorotoluene (120 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), bis(4-methoxyphenyl) disulfide (157.9 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂; hexane) to provide 3c as a colorless oil (161 mg, 61% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.23 (s, 3 H), 3.83 (s, 3 H), 6.85 (d, J = 7.2 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); ¹³C NMR (100
Following the general procedure for Table 2, [Ir(OCH₃)(C₅H₁₂)]₂ (1.1 mg, 0.0015 mmol), 4,4'-di-tert-butyl-2,2'-dipyridyl (0.9 mg, 0.003 mmol), B₂pin₂ (186 mg, 0.73 mmol) and 3-chlorotoluene (120 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), 4-aminophenyl disulfide (139.4 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 3d as a yellow solid (116 mg, 46% yield). M.P.: 66–67 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.12 (s, 3 H), 3.74 (br s, 2 H), 6.67 (dd, J = 2.0, 6.4 Hz, 2 H), 6.72-6.78 (m, 3 H), 7.20 (dd, J = 2.0, 9.2 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.0, 115.9, 118.9, 123.3, 125.4, 125.9, 134.3, 136.4, 140.0, 141.7, 147.4; HREI-MS calcd. for C₁₃H₁₂ClNS: 249.0379, Found: 249.0375.

Following the general procedure for Table 2, [Ir(OCH₃)(C₅H₁₂)]₂ (1.1 mg, 0.0015 mmol), 4,4'-di-tert-butyl-2,2'-dipyridyl (0.9 mg, 0.003 mmol), B₂pin₂ (186 mg, 0.73 mmol) and 3-chlorotoluene (120 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), bis(4-chlorophenyl) disulfide (158.0 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 3e as a colorless oil (213 mg, 79% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.26 (s, 3 H), 6.98 (s, 1 H), 7.01–7.03 (m, 2 H), 7.28 (br s, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.0, 127.0, 127.9, 129.0, 129.5, 133.0, 133.7, 134.6, 137.3, 140.6; HREI-MS calcd. for C₁₃H₁₀Cl₂S: 267.9880, Found: 267.9886.

Following the general procedure for Table 2, [Ir(OCH₃)(C₅H₁₂)]₂ (1.1 mg, 0.0015 mmol), 4,4'-di-tert-butyl-2,2'-dipyridyl (0.9 mg, 0.003 mmol), B₂pin₂ (186 mg, 0.73 mmol) and 3-chlorotoluene (120 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), 2-naphthyl disulfide
(175.2 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 3f as a colorless oil (188 mg, 66% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.24 (s, 3 H), 7.01 (m, 2 H), 7.08 (s, 1 H), 7.39 (d, J = 1.6 Hz, 1 H), 7.41-7.49 (m, 2 H), 7.74-7.81 (m, 3 H), 7.90 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.1, 126.5, 126.7, 127.5, 127.6, 127.7, 128.7, 129.1, 129.3, 131.2, 131.4, 132.5, 133.7, 134.5, 138.1, 140.5; HREI-MS calcd. for C₁₇H₁₃ClS: 284.0426, Found: 284.0418.

![3-Chloro-5-methylphenyl 4-tolyl sulfide (3g)](image)

Following the general procedure for Table 2, [Ir(OCH₃)(C₅H₅)]₂ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B₂pin₂ (186 mg, 0.73 mmol) and 3-chlorotoluene (120 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), p-tolyl disulfide (135.5 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 3g as a colorless oil (171 mg, 69% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.22 (s, 3 H), 2.33 (s, 3 H), 6.91-6.95 (m, 3 H), 7.13 (d, J = 7.2 Hz, 2 H), 7.31 (dd, J = 1.2, 6.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.0, 21.1, 125.5, 126.9, 127.5, 129.7, 130.2, 133.0, 134.4, 138.3, 139.3, 140.2; HREI-MS calcd. for C₁₇H₁₃ClS: 248.0426, Found: 248.0425.

