Supporting Information:

1-Silyl-1-boryl-2-alkenes: Novel Class of Reagents for Stereodivergent Allylation Leading to 4-Oxy-(*E*)-alkenylboronates and 4-Oxy-(*Z*)-alkenylsilanes

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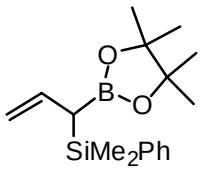
General remarks

^{1}H NMR spectra were measured on a Varian Mercury 200 (^{1}H, 200 MHz) spectrometer. Chemical shifts of ^{1}H 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. ^{13}C NMR spectra were measured on a Varian Mercury 200 (^{13}C, 50 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. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. Melting points were determined using a YANAKO MP-500D. GC analyses were measured on a SHIMADZU GC-14B. TLC analyses were performed by means of Merck Kieselgel 60 F and column chromatography was carried out using Wakogel C-200. THF and 1,4-dioxane were distilled from benzophenone and sodium under an argon atmosphere. Dichloromethane was 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. All reactions were carried out under an argon atmosphere. Cooling a reaction vessel at –98 °C or –78 °C was effected using methanol with liquid nitrogen or with dry ice, respectively.

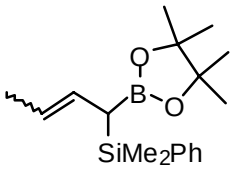
General procedure for the *gem*-silylborylation of allylic chlorides. 3-(Dimethylphenylsilyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (2a)



To a solution of allyl chloride (0.26 mL, 3.2 mmol) and (dimethylphenylsilyl)(pinacolato)borane (**1**) (0.92 g, 3.5 mmol) in THF (20 mL) at -98 °C was added a solution of LDA (3.3 mmol) in THF (8 mL). The reaction mixture was stirred for 10 min at –98 °C and then allowed to gradually warm to room temperature. Stirring the solution overnight followed by usual workup gave the crude product. Purification by column chromatography on silica gel (hexane/ethyl acetate = 9 : 1) afforded **2a** as a colorless oil (0.79 g, 82% yield).
TLC: R_f 0.45 (hexane/ethyl acetate = 9 : 1).

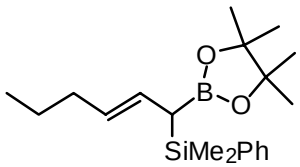
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.34 (s, 3H), 0.35 (s, 3H), 1.13 (s, 6H), 1.16 (s, 6H), 1.79 (d, *J* = 10.5 Hz, 1H), 4.74 (ddd, *J* = 16.8, 2.2, 0.6 Hz, 1H), 4.78 (dd, *J* = 10.5, 2.2 Hz, 1H), 5.85 (ddd, *J* = 16.8, 10.5, 10.5 Hz, 1H), 7.28-7.38 (m, 3H), 7.48-7.60 (m, 2H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = -3.2, -3.2, 24.7, 24.8, 82.8, 112.2, 127.4, 128.8, 133.9, 135.3, 138.0.
IR: (neat, thin layer, cm^{-1}) 2985, 1623, 1374, 1339, 1318, 1145, 839.
MS (EI, 70 eV): *m/z* 303 (M^++1, 1.3), 302 (M^+, 4.7), 301 (M^+-1, 1.0), 284 (M^+-Me, 5.6), 245 (28), 235 (M^+-Ph, 13), 202 (32), 187 (32), 160 (49), 135 ($PhMe_2Si^+$, 100).
Anal. Calcd for $C_{17}H_{27}BO_2Si$: C, 67.55; H, 9.00. Found: C, 67.29; H, 8.92.

(*E*) and (*Z*)-1-(Dimethylphenylsilyl)-1- (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butene (2b)



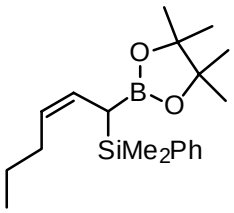
Purification: silica gel column chromatography (hexane/ethyl acetate = 19 : 1).
Yield: 86% (*E*/*Z* = 83/17).
Colorless oil.
TLC: R_f 0.44 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) (*E*-**2b**): δ = 0.35 (s, 3H), 0.37 (s, 3H), 1.15 (s, 6H), 1.18 (s, 6H), 1.63 (dd, *J* = 6.3, 1.5 Hz, 3H), 1.70 (d, *J* = 10.0 Hz, 1H), 5.15 (dq, *J* = 15.1, 6.3 Hz, 1H), 5.51 (ddq, *J* = 15.1, 10.1, 1.5 Hz, 1H), 7.28-7.38 (m, 3H), 7.48-7.60 (m, 2H).
(*Z*-**2b**) (assignable peaks): δ = 0.37 (s, 3H), 0.39 (s, 3H), 1.38 (dd, *J* = 6.6, 1.6 Hz, 3H), 2.05 (d, *J* = 11.4 Hz, 1H).
^{13}C NMR (50 MHz, $CDCl_3$) (*E*-**2b**): δ = -3.1, -3.1, 18.1, 24.8, 82.7, 122.8, 126.9, 127.3, 128.7, 134.0, 138.5.
IR: (neat, thin layer, cm^{-1}) 2978, 2989, 1655, 1641, 1589, 1371, 1348, 1313, 1252, 1144, 1113, 833, 793, 731, 698.
MS (EI, 70 eV): *m/z* 317 (M^++1, 2.6), 316 (M^+, 9.8), 301 (M^+-Me, 4.3), 216 (89), 174 (100), 135 ($PhMe_2Si^+$, 87).
Anal. Calcd for $C_{18}H_{29}BO_2Si$: C, 68.35; H, 9.24. Found: C, 68.60; H, 9.10.
The isomer ratio was determined from the integral value of the distinguishable signals in ^{1}H NMR spectra : (*E*)-**2b**: δ 1.63 (dd, *J* = 6.3, 1.5 Hz); (*Z*)-**2b**: δ 1.38 (dd, *J* = 6.6, 1.6 Hz).

(*E*) -1-(Dimethylphenylsilyl)-1- (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-hexene (2c)



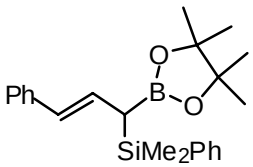
Purification: silica gel column chromatography (hexane/ethyl acetate = 9 : 1).
Yield: 75%.
Colorless oil.
TLC: R_f 0.45 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.34 (s, 3H), 0.35 (s, 3H), 0.83 (t, *J* = 7.3 Hz, 3H), 1.14 (s, 6H), 1.17 (s, 6H), 1.30 (m, 2H), 1.69 (d, *J* = 10.2 Hz, 1H), 1.93 (q, *J* = 7.0 Hz, 2H), 5.12 (dt, *J* = 15.0, 6.8 Hz, 1H), 5.46 (ddt, *J* = 15.1, 10.1, 1.2 Hz, 1H), 7.28-7.40 (m, 3H), 7.48-7.60 (m, 2H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = -3.2, -3.0, 13.6, 23.1, 24.8, 24.9, 35.0, 82.8, 126.0, 127.4, 128.5, 128.8, 134.0, 138.5.
IR: (neat, thin layer, cm^{-1}) 2980, 2960, 1650, 1379, 1372, 1356, 1316, 1248, 1143, 850, 837, 700.
MS (EI, 70 eV): *m/z* 345 (M^++1, 3.0), 344 (M^+, 9.0), 244 (61), 202 (100), 135 ($PhMe_2Si^+$, 89).
Anal. Calcd for $C_{20}H_{33}BO_2Si$: C, 69.75; H, 9.66. Found: C, 69.51; H, 9.80.

