Electronic Supplementary Material (ESI) for ChemComm.

Palladium-catalyzed thiolation of alkanes and ethers with arylsulfonyl hydrazides

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Contents

(A)Typical Experimental Procedure

1. General information:

All reagents were purchased from commercial suppliers and used without further purification. All experiments were carried out under argon. Flash chromatography was carried out with Merck silica gel 60 (63-200 mesh). Analytical TLC was performed with Merck silica gel 60 F_{254} plates. ^{1}H NMR and ^{13}C NMR (300 MHz and 75 MHz, respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants (*J*) are given in Hz.

2. Typical procedure:

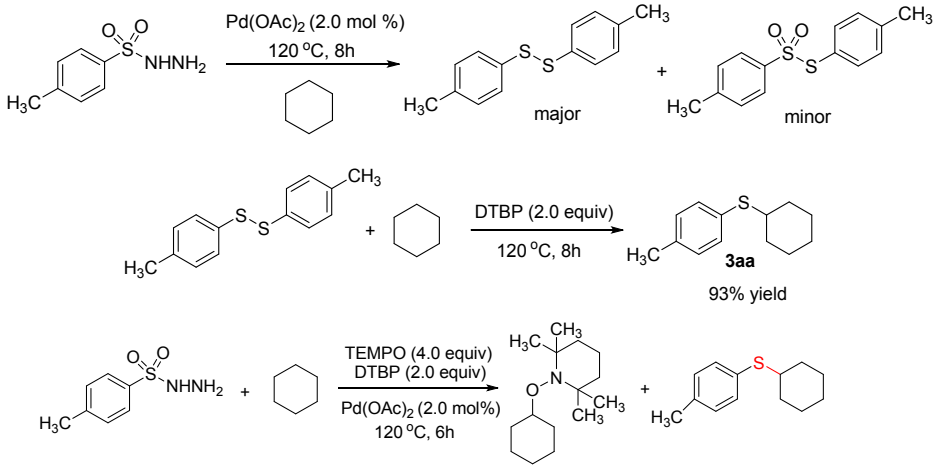
A 15-mL Schlenk tube was charged with arylsulfonyl hydrazides (***1.0 mmol***), DTBP (2 mmol), and ***alkanes*** or ***ethers (***2-3 mL) with 2 mol % $Pd(OAc)_2$ as catalyst. The resultant mixture was stirred at 120 °C for 12 h under sealed condition. After the reaction was completed by TLC monitoring, the mixture was cooled to ambient temperature, poured into 20 mL of brine, and extracted with ethyl acetate (3 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered, and all of the volatiles were removed under reduced pressure. The resulting residue was purified by flash silica gel column chromatography (eluent: hexane/EtOAc, v/v = 20/1) to afford the desired products.

3. Study of possible mechanism

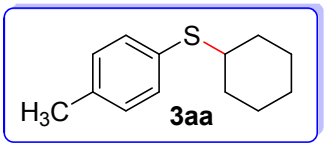
In order to explore the possible mechanism of the present transformation,

Firstly, we proved that, in the absence of DTBP, the disulfide was the main product of the model reaction with 86 % yield. The by-product of disulfide was also found during the reaction, judged by GC-MS, after 1h, the mole ratio of disulfide and **3aa** was 3:1 in the model reaction, after 2h, the mole ratio of disulfide and **3aa** was 5:3, after 4h, the disulfide disappeared. Secondly, using the byproduct of disulfide as starting material substitute for arylsulfonyl hydrazides under the same conditions, the same product was got with a 93% excellent yield.

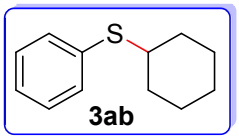
The reaction was suppressed when the TEMPO (2,2,6,6- tetramethylpiperidine-1-oxyl), a radical-trapping reagent was added into the model reaction and trapped a free radical of cyclohexane. Those result suggested that a radical process may involved in the initial steps of the transformation.



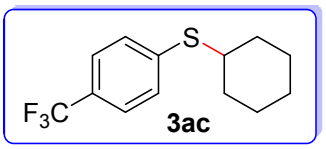
(B) Spectra Analytical data for products



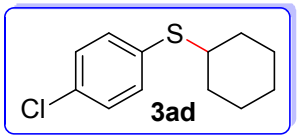
4-Methylphenyl Cyclohexyl Sulfide (3aa): [1] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 3.05 – 3.01 (m, 1H), 2.33 (s, 3H), 1.96 (d, *J* = 10.4 Hz, 2H), 1.76 (d, *J* = 5.4 Hz, 2H), 1.62 – 1.59 (m, 1H), 1.37 – 1.24 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 132.8, 131.2, 129.5, 47.1, 33.4, 26.1, 25.8, 21.1; **LRMS (ESI, 70 eV)** *m/z*: 207.2, 206.3, 124.2, 91.2, 77.2; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{13}H_{18}S$ 206.1129 found 206.1131.



