Supporting Information

Cu-catalysed Chan-Lam Synthesis of Unsymmetrical Aryl Chalcogenides under

Aqueous Micellar Conditions

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1. General remarks

The reaction substrates diorganyl diselenides and disulfides (1b, 1c, 1d, 1e, 1f, 1g, 1h and 4e) were synthesized according to literature methods.^[1-4] Water-soluble ligand PEG-1500-PyTa, PEG-2000-PyTa and PEG-5000-PyTa were synthesized according to our previously reported method.^[5] Other chemicals were commercially available and used as purchased. All ¹H, ¹³C and ⁷⁷Se NMR spectra were recorded on a Bruker ADVANCE III 500 MHz spectrometer in deuterated solvents with tetramethylsilane (TMS) as internal standard. The ⁷⁷Se NMR spectra were obtained with diphenyl diselenide ($\delta = 461$ ppm) as external standard. All ¹⁹F NMR spectra were obtained on a Bruker ADVANCE NEO 400 MHz spectrometer in deuterated solvents using CFCl₃ ($\delta = 0$ ppm) as external standard. High resolution mass spectrum of 5gu was recorded in the EI mode on an Agilent 8890 GC coupled with a 7250 Q-TOF mass spectrometer. Melting points (uncorrected) were determined on a BUCHI M-565 apparatus. UV-Vis spectrum analyses were performed on a Shimadzu UV-2600 spectrophotometer. TEM analyses were performed on a FEI Tecnai G2 F20 S-Twin microscope. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2010 Plus instrument with FID detector using a Shimadzu SH-Rtx-5 capillary column (30 m x 0.32 mm (i.d.), 0.25 µm). Flash column chromatography was performed on silica gel (200-300 mesh) with petroleum ether/ethyl acetate as eluent.

3. Characterization data for all synthesized arylselenides and arylsulfides

Note: The synthesized arylselenides and arylsulfides except for **5gu** in this paper are known compounds.



4-Methoxyphenyl phenyl selenide 3aa^[6]: Yield: 96% (101 mg); Yellow oil; ¹H NMR (500 MHz,

CDCl₃) δ 7.40-7.39 (m, 2H), 7.33 (dd, J = 7.7, 1.3 Hz, 1H), 7.27-7.19 (m, 5H), 7.06 (td, J = 7.5, 1.8 Hz, 1H), 2.39 (s, 3H) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 159.9, 136.6, 133.3, 131.0, 129.3, 126.6, 120.1, 115.3, 55.4 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 419.69 ppm.



4-Methylphenyl phenyl selenide 3ab^[6]: Yield: 94% (93 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.39 (m, 4H), 7.25-7.19 (m, 3H), 7.09 (d, J = 7.9 Hz, 2H), 2.32 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.8, 134.0, 132.2, 132.1, 130.3, 129.3, 127.0, 126.9, 21.3 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 424.97 ppm.



Diphenyl selenide 3ac^[6]: Yellow oil; ¹H NMR (500 MHz, CDCl₃); δ 7.47-7.45 (m, 4H), 7.26-7.25 (m, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 133.1, 131.3, 129.4, 127.4 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 421.37 ppm.



4-Fluorophenyl phenyl selenide 3ad^[6]: Yield: 93% (93 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.47-7.44 (m, 2H), 7.38-7.35 (m, 2H), 7.29-7.27 (m, 3H), 7.24-7.21 (m, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 162.7 (d, J = 247.7 Hz), 135.8 (d, J = 7.9 Hz), 132.4, 131.8, 129.5, 127.4, 125.3 (d, J = 3.4 Hz), 116.7 (d, J = 21.6 Hz) ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 418.44 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -113.98 ppm.



4-Chlorophenyl phenyl selenide 3ae^[6]: Yield: 97% (104 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃)

 δ 7.50-7.48 (m, 2H), 7.41-7.39 (m, 2H), 7.32-7.30 (m, 3H), 7.28-7.25 (m, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 134.2, 133.6, 133.3, 130.8, 129.7, 129.6, 127.8 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 415.05 ppm.



