Preparation of 3-Substituted (*E*)-1-Alkenylboronic Esters

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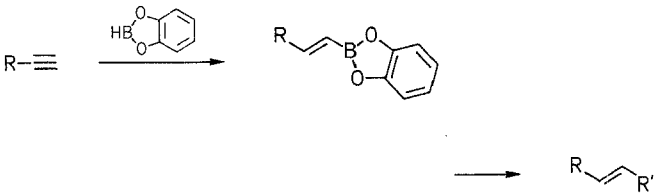
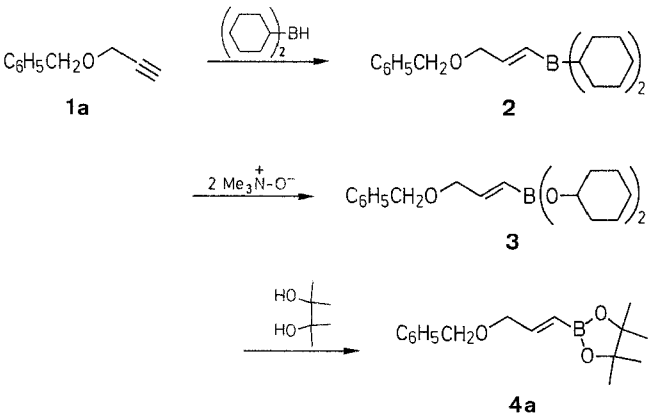
The conversion of functionalized 1-alkynes into (*E*)-1-alkenylboronic esters is achieved in a one-pot procedure consisting of hydroboration with dicyclohexylborane followed by oxidation with trimethylamine oxide.

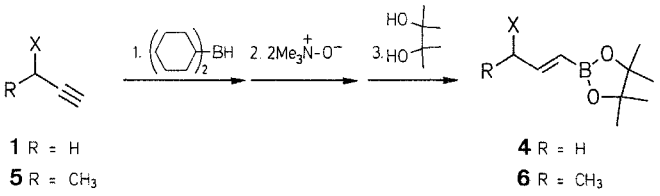
The conversion of a terminal alkyne into an *E*-alkenylboronic ester opens up various ways for subsequent transformations into other alkenyl derivatives having an *E* double bond.[1] The synthetic potential of this sequence can be utilized only if it can be applied to a variety of functionalized 1-alkynes.



The first step is usually carried out by hydroboration of the alkyne with 1,3,2-benzodioxaborole ("catechol-borane")[2] at 70°C. However, application of this technique to the functionalized alkyne **1a** resulted in no reaction under these conditions. In order to achieve the desired transformation we chose a three-step, one-pot procedure[3] using the more reactive dicyclohexylborane.[4] Even then, the hydroboration of **1a** in tetrahydrofuran proceeded rather slowly. In contrast, the thioether **1b** corresponding to **1a** reacted readily with dicyclohexylborane. We therefore assumed that coordination of the dicyclohexylborane with the ether oxyen of **1a** could be the reason for the unusually slow reaction. The specific coordination could probably be suppressed by use of a more basic solvent. Indeed, in 1,2-dimethoxyethane (DME), clean and smooth hydroboration of **1a** could be achieved.



Selective oxidation of the sp^3 C–B bonds in the resulting 1-alkenylborane **2** was possible with two equivalents of trimethylamine oxide.[5] Finally, the intermediate dicyclohexyl boronate **3** was transesterified with pinacol to the desired 2,3-dimethyl-2,3-butanediyl 1-alkenylboronate **4a**. We applied this procedure to a series of functionalized 1-alkynes and thus obtained a variety of 3-substituted 1-alkenylboronates **4** and **6**.



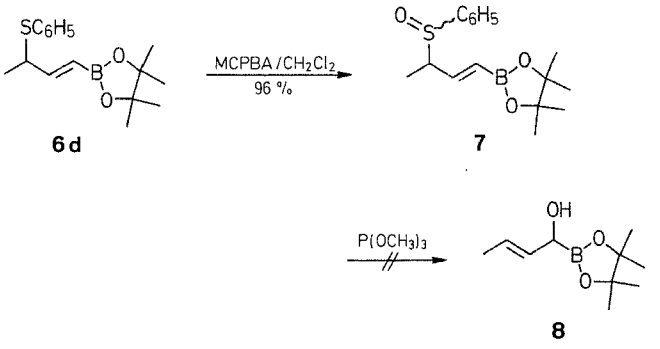
1 R = H
5 R = CH_3

4 R = H
6 R = CH_3

Product	X	Yield (%)	Product	X	Yield (%)
4a	$OCH_2C_6H_5$	70	**6d**	SC_6H_5	95
4b	$SCH_2C_6H_5$	43[a]	**6e**	$OSi(CH_3)_3$	83
4c	$OSi(CH_3)_2C_4H_9$-*t*	62	**6f**	SeC_6H_5	79
4d	SC_6H_5	52			

[a] Reaction was performed in THF.