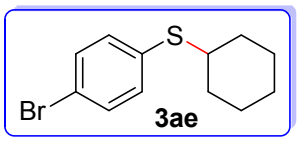
Phenyl Cyclohexyl Sulfide (3ab): [1] Colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.41-7.38 (m, 2H), 7.30-7.20 (m, 3H), 3.13-3.07 (m, 1H), 2.00-1.96 (m, 2H), 1.77-1.74 (m, 2H), 1.63-1.58 (m, 1H), 1.42-1.23 (m, 5H); **^{13}C NMR** (75 MHz, CDCl3): δ 135.3, 131.9, 128.7, 126.6, 46.6, 33.4, 26.1, 25.8; **LRMS (ESI, 70 eV)** *m/z*: 192.5, 135.3, 109.2; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{12}H_{16}S$: 192.0973; found: 192.0976.



4-Trifluoromethylphenyl Cyclohexyl Sulfide (3ac): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.53 (d, *J* = 7.5 Hz,1H), 7.46 – 7.36 (m, 2H),3.20 – 3.12 (m, 1H), 1.99 (d, *J* = 9.8 Hz, 2H), 1.75 (t, *J* = 4.8 Hz, 2H), 1.62 (t, *J* = 3.9 Hz, 1H), 1.45 – 1.25 (m, 5H); 13C NMR (126 MHz, CDCl3) δ 137.02, 134.34,129.09 (q, JC-F = 45.25 Hz). 131.58, 131.33, 131.07, 130.81 (q, JC-F = 31.5 Hz), 127.78, 127.75, 127.72, 127.69 (q, JC-F = 3.78 Hz), 127.12, 124.95, 122.78, 120.61 (q, JC-F = 273.4 Hz), 123.14, 123.11, 123.08, 123.05 (q, JC-F = 3.78 Hz), 46.47, 33.20, 25.93, 25.68; LRMS (ESI, 70 eV) m/z: 260.3, 157.5, 108.5, 81.7, 55.2, 38.7; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{13}H_{15}F_3S$ 260.0847 found 260.0845.

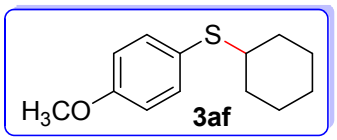


4-Chlorophenyl Cyclohexyl Sulfide (3ad): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.33 – 7.30 (q, *J* = 9.0, 2.4 Hz, 2H), 7.26 – 7.23 (q, *J* = 6.6, 1.8 Hz, 2H), 3.09-3.03 (m, 1H), 1.96 (d, *J* = 8.8 Hz, 2H), 1.77 (d, *J* = 5.4 Hz, 2H), 1.62-1.59 (m, 1H), 1.41 – 1.22 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.69, 133.27, 132.71, 128.89, 46.91, 33.26, 26.02, 25.72; **LRMS (ESI, 70 eV)** *m/z*: 226.0, 170.8, 131.0, 104.8, 81.4; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{13}H_{18}S$ 226.0583 found 226.0586.



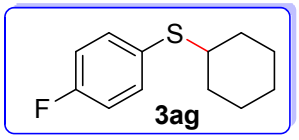
3ae

4-Bromophenyl Cyclohexyl Sulfide (3ae): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.74 – 7.68 (m, 4H), 2.89-2.82 (m, 1H), 2.05 (d, *J* = 11.2 Hz, 2H), 1.85 (d, *J* = 13.1 Hz, 2H), 1.68 (d, *J* = 9.0 Hz, 1H), 1.44 – 1.14 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 136.4, 132.3, 130.6, 128.9, 63.7, 25.6, 25.1, 25.0; **LRMS (ESI, 70 eV)** *m/z*: 272.3, 270.2, 269.3,188.3, 109.3, 81.5; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{12}H_{15}BrS$ 270.0078 found 270.0074.



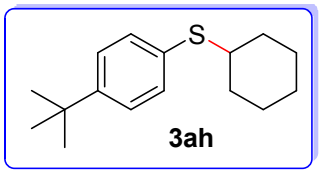
3af

4-Methoxyphenyl Cyclohexyl Sulfide (3af): [3] Colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 6.86 – 6.81 (m, 2H), 3.79 (s, 3H), 2.92 – 2.82 (m, 1H), 1.93 (d, *J* = 9.8 Hz, 2H), 1.75 (d, *J* = 5.3 Hz, 2H), 1.63 – 1.50 (m, 1H), 1.32 – 1.21 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 159.3, 135.5, 125.1, 114.3, 55.3, 47.9, 33.4, 26.1; **LRMS (ESI, 70 eV)** *m/z*: 224.2, 223.2, 222.4; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{13}H_{18}OS$ 222.1078 found 222.1075.



