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Diastereo- and Enantiomerically Pure Allylboronates: Their Synthesis and Scope

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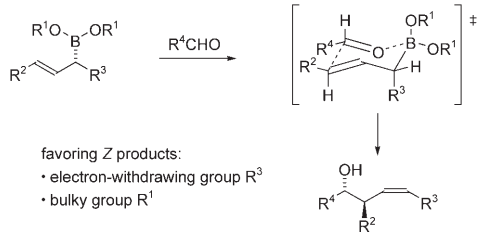
Abstract: Allylboronates are highly attractive reagents for allyl additions. Enantiomerically pure, stable reagents with a stereogenic centre in α-position to boron are especially versatile, albeit often difficult to synthesize. Starting from boron-containing allyl alcohols **6** and **7**, which are discussed in detail herein, a set of reagents were obtained via [3,3]-sigmatropic rearrangements and consecutive transformations in the side chain. The configurations could be established first by chemical correlation, but also by X-ray crystallography (**16**, **18**, **34**, and **39**). Allyl additions were performed resulting in the formation of predominantly (*Z*)-configured homoallylic alcohols (**31**, **43**–**45**) with high enantiomeric excess. Detailed investigations on the matched–mismatched interaction between the reagents **15**/**16** (and *ent*-**15**/*ent*-**16**, respectively) and isopropylidene glyceraldehyde **42d** are presented.

Keywords: allylation · asymmetric synthesis · boron · rearrangement · sigmatropic reactions

Introduction

Reagents for allyl additions are a key for the success of many syntheses. From the range of possible allyl–metal compounds, the boron derivatives are special: It can be assumed that the reliability in terms of yield, selectivity and especially predictability is one reason. The reagents are also nontoxic and usually not very costly. The transformations can be performed using rather mild reaction conditions, thus various functional groups are also tolerated.[1] The enantio- and diastereomerically pure allyl- and crotylboronic esters introduced by Roush et al. in 1985,[2] proved to be especially versatile and many applications have been reported. Related allylboranes were reported by Brown et al.[3] A common feature of these reagents is that the stereochemical information is in all cases in the periphery of the transition state for the addition. A stereogenic centre in the core of the transition state should be advantageous in terms of selectivity for the formation of the homoallylic alcohol. To achieve the goal, a substituent in position α to boron in the allyl moiety would be needed. Exemplary systematic work on the issue has been published by Hoffmann et al. who proved that by increasing the steric bulk of the boronic ester protecting group ("R^1", Scheme 1) the (*Z*)-olefinic product would be favored.[4] Furthermore, an electron-withdrawing group "R^3" will also enhance the (*Z*)-selectivity. The relative "R^2"/"R^4"-configuration is still determined by the configuration of the double bond in the reagent and the favored equatorial positioning of the bulky substituent of the aldehyde.



Scheme 1. Stereochemical reasoning of allyl additions.

Hoffmann et al. synthesized their reagents either by Matteson homologation using a diastereo- and enantiomerically pure dichloromethylboronic ester or by diastereoselective crotylation of a pure boric ester. Alternatively, appropriate enantiomerically pure alkenylboron derivatives could be rearranged using thionylchloride or sodium hydroxide. Purification proved to be difficult in all cases, the separation of diastereomers was not possible due to the lack of stability of

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the intermediates. Nevertheless, the reagents have been successfully applied in several natural product syntheses.[5] Fang and Aggarwal used enantiomerically pure sulphur ylides to perform the stereoselective rearrangement: Alkenylboron compounds were thus converted to α-substituted allylboranes.[6] Another elegant approach was recently published by Roush et al. who used the (−)-diisopinocampheylborane for the hydroboration of an allenylboronic ester thus generating an allylboronic ester. After the first addition to an aldehyde, a second allylboronic ester with a stereogenic centre α to boron is generated that adds to a second aldehyde in a highly diastereoselective manner. The configuration (also of the double bond) is determined by the steric bulk of the boronic ester. Allenes were also used as substrates for selective hydroborations or diborations including some kinetic resolutions to furnish the corresponding reagents in high optical purity.[7] The Diels–Alder reaction could also be applied to yield allylboronic esters in a highly diastereo- and enantioselective manner.[5h,8] More recently Ito et al. reported a successful allylic substitution utilizing bis(pinacolato)diborane to furnish the desired products.[9] Hoppe et al. proved that allyltitanium species—derived by enantioselective deprotonation of allylcarbonates—could not only be directly used for allyl additions, but were also transformed to enantiomerically enriched allylboronic esters or allylstannanes.[10,11] It should be noted that among other methods, allylstannanes could also be generated via Ireland and Eschenmoser rearrangement of tin-substituted allyl alcohols. More broadly applicable are the corresponding allylsilanes that are also accessible via the corresponding sigmatropic reactions.[12] Allyl additions with these reagents generally lead to (*E*)-configured homoallylic alcohols. The (*Z*)-derivatives are generally more difficult to access, an obvious advantage of bulky boron reagents.

In order to enhance the stability of boron derivatives, we introduced diol **1**—readily available in both enantiomeric forms from tartrate[13]—as a convenient protecting group for boronic acids.[13b,14] We demonstrated that a wide variety of transformations in the side-chain "R" of esters **2** and **3**, respectively, are possible, without cleaving the carbon–boron bond. We speculated that the sometimes harsh reaction conditions of [3,3]-sigmatropic rearrangements (general scheme: see Figure 1) would not be a problem for this type of compounds. Hence, the γ,δ-unsaturated esters **4** and **5** should be available from allyl alcohols **6** or **7**. Indeed, we recently demonstrated that the approach is feasible;[15] herein we describe the full details of our findings.

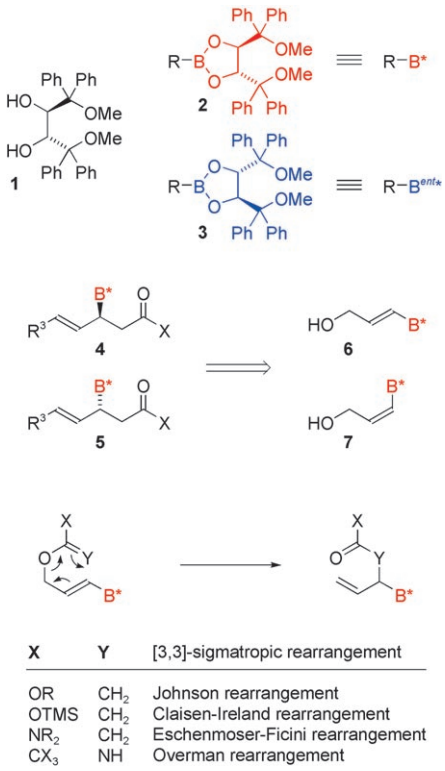
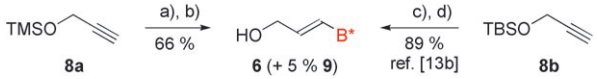


Figure 1. Abbreviations and general synthetic scheme.

Results and Discussion

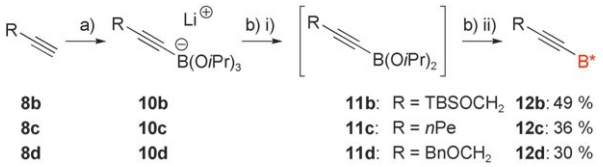
Synthesis of allyl alcohols: The (*E*)-allyl alcohol **6** is readily available from silyl-protected propargylic alcohols **8a** or **8b**, either via direct hydroboration of **8b**[13b] and consecutive deprotection or by using a conventional one-pot hydoboration (with dicyclohexylborane), oxidation (with Me_3NO), transesterification (with diol **1**) sequence with ether **8a** as substrate (Scheme 2);[14e,16] subsequent deprotection under acidic conditions furnished the desired product **6** in 66% yield. Direct hydroboration of the TMS-ether **8a** (TMS = Me_3Si) could not be achieved. While the TMS-protecting group is cheaper, the TBS route (TBS = tBuMe$_2$Si) is favored by a higher overall yield (up to 89%). The regioisomer **9** (see Scheme 5) was only isolated after the deprotection step in up to 5% yield.



Scheme 2. a) i) Cyclohexene, $H_3B{\cdot}Me_2S$, 1 h, DME, 0°C→RT; ii) **8a**, 1 h; iii) Me_3NO; iv) **1**; b) HCl, H_2O/EtOH, 66% over 2 steps; c) diol **1**, $H_3B{\cdot}Me_2S$, 3 h, CH_2Cl_2, 50°C, then **8b**, 120°C; d) HF, MeCN, 0°C, 89% over 2 steps.

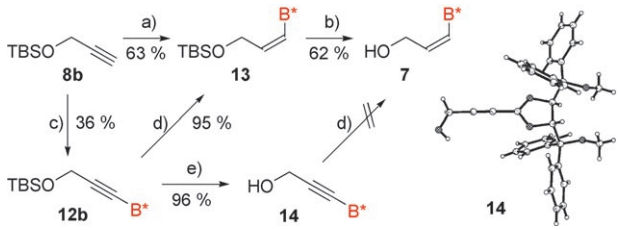
The synthesis of (*Z*)-alcohol **7** proved to be more difficult. As an alternative to the previously reported route via the corresponding vinyl iodide,[14f] we pursued a sequence involving the *syn* reduction of alkynylboronates[17] which in turn needed to be synthesized from alkyne **8** (**8**→**10**→**11**→**12**). Despite some optimization with the pentyl-derivative **8c**, we were unable to improve the yield beyond 49% (over three steps). The limiting step was the formation of ester **11** that was achieved by treatment of the ate-complex **10** with $BF_3{\cdot}Et_2O$.[18] However, omitting the step and directly performing the transesterification only led to cleavage of the

C–B bond. With protected propargylic alcohols **8b** and **8d** the yield further decreased and only 37 and 30% of alkynes **12b** and **12d** were obtained, respectively (Scheme 3). De-



Scheme 3. a) i) *n*BuLi, Et_2O, −78°C; ii) $B(OiPr)_3$; b) i) 1.33 equiv $BF_3{\cdot}Et_2O$, THF, −78°C; ii) diol **1**, THF, −78°C→RT.

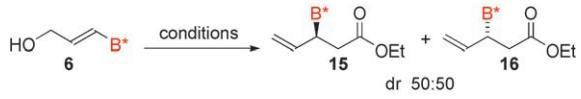
spite the fact that the reduction of alkynylboronic ester **12b** with hydrogen in the presence of Lindlar's catalyst was achieved to furnish (*Z*)-olefin **13** in high yield (95%, Scheme 4), we looked for an alternative since its deprotection yielded alcohol **7** in only 62%. On the other hand, desilylation of ether **12b** was readily achieved and product **14** was isolated in 96% yield as a crystalline solid; its structure was confirmed by X-ray crystallography. Unfortunately we were unable to successfully perform a (*Z*)-selective reduction of the triple bond of **14**; no alkenylboronic ester **7** could be isolated. In our hands, a one-pot sequence including a Rh^I-catalyzed hydroboration with catecholborane was most practical:[19] After transesterification with diol **1** the common intermediate **13** was directly obtained in moderate yield (63%; Scheme 4).[15c]



Scheme 4. a) Catecholborane, cat. $[Rh(cod)Cl]_2$, iPr_3P, Et_3N, cyclohexane, RT; ii) diol **1**, RT, 63%; b) HCl, H_2O/EtOH, 62%; c) see Scheme 3; d) H_2, Lindlar catalyst, cyclohexane, toluene, 95%; e) HCl, H_2O/MeOH, 96%.

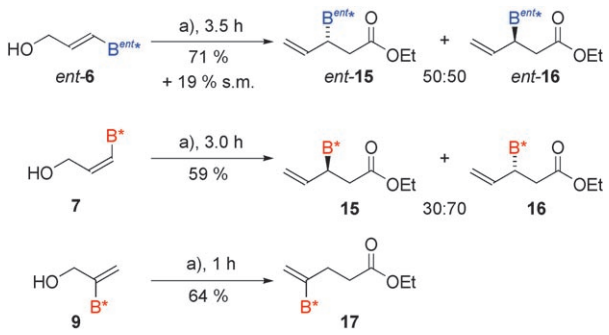
[3,3]-Sigmatropic rearrangements: Next, we investigated the possibility of [3,3]-sigmatropic rearrangements starting from alkenylboronic esters **6**, **7** and **9**.[15] The initial studies were performed utilizing alcohol **6** in a modified Johnson reaction.[20] It was immediately obvious that prolonged reaction times under the harsh reaction conditions (Table 1, entry 1) used will always lead to decomposition of boronic esters; no product **15** or **16** was obtained. While keeping the temperature high (135°C; lower temperatures dramatically decreased the rate and ultimately the yield), different acidic catalysts or catalyst loadings were tested (e.g. entries 2–4). Although both, amberlyst- and montmorillonite-catalyzed transformations provided reasonable amounts of allylboron-

Table 1. Johnson rearrangement with allyl alcohol **6**.



Entry	equiv $MeC(OEt)_3$	Catalyst	*T* [°C]	*t* [h]	Yield [%] **15**+**16**
1	8.6	0.21equiv $EtCO_2H$	135	12	0
2	7.0	Amberlyst	135	5	57
3	7.0	Montmorillonite KSF/O	135	9	65
4	7.0	0.06 equiv $EtCO_2H$	135	3.5	78(+19 **6**)

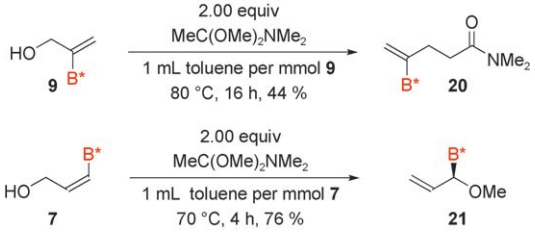
ic esters **15** or **16**, the best results were obtained when using standard conditions (entry 4: 0.06 equiv propionic acid, 3.5 h, 135°C) preventing prolonged heating and ensuring continuous removal of ethanol. Along with the 1:1 diastereomeric mixture of products (78%), 19% of the starting material **6** could be recovered. It should be noted that the highly stable and conveniently storable reagents are readily separated into the diastereo- and enantiomerically pure allylboronic esters **15** and **16** by means of MPLC. Under identical reaction conditions (Scheme 5) similar yields were obtained when utilizing allyl alcohols *ent*-**6** (yield: 71% of a 50:50 mixture of *ent*-**15**/*ent*-**16** + 19% starting material recovered), **7** (yield: 59% of a 30:70 mixture of **15**/**16**) or **9** (64% of **17**).



