Supporting Information

gem-Silylborylation of an *sp* Carbon: Novel Synthesis of 1-Boryl-1-silylallenes

Masaki Shimizu,* Takuya Kurahashi, Hirotaka Kitagawa, and Tamejiro Hiyama

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501

General remarks: All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere (deoxygenated by passing through BASF-Catalyst R3-11 column at 80 °C). ¹H NMR spectra were measured on a Varian Mercury 200 (¹H, 200 MHz) spectrometer. Chemical shifts of ¹H NMR are expressed in parts per million downfield relative to an internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet. ¹³C NMR spectra were measured on a Varian Mercury 200 (¹³C, 50 MHz) spectrometer and JEOL JMN ECP-500 (¹³C, 125 MHz) spectrometer with tetramethylsilane as an internal standard (δ = 0 ppm). Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. GC-MS analyses were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F₂₅₄ and R_f values were given. Column chromatography was carried out using Wakogel C-200. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H columns (chloroform as an eluent). Cooling a reaction vessel at –110 °C or –78 °C was effected using pentane with liquid nitrogen or methanol with dry ice, respectively.

Materials. Ethereal solvents such as THF and diethyl ether were distilled from benzophenone and sodium under an argon atmosphere. Toluene and dichloromethane were distilled from calcium hydride under an argon atmosphere. Butyllithium was purchased from Sigma-Aldrich Co. Inc., and titrated with *N*-pivaloyl-*o*-toluidine as an indicator. (Dimethylphenylsilyl)(pinacolato)borane was synthesized by the reported procedure [Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647-4649.].

General procedure for the *gem*-silylborylation of 3-chloro- or 3-alkoxy-1-alkyne.

3-Methyl-1-(dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,2-diene (5a)

To a solution of 3-chloro-3-methylbut-1-yne (**1a**) (50 mg, 0.50 mmol) in THF (3 mL) was added butyllithium in hexane (1.6 M, 0.32 mL, 0.50 mmol) dropwise at $-110\text{ }^{\circ}\text{C}$ and stirred at $-110\text{ }^{\circ}\text{C}$ for 2 min. The mixture was then treated with (dimethylphenylsilyl)(pinacolato)borane (**3**) (0.13 g, 0.50 mmol) at $-110\text{ }^{\circ}\text{C}$ followed by warming gradually to room temperature. After quenching with saturated aq. NH_4Cl (1 mL), the mixture was diluted with diethyl ether (30 mL) and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. Purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate 9 : 1) afforded **5a** as pale yellow oil (0.11 g, 70% yield). R_f 0.38 (hexane/ethyl acetate 9 : 1). ^1H NMR (CDCl_3) δ 0.37 (s, 6H), 1.18 (s, 12H), 1.60 (s, 6H), 7.26-7.39 (m, 3H), 7.51-7.61 (m, 2H). ^{13}C NMR (CDCl_3) δ -2.0, 18.8, 24.7, 83.0, 127.3, 128.5, 133.9, 139.7, 217.2. IR (neat) 2975, 2925, 1940, 1362, 1310, 1120, 1109, 856, 820, 698 cm^{-1} . MS m/z 328 (M^+ , 3), 327 (M^+-1 , 1), 313 (M^+-Me , 3), 135 (100). HRMS Calcd for $\text{C}_{19}\text{H}_{29}\text{BO}_2\text{Si}$: M^+ , 328.2030. Found: m/z 328.2052.

2-[Cyclohexylidene(dimethylphenylsilyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5c**)

Yield: 53% (BuLi); 60% (LDA). pale yellow oil. R_f 0.45 (hexane/ethyl acetate 9 : 1). ^1H NMR (CDCl_3) δ 0.40 (s, 6H), 1.17 (s, 12H), 1.20-1.70 (m, 6H), 1.96-2.12 (m, 4H), 7.24-7.38 (m, 3H), 7.50-7.62 (m, 2H). ^{13}C NMR (CDCl_3) δ -1.8, 24.6, 26.2, 27.1, 29.8, 82.9, 89.7, 127.3, 128.5, 133.9, 139.7, 213.9. IR (neat) 2928, 2856, 1933, 1304, 1142, 1113, 980, 854, 731 cm^{-1} . MS m/z 369 (M^++1 , 2), 368 (M^+ , 10), 353 (M^+-Me , 3), 226 (100), 135 (48). HRMS Calcd for $\text{C}_{22}\text{H}_{33}\text{BO}_2\text{Si}$: M^+ , 368.2343. Found: m/z 368.2333.