4-Bromophenyl phenyl selenide 3af^[6]: Yield: 91% (114 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.47-7.44 (m, 2H), 7.37-7.35 (m, 2H), 7.29-7.26 (m, 5H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 134.4, 133.5, 132.5, 131.6, 129.6, 129.3, 127.9, 121.6 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 420.18 ppm.



Phenyl 4-trifluoromethylphenyl selenide 3ag^[6]: Yield: 93% (112 mg); Yellow solid, m.p. 59-62 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.58-7.56 (m, 2H), 7.43 (q, *J* = 8.5 Hz, 4H), 7.38-7.32 (m, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.9, 135.0, 131.2, 129.9, 128.9 (q, *J* = 32.7 Hz), 128.8, 128.7, 126.0 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272.0 Hz) ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 463.50 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.54 ppm.



4-Acetylphenyl phenyl selenide 3ah^[6]: Yield: 94% (104 mg); Yellow solid, m.p. 59-63 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.79-7.77 (m, 2H), 7.60-7.58 (m, 2H), 7.40-7.33 (m, 5H), 2.55 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 197.4, 140.4, 135.3, 135.2, 130.4, 129.8, 129.0, 128.7, 128.6, 26.6 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 433.11 ppm.



4-Methoxycarbonylphenyl phenyl selenide 3ai^[6]: Yield: 95% (111 mg); White solid, m.p. 69-72 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.88-7.86 (m, 2H), 7.59-7.57 (m, 2H), 7.39-7.33 (m, 5H), 3.89 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 166.9, 139.8, 135.1, 130.5, 130.3, 129.8, 128.9, 128.6, 128.4, 52.2 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 431.88 ppm.



4-Nitrophenyl phenyl selenide 3ak^[6]: Yield: 92% (102 mg); Yellow solid, m.p. 56-58 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.03-8.01 (m, 2H), 7.46-7.43 (m, 2H), 7.41-7.39 (m, 3H), 7.36-7.33 (m, 2H) ppm;
¹³C NMR (125 MHz, CDCl₃) δ 146.3, 144.1, 136.0, 130.2, 129.8, 129.5, 127.3, 124.1 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 445.16 ppm.



2-Methylphenyl phenyl selenide 3al^[6]: Yield: 96% (95 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ
7.40-7.38 (m, 2H), 7.33 (dd, J = 7.8, 1.3 Hz, 1H), 7.28-7.19 (m, 5H), 7.06 (dt, J = 7.5, 1.8 Hz, 1H),
2.39 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 140.0, 133.8, 132.9, 131.9, 130.9, 130.4, 129.5, 127.9,
127.3, 126.9, 22.5 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 380.16 ppm.



2-Fluorophenyl phenyl selenide 3am^[6]: Yield: 93% (93 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃)
δ 7.53-7.51 (m, 2H), 7.33-7.28 (m, 3H), 7.26-7.21 (m, 2H), 7.06 (td, J = 8.5, 1.3 Hz, 1H), 7.00 (td, J =

7.6, 1.3 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 161.1 (d, J = 243.7 Hz), 134.2, 134.0 (d, J = 2.7 Hz), 129.6, 129.3 (d, J = 7.6 Hz), 128.8 (d, J = 1.6 Hz), 128.1, 125.0 (d, J = 3.5 Hz), 118.7 (d, J = 22.0 Hz), 115.6 (d, J = 23.1 Hz) ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 351.05 ppm, ¹⁹F NMR (376 MHz, CDCl₃) δ -103.90 ppm.



2-Chlorophenyl phenyl selenide 3an^[6]: Yield: 95% (102 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.62-7.60 (m, 2H), 7.40-7.31 (m, 4H), 7.09 (td, J = 7.6, 1.6 Hz, 1H), 7.00 (td, J = 7.6, 1.4 Hz, 1H),
6.961 (dd, J = 7.9, 1.6 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 136.2, 134.0, 133.7, 130.9, 129.9,
129.6, 129.0, 128.1, 127.44, 127.43 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 417.00 ppm.



