New 1,3-Disubstituted Enantiomerically Pure Allylboronic Esters by Johnson Rearrangement of Boron-Substituted Allyl Alcohols

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Dedicated to the memory of Prof. Dr. W. A. König

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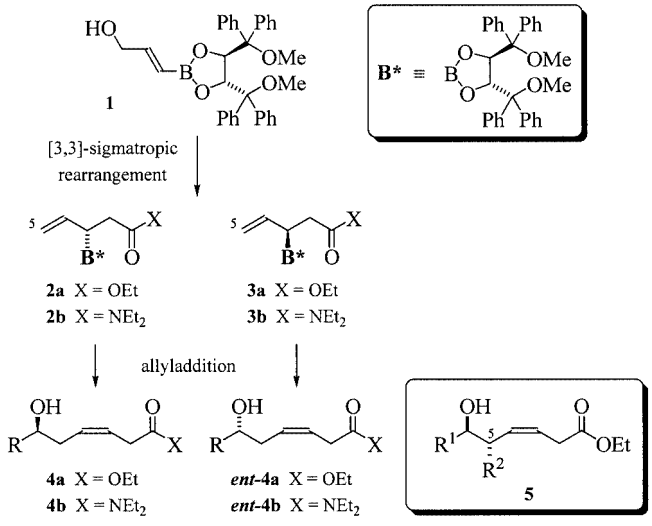
Starting from commercially available 1-substituted propargylic alcohols **6**, **18** and ***ent*-18**, stable enantio- and diastereomerically pure 1,3-disubstituted allylboronic esters **10**, **19** and **20** were synthesized. The key step – a Johnson rearrangement – was highly diastereoselective and yielded the products with almost complete transfer of the stereogenic information from the intermediate allyl alcohols. The configurations of all the new derivatives were unequivocally assigned either by chemical correlation (e.g. allylboronic ester **10** and its diastereomer **11** were independently synthesized by cross-metathesis of the known boronates **2a** and **3a** with styrene) or by analysis of the NMR data, and additionally by X-ray structural analysis (of **20**). Allyl addition to benzaldehyde in all cases yielded enantiomerically highly enriched homoallylic alcohols **15**/***ent*-15** and **21**/***ent*-21** (> 98% *ee*).

Introduction

The enantio- and diastereoselective allyl addition of allylboronic esters to carbonyl groups to give homoallyl alcohols is one of the most versatile transformations in organic synthesis. Since the transition structure is well defined, the outcome of such reactions is often predictable.[1−6] Reagents with a stereogenic center in the position α to the boronic ester moiety are special: While the selectivity of the addition is often exceptionally high, their applicability in this reaction is sometimes hampered by problems when synthesizing enantiomerically pure derivatives.[7−43] Incorporating additional functional groups into these compounds is even more difficult. Recently, we established a new route to homoallyl alcohols starting from the readily available allyl alcohol **1**: [3,3] sigmatropic rearrangements[44,45] yielded either the easily separable ester **2a/3a** (Johnson rearrangement[46]) or the amide **2b/3b** (Eschenmoser rearrangement[47,48]) in good yield.[49] The subsequent allyl addition proved to be highly enantioselective furnishing homoallyl alcohols **4**; in all cases the (*Z*) product was exclusively formed (Scheme 1). In order to extend this approach, we were interested in introducing additional substituents into the 5-position of the allylboronic esters and ultimately into the hydroxy esters **5**. In this first investigation we focused on the synthesis and structural assignment of phenyl and methyl derivatives (R^2 = Ph or Me).



Scheme 1. Synthesis of new enantiomerically pure reagents **2** and **3** for allylations by a [3,3] sigmatropic rearrangement

Results and Discussion

5-Phenyl Derivatives

First, 1-phenyl-2-propyn-1-ol (**6**) was used as a convenient starting material: Silyl-protection with *tert*-butyldimethylsilyl chloride (TBSCl) yielded **7** (97%) as the starting material for a one-pot hydroboration-oxidation-transesteri-

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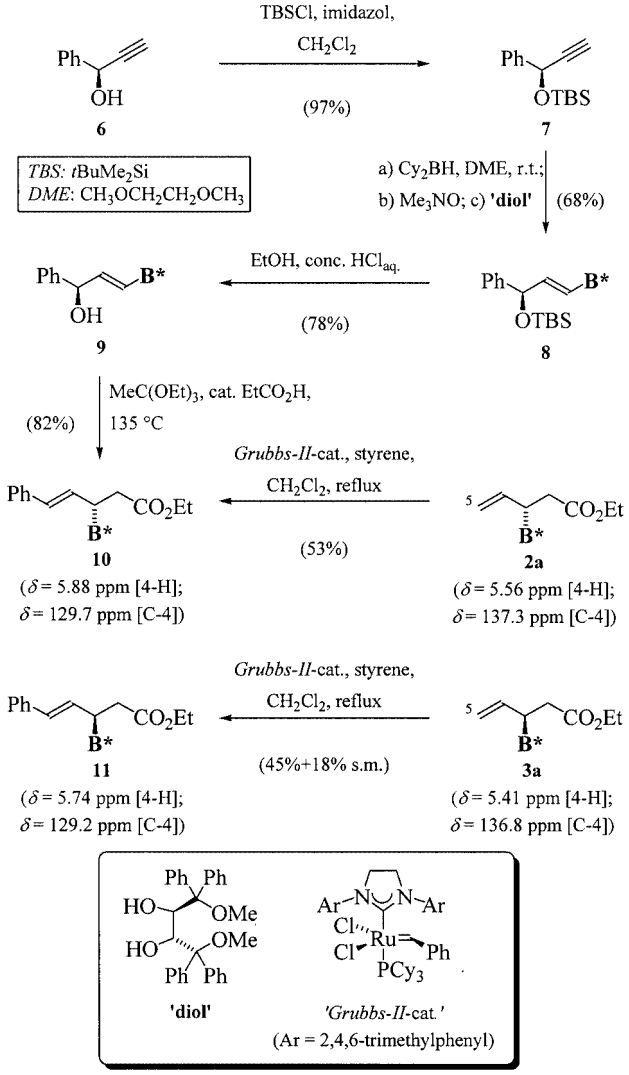
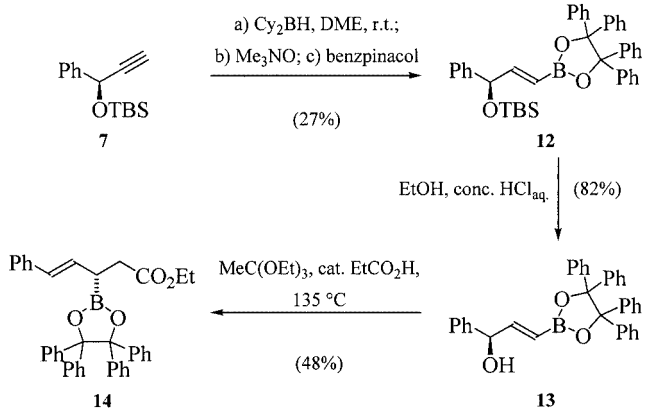
fication[22] reaction (68%) that had previously been established (Scheme 2).[50] The stable[51,52] alkenylboronic ester **8** was deprotected under acidic conditions to furnish the envisaged allyl alcohol **9** (78%). Under typical conditions of the Johnson rearrangement, this new substrate was converted in high yield (82%) to the 1,3-disubstituted allylboronic ester **10**. No trace of diastereoisomer **11** could be detected in the crude product. Note that the NMR chemical shifts for these two diastereoisomers are distinctly different, especially for 4-H/C-4 (downfield shifted for **10**); hence the NMR data should be diagnostic for a series of related reagents, as can also be seen when comparing these data with those of the parent derivatives **2a** and **3a**. To assign the absolute configurations of **10** and **11** at C-3, independent cross-metatheses were performed:[53,54] With styrene and the known **2a** and **3a** as substrates, both diastereoisomers **10** and **11** were obtained in the pure form, though in relatively poor yield (53 and 45%, respectively).



