Supporting information for

Iodine-promoted 2-arylsulfanylphenol formation using
cyclohexanones as phenol source

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**General information**

Flash column chromatography was performed over silica gel 48-75 μm. Unless otherwise noted, 1H NMR and 13C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to SiMe₄ or chloroform signals. MS analyses were performed on Agilent 5975 GC-MS instrument (EI). The new compounds were characterized by 1H NMR, 13C NMR, MS and HRMS. The structure of known compounds were further corroborated by comparing their ¹H NMR, ¹³C NMR data and MS data with those of literature. Reagents were used as received or prepared by our laboratory.

**General procedure for 3aa:**

The reaction mixture of cyclohexanone (1a, 52 μL, 0.5 mmol), p-toluenesulfonyl chloride (2a, 114 mg, 0.6 mmol), iodine (25.4 mg, 0.1 mmol) and 1,4-dioxane (1 mL) in a 10 mL oven-dried reaction vessel was stirred at 150 °C for 18 h under an air atmosphere. 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 = 95:5) to yield the desired product 3aa as pale yellow liquid (88.6 mg, 82% yield).

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

\[
\text{OH} \quad \text{S} \quad \text{Ar}
\]

¹H NMR (400 MHz, CDCl₃, ppm) δ 7.52 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.06-7.00 (m, 5H), 6.93 (t, J = 6.0 Hz, 1H), 6.53 (s, 1H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 157.1, 136.7, 136.3, 132.2, 132.1, 130.0, 127.5, 121.2, 117.2, 115.5, 21.0; MS (EI) m/z (%) 216 (100), 201, 183, 96, 91.

**4-Methyl-2-(p-tolylthio)phenol (3ba):[1]**

\[
\text{OH} \quad \text{S} \quad \text{Ar} \quad \text{Me}
\]

Pale yellow liquid; yield 80%; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.33 (s, 1H), 7.16 (d, J = 8.0
Hz, 1H), 7.06-7.01 (m, 4H), 6.95 (d, J = 8.0 Hz, 1H), 6.36 (s, 1H), 2.28 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 155.0, 136.7, 136.2, 132.8, 132.5, 130.5, 130.1, 127.6, 116.8, 115.3, 21.0, 20.4; MS (EI) m/z (%) 230 (100), 197, 110, 91, 77, 65.

4-Ethyl-2-(p-tolylthio)phenol (3ca):$^{[1]}$

Pale yellow liquid; yield 70%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.35 (s, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.06-6.97 (m, 5H), 6.36 (s, 1H), 2.58 (q, J = 8.0 Hz, 2H ) 2.28 (s, 3H), 1.21 (t, J = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 155.2, 137.1, 136.2, 135.6, 132.5, 131.6, 130.0, 127.5, 116.8, 115.4, 27.9, 21.0, 15.8; MS (EI) m/z (%) 244 (100), 229, 211, 124, 91, 77.

4-(iso-Propyl)-2-(p-tolylthio)phenol (3da):

Pale yellow liquid; yield 72%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.37 (s, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.06-6.97 (m, 5H), 6.35 (s, 1H), 2.88-2.82 (m, 1H ) 2.28 (s, 3H), 1.22 (d, J = 8.0 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 155.2, 141.8, 136.1, 134.4, 132.5, 130.3, 130.1, 127.3, 116.5, 115.3, 33.3, 24.2, 21.0; MS (EI) m/z (%) 258, 243 (100), 151, 123, 91, 79; HRMS calcd. for: C$_{16}$H$_{17}$OS [M-H]: 257.0995, found 257.0999.

4-Pentyl-2-(p-tolylthio)phenol (3ea):$^{[1]}$

Pale yellow liquid; yield 78%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.32 (s, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.06-6.96 (m, 5H), 6.36 (s, 1H), 2.53 (t, J = 8.0 Hz, 2H ), 2.28 (s, 3H), 1.61-1.57 (m, 2H),
1.33-1.27 (m, 4H), 0.88 (t, \( J = 6.0 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \( \delta \) 155.2, 136.2, 136.1, 135.8, 132.6, 132.1, 130.0, 127.4, 116.6, 115.3, 34.9, 31.4, 31.3, 22.6, 21.0, 14.0; MS (EI) m/z (%) 286, 229 (100), 137, 91, 77, 65.