(*Z*) -1-(Dimethylphenylsilyl)-1- (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-hexene (2d)



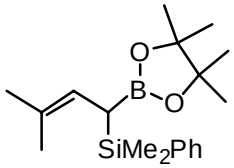
Purification: silica gel column chromatography (hexane/ethyl acetate = 9 : 1).
Yield: 75%.
Colorless oil.
TLC: R_f 0.44 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.34 (s, 3H), 0.35 (s, 3H), 0.80 (t, *J* = 7.3 Hz, 3H), 1.13 (s, 6H), 1.16 (s, 6H), 1.10-1.30 (m, 2H, overlap), 1.58-1.97 (m, 2H), 2.01 (d, *J* = 11.8 Hz, 1H), 5.20 (dt, *J* = 10.6, 7.2 Hz, 1H), 5.49 (ddt, *J* = 11.6, 10.8, 1.6 Hz, 1H), 7.28-7.42 (m, 3H), 7.48-7.62 (m, 2H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = -3.1, -3.0, 13.8, 22.6, 24.8, 29.1, 82.8, 125.6, 126.8, 127.4, 128.8, 133.9, 138.4.
IR: (neat, thin layer, cm^{-1}) 2980, 2960, 1639, 1370, 1334, 1310, 1248, 1143, 1113, 850, 836, 699.
MS (EI, 70 eV): *m/z* 345 (M^++1, 1.9), 344 (M^+, 6.7), 329 (M^+-Me, 4.2), 244 (56), 202 (97), 135 ($PhMe_2Si^+$, 100).
Anal. Calcd for $C_{20}H_{33}BO_2Si$: C, 69.75; H, 9.66. Found: C, 69.81; H, 9.42.

(*E*)-3-(Dimethylphenylsilyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (2e)



Purification: silica gel column chromatography (hexane/ethyl acetate = 19 : 1).
Yield: 75%.
White solid.
Mp 74.5 °C~75.5 °C
TLC: R_f 0.36 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.37 (s, 3H), 0.40 (s, 3H), 1.12 (s, 6H), 1.16 (s, 6H), 1.92 (d, *J* = 10.4 Hz, 1H), 6.08 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.7, 10.5 Hz, 1H), 7.04-7.17 (m, 1H), 7.17-7.27 (m, 4H), 7.27-7.38 (m, 3H), 7.46-7.60 (m, 2H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = -3.1, -3.0, 24.8, 24.9, 83.0, 125.5, 125.9, 127.5, 127.7, 128.3, 128.4, 129.0, 134.0, 137.9, 138.6.
IR: (nujol, thin layer, cm^{-1}) 1637, 1598, 1350, 1318, 1302, 1265, 1249, 1139, 1111, 813.
MS (EI, 70 eV): *m/z* 379 (M^++1, 1.2), 378 (M^+, 4.2), 236 (43), 200 (100), 135 ($PhMe_2Si^+$, 97).
Anal. Calcd for $C_{23}H_{31}BO_2Si$: C, 73.01; H, 8.26. Found: C, 72.77; H, 8.18.

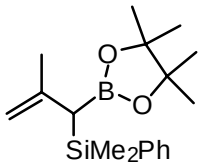
1-(Dimethylphenylsilyl)-3-methyl-1- (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butene (2f)



Purification: silica gel column chromatography (hexane/ethyl acetate = 19 : 1).
Yield: 72%.
Colorless oil.
TLC: R_f 0.45 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.33 (s, 3H), 0.37 (s, 3H), 1.15 (s, 6H), 1.18 (s, 6H), 1.30 (d, *J* = 1.0 Hz, 3H), 1.67 (d, *J* = 1.2 Hz, 3H), 1.86 (d, *J* = 11.4 Hz, 1H), 5.27 (dt, *J* = 11.4, 1.1 Hz, 1H), 7.28-7.40 (m, 3H), 7.46-7.62 (m, 2H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = -3.0, -3.0, 24.8, 24.9, 25.8, 82.8, 120.0, 127.3, 128.1, 128.7, 134.0, 138.7.
IR: (neat, thin layer, cm^{-1}) 2980, 1660, 1590, 1358, 1327, 1310, 1142, 1112, 837, 820, 699.

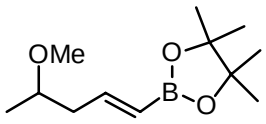
MS (EI, 70 eV): *m/z* 331 (M^++1, 1.3), 330 (M^+, 4.3), 315 (M^+-Me, 2.5), 230 (61), 188 (100), 152 (16), 135 ($PhMe_2Si^+$, 48).
Anal. Calcd for $C_{19}H_{31}BO_2Si$: C, 69.08; H, 9.46. Found: C, 69.26; H, 9.39.

3-(Dimethylphenylsilyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (2g)



Purification: silica gel column chromatography (hexane/ethyl acetate = 19 : 1).
Yield: 73%.
Colorless oil.
TLC: R_f 0.48 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.37 (s, 3H), 0.39 (s, 3H), 1.14 (s, 6H), 1.18 (s, 6H), 1.61 (s, 3H), 4.64 (s, 2H), 7.28-7.42 (m, 3H), 7.50-7.62 (m, 2H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = -2.7, 24.7, 24.9, 26.5, 82.8, 109.2, 127.4, 128.8, 134.0, 138.9, 143.3.
IR: (neat, thin layer, cm^{-1}) 2977, 1628, 1369, 1330, 1310, 1259, 1141, 1110, 699.
MS (EI, 70 eV): *m/z* 317 (M^++1, 0.1), 316 (M^+, 0.4), 315 (M^+-1, 0.2), 301 (M^+-Me, 4.6), 259 (41), 225 (21), 216 (25), 201 (96), 174 (29), 159 (15), 135 ($PhMe_2Si^+$, 100).
Anal. Calcd for $C_{18}H_{29}BO_2Si$: C, 68.35; H, 9.24. Found: C, 68.57; H, 9.36.

