

Supplementary Information

Electrochemical Hydroxylation of Organoboron Compounds

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Experimental Section

Measurements

^1H NMR spectra were recorded on a JEOL EX-270 spectrometer (270 MHz). The chemical shifts for ^1H NMR spectra were given in δ (ppm) from internal TMS, CDCl_3 . The product yields were determined by ^1H -NMR using nitromethane as an internal standard material. EI mass spectra were recorded on Shimadzu GCMS-QP5050A. Cyclic voltammetry measurements were recorded on an ALS 600A Electrochemical Analyzer. Preparative electrolysis experiments were carried out with Metronnix Corp. (Tokyo) constant current power supply model 5944 by monitoring electricity with Hokutodenko Coulomb/Amperehour meter HF-201.

Materials

All reagents and solvent were purchased commercial sources and used without further purification.

A typical procedure for cathodic hydroxylation

Constant current cathodic electrolysis of substrates (0.25 mmol) was carried out under oxygen with platinum electrodes (2 cm x 2 cm) in 0.1 M tetrabutylammonium/acetonitrile (25 ml x 2) in a divided cell at room temperature. The oxygen was continuously added during electrolysis. After electrolysis was complete, 0.1M sulfuric acid (5 ml) was added to the mixture. The product was

extract with diethyl ether and the organic layer was dried over anhydrous MgSO_4 . Then, the extracts were evaporated under reduced pressure and a crude product was obtained. ^1H -NMR yields were estimated by comparing the integration of peaks with that of nitromethane as an internal standard material. After purification by silica gel column chromatography eluting with ethyl acetate, the isolated yields of the products were determined. The known products were identified by comparison with the spectral data of the reported sample¹ and commercially available samples.

Chemical hydroxylation of **1a** with KO_2

The solution of KO_2 (80 mg, 1.13 mmol) and *p*-(methylthio)phenyl boronic acid **1a** (51.7 mg, 0.31 mmol) in acetonitrile (10 ml) under nitrogen atmosphere was stirred for 2 h at room temperature. The reaction mixture was extracted with diethylether and dried over anhydrous MgSO_4 . Then the extracts were evaporated to give the product, *p*-(methylthio)phenol **2a** (0.15 mmol, 49% ^1H -NMR yield).

Chemical hydroxylation of **1a** with hydrogen peroxide under basic conditions

p-(Methylthio)phenyl boronic acid **1a** (86.2 mg, 0.51 mmol) was dissolved in THF (6 ml) and the mixture was stirred for 30 min at 0 °C under nitrogen atmosphere. 3 M NaOH (1 ml) and 30% H_2O_2 (1.5 ml) were added to the solution and the reaction mixture was further stirred for 3 h at room temperature. Then 5 ml of water and 3M HCl (1.5 ml) were added to the mixture and the solution

was extracted with diethylether. The organic layer was dried over anhydrous MgSO_4 and concentrated in vacuo. The obtained product was a mixture of *p*-(methylsulfonyl)phenol and 2,4,6-tris[*p*-(methylsulfonyl)phenyl]boroxin determined by ^1H , ^{11}B -NMR and GC-MS.

p-(Methylsulfonyl)phenol: ^1H -NMR (270 MHz, CDCl_3) δ 7.76 (d, $J = 8.6$ Hz, 2H), 6.96 (d, $J = 8.6$ Hz, 2H), 3.04 (s, 3H), MS (m/z) 172(M^+), 157, 141, 109, 93, 65.

2,4,6-Tris[*p*-(methylsulfonyl)phenyl]boroxin: ^1H -NMR (270 MHz, CDCl_3) δ 7.53 (d, $J = 8.6$ Hz, 2H), 6.96 (d, $J = 8.6$ Hz, 2H), 2.78(s, 3H), ^{11}B -NMR (270 MHz, CDCl_3) δ 15.0.

