Electronic Supplementary Material (ESI) for Chemical Communications

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 CaH_2 and stored in the presence of activated molecular sieves.

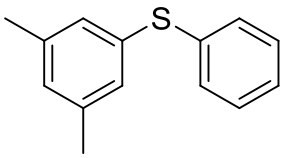
Analysis: NMR spectra were recorded on a Varian Unity Inova-600 or a Varian Mercury-400 instrument using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, 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 1: 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 ℃ 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 **3a**.

2.1 The representative example of Table 1 (entry 14)

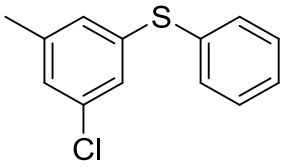
Following the general procedure for Table 1, using CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol) in DMSO (0.4 mL) and H_2O (0.2 mL), then purified by column chromatography (SiO_2, hexane) to provide **3a** as a colorless oil (188 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 6 H), 6.88 (s, 1 H), 6.99 (s, 2 H), 7.20-7.32 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol) and B_2pin_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, arene (1.0 mmol), and THF (1.5 mL) were added via syringe, and the Schrock tube was heated at 80 ℃ 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 H_2O (0.2 mL) were added, and the Schrock tube was connected to an air-filled balloon and heated at 80 ℃ 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 **3**.



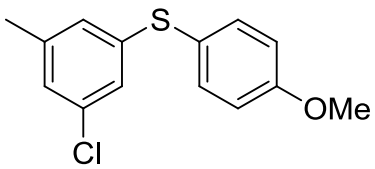
3,5-Dimethylphenyl phenyl sulfide **(3a)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (3.3 mg, 0.05 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (2.7 mg, 0.1 mmol), B_2pin_2 (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 H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3a** as a colorless oil (118 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 6 H), 6.88 (s, 1 H), 6.99 (s, 2 H), 7.20-7.32 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 126.6, 129.0, 129.1, 130.4, 134.7, 136.3, 138.8; HREI-MS calcd. for $C_{14}H_{14}S$: 214.0816, Found: 214.0809.



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

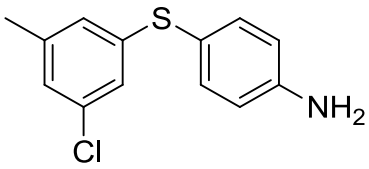
Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_2 (186 mg, 0.73 mmol) and 3-chlorotoluene (120 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), diphenyl disulfide (121.3 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3b** as a colorless oil (176 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 3 H), 6.99 (s, 2 H), 7.04 (s, 1 H), 7.27-7.38 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{13}H_{11}ClS$: 234.0270, Found: 234.0264.



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

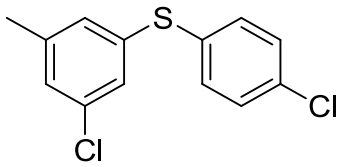
Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_2 (186 mg, 0.73 mmol) and 3-chlorotoluene (120 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), bis(4-methoxyphenyl) disulfide (157.9 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3c** as a colorless oil (161 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100

MHz, $CDCl_3$): δ = 21.1, 55.3, 115.1, 122.8, 124.2, 126.2, 126.4, 134.4, 135.9, 140.2, 140.7, 160.2; HREI-MS calcd. for $C_{14}H_{13}ClOS$: 264.0376, Found: 264.0378.



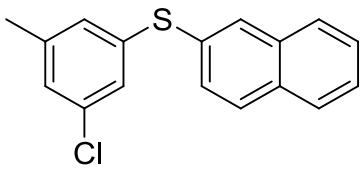
4-Aminophenyl 3-chloro-5-methylphenyl sulfide **(3d)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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), 4-aminophenyl disulfide (139.4 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3d** as a yellow solid (116 mg, 46% yield). M.P.: 66−67 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{13}H_{12}ClNS$: 249.0379, Found: 249.0375.



3-Chloro-5-methylphenyl 4-chlorophenyl sulfide **(3e)**

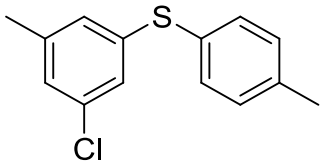
Following the general procedure for Table 2, $Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_2 (186 mg, 0.73 mmol) and 3-chlorotoluene (120 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), bis(4-chlorophenyl) disulfide (158.0 mg, 0.55mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3e** as a colorless oil (213 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 6.98 (s, 1 H), 7.01-7.03 (m, 2 H), 7.28 (br s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{13}H_{10}Cl_2S$: 267.9880, Found: 267.9886.



3-Chloro-5-methylphenyl 2-naphthyl sulfide **(3f)**

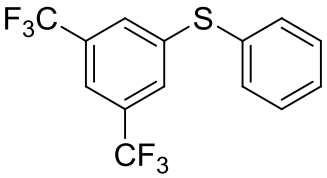
Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_2 (186 mg, 0.73 mmol) and 3-chlorotoluene (120 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, CuCl (2.9 mg, 0.05 mmol), 2,2′-bipyridyl (4.3 mg, 0.05 mmol), 2-naphthyl disulfide

(175.2 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3f** as a colorless oil (188 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{17}H_{13}ClS$: 284.0426, Found: 284.0418.



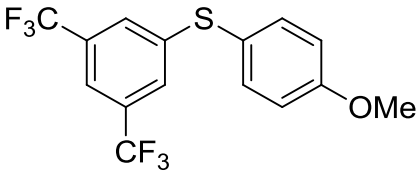
3-Chloro-5-methylphenyl 4-tolyl sulfide **(3g)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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), *p*-tolyl disulfide (135.5 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3g** as a colorless oil (171 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{13}H_{11}ClS$: 248.0426, Found: 248.0425.



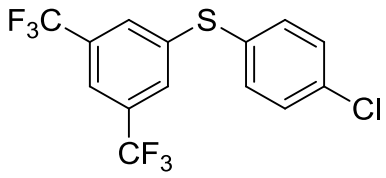
3,5-Bis(trifluoromethyl)phenyl phenyl sulfide **(3h)** [1]

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′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_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 disulfide (121.3 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3h** as a colorless oil (282 mg, 88% yield). ^{1}H NMR (600 MHz, $CDCl_3$): 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); ^{13}C NMR (125 MHz, $CDCl_3$): 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; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.7 (s).



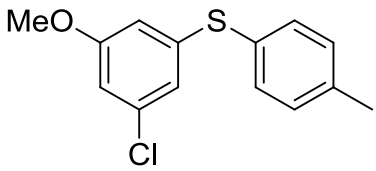
3,5-Bis(trifluoromethyl)phenyl 4-methoxyphenyl sulfide **(3i)**

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′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_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), bis(4-methoxyphenyl) disulfide (157.9 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3i** as a white solid (285 mg, 81% yield). M.P.: 54−55 °C. ^{1}H NMR (600 MHz, $CDCl_3$): 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); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.4, 115.7, 118.7, 118.8, 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; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.6 (s); HREI-MS calcd. for $C_{15}H_{10}F_6OS$: 352.0357, Found: 352.0351.



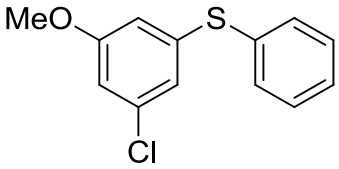
3,5-Bis(trifluoromethyl)phenyl 4-chlorophenyl sulfide **(3j)**

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′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_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), bis(4-chlorophenyl) disulfide (158.0 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3j** as a colorless oil (303 mg, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40-7.43 (m, 4 H), 7.58 (s, 2 H), 7.66 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): 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; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.7 (s); HREI-MS calcd. for $C_{14}H_7ClF_6S$: 355.9861, Found: 355.9856.



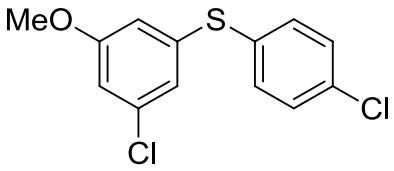
3-Chloro-5-methoxyphenyl 4-tolyl sulfide **(3k)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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), *p*-tolyl disulfide (138.2 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3k** as a colorless oil (166 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{14}H_{13}ClOS$: 264.0376, Found: 264.0370.



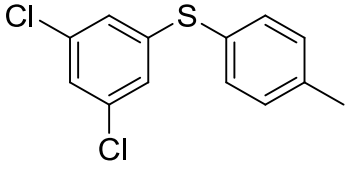
3-Chloro-5-methoxyphenyl phenyl sulfide **(3l)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **3l** as a colorless oil (217 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{13}H_{11}ClOS$: 250.0219, Found: 250.0220.



3-Chloro-5-methoxyphenyl 4-chlorophenyl sulfide **(3m)**

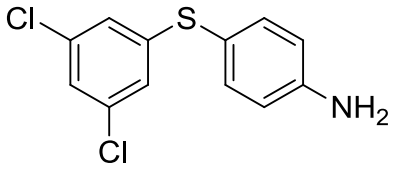
Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_2 (186 mg, 0.73 mmol) and 3-chloroanisole (125 μL, 1.0 mmol) in THF (1.5 mL)in the first step. After heating and evaporation of solvent, CuCl (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_2O (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, $CDCl_3$): δ = 3.71 (s, 3 H), 6.66 (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, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 $C_{13}H_{10}Cl_2SO$: 283.9829, Found: 283.9834.



3,5-Dichlorophenyl 4-tolyl sulfide **(3n)**

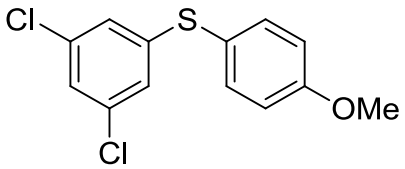
Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_2 (186 mg, 0.73 mmol) and 1,3-dichlorobenzene (114 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, 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_2O (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 21.2, 125.5, 125.6, 127.7, 130.5, 134.1, 135.2, 139.4, 142.3; HREI-MS calcd. for $C_{13}H_{10}Cl_2S$: 267.9880, Found: 267.9890.



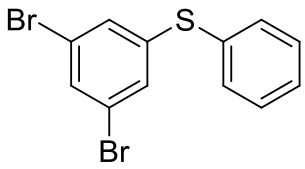
4-Aminophenyl 3,5-dichlorophenyl sulfide **(3o)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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), 4-aminophenyl disulfide (139.4 mg, 0.55 mmole), DMSO (0.4 mL) and H_2O (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 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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.



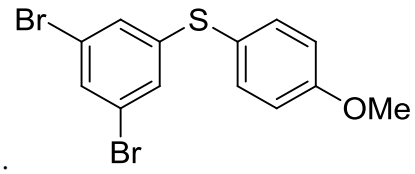
3,5-Dichlorophenyl 4-methoxyphenyl sulfide **(3p)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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), bis(4-methoxyphenyl) disulfide (157.8 mg, 0.55 mmole), DMSO (0.4 mL) and H_2O (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 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, CDCl3): δ = 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.



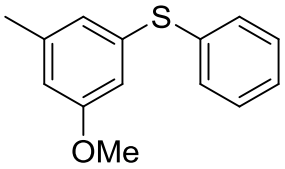
3,5-Dibromophenyl phenyl sulfide **(3q)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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_2O (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, $CDCl_3$): δ = 7.25 (d, *J* = 1.6 Hz, 2 H), 7.36-7.45 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.2,128.7, 129.7, 129.9, 131.6, 132.2, 133.2, 141.6; HREI-MS calcd. for $C_{12}H_8Br_2S$: 341.8713, Found: 341.8716.



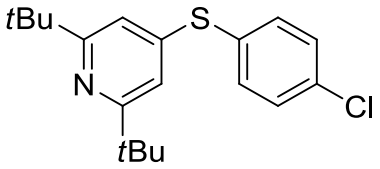
3,5-Dibromophenyl 4-methoxyphenyl sulfide (**3r)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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_2O (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 55.3, 115.4, 121.1, 123.1, 137.8, 130.6, 136.6, 143.8, 160.6; HREI-MS calcd. for $C_{13}H_{10}Br_2SO$: 371.8819, Found: 371.8820.



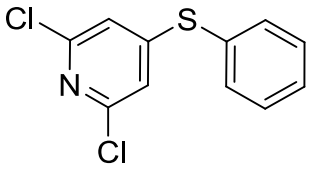
3-Methyl-5-methoxyphenyl phenyl sulfide **(3s)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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_2O (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 21.4, 55.2, 113.1, 113.8, 123.9, 127.0, 129.1, 131.1, 135.5, 136.5, 140.2, 160.0; HREI-MS calcd. for $C_{14}H_{14}OS$: 230.0765, Found: 230.0726.



2,6-Di-*tert*-butyl-4-pyridyl 4-chlorophenyl sulfide **(3t)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (20 mg, 0.03 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (16 mg, 0.06 mmol), B_2pin_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_2O (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 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.27 (s, 18H), 6.83 (s, 2 H), 7.36 (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 $C_{19}H_{24}ClNS$: 333.1318, Found: 333.1322.

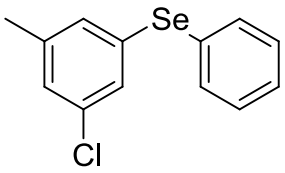


2,6-Dichloro-4-pyridyl phenyl sulfide **(3u)**

Following the general procedure for Table 2, $[Ir(OCH_3)(C_8H_{12})]_2$ (22 mg, 0.03 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (18 mg, 0.06 mmol), B_2pin_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_2O (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 $C_{11}H_7Cl_2NS$: 254.9676, Found: 254.9671.

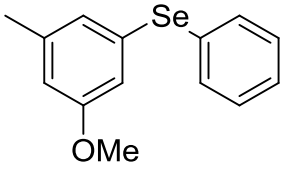
4. General procedure for Table 3: A Schrock tube equipped with a magnetic stirrer bar was charged with $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol) and B_2pin_2 (186 mg, 0.73 mmol) in a nitrogen-filled glove box.The Schrock tube was then covered 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 ℃ 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 andremoved from the glove box. Under an air atmosphere, DMSO (0.4 mL) and H_2O (0.2 mL) were added, and the Schrock tubewas connected to an air-filled balloon and heated at 80 ℃ 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**.