General procedure for the allylation of acetals in the presence of titanium tetrachloride. (*E*)-4-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene (3a)



To a solution of **2a** (0.17 g, 0.55 mmol) and acetaldehyde dimethylacetal (116 mL, 1.10 mmol) in CH_2Cl_2 (6 mL) was added a solution of $TiCl_4$ in CH_2Cl_2 (1.0 M, 0.82 mL, 0.82 mmol) at –78 °C. The solution was stirred for 15 min at –78 °C before quenching with water (0.50 mL) at –78 °C. The mixture was warmed up to room temperature, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated to give a crude product consisting of *E*/*Z* = 94 : 6 as revealed by ^{1}H NMR spectra. Purification by silica gel column chromatography (hexane/ethyl acetate = 2 : 1) afforded (*E*)-4-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene (**3a**) (97 mg, 78% yield) and (*Z*)-**3a** (4.1 mg, 3% yield).

Data of (*E*)-**3a**:

TLC: R_f 0.53 (hexane/ethyl acetate = 2 : 1).

^{1}H NMR: (200 MHz, $CDCl_3$) δ = 1.15 (d, *J* = 6.0 Hz, 3H), 1.27 (s, 12H), 2.27 (ddt, *J* = 14.4, 6.7, 1.4 Hz, 1H), 2.44 (ddt, *J* = 14.4, 6.4, 1.5 Hz, 1H), 3.32 (s, 3H), 3.42 (m, 1H), 5.50 (dt, *J* = 18.2, 1.5 Hz, 1H), 6.60 (dt, *J* = 18.0, 6.6 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$) δ = 19.1, 24.8, 42.6, 56.0, 75.9, 83.1, 150.3.

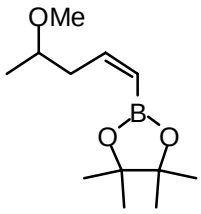
IR: (neat, thin layer, cm^{-1}) 2980, 2935, 1640, 1362, 1321, 1146, 998, 972, 852.

MS (EI, 70 eV): *m/z* 225 (M^+-1, 0.6), 211 (M^+-Me, 17), 111 (8.9), 101 (8.0), 95 (7.5), 59 (100).

Anal. Calcd for $C_{12}H_{23}BO_3$: C, 63.74; H, 10.25. Found: C, 63.62; H, 10.41.

The isomer ratio was determined from the integral value of the distinguishable signals in ^{1}H NMR spectra of the crude product mixture: (*E*)-**3a** δ 3.32 (s, 3H); (*Z*)-**3a** δ 3.35 (s, 3H).

Data of (*Z*)-**3a:**



Yield: 3%

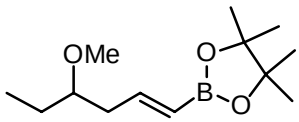
TLC: R_f 0.58 (hexane/ethyl acetate = 2 : 1).

^{1}H NMR: (200 MHz, $CDCl_3$) δ = 1.15 (d, *J* = 6.2 Hz, 3H), 1.27 (s, 12H), 2.46-2.78 (m, 2H), 3.35 (s, 3H), 3.38 (m, 1H), 5.46 (dt, *J* = 13.6, 1.3 Hz, 1H), 6.47 (dt, *J* = 13.8, 7.0 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$) δ = 19.0, 24.8, 24.9, 38.1, 56.0, 76.9, 82.9, 150.6.

MS (EI, 70 eV): *m/z* 226 (M^+, 0.03), 211 (M^+-Me, 1.0), 195 (M^+-OMe, 0.6), 110 (15), 95 (13), 59 ($MeCHOMe^+$, 100).

(*E*)-4-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene [(*E*)-3b]



Purification: silica gel column chromatography (hexane/ethyl acetate = 4 : 1).

Yield: 77%.

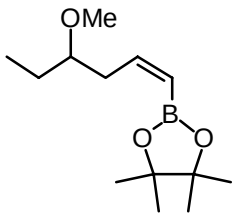
Colorless oil.

TLC: R_f 0.43 (hexane/ethyl acetate = 4 : 1).

^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.90 (t, *J* = 7.3 Hz, 3H), 1.27 (s, 12H), 1.42-1.62 (m, 2H), 2.37 (m, 2H), 3.21 (m, 1H), 3.34 (s, 3H), 5.50 (dt, *J* = 18.0, 1.4 Hz, 1H), 6.62 (dt, *J* = 18.0, 6.9 Hz, 1H).

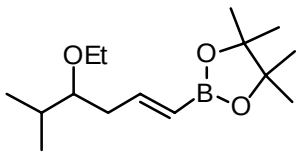
^{13}C NMR (50 MHz, $CDCl_3$) δ = 9.3, 24.7, 25.9, 39.3, 56.4, 81.0, 83.0, 150.3.
IR: (neat , thin layer, cm^{-1}) 2977, 2930, 1638, 1399, 1360, 1320, 1145, 1088, 1000, 971, 849.
MS (EI, 70 eV): *m/z* 239 (M^+-1, 0.6), 225 (M^+-Me, 20), 211 (M^+-Et, 8.6), 111 (25), 101 (9.9), 83 (13), 73 ($EtCHOMe^+$, 100).
Anal. Calcd for $C_{13}H_{25}BO_3$: C, 65.02; H, 10.49. Found: C, 64.74; H, 10.23.
The isomer ratio was determined from the integral value of the distinguishable signals in ^{1}H NMR spectra of the crude product mixture: (*E*)-**3b** δ 3.34 (s, 3H); (*Z*)-**3b** δ 3.36 (s, 3H).

(*Z*)-**3b**



Yield: 5% (isolated by second column chromatography on silica gel).
TLC: R_f 0.49 (hexane/ethyl acetate = 4 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.91 (t, *J* = 7.5 Hz, 3H), 1.27 (s, 12H), 1.51 (m, 2H), 2.64 (t, *J* = 6.6 Hz, 2H), 3.17 (m, 1H), 3.36 (s, 3H), 5.44 (d, *J* = 13.8 Hz, 1H), 6.49 (m, 1H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 9.5, 24.9, 26.1, 35.3, 56.5, 82.3, 82.9, 150.9.
MS (EI, 70 eV): *m/z* 239 (M^+-1, 0.1), 225 (M^+-Me, 4.3), 211 (M^+-Et, 5.8), 193 (25), 124 (76), 111 (67), 101 (51), 95 (68), 83 (49), 73 ($EtCHOMe^+$, 100).

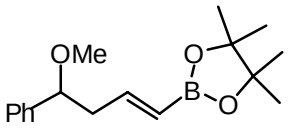
(*E*)-4-Ethoxy-5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene (3c)



Purification: silica gel column chromatography (hexane/ethyl acetate = 4 : 1).
Yield: 85% (*E* only).
Colorless oil.
TLC: R_f 0.28 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.88 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 12H), 1.78 (m, 1H), 2.35 (tt, *J* = 6.4, 1.4 Hz, 2H), 3.07 (q, *J* = 5.8 Hz, 1H), 3.43 (dq, *J* = 9.2, 7.0 Hz, 1H), 3.56 (dq, *J* = 9.2, 7.0 Hz, 1H), 5.49 (dt, *J* = 18.0, 1.4 Hz, 1H), 6.66 (dt, *J* = 17.8, 6.8 Hz, 1H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 15.6, 18.0, 18.6, 24.8, 31.0, 37.7, 65.2, 83.0, 83.7, 151.3.