Scheme 5. a) 7.00 equiv $MeC(OEt)_3$, 0.06 equiv $EtCO_2H$, 135°C.

The Eschenmoser rearrangement proved to be more challenging with alcohols **6**, **7** and **9**.[21] The temperature was crucial for the success of the transformation to allylboronic esters **18**/**19** (Table 2): At 60°C no product could be detected (entry 1); however, when increasing the temperature, ≈80°C seem (entry 2) to be the optimum, since high degree of decomposition was observed at elevated temperature (use of xylene, entry 5, but at higher temperature). While effective removal of methanol is essential in all cases, the concentration of the substrate in toluene also has a marked influence on the yield (entries 2–4). Under these reaction conditions a 50:50 separable, stable mixture of diastereomers **18**/**19** was isolated in 73% yield. While the same rearrangement led to vinylboronic ester **20** in an unoptimized 44% yield when starting from alcohol **9**, none of the expected re-

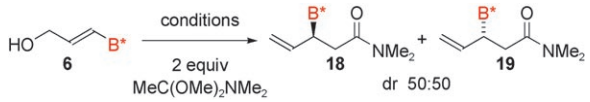
arrangement products were observed when using the (*Z*)-olefin **7** (Scheme 6). Instead, the only product we found was the highly interesting homoenolate equivalent **21**. We previ-



Scheme 6. Rearrangements using Eschenmoser conditions.[24]

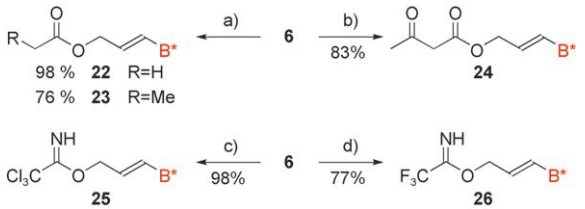
ously accounted an intramolecular complexation of the intermediate and a consecutive S_N2'-like substitution for its formation. However, a clear explanation for the high diastereoselectivity (only the shown diastereomer is formed!) is still elusive.

Table 2. Eschenmoser rearrangement with allyl alcohol **6**.



Entry	Solvent	T [°C]	t [h]	Yield [%] **18**+**19**
1	toluene (2 mL mmol^{-1} **6**)	60	18	0
2	toluene (2 mL mmol^{-1} **6**)	80	36	73
3	toluene (4 mL mmol^{-1} **6**)	78	20	45
4	toluene (1 mL mmol^{-1} **6**)	78	25	64
5	xylene (1 mL mmol^{-1} **6**)	80	24	65

Next, we looked for further alternatives to the above shown reactions including Claisen–Ireland-,[22] Carroll-,[23] and Overman-type[24] rearrangements. The syntheses of the precursors were straightforward: Direct acylation of alcohol **6** gave the desired products (yield **22**: 98%; yield **23**: 76%; Scheme 7), the β-ketoester **24** was obtained utilizing diketene (83%),[25] and the trichloro- as well as the trifluoroacetimidates **25** (98%) and **26** (77%), respectively, were synthesized according to literature procedures.[26,27] Unfortu-

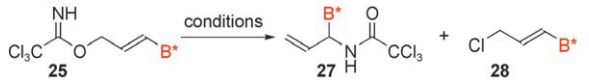


Scheme 7. a) Et_3N, cat. DMAP, CH_2Cl_2, Ac_2O for **22** or $(EtCO)_2O$ for **23**; b) THF, DMAP, diketene, RT, 23 h; c) 0.20 equiv NaH, Et_2O, 0°C, 1.20 equiv Cl_3CCN; d) 6.60 equiv F_3CCONH_2, 19.2 equiv DMSO, CH_2Cl_2, −78°C, 6.00 equiv $(COCl)_2$, 18.0 equiv Et_3N, 2.00 equiv DBU, then 1.00 equiv **6**.

nately, when treating either of the three esters **22**–**24** with base (e.g. with LDA), only decomposition of the boronic esters were observed. We then focused our efforts on the imidates **25**/**26**.

First, we tested thermal conditions to encourage the rearrangement of the chloro derivative **25** (Table 3). In refluxing toluene no conversion was observed (entry 1), only at higher temperature product formation was detected (entries 2–3). Prolonged heating led to higher conversion of **25**, but also to partial decomposition of the product. While microwave heating had no pronounced effect (entry 4), reducing the substrate concentration resulted in highest isolated yield (entry 5: 67% yield of **27** along with 10% starting material **25**). The diastereomeric ratio of crude product was deter-

Table 3. Overman rearrangement with trichloroacetimidate **25**.



Entry	Solvent (c=mmol **25** per mL)	T [°C] (t [h])	Yield [%]	dr **27**[a]
1	toluene (110 mM)	110 (11)	no conversion	–
2	1,2-dichlorobenzene (50 mM)	155 (56)	43 (**27**), 7 (**25**)	56:44
3	1,2-dichlorobenzene (30 mM)	170 (10)	52 (**27**), 22 (**25**)	59:41
4	1,2-dichlorobenzene (60 mM)	170[b] (4.4)	44% **27**, 21% **25**	57:43
5	1,2-dichlorobenzene (5 mM)	170[b] (16)	67 (**27**), 10 (**25**)	59:41
6[c]	THF (33 mM)	80 (23)	57 (**28**)	–
7[d]	toluene (67 mM)	80 (5)	**25**, decomposition	–

[a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture; [b] heated by microwave; [c] +5 mol% $[PdCl_2(MeCN)_2]$; [d] +5 mol% $[Pd(PPh_3)_4]$, K_2CO_3.

mined to be ≈60:40 in all cases. Pd-catalyzed variants (e. g. ref. [28]) that enabled lower reaction temperatures, either led to partial decomposition of the starting material or alternatively to considerable amounts of the undesired chloride **28** in 57% yield (entry 6+7). At this stage we did not further pursue the approach, since all attempts to separate the diastereomers **27** failed. We envisaged that we might overcome the problem with the related fluoro derivatives **29** (from **26**; Table 4). Again, only the thermal rearrangement was successful to a minor extent (entry 1: 20% product **29** and 14% starting material **26**) while the Pd-catalyzed reactions led to decomposition, only (entry 2+3). Separation of diastereomers was unsuccessful and consequently no further optimization was attempted.

In summary, while the boronic esters investigated proved to be more robust then previously anticipated, at this stage only few rearrangements could be successfully performed and led to separable mixtures of diastereomers. Best results were obtained utilizing standard Johnson conditions furnishing the corresponding carboxylic esters. While—not surpris-

Table 4. Overman rearrangement with trifluoroacetimidate **26**.

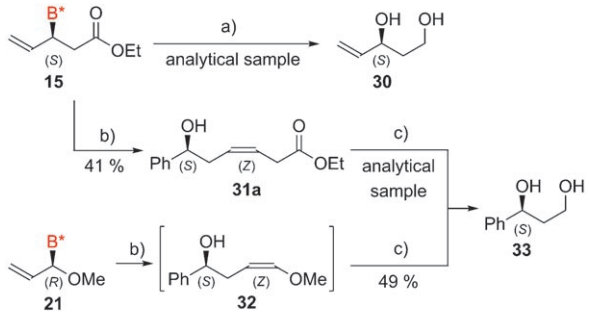
26 **29**

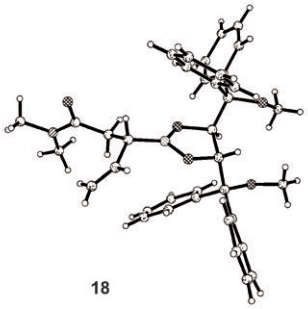
Entry	Solvent (*c*=mmol **26** per mL)	*T* [°C] (*t* [h])	Yield [%]	dr **29**[a]
1	1,2-dichlorobenzene (17 mM)	176 (11)	20 (**29**), 14 (**26**)	55:45
2[b]	toluene (67 mM)	80 (5)	decomposition	–
3[c]	toluene (67 mM)	80 (2)	decomposition	–

[a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture; [b] +5 mol% $[PdCl_2(MeCN)_2]$; [c] +5 mol% $[Pd(PPh_3)_4]$, K_2CO_3.

ingly—low auxiliary induced diastereoselectivity was observed throughout, substrate controlled rearrangements were previously shown to be highly selective furnishing one diastereomer only.[15b]

Determination of configuration: Until now all configurations presented were only assumed. In order to unequivocally assign them, we first turned to chemical correlations. Initially, compound **15** was directly converted to the known diol **30** by means of reduction with $LiAlH_4$ and oxidative work-up (Scheme 8). The small-scale transformation furnished the desired diol **30**, but unfortunately as an impure sample only. Nevertheless, the negative sign of the optical rotation[29] already hinted to the (*S*)-configuration in the allylboronic ester **15**, but it was obviously not the ultimate proof. Next, we turned to the allyl addition with reagent **15** and found the exclusive formation of the (*Z*)-olefin **31a**.





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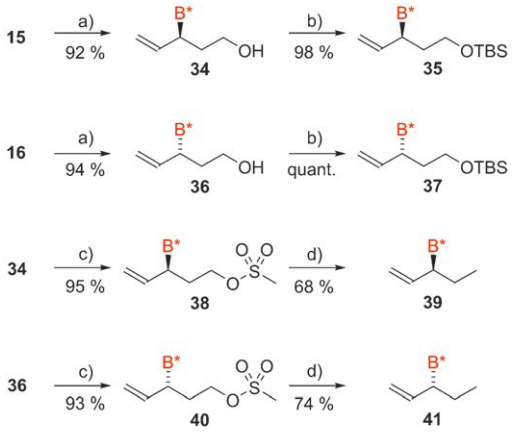
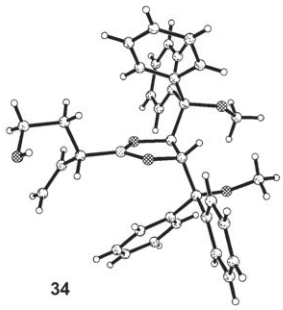
Scheme 8. Assignment of absolute configuration. a) $LiAlH_4$, THF, −78°C→RT, 2 h, then H_2O_2, 2 h; b) PhCHO, CH_2Cl_2, 0°C→RT; c) i) O_3, CH_2Cl_2, −78°C, then Me_2S; ii) $LiAlH_4$, THF 0°C, 1 h.

Ozonolysis and reduction led to the known diol **33**[30] whose configuration confirmed the structure of homoallylic alcohol **31a** and—assuming a favored transition state as depicted in Scheme 1—thus the configuration of allylboronic ester **15**. The same sequence allowed the assignment of the (*R*)-ester **21**. Later, X-ray crystallography confirmed not only the configuration of compound **16**,[15c] but also of amide **18**.[31]

Modification of side chain: Based on the knowledge that our type of boronic ester is relatively stable, we envisaged to broaden the scope of the new reagents, for example, in view of various orthogonal protecting group strategies, by simple functional group interconversions.[15a] The carboxylic ester moiety in **15** and **16** was the obvious choice for further transformations (Scheme 9). Reduction of ester **15** to the corresponding alcohol **34** was conveniently achieved by utilizing DiBAlH (92%); the introduction of a silyl-protecting group gave ether **35** in 98% yield. It should be noted that X-ray crystallography confirmed the previously assigned configuration of ester **15** by the solved structure of alcohol **34**.[31] By the same sequence as described above, ester **16** could be converted first to alcohol **36** and in a consecutive step to the new reagent **37** in 94% overall yield. Furthermore, alcohol **34** could be completely reduced by superhydride reduction of the corresponding mesylate **38** (95%) giving the ethyl derivative **39** in 68% yield; its configuration was secured by X-ray crystallography. Analogously, the diastereomeric reagent **41** was obtained from alcohol **36** via mesylate **40**.





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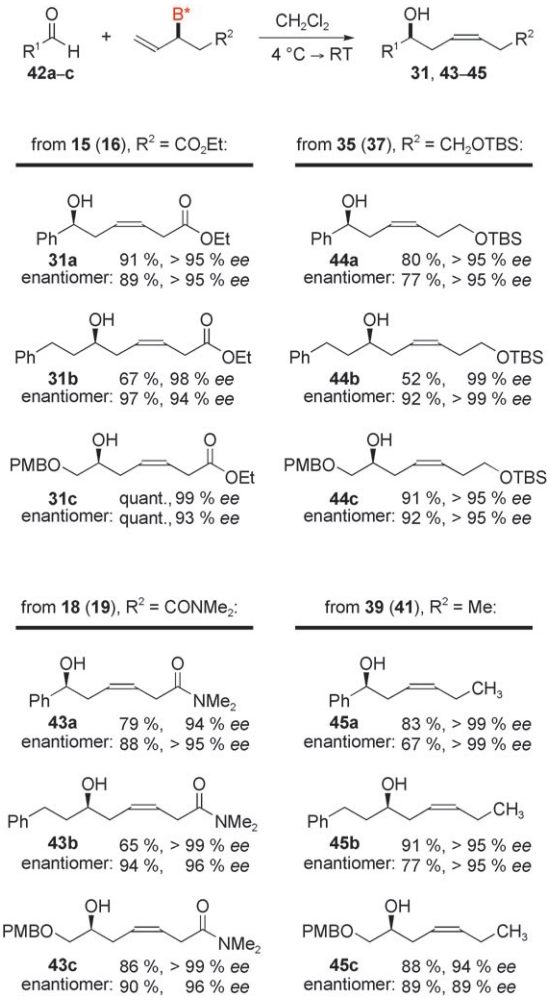
Scheme 9. a) DiBAlH, THF, −78°C; b) TBSCl, imidazole, CH_2Cl_2, 12 h; c) $MeSO_2Cl$, Et_3N, CH_2Cl_2; d) $LiEt_3BH$, THF.

