

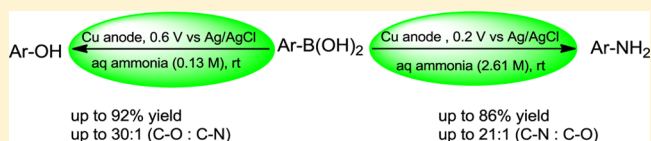
# Electrochemical Technique and Copper-Promoted Transformations: Selective Hydroxylation and Amination of Arylboronic Acids

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**S** Supporting Information

**ABSTRACT:** An efficient and selective electrochemical synthesis of phenols and anilines from arylboronic acids in aqueous ammonia is achieved in an undivided cell. By simply changing the concentration of aqueous ammonia and the anode potential, good yields of phenols and anilines can be obtained chemoselectively with high reaction rates. We propose that anodic oxidation could have played an important role in these transformations.



## INTRODUCTION

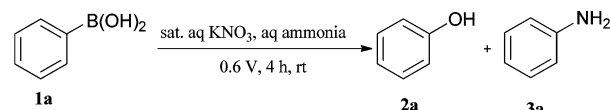
In recent years, the application of electrochemical methods to organic synthesis has received significant attention from industry and research centers worldwide, not only because electrochemical synthesis is an efficient approach to organic transformations, but also because it is a promising green method for organic synthesis.<sup>1</sup> In addition, the current and the potential of the reaction system can be easily controlled. “Constant current” reactions are commonly employed because of their high efficiencies and simple setup, while “controlled potential” reactions are preferred when selectivity is the primary concern.<sup>2</sup>

The preparation of phenols and anilines has attracted increasing attention because they are widely employed in the synthesis of natural products, materials, and biological and pharmaceutical compounds. For instance, conversion of arylboronic acids to phenols and anilines has been developed for several years,<sup>3</sup> and copper-catalyzed transformations have been recently reported.<sup>4</sup> As a consequence of our interest in the application of electrochemical methods to organic synthesis,<sup>5</sup> herein we report a highly efficient electrochemical hydroxylation and amination of arylboronic acids in aqueous ammonia. By changing the concentration of aqueous ammonia and the anode potential, phenols and arylamines were obtained chemoselectively in good yields at room temperature. Compared to reported methods, the electrochemical reactions proceeded in high rates, and no alkali base, ligand, and organic solvent were necessary.

## RESULTS AND DISCUSSION

In a one-compartment cell, Cu foils (1.5 cm<sup>2</sup> each) were chosen as the anode, and cathode and a Ag/AgCl electrode served as the reference electrode. Studies were initiated in an aqueous solution of saturated KNO<sub>3</sub> (10 mL) and 48 μL of 25% NH<sub>3</sub> (aq, final concentration of NH<sub>3</sub> 0.065 M) under a constant potential (0.6 V<sup>6</sup> vs Ag/AgCl) at room temperature (entry 1, Table 1). The electrolysis was stopped upon the complete conversion of phenylboronic acid (4 h). The composition of the crude product was determined by <sup>1</sup>H

**Table 1. Optimization of the Reaction Conditions for the Electrochemical Hydroxylation of Phenylboronic Acid<sup>a</sup>**



entry	anode—cathode	conditions	product composition <sup>b</sup> (%)	
			2a	3a
1	Cu—Cu	NH <sub>3</sub> (aq) (0.065 M)	70	3
2	Cu—Cu	NH <sub>3</sub> (aq) (0.13 M)	92	4
3	Cu—Cu	NH <sub>3</sub> (aq) (0.25 M)	65	18
4 <sup>c</sup>	Cu—Cu	NH <sub>3</sub> (aq) (0.13 M)	84	3
5 <sup>d</sup>	Cu—Cu	NH <sub>3</sub> (aq) (0.13 M)	81	5
6	Cu—Cu	NH <sub>3</sub> (aq) (1.45 M)	10	70

<sup>a</sup>Phenylboronic acid (1.0 mmol) in satd aq KNO<sub>3</sub> (10 mL) was electrolyzed at a constant potential in an undivided cell equipped with a pair of copper electrodes (1.5 cm<sup>2</sup>), Ag/AgCl as the reference electrode at rt, 4 h, air. <sup>b</sup>The product composition was determined by <sup>1</sup>H NMR spectroscopy. Benzene (<5%) was observed by GC analysis. <sup>c</sup>Potential of 0.8 V. <sup>d</sup>Potential of 0.3 V.