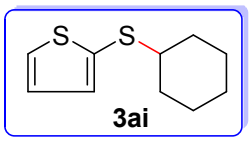
3ag

4-Fluorophenyl Cyclohexyl Sulfide (3ag): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.42 – 7.36 (m, 2H), 7.03-6.96 (m, 2H), 2.99-2.94 (m, 1H), 1.96-1.92 (m, 2H), 1.76 (d, *J* = 4.8 Hz, 2H), 1.60 (d, *J* = 9.6 Hz, 1H), 1.38 – 1.23 (m, 5H); 13C NMR (126 MHz, CDCl3) δ 163.23, 161.27 (d, JC-F = 246.96 Hz), 135.04, 134.97 (d, JC-F = 8.82 Hz), 129.83, 129.81 (d, JC-F = 2.52 Hz), 115.87, 115.70 (d, JC-F = 21.42 Hz), 47.61, 33.31, 26.05, 25.74; **LRMS (ESI, 70 eV)** *m/z*: 210.1, 128.0, 82.9; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{12}H_{15}FS$ 210.0878 found 210.0875.



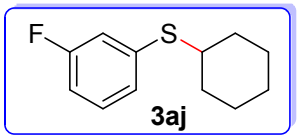
3ah

4-*tert*-Butyphenyl Cyclohexyl Sulfide (3ah): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.38 – 7.30 (m, 4H), 3.10-3.02 (m, 1H), 2.00 (d, *J* = 4.5 Hz, 2H), 1.78 (d, *J* = 5.1 Hz, 2H), 1.62 (d, *J* = 6.0 Hz 1H), 1.39 – 1.26 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.91, 132.14, 131.54, 125.80, 46.85, 34.51, 33.48, 31.34, 31.32, 26.12, 25.85; **LRMS (ESI, 70 eV)** *m/z*: 248.5, 151.3; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{16}H_{24}S$ 248.1599 found 248.1603.



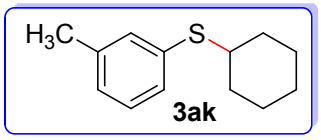
3ai

2-Thiophenyl Cyclohexyl Sulfide (3ai): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* =5.4, 1.1 Hz, 1H), 7.12 – 7.10 (q, *J* = 1.2 Hz, 1H), 7.00-6.93 (m, 1H), 2.89-2.82 (m, 1H), 2.03-1.95 (m, 2H), 1.77 (d, *J* = 5.4 Hz, 2H), 1.61-1.57 (m, 1H), 1.39 – 1.22 (m, 5H); 13C NMR (126 MHz, CDCl3) δ 134.93, 132.91, 129.68, 127.46, 49.87, 33.19, 26.06, 25.64. **LRMS (ESI, 70 eV)** *m/z*: 198.6, 124.5, 97.5, 83.5, 55.2, 40.8; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{10}H_{14}S_2$ 198.0537 found 198.0532.



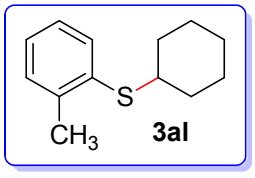
3aj

3-Fluorophenyl Cyclohexyl Sulfide (3aj): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 1H), 7.14-7.06 (m, 2H), 6.92-6.88 (m, 1H), 3.18-3.01 (m, 1H), 2.00 (d, *J* = 9.9 Hz, 2H), 1.78 (d, *J* = 4.8 Hz, 2H), 1.65-1.62 (m, 1H), 1.44 – 1.28 (m, 5H); 13C NMR (126 MHz, CDCl3) δ 163.72, 161.75 (d, JC-F = 248.2 Hz), 138.01, 137.95 (d, JC-F = 7.56 Hz), 129.98, 129.92 (d, JC-F = 7.56 Hz), 126.56, 126.54 (d, JC-F = 2.52 Hz), 117.66, 117.48 (d, JC-F = 22.68 Hz), 113.31, 113.15 (d, JC-F = 20.16 Hz), 46.26, 33.23, 25.99, 25.74. **LRMS (ESI, 70 eV)** *m/z*: 210.2; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{12}H_{15}FS$ 210.0878 found 210.0876.



