ESI for

Base-promoted silver-catalyzed protodeboronation of arylboronic acids and esters

Chun Liu,* Xinmin Li and Yonghua Wu

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

E-mail: cliu@dlut.edu.cn

Content

Materials and Methods

All arylboronic acids and esters, metal catalysts were used as received. 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}H NMR spectra were recorded on a Bruker Advance II 400 spectrometer using TMS as the internal standard. The yields of liquid products were determined by GC using biphenyl as an internal standard, and the solid products were isolated by short chromatography on a silica gel (200 – 300 mesh) column using petroleum ether (60 – 90 °C), unless otherwise noted. Compounds described in the literature were characterized by ^{1}H NMR spectra compared to reported data.

Typical procedure for protodeboronation of arylboronic acids and esters.

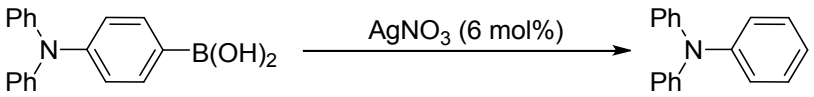
A mixture of arylboronic acid or ester (0.2 mmol), $AgNO_3$ (6 mol%), Et_3N (0.2 mmol) and EtOH/H_2O (0.5 mL/0.5 mL) was stirred at 80 ºC in air for the indicated time. The

mixture was added to brine (2 mL) and extracted three times with ethyl acetate (2 mL). The combined organic layers were dried over sodium sulfate and was analysed by gas chromatography using biphenyl as internal standard.

Typical procedure for protodeboronationof polycyclic aromatic boronic acids and esters.

A mixture of arylboronic acid or esters (0.2 mmol), $AgNO_3$ (6 mol%), Et_3N (0.2 mmol) and EtOH/H_2O (0.5 mL/0.5 mL) was stirred at 80 ºC in air for the indicated time. The mixture was added to brine (10 mL) and extracted three times with ethyl acetate (10 mL). The solvent was concentrated under vacuum, and the product was isolated by short-column chromatography.

Table S1. Effect of temperature on the protodeboronation of 4-(diphenylamino)phenylboronicacid[a]



Entry	Temperature (°C)	Time (min)	Yield (%)[b]
1	80	10	96
2	50	10	71
3	25	10	Trace

[a] Reaction conditions: 4-(diphenylamino)phenylboronic acid (0.2 mmol), $AgNO_3$ (6.0 mol%), Et_3N (0.2 mmol), EtOH/H_2O (0.5 mL/0.5 mL), 80 °C , under air. The reaction was monitored by TLC. [b] Isolated yields.

Characterization Data

Products with high volatility were analyzed by gas chromatography using biphenyl as an internal standard with standard curve method. GC conditions: injector temperature 260 °C, detector temperature 280 °C, oven temperature program; 50 °C isothermal for 3 min after injection, 30 °C/min to 280°C, hold for 2 min at 280 °C. Solid products were characterized by ^{1}H NMR.

