Unexpected Hydrazine Hydrate-Mediated Aerobic Oxidation of Aryl/Heteroaryl boronic Acids to Phenols with Ambient Air

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1. General procedure for aerobic oxidation of aryl/heteroaryl boronic acids to phenols with ambient Air. A flask was charged with aryl/heteroaryl boronic acid 1 (0.5 mmol), N₂H₄·H₂O (0.25 mmol, 14.4 µL), Cs₂CO₃ (1.0 mmol, 329.1 mg), H₂O (2.5 mmol, 45.0 µL), and PEG-400 (2.0 g). Then, the flask was stirred at 80 °C in open air for the indicated time. At the end of the reaction, the reaction mixture was acidified with dilute aqueous HCl and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate).

2. Analytical methods

¹H and ¹³C NMR spectra of solutions in CDCl₃ or DMSO-d₆ were recorded on a Bruker Avance 400 instrument. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals (CDCl₃ : H 7.24 and C 77.0 ppm; DMSO-d₆ : H 2.50 and C 39.5 ppm). The signals of water were observed at about 1.58 ppm and 3.34 ppm in CDCl₃ and DMSO-d₆, respectively. Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; ddd, doublet of doublet of doublets; tdd, doublet of doublet of triplets. Coupling constants, J, were reported in hertz unit (Hz).
3. Analytical data of products

**Dibenzothiophen-4-ol (2a):** Following general procedure, 2a was isolated as a light pink solid (86% yield), known compound. The NMR spectroscopic data agree with those described in ref. S1. 

\[
\text{H NMR (400 MHz, DMSO-}d_6\text{): }\delta 10.5 \text{ (br s, 1 H), 8.29–8.26 (m, 1 H), 8.02–7.99 (m, 1 H), 7.80 (dd, } J = 8.0, 4.0 \text{ Hz, 1 H), 7.52–7.45 (m, 2 H), 7.34 (t, } J = 8.0 \text{ Hz, 1 H), 6.95 ppm (dd, } J = 8.0, 4.0 \text{ Hz, 1 H); } \text{C NMR (100 MHz, DMSO-}d_6\text{): }\delta 152.3, 138.7, 136.9, 135.7, 126.9, 126.2, 125.6, 124.6, 123.2, 122.2, 112.9, 111.5 \text{ ppm; mp } 166.3–167.1 ^\circ \text{C (lit.}\text{S1 mp 158-160 } ^\circ \text{C).}
\]

**2,5-Dimethoxyphenol (2b):** Following general procedure, 2b was isolated as a light yellow liquid (91% yield), known compound. The NMR spectroscopic data agree with those described in ref. S2. 

\[
\text{H NMR (400 MHz, CDCl}_3\text{): }\delta 6.75 \text{ (d, } J = 8.0 \text{ Hz, 1 H), 6.54 (d, } J = 4.0 \text{ Hz, 1 H), 7.64 (dd, } J = 8.0, 4.0 \text{ Hz, 1 H), 5.65 (s, 1 H), 3.82 (s, 3 H), 3.73 ppm (s, 3 H); } \text{C NMR (100 MHz, CDCl}_3\text{): }\delta 154.5, 146.4, 140.9, 111.4, 104.2, 101.7, 56.6, 55.6 \text{ ppm.}
\]

**3,5-Dimethoxyphenol (2c):** Following general procedure, 2c was isolated as a light brown oil (92% yield), known compound. The NMR spectroscopic data agree with those described in ref. S3. 

\[
\text{H NMR (400 MHz, CDCl}_3\text{): }\delta 6.04 \text{ (t, } J = 2.0 \text{ Hz, 1 H), 6.02 (d, } J = 2.0 \text{ Hz, 2 H), 4.73 (br s, 1 H), 3.71 ppm (s, 6 H); } \text{C NMR (100 MHz, CDCl}_3\text{): }\delta 161.5, 157.6, 94.3, 92.9, 55.3 \text{ ppm.}
\]

**2,6-Dimethylphenol (2d):** Following general procedure A, 2d was isolated as a white solid (96% yield), known compound. The NMR spectroscopic data agree with those described in ref. S1. 