3-Phenyl-1-(dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propa-1,2-diene (**5d**)

Yield: 41% (BuLi); 52% (LDA). pale yellow oil. R_f 0.37 (hexane/ethyl acetate 9 : 1). ^1H NMR (CDCl_3) δ 0.42 (d, $J = 18.8$ Hz, 6H), 1.12 (d, $J = 3.6$ Hz, 12H), 5.74 (s, 1H), 7.03-7.28 (m, 8H), 7.51-7.56 (m, 2H). ^{13}C NMR (CDCl_3) δ -3.8, 23.0, 81.9, 123.7, 124.2, 125.8, 126.8, 127.2, 132.2, 132.9, 133.2, 136.7, 214.5. IR (neat) 2978, 1919, 1381, 1321, 1269, 1144, 1113, 852, 694 cm^{-1} . MS m/z 377 ($\text{M}^+ + 1$, 2), 376 (M^+ , 8), 234 (100), 135 (59). HRMS Calcd for $\text{C}_{23}\text{H}_{29}\text{BO}_2\text{Si}$: M^+ , 376.2030. Found: m/z 376.2045.

(R)-(-)-1-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,2-diene (5e)

To a solution of (*S*)-methanesulfonic acid 1-methylprop-2-ynyl ester (**1g**) (70 mg, 0.50 mmol) and (dimethylphenylsilyl)(pinacolato)borane (**3**) (0.13 g, 0.50 mmol) in THF (3 mL) was added LDA (0.50 mmol) in THF (1.0 mL) dropwise at -110 $^{\circ}\text{C}$ and stirred at -110 $^{\circ}\text{C}$ for 5 min. The mixture was then treated with chlorotrimethylsilane (60 mg, 0.55 mmol) and then warmed gradually to room temperature. After quenching with saturated aq. NH_4Cl (1 mL), the mixture was diluted with diethyl ether (30 mL) and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. Purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate 10 : 1) afforded **5e** as pale yellow oil (0.12 g, 75% yield). $[\alpha]_D^{25}$ -11.44° (c 3.20, CHCl_3). R_f 0.42 (hexane/ethyl acetate 10 : 1). ^1H NMR (CDCl_3) δ 0.40 (s, 6H), 1.21 (s, 12H), 1.60 (d, $J = 7.0$ Hz, 3H), 4.61 (q, $J = 7.0$ Hz, 1H), 7.26-7.41 (m, 3H), 7.41-7.62 (m, 2H). ^{13}C NMR (CDCl_3) δ -2.2, 12.1, 73.3, 83.4, 127.6, 129.2, 134.1, 139.2, 217.6. IR (neat) 2978, 2895, 1933, 1381, 1319, 1142, 1110, 979, 813, 779, 700 cm^{-1} . MS m/z 315 ($\text{M}^+ + 1$, 3), 314 (M^+ , 5), 299 ($\text{M}^+ - \text{Me}$, 10), 172 (100). HRMS (FAB) Calcd for $\text{C}_{18}\text{H}_{27}\text{BO}_2\text{Si}$: M^+ , 314.1873. Found: m/z 314.1868.

(R)-(-)-1-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,2-diene (5f)

Yield: 83%. Optical purity: 70% ee. pale yellow oil. $[\alpha]_D^{25}$ -9.78° (c 3.22, CHCl_3). R_f 0.52 (hexane/ethyl acetate 9 : 1). ^1H NMR (CDCl_3) δ 0.42, (s, 6H), 0.87 (t, $J = 5.0$ Hz, 3H), 1.14-1.35

(m, 18H), 1.95 (m, 2H), 4.68 (td, $J = 7.0, 1.8$ Hz, 1H), 7.29-7.33 (m, 3H), 7.56-7.60 (m, 2H). ^{13}C NMR (CDCl_3) δ -1.9, 14.2, 22.7, 24.6, 24.6, 24.7, 24.8, 24.9, 25.0, 26.9, 27.0, 29.6, 31.4, 78.9, 83.2, 127.3, 128.6, 133.9, 139.2, 216.7. IR (neat) 2928, 2856, 1933, 1427, 1389, 1304, 1269, 1142, 1113, 980, 854, 816, 779, 731, 700 cm^{-1} . MS m/z 371 ($\text{M}^+ + 1$, 21), 370 (M^+ , 60), 369 ($\text{M}^+ - 1$, 18), 355 ($\text{M}^+ - \text{Me}$, 18), 192 (100). HRMS (FAB) Calcd for $\text{C}_{22}\text{H}_{35}\text{BO}_2\text{Si}$: M^+ , 370.2499. Found: m/z 370.2508. The optical purity was determined by HPLC analysis (column: Daicel AD (0.46 $\text{cm}\phi$ x 25 cm), eluent: hexane, flow rate: 0.5 mL/min): (*R*) R_t = 17.2 min; (*S*) R_t = 15.8 min.

