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Microwave assisted synthesis of enantiomerically pure allylboronates

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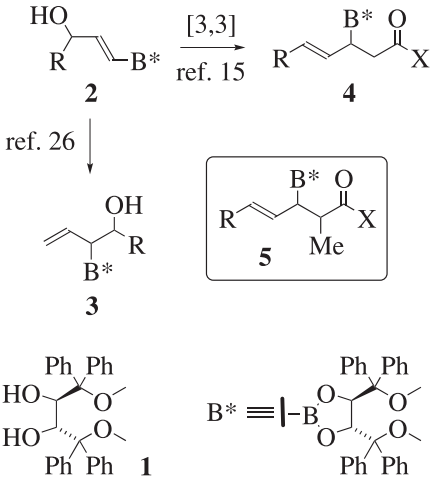
ABSTRACT

Stable allylboronates with a stereogenic centre α to the boronic ester moiety represent versatile reagents for stereoselective synthesis of homoallylic alcohols. Use of microwave irradiation in desilylation and sigmatropic rearrangement reactions allows rapid synthesis of α-chiral allylboronates utilized in the highly diastereo- and enantioselective synthesis of (*Z*)-configured homoallylic α-hydroxy esters by allyl additions to ethyl glyoxylate.

1. Introduction

During the last two decades, the application of microwave irradiation has become increasingly popular and widespread in all sectors of organic chemistry due to the benefits in comparison with conventional heating methods. Diversity- as well as target-directed synthetic organic chemistry profits from increased reaction rates, higher yields, less formation of by-products and simplified procedures for a multitude of reactions.[1–3] Among these, microwave assisted synthesis has found numerous application in sigmatropic rearrangements, due to the significance of thermal conditions for the outcome of the reaction.[4,5] Nonetheless, to the best of our knowledge no microwave assisted procedures of sigmatropic rearrangements furnishing α-chiral allylboronates have yet been presented. The conditions reported herein provide a fast and convenient way for the synthesis of the title compounds via *Johnson* rearrangement of boronate-substituted allylic alcohols.

The key to the successful synthesis of bench-stable and enantiomerically pure α-chiral allylboronates was the development of a new chiral auxiliary and protective group for boronic acids **1** (Scheme 1).[6] The necessity of orthogonal protection of the boronic acid moiety and stable boronic acid equivalents has first been served by *Genêt*'s trifluoroborates,[7,8] which have been studied intensively and have found numerous applications in synthetic chemistry. However, the purification of the trifluoroborates via chromatography still remains an issue and can confine utilization of the trifluoroborates.



Scheme 1. Diol **1**: chiral auxiliary and protective group for boronic acids.

Camphor (*Hoffmann*[9]) or tartrate (*Roush*[10]) derived dioxaborolanes were widely used in the synthesis of enantiomerically pure homoallylic alcohols, though difficulties in preparation of enantiomerically pure allylboronates, instability and arduous handling were reported as a major drawback.[11] Recently, we developed a new chiral auxiliary **1** as a protecting group for boronic acids.[6,12,13] This did not

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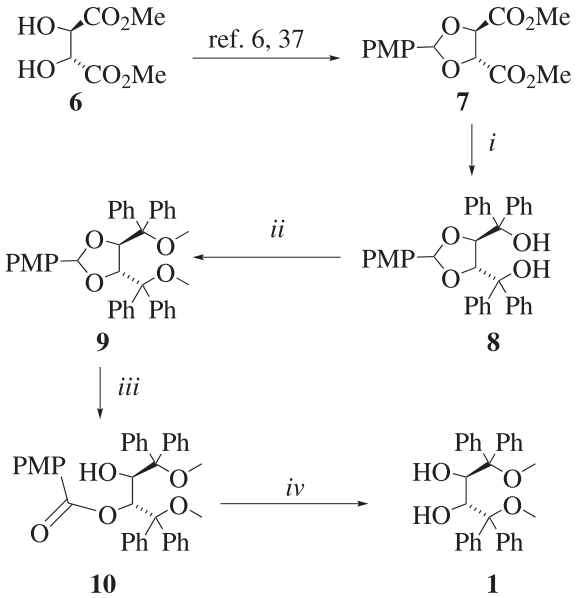
only provide access to enantiomerically pure allylboronates, but also made them easy to store and handle.[14–16] Diol **1** was first synthesized by *Nakayama* and *Rainier*,[12] and the procedure was continuously improved by Pietruszka et al.[6,17] The auxiliary **1** was successfully applied in the asymmetric synthesis of amino acids by Zhang et al.[18] While low selectivity in Diels–Alder reactions resulted in no further investigation,[19] very good selectivity was observed in the addition of enolates to furyl aldehydes bearing an adjacent boronate group.[20] The diol **1** has been applied by the *Pietruszka* group in a manifold of reactions (Scheme 1). Therein, it was not just utilized as a source of chiral information, its application as an extraordinarily stable protective group for boronic acids allowed the performance of unprecedented transformations like cyclopropanations[21–25] or carbonyl allylations[26] of allyl alcohol **2** furnishing homoallyl alcohols **3** (Scheme 1). The auxiliary **1** also enabled [3,3]-sigmatropic rearrangements of boron-containing allyl alcohol **2** leading to enantio- and diastereomerically pure allylboronic esters **4** with a stereogenic centre in the α-position to the boronic ester moiety.[14–16] Furthermore, highly selective allyl additions of allylboronic esters led to enantiomerically pure homoallylic alcohols with a (*Z*)-double bond (Scheme 13).[27] The general need for a protective group, which would allow a multitude of transformations in presence of a boronate moiety, can be measured by the attention paid to MIDA (*N*-methyliminodiacetic acid) protected boronates developed in 1986 by *Wrackmayer*[28] and recently elegantly applied by *Gillis and Burke*.[29,30]

Herein, the potential of the auxiliary **1** and its unprecedented stability was proven one more time utilizing microwave assisted conversions in the presence of the corresponding dioxaborolane. Furthermore, we wished to extend the scope of allylboronates obtained after [3,3]-sigmatropic rearrangements (**4** and **5**) by adding the reagents to ethyl glyoxylate. In doing so, the synthesis of (*Z*)-configured esters of homoallylic α-hydroxy acids would be feasable, a motif present in a number of natural products and applied in the synthesis of related substructures.[31–36]

2. Results and discussion

2.1. Synthesis of chiral auxiliary and protective group 1

The synthesis of protective group **1** for the boronic acids was further optimized commencing from (+)-dimethyl tartrate **6** (Scheme 2).[6,37] After protection of hydroxyl groups as a PMP-acetal (PMP: *p*-methoxyphenyl), acetal **7** was subjected to exhaustive Grignard addition with phenylmagnesium bromide in Me-THF. The newly generated hydroxyl groups of diol **8** were methylated using NaH/MeI giving ether **9**. Afterward, the acetal **9** was cleaved oxidatively utilizing a mixture of $NaBrO_3/Na_2S_2O_4$,[6] followed by the reduction of ester **10** with $LiAlH_4$: free diol **1** was obtained. The intermediates shown were all used without any purification, flash column chromatography on silica gel was performed only after the last step in order to isolate pure product **1** (64% yield over four steps).

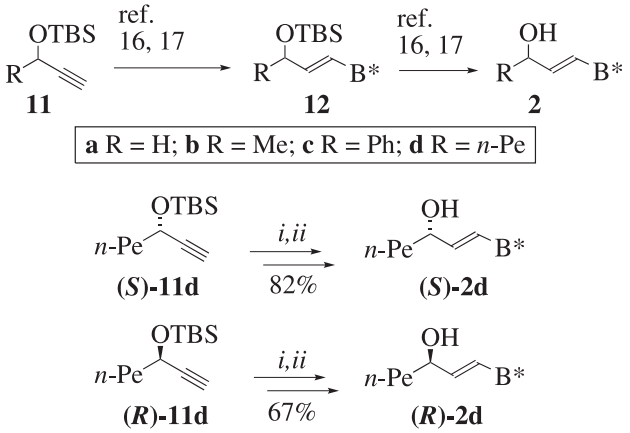


Scheme 2. Conditions: (*i*) 5.6 equiv PhMgBr, Me-THF, 0 °C to rt, 1 h; (*ii*) 3 equiv NaH, 3 equiv MeI, Me-THF, rt, 3 days; (*iii*) 3 equiv $NaBrO_3$, 3 equiv $Na_2S_2O_4$, H_2O/EtOAc, 0 °C to rt, 2 h; (*iv*) $LiAlH_4$, Me-THF, 0 °C to rt, over night (64% over four steps).

As a major difference to previously published results,[6] THF was replaced throughout by 2-methyl tetrahydrofuran (Me-THF) as solvent of choice thus considerably simplifying the work-up procedure. This proved to be especially advantageous for the Grignard reaction when using a commercially available solution of phenylmagnesium bromide in Me-THF. Therewith, the reaction time was shortened and a better separation of layers during work-up was accomplished. None the less, the choice of solvent did not influence the reaction outcome. The diol **8** could be isolated by flash column chromatography in 88% yield for Me-THF and 92% for THF. Diethyl ether seemed to be rather inappropriate due to the low solubility of substrate **7**, and agglutination of the reaction mixture was observed temporarily while adding the Grignard reagent. Nevertheless, suspension of the substrate in a threefold amount of solvent finally led to the isolation of 71% of alcohol **8** after chromatography.

2.2. Synthesis of allyl alcohols 2

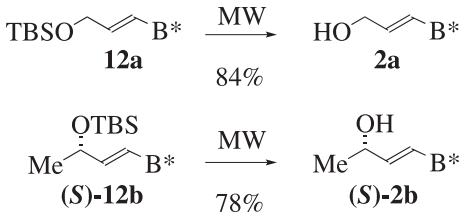
In order to obtain (*E*)-configured allyl alcohols, two well established steps were performed:[15] First, the corresponding TBS-protected propargylic alcohols **10**[16,38–40] were submitted to a one-pot hydroboration,[16,41] oxidation, and transesterification sequence, furnishing silyl-protected allyl alcohols **11**, which were directly used in the next step without any further purification (Scheme 3). Cleavage of the silyl protective group under the acidic conditions yielded free allyl alcohols **2**. Besides known allyl alcohols **2a** (R=H), **2b** (R=Me), and **2c** (R=Ph), the hydroboration was extended to new enantiomerically pure boron-containing allyl alcohols (***S***)-**2d** and (***R***)-**2d** (R=*n*-Pe: 82% and 67% yield, respectively).



Scheme 3. Conditions: (*i*) (a) 1 equiv $BH_3 \cdot SMe_2$, 2 equiv cyclohexene; 1 equiv **11**, DME, rt, 1 h; (b) 2 equiv Me_3NO; (c) 1 equiv **1**, rt; (*ii*) 0.1 M HCl, CH_2Cl_2/MeOH, rt, up to 24 h.

The deprotection of the silyl group of **12** under acidic conditions was successful, but rather slow; for the *n*-pentyl-derivative **12d** the reaction time exceeded 20 h. The addition of more equivalents of 0.1 M HCl did not accelerate the reaction considerably. Therefore, microwave (MW) assisted closed vessel desilylation was attempted and it was found that microwave irradiation accelerated the

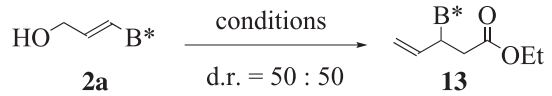
cleavage. For silyl-protected alcohols **12a** and **12b**, full conversion was detected after only 15 min stirring at 60 °C at 200 W releasing the corresponding free alcohol **2a** and (***S***)-**2b** in 84% and 78% yield (Scheme 4), respectively. For the deprotection of ether **12a** on larger scale, a microwave assisted open vessel protocol was employed without decreasing the yield (**2a**: 82%).



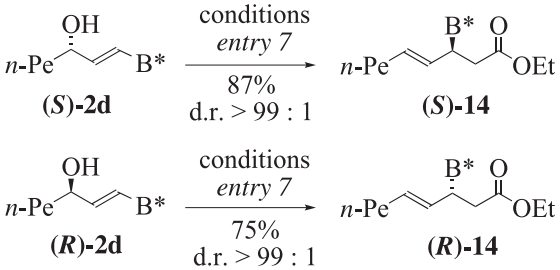
Scheme 4. Conditions (MW): 0.1 M HCl, CH_2Cl_2/MeOH, 60 °C, 200 W, 15 min.

2.3. [3,3]-Sigmatropic rearrangements

With allyl alcohols **2** in hand, [3,3]-sigmatropic rearrangements were performed. Besides conventional conditions already established in the group for the *Johnson* reaction,[14] requiring relatively long reaction times and strict exclusion of moisture, a microwave assisted closed vessel protocol was employed in the synthesis of α-chiral allylboronates (Scheme 5). The procedure was optimized for the transformation of allyl alcohol **2a** (Scheme 5, entry 1: conventional conditions, 72% yield, 4 h): We were pleased to observe that under almost identical conditions (triethylortho acetate, cat. propionic acid, 135 °C) the rearrangement was also possible in the microwave, albeit not in high yield (entry 2+3). Increasing the temperature to 160 °C (entries 4–7) furnished allylboronic esters



entry	conditions	yield [%]
1	Δ, 135 °C, 4 h cat. EtCOOH	72%
2	MW, 200W, 135 °C, 9 min DMF, cat. EtCOOH	24%
3	MW, 200W, 135 °C, 15 min DMF, cat. EtCOOH	42%
4	MW, 200W, 160 °C, 9 min DMF, cat. Montmorillonite KSF	57%
5	MW, 200W, 160 °C, 7.5 min cat. EtCOOH	63%
6	MW, 200W, 160 °C, 9 min EtOAc, cat. EtCOOH	68%
7	MW, 200W, 160 °C, 9 min DMF, cat. EtCOOH	78%

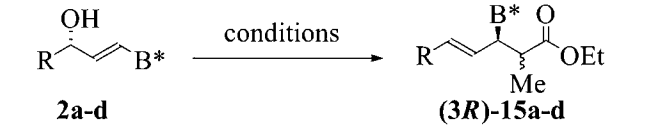


Scheme 5. Microwave assisted *Johnson* rearrangement with triethylortho acetate.

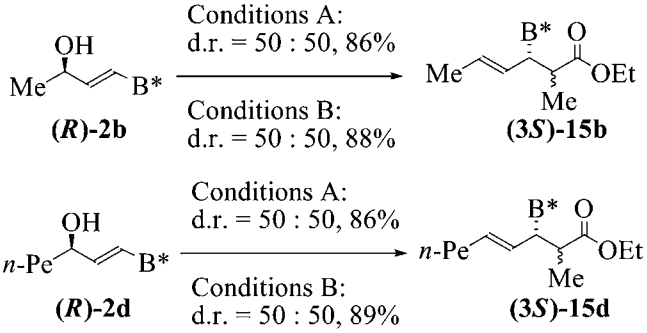
13—under the best conditions found (entry 7)—in good yield (78%) and as a 1:1 mixture of diastereoisomers in 9 min, only. The same conditions were applied for the *Johnson* rearrangement of secondary allyl alcohols (***S***)- and (***R***)-**2d** furnishing only one diastereoisomer (***S***)-**14** (87%) and (***R***)-**14** (75%), respectively. The obtained allylboronic esters were air- and moisture-stable colorless solids that were separated and purified via MPLC.

The rearrangement of the secondary allyl alcohols **2b**–**d** with triethylortho propionate allowed the introduction of an additional methyl group in 2-position of ester **15**. All conducted *Johnson* rearrangements elapsed in a very good yield (79–89%), both under conventional conditions as well as under microwave irradiation (Scheme 6, entries 1–6): The rearrangement of the (*R*)-allyl alcohols **2b** and **2d** furnished the expected 1:1 mixtures of diastereoisomers (**3*S***)-**15b** and (**3*S***)-**15d** independent of the method applied. Improved diastereoselectivity was observed for the corresponding alcohols (***S***)-**2b**, (***S***)-**2d**, and (***R***)-**2c**, respectively, furnishing (**3*R***)-**15b**–**d** allylboronic esters. Unfortunately all attempt to separate the mixtures of diastereoisomers via MPLC failed.

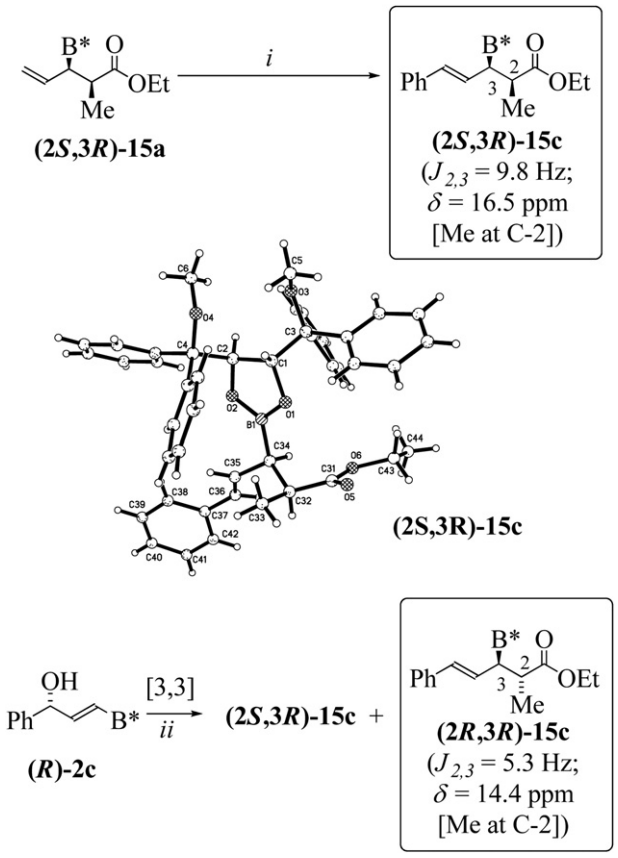
As expected, *Johnson* rearrangement of **2a** with triethylortho propionate (Scheme 6, entry 1) afforded a complex mixture including the desired four isomers. After extensive attempts to purify the crude product, we were fortunate to obtain a small sample of the pure diastereoisomer (**2*S*,3*R***)-**15a** whose configuration was confirmed after cross metathesis with styrene to yield enantiomerically pure allylboronic ester (**2*S*,3*R***)-**15c** (Scheme 7): X-ray analysis of ester (**2*S*,3*R***)-**15c** enabled the unequivocal assignment of the absolute configuration also confirming our assumption of 1,3-chirality transfer when using (***R***)-**2c** as substrate for the rearrangement.[42] On the basis of this result, we succeeded to assign the configuration of all diastereoisomers from the mixtures **15b**–**d** (see Experimental section) by comparison of the NMR data. It was found that the coupling constant $^3J_{2,3}$ in ^{1}H NMR (~10 Hz for *syn*-**15**; $^3J_{2,3}$ ~5 Hz for *anti*-**15**) and the chemical shifts of the 2-CH_3 in the ^{13}C



entry	R	conditions	*syn* : *anti*	yield [%]
1	H (**2a**)	A	[a]	[a]**15a**
2	Me (***S***)-**2b**	A	86 : 14	88 (**3*R***)-**15b**
3	Ph (***R***)-**2c**	A	72 : 28	79 (**3*R***)-**15c**
4	*n*-Pe (***S***)-**2d**	A	77 : 23	87 (**3*R***)-**15d**
5	Me (***S***)-**2b**	B	63 : 37	87 (**3*R***)-**15b**
6	*n*-Pe (***S***)-**2d**	B	60 : 40	89 (**3*R***)-**15d**



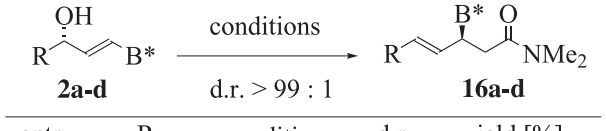
Scheme 6. Conditions: A 7 equiv $EtC(OEt)_3$, cat. $EtCO_2H$, 135 °C, 4 h; B 7 equiv $EtC(OEt)_3$, cat. $EtCO_2H$, DMF, 160 °C, 200 W, 9 min. [a] The yield was not determined since a complex mixture (including four diastereoisomers) was formed.