4-(\textit{tert}-Pentyl)-2-(\textit{p}-tolylthio)phenol (3fa):

![Chemical Structure](image)

Pale yellow liquid; yield 78%; \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \( \delta \) 7.46 (s, 1H), 7.33 (d, \( J = 8.0 \) Hz, 1H), 7.05 (d, \( J = 8.0 \) Hz, 2H), 6.98 (t, \( J = 8.0 \) Hz, 3H), 6.34 (s, 1H), 2.28 (s, 3H), 1.63-1.59 (m, 2H), 1.25 (s, 6H), 0.67 (t, \( J = 6.0 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \( \delta \) 154.8, 142.4, 136.0, 134.3, 132.6, 130.0, 129.9, 126.9, 115.9, 114.9, 37.5, 37.0, 28.6, 20.9, 9.2; MS (EI) m/z (%) 286, 257 (100), 134, 91, 77, 65.

3-(\textit{p}-Tolylthio)-[1,1'-biphenyl]-4-ol (3ga):

![Chemical Structure](image)

Pale yellow solid; yield 87%; mp 56-58 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \( \delta \) 7.78 (s, 1H), 7.61-7.53 (m, 3H), 7.41 (d, \( J = 8.0 \) Hz, 2H), 7.31 (t, \( J = 8.0 \) Hz, 1H), 7.14-7.06 (m, 5H), 6.55 (s, 1H), 2.28 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \( \delta \) 156.7, 140.0, 136.5, 135.1, 134.6, 132.2, 130.8, 130.2, 129.0, 127.8, 127.2, 126.8, 118.0 116.0, 21.1; MS (EI) m/z (%) 292 (100), 172, 139, 91, 77, 65.

3-(\textit{p}-Tolylthio)-[1,1'-biphenyl]-4,4'-diol (3ha):

![Chemical Structure](image)
White solid; yield 84%; mp 119-121 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 7.71-7.70 (m, 1H), 7.54-7.52 (m, 1H), 7.41 (d, \(J = 8.0\) Hz, 2H), 7.11-7.06 (m, 5H), 6.87 (d, \(J = 8.0\) Hz, 2H), 6.50 (s, 6H), 4.81 (s, 1H), 4.28 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\), ppm) \(\delta\) 157.0, 155.5, 136.8, 132.8, 132.0, 131.0, 130.8, 130.4, 130.2, 127.5, 127.1, 121.5, 116.5, 116.2, 21.1; MS (EI) m/z (%) 308(100), 281, 207, 188, 91, 28; HRMS calcd. for: C\(_{19}\)H\(_{15}\)O\(_2\)S [M-H]: 307.0787, found 307.0791.

**Ethyl 4-hydroxy-3-(\(p\)-tolylthio)benzoate (3ia):**[^1^]

![Chemical Structure](image1)

Pale yellow solid; yield 75%; mp 72-74 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 8.27 (s, 1H), 8.05 (d, \(J = 8.0\) Hz, 1H), 7.09-7.03 (m, 5H), 6.95 (s, 1H), 4.34 (q, \(J = 6.7\) Hz, 2H), 2.29 (s, 3H), 1.38 (t, \(J = 6.0\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\) 165.7, 160.8, 138.4, 136.8, 133.5, 131.3, 130.2, 128.1, 123.7, 118.2, 115.4, 61.0, 21.0, 14.4; MS (EI) m/z (%) 288 (100), 260, 243, 171, 91, 63.