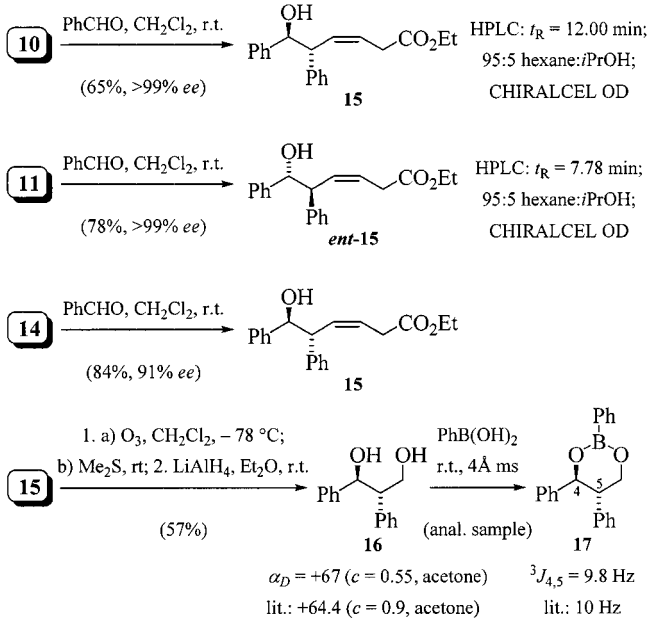
Scheme 2. Synthesis of allylboronic esters **10** and **11**; determination of their absolute configurations

In view of the complete transfer of the stereogenic information from pure allyl alcohol **9** to allylboronic ester **10**, it was questioned whether the chiral "diol" protecting group[51,55] could be replaced by a robust achiral diol such as benzpinacol. We had previously demonstrated that this type of boronic ester has a similar stability to that of chiral enantiomerically pure derivatives.[40,56] However, although its synthesis by the established sequence proved feasible, the yields were in most cases distinctly lower (Scheme 3). In particular, the synthesis of the alkenylboronic ester **12** was troublesome and only minimum amounts of product were isolated (27%). While the deprotection to **13** worked well (82%), the yield of the rearrangement to allylboronic ester **14** was moderate (48%). At this stage no definite statement with regards the enantiomeric excess could be made.

The degree of enantiomeric purity of allylboronic ester **14** was deduced by performing allyl addition with benzaldehyde (Scheme 4): Pure diastereoisomers **10** and **11** each



Scheme 3. Synthesis of benzpinacol-derived allylboronic ester **14**

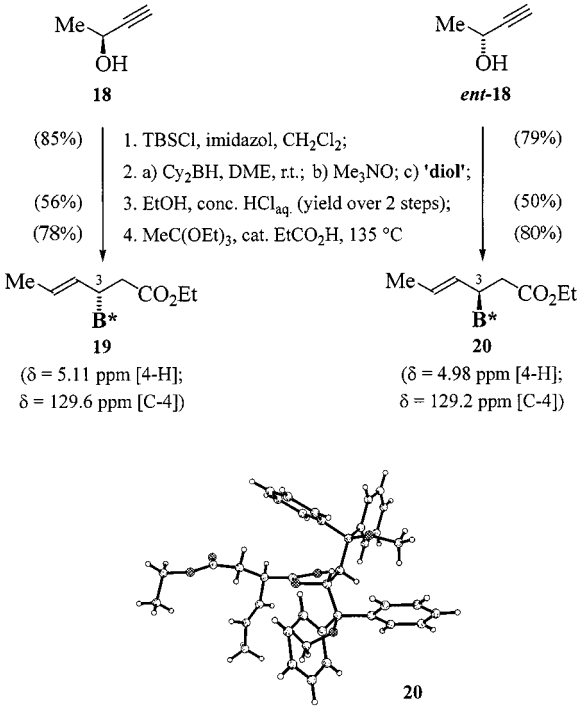


Scheme 4. Allyl additions of reagents **10**, **11** and **14**; the absolute and relative configuration of homoallyl alcohol **15** was established by chemical correlation with known diol **16** and dioxaborinane **17**

gave only one homoallyl alcohol **15** or ***ent*-15**, respectively, the configuration of the double bond being *Z* in both cases. The enantiomeric excesses were determined by means of HPLC using a chiral stationary phase (> 99% *ee*). While the yield for the allyl addition with **14** was also good (84%), the enantiomeric excess of **15** was lower (91% *ee*). Since the (*Z*) diastereoisomer was again exclusively formed, it is highly likely that the allyl addition was − as expected − completely selective, while the previous step, the rearrangement, was not. To verify the absolute and relative configurations of **15**, we converted the homoallyl alcohol to the known diol **16**[57] by an ozonolysis-reduction reaction sequence (57%). Condensation of an analytical sample of diol **16** with phenylboronic acid furnished dioxaborinane **17**; the observed coupling constant ($^3J_{4,5}$ = 9.8 Hz) also confirmed the relative configuration.[57] The optical rotation of diol **16** gave the absolute configuration.

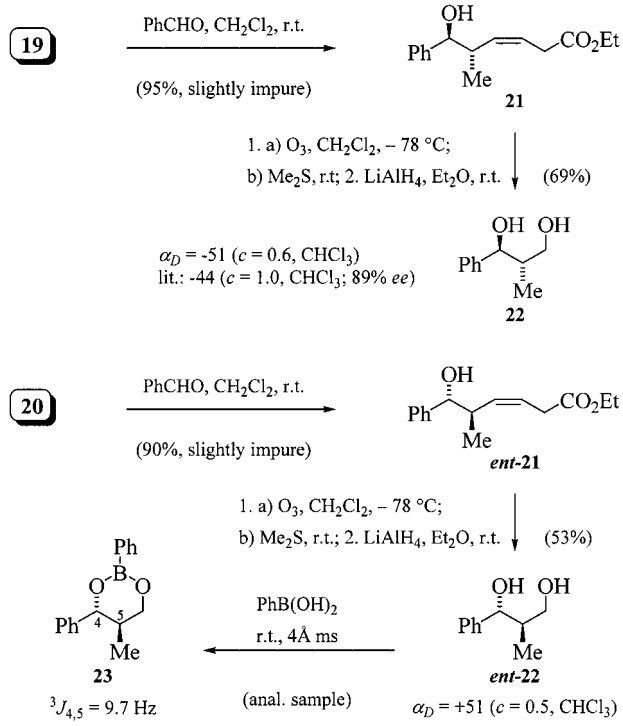
5-Methyl Derivatives

From the point of view of potential synthetic targets, the crotyl series is more versatile. Starting from the readily available 3-butyn-2-ols (**18** and ***ent*-18**), the established reaction sequence furnished the diastereomerically pure crotylboronic esters **19** and **20**, respectively (Scheme 5): After silyl protection (85/79%), hydroboration-oxidation-transesterification and deprotection (56/50% over 2 steps), Johnson rearrangement yielded the reagents (78/80%). In both cases only one diastereoisomer was detected by NMR spectroscopy of the crude product. The configuration of compounds **19** and **20** at C-3 was deduced by analogy from analysis of the NMR data (relative chemical shifts of C-4 and 4-H) and finally unambiguously by X-ray structural analysis[58] of boronic ester **20**.



Scheme 5. Synthesis of crotylboronic esters **19** and **20**; the absolute configuration of reagent **20** was established by X-ray structural analysis

Finally, allyl addition of crotylboronic esters **19** and **20** to benzaldehyde furnished slightly impure homoallyl alcohols **21** and ***ent*-21** in 95 and 90% yields, respectively (Scheme 6). Again, the (*Z*) diastereoisomers were the sole products. These results are in full agreement with those predicted for the proposed transition states of bulky allylboronic esters (the α-substituent is preferentially axial!) by Hoffmann and Weidmann.[7] The relative and absolute configurations of the two newly formed stereogenic centers were assigned by ozonolysis and reduction to the known *anti*-diols **22** and ***ent*-22**,[59][60] respectively, and by formation of the dioxaborinane **23** (which has a characteristic $^3J_{4,5}$ coupling constant of 9.7 Hz). Although the enantiomeric purities of **21/22** and ***ent*-21/22** could not be determined by direct methods completely satisfactorily (complete baseline separation of enantiomers by GLC or HPLC using chiral stationary phases was not possible), the *ee* values were confirmed from the optical rotations to be at least > 98% *ee* in both cases.



Scheme 6. Allyl additions of reagents **19** and **20**; the absolute and relative configurations of homoallyl alcohol **21**/***ent*-21** was established by chemical correlation with known diol **22**/***ent*-22** and dioxaborinane **23**

Conclusions

For the first time 1,3-disubstituted enantiomerically pure allylboronic esters **10**, **19** and **20** were synthesized by a completely selective Johnson rearrangement of boron-containing allyl alcohols (e.g. **9**). Furthermore, diastereoisomer **11** (as well as **10** from **2a**) was obtained after cross-metathesis

of the known boronic ester **3a**, thus allowing the absolute configurations of these products to be established. For the crotyl series, X-ray structural analysis of **20** allowed the unambiguous assignment of its configuration. All the allyl additions proved highly selective giving *Z*-configured homoallyl alcohols with > 98% *ee*. These results should be the basis for the future development of a plethora of highly selective *and* stable storable allylboronic esters.