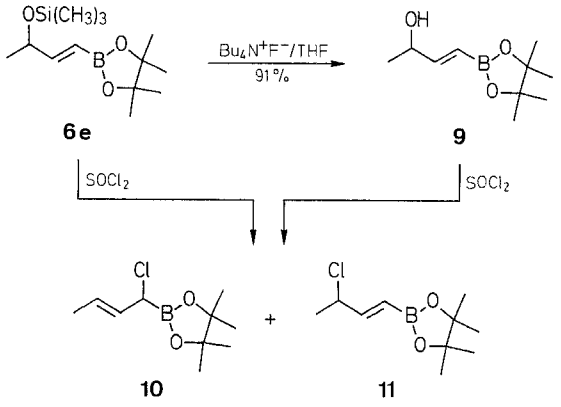
The functional groups of some of these products were further transformed: thus, the thioether **6d** was oxidized with *m*-chloroperoxybenzoic acid (MCPBA) to a mixture of the diastereoisomeric sulfoxides **7**.



Treatment of sulfoxide **7** with trimethyl phosphite[6] did not furnish the desired 1-hydroxy-2-butenylboronate **8** by [2,3]-sigmatropic rearrangement. Likewise, oxidation of **6f** with *m*-chloroperoxybenzoic acid gave crotonaldehyde instead of **8**.

Another refunctionalization, i.e., that of **6e** with thionyl chloride to give 1-chloro-2-butenylboronic ester **10**, was studied in detail. In this reaction, the main problem relates to the regiocontrol in the formation of products **10** and **11**.[7] We were specifically interested in the clean formation of 2,3-dimethyl-2,3-butanediyl (*E*)-1-chloro-2-butenylboronate (**10**) with the aim to study its addition to aldehydes.[8]

To this end, alcohol **9** was prepared in 91% yield from the 3-trimethylsiloxy-1-butenylboronic ester **6e** by reaction with tetrabutylammonium fluoride, and then treated with thionyl chloride in ether to give a 4:1 mixture of the desired boronic ester **10** and its isomer **11** in 96% yield. In order to carry out the same



reaction with enantiomerically pure material, we required reaction conditions that would minimize racemization of product **10**. Since such racemization could be caused by chloride ion,[9] and presumably as well by free hydrogen chloride, the direct conversion of **6e** into **10** seemed attractive. Indeed, reaction of **6e** with thionyl chloride led to the chloro compounds **10** and **11** in good yield, the ratio **10:11** varying from run to run. From **6e**, purified by chromatography, the undesired 3-chloro-1-butenylboronic ester **11** was obtained as the major product. However, we found that the reaction of **6e** with thionyl chloride in petroleum ether in the presence of a small amount of $Co(NO_3)_2 \cdot 6H_2O$ gave the desired product **10** consistently in > 90% yield. Probably, the controlled amount of water reacted with thionyl chloride to give a small amount of hydrogen chloride which cleaved the silyl ether **6e** to alcohol **9**. The latter reacted with thionyl chloride to give **10** whereby hydrogen chloride is regenerated. Thus, the reaction proceeded with only substoichiometric amounts of HCl. Indeed, when repeating the reaction sequence starting from enantiomerically pure 1-butyn-3-ol,[10] the 1-chloro-2-butenylboronate **10** was obtained with a high level of enantiomeric purity.

All temperatures quoted are uncorrected. Preparative GLC: Aerograph A-90-P-3, 1.5 m × 0.63 cm column with 5% Apiezon M on Chromosorb G, AW-DMCS, 150 ml He/min. ^{1}H-NMR spectra: Bruker WH-400; ^{13}C-NMR spectra: Varian CFT-20, Bruker WH-400.

