Supporting Information

A mild and highly efficient conversion of arylboronic acids into phenols oxidized by m-CPBA

Dong-Song Chen, a Jing-Mei Huang*, a

a School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong, 510640, China.

Email: chehjm@scut.edu.cn
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General methods

Commercial solvents and reagents were used without further purification, and tap water was used for the reaction.

Phenylboronic acid, \( p \)-methylthiophenylboronic acid, \( 1 \)-naphthyl boronic acid, \( p \)-chlorophenylboronic acid, \( p \)-\( \text{tert} \)-butylphenylboronic acid and \( p \)-methoxyphenylboronic acid were purchased from Alfa; \( p \)-cyanophenylboronic acid, 2,6-dimethylphenylboronic acid, \( p \)-formylphenylboronic acid, \( m \)-nitrophenylboronic acid and phenylboronic pinacol ester were purchased from J&K chemical CO., Ltd. in China. TBHP and \( m \)-CPBA were purchased from Aladdin chemical in China.

Analytical thin layer chromatography (TLC) plates and the silica gel for column chromatography were phased from Qingdao Haiyang Chemical and Special Silica Gel Co, Ltd.

Proton nuclear magnetic resonance (\( ^1 \text{H NMR} \)) and carbon nuclear magnetic resonance (\( ^{13} \text{C NMR} \)) spectroscopy were performed on Bruker Advance 400 NMR spectrometers. Chemical shifts of \( ^1 \text{H NMR} \) spectra are reported as in units of parts per million (ppm) downfield from \( \text{SiMe}_4 (\delta = 0.0) \) and relative to the signal of chloroform-\( d \) (\( \delta = 7.264 \), singlet). Multiplicities were given as: s (singlet); br s (broad singlet); d (doublet); t (triplet); dd (doublet of doublets); m (multiplets), etc. The number of protons (\( n \)) for a given resonance is indicated by \( n \text{H} \). Carbon nuclear magnetic resonance spectra (\( ^{13} \text{C NMR} \)) are reported as in units of parts per million (ppm) downfield from \( \text{SiMe}_4 (\delta = 0.0) \) and relative to the signal of chloroform-\( d \) (\( \delta = 77.03 \), triplet).

Experimental procedures

General procedure for the hydroxylation of phenylboronic acid: To the mixture of phenylboronic acid (0.5 mmol) in a \( \text{H}_2\text{O} / \text{EtOH} \) (1:2) solution (2 mL) in a round-bottom flask cell was added \( m \)-CPBA (0.5 mmol) at room temperature. When phenylboronic acid was completely consumed (monitored by TLC, 6 hrs), 0.1M aqueous sodium bicarbonate (5 mL) was added to the mixture. Then the reaction mixture was extracted with ethyl acetate (2×15 mL). The combined organic layer was washed with water (10 mL) and brine (5 mL), dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) and the corresponding phenol was obtained as a colourless solid (2a, 46 mg, 97%).
18O Labeling Experiments

Use of H2\textsuperscript{18}O

\begin{align*}
\text{B(OH)\textsubscript{3}} & \xrightarrow{m\text{-CPBA, H2\textsuperscript{18}O \ (1:2)}} \text{B(OH)\textsubscript{2}} & \text{HRMS (ESI):} m/z (M+H\textsuperscript{+}) \text{ calcd for C6H7O, 95.0498. Found: 95.0493.} \\
\text{2a (88\% yield)} & \end{align*}

HRMS (ESI): m/z (M+H\textsuperscript{+}) calcd for C\textsubscript{6}H\textsubscript{7}\textsuperscript{18}O, 97.0541. Not found.

Spectroscopic data of products

\begin{align*}
\text{phenol} & \\
\text{2a (46 mg, 97\%) colourless solid} & \\
\delta_{H} (400 MHz; CDCl\textsubscript{3}; Me\textsubscript{4}Si) & 5.65 (1 H, br s, PhOH), 6.81-6.83 (2 H, m, 2 \times Ph), 6.89-6.93 (1 H, m, 1 \times Ph), 7.18-7.22 (2 H, m, 2 \times Ph); \\
\delta_{C} (100 MHz; CDCl\textsubscript{3}; Me\textsubscript{4}Si) & 115.5, 121.1, 129.8, 155.2. \\
\text{4-hydroxybenzonitrile} & \\
\text{2b (57 mg, 96\%) yellow solid} & \\
\delta_{H} (400 MHz; CDCl\textsubscript{3}; Me\textsubscript{4}Si) & 6.94-6.97 (2 H, m, 2 \times Ph), 7.21 (1 H, br s, PhOH), 7.53-7.57 (2 H, m, 2 \times Ph). \\
\delta_{C} (100 MHz; CDCl\textsubscript{3}; Me\textsubscript{4}Si) & 102.8, 116.6, 119.4, 134.4, 160.6. \\
\text{3-nitrophenol} & \\
\text{2c (66 mg, 97\%) pale yellow solid} & \\
\delta_{H} (400 MHz; CDCl\textsubscript{3}; Me\textsubscript{4}Si) & 6.27 (1 H, br s, PhOH), 7.20-7.22 (1 H, m, 1 \times Ph), 7.40 (1 H, t, J 8.2 Hz, 1 \times Ph), 7.72 (1 H, t, J 2.2 Hz, 1 \times Ph), 7.79-7.82 (1 H, m, 1 \times Ph); \\
\delta_{C} (100 MHz; CDCl\textsubscript{3}; Me\textsubscript{4}Si) & 110.6, 115.8, 122.2, 130.3, 149.1, 156.5. 
\end{align*}
4-hydroxybenzaldehyde

