Supporting Information

Facile Synthesis of 2-(Phenylthio)phenols by Copper(I)-catalyzed Tandem Transformation of C-S Coupling/C-H Functionalization

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Experimental Details

General Information:

All reagents used in the experiments were obtained from commercial sources and used without further purification. Unless otherwise noted, all reactions were carried out at N₂ atmosphere. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. All NMR spectra were recorded on Bruker AVANCE DMX-500 spectrometry at 500 MHz and 125 MHz for ¹H and ¹³C NMR in d⁶-DMSO, respectively. The NMR chemical shift was reported in ppm relative to 2.50 and 40.70 ppm of DMSO solvent as the standards of ¹H and ¹³C NMR, respectively. The ¹H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). Melting points were tested by XT-4 apparatus without correcting temperature or cited from literature when applicable. The HRMS of new products were tested on Agilent 6210 TOF LC/MS equipped with an electrospray source.

General procedure for preparation of L1-L6:¹⁻³

Dimethylformamide dimethylacetal (DMFDMA) (10 mol, 1.19 g) and 1-(2-hydroxyphenyl) ethanone (10 mol, 1.36 g) were dissolved in *p*-xylene (2 mL). And the mixture was refluxed during a period of 5 to 12 hours, during which time the formation of yellow precipitate. The precipitate was filtered out and washed with petroleum ether three times. The solid was vacuum-dried, and 1.79 g (yield 94 %) of a yellow solid was obtained **L4** ((*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one). ¹H NMR (500 MHz, d⁶-DMSO): δ 14.51 (s, 1 H), 7.92-7.90 (t, *J* = 7.5 Hz, 2 H), 7.37-7.34 (t, *J* = 7.8 Hz, 1 H), 6.83 (d, *J* = 2.0 Hz, 2 H), 5.98-5.95 (d, *J* = 12 Hz, 1 H), 3.19 (s, 3 H), 2.98 (s, 3 H); ¹³C NMR (125 MHz, d⁶-DMSO): δ 191.1, 163.6, 156.7, 134.9, 129.9, 121.2, 119.1, 118.7, 90.4, 46.1, 38.6.

General procedures for the ¹⁸O-DMSO: ⁴

Analytical data

2-(phenylthio)phenol (3a) A mixture of thiophenol **1a** (0.5 mmol, 55.0 mg), iodobenzene **2a** (0.6 mmol, 122.4 mg), CuI (10 mol %, 9.5 mg), **L4** (10 mol %, 9.5 mg) and Cs₂CO₃ (2 equiv, 325.8 mg) in DMSO (2 mL) was stirred in N₂ at 100 °C for 10 h. After completion of the reaction, the mixture was quenched with saturated salt water (10 mL), the solution was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel to afford **3a** in 67% yield. The spectroscopic data of all the products are presented below. Colorless liquid; ¹H NMR (500 MHz, d⁶-DMSO): δ 9.96 (s, 1 H), 7.33-7.30 (m, 2 H), 7.23-7.21 (q, *J* = 7.1 Hz, 1 H), 7.20-7.17 (m, 3 H), 7.13-7.11 (q, *J* = 7.5 Hz, 1 H), 6.94-6.93 (d, *J* = 7.4 Hz, 1 H), 6.81-6.78 (t, *J* = 7.1 Hz, 1 H); ¹³C NMR (125 MHz, d⁶-DMSO): δ 157.90, 136.80, 134.60, 130.79, 130.39, 130.22, 127.47, 121.07, 120.27, 116.97. GC-MS (EI) [*M*]⁺: 202. HRMS (EI) calcd for C₁₂H₁₀OS [*M*]⁺: 202.0452; found 202.0455.