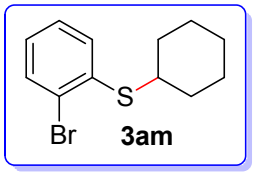
3ak

3-Methylphenyl Cyclohexyl Sulfide (3ak): [4] Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 3H), 7.03 (d, *J* = 6.3 Hz, 1H), 3.13-3.09 (m, 1H), 2.33 (s, 3H), 1.99 (d, *J* = 6.6 Hz, 2H), 1.78 (d, *J* =5.2 Hz, 2H), 1.63-1.59 (m, 1H), 1.42 – 1.26 (m, 5H); 13C NMR (126 MHz, CDCl3) δ 138.49, 134.91, 132.57, 128.87, 128.59, 127.49, 46.57, 33.42, 26.10, 25.82, 21.34; **LRMS (ESI, 70 eV)** *m/z*: 206.2, 124.0, 91.2; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{13}H_{18}S$ 206.1129 found 206.1125.

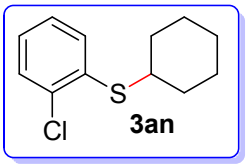


3al

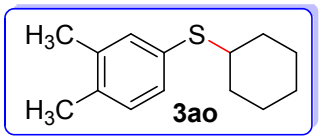
2-Methylphenyl Cyclohexyl Sulfide (3al): [4] Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 1H), 7.20 – 7.09 (m, 3H), 3.13-3.05 (m, 1H), 2.41 (s, 3H), 2.01 (d, *J* = 11.3 Hz, 2H), 1.78 (d, *J* = 5.0 Hz, 2H), 1.63-1.60 (m, 1H), 1.46 – 1.25 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 134.7, 131.5, 130.2, 126.4, 126.1, 46.1, 33.4, 26.12, 20.8; **LRMS (ESI, 70 eV)** *m/z*: 206.3, 159.7, 119.2; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{13}H_{18}S$ 206.1129 found 206.1128.



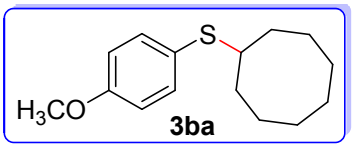
2-Bromophenyl Cyclohexyl Sulfide (3am): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.06 – 7.01 (t, *J* = 7.5 Hz, 1H), 3.21-3.27 (m, 1H), 2.03 (d, *J* = 11.3 Hz, 2H), 1.80 (d, *J* = 5.0 Hz, 2H), 1.64 (d, *J* = 5.5 Hz, 1H), 1.51 – 1.26 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 137.0, 133.2, 131.1, 127.5, 127.2, 125.8, 45.7, 33.0, 26.0, 25.8; **LRMS (ESI, 70 eV)** *m/z*: 270.3, 246.7, 207.1; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{12}H_{15}BrS$ 270.0078 found 270.0075.



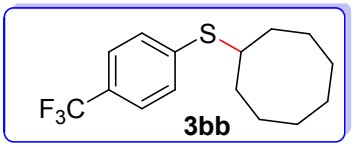
2-Chlorophenyl Cyclohexyl Sulfide (3an): Colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.23-7.10 (m, 2H), 3.28-3.21 (m, 1H), 2.01 (d, *J* = 12.2 Hz, 2H), 1.81 – 1.78 (m, 2H), 1.61 – 1.65 (m, 1H), 1.49 – 1.26 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 134.8, 131.6, 129.8, 127.2, 126.9, 45.3, 33.1, 26.0, 25.8; **LRMS (ESI, 70 eV)** *m/z*: 228.3, 226.3, 193.5, 175.5, 144.5, 108.3, 81.4; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{13}H_{18}S$ 226.0583 found 226.0585.



3,4-Dimethylphenyl Cyclohexyl Sulfide (3ao): [4] Colorless oil.^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.21 – 7.16 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 3.02 (br, 1H), 2.24 (s, 6H), 1.98 (d, *J* = 9.6 Hz, 2H), 1.77 (d, *J* =5.4 Hz, 2H), 1.61 (d, *J* =5.1 Hz, 1H), 1.40 – 1.24 (m, 5H); 13C NMR (126 MHz, CDCl3) δ 137.09, 135.58, 134.04, 131.44, 130.27, 130.03, 47.10, 33.46, 26.14, 25.84, 19.72, 19.41; **LRMS (ESI, 70 eV)** *m/z*: 221.2, 220.4, 138.2, 105.1; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{14}H_{20}S$ 220.1286 found 220.1288.

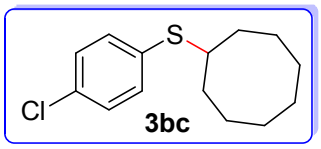


4-Methoxyphenyl Cyclooctyl Sulfide (3ba): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.25 – 3.11 (m, 1H), 1.65-1.60 (m, 2H), 1.57 – 1.48 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 159.2, 135.1, 126.2, 114.4, 55.3, 49.3, 31.9, 27.2, 25.8, 25.1; **LRMS (ESI, 70 eV)** *m/z*: 251.0, 140.7, 125.3, 96.7, 69.6; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{15}H_{22}OS$ 250.1391 found 250.1394.



