## Transition metal-free electrocatalytic halodeborylation of arylboronic acids with metal halides MX (X = I, Br) to synthesize aryl halides

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**General considerations.** The reagents used for experiments were commercially available and used as received unless otherwise noted. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). Cyclic voltammograms were obtained on a IVIUMSTAT potentiostat. Column chromatography was performed on silica gel 300-400 mesh. The yields reported are the isolated yields and the average of two runs. <sup>1</sup>H and <sup>13</sup>C NMR spectra of all compounds were recorded at 400 and 100 MHz with CDCl<sub>3</sub> as solvent respectively, except for <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound **21a**, **21b** with d<sub>6</sub>-DMSO as solvent. All coupling constants (*J* values) were reported in Herz (Hz). HRMS were performed by Shanghai Mass Spectrometry Centre, Shanghai Institute of Organic Chemistry, CAS (Chinese Academic of Sciences).

## General procedure for metal-free electrocatalytic iodination of arylboronic acids

(A) Procedure A: Arylboronic acid (0.2 mmol), NaI (0.24 mmol, 1.2 equiv) and CH<sub>3</sub>OH/H<sub>2</sub>O (6:4, 10 mL) were combined and added into oven-dried three-necked flask (25 mL) equipped with a stir bar. The flask was equipped with carbon plate (1.5 x 1.5 cm<sup>2</sup>) as the anode and glassy carbon (d = 5 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 40 °C for 2 h. When the reaction was finished, the reaction mixture was diluted with EtOAc and filtered through a short plug of silica gel that was then washed with EtOAc. The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to provide corresponding product.

## General procedure for metal-free electrocatalytic bromination of arylboronic acids

(B) Procedure B: Arylboronic acid (0.2 mmol), NaBr (0.24 mmol, 1.2 equiv),  $nBu_4NOAc$  (0.2 mmol, 1.0 equiv) and CH<sub>3</sub>OH (10 mL) were combined and added into oven-dried three-necked flask (25 mL) equipped with a stir bar. The flask was equipped with carbon plate (1.5 x 1.5 cm<sup>2</sup>) as the anode and glassy carbon (d = 5 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 40 °C for 4 h. When the reaction was finished, the reaction mixture was diluted with EtOAc and filtered through a short plug of silica gel that was then washed with EtOAc. The combined organic phases were concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to provide corresponding product.



**1-Iodo-2,4-dimethoxybenzene (1a)**. Procedure A was followed using 2,4dimethoxyphenylboronic acid (36.4 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 47.5 mg (90%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.62 (d, J = 8.8 Hz, 1 H), 6.43 (d, J = 2.4 Hz, 1 H), 6.32 (dd, J = 2.4, 8.8 Hz, 1 H), 3.85 (s, 3 H), 3.80 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  161.4, 158.9, 139.2, 107.0, 99.3, 74.8, 56.2, 55.5.

**1-Iodo-4-methoxybenzene (2a).** Procedure A was followed using 4methoxyphenylboronic acid (30.4 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 37.4 mg (80%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.56 (d, *J* = 8.8 Hz, 2 H), 6.68 (d, *J* = 8.8 Hz, 2 H), 3.78 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.5, 138.2, 116.4, 82.7, 55.3.

**1-Iodo-2-methoxybenzene (3a).** Procedure A was followed using 2methoxyphenylboronic acid (30.4 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 38.4 mg (82%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.77 (dd, J = 1.2, 7.6 Hz, 1 H), 7.31 (t, J = 8.0 Hz, 1 H), 6.83 (d, J = 8.0 Hz, 1 H), 6.72 (t, J = 7.6 Hz, 1 H), 3.88 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.0, 139.5, 129.5, 122.5, 111.0, 86.0, 56.3.

**1-Iodo-3-methoxybenzene (4a).** Procedure A was followed using 3methoxyphenylboronic acid (30.4 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 41.2 mg (88%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.29 (d, J = 7.6 Hz 1 H), 7.26 (s, 1 H), 7.00 (t, J = 8.0 Hz, 1 H), 6.87 (dd, J = 1.6, 8.4 Hz, 1 H), 3.78 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.1, 130.5, 129.8, 123.0, 113.7, 94.4, 55.4.