2-(4-chlorophenylthio)phenol (3b) Colorless liquid; ¹H NMR (500 MHz, d⁶-DMSO): δ 10.04 (s, 1 H), 7.37-7.35 (d, *J* = 8.5 Hz, 2 H), 7.25-7.20 (m, 2 H), 7.14-7.13 (d, *J* = 8.5 Hz, 2 H), 6.96-6.94 (d, *J* = 8.1 Hz, 1 H), 6.84-6.81 (t, *J* = 7.9 Hz, 1 H); ¹³C NMR (125 MHz, d⁶-DMSO): δ 158.33, 136.46, 135.42, 131.81, 131.49, 131.14, 130.26, 121.19, 119.14, 117.18. GC-MS (EI) [*M*]⁺: 236. HRMS (EI) calcd for C₁₂H₉ClOS [*M*]⁺: 236.0063; found 236.0065.

2-(4-bromophenylthio)phenol (3c) Colorless liquid; ¹H NMR (500 MHz, d⁶-DMSO): δ 10.04 (s, 1 H), 7.48-7.47 (d, *J* = 8.6 Hz, 2 H), 7.26-7.22 (m, 2 H), 7.07-7.06 (d, *J* = 8.5 Hz, 2 H),

6.97-6.95 (d, $J = 7.9$ Hz, 1 H), 6.84-6.81 (t, $J = 7.5$ Hz, 1 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 158.41, 137.14, 135.59, 133.09, 131.57, 131.28, 121.19, 120.03, 118.92, 117.21. GC-MS (EI) $[\text{M}]^+$: 280. HRMS (EI) calcd for $\text{C}_{12}\text{H}_9\text{ClOS}$ $[\text{M}]^+$: 279.9557; found 279.9560.

2-(o-tolylthio)phenol (3d) Pale yellow liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 9.93 (s, 1 H), 7.28-7.27 (d, $J = 7.3$ Hz, 1 H), 7.18-7.13 (m, 3 H), 7.02-7.01 (d, $J = 7.7$ Hz, 1 H), 6.93-6.88 (m, 2 H), 6.76-6.78 (d, $J = 8.0$ Hz, 1 H), 2.31 (s, 3 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 157.33, 139.04, 134.93, 132.91, 131.58, 131.55, 129.96, 128.13, 127.93, 121.08, 120.68, 116.76, 21.04. GC-MS (EI) $[\text{M}]^+$: 216. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12}\text{OS}$ $[\text{M}]^+$: 216.0609; found 216.0609.

2-(p-tolylthio)phenol (3e) Pale yellow liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 9.92 (s, 1 H), 7.16 (s, 4 H), 7.13-7.10 (t, $J = 7.5$ Hz, 1 H), 6.96-6.94 (d, $J = 7.8$ Hz, 1 H), 6.90-6.89 (d, $J = 8.1$ Hz, 1 H), 6.73-6.76 (t, $J = 8.0$ Hz, 1 H), 2.28 (s, 3 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 156.95, 137.67, 132.81, 132.18, 131.92, 131.19, 129.78, 122.13, 120.97, 116.67, 21.82. GC-MS (EI) $[\text{M}]^+$: 216. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12}\text{OS}$ $[\text{M}]^+$: 216.0609; found 216.0612.

2-(4-methoxyphenylthio)phenol (3f) Yellow liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 9.92 (s, 1 H), 7.34-7.32 (d, $J = 8.3$ Hz, 2 H), 7.05-7.02 (m, 1 H), 6.99-6.98 (d, $J = 7.8$ Hz, 2 H), 6.85-6.84 (d, $J = 8.0$ Hz, 1 H), 6.74-6.68 (m, 2 H), 3.77 (s, 3 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 160.43, 155.63, 135.76, 130.99, 130.34, 128.53, 124.54, 120.88, 116.37, 116.26, 56.43. GC-MS (EI) $[\text{M}]^+$: 232. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$ $[\text{M}]^+$: 232.0558; found 232.0567.

2-(2-(trifluoromethyl)phenylthio)phenol(3g) Colorless liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 10.16 (s, 1 H), 7.75-7.74 (d, $J = 7.8$ Hz, 1 H), 7.50-7.48 (d, $J = 7.7$ Hz, 1 H), 7.37-7.36 (d, $J = 7.6$ Hz, 1 H), 7.32-7.28 (m, 1 H), 7.24-7.23 (d, $J = 7.7$ Hz, 1 H), 7.00-6.98 (d, $J = 8.1$ Hz, 2 H), 6.88-6.85 (t, $J = 6.6$ Hz, 1 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 158.94, 137.50, 136.48, 134.02, 132.25, 130.87, 127.96, 127.13, 121.41, 117.36. GC-MS (EI) $[\text{M}]^+$: 270. HRMS (EI) calcd for $\text{C}_{13}\text{H}_9\text{F}_3\text{OS}$ $[\text{M}]^+$: 270.0326; found 270.0333.