3-Methylphenyl phenyl selenide 3ao^[6]: Yield: 95% (94 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.46-7.43 (m, 2H), 7.32 (s, 1H), 7.27-7.24 (m, 4H), 7.16 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H),
2.30 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 139.3, 133.9, 132.9, 131.5, 130.8, 130.4, 129.4, 129.3,
128.4, 127.3, 21.4 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 424.33 ppm.

Se F

3-Fluorophenyl phenyl selenide 3ap^[6]: Yield: 91% (91 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.30 (m, 2H), 7.22-7.17 (m, 3H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 8.1 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 163.6 (d, *J* = 206.2 Hz), 134.3, 133.9 (d, *J* = 6.9 Hz), 130.5 (d, *J* = 8.1 Hz), 129.8, 129.7, 128.2, 127.6 (d, *J* = 3.0 Hz), 118.9 (d, *J* = 22.6 Hz), 114.1 (d, *J* = 21.2 Hz) ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 431.59 ppm, ¹⁹F NMR (376 MHz, CDCl₃) δ -111.81 ppm.



3-Chlorophenyl phenyl selenide 3aq^[6]: Yield: 93% (100 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.53-7.49 (m, 2H), 7.39 (t, *J* = 1.8 Hz, 1H), 7.32-7.27 (m, 4H), 7.22-7.15 (m, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 135.1, 134.1, 133.6, 131.9, 130.4, 130.3, 129.9, 129.7, 128.2, 127.4 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 431.76 ppm.



2,6-Dimethylphenyl phenyl selenide 3ar^[6]: Yield: 86% (90 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.24-7.20 (m, 1H), 7.17-7.14 (m, 4H), 7.12-7.07 (m, 3H), 2.48 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 143.8, 133.2, 130.4, 129.19, 129.17, 128.7, 128.0, 125.5, 24.4 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 305.15 ppm.



Naphthalen-1-yl phenyl selenide 3as^[6]: Yield: 90% (102 mg); White solid, m.p. 50-53 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.34-8.32 (m, 1H), 7.84-7.82 (m, 2H), 7.60 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.50-7.48 (m, 2H), 7.37-7.32 (m, 3H), 7.21-7.16 (m, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 134.3, 134.2, 134.0, 131.9, 131.8, 129.6 129.4, 129.3, 128.7, 127.8, 127.1, 126.9, 126.5, 126.2 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 358.46 ppm.



Phenyl thiophen-3-yl selenide 3at^[6]: Yield: 95% (91 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.58 (dd, J = 2.8, 1.2 Hz, 1H), 7.57-7.55 (m, 2H), 7.58 (dd, J = 4.8, 2.8 Hz, 1H), 7.26-7.21 (m, 2H), 7.19-7.15 (m, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 132.8, 132.3, 131.0, 129.2, 126.83, 126.75, 122.7 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 336.64 ppm.



Furan-3-yl phenyl selenide 3au^[6]: Yield: 96% (86 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.58 (s, 1H), 7.52-7.50 (m, 2H), 7.44 (t, *J* = 1.6 Hz, 1H), 7.21-7.18 (m, 1H), 7.16-7.13 (m, 2H), 6.58 (d, *J* = 1.7 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.8, 144.0, 131.6, 130.0, 129.2, 127.7, 126.4, 115.7 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 246.83 ppm.



(E)-Styryl phenyl selenide 3aw^[7]: Yield: 94% (97 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ
7.54-7.52 (m, 2H), 7.32-7.25 (m, 7H), 7.23-7.20 (m, 1H), 7.16 (d, J = 15.8 Hz, 1H), 6.86 (d, J = 15.8 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.1, 135.2, 132.6, 130.2, 129.4, 128.7, 127.7, 127.5, 126.1, 119.5 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 392.10 ppm.



