Supplementary Material (ESI) for Chemical Communications

Ortho-C-H borylation of benzoate esters with bis(pinacolato)diboron catalyzed by iridium-phosphine complexes

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General. All the experiments were carried out under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions using a JEOL JNM-A400II spectrometer (400 or 100 MHz) and Me_4Si or residual protiated solvent as an internal standard. Low- and high-resolution mass spectra were obtained on a JEOL JMS-DX303. GC analyses were conducted on a Hitachi G-3500 instrument equipped with a glass column (OV-101 on Uniport B, 2 m). $[Ir(OMe)(COD)]_2$ was synthesized by the reported procedure.[1] Solvents were purified by distillation from appropriate drying agents. All of other compounds were used as received.

General procedure for the *ortho*-C-H borylation (Table 2). A flask containing $[Ir(OMe)(COD)]_2$ (9.9 mg, 0.015 mmol), tris[3,5-bis(trifluoromethyl)phenyl]phosphine (40.2 mg, 0.060 mmol), and bis(pinacolato)diboron (254 mg, 1.0 mmol) was flushed with nitrogen, and then charged with octane (6 ml) and a benzoate ester (5.0 mmol). The mixture was stirred at 80 °C for 16 h. The product was isolated by Kugelrohr distillation to give an analytically pure sample.

Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 1). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 12H), 2.94 (s, 3H), 7.39-7.43 (m, 1H), 7.49-7.51 (m, 2H), 7.94 (d, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 52.3, 84.0, 128.7, 128.9, 131.8, 132.1, 133.3, 168.0; MS (EI): *m*/*z* (%) = 262(0.8) $[M]^+$, 247(12), 204(100), 189(68), 163(41), 149(60), 131(64), 103(39), 43(57); HRMS (EI): calcd for $[C_{14}H_{19}BO_4]$: 262.1342; found: 262.1387.

Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 2). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (t, J = 7.2 Hz, 3H), 1.42 (s, 12H), 4.38 (q, J = 6.8 Hz, 2H), 7.37-7.41 (m, 1H), 7.49 (d, J = 3.6 Hz, 2H), 7.93 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 24.8, 61.2, 83.9, 128.5, 128.8, 131.7, 132.0, 133.8, 168.0; MS (EI):

m/*z* (%) = 276(0.8) $[M]^+$, 219(14), 218(100), 217(25), 189(57), 188(14), 149(29), 131(19), 103(12), 43(19); HRMS (EI): calcd for $[C_{15}H_{21}BO_4]$: 276.1533; found: 276.1534.

Isopropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 3). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (d, *J* = 6.4 Hz, 6H), 1.42 (s, 12H), 5.25 (sep, *J* = 6.4 Hz, 1H), 7.38-7.42 (m, 1H), 7.48 (d, *J* = 3.6 Hz, 2H), 7.91 (d *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9, 24.8, 68.7, 83.9, 128.3, 128.7, 131.6, 131.9, 134.3, 168.0; MS (EI): *m*/*z* (%) = 290(0.6) $[M]^+$, 233(14), 232(58), 231(20), 190(100), 149(26), 131(13); HRMS (EI): calcd for $[C_{16}H_{23}BO_4]$: 290.1689; found: 290.1707.

***tert*-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 4).** The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 12H), 1.58 (s, 9H), 7.32-7.39 (m, 1H), 7.44-7.48 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 24.8, 28.2, 81.3, 83.8, 128.0, 128.6, 131.2, 131.8, 135.9, 167.4; MS (EI): *m*/*z* (%) = 305(0.1) $[M]^+$, 246(9), 233(7), 190(100), 149(31), 131(19), 103(17), 83(30); HRMS (EI): calcd for $[C_{17}H_{25}BO_4]$: 304.1846; found: 304.1927.

Methyl 2-dimethylamino-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 5). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 12H), 2.75 (s, 6H), 3.89 (s, 3H), 7.17 (dd, *J* = 9.2 Hz, *J* = 2.0 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 9.6 Hz, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 44.8, 52.2, 83.9, 121.5, 128.0, 129.9, 132.9, 151.0, 170.7; MS (EI): *m*/*z* (%) = 305(14) $[M]^+$, 247(14), 190(24), 174(100), 173(26), 146(11), 83(13), 41(14); HRMS (EI): calcd for $[C_{16}H_{24}BNO_4]$: 305.1798; found: 305.1811.

Methyl 2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 6). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, 12H), 2.39 (s, 3H), 3.89 (s, 3H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0, 24.8, 52.1, 84.0, 129.4, 131.7, 132.7, 135.3, 170.7; MS (EI): *m*/*z* (%) = 276(0.5) $[M]^+$, 218(65), 203(39), 177(24), 163(29), 161(28), 145(49), 117(43), 83(39), 43(100); HRMS (EI): calcd for $[C_{15}H_{21}BO_4]$: 276.1533; found: 276.1545.

Methyl 2-bromo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 7). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 12H), 3.92 (s, 3H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 52.5, 84.4, 122.1, 123.3, 130.1, 133.7, 135.0, 168.3; MS (EI): *m*/*z* (%) = 340(3) $[M]^+$,

282(100), 267(29), 241(23), 227(22), 211(20), 83(22); HRMS (EI): calcd for [$C_{14}H_{18}BBrO_4$]: 340.0464; found: 340.0480.

Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-trifluoromethylbenzoate (Entry 8). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, 12H), 3.91 (s, 3H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 52.6, 84.6, 121.7, 122.8, 125.3 (q, *J*(CF) = 258 Hz), 128.3 (q, *J*(CF) = 4.9 Hz), 128.9, 138.3, 168.6; MS (EI): *m*/*z* (%) = 330(0.4) $[M]^+$, 272(100), 257(36), 211(14), 199(26), 197(12), 43(17); HRMS (EI): calcd for [$C_{15}H_{18}BF_3O_4$]: 330.1250; found: 330.1245.

Methyl 3-dimethylamino-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 9). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 12H), 2.98 (s, 6H), 3.88 (s, 3H), 6.80 (dd, *J* = 10.8 Hz, *J* = 2.8 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 40.2, 52.1, 83.4, 112.3, 114.7, 134.2, 135.9, 151.1, 169.5; MS (EI): *m*/*z* (%) = 305(62) $[M]^+$, 247(62), 246(18), 232(27), 188(100), 174(29), 148(11), 146(18); HRMS (EI): calcd for [$C_{16}H_{24}BNO_4$]: 305.1798; found: 305.1784.

Methyl 3-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 10). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 12H), 2.37 (s, 3H), 3.90 (s, 3H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.75 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 24.8, 52.2, 83.9, 129.4, 132.3, 132.5, 133.6, 139.0, 168.6; MS (EI): *m*/*z* (%) = 276(0.7) $[M]^+$, 218(87), 203(46), 177(30), 163(40), 161(39), 145(54), 43(100); HRMS (EI): calcd for [$C_{15}H_{21}BO_4$]: 276.1533; found: 276.1545.

Methyl 3-bromo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 11). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 12H), 3.92 (s, 3H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.64 (dd, *J* = 9.8 Hz, *J* = 2.0 Hz, 1H), 8.08 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 52.6, 84.3, 123.0, 131.8, 133.7, 134.7, 135.1, 173.0; MS (EI): *m*/*z* (%) = 340(2) $[M]^+$, 284(97), 282(100), 269(37), 267(39), 229(31), 227(36); HRMS (EI): calcd for [$C_{14}H_{18}BBrO_4$]: 340.0464; found: 340.0478.

Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-trifluoromethylbenzoate (Entry 12). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 12H), 3.95 (s, 3H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 8.8 Hz, *J* = 0.96 Hz, 1H), 8.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 52.7, 84.5, 125.5, 126.4 (q, *J*(CF) = 267 Hz), 128.2 (q, *J*(CF) = 3.3 Hz), 132.0

(q, *J*(CF) = 4.2 Hz), 132.8, 134.1, 167.2; MS (EI): *m*/*z* (%) = 330(3) $[M]^+$, 272(100), 257(42), 217(37), 199(18), 171(13), 43(31); HRMS (EI): calcd for $[C_{15}H_{18}BF_3O_4]$: 330.1250; found: 330.1258.

Methyl 4-dimethylamino-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 13). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 12H), 3.02 (s, 6H), 3.85 (s, 3H), 6.61 (dd, *J* = 11.2 Hz, *J* = 2.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.9, 40.0, 51.6, 83.8, 111.2, 114.2, 120.0, 130.6, 152.4, 168.5; MS (EI): *m*/*z* (%) = 305(36) $[M]^+$, 247(79), 246(41), 190(26), 174(100), 148(13), 119(12); HRMS (EI): calcd for $[C_{16}H_{24}BNO_4]$: 305.1798; found: 305.1805.

Methyl 4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 14). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 12H), 2.37 (s, 3H), 3.89 (s, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 24.9, 52.1, 84.0, 128.9, 129.6, 130.6, 132.8, 142.3, 168.4; MS (EI): *m*/*z* (%) = 276(0.7) $[M]^+$, 218(100), 203(44), 177(33), 163(33), 161(42), 145(11); HRMS (EI): calcd for $[C_{15}H_{21}BO_4]$: 276.1533; found: 276.1543.

Methyl 4-bromo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Entry 15). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 12H), 3.91 (s, 3H), 7.55 (dd, *J* = 10.4 Hz, *J* = 2.4 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 52.5, 84.4, 129.2, 130.3, 132.1, 135.1, 142.5, 173.5; MS (EI): *m*/*z* (%) = 340(3) $[M]^+$, 284(100), 281(26), 269(25), 267(26), 241(20), 227(24); HRMS (EI): calcd for $[C_{14}H_{18}BBrO_4]$: 340.0464; found: 340.0481.

Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-trifluoromethylbenzoate (Entry 16). The purity determined by NMR analyses: > 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 12H), 3.95 (s, 3H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.73 (s, 1H), 8.03 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 52.7, 84.5, 124.1 (q, *J*(CF) = 258 Hz), 126.0 (q, *J*(CF) = 4.1 Hz), 129.0, 129.1 (q, *J*(CF) = 3.3 Hz), 145.5, 154.3, 167.4; MS (EI): *m*/*z* (%) = 330(0.3) $[M]^+$, 272(100), 257(49), 217(40), 171(13), 159(15), 43(31); HRMS (EI): calcd for $[C_{15}H_{18}BF_3O_4]$: 330.1250; found: 330.1248.

References

1. R. Uson, L. A. Oro and J. A. Cabeza, *Inorg. Synth.*, 1985, **23**, 126.