2-(3-(trifluoromethyl)phenylthio)phenol (3h) Colorless liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 10.11 (s, 1 H), 7.53-7.50 (d, $J = 7.8$ Hz, 2 H), 7.38-7.30 (m, 4 H), 7.37-7.36 (d, $J = 7.6$ Hz, 1 H), 7.32-7.28 (m, 1 H), 7.24-7.23 (d, $J = 7.7$ Hz, 1 H), 7.01-7.00 (d, $J = 8.1$ Hz, 1 H), 6.89-6.86 (m, 1 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 158.94, 140.02, 136.56, 132.30, 132.20, 131.13, 124.30, 124.27, 123.28, 123.25, 121.26, 117.44, 117.36. GC-MS (EI) $[\text{M}]^+$: 270. HRMS (EI) calcd for $\text{C}_{13}\text{H}_9\text{F}_3\text{OS}$ $[\text{M}]^+$: 270.0326; found 270.0329.

5-methyl-2-(phenylthio)phenol (3i) Pale yellow liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 9.79 (s, 1 H), 7.28-7.25 (d, $J = 7.3$ Hz, 2 H), 7.16-7.12 (d, $J = 7.2$ Hz, 2 H), 7.09-7.08 (d, $J = 7.9$ Hz, 2 H), 6.77 (s, 1 H), 6.66-6.64 (d, $J = 7.8$ Hz, 1 H), 2.25 (s, 3 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 158.53, 141.43, 138.12, 136.04, 130.19, 128.78, 126.76, 122.03, 117.75, 115.71, 22.09. GC-MS (EI) $[\text{M}]^+$: 216. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12}\text{OS}$ $[\text{M}]^+$: 216.0609; found 216.0618.

2-(4-chlorophenylthio)-5-methylphenol (3j) Colorless liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 9.88 (s, 1 H), 7.33-7.31 (d, $J = 8.5$ Hz, 2 H), 7.19-7.17 (d, $J = 7.8$ Hz, 1 H), 7.06-7.05 (d, $J = 8.5$ Hz, 2 H), 6.79 (s, 1 H), 6.68-6.66 (d, $J = 7.8$ Hz, 1 H), 2.25 (s, 3 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 158.81, 142.08, 137.64, 136.55, 131.15, 130.07, 129.90, 122.15, 117.92, 114.82, 22.13. GC-MS (EI) $[\text{M}]^+$: 250. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{11}\text{ClOS}$ $[\text{M}]^+$: 250.0219; found 250.0215.

2-(4-bromophenylthio)-5-methylphenol (3k) Colorless liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 9.90 (s, 1 H), 7.45-7.43 (d, $J = 8.3$ Hz, 2 H), 7.19-7.17 (d, $J = 7.8$ Hz, 1 H), 6.99-6.97 (d, $J = 8.3$ Hz, 2 H), 6.78 (s, 1 H), 6.68-6.67 (d, $J = 7.8$ Hz, 1 H), 2.25 (s, 3 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 158.87, 142.18, 138.29, 136.68, 132.93, 130.08, 122.17, 119.31, 117.93, 114.57, 22.15. GC-MS (EI) $[\text{M}]^+$: 294. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{11}\text{BrOS}$ $[\text{M}]^+$: 293.9714; found 293.9723.