Bis(*4-methylphenyl*)*selenide 3bb*^[6]: Yield: 92% (96 mg); Yellow solid, m.p. 48-53 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 7.9 Hz, 4H), 2.30 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.3, 133.1, 130.2, 127.9, 21.2 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 285.16 ppm.



4-Acetylphenyl 4-fluorophenyl selenide 3ch^[8]: Yield: 88% (103 mg); Yellow solid, m.p. 66-71 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.0 (d, *J* = 8.5 Hz, 2H), 7.51-7.48 (m, 2H), 7.39-7.36 (m, 2H), 7.32-7.30 (m,

2H), 2.55 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 197.2, 163.2 (d, J = 247.5 Hz), 140.4, 137.6 (d, J = 8.7 Hz), 135.2, 129.8, 128.9, 122.9 (d, J = 3.7 Hz), 117.0 (d, J = 22.5 Hz), 26.9 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 424.85 ppm, ¹⁹F NMR (376 MHz, CDCl₃) δ -111.87 ppm.



4-Acetylphenyl 4-chlorophenyl selenide 3dh^[9]: Yield: 86% (107 mg); Yellow solid, m.p. 60-64 °C. ¹H
NMR (500 MHz, CDCl₃) δ 7.81 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H),
7.35-7.26 (m, 2H), 2.57 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 198.3, 139.4, 136.2, 135.5, 135.0,
130.6, 129.9, 129.0, 126.9, 27.4 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 428.43 ppm.



Mesityl 4-methoxyphenyl selenide 3ea^[6]: Yield: 90% (110 mg); White solid, m.p. 60-64 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.07-7.04 (m, 2H), 6.95 (s, 2H), 6.72-6.69 (m, 2H), 3.70 (s, 3H), 2.43 (s, 6H), 2.27 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 158.1, 143.2, 138.7, 130.7, 128.8, 127.9, 123.2, 114.9, 55.2, 24.3, 21.0 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 285.02 ppm.



4-Methylphenyl thiophen-3-yl selenide 3fb^[6]: Yield: 94% (95 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.33 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.30-7.26 (m, 3H), 7.06-7.03 (m, 3H), 2.29 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.0, 132.3, 131.9, 130.1, 128.03, 128.00, 126.6, 123.6, 21.1 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 333.92 ppm.



Benzyl 4-acetylphenyl selenide 3gh^[10]: Yield: 92% (106 mg); White solid, m.p. 103-106 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.81-7.78 (m, 2H), 7.49-7.46 (m, 2H), 7.27-7.21 (m, 5H), 4.19 (s, 2H), 2.56 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 197.4, 138.6, 137.6, 135.4, 131.4, 128.9, 128.7, 128.6, 127.2, 31.4, 26.5 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 377.05 ppm.



n-Butyl 4-methylphenyl selenide 3hb^[6]: Yield: 91% (83 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.39 (d, J = 7.7 Hz, 2H), 7.06 (d, J = 7.7 Hz, 2H), 2.86 (t, J = 7.5 Hz, 2H), 2.31 (s, 3H), 1.66 (quint, J = 6.3 Hz, 2H), 1.41 (sext, J = 6.3 Hz, 2H), 0.89 (t, J = 6.3 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 136.8, 133.1, 129.9, 126.8, 32.4, 28.1, 23.1, 21.2, 13.7 ppm; ⁷⁷Se NMR (95.5 MHz, CDCl₃) δ 284.07 ppm.



4-Methoxyphenyl phenyl sulfide 5aa^[7]: Yield: 88% (76 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.39 (m, 2H), 7.23-7.20 (m, 2H), 7.17-7.10 (m, 3H), 6.90-6.87 (m, 2H), 3.80 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 159.9, 138.6, 135.3, 128.94, 128.30, 125.8, 124.4, 115.0, 55.4 ppm.