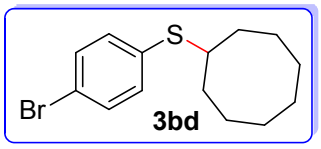
3bb

4-Trifluoromethylphenyl Cyclooctyl Sulfide (3bb): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.50 (t, *J* =7.2 Hz, 2H), 7.44-7.35 (m, 2H), 3.49– 3.43 (m, 1H), 1.98-1.92 (m, 2H), 1.76 – 1.22 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 138.05, 133.85, 133.83, 129.14, 127.25, 127.20, 127.15, 122.94, 122.89, 122.84, 122.79, 47.59, 31.95, 27.11, 25.89, 25.15; **LRMS (ESI, 70 eV)** *m/z*: 288.3, 269.8, 157.5, 111.7, 69.6; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{15}H_{19}F_3S$ 288.1160 found 288.1166.



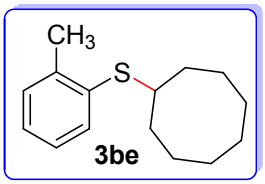
3bc

4-Chlorophenyl Cyclooctyl Sulfide (3bc): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.23 (q, *J* = 8.5 Hz, 4H), 3.38 – 3.32 (m, 1H), 1.97-1.90 (m, 2H), 1.74 – 1.49 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 134.75, 132.84, 132.52, 128.96, 48.17, 31.96, 27.15, 25.88, 25.18; **LRMS (ESI, 70 eV)** *m/z*: 254.5, 144.5, 111.8, 108.5, 69.6, 38.8; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{14}H_{19}ClS$ 254.0896 found 254.0894.



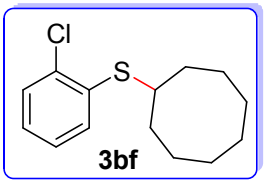
3bd

4-Bromophenyl Cyclooctyl Sulfide (3bd): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.37 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.24-7.21 (dd, *J* = 8.3, 1.5 Hz, 2H), 3.39 – 3.20 (m, 1H), 1.96-1.89 (m, 2H), 1.74 – 1.49 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 135.47, 132.96, 131.89, 120.39, 47.99, 31.96, 27.14, 25.89, 25.19; **LRMS (ESI, 70 eV)** *m/z*: 299.0, 298.0, 112.0, 38.7; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{14}H_{19}BrS$ 298.0391 found 298.0393.



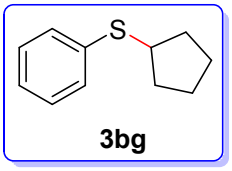
3be

2-Methylphenyl Cyclooctyl Sulfide (3be): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.35 (m, 1H), 7.18-7.12 (m, 3H), 3.48 – 3.35 (m, 1H), 2.41 (s, 3H), 1.97-1.92 (m, 2H), 1.77-1.70 (m, 4H), 1.58-1.52(m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 135.5, 131.2, 130.2, 126.3, 126.2, 47.1, 32.0, 27.2, 25.9, 25.2, 20.8; **LRMS (ESI, 70 eV)** *m/z*: 234.7, 124.5, 69.6; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{15}H_{22}S$ 234.1442 found 234.1443.



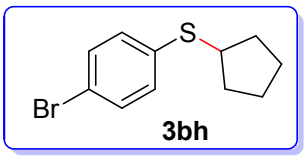
3bf

2-Chlorophenyl Cyclooctyl Sulfide (3bf): Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.35 (m, 1H), 7.20-7.12 (m, 2H), 3.54 – 3.46 (m, 1H), 2.00 -1.91 (m, 2H), 1.77-1.68 (m, 4H), 1.63-1.52 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.52, 135.39, 131.62, 129.90, 127.14, 126.97, 46.47, 31.96, 27.12, 25.96, 25.28; **LRMS (ESI, 70 eV)** *m/z*: 254.5, 253.5, 194.4, 112.0; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{14}H_{19}ClS$ 254.0896 found 254.0892.



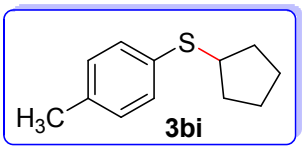
3bg

Phenyl Cyclopentyl sulfide (3bg): [2] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.38 (m, 2H), 7.30 (dd, *J* =7.2, 1.8 Hz, 2H), 7.21-7.16 (m, 1H), 3.63 – 3.57 (m, 1H), 2.08 – 2.03 (m, 2H), 1.80 – 1.75 (m, 2H), 1.67 – 1.60 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.38, 130.08, 128.79, 125.93, 46.04, 33.65, 24.87; **LRMS (ESI, 70 eV)** *m/z*: 178.7, 163.4, 135.3, 110.3; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{11}H_{14}S$ 178.0816 found 178.0817.