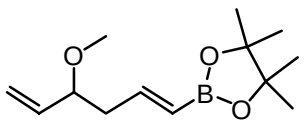
IR: (neat, thin layer, cm^{-1}) 2980, 2935, 2872, 1639, 1400, 1361, 1321, 1265, 1147, 1111, 1002, 973, 850.
MS (EI, 70 eV): *m/z* 267 (M^+-1, 0.4), 253 (M^+-Me, 15), 225 (M^+-$CHMe_2$, 25), 101 ($Me_2CHCHOEt^+$, 100), 73 (81).
Anal. Calcd for $C_{15}H_{29}BO_3$: C, 67.17; H, 10.90. Found: C, 67.41; H, 11.20.

(*E*)-4-Methoxy-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (3d)



Purification: silica gel column chromatography (hexane/ethyl acetate = 9 : 1).
Yield: 69% (*E* only).
Colorless oil.
TLC: R_f 0.43 (hexane/ethyl acetate = 4 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 1.26 (s, 12H), 2.71 (dddd, *J* = 15.2, 6.4, 5.0, 1.6 Hz, 1H), 2.67 (dddd, *J* = 15.2, 8.3, 6.7, 1.7 Hz, 1H), 3.21 (s, 3H), 4.23 (dd, *J* = 8.2, 5.0 Hz, 1H), 5.50 (dt, *J* = 17.9, 1.6 Hz, 1H), 6.63 (dt, *J* = 18.0, 6.4 Hz, 1H), 7.25-7.40 (m, 5H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 24.8, 44.6, 56.7, 82.9, 83.1, 126.6, 127.6, 128.4, 141.73, 150.2.
IR: (neat, thin layer, cm^{-1}) 2980, 2935, 2823, 1639, 1450, 1361, 1320, 1144, 1105, 971, 851, 759, 701.
MS (EI, 70 eV): *m/z* 287 (M^+-1, 0.2), 273 (M^+-Me, 13), 122 (47), 121 ($PhCHOMe^+$, 100), 105 (12), 91 (24), 77 (29).
Anal. Calcd for $C_{17}H_{25}BO_3$: C, 70.85; H, 8.74. Found: C, 70.99; H, 8.94.
The isomer ratio was determined from the integral value of the distinguishable signals in ^{1}H NMR spectra of the crude product mixture: (*E*)-**3d** δ 3.21 (s, 3H); (*Z*)-**3d** δ 3.24 (s, 3H).

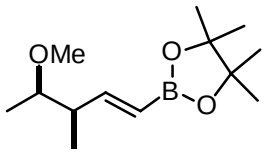
(*E*)-4-Methoxy-(4,4,5,5-tetramethyl-1,3,2-dioxaborola-2-yl)-1,5-hexadiene (3e)



Purification: silica gel column chromatography (hexane/ethyl acetate = 10 : 1).
Yield: 62%.
Colorless oil.
TLC: R_f 0.24 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 1.25 (s, 12H), 2.41 (m, 2H), 3.27 (s, 3H), 3.61 (d, *J* = 6.8 Hz, 1H), 3.68 (d, *J* = 6.8 Hz, 1H), 5.17 (ddd, *J* = 4.2, 1.8, 0.8 Hz, 1H), 5.24 (dd, *J* = 2.0, 0.6 Hz, 1H), 5.49

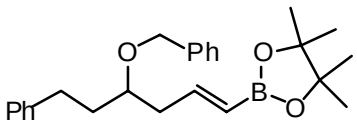
(dt, *J* = 18.0, 1.4 Hz, 1H), 5.68 (dd, *J* = 18.0, 7.4 Hz, 1H), 6.59 (dt, *J* = 18.0, 6.8 Hz, 1H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 24.7, 41.9, 56.1, 81.7, 83.1, 117.4, 117.4, 138.0, 149.7.
IR: (neat, thin layer, cm^{-1}) 3209, 3080, 2980, 2928, 1639, 1398, 1364, 1146, 1101, 1043, 851.
MS (EI, 70 eV): *m/z* 238 (M^+, 1.5), 223 (M^+-Me, 18), 71(100).
Anal. Calcd for $C_{13}H_{23}BO_3$: C, 65.57; H, 9.74. Found: C, 65.70; H, 10.02.

(*E*)-4-Methoxy-3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene (3f)



Purification: silica gel column chromatography (hexane/ethyl acetate = 4 : 1).
Yield: 81% as a diastereomer mixture (*E*, *erythro*/*E*, *threo*/others = 73 : 24 : 3).
Colorless oil.
TLC: R_f 0.38 (hexane/ethyl acetate = 4 : 1).
E, erythro:
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 1.03 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H), 1.27 (s, 12H), 2.41 (m, *J* = 6.6 Hz, 1H), 3.20 (m, *J* = 6.2 Hz, 1H), 3.33 (s, 3H), 5.46 (d, *J* = 18.2 Hz, 1H), 6.60 (dd, *J* = 18.2, 7.1 Hz, 1H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 15.1, 16.1, 24.7, 44.2, 56.2, 80.0, 82.8, 155.5.
E, threo (assignable peaks):
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 3.32 (s, 3H), 6.59 (dd, *J* = 18.1, 6.7 Hz, 1H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 13.5, 15.2, 43.4, 79.7, 155.5.
IR: (neat, thin layer, cm^{-1}) 2978, 2932, 1638, 1362, 1321, 1269, 1213, 1148, 1099, 1001, 970, 851.
MS (EI, 70 eV): *m/z* 225 (M^+-Me, 7.3), 182 (2.2), 109 (3.7), 101 (6.7), 82 (16), 67 (6.4), 56 ($MeCHOMe^+$, 100).
Anal. Calcd for $C_{17}H_{25}BO_3$: C, 65.02; H, 10.49. Found: C, 65.09; H, 10.71.
The ratio (*E*-isomer/*Z*-isomer) was determined by ^{1}H NMR.
The isomer ratio of *E*-isomers was determined by GC analysis (column: OV-1701 bonded 0.25 mmϕ x 25 m, column temperature: 120 °C constant): (*E, erythro*) R_t = 11.2 min; (*E, threo*) R_t = 10.8 min.