**5-Iodo-2-methoxybenzaldehyde (5a)**. Procedure A was followed using 3-formyl-4-methoxyphenylboronic acid (36.0 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 47.7 mg (91%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>3</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.34 (s, 1 H), 8.08 (d, J = 2.4 Hz, 1 H), 7.80 (dd, J = 2.4, 8.8 Hz, 1 H), 6.78 (d, J = 8.8 Hz, 1 H), 3.91 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  188.2, 161.4, 144.1, 137.0, 126.5, 114.1, 82.9, 55.8.

**4-Iodo-***N*,*N***-dimethylaniline (6a)**. Procedure A was followed using 4-(dimethylamino)phenylboronic acid (33.0 mg, 0.2 mmol) and NaI (72 mg, 0.48 mmol, 2.4 equiv). With stirring, the reaction mixture was performed for 1 hour instead of 2 hours. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 36.6 mg (74%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.<sup>4</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d, *J* = 8.8 Hz, 2 H), 6.50 (d, *J* = 8.8 Hz, 2 H), 2.92 (s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.0, 137.5, 114.7, 77.4, 40.4.

**2-Iodoaniline (7a)**. Procedure A was followed using 2-aminophenylboronic acid (27.4 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 37.2 mg (85%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.<sup>5 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.64 (d, J = 8.0 Hz, 1 H), 7.14 (t, J = 8.0 Hz, 1 H), 6.75 (d, J = 8.0 Hz, 1 H), 6.48 (t, J = 8.0 Hz, 1 H), 3.90 (s, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  146.7, 139.0, 129.3, 120.0, 114.7, 84.2.

**4-Iodophenol (8a)**. Procedure A was followed using 4-hydroxyphenylboronic acid (27.6 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 38.3 mg (87%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>6</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 (d, *J* = 8.8 Hz, 2 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 5.00 (s, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.3, 138.4, 117.8, 82.7.

**2,6-Dimethyl-1-iodobenzene (9a).** Procedure A was followed using 2,6-dimethylphenylboronic acid (30.0 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 34.8 mg (75%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.14 (t, *J* = 6.6 Hz, 1 H), 7.07 (d, *J* = 7.6 Hz, 2 H), 2.49 (s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  142.1, 127.6, 126.9, 108.5, 29.8.

**1-Iodo-4-methylbenzene (10a)**. Procedure A was followed using *p*-tolylboronic acid (27.2 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 26.2 mg (61%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.56 (d, *J* = 8.4 Hz, 2 H), 6.93 (d, *J* = 8.0 Hz, 2 H), 2.29 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  137.4, 137.2, 131.2, 90.2, 21.0.

**1-Iodo-2-methylbenzene (11a)**. Procedure A was followed using *o*-tolylboronic acid (27.2 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 29.6 mg (68%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.82 (d, *J* = 7.6 Hz, 1 H), 7.25 (d, *J* = 4.4 Hz, 2 H), 6.90 - 6.86 (m, 1 H), 2.45 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  141.3, 138.9, 129.8, 128.2, 127.4, 101.2, 28.2.

**1-Iodo-4-isopropylbenzene** (12a). Procedure A was followed using 4-isopropylphenylboronic acid (32.8 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 39.9 mg (81%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>7</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.60 (d, J = 8.2 Hz, 2 H), 6.98 (d, J = 8.2 Hz, 2 H), 2.89 - 2.82 (m, 1 H), 1.23 (d, J = 6.8 Hz, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.5, 137.3, 128.6, 90.6, 33.7, 23.8.

**1-Iodonaphthalene** (13a). Procedure A was followed using naphthalen-1ylboronic acid (34.4 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 46.2 mg (91%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.09 (d, J = 8.0 Hz, 2 H), 7.84 (d, J = 8.0 Hz, 1 H), 7.77 (d, J = 8.0 Hz, 1 H), 7.58 (t, J = 6.8 Hz, 1 H), 7.52 (t, J = 6.8 Hz, 1 H), 7.19 (t, J = 7.6 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  137.4, 134.3, 134.1, 132.1, 129.0, 128.5, 127.7, 126.9, 126.7, 99.6.