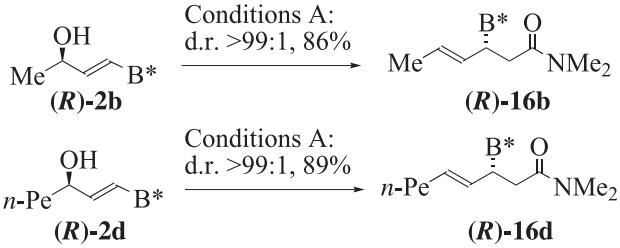
Scheme 7. Conditions: (*i*) 0.1 equiv Grubbs II catalyst, 2.0 equiv styrene, CH_2Cl_2, 40 °C, 21 h, 66%; (*ii*) 7.0 equiv $EtC(OEt)_3$, cat. $EtCO_2H$, 135 °C, 4 h, *syn*:*anti*=72:28, 79%. Crystal structure analysis[42] from allylboronate (**2*S*,3*R*)-15c** obtained by cross metathesis from alcohol (**2*S*,3*R*)-15a**.

NMR [2-CH_3 $\Delta\delta$ ~2 ppm (*syn*-**15**-*anti*-**15**)] are diagnostic for the assignment of the absolute configuration and especially the *syn*/*anti* relationship between 2-H and 3-H of the allylboronic esters **15**.

Next, the *Eschenmoser* rearrangement of allyl alcohols **2a**–**d** was investigated furnishing the corresponding diastereo- and enantiomerically pure allylboronic esters **16a**–**d** (Scheme 8): Under conventional reaction conditions (conditions A: toluene, 80 °C) the diastereomerically pure allylboronic esters **16a**–**d** were formed in good yield and perfect selectivity after 36 h. As previously reported,[15] the rearrangement of the alcohol **2a** (R=H) afforded a 1:1 mixture of diastereoisomers (entry 1; the isomers are separable by MPLC). All attempts at utilizing the microwave reactor (conditions B: 80 °C, 200 W in DMF) were unsuccessful (entry 2), no conversion was detected.

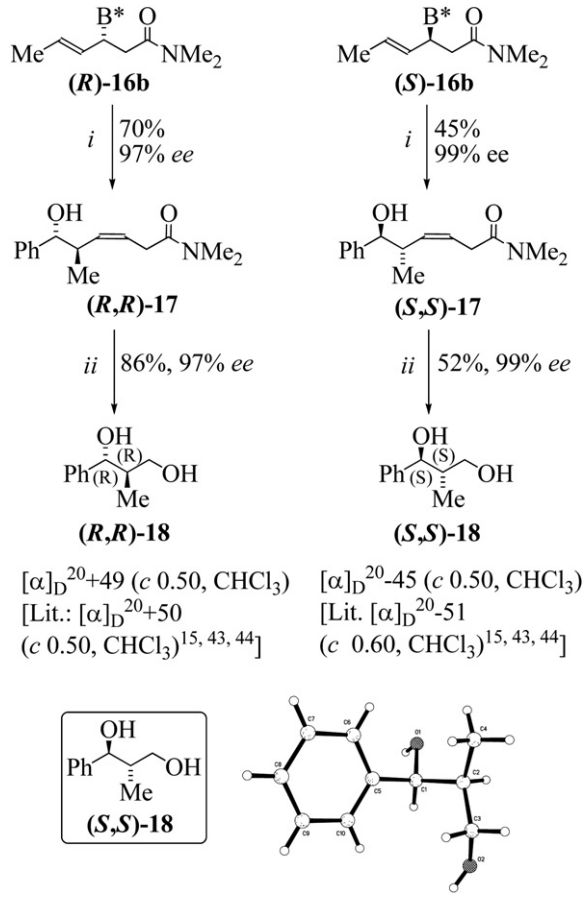


entry	R	conditions	d.r.	yield [%]
1	H (**2a**)	A	50 : 50	60 (**16a**)
2	H (**2a**)	B	-	s.m.
3	Me (***S*)-2b**	A	> 99 : 1	78 (***S*)-16b**
4	Ph (***R*)-2c**	A	> 99 : 1	63 (***S*)-16c**
5	*n*-Pe (***S*)-2d**	A	> 99 : 1	79 (***S*)-16d**



Scheme 8. Conditions: A 2 equiv $MeC(OMe)_2NMe_2$, toluene, 80 °C, 36 h; B: 2 equiv $MeC(OMe)_2NMe_2$, toluene, DMF, 80 °C, 200 W 10 min. s.m.=starting material.

The configuration of allylboronates **16b**–**d** was first assumed on the basis of the already known 1,3-chirality transfer (vide supra). In order to confirm the results, allyl additions to benzaldehyde were performed with new reagents (***R***)- and (***S***)-**16b**. As expected, (*Z*)-homoallyl alcohols **17** were formed in 45–70% yield as essentially single enantiomers (ee >97%; Scheme 9). The absolute configuration was proven by chemical correlation: ozonolysis of homoallyl alcohols (*R*,*R*)-**17** and (*S*,*S*)-**17** furnished (after reductive work-up) the corresponding known diols **18** (X-ray analysis). Based on the reported[13,43,44] optical rotation not only their configuration was determined, but also the corresponding reagents **16b** could be assigned. The rational behind it can be explained in full agreement with the findings of *Hoffmann*,[45,46] by assuming a transition state (Fig. 1) with the side chain X in **19** being in axial position.[14] The results were later further substantiated by successful X-ray structure analyses of reagents (***S***)-**16b** and (***S***)-**16c** (Figs. 2 and 3).



Scheme 9. Conditions: (*i*) 1.2 equiv PhCHO, CH_2Cl_2, 0 °C to rt; (*ii*) a O_3, CH_2Cl_2, −78 °C, 8 min; b Me_2S, rt; c $LiAlH_4$, THF, −78 °C to rt, 1 h.

To conclude, microwave assisted closed vessel conditions allowed temperatures above the boiling points of the reagents thus enabling the accelerated synthesis of the desired allylboronates via the *Johnson* albeit not via the *Eschenmoser* rearrangement. For the first case, comparing conventional conditions and microwave

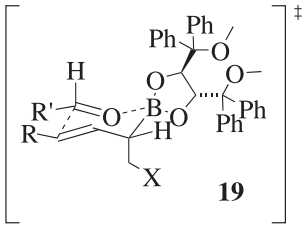


Figure 1. Favored transition state **19** for allyl additions of allylboronic esters **16** to aldehydes.

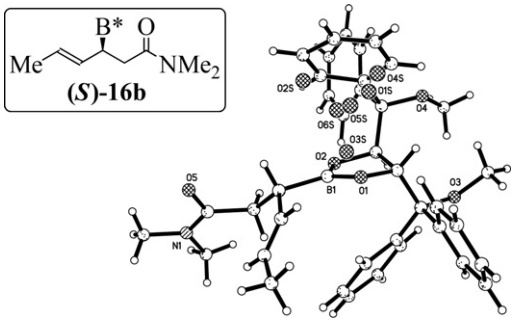


Figure 2. Crystal structure analysis of amide (***S***)-**16b**.[42]

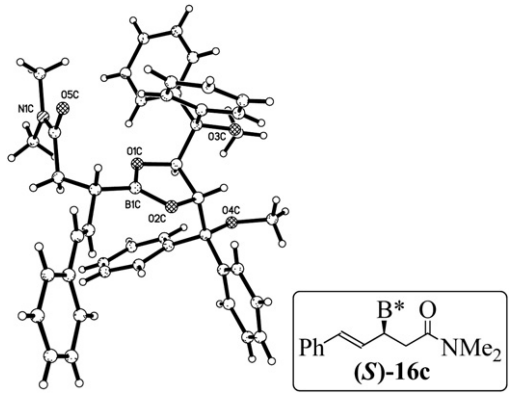


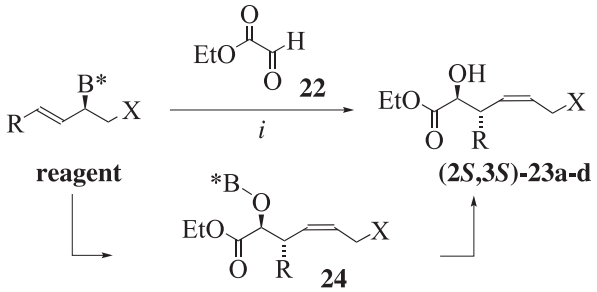
Figure 3. Crystal structure analysis of amide (***S***)-**16c**.[42]

synthesis showed that there are no major differences considering yield or selectivity. The configuration of all new reagents could be assigned either by correlation or from the X-ray structure analysis.

2.4. Allyl additions

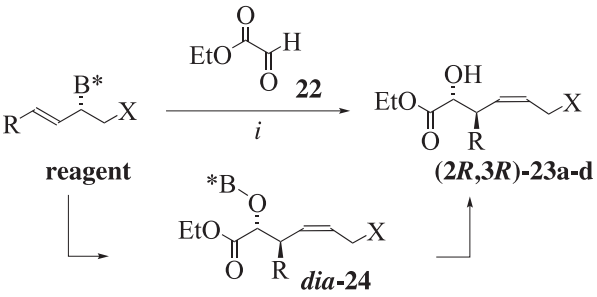
In order to gain access to acyclic (*Z*)-configured homoallylic α-hydroxy esters, we investigated the applicability of the synthesized allylboronates **13**, **16b**, **20**–**21**[14,16,27] in allyl addition using ethyl glyoxylate (**22**) as electrophile (Schemes 10 and 11). To our delight, all additions yielded exclusively the desired (*Z*)-homoallyl alcohols **23** (up to 85% yield). The selectivity given was always determined from the crude NMR spectrum of the intermediate **24** before chromatography was performed. Hydrolysis of the chiral boron auxiliary was accomplished during the chromatographic purification of intermediate **24** on silica gel to yield enantiomerically pure (*Z*)-homoallyl alcohols **23** (HPLC analysis). It should be noted that the auxiliary was recovered by reduction of all diol-containing boron residues with $LiAlH_4$ and was reused.

In the last step, it was again attempted to shorten the reaction time of the allyl addition by means of microwave heating (Scheme 12). As a matter of fact, the addition of allylboronate (***R***)-**13** to aldehyde **22** was significantly faster compared with the conventional transformation (from to 2 days to 3 h); at the same time the yields of homoallyl alcohol (**2*R***)-**23a** were comparable (rt: 83%; MW: 77%). Unfortunately selectivity decreased from 99% ee to 89% ee (Fig. 4): For comparison, the allyl addition was also performed at 65 °C using an oil bath as heating device for 3 h furnishing highly enriched product (**2*R***)-**23a** (99% ee!), albeit still contaminated with some starting material (yield not determined). The stated configuration of the ethyl glyoxylate adducts **23a** was deduced in analogy to our previous findings.



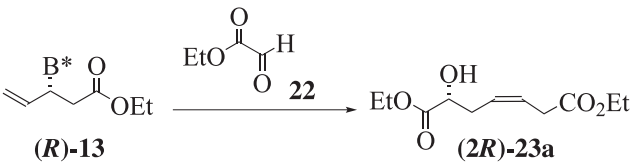
reagent	R	X	*ee* [%]	yield / **23**
(***S***)-**13**	H	CO_2Et	>99	85% (**a**)
(***S***)-**20**	H	CH_2OH	98	84% (**b**)
(***S***)-**21**	H	CH_2OTBS	97	42% (**c**)
(***S***)-**16b**	Me	$CONMe_2$	>99	56% (**d**)

Scheme 10. Conditions: (*i*) 1.2 equiv **22**, CH_2Cl_2, 0 °C to rt.



reagent	R	X	*ee* [%]	yield / **23**
(***R***)-**13**	H	CO_2Et	>99	83% (**a**)
(***R***)-**20**	H	CH_2OH	>99	77% (**b**)
(***R***)-**21**	H	CH_2OTBS	92	59% (**c**)
(***R***)-**16b**	Me	$CONMe_2$	>99	58% (**d**)

Scheme 11. Conditions: (*i*) 1.2 equiv **22**, CH_2Cl_2, 0 °C to rt.



A CH_2Cl_2, rt, 36 h, >99% *ee*, 83%;
B CH_2Cl_2, 150 W, 65 °C, 3 h, >89% *ee*, 77%

Scheme 12. Allyl additions—effect of microwave irradiation.

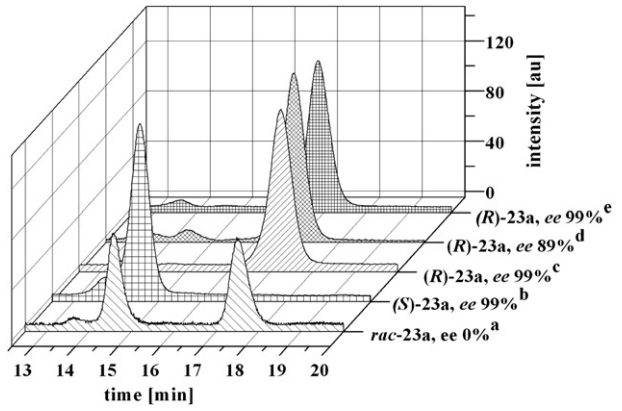


Figure 4. HPLC trace of the allyl addition of allylboronic ester **23** to ethyl glyoxylate **22**, utilizing (a) a 1:1 mixture of (***S***)-**13** and (***R***)-**13**, (b) (***S***)-**13** (0 °C to rt), (c) (***R***)-**13** (0 °C to rt), (d) (***R***)-**13** (MW, 65 °C), (e) (***R***)-**13** (oil bath, 65 °C).

3. Conclusion

In summary, we have successfully applied diol **1** in the synthesis of allylboronates **13**–**16**, proving the surprisingly high stability by utilizing microwave assisted transformations in their presence. Noteworthy are not only the successful desilylations, but especially the [3,3]-sigmatropic rearrangements toward allylboronic esters **13**–**15**. En route the synthesis of auxiliary **1** was improved, the configurations of the reagents were assigned, and the formation of essentially enantiomerically pure (*Z*)-configured homoallylic α-hydroxy esters **23** was achieved.

4. Experimental section

4.1. General methods and materials

All reagents (including Me-THF) were used as purchased from commercial suppliers without any further purification, if not indicated differently. The reactions were carried out using *Schlenk* techniques under an atmosphere of dry argon or nitrogen. Glassware was oven-dried at 120 °C over night prior to use. Solvents were dried and purified by conventional methods prior to use. Toluene, dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), and diethyl ether (Et_2O) were dried in a Solvent Purification System: *MBraun*, MB SPS-800. O_3/O_2 mixtures were generated with Ozon-Generator 500 from Fischer Technology with an oxygen stream of 150 L/h at the maximum power of the instrument. Solvent evaporation under reduced pressure was performed on rotary evaporators at 40 °C (water bath), if not indicated differently. Microwave syntheses were performed using a CEM Discover® LabMateTH/ExplorerPLS® monomode reactor. Reaction time under MW conditions corresponds to the actual reaction time at given temperature without ramp time needed to reach the desired temperature. High pressure liquid chromatography was performed on Gynkotek and Dionex systems using chiral columns Chiralcel OD, Chiralcel OD-H, Chiralpak IC, and Chiralpak IA (Daicel). As eluent, mixtures of *n*-heptane or *n*-hexane and *i*-propanol (*i*-PrOH) were used. Preparative Medium Pressure Liquid Chromatography (MPLC on silica gel 15–25 μm, 60 Å; UV detection at 254 nm) was performed on Labomatic instruments. Mixtures of petroleum ether (PE) and ethyl acetate (EtOAc) were used as eluent. Flash column chromatography was performed using silica gel 0.040–0.063 mm (400–230 mesh) from Macherey/Nagel. Crystal structure analyses were performed at the Institute for Organic Chemistry, Stuttgart using Nicolet P 3 Refractometer with graphite-monochromator, Mo- or Cu- cathode. The program SHELXS-97 was used. Melting points were measured using a Büchi Melting Point B-540 and are not corrected. Optical rotation was measured with a tempered polarimeter Perkin–Elmer (241 MC or precisely 341) at λ=589 nm (sodium-D-line) and 20 °C in a cell of 1 dm length. Infrared spectra were recorded on FTIR from Perkin–Elmer (SpectrumOne). Samples were measured either as a solution in $CHCl_3$ or neat on the ATR-sample head. The positions of the absorption bands are given in cm^{-1}. Mass spectra were measured at the Zentralabteilung für chemische Analysen des Forschungszentrums Jülich or using the following instruments (IBOC): ESI (LC/MS)—Finnigan MAT LC-Q; GC/MS (EI)—Hewlett Packard HP6890, HP5973; ESI (LC/MS-MS)—Applied Biosystems QTrap 4000. Elemental analyses were performed at the Forschungszentrums Jülich or at the Institute of Organic Chemistry, Stuttgart. NMR Spectra were recorded at 300 K using the following instruments: Bruker ARX 300; Bruker Advance/DRX 600. The chemical shifts δ are given in parts per million relative to the internal standard TMS (^{1}H: 0.00 ppm) or relative to the resonance of the solvent (e.g., ^{1}H: $CHCl_3$, 7.26 ppm; ^{13}C: $CHCl_3$, 77.0 ppm). *J* is given in hertz; in spectra of higher order the δs and *J*s were not corrected. The NMR signals were assigned by means of DEPT-, H–H-, and C–H–COSY spectra.

The following compounds were synthesized according to literature procedures.[6,14–16,27] **2a**, (***R***)-**2b**, (***R***)-**2c**, (***S***)-**2b**, (***S***)-**2c**, **7**, **11a**, (***R***)-**11b**, (***R***)-**11c**, (***S***)-**11b**, **12a**, (***R***)-**12b**, (***R***)-**12c**, (***S***)-**12b**, (***R***)-**13**, (***S***)-**13**, (***R***)-**16a**, (***S***)-**16a**, (***R***)-**20**, (***S***)-**20**; (***R***)-**21**, (***S***)-**21**.