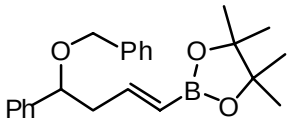
General procedure for the allylation of aldehyde in the presence of trimethylsilyl trifluoromethanesulfonate and benzyl trimethylsilyl ether.
(*E*)- 4-Benzyloxy-6-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene (3g)



To a solution of benzyl trimethylsilyl ether (47 μL, 0.24 mmol) and 3-phenylpropanal (25 μL, 0.19 mmol) in CH_2Cl_2 (2 mL) was added trimethylsilyl trifluoromethanesulfonate (TMSOTf) (34 μL, 0.19 mmol) at –78 °C. The solution was stirred at –78 °C for 6 h before the addition of **2a** (57 mg, 0.19 mmol) at –78 °C. The resulting mixture was stirred at –78 °C for 12 h and then quenched with water (0.5 mL) at –78 °C. The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Purification by silica gel column chromatography (hexane/ethyl acetate = 10 : 1) afforded (*E*)-4-benzyloxy-6-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene (**3g**) (63 mg, 85% yield).

Colorless oil.
TLC: R_f 0.30 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 1.26 (s, 12H), 1.85 (m, 2H), 2.49 (m, 2H), 2.69 (m, 2H), 3.53 (m, 1H), 4.46 (d, *J* = 11.4 Hz, 1H), 4.60 (d, *J* = 11.4 Hz, 1H), 5.52 (dt, *J* = 18.0, 1.4 Hz, 1H), 6.64 (dt, *J* = 18.0, 7.0 Hz, 1H), 7.19-7.40 (m, 10H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 24.8, 31.7, 35.8, 40.4, 70.8, 77.2, 83.1, 125.7, 126.1, 127.5, 127.8, 128.3, 128.4, 129.1, 138.7, 142.2, 150.1.
IR: (neat, thin layer, cm^{-1}) 3062, 3027, 2929, 1638, 1362, 1143, 908, 698.
MS (EI, 70 eV): *m/z* 377 (M^+-Me, 7.2), 117 (93), 91(100).
Anal. Calcd for $C_{25}H_{33}BO_3$: C, 76.53; H, 8.48. Found: C, 76.78; H, 8.51.

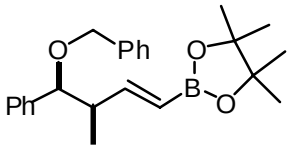
(*E*)- 4-Benzyloxy-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (3h)



Purification: silica gel column chromatography (hexane/ethyl acetate = 10 : 1).
Yield: 88%.
Colorless oil.
TLC: R_f 0.30 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 1.26 (s, 12H), 2.62 (m, 2H), 4.27 (d, *J* = 11.8 Hz, 1H), 4.41 (dd, *J* = 8.0, 5.4 Hz, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 5.49 (dt, *J* = 18.0, 1.4 Hz, 1H), 6.64 (dt, *J* = 18.0, 6.6 Hz, 1H), 7.29-7.45 (m, 10H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 24.7, 44.7, 70.2, 80.6, 83.0, 126.8, 127.4, 127.6, 127.7, 127.9, 128.2, 128.4, 138.5, 141.8, 150.3.
IR: (neat, thin layer, cm^{-1}) 3062, 3028, 2978, 1638, 1495, 1362, 1323, 1143, 1094, 1070, 910, 700.

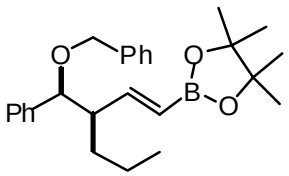
MS (EI, 70 eV): *m/z* 349 (M^+-Me, 2.6), 197 (29), 91(100).
Anal. Calcd for $C_{23}H_{29}BO_3$: C, 75.83; H, 8.02. Found: C, 75.59; H, 7.76.

(*E*)- 4-Benzyloxy-3-methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (3i)



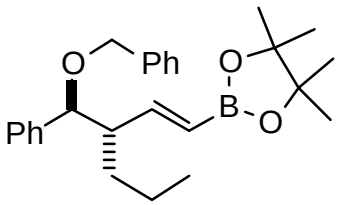
Purification: silica gel column chromatography (hexane/ethyl acetate = 10 : 1).
Yield: 81% as a diastereomer mixture (*E, erythro*/ *E, threo* = 84 : 16).
Colorless oil.
TLC: R_f 0.33 (hexane/ethyl acetate = 9 : 1).
E, erythro:
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 1.09 (d, *J* = 6.8 Hz, 3H), 1.24 (s, 12H), 2.62 (m, 1H), 4.25 (d, *J* = 12.2 Hz, 1H), 4.25 (d, *J* = 6.0 Hz, 1H), 4.50 (d, *J* = 12.2 Hz, 1H), 5.34 (d, *J* = 18.0 Hz, 1H), 6.57 (dd, *J* = 18.0, 6.0 Hz, 1H), 7.26-7.61 (m, 10H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.6, 24.7, 46.4, 70.5, 82.9, 84.4, 127.3, 127.4, 127.5, 127.6, 127.7, 128.0, 128.2, 138.6, 140.5, 155.9.
E, threo:
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.81 (d, *J* = 6.8 Hz, 3H), 1.29 (s, 12H), 2.84 (m, 1H), 4.12 (d, *J* = 7.8 Hz, 1H), 4.13 (d, *J* = 7.0 Hz, 1H), 4.20 (d, *J* = 7.8 Hz, 1H), 5.48 (d, *J* = 18.0 Hz, 1H), 6.77 (d, *J* = 18.0 Hz, 1H). 7.26-7.61 (m, 10H).
^{13}C NMR (50 MHz, $CDCl_3$) δ =16.0, 24.8, 46.1, 70.3, 77.2, 85.2, 126.3, 126.5, 126.7, 127.0,127.0, 128.3, 128.4, 139.2, 140.4, 156.8.
IR: (neat, thin layer, cm^{-1}) 3063, 3028, 2976, 2930, 1638, 1360, 1321, 1146, 1067, 970, 700.
MS (EI, 70 eV): *m/z* 363 (M^+-Me, 2.7), 197 (32), 91 (100).
Anal. Calcd for $C_{24}H_{31}BO_3$: C, 76.20; H, 8.26. Found: C, 76.45; H, 8.08.
The isomer ratio was determined by GC analysis (column: OV-1701 bonded 0.25 mmϕ x 25 m, column temperature: 200 °C constant): (*E, erythro*) R_t = 14.1 min; (*E, threo*) R_t = 14.6 min.

***erythro*-(*E*)-3-[Benzoxy(phenyl)methyl] -1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene (3j)**



Purification: silica gel column chromatography (hexane/ethyl acetate = 10 : 1).
Yield: 83%.
Colorless oil.
TLC: R_f 0.33 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.81 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 12H), 1.40 (m, 2H), 1.67 (m, 2H), 2.47 (m, 1H), 4.26 (d, *J* = 11.8 Hz, 1H), 4.28 (d, *J* = 6.4 Hz, 1H), 4.50 (d, *J* = 11.8 Hz, 1H), 5.25 (dd, *J* = 18.0, 0.8 Hz, 1H), 7.24-7.38 (m, 10H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.1, 20.3, 24.6, 31.3, 53.0, 70.5, 82.9, 84.0, 127.3, 127.5, 127.6, 127.7, 127.9, 128.1, 128.2, 138.6, 140.6, 154.6.
IR: (neat, thin layer, cm^{-1}) 3063, 3028, 2976, 2930, 2870, 1638, 1364, 1146, 1067, 897, 700.
MS (EI, 70 eV): *m/z* 391 (M^+-Me, 2.0), 197 (33), 91 (100).
The isomer ratio was determined by GC analysis (column: OV-1701 bonded 0.25 mmϕ x 25 m, column temperature: 220 °C constant): (*E, erythro*) R_t = 17.8 min; (*E, threo*) R_t = 18.4 min.