Experimental Section

General Remarks: All reagents were used as purchased from commercial suppliers without further purification. The reactions were carried out by using standard Schlenk techniques under dry nitrogen. Glassware was oven-dried at 112 °C overnight. Solvents were dried and purified by conventional methods prior to use; diethyl ether (Et_2O), 1,2-dimethoxyethane (DME), and tetrahydrofuran (THF) were freshly distilled from sodium/benzophenone. Petroleum ether refers to the fraction with a boiling point between 40−60 °C. Flash-column chromatography: Merck silica gel 60, 0.040−0.063 mm (230−400 mesh). TLC: Pre-coated sheets, Polygram® SIL G/UV$_{254}$ Macherey−Nagel; detection by UV or by cerium molybdenum solution [phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), concd. H_2SO_4 (60 mL), H_2O (940 mL)]. Preparative MPLC: Labomatic (MD80/100) with a packed column (39 × 400 mm or 23 × 250 mm), LiChroprep, Si60 (15−25 μm) and UV detector (254 nm). HPLC: Pharmacia, equipped with a CHIRALCEL OD column. ^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ with a Bruker ARX 500/300. Chemical shifts δ are given in ppm relative to TMS as internal standard or relative to the resonance of the solvent (^{13}C: $CDCl_3$, δ = 77.0 ppm); coupling constants *J* are given in Hz. Higher order δ and *J* values are not corrected. ^{13}C signals were assigned by means of C−H and H−H COSY spectroscopy. Microanalyses were performed at the Institut für Organische Chemie, Stuttgart. Melting points (Büchi 510) are not corrected. Specific rotations were measured at 20 °C unless otherwise stated.

X-ray Crystallographic Analysis:[58] The crystal data for compound **20** were determined with a Siemens P4 diffractometer with graphite monochromator in the ω-scan mode with Cu-K_α (λ = 1.54178 Å) radiation. $C_{38}H_{41}BO_6$, M_r = 604.5, colorless, *T* = 293 K, crystal size 0.35 × 0.25 × 0.1 mm, orthorhombic, $P2_12_12_1$, *a* = 9.3668(6), *b* = 17.7165(17), *c* = 19.9587(16) Å, *V* = 3312.1(5) Å^3, *Z* = 4, $D_{calcd.}$ = 1.212 g·cm^{-3}, μ = 0.641 mm^{-1}, *F*(000) = 1288, θ range = 3.34−64.99°, 3524 measured/independent reflections, 2162 reflections with [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 for all data weights to *R* = 0.098, *wR* = 0.199(6), *S* = 1.030, H atoms were treated as riding atoms, max. shift/error < 0.001, residual $\rho_{max.}$ = 0.248 A^{-3}.

(*R*)-*tert*-Butyldimethyl(1-phenylprop-2-ynyloxy)silane (7): Under dry nitrogen, alcohol **6** (400 mg, 3.02 mmol) was dissolved in CH_2Cl_2 (2.5 mL) and imidazole (226 mg, 3.32 mmol) was added at 0 °C. After addition of *tert*-butyldimethylsilyl chloride (456 mg, 3.02 mmol; TBSCl), the mixture was stirred for 5 h. Hydrolysis with water (2.5 mL) was followed by extraction with pentane (3 × 10 mL). The combined organic layers were dried with $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude product was purified by flash-column chromatography (pentane/Et_2O, 98:2); the experimental data are in full agreement with those previously reported.[61] Yield: 724 mg (2.94 mmol, 97%), yellowish oil.

Alkenylboronic Ester 9: Under dry nitrogen, $BH_3 \cdot SMe_2$ complex (100 μL of a 10 M solution in dimethyl sulfide, 1.00 mmol) in 1,2-dimethoxyethane (1 mL; DME) was stirred at room temperature. After addition of cyclohexene (203 μL, 164 mg, 2.00 mmol), a colorless precipitate formed within 1 h; alkyne **7** (246 mg, 1.00 mmol) was then added. Stirring was continued until a clear solution formed. First, trimethylamine *N*-oxide dihydrate[62−64](222 mg, 2.00 mmol; water was removed prior to addition by Dean−Stark distillation with toluene) and after 1 h the "diol" (455 mg, 1.00 mmol) was added. The reaction mixture was stirred until no further consumption (as judged by TLC) of diol was indicated. The solvent was removed under reduced pressure and the crude product subjected to flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 98:2). Yield of **8**: 483 mg (0.68 mmol, 68%), colorless foam. This silyl ether was deprotected by dissolving alkenylboronic ester **8** (483 mg, 0.68 mmol) in a minimum amount of CH_2Cl_2 and ethanol (7.64 mL). Concentrated hydrochloric acid (159 μL) in ethanol (1.43 mL) was then added dropwise. After 1 h, complete consumption (as judged by TLC) of the starting material was detected. Saturated aqueous sodium hydrogencarbonate (2.50 mL) was added and the volume of the solvent reduced under reduced pressure. Water was added and the aqueous layer extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with saturated brine, dried with $MgSO_4$ and subjected to flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 85:15). Yield of **9**: 318 mg (0.53 mmol, 78%), colorless foam. Softening range 79−93 °C. $[\alpha]_D^{20}$ = −16 (*c* = 1.12, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3560, 3070, 3040, 3005, 2960, 2940, 2920, 2880, 2805, 1630, 1590, 1570, 1480, 1435, 1390, 1365, 1340, 1310, 1270, 1225, 1160, 1060 cm^{-1}. MS (FAB, NBA + NaI): *m*/*z* (%) = 619 (11) [M + Na]$^+$, 197 (100) [CPh_2OMe]$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.83 (d, *J* = 3.9 Hz, 1 H, O*H*), 2.99 (s, 6 H, OC*H*$_3$), 5.02 (ddd, *J* = 5.1, *J* = 3.9, *J* = 1.6 Hz, 1 H, 1-H), 5.35 (s, 2 H, 4′-H, 5′-H), 5.37 (dd, *J* = 18.0, *J* = 1.6 Hz, 1 H, 3-H), 6.28 (dd, *J* = 18.0, *J* = 5.1 Hz, 1 H, 2-H), 7.16−7.34 (m, 25 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 51.8 (O*C*H$_3$), 75.8 (C-1), 77.6 (C-4′, C-5′), 83.3 (*C*Ph$_2$OMe), 116.5 (C-3), 126.5, 127.2, 127.2, 127.5, 127.8, 127.8, 128.4, 128.4, 129.7 (arom. *C*H), 141.0, 141.2, 141.9 (arom. C_{ipso}), 153.1 (C-2) ppm. $C_{39}H_{37}BO_5$ (596.52): calcd. C 78.53, H 6.25; found C 78.36, H 6.30.

Allylboronic Ester 10. Method A (Johnson Rearrangement): Allyl alcohol **9** (276 mg, 0.46 mmol), triethyl orthoacetate (525 mg, 3.24 mmol) and propionic acid (2 mg, 2 μL, 0.03 mmol) were placed in an oven-dried flask equipped with a magnetic stirrer bar and a Claisen condenser. The mixture was stirred at 135 °C for 3 h. After cooling to room temperature, the residue was co-distilled several times with CH_2Cl_2 to remove the orthoester and propionic acid. After flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 95:5) the product was obtained. Yield of **10**: 253 mg (0.38 mmol, 82%), colorless foam. **Method B (Cross-Metathesis):** Under dry N_2, allylboronic ester **2a**[49] (207 mg, 0.35 mmol) was dissolved in CH_2Cl_2 (3.5 mL) in a 25-mL Schlenk flask equipped with a magnetic stirrer bar and a reflux condenser. Styrene (81 μL, 73 mg, 0.70 mmol) and "Grubbs-II catalyst" (30 mg, 35 μmol) was added and the mixture heated to 40 °C. The reaction was incomplete (as judged by TLC) after 22 h; however, neither addition of styrene (323 μL, 292 mg, 2.81 mmol) nor catalyst (6 mg, 7 μmol) changed the product distribution. After 2 d, the volatiles were removed under reduced pressure and the residue subjected first to flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 95:5) and then MPLC (petroleum ether/ethyl acetate, 95:5). Yield of **10**: 125 mg (0.19 mmol, 53%). Softening range 44−61 °C. $[\alpha]_D^{20}$ = −20 (*c* = 1.00, $CHCl_3$). IR (KBr):

