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). $^1$H 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 $^1$H 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 °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)$^{[1]}$

![Chemical structure](image)

$^1$H 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%).

\[ \text{1H NMR (400 MHz, CDCl}_3, \text{ ppm) } \delta 7.32 \text{ (s, 1H), 7.14 (d, } J = 7.2 \text{ Hz, 1H), 7.06-7.00 (m, 4H), 6.94 (d, } J = 8.0 \text{ Hz, 1H), 6.35 \text{ (s, 1H), 2.28 (s, 3H), 2.27 (s, 3H); 13C NMR (100 MHz, CDCl}_3, \text{ ppm) } \delta 154.8, 136.6, 136.1, 132.7, 132.3, 130.5, 129.9, 127.4, 116.6, 115.1, 20.9, 20.3; \text{ IR (neat, cm}^{-1} \text{) 3425, 3022, 2920, 2863, 1485, 1175; Anal. Calcd for C}_{14}\text{H}_{14}\text{OS: C, 73.01; H, 6.13; S, 13.92. found: C, 73.36; H, 6.29; S, 14.22. HRMS (ESI, m/z): calcd. for C}_{14}\text{H}_{13}\text{OS [M-H]}^\text{-} 229.0682, \text{ found 229.0682.} \]

4-Ethyl-2-((p-tolylthio)phenol (3c)

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%).

\[ \text{1H NMR (400 MHz, CDCl}_3, \text{ ppm) } \delta 7.34 \text{ (s, 1H), 7.18 (d, } J = 6.8 \text{ Hz, 1H), 7.06-6.96 (m, 5H), 6.35 \text{ (s, 1H), 2.58 (q, } J = 7.6 \text{ Hz, 2H) 2.28 (s, 3H), 1.20 (t, } J = 7.4 \text{ Hz, 3H); 13C NMR (100 MHz, CDCl}_3, \text{ ppm) } \delta 155.1, 137.0, 136.1, 135.5, 132.4, 131.5, 130.0, 127.4, 116.7, 115.2, 27.8, 20.9, 15.6; \text{ MS (EI) m/z (%) 244(100), 229, 211, 124, 91.} \]

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 μL, 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%).

\[ \text{The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product 3d as pale yellow liquid (107.3 mg, 75%).} \]

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

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

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

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

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

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

\[ \text{H NMR (400 MHz, CDCl} \text{3, ppm) } \delta 7.32 \text{ (s, 1H), 7.16 (d, } J = 8.0 \text{ Hz, 1H), 7.06-6.95 (m, 5H), 6.35 \text{ (s, 1H), 2.52 (t, } J = 7.6 \text{ Hz, 2H), 2.28 (s, 3H), 1.61-1.59 (m, 2H), 1.33-1.30 (m, 4H), 0.88 (t, } J = 6.6 \text{ Hz, 3H); } ^{13}\text{C NMR (100 MHz, CDCl} \text{3, ppm) } \delta 155.1, 136.1, 136.1, 135.7, 132.5, 132.0, 130.0, 127.4, 116.6, 115.2, 34.8, 31.4, 31.2, 22.5, 20.9, 14.0; \text{ IR (neat, cm}^{-1}) 3430, 3022, 2955, 2925, 2855, 1485, 1174; \text{ Anal. Calcd for C}_{18}\text{H}_{22}\text{OS: C, 75.48; H, 7.74; S, 11.19. found: C, 75.76; H, 7.92; S, 11.29. HRMS (ESI, m/z): calcd. for C}_{18}\text{H}_{21}\text{OS } [\text{M-H}^-] 285.1308, \text{ found 285.1310.} \]
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%).

\[
\begin{align*}
1^1\text{H NMR (400 MHz, CDCl}_3, \text{ppm) } & \delta 7.78 (s, 1H), 7.60-7.53 (m, 3H), 7.41 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.13-7.06 (m, 5H), 6.54 (s, 1H), 2.28 (s, 3H); \\
1^3\text{C NMR (100 MHz, CDCl}_3, \text{ppm) } & \delta 156.4, 139.8, 136.4, 134.9, 134.4, 131.9, 130.6, 130.0, 128.8, 127.6, 127.0, 126.6, 117.7, 115.8, 20.9; \\
\text{IR (neat, cm}^{-1}) & \text{ 3407, 3029, 2921, 2859, 1471, 1177;} \\
\text{Anal. Calcd for C}_{19}\text{H}_{15}\text{OS: } & \text{C, 78.5; H, 5.52; S, 10.97. found: C, 78.27; H, 5.70; S, 11.25. HRMS (ESI, m/z): calcd. for C}_{19}\text{H}_{15}\text{OS [M-H]}' 291.0838, \text{found 291.0840.}
\end{align*}
\]

\[\text{N-(4-hydroxy-3-(p-tolylthio)phenyl)acetamide (3g)}\]

\[
\begin{align*}
\text{The reaction was conducted with 4-methylbenzenethiol (2a, 62 mg, 0.5 mmol) and N-(4-oxocyclohexyl)acetamide (1g, 155 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) afforded the product 3g as pale yellow solid (80.6 mg, 62%).} \\
\text{1^1\text{H NMR (400 MHz, CDCl}_3, \text{ppm) } & \delta 7.61 (s, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.16-6.99 (m, 6H), 6.41 (s, 1H), 2.28 (s, 3H), 2.14 (s, 3H); \\
\text{1^3\text{C NMR (100 MHz, CDCl}_3, \text{ppm) } & \delta 168.7, 153.7, 136.6, 131.6, 131.2, 130.0, 128.1, 127.9, 124.4, 118.0, 115.5, 24.0, 20.8; \\
\text{IR (neat, cm}^{-1}) & \text{ 3286, 3192, 3073, 2920, 2858, 1656, 1486, 1178;} \\
\text{Anal. Calcd for C}_{15}\text{H}_{15}\text{O}_2\text{NS: } & \text{C, 65.91; H, 5.53; N, 5.12; S, 11.73. found: C, 66.18; H, 5.76; N, 5.38; S, 12.01. HRMS (ESI, m/z): calcd. for C}_{15}\text{H}_{14}\text{O}_2\text{NS}
\end{align*}
\]
[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 μL, 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%).