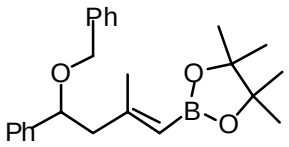
threo-(_E_)-3-[Benzoxy(phenyl)methyl] -1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene (3k)



Purification: silica gel column chromatography (hexane/ethyl acetate = 10 : 1).
Yield: 94%.
Colorless oil.
TLC: R_f 0.27 (hexane/ethyl acetate = 10 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.76 (t, *J* = 7.0 Hz, 3H), 1.18 (m, 4H), 1.27 (s, 12H), 2.51 (m, 1H), 4.21 (d, *J* = 12.2 Hz, 1H), 4.21 (d, *J* = 7.6 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 5.44 (dd, *J* = 18.8, 1.0 Hz, 1H), 6.54 (dd, *J* = 18.8, 8.8 Hz, 1H), 7.24-7.48 (m, 10H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 13.9, 20.1, 24.8, 32.3, 52.7, 70.3, 82.9, 84.2, 127.2, 127.3, 127.6, 127.7, 127.9, 128.1, 128.1, 138.7, 140.6, 155.4.
IR: (neat, thin layer, cm^{-1}) 3063, 3028, 2976, 2959, 2931, 2870, 1638, 1454, 1367, 1321, 1146, 1094, 999, 849, 700.
MS (EI, 70 eV): *m/z* 391 (M^+-Me, 7.0), 197 (89), 91 (100).

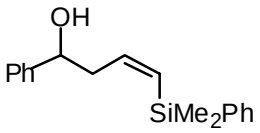
The isomer ratio was determined by GC analysis (column: OV-1701 bonded 0.25 mmϕ x 25 m, column temperature: 220 °C constant): (*E*, *erythro*) R_t = 17.8 min; (*E*, *threo*) R_t = 18.4 min.

(*E*)- 4-Benzyloxy-2-methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (3l)



Purification: silica gel column chromatography (hexane/ethyl acetate = 10 : 1).
Yield: 70%.
Colorless oil.
TLC: R_f 0.33 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ =1.26 (s, 12H), 1.96 (s, 3H), 2.42 (dd, *J* = 14.4, 5.0 Hz, 1H), 2.68 (dd, *J* = 14.4, 8.4 Hz, 1H), 4.26 (d, *J* = 11.6 Hz, 1H), 4.44 (d, *J* =11.6 Hz, 1H), 4.51 (dd, *J* = 8.6, 4.8 Hz, 1H), 7.19-7.42 (m, 10H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 21.8, 24.8, 50.9, 70.3, 80.5, 82.6, 126.0, 126.7, 127.6, 127.6, 127.6, 128.2, 128.4, 138.5, 142.3, 159.3.
IR: (neat, thin layer, cm^{-1}) 3063, 3030, 2978, 2930, 1638, 1495, 1369, 1319, 1265, 1144, 1105, 1070, 853, 698.
MS (EI, 70 eV): *m/z* 363 (M^+-Me, 1.4), 197 (27), 91 (100).
Anal. Calcd for $C_{24}H_{31}BO_3$: C, 76.20; H, 8.26. Found: C, 76.08; H, 8.07.

General procedure for the allylation of aldehydes upon heating.
(*Z*)-4-(Dimethylphenylsilyl)-1-phenyl-3-buten-1-ol (4b)



A solution of **2a** (0.13 g, 0.42 mmol) and benzaldehyde (47 L, 0.46 mmol) in THF (4 mL) was stirred at 100 °C (oil bath) for 24 h. To the reaction mixture ethanolamine (42 L) was added at room temperature, and the resulting milky suspension was stirred for 30 min. Filtration of the insoluble material followed by concentration of the filtrate gave a crude product whose ^{1}H NMR spectra provided isomeric ratio of *E*/*Z* = 3 : 97. Purification by silica gel column chromatography (hexane/ethyl acetate = 4 : 1) gave 4-(dimethylphenylsilyl)-1-phenyl-3-buten-1-ol (**4b**) as a colorless oil (0.11 g, 89% yield, *E*/*Z* = 9/91).
TLC: R_f 0.31 (hexane/ethyl acetate = 4 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.38 (s, 6H), 1.77 (brs, 1H), 2.35-2.65 (m, 2H), 4.64 (dd, *J* = 7.4,

5.6 Hz, 1H), 5.85 (dt, *J* = 13.9, 1.3 Hz, 1H), 6.46 (dt, *J* = 13.9, 7.4 Hz, 1H), 7.16-7.42 (m, 8H), 7.48-7.58 (m, 2H).

^{13}C NMR (50 MHz, $CDCl_3$) δ = -1.0, 1.0, 43.0, 73.6, 125.7, 127.4, 127.8, 128.3, 128.9, 130.6, 133.7, 139.3, 143.8, 145.6.

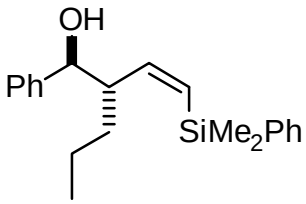
IR: (neat, thin layer, cm^{-1}) 3400 (br), 3070, 3035, 2965, 2900, 1608, 1428, 1250, 1114, 1053, 822.

MS (EI, 70 eV): *m/z* 283 (M^++1, 0.3), 282 (M^+, 0.5), 281 (M^+-1, 1.9), 264 (M^+-H_2O, 13), 249 (M^+-H_2O-Me, 16), 241 (34), 173 (52), 145 (36), 135 ($PhMe_2Si^+$, 91), 121 (47), 107 ($PhCHOH^+$, 100).

Anal. Calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85. Found: C, 76.82; H, 7.88.

The isomer ratio was determined from the integral value of the distinguishable signals in ^{1}H NMR spectra : (*E*)-**4b**: δ 6.08 (dt, *J* = 18.6, 6.4 Hz); (*Z*)-**4b** δ 6.46 (dt, *J* = 13.8, 7.3 Hz).

***threo*-(*Z*)-4-(Dimethylphenylsilyl)-1-phenyl-2-propyl-3-buten-1-ol (4c)**



Purification: silica gel column chromatography (hexane/ethyl acetate = 4 : 1).

Yield: 87% (*E/Z* = 7 : 93).

Colorless oil.

TLC: R_f 0.44 (hexane/ethyl acetate = 4 : 1).