4.1.1. General procedure 1: introduction of silyl-protecting groups. In a Schlenk-flask equipped with a magnetic stirrer bar and a septum, the corresponding alcohol (1.00 equiv) was dissolved in abs CH_2Cl_2 (0.75 mL/mmol alcohol) under an inert atmosphere of argon. The solution was cooled to 0 °C before imidazole (1.10 equiv) and subsequently TBSCl (1.00 equiv) was added. A colorless precipitate was formed and the reaction mixture was stirred at room temperature over night. Hydrolysis with water was followed by extraction with *n*-pentane. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvents were evaporated under reduced pressure and the crude product was purified either by flash column chromatography on silica gel or by distillation as indicated.

4.1.2. General procedure 2: hydroboration of alkynes. In a Schlenk-flask equipped with a stirrer bar and a septum were placed abs cyclohexene (2.00 equiv) and abs 1,2-dimethoxyethane (DME) (2 mL/mmol alkyne) under an atmosphere of dry nitrogen. The mixture was treated at 0 °C with 10 M $BH_3{\cdot}SMe_2$ (1.00 equiv); a colorless precipitate formed within 30 min. The reaction mixture was warmed to room temperature before the corresponding alkyne (1.00 equiv) was added. Stirring was continued for 1 h at room temperature; the precipitate dissolved within the hour. The reaction mixture was treated with $Me_3NO{\cdot}2H_2O$ (1.90 equiv), stirred for 1 h, and diol **1** (1.00 equiv) was added. After complete consumption of the starting material was indicated by TLC, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel as indicated.

4.1.3. General procedure 3: deprotection of silyl-protected allyl alcohols with HCl. The corresponding silyl ether was dissolved in a minimum amount of CH_2Cl_2 and ethanol or methanol (7.64 mL/mmol of silyl ether) before it was treated with a solution of concd hydrochloric acid (159 μL/mmol silyl ether, ~2.30 mmol) in ethanol or methanol (1.43 mL/mmol silyl ether). The reaction mixture was stirred at room temperature; the reaction was quenched with $NaHCO_3$ (aq) after complete consumption of starting material (as judged by TLC). The volume of the solvent was reduced under reduced pressure and water was added. The aqueous layer was extracted three times with Et_2O. The combined organic layer was

washed with brine and dried over $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel as indicated.

4.1.4. General procedure 4: deprotection of silyl-protected allyl alcohols in a microwave reactor. In a microwave vessel equipped with a stirrer bar and a septum the corresponding silyl ether (1.00 equiv) was dissolved in a minimum amount of CH_2Cl_2 and methanol (7.64 mL/mmol of silyl ether) before it was treated with a solution of concd hydrochloric acid (159 μL/mmol silyl ether, ~1.92 mmol) in ethanol (1.43 mL/mmol silyl ether). The reaction was carried out according to the closed vessel method at 60 °C, 200 W for 15 min in a CEM Microwave. After cooling to room temperature, the reaction was quenched by addition of saturated $NaHCO_3$ (aq) and the volume of the solvent was reduced under reduced pressure. Water was added and the aqueous layer was extracted three times with Et_2O. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel as indicated.

4.1.5. General procedure 5: microwave assisted Johnson rearrangement. In a microwave vessel equipped with a stirrer bar and a septum the corresponding allyl alcohol (1.00 equiv) was dissolved in triethyl orthoacetate (7.10 equiv) or triethyl orthopropionate (7.10 equiv) containing a catalytic amount of propionic acid (4.34 μL/mmol allyl alcohol) and *N*,*N*-dimethylformamide (DMF) (1.35 mL/mmol allyl alcohol). The reaction was carried out according to the closed vessel method at 160 °C, 200 W for 9 min in a CEM Microwave. After cooling to room temperature, the solvent was removed under reduced pressure (10^{-3} hPa). The diastereomeric ratio of the crude product was determined by ^1H and ^{13}C NMR spectroscopy. The crude sample was purified by flash column chromatography on silica gel as indicated.

4.1.6. General procedure 6: Johnson rearrangement (standard conditions). In a round-bottom flask equipped with a magnetic stirrer bar, Claisen condenser and a drying tube, the corresponding allyl alcohol (1.00 equiv) was dissolved in triethyl orthopropionate or triethyl orthoacetate (7.10 equiv) containing a catalytic amount of propionic acid (4.34 μL/mmol allyl alcohol) under an atmosphere of dry nitrogen. The reaction mixture was then heated (exactly 135 °C) for up to 4 h. During the first 2 h of the reaction, the attached Claisen condenser was heated to accelerate the removal of the formed ethanol (EtOH). The progress of the reaction was monitored by TLC. After complete conversion was determined, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure (10^{-3} hPa). The diastereomeric ratio of the crude product was determined by ^1H and ^{13}C NMR spectroscopy. The crude product was purified by flash column chromatography on silica gel and MPLC as indicated.

4.1.7. General procedure 7: Eschenmoser rearrangement. In a round-bottom flask equipped with a magnetic stirrer bar, Claisen condenser and a drying tube, the corresponding allyl alcohol (1.00 equiv) was dissolved in toluene (2.00 mL/mmol allyl alcohol) under an atmosphere of dry nitrogen. The solution was treated with a 90% solution of *N*,*N*-dimethylacetamide dimethyl acetal (2.00 equiv) and was then heated (exactly 80 °C) for 24–36 h. During the first 2 h of the reaction, the attached Claisen condenser was heated to accelerate the removal of the formed methanol. The progress of the reaction was monitored by TLC. After the complete conversion was determined, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure (10^{-3} hPa). The diastereomeric ratio of the crude product was determined by ^1H and ^{13}C NMR spectroscopy. The crude product was purified by flash column chromatography on silica gel and MPLC as indicated.

4.1.8. General procedure 8: allyl addition. In a Schlenk-flask equipped with a stirrer bar and a septum, the corresponding allylboronic ester (1.00 equiv) was dissolved in CH_2Cl_2 (0.50 mL/mmol ester) under an atmosphere of dry argon. The solution was treated with the appropriate aldehyde (1.10–1.50 equiv) at 0 °C and was warmed over night to room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was determined, the solvent was removed under reduced pressure. The diastereomeric ratio of the crude product was determined by ^1H and ^{13}C NMR spectroscopy. The crude product was purified by flash column chromatography on silica gel as indicated.

4.2. Synthesis of chiral auxiliary and protective group (1)

*4.2.1. (4R,5R)-(2-(4-Methoxyphenyl)-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) (**8**).* A 500 mL Schlenk flask was charged with dicarboxylate **7**[6] (10.0 g, 33.8 mmol) and Me-THF (60 mL) and cooled to 0 °C. A solution of phenylmagnesium bromide in Me-THF (45%, 68 mL, 197 mmol) was added via a double-tipped cannula to the stirred solution. After removal of the ice-bath stirring was continued for 1 h at room temperature; TLC indicated complete conversion of diester **7**. The mixture was diluted with Me-THF (40 mL) and quenched by adding 75% satd aqueous NH_4Cl (260 mL). The two layers were separated and the aqueous layer was extracted with Me-THF (5×40 mL). The combined organic layer was washed with brine (140 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to yield 20.2 g of crude bis(diphenylmethanol) **8** as a yellow foam, which was used in the next step without further purification.

Solvent screening for 2-Me-THF, THF, and diethyl ether:

A 100 mL Schlenk flask was charged with dicarboxylate **7**[6] (1.5 g, 5.06 mmol) and the appropriate solvent (Me-THF and THF: 8.5 mL; Et_2O: 25.5 mL). The stirred solution/suspension was cooled to 0 °C and a solution of phenylmagnesium bromide (Me-THF 45%; Et_2O 45%; THF 17%) (28.35 mmol) was added. The cooling bath was removed and after 45 min (Me-THF/THF) or 2 h (Et_2O), the reaction was quenched by addition of 75% satd aqueous NH_4Cl (8 mL/mmol PhMgBr). The aqueous layer was extracted with the solvent used (5×10 mL), the combined organic layer was washed with brine (25 mL) and dried over $MgSO_4$. Flash column chromatography (90% PE/EtOAc to 80% PE/EtOAc) yielded 2.42 g (Me-THF: 4.44 mmol, 88%), 2.54 g (THF: 4.66 mmol, 92%), and 1.97 g (Et_2O: 3.62 mmol, 71%) of compound **8** as a colorless foam. All spectroscopic data are in full agreement with literature data.[12]

*4.2.2. (4R,5R)-4,5-Bis(methoxydiphenylmethyl)-2-(4′-methoxyphenyl)-1,3-dioxolane (**9**).* A flame dried 500 mL Schlenk-flask equipped with a magnetic stirrer bar and a rubber septum was charged with crude bis(diphenylmethanol) **8** (20.2 g) obtained in the previous step and Me-THF (75 mL). After the addition of NaH (95%; 2.53 g, 100.1 mmol) at 0 °C, the solution was stirred at room temperature for 30 min, then MeI (6.2 mL, 100 mmol) was added and stirred at room temperature over night. NaH (2.53 g, 100.1 mmol) and MeI were added, and after stirring for 2 days at room temperature the same amount of NaH and MeI was added once more. After stiring over night, the reaction mixture was diluted with 85 mL of Me-THF and quenched carefully by initially adding H_2O (85 mL) dropwise. The aqueous layer was extracted with Me-THF (3×85 mL), and the combined organic layer was washed with H_2O (5×65 mL), brine (70 mL), and dried over $MgSO_4$. Evaporation of the solvent yielded the crude product **9** (19.0 g) as

a yellow foam. The product was used in the next step without further purification.

*4.2.3. (2R,3R)-3-Hydroxy-1,4-dimethoxy-1,1,4,4-tetraphenylbutan-2-yl 4-methoxybenzoate (**10**).* A 250 mL round-bottom flask equipped with a magnetic stirrer bar and a pressure-equalizing addition funnel was charged with crude dimethyl ether **9** (19.0 g) and EtOAc (65 mL). A solution of $NaBrO_3$ (15.1 g, 100 mmol in 50 mL H_2O) was added within 15 min. The two-phase mixture was cooled to 0 °C and a solution of $Na_2S_2O_4$ (17.4 g, 100 mmol in 50 mL H_2O) was added dropwise while stirring continuously. Upon complete addition of the dithionite solution the deep red color vanished, and more of the $NaBrO_3$ solution (5.00 g, 33.1 mmol in 20 mL H_2O) was added. The red color persisted and after 2 h of vigorous stirring at room temperature TLC indicated complete conversion of the starting material. The mixture was diluted with EtOAc (65 mL) and the aqueous layer was extracted with EtOAc (3×85 mL). The combined organic layer was washed with aqueous 2 M $Na_2S_2O_3$ solution (12×60 mL) and brine (2×60 mL), dried over $MgSO_4$, and concentrated to yield the crude product **10** as a yellow foam. It was dissolved in CH_2Cl_2 (130 mL) and refluxed with charcoal (1.3 g) for 1 h. The mixture was cooled to room temperature and filtered through a pad of Celite®. The solvent was removed under reduced pressure. The resulting pale yellow foam was used in the next step without further purification.

*4.2.4. (2R,3R)-1,4-Dimethoxy-1,1,4,4-tetraphenylbutane-2,3-diol (**1**).* A 250 mL Schlenk-flask equipped with a magnetic stirrer bar and a rubber septum was charged with 4-methoxybenzoate **10** and Me-THF (140 mL). The mixture was cooled to 0 °C, $LiAlH_4$ (3.8 g, 100.1 mmol) was added and stirred over night. The mixture was diluted with Me-THF (35 mL), the reductant was hydrolyzed by addition of H_2O (3.7 mL), aqueous 15% NaOH (3.7 mL), and H_2O (3.7 mL). The formed precipitate was removed by filtration through a pad of Celite®, and the filter cake was thoroughly washed with Me-THF. The filtrate was dried over $MgSO_4$ and concentrated under reduced pressure to yield the crude compound **1** as a yellowish resin. Flash column chromatography (93% PE/EtOAc) of the crude product led to the isolation of 9.8 g (21.56 mmol, 64%) of diol **1** as a colorless foam. $[\alpha]_D^{20}$ +60.0 (*c* 1.0, $CHCl_3$) All spectroscopic data are in full agreement with those previously published.[6]

4.3. Synthesis of allyl alcohols (2)

*4.3.1. (S)- and (R)-tert-Butyldimethyl(oct-1-yn-3-yloxy)silane [(**S**)-**11d**] and [(**R**)-**11d**].* According to general procedure 1 (*S*)-1-octyn-3-ol (800 mg, 6.34 mmol, 1.00 equiv) in abs CH_2Cl_2 (13.0 mL) was treated with imidazole (453 mg, 6.65 mmol, 1.10 equiv) and TBSCl (1.11 g, 6.97 mmol, 1.00 equiv) at 0 °C. The reaction mixture was stirred at room temperature for 6 h. The crude product was purified by flash column chromatography on silica gel (98% *n*-pentane/Et_2O) to yield ether (***S***)-**11d** as a light yellow liquid (1.41 g, 6.21 mmol, 98%). *Enantiomer* (general procedure 1): (*R*)-(+)-1-octyn-3-ol (952 mg, 7.54 mmol, 1.0 equiv) in abs CH_2Cl_2 (15.0 mL) was treated with imidazole (565 mg, 8.29 mmol, 1.1 equiv) and TBSCl (1.14 g, 7.54 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 5 h. The crude product was purified by flash column chromatography on silica gel (98% *n*-pentane/Et_2O) to yield (***R***)-**11d** as a yellow liquid (1.54 g, 6.41 mmol, 85%). The analytical data are in full agreement to those reported in the literature.[38–40] [Found: C, 69.82; H, 11.81. $C_{14}H_{28}OSi$ requires C, 69.93; H, 11.74%]; R_f (90% PE/EtOAc) 0.84; $[\alpha]_D^{20}$ −41 [*c* 1.20, $CHCl_3$, (***S***)-**11d**]; $[\alpha]_D^{20}$ +41 [*c* 1.06, $CHCl_3$, (***R***)-**11d**]; ν_{max} (liquid film): 3313, 2960, 2860, 1472, 1253, 1120, 1092, 839, 778 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) 0.11 (3H, s, CH_3Si), 0.13 (3H, s, CH_3Si), 0.91 (9H, s, (CH_3)$_3$CSi), 1.20 (3H, t, ^3J 6.8 Hz, CH_3), 1.26–1.45 (6H, m, $CH_3CH_2CH_2CH_2CH_2$), 1.66 (2H, m, $CH_3CH_2CH_2CH_2CH_2$), 2.37 (1H, d, ^4J 2.1 Hz, C≡C*H*), 4.33 (1H, td, ^3J 6.5 Hz, ^4J 2.1 Hz, C*H*OTBS); ^{13}C NMR ($CDCl_3$, 151 MHz) −5.0 (CH_3Si), −4.6 (*C*H_3Si), 14.0, 18.2 ((CH_3)$_3$CSi), 22.5 (CH_3), 24.7, 25.7, 31.4, 38.5 ($CH_3CH_2CH_2CH_2CH_2$), 62.7 (CHOTBS), 71.8, 85.7 (CHC≡*C*H); GC/MS (EI, 70 eV, H_2): t_{ret} 7.7 min, *m*/*z* 183 (10) [($C_{10}H_{19}OSi$)$^+$], 169 (12) [($C_9H_{17}OSi$)$^+$], 113 (100), 107 (5), 83 (45), 75 (100), 55 (10).

*4.3.2. (E,4′R,5′R)-3-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]prop-2-en-1-ol (**2a**).* According to general procedure 4 silyl ether **12a**[14,17] (250 mg, 0.39 mmol) was dissolved in a minimum amount of CH_2Cl_2 and solution of concd hydrochloric acid (97 μL, approx. 1.18 mmol) in methanol (0.56 mL) was added. The mixture was irradiated and worked up as described. Flash column chromatography (90% PE/EtOAc to 70% PE/EtOAc) yielded 172.4 mg (0.33 mmol, 84%) of compound **2a** as a colorless foam.

Open vessel protocol: A 100 mL round-bottom flask was charged with a stirrer bar and silyl ether **12a**[14,17] (11.70 g, 18.37 mmol) was dissolved in a minimum amount of CH_2Cl_2. A solution of concd hydrochloric acid (4.56 mL, 55.1 mmol) in methanol (26.3 mL) was added. The flask was placed in a microwave reactor and equipped with a reflux condenser. The reaction mixture was irradiated for 6 min with a fixed power of 200 W, reaching a measured temperature of 68 °C. The mixture was cooled down and saturated aqueous $NaHCO_3$ was added until neutral. The layers were separated and the aqueous phase was extracted with diethyl ether (4×150 mL). The combined organic layer was dried over $MgSO_4$ and evaporated to give the crude product. Flash column flash chromatography (90% PE/EtOAc to 70% PE/EtOAc) yielded 7.85 g (15.08 mmol, 82%) of title compound **2a** as a colorless foam. $[\alpha]_D^{20}$ −81 (*c* 1.0, $CHCl_3$). All spectroscopic data are in full agreement with those previously published.[14]

*4.3.3. (3S,E,4′R,5′R)-4-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]but-3-en-2-ol [(**S**)-**2b**].* According to general procedure 3 silyl ether (***S***)-**12b**[16] (6.29 g, 9.70 mmol, 1.00 equiv) was dissolved in a minimum amount of CH_2Cl_2 and methanol (74.0 mL) was added; the mixture was treated with a solution of concd hydrochloric acid (1.84 mL, 22.3 mmol, 2.30 equiv) in methanol (14.0 mL) for 4 h. The crude product was purified by flash column chromatography on silica gel (85% PE/EtOAc) affording alcohol (***S***)-**2b** as a colorless foam (2.14 g, 3.98 mmol, 41%).

According to general procedure 4 silyl ether (***S***)-**12b**[16] (68.9 mg, 0.11 mmol, 1.0 equiv) was dissolved in a minimum amount of CH_2Cl_2 and methanol (0.80 mL), and treated with a solution of concd hydrochloric acid (16.9 μL) in methanol (0.15 mL). The crude product was purified by flash column chromatography on silica gel (85% PE/EtOAc) affording alcohol (***S***)-**2b** as a colorless foam (44.2 mg, 0.08 mmol, 78%). The analytical data are in full agreement with those reported in the literature.[47,16] [Found: C, 76.30; H, 6.65. $C_{34}H_{35}BO_5$ requires C, 76.41; H, 6.60%]; R_f (85% PE/EtOAc) 0.11; $[\alpha]_D^{20}$ −74 (*c* 1.02, $CHCl_3$); mp=80–95 °C; *m*/*z* (ESI, positive ion, N_2) 557 (18) [(M+Na)$^+$], 197 (100) [(CPh_2OMe)$^+$], 167 (10) [($C_{13}H_{11}$)$^+$], 105 (18) [(PhCO)$^+$].