(*E*)-2-(3-Benzyloxy-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a):

Under an atmosphere of nitrogen, dimethyl sulfide-borane complex (21.1 mL, 0.15 mol) is dissolved in DME (300 mL). Cyclohexene (24.6 g, 0.3 mol) is added at 0 °C. After 15 min, the mixture is allowed to reach room temperature. The resultant suspension of dicyclohexylborane is stirred for 1 h, then cooled to 0 °C. Benzyl 2-propynyl ether[11] (**1a**; 21.9 g, 0.15 mol) is added and the mixture is allowed to warm to room temperature whereupon the dicyclohexylborane dissolves. After 1 h, anhydrous trimethylamine oxide[12] (22.5 g, 0.30 mol) is added in small portions in such a manner that the solution is maintained under gentle reflux. The mixture is then cooled to room temperature, stirred for 1 h, and 2,3-dimethyl-2,3-butanediol (17.7 g, 0.15 mol) is added. After 12 h, the solution is filtered and the filtrate is concentrated and fractionally distilled at 0.3 Torr. After a forerun of cyclohexanol, product **4a** is obtained; yield: 28.7 g (70%); bp 138–143 °C/0.3 Torr. For analysis, a small sample is purified by GLC (180 °C).

$C_{16}H_{23}BO_3$	calc.	C 70.09	H 8.46
(274.2)	found	69.94	8.54

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 12 H), 4.10 (dd, 2 H, J = 4.7, 1.8 Hz); 4.53 (s, 2 H); 5.75 (dt, 1 H, J = 18.1, 1.8 Hz); 6.47 (dt, 1 H, J = 18.1, 4.7 Hz); 7.26–7.38 (m, 5 H).

^{13}C-NMR (20 MHz, $CDCl_3$): δ = 24.7, 71.7, 72.2, 83.2, 127.5, 128.3, 138.2, 149.0.

(*E*)-2-(3-Benzylthio-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b):

Dimethyl sulfide-borane complex (1.2 mL, 12 mmol), THF (20 mL), cyclohexene (2.0 g, 24 mmol), benzyl 2-propynyl sulfide[13] (**1b**; 2.0 g, 12 mmol), trimethylamine oxide[12] (1.9 g, 24 mmol), and 2,3-dimethyl-2,3-butanediol (1.5 g, 12 mmol) are treated as described in the procedure for **4a** to give crude **4b** as a colorless oil; yield: 0.81 g (43%); bp 152 °C/0.3 Torr. For analysis, a small sample is purified by GLC (185 °C).

$C_{16}H_{23}BO_2S$	calc.	C 66.21	H 7.98
(290.2)	found	66.34	8.16

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 12 H); 3.08 (dd, 2 H, J = 6.9, 1.3 Hz); 3.62 (s, 2 H); 5.49 (dt, 1 H, J = 17.7, 1.3 Hz); 6.54 (dt, 1 H, J = 17.7, 6.9 Hz); 7.19–7.31 (m, 5 H).

^{13}C-NMR (20 MHz, $CDCl_3$): δ = 24.6, 34.8, 35.3, 82.9, 126.6, 128.1, 128.8, 138.0, 148.1.

(*E*)-2-(3-*tert*-Butyldimethylsiloxy-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c):

Dimethyl sulfide-borane complex (10.5 mL, 49 mmol), DME (100 mL), cyclohexene (15.9 g, 98 mmol), 3-(*tert*-butyldimethylsiloxy)propyne[14] (**1c**; 8.0 g, 49 mmol), trimethylamine oxide[12] (7.28 g, 98 mmol), and 2,3-dimethyl-2,3-butanediol (5.72 g, 48.5 mmol) are treated as described in the procedure for **4a** to give **4c** as a colorless oil; yield: 9.83 g (62%); bp 108–110 °C/0.3 Torr. For analysis, a small sample is purified by GLC (180 °C).

$C_{15}H_{31}O_3Si$	calc.	C 60.39	H 10.47
(298.3)	found	60.31	10.64

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 6 H); 0.89 (s, 9 H); 1.25 (s, 12 H); 4.23 (dd, 2 H, J = 3.5, 2.1 Hz); 5.74 (dt, 1 H, J = 17.9, 2.1 Hz); 6.66 (dt, 1 H, J = 17.9, 3.5 Hz).