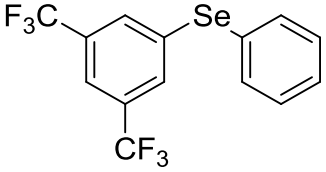
3-Chloro-5-methylphenyl phenyl selenide **(4a)**

Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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_2O (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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)**

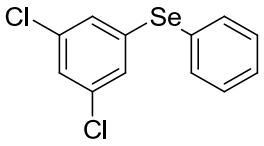
Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_2 (186 mg, 0.73 mmol) and 1,3-dichlorobenzene (114 μL, 1.0 mmol) in THF (1.5 mL) in the first step. After heating and evaporation of solvent, 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_2O (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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)**

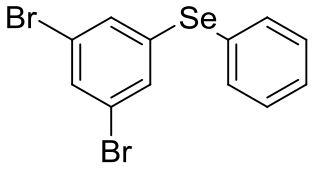
Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (0.7 mg, 0.001 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_2 (186 mg, 0.73 mmol) and 1,3-bis(trifluoromethyl)benzene (160 μL, 1.0 mmol) in THF (1.5 mL) in

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 H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **4c** as a colorless oil (270 mg, 73% yield). ^{1}H NMR (600 MHz, $CDCl_3$): 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); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 120.3, 120.4, 120.4, 120.4, 120.4, 122.9 (q, *J* = 27.6 Hz), 127.7, 129.2, 130.0, 130.6, 130.6, 132.2 (q, *J* = 27.6 Hz), 135.0, 135.0, 135.0, 135.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.7 (s); HREI-MS calcd. for $C_{14}H_8F_6Se$: 369.9695, Found: 369.9699.



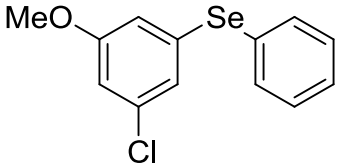
3,5-Dichlorophenyl phenyl selenide **(4d)**

Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **4d** as a colorless oil (245 mg, 81 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.8, 128.4, 128.6, 129.0, 129.7, 134.6, 135.3, 135.3; HREI-MS calcd. for $C_{12}H_8Cl_2Se$: 301.9168, Found: 301.9164.



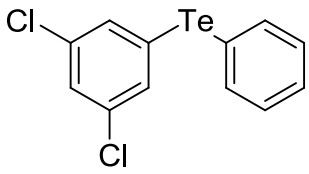
3,5-Dibromophenyl phenyl selenide **(4e)**

Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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 diselenide (175.1 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **4e** as a colorless oil (384 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.3, 128.5, 128.5 129.6, 132.1, 132.2, 134.4, 135.8; HREI-MS calcd. for $C_{12}H_8Br_2Se$: 389.8158, Found: 389.8162.



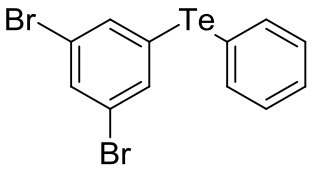
3-Chloro-5-methoxyphenyl phenyl selenide **(4f)**

Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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_2O (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, 128.1, 129.4, 129.5, 134.0, 134.1, 135.2, 160.4; HREI-MS calcd. for $C_{13}H_{11}ClOSe$: 297.9664, Found: 297.9658.



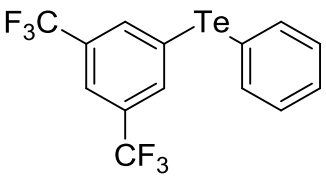
3,5-Dichlorophenyl phenyl telluride **(4g)**

Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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_2O (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), 7.76-7.80 (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 $C_{12}H_8Cl_2Te$: 351.9065, Found: 351.9076.



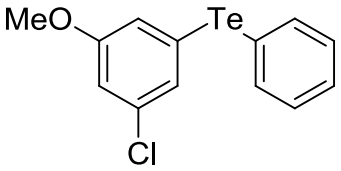
3,5-Dibromophenyl phenyl telluride **(4h)**

Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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_2O (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 $C_{12}H_8Br_2Te$: 439.8055, Found: 439.8056.



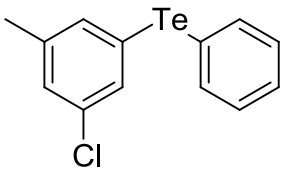
3,5-Bis(trifluoromethyl)phenyl phenyl telluride **(4i)**

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′-dipyridyl (0.5 mg, 0.002 mmol), B_2pin_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 ditelluride (232.1 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **4i** as a yellow oil (278 mg, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 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}C NMR (125 MHz, $CDCl_3$): δ = 112.7, 117.9, 121.3, 121.3, 121.3, 121.3, 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}F NMR (376 MHz, $CDCl_3$): δ = -64.6 (s); HREI-MS calcd. for $C_{14}H_8F_6Te$: 419.9592, Found: 419.9601.



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

Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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 ditelluride (229.7 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to provide **4j** as a yellow oil (207 mg, 60 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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}C NMR (100 MHz, $CDCl_3$): δ = 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 $C_{13}H_{11}ClOTe$: 347.9561, Found: 347.9568.



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

Following the general procedure for Table 3, $[Ir(OCH_3)(C_8H_{12})]_2$ (1.1 mg, 0.0015 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.9 mg, 0.003 mmol), B_2pin_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 ditelluride (232.1 mg, 0.55 mmol), DMSO (0.4 mL) and H_2O (0.2 mL) then purified by column chromatography (SiO_2, hexane) to

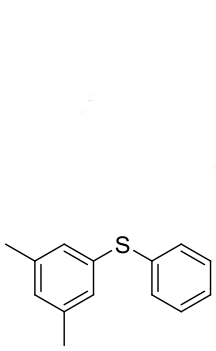
provide **4k** as a yellow oil (138 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 3 H), 7.05 (s, 1 H), 7.21-7.52 (m, 2 H), 7.29-7.31 (m, 1 H), 7.36 (s, 1 H), 7.43 (s, 1 H), 7.72 (dd, *J* = 1.2, 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 114.0, 115.7, 128.2, 128.7, 129.6, 134.0, 134.5, 136.2, 138.4, 140.7; HREI-MS calcd. for $C_{13}H_{11}ClTe$: 331.9612, Found: 331.9608.

5. Reference

1. N. Kornblum, L. Cheng, R. C. Kerber, M. M. Kestner, B. N. Newton, H. W. Pinnick, R. G. Smith and P. A. Wade, *J. Org. Chem.*, 1976, **41**, 1560.

6. Spectra data for new compounds

3,5-Dimethylphenyl phenylsulfide



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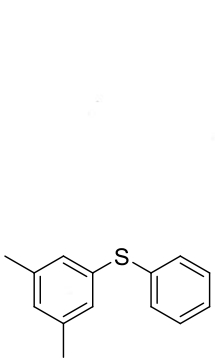
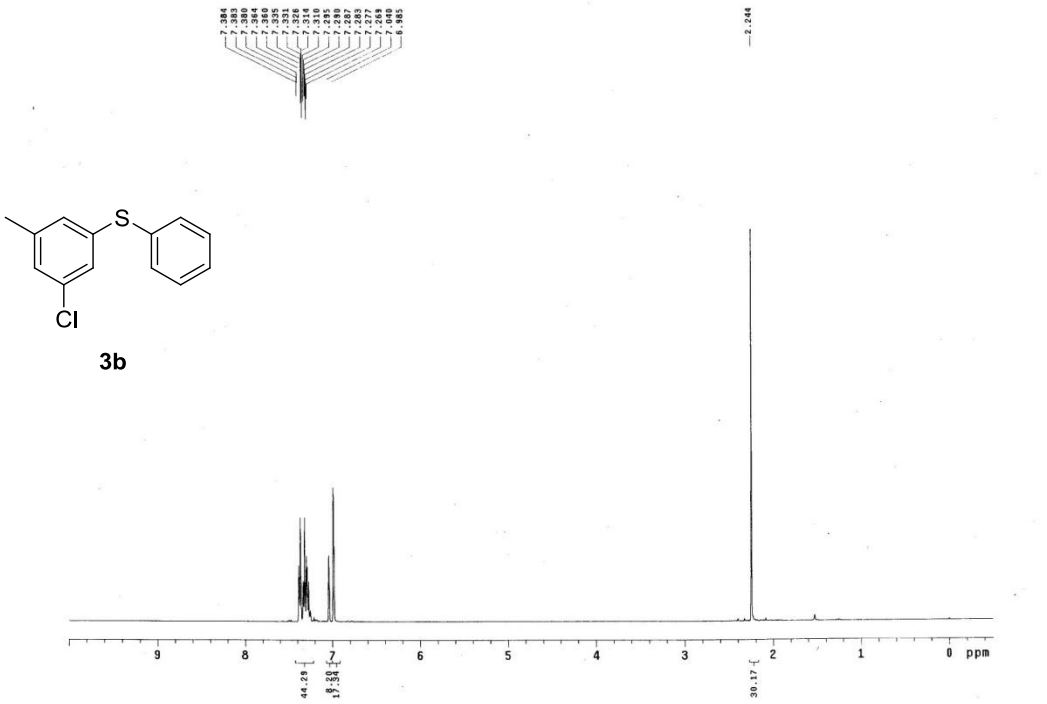
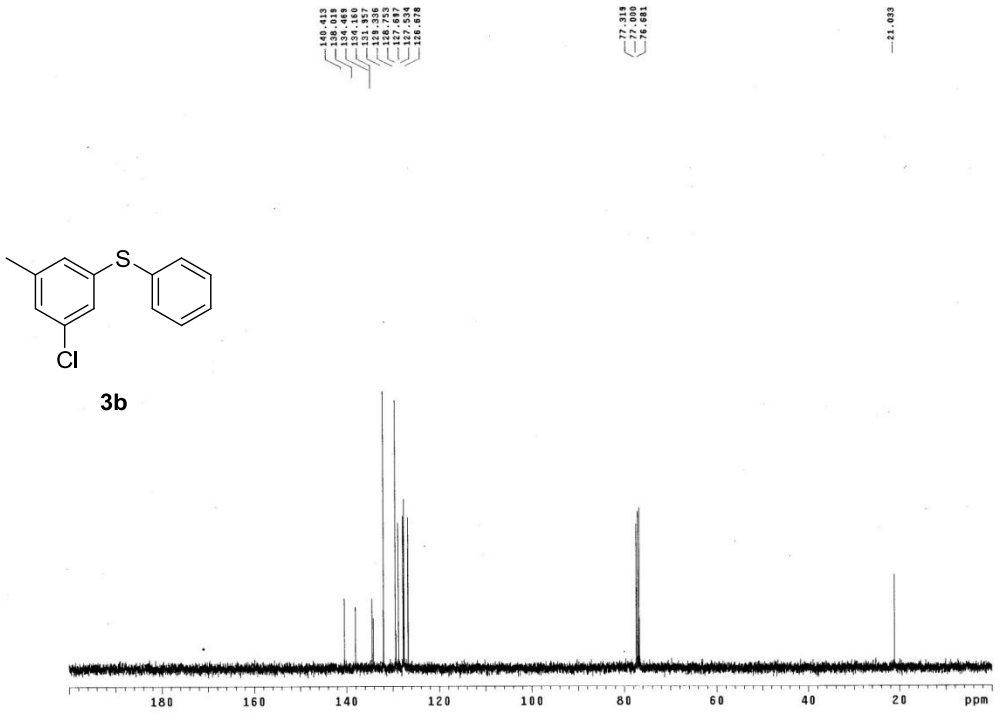