$\tilde{\nu}$ = 3070, 3040, 3010, 2960, 2920, 2880, 2810, 1730, 1630, 1590, 1570, 1480, 1435, 1360, 1265, 1220, 1190, 1120, 1060 cm^{-1}. MS (FAB, NBA + NaI): *m*/*z* (%) = 689 (27) $[M + Na]^+$, 197 (100) $[CPh_2OMe]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.10 (t, *J* = 7.1 Hz, 3 H, 2′′-H), 2.07−2.21 (m, 3 H, 2-H, 3-H), 3.00 (s, 6 H, OCH_3), 3.92 (dq, *J* = 10.8, *J* = 7.1 Hz, 1 H, 1′′-H_a), 3.93 (dq, *J* = 10.8, *J* = 7.1 Hz, 1 H, 1′′-H_b), 5.34 (s, 2 H, 4′-H, 5′-H), 5.88 (dd, *J* = 16.0, *J* = 7.0 Hz, 1 H, 4-H), 6.08 (d, *J* = 16.0 Hz, 1 H, 5-H), 7.10−7.33 (m, 25 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2 (OCH_2CH_3), 24.4 (C-3), 34.0 (C-2), 51.7 (OCH_3), 60.1 (OCH_2CH_3), 78.0 (C-4′, C-5′), 83.3 (CPh_2OMe), 125.9, 126.5, 127.3, 127.4, 127.6, 127.8, 128.3, 128.4, 129.6 (arom. *C*H), 128.6 (C-5), 129.7 (C-4), 137.9, 141.0, 141.0 (arom. C_{ipso}), 172.9 (C-1) ppm. $C_{43}H_{43}BO_6$ (666.61): calcd. C 77.48, H 6.50; found C 77.43, H 6.76.

Allylboronic Ester 11. Method B (Cross-Metathesis): Under dry N_2, allylboronic ester **3a** (200 mg, 0.34 mmol) was dissolved in CH_2Cl_2 (3.4 mL) in a 25-mL Schlenk flask equipped with a magnetic stirrer bar and a reflux condenser. Styrene (78 μL, 71 mg, 0.68 mmol) and "Grubbs-II catalyst" (29 mg, 34 μmol) was added and the mixture heated to 40 °C. The reaction was incomplete (as judged by TLC) after 22 h; however, neither addition of styrene (311 μL, 282 mg, 2.71 mmol) nor catalyst (13 mg, 15 μmol) changed the product distribution. After 2 d, the volatiles were removed under reduced pressure, the residue subjected first to flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 95:5) and then MPLC (petroleum ether/ethyl acetate, 95:5). Yield of **11**: 102 mg (0.15 mmol, 45%). Softening range 52−70 °C. $[\alpha]_D^{20}$ = −41 (*c* = 0.98, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3070, 3040, 3010, 2960, 2920, 2880, 2810, 1730, 1630, 1590, 1570, 1480, 1435, 1360, 1310, 1265, 1220, 1190, 1120, 1060 cm^{-1}. MS (FAB, NBA + NaI): *m*/*z* (%) = 689 (61) $[M + Na]^+$, 197 (100) $[CPh_2OMe]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.1 Hz, 3 H, 2′′-H), 2.07−2.16 (m, 3 H, 2-H, 3-H), 3.00 (s, 6 H, OCH_3), 3.98 (q, *J* = 7.1 Hz, 2 H, 1′′-H), 5.34 (s, 2 H, 4′-H, 5′-H), 5.74 (dd, *J* = 15.9, *J* = 7.8 Hz, 1 H, 4-H), 6.06 (dd, *J* = 15.9, *J* = 0.5 Hz, 1 H, 5-H), 7.13−7.34 (m, 25 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2 (OCH_2CH_3), 24.6 (C-3), 34.5 (C-2), 51.8 (OCH_3), 60.1 (OCH_2CH_3), 77.9 (C-4′, C-5′), 83.3 (CPh_2OMe), 126.0, 126.5, 127.3, 127.4, 127.6, 127.8, 128.2, 128.4, 129.7 (arom. *C*H), 129.2 (C-5), 129.2 (C-4), 137.9, 141.1, 141.1 (arom. C_{ipso}), 172.8 (C-1) ppm. $C_{43}H_{43}BO_6$ (666.61): calcd. C 77.48, H 6.50; found C 77.29, H 6.52.

Alkenylboronic Ester 13: Under dry nitrogen, $BH_3{\cdot}SMe_2$ complex (100 μL of a 10 M solution in dimethyl sulfide, 1.00 mmol) in 1,2-dimethoxyethane (1 mL; DME) was stirred at room temperature. After addition of cyclohexene (203 μL, 164 mg, 2.00 mmol) a colorless precipitate formed within 1 h; alkyne **7** (246 mg, 1.00 mmol) was then added. Stirring was continued until a clear solution formed. First, trimethylamine *N*-oxide dihydrate[62−64](222 mg, 2.00 mmol; water was removed prior to addition by Dean−Stark-distillation with toluene) was added and then, after 1 h, benzpinacol (440 mg, 1.20 mmol). The reaction mixture was refluxed for 8 h until no further consumption (as judged by TLC) of diol was detected. The solvent was then removed under reduced pressure and the crude product subjected to flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 98:2) and MPLC (petroleum ether/ethyl acetate, 99:1). Yield of **12**: 168 mg (0.27 mmol, 27%), colorless foam. Softening range 45−57 °C. $[\alpha]_D^{20}$ = +29 (*c* = 1.16, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3420, 3070, 3040, 3005, 2935, 2905, 2860, 2840, 1625, 1590, 1570, 1480, 1460, 1450, 1435, 1385, 1355, 1330, 1270, 1240, 1210, 1160, 1100 cm^{-1}. MS (FAB, NBA + NaI): *m*/*z* (%) = 645 (13) $[M + Na]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = −0.07, 0.05 [2 s, 6 H, $Si(CH_3)_2$], 0.87 [s, 9 H, $C(CH_3)_3$], 5.27 (dd, *J* = 4.6, *J* = 1.5 Hz, 1 H, 1-H), 6.03 (dd, *J* = 17.8, *J* = 1.7 Hz, 1 H, 3-H), 6.94−7.34 (m, 26 H, 2-H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = −4.8, −4.6 [$Si(CH_3)_2$], 18.4 [$C(CH_3)_3$], 25.9 [$C(CH_3)_3$], 76.7 (C-1), 95.9 (CPh_2), 115.1 (C-3), 126.4, 126.9, 126.9, 127.2, 127.3, 128.3, 128.5 (arom. *C*H), 142.6, 142.5, 142.8 (arom. C_{ipso}), 157.3 (C-2) ppm. $C_{41}H_{43}BO_3Si$ (622.67): calcd. C 79.08, H 6.96; found C 78.90, H 6.97. The silyl ether was deprotected by dissolving alkenylboronic ester **12** (188 mg, 0.30 mmol) in a minimum amount of CH_2Cl_2 and ethanol (7.64 mL). Concentrated hydrochloric acid (159 μL) in ethanol (1.43 mL) was then added dropwise. After 1 h, complete consumption (as judged by TLC) of the starting material was detected. Saturated aqueous sodium hydrogencarbonate (637 μL) was added and the volume of the solvent reduced under reduced pressure. Water was added and the aqueous layer extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with saturated brine, dried with $MgSO_4$ and subjected to flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 85:15) to furnish the spectroscopically pure product. Yield of **13**: 129 mg (0.25 mmol, 82%), colorless foam. An analytical sample was further purified by MPLC (petroleum ether/ethyl acetate, 85:15). M.p. 156−158 °C. $[\alpha]_D^{20}$ = +17 (*c* = 1.10, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3550, 3400, 3070, 3040, 3010, 2980, 1630, 1590, 1575, 1480, 1435, 1385, 1350, 1320, 1295, 1270, 1220, 1210, 1160, 1060 cm^{-1}. MS (CI, CH_4: T_{source} = 410 K, T_{sample} = 455 K): *m*/*z* (%) = 508 (57) $[M]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.14 (d, *J* = 3.6 Hz, 1 H, O*H*), 5.37 (ddd, *J* = 5.0, *J* = 3.6, *J* = 1.6 Hz, 1 H, 1-H), 6.14 (dd, *J* = 18.0, *J* = 1.6 Hz, 1 H, 3-H), 7.16 (dd, *J* = 18.0, *J* = 5.0 Hz, 1 H, 2-H), 7.02−7.42 (m, 25 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 76.1 (C-1), 96.0 (CPh_2), 116.8 (C-3), 126.6, 126.9, 126.9, 127.2, 128.0, 128.5, 128.5, 128.7 (arom. *C*H), 141.8, 142.4, 142.5 (arom. C_{ipso}), 155.5 (C-2) ppm. $C_{35}H_{29}BO_3$ (508.41): calcd. C 82.68, H 5.75; found C 82.44, H 5.85.