\[
\text{H NMR (400 MHz, CDCl}_3\text{): }\delta 6.96 \text{ (d, } J = 8.0 \text{ Hz, 2 H), 6.74 (t, } J = 8.0 \text{ Hz, 1 H), 4.58 (br s, 1 H), 2.24 ppm (s, 6 H); } \text{C NMR (100 MHz, CDCl}_3\text{): }\delta 152.1, 128.6, 122.9, 120.2, 15.8 \text{ ppm; mp 42.8–44.2 } ^\circ \text{C (lit.}\text{S1 mp 43-45 } ^\circ \text{C).}
\]
2-Methoxyphenol (2e): Following general procedure, 2e was isolated as a light yellow oil (97% yield), known compound. The NMR spectroscopic data agree with those described in ref.\textsuperscript{S1} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 6.94–6.91\) (m, 1 H), \(6.89–6.84\) (m, 3 H), \(5.64\) (br s, 1 H), \(3.87\) ppm (s, 3 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 146.5, 145.6, 121.4, 120.1, 114.5, 110.7, 55.8\) ppm.

\begin{center}
\includegraphics[width=0.2\textwidth]{2e}
\end{center}

3-Methoxyphenol (2f): Following general procedure, 2f was isolated as a light yellow oil (83% yield), known compound. The NMR spectroscopic data agree with those described in ref.\textsuperscript{S1} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 7.11\) (t, \(J = 8.0\) Hz, 1 H), \(6.49–6.30\) (m, 3 H), \(4.14\) (br s, 1 H), \(3.76\) ppm (s, 3 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 160.9, 156.9, 130.1, 107.9, 106.3, 101.6, 55.3\) ppm.

\begin{center}
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\end{center}

4-Methoxyphenol (2g): Following general procedure, 2g was isolated as a low melting point solid (98% yield), known compound. The NMR spectroscopic data agree with those described in ref.\textsuperscript{S1} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 6.79–6.73\) (m, 4 H), \(4.86\) (br s, 1 H), \(3.75\) ppm (s, 3 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 153.7, 149.4, 116.0, 114.8, 55.8\) ppm.

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\end{center}

3-Aminophenol (2h): Following general procedure, 2h was isolated as a white solid (85% yield), known compound. The NMR spectroscopic data agree with those described in ref.\textsuperscript{S4} \textsuperscript{1}H NMR (400 MHz, DMSO-\textsubscript{d}\textsubscript{3}): \(\delta 8.86\) (br s, 1 H), \(6.80–6.76\) (m, 1 H), \(6.02–6.00\) (m, 2 H), \(5.96–5.93\) (m, 1 H), \(4.92\) ppm (br s, 2 H); \textsuperscript{13}C NMR (100 MHz, DMSO-\textsubscript{d}\textsubscript{3}): \(\delta 158.1, 149.8, 129.5, 105.6, 103.5, 101.1\) ppm; mp 118.8–120.2 °C (lit.\textsuperscript{S4} mp 120–121 °C).

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\includegraphics[width=0.2\textwidth]{2h}
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2-Methylphenol (2i): Following general procedure, 2i was isolated as a low melting point solid (91% yield), known compound. The NMR spectroscopic data agree with those described in ref.\textsuperscript{S5} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 7.13–7.06\) (m, 2 H), \(6.85\) (td, \(J = 8.0, 0.8\) Hz, 1 H), \(6.76\) (d, \(J = 8.0\) Hz, 2 H), \(4.78\) (br s, 1 H), \(2.25\) ppm (s, 3 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 153.7, 131.0, 127.1, 123.7, 120.7, 114.8, 15.7\) ppm.
3-Methylphenol (2j): Following general procedure, 2j was isolated as a colorless oil (95% yield), known compound. The NMR spectroscopic data agree with those described in ref. S6. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.13 (t, $J = 8.0$ Hz, 1 H), 6.76 (d, $J = 8.0$ Hz, 1 H), 6.67–6.64 (m, 2 H), 4.89 (br s, 1 H), 2.30 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.3, 139.8, 129.4, 121.6, 116.0, 112.3, 21.3 ppm.