![3,5-Bis(trifluoromethyl)phenyl phenyl sulfide (3h)](image)

Following the general procedure for Table 2, [Ir(OCH₃)(C₅H₅)]₂ (0.7 mg, 0.001 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.5 mg, 0.002 mmol), B₂pin₂ (186 mg, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (160 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), diphenyl disulfide (121.3 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 3h as a colorless oil (282 mg, 88% yield). ¹H NMR (600 MHz, CDCl₃): δ = 7.41-7.43 (m, 3 H), 7.47-7.49 (m, 2 H), 7.55 (s, 2 H), 7.61 (s, 1 H); ¹³C NMR (125 MHz, CDCl₃): δ = 119.5, 119.6, 119.6, 123.0 (q, J = 226.1 Hz), 127.8, 129.4, 130.0, 131.2, 132.2 (q, J = 27.9 Hz), 133.8, 141.8; ¹⁹F NMR (376 MHz, CDCl₃): δ = -64.7 (s).

![3,5-Bis(trifluoromethyl)phenyl 4-methoxyphenyl sulfide (3i)](image)
Following the general procedure for Table 2, [Ir(OCH₃)(C₅H₁₂)]₂ (0.7 mg, 0.001 mmol), 4,4’-di-tert-butyl-2,2’-dipyridyl (0.5 mg, 0.002 mmol), B₂pin₂ (186 mg, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (160 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2’-bipyridyl (4.3 mg, 0.05 mmol), bis(4-methoxyphenyl) disulfide (157.9 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 3i as a white solid (285 mg, 81% yield). M.P.: 54–55 °C. ¹H NMR (600 MHz, CDCl₃): δ = 3.87 (s, 3 H), 6.98 (dd, J = 2.4, 6.6 Hz, 2 H), 7.44 (s, 2 H), 7.48 (dd, J = 2.4, 6.6 Hz, 2 H), 7.56 (s, 1 H); ¹³C NMR (125 MHz, CDCl₃): δ = 55.4, 115.7, 118.7, 118.8, 120.3, 122.1, 123.9, 125.8, 126.0, 132.0 (q, J = 27.9 Hz), 136.8, 143.6, 161.0; ¹⁹F NMR (376 MHz, CDCl₃): δ = -64.6 (s); HREI-MS calcd. for C₄₃H₁₀F₆OS: 352.0357, Found: 352.0351.

Following the general procedure for Table 2, [Ir(OCH₃)(C₅H₁₂)]₂ (0.7 mg, 0.001 mmol), 4,4’-di-tert-butyl-2,2’-dipyridyl (0.5 mg, 0.002 mmol), B₂pin₂ (186 mg, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (160 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2’-bipyridyl (4.3 mg, 0.05 mmol), bis(4-chlorophenyl) disulfide (158.0 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 3j as a colorless oil (303 mg, 85% yield). ¹H NMR (600 MHz, CDCl₃): δ = 7.40-7.43 (m, 4 H), 7.58 (s, 2 H), 7.66 (s, 1 H); ¹³C NMR (125 MHz, CDCl₃): δ = 120.0, 120.0, 120.0, 120.0, 120.1, 122.9 (q, J = 226.4 Hz), 128.1, 128.1, 129.9, 130.2, 132.4 (q, J = 27.9 Hz), 134.8, 135.7, 140.9; ¹⁹F NMR (376 MHz, CDCl₃): δ = -64.7 (s); HREI-MS calcd. for C₃₄H₁₇Cl₂F₂OS: 355.9861, Found: 355.9856.