2d (52 mg, 85%) pale yellow solid

$\delta_{H}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 7.00 (2 H, dd, $J$ 8.4 Hz, 2 × Ph), 7.17 (1 H, br s, 1 × PhOH), 7.82 (2 H, dd, $J$ 8.4 Hz, 2 × Ph); $\delta_{C}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 116.1, 129.6, 132.7, 162.1, 191.6.

4-chlorophenol

2e (61 mg, 95%) white solid

$\delta_{H}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 5.37 (1 H, br s, 1 × PhOH), 6.76 (2 H, d, $J$ 8.8 Hz, 2 × Ph), 7.18 (2 H, d, $J$ 8.8 Hz, 2 × Ph); $\delta_{C}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 116.7, 125.8, 129.6, 153.9.

4-methoxyphenol

2f (56 mg, 91%) colourless solid

$\delta_{H}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 3.76 (3 H, s, 3 × PhOCH$_3$), 6.75-6.81 (4 H, m, 4 × Ph); $\delta_{C}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 55.9, 114.9, 116.1, 149.6, 153.7.

2,6-dimethylphenol

2g (57 mg, 94%) white solid

$\delta_{H}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.25 (6 H, s, 2 × Ph(CH$_3$)), 4.64 (1 H, br s, 1 × PhOH), 6.74-6.77 (1 H, m, 1 × Ph), 6.97-6.98 (2 H, m, 2 × Ph); $\delta_{C}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 15.9, 120.2, 123.0, 128.6, 152.2.

4-tert-butylphenol

2h (75 mg, quant) colourless solid

$\delta_{H}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.29 (9 H, s, 3 × C(CH$_3$)$_3$), 6.77 (2 H, d, $J$ 8.0 Hz, 2 × Ph), 7.25 (2 H, d, $J$ 8.0 Hz, 2 × Ph); $\delta_{C}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 31.6, 34.1, 114.8, 126.4, 143.5, 153.2.
4-(methylthio)phenol
2i (56 mg, 80%) yellow solid
δ_H (400 MHz; CDCl₃; Me₄Si) 2.44 (3 H, s, 3 × PhSCH₃), 6.77-6.81 (2 H, m, 2 × Ph), 7.21-7.24 (2 H, m, 2 × Ph);
δ_C (100 MHz; CDCl₃; Me₄Si) 18.1, 116.1, 130.4, 131.0, 154.3.

Naphthalen-1-ol
2j (72 mg, quant) colourless solid
δ_H (400 MHz; CDCl₃; Me₄Si) 5.43 (1 H, br s, 1 × PhOH), 6.75-6.76 (1 H, m, 1 × Ph), 7.25-7.29 (1 H, m, 1 × Ph),
7.41-7.47 (3 H, m, 3 × Ph), 7.78-7.81 (1 H, m, 1 × Ph), 8.15-8.18 (1 H, m, 1 × Ph);
δ_C (100 MHz; CDCl₃; Me₄Si) 108.8, 120.8, 121.6, 124.4, 125.4, 125.9, 126.5, 127.8, 134.8, 151.4.

Cyclohexanol
2l (30 mg, 60%) colourless oil
δ_H (400 MHz; CDCl₃; Me₄Si) 1.12-1.33 (5 H, m, 5 × cyclohexyl), 1.53-1.56 (1 H, m, 1 × cyclohexyl),
1.72-1.75 (2 H, m, 2 × cyclohexyl), 1.87-1.90 (2 H, m, 2 × cyclohexyl), 2.25 (1 H, s, cyclohexyl-OH),
3.57-3.63 (1 H, m, 1 × cyclohexyl);
δ_C (100 MHz; CDCl₃; Me₄Si) 24.2, 25.5, 35.5, 70.2.
NMR spectra of synthesized compounds
Two chemical structures and their corresponding 1D NMR spectra are shown on the page. The structures are connected to the spectra, indicating the chemical shifts and peak assignments for each peak in the spectra.