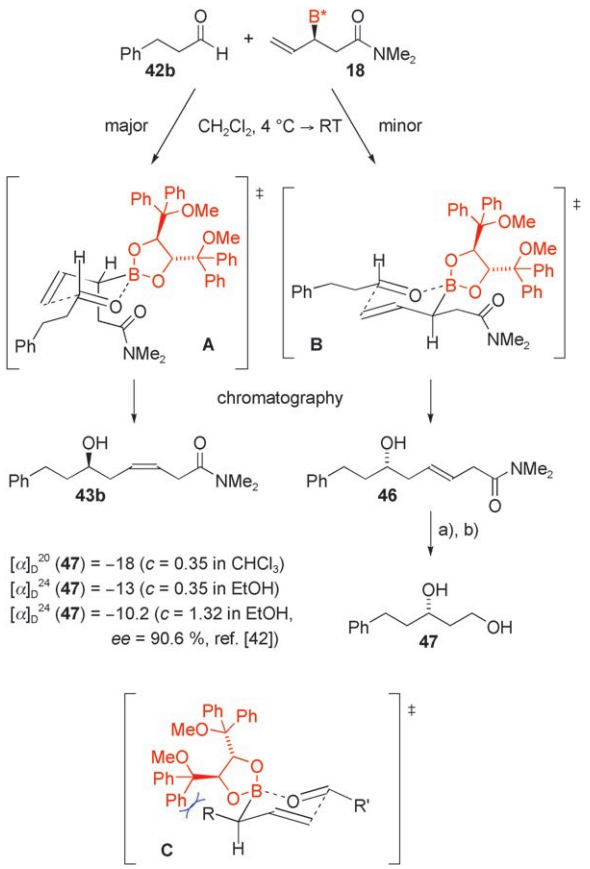
Allyl additions: With a plethora of reagents in our hands and the configurations completely assigned, we turned our attention to allyl additions utilizing all allylboronic esters synthesized (Scheme 10).



Scheme 10. Yields of allyl additions and *ee* values of their products.

In general, allyl additions of reagents **15**, **18**, **35** and **39** [abbreviated as the (*S*)-series] to benzaldehyde **42a** were unproblematic, the products were formed exclusively (as detected by NMR of the crude products) as the (*Z*)-configured olefins **31a**, **43–45a** (yield: 79–91 %; *ee* > 94 %). Similarly, the enantiomers *ent*-**31a** and *ent*-**43–45a** were obtained (yield: 67–89 %; *ee* > 95 %) from the diastereomeric boronic esters **16**, **19**, **37** and **41** [the (*R*)-series]. The most unreliable substrate proved to be aldehyde **42b**: Especially with the (*S*)-series of reagents major amounts of the (*E*)-olefin were detected in the crude product [crude **31b**: 93 %, *Z*/*E* 86:14; crude **43b**: 98 %, *Z*/*E* 70:30; crude **44b**: 89 %, *Z*/*E* 87:13]; yields given in Scheme 10 refer to isolated (*Z*)-products. It should be noted that (*E*)-**43b** was the only (*E*)-isomeric compound that could be obtained in pure form. When isolating product **45b** (91 %) no second diastereomer was detected. However, the enantiomeric ratio was surprisingly low (84 % *ee*). Within the (*R*)-series no such problems occurred and the homoallylic alcohols *ent*-**31b** and *ent*-**43–45b** were formed exclusively as the (*Z*)-diastereomers (yield: 77–97 %; *ee* > 94 %). The general trend also remained when using aldehyde **42c** albeit to a lesser extent: Whereas in the (*S*)-series regularly marginal amounts of the (*E*)-side-product could be detected [yields of **31c** and **43–45c**: 86–92 %; *ee* > 94 %], the (*R*)-series furnished the pure (*Z*)-products *ent*-**31c** and *ent*-**43–45c** (yield: 89–92 %; *ee* > 87 %). In a preliminary experiment it was also found that triethylsilyl-protected glycolic aldehyde was not a suitable substrate for allyl additions; the yields were low.

The reason for the relatively high (*E*)-selectivity—especially when using aldehyde **42b** and reagent **18**—is not completely understood (Scheme 11). The favored transition states **A** and **B** en route to homoallylic alcohols **43b** and **46** (the configuration was confirmed by transformation to the known diol **47** and comparison of the optical rotation) are obvious; however, why these substituents support the pseudo-equatorial positioning of all substituents (in **B**) remains unclear. Nevertheless, when comparing transition state **B** with the related transition state **C** for the (*R*)-series, a notable difference became obvious: One bulky group of the remote auxiliary [**C**; (*R*)-series only] is situated in the vicinity of the residue in equatorial position thus rendering this route irrelevant.

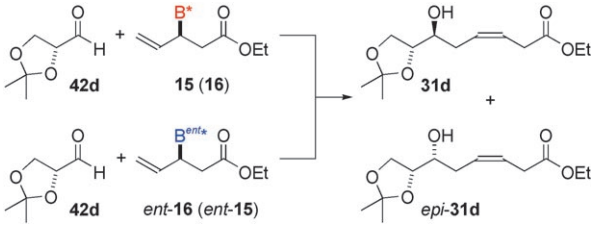


Scheme 11. a) O_3, CH_2Cl_2, –78 °C; Me_2S. b) $LiAlH_4$, THF, 56 % over 2 steps.

Allyl additions using isopropylidene glyceraldehyde: Finally, we investigated matched/mismatched interactions between diastereomeric reagents and an aldehyde bearing a stereogenic centre. Since the substrate selectivity is usually relatively difficult to overcome when using isopropylidene glyceraldehyde (**42d**),[32] we took this aldehyde for our studies.

First, we looked at the ester reagents **15** and **16** (Table 5). The (*E*)-product was not observed in any case; the yields were generally high (86–92%). Substrate-controlled addition leads to the *anti*-product **31d**, while reagent control will either favor **31d** (entry 1: reagent **15**; dr 97:3) or *epi*-**31d** (entry 2: reagent **16**; dr 30:70). Obviously, the directing effect of the substrate cannot be overruled completely in any case; however, with reagent **16** favoring the (*R*)-product *epi*-**31d** a distinct preference for its formation was found. Beside the influence of the stereogenic centre in α-position to the boron moiety, the configuration of the auxiliary could also have a directing effect. Hence we turned our attention to the enantiomeric reagents *ent*-**15** and *ent*-**16** (entry 3+4), respectively. The effect of the auxiliary is small, but distinct: Within the limits of NMR spectroscopy only one diastereomer **31** could be detected when utilizing allylboronic ester *ent*-**16**, while the *syn*-product *epi*-**31d** was formed with lower selectivity (as compared to entry 2) with reagent *ent*-**15** (entry 3: dr 35:65). In summary, substrate control was best matched with the (3*S*,4′*S*,5′*S*)-reagent *ent*-**16**.

Table 5. Allyl additions of reagents **15**, **16** *ent*-**15** and *ent*-**16** to aldehyde **42d**.

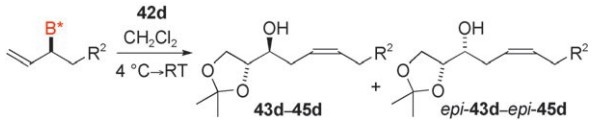


Entry	Reagent	Yield [%]	dr **31d**/*epi*-**31d**[a]
1	**15**	86	97:3
2	**16**	89	30:70
3	*ent*-**15**	92	35:65
4	*ent*-**16**	91	>99:1

[a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

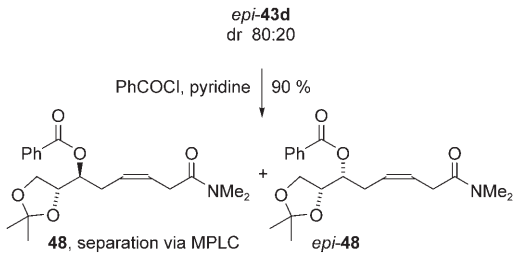
The same trend was observed when aldehyde **42d** was treated with the remaining sets of reagents (Table 6): Again, only (*Z*)-products were observed in moderate to high yield (63–91%). In all cases the *anti*-products **43d**–**45d** were predominantly formed with good to excellent selectivity when utilizing allylboronic esters of the (*S*)-series (entries 1,3,5), while the (*R*)-series led to the *syn*-products *epi*-**43d**–*epi*-**45d**, albeit with low diastereoselectivity (entries 2,4,6). Although diastereomerically pure products were obtained in some cases, it should be noted that the diastereomers are not always easily separated by column chromatography. In one case a further derivatization was performed in order to obtain a complete set of analytical data for the diastereoisomers: An 80:20 diastereomeric mixture of homoallyl alcohols *epi*-**43d** and **43d** were benzoylated furnishing esters *epi*-**48** and **48** in 90% yield; the products are readily separable by means of MPLC.

Table 6. Allyl additions of reagents **15**, **16**, *ent*-**15** and *ent*-**16** to aldehyde **42d**.



Entry	Reagent	R^2	Yield [%]	Product	dr[a]
1	**18**	$CONMe_2$	63	**43d**/*epi*-**43d**	>99:1
2	**19**	$CONMe_2$	75	**43d**/*epi*-**43d**	27:73
3	**35**	CH_2OTBS	69	**44d**/*epi*-**44d**	89:11
4	**37**	CH_2OTBS	90	**44d**/*epi*-**44d**	29:71
5	**39**	CH_3	81	**45d**/*epi*-**45d**	95:5
6	**41**	CH_3	91	**45d**/*epi*-**45d**	30:70

[a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture.



Conclusion

We have reported the synthesis of a set of new enantio- and diastereomerically pure boron reagents for allyl additions as well as their configurational assignment. Key reactions were [3,3]-sigmatropic rearrangements followed by standard transformations, albeit in the presence of the boronic ester moiety. The scope of the consecutive allylation was shown in detail proving that the additions were dominated by the stereogenic centre in α-position to boron thus furnishing predominantly (*Z*)-homoallylic alcohols. In some cases the products were obtained in up to quantitative yield and/or as a single enantiomer. With a dominant chiral substrate **42d** a conclusive investigation of matched/mismatched interaction was performed leading either exclusively to the *anti*-products or—overcoming to some extent the substrate-selectivity—with low selectivity for the *syn*-products.

Experimental Section

Unless specified the reactions were carried out by using standard Schlenk techniques under dry N_2 with magnetic stirring. Glassware was oven-dried at 120°C over night. Solvents were dried and purified by conventional methods prior to use; tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Common solvents for chromatography (petroleum ether 40–60°C, EtOAc) were distilled prior to use. Column chro-

matography and flash column chromatography were performed on silica gel 60, 0.040–0.063 mm (230–400 mesh). TLC (monitoring the course of the reactions) was performed on pre-coated plastic sheets (Polygram SIL G/UV254, Macherey-Nagel) with detection by UV (254 nm) or by coloration with cerium molybdenum solution [phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), concd. H_2SO_4 (60 mL), H_2O (940 mL)]. Preparative medium pressure liquid chromatography (MPLC) was performed with a Labomatic pump (MD-50/80/100), a packed column (25×300 mm or 40×475 mm), LiChroprep, Si 60 (15–25 μm) and UV detector (254 nm). HPLC was performed on a Pharmacia device equipped with a Chiralcel OD or a Dionex/Gynkotek device with a Chiralcel OD-H column. ^1H and ^{13}C NMR spectra were recorded at RT in $CDCl_3$ with a Bruker ARX 300/500 or a Varian Inova 400. Chemical shifts are given in ppm relative to TMS as internal standard [^1H: $Si(CH_3)_4 = 0.00$ ppm] or relative to the resonance of the solvent (^{13}C: $CDCl_3 = 77.0$ ppm); coupling constants J are given in Hz. Higher order δ and J values are not corrected. ^{13}C signals were assigned by means of H,H COSY and HSQC or HMBC spectroscopy. Microanalyses and gas chromatographic determinations were performed at the Institut für Organische Chemie, Stuttgart. Melting points or softening ranges (Büchi 510 and B-540) are not corrected respectively. Specific rotations were measured at 20 °C. IR spectra were obtained on a Perkin–Elmer 283, Bruker IFS 28 or a Perkin–Elmer Spectrum One. MS were recorded on a Finnigan MAT 95 [FAB (NBA: 3-nitrobenzyl alcohol), EI, CI], a Varian MAT 711 (EI), a Finnigan MAT LC-Q (ESI-1, LC-MS-MS) or a Applied Biosystems/MDS SCIEX 4000 Q TRAP (ESI-2, LC-MS-MS); for HRMS perfluorokerosene was the reference; directly injected solution for LC-MS-MS: one part of a 0.5 mM solution of the substance in CH_3CN, three parts CH_3CN, one part 0.1% aqueous NH_4HCO_2 solution. For convenience and data comparison the boronate moieties B* and B^{ent}* are set to the last priority of substituents contradicting the IUPAC nomenclature. Diol **1** and diol *ent*-**1** were synthesized according to literature procedures.[13] 1-Heptyne (**8c**) is commercially available. Benzyl propargyl ether (**8d**) was prepared according to a literature procedure, but with THF as the only solvent.[33] The analytical data are in full agreement to those previously reported.[34] (*R*)-Isopropylidene glycerine aldehyde (**42d**) was prepared according to literature procedures.[35] Triethylorthoacetate was distilled prior to use, whereas *N*,*N*-dimethylacetamiddimethylacetal was used as purchased (90% purity). O_3/O_2-mixtures were prepared with the Ozon generator 500 (Fischer technology) with an O_2 stream of 150 L h^{-1} (the device was adjusted to full power) or with the Sander Labor-Ozonisator 300.5 with an O_2 stream of 100 L h^{-1} and adjusted to 0.33 A.