*4.3.4. (3S,E,4′R,5′R)-1-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]oct-1-en-3-ol [(**S**)-**2d**].* According to general procedure 2 a mixture of abs cyclohexene (1.52 mL, 1.23 g, 14.9 mmol, 2.0 equiv) and abs DME (15.0 mL) was treated with 10 M $BH_3 \cdot SMe_2$ (0.79 mL, 569 mg, 7.48 mmol, 1.0 equiv). Alkyne (***S***)-**11d** (1.80 g, 7.48 mmol, 1.0 equiv) was added at room temperature. After 1 h the reaction mixture was treated with trimethylamine *N*-oxide dihydrate $Me_3NO \cdot 2H_2O$ (1.66 g, 14.9 mmol, 2.0 equiv) and was stirred for 1 h. Diol **1** (3.40 g, 7.48 mmol, 1.0 equiv) was added and stirring was continued for 2 days. After solvent evaporation, a yellow foam of boronic ester (***S***)-**12d** was obtained, which was used in the

following step without any further purification. R_f (85% PE/EtOAc) 0.69.

According to general procedure 3 silyl ether (***S***)-**12d** (4.24 g, 6.01 mmol, 1.00 equiv) was dissolved in a minimum amount of CH_2Cl_2 and ethanol (40.0 mL), followed by treatment with a solution of concd hydrochloric acid (1.16 mL, 13.9 mmol, 2.91 equiv) in ethanol (7.37 mL). The reaction mixture was stirred for 24 h. Flash column chromatography on silica gel (85% PE/EtOAc) afforded the pure product (***S***)-**2d** as a colorless solid (2.91 g, 4.93 mmol, 82% over two steps). [Found: C, 76.90; H, 7.39. $C_{38}H_{43}BO_5$ requires C, 77.28; H, 7.34%]; R_f (85% PE/EtOAc) 0.17; $[\alpha]_D^{20}$ −53 (*c* 1.06, $CHCl_3$); mp 68–71 °C; ν_{max} (liquid film): 3551 (br, O–H- ν), 3083, 3058, 3012 (arom C–H-ν), 2970, 2932, 2855, 2830 (aliph. C–H-ν), 1642 (olef. C=C-ν), 1598, 1494 (arom. C=C-ν), 1446, 1398, 1369, 1347, 1284, 1234, 1196, 1177, 1075 (C–O–C), 1032, 1015, 993, 966, 917, 895, 846, 794, 757 (Ph, C–H-$\delta_{out\ of\ plane}$), 732, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 0.86 (3H, t, ^3J 7.1 Hz, CH_3), 1.21–1.41 (8H, m, $CH_3CH_2CH_2CH_2CH_2$), 1.29 (1H br, OH), 2.98 (6H, s, OCH_3); 3.99 (1H, m, *CH*OH), 5.22 (1H, dd, ^3J 18.1 Hz, ^4J 1.3 Hz, CH=C*H*-B*), 5.35 (2H, s, C*H*CPh$_2$OMe), 6.16 (1H, dd, ^3J 18.1, 5.3 Hz, C*H*=CH-B*), 7.24–7.35 (20H, m, arom. CH); ^{13}C NMR ($CDCl_3$, 151 MHz) 14.0 (CH_3), 22.6, 24.7, 31.7, 36.5 ($CH_3CH_2CH_2CH_2CH_2$), 51.8 (OCH_3), 77.6 (*C*HCPh$_2$OMe), 83.3 (*C*Ph$_2$OCH$_3$), 116.8 (CH=*C*H-B*), 127.2, 127.3, 127.5, 127.8, 128.4, 129.6 (arom. CH), 141.0, 141.3 (arom. C_{ipso}), 154.8 (*C*H=CH-B*); *m*/*z* (ESI, positive ion, N_2) 608 (100) [$(M+H_2O)^+$], 564 (48), 167 (17) [$(C_{13}H_{11})^+$].

*4.3.5. (3R,E,4′R,5′R)-1-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]oct-1-en-3-ol ((**R**)-**2d**).* According to general procedure 2 a mixture of abs cyclohexene (1.30 mL, 1.04 g, 12.7 mmol, 2.05 equiv) and abs DME (6.40 mL) was treated with 10 M $BH_3{\cdot}SMe_2$ (0.68 mL, 535 mg, 6.34 mmol, 1.02 equiv). Alkyne (***R***)-**11d** (1.49 g, 6.18 mmol, 1.00 equiv) was added at room temperature, followed by treatment with trimethylamine *N*-oxide dihydrate $Me_3NO{\cdot}2H_2O$ (953 mg, 12.7 mmol, 2.05 equiv) after 1 h. After stirring for 1 h, diol **1** (2.88 g, 6.34 mmol, 1.02 equiv) was added. The yellow oily crude product (***R***)-**12d** obtained after 25 h was used in the next step without further purification. R_f (85% PE/EtOAc) 0.70; ^1H NMR ($CDCl_3$, 300 MHz) −0.09 [9H, s, $(CH_3)_3CSi$], −0.06 (3H, s, C*H*$_3$Si), −0.04 (3H, s, C*H*$_3$Si), 0.85 (3H, t, ^3J 6.8 Hz, CH_3), 1.16–1.49 (8H, m, $CH_3CH_2CH_2CH_2CH_2$), 2.96 (6H, s, OCH_3), 3.91 (1H, m, *CH*OTBS), 5.10 (1H, dd, ^3J 17.9 Hz, ^4J 1.3 Hz, CH=C*H*-B*), 5.22 (2H, s, C*H*CPh$_2$OMe), 6.08 (1H, dd, ^3J 17.9, 5.5 Hz, C*H*=CH-B*), 7.20–7.34 (20H, m, arom. CH).

According to general procedure 3 silyl ether (***R***)-**12d** (3.20 g, 4.54 mmol, 1.0 equiv) was dissolved in a minimum amount of CH_2Cl_2 and ethanol (43.0 mL), and treated with a solution of concd hydrochloric acid (877 μL) in ethanol (8.00 mL). The reaction mixture was stirred for 21 h. Flash column chromatography on silica gel (85% PE/EtOAc) afforded the pure product (***R***)-**2d** as a colorless foam (1.80 g, 3.04 mmol, 67%; 50% over two steps). [Found: C, 77.22; H, 7.35. $C_{38}H_{43}BO_5$ requires C, 77.28; H, 7.34%]; R_f (85% PE/EtOAc) 0.23; $[\alpha]_D^{20}$ −60 (*c* 0.11, $CHCl_3$); mp 66–73 °C; ν_{max} (liquid film): 3402 (br, O–H- ν), 3083, 3063, 3022 (arom C–H-ν), 2968, 2926, 2825 (aliph. C–H-ν), 1643 (olef. C=C-ν), 1494 (arom. C=C-ν), 1446, 1400, 1367, 1350, 1317, 1282, 1237, 1181, 1074 (C–O–C), 1032, 1011, 995, 967, 938, 917, 895, 844, 757 (Ph, C–H-$\delta_{out\ of\ plane}$),733, 698, 668 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 0.87 (3H, t, ^3J 7.1 Hz, CH_3),1.21–1.29 (6H, m, $CH_3CH_2CH_2CH_2CH_2$), 1.32 (1H, br, OH), 1.38 (2H, m, $CH_3CH_2CH_2CH_2CH_2$), 2.99 (6H, s, OCH_3), 3.98 (1H, m, *CH*OH), 5.19 (1H, dd, ^3J 18.1 Hz, ^4J 1.5 Hz, CH=C*H*-B*), 5.35 (2H, s, C*H*CPh$_2$OMe), 6.17 (1H, dd, ^3J 18.1, 5.7 Hz, C*H*=CH-B*), 7.24–7.36 (20H, m, arom. CH); ^{13}C NMR ($CDCl_3$, 151 MHz) 14.0 (CH_3), 22.6, 24.7, 31.7, 36.4 ($CH_3CH_2CH_2CH_2CH_2$), 51.8 (OCH_3), 73.6 (*C*HCPh$_2$OMe), 83.3 (*C*Ph$_2$OCH$_3$), 116.5 (CH=*C*H-B*), 127.2, 127.3, 127.5, 127.8, 128.4, 129.6 (arom. *C*H), 141.0, 141.3 (arom. C_{ipso}), 154.8 (*C*H=CH-B*); *m*/*z* (ESI, positive ion, N_2) 608 (100) [$(M+H_2O)^+$], 558 (20) [$(M-CH_3O)^+$], 529 (20) [$(M-2CH_3O)^+$], 197 (12) [$(CPh_2OMe)^+$], 67 (12) [$(C_{13}H_{11})^+$].

4.4. [3,3]-Sigmatropic rearrangements

*4.4.1. (3S)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]pent-4-enoate [(**S**)-**13**] and (3R)-ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]pent-4-enoate [(**R**)-**13**].* According to general procedure 5 a 10 mL microwave vessel equipped with a stirrer bar was charged with allyl alcohol **2a** (250 mg, 0.48 mmol), triethylortho acetate (625 μL, 553 mg, 3.41 mmol), propionic acid (2.1 μL, 2.1 mg, 28.5 μmol), and DMF (649 μL). The vessel was exposed to microwave irradiation for 9 min, reaching a temperature of 160 °C. After removal of volatile compounds in vacuo and subsequent flash column chromatography (90% PE/EtOAc to 75% PE/EtOAc) 222.6 mg (0.38 mmol, 78%) of (***S***)-**13** and (***R***)-**13** were isolated as a 1:1 mixture of diastereomers. The diastereomers (***S***)-**13** and (***R***)-**13** were separated by means of MPLC (98% PE/EtOAc). (***S***)-**13**: $[\alpha]_D^{20}$ −108.6 (*c* 1.0, $CHCl_3$); (***R***)-**13**: $[\alpha]_D^{20}$ −97.1 (*c* 1.0, $CHCl_3$). All spectroscopic data are in full agreement with those previously reported.[14,16,27]

*4.4.2. (3S,4E,4′R,5′R)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]dec-4-enoate [(**S**)-**14**].* According to general procedure 5 alcohol (***S***)-**2d** (500 mg, 0.85 mmol, 1.0 equiv), triethyl orthoacetate (1.80 mL, 5.92 mmol, 7.0 equiv), a catalytic amount of propionic acid (3.67 μL), and DMF (1.14 mL) were heated in a microwave. ^1H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be >99:1. The crude sample was purified by flash column chromatography (95% PE/EtOAc) to yield boronic ester (***S***)-**14** as a colorless foam (486 mg, 0.735 mmol, 87%). [Found: C, 76.40; H, 7.51. $C_{42}H_{49}BO_6$ requires C, 76.36; H, 7.48%]; R_f (85% PE/EtOAc) 0.49; $[\alpha]_D^{20}$ −72 (*c* 2.18, $CHCl_3$); ν_{max} (liquid film): 3088, 3058, 3027 (arom. C–H-ν), 2951, 2929, 2860, 2830 (aliph. C–H-ν), 1735 (C=O-ν), 1494, 1461, 1446 (arom. C=C-ν), 1369, 1330, 1274, 1229, 1198, 1138, 1076 (C–O–C), 1033, 1016, 967; 917, 895, 844, 758, 733, 703 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 0.79 (3H, t, ^3J 7.2 Hz, CH_3), 1.13 (3H, t, ^3J 7.2 Hz, $CO_2CH_2CH_3$), 1.08–1.26 (6H, m, $CH_3CH_2CH_2CH_2CH_2$), 1.84 (3H, m, *CH*-B*, *n*-Bu*CH*$_2$CH), 1.94 (1H, dd, ^2J 15.5 Hz, ^3J 10.6 Hz, *CH*$_{2a}$COEt), 2.06 (1H, dd, ^2J 15.5 Hz, ^3J 4.5 Hz, *CH*$_{2b}$COEt), 2.99 (6H, s, OCH_3), 3.93 (2H, q, ^3J 7.2 Hz, $CO_2CH_2CH_3$), 5.09 (2H, m, 2H, C*H*=C*H*), 5.28 (2H, s, C*H*CPh$_2$OMe), 7.23–7.31 (20H, m, arom. C*H*); ^{13}C NMR ($CDCl_3$, 151 MHz) 13.9 (CH_3), 14.2 ($CO_2CH_2CH_3$), 22.4, 29.1, 31.1 ($CH_3CH_2CH_2CH_2CH_2$), 23.8 (*C*H-B*), 32.5 ($CH_3CH_2CH_2CH_2CH_2$), 34.3 (*C*H$_2$COEt), 51.7 (OCH_3), 59.9 ($CO_2CH_2CH_3$), 77.9 (*C*HCPh$_2$OMe), 83.3 (*C*Ph$_2$OCH$_3$), 128.4 (*C*H=*C*H), 127.3, 127.3, 127.5, 127.8, 129.4, 129.7 (arom. *C*H); 141.1, 141.2 (arom. C_{ipso}), 173.2 (*C*O$_2$OEt); *m*/*z* (ESI, positive ion, N_2) 678 (100) [$(M+H_2O)^+$], 683 (40) [$(M+Na)^+$], 403 (19), 197 (5) [$(CPh_2OMe)^+$].

*4.4.3. (3R,4E,4′R,5′R)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]dec-4-enoate [(**R**)-**14**].* According to the general procedure 5 alcohol (***R***)-**2d** (500 mg, 0.85 mmol, 1.00 equiv), triethyl orthoacetate (1.8 mL, 5.92 mmol, 7.00 equiv), a catalytic amount of propionic acid (3.67 μL), and DMF (1.14 mL) were heated in a microwave. ^1H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be >99: 1. The crude sample was purified by flash column chromatography (95% PE/EtOAc) to yield boronate (***R***)-**14** as a colorless foam (419 mg, 0.63 mmol, 75%). R_f (85% PE/EtOAc) 0.46; $[\alpha]_D^{20}$ +70 (*c* 1.99, $CHCl_3$); ν_{max} (liquid film): 3093, 3058, 3027 (arom. C–H-ν), 2951, 2929, 2855, 2830 (aliph. C–H-ν), 1736 (C=O-ν), 1494, 1461, 1446 (arom. C=C-ν), 1368, 1327, 1278, 1230, 1201, 1139, 1076 (C–O–C), 1033, 1014, 967, 915, 895, 842, 794, 758, 733, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 0.84 (3H, t, ^3J 7.1 Hz, CH_3), 1.15 (3H, t, ^3J 7.1 Hz, $CO_2CH_2CH_3$), 1.12–1.28 (6H, m,

$CH_3CH_2CH_2CH_2CH_2$), 1.80–1.85 (3H, m, C*H*-B*, $CH_3CH_2CH_2CH_2CH_2$), 1.98 (1H, dd, ^2J 15.5 Hz, ^3J 10.9 Hz, CH_bH_aCOEt), 2.05 (1H, dd, ^2J 15.5 Hz, ^3J 4.5 Hz, CH_aH_bCOEt), 2.99 (6H, s, OCH_3), 3.99 (2H, q, ^3J 7.1 Hz, $CO_2CH_2CH_3$), 4.94 (1H, ddt, ^3J 15.3 Hz, ^3J 8.3 Hz, ^4J 1.5 Hz, CH=C*H*CHB*), 5.08 (1H, dtd, ^3J 15.3 Hz, ^3J 6.8 Hz, ^4J 1.1 Hz, CH_2CH=CH), 5.28 (2H, s, 2H, C*H*CPh_2OMe), 7.23–7.31 (20H, m, arom. CH); ^{13}C NMR ($CDCl_3$, 151 MHz) 14.1 (CH_3), 14.2 ($CO_2CH_2CH_3$), 22.5, 29.2, 31.1 ($CH_3CH_2CH_2CH_2CH_2$), 24.4 (*C*H-B*); 32.5 ($CH_3CH_2CH_2CH_2CH_2$), 34.9 (CH_2COEt), 51.7 (OCH_3),59.9 ($CO_2CH_2CH_3$), 77.7 (*C*HCPh_2OMe), 83.3 (*C*Ph_2OCH_3), 127.5 (CH=*C*HCHB*), 130.1 (*C*H=CHCHB*), 127.2, 127.3, 127.7, 128.1, 128.4, 129.7 (arom. CH), 141.3 (arom. C_{ipso}), 173.2 (CO_2OEt); *m*/*z* (ESI, positive ion, N_2) 678 (100) [$(M+H_2O)^+$], 645 (20) [$(M-CH_3)^+$], 403 (17), 197 (8) [$(CPh_2OMe)^+$]. HRMS (ESI, positive ion): MNa^+, found 683.35138. $C_{42}H_{49}BO_6Na$ requires 683.35199.

*4.4.4. (2R,3S,E,4′R,5′R)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-2-methylpent-4-enoate [(**2S**,**3R**)-**15a**].* According to general procedure 6 alcohol **2a** (500 mg, 0.96 mmol, 1.0 equiv), triethyl orthopropionate (1.34 mL, 1.19 g, 6.73 mmol, 7.0 equiv), and a catalytic amount of propionic acid (4 μL) were heated at 135 °C for 4 h. After work-up a complex mixture of slightly impure diastereoisomers (405 mg, ~70%) was obtained. After extensive chromatographic purification [flash column chromatography (95% PE/EtOAc)/MPLC (98% PE/EtOAc)] a small sample of the allylboronic ester (**2S**,**3R**)-**15a** was isolated: [Found: C, 75.20; H, 6.84. $C_{38}H_{41}BO_6$ requires C, 75.50; H, 6.48%]; R_f (85% PE/EtOAc) 0.43; $[\alpha]_D^{20}$ −116 (*c* 1.10, $CHCl_3$); ν_{max} (liquid film): 3083, 3063, 3022 (arom C–H-ν), 2978, 2936, 2906, 2834 (aliph. C–H-ν), 1732 (C=O-ν), 1636, 1600, 1577, 1494, 1446 (arom. C=C-ν), 1368, 1332, 1347, 1231, 1198, 1186, 1076 (C–O–C), 1051, 1033, 1015, 967 (CH=CH_2, C–H-$\delta_{out\ of\ plane}$), 907, 857, 794, 757, 703, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) 0.69 (3H, d, ^3J 6.9 Hz, CH_3CHCO_2Et), 1.10 (3H, dd, ^3J 7.1, 7.1 Hz, $CO_2CH_2CH_3$), 1.77 (dddd, ^3J 9.6, 9.1 Hz, ^4J 1.2, 0.8 Hz, C*H*-B*), 2.24 (dq, ^3J 9.6, 6.9 Hz, *CH*CO_2Et), 2.99 (6H, s, OCH_3), 3.85 (1H, dq, ^2J 10.8 Hz, ^3J 7.1 Hz, $CO_2CH_bH_aCH_3$), 3.89 (1H, dq, ^2J 10.8 Hz, ^3J 7.1 Hz, $CO_2CH_aH_bCH_3$), 4.70 (1H, ddd, ^3J 17.1 Hz, ^2J 1.8 Hz, ^4J 0.8 Hz, CH=CH_EH_Z), 4.74 (1H, ddd, ^3J 10.3 Hz, ^2J 1.8 Hz, ^4J 1.2 Hz, CH=CH_ZH_E), 5.31 (2H, s, C*H*CPh_2OMe), 5.50 (1H, ddd, ^3J 17.1, 10.3 Hz, ^3J 9.1 Hz, C*H*=CH_2), 7.23–7.36 (20H, m, arom. C*H*); ^{13}C NMR ($CDCl_3$, 151 MHz) 14.1 ($CO_2CH_2CH_3$), 16.3 (CH_3CHCO_2Et), 33.6 (*C*H-B*), 40.3 (*C*HCO_2Et), 51.7 (OCH_3), 59.8 ($CO_2CH_2CH_3$), 77.7 (*C*HCPh_2OMe), 83.4 (*C*Ph_2OCH_3), 114.4 (CH=CH_2), 127.3, 127.4, 127.5, 127.7, 128.5, 129.7 (arom. *C*H), 136.9 (*C*H=CH_2), 141.3, 141.3 (arom. C_{ipso}), 175.9 (CO_2Et); *m*/*z* (ESI, positive ion, N_2) 627 (100) [$(M+Na)^+$].

