Supporting Information
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An Iodide Mediated Transition Metal-Free Strategy towards Unsymmetrical Diaryl Sulfides via Aryl hydrazines and Thiols

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1 General remarks: The following includes general experimental procedures, specific details for representative reactions, isolation and spectroscopic information for the compounds. All reagents were commercially available and used as received. Column chromatography was carried out on silica gel (230–400 mesh). TLC was conducted on silica gel 250 micron, F254 plates. 1H NMR spectra were recorded at room temperature on Bruker 500 MHz spectrometer, using DMSO-d6 and CDCl3 as solvent. Chemical shifts are reported in ppm with TMS as an internal standard (TMS: δ 0.0 ppm). 13C NMR spectra are referenced from the solvent central peak (77.23 ppm). Chemical shifts are given in ppm. Elemental analyses (CHN) were recorded on a Thermo Finnigan Flash EA 1112 elemental analyzer.

2 Typical Experimental Procedure for Metal-Free Cross-Coupling of Arylhydrazines and Thiols. A vial equipped with a stir bar was charged with thiol (0.2 mmol, 2 equiv), arylhydrazine (0.1 mmol, 1 equiv), Cs2CO3 (1 equiv), KI (50 mol %) and TBHP (4 equiv). H2O (0.3 mL) was added and the vial was capped. The resulting mixture was stirred at room temperature for 20 h. Upon completion of the reaction, the resulting mixture was extracted with ethyl acetate. The combined organic layers was dried over anhydrous Na2SO4. After the removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (EtOAc/hexane gradient) to provide the desired products.

3 Compounds characterization data

(3-Methoxyphenyl)(phenyl)sulfane (3a). Pale yellow oil; Yield= 87% (19 mg); 1H NMR (500 MHz, CDCl3): δ 3.78 (s, 3H), 6.82 (dd, J = 8.3, 2.5 Hz, 1H), 6.91-6.93 (m, 1H), 6.94-6.97 (m, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.30 (d, J = 7.1 Hz, 1H), 7.35 (t, J = 8.0 Hz, 2H), 7.42 (d, J = 7.4 Hz, 2H); 13C NMR (125 MHz, CDCl3): δ 55.2, 112.8, 115.9, 123.0, 127.2, 129.2, 129.9, 131.4, 135.3, 137.2, 160.1; Anal. Calcd for C13H12OS: C, 72.19; H, 5.59; Found: C, 71.83; H, 5.50.

Phenyl(p-tolyl)sulfane (3b). White solid; Yield= 85% (17 mg); mp 88-90 °C (Ref. 1 90-93 °C); 1H NMR (500 MHz, CDCl3): δ 2.41 (s, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.84 (d, J = 8.0 HZ, 2H), 7.32 (d, J = 7.4 Hz, 2H); 13C NMR (125 MHz, CDCl3): δ 21.5, 127.5, 127.7, 129.2, 129.9, 133.0, 138.7, 142.0, 144.2; Anal. Calcd for C13H12S: C, 77.95; H, 6.04; Found: C, 78.25; H, 6.13.

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(3-Methoxyphenyl)(p-tolyl)sulfane (3c). Colorless oil; Yield = 83% (19 mg); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.39 (s, 3H), 3.78 (s, 3H), 6.75-6.79 (m, 1H), 6.86 (t, $J$ = 1.8 Hz, 1H), 6.87-6.91 (m, 1H), 7.16-7.24 (m, 3H), 7.36-7.40 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 21.2, 55.2, 112.1, 114.8, 121.8, 129.8, 130.1, 130.8, 132.6, 137.8, 138.6, 160.0; Anal. Calcd for C$_{14}$H$_{14}$OS: C, 73.01; H, 6.13; Found: C, 72.83; H, 6.02.

(4-Bromophenyl)(p-tolyl)sulfane (3d). White solid; Yield = 84% (24 mg); mp 75-77 °C (Ref. 2); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.38 (s, 3H), 7.13 (d, $J$ = 8.5 Hz, 2H), 7.18 (d, $J$ = 7.9 Hz, 2H), 7.33 (d, $J$ = 7.9 Hz, 2H), 7.39 (d, $J$ = 8.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 21.2, 120.1, 130.2, 130.9, 132.0, 132.7, 136.8, 138.2; Anal. Calcd for C$_{13}$H$_{11}$BrS: C, 55.93; H, 3.97; Found: C, 56.33; H, 4.13.