X-ray crystallographic analysis:[31] The crystal data for compounds **14**, **18** and **34** were determined with a Siemens P4 diffractometer with graphite monochromator in the ω-scan mode with $Cu_{K\alpha}$ ($\lambda = 1.54178$ Å) radiation. Alkynylboronate **14**:[31] $C_{33}H_{31}BO_5$, $M_r = 518.41$, colorless, $T = 293$ K, crystal size 0.50×0.10×0.10 mm, orthorhombic, $P2_12_12_1$, $a = 10.1832(6)$, $b = 15.8268(7)$, $c = 17.6158(15)$ Å, $V = 2839.1(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.212$ g cm^{-3}, $\mu = 0.641$ mm^{-1}, $F(000) = 1096$, θ range = 3.75 to 59.95°, 2270 measured/independent reflections, 1477 reflections with [$I > 2\sigma(I)$]; the structure was solved by direct methods and refined by full-matrix least-squares on F^2 for all data weights to $R = 0.0952$, $wR = 0.2081$, $S = 1.045$, H atoms were treated as riding atoms, max. shift/error < 0.001, residual $\rho_{max} = 0.197$ Å^{-3}. Alkynylboronate **18**:[31] $C_{37}H_{40}BNO_5$, $M_r = 589.53$, colorless, $T = 293$ K, crystal size 0.20×0.15×0.05 mm, orthorhombic, $P2_12_12_1$, $a = 10.7765(5)$, $b = 14.7879(9)$, $c = 20.8366(10)$ Å, $V = 3320.6(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.179$ g cm^{-3}, $\mu = 0.613$ mm^{-1}, $F(000) = 1256$, θ range = 3.67 to 59.99°, 3200 measured/independent reflections, 1318 reflections with [$I > 2\sigma(I)$]; the structure was solved by direct methods and refined by full-matrix least-squares on F^2 for all data weights to $R = 0.1887$, $wR = 0.2528$, $S = 1.068$, H atoms were treated as riding atoms, max. shift/error < 0.001, residual $\rho_{max} = 0.308$ Å^{-3}. Allylboronate **34**:[31] $C_{35}H_{37}BO_5$, $M_r = 548.48$, colorless, $T = 293$ K, crystal size 0.55×0.10×0.07 mm, monoclinic, $P2_1$, $a = 18.556(2)$, $b = 9.2194(18)$, $c = 19.929(3)$ Å, $V = 3038.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.199$ g cm^{-3}, $\mu = 0.623$ mm^{-1}, $F(000) = 1168$, θ range = 2.49 to 57.50°, 4994 measured/independent reflections, 2513 reflections with [$I > 2\sigma(I)$]; the structure was solved by direct methods and refined by full-matrix least-squares on F^2 for all data weights to $R = 0.1255$, $wR = 0.1666$, $S = 0.942$, H atoms were treated as riding atoms, max. shift/error < 0.001, residual $\rho_{max} = 0.241$ Å^{-3}.

Synthesis of allyl alcohols

(4′*R*,5′*R*,2*E*)-3-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]prop-2-en-1-ol (6) and (4′*R*,5′*R*)-2-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]prop-2-en-1-ol (9) and their enantiomers (*ent*-6 and *ent*-9): Hydroboration:[14e,16a] A solution of cyclohexene (8.92 mL, 7.23 mg, 88.0 mmol, 2.00 equiv) and 1,2-dimethoxyethane (88.0 mL) was cooled to 0 °C and stirred vigorously. $H_3B \cdot Me_2S$ (4.40 mL of a 10 M solution in Me_2S, 44.0 mmol, 1.00 equiv) was added via syringe; dicyclohexylborane was formed as a colorless precipitate. After 15 min the reaction mixture was warmed to RT and stirring was continued for 1 h. Alkyne **8a**[16a,36] (5.64 g, 44.0 mmol, 1.00 equiv) was added and stirring continued for 1 h while the colorless solid disappeared. Anhydrous Me_3NO[37] (6.28 g, 83.6 mmol, 1.90 equiv) was added slowly (exothermic reaction!) to the stirred mixture, followed by (after 1 h) diol **1** (20.0 g, 44.0 mmol, 1.00 equiv). After 12 h the mixture was concentrated under reduced pressure. Flash column chromatography (520 g silica gel, petroleum ether/EtOAc 90:10) gave a mixture of compounds (24.9 g) that was directly used for the next step.

Deprotection: The mixture was dissolved in a minimum amount of CH_2Cl_2 and ethanol (240 mL) and a solution of concentrated HCl (7 mL) in ethanol (22 mL) was added. After 45 min saturated aqueous $NaHCO_3$ solution (22 mL) was added and the organic solvent almost completely removed under reduced pressure. After dilution with H_2O, the aqueous phase was extracted three times with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography (900 g silica gel, petroleum ether/EtOAc 85:15 → 80:20) led to a spectroscopically pure colorless solid foam (15.0 g, 28.9 mmol, 66% **6** over two steps). $R_f = 0.28$ (petroleum ether/EtOAc 85:15); spectroscopic data is in agreement with literature data.[13b] The regioisomer **9** was also isolated as a spectroscopically pure colorless solid foam (7% **9**, 1.53 g, 2.94 mmol) MPLC (petroleum ether/EtOAc 85:15) afforded an analytically pure colorless solid foam. $R_f = 0.36$ (petroleum ether/EtOAc 85:15); all spectroscopic data are in full agreement with those previously published {[α] (**6**) = −84 ($c = 0.50$ in $CHCl_3$); $[\alpha]_D^{20}$ (**9**) = −144 ($c = 1.0$ in $CHCl_3$); $[\alpha]_D^{20}$ (*ent*-**6**) = +84 ($c = 1.12$ in $CHCl_3$) (obtained when starting from *ent*-**1**)}.[14g]

Synthesis of lithium alkynylboronates 10 (General procedure A):[38] Alkyne **8** (1.00 equiv) was dissolved in Et_2O (1.40 mL per mmol **8**) and cooled to −78 °C. *n*BuLi (1.00 equiv, 1.6 M in hexane) was added and the reaction mixture was stirred for 30 min. In a second flask $B(OiPr)_3$ (1.00 equiv) was dissolved in Et_2O and the solution was also cooled to −78 °C. The alkynyllithium solution was added via insulated transfer cannula to the $B(OiPr)_3$ solution whereupon lithium alkynylboronate **10** precipitated. The suspension was first stirred at −78 °C for 1 h, followed by 4 h at RT. After concentration under reduced pressure the remaining solid was dried for 3 h under high vacuum, stored under N_2 at −20 °C and used without further purification and characterization.

Synthesis of alkynylboronate 12 (General procedure B):[39] Lithium alkynylboronate **10** (1.00 equiv) was suspended in THF (1.65 mL per mmol **10**) and cooled to −78 °C. $BF_3 \cdot Et_2O$ (1.33 equiv) was added dropwise; the flask was briefly taken out of the cooling bath to dissolve the solid and was then recooled to −78 °C. In a second flask was placed diol **1** (1.66 equiv) in THF (6.25 mL per mmol **1**) at −78 °C. The solution was added via insulated transfer cannula dropwise to the boronate solution. Stirring was continued for 1 h and at RT for 30 min followed by concentration of the mixture under reduced pressure and drying under high vacuum.

(4′*R*,5′*R*)-(*tert*-Butyldimethylsilyl)-3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]propargyl ether (12b): According to GP A, alkyne **8b**[40] (2.03 mL, 1.70 g, 10.0 mmol) in Et_2O (14 mL) and *n*BuLi (6.7 mL of a 1.6 M solution in hexane, 10 mmol) were used in the first flask. In a second flask $B(OiPr)_3$ (2.30 mL, 1.88 g, 10.0 mmol) was dissolved in Et_2O (33 mL). Lithium alkynylboronate **10b** (≈10 mmol) precipitated. According to GP B, lithium alkynylboronate **10b** (346 μg, 0.95 mmol) in THF (1.57 mL) was used. The suspension was treated with $BF_3 \cdot Et_2O$ (156 μL, 180 mg, 1.27 mmol) and diol **1** (682 mg, 1.50 mmol) in

THF (10 mL). Chromatography (57 g silica gel, petroleum ether/EtOAc 97:3, 85:15, 70:30) and MPLC furnished an analytically pure colorless solid foam (220 mg, 0.29 mmol, 37%). R_f=0.55 (petroleum ether/EtOAc 90:10); softening range 72–80°C; $[\alpha]_D^{20}=-17$ (c=1.00 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.04 [s, 6H, Si(CH_3)$_2$], 0.85 (s, 9H, C(CH_3)$_3$), 2.99 (s, 6H, OCH_3), 4.18 (s, 2H, 1-H), 5.34 (s, 2H, 4′-H, 5′-H), 7.22–7.38 ppm (m, 20H, arom. CH); ^{13}C NMR (126 MHz, $CDCl_3$): δ=−5.2 [(Si(CH_3)$_2$], 18.2 [C(CH$_3$)$_3$], 25.7 [C(CH_3)$_3$], 51.8 (OCH_3, C-1), 78.0 (C-4′,C-5′), 83.2 (CPh_2OCH_3), 100.8 (C-2), 127.5, 127.5, 127.5, 127.8, 128.4, 129.6 (arom. CH), 140.8, 141.0 ppm (arom. C_{ipso}); C-3 was not detected; IR (KBr): $\tilde{\nu}$=3420 (br); 3065, 3040, 3000 (arom. C-H-ν); 2940, 2910, 2875, 2835 (aliph. C-H-ν); 2805 (OCH_3, C-H-ν); 2180 (C≡C-ν); 1590, 1575, 1480 (arom. C=C-ν); 1440; 1380; 1360; 1325; 1215; 1060 (C-O-C); 820, 795, 760 (TBS); 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 (Ph, ring-δ); 615 cm^{-1}; MS (FAB, matrix: NBA+NaI): m/z (%): 788 (2), 661 (2), 655 (7) [M+Na$^+$], 638 (9), 197 (100) [Ph_2COMe^+], 167 (11) [Ph_2CH^+], 105 (11) [PhCO$^+$], 77 (5) [Ph$^+$]; elemental analysis calcd (%) for $C_{39}H_{45}BO_5Si$ (632.7): C 74.04, H 7.17, found: C 73.86, H 7.23.

(4′*R*,5′*R*)-1-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]hept-1-yne (12c): According to GP A, 1-heptyne (**8b**) (1.31 mL, 963 mg, 10.0 mmol) in Et_2O (14 mL) and nBuLi (6.7 mL of a 1.6 M solution in hexane, 10 mmol) were used in the first flask. In a second flask B(OiPr)$_3$ (2.30 mL, 1.88 g, 10.0 mmol) was dissolved in Et_2O (33 mL). Lithium 1-heptyn-1-ylboronate (**10c**) (≈10 mmol) precipitated. According to (GP B), **10c** (279 μg, 0.96 mmol) in THF (1.58 mL) was used. The suspension was treated with BF_3·Et_2O (157 μL, 182 mg, 1.28 mmol) and diol **1** (727 mg, 1.60 mmol) in THF (10 mL). Chromatography (50 g silica gel, petroleum ether/EtOAc 95:5) yielded an analytically pure colorless solid foam (262 mg, 0.47 mmol, 49%). R_f=0.69 (petroleum ether/EtOAc 85:15); softening range 84–88°C; $[\alpha]_D^{20}=-21$ (c=0.26 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.04 (t, ^3J=7.0 Hz, 3H, 7-H), 1.26 (m, 4H, 5-H, 6-H), 1.39–1.43 (m, 2H, 4-H), 2.08 (t, ^3J=7.2 Hz, 2H, 3-H), 2.99 (s, 6H, OCH_3), 5.33 (s, 2H, 4′-H, 5′-H), 7.24–7.37 ppm (m, 20H, arom. CH); ^{13}C NMR (126 MHz in $CDCl_3$): δ=13.9 (C-7), 19.4 (C-3), 22.1 (C-6), 27.6 (C-4), 30.8 (C-5), 51.8 (OCH_3), 77.8 (C-4′, C-5′), 83.1 (CPh_2OCH_3), 104.4 (C-2), 127.5, 127.5, 127.8, 128.4, 129.7 (arom. CH), 140.8, 141.0 ppm (arom. C_{ipso}), C-1 was not detected; IR (KBr): $\tilde{\nu}$=3410 (br), 3065, 3035, 3000 (arom. C-H-ν), 2935, 2910, 2835 (aliph. C-H-ν), 2805 (OCH_3, C-H-ν), 2175 (C≡C-ν), 1590, 1575, 1485 (arom. C=C-ν), 1435, 1330, 1210, 1060 (C-O-C); 1020, 950, 740 (Ph, C-H-$\delta_{out\ of\ plane}$), 680 (Ph, ring-δ), 615 cm^{-1}; MS (EI, 70 eV): m/z (%): 558 (0.2) [M^+], 526 (2) [M−MeOH$^+$], 197 (100) [Ph_2COMe^+], 167 (1) [Ph_2CH^+], 105 (4) [PhCO$^+$], 77 (1) [Ph$^+$]; elemental analysis calcd (%) for $C_{37}H_{39}BO_4$ (558.5): C 79.57, H 7.04, found: C 79.46, H 7.06.