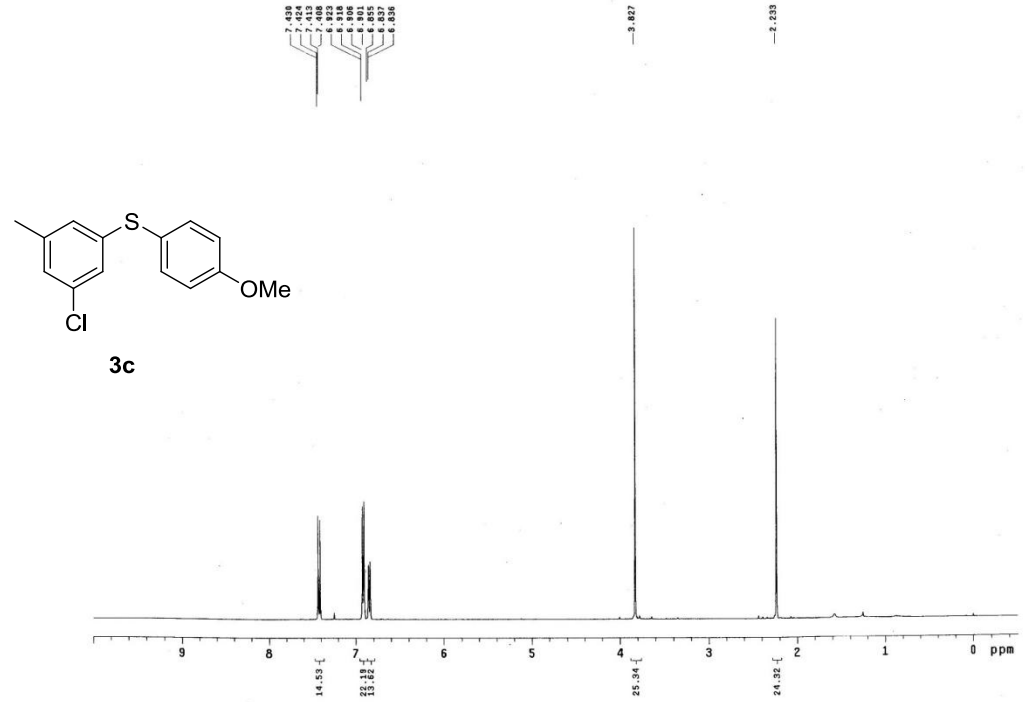
3a

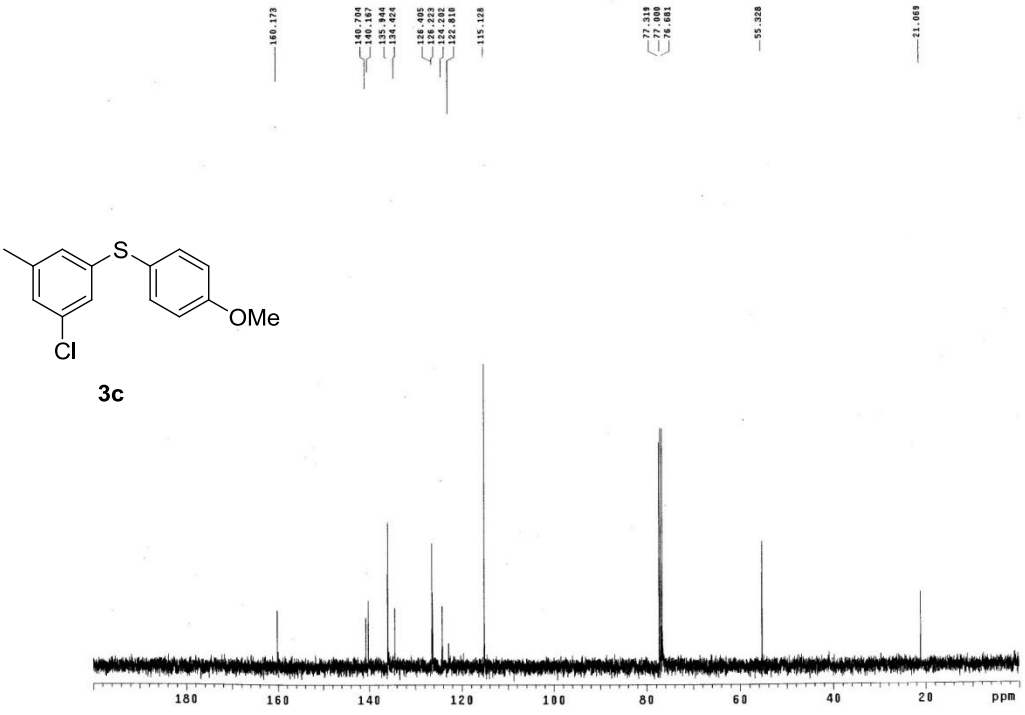
3-Chloro-5-methylphenyl phenyl sulfide



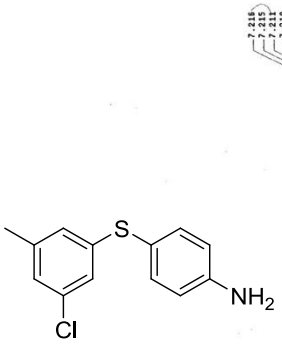


3-Chloro-5-methylphenyl 4-methoxyphenyl sulfide





4-Aminophenyl 3-chloro-5-methylphenylsulfide



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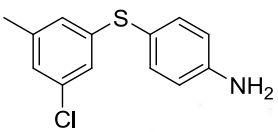
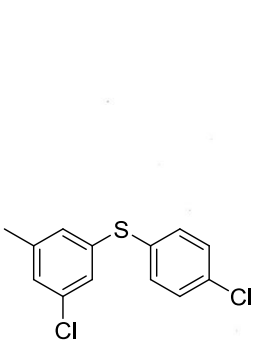


3d

3-Chloro-5-methylphenyl 4-chlorophenyl sulfide



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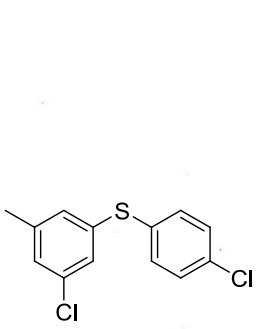
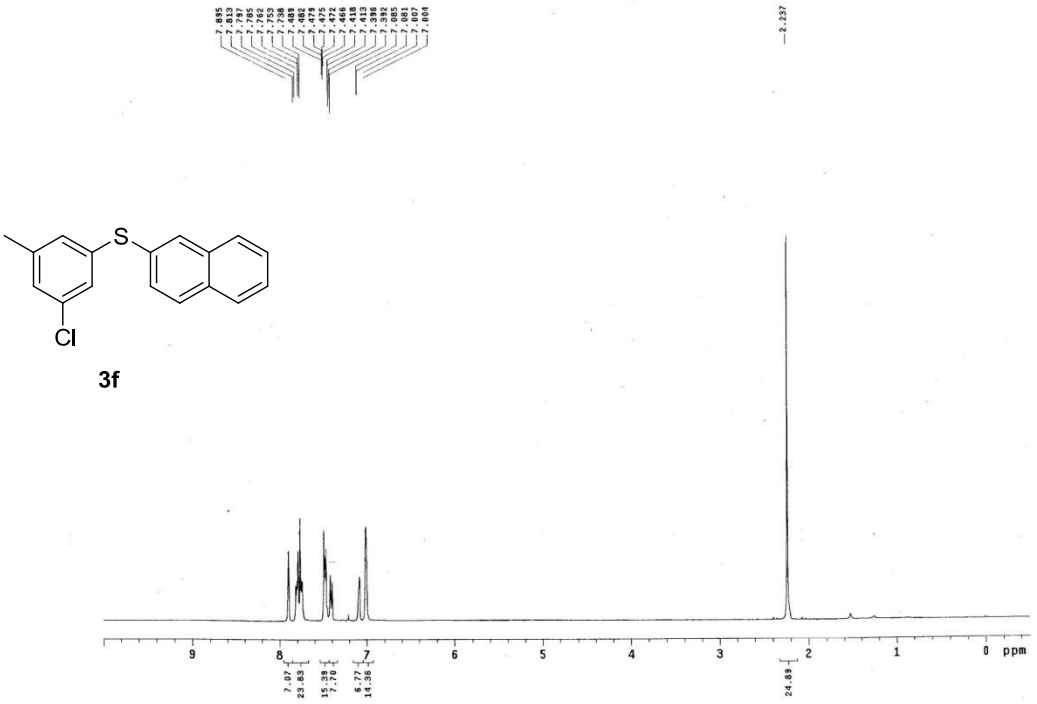
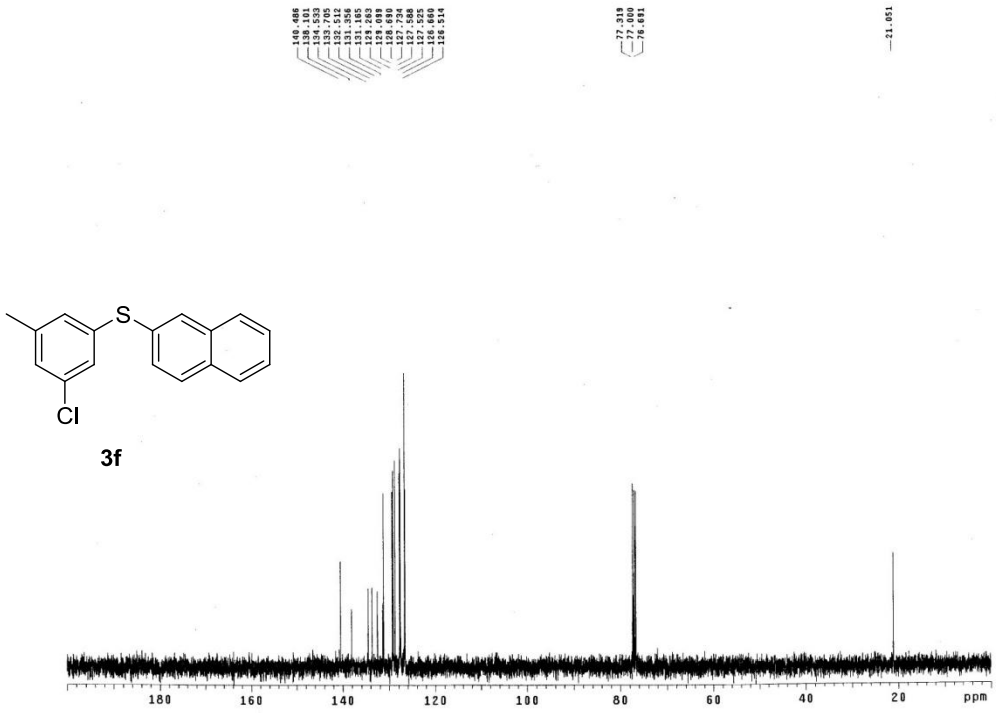


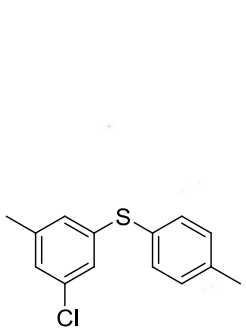
3e

3-Chloro-5-methylphenyl 2-naphthal sulfide





3-Chloro-5-methylphenyl 4-tolyl sulfide



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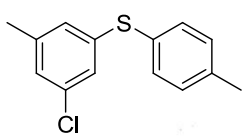

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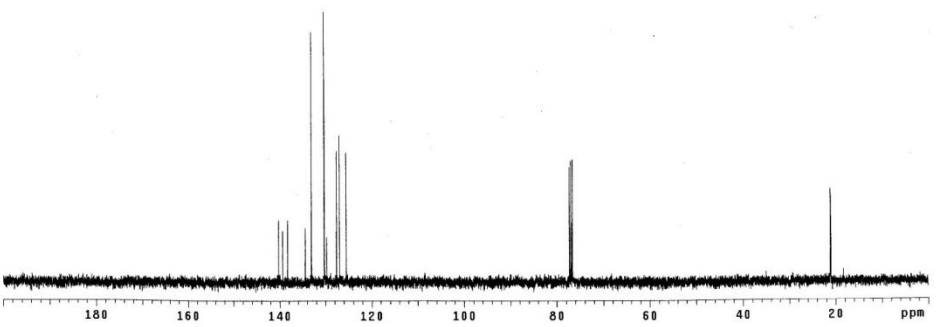
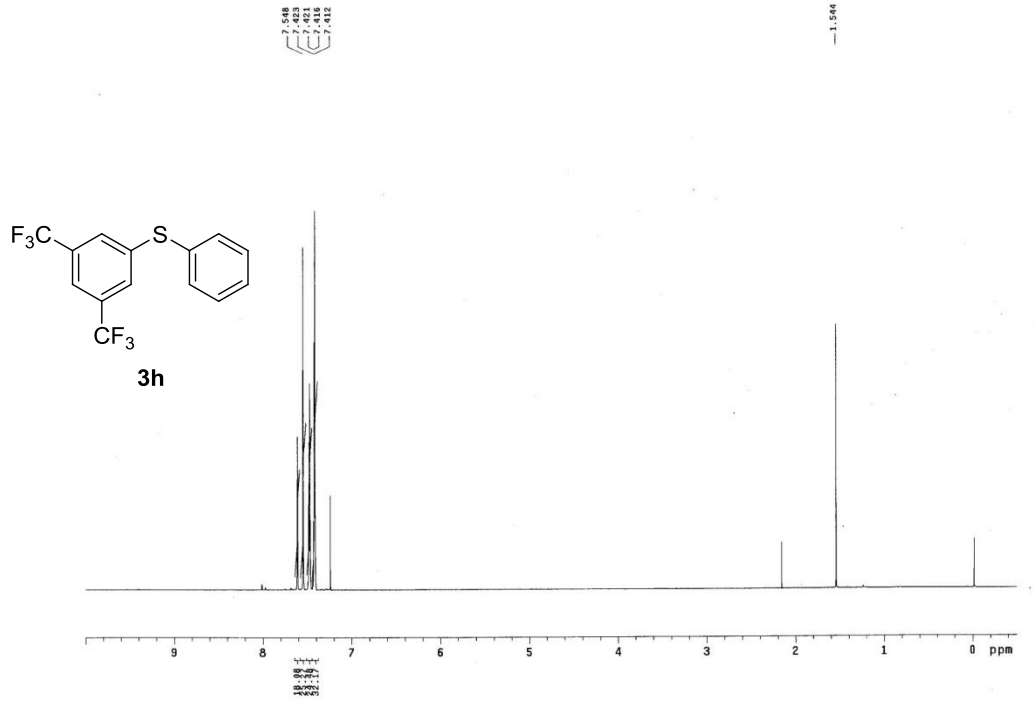
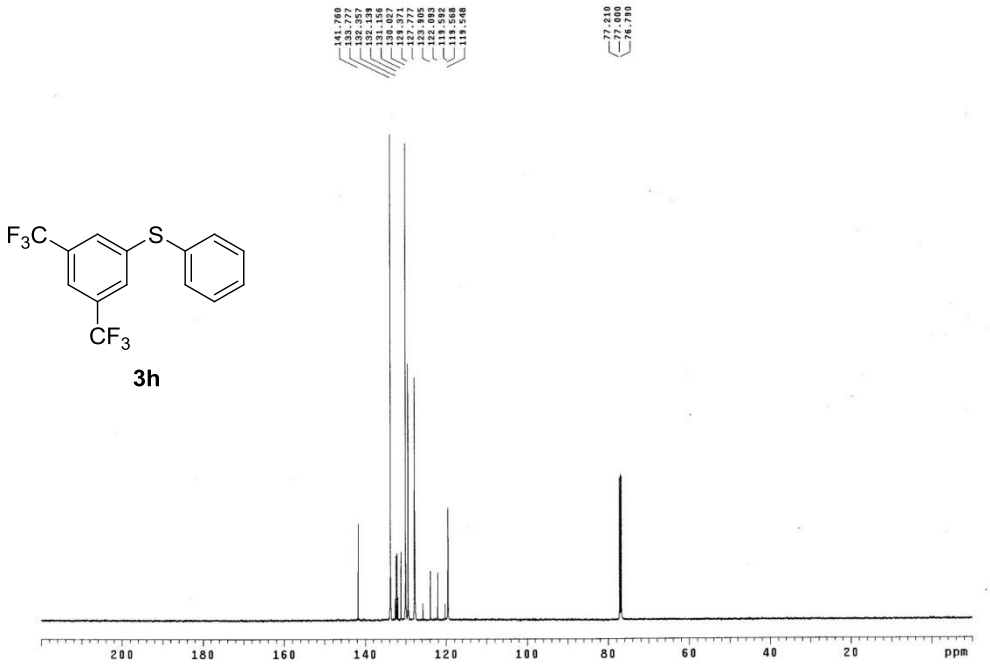
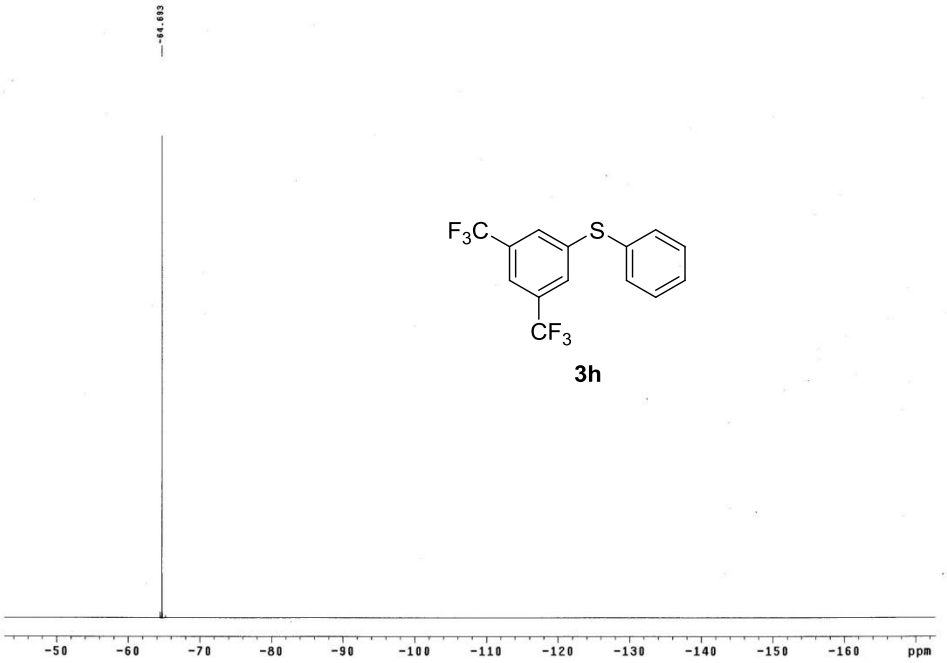


