Supporting Information
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Synthesis of Tetra-ortho-substituted Biaryls with Aryltriolborates

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Supporting Information

General

$^1$H NMR spectra were recorded on a JEOL JNM-400II spectrometer (400 MHz) in CDCl$_3$ ($\delta_H = 7.25$ ppm) with tetramethylsilane as an internal standard. Chemical shifts were reported in parts per million (ppm), and signals are expressed as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). $^{13}$C NMR spectra were recorded on JEOL JNM-400II spectrometer (100 MHz) in CDCl$_3$ ($\delta_C = 77.0$ ppm) with tetramethylsilane as an internal standard. Chemical shifts were reported in parts per million (ppm). High-resolution mass spectrometry (HRMS) was performed on a JEOL JMS AX-500 or a JEOL JMSSX102A mass spectrometer at the Center for Instrumental Analysis, Hokkaido University. Kanto Chemical silica gel 60 (particle size 0.063-0.210 mm) was used for flash column chromatography. DMF was distilled from calcium hydride under argon. All other chemicals were purchased from Aldrich, Wako Chemicals, and TCI and used as without further purification.

Synthesis of potassium aryltriolborates

Potassium 2, 6-dimethylphenyl triolborate (7)

2,6-Dimethylbenzyl boronic acid (1) (100 mmol) and 1,1,1-tris(hydroxymethyl)ethane (100 mmol) were dissolved in toluene (200 mL). Water was removed by azeotropic distillation by the Dean-Stark method for 4h. Solvent was removed, giving crude product 4 (99%). Crude product 4 without further purification and KOH (90 mmol) were dissolved in toluene and heat at reflux for 4h by the Dean-Stark method. The potassium triolborate 7 was precipitated. After cooling to room temperature, acetone was added until the potassium triolborate was almost fully dissolved. By filtration, insoluble compounds were removed. The filtrate was concentrated under reduced pressure. 100 mL diethyl ether was added and stirred for
1h under nitrogen atmosphere at room temperature. The pure cyclic 2, 6-dimethylbenzyltrialborate 7 (82%) was collected by filtration, washed with diethyl ether and dried under reduced pressure. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ = 0.43 (s, 3H), 2.37 (s, 6H), 3.56 (s, 6H), 6.52-6.54 (m, 2H), 6.55-6.63 (m, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ = 17.0, 24.5, 34.7, 74.0, 124.2, 126.9, 142.5 ppm (C-B is not observed). $^{11}$B NMR (128 MHz, DMSO-d$_6$): $\delta$ = 2.56 ppm; HRMS (FAB$^-$): m/z calcd for C$_{13}$H$_{18}$BO$_3$: 233.1354; found: 233.1341; elemental analysis: calcd (%) for C$_{13}$H$_{18}$BKO$_3$: C, 57.36; H, 6.67; found: C, 56.73; H, 6.67.

Potassium 2, 4, 6-trimethylbenzyl triolborate (8)

The synthesis of 8 (73%) was same as the synthesis of 7. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ = 0.46 (s, 3H), 2.07 (s, 3H), 2.37 (s, 6H), 3.58 (s, 6H), 6.40 (s, 2H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ = 16.5, 20.7, 23.8, 34.1, 73.5, 127.3, 131.3, 142.0 ppm (C-B is not observed). $^{11}$B NMR (128 MHz, DMSO-d$_6$): $\delta$ = 2.69 ppm; HRMS (FAB$^-$): m/z calcd for C$_{14}$H$_{20}$BO$_3$: 247.1511; found: 247.1503; elemental analysis: calcd (%) for C$_{14}$H$_{20}$BKO$_3$: C, 58.75; H, 7.04; found: C, 57.94; H, 7.19.

Potassium 2-methyl-1-naphthalenyl triolborate (9)

2-Methylnaphthalene boronic acid (3) (100 mmol) and 1,1,1-tris(hydroxymethyl)ethane (100 mmol) were dissolved in toluene (200 mL). Water was removed by azeotropic distillation by the Dean-Stark method for 4h. Solvent was removed, giving crude product 6 (99%). Crude product 3b without further purification and KOH (90mmol) were dissolved in toluene and heated at reflux for 4h by the Dean-Stark method. The potassium triolborate 9 was collected by filtration, washed with diethyl ether and dried under reduced pressure (87%). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ = 0.53 (s, 3H), 2.63 (s, 3H), 3.69 (s, 6H), 7.0 (s, 1H), 7.1 (s, 2H), 7.34 (s, 1H), 7.50(s, 1H), 9.33 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$=16.5, 24.0, 34.3, 73.5, 122.0, 122.3, 124.3, 126.5, 129.8, 131.5, 132.8, 138.5, 138.8 ppm (C-B is not observed); $^{11}$B NMR (128 MHz, DMSO-d$_6$): $\delta$ = 3.49 ppm; HRMS (FAB$^-$): m/z calcd for C$_{16}$H$_{18}$BO$_3$: 269.1354; found: 269.1355; elemental analysis: calcd (%) for C$_{16}$H$_{18}$BKO$_3$: C, 62.35; H, 5.89; found: C, 58.70; H, 5.91.