(4″*R*,5″*R*)-Benzyl-3-[4″,5″-bis(methoxydiphenylmethyl)-1″,3″,2″-dioxaborolan-2″-yl] propargyl ether (12d): According to GP A, benzyl protected propargylic alcohol **8d** (1.46 g, 10.0 mmol, 1.00 equiv) in Et_2O (14 mL, 1.40 mL per mmol **8d**) and nBuLi (6.7 mL of a 1.6 M solution in hexane, 10 mmol) were used in the first flask. In a second flask B(OiPr)$_3$ (2.30 mL, 1.88 g, 10.0 mmol) was dissolved in Et_2O (33 mL). Lithiumalkynyl boronate **10d** (≈10 mmol) precipitated. According to GP B, **10d** (323 μg, 0.95 mmol) in THF (1.58 mL) was used. The suspension was treated with BF_3·Et_2O (156 μL, 180 mg, 1.27 mmol) and diol **1** (682 mg, 1.50 mmol, 1.58 equiv) in THF (10 mL). Chromatography (60 g silica gel, petroleum ether/EtOAc 97:3) and MPLC yielded an analytically pure colorless solid foam (175 mg, 0.29 mmol, 30%). R_f=0.42 (petroleum ether/EtOAc 90:10); softening range 67–80°C; $[\alpha]_D^{20}=-3$ (c=0.80 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.00 (s, 6H, OCH_3), 4.04 (s, 2H, 1-H), 4.48 (s, 2H, 1′-H), 5.38 (s, 2H, 4″-H, 5″-H), 7.23–7.39 ppm (m, 25H, arom. CH); ^{13}C NMR (126 MHz, $CDCl_3$): δ=51.8 (OCH_3), 57.3 (C-1), 71.3 (C-1′), 78.1 (C-4″, C-5″), 83.1 (CPh_2OCH_3), 97.9 (C-2), 127.5, 127.5, 127.6, 127.9, 127.9, 128.1, 128.4, 128.4, 129.6 (arom. CH), 137.2, 140.7, 140.8 ppm (arom. C_{ipso}); C-3 was not detected; IR (KBr): $\tilde{\nu}$=3435 (br); 3065, 3040, 3010 (arom. C-H-ν); 2950, 2920, 2880 (aliph. C-H-ν); 2815 (OCH_3, C-H-ν); 2180 (C≡C-ν); 1590, 1575, 1480 (arom. C=C-ν); 1435; 1380; 1360; 1325; 1215; 1060 (C-O-C); 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 (Ph, ring-δ); 610; 555; 465 cm^{-1}; MS (FAB, matrix: NBA+NaI): m/z (%): 788 (2), 661 (1), 638 (11), 631 (4) [M+Na$^+$], 197 (100) [Ph_2COMe^+], 167 (13) [Ph_2CH^+], 105 (21) [PhCO$^+$]; elemental analysis calcd (%) for $C_{40}H_{37}BO_5$ (608.5): C 78.95, H 6.13, found: C 78.89, H 6.18.

(4′*R*,5′*R*,2*Z*)-*tert*-Butyldimethylsilyl-3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl] prop-2-en-1-yl ether (13): ***Procedure 1***:[19] To a solution of [Rh(cod)Cl]$_2$ (7 mg, 14 μmol) in cyclohexane (3.00 mL) was added successively (iPr)$_3$P (13 μL, 11 mg, 60 μmol, purity: 90%), Et_3N (139 μL, 101 mg, 1.00 mmol) and catecholborane (120 mg, 1.00 mmol). After 30 min alkyne **8b** (243 μL, 204 mg, 1.20 mmol) was added in one batch. Diol **1** (681 mg, 1.50 mmol) was added after 5 h. After 12 h the mixture was concentrated under reduced pressure. Purification by flash column chromatography (30 g silica gel, petroleum ether/EtOAc 95:5) gave a slightly impure yellowish solid foam (63% **13**, 398 mg, 0.63 mmol). When increasing the amount of catalyst {0.03 equiv [Rh(cod)Cl]$_2$, 0.12 equiv (iPr)$_3$P and 2.00 equiv Et_3N} an improved yield (81%) was observed in one case. ***Procedure 2***: Lindlar catalyst (5 mg) and alkyne **12b** (32 mg, 0.05 mmol) were suspended/dissolved in toluene (2 mL). The flask was briefly evacuated and flooded with H_2 for several times. The reaction mixture was stirred for 1 h while the flask was connected to a ballon containing H_2. The mixture was directly loaded on a column conditioned with petroleum ether (10 g silica gel); elution with petroleum ether/EtOAc 97:3 furnished a slightly impure (the consecutive MPLC a spectroscopically pure) colorless solid foam (95%, 30 mg, 50 μmol). R_f=0.78 (petroleum ether/EtOAc 85:15); ^{1}H NMR (500 MHz in $CDCl_3$): δ=−0.12, −0.10 [2s, 6H, Si(CH_3)$_2$], 0.82 [s, 9H, C(CH_3)$_3$], 3.01 (s, 6H, OCH_3), 3.93 (ddd, ^2J=15.0, ^3J=5.3, ^4J=1.9 Hz, 1H, 1-H$_a$), 4.03 (ddd, ^2J=15.0, ^3J=5.6, ^4J=1.9 Hz, 1H, 1-H$_b$), 4.94 (ddd, ^3J=13.9, ^4J=1.9, ^4J=1.9 Hz, 1H, 3-H), 5.34 (s, 2H, 4′-H, 5′-H), 6.24 (ddd, ^3J=13.9, ^3J=5.6, ^3J=5.3 Hz, 1H, 2-H), 7.23–7.35 ppm (m, 20H, arom. CH); ^{13}C NMR (126 MHz in $CDCl_3$): δ=−5.3, −5.2 [Si(CH_3)$_2$], 18.3 [C(CH$_3$)$_3$], 25.9 [C(CH_3)$_3$], 51.7 (OCH_3), 63.0 (C-1), 77.4 (C-4′, C-5′), 83.3 (CPh_2OCH_3), 115.7 (C-3), 127.3, 127.3, 127.5, 127.8, 128.3, 129.6 (arom. CH), 141.1, 141.3 (arom. C_{ipso}), 154.7 ppm (C-2); IR (KBr): $\tilde{\nu}$=3420 (br), 3070, 3040, 3000 (arom. C-H-ν), 2940, 2910, 2875 (aliph. C-H-ν), 2810 (OCH_3, C-H-ν), 1620 (olef. C=C-ν), 1590, 1570, 1485 (arom. C=C-ν), 1435, 1410, 1245, 1170, 1070, 1060, 820, 795, 755 (TBS), 740 (Ph, C-H-$\delta_{out\ of\ plane}$), 680 cm^{-1} (Ph, ring-δ).

(4′*R*,5′*R*)-3-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl] prop-2-yn-1-ol (14): TBS-protected propargyl alcohol **12b** (260 mg, 0.41 mmol) was dissolved in MeOH (3 mL, 7.32 mL per mmol **12b**) and a solution of concentrated HCl (51 μL) in MeOH (0.45 mL) was added. After 5 min the reaction mixture was diluted with CH_2Cl_2 and 5% aqueous $NaHCO_3$ solution (1.4 mL) was added. The aqueous layer was extracted twice with CH_2Cl_2 (5 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Chromatography (20 g silica gel, petroleum ether/EtOAc 85:15) gave an analytically pure colorless solid foam (205 mg, 0.40 mmol, 96%). R_f=0.07 (petroleum ether/EtOAc 90:10); m.p. 196–198°C; $[\alpha]_D^{20}=-36$ (c=0.50 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.39 (t, ^3J=6.3 Hz, 1H, OH), 3.00 (s, 6H, OCH_3), 4.14 (d, ^3J=6.3 Hz, 2H, 1-H), 5.36 (s, 2H, 4′-H, 5′-H), 7.23–7.34 ppm (m, 20H, arom. CH); ^{13}C NMR (126 MHz, $CDCl_3$): δ=51.3 (C-1), 51.8 (OCH_3), 78.1 (C-4′,C-5′), 83.1 (CPh_2OCH_3), 127.5, 127.6, 127.6, 127.9, 128.4, 129.6 (arom. CH), 140.7, 140.8 ppm (arom. C_{ipso}), C-2 and C-3 were not detected; IR (KBr): $\tilde{\nu}$=3550 (br, O-H-ν); 3500 (br); 3070, 3040, 3015, 3005 (arom. C-H-ν); 2955, 2950, 2915, 2880, 2840, 2830 (aliph. C-H-ν); 2805 (OCH_3, C-H-ν); 2180 (C≡C-ν); 1590, 1570, 1485 (arom. C=C-ν); 1450; 1390; 1365; 1330; 1220; 1065 (C-O-C); 1015; 1000; 950; 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 690 (Ph, ring-δ); 615 cm^{-1}; MS (EI, 70 eV): m/z (%): 518 (0.03) [M^+], 486 (2) [M−MeOH$^+$], 197 (100) [Ph_2COMe^+], 167 (3) [Ph_2CH^+], 105 (12) [PhCO$^+$], 77 (5) [Ph$^+$]; elemental analysis calcd (%) for $C_{33}H_{31}BO_5$ (518.4): C 76.46, H 6.03, found: C 76.38, H 6.12.

(4′*R*,5′*R*,2*Z*)-3-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]prop-2-en-1-ol (7): Silylether **13** (561 mg, 0.88 mmol, 1.00 equiv) was dissolved in the minimal amount of CH_2Cl_2 and EtOH (6.70 mL). A solution of concentrated HCl (140 μL) in EtOH (1.30 mL) was added. After 1 h the mixture was neutralized with saturated aqueous $NaHCO_3$ solution (1 mL); the solvents were removed under reduced pressure. After addition of H_2O the aqueous layer was extracted three times with Et_2O. The

combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography (17 g silica gel, petroleum ether/EtOAc 87:13) gave a spectroscopically pure colorless solid foam (340 mg, 0.65 mmol, 74%). $R_f = 0.22$ (petroleum ether/EtOAc 85:15); softening range 60–78 °C, $[\alpha]_D^{20} = -148$ ($c = 0.36$ in $CHCl_3$), spectroscopic data are in full agreement to those previously reported.[14f]

[3,3]-Sigmatropic rearrangements

Johnson rearrangement (General procedure C): In a flask, fitted to a Claisen condenser and a drying tube, the appropriate allyl alcohol (1.00 equiv) was dissolved in freshly distilled triethylorthoacetate (7.00 equiv); propionic acid (0.06 equiv) was added. The reaction mixture was heated to 135 °C for the time indicated and the generated EtOH was removed. The reaction mixture was cooled, concentrated under reduced pressure and subjected to chromatographic purification.