Following the general procedure for Table 2, [Ir(OCH₃)(C₅H₁₂)]₂ (1.1 mg, 0.0015 mmol), 4,4’-di-tert-butyl-2,2’-dipyridyl (0.9 mg, 0.003 mmol), B₂pin₂ (186 mg, 0.73 mmol) and 3-chloroanisole (125 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2’-bipyridyl (4.3 mg, 0.05 mmol), p-tolyl disulfide (138.2 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 3k as a colorless oil (166 mg, 63% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.36 (s, 3 H), 3.71 (s, 3 H), 6.61 (s, 1 H), 6.67 (s, 1 H), 6.73 (s, 1 H), 7.17 (d, J = 8.0 Hz, 2 H), 7.35 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.2, 55.5, 111.9, 112.4, 120.3, 129.0, 130.3, 133.6, 135.2, 138.7, 140.9, 160.3; HREI-MS calcd. for C₁₈H₁₈Cl₂OS: 264.0376, Found: 264.0370.
Following the general procedure for Table 2, [Ir(OCH$_3$)$_3$(C$_9$H$_{12}$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 3-chloroanisole (125 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), diphenyl disulfide (121.3 mg, 0.55 mmol), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 3I as a colorless oil (217 mg, 87% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.72 (s, 3 H), 6.68 (t, $J = 2.0$ Hz, 1 H), 6.72 (t, $J = 2.0$ Hz, 1 H), 6.81 (t, $J = 1.6$ Hz, 1 H)7.29-7.37 (m, 3 H), 7.40-7.43 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.5, 112.4, 113.3, 121.3, 128.1, 129.4, 132.6, 133.3, 135.2, 139.6, 160.4; HREI-MS calcd. for C$_{13}$H$_7$ClOS: 250.0219, Found: 250.0220.

Following the general procedure for Table 2, [Ir(OCH$_3$)$_3$(C$_9$H$_{12}$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 3-chloroanisole (125 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), bis(4-chlorophenyl) disulfide (157.3 mg, 0.55 mmole), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 3m as a colorless oil (227 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.71 (s, 3 H), 6.68 (t, $J = 1.6$ Hz, 1 H), 6.66 (t, $J = 2.2$ Hz, 1 H), 6.80 (t, $J = 1.8$ Hz, 1 H)7.26-7.32 (m, 3 H), 7.38-7.43 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.5, 112.8, 113.7, 121.6, 129.6, 132.2, 133.6, 134.2, 135.4, 138.8, 160.5; HREI-MS calcd. for C$_{19}$H$_{16}$Cl$_2$SO: 283.9829, Found: 283.9834.

Following the general procedure for Table 2, [Ir(OCH$_3$)$_3$(C$_9$H$_{12}$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 1,3-dichlorobenzene (114 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-Bipyridyl (4.3 mg, 0.05 mmol), p-Tolyl disulfide (138.2 mg, 0.55 mmole), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 3n as a colorless oil (188 mg, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.36 (s, 3 H), 6.97 (d, $J = 1.6$ Hz, 2 H),
7.07 (t, $J = 2.0$ Hz, 1 H), 7.18 (d, $J = 8.0$ Hz, 2 H), 7.35 (d, $J = 8.0$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.2, 125.5, 125.6, 127.7, 130.5, 134.1, 139.4, 142.3$; HREI-MS calcd. for $C_{13}H_{10}Cl_2S$: 267.9880, Found: 267.9890.

4-Aminophenyl 3,5-dichlorophenyl sulfide (3o)

Following the general procedure for Table 2, [Ir(OCH$_3$)$_3$(C$_8$H$_{12}$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 1,3-dichlorobenzene (114 $\mu$L, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), 4-aminophenyl disulfide (139.4 mg, 0.55 mmole), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 3o as a yellow solid (156 mg, 58% yield). M.P.: 72−73 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.90$ (bs, 2 H), 6.69 (d, $J = 8.0$ Hz, 2 H), 6.88 (s, 2 H), 7.03 (s, 1 H), 7.30 (d, $J = 8.4$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 116.0, 117.3, 124.0, 124.8, 135.1, 137.0, 144.3, 147.9$; HREI-MS calcd. for $C_{12}H_9Cl_2NS$: 268.9833, Found: 268.9840.

3,5-Dichlorophenyl 4-methoxyphenyl sulfide (3p)

Following the general procedure for Table 2, [Ir(OCH$_3$)$_3$(C$_8$H$_{12}$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 1,3-dichlorobenzene (114 $\mu$L, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), bis(4-methoxyphenyl) disulfide (157.8 mg, 0.55 mmole), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 3p as a white solid (213 mg, 75% yield). M.P.: 59−60 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.82$ (s, 3 H), 6.90 (s, 2 H), 6.93 (d, $J = 7.6$ Hz, 2 H), 7.05 (s, 1 H), 7.43 (d, $J = 7.8$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 55.3, 115.4, 121.0, 124.5, 125.2, 135.1, 136.6, 143.3, 160.6$; HREI-MS calcd. for $C_{13}H_{10}Cl_2SO$: 283.9829, Found: 283.9837.