Stereochemical assignment of (5e) and (5f).

Propargylation of cyclohexanecarbaldehyde.

A solution of **5e** (90 mg, 0.30 mmol) and cyclohexanecarbaldehyde (50 mg, 0.45 mmol) in toluene (2.0 mL) was stirred at -20°C for 24 h. After quenching with water (1 mL), the mixture was diluted with diethyl ether (40 mL) and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The diastereomer ratio was determined from the integral value of the distinguishable signals in ^1H NMR spectra of the crude product: **anti-6e**: δ 3.10 (dd, $J = 6.8, 4.4$ Hz, 1H); **syn-6e**: δ 3.37 (dd, $J = 6.0, 6.0$ Hz, 1H). Diastereomer **anti-6e** and **syn-6e** were separated and isolated by column chromatography on silica gel (hexane/ethyl acetate 10 : 1) as pale yellow oil (80 mg, 92% yield, *anti* : *syn* = 93 : 7).

anti-1-Cyclohexyl-4-(dimethylphenylsilyl)-2-methylbut-3-yn-1-ol (anti-6e)

Yield: 86%. pale yellow oil. $[\alpha]_D^{25} -1.39^\circ$ (c 3.51, CHCl_3). R_f 0.27 (hexane/ethyl acetate 10 : 1). ^1H NMR (CDCl_3) δ 0.40 (s, 6H), 1.00-1.81 (m, 14H), 1.92 (d, $J = 11.4$ Hz, 1H), 2.80 (m, 1H), 3.10 (dd, $J = 6.8, 4.4$ Hz, 1H), 7.31-7.50 (m, 3H), 7.56-7.70 (m, 2H). ^{13}C NMR (CDCl_3) δ -0.65, 26.0, 26.3, 28.1, 29.7, 31.2, 41.2, 78.5, 85.4, 109.6, 127.8, 129.3, 133.6, 137.3. IR (neat) 3441, 2926, 2853, 2164, 1448, 1427, 1248, 1114, 1049, 991, 974, 829, 779, 700 cm^{-1} . MS (FAB) m/z 301 (MH^+ , 17), 223 (28), 135 (100). HRMS (FAB) Calcd for $\text{C}_{19}\text{H}_{29}\text{OSi}$: MH^+ , 301.1988. Found: m/z 301.1991.

syn-1-Cyclohexyl-4-(dimethylphenylsilyl)-2-methylbut-3-yn-1-ol (syn-6e)

Yield: 6%. pale yellow oil. $[\alpha]_D^{25} -3.58^\circ$ (c 0.67, CHCl_3). R_f 0.20 (hexane/ethyl acetate 10 : 1). ^1H NMR (CDCl_3) δ 0.39 (s, 6H), 0.81-1.84 (m, 14H), 1.95 (m, 1H), 2.71 (m, 1H), 3.37 (dd, J = 6.0, 6.0 Hz, 1H), 7.31-7.50 (m, 3H), 7.55-7.71 (m, 2H). ^{13}C NMR (CDCl_3) δ -0.5, 15.2, 26.1, 26.5, 27.7, 29.8, 31.3, 40.1, 78.1, 84.3, 111.3, 127.3, 129.2, 133.5, 137.3. IR (neat) 3385, 2928, 2853, 2164, 1450, 1427, 1249, 1117, 1067, 837, 700 cm^{-1} . MS (FAB) m/z 301 (MH^+ , 15), 223 (26), 135 (100). HRMS (FAB) Calcd for $\text{C}_{19}\text{H}_{29}\text{OSi}$: MH^+ , 301.1988. Found: m/z 301.1985.

***anti*-1-Cyclohexyl-4-(dimethylphenylsilyl)-2-pentylbut-3-yn-1-ol (*anti*-6f)**

The diastereomer ratio was determined from the integral value of the distinguishable signals in ^1H NMR spectra of the crude: ***anti*-6f**: δ 3.15 (m, 1H); ***syn*-6f**: δ 3.40 (m, 1H).