3,5-Bis(trifluoromethyl)phenyl phenyl sulfide

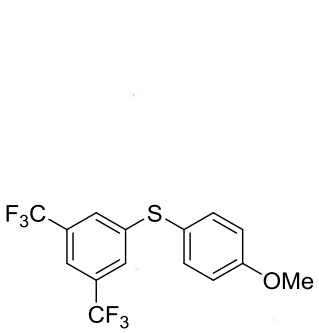






3h

3,5-Bis(trifluoromethyl)phenyl 4-methoxyphenyl sulfide



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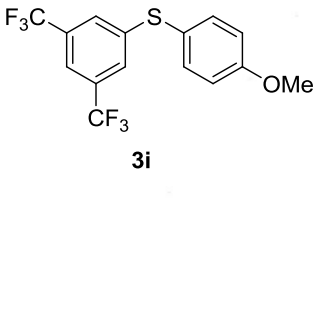

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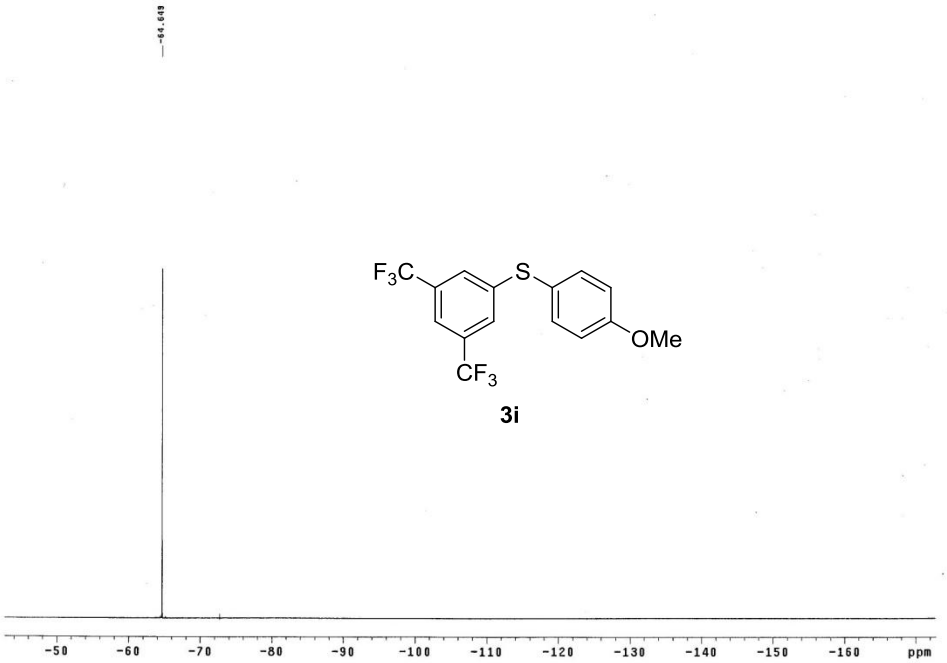
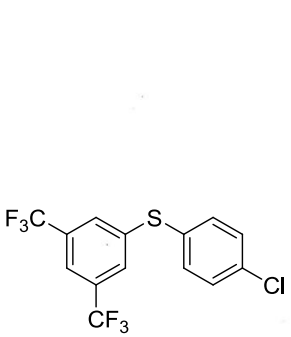


3i

3,5-Bis(trifluoromethyl)phenyl4-chlorophenyl sulfide



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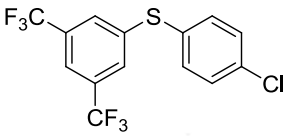

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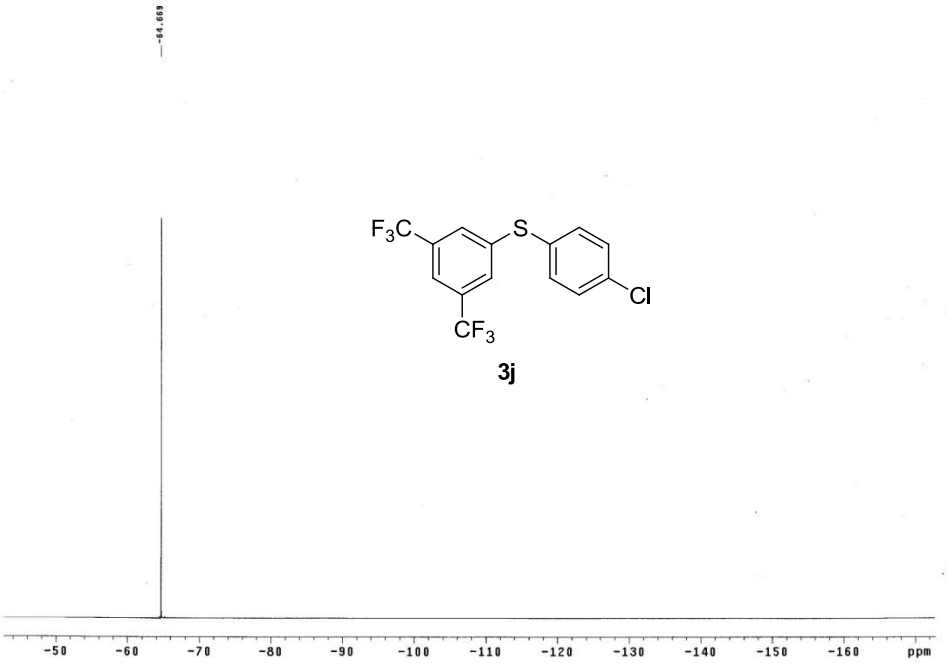

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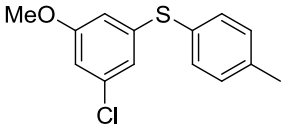
3-Chloro-5-methoxyphenyl 4-tolyl sulfide



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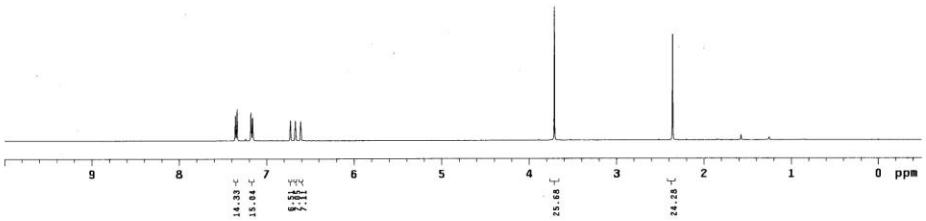

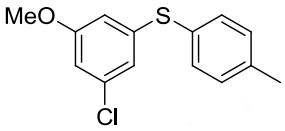

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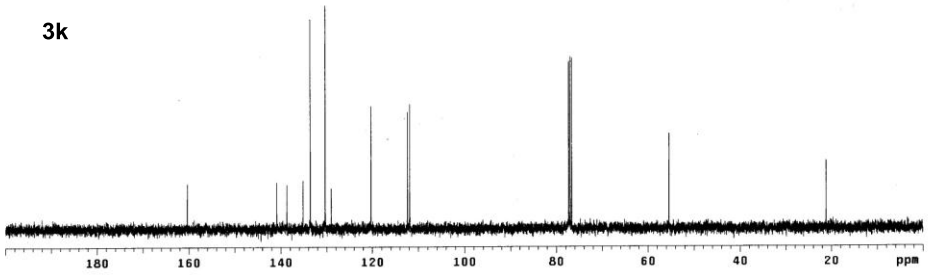
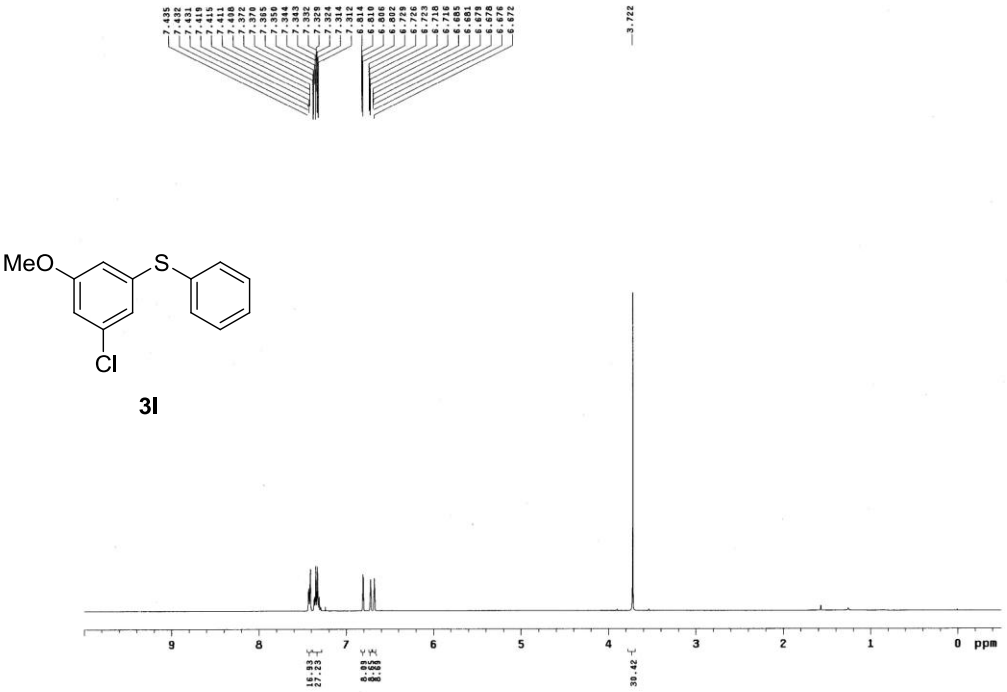
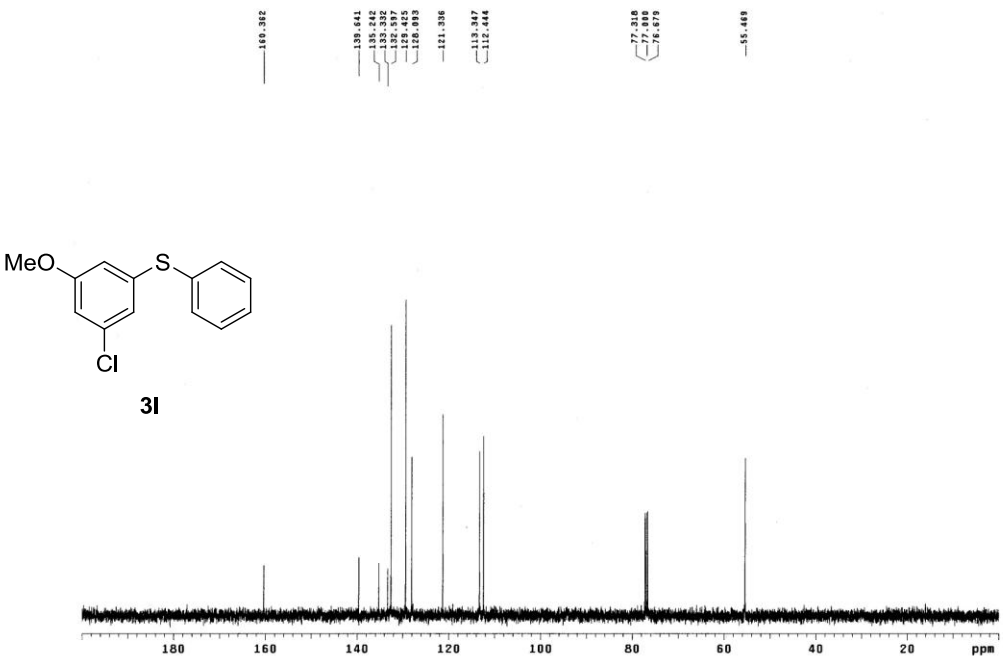
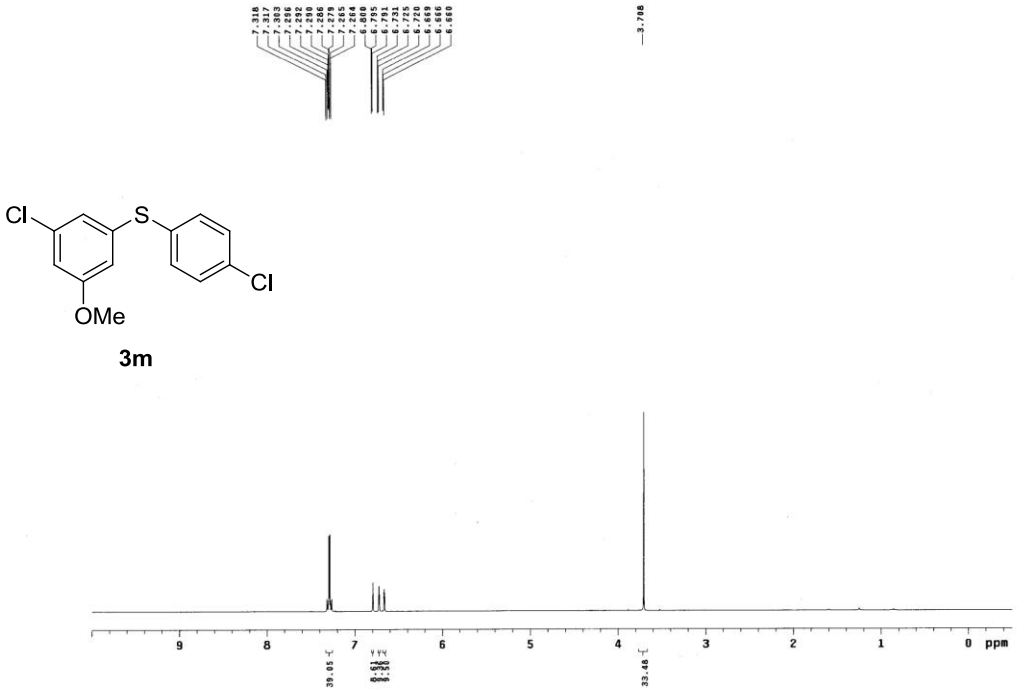


