Supplementary Material for Chemical Communications

Synthesis of bi- and tricyclic arylboronates via Cp*RuCl-catalyzed cycloaddition of α,ω-diynes with ethynylboronate

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Supplementary Information

General Considerations.

Column chromatography was performed with silica gel (Cica silica gel 60N) or alumina (Merck aluminium oxide 90 standardized) eluted with mixed solvents [hexane / ethyl acetate]. ^{1}H and ^{13}C NMR spectra were obtained for samples in $CDCl_3$ solution at 25 ˚C. ^{1}H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at 7.26 ppm for chloroform. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. Coupling constants are reported in Hz. ^{13}C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ = 77.0 ppm for $CDCl_3$. Elemental analyses were performed by the Instrumental Analysis Facility of Nagoya University. Melting points were obtained in capillary tubes and are uncorrected. 1,2-Dichloroethane and DMF were distilled from CaH_2, and degassed before use. MeOH was distilled from Mg. Cp*RuCl(cod) (Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161-1164.) and $Pd_2(dba)_3$•$CHCl_3$ (Ukai, T.; Kawazura, T.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253-266.) were prepared according to the established procedure.

Representative Procedure for Cycloaddition of α,ω-Diyne with Ethynylboronate: Synthesis of Arylboronate 4a from Ethynylboronate 2 and Dipropargylmalonate 3a. To a solution of Cp*RuCl(cod) (**1**) (17.1 mg, 0.045 mmol) and ethynylboronate **2** (248.2 mg, 1.80 mmol) in dry

degassed 1,2-dichloroethane (4.5 mL) was added a solution of diyne **3a** (187.4 mg, 0.90 mmol) in dry degassed 1,2-dichloroethane (6 mL) over 1 h via syringe pump at room temperature under Ar atmosphere. The solution was stirred at room temperature under Ar atmosphere for 1 h, and then, the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane-AcOEt 15:1) to give **4a** (266.5 mg, 86%) as colorless solids (mp. 133.6-133.7 ˚C): IR (neat) 1732 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (s, 6 H), 3.59 (s, 2 H), 3.60 (s, 2 H), 3.73 (s, 6 H), 3.75 (s, 4 H), 7.19 (d, J = 7.5 Hz, 1 H), 7.62 (d, J = 7.5 Hz, 1 H), 7.64 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.87, 31.85, 40.38, 40.71, 52.85, 60.23, 72.17, 123.32, 129.40, 132.54, 138.92, 142.46, 171.80; MS (EI): *m*/*z* (%): 346 (29) [M^+], 286 (100) [M^+-H-CO_2Me], 227 (13) [M^+-H-2CO_2Me]; EA calcd (%) for $C_{18}H_{23}BO_6$ (346.18): C 62.45, H 6.70; found: C 62.41, H 6.69.

4b: mp. 116.8-116.9 ˚C; IR ($CHCl_3$) 1699 (COMe) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (s, 6 H), 2.16 (s, 6 H), 3.49 (s, 2 H), 3.51 (s, 2 H), 3.76 (s, 4 H), 7.19 (d, J = 7.5 Hz, 1 H), 7.62 (d, J = 7.5 Hz, 1 H), 7.64 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.90, 26.58, 31.88, 37.52, 37.82, 72.22, 74.51, 123.58, 129.65, 132.66, 138.81, 142.38, 204.70; MS (EI): *m*/*z* (%): no molecular ion peak 271 (100) [M^+-COMe], 256 (41) [M^+-Me-COMe], 228 (18) [M^+-2COMe]; EA calcd (%) for $C_{18}H_{23}BO_4$ (314.18): C 68.81, H 7.38; found: C 68.85, H 7.46.

4c: mp. 169.1-169.3 ˚C; IR ($CHCl_3$) 2967 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.03 (s, 6 H), 3.72 (s, 2 H), 3.73 (s, 2 H), 3.77 (s, 4 H), 7.28 (d, J = 7.5 Hz, 1 H), 7.73 (s, 1 H), 7.75 (d, J = 7.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.91, 31.84, 33.61, 44.56, 44.80, 72.30, 116.25, 123.88, 129.96, 134.04, 135.37, 138.47; MS (EI): *m*/*z* (%): 280 (100) [M^+], 237 (18) [M^+-MeCHMe]; EA calcd (%) for $C_{16}H_{17}BN_2O_2$ (280.13): C 68.60, H 6.12, N 10.00; found: C 68.32, H 6.20, N 9.98.

4d: mp. 111.4-111.5 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (s, 6 H), 2.06 (quint, *J* = 7.5 Hz, 2 H), 2.92 (t, *J* = 7.5 Hz, 4 H), 3.77 (s, 4 H), 7.24 (d, *J* = 7.5 Hz, 1 H), 7.60 (d, *J* = 7.5 Hz, 1 H), 7.69 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.95, 25.33, 31.92, 32.62, 33.09, 72.23, 123.60, 129.61, 131.70, 143.27, 147.00; MS (EI): *m*/*z* (%): 230 (100) [M^+], 187 (35) [M^+-MeCHMe]; EA calcd (%) for $C_{14}H_{19}BO_2$ (230.11): C 73.07, H 8.32; found: C 73.00, H 8.47.