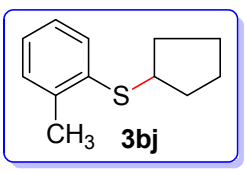
3bh

4-Bromophenyl Cyclopentyl sulfide (3bh): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, J=1.9, 8.5 Hz, 2H), 7.22 (dd, J=1.8, 8.6 Hz, 2H), 3.61 – 3.52 (m, 1H), 2.08-1.99 (m, 2H), 1.79 – 1.74 (m, 2H), 1.67 – 1.54 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.65, 131.81, 131.47, 119.75, 46.06, 33.53, 24.84; **LRMS (ESI, 70 eV)** *m/z*: 258.3, 256.9, 256.0, 110.2. **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{11}H_{13}BrS$ 255.9921 found 255.9925.



3bi

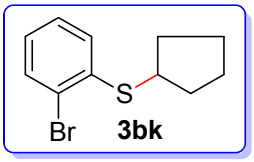
4-Methylphenyl Cyclopentyl Sulfide (3bi) [1]**:** Colorless liquid,^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 3.53-3.52 (m, 1H), 2.33 (s, 3H), 2.03 – 1.98 (m, 2H), 1.79 – 1.74 (m, 2H), 1.66 – 1.59 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.17, 133.37, 131.06, 129.56, 46.75, 33.60, 24.79, 21.05; **LRMS (ESI, 70 eV)** *m/z*: 192.5, 190.8, 170.6, 150.5, 89.2; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{12}H_{16}ClS$ 192.0973 found 192.0976.



3bj

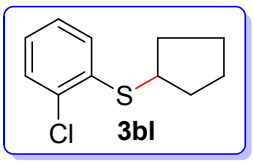
2-Methylphenyl Cyclopentyl Sulfide (3bj) : Colorless liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.3 Hz, 1H), 7.19 – 7.07 (m, 3H), 3.63 – 3.57 (m, 1H), 2.38 (s, 3H), 2.15 – 2.06

(m, 2H), 1.82 (s, 2H), 1.71 – 1.64 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.71, 136.79, 130.04, 129.11, 126.26, 125.56, 45.11, 33.66, 24.91, 20.52; **LRMS (ESI, 70 eV)** *m/z*: 192.5, 147.3, 89.3; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{12}H_{16}ClS$ 192.0973 found 192.0975.



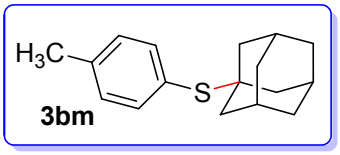
3bk

2-Bromophenyl Cyclopentyl Sulfide (3bk) : Colorless liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.32 – 7.23 (m, 2H), 7.03 – 6.97 (m, 1H), 3.70 – 3.61 (m, 1H), 2.17 – 2.10 (m, 2H), 1.83-1.78 (m, 2H), 1.73 – 1.63 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.15, 132.95, 128.93, 127.60, 126.30, 123.49, 44.83, 33.37, 25.02; **LRMS (ESI, 70 eV)** *m/z*: 256.9, 256.0, 112.3. **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{11}H_{13}BrS$ 255.9921 found 255.9920.



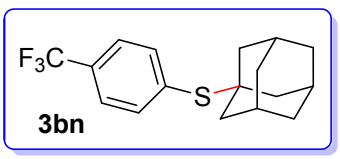
3bl

2-Chlorophenyl Cyclopentyl Sulfide (3bl) : Colorless liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.23 – 7.18 (m, 1H), 7.12 – 7.06 (m, 1H), 3.69 – 3.62(m, 1H), 2.17 – 1.95 (m, 2H), 1.87-1.82 (m, 2H), 1.72 – 1.62 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.64, 129.31, 126.97, 126.23, 44.46, 33.44, 24.98; **LRMS (ESI, 70 eV)** *m/z*: 212.5, 166.8; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{11}H_{13}ClS$ 212.0426 found 212.0424



3bm

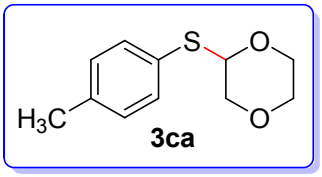
4-Methylphenyl adamantanyl sulfide (3bm): oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H), 2.00 (s, 3H), 1.80 (d, *J* = 2.4 Hz, 6H), 1.66-1.54 (m, 6H); 13C NMR (126 MHz, CDCl3) δ 138.60, 137.59, 129.12, 127.03, 47.56, 43.58, 36.21, 29.99, 21.24; **LRMS (ESI, 70 eV)** *m/z*: 258.7, 135.7, 79.3; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{17}H_{22}S$ 258.1442 found 258.1445.