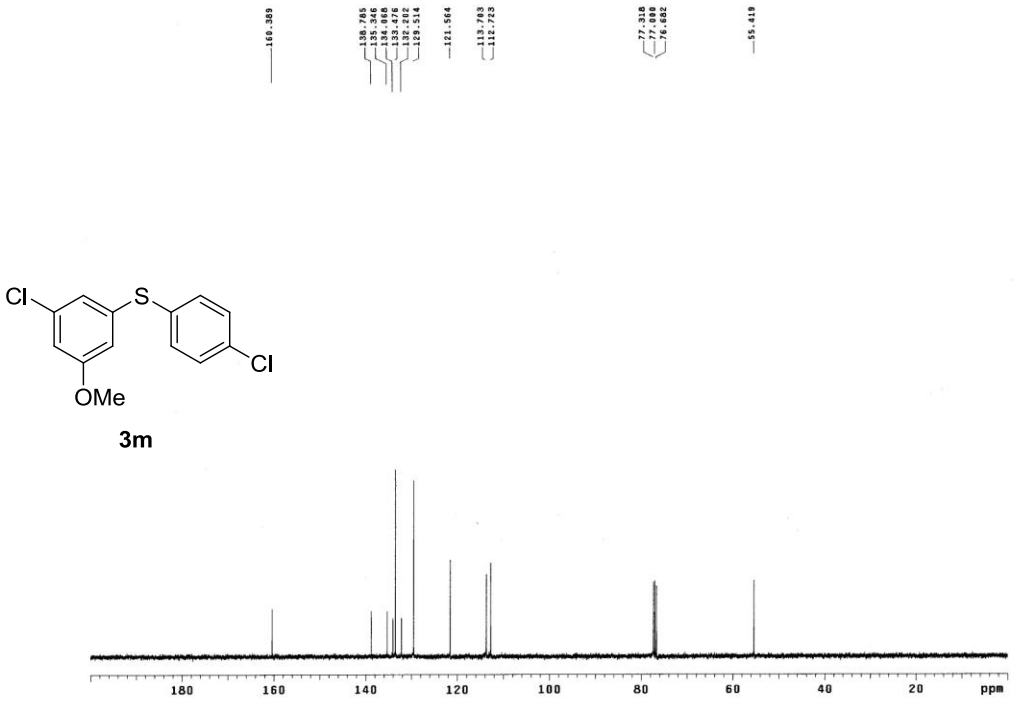
3-Chloro-5-methoxyphenylphenyl sulfide



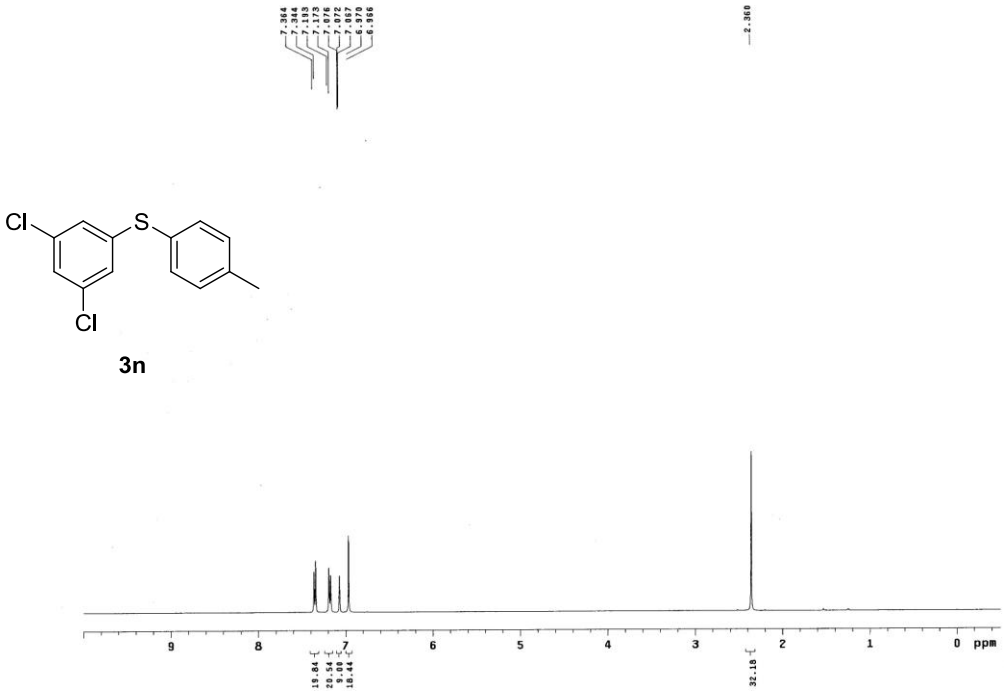


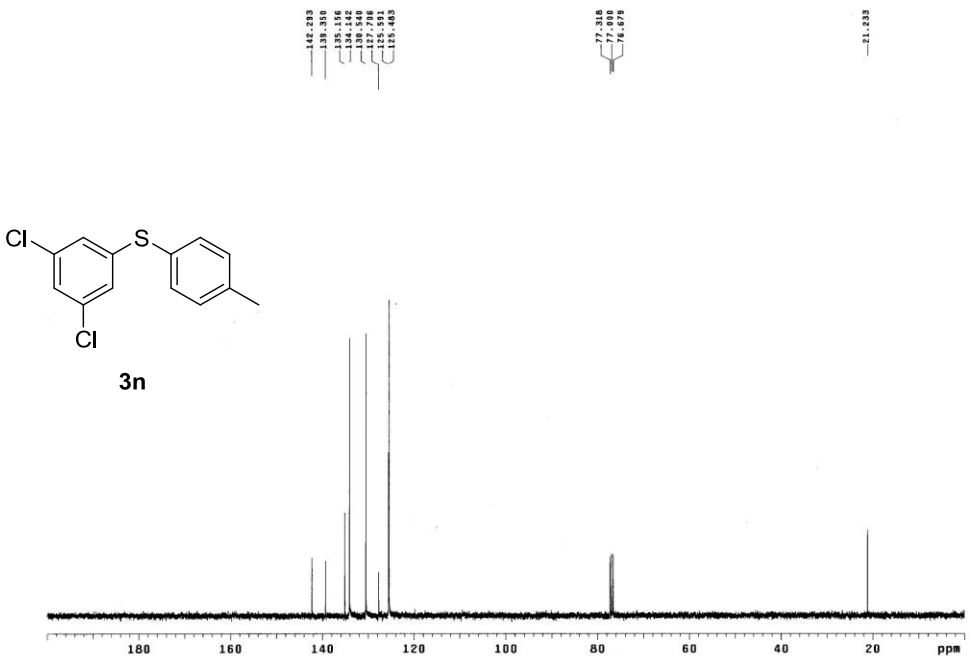
3-Chloro-5-methoxyphenyl4-chlorophenyl sulfide



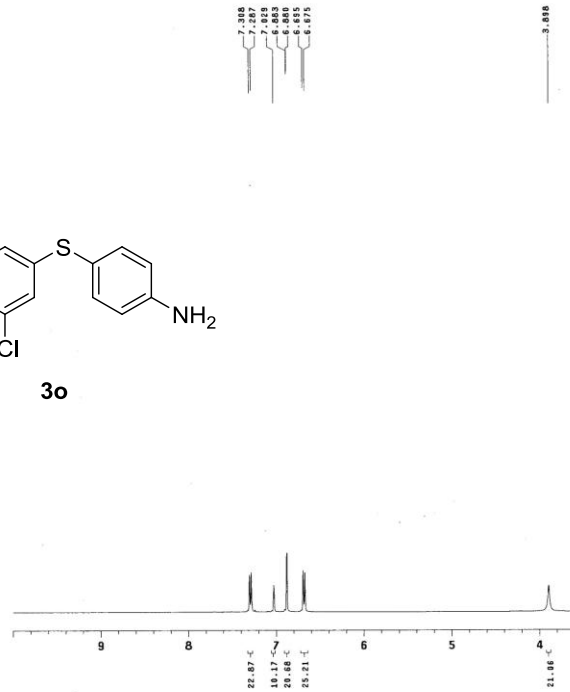


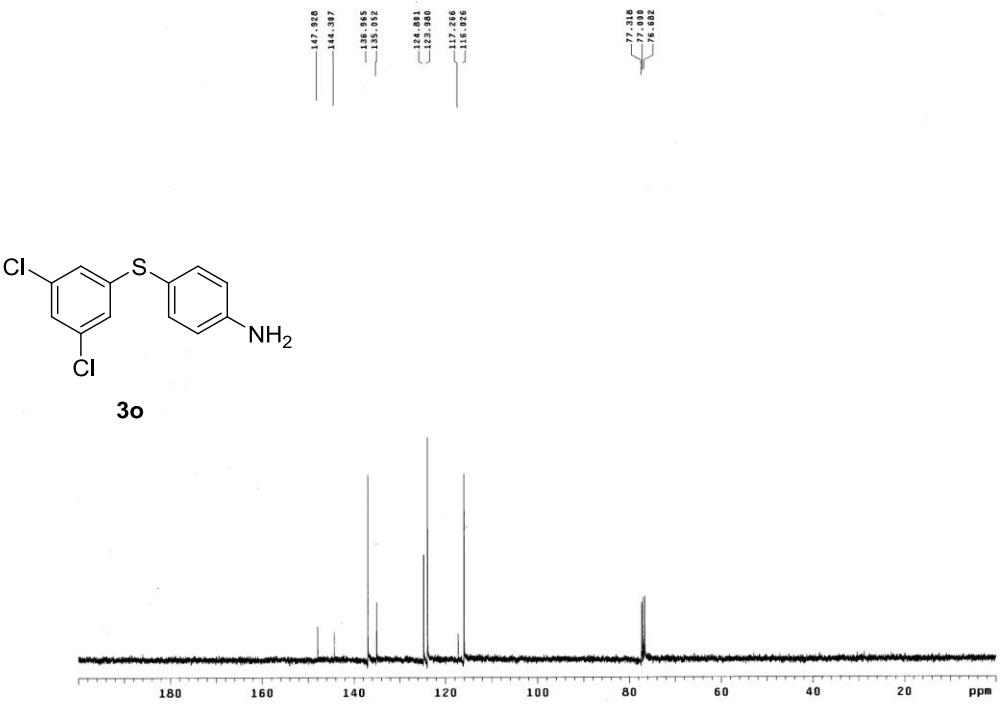
3,5-Dichlorophenyl 4-tolyl sulfide



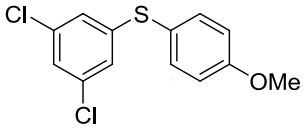


4-Aminophenyl 3,5-dichlorophenylsulfide





3,5-Dichlorophenyl 4-methoxyphenylsulfide



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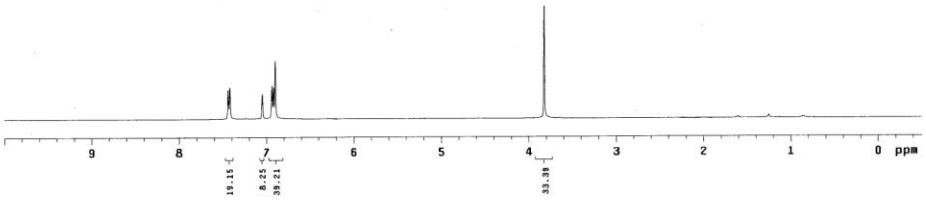

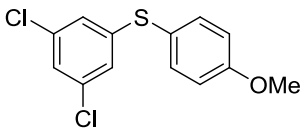

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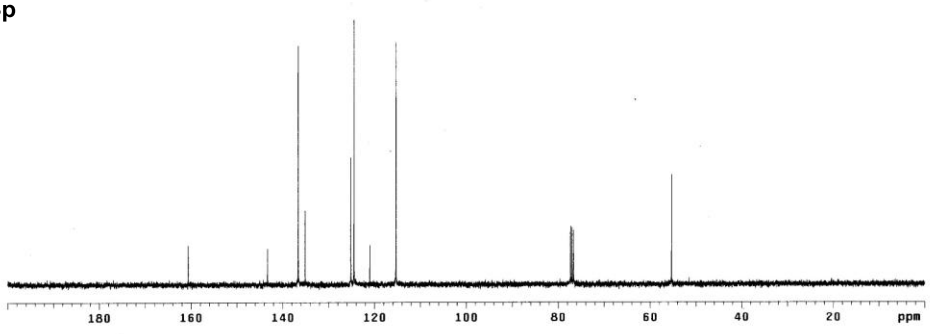
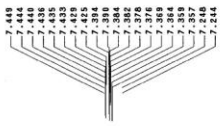
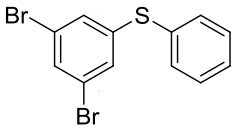