2-(o-tolylthio)-5-methylphenol (3l) Pale yellow liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 9.76 (s, 1 H), 7.23-7.22 (d, $J = 6.9$ Hz, 1 H), 7.12-7.06 (m, 2 H), 6.95-6.93 (d, $J = 7.8$ Hz, 1 H), 6.86-6.84 (d, $J = 7.0$ Hz, 1 H), 6.76 (s, 1 H), 6.63-6.62 (d, $J = 7.8$ Hz, 1 H), 2.29 (s, 3 H), 2.24 (s, 3 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 158.10, 140.71, 137.58, 136.40, 134.76, 131.32, 129.61, 127.72, 127.17, 122.06, 117.63, 115.97, 22.03, 20.91. GC-MS (EI) $[\text{M}]^+$: 216. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{OS}$ $[\text{M}]^+$: 216.0609; found 216.0618.

2-(p-tolylthio)-5-methylphenol (3m) Pale yellow liquid; ^1H NMR (500 MHz, d^6 -DMSO): δ 9.75 (s, 1 H), 7.11-7.10 (d, $J = 8.1$ Hz, 2 H), 7.06-7.04 (d, $J = 8.1$ Hz, 2 H), 6.99-6.98 (d, $J = 8.3$ Hz, 1 H), 6.73 (s, 1 H), 6.61-6.59 (d, $J = 7.8$ Hz, 1 H), 2.25 (s, 3 H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, d^6 -DMSO): δ 157.76, 140.52, 136.77, 134.63, 133.71, 131.97, 131.33, 130.97, 130.26, 121.92, 117.55, 117.33, 22.04, 21.75. GC-MS (EI) $[\text{M}]^+$: 230. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{OS}$ $[\text{M}]^+$: 230.0765; found 230.0766.

2-(4-methoxyphenylthio)-5-methylphenol (3n) Yellow liquid; ^1H NMR (500 MHz, d^6 -DMSO): δ 9.75 (s, 1 H), 7.24-7.22 (d, $J = 8.6$ Hz, 2 H), 6.94-6.93 (d, $J = 8.6$ Hz, 2 H), 6.80-6.79 (d, $J = 7.8$ Hz, 1 H), 6.69 (s, 1 H), 6.57-6.55 (d, $J = 7.5$ Hz, 1 H), 3.76 (s, 3H), 2.19 (s, 3 H); ^{13}C NMR (125 MHz, d^6 -DMSO): δ 159.90, 156.48, 139.15, 134.17, 132.26, 126.12, 121.75, 119.80, 117.20, 116.17, 56.39, 21.91. GC-MS (EI) $[\text{M}]^+$: 246. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$ $[\text{M}]^+$: 246.0715; found 246.0715.

2-(2-(trifluoromethyl)phenylthio)-5-methylphenol (3o) Colorless liquid; ^1H NMR (500 MHz, d^6 -DMSO): δ 10.04 (s, 1 H), 7.72-7.70 (d, $J = 7.7$ Hz, 1 H), 7.48-7.45 (t, $J = 7.5$ Hz, 1 H), 7.32-7.29 (t, $J = 7.0$ Hz, 1 H), 7.22-7.20 (d, $J = 7.0$ Hz, 1 H), 6.90-6.88 (d, $J = 8.0$ Hz, 1 H), 6.82 (s, 1 H), 6.72-6.70 (d, $J = 7.7$ Hz, 1 H), 2.28(s, 3 H); ^{13}C NMR (125 MHz, d^6 -DMSO): δ 159.16, 142.69, 138.42, 137.20, 133.68, 129.42, 127.59, 126.32, 122.23, 117.85, 113.11. GC-MS (EI) $[\text{M}]^+$: 284. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{11}\text{F}_3\text{OS}$ $[\text{M}]^+$: 284.0483; found 284.0489.

2-(4-bromophenylthio)-4-methylphenol (3p) Colorless liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 9.75 (s, 1 H), 7.55-7.46 (d, J = 8.5 Hz, 2 H), 7.08-7.07 (d, J = 8.5 Hz, 2 H), 7.04-7.03 (d, J = 8.3 Hz, 2 H), 6.86-6.84 (d, J = 8.1 Hz, 1 H), 2.17 (s, 3 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 156.40, 137.56, 136.10, 133.01, 132.35, 130.81, 129.87, 119.70, 118.04, 117.12. GC-MS (EI) $[\text{M}]^+$: 294. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{11}\text{BrOS}$ $[\text{M}]^+$: 293.9714; found 293.9716.

