Electronic Supplementary Information

~ Experimental Procedures and Spectral/Analytical Data ~

General Comments

Melting points (mp) were determined with a Yazawa micro melting point apparatus and uncorrected. Infrared (IR) data were recorded on SensIR ATR (Attenuated Total Reflectance) FT-IR. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). NMR data were recorded on a JEOL AL400 spectrometer. Chemical shifts are expressed in δ (parts per million, ppm) values and coupling constants are expressed in herts (Hz). ^{1}H NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal ($CDCl_3$: 77.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, br = broad singlet. Low and high resolution mass spectra (LRMS and HRMS) were obtained from Mass Spectrometry Resource, Graduate School of Pharmaceutical Sciences, Tohoku University, on a JEOL JMS-DX 303 and JMS-700/JMS-T 100 GC spectrometer respectively.

Materials

Boronic acids and other commercially available materials including copper salts were purchased from Tokyo Kasei Co., Aldrich Inc. and other commercial suppliers and were used as received. Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neutral, 70−230 mesh).

Representative Procedure for Oxidative Hydroxylation of 4-Methoxyphenylboronic Acid (Table 1, Entry 8)

Under an O_2 atmosphere, a mixture of 4-methoxyphenylboronic acid (45.6 mg, 0.30 mmol), $CuCl_2$ (2.0 mg, 0.015 mmol) and Brij S-100 (140.1 mg, 0.030 mmol) in H_2O (4 mL) was stirred for 6 h at rt. The reaction mixture was diluted with brine and extracted with AcOEt (30 mL × 3), and then the combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by SiO_2 column chromatography (gradient elution; 10–30% AcOEt in hexane) to give 4-methoxyphenol (34.9 mg, 95%).

4-Methoxyphenol (2a)

Obtained as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.76 (s, 3H), 4.43 (br, 1H), 6.75–6.80 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 55.8, 114.9, 116.1, 149.6, 153.4.

LRMS (EI) *m/z*: 124 (M^+).

HRMS Calcd. for $C_7H_8O_2$: 124.0524, found: 124.0527.

IR (neat): 3384, 2955, 2835, 1605, 1441, 1233, 1180, 1035, 826, 734 cm^{-1}.

4-Methylphenol (2b)

Obtained as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.27 (s, 3H), 4.56 (s, 1H), 6.73 (d, 2H, *J* = 8.3 Hz), 7.03 (d, 2H, *J* = 8.3 Hz).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 20.4, 115.1, 129.97, 130.05, 153.2.

LRMS (EI) *m/z*: 108 (M^+).

HRMS Calcd. for C_7H_8O: 108.0575, found: 108.0550.

IR (neat): 3401, 3293, 3204, 2924, 1614, 1361, 1221, 1170, 811, 738 cm^{-1}.

3-Methylphenol (2c)

Obtained as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.31 (s, 3H), 4.61 (s, 1H), 6.62–6.66 (m, 2H), 6.75 (d, 1H, *J* = 7.8 Hz), 7.11 (t, 1H, *J* = 7.8 Hz).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 21.3, 112.3, 116.0, 121.6, 129.4, 139.8, 155.4.

LRMS (EI) *m/z*: 108 (M^+).

HRMS Calcd. for C_7H_8O: 108.0575, found: 108.0556.

IR (neat): 3356, 2923, 2855, 1703, 1614, 1463, 1268, 1247, 928, 733 cm^{-1}.

2-Methylphenol (2d)

Obtained as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.25 (s, 3H), 4.64 (s, 1H), 6.77 (d, 1H, *J* = 7.8 Hz), 6.85 (dd, 1H, *J* = 7.8 Hz), 7.06–7.13 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 15.7, 114.9, 120.7, 123.7, 127.1, 131.0, 153.7.

LRMS (EI) *m/z*: 108 (M^+).

HRMS Calcd. for C_7H_8O: 108.0575, found: 108.0562.

IR (neat): 3506, 3299, 2958, 2924, 1443, 1346, 1169, 1006, 930, 751 cm^{-1}.