4-Methylphenyl phenyl sulfide 5ab^[7]: Yield: 90% (72 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.29 (d, *J* = 8.2 Hz, 2H), 7.27-7.22 (m, 4H), 7.20 -7.15 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.6, 137.2, 132.3, 131.4, 130.1, 129.85, 129.08, 126.5, 21.2 ppm.



Diphenyl sulfide 5ac^[7]: Yield: 89% (66 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.32 (m, 4H), 7.29-7.25 (m, 4H), 7.23-7.20 (m, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 135.9, 131.1, 129.2, 127.1 ppm.



4-Chlorophenyl phenyl sulfide 5ae^[7]: Yield: 80% (71 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.29 (m, 2H), 7.27-7.24 (m, 2H), 7.22-7.20 (m, 1H), 7.19 (s, 4H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 135.3, 134.8, 133.1, 132.1, 131.4, 129.46, 129.43, 127.5 ppm.



4-Bromophenyl phenyl sulfide 5af^[7]: Yield: 74% (78 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.31 (m 4H), 7.28-7.25 (m, 2H), 7.24-7.20 (m, 1H), 7.13-7.11 (m, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 135.6, 135.0, 132.33, 132.18, 131.7, 129.5, 127.7, 121.0 ppm.



4-Acetylphenyl phenyl sulfide 5ah^[11]: Yield: 75% (68 mg); White solid, m.p. 64-67 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, J = 8.4 Hz, 2H), 7.50-7.48 (m, 2H), 7.41-7.38 (m, 3H), 7.21 (d, J = 8.5 Hz, 2H), 2.54 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 197.0, 144.9, 134.6, 133.8, 132.2, 129.7, 128.89, 128.77, 127.5, 26.4 ppm.



4-Nitrophenyl phenyl sulfide 5ak^[12]: Yield: 51% (47 mg); White solid, m.p. 121-123 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.06-8.03 (m, 2H), 7.55-7.52 (m, 2H), 7.46-7.44 (m, 3H), 7.18-7.15 (m, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 148.5, 145.4, 134.7, 130.52, 130.04, 129.7, 126.7, 124.0 ppm.



2-Methylphenyl phenyl sulfide 5al^[7]: Yield: 83% (66 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.29 (dd, J = 7.7, 1.3 Hz, 1H), 7.26-7.22 (m, 3H), 7.21-7.15 (m, 4H), 7.12 (dt, J = 7.3, 1.3 Hz, 1H), 2.37 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 140.0, 136.3, 133.8, 133.1, 130.7, 129.7, 129.2, 128.0, 126.78, 126.39, 20.7 ppm.



2,6-Dimethylphenyl phenyl sulfide 5ar^[12]: Yield: 57% (49 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.24-7.15 (m, 5H), 7.05 (dt, *J* = 7.4, 1.2 Hz, 1H), 6.97-6.86 (m, 2H), 2.42 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 143.9, 138.1, 130.6, 129.3, 128.9, 128.5, 125.7, 124.6, 21.8 ppm.



Phenyl thiophen-3-yl sulfide 5at^[11]: Yield: 86% (66 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.32 (m, 2H), 7.24-7.19 (m, 4H), 7.16-7.12 (m, 1H), 7.02 (dd, *J* = 4.9, 1.3 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.4, 131.31, 129.44, 129.08, 128.52, 128.25, 126.8, 126.2 ppm.

S C

Furan-3-yl phenyl sulfide 5au^[13]: Yield: 73% (51 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (s, 1H), 7.50 (s, 1H), 7.26-7.19 (m, 4H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 0.9 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.1, 144.2, 137.3, 128.9, 127.3, 125.8, 114.7, 114.0 ppm.



(*E*)-Styryl phenyl sulfide 5aw^[7]: Yield: 60% (51 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.54-7.52 (m, 2H), 7.32-7.19 (m, 8H), 7.16 (d, J = 15.8 Hz, 1H), 6.86 (d, J = 15.8 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.1, 135.2, 132.6, 130.3, 129.4, 128.7, 127.72, 127.48, 126.2, 119.5 ppm.