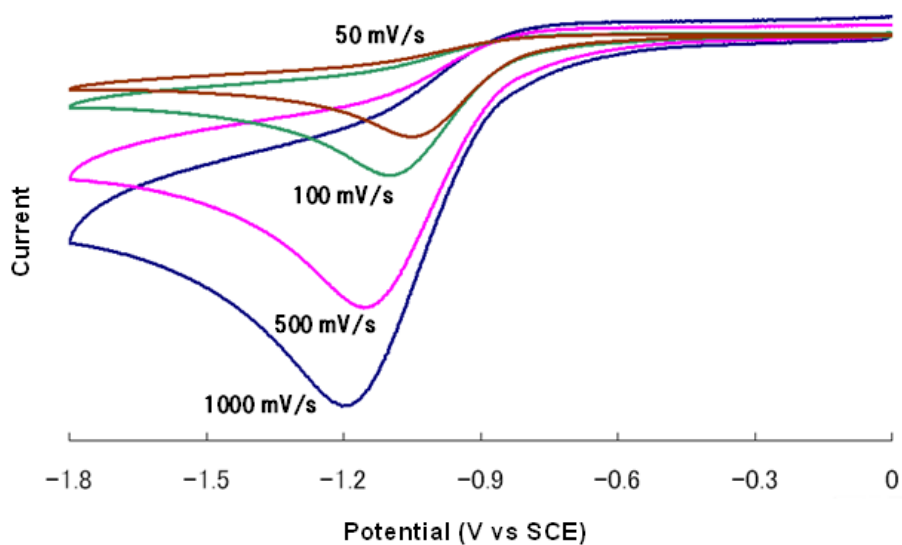


Figure S1. Cyclic voltammograms of oxygen in the presence of **1a**, measured in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{acetonitrile}$ with GC disk working electrode at various scan rate.

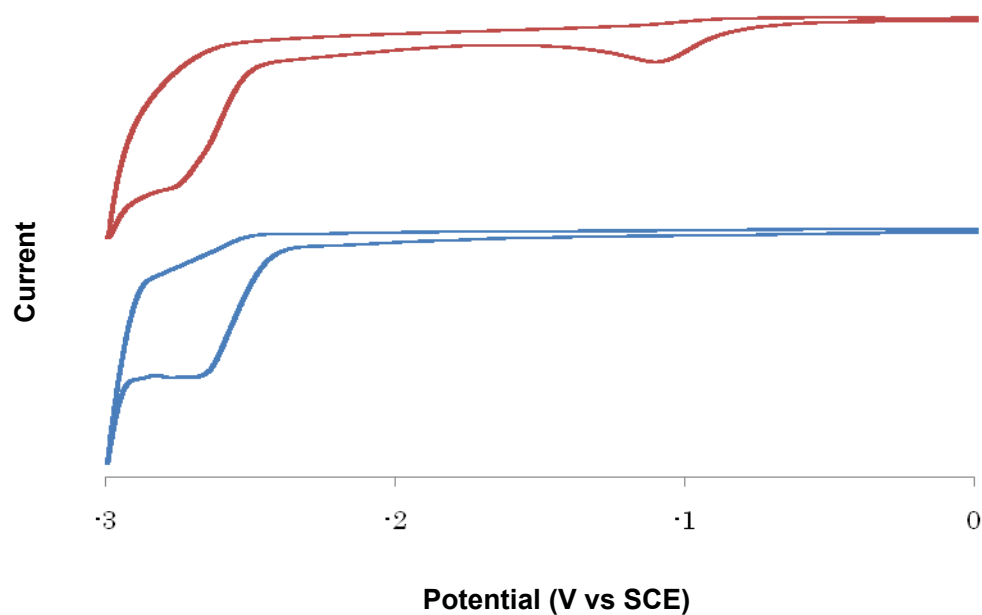


Figure S2. Cyclic voltammograms of 4-(methylthio)phenylboronic acid **1a** in the presence (upper) and absence (lower) of oxygen, measured in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{acetonitrile}$ with GC disk working electrode at 100 mV/s.

Reference

1. E. Nomura, A. Hosoda, H. Mori, H. Taniguchi, *Green Chemistry*, 2005, **7**, 863.