3,5-Dibromophenyl phenyl sulfide (3q)

Electronic Supplementary Material (ESI) for Chemical Communications
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Following the general procedure for Table 2, [Ir(OCH$_3$)(C$_6$H$_5$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4’-di-tert-butyl-2,2’-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 1,3-dibromobenzene (125 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2’-bipyridyl (4.3 mg, 0.05 mmol), diphenyl disulfide (121.3 mg, 0.55 mmole), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 3q as a colorless oil (275 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.25 (d, $J$ = 1.6 Hz, 2 H), 7.36-7.45 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 123.2, 128.7, 129.7, 129.9, 131.6, 132.2, 133.2, 141.6; HREI-MS calcd. for C$_{12}$H$_8$Br$_2$S: 341.8713, Found: 341.8716.

![3q](image)

3,5-Dibromophenyl 4-methoxyphenyl sulfide (3r)

Following the general procedure for Table 2, [Ir(OCH$_3$)(C$_6$H$_5$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4’-di-tert-butyl-2,2’-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 1,3-dibromobenzene (125 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2’-bipyridyl (4.3 mg, 0.05 mmol), bis(4-methoxyphenyl) disulfide (157.8 mg, 0.55 mmole), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 3r as a white solid (295 mg, 79% yield). M.P.: 80–81 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.83 (s, 3 H), 6.94 (d, $J$ = 8.0 Hz, 2 H), 7.10 (d, $J$ = 1.6 Hz, 2 H), 7.36 (t, $J$ = 1.4 Hz, 1H), 7.43 (d, $J$ = 8.8 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.3, 115.4, 121.1, 123.1, 137.8, 130.6, 136.6, 143.8, 160.6; HREI-MS calcd. for C$_{13}$H$_{10}$Br$_2$SO: 371.8819, Found: 371.8820.

![3r](image)

3-Methyl-5-methoxyphenyl phenyl sulfide (3s)

Following the general procedure for Table 2, [Ir(OCH$_3$)(C$_6$H$_5$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4’-di-tert-butyl-2,2’-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 3-methylanisole (127 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2’-bipyridyl (4.3 mg, 0.05 mmol), diphenyl disulfide (121.3 mg, 0.55 mmol), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 3s as a colorless oil (128 mg, 55% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.29 (s, 3 H), 3.74 (s, 3 H), 6.62 (s, 1 H), 6.70 (s, 1 H), 6.78 (s, 1 H), 7.25-7.27 (m, 1 H), 7.29-7.33 (m, 2 H), 7.36-7.38 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.4, 55.2, 113.1, 113.8, 123.9, 127.0, 129.1, 131.1, 134.5, 136.5, 140.2, 160.0; HREI-MS calcd. for C$_{14}$H$_{14}$OS: 230.0765, Found: 230.0726.
Following the general procedure for Table 2, [Ir(OCH$_3$)(C$_6$H$_{12}$)$_2$]$_2$ (20 mg, 0.03 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (16 mg, 0.06 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 2,6-di-tert-butylpyridine (232 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), bis(4-chlorophenyl) disulfide (158.0 mg, 0.55 mmole), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 3t as a white solid (226 mg, 68% yield). M.P.: 88–89 °C. $^1$H NMR (600 MHz, CDCl$_3$): δ = 1.27 (s, 18H), 6.83 (d, J = 8.4 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 2 H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 30.0, 37.7, 113.8, 129.7, 135.0, 135.2, 147.6, 168.1; HREI-MS calcd. for C$_{15}$H$_{25}$ClINS: 333.1318, Found: 333.1322.

Following the general procedure for Table 2, [Ir(OCH$_3$)(C$_6$H$_{12}$)$_2$]$_2$ (22 mg, 0.03 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (18 mg, 0.06 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 2,6-dichloropyridine (83 mg, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), diphenyl disulfide (121.3 mg, 0.55 mmol), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 3u as a colorless oil (153 mg, 60% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ = 6.82 (s, 2 H), 7.48–7.57 (m, 5 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 118.6, 127.3, 130.3, 130.6, 135.5, 150.4, 156.6; HREI-MS calcd. for C$_{11}$H$_{20}$Cl$_2$NS: 254.9676, Found: 254.9671.