3,5-Dibromophenyl phenyl sulfide





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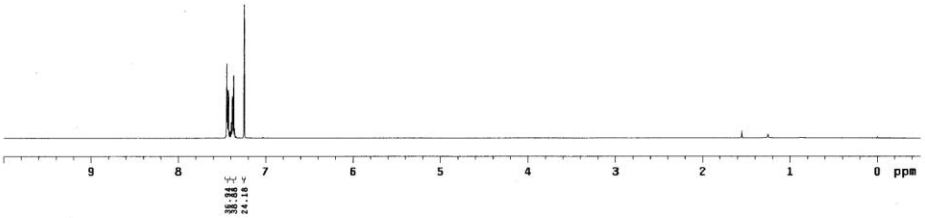

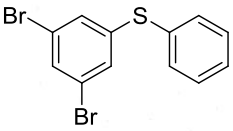

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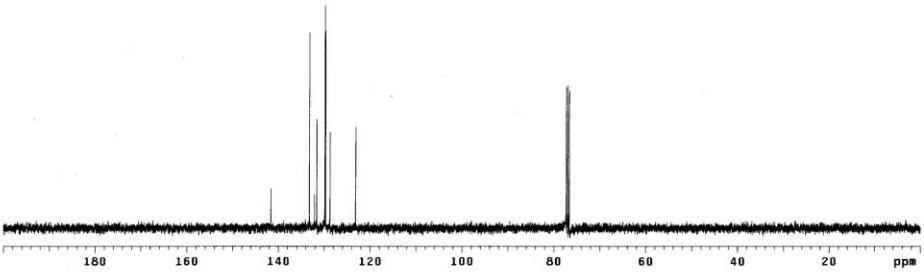
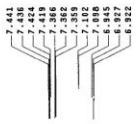
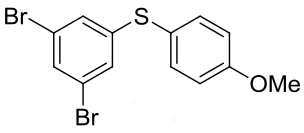


3,5-Dibromophenyl 4-methoxyphenylsulfide





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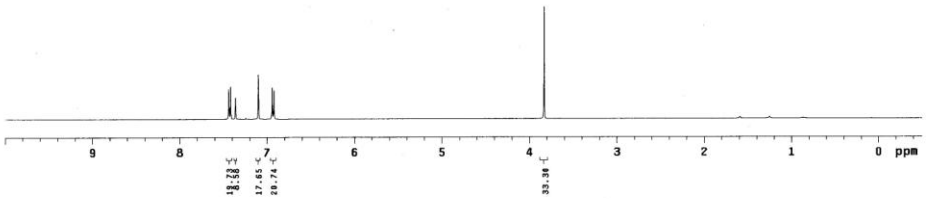

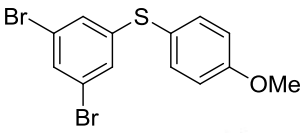

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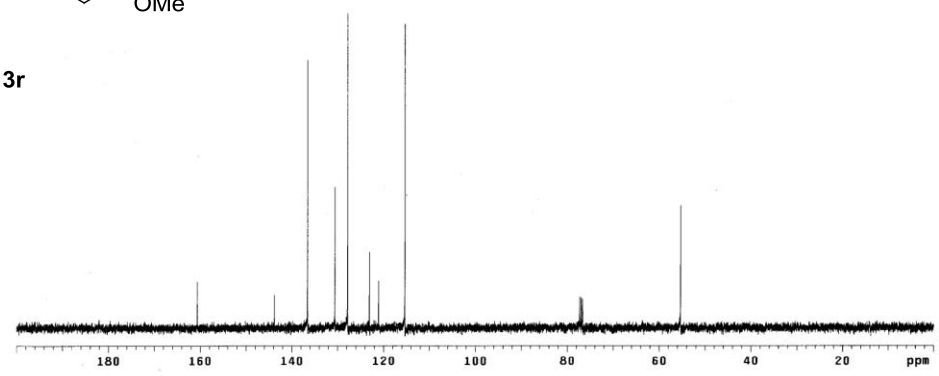
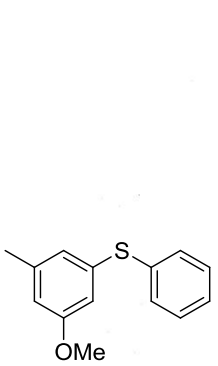
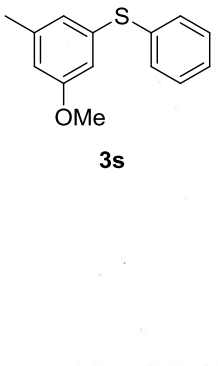


3-Methyl-5-methoxyphenyl phenyl sulfide

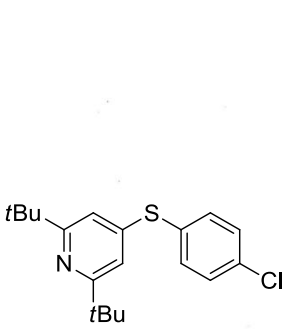


3s



3s

2,6-Di-*tert*-butyl-4-pyridyl4-chlorophenyl sulfide



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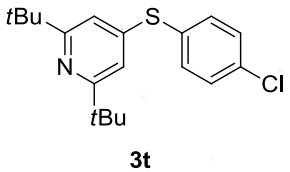
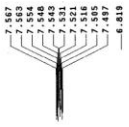
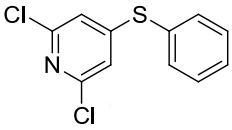


3t

2,6-Dichloro-4-pyridyl phenyl sulfide





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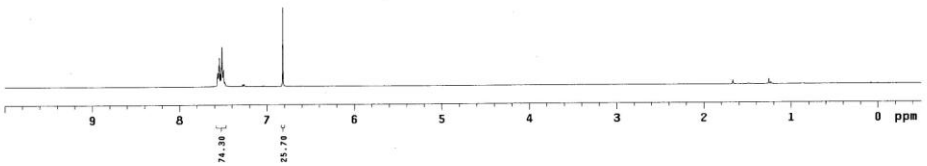

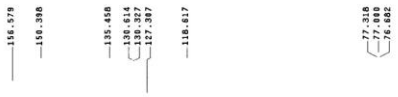

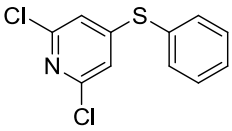

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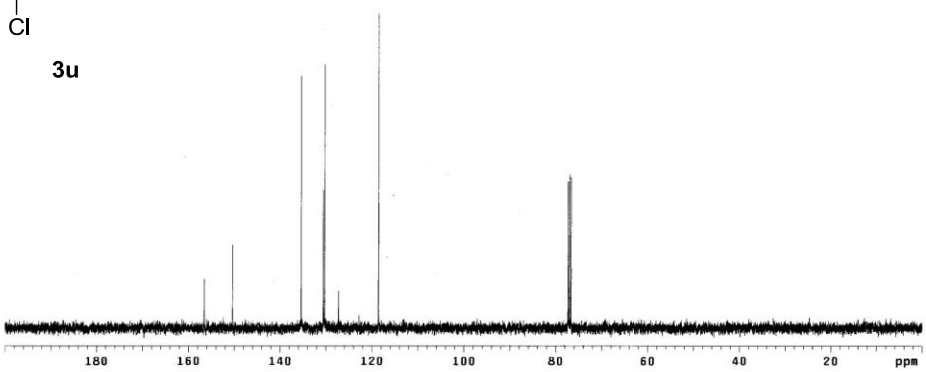
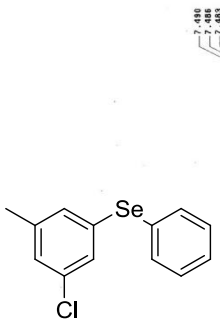
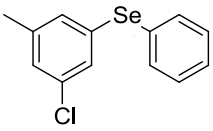


3-Chloro-5-methylphenyl phenylselenide



4a



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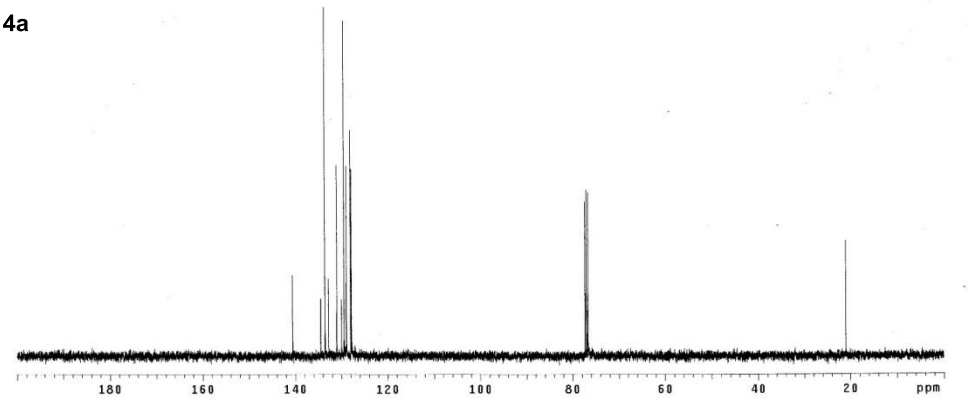
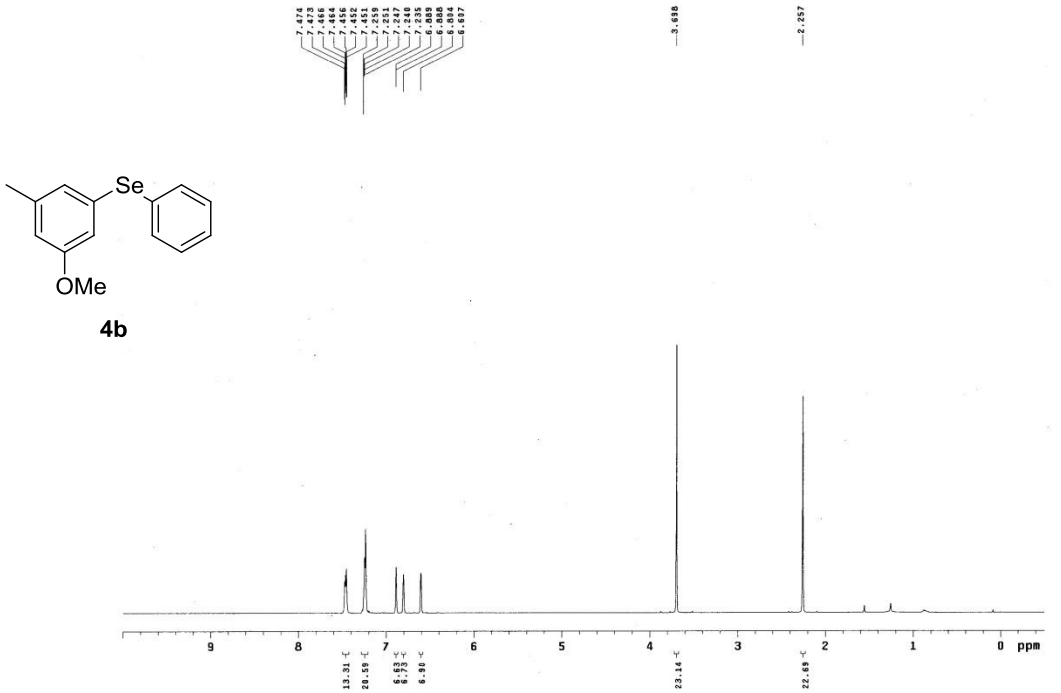


3-Methoxy-5methylphenyl phenylselenide



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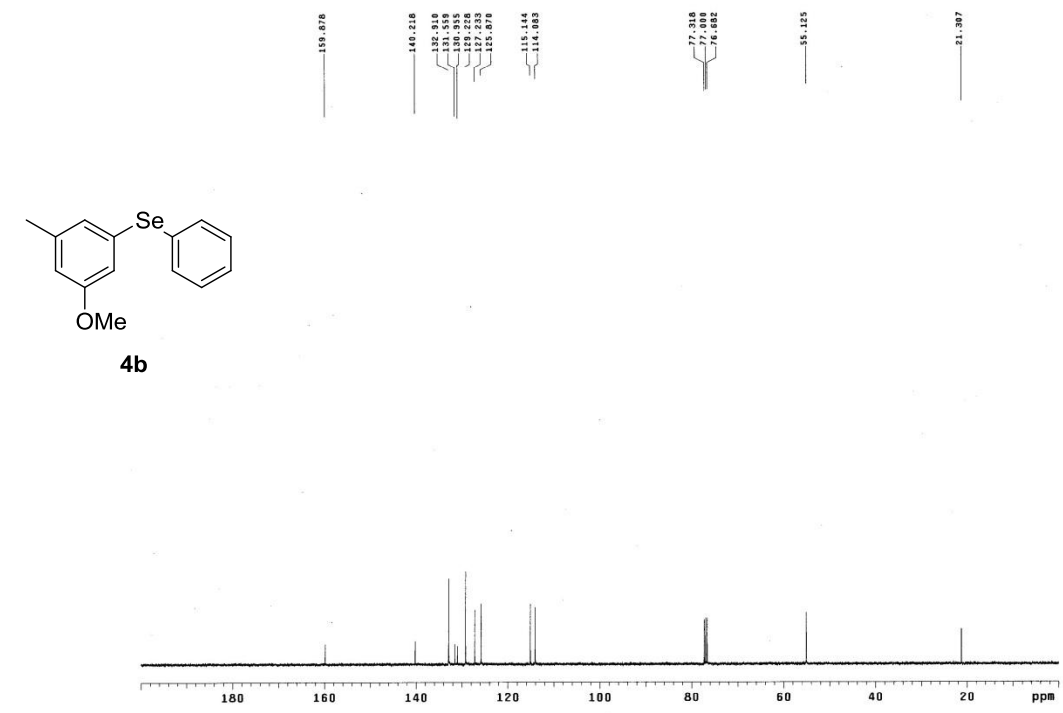
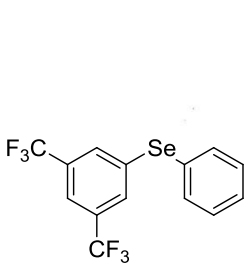