*4.4.5. (2R,3S,E,4′R,5′R)- and (2S,3S,E,4′R,5′R)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-2-methylhex-4-enoate [(**3S**)-**15b**].* According to general procedure 5 alcohol (***R***)-**2b**[16] (150 mg, 0.28 mmol, 1.00 equiv), triethyl orthopropionate (308 μL, 351 mg, 1.99 mmol, 7.10 equiv), a catalytic amount of propionic acid (1.22 μL), and DMF (0.38 mL) were heated in a microwave reactor. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be 50:50. The crude product was purified by flash column chromatography (95% PE/EtOAc) and MPLC (98% PE/EtOAc) to yield a 1:1 mixture of the diastereoisomers (**2R**,**3S**)- and (**2S**,**3S**)-**15b** (152 mg, 0.25 mmol, 88%) as a colorless solid.

According to general procedure 6 alcohol (***R***)-**2b**[16] (1.00 g, 1.87 mmol, 1.00 equiv), triethyl orthopropionate (2.64 mL, 2.34 g, 13.3 mmol, 7.10 equiv), and a catalytic amount of propionic acid (8.12 μL) were heated at 135 °C for 4 h. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be 50:50. The crude product was purified by flash column chromatography (85% PE/EtOAc) and MPLC (98% PE/EtOAc) to yield a 1:1 mixture of diastereoisomers (**2R**,**3S**)- and (**2S**,**3S**)-**15b** (0.99 g, 1.61 mmol, 86%) as a colorless solid. [Found: C, 75.73; H, 7.01. $C_{39}H_{43}BO_6$ requires C, 75.73; H, 7.01%]; R_f (85% PE/EtOAc) 0.52; ν_{max} (liquid film): 3457 (br), 3083, 3053, 3022 (arom. C–H-ν), 2977, 2937, 2830, (aliph. C–H-ν), 1732 (C=O-ν), 1600, 1580 (arom. C=C-ν), 1489, 1446, 1376, 1350, 1332, 1282, 1233, 1177, 1150, 1076 (C–O–C), 1033, 1014, 1001, 967 (CH=CH_2, C–H-$\delta_{out\ of\ plane}$), 920, 900, 859, 842, 791, 758, 730, 703, 698 cm^{-1}; ^{1}H NMR [$CDCl_3$, 600 MHz, (**2R**,**3S**)-**15b**] 0.67 (3H, d, ^3J 6.8 Hz, CH_3CHCO_2Et), 1.12 (3H, m, $CO_2CH_2CH_3$), 1.46 (3H, dd, ^3J 6.4, 1.5 Hz, CH_3CH=CH), 1.58 (1H, dd, ^3J 10.5, 9.6 Hz C*H*-B*), 2.28 (1H, qd, ^3J 6.8, 10.5 Hz, *CH*CO_2Et), 2.98 (6H, s, OCH_3), 3.94 (2H, m, $CO_2CH_2CH_3$), 4.93 (1H, ddq, ^3J 15.1, 9.6 Hz, ^4J 1.5 Hz, MeCH=C*H*), 5.07 (1H, dq, ^3J 15.1 6.4 Hz, Me*CH*=CH), 5.29 (2H, s, C*H*CPh_2OMe), 7.25–7.35 (20H, m, arom. C*H*); ^{1}H NMR [$CDCl_3$, 600 MHz, (**2S**,**3S**)-**15b**] 0.77 (3H, d, ^3J 7.2 Hz, CH_3CHCO_2Et), 1.12 (3H, m, $CO_2CH_2CH_3$), 1.51 (3H, dd, ^3J 6.4, 1.5 Hz, CH_3CH=CH), 1.90 (1H, dd, ^3J 9.4, 4.9 Hz, C*H*-B*), 2.17 (1H, qd, ^3J 7.2, 4.9 Hz, *CH*CO_2Et), 2.98 (6H, s, OCH_3), 3.94 (2H, m, $CO_2CH_2CH_3$), 4.95 (1H, ddq, ^3J 15.1, 9.6 Hz, ^4J 1.5 Hz, MeCH=C*H*), 5.07 (1H, dq, ^3J 15.1, 6.4 Hz, Me*CH*=CH), 5.31 (2H, s, C*H*CPh_2OMe), 7.25–7.35 (20H, m, arom. C*H*); ^{13}C NMR [$CDCl_3$, 151 MHz, mixture of *syn*-(**2R**,**3S**)-**15b** and *anti*-(**2S**,**3S**)-**15b**] 13.9 (CH_3CHCO_2Et-*anti*), 14.1, 14.2 ($CO_2CH_2CH_3$), 16.4 (CH_3CHCO_2Et-*syn*), 18.0, 18.1 (CH_3CH=CH), 31.4 (*C*H-B*-*anti*), 32.7 (*C*H-B*-*syn*), 39.3 (*C*HCO_2Et-*anti*), 41.1 (*C*HCO_2Et-*syn*), 51.8, 51.9 (OCH_3), 59.6, 59.8 ($CO_2CH_2CH_3$), 77.7, 77.8 (*C*HCPh_2OMe), 83.4, 83.5 (*C*Ph_2OCH_3), 125.3, 126.8, (Me*C*H=CH), 126.6 (MeCH=*C*H-*anti*), 128.5 (MeCH=*C*H-*syn*), 127.1, 127.2, 127.3, 127.4, 127.4, 127.5, 127.7, 128.6, 129.7 (arom. *C*H), 141.2, 141.3, 141.4, 141.5 (arom. C_{ipso}), 175.6 ($CO_2CH_2CH_3$-*anti*), 175.9 ($CO_2CH_2CH_3$-*syn*), *m*/*z* (ESI, positive ion, N_2) 636 (100) [$(M+H_2O)^+$], 361 (47) [$(C_{28}H_{25})^+$], 197 (8) [$(CPh_2OMe)^+$].

*4.4.6. (2S,3R,E,4′R,5′R)- and (2R,3R,E,4′R,5′R)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-2-methylhex-4-enoate [(**3R**)-**15b**].* According to general procedure 5 alcohol (***S***)-**2b**[16] (100 mg, 0.19 mmol, 1.0 equiv), triethyl orthopropionate (264 μL, 234 mg, 1.33 mmol, 7.1 equiv), a catalytic amount of propionic acid (0.82 μL), and DMF (0.26 mL) were heated in a microwave reactor. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be 63:37. The crude product was purified by flash column chromatography (95% PE/EtOAc) and MPLC (98% PE/EtOAc) to yield a 63:37 mixture of diastereoisomers (**2S**,**3R**)- and (**2R**,**3R**)-**15b** (99.8 mg, 0.16 mmol, 87%) as a colorless solid.

According to general procedure 6 alcohol (***S***)-**2b**[16] (500 mg, 0.94 mmol, 1.0 equiv), triethyl orthopropionate (1.30 mL, 1.15 g, 6.55 mmol, 7.0 equiv), and a catalytic amount of propionic acid (4.05 μL) were heated at 135 °C for 4 h. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be 86:14. The crude product was purified by flash column chromatography (95% PE/EtOAc) and MPLC (98% PE/EtOAc) to yield a 86:14 mixture of diastereoisomers (**2S**,**3R**)- and (**2R**,**3R**)-**15b** (509 mg, 0.82 mmol, 88%) as a colorless solid. [Found: C, 75.51; H, 6.99. $C_{39}H_{43}BO_6$ requires C, 75.73; H, 7.01%]; R_f (85% PE/EtOAc) 0.47; ν_{max} (liquid film): 3457 (br), 3083, 3048, 3027 (arom C–H-ν), 2970, 2936, 2834, (aliph. C–H-ν), 1736 (C=O-ν), 1590, 1570, 1519, 1494 (arom. C=C-ν), 1446, 1366, 1355, 1266, 1229, 1217, 1204, 1155, 1075 (C–O–C), 1032, 1014, 1001, 966 (CH=CH_2, C–H-$\delta_{out\ of\ plane}$), 921, 901, 857, 839, 795, 758, 734, 698 cm^{-1}; ^{1}H NMR [$CDCl_3$, 600 MHz, (**2S**,**3R**)-**15b**] 0.65 (3H, d, ^3J 6.9 Hz, CH_3CHCO_2Et), 1.09 (3H, t, ^3J 7.2 Hz, $CO_2CH_2CH_3$), 1.48 (3H, m, CH_3CH=CH), 1.65 (1H, dd, ^3J 9.3, 9.8 Hz, C*H*-B*), 2.18 (1H, qd, ^3J 6.8, 9.8 Hz, *CH*CO_2Et), 2.97 (6H, s, OCH_3), 3.86 (2H, m, $CO_2CH_2CH_3$), 5.08 (1H, ddq, ^3J 15.1, 9.3 Hz, ^4J 2.1 Hz, MeCH=C*H*), 5.12 (1H, dq, ^3J 15.1, 6.8 Hz, Me*CH*=CH), 5.29 (2H, s, C*H*CPh_2OMe), 7.23–7.35 (20H, m, arom. C*H*); ^{13}C NMR [$CDCl_3$, 151 MHz (**2S**,**3R**)-**15b**] 14.2 ($CO_2CH_2CH_3$), 16.4 (CH_3CHCO_2Et), 17.8 (CH_3CH=CH), 32.7 (*C*H-B*), 41.1 (*C*HCO_2Et), 51.7 (OCH_3), 59.8 ($CO_2CH_2CH_3$), 77.7 (*C*HCPh_2OMe), 83.4 (*C*Ph_2OCH_3), 125.2 (Me*C*H=CH), 127.2, 127.3, 127.5, 127.7, 128.6, 129.7 (arom. *C*H), 129.1 (MeCH=*C*H), 141.3, 141.4 (arom. C_{ipso}), 176.1 (CO_2Et); ^{1}H NMR [$CDCl_3$, 600 MHz, (**2R**,**3R**)-**15b**] 0.69 (3H, d, ^3J

6.8 Hz, C*H*$_3$CHCO$_2$Et), 1.21 (3H, t, ^3J 7.2 Hz, CO$_2$CH$_2$C*H*$_3$), 1.49 (3H, m, C*H*$_3$CH=CH), 1.84 (1H, dd, ^3J 9.8, 4.9 Hz, C*H*-B*), 2.30 (1H, qd, ^3J 6.9, 5.1 Hz, C*H*CO$_2$Et), 2.98 (6H, s, OC*H*$_3$), 3.86 (2H, m, CO$_2$C*H*$_2$CH$_3$), 5.04 (1H, ddq, ^3J 15.1, 9.8 Hz, ^4J 1.5 Hz, MeCH=C*H*), 5.13 (1H, ddq, ^3J 15.1, 6.8 Hz, ^4J 0.8 Hz MeC*H*=CH), 5.29 (2H, s, C*H*CPh$_2$OMe), 7.23–7.35 (20H, m, arom. C*H*); ^{13}C NMR [CDCl$_3$, 151 MHz, (**2*R*,3*R***)-**15b**] 13.9 (C*H*$_3$CHCO$_2$Et), 14.2 (CO$_2$CH$_2$C*H*$_3$), 18.0 (*C*H$_3$CH=CH), 31.4 (*C*H-B*), 39.3 (*C*HCO$_2$Et), 51.7 (OCH$_3$), 59.7 (CO$_2$*C*H$_2$CH$_3$), 77.8 (*C*HCPh$_2$OMe), 83.3 (*C*Ph$_2$OCH$_3$), 125.2 (MeCH=CH), 127.2, 127.3, 127.4, 127.7, 128.5, 129.6 (arom. *C*H), 127.0 (MeCH=*C*H), 141.1, 141.3 (arom. C_{ipso}), 176.0 (*C*O$_2$Et); *m*/*z* (ESI, positive ion, N$_2$) 636 (100) [(M+H$_2$O)$^+$], 361 (50) [(C$_{28}$H$_{25}$)$^+$], 197 (9) [(CPh$_2$OMe)$^+$].

*4.4.7. (2S,3S,E,4′R,5′R)- and (2S,3R,E,4′R,5′R)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-2-methyl-5-phenylpent-4-enoate [(**3R**)-**15c**].* According to general procedure 6 alcohol (***R***)-**2c**[16] (1.16 g, 1.94 mmol, 1.0 equiv), triethyl orthopropionate (1.30 mL, 1.15 g, 6.55 mmol, 7.0 equiv), and a catalytic amount of propionic acid (1.58 μL) were heated at 135 °C for 3 h. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be 72:28. The crude product was purified by flash column chromatography (95% PE/EtOAc) and MPLC to yield a 1:1 mixture of diastereoisomers (**2*S*,3*R***)- and (**2*R*,3*R***)-**15c** (1.04 g, 1.53 mmol, 79%) as a colorless solid. [Found: C, 77.21; H, 6.62. C$_{44}$H$_{45}$BO$_6$ requires C, 77.64; H, 6.66%]; R_f (85% PE/EtOAc) 0.15; $[\alpha]_D^{20}$ −50 (*c* 1.04, CHCl$_3$); ν_{max} (liquid film): 3458 (br), 3083, 3027, 3002 (arom C–H-ν), 2970, 2941 (aliph. C–H-ν), 1734 (C=O-ν), 1489 (arom. C=C-ν), 1446, 1408, 1375, 1365, 1229, 1217, 1203, 1165, 1150, 1087, 1075 (C–O–C), 1032, 1012, 965 (CH=CH$_2$, C–H-$\delta_{out\ of\ plane}$), 903, 895, 795, 755, 733, 698, 668 cm^{-1}; ^{1}H NMR [CDCl$_3$, 600 MHz (**2*R*,3*R***)-**15c**] 0.79 (3H, d, ^3J 7.2 Hz, C*H*$_3$CHCO$_2$Et), 1.03 (3H, t, ^3J 7.2, CO$_2$CH$_2$C*H*$_3$), 2.05 (1H, dd, ^3J 9.4, 5.3 Hz, C*H*-B*), 2.39 (1H, qd, ^3J 7.2, 5.3 Hz, C*H*CO$_2$Et), 2.99 (6H, s, OCH$_3$), 3.83 (2H, m, CO$_2$C*H*$_2$CH$_3$), 5.34 (2H, s, C*H*CPh$_2$OMe), 5.80 (1H, dd, ^3J 15.6, 9.4 Hz, PhCH=C*H*), 6.10 (1H, d, ^3J 15.8 Hz, PhC*H*=CH), 7.11–7.35 (25H, m, arom. CH); ^{13}C NMR [CDCl$_3$, 151 MHz (**2*R*,3*R***)-**15c**] 14.2 (CO$_2$CH$_2$*C*H$_3$), 14.4 (*C*H$_3$CHCO$_2$Et), 31.7 (*C*H-B*), 39.2 (*C*HCO$_2$Et), 51.8 (OCH$_3$), 60.0 (CO$_2$*C*H$_2$CH$_3$), 78.0 (*C*HCPh$_2$OMe), 83.4, 83.5 (*C*Ph$_2$OCH$_3$), 125.9, 126.6, 127.3, 127.5, 127.7, 128.3, 128.5, 129.6, 129.7 (arom. *C*H), 126.8 (PhCH=*C*H), 131.6 (Ph*C*H=CH), 141.0, 141.2 (arom. C_{ipso}), 175.7 (*C*O$_2$Et); *m*/*z* (ESI, positive ion, N$_2$) 703 (100) [(M+Na)$^+$], 698 (55) [(M+H$_2$O)$^+$], 719 (20) [(M+K)$^+$], 423 (18) [(C$_{28}$H$_{22}$O$_4$)$^+$]. The analytical data of (**2*S*,3*R***)-**15c** are described below.

Synthesis via cross metathesis: Under an atmosphere of dry nitrogen in a 25 mL *Schlenk*-flask equipped with a magnetic stirrer bar and a reflux condenser, the allylboronic ester (**2*S*,3*R***)-**15a** (300 mg, 0.49 mmol, 1.00 equiv) was dissolved in abs CH$_2$Cl$_2$ (5.00 mL). The solution was treated with styrene (114 μL, 103.4 mg, 0.99 mmol, 2.00 equiv) and the *Grubbs* II catalyst (42.1 mg, 49.6 μmol, 0.10 equiv); the mixture was stirred for 21 h at 40 °C. After cooling to room temperature, the solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography on silica gel (98% PE/EtOAc) to yield (**2*S*,3*R***)-**15c** as a colorless solid (223 mg, 0.33 mmol, 66%). An X-ray crystal structure analysis of a single diastereoisomer (**2*S*,3*R***)-**15c** was obtained.[42] [Found: C, 77.64; H, 6.66. C$_{44}$H$_{45}$BO$_6$ requires C, 77.27; H, 6.68%]; R_f (85% PE/EtOAc) 0.44; $[\alpha]_D^{20}$ −44 (*c* 1.00, CHCl$_3$); ν_{max} (liquid film): 3458 (br), 3083, 3027, 3002 (arom C–H-ν), 2970, 2941 (aliph. C–H-ν), 1739 (C=O-ν), 1489 (arom. C=C-ν), 1447, 1413, 1375, 1365, 1229, 1217, 1208, 1165, 1150, 1092, 1077 (C–O–C), 1034, 1008, 963 (CH=CH$_2$, C–H-$\delta_{out\ of\ plane}$), 903, 895, 757, 733, 700 cm^{-1}; ^{1}H NMR [CDCl$_3$, 600 MHz *syn*-(**2*S*,3*R***)-**15c**] 0.73 (3H, d, ^3J 6.8 Hz, C*H*$_3$CHCO$_2$Et), 1.03 (3H, t, ^3J 7.2 Hz, CO$_2$CH$_2$C*H*$_3$), 1.90 (1H, dd, ^3J 9.8, 9.4 Hz, C*H*-B*), 2.33 (1H, qd, ^3J 9.8, 6.8 Hz, C*H*CO$_2$Et), 2.98 (6H, s, OC*H*$_3$), 3.83 (2H, m, CO$_2$C*H*$_2$CH$_3$), 5.29 (2H, s, C*H*CPh$_2$OMe), 5.84 (1H, dd, ^3J 15.6, 9.4 Hz, PhCH=C*H*), 6.05 (1H, d, ^3J 15.8 Hz, PhC*H*=CH), 7.13–7.35 (25H, m, arom. CH); ^{13}C NMR [CDCl$_3$, 151 MHz *syn*-(**2*S*,3*R***)-**15c**] 14.2 (CO$_2$CH$_2$*C*H$_3$), 16.5 (*C*H$_3$CHCO$_2$Et), 33.1 (*C*H-B*), 40.9 (*C*HCO$_2$Et), 51.8 (OCH$_3$), 59.9 (CO$_2$*C*H$_2$CH$_3$), 77.9 (*C*HCPh$_2$OMe), 83.5 (*C*Ph$_2$OCH$_3$), 125.9, 126.5, 127.3, 127.4, 127.5, 127.8, 128.2, 128.6, 129.3 (arom. CH), 129.3 (PhCH=*C*H), 130.0 (Ph*C*H=CH), 138.0, 141.1, 141.3 (arom. C_{ipso}); 175.9 (*C*O$_2$Et); *m*/*z* (ESI, positive ion, N$_2$) 698 (52) [(M+H$_2$O)$^+$], 719 (25) [(M+K)$^+$], 423 (21) [(C$_{28}$H$_{22}$O$_4$)$^+$].

