

Supporting information for

Iodine-catalyzed Efficient 2-Arylsulfanylphenol Formation from Thiols and Cyclohexanones

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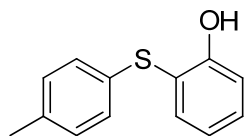
General information:

All reactions were carried out under an atmosphere of oxygen unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra was measured on Agilent 5975 GC-MS instrument (EI). Infrared spectra was measured on Nicolet 6700 FT-IR. High-resolution mass spectra were recorded at Institute of Chemistry, Chinese Academy of Sciences. The structure of known compounds were further corroborated by comparing their ^1H NMR, ^{13}C NMR data and MS data with those of literature. All reagents were obtained from commercial suppliers and used without further purification.

General procedure (3a):

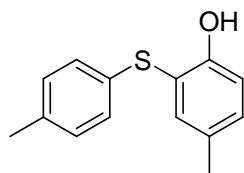
4-Methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and iodine (25.4 mg, 0.1 mmol) were added to a 25 mL oven-dried reaction vessel. The reaction vessel was purged with oxygen for three times and was added cyclohexanone (**1a**, 103.6 μL , 1.0 mmol) and NMP (2.0 mL) by syringe. The reaction vessel with an oxygen balloon was stirred at 160 $^\circ\text{C}$ for 20 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) to yield the desired product **3a** as pale yellow liquid (81 mg, 75% yield).

2-(*p*-Tolylthio)phenol (**3a**, CAS: 59010-83-2)^[1]



^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.51 (d, $J = 7.6$ Hz, 1H), 7.35 (t, $J = 6.8$ Hz, 1H), 7.06-7.00 (m, 5H), 6.93 (t, $J = 7.2$ Hz, 1H), 6.53 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 157.1, 136.6, 136.3, 132.1, 132.0, 130.0, 127.5, 121.2, 117.2, 115.4, 20.9; MS (EI) m/z (%) 216(100), 201, 183, 96, 91.

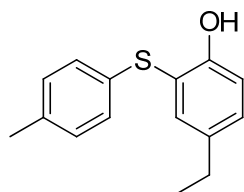
4-Methyl-2-(*p*-tolylthio)phenol (**3b**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4-methylcyclohexanone (**1b**, 122.5 μL , 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3b** as pale yellow liquid (80.5 mg, 70%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.32 (s, 1H), 7.14 (d, $J = 7.2$ Hz, 1H), 7.06-7.00 (m, 4H), 6.94 (d, $J = 8.0$ Hz, 1H), 6.35 (s, 1H), 2.28 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 154.8, 136.6, 136.1, 132.7, 132.3, 130.5, 129.9, 127.4, 116.6, 115.1, 20.9, 20.3; IR (neat, cm^{-1}) 3425, 3022, 2920, 2863, 1485, 1175; Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{OS}$: C, 73.01; H, 6.13; S, 13.92. found: C, 73.36; H, 6.29; S, 14.22. HRMS (ESI, m/z): calcd. for $\text{C}_{14}\text{H}_{13}\text{OS}$ $[\text{M}-\text{H}]^-$ 229.0682, found 229.0682.

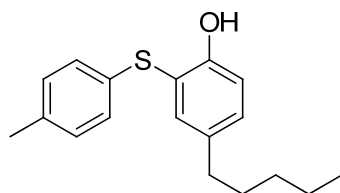
4-Ethyl-2-(*p*-tolylthio)phenol (**3c**)^[2]



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4-ethylcyclohexanone (**1c**, 141 μL , 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3c** as pale yellow liquid (87.8 mg, 72%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.34 (s, 1H), 7.18 (d, $J = 6.8$ Hz, 1H), 7.06-6.96 (m, 5H), 6.35 (s, 1H), 2.58 (q, $J = 7.6$ Hz, 2H), 2.28 (s, 3H), 1.20 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 155.1, 137.0, 136.1, 135.5, 132.4, 131.5, 130.0, 127.4, 116.7, 115.2, 27.8, 20.9, 15.6; MS (EI) m/z (%) 244(100), 229, 211, 124, 91.