Lithium 3-methyl-2-pyridyl triolborate (11)

n-BuLi (5 mmol) in hexane was added to a stirred solution of 3-methyl-2-bromopyridine (10) (5 mmol) in THF (20 mL) at -78 ºC. The resulting mixture was stirred for 45 min at -78 ºC. Triisopropylborate (5 mmol) was added, and then the mixture was allowed to naturally warm to room temperature. 1,1,1-Tris(hydroxymethyl)ethane (5 mmol) was then added, and the resulting mixture was stirred for 1 h at 60ºC. Concentration to dryness under reduced pressure gave lithium 3-methyl-2-pyridyl triolborate (11) (91%). $^1$H NMR (400 MHz, DMSO-d$_6$):
δ = 0.54 (s, 3H), 2.41 (s, 3H), 3.69 (s, 6H), 6.96 (s, 1H), 7.28 (s, 2H), 8.06 (s, 1H); 13C NMR (100 MHz, DMSO-d6): δ = 15.8, 19.7, 34.4, 73.3, 120.2, 135.5, 137.0, 143.6 ppm (C-B is not observed); 11B NMR (128 MHz, DMSO-d6): δ = 1.03 ppm; HRMS (FAB): m/z calcd for C16H18BO3: 220.1150; found: 220.1149; elemental analysis: calcd (%) for C16H18BKO3: C, 58.20; H, 6.66; N, 6.17 found: C, 54.93; H, 6.63; N, 5.26.

**General procedure for synthesis of ortho-substituted biaryls**

The aryl bromide (0.5 mmol), aryltriolborate (0.75 mmol), palladium acetate (5 mol %), BIPHEP (5.5 mol %), CuCl (0.1 mmol) were placed in a flash under nitrogen atmosphere. dry DMF (5 mL) was added. The mixture was stirred at 80 ºC for 14 h. After cooling to rt, the crude mixture was filtered through a plug of celite and washed with ether. The filtrate was then concentrated in vacuo to afford the crude product, which was further purified by chromatography on silica gel with hexanes/EtOAc (99:1-10:1).

The spectra of compounds 13, 14, 15, 16, 17, 22, 25, 28, 29, 30, 33 are identical to those reported in the literatures.

![Structure of 2-(2,6-dimethylphenyl)-3-methylthiophene (18)](image)

**1H NMR (400 MHz, CDCl3):** δ = 1.94 (s, 3H), 2.08 (s, 6H), 6.94–6.95 (d, J = 5.2 Hz, 1H), 7.09–7.11 (m, 2H), 7.16–7.18 (m, 1H), 7.26–7.28 (m, 1H); 13C NMR (100 MHz, CDCl3): δ = 13.7, 20.4, 123.8, 127.2, 128.0, 129.5, 133.3, 133.9, 135.7, 138.8 ppm. HRMS (EI): m/z calcd for C13H14S: 202.0816; found: 202.0816.

![Structure of Methyl 2,2',6'-trimethylbiphenyl-4-carboxylate (19)](image)

**1H NMR (400 MHz, CDCl3):** δ = 1.92 (s, 6H), 2.02 (s, 3H), 3.94 (s, 3H), 7.09–7.18 (m, 4H), 7.91–7.99 (m, 2H); 13C NMR (100 MHz, CDCl3): δ = 19.3, 20.2, 52.0, 127.3, 127.3, 127.4, 128.9, 129.1, 131.2, 135.3, 136.2, 140.0, 145.7, 167.3 ppm. HRMS (EI): m/z calcd for C17H16O2: 254.1307; found: 254.1302.

![Structure of 1-(2',6'-Dimethylbiphenyl-4-yl)ethanone (20)](image)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.02 (s, 6H), 2.66 (s, 3H), 7.11–7.13 (m, 2H), 7.17–7.25 (m, 1H), 7.26–7.28 (d, $J$ = 8 Hz, 2H), 8.03–8.05 (d, $J$ = 8 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 20.7, 26.6, 127.4, 127.5, 128.6, 129.4, 135.6, 135.6, 140.7, 146.4, 197.9 ppm. HRMS (EI): m/z calcd for C$_{16}$H$_{16}$O: 224.1201; found: 224.1297.

1-mesityl-2-methoxynaphthalene (21)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.85 (s, 6H), 2.38 (s, 3H), 3.82 (s, 3H), 7.00 (s, 2H), 7.10–7.19 (m, 1H), 7.27–7.38 (m, 3H), 7.80–7.88 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 20.0, 21.2, 56.3, 113.5, 123.3, 123.4, 124.5, 126.4, 127.9, 128.1, 128.7, 129.1, 132.6, 133.0, 136.7, 137.2, 153.6 ppm. HRMS (EI): m/z calcd for C$_{20}$H$_{20}$O: 276.1514; found: 276.1514.