3bn

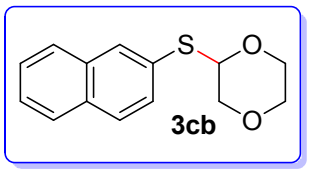
4-Trifluoromethylphenyl adamantanyl Sulfide (3bn): oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 2.03 (s, 3H), 1.80 (d, *J* = 2.8 Hz, 6H), 1.68-1.57 (m, 6H); 13C NMR (126 MHz, CDCl3) δ 140.79, 132.03,

128.65, 122.76 (q, JC-F = 54.82 Hz), 134.07, 134.04, 134.01, 133.98 (q, JC-F = 3.78 Hz), 133.26, 130.89, 130.65, 129.14 (q, JC-F =32.76 Hz), 125.39, 124.92 (q, JC-F = 59.22 Hz), 125.37, 125.34 (d, JC-F = 3.78 Hz), 48.58, 43.61, 36.06, 29.98; **LRMS (ESI, 70 eV)** *m/z*: 312.5, 177.3, 135.2; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{17}H_{19}F_3S$ 312.1160 found 312.1166.



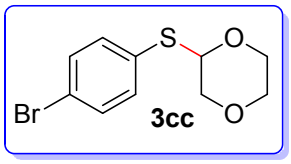
3ca

2-(p-tolylthio)-1,4-dioxane (3ca): Colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 5.04-5.01 (m, 1H), 4.22-4.17 (m, 1H), 3.99-3.94 (dd, *J* = 11.8, 2.8 Hz, 1H), 3.72-3.64 (m, 4H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 137.69, 132.41, 130.01, 129.78, 83.57, 69.96, 66.49, 64.08; **LRMS (ESI, 70 eV)** *m/z*: 210.7, 209.7, 149.5, 124.5, 86.5, 73.5, 65.3; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{11}H_{14}O_2S$ 210.0715 found 210.0719.



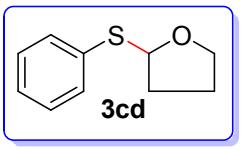
3cb

2-(naphthalen-2-ylthio)-1,4-dioxane(3cb): Light-yellow solid, m.p. 103-104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.2 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 3H), 7.57 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.50 – 7.46 (m, 2H), 5.25-5.22 (m, 1H), 4.36 – 4.24 (m, 1H), 4.03 (dd, *J* = 11.7, 2.9 Hz, 1H), 3.81 – 3.69 (m, 4H); ^{13}C NMR (126 MHz, CDCl3) δ 133.66, 132.42, 131.30, 130.37, 129.08, 128.51, 127.71, 127.47, 126.55, 126.21, 83.32, 70.03, 66.54, 63.86. **LRMS (ESI, 70 eV)** *m/z*: 246.3, 160.3, 115.3, 87.5; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{14}H_{14}O_2S$ 246.0715 found 246.0712.



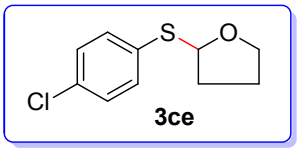
3cc

2-(4-bromophenylthio)-1,4-dioxane(3ae): Light-yellow solid, m.p. 75-76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 6.6, 1.8 Hz, 2H), 7.35 (dd, *J* = 6.6, 2.1 Hz, 2H), 5.11-5.08 (m, 1H), 4.26 – 4.18 (m, 1H), 3.97 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.75 – 3.65 (m, 4H); 13C NMR (126 MHz, CDCl3) δ 133.09, 132.03, 129.46, 121.54, 83.19, 69.83, 66.53, 63.52; **LRMS (ESI, 70 eV)** *m/z*: 273.9, 272.8, 108.2, 87.3, 73.5; **HRMS (TOF, EI$^+$)** *m/z* calcd for $C_{10}H_{11}BrO_2S$ 273.9663 found 273.9667.



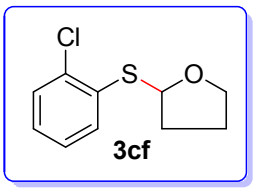
3cd

2-(phenylthio)tetrahydrofuran (3cd): Colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.33-7.23 (m, 3H), 5.68-5.64 (m, 1H), 4.05-3.96 (m, 2H), 2.40-2.33 (m, 1H), 2.02-1.92 (m, 3H); 13C NMR (126 MHz, CDCl3) δ 135.70, 131.10, 128.82, 126.81, 87.17, 67.29, 32.67, 24.87; **LRMS (ESI, 70 eV)** m/z: 180.2, 109.3, 71.2, 65.2; **HRMS (TOF, EI+)** m/z calcd for C10H12OS 180.0609 found 180.0611.