4-Methoxyphenyl 4-methylphenyl sulfide 5ba^[11]: Yield: 87% (80 mg); Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.33 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.86-6.83 (m, 2H), 3.77 (s, 3H), 2.28 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 159.5, 136.1, 134.40, 134.37, 129.82, 129.46, 125.7, 114.9, 55.4, 21.0.



4-Chlorophenyl 4-methoxyphenyl sulfide 5ca^[11]: Yield: 72% (72 mg); White solid, m.p. 59-62 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.38 (m, 2H), 7.20-7.17 (m, 2H), 7.08-7.05 (m, 2H), 6.91-6.88 (m, 2H), 3.81 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 160.1, 137.4, 135.5, 131.6, 129.36, 129.01, 123.8, 115.2, 55.4 ppm.



2-Aminophenyl 4-methoxyphenyl sulfide 5da^[12]: Yield: 46% (43 mg); Yellow oil; ¹H NMR (500 MHz,

CDCl₃) δ 7.39 (dd, J = 7.7, 1.6 Hz, 1H), 7.16 (dt, J = 7.7, 1.6 Hz, 1H), 7.13-7.10 (m, 2H), 6.80-6.77 (m, 2H), 6.74-6.69 (m, 2H), 4.25 (s, br, 2H), 3.74 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 158.4, 148.1, 136.3, 130.4, 129.7, 126.9, 118.7, 116.8, 115.4, 114.8, 55.4 ppm.



4-Methoxycarbonylphenyl 4-fluorophenyl sulfide 5ed^[14]: Yield: 53% (56 mg); White solid, m.p. 81-85 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.50-7.46 (m 2H), 7.141-7.07 (m, 4H), 3.88 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 166.6, 163.2 (d, *J* = 248.7 Hz), 144.7, 136.3 (d, *J* = 8.7 Hz), 130.1, 127.4, 127.2 (d, *J* = 3.7 Hz), 126.9, 116.9 (d, *J* = 22.5 Hz), 52.05 ppm, ¹⁹F NMR (376 MHz, CDCl₃) δ -111.58 ppm.



4-Methoxyphenyl 2-methylfuran-3-yl sulfide 5fa^[15]: Yield: 87% (77 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.16 (d, J = 2.0 Hz, 1H), 7.14-7.11 (m, 2H), 6.81-6.78 (m, 2H), 6.32 (d, J = 2.0 Hz, 1H), 3.76 (s, 3H), 2.35 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 158.2, 155.7, 141.0, 129.4, 128.3, 115.1, 114.6, 109.8, 55.4, 11.8 ppm.



Thiophen-2-yl 4-methoxyphenyl sulfide 5ga^[11]: Yield: 94% (84 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.34 (dd, *J* = 5.4, 1.3 Hz, 1H), 7.28-7.25 (m, 2H), 7.19 (dd, *J* = 3.6, 1.3 Hz, 1H), 6.97 (dd, *J* = 5.4, 3.6 Hz, 1H), 6.81-6.78 (m, 2H), 3.80 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 159.0, 134.4, 133.9, 131.2, 130.1, 128.4, 127.7, 114.8, 55.4 ppm.



Furan-3-yl thiophen-2-yl sulfide 5gu: Yield: 92% (67 mg); Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.49 (s, 1H), 7.38 (t, J = 1.8 Hz, 1H), 7.31 (dd, J = 5.3, 1.3 Hz, 1H), 7.15 (dd, J = 3.6, 1.3 Hz, 1H), 6.94 (dd, J = 5.3, 3.6 Hz, 1H), 6.40 (dd, J = 1.9, 0.8 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 143.7, 143.3, 134.3, 132.5, 129.2, 127.5, 118.2, 113.2 ppm. HRMS (EI-TOF) m/z: [M⁺] Calculated for C₈H₆OS₂ 181.9860, found 181.9859.