Allylboronic Ester 14: Allyl alcohol **13** (85 mg, 0.17 mmol), triethyl orthoacetate (190 mg, 1.17 mmol) and propionic acid (1 mg, 1 μL, 10 μmol) were placed in a flask equipped with a magnetic stirrer bar and a Claisen condenser. The mixture was stirred at 135 °C for 3 h. After cooling to room temperature, the residue was co-distilled several times with CH_2Cl_2 to remove the orthoester and propionic acid. After flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 90:10) the slightly impure product was obtained. Yield of **14**: 76 mg (0.13 mmol, 79%), colorless foam. An analytical sample was further purified by means of MPLC (petroleum ether/ethyl acetate, 98:2); yield: 46 mg (80 μmol, 48%). Softening range 38−62 °C. $[\alpha]_D^{20}$ = −19 (*c* = 0.72, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3070, 3040, 3000, 2960, 2910, 2880, 1725, 1630, 1590, 1570, 1480, 1435; 1410, 1355, 1320, 1295, 1270, 1250, 1205, 1165, 1080, 1065, 1015 cm^{-1}. MS (EI, 70 eV: T_{source} = 420 K, T_{sample} = 420 K): *m*/*z* (%) = 578 (28) $[M]^+$, 533 (4) $[M - OEt]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.1 Hz, 3 H, 2′′-H), 2.74−2.84 (m, 1 H, 2-H_a), 2.92−3.01 (m, 2 H, 3-H, 2-H_b), 4.14 (dq, *J* = 10.8, *J* = 7.1 Hz, 1 H, 1′′-H_a), 4.17 (dq, *J* = 10.8, *J* = 7.1 Hz, 1 H, 1′′-H_b), 6.46 (dd, *J* = 16.0, *J* = 7.9 Hz, 1 H, 4-H), 6.59 (d, *J* = 16.0 Hz, 1 H, 5-H), 6.99−7.36 (m, 25 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (C-2′′), 25.1 (C-3), 35.1 (C-2), 60.5 (C-1′′), 96.5 (CPh_2), 126.0, 126.8, 126.9, 127.0, 127.1, 127.1, 128.5, 128.5, 128.6 (arom. *C*H), 129.1 (C-4), 130.4 (C-5), 137.7, 142.2, 142.5 (arom. C_{ipso}), 173.2 (C-1) ppm. $C_{39}H_{35}BO_4$ (578.50): calcd. C 80.97, H 6.10; found C 80.74, H 6.11.

Ethyl (*Z*,5*R*,6*S*)-6-Hydroxy-5,6-diphenylhex-3-enoate (15): Allylboronic ester **10** (152 mg, 0.23 mmol) was dissolved in CH_2Cl_2 (114

μL) in a Schlenk flask equipped with stirrer bar and septum. Benzaldehyde (29 mg, 28 μL, 0.27 mmol) was added at 0 °C and the mixture warmed to room temperature overnight. After complete consumption of reagent **10** (as judged by TLC), the solvents were removed under reduced pressure and the crude product subjected to thorough flash-column chromatography and MPLC (petroleum ether/ethyl acetate, 85:15) to furnish the pure product. Yield of **15**: 46 mg (0.15 mmol, 65%, > 99% *ee*), colorless oil. $[\alpha]_D^{20} = -97$ (*c* = 0.54, $CHCl_3$; > 99% *ee*). HPLC (CHIRALCEL OD, hexane/*i*PrOH, 95:5): t_R = 12.00 min. IR (neat): $\tilde{\nu}$ = 3477, 3090, 3060, 3030, 2980, 2935, 2905, 2870, 1734, 1600, 1585, 1495, 1450, 1400, 1370, 1325, 1300, 1260, 1175, 1095, 1030 cm^{-1}. MS (EI, 70 eV: T_{source} = 390 K, T_{sample} = 360 K): *m*/*z* (%) = 310 (0.3) $[M]^+$, 292 (0.1) $[M - H_2O]^+$, 265 (1) $[M - OEt]^+$, 247 (1) $[M - (H_2O + EtO)]^+$, 204 (95) $[M - PhCHO]^+$, 130 (100) $[C_{10}H_{10}]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.1 Hz, 3 H, 2′-H), 2.63 (d, *J* = 3.1 Hz, 1 H, O*H*), 2.98 (ddd, *J* = 17.0, *J* = 6.9, *J* = 1.6 Hz, 1 H, 2-H_a), 3.08 (ddd, *J* = 17.0, *J* = 7.7, *J* = 1.7 Hz, 1 H, 2-H_b), 3.80 (ddd, *J* = 10.2, *J* = 7.3, *J* = 1.0 Hz, 1 H, 5-H), 4.09 (q, *J* = 7.1 Hz, 2 H, 1′-H), 4.84 (dd, *J* = 7.3, *J* = 3.1 Hz, 1 H, 6-H), 5.83 (dddd, *J* = 10.8, *J* = 7.7, *J* = 6.9, *J* = 1.0 Hz, 1 H, 3-H), 6.11 (dddd, *J* = 10.8, *J* = 10.2, *J* = 1.7, *J* = 1.6 Hz, 1 H, 4-H), 7.06−7.22 (m, 10 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (C-2′), 33.1 (C-2), 52.7 (C-5), 60.8 (C-1′), 77.9 (C-6), 124.3 (C-3), 126.5, 126.6, 127.4, 127.9, 128.3, 128.4 (arom. *C*H), 132.3 (C-4), 140.7, 142.0 (arom. C_{ipso}), 171.6 (C-1) ppm. $C_{20}H_{22}O_3$ (310.39): calcd. C 77.39, H 7.14; found C 77.32, H 7.20. According to the same procedure, homoallyl alcohol ***ent*-15** (75 mg, 0.24 mmol, 78%, > 99% *ee*) was obtained from allylboronic ester **11** (206 mg, 0.31 mmol). $[\alpha]_D^{20} = +98$ (*c* = 1.16, $CHCl_3$; > 99% *ee*). HPLC (CHIRALCEL OD, hexane/*i*PrOH, 95:5): t_R = 7.78 min. Starting with reagent **14** (40 mg, 69 μmol), alcohol **15** (18 mg, 58 μmol, 84%, *ee* = 91%) was isolated.

(1*S*,2*S*)-1,2-Diphenylpropane-1,3-diol (16): Homoallyl alcohol **15** (26 mg, 84 μmol) was first dissolved in CH_2Cl_2 (10 mL). Ozone was then bubbled through the solution at −78 °C until a blue color persisted. Excess ozone was removed by passing a continuous stream of oxygen through the solution. After reductive work up with Me_2S (1 mL), the mixture was warmed to room temperature and the volatiles removed under reduced pressure. The residue was dissolved in THF (10 mL) and $LiAlH_4$ (100 mg, 2.64 mmol) was added. After 1 h, the mixture was diluted with Et_2O (5 mL) and treated successively with H_2O (250 μL), 2 N aqueous NaOH (500 μL) and H_2O (500 μL). The solids were filtered off, washed thoroughly and the filtrate dried with sodium sulfate. Filtration and removal of the solvents under reduced pressure furnished the product. After MPLC (petroleum ether/ethyl acetate, 60:40) a spectroscopically pure product was obtained. Yield of **16**: 11 mg (48 μmol, 57%), colorless solid, spectroscopic data were in good agreement with those previously reported.[57] $[\alpha]_D^{20} = +92$ (*c* = 0.55, $CHCl_3$); +67 (*c* = 0.55, acetone) [ref.[57] for ***ent*-16**: −64 (*c* = 0.90, acetone)]. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.95 (br. s, 2 H, O*H*), 3.16 (ddd, *J* = 8.8, *J* = 7.7, *J* = 4.5 Hz, 1 H, 2-H), 3.97 (dd, *J* = 11.1, *J* = 4.5 Hz, 1 H, 3-H_a), 4.20 (dd, *J* = 11.1, *J* = 7.7 Hz, 1 H, 3-H_b), 5.03 (d, *J* = 8.8 Hz, 1 H, 1-H), 7.01−7.53 (m, 10 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 54.9 (C-2), 66.3 (C-3), 79.6 (C-1), 126.5, 126.9, 127.7, 128.1, 128.4, 128.5 (arom. *C*H), 139.2, 142.7 (arom. C_{ipso}) ppm.