**2-(Phenylthio)phenol (3ab, CAS: 55214-86-3):**[^2^]

![Chemical Structure](image2)

Pale yellow liquid; yield 65%; \(^1^H\) NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 7.54 (d, \(J = 8.0\) Hz, 1H), 7.38 (t, \(J = 8.0\) Hz, 1H), 7.24-7.22 (m, 2H), 7.17-7.13 (m, 1H), 7.09-7.07 (m, 3H) 6.96 (t, \(J = 8.0\) Hz, 1H), 6.52 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\) 157.3, 136.9, 135.9, 132.3, 129.2, 127.0, 126.2, 121.3, 116.5, 115.6; MS (EI) m/z (%) 202 (100), 169, 141, 96, 77, 51.

**2-((4-Ethylphenyl)thio)phenol (3ac):**

![Chemical Structure](image3)

Pale yellow liquid; yield 83%; \(^1^H\) NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 7.52 (d, \(J = 8.0\) Hz, 1H), 7.36
(t, J = 8.0 Hz, 1H), 7.08-7.02 (m, 5H), 6.94 (t, J = 8.0 Hz, 1H), 6.55 (s, 1H); 2.61-2.55 (m, 2H), 1.18 (d, J = 8.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 157.2, 142.7, 136.7, 132.4, 132.0, 128.8, 127.6, 121.1, 117.3, 115.5, 28.3, 15.4; MS (EI) m/z (%) 230 (100), 215, 105, 91, 77, 63; HRMS calcd. for: C$_{14}$H$_{13}$OS [M-H]$^-$: 229.0682, found 229.0686.

2-((4-(tert-Butyl)phenyl)thio)phenol (3ad, CAS: 2976-28-5):$^{[3]}$

Pale yellow liquid; yield 85%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.53 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.28-7.26 (m, 2H), 7.08-7.03 (m, 3H), 6.95 (t, J = 8.0 Hz, 1H), 6.55 (s, 1H), 1.27 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 157.3, 149.5, 136.9, 132.3, 132.2, 127.0, 126.4, 121.3, 116.9, 115.6, 34.5, 31.3; MS (EI) m/z (%) 258, 243(100), 125, 108, 97, 77.

2-((4-Methoxyphenyl)thio)phenol (3ae):$^{[1]}$

Pale yellow solid; yield 64%; mp 62-64°C; $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.50 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 1H), 6.91 (t, J = 8.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 2H), 6.57 (s, 1H), 3.76 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 159.0, 156.8, 136.1, 131.6, 130.3, 126.2, 121.2, 118.8, 115.5, 115.1, 55.4; MS (EI) m/z (%) 232 (100), 217, 171, 108, 96.

2-((4-Fluorophenyl)thio)phenol (3af):$^{[1]}$

Pale yellow liquid; yield 80%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.51 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.11-7.06 (m, 3H), 6.97-6.93 (m, 3H), 6.49 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 161.7 (d, J = 243.0 Hz), 157.1, 136.6, 132.3, 130.9 (d, J = 3.0 Hz), 129.3 (d, J =
8.0 Hz), 121.4, 117.1, 116.4 (d, $J = 22.0$ Hz), 115.7; MS (EI) $m/z$ (%) 220, 128, 96 (100), 75, 61.

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

![Structural formula of 2-((4-Bromophenyl)thio)phenol (3ag)]

Pale yellow liquid; yield 70%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.51 (d, $J = 8.0$ Hz, 1H), 7.42-7.34 (m, 3H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.99-6.92 (m, 3H), 6.42 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 157.3, 136.9, 135.2, 132.7, 132.3, 128.4, 121.6, 120.0, 115.8, 115.8; MS (EI) $m/z$ (%) 282, 280, 201, 168, 96 (100).

2-((4-(Trifluoromethoxy)phenyl)thio)phenol (3ah):

![Structural formula of 2-((4-(Trifluoromethoxy)phenyl)thio)phenol (3ah)]

Pale yellow liquid; yield 66%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.53 (d, $J = 8.0$ Hz, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.10-7.08 (m, 5H), 6.98 (d, $J = 8.0$ Hz, 1H), 6.45 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$, ppm) $\delta$ 157.3, 147.6, 136.9, 134.7, 132.7, 128.0, 121.9, 121.6, 120.4 (q, $J = 256.0$ Hz), 115.8, 115.7; MS (EI) $m/z$ (%) 286 (100), 201, 171, 128, 96; HRMS calcd. for: C$_{13}$H$_8$O$_2$F$_3$S [M-H]$^-$: 285.0192, found 285.0195.

