

Supporting Information
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Supporting Information

Ligand-Free Copper-Catalyzed Synthesis of Diaryl Thioethers from Aryl Halides and Thioacetamide

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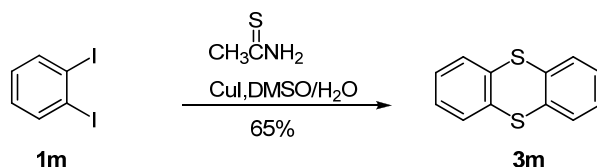
General experimental procedures

All reactions were carried out in an oven-dried Schlenk tube under argon atmosphere. All chemicals were obtained from commercial source and used without further purification. Flash column chromatography was performed on silica 230–400 mesh. ¹H-NMR, ¹³C-NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature in CDCl₃. Chemical shifts are reported in ppm relative to TMS. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System.

Coupling of aryl halides with thioacetamide; General procedure:

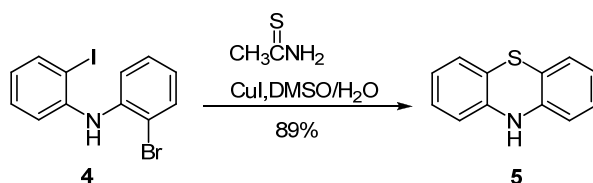
An oven-dried Schlenk tube was charged with CuI (18 mg, 10 mol%), CH₃CSNH₂ (75 mg, 1.0mmol), Cs₂CO₃ (978 mg, 3.0 mmol) and aryl halide (2.5 mmol). The tube was evacuated and backfilled with argon. Then, DMSO/H₂O (0.5 mL/0.25 mL) were added under argon. The tube was sealed and the reaction mixture was stirred at 120°C for 24-36 hours. The reaction mixture was quenched with water, extracted with diethyl ether and dried over anhydrous MgSO₄. The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, EtOAc-PE) to afford the product.

Coupling of 1,2-diiodobenzene with thioacetamide:

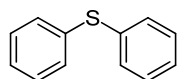


An oven-dried Schlenk tube was charged with CuI (18 mg, 10 mol%), CH₃CSNH₂ (225 mg, 3.0mmol), Cs₂CO₃ (978 mg, 3.0 mmol). The tube was evacuated and backfilled with argon. Then, 1,2-diiodobenzene (1.0mmol) and DMSO/H₂O (0.5 mL/0.25 mL) were added under argon. The tube was sealed and the reaction mixture was stirred at 120°C for 36 hours. The reaction mixture was quenched with water, extracted with diethyl ether and dried over anhydrous MgSO₄. The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, Petroleum ether) to afford the product.

Coupling of 2-bromo-N-(2-iodophenyl)aniline with thioacetamide:

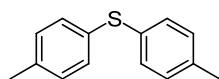


An oven-dried Schlenk tube was charged with CuI (18 mg, 10 mol%), CH_3CSNH_2 (225 mg, 3.0 mmol), Cs_2CO_3 (978 mg, 3.0 mmol). The tube was evacuated and backfilled with argon. Then, 2-bromo-N-(2-iodophenyl)aniline (374 mg, 1.0 mmol) and $\text{DMSO}/\text{H}_2\text{O}$ (0.5 mL/0.25 mL) were added under argon. The tube was sealed and the reaction mixture was stirred at 120°C for 20 hours. The reaction mixture was quenched with water, extracted with diethyl ether and dried over anhydrous MgSO_4 . The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, EtOAc-PE) to afford the product.



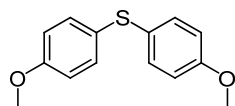
diphenylsulfane (3a)¹:

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32 (d, $J = 6.7$ Hz, 4H), 7.25 (t, $J = 7.2$ Hz, 4H), 7.19 (dd, $J = 9.3, 5.0$ Hz, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 135.9, 131.1, 129.2, 127.1. GC-MS (EI): $m/z = 186.15$ [M]⁺



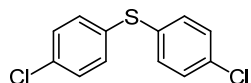
dip-tolylsulfane (3b)¹:

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.28 – 7.20 (m, 4H), 7.09 (d, $J = 7.4$ Hz, 4H), 2.31 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 137.0, 132.8, 131.2, 130.0, 21.2. GC-MS (EI): $m/z = 214.09$ [M]⁺



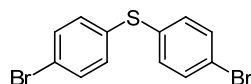
bis(4-methoxyphenyl)sulfane (3c)²:

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.27 (d, $J = 8.8$ Hz, 4H), 6.82 (d, $J = 8.7$ Hz, 4H), 3.77 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.1, 132.8, 127.5, 114.8, 55.4. GC-MS (EI): $m/z = 246.09$ [M]⁺



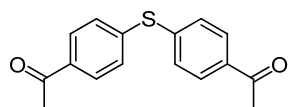
bis(4-chlorophenyl)sulfane (3d)³:

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 – 7.19 (m, 8H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 134.0, 133.6, 132.4, 129.6. GC-MS (EI): $m/z = 254.03, 256.01, 258.05$ [M]⁺



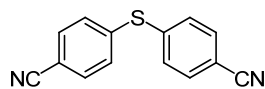
bis(4-bromophenyl)sulfane (3e)³:

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.5$ Hz, 4H), 7.17 (d, $J = 8.5$ Hz, 4H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 134.6, 132.7, 132.5, 121.6. GC-MS (EI): $m/z = 341.96, 343.93, 345.89$ [M]⁺



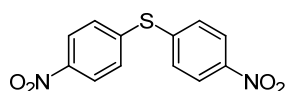
1,1'-(4,4'-thiobis(4,1-phenylene))diethanone (3f)³:

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.3 Hz, 4H), 7.41 (d, *J* = 8.3 Hz, 4H), 2.59 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 197.2, 141.1, 136.1, 130.7, 129.3, 26.7. GC-MS (EI): *m/z* = 270.08 [M]⁺



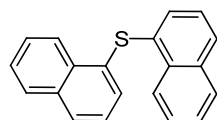
4,4'-thiodibenzonitrile (3g)⁴:

¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.1 Hz, 4H), 7.42 (d, *J* = 8.2 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 133.0, 131.2, 118.2, 111.5. GC-MS (EI): *m/z* = 236.09 [M]⁺



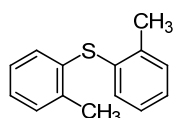
bis(4-nitrophenyl)sulfane (3h)³:

¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.8 Hz, 4H), 7.50 (d, *J* = 8.8 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 142.8, 131.2, 124.7. GC-MS (EI): *m/z* = 276.07 [M]⁺



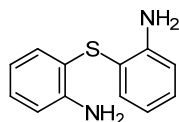
dinaphthalen-1-ylsulfane (3i)⁵:

¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 2H), 7.83 (d, *J* = 3.2 Hz, 2H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.53 – 7.43 (m, 4H), 7.33 – 7.21 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 134.2, 132.7, 132.5, 130.0, 128.7, 128.1, 126.8, 126.5, 125.9, 125.2. GC-MS (EI): *m/z* = 286.16 [M]⁺



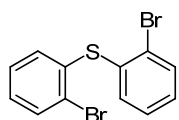
dio-tolylsulfane (3j)⁶:

¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.0 Hz, 2H), 7.07 (q, *J* = 7.7 Hz, 4H), 2.37 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 139.0, 134.5, 131.3, 130.6, 127.2, 126.8, 20.5. GC-MS (EI): *m/z* = 214.09 [M]⁺



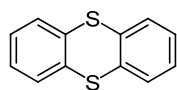
2,2'-thiodianiline (3k)⁷:

¹H NMR (400 MHz, CDCl₃) δ 7.20 (t, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.68 (dd, *J* = 11.7, 6.0 Hz, 4H), 4.08 (s, br, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 146.8, 133.5, 129.3, 119.1, 117.3, 115.6. GC-MS (EI): *m/z* = 216.07 [M]⁺



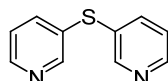
bis(2-bromophenyl)sulfane (3l)⁸:

^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 7.8$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 2H), 7.13 (t, $J = 7.5$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.8, 133.6, 132.5, 128.9, 128.2, 125.9. GC-MS (EI): $m/z = 342.00, 343.93, 345.89$ $[\text{M}]^+$



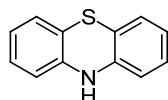
thianthrene (3m)⁹:

^1H NMR (400 MHz, CDCl_3) δ 7.47 (dd, $J = 5.4, 3.6$ Hz, 4H), 7.22 (dd, $J = 5.4, 3.6$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.7, 128.8, 127.8. GC-MS (EI): $m/z = 216.07$ $[\text{M}]^+$



dipyridin-3-ylsulfane (3n)¹⁰:

^1H NMR (400 MHz, CDCl_3) δ 8.58 (d, $J = 34.8$ Hz, 4H), 7.65 (d, $J = 7.9$ Hz, 2H), 7.27 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 148.6, 138.7, 132.0, 124.2. GC-MS (EI): $m/z = 188.06$ $[\text{M}]^+$



10H-phenothiazine (5)¹¹:

^1H NMR (400 MHz, CD_3COCD_3) δ 7.79 (s, 1H), 7.03 – 6.88 (m, 4H), 6.78 (t, $J = 7.5$ Hz, 2H), 6.71 (d, $J = 7.9$ Hz, 2H). ^{13}C NMR (100 MHz, CD_3COCD_3) δ 143.3, 128.3, 127.2, 122.8, 118.3, 115.4. GC-MS (EI): $m/z = 199.10$ $[\text{M}]^+$

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