Phenol (2e)

Obtained as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.69 (s, 1H), 6.83 (d, 2H, *J* = 7.5 Hz), 6.93 (t, 1H, *J* = 7.5 Hz), 7.22–7.26 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 115.3, 120.8, 129.6, 155.5.

LRMS (EI) *m/z*: 94 (M^+).

HRMS Calcd. for C_6H_6O: 94.0419, found: 94.0404.

IR (neat): 3333, 2360, 1933, 1596, 1474, 1367, 1229, 1071, 810, 690 cm^{-1}.

4-Fluorophenol (2f)

Obtained as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.66 (s, 1H), 6.75–6.79 (m, 2H), 6.90–6.95 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 116.0 (d, J_{FC} = 22.9 Hz), 116.2 (d, J_{FC} = 8.2 Hz), 151.6 (d, J_{FC} = 2.5 Hz), 157.3 (d, J_{FC} = 238.4 Hz).

LRMS (EI) *m/z*: 112 (M^+).

HRMS Calcd. for C_6H_5FO: 112.0324, found: 112.0336.

IR (neat): 3403, 2924, 2853, 2362, 1724, 1497, 1457, 1288, 1199, 669 cm^{-1}.

4-Chlorophenol (2g)

Obtained as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.75 (s, 1H), 6.77 (d, 2H, *J* = 8.8 Hz), 7.19 (d, 2H, *J* = 8.8 Hz).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 116.6, 125.7, 129.5, 154.1.

LRMS (EI) *m/z*: 128 (M^+).

HRMS Calcd. for C_6H_5ClO: 128.0029, found: 128.0000.

IR (neat): 3323, 3252, 2922, 2853, 1493, 1359, 1224, 1092, 824, 719 cm^{-1}.

4-Bromophenol (2h)

Obtained as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.75 (s, 1H), 6.72 (d, 2H, *J* = 9.0 Hz), 7.33 (d, 2H, *J* = 9.0 Hz).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 112.9, 117.2, 132.5, 154.6.

LRMS (EI) *m/z*: 172 (M^+).

HRMS Calcd. for C_6H_5BrO: 171.9524, found: 171.9549.

IR (neat): 3398, 3191, 3092, 1487, 1252, 1157, 1070, 822, 768, 680 cm^{-1}.

4-Iodophenol (2i)

Recrystallized from hexane, colorless prisms, mp 66 °C (lit.[1)] mp 89–90 ºC).

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.71 (s, 1H), 6.62 (d, 2H, *J* = 8.8 Hz), 7.52 (d, 2H, *J* = 8.8 Hz).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 82.6, 117.8, 138.4, 155.3.

LRMS (EI) *m/z*: 220 (M^+).

HRMS Calcd. for C_6H_5IO: 219.9385, found: 219.9381.

IR (neat): 3372, 2353, 2342, 671 cm^{-1}.

4-Ethoxycarbonylphenol (2j)

Recrystallized from AcOEt/hexane, yellow plates, mp 116 °C (lit.[2] mp 116–118 ºC).

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.38 (t, 3H, *J* = 7.2 Hz), 4.34 (q, 2H, *J* = 7.2 Hz), 5.14 (s, 1H), 6.85 (d, 2H, *J* = 8.8 Hz), 7.97 (d, 2H, *J* = 8.8 Hz).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 14.3, 61.0, 115.3, 122.4, 131.9, 160.4, 167.2.

LRMS (EI) *m/z*: 166 (M^+).

HRMS Calcd. for $C_9H_{10}O_3$: 166.0630, found: 166.0634.

IR (neat): 3219, 3152, 2928, 1668, 1590, 1444, 1234, 1105, 954, 697 cm^{-1}.

4-Acethylphenol (2k)

Recrystallized from AcOEt/hexane, colorless prisms, mp 110 °C (lit.[3] mp 115–117 ºC).

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.56 (s, 3H), 5.88 (s, 1H), 6.89 (d, 2H, *J* = 8.8 Hz), 7.91 (d, 2H, *J* = 8.8 Hz).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 26.3, 115.3, 130.4, 131.0, 160.2, 197.1.

LRMS (EI) *m/z*: 136 (M^+).

HRMS Calcd. for $C_8H_8O_2$: 136.0524, found: 136.0529.