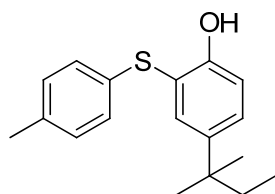
4-Pentyl-2-(*p*-tolylthio)phenol (**3d**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4-pentylcyclohexanone (**1d**, 190 μ L, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3d** as pale yellow liquid (107.3 mg, 75%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.32 (s, 1H), 7.16 (d, $J = 8.0$ Hz, 1H), 7.06-6.95 (m, 5H), 6.35 (s, 1H), 2.52 (t, $J = 7.6$ Hz, 2H), 2.28 (s, 3H), 1.61-1.59 (m, 2H), 1.33-1.30 (m, 4H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 155.1, 136.1, 136.1, 135.7, 132.5, 132.0, 130.0, 127.4, 116.6, 115.2, 34.8, 31.4, 31.2, 22.5, 20.9, 14.0; IR (neat, cm^{-1}) 3430, 3022, 2955, 2925, 2855, 1485, 1174; Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{OS}$: C, 75.48; H, 7.74; S, 11.19. found: C, 75.20; H, 7.96; S, 11.34. HRMS (ESI, m/z): calcd. for $\text{C}_{18}\text{H}_{21}\text{OS}$ $[\text{M}-\text{H}]^-$ 285.1308, found 285.1310.

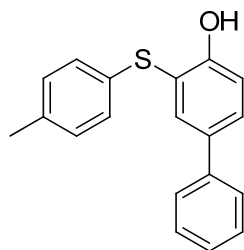
4-(*tert*-Pentyl)-2-(*p*-tolylthio)phenol (**3e**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4-(*tert*-pentyl)cyclohexanone (**1e**, 183 μ L, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3e** as pale yellow liquid (101.5 mg, 71%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.45 (s, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 7.05 (d, $J = 8.0$ Hz, 2H), 7.00-6.96 (m, 3H), 6.33 (s, 1H), 2.28 (s, 3H), 1.63-1.59 (m, 2H), 1.25 (s, 6H), 0.67 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 154.8, 142.4, 136.0, 134.2, 132.6, 129.9, 129.8, 127.0, 116.0, 114.9, 37.4, 36.9, 28.5, 20.8, 9.06; IR (neat, cm^{-1}) 3431, 2962, 2920, 2873, 1484, 1183; Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{OS}$: C, 75.48; H, 7.74; S, 11.19. found: C, 75.76; H, 7.92; S, 11.29. HRMS (ESI, m/z): calcd. for $\text{C}_{18}\text{H}_{21}\text{OS}$ $[\text{M}-\text{H}]^-$ 285.1308, found 285.1310.

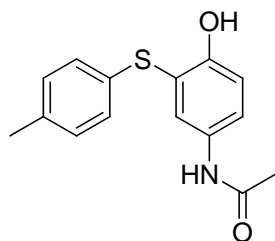
3-(*p*-Tolylthio)-[1,1'-biphenyl]-4-ol (**3f**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4-phenylcyclohexanone (**1f**, 174 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3f** as pale yellow liquid (116.8 mg, 80%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.78 (s, 1H), 7.60-7.53 (m, 3H), 7.41 (d, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.2$ Hz, 1H), 7.13-7.06 (m, 5H), 6.54 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 156.4, 139.8, 136.4, 134.9, 134.4, 131.9, 130.6, 130.0, 128.8, 127.6, 127.0, 126.6, 117.7, 115.8, 20.9; IR (neat, cm^{-1}) 3407, 3029, 2921, 2859, 1471, 1177; Anal. Calcd for $\text{C}_{19}\text{H}_{16}\text{OS}$: C, 78.05; H, 5.52; S, 10.97. found: C, 78.27; H, 5.70; S, 11.25. HRMS (ESI, m/z): calcd. for $\text{C}_{19}\text{H}_{15}\text{OS}$ $[\text{M}-\text{H}]^-$ 291.0838, found 291.0840.

N-(4-hydroxy-3-(*p*-tolylthio)phenyl)acetamide (**3g**)

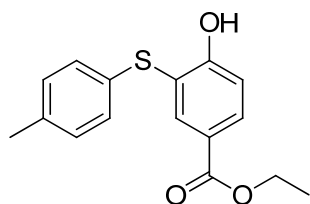


The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and *N*-(4-oxocyclohexyl)acetamide (**1g**, 155 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) afforded the product **3g** as pale yellow solid (80.6 mg, 62%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.61 (s, 1H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.16-6.99 (m, 6H), 6.41 (s, 1H), 2.28 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 168.7, 153.7, 136.6, 131.6, 131.2, 130.0, 128.1, 127.9, 124.4, 118.0, 115.5, 24.0, 20.8; IR (neat, cm^{-1}) 3286, 3192, 3073, 2920, 2858, 1656, 1486, 1178; Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{NS}$: C, 65.91; H, 5.53; N, 5.12; S, 11.73. found: C, 66.18; H, 5.76; N, 5.38; S, 12.01. HRMS (ESI, m/z): calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{NS}$

[M-H]⁻ 272.0740, found 272.0740.