NMR spectroscopy to give a yield of 70% for phenol and 3% for aniline.<sup>7</sup> When the concentration of NH<sub>3</sub>(aq) was raised to 0.13 M (entry 2, Table 1, condition A), the yield of phenol improved to 92% with 4% aniline as a byproduct. However, a further increase of the concentration of NH<sub>3</sub>(aq) resulted in a decrease of phenol and an increase of aniline (entry 3, Table 1). This indicated that the concentration of NH<sub>3</sub>(aq) had a significant effect on the reaction efficiency and chemoselectivity. Studies on the effect of the anode potential (entries 4 and 5, Table 1) showed that an increase or decrease of the anode potential resulted in a decrease in the yield of phenol and a slight change of the ratio of 2a to 3a.

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It was interesting to observe that the yield of aniline<sup>7</sup> rose significantly to 70% when the concentration of NH<sub>3</sub>(aq) increased to 1.45 M (entry 6, Table 1). By modulating the potential and ammonia concentration, it was found that 0.2 V<sup>6</sup> vs Ag/AgCl and 2.61 M NH<sub>3</sub>(aq) (condition B) were the best conditions for the synthesis of aniline with 86% yield in 2 h (Table 2). Thus, the optimized reaction conditions of phenol

**Table 2. Optimization of the Reaction Conditions for the Electrochemical Amination of Phenylboronic Acid<sup>a</sup>**

entry	anode–cathode	conditions	product composition <sup>b</sup> (%)	
			2a	3a
1	Cu–Cu	NH <sub>3</sub> (aq) (1.45 M)	12	72
2	Cu–Cu	NH <sub>3</sub> (aq) (2.61 M)	8	86
3	Cu–Cu	NH <sub>3</sub> (aq) (3.57 M)	12	84
4 <sup>c</sup>	Cu–Cu	NH <sub>3</sub> (aq) (2.61 M)	8	82
5 <sup>d</sup>	Cu–Cu	NH <sub>3</sub> (aq) (2.61 M)	13	82

<sup>a</sup>Phenylboronic acid (1.0 mmol) in satd aq KNO<sub>3</sub> (8 mL) was electrolyzed at a constant potential in an undivided cell equipped with a pair of copper electrodes (1.5 cm<sup>2</sup>), Ag/AgCl as the reference electrode at rt, 2 h, air. <sup>b</sup>The product composition was determined by <sup>1</sup>H NMR spectroscopy. Benzene (<5%) was observed by GC analysis. <sup>c</sup>Potential of 0.1 V. <sup>d</sup>Potential of 0.3 V.

and aniline were established. It was noted that oligomeric, polymeric, biphenyl and N,O-diarylated products were not detected in both conditions A and B. Copper consumptions at the anode were 25 and 60 mmol % for conditions A and B, respectively, based on arylboronic acid.<sup>8</sup>

Subsequently, a variety of boronic acids were examined to generate the hydroxylation and amination products under the optimized conditions. The results are summarized in Tables 3 (2a–2k) and 4 (3a–3j).<sup>9</sup> Substituted aromatic boronic acids bearing electron-deficient or electron-rich groups were converted to the corresponding phenols and aromatic amines smoothly with good yields and good chemoselectivities. For instance, *p*-cyanophenol was obtained in 90% yield and the 2b:3b selectivity was 30:1 under condition A, and *p*-cyanoaniline was obtained in 82% yield and the 3b:2b selectivity was 21:1 under condition B. Functional groups which are easily reduced or oxidized, such as cyano, nitro, methylthio, and aldehyde, were tolerated in these mild electrochemical processes.<sup>1d,3a</sup> Due to the formation of protodeboronation byproducts,<sup>10</sup> slightly lower yields (ranging from 71% to 80%) were obtained for *p*-(methylthio)-phenylboronic acid and 1-naphthylboronic acid. 2,6-Dimethylphenylboronic acid and *p*-*tert*-butylphenylboronic acid afforded the products with lower yields because of steric hindrance. The results for the aliphatic boronic acid were significantly different from those for cyclohexanol. Cyclohexanol was obtained exclusively in 35% yield when the concentration of NH<sub>3</sub>(aq) was increased to 10.2 M at a constant potential of 0.6 V vs Ag/AgCl, and cyclohexylamine could not be obtained at any concentration of NH<sub>3</sub>(aq) at 0.2 V vs Ag/AgCl or 0.6 V vs Ag/AgCl. Both conditions A and B were inapplicable to the heteroarylboronic acids and primary alkylboronic acids.

**Table 3. Copper-Promoted Electrochemical Hydroxylation of Boronic Acids in Aqueous Ammonia Solution<sup>a,b</sup>**

2a 92%	2b 90%	2c 85%	2d 83%
2a:3a 23:1	2b:3b 30:1	2c:3c 21:1	2d:3d 19:1
2e 82%	2f 85%	2g 70%	2h 72%
2e:3e 30:1	2f:3f 22:1	2g:3g 10:1	2h:3h 13:1
2i 70%	2j 77%	2k <sup>c</sup> 35%	
2i:3i 9:1	2j:3j 15:1	2k:3k 100:0	

<sup>a</sup>Condition A: boronic acids (1.0 mmol), satd aq KNO<sub>3</sub> (10 mL) with 25% aqueous ammonia (0.13 M), copper electrodes (1.5 cm<sup>2</sup>), Ag/AgCl as the reference electrode, constant potential (0.6 V), an undivided cell, air, 4 h, rt. <sup>b</sup>The selectivity was determined by crude <sup>1</sup>H NMR. <sup>c</sup>Satd KNO<sub>3</sub> (2 mL), 25% aqueous ammonia (8 mL).