4b

3,5-Bis(trifluoromethyl)phenyl phenyl selenide



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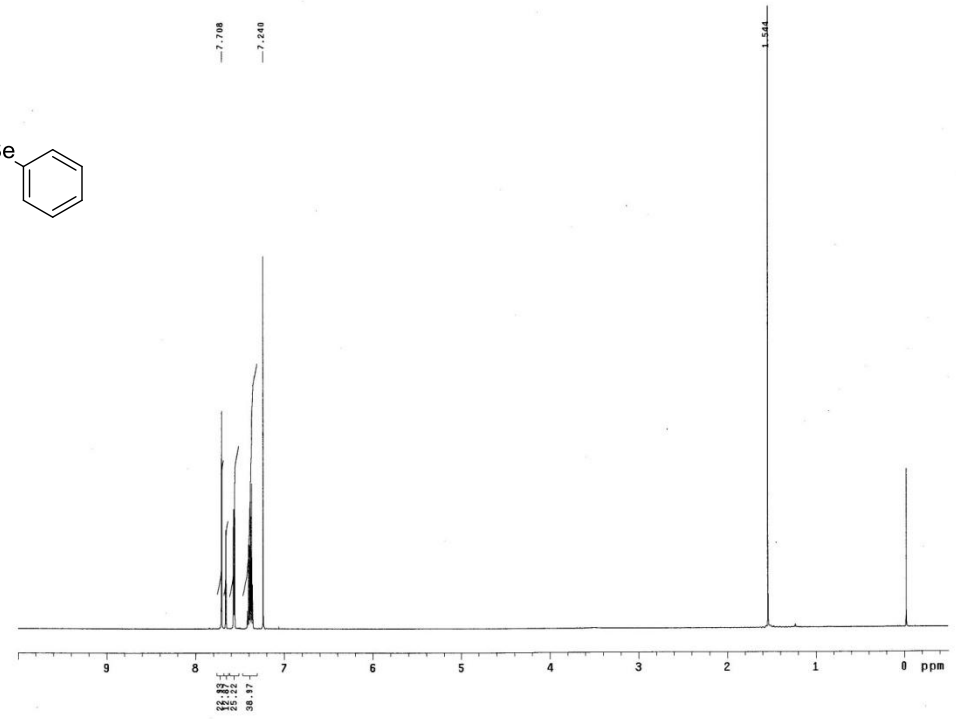

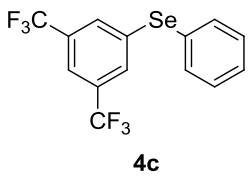

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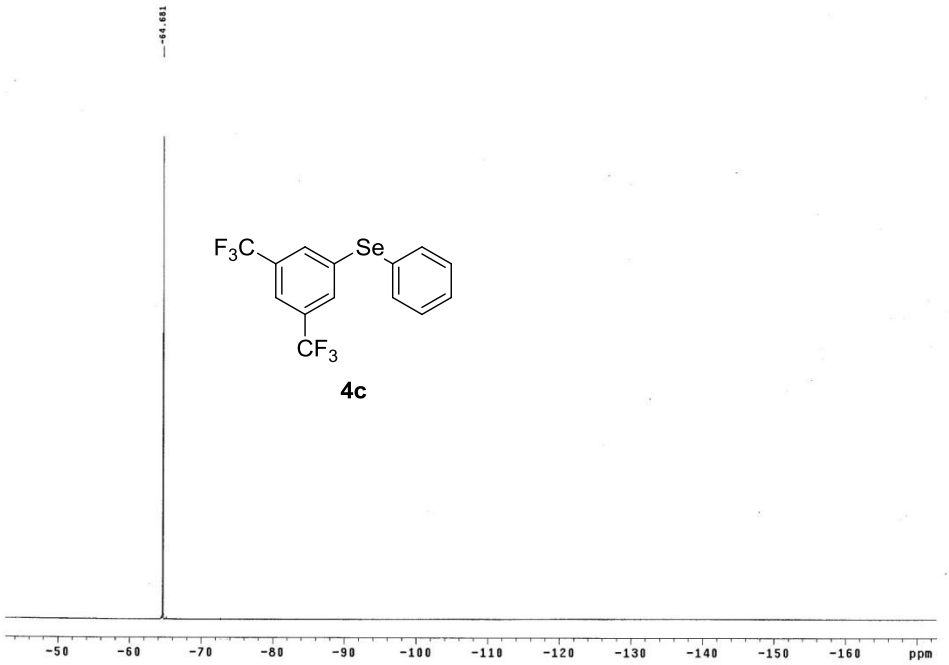
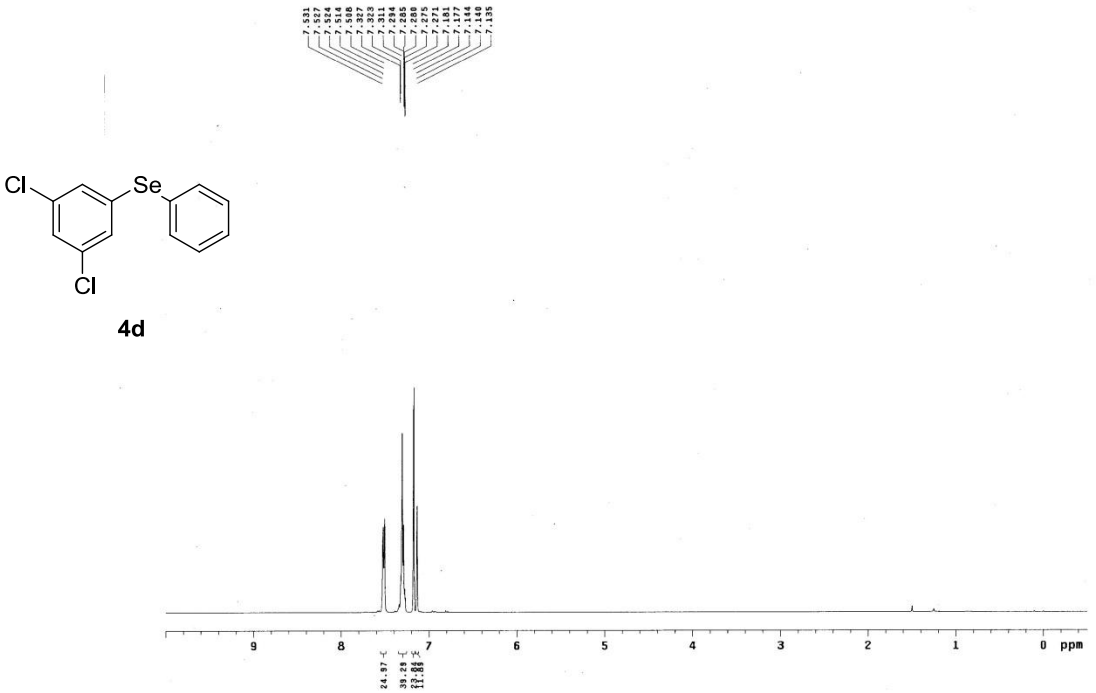
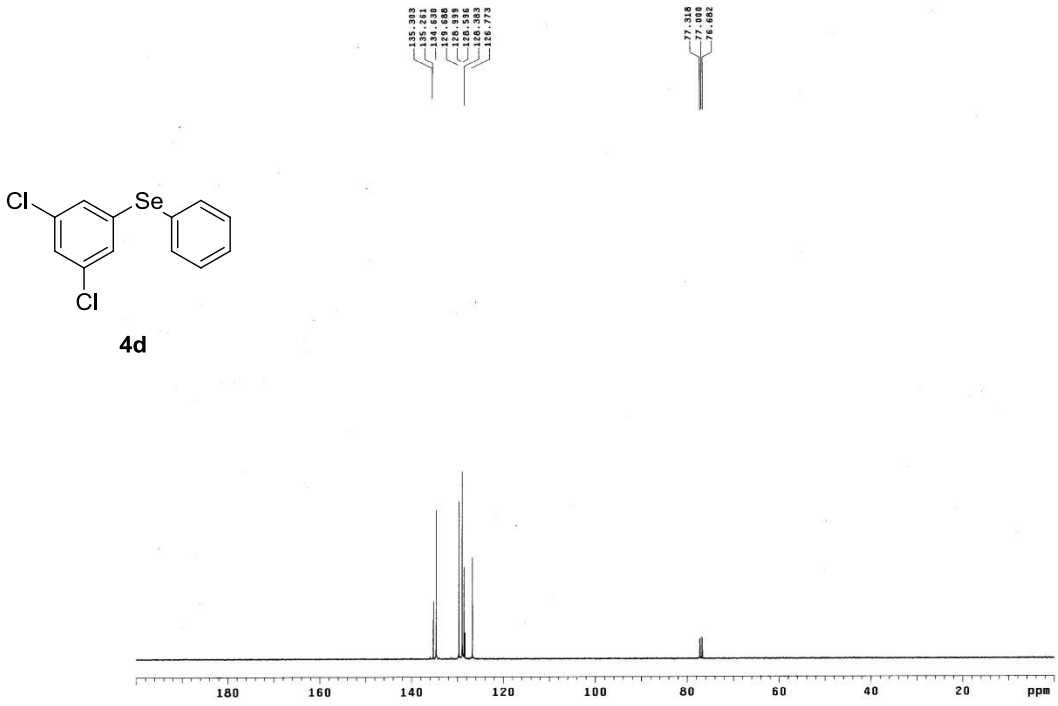


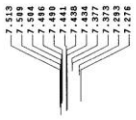
4c

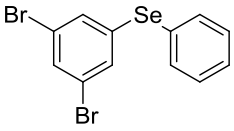
3,5-Dichlorophenyl phenyl selenide



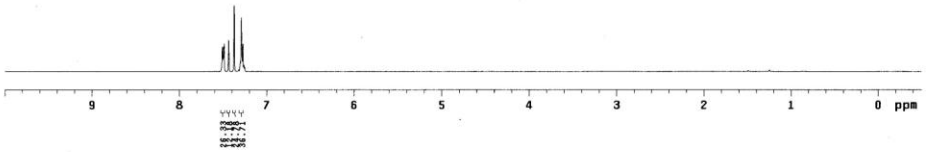


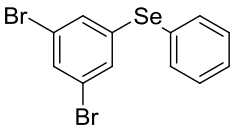
3,5-Dibromophenyl phenyl selenide





4e





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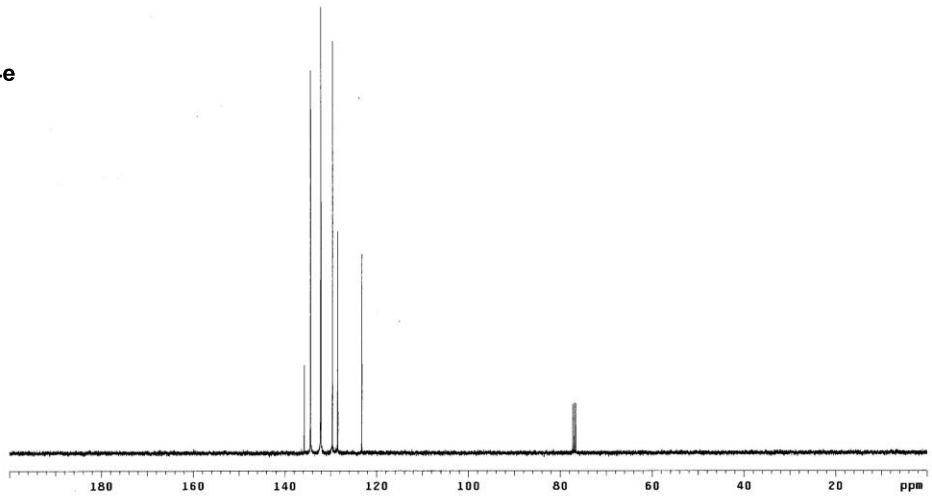
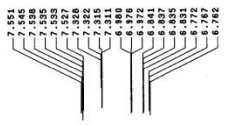
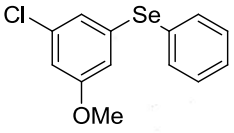


3-Chlore-5-methoxyphenyl phenyl selenide





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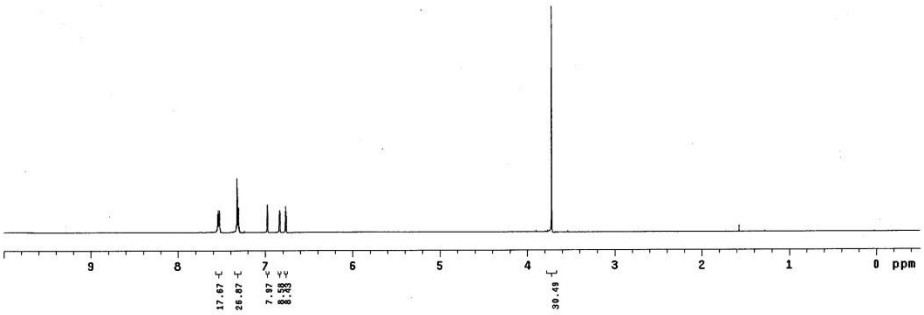

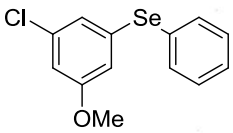

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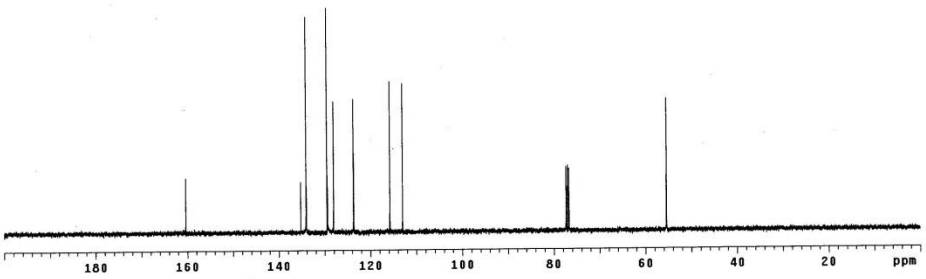
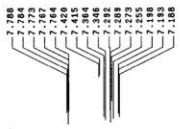
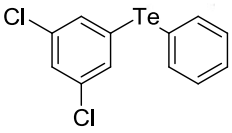