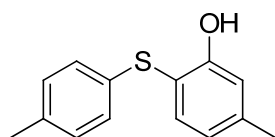
Ethyl 4-hydroxy-3-(*p*-tolylthio)benzoate (**3h**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and ethyl 4-oxocyclohexanecarboxylate (**1h**, 159.3 μ L, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded the product **3h** as white solid (87.8 mg, 61%).

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.26 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.08-7.02 (m, 5H), 6.93 (s, 1H), 4.34 (q, J = 7.0 Hz, 2H), 2.29 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 165.6, 160.7, 138.4, 136.8, 133.5, 131.2, 130.1, 128.0, 123.8, 118.0, 115.3, 60.9, 20.9, 14.3; IR (neat, cm⁻¹) 3361, 3038, 2978, 2932, 1681, 1257, 1172, 1012; Anal. Calcd for C₁₆H₁₆O₃S: C, 66.64; H, 5.59; S, 11.12. found: C, 66.39; H, 5.80; S, 11.49. HRMS (ESI, m/z): calcd. for C₁₆H₁₅O₃S [M-H]⁻ 287.0736, found 287.0739.

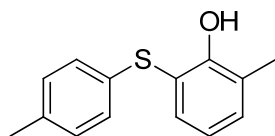
5-Methyl-2-(*p*-tolylthio)phenol (**3i**, CAS:1254831-65-6)^[1]



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 3-methylcyclohexanone (**1i**, 122.7 μ L, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1) afforded the product **3i** as pale yellow liquid (77.0 mg, 67%).

¹H NMR (400 MHz, CDCl₃, ppm) δ 7.39 (d, J = 7.6 Hz, 1H), 7.05-6.98 (m, 4H), 6.88 (s, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.46 (s, 1H), 2.35 (s, 3H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 157.0, 142.8, 136.4, 136.1, 132.7, 129.9, 127.2, 122.2, 116.0, 113.7, 21.5, 20.9; MS (EI) m/z (%) 230 (100), 215, 197, 110, 91.

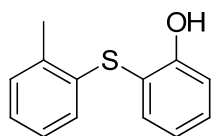
2-Methyl-6-(*p*-tolylthio)phenol (**3j**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 2-methylcyclohexanone (**1j**, 121.7 μL , 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 500:1) afforded the product **3j** as pale yellow liquid (46.0 mg, 40%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.36 (d, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 7.2$ Hz, 1H), 7.06-7.00 (m, 4H), 6.83 (t, $J = 7.6$ Hz, 1H), 6.65 (m, 1H), 2.29 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 157.0, 142.8, 136.4, 136.1, 132.7, 129.9, 127.2, 122.2, 116.0, 113.7, 21.5, 20.9; IR (neat, cm^{-1}) 3418, 3020, 2919, 2861, 1220, 1183; Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{OS}$: C, 73.01; H, 6.13; S, 13.92. found: C, 73.25; H, 6.35; S, 14.15. HRMS (ESI, m/z): calcd. for $\text{C}_{14}\text{H}_{13}\text{OS}$ [$\text{M}-\text{H}$] 229.0682, found 229.0681.

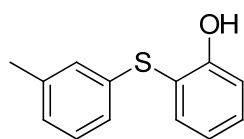
2-(*o*-Tolylthio)phenol (**3k**)^[1]



The reaction was conducted with 2-methylbenzenethiol (**2b**, 58.8 μL , 0.5 mmol) and cyclohexanone (**1a**, 103.6 μL , 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3k** as white liquid (64.8 mg, 60%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.48 (d, $J = 7.2$ Hz, 1H), 7.38 (t, $J = 7.4$ Hz, 1H), 7.17 (d, $J = 7.2$ Hz, 1H), 7.09-6.95 (m, 4H), 6.66 (d, $J = 7.2$ Hz, 1H), 6.40 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 157.3, 136.8, 135.5, 134.9, 134.9, 132.1, 130.3, 126.8, 125.8, 125.8, 121.4, 115.5, 20.0; MS (EI) m/z (%) 216 (100), 201, 122, 96, 91.