4e: mp. 195.8-196.1 ˚C; IR ($CHCl_3$) 1320, 1163 (NTs) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (s, 6 H), 2.39 (s, 3 H), 3.74 (s, 4 H), 4.62 (s, 4 H), 7.15 (d, *J* = 7.5 Hz, 1 H), 7.30 (d, *J* = 8.1 Hz, 1 H), 7.60 (s, 1 H), 7.66 (d, *J* = 7.5 Hz, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.57, 21.92, 31.95, 53.64, 53.90, 72.31, 121.70, 127.45, 127.86, 129.67, 133.17, 133.62, 135.28, 138.46, 143.46; MS (EI): *m*/*z* (%): 385 (91) [M^+], 330 (100) [M^+-NTs]; EA calcd (%) for $C_{20}H_{24}BNO_4S$ (385.28): C 62.35, H 6.28, N 3.64; found: C 62.28, H 6.34, N 3.56.

4f: mp. 117.6-117.8 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.03 (s, 6 H), 3.78 (s, 4 H), 5.11 (s, 4 H), 7.23 (d, *J* = 7.5 Hz, 1 H), 7.68 (s, 1 H), 7.71 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.97, 31.96, 72.31, 73.45, 73.60, 120.07, 126.16, 132.85, 138.25, 141.61; MS (EI): *m*/*z* (%): 232 (100) [M^+], 217 (22) [M^+-Me], 204 (93) [M^+-CO]; EA calcd (%) for $C_{13}H_{17}BO_3$ (232.08): C 67.28, H 7.38; found: C 67.09, H 7.57.

4g: mp. 116.7-116.8 ˚C; IR ($CHCl_3$) 1732 (CO_2Et) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (s, 6 H), 1.20 (t, *J* = 7.2 Hz, 12 H), 3.52 (s, 2 H), 3.54 (s, 2 H), 3.75 (s, 4 H), 4.12-4.23 (m, 8 H), 7.07 (d, *J* = 7.5 Hz, 1 H), 7.52 (s, 1 H), 7.53 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.87, 21.97, 31.92, 34.59, 34.92, 57.46, 61.72, 72.25, 127.39, 131.37, 131.65, 133.79, 135.33, 169.71,

169.76; MS (EI): *m*/*z* (%): 532 (42) [M^+], 487 (32) [M^+-OEt], 459 (31) [M^+-CO_2Et], 413 (70) [M^+-HOEt-CO_2Et], 385 (50) [M^+-H-2CO_2Et], 339 (100) [M^+-2H-OEt-2CO_2Et]; EA calcd (%) for $C_{27}H_{37}BO_{10}$ (532.39): C 60.91, H 7.01; found: C 61.11, H 7.25.

4h: mp. 192.6-193.0 ˚C; IR ($CHCl_3$) 1673 (quinone) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 6 H), 3.83 (s, 4 H), 7.78-7.82 (m, 2 H), 8.20 (dd, *J* = 7.8, 1.2 Hz, 1 H), 8.28 (dd, *J* = 7.8, 0.3 Hz, 1 H), 8.30-8.35 (m, 2 H), 8.75 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.92, 31.95, 72.37, 125.86, 126.93, 127.03, 132.15, 132.70, 133.39, 133.42, 133.73, 133.86, 134.52, 139.07, 183.01, 183.20; MS (EI): *m*/*z* (%): 320 (100) [M^+], 280 (85) [M^+-C_3H_4], 235 (95) [M^+-$CH_2C(Me)_2CHO$]; EA calcd (%) for $C_{19}H_{17}BO_4$ (320.15): C 71.28, H 5.35; found: C 71.05, H 5.53.

6: mp. 160.1-160.5 ˚C; IR ($CHCl_3$) 1732 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): meta-**6** δ 1.01 (s, 6 H), 2.26 (s, 3 H), 3.54 (s, 2 H), 3.60 (s, 2 H), 3.74 (s, 6 H), 3.75 (s, 4 H), 7.43 (s, 1 H), 7.47 (s, 1 H); ortho-**6** δ 1.02 (s, 6 H), 2.42 (s, 3 H), 3.55 (s, 2 H), 3.60 (s, 2 H), 3.74 (s, 6 H), 3.76 (s, 4 H), 7.01 (d, *J* = 7.5 Hz, 1 H), 7.57 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): meta-**6** δ 18.91, 21.91, 31.89, 39.63, 40.63, 52.94, 59.80, 72.23, 120.54, 126.75, 133.31, 138.81, 141.51, 172.00; ortho-**6** δ 18.51, 21.91, 31.63, 39.87, 40.97, 52.94, 59.54, 72.20, 132.72, 134.02, 138.73, 139.46, 141.44, 172.06; MS (EI): *m*/*z* (%): 360 (31) [M^+], 300 (100) [M^+-H-CO_2Me]; EA calcd (%) for $C_{19}H_{25}BO_6$ (360.21): C 63.35, H 7.00; found: C 63.27, H 7.01.