(3*S*,4′*R*,5′*R*)- and (3*R*,4′*R*,5′*R*)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]pent-4-enoate (15 and 16) and their enantiomers (*ent*-15 and *ent*-16): According to GP C allyl alcohol **6** (26.0 g, 50.0 mmol) was treated with triethylorthoacetate (63.9 mL, 65.5 g, 40.4 mmol,) under catalysis of propionic acid (225 μL, 222 mg, 3.00 mmol). The reaction mixture was heated for 3.5 h; the dr (as determined by proton NMR of the crude mixture) was 50:50. Chromatography (700 g silica gel, petroleum ether/EtOAc 98:2 → 85:15) gave the mixture of diastereomers **15/16** (23.1 g, 39.1 mmol, 78%) and starting material **6** (5.05 g, 9.70 mmol, 19%). MPLC (petroleum ether/EtOAc 98:2) gave two analytically pure solid foams (**15** and **16**). Allylboronate **15**: $R_f = 0.68$ (petroleum ether/EtOAc 85:15); softening range: 49–62 °C; $[\alpha]_D^{20}$ (**15**) = −108 ($c = 0.67$ in $CHCl_3$); $[\alpha]_D^{20}$ (*ent*-**15**) = +110 ($c = 1.19$ in $CHCl_3$) (obtained when starting from *ent*-**6**); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.13$ (t, $^3J = 7.1$ Hz, 3H, 2″-H), 1.90–1.94 (m, 1H, 3-H), 1.98–2.10 (m, 2H, 2-H), 3.00 (s, 6H, OCH_3), 3.93 (q, $^3J = 7.1$ Hz, 2H, 1″-H), 4.70 (ddd, $^3J = 17.2$, $^2J = 1.5$, $^4J = 1.5$ Hz, 1H, 5-H_Z), 4.77 (ddd, $^3J = 10.5$, $^2J = 1.5$, $^4J = 1.5$ Hz, 1H, 5-H_E), 5.30 (s, 2H, 4′-H, 5′-H), 5.56 (ddd, $^3J = 17.2$, $^3J = 10.5$, $^3J = 6.9$ Hz, 1H, 4-H); 7.24–7.35 ppm (m, 20H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 14.1$ (C-2″), 25.0 (C-3), 33.0 (C-2), 51.7 (OCH_3), 60.0 (C-1″), 77.9 (C-4′, C-5′), 83.2 (CPh_2OCH_3), 112.7 (C-5), 127.3, 127.4, 127.5, 127.8, 128.4, 129.7 (arom. *C*H), 137.3 (C-4), 141.1, 141.1 (arom. C_{ipso}), 173.1 ppm (C-1); IR (KBr): $\tilde{\nu} = 3430$ (br); 3060, 3040, 3000 (arom. C-H-ν); 2960, 2920, 2880 (aliph. C-H-ν); 2805 (OCH_3, C-H-ν); 1730 (C=O-ν); 1625 (olef. C=C-ν); 1590, 1570, 1480 (arom. C=C-ν); 1440; 1360; 1060 (C-O-C); 1020; 985, 950 ($CH{=}CH_2$, C-H-$\delta_{out\ of\ plane}$); 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 690 cm^{-1} (Ph, ring-δ); MS (FAB, matrix: NBA + NaI): *m*/*z* (%): 613 (14) [*M* + Na^+], 333 (10), 197 (100) [CPh_2OMe^+], 167 (5) [Ph_2CH^+], 105 (11) [$PhCO^+$], 77 (5) [Ph^+]; elemental analysis calcd (%) for $C_{37}H_{39}BO_6$ (590.5): C 75.26, H 6.66, found: C 75.25, H 6.67. Allylboronate **16**: $R_f = 0.68$ (petroleum ether/EtOAc 85:15); softening range: 41–60 °C; $[\alpha]_D^{20}$ (**16**) = −98 ($c = 0.32$ in $CHCl_3$), $[\alpha]_D^{20}$ (*ent*-**16**) = +102 ($c = 1.19$ in $CHCl_3$) (obtained when starting from *ent*-**6**); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.13$ (t, $^3J = 7.1$ Hz, 3H, 2″-H), 1.90–1.94 (m, 1H, 3-H), 2.05–2.14 (m, 2H, 2-H), 2.99 (s, 6H, OCH_3), 3.99 (q, $^3J = 7.1$ Hz, 2H, 1″-H), 4.70 (ddd, $^3J = 17.2$, $^2J = 1.4$, $^4J = 1.4$ Hz, 1H, 5-H_Z), 4.75 (ddd, $^3J = 10.3$, $^2J = 1.4$, $^4J = 1.4$ Hz, 1H, 5-H_E), 5.32 (s, 2H, 4′-H, 5′-H), 5.41 (ddd, $^3J = 17.2$, $^3J = 10.3$, $^3J = 7.8$ Hz, 1H, 4-H), 7.25–7.32 ppm (m, 20H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 14.2$ (C-2″), 25.4 (C-3), 33.8 (C-2), 51.8 (OCH_3), 60.0 (C-1″), 77.9 (C-4′, C-5′), 83.3 (CPh_2OCH_3), 113.6 (C-5), 127.4, 127.4, 127.6, 127.8, 128.4, 129.7 (arom. *C*H), 136.8 (C-4), 141.2, 141.2 (arom. C_{ipso}), 172. 9 ppm (C-1); IR (KBr): $\tilde{\nu} = 3420$ (br); 3065, 3040, 3005 (arom. C-H-ν); 2960, 2915, 2880 (aliph. C-H-ν); 2805 (OCH_3, C-H-ν); 1730 (C=O-ν); 1625 (olef. C=C-ν); 1590, 1575, 1482 (arom. C=C-ν); 1450; 1437; 1360; 1060 (C-O-C); 1020; 985, 950 ($CH{=}CH_2$, C-H-$\delta_{out\ of\ plane}$); 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 690 cm^{-1} (Ph, ring-δ); MS (FAB, matrix: NBA + NaI): *m*/*z* (%): 613 (12) [*M* + Na^+], 333 (6), 197 (100) [CPh_2OMe^+], 167 (6) [Ph_2CH^+], 105 (11) [$PhCO^+$], 77 (4) [Ph^+]; elemental analysis calcd (%) for $C_{37}H_{39}BO_6$ (590.5): C 75.26, H 6.66, found: C 75.32, H 6.68.

(3*S*,4′*R*,5′*R*)- and (3*R*,4′*R*,5′*R*)-Ethyl 3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]pent-4-enoate (15 and 16): According to GP C, allyl alcohol **7** (101 mg, 0.19 mmol) was treated with triethylorthoacetate (248 μL, 220 mg, 1.36 mmol,) under catalysis of propionic acid (1 μL, 1 mg, 0.01 mmol). The reaction mixture was heated for 3 h; dr 30:70 (determined by proton NMR of the crude mixture). Chromatography (4 g silica gel, petroleum ether/EtOAc 93:7) yielded the mixture of diastereomers **15/16** (68 mg, 0.12 mmol, 59%) as a slightly impure colorless solid foam. Analytical data: see above.

(4′*R*,5′*R*)-Ethyl 4-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]pent-4-enoate (17): According to GP C, allyl alcohol **9** (239 mg, 0.46 mmol) was treated with triethylorthoacetate (587 μL, 522 mg, 3.21 mmol) under catalysis of propionic acid (2 μL, 2 mg, 0.03 mmol.). The reaction mixture was heated for 1 h. Chromatography (25 g silica gel, petroleum ether/EtOAc 95:5) gave a slightly impure colorless solid foam of **17** (184 mg, 0.31 mmol, 68%), MPLC (petroleum ether/EtOAc 98:2) furnished an analytically pure sample. $R_f = 0.61$ (petroleum ether/EtOAc 85:15); softening range: 37–43 °C; $[\alpha]_D^{20} = -122$ ($c = 0.94$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.20$ (t, $^3J = 7.1$ Hz, 3H, 2″-H), 2.00–2.15 (m, 4H, 2-H, 3-H), 2.99 (s, 6H, OCH_3), 4.05 (q, $^3J = 7.1$ Hz, 2H, 1″-H), 5.35 (s, 2H, 4′-H, 5′-H), 5.40 (s, 2H, 5-H), 7.23–7.36 ppm (m, 20H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 14.2$ (C-2″), 29.8 (C-3), 33.4 (C-2), 51.8 (OCH_3), 60.0 (C-1″), 77.8 (C-4′, C-5′), 83.3 (CPh_2OCH_3), 127.2, 127.3, 127.5, 127.8, 128.4, 129.6 (arom. *C*H), 130.0 (C-5), 141.2, 141.4 (arom. C_{ipso}), 173.4 ppm (C-1), C-4 was not detected; IR (KBr): $\tilde{\nu} = 3440$ (br); 3070, 3045, 3010 (arom. C-H-ν); 2960, 2920, 2890 (aliph. C-H-ν); 2815 (OCH_3, C-H-ν); 1730 (C=O-ν); 1610 (olef. C=C-ν); 1590, 1570, 1480 (arom. C=C-ν); 1435; 1410; 1370; 1210; 1160; 1060 (C-O-C); 1015; 1000; 950; 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 685 cm^{-1} (Ph, ring-δ); MS (FAB, matrix: NBA + NaI): *m*/*z* (%): 613 (54) [*M* + Na^+], 333 (6), 197 (100) [CPh_2OMe^+], 167 (7) [Ph_2CH^+], 105 (15) [$PhCO^+$], 77 (6) [Ph^+]; elemental analysis calcd (%) for $C_{37}H_{39}BO_6$ (590.5): C 75.26, H 6.66, found: C 75.29, H 6.65.

(3*S*,4′*R*,5′*R*)- and (3*R*,4′*R*,5′*R*)-3-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-*N*,*N*-dimethylpent-4-enamide (18 and 19): A flask containing allyl alcohol **6** (500 mg 0.96 mmol) dissolved in toluene (2 mL) and *N*,*N*-dimethylacetamide dimethylacetal (281 μL, 255 mg, 1.92 mmol) was fitted to a Claisen condenser and a drying tube. The reaction mixture was heated for 36 h at precisely 80 °C and the evolving MeOH was removed. The mixture was concentrated under reduced pressure; the dr (as determined by proton NMR of the crude mixture) was 50:50. Chromatography (25 g silica gel, petroleum ether/EtOAc 70:30) yielded the slightly impure mixture of diastereomers **18/19**, (415 mg, 0.71 mmol, 73%) and **2** (R = OH: 175 mg, 0.16 mmol, 16%). MPLC (petroleum ether/EtOAc 70:30) furnished two analytically pure solid foams (**18** and **19**). Allylboronate **18**: $R_f = 0.11$ (petroleum ether/EtOAc 85:15); softening range: 51–72 °C; $[\alpha]_D^{20} = -124$ ($c = 0.25$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.98$ (d, $^3J = 7.5$ Hz, 2H, 2-H), 2.10 (td, $^3J = 7.2$, $^3J = 6.7$ Hz, 1H, 3-H), 2.67, 2.74 [2s, 6H, $N(CH_3)_2$)], 3.00 (s, 6H, OCH_3), 4.66 (ddd, $^3J = 17.2$, $^2J = 1.6$, $^4J = 1.6$ Hz, 1H, 5-H_Z), 4.76 (ddd, $^3J = 10.5$, $^2J = 1.6$, $^4J = 1.6$ Hz, 1H, 5-H_E), 5.30 (s, 2H, 4′-H, 5′-H), 5.62 (ddd, $^3J = 17.2$, $^3J = 10.5$, $^3J = 6.7$ Hz, 1H, 4-H), 7.24–7.33 ppm (m, 20H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 24.9$ (C-3), 30.8 (C-2), 35.4, 37.3 [N-(CH_3)$_2$], 51.7, 51.7 (OCH_3), 77.8 (C-4′, C-5′), 83.2 (CPh_2OCH_3), 112.0 (C-5), 127.2, 127.3, 127.5, 127.8, 128.5, 129.7 (arom. *C*H), 138.3 (C-4), 141.0, 141.1 (arom. C_{ipso}), 172.3 ppm (C-1); IR (KBr): $\tilde{\nu} = 3420$ (br); 3070, 3040, 3005 (arom. C-H-ν); 2960, 2920, 2890 (aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1640 (C=O-ν); 1590, 1570, 1480 (arom. C=C-ν); 1450, 1435; 1380; 1360; 1340; 1220; 1185; 1060 (C-O-C); 1015; 985, 950 ($CH{=}CH_2$, C-H-$\delta_{out\ of\ plane}$); 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 690 (Ph, ring-δ); 680; 615; 590 cm^{-1}; MS (FAB, matrix: NBA + NaI): *m*/*z* (%): 612 (100) [*M* + Na^+], 332 (17), 197 (24) [CPh_2OMe^+], 168 (6) [$Ph_2CH_2^+$], 105 (5) [$PhCO^+$], 77 (3) [Ph^+]; elemental analysis calcd (%) for $C_{37}H_{40}BNO_5$ (589.5): C 75.38, H 6.84, N 2.38, found: C 75.10, H 6.96, N 2.38.

Allylboronate **19**: $R_f = 0.08$ (petroleum ether/EtOAc 85:15); softening range: 52–71 °C; $[\alpha]_D^{20} = -108$ ($c = 0.16$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.03$ (ddd, $^3J = 11.4$,$^3J = 7.7$, $^3J = 3.2$ Hz, 1H, 3-H), 2.04 (dd, $^2J = 15.8$, $^3J = 3.2$ Hz, 1H, 2-H_a), 2.15 (dd, $^2J = 15.8$, $^3J = 11.4$ Hz, 1H, 2-H_b), 2.84, 2.84 [2s, 6H, $N(CH_3)_2$], 2.99 (s, 6H, OCH_3), 4.68 (ddd, $^3J = 17.1$, $^2J = 1.5$, $^4J = 1.5$ Hz, 1H, 5-H_Z), 4.74 (ddd, $^3J = 10.2$, $^2J = 1.5$, $^4J = 1.5$ Hz, 1H, 5-H_E), 5.32 (s, 2H, 4′-H, 5′-H), 5.44 (ddd, $^3J = 17.1$, $^3J = 10.2$, $^3J = 7.7$ Hz, 1H, 4-H), 7.24–7.34 ppm (m, 20H, arom. C*H*); ^{13}C NMR

(126 MHz, $CDCl_3$): δ = 25.3 (C-3), 32.3 (C-2), 35.4, 37.2 [$N(CH_3)_2$], 51.8 (OCH_3), 77.9 (C-4′, C-5′), 83.4 (CPh_2OCH_3), 113.6 (C-5), 127.3, 127.4, 127.5, 127.8, 128.4, 129.7 (arom. *C*H), 137.5 (C-4), 141.1, 141.2 (arom. C_{ipso}), 172.1 ppm (C-1); IR (KBr): $\tilde{\nu}$ = 3430 (br); 3070, 3040, 3010 (arom. C-H-ν); 2920, 2890 (aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1640 (C=O-ν); 1590, 1575, 1480 (arom. C=C-ν); 1450, 1435; 1380; 1360; 1340; 1220; 1185; 1060 (C-O-C); 1020; 1000; 985, 950 (CH=CH_2, C-H-$\delta_{out\ of\ plane}$); 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 690 (Ph, ring-δ); 680; 610; 585 cm^{-1}; MS (FAB, matrix: NBA + NaI): 612 (100) [*M*+Na^+], 332 (46), 197 (49) [CPh_2OMe^+], 168 (13) [$Ph_2CH_2^+$], 105 (6) [$PhCO^+$], 77 (3) [Ph^+]; elemental analysis calcd (%) for $C_{37}H_{40}BNO_5$ (589.5): C 75.38, H 6.84, N 2.38, found: C 75.15, H 6.94, N 2.19.