$^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 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); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 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, 1261, 1272, 1112; Anal. Calcd for C$_{16}$H$_{15}$O$_3$S: 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 C$_{16}$H$_{15}$O$_3$S [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 μL, 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%).

$^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 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); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 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%).

$^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 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) $\delta$ 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 C$_{14}$H$_{14}$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 C$_{14}$H$_{13}$OS [M-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%).

$^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 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) $\delta$ 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%). 

\(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 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) \(\delta\) 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 C\(_{13}\)H\(_{12}\)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 C\(_{13}\)H\(_{11}\)OS [M-H]\(^{-}\) 215.0525, found 215.0525.

2-((4-Methoxyphenyl)thio)phenol (3m)\(^{[1]}\)

\[
\text{H}_{3}\text{CO} \quad \begin{array}{c}
\text{S} \\
\text{OH}
\end{array}
\]

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%). 

\(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 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) \(\delta\) 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)phenyl)acetamide (3n)

\[
\text{O} \quad \begin{array}{c}
\text{N} \\
\text{H}
\end{array}
\]

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%). 

\(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 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); ¹³C NMR (100 MHz, CDCl₃, 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 C₁₄H₁₃O₂NS: 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 C₁₄H₁₂O₂NS [M-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, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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 C₁₂H₉OF$:
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\textsubscript{12}H\textsubscript{8}OFS [M-H]- 219.0274, found 219.0273.

2-((4-Chlorophenyl)thio)phenol (3q, CAS: 59010-71-8)\textsuperscript{[1]}

![2-((4-Chlorophenyl)thio)phenol](image)

The reaction was conducted with 4-chlorobenzenethiol (2h, 72.3 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 = 100:1) afforded the product 3q as pale yellow liquid (73.3 mg, 62%).

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}, ppm) \(\delta\) 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); \(^1^3\)C NMR (100 MHz, CDCl\textsubscript{3}, ppm) \(\delta\) 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)\textsuperscript{[1]}

![2-((4-Bromophenyl)thio)phenol](image)

The reaction was conducted with 4-bromobenzenethiol (2i, 94.5 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 = 100:1) afforded the product 3r as pale yellow liquid (99.4 mg, 71%).

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}, ppm) \(\delta\) 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); \(^1^3\)C NMR (100 MHz, CDCl\textsubscript{3}, ppm) \(\delta\) 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 μL, 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%).

\[ \text{1H NMR (400 MHz, CDCl}_3, \text{ ppm) } \delta \text{ 7.76-7.57 (m, 4H), 7.49-7.39 (m, 4H), 7.22 (d, } J = 8.4 \text{ Hz, 1H), 7.10 (d, } J = 8.0 \text{ Hz, 1H), 6.98 (t, } J = 7.4 \text{ Hz, 1H), 6.54 (s, 1H); }^{13}\text{C NMR (100 MHz, CDCl}_3, \text{ ppm) } \delta \text{ 157.3, 136.8, 133.7, 133.2, 133.2, 131.9, 128.9, 127.7, 127.1, 126.7, 125.8, 125.3, 125.2, 121.3, 116.5, 115.7; } \text{IR (neat, cm}^{-1}) \text{ 3417, 3052, 1623, 1573, 1468, 1186; Anal. Calcd for } C_{16}H_{13}OS: \text{ C, 76.16; H, 4.79; S, 12.71. found: C, 76.46; H, 5.10; S, 13.09. HRMS (ESI, m/z): calcd. for } C_{16}H_{12}OS [M-H]^- 251.0525, \text{ found 251.0527.} \]

2-(Cyclohexylthio)phenol (3t, CAS: 56484-57-2)

The reaction was conducted with cyclohexanethiol (2k, 61.2 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 3t as pale yellow liquid (52.0 mg, 50%).

\[ \text{1H NMR (400 MHz, CDCl}_3, \text{ ppm) } \delta \text{ 7.44 (d, } J = 7.6 \text{ Hz, 1H), 7.29-7.25 (m, 1H), 6.99 (d, } J = 8.0 \text{ Hz, 1H), 6.88-6.84 (m, 2H), 2.81 (m, 1H), 1.94-1.91 (m, 2H), 1.76-1.74 (m, 2H), 1.38-1.17 (m, 6H); }^{13}\text{C NMR (100 MHz, CDCl}_3, \text{ ppm) } \delta \text{ 157.5, 136.9, 131.1, 120.4, 117.7, 114.5, 48.7, 33.6, 26.1, 25.5; MS (EI) m/z (\%) 208, 137, 126 (100), 97, 83.} \]
References


Copies of $^1$H and $^{13}$C NMR spectra of all products
3p

3p