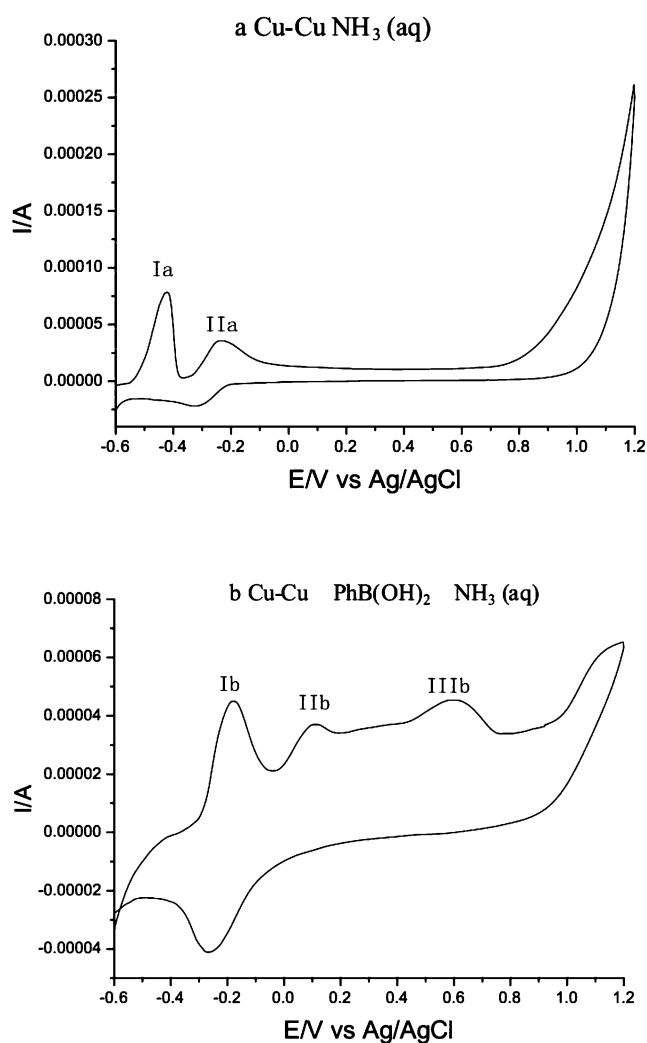
**Table 4. Copper-Promoted Electrochemical Amination of Boronic Acids in Aqueous Ammonia Solution<sup>a,b</sup>**

3a 86%	3b 82%	3c 81%	3d 70%
3a:2a 11:1	3b:2b 21:1	3c:2c 15:1	3d:2d 10:1
3e 80%	3f 85%	3g 73%	3h 73%
3e:2e 20:1	3f:2f 20:1	3g:2g 10:1	3h:2h 11:1
3i 79%	3j 70%		
3i:2i 15:1	3j:2j 12:1		

<sup>a</sup>Condition B: boronic acids (1.0 mmol), satd aq KNO<sub>3</sub> (8 mL) with 25% aqueous ammonia (2.61 M), copper electrodes (1.5 cm<sup>2</sup>), Ag/AgCl as the reference electrode, constant potential (0.2 V), an undivided cell, air, 2 h, rt. <sup>b</sup>The selectivity was determined by crude <sup>1</sup>H NMR.

Further studies were carried out using cyclic voltammetry (CV) measurements and control reactions for the transformations of phenylboronic acid to phenol and aniline, respectively.<sup>11</sup>

Figure 1 shows the CV diagrams of solutions obtained from condition A for the synthesis of phenol. CV curves a and b were recorded on the solutions, which were taken up from the reaction mixtures when the electrolysis had proceeded for 10 min. In solution a, phenylboronic acid was not added and two oxidative waves were observed (Figure 1a), which corre-



**Figure 1.** Cyclic voltammograms of the solutions from condition A and its control: (a) without PhB(OH)<sub>2</sub>; (b) with PhB(OH)<sub>2</sub>. Solutions were taken from the cell after the electrolysis had proceeded for 10 min. The cyclic voltammograms were recorded at a scan rate of 40 mV s<sup>-1</sup> at rt with two platinum electrodes.

sponded to the oxidation of copper species from Cu<sup>0</sup> to Cu<sup>I</sup> at -0.45 V vs Ag/AgCl (peak Ia) and from Cu<sup>I</sup> to Cu<sup>II</sup> at -0.20 V vs Ag/AgCl (peak IIa), respectively. In contrast with curve b from the solution with phenylboronic acid, three oxidative waves were observed with one more oxidative peak at a potential in the vicinity of 0.59 V vs Ag/AgCl (peak IIIb).<sup>12</sup> The additional wave (peak IIIb) might be associated with the formation of a new reaction intermediate derived from phenylboronic acid.