*4.4.8. (2R,3S,E,4′R,5′R)- and (2S,3S,E,4′R,5′R)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-2-methyldec-4-enoate [(**3S**)-**15d**].* According to general procedure 5 alcohol (***R***)-**2d** (100 mg, 0.17 mmol, 1.0 equiv), triethyl orthopropionate (240 μL, 212.6 mg, 1.19 mmol, 7.1 equiv), a catalytic amount of propionic acid (0.73 μL), and DMF (0.23 mL) were heated in a microwave reactor. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be 50:50. The crude product was purified by flash column chromatography (95%, PE/EtOAc) to yield a 1:1 mixture of diastereoisomers (**2*R*,3*S***)- and (**2*S*,3*S***)-**15d** (101 mg, 0.15 mmol, 89%) as a colorless foam.

According to general procedure 6 alcohol (***R***)-**2d** (1.19 g, 2.02 mmol, 1.0 equiv), triethyl orthopropionate (2.85 mL, 2.53 g, 14.3 mmol, 7.1 equiv), and a catalytic amount of propionic acid (8.8 μL) were heated at 135 °C for 4 h. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be 50:50. The crude product was purified by flash column chromatography (85% PE/EtOAc) and MPLC (98% PE/EtOAc) to yield a 1:1 mixture of diastereoisomers (**2*R*,3*S***)- and (**2*S*,3*S***)-**15d** (1.18 g, 1.74 mmol, 86%) as a colorless foam. [Found: C, 76.31; H, 7.57. C$_{43}$H$_{51}$BO$_6$ requires C, 76.55; H, 7.62%]; R_f (85% PE/EtOAc) 0.47; ν_{max} (liquid film): 3457 (br), 3093, 3058, 3027 (arom C–H-ν), 2956, 2932, 2850, 2830 (aliph. C–H-ν), 1733 (C=O-ν), 1598, 1577, 1494 (arom. C=C-ν), 1447, 1374, 1330, 1279, 1231, 1188, 1148, 1076 (C–O–C), 1033, 1014, 967 (CH=CH$_2$, C–H-$\delta_{out\ of\ plane}$), 915, 897, 839, 794, 728, 705, 665 cm^{-1}; ^{1}H NMR [CDCl$_3$, 600 MHz *syn*-(**2*R*,3*S***)- and *anti*-(**2*S*,3*S***)-**15d**] 0.70 (3H, ^3J 6.8 Hz, C*H*$_3$CHCO$_2$Et-*syn*), 0.80 (3H, d, ^3J 7.2 Hz, *CH*$_3$CHCO$_2$Et-*anti*), 0.87 (3H, t, ^3J 7.2 Hz, *CH*$_3$CH$_2$CH$_2$CH$_2$CH$_2$), 1.11–1.27 (6H, m, CH$_3$C*H*$_2$CH$_2$CH$_2$CH$_2$), 1.13 (3H, t, ^3J 7.2 Hz, CO$_2$CH$_2$C*H*$_3$), 1.56 (1H, t, ^3J 10.2 Hz, C*H*-B*-*syn*), 1.78 (2H, m, *n*-BuC*H*$_2$CH), 1.86 (1H, ^3J 9.8, 5.6 Hz, C*H*-B*-*anti*), 2.28 (1H, qd, ^3J 10.9, 6.8 Hz, C*H*CO$_2$Et-*syn*), 2.29 (1H, qd, ^3J 7.5, 5.6 Hz, C*H*CO$_2$Et-*anti*), 2.98 (6H, s, OC*H*$_3$), 3.93 (2H, q, ^3J 7.2 Hz, CO$_2$C*H*$_2$CH$_3$), 4.87 (1H, ddt, ^3J 15.3, 9.6 Hz, ^4J 1.3 Hz, *n*-PeCH=C*H*-*syn*), 5.07 (1H, dtd, ^3J 15.3, 6.4 Hz, ^4J 0.8 Hz, *n*-PeC*H*=CH-*syn*), 4.91 (1H, ddt, ^3J 15.1, 10.2 Hz, ^4J 1.3 Hz, *n*-PeCH=C*H*-*anti*), 5.10 (1H, dtd, ^3J 15.1, 6.8 Hz, ^4J 0.8 Hz, *n*-PeC*H*=CH-*anti*), 5.28 (2H, s, C*H*CPh$_2$OMe), 7.23–7.34 (20H, m, arom. C*H*); ^{13}C NMR [CDCl$_3$, 151 MHz mixture of *syn*-(**2*R*,3*S***)-**15d** and *anti*-(**2*S*,3*S***)-**15d**] 14.5 (*C*H$_3$CHCO$_2$Et-*anti*), 14.0, 14.0 (*C*H$_3$CH$_2$CH$_2$CH$_2$CH$_2$), 14.1, 14.2 (CO$_2$CH$_2$*C*H$_3$), 17.0 (*C*H$_3$CHCO$_2$Et-*syn*), 22.3, 22.5, 29.0, 29.1, 22.4, 22.5 (CH$_3$CH$_2$CH$_2$*C*H$_2$CH), 31.0 (*C*H-B*-*anti*), 33.1 (*C*H-B*-*syn*), 32.4 (*n*-BuCH$_2$-*syn*), 32.5 (*n*-BuCH$_2$-*anti*), 39.3 (*C*HCO$_2$Et-*anti*), 40.9 (*C*HCO$_2$Et-*syn*), 51.8, 53.4 (OCH$_3$), 59.6 (CO$_2$CH$_2$CH$_3$-*syn*), 59.8 (CO$_2$CH$_2$CH$_3$-*anti*), 77.6, 77.8 (*C*HCPh$_2$OMe), 83.3, 83.4 (*C*Ph$_2$OCH), 127.1, 127.2, 127.3, 127.4, 127.4, 127.4, 127.7, 127.7, 128.5, 128.5, 129.6, 129.7 (arom. *C*H), 125.7 (*n*-PeCH=*C*H-*anti*), 127.3 (*n*-PeCH=*C*H-*syn*), 131.3 (*n*-PeC*H*=CH-*syn*), 132.5 (*n*-PeCH=CH-*anti*), 141.3, 141.3, 141.4, 141.4 (arom. C_{ipso}), 175.8 (*C*O$_2$Et-*anti*), 176.5 (*C*O$_2$Et-*syn*); *m*/*z* (ESI, positive ion, N$_2$) 697 (80) [(M+Na)$^+$], 729 (100) [(M+3H$_2$O)$^+$].

*4.4.9. (2S,3R,E,4′R,5′R)- and (2R,3R,E,4′R,5′R)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-2-methyldec-4-enoate [(**3R**)-**15d**].* According to general procedure 5 alcohol (***S***)-**2d** (100 mg, 0.17 mmol, 1.0 equiv), triethyl orthopropionate (240 μL, 213 mg, 1.20 mmol, 7.1 equiv), a catalytic amount of propionic acid (0.73 μL), and DMF (0.23 mL) were heated in a microwave reactor. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric

ratio to be 60:40. The crude product was purified by flash column chromatography (95% PE/EtOAc) and MPLC (98% PE/EtOAc) to yield a 60:40 mixture of diastereoisomers (**2*S*,3*R***)-**15d** and (**2*R*,3*R***)-**15d** (101.4 mg, 0.15 mmol, 89%) as a colorless solid.

According to general procedure 6 alcohol (***S***)-**2d** (500 mg, 0.86 mmol, 1.0 equiv), triethyl orthopropionate (1.18 mL, 1.05 g, 5.93 mmol, 7.0 equiv), and a catalytic amount of propionic acid (3.74 μL) were heated at 135 °C for 4 h. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be 77:23. The crude product was purified by flash column chromatography (95% PE/EtOAc) and MPLC (98% PE/EtOAc) to yield a 77:23 mixture of diastereoisomers (**2*S*,3*R***)-**15d** and (**2*R*,3*R***)-**15d** (506 mg, 0.75 mmol, 87%) as a colorless solid. Even though the MPLC separation was not completely successful, a small amount of enriched diastereoisomer (**2*S*,3*R***)-**15d** was isolated. [Found: C, 76.31; H, 7.57. $C_{43}H_{51}BO_6$ requires C, 76.55; H, 7.62%]; R_f (85% PE/EtOAc) 0.47; ν_{max} (liquid film): 3457 (br); 3093, 3058, 3027 (arom C–H-ν), 2956, 2932, 2850, 2830 (aliph. C–H-ν), 1733 (C=O-ν), 1598, 1577, 1494 (arom. C=C-ν), 1447, 1374, 1330, 1279, 1231, 1188, 1148, 1076 (C–O–C), 1033, 1014, 967 (CH=CH_2, C–H-$\delta_{out\ of\ plane}$), 915, 897, 839, 794, 728, 705, 665 cm^{-1}; ^{1}H NMR [$CDCl_3$, 600 MHz, (**2*S*,3*R***)-**15d**] 0.66 (3H, d, ^3J 6.9 Hz, CH_3CHCO$_2$Et), 0.85 (3H, t, ^3J 7.2 Hz, CH_3CH$_2$CH$_2$CH$_2$CH$_2$), 1.10 (3H, t, ^3J 7.2, CO$_2$CH$_2$CH_3), 1.13–1.27 (6H, m, CH$_3$CH_2CH_2CH_2CH$_2$), 1.67 (3H, t, ^3J 9.8, C*H*-B*), 1.81 (2H, m, *n*-BuCH_2), 2.18 (1H, qd, ^3J 6.9, 9.8 Hz, C*H*CO$_2$Et), 2.98 (6H, s, OCH_3), 3.87 (2H, m, CO$_2$CH_2CH$_3$), 5.06 (2H, m, *n*-PeC*H*=C*H*), 5.28 (2H, s, 2H, C*H*CPh$_2$OMe), 7.23–7.34 (20H, m, arom. C*H*); ^{1}H NMR [$CDCl_3$, 600 MHz, (**2*R*,3*R***)-**15d**] 0.71 (3H, d, ^3J 6.8 Hz, CH_3CHCO$_2$Et), 0.79 (3H, t, ^3J 7.2 Hz, CH_3CH$_2$CH$_2$CH$_2$CH$_2$), 1.11 (3H, t, ^3J 7.2, CO$_2$CH$_2$CH_3), 1.13–1.27 (6H, m, CH$_3$CH_2CH_2CH_2CH$_2$), 1.81 (2H, m, *n*-BuCH_2), 1.84 (3H, t, ^3J 9.4, ^3J 5.3 Hz,C*H*-B*), 2.29 (1H, qd, ^3J 6.8, 5.3 Hz, C*H*CO$_2$Et), 2.98 (6H, s, OCH_3), 3.87 (2H, m, CO$_2$CH_2CH$_3$), 5.00 (1H, ddt, ^3J 15.1, 9.4 Hz, ^4J 1.3 Hz, *n*-PeCH=C*H*), 5.10 (1H, dt, ^3J 15.1, 6.8 Hz, *n*-PeC*H*=CH), 5.30 (2H, s, 2H, C*H*CPh$_2$OMe), 7.23–7.34 (20H, m, arom. C*H*); ^{13}C NMR [$CDCl_3$, 151 MHz mixture of *syn*-(**2*S*,3*R***)-**15d** and *anti*-(**2*R*,3*R***)-**15d**] 13.9 (*C*H$_3$CHCO$_2$Et-*anti*), 14.0, 14.0 (*C*H$_3$CH$_2$CH$_2$CH$_2$CH$_2$), 14.1, 14.2 (CO$_2$CH$_2$CH$_3$), 16.4 (*C*H$_3$CHCO$_2$Et-*syn*), 22.3, 22.5, 29.1, 29.1, 31.0, 31.1 (CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$), 32.3 (*C*H-B*-*syn*), 32.6 (*C*H-B*-*anti*), 32.4, 32.6 (*n*-BuCH$_2$), 39.1 (*C*HCO$_2$Et-*anti*), 41.1 (*C*HCO$_2$Et-*syn*), 51.7, 53.4 (OCH$_3$), 59.7, 59.7 (CO$_2$CH$_2$CH$_3$), 77.6, 77.8 (*C*HCPh$_2$OMe), 83.3, 83.4 (*C*Ph$_2$OCH), 127.2, 127.2, 127.3, 127.3, 127.4, 127.4, 127.7, 127.7, 127.8, 128.5, 129.6, 129.7 (arom. *C*H), 125.2, 132.6 (*n*-PeCH=*C*H*-*anti*), 128.1, 130.6 (*n*-PeCH=*C*H-*syn*), 141.2, 141.3, 141.4, 141.4 (arom. C_{ipso}), 176.0 (*C*O$_2$Et -*anti*), 176.2 (*C*O$_2$Et-*syn*); *m*/*z* (ESI, positive ion, N_2) 692 (100) [(M+H_2O)$^+$], 197 (6) [(CPh$_2$OMe)$^+$].

*4.4.10. (3S,4E,4′R,5′R)-3-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-N,N-dimethylhex-4-enamide [(**S**)-**16b**].* According to general procedure 7 alcohol (***S***)-**2b**[16] (1.00 g, 1.87 mmol, 1.0 equiv) was dissolved in abs toluene (3.60 mL) and treated with a 90% solution of *N*,*N*-dimethylacetamide dimethyl acetal (0.61 mL, 497 mg, 3.74 mmol, 2.0 equiv). The reaction mixture was stirred at 80 °C for 45 h. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be >99:1. The crude product was purified by flash column chromatography (80% PE/EtOAc to 70% PE/EtOAc) to yield (***S***)-**16b** as a yellowish oil (880 mg, 1.46 mmol, 78%). From the allylboronic ester (***S***)-**16b** a crystal structure analysis was obtained.[42] [Found: C, 75.19; H, 7.02; N, 2.23. $C_{38}H_{42}BNO_5$ requires C, 75.62; H, 7.01; N, 2.32%]; R_f (70% PE/EtOAc) 0.27; $[\alpha]_D^{20}$ −100 (*c* 1.02, $CHCl_3$); softening range 47–62 °C; ν_{max} (liquid film): 3091, 3058, 3029 (arom. C–H-ν), 2980, 2958, 2937, 2915, 2857, 2825 (aliph. C–H-ν), 1643 (C=O-ν), 1494, 1466, 1446 (arom. C=C-ν), 1390, 1381, 1370, 1354, 1319, 1267, 1230, 1196, 1158, 1130, 1076 (C–O–C), 1033, 1019, 1001, 967 (CH=CH_2, C–H-$\delta_{out\ of\ plane}$), 938, 923, 901, 857, 826, 796, 757, 734, 705, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) 1.50 (3H, d, ^3J 6.0 Hz, CH_3CH),1.93 (1H, dd, ^2J 14.8 Hz, ^3J 9.2 Hz, CH$_b$H$_a$CONMe$_2$), 1.96 (1H, dd, ^2J 14.8 Hz, ^3J 5.5 Hz, CH$_a$H$_b$-CONMe$_2$), 2.01 (1H, m, C*H*B*), 2.69 (3H, s, NCH_{a3}), 2.75 (3H, s, NCH_{b3}), 2.99 (6H, s, OCH_3), 5.08 (1H, dqd, ^3J 15.3, 6.1 Hz, ^4J 1.13 Hz, CH$_3$C*H*=CH), 5.15 (1H, ddq, ^3J 15.3, 6.9 Hz, ^4J 1.5 Hz, CH$_3$CH=C*H*), 5.29 (2H, s, 2H, C*H*CPh$_2$OMe), 7.24–7.32 (20H, m, arom. C*H*); ^{13}C NMR ($CDCl_3$, 151 MHz) 18.1 (*C*H$_3$CH), 23.4 (*C*HB*), 32.1 (*C*H$_2$CONMe$_2$), 35.4, 37.3 [(NCH$_3$)$_2$], 51.8 (OCH$_3$), 77.9 (*C*HCPh$_2$OMe), 83.4 (*C*Ph$_2$OCH$_3$), 123.1 (CH$_3$*C*H=CH), 127.2, 127.3, 127.5, 127.8, 128.6, 129.7 (arom. *C*H), 130.5 (CH$_3$CH=*C*H), 141.0, 141.2 (arom. C_{ipso}), 172.6 (*C*ONMe$_2$); *m*/*z* (ESI, positive ion, N_2) 626 (35) [(M+H_2O)$^+$], 603 (30) [M$^+$], 346 (100) [($C_{22}H_{18}O_4$)$^+$].