2-((4-(Trifluoromethyl)phenyl)thio)phenol (3ai):

![Structural formula of 2-((4-(Trifluoromethyl)phenyl)thio)phenol (3ai)]

Pale yellow liquid; yield 46%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.53 (d, $J = 8.0$ Hz, 1H), 7.48-7.43 (m, 3H), 7.12 (d, $J = 8.0$ Hz, 3H), 7.01 (t, $J = 8.0$ Hz, 1H), 6.37 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$, ppm) $\delta$ 157.4, 141.2, 137.1, 133.0, 128.1 (q, $J = 32.0$ Hz), 126.1, 126.0 (q, $J = 3.7$ Hz), 124.0 (q, $J = 270.0$ Hz), 121.7, 116.0, 114.5; MS (EI) $m/z$ (%) 270 (100), 251, 171, 96, 69; HRMS calcd. for: C$_{13}$H$_8$OF$_3$S [M-H]$^-$: 269.0243, found 269.0247.
2-((4-Nitrophenyl)thio)phenol (3aj):[4]

Yellow solid; yield 36%; mp 99-101 °C; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 8.09 (d, $J$ = 8.0 Hz, 2H), 7.54-7.46 (m, 2H), 7.15-7.11 (m, 3H), 7.04 (t, $J$ = 8.0 Hz, 1H), 6.25 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 157.5, 145.9, 137.1, 133.4, 126.5, 126.0, 124.4, 124.2, 121.9, 116.3; MS (EI) $m/z$ (%) 247 (100), 230, 200, 171, 97.

4-((2-Hydroxyphenyl)thio)benzonitrile (3ak):[5]

Pale yellow solid; yield 42%; mp 82-84 °C; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.52-7.44 (m, 4H), 7.13-7.07 (m, 3H), 7.02 (t, $J$ = 8.0 Hz, 1H), 6.29 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 157.5, 143.5, 137.1, 133.3, 132.8, 132.6, 126.7, 126.3, 121.8, 118.5, 116.2; MS (EI) $m/z$ (%) 227 (100), 198, 166, 96, 63.

2-(Mesitylthio)phenol (3al):

Pale yellow solid; yield 75%; mp 61-63 °C; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.08 (t, $J$ = 8.0 Hz, 1H), 6.96 (s, 2H), 6.90 (d, $J$ = 8.0 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 6.74 (t, $J$ = 6.0 Hz, 1H), 5.84 (s, 1H), 2.39 (s, 6H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 154.1, 142.9, 139.1, 129.9, 129.7, 127.9, 122.2, 121.4, 115.4, 110.0, 21.9, 21.1; MS (EI) $m/z$ (%) 244, 150, 120 (100), 105, 91, 77; HRMS calcd. for: C$_{15}$H$_{15}$OS [M-H]: 243.0838, found 243.0842.

2-(Naphthalen-1-ylthio)phenol (3am):


Pale yellow solid; yield 73%; mp 87-89°C; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 8.35 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.63-7.54 (m, 3H), 7.41 (t, $J = 6.0$ Hz, 1H), 7.30-7.28 (m, 1H), 7.11 (d, $J = 8.0$ Hz, 1H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 6.46 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 157.4, 136.9, 134.1, 133.0, 132.2, 131.4, 128.8, 126.9, 126.7, 126.5, 126.0, 124.6, 124.0, 121.6, 116.3, 115.9; MS (EI) $m/z$ (%) 252, 189, 128 (100), 115, 77; HRMS calcd. for: C$_{16}$H$_{11}$OS $[M-H]^{-}$: 251.0525, found 251.0530.