Other control reactions for phenol transformation were carried out (Table 5). Without aqueous ammonia, a 40% yield of phenol was obtained after electrolysis for 4 h, and a trace amount of benzene could be detected (entry 1, Table 5). The composition of the crude product (2a, 3a, and 5a) was determined by <sup>1</sup>H NMR spectroscopy. The yield of benzene was determined by GC analysis. Conducting the reaction under a N<sub>2</sub> atmosphere did not yield any phenol or aniline, and 8% benzene could be detected (entry 2, Table 5). The solution was colorless throughout the electrolysis, and the deposition of Cu<sup>0</sup> on the cathode was observed. This suggests that that, in the absence of air, Cu<sup>I</sup> could not be oxidized to Cu<sup>II</sup>,<sup>13</sup> and the

reaction of phenyl-Cu<sup>I</sup> complex leading to phenol could not occur. We also attempted the reaction under a N<sub>2</sub> atmosphere without adding NH<sub>3</sub>(aq), and no phenol, aniline, and benzene were observed. When the Cu foils were replaced with Pt foils, only trace conversion of the starting material to phenol (5%) and benzene (15%) was observed (entry 3, Table 5). By adding Cu<sub>2</sub>O powder into the anode chamber (to avoid reducing copper cation on the platinum cathode), the yield of phenol reached 82% with 8% aniline (entry 4, Table 5). Under nonelectrochemical conditions (entries 5–7),<sup>14</sup> Cu<sub>2</sub>O, Cu powder, and CuSO<sub>4</sub> were employed, and the yields and selectivities were inferior to those under electrochemical conditions.

Figure 2 shows the CV studies for the solutions under condition B. Similar results of CV measurements were obtained as shown in Figure 2.<sup>15</sup> Peak Ia and peak Ib were attributed to the Cu<sup>0</sup>/Cu<sup>I</sup> redox couple, while peak IIa and peak IIb were attributed to the Cu<sup>I</sup>/Cu<sup>II</sup>. Similarly, a third peak IIIb could be observed in the presence of phenylboronic acid.

For the electrochemical amination of arylboronic acids, similar control reactions were carried out. The reaction conducted under a N<sub>2</sub> atmosphere was similar to that of the electrochemical hydroxylation, with benzene as the only product (15%) (entry 1, Table 6). The solution was colorless during the electrolysis for 2 h. This suggests that oxygen is essential in the electrochemical amination reaction. All other control reactions (entries 2–6, Table 6)<sup>16</sup> exhibited results similar to those in Table 5. The results of the control reactions in Tables 5 and 6 showed that anodic oxidation improves the efficiency of the redox cycle of copper species.

## CONCLUSION

In conclusion, an efficient and selective electrosynthesis of phenols and arylamines from arylboronic compounds in aqueous ammonia has been developed. Undivided-cell equipment and rough metals were used, and the reactions were carried out in readily available electrolytes. By simply changing the concentration of ammonia and the potential, phenols and arylamines were obtained selectively with high reaction rates. CV studies and control reactions were performed to show that anodic oxidation improves the efficiency of the redox cycle of copper species.