*4.4.11. (3R,4E,4′R,5′R)-3-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-N,N-dimethylhex-4-enamide ((**R**)-**16b**).* According to general procedure 7 alcohol (***R***)-**2b**[16] (200 mg, 0.37 mmol, 1.0 equiv) dissolved in abs toluene (0.75 mL) was treated with a 90% solution of *N*,*N*-dimethylacetamide dimethyl acetal (122 μL, 111 mg, 0.74 mmol, 2.0 equiv). The reaction mixture was stirred at 80 °C for 22 h. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be >99:1. The crude product was purified by flash column chromatography (85% PE/EtOAc with a gradient to 70% PE/EtOAc) to yield (***R***)-**16b** as a yellow oil (194 mg, 0.32 mmol, 86%). [Found: C, 75.61; H, 7.02; N, 2.22. $C_{38}H_{42}BNO_5$ requires C, 75.62; H, 7.01; N, 2.32%]; R_f (60% PE/EtOAc) 0.19; $[\alpha]_D^{20}$ −91 (*c* 1.00, $CHCl_3$); ν_{max} (liquid film): 3083, 3063, 3022 (arom. C–H-ν), 2980, 2937, 2915, 2855, 2820 (aliph. C–H-ν), 1648 (C=O-ν), 1494, 1466, 1446 (arom. C=C-ν), 1390, 1381, 1370, 1353, 1319, 1266, 1232, 1198, 1158, 1130, 1076 (C–O–C), 1033, 1019, 1001, 967 (CH=CH_2, C–H-$\delta_{out\ of\ plane}$), 938, 923, 901, 857, 826, 796, 759, 733, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) 1.50 (3H, ddd, ^3J 6.0 Hz, ^4J 1.3 Hz, ^5J 0.8 Hz, CH_3CH), 1.96 (2H, m, CH$_b$H$_a$CONMe$_2$, C*H*B*), 2.08 (1H, dd, ^2J 15.8 Hz, ^3J 11.7 Hz, CH$_a$H$_b$CONMe$_2$), 2.82 (3H, s, NCH_{a3}), 2.84 (3H, s, NCH_{b3}), 2.98 (6H, s, 6H, OCH_3), 5.01 (1H, ddq, ^3J 15.3, 7.7 Hz, ^4J 1.3 Hz, CH$_3$CH=C*H*), 5.06 (1H, dqd, ^3J 15.3, 6.0 Hz, ^4J 0.8 Hz, CH$_3$C*H*=CH), 5.29 (2H, s, C*H*CPh$_2$OMe), 7.24–7.35 (20H, m, arom. C*H*); ^{13}C NMR ($CDCl_3$, 151 MHz) 18.1 (*C*H$_3$CH), 24.0 (*C*HB*), 33.1 (*C*H$_2$CONMe$_2$), 35.4, 37.3 [(NCH$_3$)$_2$], 51.8 (OCH$_3$), 77.9 (*C*HCPh$_2$OMe), 83.4 (*C*Ph$_2$OCH$_3$), 124.1 (CH$_3$*C*H=CH), 127.2, 127.3, 127.5, 127.6, 128.5, 129.7 (arom. *C*H), 129.8 (CH$_3$CH=*C*H); 141.2, 141.3 (arom. C_{ipso}), 172.4 (*C*ONMe$_2$); *m*/*z* (ESI, positive ion, N_2) 626 (10) [(M+H_2O)$^+$], 604 (30) [(M+1)$^+$], 346 (100) [($C_{22}H_{18}O_4$)$^+$], 168 (22) [($C_{13}H_{112}$)$^+$].

*4.4.12. (3S,4E,4′R,5′R)-3-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-N,N-dimethyl-5-phenylpent-4-enamide [(**S**)-**16c**].* According to general procedure 7 alcohol (***R***)-**2c**[16] (145 mg, 0.24 mmol, 1.0 equiv) dissolved in abs toluene (0.50 mL) was treated with a 90% solution of *N*,*N*-dimethylacetamide dimethyl acetal (78.8 μL, 64.6 mg, 0.48 mmol, 2.0 equiv). The reaction mixture was stirred at 80 °C for 24 h. ^{1}H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be >99:1. The crude product was purified by flash column chromatography (85% PE/EtOAc) to yield product (***S***)-**16c** as a light brown solid (99.9 mg, 0.15 mmol, 62%). From the allylboronic ester (***S***)-**16c** a crystal structure analysis was obtained.[42] R_f (85% PE/EtOAc) 0.20; $[\alpha]_D^{20}$ −46 (*c* 1.01, $CHCl_3$); mp 58–75 °C; ν_{max} (liquid film): 3083, 3058, 3032 (arom. C–H-ν), 2980, 2967, 2946, 2901, 2855, 2830 (aliph. C–H-ν), 2324, 2298 (OCH$_3$, C–H-ν), 1744, 1635 (C=O-ν), 1595, 1524, 1491, 1466, 1458, 1443 (arom. C=C-ν), 1390, 1373, 1350, 1319, 1264, 1231, 1198, 1158, 1148, 1075 (C–O–C), 1031, 1021, 1001, 963 (CH=CH_2, C–H-$\delta_{out\ of\ plane}$), 938, 923, 900, 887, 834, 799, 758, 735, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) 2.05 (1H, dd, ^2J 14.7 Hz, ^3J 7.9 Hz, CH$_b$H$_a$CONMe$_2$), 2.08 (1H, dd, ^2J 14.7 Hz, ^3J 6.49 Hz, 1H, CH$_a$H$_b$CONMe$_2$), 2.27 (1H, m, C*H*B*), 2.67 (3H, s, NCH_{a3}), 2.76 (3H, s, NCH_{b3}), 3.01 (6H, s, OCH_3), 5.30 (2H, s, C*H*CPh$_2$OMe), 5.94 (1H, dd, ^3J 15.9, 7.2 Hz, PhCH=C*H*), 6.06 (1H, d, ^3J 15.9 Hz, PhC*H*=CH), 7.09–7.39 (5H, m, arom. C*H*), 7.25–7.39 (20H, arom. C*H*); ^{13}C NMR ($CDCl_3$, 151 MHz) 24.4 (*C*HB*),

31.9 (CH_2CONMe_2), 35.5, 37.4 [$(NCH_3)_2$], 51.8 (OCH_3), 78.1 ($CHCPh_2OMe$), 83.4 (CPh_2OCH_3), 128.1 (PhCH=CH), 125.9, 126.4, 127.3, 127.4, 127.6, 127.8, 128.3, 128.6, 129.7 (arom. *C*H), 130.9 (PhCH=*C*H), 138.2, 140.9, 141.1 (arom. C_{ipso}), 172.2 ($CONMe_2$); *m*/*z* (ESI, positive ion, N_2) 666 (20) [$(M+1)^+$]. HRMS (ESI, positive ion): MNa^+, found 688.32035. $C_{43}H_{44}BNO_5Na$ requires 688.32102.

*4.4.13. (3S,4E,4′R,5′R)-3-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-N,N-dimethyldec-4-enamide [(**S**)-**16d**].* According to general procedure 7 (***S***)-**2d** (500 mg, 0.85 mmol, 1.00 equiv) dissolved in abs toluene (1.70 mL) was treated with a 90% solution of *N*,*N*-dimethylacetamide dimethyl acetal (275 μL, 225 mg, 1.70 mmol, 2.00 equiv). The reaction mixture was stirred at 80 °C for 24 h. ^1H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be >99:1. The crude product was purified by flash column chromatography (70%PE/EtOAc) to yield (***S***)-**16d** as a colorless solid (440 mg, 0.67 mmol, 79%). [Found: C, 76.35; H, 7.67; N, 2.17. $C_{42}H_{50}BNO_5$ requires C, 76.47; H, 7.64; N, 2.12%]; R_f (50% PE/EtOAc) 0.56; $[\alpha]_D^{20}$ −94 (*c* 1.05, $CHCl_3$); ν_{max} (liquid film): 3457 (br), 3091, 3053, 3012 (arom. C−H-ν), 2958, 2928, 2876, 2854, 2836 (aliph. C−H-ν), 1643 (C=O-ν), 1493, 1463, 1446 (arom. C=C-ν), 1392, 1368, 1317, 1264, 1228, 1198, 1153, 1130, 1075 (C−O−C), 1032, 1017, 966 ($CH=CH_2$, C−H-$\delta_{out\ of\ plane}$), 922, 901, 827, 796, 758, 733, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 0.79 (3H, t, ^3J 7.1 Hz, $CH_3CH_2CH_2CH_2CH_2$), 1.14 (6H, m, $CH_3CH_2CH_2CH_2CH_2$), 1.81 (2H, m, *n*-BuCH_2), 1.95 (2H, m, CH_2CONMe_2), 2.02 (1H, m, *C*HB*), 2.66 (3H, s, NCH_{a3}), 2.72 (3H, s, NCH_{b3}), 2.99 (6H, s, OCH_3), 5.07 (1H, dtd, ^3J 15.5, 6.1 Hz, ^4J 1.1 Hz, *n*-PeC*H*=CH), 5.13 (1H, ddt, ^3J 15.5, 6.8 Hz, ^4J 1.1 Hz, *n*-PeCH=C*H*), 5.28 (2H, s, *CH*CPh_2OMe), 7.23–7.36 (20H, m, arom. *CH*); ^{13}C NMR ($CDCl_3$, 151 MHz) 14.0 ($CH_3CH_2CH_2CH_2CH_2$), 22.4, 27.5, 29.2 ($CH_3CH_2CH_2CH_2CH_2$), 24.2 (*CH*B*), 31.1 (*n*-BuCH_2), 32.6 (CH_2CONMe_2), 35.4, 35.7 [$(NCH_3)_2$], 51.7 (OCH_3), 77.9 ($CHCPh_2OMe$), 83.3 (CPh_2OCH_3), 128.2 (*n*-PeCH=*C*H), 129.2 (*n*-PeCH=CH), 127.2, 127.3, 127.5, 127.7, 127.8, 129.6 (arom. *C*H), 141.0, 141.6 (arom. C_{ipso}), 172.8 ($CONMe_2$); *m*/*z* (ESI, positive ion, N_2) 682 (100) [$(M+Na)^+$], 659 (20) [M^+], 629 (9), 403 (38), 224 (7).

*4.4.14. (3R,4E,4′R,5′R)-3-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-N,N-dimethyldec-4-enamide ((**R**)-**16d**).* According to general procedure 7 alcohol (***R***)-**2d** (200 mg, 0.34 mmol, 1.0 equiv) dissolved in abs toluene (0.70 mL) was treated with a 90% solution of *N*,*N*-dimethylacetamide dimethyl acetal (110 μL, 100.2 mg, 0.68 mmol, 2.0 equiv). The reaction mixture was stirred at 80 °C for 21 h. ^1H and ^{13}C NMR of the crude product proved the diastereomeric ratio to be >99:1. The crude product was purified by flash column chromatography (90% PE/EtOAc with the gradient to 70% PE/EtOAc) to yield (***R***)-**16d** as a yellowish oil (197 mg, 0.29 mmol, 88%). [Found: C, 76.01; H, 7.65; N, 2.11. $C_{42}H_{50}BNO_5$ requires C, 76.47; H, 7.64; N, 2.12%]; R_f (70% PE/EtOAc) 0.20; $[\alpha]_D^{20}$ +92 (*c* 1.00, $CHCl_3$); ν_{max} (liquid film): 3457 (br), 3091, 3053, 3026 (arom. C−H-ν), 2957, 2929, 2876, 2856, 2836 (aliph. C−H-ν), 1641 (C=O-ν), 1522, 1493, 1463, 1446 (arom. C=C-ν), 1392, 1366, 1265, 1229, 1217, 1205, 1198, 1153, 1075 (C−O−C), 1033, 1014, 966 ($CH=CH_2$, C−H-$\delta_{out\ of\ plane}$), 920, 900, 725, 758, 733, 698, 670 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 0.84 (3H, t, ^3J 7.2 Hz, $CH_3CH_2CH_2CH_2CH_2$), 1.20 (6H, m, $CH_3CH_2CH_2CH_2CH_2$), 1.81 (2H, dt, ^3J 6.8, 6.8 Hz, *n*-BuCH_2), 1.94 (1H, ddt, ^3J 11.5, 7.9, 3.2 Hz, *C*HB*), 2.00 (1H, dd, ^2J 15.1 Hz, ^3J 3.5 Hz, $CH_bH_aCONMe_2$), 2.1 (1H, dd, ^2J 15.1 Hz, ^3J 10.9 Hz, $CH_aH_bCONMe_2$), 2.82 (3H, s, NCH_{a3}), 2.83 (3H, s, NCH_{b3}), 2.99 (6H, s, 6H, OCH_3), 4.98 (1H, ddt, ^3J 15.1, 8.3 Hz, ^4J 1.3 Hz, *n*-PeCH=C*H*), 5.07 (1H, dtd, ^3J 15.1, 5.7 Hz, ^4J 0.9 Hz, *n*-PeC*H*=CH), 5.30 (2H, s, *CH*CPh_2OMe), 7.23–7.34 (20H, m, arom. *CH*); ^{13}C NMR ($CDCl_3$, 151 MHz) 14.1 ($CH_3CH_2CH_2CH_2CH_2$), 22.5, 29.2, 31.2 ($CH_3CH_2CH_2CH_2CH_2$), 24.4 (*CH*B*), 32.5 (*n*-BuCH_2), 33.3 (CH_2CONMe_2), 35.4, 37.4 [$(NCH_3)_2$], 51.8 (OCH_3), 77.8 (*C*HCPh_2OMe), 83.4 (CPh_2OCH_3), 128.6 (*n*-PeCH=*C*H), 130.1 (*n*-PeC*H*=CH), 127.2, 127.3, 127.5, 127.8, 128.5, 129.7 (arom. *C*H), 141.3, 141.4 (arom. C_{ipso}), 172.5 ($CONMe_2$); *m*/*z* (ESI, positive ion, N_2) 682 (30) [$(M+K)^+$], 698 (100) [$(M+Na)^+$].

4.5. Allyl additions

*4.5.1. (5R,6R,Z)- and (5S,6S,Z)-6-Hydroxy-N,N-dimethyl-5,6-diphenylhex-3-enamide [(**R**,**R**)-**17**] and [(**S**,**S**)-**17**].* According to general procedure 8 allylboronic ester (***R***)-**16b** (70.0 mg, 0.12 mmol, 1.0 equiv) was treated with benzaldehyde (14.1 μL, 14.8 mg, 0.14 mmol, 1.2 equiv) in abs CH_2Cl_2 (258 μL). The reaction mixture was stirred for 7 days. ^1H and ^{13}C NMR of the crude product confirmed the (*Z*)/(*E*) diastereomeric ratio to be >99:1. The crude product was purified by flash column chromatography on silica gel (40% PE/EtOAc) to yield (***R***,***R***)-**17** as a colorless oil (19.9 mg, 0.08 mmol, 70%).

According to general procedure 8 allylboronic ester (***S***)-**16b** (272 mg, 0.45 mmol, 1.0 equiv) was treated with benzaldehyde (54.6 μL, 57.3 mg, 0.54 mmol, 1.2 equiv) in abs CH_2Cl_2 (1.10 mL). The reaction mixture was stirred for 7 days. ^1H and ^{13}C NMR of the crude product confirmed the (*Z*)/(*E*) diastereomeric ratio to be >99:1. The crude product was purified by flash column chromatography on silica gel (60% PE/EtOAc with a gradient to 30% PE/EtOAc) to yield (***S***,***S***)-**17** as a colorless oil (50.5 mg, 0.20 mmol, 45%). [Found: C, 72.50; H, 8.53; N, 5.55. $C_{15}H_{21}NO_2$ requires C, 72.84; H, 8.56; N, 5.55%]. HRMS (ESI, positive ion): $[M+Na]^+$, found 270.14648; $[M-OH]^+$, found 230.15396. $[M+Na]^+$, requires 270.14645; $[M-OH]^+$, requires 230.15394; R_f (50% PE/EtOAc) 0.06; R_f (30% PE/EtOAc) 0.14; $[\alpha]_D^{20}$ +181 [*c* 1.04, $CHCl_3$, (***R***,***R***)-**17**]; $[\alpha]_D^{20}$ −153 [*c* 1.44, $CHCl_3$, (***S***,***S***)-**17**]; ν_{max} (liquid film): 3442 (br), 3367 (O−H-ν, br), 3070, 3040, 3026 (arom. C−H-ν), 2970, 2940, 2926, 2860 (aliph. C−H-ν), 1739 (C=O-ν), 1625 (olef. C=C-ν), 1492 (arom. C=C-ν), 1450, 1435, 1366, 1259, 1216, 1228, 1203, 1144, 1092, 1074, 1054, 1024, 988, 932, 907, 824, 799, 762 (Ph, C−H-$\delta_{out\ of\ plane}$), 720, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 0.80 (3H, d, ^3J 6.4 Hz, $CHCH_3$), 2.73 (1H, m, *C*HCH_3), 2.96 (3H, s, NCH_{3a}), 3.03 (3H, s, NCH_{3b}), 3.13 (2H, dd, ^3J 7.2, 1.1 Hz, CH_2CONMe_2), 3.65 (1H, br, O*H*), 4.28 (1H, d, ^3J 8.3 Hz, *CH*OH), 5.58 (1H, td, ^3J 10.1 Hz, ^4J 1.5 Hz, *CH*=$CHCH_2$), 5.71 (1H, dtd, ^3J 10.1, 7.2 Hz, ^4J 0.8 Hz, CH=*CH*CH_2), 7.24–7.36 (5H, m, arom. *CH*); ^{13}C NMR ($CDCl_3$, 151 MHz) 17.4 ($CHCH_3$), 32.1 (CH_2CONMe_2), 35.7 (NCH_{3a}), 37.4 (NCH_{3b}), 40.8 (*C*HCH_3), 78.6 (*C*HOH), 123.5 (CH=*C*HCH_2), 126.9, 127.4, 128.1 (arom. *C*H), 136.3 (*C*H=$CHCH_2$), 143.2 (arom. C_{ipso}), 171.5 ($CONMe_2$); *m*/*z* (ESI, positive ion, N_2) 248 (100) [$(M+H)^+$], 230 (30) [$(M-OH)^+$]; HPLC (Chiracel OD-H, 90% *n*-hexane/*i*-PrOH, flow rate 0.5 mL/min, detection UV 220 nm) t_R (***R***,***R***)-**17** 33.1 min, ee >97%; t_R (***S***,***S***)-**17** 27.7 min, ee >99%.

*4.5.2. (1R,2R)- and (1S,2S)-2-Methyl-1-phenylpropane-1,3-diol [(**R**,**R**)-**18**] and [(**S**,**S**)-**18**].* In a Schlenk tube homoallylic alcohol (***R***,***R***)-**17** or (***S***,***S***)-**17** (49.5 mg, 0.20 mmol) was dissolved in abs CH_2Cl_2 (20.0 mL) under an atmosphere of dry argon. Ozone was passed through the solution at −78 °C and the reaction progress was monitored by TLC. After 8 min the excess of the ozone was removed by passing a continuous stream of argon through the solution. After the reductive work-up with Me_2S (2.0 mL), the reaction mixture was warmed to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in abs THF (20 mL) under an atmosphere of dry argon and was treated with $LiAlH_4$ (200 mg, 5.28 mmol) at −78 °C. The mixture was warmed to room temperature. After 1 h it was diluted with Et_2O (20.0 mL) and quenched at 0 °C with H_2O (242 μL), 15% NaOH (aq) (242 μL), and H_2O (716 μL). After stirring for approximately 30 min, the formed precipitate was filtered off and washed thoroughly. The filtrate was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (60% PE/EtOAc) to yield diol (***R***,***R***)-**18** (28.5 mg, 0.17 mmol, 86%) as a colorless solid, and (***S***,***S***)-**18** (17.2 mg,

0.10 mmol, 52%), respectively. The analytical data are in full agreement with those reported in the literature.[14,16,44] A crystal structure analysis of (**S**,**S**)-**18** was obtained.[42] [Found: C, 71.91; H, 8.46. $C_{10}H_{14}O_2$ requires C, 72.26; H, 8.46%]; R_f (50% PE/EtOAc) 0.28; $[\alpha]_D^{20}$ +49 [*c* 0.50, $CHCl_3$, (**R**,**R**)-**18**]; [a]$_D^{20}$ −45 [*c* 0.50, $CHCl_3$, (**S**,**S**)-**18**]; ν_{max} (liquid film): 3333 (O–H-ν, br), 3083, 3063, 3027 (arom. C–H-ν), 2956, 2926, 2879 (aliph. C–H-ν), 1489 (arom. C=C-ν), 1454, 1431, 1378, 1340, 1276, 1198, 1084, 1064, 1020, 976, 928, 912, 761 (Ph, C–H-$\delta_{out\ of\ plane}$), 698 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 0.71 (3H, t, ^3J 7.2 Hz, CH_3), 2.06 (1H, m, C*H*Me), 2.82 (2H, br, O*H*), 3.73 (1H, dd, ^2J 10.9 Hz, ^3J 7.6 Hz, CH_aH$_b$), 3.78 (1H, d, ^2J 10.9 Hz, CH_bH$_a$), 4.56 (1H, d, ^3J 8.3 Hz, C*H*OH), 7.27–7.38 (5H, m, arom. C*H*); ^{13}C NMR ($CDCl_3$, 151 MHz) 13.8 (*C*H_3), 41.7 (*C*HCH$_3$), 67.9 (*C*H$_2$), 80.8 (*C*HOH), 126.7, 127.8, 128.4 (arom. *C*H), 143.3 (arom. C_{ipso}); HPLC (Chiralpak IC, 90% *n*-hexane/*i*-PrOH, flow rate 1.0 mL/min, detection UV at 220 nm) t_R (**R**,**R**)-**18** 14.8 min, ee >97%; t_R (**S**,**S**)-**18** 11.4 min, ee >99%.