^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.42 (s, 6H), 0.70 (t, *J* = 6.7 Hz, 3H), 0.80-1.30 (m, 4H), 1.99 (d, *J* = 2.2 Hz, 1H), 2.30-2.50 (m, 1H), 4.24 (dd, *J* = 8.2, 2.2 Hz, 1H), 5.95 (d, *J* = 14.0 Hz, 1H), 6.22 (dd, *J* = 14.3, 10.3 Hz, 1H), 7.08-7.20 (m, 2H), 7.20-7.31 (m, 3H), 7.30-7.42 (m, 3H), 7.50-7.63 (m, 2H).

^{13}C NMR (50 MHz, $CDCl_3$) δ = -0.9, -0.8, 14.3, 20.4, 33.1, 51.1, 76.8, 127.1, 127.5, 127.9, 128.1, 129.0, 131.9, 133.8, 139.3, 142.3, 150.7.

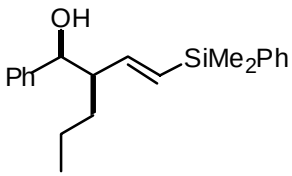
IR: (neat, thin layer, cm^{-1}) 3450 (br), 2962, 2938, 2878, 1607, 1457, 1430, 1250, 1113, 838, 822, 783, 735, 701.

MS (EI, 70 eV): *m/z* 306 (M^+-H_2O, 0.8), 281 (M^+-Pr, 1.9), 241 (11), 218 (7.9), 135 ($PhMe_2Si^+$, 100), 121 (13), 107 ($PhCHOH^+$, 29).

Anal. Calcd for $C_{21}H_{28}OSi$: C, 77.72; H, 8.70. Found: C, 77.43; H, 8.67.

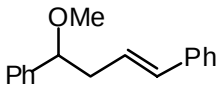
The isomer ratio was determined from the integral value of the distinguishable signals in ^{1}H NMR spectra: (*E*)-**4c** δ 4.45 (d, *J* = 7.4 Hz); (*Z*)-**4c** δ 4.24 (d, *J* = 8.2 Hz).

***erythro*-(*E*)-4-(Dimethylphenylsilyl)-1-phenyl-2-propyl-3-buten-1-ol (4d)**



Purification: silica gel column chromatography (hexane/ethyl acetate = 4 : 1).
Yield: 46%.
Colorless oil.
TLC: R_f 0.36 (hexane/ethyl acetate = 4 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.23 (s, 3H), 0.25 (s, 3H), 0.87 (t, *J* = 6.9 Hz, 3H), 1.10-1.70 (m, 4H), 2.11 (d, *J* = 3.0 Hz, 1H), 2.38-2.58 (m, 1H), 4.55 (dd, *J* = 5.8, 2.2 Hz, 1H), 5.65 (d, *J* = 18.8 Hz, 1H), 5.71 (dd, *J* = 18.6, 7.8 Hz, 1H), 7.16-7.40 (m, 10H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = -2.5, 14.1, 20.5, 32.0, 54.2, 77.0, 126.7, 127.3, 127.6, 127.9, 128.8, 131.0, 133.7, 138.8, 142.7, 148.6.
IR: (neat, thin layer, cm^{-1}) 3420 (br), 2965, 2880, 1617, 1458, 1430, 1251, 1117, 1030, 995, 846, 787, 763, 734, 702.
MS (EI, 70 eV): *m/z* 323 (M^+-1, 0.8), 306 (M^+-H_2O, 4.1), 281 (M^+-Pr, 2.0), 241 (12), 218 (7.1), 215 (11), 170 (8.9), 135 ($PhMe_2Si^+$, 100), 121 (20), 107 ($PhCHOH^+$, 25), 105 (24).
Anal. Calcd for $C_{21}H_{28}OSi$: C, 77.72; H, 8.70. Found: C, 77.51; H, 8.56.
The isomer ratio was determined from the integral value of the distinguishable signals in ^{1}H NMR spectra: (*E*, *erythro*) δ 4.55 (dd, *J* = 5.8, 2.2 Hz, 1H); (*Z*, *threo*) δ 4.24 (dd, *J* = 8.2, 2.2 Hz, 1H).

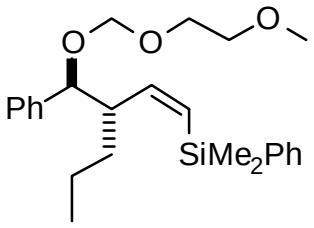
4-Methoxy-1,4-diphenyl-1-pentene (5)



To a solution of **3d** (0.20 g, 0.88 mmol), iodobenzene (0.11 mL, 0.95 mmol), $Pd(PPh_3)_4$ (50 mg, 0.043 mmol) in dioxane (5 mL) was added an aqueous KOH solution (1.2 N, 2.2 mL), and the resulting mixture was stirred at 100°C (bath) for 24 h. The solution was neutralized with a saturated NH_4Cl solution and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and purified by silica gel column chromatography (hexane/ethyl acetate = 4 : 1) to give **5** (0.13 g) in 86% yield.
Colorless oil.
TLC: R_f 0.46 (hexane/ethyl acetate = 4 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 1.19 (d, *J* = 6.2 Hz, 3H), 2.22-2.58 (m, 2H), 3.37 (s, 3H), 3.44 (m, 1H), 6.22 (dt, *J* = 15.8, 7.1 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 7.14-7.44 (m, 5H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 19.0, 39.7, 56.1, 76.6, 126.0, 126.7, 127.0, 128.4, 132.0, 137.6.
IR: (neat, thin layer, cm^{-1}) 3025, 2970, 2927, 2820, 1598, 1493, 1448, 1373, 1135, 1092, 966, 742, 691.

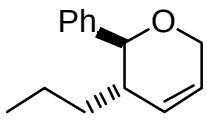
MS (EI, 70 eV): *m/z* 177 (M^++1, 1.5), 176 (M^+, 12), 145 (M^+-OMe, 3.1), 117 ($PhCH{=}CHCH_2^+$, 11), 115 (15), 91 ($PhCH_2^+$, 8.0), 77 (Ph^+, 2.6), 59 (CH_3CHOMe^+, 100).
Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.91; H, 9.34.