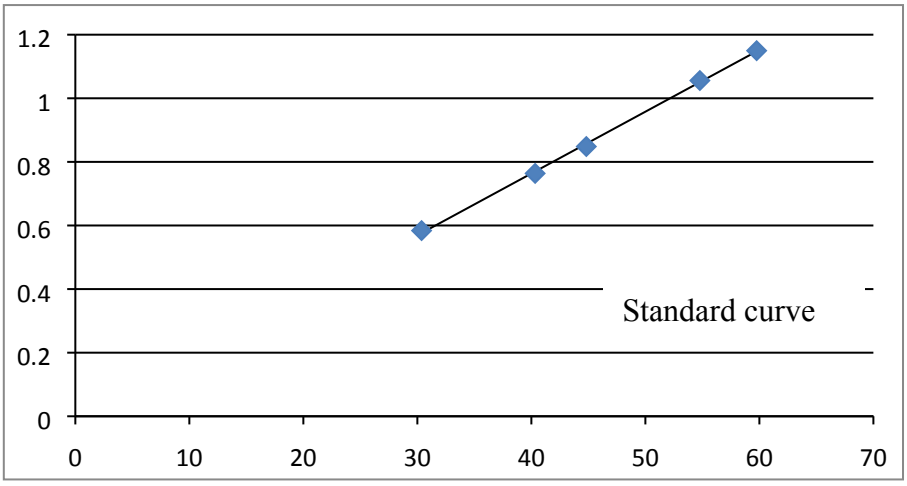


Figure S1 GC standard curve of anisole

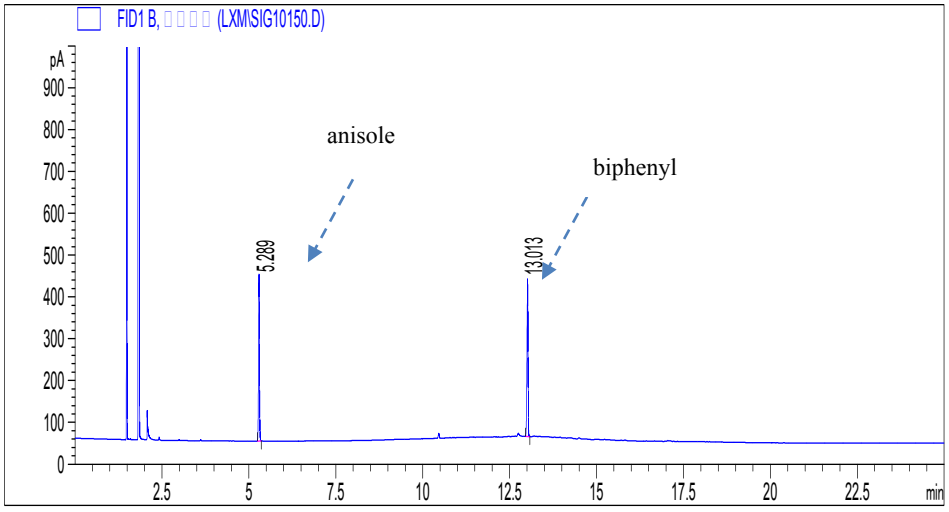
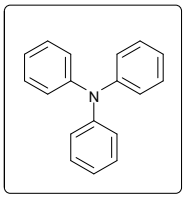
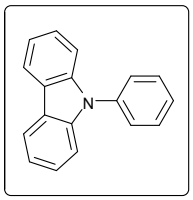


Figure S2 GC spectrum of the reaction mixture of (4-methoxyphenyl)boronic acid after 10 min



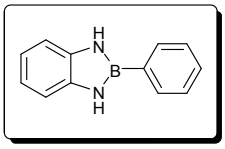
Triphenylamine[1]

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.23 (d, *J* = 7.7 Hz, 5H), 7.08 (d, *J* = 8.2 Hz, 6H), 7.00 (t, *J* = 7.3 Hz, 3H).



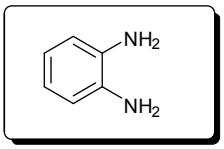
9-phenyl-9H-carbazole[2]

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 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).



2-Phenyl-2,3-dihydro-1H-1,3,2-benzodiazaborole[3]

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 (dd, *J* = 6.4, 3.0 Hz, 2H,), 7.43 (dd, *J* = 6.2, 2.6 Hz, 3H), 7.16-7.10 (m, 2H)，7.01 – 6.94 (m, 2H)，6.79 (s, 2H).



Benzene-l,2-diainine[3]

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.00 – 6.50 (m, 4H), 3.37 (s, 4H).