**4-Iododibenzofuran (14a)**. Procedure A was followed using dibenzo[b,d]furan-4ylboronic acid (42.4 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 51.2 mg (87%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl3):  $\delta$  7.92 (t, *J* = 7.2 Hz, 2 H), 7.81 (d, *J* = 7.6 Hz, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.37 (t, *J* = 7.6 Hz, 1 H), 7.11 (t, *J* = 7.6 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  156.4, 155.6, 135.9, 127.7, 124.5, 124.5, 124.4, 123.1, 121.1, 120.5, 112.1, 75.4. **Iodobenzene (15a)**. Procedure A was followed using phenylboronic acid (24.4 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 24.5 mg (60%) of the product as yellow liquid. Exhibited spectral data in accordance with previous report.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.71 (d, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 7.11 (t, *J* = 8.0 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  137.5, 130.2, 127.4, 94.4.

**1-Bromo-4-iodobenzene** (16a). Procedure A was followed using 4bromophenylboronic acid (40.0 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 47.5 mg (84%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.<sup>8</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.54 (d, *J* = 8.8 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  139.0, 133.4, 122.2, 92.1.

**1-Bromo-2-iodobenzene** (17a). Procedure A was followed using 2bromophenylboronic acid (40.0 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 48.5 mg (86%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl3):  $\delta$  7.86 (dd, J = 1.2, 8.0 Hz, 1 H), 7.62 (dd, J = 1.2, 8.0 Hz, 1 H), 7.21 (td, J = 1.2, 7.6 Hz 1 H), 7.00 (td, J = 1.2, 7.6 Hz 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.3, 132.7, 129.7, 129.4, 128.4, 101.2.

**1-Chloro-4-iodobenzene** (18a). Procedure A was followed using 4chlorophenylboronic acid (31.2 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 32.4 mg (68%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.<sup>9</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.60 (d, J = 8.8 Hz, 2 H), 7.08 (d, J = 8.4 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  138.7, 134.2, 130.5, 91.2.

**1-Chloro-3-iodobenzene** (19a). Procedure A was followed using 3chlorophenylboronic acid (31.2 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 28.1 mg (59%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.72 (s, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.02 (t, J = 8.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  137.1, 135.6, 135.0, 131.0, 128.0, 94.1.

**4-Iodobenzoic acid methyl ester (20a)**. Procedure A was followed using 4-(methoxycarbonyl)phenylboronic acid (36.0 mg, 0.2 mmol) and NaI (108 mg, 0.72 mmol, 3.6 equiv). With stirring, the reaction mixture was performed for 14 hours

instead of 2 hours and constant current 15 mA instead of 10 mA. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 41.9 mg (80%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.79 (d, J = 8.4 Hz, 2 H), 7.73 (d, J = 8.4 Hz, 2 H), 3.90 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  166.6, 137.7, 131.0, 129.5, 100.8, 52.3.

**4-Iodobenzoic acid (21a).** Procedure A was followed using 4-boronobenzoic acid (33.2 mg, 0.2 mmol) and NaI (108 mg, 0.72 mmol, 3.6 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 2 hours and constant current 15 mA instead of 10 mA. The reaction mixture was purified by flash column chromatography on silica gel (15% EtOAc in petroleum ether) to afford 44.6 mg (90%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>10</sup> <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  13.16 (s, 1 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, DMSO):  $\delta$  167.4, 138.0, 131.5, 130.6, 101.7.

**4-Iodobenzonitrile (22a)**. Procedure A was followed using 4-cyanophenylboronic acid (33.2 mg, 0.2 mmol) and NaI (108 mg, 0.72 mmol, 3.6 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 2 hours and constant current 15 mA instead of 10 mA. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 44.0 mg (96%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>7</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.82 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  138.5, 133.2, 118.3, 111.7, 100.4.

**1-Iodo-3-nitrobenzene** (23a). Procedure A was followed using 3nitrophenylboronic acid (33.4 mg, 0.2 mmol) and NaI (108 mg, 0.72 mmol, 3.6 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 2 hours and constant current 15 mA instead of 10 mA. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 47.8 mg (96%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.56 (s, 1 H), 8.20 (d, *J* = 8.0 Hz, 1 H), 8.03 (d, *J* = 7.6 Hz, 1 H), 7.29 (t, *J* = 8.0 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.5, 143.5, 132.4, 130.7, 122.7, 93.5.