4. General procedure for Table 3: A Schrock tube equipped with a magnetic stirrer bar was charged with [Ir (OCH$_3$)(C$_6$H$_{12}$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol) and B$_2$pin$_2$ (186 mg, 0.73 mmol) in a nitrogen-filled glove box. The Schrock tube was then covered with a rubber septum and removed from the glove box. Under a nitrogen atmosphere, arenes (1.0 mmol), and THF (1.5 mL) were added via syringe, and the Schrock 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 and the solution was concentrated under vacuum. This Schrock tube was returned to the glove box, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), diselenide or ditelluride (0.55 mmol) were added, the Schrock tube was then covered with a rubber septum and removed from the glove box. Under an air atmosphere, DMSO (0.4 mL) and H$_2$O (0.2 mL) were added, and the Schrock tube was connected to an air-filled balloon and heated at 80 °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 Celite 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 phenyl selenide (4a)](image)

Following the general procedure for Table 3, [Ir(OCH$_3$)$_3$(C$_8$H$_{12}$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4'-di-$t$-butyl-2,2'-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 3-chlorotoluene (120 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), diphenyl diselenide (173.4 mg, 0.55 mmol), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 4a as a colorless oil (233 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.23 (s, 3 H), 7.01 (dd, $J$ = 0.8, 1.2 Hz, 1 H), 7.12 (m, 1 H), 7.18-7.19 (m, 1 H), 7.26-7.28 (m, 3 H), 7.47-7.49 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.0, 127.8, 128.0, 128.9, 129.4, 130.0, 131.0, 132.7, 133.6, 134.5, 140.5; HREI-MS calcd. for C$_{13}$H$_{11}$ClSe: 281.9714, Found: 281.9716.

![3-Methoxy-5-methylphenyl phenyl selenide (4b)](image)

Following the general procedure for Table 3, [Ir(OCH$_3$)$_3$(C$_8$H$_{12}$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4'-di-$t$-butyl-2,2'-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 1,3-dichlorobenzene (114 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), diphenyl diselenide (175.1 mg, 0.55 mmol), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 4b as a colorless oil (245 mg, 81 % yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.26 (s, 3 H), 3.70 (s, 3 H), 6.61 (s, 1 H), 6.80 (s, 1 H), 6.89 (s, 1 H), 7.24-7.26 (m, 3 H), 7.45-7.47 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.3, 55.1, 114.1, 115.1, 125.9, 127.2, 129.2, 131.0, 131.6, 132.9, 140.2, 159.9; HREI-MS calcd. for C$_{14}$H$_{14}$OSe: 278.0210, Found: 278.0204.

![3,5-Bis(trifluoromethyl)phenyl phenyl selenide (4c)](image)

Following the general procedure for Table 3, [Ir(OCH$_3$)$_3$(C$_8$H$_{12}$)$_2$]$_2$ (0.7 mg, 0.001 mmol), 4,4'-di-$t$-butyl-2,2'-dipyridyl (0.5 mg, 0.002 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (160 μL, 1.0 mmol) in THF (1.5 mL) in
the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), diphenyl diselenide (173.4 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 4c as a colorless oil (270 mg, 73% yield). ¹H NMR (600 MHz, CDCl₃): δ = 7.36-7.42 (m, 3 H), 7.56-7.58 (m, 2 H), 7.66 (s, 1 H), 7.71 (s, 2 H); ¹³C NMR (125 MHz, CDCl₃): δ = 120.3, 120.4, 120.4, 120.4, 122.9 (q, J = 27.6 Hz), 127.7, 129.2, 130.0, 130.6, 132.2 (q, J = 27.6 Hz), 135.0, 135.0, 135.0, 135.9; ¹⁹F NMR (376 MHz, CDCl₃): δ = -64.7 (s); HREI-MS calcd. for C₁₃H₁₂F₆Se: 369.9699, Found: 369.9699.