References

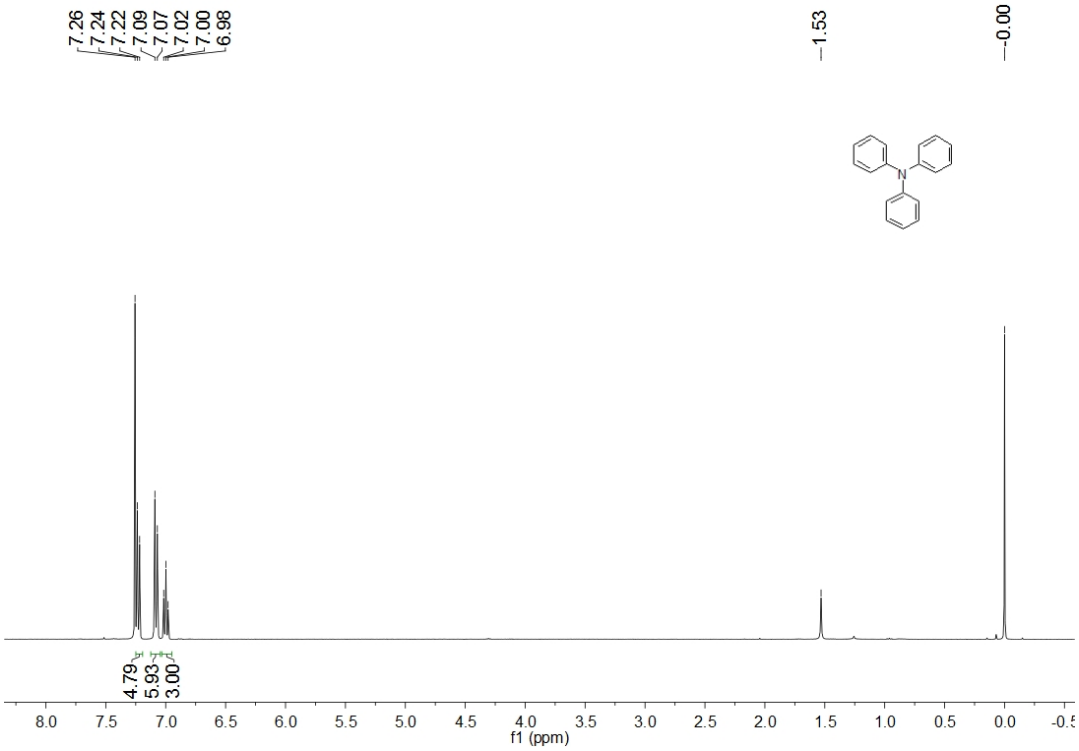
1. Tlili, A.; Monnier, F.; Taillefer, M., *Chem. Commun.*, 2012**, 48**, 6408-6410.

2. Kim, S. H.; Cho, I.; Sim, M. K.; Park, S.; Park, S. Y., *J. Mater. Chem.*, 2011**, 21**, 9139-9148.

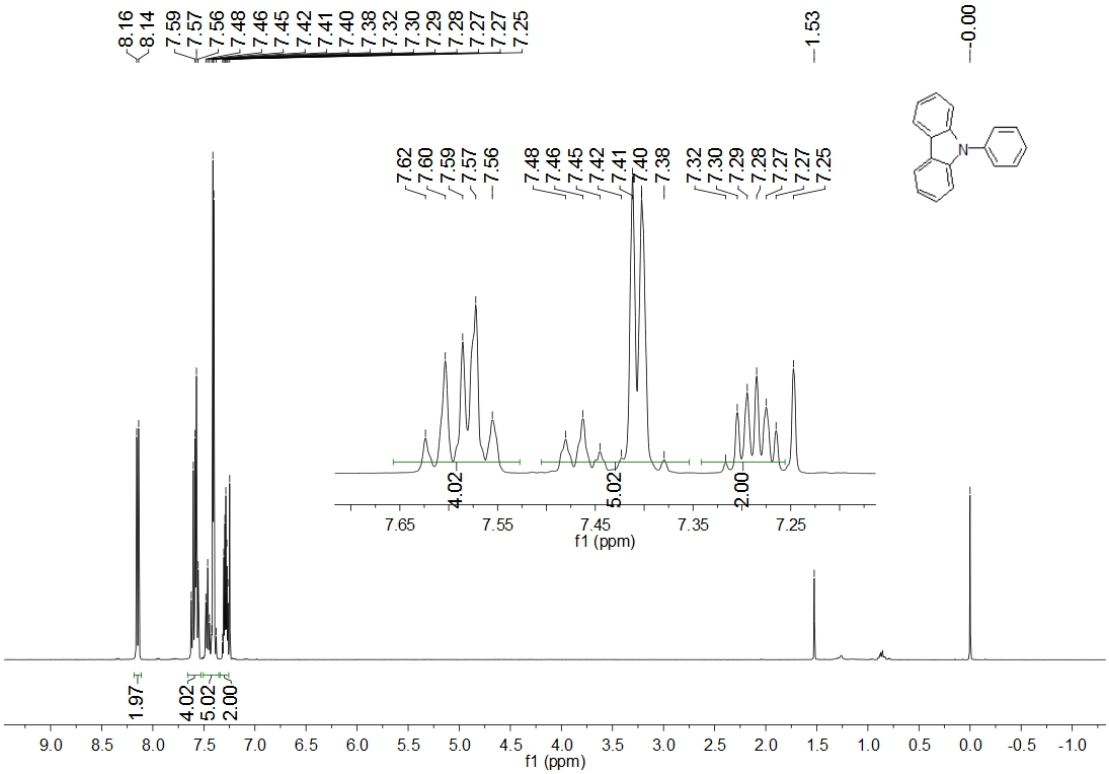
3. Kaupp, G.; Naimi‐Jamal, M. R.; Stepanenko, V., *Chem. - Eur. J.*, 2003**, 9**, 4156-4161.