**2-Iodobenzofuran (24a)**. Procedure A was followed using benzofuran-2-ylboronic acidacid (32.4 mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 43.4 mg (89%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.54 - 7.46 (m, 2 H), 7.25 - 7.19 (m, 2 H), 6.96 (s, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.2, 129.2, 124.2, 123.1, 119.7, 117.2, 110.8, 95.9.

**3-Iodobenzofuran (25a)**. Procedure A was followed using benzofuran-3-ylboronic acid (32.4mg, 0.2 mmol) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 30.7 mg (63%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>11</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.66 (s, 1 H), 7.50 (d, *J* = 7.6 Hz, 1 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.38 (t, *J* = 6.0 Hz, 1 H), 7.33 (t, *J* = 7.2 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.4, 147.0, 129.6, 125.4, 123.5, 121.3, 111.5, 64.3.

**1-Bromo-4-methoxybenzene (2b)**. Procedure B was followed using 4methoxyphenylboronic acid (30.4 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 34.0 mg (91%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>12</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.38 (d, J = 9.2 Hz, 2 H), 6.79 (d, J = 8.8 Hz, 2 H), 3.78 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.7, 132.2, 115.7, 112.8, 55.4.

**1-Bromo-2-methoxybenzene (3b)**. Procedure B was followed using 2methoxyphenylboronic acid (30.4 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 29.1 mg (78%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>12</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.54 (dd, J = 7.8, 1.4 Hz, 1H), 7.29 (d, J = 6.8 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.84 (td, J = 1.2, 7.8 Hz, 1H), 3.90 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.8, 133.3, 128.5, 121.8, 111.9, 111.6, 56.1.

**5-Bromo-2-methoxybenzaldehyde (5b)**. Procedure B was followed using 3-formyl-4-methoxyphenylboronic acid (36.0 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 38.3 mg (89%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>13</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.37 (s, 1 H), 7.90 (d, J = 2.4 Hz, 1 H), 7.62 (dd, J = 2.4, 8.8 Hz, 1 H), 6.89 (d, J = 8.8 Hz, 1 H), 3.92 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  188.3, 160.7, 138.2, 131.0, 126.1, 113.7, 113.4, 55.9.

**2,6-Dimethyl-1-bromobenzene (9b)**. Procedure B was followed using 2,6-dimethylphenylboronic acid (30.0 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 25.9 mg (70%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>14</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.10 - 7.06 (m, 3 H), 2.43 (s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  138.3, 128.1, 127.6, 126.6, 23.9.

**1-Bromo-4-methylbenzene (10b)**. Procedure B was followed using *p*-tolylboronic acid (27.2 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 26.0 mg (76%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>15</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.37 (d, *J* = 8.4 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 2.31 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  136.7, 131.2, 130.8, 119.0, 20.9.

**1-Bromo-2-methyl benzene (11b)**. Procedure B was followed using *o*-tolylboronic acid (27.2 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 19.2 mg (56%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>14</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (d, *J* = 8.0 Hz, 1 H), 7.25 - 7.16 (m, 2 H), 7.05 (td, *J* = 1.6, 6.8 Hz, 1 H), 2.41 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  137.8, 132.3, 130.8, 127.3, 127.2, 124.9, 22.9.

**1-Bromo-4-isopropylbenzene (12b)**. Procedure B was followed using 4-isopropylphenylboronic acid (32.8 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 33.8 mg (85%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>16</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.40 (d, J = 8.4 Hz, 2 H), 7.10 (d, J = 8.4 Hz, 2 H), 2.91 - 2.84 (m, 1 H), 1.23 (d, J = 6.8 Hz, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  147.8, 131.3, 128.2, 119.3, 33.6, 23.8.

**1-Bromonaphthalene (13b)**. Procedure B was followed using naphthalen-1ylboronic acid (34.4 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 38.1 mg (92%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.<sup>14</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 8.34 (d, J = 8.4 Hz, 1 H), 7.88 - 7.83 (m, 3 H), 7.66 (td, J = 1.2, 7.2 Hz, 1 H), 7.58 (td, J = 1.2, 8.0 Hz, 1 H), 7.35 (t, J = 8.0 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  134.7, 132.1, 130.0, 128.4, 128.0, 127.4, 127.2, 126.8, 126.2, 122.9.