(4′*R*,5′*R*)-4-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-*N*,*N*-dimethylpent-4-enamide (20): Allyl alcohol **9** (297 mg, 0.57 mmol) was dissolved in toluene (570 μL) and *N*,*N*-dimethylformamide dimethylacetal (167 μL, 152 mg, 1.14 mmol) was added. The reaction mixture was heated for 16 h to 70 °C and was concentrated under reduced pressure. Chromatography (19 g silica gel, petroleum ether/EtOAc 70:30 → 60:40) gave an analytically pure colorless solid foam of amide **20** (147 mg, 0.25 mmol, 44 %). R_f = 0.09 (petroleum ether/EtOAc 70:30); softening range: 49–65 °C; $[\alpha]_D^{20}$ = −128 (*c* = 0.54 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.90–2.13 (m, 4H, 2-H, 3-H), 2.71, 2.85 [2s, 6H, $N(CH_3)_2$], 3.01 (s, 6H, OCH_3), 5.37 (s, 2H, 4′-H, 5′-H), 5.40 (d, ^2J = 3.4 Hz, 1H, 5-H_a), 5.45 (d, ^2J = 3.4 Hz), 7.24–7.35 ppm (m, 20H, arom. *C*H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 31.3 (C-3), 33.5 (C-2), 35.2, 37.1 [$N(CH_3)_2$], 51.8 (OCH_3), 77.8 (C-4′, C-5′), 83.4 (CPh_2OCH_3), 127.2, 127.3, 127.5, 127.8, 128.5, 129.7 (arom. *C*H), 130.7 (C-5), 141.1, 141.3 (arom. C_{ipso}), 173.0 ppm (C-1), C-4 was not detected; IR (KBr): $\tilde{\nu}$ = 3420 (br); 3070, 3040, 3010 (arom. C-H-ν); 2920 (br, aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1650 (amide I, C=O-ν); 1640 (amide II, N-H-bending); 1590, 1570, 1480 (arom. C=C-ν); 1435; 1210; 1185; 1060 (C-O-C); 1020; 1000; 950; 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 cm^{-1} (Ph, ring-δ); MS (FAB, matrix: NBA + NaI): *m*/*z* (%): 612 (89) [*M*+Na^+], 332 (96), 197 (100) [CPh_2OMe^+], 168 (18) [$Ph_2CH_2^+$], 105 (10) [$PhCO^+$], 77 (7) [Ph^+]; elemental analysis calcd (%) for $C_{37}H_{40}BNO_5$ (589.5): C 75.38, H 6.84, N 2.38, found: C 75.25, H 6.94, N 2.22.

(1*R*,4′*R*,5′*R*)-1-(4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl)-1-methoxy-2-propene (21): Allyl alcohol **7** (160 mg, 0.31 mmol) was dissolved in toluene (300 μL) and *N*,*N*-dimethylformamide dimethylacetal (90 μL, 82 mg, 0.62 mmol) was added. The reaction mixture was heated to 70 °C for 4 h, concentrated under reduced pressure. Chromatography (12 g silica gel, petroleum ether/EtOAc 95:5) gave a slightly impure, MPLC (petroleum ether/EtOAc 95:5) an analytically pure colorless solid foam of ether **21** (92 mg, 0.17 mmol, 56 %). R_f = 0.38 (petroleum ether/EtOAc 90:10); softening range: 50–67 °C; $[\alpha]_D^{20}$ = −124 (*c* = 0.54 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.00 (s, 6H, OCH_3), 3.09 (ddd, ^3J = 6.8, ^4J = 1.6, ^4J = 1.6 Hz, 1H, 1-H), 3.12 (s, 3H, 1-OCH_3), 4.97 (ddd, ^3J = 10.5, ^2J = 1.7, ^4J = 1.6 Hz, 1H, 3-H_E), 4.98 (ddd, ^3J = 17.2, ^2J = 1.7, ^4J = 1.6 Hz, 1H, 3-H_Z), 5.36 (s, 2H, 4′-H, 5′-H), 5.48 (ddd, ^3J = 17.2, ^3J = 10.5, ^3J = 6.8 Hz, 1H, 2-H), 7.23–7.36 ppm (m, 20H, arom. *C*H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 51.7 (OCH_3), 58.0 (1-OCH_3), 72.4 (C-1), 78.0 (C-4′, C-5′), 83.2 (CPh_2OCH_3), 114.3 (C-3), 127.4, 127.4, 127.5, 127.8, 128.4, 129.7 (arom. *C*H), 135.5 (C-2), 141.0, 141.1 ppm (arom. C_{ipso}); IR (KBr): $\tilde{\nu}$ = 3420 (br); 3070, 3040, 3010 (arom. C-H-ν); 2960, 2920 (aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1630 (olef. C=C-ν); 1590, 1570, 1480 (arom. C=C-ν); 1435; 1370; 1225; 1285; 1260; 1060 (C-O-C); 1020; 1000; 985, 950 (CH=CH_2, C-H-$\delta_{out\ of\ plane}$); 900; 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 (Ph, ring-δ); 615; 590 cm^{-1}; MS (FAB, matrix: NBA + NaI): *m*/*z* (%): 557 (26) [*M*+Na^+], 197 (100) [CPh_2OMe^+], 167 (9) [Ph_2CH^+], 105 (9) [$PhCO^+$], 77 (3) [Ph^+]; elemental analysis calcd (%) for $C_{34}H_{35}BO_5$ (534.5): C 76.41, H 6.60, found: C 76.22, H 6.82.

(4″*R*,5″*R*,2′*E*)-3′-[4″,5″-Bis(methoxydiphenylmethyl)-1″,3″,2″-dioxaborolan-2″-yl]prop-2′-en-1′-yl acetate (22): Allyl alcohol **6** (520 mg 1.00 mmol) was dissolved in CH_2Cl_2 (2 mL) and Et_3N (277 μL, 202 mg, 2.00 mmol), DMAP (12 mg, 0.10 mmol) and acetic anhydride (189 μL, 204 mg, 2.00 mmol) were added. After 15 min saturated aqueous $NaHCO_3$ solution (5 mL) was added. The aqueous phase was extracted thrice with CH_2Cl_2. The combined organic phase was washed with saturated aqueous NH_4Cl solution and H_2O, dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography (10 g silica gel, petroleum ether/EtOAc 93:7) yielded an analytically pure colorless solid foam of acetate **22** (554 mg, 0.70 mmol, 98 %). R_f = 0.58 (petroleum ether/EtOAc 85:15); softening range: 61–67 °C; $[\alpha]_D^{20}$ = −68 (c = 1.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 3H, 2-H), 3.00 (s, 6H, OCH_3), 4.47 (m, 2H, 1′-H), 5.28 (dt, ^3J = 18.1, ^4J = 1.8 Hz, 1H, 3′-H), 5.35 (s, 2H, 4″-H, 5″-H), 6.17 (dt, ^3J = 18.1, ^3J = 4.6 Hz, 1H, 2′-H), 7.23–7.35 ppm (m, 20H, arom *C*H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.8 (C-2), 51.8 (OCH_3), 65.2 (C-1′), 77.7 (C-4″, C-5″), 83.3 (CPh_2OCH_3), 119.1 (C-3′), 127.3, 127.3, 127.5, 127.8, 128.4, 129.6 (arom. *C*H), 141.0, 141.2 (arom. C_{ipso}), 145.4 (C-2′), 170.4 ppm (C-1); IR (KBr): $\tilde{\nu}$ = 3320 (br); 3070, 3040, 3000 (arom. C-H-ν); 2940, 2910, 2880 (aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1740 (C=O-ν); 1640 (olef. C=C-ν); 1590, 1575, 1485 (arom. C=C-ν); 1440; 1395; 1360; 1335; 1220; 1175; 1060 (C-O-C); 1020; 1000; 985; 950; 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 690 (Ph, ring-δ); 680; 615; 590 cm^{-1}; MS (FAB, matrix: NBA + NaI): *m*/*z* (%): 585 (32) [*M*+Na^+], 197 (100) [CPh_2OMe^+], 167 (9) [Ph_2CH^+], 105 (12) [$PhCO^+$], 77 (5) [Ph^+]; elemental analysis calcd (%) for $C_{35}H_{35}BO_6$ (562.5): C 74.74, H 6.27, found: C 74.82, H 6.49.

(4″*R*,5″*R*,2′*E*)-3′-[4″,5″-Bis(methoxydiphenylmethyl)-1″,3″,2″-dioxaborolan-2″-yl]prop-2′-en-1′-yl propionate (23): Allyl alcohol **6** (500 mg, 0.96 mmol) was dissolved in CH_2Cl_2 (2 mL) and Et_3N (250 μL, 183 mg, 1.80 mmol), DMAP (12 mg, 0.10 mmol) and propionic anhydride (230 μL, 232 mg, 1.78 mmol) were added. After 15 min saturated aqueous $NaHCO_3$ solution (5 mL) was added. The aqueous phase was extracted thrice with CH_2Cl_2. The combined organic phase was washed with saturated aqueous NH_4Cl solution and H_2O, dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography (15 g silica gel, petroleum ether/EtOAc 93:7) yielded an analytically pure colorless solid foam of propionate **23** (420 mg, 0.73 mmol, 76 %). R_f = 0.65 (petroleum ether/EtOAc 85:15); softening range: 50–63 °C; $[\alpha]_D^{20}$ = −65 (c = 1.13 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11 (t, ^3J = 7.6 Hz, 3H, 3-H), 2.31 (q, ^3J = 7.6 Hz, 2H, 2-H), 3.00 (s, 6H, OCH_3), 4.48 (m, 2H, 1′-H), 5.28 (dt, ^3J = 18.1, ^3J = 1.9 Hz, 1H, 3′-H), 5.35 (s, 2H, 4″-H, 5″-H), 6.17 (dt, ^3J = 18.1, ^3J = 4.6 Hz, 1H, 2′-H), 7.24–7.36 ppm (m, 20H, arom. *C*H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 9.0 (C-3), 27.4 (C-2), 51.8 (OCH_3), 65.1 (C-1′), 77.7 (C-4″, C-5″), 83.3 (CPh_2OCH_3), 119.0 (C-3′), 127.3, 127.3, 127.5, 127.8, 128.4, 129.7 (arom. *C*H), 141.0, 141.2 (arom. C_{ipso}), 145.6 (C-2′), 173.8 ppm (C-1); IR (KBr): $\tilde{\nu}$ = 3450 (br); 3070, 3040, 3010 (arom. C-H-ν); 2960, 2920, 2890 (aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1740 (C=O-ν); 1640 (olef. C=C-ν); 1590, 1573, 1483 (arom. C=C-ν); 1440; 1395; 1375; 1360; 1230; 1170; 1065 (C-O-C); 1020; 1000; 985; 950; 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 690 (Ph-ring-δ); 680; 615; 590 cm^{-1}; MS (FAB, matrix: NBA + NaI): *m*/*z* (%): 599 (9) [*M*+Na^+], 197 (100) [CPh_2OMe^+], 167 (9) [Ph_2CH^+], 105 (13) [$PhCO^+$], 77 (4) [Ph^+]; elemental analysis calcd (%) for $C_{36}H_{37}BO_6$ (576.5): C 75.00, H 6.47, found: C 74.76, H 6.47.

(4″*R*,5″*R*)-3′-[4″,5″-Bis(methoxydiphenylmethyl)-1″,3″,2″-dioxaborolan-2″-yl] allyl 3-oxobutyrate (24): Allyl alcohol **6** (500 mg, 0.96 mmol) was dissolved in THF (5 mL) and DMAP (11 mg, 0.09 mmol) and diketene (83.5 μL, 91.6 mg, 1.09 mmol) were added, whereupon the reaction mixture got warm. After 23 h to the mixture was added 0.1 % aqueous NaOH solution and Et_2O. The organic phase was washed with 0.1 % aqueous NaOH solution and saturated aqueous NaCl solution, dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography (40 g silica gel, petroleum ether/EtOAc 83:17) gave a slightly impure colorless solid foam (83 % **24**, 485 mg, 0.80 mmol), MPLC (petroleum ether/EtOAc 85:15) furnished an analytically pure sample. The ratio of keto to enol form is 9:1 in favor of keto form (^{1}H NMR). R_f = 0.36 (petroleum ether/EtOAc 85:15); softening range: 52–67 °C; $[\alpha]_D^{20}$ = −62 (c = 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) keto form: δ = 2.23 (s, 3H, 4-H), 2.99 (s, 6H, OCH_3), 3.42 (s, 2H, 2-H), 4.53 (dd, ^3J = 4.8, ^4J = 1.7 Hz, 2H, 1′-H), 5.29 (dt, ^3J = 18.1, ^4J = 1.7 Hz, 3′-H), 5.35 (s, 2H, 4″-H, 5″-H), 6.15 (dt, ^3J = 18.1, ^3J = 4.8 Hz, 1H, 2′-H), 7.24–7.35 ppm (m, 20H, arom. *C*H); different signals in enol form: δ = 1.94 (s, 3H, 4-H); 4.96 (s, 1H, 2-H); 6.15 ppm (dt, ^3J = 18.1, ^3J = 4.6 Hz, 1H, 2′-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 30.1 (C-4), 49.8 (C-2), 51.8 (OCH_3), 66.1 (C-1′), 77.8 (C-4″, C-5″), 83.3 (CPh_2OCH_3), 120.0 (C-3′), 127.3, 127.3, 127.5, 127.8, 128.4, 129.7 (arom. *C*H), 141.0, 141.2 (arom. C_{ipso}), 144.5 (C-2′), 166.5 (C-1), 200.2 ppm (C-3); IR (KBr): $\tilde{\nu}$ = 3420 (br); 3070, 3040, 3010 (arom. C-H-

ν); 2940, 2920, 2890 (aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1740 (ester, C=O-ν); 1715 (keton, C=O-ν); 1635 (olef. C=C-ν); 1590, 1570, 1480 (arom. C=C-ν); 1435; 1370; 1335; 1230; 1170; 1060 (C-O-C); 1020; 1000; 950; 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 690 (Ph, Ring-δ); 680; 615; 590 cm^{-1}; MS (FAB, matrix: NBA+NaI): *m/z* (%): 627 (71) [*M*+Na^+], 401 (5), 197 (100) [CPh_2OMe^+], 167 (8) [Ph_2CH^+], 105 (12) [$PhCO^+$], 77 (6) [Ph^+]; elemental analysis calcd (%) for $C_{37}H_{37}BO_7$ (604.5): C 73.52, H 6.17, found: C 73.55, H 6.19.