*4.5.3. (2S,Z)- and (2R,Z)-Diethyl 2-hydroxyhept-4-enedioate [(**2S**)-**23a**] and [(**2R**)-**23a**].* According to general procedure 8 allylboronate (**S**)-**13** or (**R**)-**13** (400 mg, 0.68 mmol) was dissolved in CH_2Cl_2 (340 μL) at 0 °C, before a solution of ethyl glyoxylate (**22**) in toluene (50%, 175 μL, 0.88 mmol) was added. After 2 days stirring at room temperature solvents were removed under reduced pressure. Repeated flash column chromatography (90% PE/EtOAc to 80 PE/EtOAc) furnished diester (**2S**)-**23a** (132.8 mg 0.58 mmol, 85%, ee >99%) and (**2R**)-**23a** (128.9 mg 0.56 mmol, 83%, ee >99%) as a clear liquid.

Microwave assisted addition: A 10 mL microwave vessel equipped with a stirrer bar was charged with allylboronate (**R**)-**13** (200 mg, 0.34 mmol), a solution of ethyl glyoxylate (**22**) in toluene (50%, 134 μL, 0.68 mmol), and 0.51 mL CH_2Cl_2. The vessel was closed with an IntelliVent© septum and heated to a temperature of 65 °C using a microwave reactor. Herein, the power was limited to 150 W, the 'cooling' function was on permanently. After 3 h of irradiation, all volatile compounds were removed under reduced pressure. After repeated flash column chromatography (90% PE/EtOAc to 80% PE/EtOAc) product (**2R**)-**23a** (60.3 mg, 0.26 mmol, 77%, 89% ee) was isolated as a colorless liquid.

Thermal conditions: A 10 mL microwave vessel equipped with a stirrer bar was charged with allylboronate (**R**)-**13** (200 mg, 0.34 mmol) and 0.51 mL CH_2Cl_2. It was closed with an IntelliVent© septum and heated to 65 °C in an oil bath. After 30 min a solution of ethyl glyoxylate (**22**) in toluene (50%, 134 μL, 0.68 mmol) was added to the closed vessel through a cannula. After stirring for 3 h, the vessel was removed from the oil-bath and freed from all volatile compounds under reduced pressure. NMR of the crude product indicated incomplete conversion; a sample of (**2R**)-**23a** was isolated by flash column chromatography (90% *n*-pentane/MTBE to 70% *n*-pentane/MTBE) and submitted to HPLC: 99% ee. [Found: C, 57.63; H, 7.74. $C_{11}H_{18}O_5$ requires C, 57.38; H, 7.88%]; R_f (80% PE/EE) 0.09; $[\alpha]_D^{20}$ +1.0 [*c* 1.4, $CHCl_3$, (**2S**)-**23a**]; $[\alpha]_D^{20}$ −1.1 [*c* 1.2, $CHCl_3$, (**2R**)-**23a**]; ν_{max} (liquid film) 3650–3200 (br), 2983, 2937, 2906, 1734, 1254, 1196, 1180, 1105, 1031, 860, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 1.26 (3H, t, ^3J 7.1 Hz, β-OCH_3CH$_2$), 1.30 (3H, t, ^3J 7.1 Hz, α-OCH_3CH$_2$), 2.46–2.60 (2H, m$_c$, CH(OH)CH_2), 3.11 (1H, ddd, ^2J 15.5 Hz, ^3J 7.3 Hz, ^4J 1.5 Hz, CH_aH$_b$COOEt), 3.12 (1H, ddd, ^2J 15.5 Hz, ^3J 7.3 Hz, ^4J 1.5 Hz, CH$_a$H$_b$COOEt), 4.15 (2H, q, ^3J 7.1 Hz, β-OCH_2CH$_3$), 4.22–4.28 (3H, m, C*H*OH and α-OCH_2CH$_3$), 5.63 (1H, dtt, ^4J 1.5 Hz, ^3J 10.8, 7.5 Hz, C*H*=CHCH$_2$COOEt), 5.77 (1H, dtt, ^4J 1.5 Hz, ^3J 10.8, 7.3 Hz, CH=C*H*CH$_2$COOEt); ^{13}C NMR ($CDCl_3$, 151 MHz) 14.2 (α-OCH$_2$*C*H$_3$), 14.2 (β-OCH$_2$*C*H$_3$), 32.3 (CH(OH)*C*H$_2$), 33.1 (*C*H$_2$COOEt), 60.8 (β-O*C*H$_2$CH$_3$), 61.8 (α-O*C*H$_2$CH$_3$), 69.9 (*C*HOH), 124.9 (CH=*C*HCH$_2$COOEt), 126.7 (*C*H=CHCH$_2$COOEt), 171.7 (β-*C*OOEt), 174.3 (α-*C*OOEt). HRMS (ESI): $[M+Na]^+$, found 253.1048. $C_{11}H_{18}O_5$^{23} Na $[M+Na]^+$, requires 253.1047; HPLC (Chiracel OD-H, 90% *n*-hexane/*i*-PrOH, flow rate 0.5 mL/min, detection 210 nm) t_R (**2S**)-**23a** 14.6 min; t_R (**2R**)-**23a** 17.3 min.

*4.5.4. (2S,Z)- and (2R,Z)-Ethyl 2,7-dihydroxyhept-4-enoate [(**2S**)-**23b**] and [(**2R**)-**23b**].* According to general procedure 8 allylboronate (**S**)-**20** or (**R**)-**20** (400 mg, 0.73 mmol) was dissolved in CH_2Cl_2 (365 μL) at 0 °C, before a solution of ethyl glyoxylate (**22**) in toluene (50%, 188 μL, 0.95 mmol, 1.3 equiv) was added. After 3 days stirring at room temperature and removal of solvents under reduced pressure, ester (**2S**)-**23b** was isolated by flash column chromatography (70% PE/EtOAc to 30% PE/EtOAc) (115.4 mg, 0.61 mmol, 84%, ee 98%) as a clear liquid; ester (**2R**)-**23b** was obtained in 77% (105.4 mg, 0.56 mmol, ee 99%). [Found: C, 57.27; H, 8.50. $C_9H_{16}O_4$ requires C, 57.43; H, 8.57%] R_f (30% PE/EtOAc) 0.14; $[\alpha]_D^{20}$ −30.2 [*c* 1.1, $CHCl_3$, (**2S**)-**23b**]; $[\alpha]_D^{20}$ +30.4 [*c* 1.1, $CHCl_3$, (**2R**)-**23b**]; ν_{max} (liquid film) 3600–3050 (br), 2982, 2938, 2901, 1730, 1267, 1199, 1111, 1083, 1034, 862, 721 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 1.26 (3H, t, ^3J 7.1 Hz, OCH$_2$CH_3), 2.36 (2H, ddd, ^3J 7.5, 6.2 Hz, ^4J 1.2 Hz, CH_2CH$_2$OH), 2.49 (1H, ddd, ^2J 14.5 Hz, ^3J 7.5 Hz, ^4J 1.2 Hz, CH(OH)CH_aH$_b$), 2.53 (1H, s br, O*H*), 2.57 (1H, ddd, ^2J 14.5 Hz, ^3J 7.5 Hz, ^4J 1.2 Hz, CH(OH)CH$_a$$H_b$), 3.45 (1H, s br, O*H*), 3.67 (2H, t, ^3J 6.2 Hz, CH_2OH), 4.20 (2H, q, ^3J 7.1 Hz, OCH_2CH$_3$), 4.22 (1H, m, C*H*(OH)), 5.51 (1H, dtt, ^3J 11.0 Hz, ^3J 7.5 Hz, ^4J 1.2 Hz, C*H*C=CHCH$_2$CH$_2$OH), 5.57 (1H, dtt, ^3J 11.0, 7.5 Hz, ^4J 1.2 Hz, CHC=C*H*CH$_2$CH$_2$OH); ^{13}C NMR ($CDCl_3$, 151 MHz) 14.2 (OCH$_2$*C*H$_3$), 30.61 (*C*H$_2$CH$_2$OH), 32.06 (C(OH)H*C*H$_2$), 61.69 (*C*H$_2$OH), 61.71 (O*C*H$_2$CH$_3$), 70.0 (*C*(OH)H), 126.3 (*C*HC=CHCH$_2$CH$_2$OH), 130.0 (CHC=*C*HCH$_2$CH$_2$OH), 174.4 (*C*O$_2$Et). HRMS (ESI): $[M+Na]^+$, found 211.0942. $C_9H_{16}O_4$^{23}Na $[M+Na]^+$, requires 211.0941; HPLC (Chiracel OD-H, 90% *n*-hexane/*i*-PrOH, flow rate 0.5 mL/min, detection 202 nm) t_R (**2S**)-**23b** 17.0 min, t_R (**2R**)-**23b** 29.4 min.

*4.5.5. (2S,Z)- and (2R,Z)-Ethyl 7-(tert-butyldimethylsilyloxy)-2-hydroxyhept-4-enoate [(**2S**)-**23c**] and [(**2R**)-**23c**].* According to general procedure 8 allylboronate (**S**)-**21** or (**R**)-**21** (440.0 mg, 0.66 mmol) was dissolved in CH_2Cl_2 (330 μL) at 0 °C before a solution of ethyl glyoxylate (**22**) in toluene (50%, 171 μL, 0.86 mmol, 1.3 equiv) was added. After 4 days stirring at room temperature, the solvents were removed under reduced pressure. Repeated flash column chromatography (95% PE/EtOAc to 80% PE/EtOAc) yielded (**2S**)-**23c** as a clear liquid (84.0 mg 0.28 mmol, 42%, ee 97%); ester (**2R**)-**23c** was obtained in 59% (119.4 mg 0.39 mmol, ee 92%). [Found: C, 59.35; H, 9.86. $C_{15}H_{30}O_4Si$ requires C, 59.56; H, 10.00%]; R_f (80% PE/EtOAc) 0.30; $[\alpha]_D^{20}$ −0.2 [*c* 0.7, $CHCl_3$, (**2S**)-**23**]; $[\alpha]_D^{20}$ +0.1 [*c* 0.9, $CHCl_3$, (**2R**)-**23c**]; ν_{max} (liquid film) 3550–3200 (br), 2930, 2891, 2858, 1734, 1254, 1201, 1189, 1035, 832, 775, 737 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) 0.06 (3H, s, Si(CH_3)), 0.06 (3H, s, Si(CH_3)), 0.89 (9H, s, C(CH_3)$_3$), 1.30 (3H, t, ^3J 7.2 Hz, OCH$_2$CH_3), 2.28 (1H, dddd, ^2J 14.2 Hz, ^3J 7.4, 6.7 Hz, ^4J 1.4 Hz, CH_aH$_b$CH$_2$OTBS), 2.32 (1H, dddd, ^2J 14.2 Hz, ^3J 7.4, 6.7 Hz, ^4J 1.4 Hz, CH$_a$$H_bCH_2$OTBS), 2.43 (1H, dddd, ^2J 14.6 Hz, ^3J 7.5, 6.9 Hz, ^4J 1.4 Hz, CH(OH)CH_aH$_b$), 2.52 (1H, dddd, ^2J 14.6 Hz, ^3J 7.5, 6.9 Hz, ^4J 1.4 Hz, CH(OH)CH$_a$$H_b$), 2.88 (1H, d, ^3J 6.2 Hz, O*H*), 3.57 (2H, t, ^3J 6.7 Hz, CH_2OTBS), 4.24 (1H, ddd, ^3J 6.9, 6.2 Hz, ^4J 0.7 Hz, C*H*(OH)), 4.24 (2H, dq, ^3J 7.2 Hz, ^4J 0.7 Hz, OCH_2CH$_3$), 5.44 (1H, dtt, ^3J 10.9, 7.5 Hz, ^4J 1.5 Hz, CH=C*H*CH$_2$C(OH)H), 5.53 (1H, dtt, ^3J 10.9, 7.4 Hz, ^4J 1.4 Hz, C*H*=CHCH$_2$C(OH)H); ^{13}C NMR ($CDCl_3$, 151 MHz), −5.3 (Si(*C*H$_3$)$_2$), 14.2 (OCH$_2$*C*H$_3$), 18.4 (Si*C*(CH$_3$)$_3$), 26.0 (SiC(*C*H$_3$)$_3$), 31.1 (*C*H$_2$CH$_2$OTBS), 32.3 (CH(OH)*C*H$_2$), 61.6 (O*C*H$_2$CH$_3$), 62.7 (*C*H$_2$OTBS), 70.2 (*C*HOH), 124.8 (CH=*C*HCH$_2$C(OH)H), 130.1 (*C*H=CHCH$_2$C(OH)H), 174.5 (*C*OOEt). HRMS (ESI): $[M+Na]^+$, found 325.1805. $C_{15}H_{30}O_4$^{23}Na^{28}Si $[M+Na]^+$, requires 325.1806; HPLC (Chiracel OD-H, 98% *n*-hexane/*i*-PrOH, flow rate 0.5 mL/min, detection 210 nm) t_R (**2S**)-**23c** 11.1 min, t_R (**2R**)-**23c** 13.1 min.

*4.5.6. (2R,3R,Z)- and (2S,3S,Z)-Ethyl 7-(dimethylamino)-2-hydroxy-3-methyl-7-oxohept-4-enoate [(**R**,**R**)-**23d**] and [(**S**,**S**)-**23d**].* According to general procedure 8 allylboronic ester (**R**)-**16b** or (**S**)-**16b** (150 mg, 0.25 mmol, 1.0 equiv) was dissolved in abs CH_2Cl_2 (124 μL) and treated with a 50% solution of ethyl glyoxylate (**22**) in toluene (54.2 μL, 27.9 mg, 0.27 mmol, 1.1 equiv). The reaction mixture was

stirred for 2 days. ^{1}H and ^{13}C NMR of the crude product confirmed the (*Z*)/(*E*) diastereomeric ratio to be >99:1. The crude product was purified by flash column chromatography on silica gel (85% PE/EtOAc) to yield amide (***R*,*R***)-**23d** as a colorless oil (33.8 mg, 0.14 mmol, 56%); amide (***S*,*S***)-**23d** was obtained in 58% (40.1 mg, 0.16 mmol). The product could even at 0 °C not be stored longer than 2 months. [Found: C, 59.41; H, 8.63; N, 5.71. $C_{12}H_{21}NO_4$ requires C, 59.246; H, 8.70; N, 5.71%]; R_f (50% PE/EtOAc) 0.04; R_f (30% *n*-Pe/Et_2O) 0.02; $[\alpha]_D^{20}$ +12 [*c* 1.26, $CHCl_3$, (***R*,*R***)-**23d**]; $[\alpha]_D^{20}$ +12 [*c* 1.02, $CHCl_3$, (***S*,*S***)-**23d**]; ν_{max} (liquid film): 3397 (O–H-ν, br), 2971, 2931, 2875 (aliph. C–H-ν), 1737 (C=O-ν), 1628 (olef. C=C-ν), 1499, 1453, 1399, 1370, 1262, 1223, 1204, 1145, 1112, 1027, 991, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) 1.08 (3H, d, ^3J 6.8 Hz, C*H*$_3$), 1.29 (3H, t, ^3J 7.2 Hz, $COCH_2CH_3$), 2.72 (1H, br, O*H*), 2.92 (1H, m, C*H*CH_3), 2.95 (3H, s, NCH_3), 3.03 (3H, s, NCH_3), 3.07 (1H, ddd, ^2J 15.8 Hz, ^3J 6.8 Hz, ^4J 1.5 Hz, CH_aH_b), 3.18 (1H, ddd, ^2J 15.8 Hz, ^3J 7.2 Hz, ^4J 1.5 Hz, CH_bH_a), 4.04 (1H, d, ^3J 4.9 Hz, C*H*OH), 4.22 (2H, m, $COCH_2CH_3$), 5.54 (1H, ddt, ^3J 10.9, 7.3 Hz, ^4J 1.5 Hz, C*H*=$CHCH_2$), 5.65 (1H, dtd, ^3J 10.9, 7.2 Hz, ^4J 0.8 Hz, CH=C*H*CH_2); ^{13}C NMR ($CDCl_3$, 151 MHz) 14.2 ($COCH_2CH_3$), 16.9 (CH_3), 32.6 (CH_2), 35.6 (NCH_3), 36.4 ($CHCH_3$), 37.3 (NCH_3), 61.5 ($CO_2CH_2CH_3$), 74.6 (*C*HOH), 123.5 (CH=$CHCH_2$), 132.7 (*C*H=$CHCH_2$), 171.1, 173.9 (CO_2Et, CO_2NMe_2); *m*/*z* (GC/MS, EI, 70 eV) 243 (0.2) [M^+], 223 (8), 205 (5), 149 (100); *m*/*z* (ESI, positive ion, N_2) 244 (100) [$(M+H)^+$]; HPLC (Chiracel OD-H, 90% *n*-hexane/*i*-PrOH, flow rate 0.5 mL/min, detection UV 220 nm) t_R (***R*,*R***)-**23d** 45.2 min, ee >99%; t_R (***S*,*S***)-**23d** 28.8 min, ee >99%.

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Supplementary data

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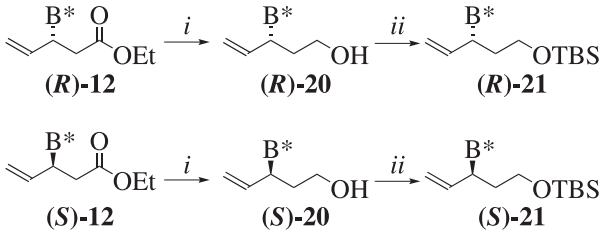

Scheme 13. Conditions: (*i*) 2.00 equiv DiBAlH, −78 °C to rt, CH_2Cl_2, 2 h; (*ii*) 1.10 equiv TBSCl, 1.05 equiv imidazole, CH_2Cl_2, 0 °C to rt, over night.

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