(4*S*,5*S*)-2,4,5-Triphenyl-1,3,2-dioxaborinane (17): Diol **16** (11 mg, 48 μmol) and phenylboronic acid (7 mg, 53 μmol) were dissolved in CH_2Cl_2 (526 μL) and two spheres of molecular sieves (4 Å) were added. The mixture was stirred overnight, filtered and the solvent removed under reduced pressure. The spectroscopic data of the crude product (quant. conversion) are in good agreement with those previously published.[57] ^1H NMR (500 MHz, $CDCl_3$): δ = 3.13 (ddd, *J* = 10.8, *J* = 9.7, *J* = 4.6 Hz, 1 H, 5-H), 4.27 (dd, *J* = 11.4, *J* = 4.6 Hz, 1 H, 6-H_a), 4.41 (dd, *J* = 11.4, *J* = 10.8 Hz, 1 H, 6-H_b), 5.30 (d, *J* = 9.7 Hz, 1 H, 4-H), 7.04−7.91 (m, 15 H, arom C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 51.3 (C-5), 66.3 (C-6), 78.8 (C-4), 126.4, 127.4, 127.6, 127.6, 128.0, 128.5, 128.7, 130.9, 134.1, 137.4, 140.9 (arom. *C*H, arom. C_{ipso}) ppm.

Allylboronic Esters 19 and 20: Under dry nitrogen alcohol, **18** (100 mg, 1.43 mmol) was dissolved in CH_2Cl_2 (1.1 mL) and imidazole (107 mg, 1.57 mmol) was added at 0 °C. After addition of *tert*-butyldimethylsilyl chloride (215 mg, 1.43 mmol; TBSCl), the mixture was stirred at room temperature for 5 h. Hydrolysis with water (1.5 mL) was followed by extraction with pentane (3 × 5 mL). The combined organic layers were washed with brine, dried with $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude product was purified by flash-column chromatography (pentane/Et_2O, 98:2); the spectroscopic data are in full agreement with those previously reported.[61] Yield: 223 mg (1.21 mmol, 85%), colorless oil. Starting from ***ent*-18** (100 mg, 1.43 mmol), 208 mg (1.13 mmol, 79%) of a colorless oil was obtained. Under dry nitrogen $BH_3{\cdot}SMe_2$ complex (100 μL of a 10 M solution in dimethyl sulfide, 1.00 mmol) in 1,2-dimethoxyethane (1 mL; DME) was stirred at room temperature. After addition of cyclohexene (203 μL, 164 mg, 2.00 mmol) a colorless precipitate formed within 1 h; the silyl-protected alkyne (184 mg, 1.00 mmol) was then added. Stirring was continued until a clear solution formed. Next, trimethylamine *N*-oxide dihydrate[62−64] (222 mg, 2.00 mmol; water was removed prior to addition by Dean−Stark-distillation with toluene) was added and after 1 h the "diol" (455 mg, 1.00 mmol) was added. The reaction mixture was stirred until no further consumption (as judged by TLC) of diol was detected. The solvent was removed under reduced pressure and the crude product subjected to flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 98:2 to 90:10). An analytical sample was purified by MPLC (petroleum ether/ethyl acetate, 99:1). **(3*E*,2*S*,4′*R*,5′*R*)-(*tert*-Butyldimethylsilyl) 4-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]but-3-en-2-yl Ether:** Softening range 57−69 °C. $[\alpha]_D^{20}$ = −48 (*c* = 1.08, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3070, 3040, 3010, 2940, 2910, 2880, 2840, 2810, 1630, 1590, 1570, 1480, 1460, 1450, 1435, 1390, 1370, 1360, 1330, 1270, 1240, 1220, 1170, 1130, 1060, 1020, 1000 cm^{-1}. MS (FAB, NBA + NaI): *m*/*z* (%) = 671 (7) $[M + Na]^+$, 197 (100) $[CPh_2OMe]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = −0.04, −0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.83 [s, 9 H, $C(CH_3)_3$], 1.07 (d, $^3J_{1,2}$ = 6.4 Hz, 3 H, 1-H), 3.00 (s, 6 H, OCH_3), 4.13 (qdd, *J* = 6.4, *J* = 4.6, *J* = 1.6 Hz, 1 H, 2-H), 5.21 (dd, *J* = 17.9, *J* = 1.6 Hz, 1 H, 4-H), 5.35 (s, 2 H, 4′-H, 5′-H), 6.17 (dd, *J* = 17.9, *J* = 4.6 Hz, 1 H, 3-H), 7.22−7.37 (m, 20 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = −5.0, −4.7 [$Si(CH_3)_2$], 18.3 [$C(CH_3)_3$], 23.8 (C-1), 25.9 [$C(CH_3)_3$], 51.8 (OCH_3), 70.0 (C-2), 77.6 (C-4′, C-5′), 83.4 (CPh_2OMe), 114.5 (C-4), 127.2, 127.2, 127.5, 127.8, 128.5, 129.7 (arom. *C*H), 141.1, 141.4 (arom. C_{ipso}), 156.5 (C-3) ppm. $C_{40}H_{49}BO_5Si$ (648.71): calcd. C 74.06, H 7.61; found C 73.95, H 7.62. The (3*E*,2*R*,4′*R*,5′*R*) diastereoisomer was obtained starting from the corresponding silyl ether (188 mg, 1.02 mmol) and "diol" (464 mg, 1.02 mmol). **(3*E*,2*R*,4′*R*,5′*R*)-(*tert*-Butyldimethylsilyl) 4-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]but-3-en-2-yl Ether:** Softening range 58−68 °C. $[\alpha]_D^{20}$ = −58 (*c* = 1.10, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3070, 3040, 3010, 2940, 2920, 2880, 2840, 2810, 1630, 1590, 1570, 1480, 1460, 1450, 1435, 1390, 1370, 1360, 1330, 1270, 1240, 1225, 1165, 1130, 1060, 1020, 1000 cm^{-1}. MS (CI, NH_3: T_{source} = 395 K, T_{sample} = 475 K): *m*/*z* (%) = 666 (7) [M