**4-Bromodibenzofuran** (14b). Procedure B was followed using dihydrodibenzo[b,d]furan-4-ylboronic acid (42.8 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 44.5 mg (90%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>17</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.93 (d, J = 7.6 Hz, 1 H), 7.88 (dd, J = 1.2, 8.0 Hz, 1 H), 7.66 (d, J = 8.4 Hz, 1 H), 7.61 (dd, J = 1.2, 8.0 Hz, 1 H), 7.50 (td, J = 1.2, 8.4 Hz 1 H), 7.38 (t, J = 8.0 Hz 1 H), 7.23 (t, J = 8.0 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  156.0, 153.2, 130.0, 127.8, 125.7, 124.1, 123.9, 123.2, 121.0, 119.6, 112.1, 104.4.

**Bromobenzene (15b)**. Procedure B was followed using phenylboronic acid (24.4 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 4 hours. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 15.7 mg (50%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>13</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.50 (d, J = 7.2 Hz, 2H), 7.28 (d, J = 6.8 Hz, 1H), 7.24 (d, J = 7.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  131.5, 130.0, 126.9, 122.5.

**1,4-Dibromobenzene** (16b). Procedure B was followed using 4bromophenylboronic acid (40.2 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 4 hours. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 42.0 mg (89%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>14</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  133.1, 121.0.

**1,2-Dibromobenzene** (17b). Procedure B was followed using 2bromophenylboronic acid (36.0 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 4 hours. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 37.3 mg (79%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>18</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.64 - 7.60 (m, 2 H), 7.19 - 7.15 (m, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 133.7, 128.5, 124.8.

**1-Bromo-4-chlorobenzene** (18b). Procedure B was followed using 4-chlorophenylboronic acid (31.2 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 4 hours. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 30.2 mg (79%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>14</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.42 (d, *J* = 8.8 Hz, 2 H), 7.21 (d, *J* = 8.8 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  133.2, 132.7, 130.2, 120.2.

**1-Bromo-3-chlorobenzene** (19b). Procedure B was followed using 3-chlorophenylboronic acid acid (31.2 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 4 hours. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 26.7 mg (70%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>19</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (s, 1 H), 7.39 (d, *J* = 8.0 Hz, 1 H), 7.29 (d, *J* = 8.0 Hz, 1 H), 7.17 (t, *J* = 8.0 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  135.2, 131.5, 130.7, 129.8, 127.3, 122.8.

**4-Bromo-benzoic acid methyl ester (20b)**. Procedure B was followed using 4methoxycarbonylphenylboronic acid (36.0 mg, 0.2 mmol) and NaBr (74.1 mg, 0.72 mmol, 3.6 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 4 hours and constant current 30 mA instead of 10 mA. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 36.6 mg (85%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>12</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.89 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 8.8 Hz, 2 H), 3.90 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  166.3, 131.7, 131.1, 129.0, 128.0, 52.2.

**4-Bromobenzoic** acid (21b). Procedure В was followed using 4methoxycarbonylphenylboronic acid (36.0 mg, 0.2 mmol) and NaBr (74.1 mg, 0.72 mmol, 3.6 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 4 hours and constant current 30 mA instead of 10 mA. The reaction mixture was purified by flash column chromatography on silica gel (15% EtOAc in petroleum ether) to afford 37.4 mg (93%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>10</sup> <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  13.20 (s, 1 H), 7.87 (d, J = 7.2 Hz, 2 H), 7.70 (d, J = 7.2 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, DMSO):  $\delta$ 167.0, 132.1, 131.7, 130.5, 127.3.

**4-Bromobenzonitrile** (22b). Procedure B was followed using 4cyanophenylboronic acid (29.4 mg, 0.2 mmol) and NaBr (74.1 mg, 0.72 mmol, 3.6 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 4 hours and constant current 30 mA instead of 10 mA. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 29.8 mg (82%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>12</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.63 (d, *J* = 8.4 Hz, 2 H), 7.52 (d, *J* = 8.4 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  133.4, 132.6, 128.0, 118.0, 111.2.

