

## ESI for

# Copper-catalyzed protodeboronation of arylboronic acids in aqueous media

Chun Liu\*, Xinmin Li, Yonghua Wu and Jieshan Qiu

State Key Lab of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Linggong Road 2, Dalian 116024, China

E-mail: [chunliu70@yahoo.com](mailto:chunliu70@yahoo.com)

Materials and Methods and Experimental Procedure	S1-S2
Control Experiments in Different Conditions	S2
Characterization Data	S2-S3
NMR Spectra for Protodeboronation Products	S4-S5

### Materials and Methods

All arylboronic acids and metal catalysts were used as received (Alfa Aesar, Avocado). Other reagents and solvents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature.  $^1\text{H}$  NMR spectra were recorded on a Bruker Advance II 400 spectrometer using TMS as internal standard. GC analysis was performed on Agilent GC-7890A with biphenyl as internal standard. The isolated yield of product were obtained by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C), unless otherwise noted.

### Typical procedure for protodeboronation of arylboronic acids

A mixture of arylboronic acid (0.2 mmol),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (1 mol%),  $(i\text{-Pr})_2\text{NH}$  (0.2 mmol) and EtOH/ $\text{H}_2\text{O}$  (0.5 mL/0.5 mL) was stirred at 80 °C in air for 1.5 h. The

mixture was added to brine (2 mL) and extracted two times with ethyl acetate (2 mL). The combined organic layers were dried over sodium sulfate and the yield of protodeboronation product was determined by GC analysis with biphenyl as internal standard.

### Typical procedure for protodeboronation of polycyclic aromatic boronic acids

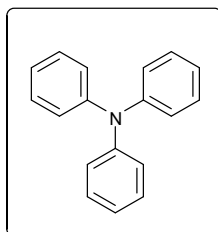
A mixture of arylboronic acid (0.2 mmol),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (1 mol%),  $(i\text{-Pr})_2\text{NH}$  (0.2 mmol) and EtOH/ $\text{H}_2\text{O}$  (0.5 mL/0.5 mL) was stirred at 80 °C in air for 1.5 h. The mixture was added to brine (2 mL) and extracted two times with ethyl acetate (2×2 mL). The solvent was concentrated under vacuum, and the product was isolated by short-column chromatography on silica gel (200–300 mesh).

### Control Experiments

*Protodeboronation of 4-(diphenylamino)phenylboronic acid performed in oxygen for example:*

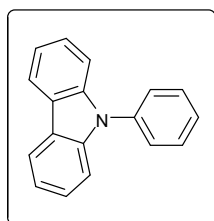
A mixture of 4-(diphenylamino)phenylboronic acid (0.2 mmol),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (1 mol%),  $(i\text{-Pr})_2\text{NH}$  (0.2 mmol) and EtOH/ $\text{H}_2\text{O}$  (0.5 mL/0.5 mL) at 80 °C for 1.5 h with a balloon full of oxygen. The mixture was added to brine (10 mL) and extracted two times with ethyl acetate (2 × 2 mL), the solvent was evaporated *in vacuo* and the product was isolated by short column chromatography.

### Characterization Data



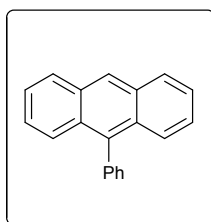
#### Triphenylamine<sup>1</sup>

<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.23 (d,  $J = 7.7$  Hz, 5H), 7.08 (d,  $J = 8.2$  Hz, 6H), 7.00 (t,  $J = 7.3$  Hz, 3H).



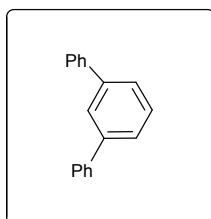
#### 9-phenyl-9H-carbazole<sup>2</sup>

<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.15 (d,  $J = 7.8$  Hz, 2H), 7.66 – 7.53 (m, 4H), 7.51 – 7.35 (m, 5H), 7.34 – 7.26 (m, 2H).



### 9-phenylanthracene<sup>3</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 8.50 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.56 (dt, *J* = 13.8, 7.0 Hz, 3H), 7.49 – 7.40 (m, 4H), 7.39 – 7.29 (m, 2H).



### 1,3-Diphenylbenzene<sup>4</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ 7.81 (s, 1H), 7.65 (d, *J* = 7.4 Hz, 4H), 7.58 (dd, *J* = 6.7, 1.6 Hz, 2H), 7.54 – 7.42 (m, 5H), 7.37 (t, *J* = 7.3 Hz, 2H).

## Reference

1. A. Tlili, F. Monnier and M. Taillefer, *Chem. Commun.*, 2012,**48**, 6408-6410.
2. S. H. Kim, I. Cho, M. K. Sim, S. Park and S. Y. Park, *J. Mater. Chem.*, 2011, **21**, 9139–9148.
3. T. E. Schmid, D. C. Jones, O. Songis, O. Diebolt, M. R. L. Furst, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans.*, 2013,**42**, 7345-7353.
4. P. K. Mandali, D. K. Chand, *Catal. Commun.*, 2013,**31**,16– 20.