+ $NH_4]^+$, 197 (100) $[CPh_2OMe]^+$. ^1H NMR (500 MHz, $CDCl_3$): $\delta = -0.03, -0.03$ [2 s, 6 H, $Si(CH_3)_2$], 0.85 [s, 9 H, $C(CH_3)_3$], 1.07 (d, $J = 6.5$ Hz, 3 H, 1-H), 2.99 (s, 6 H, OCH_3), 4.14 (qdd, $J = 6.5$, $J = 4.7$, $J = 1.5$ Hz, 1 H, 2-H), 5.17 (dd, $J = 17.9$, $J = 1.5$ Hz, 1 H, 4-H), 5.33 (s, 2 H, 4′-H, 5′-H), 6.16 (dd, $J = 17.9$, $J = 4.7$ Hz, 1 H, 3-H), 7.23−7.37 (m, 20 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -5.0, -4.7$ [$Si(CH_3)_2$], 18.3 [$C(CH_3)_3$], 23.8 (C-1), 25.9 [$C(CH_3)_3$], 51.8, 51.8 (OCH_3), 70.2 (C-2), 77.7 (C-4′, C-5′), 83.4 (CPh_2OMe), 114.6 (C-4), 127.2, 127.2, 127.4, 127.8, 128.5, 129.7 (arom. *C*H), 141.1, 141.5 (arom. C_{ipso}), 156.5 (C-3) ppm. $C_{40}H_{49}BO_5Si$ (648.71): calcd. C 74.06, H 7.61; found C 73.93, H 7.57. The silyl ether was deprotected by dissolving the crude alkenylboronic ester (531 mg) in a minimum amount of CH_2Cl_2 and ethanol (7.64 mL). Concentrated hydrochloric acid (159 μL, 1.92 mmol) in ethanol (1.43 mL) was then added dropwise. After 1 h, complete consumption (as judged by TLC) of the starting material was detected. Saturated aqueous sodium hydrogencarbonate (637 μL) was added and the volume of the solvent reduced under reduced pressure. Water was then added and the aqueous layer extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with saturated brine, dried with $MgSO_4$ and subjected to flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 85:15) to furnish the spectroscopically pure product. Yield (over 2 steps): 298 mg (0.56 mmol, 56%), colorless foam. An analytical sample was further purified by MPLC (petroleum ether/ethyl acetate, 85:15). **(3*E*,2*S*,4′*R*,5′*R*)-4-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]but-3-en-2-ol:** Softening range 80−95 °C. $[\alpha]_D^{20} = -74$ ($c = 1.02$, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3560, 3400, 3070, 3040, 3010, 2950, 2920, 2880, 2815, 1635, 1590, 1570, 1480, 1435, 1390, 1360, 1340, 1310, 1270, 1225, 1170, 1140, 1060, 1020, 1000 cm^{-1}. MS (FAB, NBA + NaI): *m*/*z* (%) = 557 (18) $[M + Na]^+$, 197 (100) $[CPh_2OMe]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, $J = 6.5$ Hz, 3 H, 1-H), 1.50 (br. s, 1 H, O*H*), 3.00 (s, 6 H, OCH_3), 4.14 (qdd, $J = 6.5$, $J = 5.0$, $J = 1.5$ Hz, 1 H, 2-H), 5.20 (dd, $J = 18.1$, $J = 1.5$ Hz, 1 H, 4-H), 5.35 (s, 2 H, 4′-H, 5′-H), 6.21 (dd, $J = 18.1$, $J = 5.0$ Hz, 1 H, 3-H), 7.23−7.36 (m, 20 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.7 (C-1), 51.8, 51.8 (OCH_3), 69.4 (C-2), 77.7 (C-4′, C-5′), 83.3 (CPh_2OMe), 115.4 (C-4), 127.2, 127.3, 127.5, 127.8, 128.5, 129.7 (arom. *C*H), 141.0, 141.3 (arom. C_{ipso}), 155.7 (C-3). $C_{34}H_{35}BO_5$ (534.45): calcd. C 76.41, H 6.60; found C 76.30, H 6.65. The (3*E*,2*R*,4′*R*,5′*R*) diastereoisomer was obtained in the same way in 50% yield (274 mg, 0.51 mmol) over two steps. **(3*E*,2*S*,4′*R*,5′*R*)-4-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]but-3-en-2-ol:** Softening range 81−91 °C. $[\alpha]_D^{20} = -80$ ($c = 1.25$, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3560, 3410, 3070, 3040, 3010, 2950, 2920, 2880, 2810, 1635, 1590, 1570, 1480, 1450, 1435, 1390, 1360, 1340, 1315, 1270, 1225, 1170, 1140, 1060, 1020, 1000 cm^{-1}. MS (FAB, NBA + NaI): *m*/*z* (%) = 557 (37) $[M + Na]^+$, 197 (100) $[CPh_2OMe]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, $J = 6.5$ Hz, 3 H, 1-H), 1.43 (br, 1 H, O*H*), 3.00 (s, 6 H, OCH_3), 4.15 (qdd, $J = 6.5$, $J = 4.9$, $J = 1.5$ Hz, 1 H, 2-H), 5.20 (dd, $J_{4,3} = 18.1$, $J = 1.5$ Hz, 1 H, 4-H), 5.35 (s, 2 H, 4′-H, 5′-H), 6.22 (dd, $J = 18.1$, $J = 4.9$ Hz, 1 H, 3-H), 7.23−7.36 (m, 20 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.6 (C-1), 51.8 (OCH_3), 69.4 (C-2), 77.7 (C-4′, C-5′), 83.4 (CPh_2OMe), 115.3 (C-4), 127.2, 127.3, 127.5, 127.8, 128.5, 129.7 (arom. *C*H), 141.1, 141.3 (arom. C_{ipso}), 155.7 (C-3) ppm. $C_{34}H_{35}BO_5$ (534.45): calcd. C 76.41, H 6.60; found C 75.62, H 6.53. The above-formed allyl alcohol (277 mg, 0.52 mmol), triethyl orthoacetate (376 mg, 2.32 mmol) and propionic acid (1.5 mg, 1.5 μL, 0.02 mmol) were added to a flask equipped with a magnetic stirrer bar and a Claisen condenser. The mixture was stirred at 135 °C for 3 h. After cooling to room temperature, the residue was co-distilled several times with CH_2Cl_2 to remove the orthoester and propionic acid. After flash-column chromatography on silica gel (petroleum ether/ethyl acetate, 95:5) the spectroscopically pure product was obtained. Yield of **19**: 244 mg (0.40 mmol, 78%), colorless foam. An analytically pure sample was obtained after MPLC (petroleum ether/ethyl acetate, 98:2). **19:** Softening range 41−57 °C. $[\alpha]_D^{20} = -86$ ($c = 1.15$, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3070, 3040, 3005, 2960, 2920, 2890, 2810, 1730, 1590, 1570, 1480, 1435, 1370, 1360, 1340, 1305, 1260, 1215, 1190, 1160, 1120, 1070, 1060, 1015, 1000 cm^{-1}. MS (FAB, NBA + NaI): *m*/*z* (%) = 627 (3) $[M + Na]^+$, 197 (100) $[CPh_2OMe]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, $J = 7.1$ Hz, 3 H, 2′′-H), 1.50 (m, 3 H, 6-H), 1.84 (m, 1 H, 3-H), 1.94 (dd, $J = 15.4$, $J = 10.7$ Hz, 1 H, 2-H_a), 2.07 (dd, $J = 15.4$, $J = 4.5$ Hz, 1 H, 2-H_b), 2.99 (s, 6 H, OCH_3), 3.92 (dq, $J = 10.8$, $J = 7.1$ Hz, 1 H, 1′′-H_a), 3.94 (dq, $J = 10.8$, $J = 7.1$ Hz, 1 H, 1′′-H_b), 5.11 (m, 2 H, 4-H, 5-H), 5.29 (s, 2 H, 4′-H, 5′-H), 7.25−7.34 (m, 20 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2 (C-2′′), 18.0 (C-6), 23.9 (C-3), 34.3 (C-2), 51.7, 51.7 (OCH_3), 59.9 (C-1′′), 77.9 (C-4′, C-5′), 83.3 (CPh_2OMe), 123.8 (C-5), 127.3, 127.3, 127.5, 127.8, 128.4, 129.7 (arom. *C*H), 129.6 (C-4), 141.1, 141.2 (arom. C_{ipso}), 173.2 (C-1). $C_{38}H_{41}BO_6$ (604.54): calcd. C 75.50, H 6.84; found C 75.36, H 6.86. The spectroscopically pure diastereoisomer **20** was formed in 80% yield (231 mg, 0.38 mmol) after Johnson rearrangement of the appropriate allyl alcohol (255 mg, 0.48 mmol). An analytically pure sample was obtained after MPLC (petroleum ether/ethyl acetate, 98:2). Recrystallization from pentane/ethanol yielded crystals suitable for X-ray structural analysis. **20:** M.p. 150−152 °C. $[\alpha]_D^{20} = -98$ ($c = 1.30$, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3070, 3040, 3005, 2960, 2940, 2920, 2890, 2835, 2810, 1730, 1590, 1570, 1480, 1435, 1370, 1360, 1345, 1325, 1305, 1270, 1220, 1195, 1165, 1125, 1070, 1060, 1020, 1000 cm^{-1}. MS (FAB, NBA + NaI): *m*/*z* (%) = 627 (50) $[M + Na]^+$, 197 (100) $[CPh_2OMe]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.14 (t, $J = 7.1$ Hz, 3 H, 2′′-H), 1.50 (m, 3 H, 6-H), 1.86 (m, 1 H, 3-H), 2.00 (d, $J = 9.1$ Hz, 1 H, 2-H_a), 2.00 (d, $J = 6.1$ Hz, 1 H, 2-H_b), 2.99 (s, 6 H, OCH_3), 4.04 (dq, $J = 10.8$, $J = 7.1$ Hz, 1 H, 1′′-H_a), 4.06 (dq, $J = 10.8$, $J = 7.1$ Hz, 1 H, 1′′-H_b), 4.98 (ddq, $J = 15.3$, $J = 7.9$, $J = 1.5$ Hz, 1 H, 4-H), 5.09 (dqd, $J = 15.3$, $J = 6.3$, $J = 1.0$ Hz, 1 H, 5-H), 5.30 (s, 2 H, 4′-H, 5′-H), 7.23−7.34 (m, 20 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2 (C-2′′), 17.9 (C-6), 24.1 (C-3), 34.7 (C-2), 51.8 (OCH_3), 59.9 (C-1′′), 77.9 (C-4′, C-5′), 83.4 (CPh_2OMe), 124.2 (C-5), 127.2, 127.3, 127.5, 127.8, 128.5, 129.7 (arom. *C*H), 129.2 (C-4), 141.2, 141.3 (arom. C_{ipso}), 173.1 (C-1) ppm. $C_{38}H_{41}BO_6$ (604.54): calcd. C 75.50, H 6.84; found C 75.44, H 6.86.