3,5-Dichlorophenyl phenyl selenide (4d)

Following the general procedure for Table 3, [Ir(OCH₃)(C₅H₅)₂]₂ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B₂pin₂ (186 mg, 0.73 mmol) and 1,3-dichlorobenzene (114 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), diphenyl diselenide (175.1 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 4d as a colorless oil (245 mg, 81 % yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.14 (t, J = 2.0 Hz, 1 H), 7.18 (d, J =1.6 Hz, 2 H), 7.27-7.33 (m, 3 H), 7.51-7.53 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ = 126.8, 128.4, 128.6, 129.0, 129.7, 134.6, 135.3, 135.3; HREI-MS calcd. for C₁₃H₁₂Cl₂Se: 301.9168, Found: 301.9164.

3,5-Dibromophenyl phenyl selenide (4e)

Following the general procedure for Table 3, [Ir(OCH₃)(C₅H₅)₂]₂ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B₂pin₂ (186 mg, 0.73 mmol) and 1,3-dibromobenzene (125 µL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), diphenyl diselenide (175.1 mg, 0.55 mmol), DMSO (0.4 mL) and H₂O (0.2 mL) then purified by column chromatography (SiO₂, hexane) to provide 4e as a colorless oil (384 mg, 98% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.25-7.32 (m, 3 H), 7.38 (d, J = 1.6 Hz, 2 H), 7.44 (s, 1 H), 7.49-7.52 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ = 13.3, 128.5, 128.5 129.6, 132.1, 132.2, 134.4, 135.8; HREI-MS calcd. for C₁₃H₁₂Br₂Se: 389.8158, Found: 389.8162.

3-Chloro-5-methoxyphenyl phenyl selenide (4f)
Following the general procedure for Table 3, [Ir(OCH$_3$)(C$_5$H$_5$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 3-chloroanisole (125 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), diphenyl diselenide (175.1 mg, 0.55 mmol), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 4f as a colorless oil (232 mg, 78 % yield). $^1$H NMR (400 MHz, CDCl$_3$): δ = 3.72 (s, 3 H), 6.77 (t, $J$ = 2.0 Hz, 1 H), 6.84 (t, $J$ = 1.6 Hz, 1 H), 6.98 (t, $J$ = 1.6 Hz, 1 H), 7.30-7.34 (m, 3 H), 7.52-7.56 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 55.4, 113.0, 115.8, 123.7, 134.0, 134.1, 135.2, 160.4; HREI-MS calcd. for C$_{13}$H$_{15}$ClOSe: 297.9664, Found: 297.9658.

![3,5-Dichlorophenyl phenyl telluride (4g)](image)

Following the general procedure for Table 3, [Ir(OCH$_3$)(C$_5$H$_5$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 1,3-dichlorobenzene (114 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), diphenyl ditelluride (229.7 mg, 0.55 mmol), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 4g as a yellow oil (224 mg, 64 % yield). $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.19 (t, $J$ = 2.0 Hz, 1 H), 7.26-7.29 (m, 2 H), 7.34-7.36 (m, 1 H), 7.42 (d, $J$ = 2.0 Hz, 2 H), 7.67-7.80 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 113.2, 117.6, 127.6, 128.8 129.8, 134.1, 135.2, 139.3; HREI-MS calcd. for C$_{13}$H$_{15}$Te: 351.9065, Found: 351.9076.

![3,5-Dibromophenyl phenyl telluride (4h)](image)