## EXPERIMENTAL SECTION

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

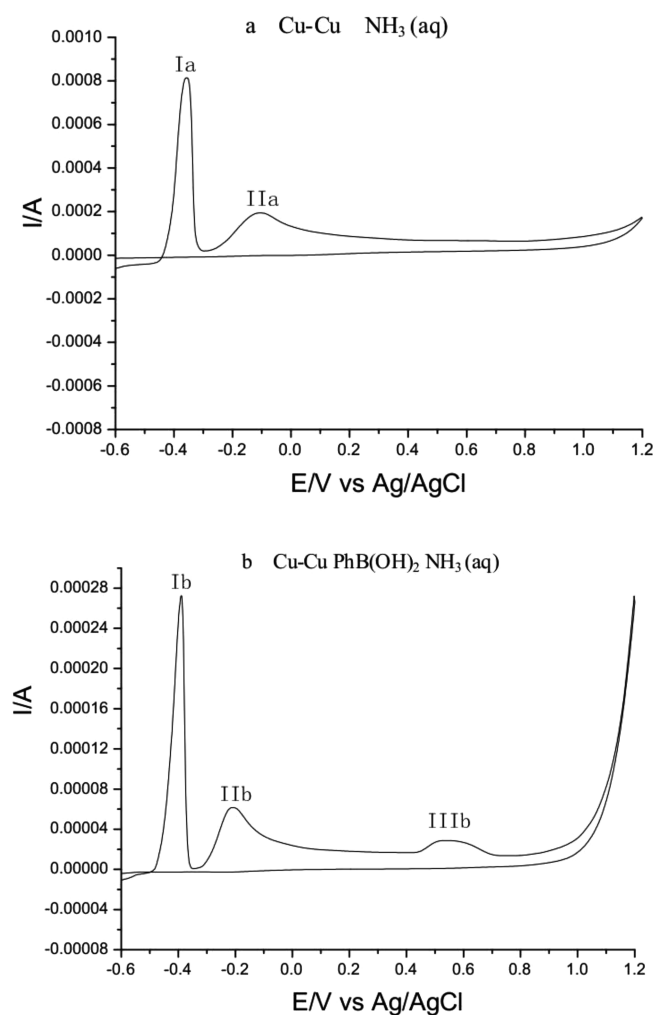
Electrolysis and cyclic voltammetric (CV) experiments were carried out in a classical three-electrode cell in the presence of a supporting electrolyte. Both the anodic electrode and the cathodic electrode were copper foils (99.9%), while a Ag/AgCl electrode was used as the reference electrode in the electrolysis experiments. In the CV experiments, a platinum disk electrode (*d* = 2 mm) and a platinum wire electrode (*d* = 0.2 mm) were employed as the anodic electrode and cathodic electrode, respectively. A Ag/AgCl electrode was used as the reference electrode in the CV experiments. Analytical thin-layer chromatography (TLC) plates and the silica gel for column chromatography were commercially available.

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) and carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectroscopies were performed on 400 MHz NMR spectrometers. Chemical shifts of <sup>1</sup>H NMR spectra are reported in units of parts per million downfield from SiMe<sub>4</sub> ( $\delta$  0.0) and relative to the signal of chloroform-*d* ( $\delta$  7.264, singlet). Multiplicities are given as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), etc. The number of protons (*n*) for a given resonance is indicated by *n*H.

Table 5. Control Reactions for the Electrochemical Hydroxylation of Phenylboronic Acid<sup>a</sup>

entry	anode– cathode	conditions	product composition <sup>b</sup> (%)				
			1a	2a	3a	4a	5a
1	Cu–Cu	no NH <sub>3</sub> (aq)	10	40	0	trace	20
2	Cu–Cu	NH <sub>3</sub> (aq) (0.13 M), N <sub>2</sub>	85	0	0	8	0
3 <sup>c</sup>	Pt–Pt	NH <sub>3</sub> (aq) (0.13 M)	70	5	0	15	0
4 <sup>d</sup>	Pt–Pt	NH <sub>3</sub> (aq) (0.13 M), Cu <sub>2</sub> O (12.5 mmol %)	0	82	8	trace	0
5 <sup>e</sup>		NH <sub>3</sub> (aq) (0.13 M), Cu <sub>2</sub> O (12.5 mmol %)	20	45	16	10	0
6 <sup>e</sup>		NH <sub>3</sub> (aq) (0.13 M), Cu powder (25 mmol %)	25	42	12	13	0
7 <sup>e</sup>		NH <sub>3</sub> (aq) (0.13 M), CuSO <sub>4</sub> (25 mmol %)	22	53	4	15	0

<sup>a</sup>Standard conditions: phenylboronic acid (1.0 mmol) in satd aq KNO<sub>3</sub> (10 mL), 25% aqueous ammonia. <sup>b</sup>The product composition was determined by <sup>1</sup>H NMR spectroscopy. The yield of benzene was determined by GC analysis. <sup>c</sup>The solution was electrolyzed at a constant potential of 0.6 V vs Ag/AgCl in an undivided cell. Two platinum electrodes (1.5 cm<sup>2</sup>). <sup>d</sup>Electrolyzed at a constant potential of 0.6 V vs Ag/AgCl in a divided cell with a salt bridge connecting the anode chamber and the cathode chamber. Anode chamber: phenylboronic acid (1.0 mmol) in satd aq KNO<sub>3</sub> (10 mL), 25% aqueous ammonia. Cathode chamber: satd aq KNO<sub>3</sub> (10 mL). Two platinum foils (1.5 cm<sup>2</sup>). <sup>e</sup>Phenylboronic acid was added after the copper catalyst was completely dissolved in the ammonia solution.



**Figure 2.** Cyclic voltammograms of the solutions from condition B and its control: (a) without PhB(OH)<sub>2</sub>; (b) with PhB(OH)<sub>2</sub>. Solutions were taken from the cell after the electrolysis had proceeded for 10 min. The cyclic voltammograms were recorded at a scan rate of 40 mV s<sup>-1</sup> at rt with two platinum electrodes.