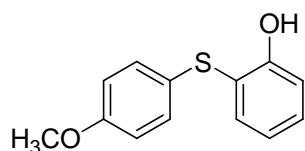
2-(*m*-Tolylthio)phenol (**3l**)



The reaction was conducted with 3-methylbenzenethiol (**2c**, 59.4 μL , 0.5 mmol) and

cyclohexanone (**1a**, 103.6 μL , 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3l** as white liquid (69.0 mg, 64%). ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.53 (d, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.14-7.06 (m, 2H), 6.97-6.86 (m, 4H), 6.52 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 157.2, 139.1, 136.8, 135.5, 132.2, 129.0, 127.6, 127.1, 124.0, 121.2, 116.5, 115.5, 21.3; IR (neat, cm^{-1}) 3419, 3055, 2920, 1592, 1573, 1469, 1185; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{OS}$: C, 72.19; H, 5.59; S, 14.82. found: C, 72.06; H, 5.62; S, 15.01. HRMS (ESI, m/z): calcd. for $\text{C}_{13}\text{H}_{11}\text{OS}$ $[\text{M}-\text{H}]^-$ 215.0525, found 215.0525.

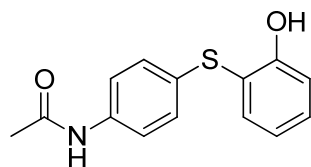
2-((4-Methoxyphenyl)thio)phenol (**3m**)^[1]



The reaction was conducted with 4-methoxybenzenethiol (**2d**, 61.4 μL , 0.5 mmol) and cyclohexanone (**1a**, 103.6 μL , 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded the product **3m** as pale yellow liquid (60.3 mg, 52%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.49 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.13 (d, $J = 8.8$ Hz, 2H), 7.03 (d, $J = 8.0$ Hz, 1H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.80 (d, $J = 8.4$ Hz, 2H), 6.56 (s, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 158.8, 156.7, 136.1, 131.6, 130.1, 126.0, 121.1, 118.5, 115.4, 114.9, 55.3; MS (EI) m/z (%) 232 (100), 217, 171, 108, 96.

N-4-((2-hydroxyphenyl)thio)phenylacetamide (**3n**)

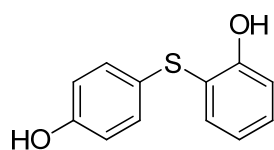


The reaction was conducted with *N*-(4-mercaptophenyl)acetamide (**2e**, 78.5 mg, 0.5 mmol) and cyclohexanone (**1a**, 103.6 μL , 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) afforded the product **3n** as pale yellow solid (93.3 mg, 72%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.50 (d, $J = 7.6$ Hz, 1H), 7.39-7.34 (m, 3H), 7.08-7.04 (m,

3H), 6.94 (t, $J = 7.4$ Hz, 1H), 6.54 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 168.7, 157.0, 136.5, 136.4, 131.9, 130.8, 128.4, 121.2, 120.9, 117.3, 115.6, 24.3; IR (neat, cm^{-1}) 3245, 3174, 2929, 2873, 1652, 1492, 1155; Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{O}_2\text{NS}$: C, 64.84; H, 5.05; N, 5.40; S, 12.36. found: C, 65.05; H, 5.15; S, 12.68. HRMS (ESI, m/z): calcd. for $\text{C}_{14}\text{H}_{12}\text{O}_2\text{NS}$ $[\text{M}-\text{H}]^-$ 258.0583, found 258.0584.

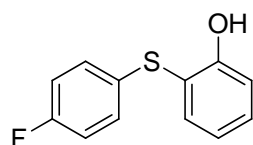
2-((4-Hydroxyphenyl)thio)phenol (**3o**, CAS: 17755-37-2)^[3]



The reaction was conducted with 4-mercaptophenol (**2f**, 63 mg, 0.5 mmol) and cyclohexanone (**1a**, 103.6 μL , 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) afforded the product **3o** as white solid (88.3 mg, 81%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.49 (d, $J = 7.6$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 1H), 7.09-7.02 (m, 3H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.73 (t, $J = 8.4$ Hz, 2H), 6.56 (s, 1H), 5.02 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 156.5, 154.8, 136.0, 131.6, 130.4, 126.1, 121.2, 118.6, 116.4, 115.4; MS (EI) m/z (%) 218 (100), 185, 157, 125, 94.