2-(4-methoxyphenylthio)-4-methylphenol (3q) Yellow liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 9.61 (s, 1 H), 7.31-7.28 (t, J = 8.6 Hz, 2 H), 6.97-6.95 (d, J = 8.6 Hz, 2 H), 6.86-6.84 (d, J = 8.0 Hz, 1 H), 7.75-7.73 (d, J = 8.1 Hz, 1 H), 6.63 (s, 1 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 160.21, 153.83, 135.12, 131.34, 129.42, 125.14, 123.57, 116.28, 56.42, 21.28. GC-MS (EI) $[\text{M}]^+$: 246. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$ $[\text{M}]^+$: 246.0715; found 246.0718.

5-chloro-2-(phenylthio)phenol (3r) Colorless liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 10.52 (s, 1 H), 7.37-7.32 (d, J = 8.5 Hz, 2 H), 7.26-7.25 (d, J = 8.0 Hz, 1 H), 7.23-7.21 (m, 2 H), 7.09-7.07 (d, J = 8.5 Hz, 1 H), 6.96-6.95 (d, J = 2.0 Hz, 1 H), 6.87-6.84 (d, J = 8.1 Hz, 1 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 158.44, 135.86, 135.24, 134.35, 130.74, 130.52, 127.90, 120.96, 120.29, 116.59. GC-MS (EI) $[\text{M}]^+$: 236. HRMS (EI) calcd for $\text{C}_{12}\text{H}_9\text{ClOS}$ $[\text{M}]^+$: 236.0063; found 236.0066.

2-(4-chlorophenylthio)-5-chlorophenol (3s) Colorless liquid; ^1H NMR (500 MHz, d^6 -DMSO): δ 10.60 (s, 1 H), 7.75-7.73 (d, $J = 8.5$ Hz, 1 H), 7.53-7.44 (m, 3 H), 7.39-7.33 (m, 3 H), 6.96 (d, $J = 2.0$ Hz, 1 H), 6.90-6.88 (d, $J = 8.1$ Hz, 1 H); ^{13}C NMR (125 MHz, d^6 -DMSO): δ 158.92, 136.13, 135.53, 135.06, 133.68, 131.67, 130.83, 130.39, 121.07, 116.80. GC-MS (EI) $[\text{M}]^+$: 270. HRMS (EI) calcd for $\text{C}_{12}\text{H}_8\text{Cl}_2\text{OS}$ $[\text{M}]^+$: 269.9673; found 269.9676.

2-(4-bromophenylthio)-5-chlorophenol (3t) Colorless liquid; ^1H NMR (500 MHz, d^6 -DMSO): δ 10.52 (s, 1 H), 7.37-7.32 (d, $J = 8.5$ Hz, 2 H), 7.26-7.21 (m, 3 H), 7.09-7.07 (d, $J = 8.5$ Hz, 1 H), 6.96-6.95 (d, $J = 2.4$ Hz, 1 H), 6.87-6.84 (d, $J = 8.1$ Hz, 1 H); ^{13}C NMR (125 MHz, d^6 -DMSO): δ 158.44, 135.86, 135.24, 134.35, 130.74, 130.52, 127.90, 120.96, 120.29, 116.59. GC-MS (EI) $[\text{M}]^+$: 314. HRMS (EI) calcd for $\text{C}_{12}\text{H}_8\text{BrClOS}$ $[\text{M}]^+$: 313.9618; found 313.9621.

5-bromo-2-(phenylthio)phenol (3u) Colorless liquid; ^1H NMR (500 MHz, d^6 -DMSO): δ 10.51 (s, 1 H), 7.56-7.54 (d, $J = 8.5$ Hz, 1 H), 7.34-7.33 (d, $J = 8.0$ Hz, 2 H), 7.24-7.08 (m, 2 H), 6.98 (s, 1 H), 6.97 (s, 1 H), 7.00-6.98 (d, $J = 8.1$ Hz, 2 H), 6.88-6.85 (t, $J = 6.6$ Hz, 1 H); ^{13}C NMR (125 MHz, d^6 -DMSO): δ 158.40, 135.22, 133.54, 133.15, 132.65, 130.99, 130.95, 130.57, 128.04, 123.84, 119.38. GC-MS (EI) $[\text{M}]^+$: 280. HRMS (EI) calcd for $\text{C}_{12}\text{H}_9\text{BrOS}$ $[\text{M}]^+$: 279.9557; found 279.9560.