IR (neat): 3313, 2996, 2360, 1662, 1577, 1357, 1279, 1108, 962, 668 cm^{-1}.

4-Cyanophenol (2l)

Recrystallized from Et_2O/hexane, colorless prisms, mp 111–113 °C (lit.[4] mp 111–112 ºC).

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 6.17 (s, 1H), 6.92 (d, 2H, *J* = 8.7 Hz), 7.56 (d, 2H, *J* = 8.7 Hz).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 103.7, 116.4, 119.1, 134.3, 159.8.

LRMS (EI) *m/z*: 119 (M^+).

HRMS Calcd. for C_7H_5NO: 119.0371, found: 119.0369.

IR (neat): 3321, 3226, 2231, 1510, 1374, 1282, 1167, 1006, 835, 772 cm^{-1}.

References

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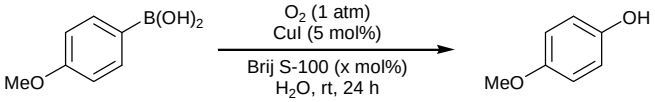
[4] V. S. Chankeshwara, R. Chebolu and K. A. Chakraborti, *J. Org. Chem.*, 2008, **73**, 8615.

Effect of Concentration of Brij S-100



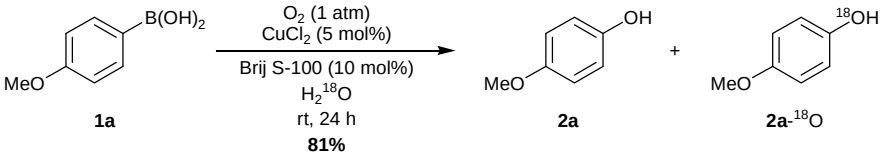
1a **2a**

Entry	x (mol%)	Yield (%)[a]
1	0	0
2	0.01	55
3	0.1	56
4	1	56
5	2	52
6	5	67
7	10	95
8	30	66

[a] Isolated yield.

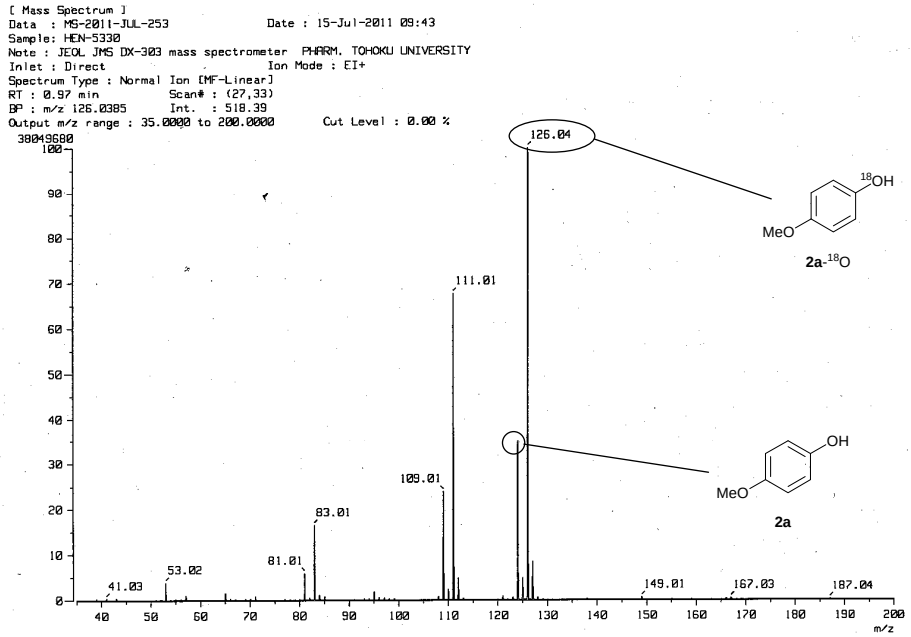
Mechanistic Studies

~ Use of $H_2{}^{18}O$ ~



1a **2a** **2a**-^{18}O

(**2a** : **2a**-^{18}O = *ca.* 1 : 3)



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