3,5-Dichlorophenyl phenyl telluride





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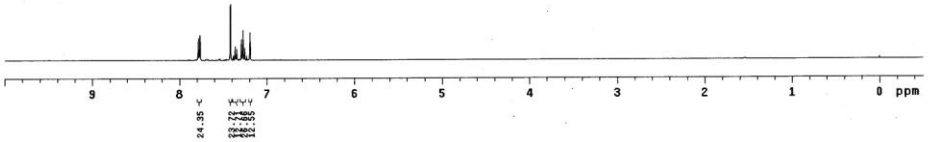

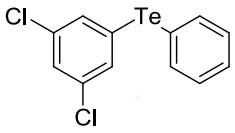

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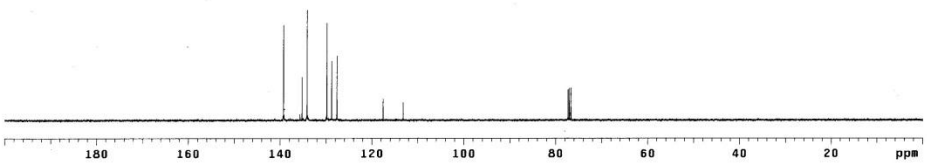
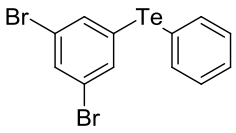


3,5-Dibromophenyl phenyl telluride



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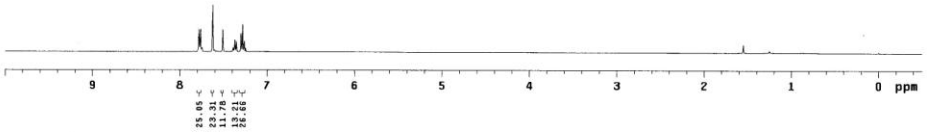

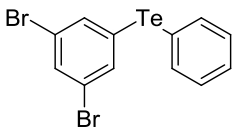

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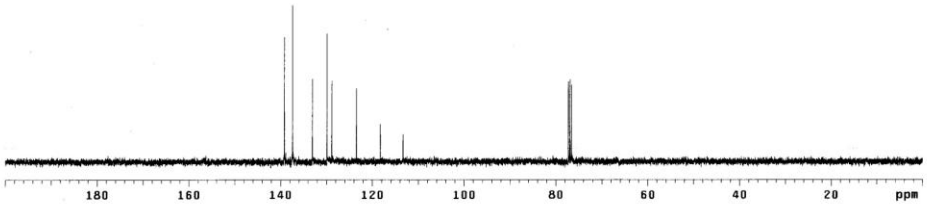
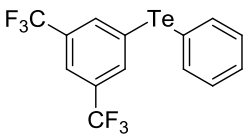


3,5-Bis(trifluoromethyl)phenyl phenyl telluride



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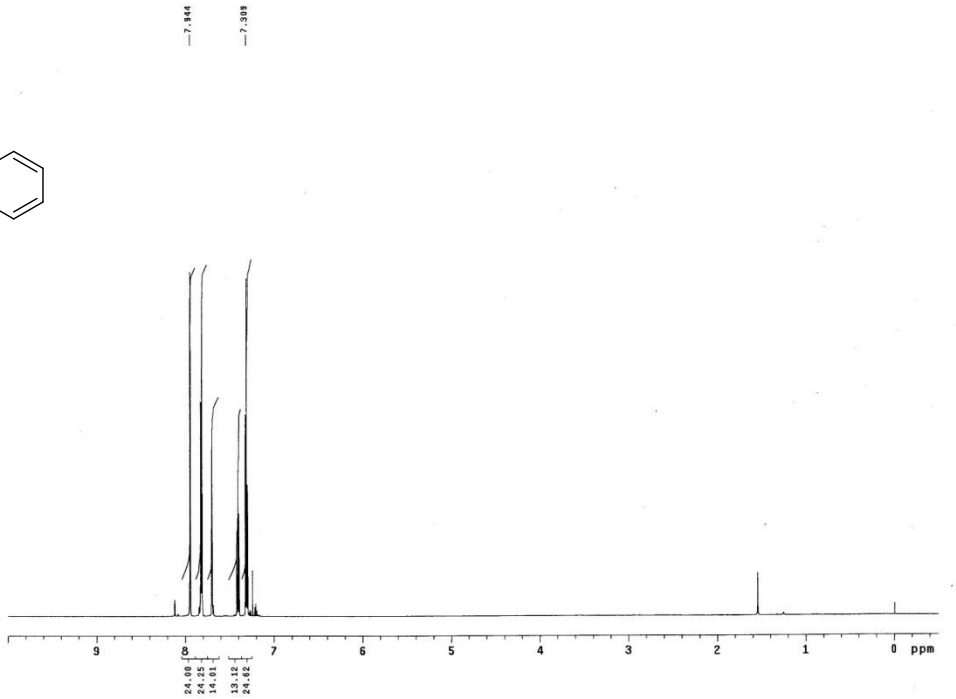

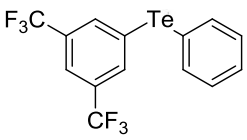

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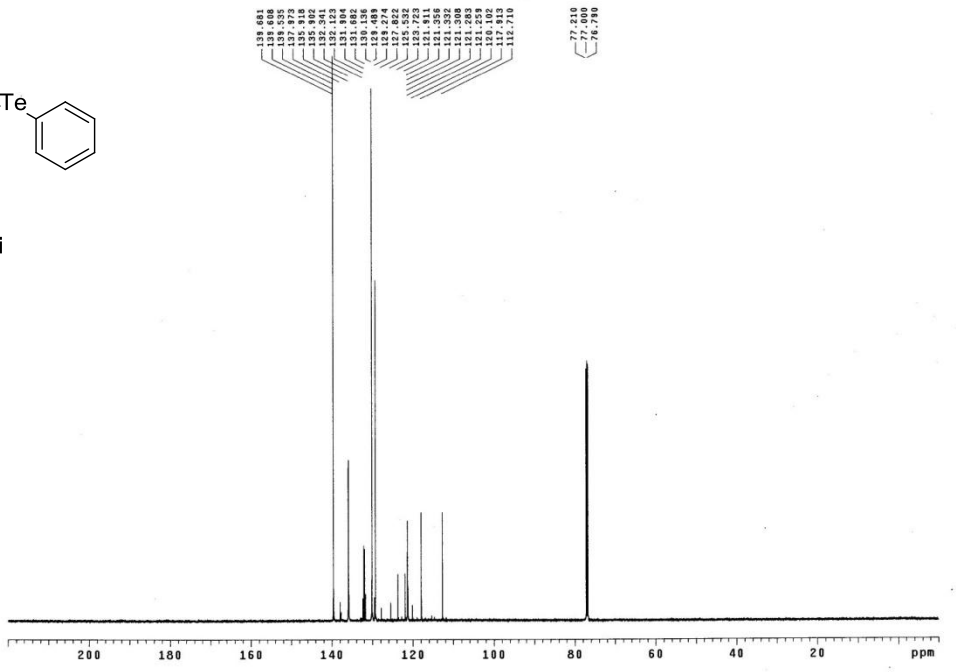

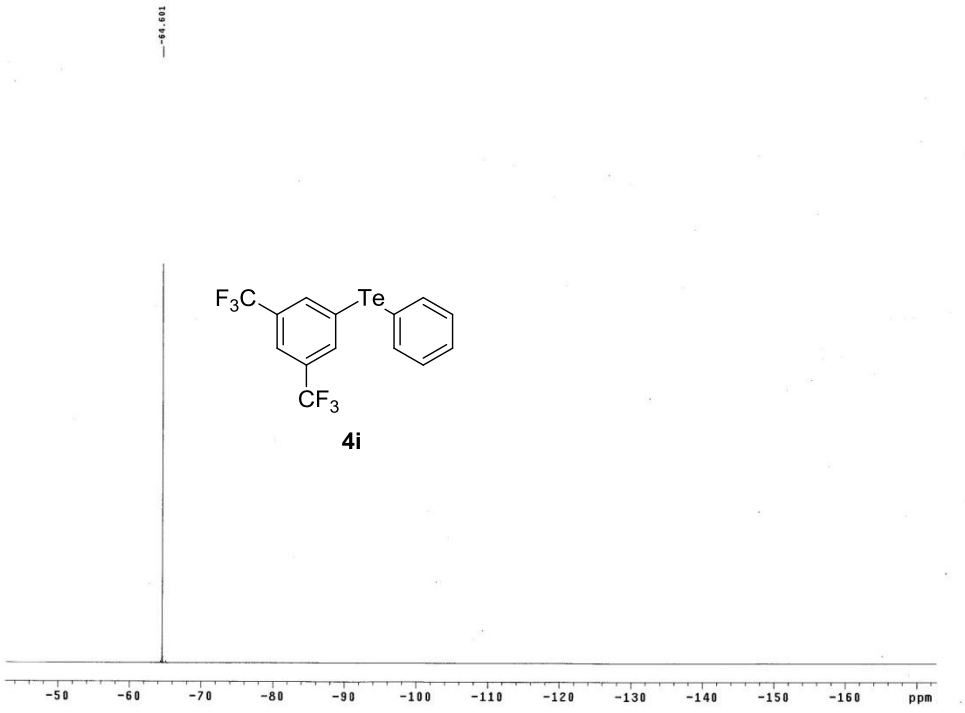

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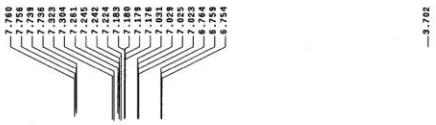
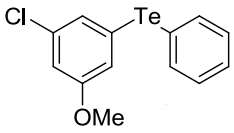
3-Chlore-5-methoxyphenyl phenyl telluride





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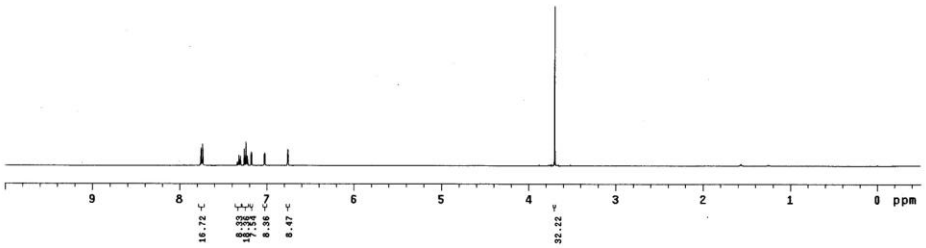

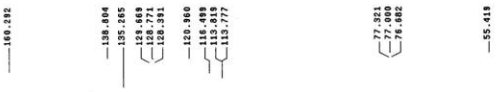

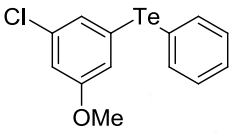

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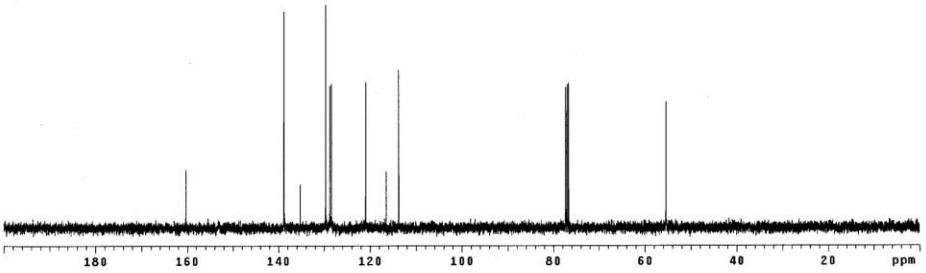
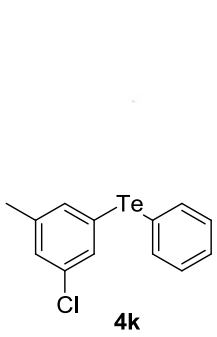


3-Chloro-5-methylphenyl phenyl telluride



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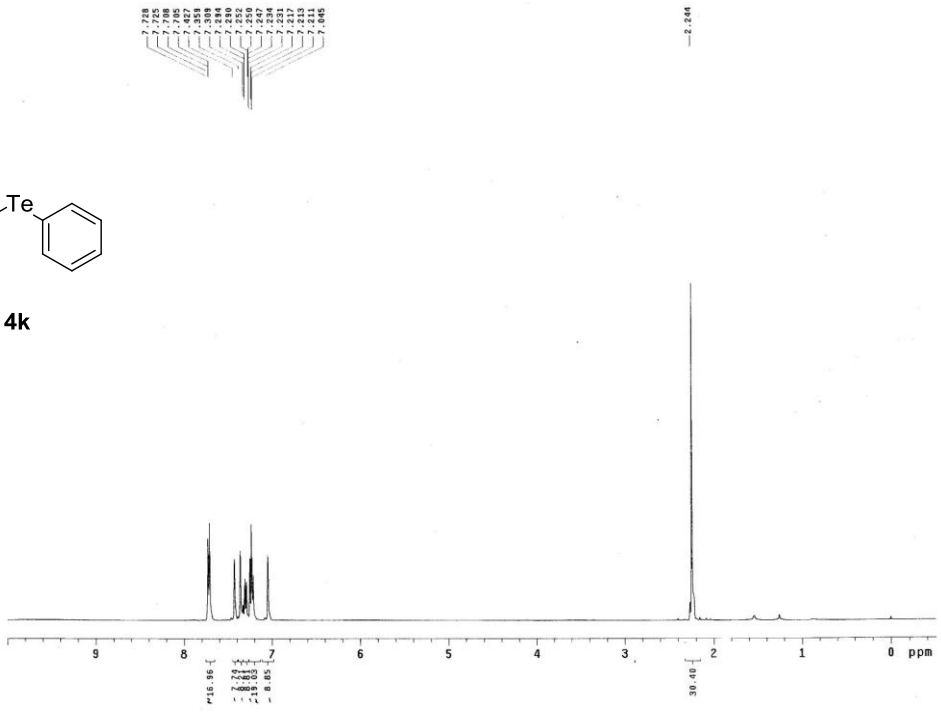

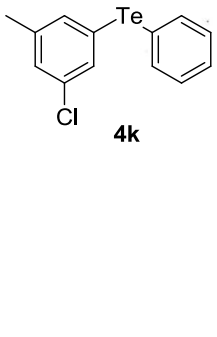

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