**1-Bromo-3-nitrobenzene** (23b). Procedure B was followed using 3nitrophenylboronic acid (33.4 mg, 0.2 mmol) and NaBr (74.1 mg, 0.72 mmol, 3.6 equiv). With stirring, the reaction mixture was performed for 14 hours instead of 4 hours and constant current 30 mA instead of 10 mA. The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 33.0 mg (82%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.<sup>12</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.37 (s, 1 H), 8.17 (d, *J* = 8.4 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.44 (t, *J* = 8.4 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.7, 137.6, 130.6, 126.7, 122.8, 122.1.

**3-Bromobenzofuran (25b)**. Procedure B was followed using benzofuran-3-ylboronic acid (32.4 mg, 0.2 mmol) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford 33.5 mg (85%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>20</sup> <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>):  $\delta$  7.66 (s, 1 H), 7.57 (d, J = 7.2 Hz, 1 H), 7.51 (d, J = 8.0 Hz, 1 H), 7.39 - 7.32 (m, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.4, 142.6, 127.1, 125.4, 123.4, 119.8, 111.7, 97.9.

The procedure for metal-free electrocatalytic iodination of alkylboronic acids **26.** Phenethylboronic acid (30.0 mg, 0.2 mmol), NaI (36 mg, 0.24 mmol, 1.2 equiv) and CH<sub>3</sub>OH/H<sub>2</sub>O (6:4, 10 mL) were combined and added into oven-dried three-necked flask (25 mL) equipped with a stir bar. The flask was equipped with carbon plate (1.5 x 1.5 cm<sup>2</sup>) as the anode and glassy carbon (d = 5 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 40 °C for 4 h. When the reaction was finished, the reaction mixture was diluted with EtOAc and filtered through a short plug of silica gel that was then washed with EtOAc. The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel (petroleum ether) to afford 21.8 mg (47%) of the product **26a** as colorless liquid. Exhibited spectral data in accordance with previous report.<sup>21 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.33 (t, *J* = 6.8 Hz, 2 H), 7.28 (d, *J* = 7.2 Hz, 1 H), 7.20 (d, *J* = 6.8 Hz, 2 H), 3.36 (t, *J* = 7.8 Hz, 2 H), 3.19 (t, *J* = 7.8 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.6, 128.6, 128.3, 126.8, 40.3, 5.6.

The procedure for metal-free electrocatalytic bromination of alkylboronic acids 26. Phenethylboronic acid (30.0 mg, 0.2 mmol), NaBr (24.7 mg, 0.24 mmol, 1.2 equiv), *n*Bu<sub>4</sub>NOAc (0.2 mmol) and CH<sub>3</sub>OH (10 mL) were combined and added into oven-dried three-necked flask (25 mL) equipped with a stir bar. The flask was equipped with carbon plate (1.5 x 1.5 cm<sup>2</sup>) as the anode and glassy carbon (d = 5 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 40 °C for 4 h. When the reaction was finished, the reaction mixture was diluted with EtOAc and filtered through a short plug of silica gel that was then washed with EtOAc. The combined organic phases were concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel (petroleum ether) to afford 18.5 mg (50%) of the product **26b** as a colorless liquid. Exhibited spectral data in accordance with previous report.<sup>22</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.34 (t, *J* = 7.2 Hz, 2 H), 7.28 (d, *J* = 6.8 Hz, 1 H), 7.22 (d, *J* = 6.8 Hz, 2 H), 3.58 (t, *J* = 7.6 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  138.9, 128.7, 128.6, 126.9, 39.4, 33.0.

**Gram-scale** synthesis of 1-iodo-2,4-dimethoxybenzene 1a. 2,4-Dimethoxyphenylboronic acid (5.0 mmol), NaI (6 mmol) and MeOH/H<sub>2</sub>O (6:4, 250 mL) were combined and added into an oven-dried three-necked flask (500 mL) with a stir bar. The flask was equipped with carbon plate (1.5 x 1.5 cm<sup>2</sup>) as the anode and glassy carbon (d = 5 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA (The dual display potentiostat was operating in constant current mode) under room temperature for 36 h. When the reaction was finished, the solution was extracted with EtOAc (3 x 150 mL). The combined organic phases were dried with  $Na_2SO_4$  and then filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel (petroleum ether) to afford 1.21 g (92%) of the product.