^{1}H NMR Spectra for Solid Products

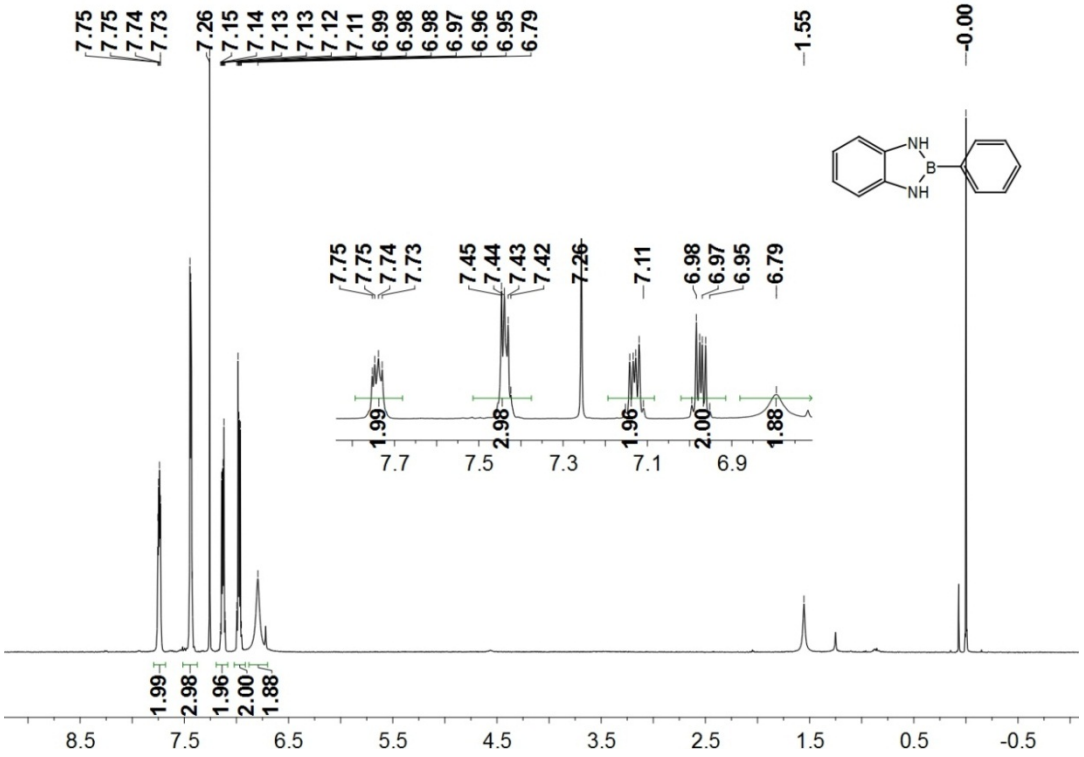
Triphenylamine



9-phenyl-9H-carbazole



2-Phenyl-2,3-dihydro-1H-1,3,2-benzodiazaborole



Benzene-l,2-diainine