^{13}C-NMR (20 MHz, $CDCl_3$): δ = −5.4, 18.3, 24.7, 25.9, 64.4, 83.0, 152.0.

(*E*)-2-(3-Phenylthio-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d):

Dimethyl sulfide-borane complex (11 mL, 110 mmol), DME (250 mL), cyclohexene (18.20 g, 222 mmol), 3-phenylthiopropyne[13] (**1d**; 16.40 g, 111 mmol) trimethylamine oxide[12] (16.60 g, 222 mmol), and 2,3-dimethyl-2,3-butanediol (13.10 g, 111 mmol) are treated as described in the procedure for **4a** to give **4d** as a slightly yellowish viscous oil; yield: 16.0 g (52%); bp 140 °C/0.3 Torr.

$C_{15}H_{21}BO_2S$	calc.	C 65.22	H 7.66
(276.2)	found	65.20	7.65

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 12 H), 3.60 (dd, 2 H, J = 6.6, 1.4 Hz); 5.55 (dt, 1 H, J = 17.4, 1.4 Hz); 6.62 (dt, 1 H, J = 17.4, 6.6 Hz); 7.24 (m, 5 H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 24.6, 38.4, 83.1, 125.9, 128.6, 129.2, 135.9, 147.4.

3-Trimethylsiloxy-1-butyne (5e):

3-Hydroxy-1-butyne (16.58 g, 236.5 mmol) and hexamethyldisilazane (19.09 g, 118 mmol) are heated at 110 °C for 12 h. The mixture is then filtered by suction through a small plug of silica gel to give **5e** as an almost colorless liquid; yield: 33.30 g (99%). This product is used without further purification. [The compound was identified by its ^{1}H-NMR-spectrum.[15]].

(*E*)-2-(3-Trimethylsiloxy-1-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6e):

Dimethyl sulfide-borane complex (8.4 mL, 84 mmol), DME (120 mL), cyclohexene (13.80 g, 168 mol), 3-trimethylsiloxy-1-butyne (**5e**; 15.0 g, 84 mmol), trimethylamine oxide[12] (12.65 g, 168 mmol), and 2,3-dimethyl-2,3-butanediol (10.0 g, 84 mmol) are treated as described in the procedure for **4a** to give **6e**; yield: 18.60 g (83%); bp 68 °C/0.1 Torr. For analysis, a small sample is purified by GLC (180 °C).

$C_{13}H_{27}BO_3Si$	calc.	C 57.78	H 10.07
(270.3)	found	57.71	10.16

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 9 H); 1.20 (d, 3 H, J = 6.5 Hz); 1.25 (s, 12 H); 4.30 (ddq, 1 H, J = 6.5, 4.3, 1.7 Hz); 5.58 (dd, 1 H, J = 17.9, 1.7 Hz); 6.58 (dd, 1 H, J = 17.9, 4.3 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 0.0, 23.5, 24.7, 69.6, 83.0, 156.5.

The distilled product **6e** still contains traces of trimethylamine; these are removed by the following procedure: a solution of **6e** (5.0 g) in petroleum ether (bp 40–60 °C) (50 mL) is washed with 5% AcOH

(10 mL), 4% $NaHCO_3$ solution (10 mL), and saturated Na_2SO_4 solution (10 mL). The aqueous phases are back-extracted each time with petroleum ether (bp 40–60 °C; 10 mL each). The combined organic phase is dried ($MgSO_4$) and concentrated *in vacuo* to give pure **6e**: yield: 4.84 g. This product is used for the preparation of **10**.

(*E*)-2-[(*R*)-3-Trimethylsiloxy-1-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*R*)-6e]:

Prepared similarly starting from (*R*)-3-trimethylsiloxy-1-butyne;[10] yield: 80%; $[\alpha]_\lambda^{20}$ (*c* = 10, toluene): −8.9° (589), −9.4° (578), −11.2° (546), −23.3° (436), −46.4° (365 nm).

(*E*)-2-(3-Phenylthio-1-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6d):

Dimethyl sulfide-borane complex (6.2 mL, 62 mmol), DME (100 mL), cyclohexene (10.20 g, 124 mmol), 3-phenylthio-1-butyne[13] (10.00 g, 62 mmol), trimethylamine oxide[12] (9.30 g, 124 mmol), and 2,3-dimethyl-2,3-butanediol (7.33 g, 62 mmol) are treated as described in the procedure for **4a** to give **6d**: yield: 17.03 g (95%); bp 135 °C/0.1 Torr.