2-(Naphthalen-2-ylthio)phenol (3an):$[^1]$}

Pale yellow liquid; yield 79%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.77-7.58 (m, 4H), 7.48-7.40 (m, 4H), 7.24-7.21 (m, 1H), 7.11 (d, $J = 8.0$ Hz, 1H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.54 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 157.4, 136.9, 133.8, 133.2, 132.3, 132.3, 131.9, 129.0, 127.8, 127.2, 126.8, 125.9, 125.4, 125.3, 121.4, 116.6, 115.8; MS (EI) $m/z$ (%) 252, 219, 128 (100), 115, 77.

2-((4-Bromo-3-fluorophenyl)thio)phenol (3ao):

Pale yellow liquid; yield 56%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.51 (d, $J = 8.0$ Hz, 1H), 7.45-7.38 (m, 2H), 7.10 (d, $J = 8.0$ Hz, 1H), 7.00 (t, $J = 8.0$ Hz, 1H), 6.77-6.74 (m, 2H), 6.35 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 159.4 (d, $J = 248.0$ Hz), 157.3, 138.0 (d, $J = 6.0$ Hz), 136.9, 133.9, 133.0, 123.4 (d, $J = 4.0$ Hz), 121.7, 116.1, 115.0, 114.7 (d, $J = 25.0$ Hz), 106.4 (d, $J = 21.0$ Hz); MS (EI) $m/z$ (%) 300 (100), 218, 186, 109, 96, 63; HRMS calcd. for: C$_{12}$H$_7$BrFOS $[M-H]^{-}$: 296.9380, found 296.9382.
2-(Thiophen-2-ylthio)phenol (3ap):

Pale yellow solid; yield 43%; mp 39-41 °C; \(^1\)H NMR (400 MHz, CDCl₃, ppm) \(\delta\) 7.52 (d, \(J = 8.0\) Hz, 1H), 7.30-7.29 (m, 2H), 7.15 (s, 1H), 7.00-6.87 (m, 3H), 6.48 (s, 1H); \(^1^3\)C NMR (100 MHz, CDCl₃, ppm) \(\delta\) 156.0, 134.9, 133.6, 132.1, 131.5, 129.1, 127.6, 121.2, 120.4, 115.7; MS (EI) m/z (%) 208 (100), 175, 147, 96, 84, 71; HRMS calcd. for: C\(_{10}\)H₇OS₂ [M-H]: 206.9933, found 206.9935.

2-(Ethylthio)phenol (3aq, CAS: 29549-60-8)\(^6\):

Pale yellow liquid; yield 43%; \(^1\)H NMR (400 MHz, CDCl₃, ppm) \(\delta\) 7.47 (d, \(J = 8.0\) Hz, 1H), 7.32-7.26 (m, 1H), 6.99 (d, \(J = 8.0\) Hz, 1H), 6.88 (t, \(J = 6.0\) Hz, 1H), 6.77 (s, 1H), 2.72 (q, \(J = 8.0\) Hz, 2H), 1.22 (t, \(J = 6.0\) Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl₃, ppm) \(\delta\) 157.1, 136.1, 131.1, 120.7, 118.8, 114.7, 30.8, 14.9; MS (EI) m/z (%) 154 (100), 139, 126, 97, 53.

**General procedure (5aa):**

Iodine (15.3 mg, 0.06 mmol) and \(p\)-toluenesulfinic acid sodium (4a, 107 mg, 0.6 mmol) were added to a 10 mL oven-dried reaction vessel. The reaction vessel was purged with argon for three times and was added diether phosphite (50 \(\mu\)L, 0.4 mmol), cyclohexanone (1a, 21 \(\mu\)L, 0.2 mmol), DMSO (0.1 mL) and toluene (0.5 mL) by syringe. The reaction mixture was stirred at 130 °C for 24 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 = 98:2) to yield the desired product 5aa as pale yellow liquid (30.6 mg, 71% yield). The product is same as 3aa.
4-Methyl-2-\((\rho\text{-tolylthio})\)phenol (5ba):\cite{1}

\[
\begin{array}{c}
\text{OH} \\
\text{Me}
\end{array}
\]

Pale yellow liquid; yield 75%. The product is same as 3ba.