4-Methylphenol (2k): Following general procedure, 2k was isolated as a low melting point solid (90% yield), known compound. The NMR spectroscopic data agree with those described in ref. S6. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.02–6.91 (dd, $J = 8.0$, 0.8 Hz, 2 H), 6.72 (d, $J = 8.0$ Hz, 2 H), 4.49 (br s, 1 H), 2.26 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.2, 130.0, 129.9, 115.0, 20.4 ppm.

Phenol (2l): Following general procedure A, 2l was isolated as a white yellow solid (87% yield), known compound. The NMR spectroscopic data agree with those described in ref. S1. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.24 (t, $J = 8.0$ Hz, 2 H), 6.93 (t, $J = 8.0$ Hz, 1 H), 6.83 (d, $J = 8.0$ Hz, 2 H), 4.84 ppm (br s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.3, 129.7, 120.8, 115.3 ppm; mp 41.2–42.6 °C (lit. S1 mp 40–42 °C).

4-Iodophenol (2m): Following general procedure A, 2m was isolated as a light yellow solid (98% yield), known compound. The NMR spectroscopic data agree with those described in ref. S1. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.49 (d, $J = 8.0$ Hz, 2 H), 6.61 (d, $J = 8.0$ Hz, 2 H), 5.03 ppm (br s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.3, 138.4, 117.8, 82.7 ppm; mp 63.3–64.2 °C (lit. S1 mp 90–93 °C).

4-Bromophenol (2n): Following general procedure, 2n was isolated as a light yellow solid (96%
yield), known compound. The NMR spectroscopic data agree with those described in ref. S1. 1H NMR (400 MHz, CDCl3): δ 7.31 (d, J = 8.0 Hz, 2 H), 6.71 (d, J = 8.0 Hz, 2 H), 4.83 ppm (br s, 1 H); 13C NMR (100 MHz, CDCl3): δ 154.6, 132.4, 117.2, 112.9 ppm; mp 54.3–56.2 °C (lit. S1 mp 55–58 °C).

3-Hydroxyacetophenone (2o): Following general procedure, 2o was isolated as a white solid (95% yield), known compound. The NMR spectroscopic data agree with those described in ref. S7. 1H NMR (400 MHz, DMSO-d6): δ 9.79 (s, 1 H), 7.41 (dt, J = 8.0, 4.0 Hz, 1 H), 7.32 (t, J = 8.0 Hz, 2 H), 7.03 (ddd, J = 8.0, 4.0, 2.0 Hz, 1 H), 2.52 ppm (s, 3 H); 13C NMR (100 MHz, DMSO-d6): δ 197.8, 157.6, 138.3, 129.8, 120.3, 119.3, 114.3, 26.8 ppm; mp 85.8–86.2 °C (lit. S7 mp 92–95 °C).

Methyl 4-Hydroxybenzoate (2p): Following general procedure, 2p was isolated as a white solid (97% yield), known compound. The NMR spectroscopic data agree with those described in ref. S1. 1H NMR (400 MHz, CDCl3): δ 7.94 (d, J = 8.0 Hz, 2 H), 6.84 (d, J = 8.0 Hz, 2 H), 5.51 (br s, 1 H), 3.87 ppm (s, 1 H); 13C NMR (100 MHz, CDCl3): δ 167.3, 160.1, 131.9, 122.4, 115.2, 52.0 ppm; mp 112.0–113.1 °C (lit. S1 mp 121–123 °C).

4-Hydroxybenzonitrile (2q): Following general procedure, 2q was isolated as a light yellow solid (98% yield), known compound. The NMR spectroscopic data agree with those described in ref. S1. 1H NMR (400 MHz, CDCl3): δ 7.53 (d, J = 8.0 Hz, 2 H), 6.92 (d, J = 8.0 Hz, 2 H), 6.34 ppm (br s, 1 H); 13C NMR (100 MHz, CDCl3): δ 160.4, 134.3, 119.3, 116.5, 102.8 ppm; mp 109.1–111.2 °C (lit. S1 mp 107–109 °C).