9-mesitylanthracene (23)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.70 (s, 6H), 2.45 (s, 3H), 7.08 (s, 2H), 7.30–7.34 (t, $J$ = 8 Hz, 2H), 7.43–7.48 (m, 4H), 8.04–8.06 (d, $J$ = 8.4 Hz, 2H), 8.47 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.9, 21.2, 125.1, 125.5, 126.0, 126.0, 128.2, 128.6, 129.7, 131.6, 134.5, 135.7, 137.1, 137.6 ppm. HRMS (EI): m/z calcd for C$_{23}$H$_{20}$: 296.1565; found: 296.1557.

1-mesityl-2-naphthaldehyde (24)

$^1$H NMR (400 MHz, CDCl$_3$): 1.82 (s, 6H), 2.41 (s, 3H), 7.04 (s, 2H), 7.42–7.46 (m, 2H), 7.60–7.63 (m, 2H), 8.06–8.08 (d, $J$ = 8.4 Hz, 1H), 9.78 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 20.4, 21.2, 122.2, 126.5, 127.1, 128.1, 128.3, 128.4, 129.0, 130.9, 131.3, 131.9, 136.5, 137.1, 138.0, 146.2, 192.8 ppm; HRMS (EI): m/z calcd for C$_{20}$H$_{18}$O: 274.1358; found: 274.1358.
2,2',4,4',6,6'-hexamethylbiphenyl (26)

$^1$H NMR (400 MHz, CDCl$_3$): 1.86 (s, 12H), 2.33 (s, 6H), 6.93 (s, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.8, 21.1, 128.1, 135.5, 136.0, 137.0 ppm. HRMS (EI): m/z calcd for C$_{18}$H$_{22}$: 238.1722; found: 238.1717.

2-mesityl-3-methylthiophene (27)

$^1$H NMR (400 MHz, CDCl$_3$): 1.93 (s, 1H), 2.05 (s, 6H), 2.32 (s, 3H), 6.93-6.94 (m, 3H), 7.24-7.25 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 13.7, 20.3, 21.1, 123.7, 128.0, 129.5, 130.2, 134.0, 135.8, 137.7, 138.6 ppm. HRMS (EI): m/z calcd for C$_{14}$H$_{16}$S: 216.0973; found: 216.0968.

1-(2,6-dimethoxyphenyl)-2-methylnaphthalene (31)

$^1$H NMR (400 MHz, CDCl$_3$): 2.19 (s, 3H), 3.60 (s, 3H), 6.69-6.71 (d, $J$ = 4.4 Hz, 1H), 7.29-7.43 (m, 4H), 7.75-7.77 (d, $J$ = 8 Hz, 1H), 7.79-7.81 (d, $J$ = 8 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.9, 55.42, 103.7, 115.9, 124.0, 125.1, 125.1, 126.7, 127.5, 128.1, 128.6, 130.4, 131.5, 132.4, 134.0, 157.8 ppm. HRMS (EI): m/z calcd for C$_{19}$H$_{18}$O$_2$: 278.1307; found: 278.1300.

3-methyl-2-(2-methylnaphthalen-1-yl)thiophene (32)

$^1$H NMR (400 MHz, CDCl$_3$): 1.91 (s, 3H), 2.28 (s, 3H), 7.02-7.04 (d, $J$ = 5.6 Hz, 1H), 7.21-7.41 (m, 4H), 7.47-7.49 (d, $J$ = 8 Hz, 1H), 7.78-7.83 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 13.5, 20.1, 124.0, 124.5, 125.3, 125.8, 127.3, 127.9, 129.1, 129.2, 131.5, 133.5, 133.8, 135.1, 136.0 ppm. HRMS (EI): m/z calcd for C$_{14}$H$_{16}$S: 238.0816; found: 238.0815.
3-methyl-2-(1,3,5-trimethyl-1H-pyrazol-4-yl)pyridine (34)

$^1$H NMR (400 MHz, CDCl$_3$): 2.11 (s, 3H), 2.12 (s, 3H), 2.19 (s, 3H), 77 (s, 3H), 7.15 (dd, $J = 4.98$, 7.70 Hz, 1H), 7.57 (d, $J = 7.70$ Hz, 1H), 8.50 (d, $J = 4.98$ Hz, 1H);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 10.1$, 12.3, 18.9, 35.8, 118.4, 121.7, 132.8, 137.1, 137.6, 145.4, 146.9, 152.9 ppm. HRMS (EI): m/z calcd for C$_{12}$H$_{15}$N$_3$: 201.1266; found: 201.1266.

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