4-Ethyl-2-\((\rho\text{-tolylthio})\)phenol (5ca):\cite{1}

\[
\begin{array}{c}
\text{OH} \\
\text{Et}
\end{array}
\]

Pale yellow liquid; yield 83%. The product is same as 3ca.

4-(\textit{iso}-Propyl)-2-\((\rho\text{-tolylthio})\)phenol (5da):

\[
\begin{array}{c}
\text{OH} \\
\text{Me}
\end{array}
\]

Pale yellow liquid; yield 81%. The product is same as 3da.

4-Pentyl-2-\((\rho\text{-tolylthio})\)phenol (5ea):\cite{1}

\[
\begin{array}{c}
\text{OH} \\
\text{n-C}_5\text{H}_{11}
\end{array}
\]

Pale yellow liquid; yield 83%. The product is same as 3ea.

4-(\textit{tert}-Pentyl)-2-\((\rho\text{-tolylthio})\)phenol (5fa):\cite{1}

\[
\begin{array}{c}
\text{OH} \\
\text{tert-C}_5\text{H}_{11}
\end{array}
\]
Pale yellow liquid; yield 85%. The product is same as 3fa.

3-((p-Tolylthio)-[1,1'-biphenyl]-4-ol (5ga):[1]

Pale yellow solid; yield 80%. The product is same as 3ga.

3-((p-Tolylthio)-[1,1'-biphenyl]-4,4'-diol (5ha):

White solid; yield 68%. The product is same as 3ha.

N-(4-Hydroxy-3-(p-tolylthio)phenyl)acetamide (5ia):[1]

Pale yellow liquid; yield 50%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.62 (s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.05-6.99 (m, 6H), 6.38 (s, 1H), 2.28 (s, 3H), 2.14 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 168.5, 153.8, 136.6, 131.7, 131.2, 130.1, 128.1, 128.0, 124.5, 117.9, 115.6, 24.2, 21.0; MS (EI) m/z (%) 273 (100), 231, 207, 139, 111, 91.

2-(Phenylthio)phenol (5ab, CAS: 55214-86-3):[2]

Pale yellow liquid; yield 64%. The product is same as 3ab.
2-((4-Fluorophenyl)thio)phenol (5ac):\textsuperscript{[1]}

Pale yellow liquid; yield 75%. The product is same as 3af.

2-((4-Chlorophenyl)thio)phenol (5ad, CAS: 59010-71-8):\textsuperscript{[1]}

Pale yellow liquid; yield 70%; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm) δ 7.51 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.19 (t, J = 8.0 Hz, 2H), 7.09-6.95 (m, 4H), 6.43 (s, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, ppm) δ 157.2, 136.8, 134.5, 132.5, 132.3, 129.3, 128.3, 121.4, 116.2, 115.8; MS (EI) m/z (%) 236 (100), 220, 200, 168, 96.

2-((4-Bromophenyl)thio)phenol (5ae, CAS: 1254831-59-8):\textsuperscript{[1]}

Pale yellow liquid; yield 68%; The product is same as 3ag.

2-((4-(Trifluoromethyl)phenyl)thio)phenol (5af):

Pale yellow liquid; yield 42%. The product is same as 3ai.

2-(p-Tolythio)phenol (5ag):\textsuperscript{[1]}
Pale yellow liquid; yield 56%; $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.48 (d, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.17 (d, $J = 8.0$ Hz, 1H), 7.09-6.95 (m, 4H), 6.66 (d, $J = 8.0$ Hz, 1H), 6.40 (s, 1H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 157.4, 136.8, 135.7, 134.9, 134.9, 132.0, 130.4, 126.8, 126.2, 126.0, 121.4, 115.6, 20.0; MS (EI) m/z (%) 216 (100), 201, 122, 96, 91.

References

$^1$H NMR and $^{13}$C NMR spectra
GC analysis for 3ja and 3ja'