3-Nitrophenol (2r): Following general procedure, 2r was isolated as a light yellow solid (89% yield), known compound. The NMR spectroscopic data agree with those described in ref. S1. 1H NMR (400 MHz, CDCl3): δ 7.79 (ddd, J = 8.0, 4.0, 2.0 Hz, 1 H), 7.70 (t, J = 8.0 Hz, 1 H), 7.39 (t, J = 8.0, 4.0, 2.0 Hz, 1 H), 7.19 (ddd, J = 8.0, 4.0, 2.0 Hz, 1 H), 5.97 ppm (br s, 1 H); 13C NMR (100 MHz, CDCl3): δ 156.3, 149.0, 130.3, 122.1, 115.9, 110.5 ppm; mp 99.0–100.1 °C (lit. S1 mp 96–99 °C).
**2-Napthol (2s):** Following general procedure, 2s was isolated as a white solid (97% yield), known compound. The NMR spectroscopic data agree with those described in ref. 81. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (t, $J = 8.0$ Hz, 2 H), 7.66 (d, $J = 8.0$ Hz, 1 H), 7.44–7.30 (m, 1 H), 7.13 (d, $J = 4.0$ Hz, 1 H), 7.11 (td, $J = 8.0$, 4.0 Hz, 2 H), 4.86 ppm (br s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.3, 134.6, 129.8, 128.9, 127.7, 126.5, 126.4, 123.6, 117.7, 109.5 ppm; mp 116.0–116.8 °C (lit. 81 mp 121–123 °C).

![2s](image) $\text{H}_2\text{N}$

**4-(Methylmercapto)phenol (2t):** Following general procedure A, 2t was isolated as a white solid (85% yield), known compound. The NMR spectroscopic data agree with those described in ref. 88. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.20 (d, $J = 8.4$ Hz, 2 H), 6.77 (d, $J = 8.4$ Hz, 2 H), 5.18 (br s, 1 H), 2.42 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.0, 130.3, 128.8, 116.1, 18.0 ppm; mp 83.4–84.3 °C (lit. 88 mp 83-85 °C).

![2t](image) $\text{H}_2\text{N}$

**Dibenzofuran-4-ol (2u):** Following general procedure, 2u was isolated as a white solid (83% yield), known compound. The NMR spectroscopic data agree with those described in ref. 81. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J = 8.0$ Hz, 1 H), 7.57 (d, $J = 8.0$ Hz, 1 H), 7.51 (dd, $J = 8.0$, 4.0 Hz, 1 H), 7.45 (td, $J = 8.0$, 2.0 Hz, 1 H), 7.34 (td, $J = 8.0$, 2.0 Hz, 1 H), 7.21 (t, $J = 8.0$ Hz, 1 H), 7.02 (dd, $J = 8.0$, 4.0 Hz, 1 H), 5.49 ppm (br s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 156.0, 144.0, 141.1, 127.3, 125.7, 124.6, 123.7, 122.9, 121.0, 113.6, 112.8, 111.8 ppm; mp 98.2–100.1 °C (lit. 81 mp 98–100 °C).

![2u](image) $\text{H}_2\text{N}$

**Pyridin-3-ol (2v):** Following general procedure, 2v was isolated as a white solid (91% yield), known compound. The NMR spectroscopic data agree with those described in ref. 87. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.27 (d, $J = 4.0$ Hz, 1 H), 8.08 (dd, $J = 8.0$, 4.0 Hz, 1 H), 7.32–7.25 ppm (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.1, 139.3, 136.5, 125.2, 125.1 ppm; mp 125.0–126.2 °C (lit. 87 mp 127 °C).

![2v](image) $\text{H}_2\text{N}$

**1H-indazol-6-ol (2w):** Following general procedure, 2w was isolated as a light yellow solid (96% yield), known compound (CAS: 23244-88-4). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 12.58 (br s, 1 H),
9.57 (br s, 1 H), 7.86 (s, 1 H), 7.52 (d, J = 8.0 Hz, 1 H), 6.78 (s, 1 H), 6.64 ppm (dd, J = 8.0, 2.0 Hz, 1 H); \(^{13}\text{C}\) NMR (100 MHz, DMSO-d<sub>6</sub>): δ 156.5, 141.5, 133.3, 121.1, 117.0, 112.3, 93.2 ppm; mp 161.8–164.2 °C.

4. References
5. Copies of NMR Spectra

![NMR Spectra Image]