Yield: 70%. colorless oil. $[\alpha]_D^{26} 16.91^\circ$ (c 2.56, CHCl_3). R_f 0.38 (hexane/ethyl acetate 10 : 1). ^1H NMR (CDCl_3) δ 0.41 (s, 6H), 0.87-1.80 (m, 22H), 1.97 (d, J = 11.2 Hz, 1H), 2.68 (m, 1H), 3.15 (m, 1H), 7.26-7.41 (m, 3H), 7.59-7.66 (m, 2H). ^{13}C NMR (CDCl_3) δ -0.6, 14.0, 22.6, 26.0, 26.3, 26.4, 27.2, 28.5, 29.6, 31.6, 32.1, 37.2, 42.2, 86.5, 108.7, 127.8, 129.3, 133.6, 137.4, 144.6. IR (neat) 3441, 3068, 2924, 2855, 2164, 1450, 1248, 1115, 837, 814, 731 cm^{-1} . MS (FAB) m/z 357 (MH^+ , 15), 279 (18), 135 (100) 75 (51). HRMS (FAB) Calcd for $\text{C}_{23}\text{H}_{37}\text{OSi}$: MH^+ , 357.2614. Found: m/z 357.2612.

***syn*-Cyclohexyl-4-(dimethylphenylsilyl)-2-pentylbut-3-yn-1-ol (*syn*-6f)**

Yield: 9%. colorless oil. $[\alpha]_D^{26} 8.03^\circ$ (c 1.22, CHCl_3). R_f 0.38 (hexane/ethyl acetate 10 : 1). ^1H NMR (CDCl_3) δ 0.39 (s, 6H), 0.81-1.89 (m, 22H), 1.93 (d, J = 11.6 Hz, 1H), 2.61 (m, 1H), 3.40 (m, 1H), 7.26-7.39 (m, 3H), 7.60-7.65 (m, 2H). ^{13}C NMR (CDCl_3) δ -0.6, 14.0, 22.6, 26.0, 26.3, 27.1, 27.2, 29.8, 31.7, 37.2, 40.2, 85.5, 110.2, 127.8, 129.3, 133.6, 137.5, 139.0. IR (neat) 3385, 2926, 2855, 2166, 1448, 1248, 1115, 814, 779, 729, 698 cm^{-1} . MS (FAB) m/z 357 (MH^+ , 13), 279 (41), 135 (100) 75 (77). HRMS (FAB) Calcd for $\text{C}_{23}\text{H}_{37}\text{OSi}$: MH^+ , 357.2614. Found: m/z

357.2608.

Protodesilylation

anti-1-Cyclohexyl-2-methylbut-3-yn-1-ol (*anti*-7e)

To a solution of *anti*-6e (80 mg, 0.25 mmol) in THF (2 mL) was added 1.0 M solution of tetrabutylammonium fluoride in THF (0.25 mL, 0.25 mmol), and the resulting solution was stirred at 0 °C for 6 h. After quenching with water (1 mL), the mixture was diluted with diethyl ether (30 mL) and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. Purification by column chromatography on silica gel (hexane/ethyl acetate 10 : 1) afforded *anti*-7e as colorless oil (30 mg, 72% yield). Optical purity: 74% ee. $[\alpha]_D^{27} -3.21^\circ$ (*c* 1.37, CHCl₃). *R*_f 0.21 (hexane/ethyl acetate 10 : 1). ¹H NMR (CDCl₃) δ 0.95-1.80 (m, 14H), 1.96 (d, *J* = 12.3 Hz, 1H), 2.20 (d, *J* = 2.4 Hz, 1H), 2.72 (m, 1H), 3.03 (m, 1H). The optical purity was determined by GC analysis (column: Chiral-DEX CB (0.25 mm ϕ x 25 m), column temperature: 120 °C constant): (1*R*, 2*S*) *R*_t = 15.0 min; (1*S*, 2*R*) *R*_t = 13.9 min. The Registry Number for *anti*-7e: [200440-86-4].

anti-1-Cyclohexyl-2-pentylbut-3-yn-1-ol (*anti*-7f)

Yield: 82%. Optical purity: 70% ee. $[\alpha]_D^{27} 5.38^\circ$ (*c* 1.20, CHCl₃). *R*_f 0.30 (hexane/ethyl acetate 10 : 1). ¹H NMR (CDCl₃) δ 0.89 (t, *J* = 6.6 Hz, 3H), 0.90-1.84 (m, 19H), 1.99 (m, 1H), 2.11 (d, *J* = 2.4 Hz, 1H), 2.56 (m, 1H), 3.13 (ddd, *J* = 8.1, 8.1, 3.3 Hz). The optical purity was determined by GC analysis (column: Chiral-DEX CB (0.25 mm ϕ x 25 m), column temperature: 130 °C constant): (1*R*, 2*S*) *R*_t = 17.2 min; (1*S*, 2*R*) *R*_t = 16.5 min. The Registry Number for *anti*-7f: [252234-97-2].