General procedure for cyclic voltammetry (CV). CV was performed in a three electrode cell connected to a schlenk line under room temperature. Glassy carbon electrode was used as working electrode, and platinum wire was employed as counter electrode. Ag/AgCl reference electrode was submerged in saturated aqueous KCl solution and separated from reaction by a salt bridge. The mixture of MeOH/H<sub>2</sub>O (9:1) containing 0.1 M  $nBu_4NBF_4$  was poured into the electrochemical cell in all experiments. The scan rate was 100 mV/s ranging from -2.0 V to 3.0 V.



**Figure 1.** Cyclic voltammograms of substrates: (a) background ( $nBu_4NBF_4$  0.1 M in MeOH/H<sub>2</sub>O); (b) 4-methoxyphenylboronic acid **2** (0.05 mmol/mL); (c) NaI (0.06 mmol/mL).

Notes and references

- 1 G. J. P. Perry, J. M. Quibell, A. Panigrahi and I. Larrosa, J. Am. Chem. Soc., 2017, 139, 11527.
- 2 H. J. Yang, Y. Li, M. Jiang, J. M. Wang and H. Fu, *Chem. Eur. J.*, 2011, 17, 5652.
- 3 D. T. Racys, C. E. Warrilow, S. L. Pimlott and A. Sutherland, *Org. Lett.*, 2015, 17, 4782.
- 4 Y. Shi, Z. Ke and Y. Y. Yeung, Green Chem., 2018, 20, 4448.
- 5 S. Ahammed, A. Saha and B. C. Ranu, J. Org. Chem., 2011, 76, 7235.
- 6 G. A. Molander and L. N. Cavalcanti, J. Org. Chem., 2011, 76, 623.
- 7 W. Liu, X. Yang, Y. Gao and C-J. Li, J. Am. Chem. Soc., 2017, 139, 8621.
- 8 R. H. Tale, G. K. Toradmal and V. B. Gopula, RSC Adv., 2015, 5, 84910.
- 9 C. Dong, K. Nakamura, T. Taniguchi, S. Mita, S. Kodama, S. Kawaguchi, A. Nomoto, A. Ogawa and T. Mizuno, *ACS Omega.*, 2018, **3**, 9814.
- 10 K. Kobayashi, Y. Kondo, Org. Lett., 2009, 11, 9.
- 11 H. Kanno, K. Nakamura, K. Noguchi, Y. Shibata and K. Tanaka, Org. Lett., 2016, 18, 1654.
- 12 W. He, R. Zhang and M. Cai, RSC Adv., 2017, 7, 764.
- 13 M. Dabrowski, J. Kubicka, S. Lulin'ski and J. Serwatowski, *Tetrahedron.*, 2005, 61, 6590.
- 14 G. W. Kabalka and A. Mereddy, Organometallics., 2004, 23, 4519.
- 15 C-T. Yang, Z-Q. Zhang, Y-C. Liu and L. Liu, Angew. Chem., Int. Ed., 2011, 50, 3904.
- 16 T. N. Gieshoff, U. Chakraborty, M. Villa and A. Wangelin, *Angew. Chem., Int. Ed.*, 2017, **56**, 3585.
- 17 H. Gao, D. H. Ess, M. Yousufuddin and L. Kürti, J. Am. Chem. Soc., 2013, 135, 7086.
- 18 V. Diemer, F. R. Leroux and F. Colobert, Eur. J. Org. Chem., 2011, 327.
- 19 H. Kim and C. Lee, Angew. Chem. Int. Ed., 2012, 51, 12303.
- 20 S. Shiotani and H. Morita, J. Heterocyclic Chem., 1990, 27, 637.
- 21 N. Sakai, Y. Matsushita, T. Konakahara, Y. Ogiwara and K. Hirano, *Eur. J. Org. Chem.*, 2015, 1591.
- 22 G. Cahiez, O. Gager, A. Moyeux and T. Delacroix, *Adv. Synth. Catal.*, 2012, **354**, 1519.







S16







S19

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200 190 180 170 160 150 140 130 120 110 100 90 80 70 60











































































































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