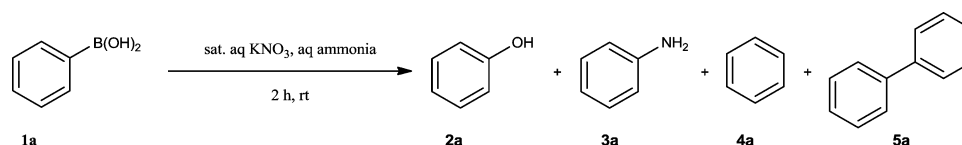
Carbon nuclear magnetic resonance spectra (<sup>13</sup>C NMR) are reported as units of parts per million downfield from SiMe<sub>4</sub> ( $\delta$  0.0) and relative to the signal of chloroform-*d* ( $\delta$  77.03, triplet).

**General Procedure for the Hydroxylation of Phenylboronic Acid.** To a 25 mL round-bottom flask cell were added saturated aqueous KNO<sub>3</sub> solution (10 mL) and 96  $\mu$ L of 25% NH<sub>3</sub>(aq) (final concentration of NH<sub>3</sub> 0.13 M). Then phenylboronic acid (1.0 mmol) was dissolved in the above mixture. The resulting solution was equipped with a pair of copper electrodes (1.5 cm<sup>2</sup>) as the anodic and cathodic electrodes. A Ag/AgCl electrode was used as the reference electrode. To control the current at about 1.5 mA, a 6 k $\Omega$  resistance was added in the cathode loop.<sup>17</sup> The solution was electrolyzed at a constant potential (0.6 V vs Ag/AgCl) at ambient temperature (25–30 °C) until phenylboronic acid was completely consumed (monitored by TLC, 4 h, 0.23 F mol<sup>-1</sup>). The reaction mixture was extracted with ethyl acetate (2  $\times$  15 mL). The combined organic extracts were washed with 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 colorless solid (2a, 86 mg, 92%).

**General Procedure for the Amination of Phenylboronic Acid.** To a 25 mL round-bottom flask cell were added saturated aqueous KNO<sub>3</sub> solution (8 mL) and 1.92 mL of 25% NH<sub>3</sub>(aq) (final concentration of NH<sub>3</sub> 2.61 M). Then phenylboronic acid (1.0 mmol) was dissolved in the above mixture. The resulting solution was equipped with a pair of copper electrodes (1.5 cm<sup>2</sup>) as the anodic and cathodic electrodes. A Ag/AgCl electrode was used as the reference electrode. To control the current at about 2.5 mA, a 3 k $\Omega$  resistance was added in the cathode loop.<sup>17</sup> The solution was electrolyzed at a constant potential (0.2 V vs Ag/AgCl) at ambient temperature (25–30 °C) until phenylboronic acid was completely consumed (monitored by TLC, 2 h, 0.18 F mol<sup>-1</sup>). The reaction mixture was extracted with ethyl acetate (2  $\times$  15 mL). The combined organic extracts were washed with 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, 3:1), and the corresponding aniline was obtained as a colorless oil (3a, 81 mg, 86%).

**Data for phenol (2a):**<sup>4g</sup> yield 86 mg, 92%; colorless solid;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 5.65 (s, 1 H), 6.82 (d, *J* = 8.0 Hz, 2 H), 6.91 (t, *J* = 8.0 Hz, 1 H), 7.21 (t, *J* = 8.0 Hz, 2 H);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 115.5, 121.1, 129.9, 155.3.

**Data for 4-hydroxybenzonitrile (2b):**<sup>4j</sup> yield 107 mg, 90%; yellow solid;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 6.95 (d, *J* = 8.4 Hz, 2 H),

Table 6. Control Reactions for the Electrochemical Amination of Phenylboronic Acid<sup>a</sup>

entry	anode– cathode	conditions	product composition <sup>b</sup> (%)				
			1a	2a	3a	4a	5a
1	Cu–Cu	NH <sub>3</sub> (aq) (2.61 M), N <sub>2</sub>	80	0	0	15	0
2 <sup>c</sup>	Pt–Pt	NH <sub>3</sub> (aq) (2.61 M)	65	6	0	25	0
3 <sup>d,e</sup>	Pt–Pt	NH <sub>3</sub> (aq) (2.61 M), Cu <sub>2</sub> O (30 mmol %)	0	20	70	trace	0
4 <sup>e</sup>		NH <sub>3</sub> (aq) (2.61 M), Cu <sub>2</sub> O (30 mmol %)	20	10	44	18	0
5 <sup>e</sup>		NH <sub>3</sub> (aq) (2.61 M), Cu powder (60 mmol %)	15	5	50	20	0
6 <sup>e</sup>		NH <sub>3</sub> (aq) (2.61 M), CuSO <sub>4</sub> (60 mmol %)	35	15	15	25	0