Following the general procedure for Table 3, [Ir(OCH$_3$)(C$_5$H$_5$)$_2$]$_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B$_2$pin$_2$ (186 mg, 0.73 mmol) and 1,3-dibromobenzene (125 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), diphenyl ditelluride (229.7 mg, 0.55 mmol), DMSO (0.4 mL) and H$_2$O (0.2 mL) then purified by column chromatography (SiO$_2$, hexane) to provide 4h as a colorless oil (352 mg, 80 % yield). $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.24-7.39 (m, 2 H), 7.29 (d, $J$ = 7.2 Hz, 1 H), 7.52 (s, 1 H), 7.63 (d, $J$ = 2.0 Hz, 2 H), 7.74-7.78 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 113.3, 118.2, 123.5, 128.8, 129.9, 133.1, 137.4, 139.2; HREI-MS calcd. for C$_{12}$H$_{16}$Br$_2$Te: 439.8055, Found: 439.8056.
Following the general procedure for Table 3, \([\text{Ir(OCH}_3\text{)}(\text{C}_6\text{H}_5)_2]\)_2 (0.7 mg, 0.001 mmol), 4,4'-di-\text{tert}-butyl-2,2'-dipyridyl (0.5 mg, 0.002 mmol), \(\text{B}_3\text{pin}_2\) (186 mg, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (160 \(\mu\)L, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), diphenyl ditelluride (232.1 mg, 0.55 mmol), DMSO (0.4 mL) and \(\text{H}_2\text{O}\) (0.2 mL) then purified by column chromatography (SiO\(_2\), hexane) to provide 4i as a yellow oil (278 mg, 67% yield). \(^1\text{H}\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.29-7.33\) (m, 2 H), 7.39-7.42 (m, 1 H), 7.70 (s, 1 H), 7.81-7.83 (m, 2 H), 7.94 (s, 2 H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\)): \(\delta = 112.7, 117.9, 121.3, 121.3, 121.4, 121.4, 122.8\) (q, \(J = 226.1\) Hz), 129.3, 130.1, 132.0 (q, \(J = 27.5\) Hz), 135.9, 135.9, 139.5, 139.6, 139.7; \(^{19}\text{F}\) NMR (376 MHz, CDCl\(_3\)): \(\delta = -64.6\) (s); HREI-MS calcd. for \(\text{C}_{14}\text{H}_8\text{F}_6\text{Te}\): 419.9592, Found: 419.9601.

![3,5-Bis(trifluoromethyl)phenyl phenyl telluride (4i)](image)

3-Chloro-5-methoxyphenyl phenyl telluride (4j)

Following the general procedure for Table 3, \([\text{Ir(OCH}_3\text{)}(\text{C}_6\text{H}_5)_2]\)_2 (1.1 mg, 0.0015 mmol), 4,4'-di-\text{tert}-butyl-2,2'-dipyridyl (0.9 mg, 0.003 mmol), \(\text{B}_3\text{pin}_2\) (186 mg, 0.73 mmol) and 3-chloroanisole (125 \(\mu\)L, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), diphenyl ditelluride (229.7 mg, 0.55 mmol), DMSO (0.4 mL) and \(\text{H}_2\text{O}\) (0.2 mL) then purified by column chromatography (SiO\(_2\), hexane) to provide 4j as a yellow oil (207 mg, 60 % yield). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.70\) (s, 3 H), 6.76 (t, \(J = 2.0\) Hz, 1 H), 7.03 (dd, \(J = 0.8, 2.4\) Hz, 1 H), 7.18 (dd, \(J = 1.2, 1.6\) Hz, 1 H), 7.22-7.27 (m, 2 H), 7.32 (tt, \(J = 1.2, 7.2\) Hz, 1 H), 7.74-7.76 (m, 2 H). \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta = 55.4, 113.8, 113.8, 116.5, 121.0, 128.4, 128.8, 129.7, 135.3, 138.8, 160.3\); HREI-MS calcd. for \(\text{C}_{14}\text{H}_9\text{ClO}_{1}\text{Te}\): 347.9561, Found: 347.9568.

![3-Chloro-5-methylphenyl phenyl telluride (4k)](image)

3-Chloro-5-methylphenyl phenyl telluride (4k)

Following the general procedure for Table 3, \([\text{Ir(OCH}_3\text{)}(\text{C}_6\text{H}_5)_2]\)_2 (1.1 mg, 0.0015 mmol), 4,4'-di-\text{tert}-butyl-2,2'-dipyridyl (0.9 mg, 0.003 mmol), \(\text{B}_3\text{pin}_2\) (186 mg, 0.73 mmol) and 3-chlorotoluene (120 \(\mu\)L, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2'-bipyridyl (4.3 mg, 0.05 mmol), diphenyl ditelluride (232.1 mg, 0.55 mmol), DMSO (0.4 mL) and \(\text{H}_2\text{O}\) (0.2 mL) then purified by column chromatography (SiO\(_2\), hexane) to
provide 4k as a yellow oil (138 mg, 42% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.24$ (s, 3 H), 7.05 (s, 1 H), 7.21-7.52 (m, 2 H), 7.29-7.31 (m, 1 H), 7.36 (s, 1 H), 7.43 (s, 1 H), 7.72 (dd, $J = 1.2, 8.0$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 20.9, 114.0, 115.7, 128.2, 128.7, 129.6, 134.0, 134.5, 136.2, 138.4, 140.7$; HREI-MS calcd. for C$_{13}$H$_{11}$CITE: 331.9612, Found: 331.9608.