***threo*-(*Z*)-1-Dimethylphenylsilyl-3-[(2-methoxyethoxy)phenylmethyl]-hex-1-ene**



To a solution of **4c** (0.24 g, 0.74 mmol) in THF (5 mL) was added NaH (ca. 60wt%, 0.15 g), and stirred at room temperature for 2 h. 2-Methoxyethoxymethyl chloride (0.79 mL, 4.5 mmol) was added to the mixture, and the resulting mixture was stirred for 1 h. Usual work-up and silica gel column chromatography (hexane/ethyl acetate = 6 : 1) afforded the corresponding product (0.17 g, 55% yield).
Colorless oil.
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.28 (s, 6H), 0.73 (t, *J* = 5.6 Hz, 3H), 0.90-1.40 (m, 4H), 2.49 (m, 1H), 3.34 (s, 3H), 3.36-3.55 (m, 3H), 3.65-3.90 (m, 1H), 4.44 (d, *J* = 6.4 Hz, 1H), 4.49 (d, *J* = 7.0 Hz, 1H), 4.55 (d, *J* = 7.0 Hz, 1H), 5.70 (d, *J* = 14.4 Hz, 1H), 6.22 (dd, *J* = 14.4, 10.4 Hz, 1H), 7.10-7.40 (m, 8H), 7.40-7.58 (m, 2H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = -1.0, -0.7, 14.3, 20.2, 33.6, 49.2, 59.0, 66.9, 71.7, 80.7, 93.2, 127.4, 127.6, 127.9, 127.9, 128.7, 128.8, 133.9, 139.8, 140.7, 150.8.
IR: (neat, thin layer, cm^{-1}) 2955, 2932, 2874, 1611, 1454, 1427, 1246, 1111, 1042, 1024, 820, 781, 731, 700.
MS (EI, 70 eV): *m/z* 367 (M^+-$MeOCH_2$, 0.13), 307 (M^+-MEMO, 1.7), 195 (27), 135 ($PhMe_2Si^+$, 41), 121 (16), 89 ($MeOCH_2CH_2OCH_2^+$, 100), 59 ($MeOCH_2CH_2^+$, 52).
Anal. Calcd for $C_{25}H_{36}O_3Si$: C, 72.77; H, 8.79. Found: C, 72.81; H, 8.62.

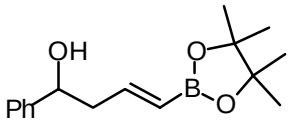
***trans*-6-Phenyl-5-propyl-5,6-dihydro-2*H*-pyran (6)**



To a solution of the MEM ether (0.10 g, 0.25 mmol) in CH_2Cl_2 (4 mL) was added a solution of $TiCl_4$ in CH_2Cl_2 (1.0 M, 0.75 mL, 0.75 mmol) at –78°C. The solution was stirred at –78 °C for 15 min before quenching by the addition of water (0.5 mL) at –78 °C. After warming up the mixture to room temperature, usual workup and purification by silica gel column chromatography

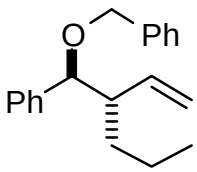
(hexane/ethyl acetate = 9 : 1) gave **6** (42 mg) in 82% yield.
Colorless oil.
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.79 (t, *J* = 6.9 Hz, 3H), 0.94–1.54 (m, 4H), 2.32–2.54 (m, 1H), 4.11 (d, *J* = 9.2 Hz, 1H), 4.20–4.34 (m, 2H), 5.81 (dq, *J* = 10.2, 2.2 Hz, 1H), 5.90 (dt, *J* = 10.3, 1.7 Hz, 1H), 7.20–7.42 (m, 5H)
^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.2, 19.1, 32.9, 40.3, 66.2, 81.6, 125.8, 127.5, 127.9, 128.3, 128.9, 141.2.
IR: (neat, thin layer, cm^{-1}) 3025, 2955, 2923, 2864, 2806, 1451, 1133, 1091, 1022, 753, 697.
MS (EI, 70 eV): *m/z* 202 (M^+, 0.37), 184 (0.18), 173 (M^+-Et, 0.32), 159 (M^+-Pr, 2.2), 96 (100), 81 (76), 67 (54), 54 (79).
Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.04; H, 9.21.

(*E*)-1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-but-3-en-1-ol (7)



To a solution of **h** (0.015 g, 0.04 mmol) in CH_2Cl_2 (1 mL) was added Me_3SiI (0.05 mmol) at room temperature. The solution was stirred at room temperature for 30 min before quenching with water (0.5 mL). Usual workup and purification by silica gel column chromatography (hexane/ethyl acetate = 9 : 1) gave **7** (8 mg) in 73% yield.
Colorless oil.
TLC: R_f 0.55 (hexane/ethyl acetate = 4 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 1.25 (s, 12H), 2.98-3.31 (m, 2H), 5.16 (t, *J* = 7.6 Hz, 1H), 5.53 (t, *J* = 18.0 Hz, 1H), 6.46 (dt, *J* = 18.0, 6.6 Hz, 1H), 7.22-7.48 (m, 5H).
^{13}C NMR (50 MHz, $CDCl_3$) δ = 24.7, 29.7, 47.1, 79.6, 127.1, 128.0, 128.4, 128.7, 139.7, 149.3.
IR: (neat, thin layer, cm^{-1}) 3396, 2926, 2855, 1456, 1371, 1142, 698.
MS (EI, 70 eV): *m/z* 256 (M^+-H_2O, 75), 156 (100), 129 (89), 84 (87).

***threo*-3-[Benzyloxy(phenyl)methyl]-1-hexene [reference 17]**



Protodeborylation of 3k

To a solution of **3k** (0.02 g, 0.05 mmol) in THF (2 mL) was added butyllithium in hexane (1.56 M, 96 μL, 0.15 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h before the addition of a 6 M

aqueous KOH solution. The resulting mixture was stirred for 2 h at 0 °C. Usual workup and purification by silica gel column chromatography (hexane/ethyl acetate = 9 : 1) gave 3-[benzyloxy(phenyl)methyl]-1-hexene (8 mg) in 58% yield.

Benzylation and protodesilylation of 4c

To a solution of **4c** (0.03 g, 0.09 mmol) in THF (4 mL) was added benzyl bromide (0.45 mmol) and powder KOH (9.0 mmol). The reaction mixture was stirred at 100 °C for 36 h. Usual workup and purification by silica gel column chromatography (hexane/ethyl acetate = 9 : 1) gave *threo*-3-[benzyloxy(phenyl)methyl]-1-hexene which was consistent with the stereoisomer obtained from **3k** (20 mg) in 77% yield.

Colorless oil.
TLC: R_f 0.41 (hexane/ethyl acetate = 9 : 1).
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 0.79 (t, *J* = 5.6 Hz, 3H), 1.06-1.21 (m, 4H), 2.35-2.47 (m, 1H), 4.22 (d, *J* = 12.6 Hz, 1H), 4.22 (s, 1H), 4.49 (d, *J* = 12.6 Hz, 1H), 4.93 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.06 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.67 (dt, *J* = 17.2, 7.0 Hz, 1H), 7.24-7.43 (m, 10H)
^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.0, 20.2, 32.8, 50.9, 70.4, 84.1, 116.2, 127.3, 127.4, 127.6, 127.6, 128.0, 128.2, 138.7, 139.4, 140.8.
IR: (neat, thin layer, cm^{-1}) 3064, 3030, 2957, 2929, 2870, 1495, 1454, 1094, 1069, 1028, 912, 700.
MS (EI, 70 eV): *m/z* 253 (M^+-C_2H_3, 1.3), 197 (4.5), 149 (100), 91 (21).