(3-Methoxyphenyl)(phenyl)sulfane (3e). Yellow oil; Yield = 86% (19 mg); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.85 (s, 3H), 6.94-6.96 (m, 2H), 7.17-7.24 (m, 3H), 7.27-7.29 (m, 2H), 7.46-7.48 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 55.4, 115.1, 124.4, 125.8, 128.3, 129.0, 135.4, 138.7, 159.9; Anal. Calcd for C$_{13}$H$_{12}$OS: C, 72.19; H, 5.59; Found: C, 72.59; H, 5.68.

(3-Methoxyphenyl)(p-tolyl)sulfane (3f). White solid; Yield = 88% (20 mg); mp 47-49 °C (Ref. 3); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.35 (s, 3H), 3.84 (s, 3H), 6.92 (d, $J$ = 8.7 Hz, 2H), 7.12 (d, $J$ = 8.1 Hz, 2H), 7.20 (d, $J$ = 8.1 Hz, 2H), 7.42 (d, $J$ = 8.8 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 21.2, 55.3, 114.9, 125.7, 129.4, 129.8, 134.4, 134.4, 136.1, 159.5; Anal. Calcd for C$_{14}$H$_{14}$OS: C, 73.01; H, 6.13; Found: C, 73.33; H, 6.23.

(4-Chlorophenyl)(2-fluorophenyl)sulfane (3g). Pale yellow oil; Yield = 82% (20 mg); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.10-7.16 (m, 2H), 7.25-7.30 (m, 4H), 7.30-7.35 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 116.1 (d, $J$ = 21.2 Hz), 122.0 (d, $J$ = 17.5 Hz), 124.8 (d, $J$ = 3.7 Hz), 129.4, 129.9 (d, $J$ = 7.5 Hz), 131.9, 133.1 (d, $J$ = 2.5 Hz), 133.3, 133.8, 161.3 (d, $J$ = 246.2 Hz); Anal. Calcd for C$_{12}$H$_8$ClFS: C, 60.38; H, 3.38; Found: C, 61.95; H, 4.30.

(4-Chlorophenyl)(4-fluorophenyl)sulfane (3h). White solid; Yield = 84% (20 mg); mp 38-40 °C (Ref. 4); $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.21-7.26 (m, 4H), 7.37 (d, $J$ = 8.6 Hz, 2H), 7.43-7.46 (m, 2H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$ 117.3 (d, $J$ = 22.5 Hz), 129.4 (d, $J$ = 3.7 Hz), 129.8, 131.4, 132.2, 134.0,
135.0 (d, \( J = 8.7 \) Hz), 162.5 (d, \( J = 243.7 \) Hz); Anal. Calcd for C\(_{12}\)H\(_8\)ClFS: C, 60.38; H, 3.38; Found: C, 60.68; H, 3.47.

(4-Chlorophenyl)(4-nitrophenyl)sulfane (3i). Yellow solid; Yield= 63\% (17 mg); mp 86-88\(^\circ\)C (Ref.\(^5\) 90 \(^\circ\)C); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.20 (d, \( J = 8.9 \) Hz, 2H), 7.44 (d, \( J = 8.5 \) Hz, 2H), 7.48 (d, \( J = 8.5 \) Hz, 2H), 8.09 (d, \( J = 8.9 \) Hz, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 124.1, 126.9, 129.1, 130.3, 135.9, 136.1, 145.6, 147.6; Anal. Calcd for C\(_{12}\)H\(_8\)ClNO\(_2\)S: C, 54.24; H, 3.03; N, 5.27; Found: C, 54.64; H, 3.18; N, 5.57.

(4-Chlorophenyl)(o-tolyl)sulfane (3j). White oil; Yield= 83\% (20 mg); \(^1\)H NMR (500 MHz, DMSO-\( \text{d}_6 \)): \( \delta \) 2.29 (s, 3H), 7.13 (d, \( J = 8.5 \) Hz, 2H), 7.21 (t, \( J = 7.7 \) Hz, 1H), 7.28-7.31 (m, 2H), 7.34 (d, \( J = 8.5 \) Hz, 2H); \(^{13}\)C NMR (125 MHz, DMSO-\( \text{d}_6 \)): \( \delta \) 20.6, 127.7, 129.2, 129.8, 130.8, 131.4, 131.4, 132.4, 133.7, 135.1, 140.2; Anal. Calcd for C\(_{13}\)H\(_{11}\)ClS: C, 66.52; H, 4.72; Found: C, 66.92; H, 4.87.