$C_{16}H_{23}BO_2S$	calc.	C 66.21	H 7.98
(290.2)	found	66.14	7.86

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.23 (s, 12H); 1.38 (d, 3H, *J* = 6.9 Hz); 3.76 (ddq, 1H, *J* = 7.6, 6.9, 1.1 Hz); 5.30 (dd, 1H, *J* = 17.8, 1.1 Hz); 6.55 (dd, 1H, *J* = 17.8, 7.6 Hz); 7.23 (m, 3H); 7.36 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 19.6, 24.6, 47.6, 83.1, 127.1, 128.6, 132.6, 134.5, 153.3.

(*E*)-2-(3-Phenylseleno-1-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6f):

Dimethyl sulfide-borane complex (2.4 mL, 24 mmol), DME (100 mL), cyclohexane (3.93 g, 48 mmol), 3-phenylseleno-1-butyne[13] (5.00 g, 24 mmol), trimethylamine oxide[12] (3.60 g, 48 mmol), 2,3-dimethyl-2,3-butanediol (2.84 g, 24 mmol) are treated as described in the procedure for **4a** give **6f** as a yellowish viscous oil; yield: 6.37 g (79%); bp 126 °C/0.1 Torr. For analysis, a small sample is purified by GLC (165 °C).

$C_{16}H_{23}BO_2Se$	calc.	C 57.00	H 6.88
(337.1)	found	56.87	6.91

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 12H); 1.48 (d, 3H, *J* = 6.8 Hz); 3.88 (dq, 1H, *J* = 7.9, 6.8 Hz); 5.13 (d, 1H, *J* = 17.9 Hz); 6.66 (dd, 1H, *J* = 17.9, 7.9 Hz); 7.24 (m, 5H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 19.7, 24.6, 42.5, 82.9, 127.6, 128.6, 128.9, 131.3, 135.5, 153.5.

Oxidation of (*E*)-2-(3-phenylthio-1-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6d) to (*E*)-2-(3-Phenylsulfinyl-1-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7):

To a stirred solution of **6d** (3.00 g, 10.3 mmol) in CH_2Cl_2 (30 mL) at 0 °C is added 80% MCPBA (2.20 g, 10.3 mmol). After 2 h, the mixture is washed with 4% $NaHCO_3$ solution (2 × 10 mL) and the organic phase is dried ($MgSO_4$). Evaporation affords a 55:45 mixture of two diastereomeric sulfoxides **7** as a colorless oil; yield: 3.02 g (96%). This product is not analytically pure.

^{1}H-NMR (400 MHz, $CDCl_3$):

Diastereoisomer A: δ = 1.25 (s, 12H); 1.32 (d, 3H, *J* = 6.9 Hz); 3.41 (ddq, 1H, *J* = 7.7, 6.9, 1.1 Hz); 5.49 (dd, 1H, *J* = 18.0, 1.1 Hz); 6.41 (dd, 1H, *J* = 18.0, 7.7 Hz); 7.40–7.60 (m, 5H).

Diastereoisomer B: δ = 1.24 (s, 12H); 1.29 (d, 3H, *J* = 6.9 Hz); 3.55 (ddq, 1H, *J* = 7.6, 6.9, 1.1 Hz); 5.47 (dd, 1H, *J* = 18.0, 1.1 Hz); 6.33 (dd, 1H, *J* = 18.0, 7.6 Hz); 7.40–7.60 (m, 5H).

^{13}C-NMR (100 MHz, $CDCl_3$):

Diastereoisomer A: δ = 11.18, 24.43, 64.98, 83.06, 124.87, 128.24, 130.88, 141.09, 145.58.

Diastereoisomer B: δ = 11.10, 24.43, 63.67, 83.06, 124.91, 128.28, 130.83, 140.21, 145.00.

(*E*)-2-(1-Chloro-2-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10):

The thionyl chloride used in this procedure should be freshly distilled and contact of this reagent with metal surfaces should be avoided.

To a stirred solution of **6e** (5.70 g, 21.1 mmol) in petroleum ether (bp 40–60 °C; 130 mL), $Co(NO_3)_2 \times 6H_2O$ (~ 20 mg) is added, followed immediately by $SOCl_2$ (2.75 g, 23.1 mmol). Slow evolution of SO_2 begins; it ceases after 4 h. The mixture is then filtered and concentrated to give the crude product **10**; yield: 4.39 g (96%). For analysis, a small sample is purified by bulb-to-bulb distillation at 30 °C/0.1 Torr.