Benzyl phenyl sulfide 5hc^[16]: Yield: 43% (35 mg); Yellow solid, m.p. 41-44 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.26 (m, 6H), 7.24-7.20 (m, 3H), 7.17-7.14 (m, 1H), 4.09 (s, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.5, 136.5, 129.9, 128.88, 128.87, 128.53, 127.2, 126.4, 39.1 ppm.

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3. ¹H NMR and ¹³C NMR Spectra









Figure S8 ¹³C NMR (125 MHz) spectrum of 3ad in CDCl₃



Figure S10 ¹³C NMR (125 MHz) spectrum of 3ae in CDCl₃



Figure S12 ¹H NMR (500 MHz) spectrum of 3af in CDCl₃



Figure S14 ¹³C NMR (125 MHz) spectrum of 3ag in CDCl₃





100 90 f1 (ppm)

Figure S18 ¹³C NMR (125 MHz) spectrum of **3ai** in CDCl₃







100 90 f1 (ppm)

Figure S24 ¹³C NMR (125 MHz) spectrum of 3am in CDCl₃



100 90 f1 (ppm)

Figure S26 ¹³C NMR (125 MHz) spectrum of 3an in CDCl₃





100 90 f1 (ppm)

Figure S30 ¹³C NMR (125 MHz) spectrum of **3ap** in CDCl₃



100 90 f1 (ppm)

Figure S32 ¹³C NMR (125 MHz) spectrum of 3aq in CDCl₃



Figure S34 ¹³C NMR (125 MHz) spectrum of 3ar in CDCl₃









100 90 f1 (ppm)

Figure S36 ¹³C NMR (125 MHz) spectrum of 3as in CDCl₃





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Figure S42 ¹³C NMR (125 MHz) spectrum of **3aw** in CDCl₃



Figure S44 ¹³C NMR (125 MHz) spectrum of **3bb** in CDCl₃





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Figure S56 ¹³C NMR (125 MHz) spectrum of **3hb** in CDCl₃







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Figure S70 13 C NMR (125 MHz) spectrum of 5ak in CDCl₃



Figure S72 ¹³C NMR (125 MHz) spectrum of 5al in CDCl₃



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Figure S78 ¹³C NMR (125 MHz) spectrum of 5au in CDCl₃





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Figure S84 ¹³C NMR (125 MHz) spectrum of 5ca in CDCl₃





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Figure S90 ¹³C NMR (125 MHz) spectrum of 5fa in CDCl₃





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4. ⁷⁷Se NMR spectra





Figure S100 ⁷⁷Se NMR (95.5 MHz) spectrum of **3ad** in CDCl₃



Figure S102 ⁷⁷Se NMR (95.5 MHz) spectrum of **3af** in CDCl₃



Figure S104 ⁷⁷Se NMR (95.5 MHz) spectrum of **3ah** in CDCl₃



Figure S106⁷⁷Se NMR (95.5 MHz) spectrum of **3ak** in CDCl₃



Figure S108 ⁷⁷Se NMR (95.5 MHz) spectrum of 3am in CDCl₃



Figure S110 ⁷⁷Se NMR (95.5 MHz) spectrum of **3ao** in CDCl₃



Figure S112 ⁷⁷Se NMR (95.5 MHz) spectrum of 3aq in CDCl₃


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Figure S116 ⁷⁷Se NMR (95.5 MHz) spectrum of **3au** in CDCl₃



Figure S118 ⁷⁷Se NMR (95.5 MHz) spectrum of **3bb** in CDCl₃



Figure S120 ⁷⁷Se NMR (95.5 MHz) spectrum of **3dh** in CDCl₃



Figure S122 ⁷⁷Se NMR (95.5 MHz) spectrum of **3fb** in CDCl₃



Figure S124 ⁷⁷Se NMR (95.5 MHz) spectrum of **3hb** in CDCl₃

5. ¹⁹F NMR Spectra of 3ad, 3ag, 3am, 3ap, 3ch and 5ed





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