<sup>a</sup>Phenylboronic acid (1.0 mmol) in satd aq KNO<sub>3</sub> (8 mL) with 25% aqueous ammonia. <sup>b</sup>The product composition was determined by <sup>1</sup>H NMR spectroscopy. The yield of benzene was determined by GC analysis. <sup>c</sup>The solution was electrolyzed at a constant potential of 0.2 V vs Ag/AgCl in an undivided cell. Two platinum foils (1.5 cm<sup>2</sup>). <sup>d</sup>The solution was electrolyzed at a constant potential of 0.2 V vs Ag/AgCl in a divided cell with a salt bridge connecting the anode chamber and the cathode chamber. Anode chamber: phenylboronic acid (1.0 mmol) in satd aq KNO<sub>3</sub> (8 mL), 25% aqueous ammonia. Cathode chamber: satd aq KNO<sub>3</sub> (10 mL). Two platinum foils (1.5 cm<sup>2</sup>). <sup>e</sup>Phenylboronic acid was added after the copper catalyst was dissolved in the ammonia solution.

7.21 (s, 1 H), 7.55 (d, *J* = 8.8 Hz, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 102.8, 116.7, 119.5, 134.5, 160.7.

**Data for 3-nitrophenol (2c):**<sup>4g</sup> yield 118 mg, 85%; pale yellow solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 6.27 (s, 1 H), 7.19–7.22 (m, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 7.72 (t, *J* = 2.0 Hz, 1 H), 7.71–7.79 (m, 1 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 110.7, 116.0, 122.3, 130.5, 149.2, 156.6.

**Data for 4-hydroxybenzaldehyde (2d):**<sup>4g</sup> yield 101 mg, 83%; pale yellow solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.00 (d, *J* = 7.2 Hz, 2 H), 7.17 (s, 1 H), 7.82 (d, *J* = 8.4 Hz, 2 H), 9.83 (s, 1 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 116.3, 129.7, 132.8, 162.3, 191.7.

**Data for 4-chlorophenol (2e):**<sup>3g</sup> yield 105 mg, 82%; white solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 5.40 (s, 1 H), 6.78 (d, *J* = 8.8 Hz, 2 H), 7.20 (d, *J* = 8.8 Hz, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 116.8, 125.9, 129.7, 154.0.

**Data for 4-methoxyphenol (2f):**<sup>3g</sup> yield 105 mg, 85%; colorless solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 3.77 (s, 3 H), 6.76–6.81 (m, 4 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 56.0, 115.0, 116.2, 149.7, 153.8.

**Data for 2,6-dimethylphenol (2g):**<sup>4g</sup> yield 86 mg, 70%; white solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 2.27 (s, 6 H), 4.67 (s, 1 H), 6.78 (t, *J* = 7.2 Hz, 1 H), 7.00 (d, *J* = 7.6 Hz, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 16.0, 120.4, 123.2, 128.8, 152.3.

**Data for 4-tert-butylphenol (2h):** yield 108 mg, 72%; colorless solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 1.30 (s, 9 H), 6.77 (d, *J* = 7.2 Hz, 2 H), 7.26 (d, *J* = 6.8 Hz, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 31.7, 34.2, 114.9, 126.5, 143.6, 153.3.

**Data for 4-(methylthio)phenol (2i):**<sup>3f</sup> yield 98 mg, 70%; yellow solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 2.44 (s, 3 H), 6.78–6.80 (m, 2 H), 7.22–7.24 (m, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 18.3, 116.2, 130.6, 131.0, 154.4.

**Data for naphthalen-1-ol (2j):**<sup>3g</sup> yield 110 mg, 77%; colorless solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 5.51 (s, 1 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 7.35 (t, *J* = 8.0 Hz, 1 H), 7.49–7.57 (m, 3 H), 7.86–7.89 (m, 1 H), 8.23–8.25 (m, 1 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 108.7, 120.7, 121.5, 124.3, 125.3, 125.8, 126.4, 127.7, 134.7, 151.3.

**Data for cyclohexanol (2k):** yield 35 mg, 35%; colorless oil; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 1.11–1.29 (m, 5 H), 1.49–1.52 (m, 1 H), 1.69–1.71 (m, 2 H), 1.84–1.85 (m, 2 H), 2.21 (s, 1 H), 3.53–3.59 (m, 1 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 24.2, 25.5, 35.6, 70.3.

**Data for aniline (3a):**<sup>4f</sup> yield 80 mg, 86%; colorless oil; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 3.46 (s, 2 H), 6.66 (d, *J* = 8.4 Hz, 2 H), 6.76 (t, *J* = 7.6 Hz, 1 H), 7.16 (t, *J* = 8.0 Hz, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 115.1, 118.5, 129.3, 146.4.