$C_{10}H_{18}BClO_2$	calc.	C 55.47	H 8.38
(216.5)	found	55.50	8.64

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 12H); 1.71 (ddd, 3H, *J* = 6.4, 1.5, 0.8 Hz); 3.94 (d, 1H, *J* = 9.2 Hz); 5.65 (ddq, 1H, *J* = 15.1, 9.2, 1.5 Hz); 5.78 (ddq, 1H, *J* = 15.1, 6.4, 0.8 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 17.7, 24.4, 84.4, 128.1, 129.0.

(*E*)-2-[(*S*)-1-Chloro-2-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-10]:

This compound is prepared in an analogous manner starting from (*R*)-**6e** of > 97% ee; yield: 87%; colorless oil.

$[\alpha]_\lambda^{20}$ (*c* = 10, toluene): −39.7° (589), −42.0° (578), −96.1° (436), −166.9° (365 nm).

(*E*)-2-(3-Chloro-1-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11):

Compound **6e** is chromatographed over silica gel (120 g) using petroleum ether/Et_2O (4:1) as eluent. The resultant pure compound **6e** (1.50 g, 5.5 mmol) is dissolved in petroleum ether (bp 40–60 °C; 10 mL) and $SOCl_2$ (0.70 g, 5.9 mmol) is added with stirring. After 12 h, the solvents are removed *in vacuo*. The residue is a mixture of **10** and **11** according to ^{1}H-NMR analysis. It is column chromatographed on silica gel (120 g) using petroleum ether (bp 40–60 °C)/Et_2O (4:1) as eluent to give product **11**; yield: 0.69 g (58%); colorless oil. For analysis, a small sample is purified by GLC (120 °C).

$C_{10}H_{18}BClO_2$	calc.	C 55.47	H 8.38	Cl 16.37
(216.5)	found	55.60	8.39	16.31

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 12H); 1.58 (d, 3H, *J* = 6.7 Hz); 4.51 (ddq, 1H, *J* = 6.8, 6.7, 1.2 Hz); 5.60 (dd, 1H, *J* = 17.7, 1.2 Hz); 6.60 (dd, 1H, *J* = 17.7, 7.0 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 24.2, 24.7, 58.2, 83.4, 152.2.

(*E*)-2-(3-Hydroxy-1-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9):

A solution of **6e** (4.00 g, 15.0 mmol) in THF (15 mL) is treated at 20 °C with a 1.0 M solution of tetrabutylammonium fluoride in THF (15.00 mL, 15.0 mmol). After 1 h, 2N HCl (20 mL) is added. The aqueous phase is extracted with Et_2O (3 × 40 mL). The combined organic phase is dried ($MgSO_4$) and concentrated to give **9** as a colorless oil; yield: 2.68 g (91%). For analysis, a small sample is purified by GLC (140 °C).

$C_{10}H_{19}BO_3$	calc.	C 60.64	H 9.67
(198.1)	found	60.66	9.74

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 12H); 1.25 (d, 3H, *J* = 6.5 Hz); 1.79 (d, 1H, *J* = 4.0 Hz); 4.30 (m, 1H); 5.58 (dd, 1H, *J* = 18.1, 1.6 Hz); 6.62 (dd, 1H, *J* = 18.1, 4.9 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 22.5, 24.6, 69.3, 83.1, 156.3.

(*E*)-2-[(*R*)-3-Hydroxy-1-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*R*)-9]:

This compound is similarly obtained from (*R*)-**6e**; yield: 90%. The enantiomeric purity is determined by conversion of **9** (20 µL) into a corresponding mixture of diastereoisomeric carbamates by reaction with (*S*)-1-phenylethyl isocyanate (Fluka; 30 µL) for 1 h at 60 °C. After dilution with CH_2Cl_2 (1 mL), the ratio of diastereoisomers is determined to be 99:1 by GLC on a 40 m × 0.33 mm glass capillary column with SE 52, 2.1 bar He (250 °C).

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Dedicated to Professor H. Dörfel with best wishes on the occasion of his 60th birthday.

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(1) See for instance:
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