Ethyl (3*Z*,5*S*,6*S*)-6-Hydroxy-5-methyl-6-phenylhex-3-enoate (21): Allylboronic ester **19** (341 mg, 0.56 mmol) was dissolved in CH_2Cl_2 (282 μL) in a Schlenk flask equipped with a stirrer bar and septum. Benzaldehyde (69 μL, 72 mg, 0.68 mmol) was added at 0 °C and the mixture warmed to room temperature overnight. After complete consumption of reagent **19** (as judged by TLC) the solvents were removed under reduced pressure and the crude product subjected to thorough flash-column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) to furnish a slightly impure product. Yield of **21**: 133 mg (0.54 mmol, 95%, > 97% *ee*), colorless oil. An analytically pure sample was obtained after purification by means of MPLC (petroleum ether/ethyl acetate, 85:15). **21:** $[\alpha]_D^{20} = -130$ (c = 1.55, $CHCl_3$, > 97% *ee*). HPLC (CHIRALCEL OD, hexane/*i*PrOH, 98:2): t_R = 9.73 min (no baseline separation). IR (film): $\tilde{\nu}$ = 3460, 3070, 3040, 3005, 2955, 2905, 2880, 2850, 1730, 1590, 1575, 1480, 1440, 1390, 1360, 1315, 1240, 1160, 1080, 1020 cm^{-1}. MS (EI, 70 eV: T_{source} = 400 K, T_{sample} = 315 K): *m*/*z* (%) = 248 (2) $[M]^+$, 230 (0.1) $[M - H_2O]^+$, 203 (1) $[M - OEt]^+$, 185 (2) $[M - (H_2O + EtO)]^+$, 142 (100) $[M - PhCHO]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.81 (d, $J = 6.7$ Hz, 3 H, CH_3), 1.26 (t, $J = 7.1$ Hz,

3 H, 2′-H), 2.64 (d, J = 2.1 Hz, 1 H, O*H*), 2.71 (ddqd, J = 10.1, J = 8.1, J = 6.7, J = 1.0 Hz, 1 H, 5-H), 3.08 (ddd, J = 16.7, J = 7.2, J = 1.5 Hz, 1 H, 2-H_a), 3.13 (ddd, J = 16.7, J = 7.6, J = 1.6 Hz, 1 H, 2-H_b), 4.15 (q, J = 7.1 Hz, 2 H, 1′-H), 4.32 (dd, J = 8.1, J = 2.1 Hz, 1 H, 6-H), 5.55 (dddd, J = 10.8, J = 10.1, J = 1.6, J = 1.5 Hz, 1 H, 4-H), 5.73 (dddd, J = 10.8, J = 7.6, J = 7.2, J = 1.0 Hz, 1 H, 3-H), 7.25−7.34 (m, 5 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (C-2′), 17.1 (*C*H_3), 33.2 (C-2), 40.6 (C-5), 60.8 (C-1′), 78.4 (C-6), 123.2 (C-3), 126.9, 127.6, 128.2 (arom. *C*H), 135.9 (C-4), 142.5 (arom. C_{ipso}), 171.9 (C-1) ppm. $C_{15}H_{20}O_3$ (248.32): calcd. C 72.55, H 8.12; found C 72.47, H 8.07. According to the same procedure, homoallyl alcohol ***ent*-21** (58 mg, 0.23 mmol, 90%, > 97% *ee*) was obtained from allylboronic ester **20** (157 mg, 0.26 mmol). $[\alpha]_D^{20}$ = +137 (c = 0.88, $CHCl_3$, > 97% *ee*). HPLC (CHIRALCEL OD, hexane/*i*PrOH, 98:2): t_R = 9.11 min (no baseline separation).

(1*S*,2*S*)-2-Methyl-1-phenylpropane-1,3-diol (22): Homoallyl alcohol **21** (39 mg, 0.16 mmol) was first dissolved in CH_2Cl_2 (10 mL). Ozone was then bubbled through the solution at −78 °C until a blue color persisted. Excess ozone was removed by passing a continuous stream of oxygen through the solution. After reductive work up with Me_2S (1 mL), the mixture was warmed to room temperature and the volatiles removed under reduced pressure. The residue was dissolved in Et_2O (5 mL) and $LiAlH_4$ (60 mg, 1.57 mmol) was added. After 1 h, the mixture was diluted with Et_2O (5 mL) and treated successively with H_2O (100 μL), 2 N aqueous NaOH (200 μL) and H_2O (200 μL). The solids were filtered off, washed thoroughly and the filtrate dried with sodium sulfate. Filtration and removal of the solvents under reduced pressure furnished the product. After MPLC (petroleum ether/ethyl acetate, 60:40), a spectroscopically pure product was obtained. Yield of **22**: 18 mg (0.11 mmol, 69%, > 98% *ee*), colorless oil. The spectroscopic data are in good agreement with those previously reported.[59][60] $[\alpha]_D^{20}$ = −51 (c = 0.60, $CHCl_3$) [lit.[60] for **22**: −44 (c = 1.04, $CHCl_3$), *ee* = 89%]. GLC (Bondex-un-α/β, 100 °C, 1′ iso, then 2.5 °C·min^{-1}): t_R = 23.11 min (no complete baseline separation). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.69 (d, J = 7.0 Hz, 3 H, C*H*$_3$), 2.04 (m_c, 1 H, 2-H), 3.10, 3.19 (2 br. s, 2 H, O*H*), 3.69 (dd, J = 10.8, J = 7.5 Hz, 1 H, 3-H_a), 3.75 (d, J = 10.8 Hz, 1 H, 3-H_b), 4.52 (d, J = 8.4 Hz, 1 H, 1-H), 7.26−7.37 (m, 5 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (*C*H_3), 41.7 (C-2), 67.9 (C-3), 80.8 (C-1), 126.7, 127.8, 128.4 (arom. *C*H), 143.4 (arom. C_{ipso}). According to the same procedure, diol ***ent*-22** (10 mg, 60 μmol, 53%, > 98% *ee*) was obtained from homoallyl alcohol ***ent*-21** (28 mg, 0.11 mmol). $[\alpha]_D^{20}$ = +50 (c = 0.50, $CHCl_3$, > 98% *ee*). GLC (Bondex-un-α/β, 100 °C, 1′ iso, then 2.5 °C·min^{-1}): t_R = 22.89 min (no baseline separation).

(4*R*,5*R*)-5-Methyl-2,4-diphenyl-1,3,2-dioxaborinane (23): Diol ***ent*-22** (8 mg, 48 μmol) and phenylboronic acid (7 mg, 53 μmol) were dissolved in CH_2Cl_2 (480 μL) and two spheres of molecular sieves (4 Å) were added. The mixture was stirred overnight, filtered and the solvent removed under reduced pressure. The NMR data of the crude product (quant. conversion) were obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (d, J = 6.8 Hz, 3 H, C*H*$_3$), 2.08 (ddqd, J = 10.3, J = 9.1, J = 6.8, J = 4.4 Hz, 1 H, 5-H), 3.87 (dd, J = 11.2, J = 10.3 Hz, 1 H, 6-H_a), 4.12 (dd, J = 11.2, J = 4.4 Hz, 1 H, 6-H_b), 4.74 (d, J = 9.1 Hz, 1 H, 4-H), 7.31−7.86 (m, 10 H, arom. C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.3 (*C*H_3), 38.5 (C-5), 67.4 (C-6), 80.0 (C-4), 126.6, 127.6, 127.9, 128.3, 130.7, 133.9, 141.4 (arom *C*H, arom. C_{ipso}) ppm.

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