Experimental procedure for Suzuki-Miyaura coupling of 4a.

To a solution of arylboronate **4a** (104.0 mg, 0.30 mmol) and *p*-iodoacetophenone (111.8 mg, 0.45 mmol) in dry DMF (2 mL) was added $Pd_2(dba)_3$•$CHCl_3$ (8.0 mg, 0.0077 mmol), PCy_3 (8.7 mg, 0.041 mmol), and K_3PO_4 (99.2 mg, 0.47 mmol). The mixture was degassed at -78 ˚C, and stirred at 100 ˚C

under Ar atmosphere for 4 h. The reaction mixture was diluted with distilled water (10 mL) and extracted with AcOEt (5 mL × 3). The organic layer was washed with brine (5 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane-AcOEt 20:1) to give **10** (82.9 mg, 80%) as colorless solids (mp. 98.8-99.4 ˚C): IR ($CHCl_3$) 1733 (CO_2Me), 1680 (COMe) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.63 (s, 3 H), 3.65 (s, 2 H), 3.67 (s, 2 H), 3.77 (s, 6 H), 7.29 (d, *J* = 8.1 Hz, 1 H), 7.44 (d, *J* = 8.1 Hz, 1 H), 7.45 (s, 1 H), 7.65 (d, *J* = 8.4 Hz, 2 H), 8.01 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.73, 40.41, 40.60, 53.09, 60.47, 123.03, 124.61, 126.24, 127.05, 127.34, 128.77, 135.60, 138.89, 140.06, 140.72, 145.68, 171.78, 197.50; MS (EI): *m*/*z* (%): 352 (79) [M^+], 292 (100) [M^+-H-CO_2Me], 277 (22) [M^+-H-CO_2Me-Me]; EA calcd (%) for $C_{21}H_{20}O_5$ (352.38): C 71.58, H 5.72; found: C 71.68, H 5.60.

Experimental procedure for methoxycarbonylation of arylboronates.

To a solution of arylboronate **4a** (104.4 mg, 0.30 mmol) in dry MeOH (3 mL) was added $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), PPh_3 (9.3 mg, 0.035 mmol), and *p*-benzoquinone (32.6 mg, 0.30 mmol). The mixture was stirred at room temperature under CO atmosphere for 1.5 h. The reaction mixture was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane-AcOEt 15:1) to give **11** (68.4 mg, 77%) as colorless solids (mp. 90.1-90.3 ˚C): IR ($CHCl_3$) 1735 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.63 (s, 4 H), 3.75 (s, 6 H), 3.89 (s, 3 H), 7.26 (d, *J* = 8.1 Hz, 1 H), 7.86-7.88 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.19, 40.57, 52.02, 53.06, 60.29, 124.00, 125.30, 128.60, 129.04, 140.11, 145.23, 166.80, 171.47; MS (EI): *m*/*z* (%): 292 (39) [M^+], 261 (23) [M^+-OMe], 232 (100) [M^+-H-CO_2Me], 201 (43) [M^+-HOMe-CO_2Me], 173 (51) [M^+-H-2CO_2Me]; EA calcd (%) for $C_{15}H_{15}O_6$ (292.28): C 61.64, H 5.52; found: C 61.50, H 5.62.

The methoxycarbonylation of **4g** was carried out in a similar manner. The spectral data for **13** was in good agreement with those reported previously (T. Sugaya, N. Kato, A. Sakaguchi and S. Tomioka, *Synthesis*, 1995, 1257.).

Experimental procedure for oxidation of arylboronates.

To a solution of arylboronate **4a** (104.0 mg, 0.30 mmol) in THF (3.5 mL) was added a basic solution of H_2O_2 (30% aq. H_2O_2 0.5 mL + 1 N NaOH 1 mL) at room temperature. The mixture was stirred at room temperature for 15 min. The reaction mixture was diluted with sat. NH_4Cl (5 mL) and extracted with AcOEt (5 mL × 3). The organic layer was washed with brine (5 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane-AcOEt 10:1) to give **12** (69.5 mg, 93%) as colorless oil: IR (neat) 2449 (OH), 1723 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.51 (s, 2 H), 3.54 (s, 2 H), 3.74 (s, 6 H), 4.57 (br s, 1 H), 6.63 (dd, J = 8.4, 2.7 Hz, 1 H), 6.67 (m, 1 H), 7.03 (d, J = 8.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.80, 40.61, 53.07, 60.80, 111.11, 114.12, 124.79, 131.37, 141.26, 155.01, 172.09; MS (EI): m/z (%): 250 (35) [M^+], 190 (100) [M^+-H-CO_2Me], 131 (55) [M^+-H-2CO_2Me]; EA calcd (%) for $C_{13}H_{14}O_5$ (250.25): C 62.39, H 5.64; found: C 62.37, H 5.67.

The oxidation of **4g** was carried out in a similar manner. The spectral data for **14** was in good agreement with those reported previously (G. G. Mihai, P. G. Tarassoff and N. Filipescu, *J. Chem. Soc., Perkin 1*, 1975, 1374.).