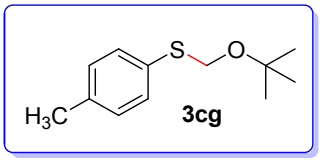
3ce

2-(4-Chlorophenylthio)tetrahydrofuran (3ce): Colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.28-7.23 (m, 1H), 5.62-5.58 (m, 1H), 4.02-3.93 (m, 2H), 2.40-2.36 (m, 1H), 2.01-1.88 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 135.59, 134.02, 130.86, 129.56, 127.28, 127.23, 85.56, 67.53, 32.65, 24.83. **LRMS (ESI, 70 eV)** *m/z*: 214.3, 140.1, 71.3, 65.1; **HRMS (TOF, EI^{+})** *m/z* calcd for $C_{10}H_{11}ClOS$ 214.0219 found 214.0223.



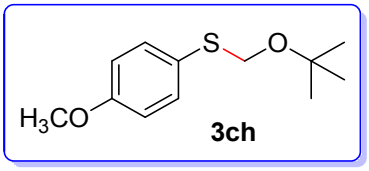
3cf

2-(2-Chlorophenylthio)tetrahydrofuran (3cf): Colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.35 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.25-7.20 (m, 1H), 7.16-7.13 (m, 1H), 5.78-5.75 (m, 1H), 4.07-3.95 (m, 2H), 2.44-2.39 (m, 1H), 2.10-1.88 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 135.59, 134.02, 130.86, 129.56, 127.28, 127.23, 85.56, 67.53, 32.65, 24.83. **LRMS (ESI, 70 eV)** *m/z*: 214.3, 213.8, 140.3, 71.2, 65.6; **HRMS (TOF, EI^{+})** *m/z* calcd for $C_{10}H_{11}ClOS$ 214.0219 found 214.0220.



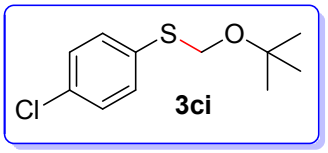
3cg

4-Methylphenyl *tert*-butoxymethyl sulfide(3cg): Colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 4.85 (s, 2H), 2.32 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 136.60, 132.87, 130.78, 129.55, 75.23, 68.86, 27.90, 21.06, 21.04; **LRMS (ESI, 70 eV)** *m/z*: 210.3, 180.4, 137.3, 124.3, 91.5, 63.2. **HRMS (TOF, EI^{+})** *m/z* calcd for $C_{12}H_{18}OS$ 210.1087 found 210.1086.



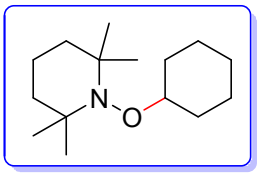
3ch

4-Methoxyphenyl *tert*-butoxymethyl sulfide(3ch): Colorless oil,^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.77 (s, 2H), 3.78 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 159.26, 133.60, 126.74, 114.44, 75.13, 69.71, 55.34, 55.31, 27.89; **LRMS (ESI, 70 eV)** *m/z*: 226.3, 196.2, 153.5, 140.8, 108.2, 93.2, 58.2, 43.3; **HRMS (TOF, EI^{+})** *m/z* calcd for $C_{12}H_{18}O_2S$ 226.1028 found 226.1032.



3ci

4-Chlorophenyl *tert*-butoxymethyl sulfide(3ci): Colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 6.3, 1.8 Hz, 2H), 7.24 (dd, *J* = 6.6, 1.8 Hz, 2H), 4.86 (s, 2H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 135.23, 132.61, 131.45, 128.91, 75.53, 68.38, 27.88; **LRMS (ESI, 70 eV)** *m/z*: 230.3, 200.8, 144.3, 108.7,63.4; **HRMS (TOF, EI^{+})** *m/z* calcd for $C_{11}H_{15}ClOS$ 230.0532 found 230.0538.



1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine: oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61-3.56 (m, 1H), 2.07-2.04 (m, 2H), 1.73 (d, *J* = 4.2 Hz, 2H), 1.66-1.62 (m, 2H), 1.47 (d, *J* = 5.2 Hz, 4H), 1.29-1.21 (m, 4H), 1.14 (s, 14H); 13C NMR (101 MHz, CDCl3) δ 81.71, 59.59, 40.27, 34.46, 32.89, 25.96, 25.09, 20.26, 17.33; **LRMS (ESI, 70 eV)** m/z: 240.1, 157.0, 142.1, 109.2, 83.1. **HRMS (TOF, EI+)** m/z calcd for C15H29NO 239.2249 found 239.2246.

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(C) Original spectra