5. Reference

6. Spectra data for new compounds

3,5-Dimethylphenyl phenylsulfide

3a
3-Chloro-5-methylphenyl phenyl sulfide
3-Chloro-5-methylphenyl 4-methoxyphenyl sulfide
4-Aminophenyl 3-chloro-5-methylphenylsulfide

S19
3-Chloro-5-methylphenyl 4-chlorophenyl sulfide
3-Chloro-5-methylphenyl 2-naphthal sulfide
3-Chloro-5-methylphenyl 4-tolyl sulfide
3,5-Bis(trifluoromethyl)phenyl phenyl sulfide

\[ \text{F}_3\text{C}-\begin{array}{c} \text{S} \\ \text{CF}_3 \end{array}-\text{S}-\begin{array}{c} \text{CF}_3 \\ \text{C} \end{array} \]

3h
3,5-Bis(trifluoromethyl)phenyl 4-methoxyphenyl sulfide
3,5-Bis(trifluoromethyl)phenyl4-chlorophenyl sulfide
3-Chloro-5-methoxyphenyl 4-tolyl sulfide

3k
3-Chloro-5-methoxyphenylphenyl sulfide
3-Chloro-5-methoxyphenyl4-chlorophenyl sulfide
3,5-Dichlorophenyl 4-tolyl sulfide
4-Aminophenyl 3,5-dichlorophenylsulfide
3,5-Dichlorophenyl 4-methoxyphenylsulfide
3,5-Dibromophenyl phenyl sulfide

3q
3.5-Dibromophenyl 4-methoxyphenylsulfide
3-Methyl-5-methoxyphenyl phenyl sulfide
2,6-Di-tert-butyl-4-pyridyl4-chlorophenyl sulfide

3t
2.6-Dichloro-4-pyridyl phenyl sulfide

![Chemical structure of 2.6-Dichloro-4-pyridyl phenyl sulfide](image1)

![NMR spectrum of 2.6-Dichloro-4-pyridyl phenyl sulfide](image2)

![Chemical structure of 2.6-Dichloro-4-pyridyl phenyl sulfide](image3)
3-Chloro-5-methylphenyl phenylselenide
3-Methoxy-5-methylphenyl phenylselenide

Electronic Supplementary Material (ESI) for Chemical Communications
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3,5-Bis(trifluoromethyl)phenyl phenyl selenide
3,5-Dichlorophenyl phenyl selenide

![Chemical structure of 3,5-Dichlorophenyl phenyl selenide](image)

![NMR spectrum of 3,5-Dichlorophenyl phenyl selenide](image)
3,5-Dibromophenyl phenyl selenide

**Chemical Structure**

![Chemical Structure Image]

**NMR Spectra**

The NMR spectra show distinct peaks at specific ppm values, indicating the presence of the 3,5-Dibromophenyl phenyl selenide compound.
3-Chloro-5-methoxyphenyl phenyl selenide

![3-Chloro-5-methoxyphenyl phenyl selenide](image1)

![3-Chloro-5-methoxyphenyl phenyl selenide](image2)
3,5-Dichlorophenyl phenyl telluride
3,5-Dibromophenyl phenyl telluride

![Chemical structure of 3,5-Dibromophenyl phenyl telluride](image)

![NMR spectrum of 3,5-Dibromophenyl phenyl telluride](image)
3,5-Bis(trifluoromethyl)phenyl phenyl telluride

![Chemical structure](image1)

![Chemical structure](image2)
3-Chloro-5-methoxyphenyl phenyl telluride
3-Chloro-5-methylphenyl phenyl telluride