(4-Chlorophenyl)(3-methoxyphenyl)sulfane (3k). Yellow oil; Yield= 81\% (20 mg); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 3.79 (s, 3H), 6.84 (dd, \( J = 8.3, 2.7 \) Hz, 1H), 6.91 (d, \( J = 2.3 \) Hz, 1H), 6.95 (d, \( J = 7.1 \) Hz, 1H), 7.23-7.27 (m, 1H), 7.28-7.34 (m, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 55.3, 113.1, 116.3, 123.2, 129.3, 130.1, 132.4, 133.2, 134.2, 136.5, 160.1; Anal. Calcd for C\(_{13}\)H\(_{11}\)ClOS: C, 62.27; H, 4.42; Found: C, 61.95; H, 4.30.

(2-Nitrophenyl)(phenyl)sulfane (3l). Yellow solid; Yield= 65\% (15 mg); mp 79-81 \(^\circ\)C (Ref.\(^6\) 80-82 \(^\circ\)C); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 6.88 (d, \( J = 8.2 \) Hz, 1H), 7.23 (t, \( J = 7.7 \) Hz, 1H), 7.35 (t, \( J = 7.8 \) Hz, 1H), 7.48-7.53 (m, 3H), 7.58-7.62 (m, 2H), 8.24 (d, \( J = 8.3 \) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 125.0, 125.7, 128.3, 130.1, 130.2, 131.0, 133.5, 136.0, 139.5, 144.9; Anal. Calcd for C\(_{12}\)H\(_9\)NO\(_2\)S: C, 62.32; H, 3.92; N, 6.06; Found: C, 62.63; H, 4.01; N, 6.26.

(4-Chlorophenyl)(2-nitrophenyl)sulfane (3m). Yellow solid; Yield= 76\% (21 mg); mp 93-95\(^\circ\)C (Ref.\(^6\) 94-96 \(^\circ\)C); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 6.87 (d, \( J = 8.2 \) Hz, 1H), 7.25 (t, \( J = 7.8 \) Hz, 1H), 7.38 (t, \( J = 7.6 \) Hz, 1H), 7.46 (d, \( J = 8.2 \) Hz, 2H), 7.52 (d, \( J = 8.2 \) Hz, 2H), 8.22 (d, \( J = 8.2 \) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 125.3, 125.8, 128.2, 129.6, 130.4, 133.6, 136.5, 137.1, 138.7, 145.0; Anal. Calcd for C\(_{12}\)H\(_8\)ClNO\(_2\)S: C, 54.24; H, 3.03; N, 5.27; Found: C, 54.64; H, 3.18; N, 5.57.
(4-Nitrophenyl)(phenyl)sulfane (3n). Yellow solid; Yield = 72% (17 mg); mp 55-57 °C (Ref. 7 55-56 °C); ¹H NMR (500 MHz, CDCl₃): δ 7.18 (d, J = 9.0 Hz, 2H), 7.43-7.49 (m, 3H), 7.52-7.57 (m, 2H), 8.05 (d, J = 9.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 124.0, 126.7, 129.7, 130.0, 130.5, 134.7, 145.4, 148.5; Anal. Calcd for C₁₂H₉NO₂S: C, 62.32; H, 3.92; N, 6.06; Found: C, 62.72; H, 4.07; N, 6.36.

(2,4-Dinitrophenyl)(phenyl)sulfane (3o). Yellow solid; Yield = 75% (21 mg); mp 118-120 °C (Ref. 8 120-121 °C); ¹H NMR (500 MHz, CDCl₃): δ 7.01 (d, J = 9.0 Hz, 1H), 7.55-7.64 (m, 5H), 8.13 (dd, J = 9.0, 2.5 Hz, 1H), 9.07 (d, J = 2.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 121.4, 126.9, 128.9, 129.0, 130.7, 131.1, 135.9, 143.8, 144.3, 148.4; Anal. Calcd for C₁₂H₈N₂O₄S: C, 52.17; H, 2.92; N, 10.14; Found: C, 52.47; H, 3.01; N, 10.34.

Naphthalen-2-yl(p-tolyl)sulfane (3p). White solid; Yield = 80% (20 mg); mp 68-70 °C (Ref. 9 67-69 °C); ¹H NMR (500 MHz, DMSO-d₆): δ 2.30 (s, 3H), 7.21-7.23 (m, 2H), 7.30-7.33 (m, 3H), 7.48-7.52 (m, 2H), 7.81-7.83 (m, 2H), 7.86-7.89 (m, 2H); ¹³C NMR (125 MHz, DMSO-d₆) δ 21.1, 126.7, 127.3, 127.7, 128.0, 128.5, 129.5, 130.8, 131.0, 132.1, 132.2, 133.8, 133.9, 138.0; Anal. Calcd for C₁₇H₁₄S: C, 81.56; H, 5.64; Found: C, 81.96; H, 5.79.