2-(p-tolylthio)-5-bromophenol (3v) Colorless liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 10.50 (s, 1 H), 7.21-7.17 (m, 4 H), 7.04 (s, 1 H), 6.93-6.92 (d, $J = 7.0$ Hz, 1 H), 6.81-6.80 (d, $J = 8.3$ Hz, 1 H), 2.29 (s, 3 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 157.41, 138.34, 133.33, 132.69, 131.38, 130.89, 123.71, 122.95, 121.39, 119.03, 21.83. GC-MS (EI) $[\text{M}]^+$: 294. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{11}\text{BrOS}$ $[\text{M}]^+$: 293.9714; found 293.9716.

2-(4-bromophenylthio)-5-bromophenol (3w) Colorless liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 10.60 (s, 1 H), 7.51-7.49 (m, 2 H), 7.12-7.10 (t, $J = 8.4$ Hz, 4 H), 7.02-7.00 (t, $J = 8.3$ Hz, 1 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 158.98, 136.37, 135.97, 133.30, 131.97, 124.00, 123.45, 120.65, 119.65, 119.51. GC-MS (EI) $[\text{M}]^+$: 358. HRMS (EI) calcd for $\text{C}_{12}\text{H}_8\text{Br}_2\text{OS}$ $[\text{M}]^+$: 357.8663; found 357.8668.

2-(4-chlorophenylthio)-5-bromophenol (3x) Colorless liquid; ^1H NMR (500 MHz, $\text{d}^6\text{-DMSO}$): δ 10.60 (s, 1 H), 7.39-7.38 (d, $J = 8.6$ Hz, 2 H), 7.20-7.18 (d, $J = 8.5$ Hz, 2 H), 7.10-7.08 (t, $J = 7.5$ Hz, 2 H), 7.02-7.00 (d, $J = 8.3$ Hz, 1 H); ^{13}C NMR (125 MHz, $\text{d}^6\text{-DMSO}$): δ 158.88, 136.16, 135.28, 132.41, 131.88, 130.44, 123.98, 123.32, 119.80, 119.61. GC-MS (EI) $[\text{M}]^+$: 314. HRMS (EI) calcd for $\text{C}_{12}\text{H}_8\text{BrClOS}$ $[\text{M}]^+$: 313.9618; found 313.9178.

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Spectrum

3a

3b

3c

3d

3e

3f

3g

3h

3i

3j

3k

31

3m

3n

30

3p

3q

3r

3s

3t

3u

3v

3w

3x

3a MS² (using DMSO as the solvent)

3a MS² (using ¹⁸O-DMSO as the solvent)

Proof of the OH is in thiophenol ring

¹H and ¹³C NMR Data of **3r**

Position	3r	
	δ H (mult, <i>J</i> in Hz)	δ C
1		120.3
2		158.4
3	6.96-6.95 (1 H, d, 2.2)	116.6
4		134.4
5	6.87-6.84 (1 H, dd, 8.5, 2.2)	121.0
6	7.09-7.07 (1 H, d, 8.5)	135.2
1'		135.9
2'	7.37-7.32 (2 H, dd, 8.5, 2.2)	130.5
3'	7.25-7.21 (2 H, dd, 8.5, 2.2)	130.7
4'	7.26-7.25 (1 H, dd, 8.5, 2.2)	127.9
OH	10.52 (1 H, s)	

¹H NMR spectra were measured at 500 MHz, ¹³C NMR spectra were run at 125 MHz.

¹H-¹H COSY spectrum of **3r**

HMQC spectrum of 3r

HMBC spectrum of 3r