2-((4-Fluorophenyl)thio)phenol (**3p**)

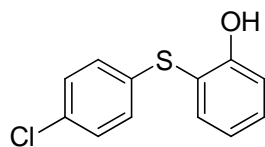


The reaction was conducted with 4-fluorobenzenethiol (**2g**, 53.3 μL , 0.5 mmol) and cyclohexanone (**1a**, 103.6 μL , 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3p** as pale yellow liquid (77.0 mg, 70%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.52 (d, $J = 8.0$ Hz, 1H), 7.37 (t, $J = 7.8$ Hz, 1H), 7.12-7.05 (m, 3H), 6.97-6.93 (m, 3H), 6.49 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 159.9 (d, $J = 244.8$ Hz), 157.0, 136.6, 132.3, 130.8 (d, $J = 3.2$ Hz), 129.2 (d, $J = 8.0$ Hz), 121.4, 117.0, 116.3 (d, $J = 22.1$ Hz), 115.6; IR (neat, cm^{-1}) 3414, 3067, 1588, 1487, 1224, 1155; Anal. Calcd for $\text{C}_{12}\text{H}_9\text{OF}_\text{S}$:

C, 65.43; H, 4.12; S, 14.56. found: C, 65.27; H, 4.28; S, 14.80. HRMS (ESI, m/z): calcd. for $C_{12}H_8OFS$ $[M-H]^-$ 219.0274, found 219.0273.

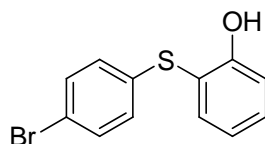
2-((4-Chlorophenyl)thio)phenol (3q, CAS: 59010-71-8)^[1]



The reaction was conducted with 4-chlorobenzenethiol (**2h**, 72.3 mg, 0.5 mmol) and cyclohexanone (**1a**, 103.6 μ L, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3q** as pale yellow liquid (73.3 mg, 62%).

1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.8$ Hz, 1H), 7.20 (t, $J = 6.8$ Hz, 2H), 7.09-6.95 (m, 4H), 6.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.2, 136.8, 134.5, 132.5, 132.2, 129.3, 128.2, 121.4, 116.1, 115.8; MS (EI) m/z (%) 236 (100), 220, 200, 168, 96.

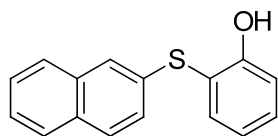
2-((4-Bromophenyl)thio)phenol (3r, CAS: 1254831-59-8)^[1]



The reaction was conducted with 4-bromobenzenethiol (**2i**, 94.5 mg, 0.5 mmol) and cyclohexanone (**1a**, 103.6 μ L, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3r** as pale yellow liquid (99.4 mg, 71%).

1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, $J = 7.6$ Hz, 1H), 7.41-7.34 (m, 3H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.98-6.93 (m, 3H), 6.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.1, 136.8, 135.1, 132.5, 132.2, 130.5, 128.3, 121.4, 119.9, 115.7; MS (EI) m/z (%) 282, 280, 201, 168, 96 (100).

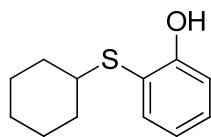
2-(Naphthalen-2-ylthio)phenol (3s)



The reaction was conducted with naphthalene-2-thiol (**2j**, 80.0 mg, 0.5 mmol) and cyclohexanone (**1a**, 103.6 μ L, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3s** as pale yellow liquid (76.9 mg, 61%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.76-7.57 (m, 4H), 7.49-7.39 (m, 4H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 6.98 (t, $J = 7.4$ Hz, 1H), 6.54 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 157.3, 136.8, 133.7, 133.2, 133.2, 131.9, 128.9, 127.7, 127.1, 126.7, 125.8, 125.3, 125.2, 121.3, 116.5, 115.7; IR (neat, cm^{-1}) 3417, 3052, 1623, 1573, 1468, 1186; Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{OS}$: C, 76.16; H, 4.79; S, 12.71. found: C, 76.46; H, 5.10; S, 13.09. HRMS (ESI, m/z): calcd. for $\text{C}_{16}\text{H}_{11}\text{OS}$ [$\text{M}-\text{H}$] $^-$ 251.0525, found 251.0527.

2-(Cyclohexylthio)phenol (**3t**, CAS: 56484-57-2)^[4]



The reaction was conducted with cyclohexanethiol (**2k**, 61.2 μ L, 0.5 mmol) and cyclohexanone (**1a**, 103.6 μ L, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3t** as pale yellow liquid (52.0 mg, 50%).

^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.44 (d, $J = 7.6$ Hz, 1H), 7.29-7.25 (m, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.88-6.84 (m, 2H), 2.81 (m, 1H), 1.94-1.91 (m, 2H), 1.76-1.74 (m, 2H), 1.38-1.17 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 157.5, 136.9, 131.1, 120.4, 117.7, 114.5, 48.7, 33.6, 26.1, 25.5; MS (EI) m/z (%) 208, 137, 126 (100), 97, 83.

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Copies of ^1H and ^{13}C NMR spectra of all products