**Data for 4-aminobenzonitrile (3b):**<sup>4h</sup> yield 97 mg, 82%; yellow solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.22 (s, 2 H), 6.65 (d, *J* = 7.2 Hz,

2 H), 7.40 (d, *J* = 7.2 Hz, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 100.1, 114.6, 120.3, 133.9, 150.6.

**Data for 3-nitroaniline (3c):**<sup>4j</sup> yield 112 mg, 81%; yellow solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.06 (s, 2 H), 6.98 (d, *J* = 8.0 Hz, 1 H), 7.30 (t, *J* = 8.4 Hz, 1 H), 7.51 (d, *J* = 3.6 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 109.0, 113.1, 120.7, 129.9, 147.5, 149.4.

**Data for 4-aminobenzaldehyde (3d):**<sup>4f</sup> yield 85 mg, 70%; yellow solid; δ<sub>H</sub> (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, Me<sub>4</sub>Si) 7.00–7.04 (m, 2 H), 7.81 (d, *J* = 9.6 Hz, 2 H), 9.85 (s, 1 H); δ<sub>C</sub> (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, Me<sub>4</sub>Si) 117.9, 118.5, 134.2, 136.2, 192.8.

**Data for 4-chloroaniline (3e):**<sup>4h</sup> yield 102 mg, 80%; white solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 3.39 (s, 2 H), 6.77 (m, 2 H), 7.19 (m, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 116.4, 123.4, 129.3, 145.0.

**Data for 4-methoxyaniline (3f):**<sup>4h</sup> yield 104 mg, 85%; colorless oil; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 3.44 (s, 2 H), 3.75 (s, 3 H), 6.65–6.77 (m, 4 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 55.8, 114.9, 116.6, 139.9, 152.9.

**Data for 2,6-dimethylaniline (3g):**<sup>4f</sup> yield 88 mg, 73%; yellow oil; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 2.25 (s, 6 H), 3.57 (s, 2 H), 6.72 (t, *J* = 8.0 Hz, 1 H), 7.02 (d, *J* = 8.0 Hz, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 17.6, 118.0, 121.6, 128.2, 142.7.

**Data for 4-tert-butylaniline (3h):** yield 109 mg, 73%; red solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 1.29 (s, 9 H), 6.66 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 31.7, 34.0, 115.1, 126.2, 141.6, 143.9.

**Data for 4-(methylthio)aniline (3i):** yield 110 mg, 79%; colorless oil; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 2.42 (s, 3 H), 3.52 (s, 2 H), 6.64 (d, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 18.9, 115.9, 126.0, 131.2, 145.2.

**Data for naphthalen-1-amine (3j):**<sup>4j</sup> yield 100 mg, 70%; white solid; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.16 (s, 2 H), 6.80 (d, *J* = 6.8 Hz, 1 H), 7.29–7.36 (m, 2 H), 7.47–7.48 (m, 2 H), 7.83–7.84 (m, 2 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 109.8, 119.1, 120.9, 123.8, 125.0, 126.0, 126.5, 128.7, 134.6, 142.2.

## ■ ASSOCIATED CONTENT

### Supporting Information

Diagram of the experimental device and NMR spectra of the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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- (6) The output potential (0.2 V vs Ag/AgCl and 0.6 V vs Ag/AgCl) was offered by an electrochemical workstation; see the Supporting Information.
- (7) A control reaction was conducted to show that phenol could not be converted to aniline under condition B.
- (8) For the synthesis of phenol, the mass of the anode decreased by ~16.0 mg (0.25 mmol) after the reaction. For the synthesis of aniline, the mass of the anode decreased by ~38.0 mg (0.6 mmol) after the reaction.
- (9) Pinacolyl boronate ester was also suitable for these reactions. For example, phenol and arylamine were obtained from phenylboronic acid pinacol ester in 75% and 70% yield, respectively.
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- (14) Under nonelectrochemical conditions, the following reaction was also studied: After complete conversion of the phenylboronic acid into phenol under standard electrochemical condition A, the solution was used again by just adding phenylboronic acid without power applied. A 65% yield of phenol and 10% yield of aniline were obtained after 9 h.
- (15) In Figure 2, the lines of the voltammograms cross. This is due to the change of the adsorption on the electrode surface during the reverse scan and the increase of the thickness of the electrical double layer, resulting in a decrease of the capacitive current.
- (16) Under nonelectrochemical conditions, the following reaction was also studied: After complete conversion of the phenylboronic acid into aniline under standard electrochemical condition B, the solution was used again by just adding phenylboronic acid without power applied. A 30% yield of phenol and 45% yield of aniline were obtained after 5 h.
- (17) See the Supporting Information for a diagram of the experimental device.