Supplementary Material (ESI) for Chemical Communications

Supporting Information

Copper-catalyzed addition of diboron reagents to α,β-acetylenic esters: Efficient synthesis of β-boryl-α,β-ethylenic esters

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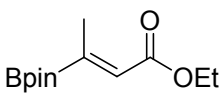
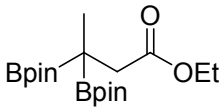
General Methods. THF was distilled from sodium benzophenone ketyl under nitrogen. CuCl, NaO*t*-Bu, bis(pinacolato)diboron and other commercial substrates were purchased from Aldrich and used as received. All reactions were carried out under a nitrogen atmosphere, in an oven-dried Schlenk tube and run two or more times. Flash chromatography was performed on silica gel from Merck (70–230 mesh). All ^{1}H NMR spectra were obtained on Varian Mercury 300 systems and reported in parts per million (ppm) downfield from tetramethylsilane. ^{13}C NMR spectra are reported in ppm referenced to deuteriochloroform (77.2 ppm). High resolution mass spectra (HRMS) were obtained at Korea Basic Science Institute (Daegu, Korea) and reported in the form of m/z (intensity relative to base peak = 100).

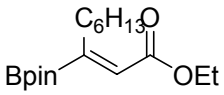
General Procedure for the β-boration of α,β-acetylenic esters: CuCl (0.015 mmol, 1.5 mg), NaO*t*-Bu (0.030 mmol, 2.9 mg) and Xantphos ligand (0.015 mmol, 8.7 mg) were placed in an oven-dried Schlenk tube and THF (0.45mL) were added under nitrogen. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron (0.55 mmol, 140 mg) and THF (0.30 mL) were added. The reaction mixture was stirred for 10 min and α,β-acetylenic ester compound (0.50 mmol) was added, followed by MeOH (1.0 mmol, 40 μL). The reaction tube was washed with THF (0.20 mL), sealed, and stirred until no starting material was detected by TLC. The reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.



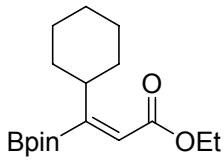
(*Z*)-ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (2a).[1] Using the general procedure, the title compound was prepared as a colorless oil in 85% yield (102 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ =1.20−1.30 (m, 15H), 2.17 (s, 3H), 4.18 (q, *J* = 6.9 Hz, 2H), 6.45 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =166.0, 147.0 (C–B), 130.5, 84.0, 60.0, 24.7, 16.2, 14.2; *m/z* 241 (M^+, 100%), 195 (33), 111 (18).



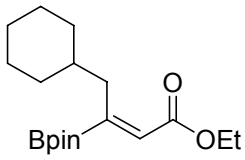
β,β-Diboryrated product (2a'): Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (s, 3H) 1.03−1.37 (m, 27H), 2.59 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 2H); *m/z* 368 (M^+, 14%), 310 (64), 252 (21), 156 (25), 83 (100).



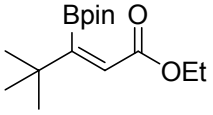
(*Z*)-ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-2-enoate (2b). Using the general procedure, the title compound was prepared as a colorless oil in 93% yield (144 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ =0.87 (t, *J* = 6.6 Hz, 3H), 1.27−1.34 (m, 23H), 2.66 (t, *J* = 7.2 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 6.40 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =165.9, 162.0 (C–B), 129.8, 84.0, 59.6, 31.8, 30.0, 29.6, 29.5, 24.7, 14.3, 14.1; *m/z* 311 (M^+, 32%), 265 (14), 210 (100), 181 (56), 167 (33), 83 (13).



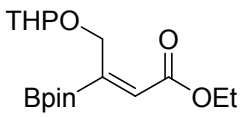
(*Z*)-ethyl 3-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2c). Using the general procedure, the title compound was prepared as a colorless oil in 99% yield (153 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ =1.25−1.30 (m, 15H), 1.48−1.55 (m, 6H), 1.65−1.74 (m, 5H), 4.16 (q, *J* = 7.2 Hz, 2H), 6.24 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =166.1, 158.0 (C–B), 127.9, 83.9, 59.8, 40.0, 31.5, 26.4, 26.1, 24.8, 14.4; *m/z* 309 (M^+, 12%), 208 (100), 180 (32), 112 (13).