(4-Fluorophenyl)(napthalen-2-yl)sulfane (3q). White solid; Yield = 70% (18 mg); mp 67-68 °C (Ref. 10 66-68 °C); ¹H NMR (500 MHz, CDCl₃): δ 7.10-7.12 (m, 2H), 7.43-7.45 (m, 1H), 7.48-7.56 (m, 4H), 7.78-7.87 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 116.6 (d, J = 21.2 Hz), 126.3, 126.8, 127.4, 127.8, 127.9, 128.7, 129.0, 132.4, 133.9, 134.0 (d, J = 7.5 Hz), 162.4 (d, J = 246.2 Hz); Anal. Calcd for C₁₆H₉FS: C, 75.56; H, 4.36; Found: C, 75.86; H, 4.47.

Benzyl(phenyl)sulfane (3r). White solid; Yield = 82% (17 mg); mp 40-42 °C (Ref. 11 42 °C); ¹H NMR (500 MHz, CDCl₃): δ 4.15 (s, 2H), 7.20-7.23 (m, 1H), 7.27-7.35 (m, 9H); ¹³C NMR (125 MHz, CDCl₃): δ 39.1, 126.4, 127.2, 128.5, 128.90, 128.91, 129.9, 136.5, 137.5; Anal. Calcd for C₁₃H₁₂S: C, 77.95; H, 6.04; Found: C, 78.25; H, 6.13.
(4-Methylbenzyl)(phenyl)sulfane (3s). White solid; Yield = 83% (18 mg); mp 66-67°C (Ref.12 66-67 °C); ¹H NMR (500 MHz, DMSO-d₆): δ 7.26 (s, 3H), 4.20 (s, 2H), 7.09 (d, J = 7.5 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.24 (d, J = 7.6 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H); ¹³C NMR (125 MHz, DMSO-d₆): δ 25.9, 41.7, 130.1, 133.5, 133.9, 134.1, 134.1, 139.6, 141.4, 141.6; Anal. Calcd for C₁₄H₁₄S: C, 78.46; H, 6.58; Found: C, 78.76; H, 6.67.

Butyl(phenyl)sulfane (3t). Yellow oil; Yield = 80% (14 mg); ¹H NMR (500 MHz, CDCl₃): δ 0.95 (t, J = 7.2 Hz, 3H), 1.42-1.51 (m, 2H), 1.61-1.69 (m, 2H), 2.94 (t, J = 7.3 Hz, 2H), 7.26-7.31 (m, 2H), 7.32-7.36 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 13.6, 21.9, 31.2, 33.2, 125.6, 128.8, 128.8, 137.0; Anal. Calcd for C₁₀H₁₄S: C, 72.23; H, 8.49; Found: C, 71.92; H, 8.38.

(2-Chlorophenyl)(2,4-dimethylphenyl)sulfane (3u). Brown oil; Yield = 65% (16 mg); ¹H NMR (500 MHz, CDCl₃): δ 2.28 (s, 3H), 2.48 (s, 3H), 6.57 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.93 (s, 1H), 7.03 (dd, J = 9.1, 1.65 Hz, 2H), 7.12 (dd, J = 9.1, 1.3 Hz, 1H), 7.30 (t, J = 8.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 20.0, 20.1, 113.8, 116.5, 122.0, 125.8, 127.6, 129.6, 131.4, 131.8, 135.8, 136.0, 140.4, 158.9; Anal. Calcd for C₁₄H₁₃ClS: C, 67.59; H, 5.27; Found: C, 67.99; H, 5.36.

4 References


5 Copies of $^1$H NMR and $^{13}$C NMR spectra
Compound 3a
Compound 3a
Compound 3b
Compound 3c
Compound 3c
Compound 3d
Compound 3d
Compound 3e
Compound 3e
Compound 3f
Compound 3f
Compound 3g
Compound 3h
Compound 3h
Compound 3i

[Chemical structure diagram]

[Spectrum graph]

S24
Compound 3i
Compound 3j
Compound 3k
Compound 3k
Compound 3l

![Compound 3l diagram]

[Chemical structure of Compound 3l with 1H NMR spectrum]
Compound 3l
Compound 3m
Compound 3m
Compound 3n
Compound 3n
Compound 3o
Compound 3o
Compound 3q
Compound 3r
Compound 3r
Compound 3s
Compound 3s
Compound 3t
Compound 3t
Compound 3u