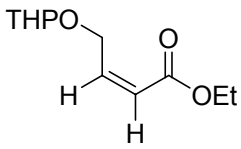
(*Z*)-ethyl 4-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (2d). Using the general procedure, the title compound was prepared as a colorless oil in 88% yield (142 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ =1.17−1.18 (m, 2H), 1.20−1.30 (m, 16H), 1.63−1.68 (m, 5H), 4.16 (q, *J* = 7.2 Hz, 2H), 6.44 (s, 1H) (the irradiation of the vinylic proton at 6.44 ppm resulted in no enhancement of the allylic proton signal); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =166.0, 151.7 (C–B), 130.4, 84.0, 59.8, 38.9, 37.2, 33.4, 26.6, 26.5, 24.7, 14.3; HRMS(EI) calcd for $C_{18}H_{31}BO_4$ 322.2315, found 322.2318.



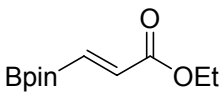
(*E*)-ethyl 4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-enoate (2f). Using the general procedure, the title compound was prepared as a colorless oil in 71% yield (100 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ =1.21−1.29 (m, 24H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.23 (s, 1H) (the irradiation of the vinylic proton at 6.23 ppm resulted in a 3.4% enhancement of the *t*-butyl proton signal at 1.24 ppm); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =168.9, 152.0 (C–B), 128.1, 83.7, 60.4, 36.1, 29.6, 25.0, 14.1; HRMS(EI) calcd for $C_{15}H_{27}BO_4$ 288.2002, found 288.2004.



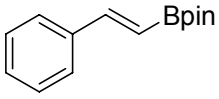
(*Z*)-ethyl 4-(tetrahydro-2H-pyran-2-yloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (2e). Using the general procedure, the title compound was prepared as a colorless oil in 77% yield (131 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ =1.24−1.42 (m, 15H), 1.47−1.90 (m, 6H), 3.47−3.57 (m, 1H), 3.88−3.96 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.61−4.71 (m, 2H), 4.81 (dd, *J* = 12.3 Hz, 2.1 Hz, 1H), 6.29 (s, 1H) (the irradiation of the vinylic proton at 6.29 ppm resulted in no enhancement of the allylic proton signal); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =165.6, 150.0 (C–B), 128.5, 98.2, 84.0, 65.7, 61.4, 60.1, 30.4, 25.5, 24.7, 19.0, 14.2; HRMS(EI) calcd for $C_{17}H_{29}BO_6$ 340.2057, found 340.2057.



Protodeboronated product of 2e: (*Z*)-ethyl 4-(tetrahydro-2H-pyran-2-yloxy)but-2-enoate. ^{1}H NMR (300MHz, $CDCl_3$): δ =1.29 (t, *J* = 7.2 Hz, 3H), 1.55−1.61 (m, 4H), 1.71−1.85 (m, 2H), 3.50−3.57 (m, 1H), 3.82−3.90 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.63−4.71 (m, 2H), 4.75−4.82 (m, 1H), 5.80 (td, *J* = 11.7 Hz, 2.7 Hz, 1H), 6.42 (td, *J* = 11.7 Hz, 5.1 Hz, 1H)



(*E*)-ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2g). Using the general procedure, the title compound was prepared as a colorless oil in 65% yield (73.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ =1.24−1.35 (m, 15H), 4.21(q, *J* = 7.2 Hz, 2H), 6.62 (d, *J* = 18.3 Hz, 1H), 6.78 (d, *J* = 18.3 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =166.0, 138.8, 134.1 (C–B), 84.1, 60.6, 24.8, 14.2; *m/z* 227(M^+, 100%), 211 (42), 182 (11), 127 (6), 111 (31).



(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane[2]

Using the general procedure, the title compound was prepared as a colorless oil in 99% yield (114 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ =1.25−1.38 (m, 12H), 6.17 (d, *J* = 18.3 Hz, 1H), 7.30−7.51 (m, 6H);^{13}C NMR (75.4 MHz, $CDCl_3$): δ =149.6, 137.4, 129.0, 128.6, 127.1, 116.2 (C–B), 83.3, 24.8; *m/z* 230 (M^+, 47%), 215 (21), 144 (100), 131 (23), 77 (6).

References:

1. T. Ishiyama, J. Takagi, A. Kamon, N. Miyaura, *J. Organomet. Chem*., 2003, **687**, 284−290.
2. C. E. Tucker, J. Davidson and P. Knochel. *J. Org. Chem*., 1992, **57**, 3482−3485.