(4″*R*,5″*R*,2′*E*)-3′-[4″,5″-Bis(methoxydiphenylmethyl)-1″,3″,2″-dioxaborolan-2″-yl]-2′-propen-1′-yl 2,2,2-trichloroacetimidate (25): NaH (10 mg, 0.40 mmol) was suspended in Et_2O (2 mL) and a solution of allyl alcohol **6** (1.04 g, 2.00 mmol) in Et_2O (3 mL) was slowly dropwise. After 30 min the reaction mixture was cooled to 0 °C and Cl_3CCN (241 μL, 347 mg, 2.40 mmol) was added dropwise. After 1 h at 0 °C and 2 h at RT the reaction mixture was concentrated under reduced pressure. Chromatography (70 g silica gel, petroleum ether/EtOAc 85:15) furnished an analytically pure colorless solid foam of trichloroacetimidate **25** (1.30 g, 1.96 mmol, 98 %). R_f=0.40 (petroleum ether/EtOAc 90:10); softening range: 80–90 °C; $[\alpha]_D^{20}=-54$ (*c*=1.00 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 3.00 (s, 6H, OCH_3), 4.68 (dd, ^3J=4.6, ^4J=1.8 Hz, 2H, 1′-H), 5.34 (s, 2H, 4″-H, 5″-H), 5.42 (dt, ^3J=18.1, ^4J=1.8 Hz, 1H, 3′-H), 6.24 (dt, ^3J=18.1, ^3J=4.6 Hz, 1H, 2′-H), 7.24–7.35 (m, 20H, arom. C*H*), 8.26 ppm (s, 1H, N*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ=51.8 (OCH_3), 69.9 (C-1′), 77.8 (C-4″, C-5″), 83.3 (CPh_2OCH_3), 91.3 (C-2), 119.9 (C-3′), 127.3, 127.3, 127.5, 127.8, 128.4, 129.7 (arom. *C*H), 141.0, 141.2 (arom. C_{ipso}), 144.3 (C-2′), 162.3 ppm (C-1); IR (KBr): $\tilde{\nu}$=3420 (br); 3325 (N-H-ν); 3065, 3040, 3010 (arom. C-H-ν); 2935, 2915, 2880 (aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1660 (C=N-ν); 1635 (olef. C=C-ν); 1590, 1575, 1480 (arom. C=C-ν); 1435; 1370; 1360; 1340; 1295; 1230; 1175; 1060 (C-O-C); 1020; 1000; 975; 950; 810; 780; 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 (Ph, ring-δ); 630 (C-Cl); 615 cm^{-1}; MS (FAB, matrix: NBA+NaI): *m/z* (%): 688 (84) [*M*+Na^+], 471 (2), 197 (100) [CPh_2OMe^+], 167 (7) [Ph_2CH^+], 105 (11) [$PhCO^+$], 77 (6) [Ph^+]; elemental analysis calcd (%) for $C_{35}H_{33}BCl_3NO_5$ (664.8): C 63.23, H 5.00, N 2.11, found: C 63.28, H 5.14, N 2.10.

(4″*R*,5″*R*,2′*E*)-3′-[4″,5″-Bis(methoxydiphenylmethyl)-1″,3″,2″-dioxaborolan-2″-yl]-2′-propen-1′-yl 2,2,2-trifluoroacetimidate (26): In a 50 mL three-necked round-bottom flask equipped with a stirring bar, a thermometer, a septum and a nitrogen inlet were introduced trifluoroacetamide (746 mg, 6.60 mmol), DMSO (1.36 mL, 1.50 g, 19.2 mmol, 19.2 equiv) and CH_2Cl_2 (25 mL). The solution was cooled down to −75 °C (internal) and a solution of $(COCl)_2$ (516 μL, 762 mg, 6.00 mmol) in CH_2Cl_2 (2 mL) and a solution of Et_3N (2.51 mL, 1.82 g, 18.0 mmol) in CH_2Cl_2 (1 mL) were added slowly; no rise in temperature was observed during this process. Stirring was continued at −78 °C for 30 min, DBU (298 μL, 304 mg, 2.00 mmol) and a solution of alcohol **6** (520 mg, 1.00 mmol) in CH_2Cl_2 (4 mL) were added slowly via syringe. The reaction mixture was stirred at −78 °C and was then allowed to reach room temperature over 10 h. Water was added and the aqueous layer was extracted twice with CH_2Cl_2 (15 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Chromatography (108 g silica gel, petroleum ether/EtOAc 90:10) yielded a spectroscopically pure colorless solid foam of trifluoroacetimidate **26** (471 mg, 0.77 mmol, 77 %), MPLC (petroleum ether/EtOAc 95:5) furnished an analytically pure sample. R_f=0.38 (petroleum ether/EtOAc 90:10); softening range: 60–64 °C; $[\alpha]_D^{20}=-61$ (*c*=0.50 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.00 (s, 6H, OCH_3), 4.65 (dd, ^3J=4.8, ^4J=1.8 Hz, 2H, 1′-H), 5.36 (s, 2H, 4″-H, 5″-H), 5.36 (dt, ^3J=18.1, ^4J=1.8 Hz, 1H, 3′-H), 6.21 (dt, ^3J=18.1, ^3J=4.8 Hz, 1H, 2′-H), 7.24–7.35 (m, 20H, arom. C*H*), 8.14 ppm (s, 1H, N*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ=51.8 (OCH_3), 68.3 (C-1′), 77.8 (C-4″, C-5″), 83.3 (CPh_2OCH_3), 115.5 (q, $^1J_{C,F}$=280 Hz, C-2), 120.3 (C-3′), 127.3, 127.3, 127.5, 127.8, 128.4, 129.7 (arom. *C*H), 141.0, 141.2 (arom. C_{ipso}), 143.8 (C-2′), 157.5 ppm (q, $^2J_{C,F}$=38 Hz, C-1); IR (KBr): $\tilde{\nu}$=3410 (br); 3330 (N-H-ν); 3070, 3040, 3015, 3000 (arom. C-H-ν); 2940, 2915, 2880 (aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1680 (C=N-ν); 1640 (olef. C=C-ν); 1590, 1570, 1480 (arom. C=C-ν); 1435; 1365; 1330; 1230, 1190, 1155 (br, C-F); 1060 (C-O-C); 1020; 1000; 950; 830; 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 (Ph, ring-δ); 615 cm^{-1}; MS (FAB, matrix: NBA+NaI): *m/z* (%): 638 (7) [*M*+Na^+], 197 (100) [CPh_2OMe^+], 167 (8) [Ph_2CH^+], 105 (15) [$PhCO^+$], 77 (6) [Ph^+]; elemental analysis calcd (%) for $C_{35}H_{33}BF_3NO_5$ (615.5): C 68.30, H 5.40, N 2.28, found: C 68.21, H 5.43, N 2.18.

(1′*R*,4″*R*,5″*R*)- and (1′*S*,4″*R*,5″*R*)-*N*-{1′-[4″,5″-Bis(methoxydiphenylmethyl)-1″,3″,2″-dioxaborolan-2″-yl]prop-2′-en-1′-yl}-2,2,2-trichloroacetamide (27): Trichloroacetimidate **25** (50 mg, 0.08 mmol) was dissolved in 1,2-dichlorobenzene (15 mL). The solution was heated to 171 °C for 10 h and cooled to RT. The reaction mixture was loaded directly on a column (10 g silica gel) which was conditioned with petroleum ether. Chromatography (petroleum ether to petroleum ether/EtOAc 90:10) gave a mixture of starting material **25** and product **27** (16:84), whereas the product **27** was a 59:41 diastereomeric mixture. The diastereomers could not be separated by MPLC, but the product **27** was furnished as an analytically pure colorless solid foam with dr 59:41 (34 mg, 0.05 mmol, 67 %); starting material **25** was recovered (5 mg, 8 μmol, 10 %). R_f=0.48 (petroleum ether/EtOAc 90:10); melting range: 120–126 °C; diastereomer A: ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.00 (s, 6H, OCH_3), 3.81 (m, 1H, 1′-H), 4.85 (ddd, ^3J=17.1, ^2J=2.3, ^4J=0.8 Hz, 1H, 3′-H_Z), 4.90 (ddd, ^3J=10.5, ^2J=2.3, ^4J=0.8 Hz, 1H, 3′-H_E), 5.35 (ddd, ^3J=17.1, ^3J=10.5, ^3J=4.8 Hz, 1H, 2′-H), 5.43 (s, 2H, 4″-H, 5″-H), 6.49 (d, ^3J=7.2 Hz, 1H, N*H*), 7.24–7.42 ppm (m, 20H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ=40.2 (C-1′), 51.9 (OCH_3), 78.7 (C-4′, C-5′), 83.2 (CPh_2OCH_3), 92.7 (C-2), 113.1 (C-3′), 127.7, 127.7, 127.8, 127.9, 128.3, 129.6 (arom. *C*H), 132.9 (C-2′), 140.4, 140.6 (arom. C_{ipso}), 161.2 ppm (C-1); diastereomer B: ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.02 (s, 6H, OCH_3), 3.75 (m, 1H, 1′-H), 4.90 (ddd, ^3J=17.1, ^2J=2.4, ^4J=0.9 Hz, 1H, 3′-H_Z), 4.94 (ddd, ^3J=10.5, ^2J=2.4, ^4J=0.9 Hz, 1H, 3′-H_E), 5.40 (s, 2H, 4″-H, 5″-H), 5.54 (ddd, ^3J=17.1, ^3J=10.5, ^4J=4.6 Hz, 1H, 2′-H), 6.38 (d, ^3J=7.8 Hz, 1H, N*H*), 7.24–7.42 ppm (m, 20H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ=40.2 (C-1), 51.8 (OCH_3), 78.7 (C-4″, C-5″), 83.3 (CPh_2OCH_3), 92.7 (C-2), 112.4 (C-3′), 127.6, 127.7, 127.8, 127.9, 128.2, 129.6 (arom. *C*H), 132.3 (C-2′), 140.5, 140.7 (arom. C_{ipso}), 161.5 ppm (C-1); IR (film, ATR): $\tilde{\nu}$=3430 (N-H-ν); 3085, 3060, 3030 (arom. C-H-ν); 2985, 2960, 2940, 2910 (aliph. C-H-ν); 2835 (OCH_3, C-H-ν); 1720 (CONH, amide I); 1655 (olef. C=C-ν); 1600, 1585, 1495 (arom. C=C-ν); 1510 (CONH, amide II); 1445; 1390; 1350; 1240; 1200; 1075 (C-O-C); 1030; 1010; 820; 760 (Ph, C-H-$\delta_{out\ of\ plane}$); 700 (Ph, ring-δ); 635 cm^{-1}; MS (FAB, matrix: NBA+NaI): *m/z* (%): 688 (25) [*M*+Na^+], 197 (100) [CPh_2OMe^+], 167 (8) [Ph_2CH^+], 105 (22) [$PhCO^+$], 77 (10) [Ph^+]; elemental analysis calcd (%) for $C_{35}H_{33}BCl_3NO_5$ (664.8): C 63.23, H 5.00, N 2.11, found: C 63.45, H 5.10, N 1.97.

(4′*R*,5′*R*,1*E*)-1-[4′,5′-Bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-3-chloro-2-propene (28): Trichloroacetimidate **25** (100 mg, 0.15 mmol) was dissolved in THF (2.5 mL) and cooled to 0 °C. A suspension of $[PdCl_2(CH_3CN)_2]$ (2 mg, 8 μmol) in THF (2 mL) was added and as no reaction occured, the reaction mixture was heated to 80 °C for 23 h, cooled to RT and concentrated under reduced pressure. Chromatography (41 g silica gel, petroleum ether/EtOAc 95:5) gave a spectroscopically pure colorless solid foam (57 %, 46 mg, 0.09 mmol), MPLC yielded an analytically pure sample. R_f=0.60 (petroleum ether/EtOAc 90:10); softening range: 80–90 °C; $[\alpha]_D^{20}=-65$ (*c*=0.90 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.00 (s, 6H, OCH_3), 3.91 (dd, ^3J=6.1, ^4J=1.2 Hz, 2H, 3-H), 5.32 (dt, ^3J=17.6, ^4J=1.2 Hz, 1H, 1-H), 5.36 (s, 2H, 4′-H, 5′-H), 6.18 (dt, ^3J=17.6, ^3J=6.1 Hz, 1H, 2-H), 7.26–7.41 ppm (m, 20H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ=45.9 (C-3), 51.8 (OCH_3), 77.7 (C-4′, C-5′), 83.3 (CPh_2OCH_3), 121.3 (C-1), 127.3, 127.3, 127.5, 127.8, 128.4, 129.6 (arom. *C*H), 140.9, 141.2 (arom. C_{ipso}), 146.2 ppm (C-2); IR (film, ATR): $\tilde{\nu}$= 3390 (br); 3090, 3055, 3025 (arom. C-H-ν); 2955, 2940, 2905 (aliph. C-H-ν); 2830 (OCH_3, C-H-ν); 1645 (olef. C=C-ν); 1600, 1580, 1495 (arom. C=C-ν); 1445; 1400; 1375; 1355; 1240; 1200; 1075 (C-O-C); 1030; 1015; 760 (Ph, C-H-$\delta_{out\ of\ plane}$); 700 cm^{-1} (Ph, ring-δ); MS (FAB, matrix: NBA+NaI): *m/z* (%): 561 (8) [*M*+Na^+], 197 (100) [CPh_2OMe^+], 167 (10) [Ph_2CH^+], 105 (16) [$PhCO^+$], 77 (7) [Ph^+]; elemental analysis calcd (%) for $C_{33}H_{32}BClO_4$ (538.9): C 73.55, H 5.99, found: C 73.52, H 6.04.

(1′*R*,4″*R*,5″*R*)- and (1′*S*,4″*R*,5″*R*)-*N*-{1′-[4″,5″-Bis(methoxydiphenylmethyl)-1″,3″,2″-dioxaborolan-2″-yl]prop-2′-en-1′-yl}–2,2,2-trifluoroacetamide (29): Trifluoroacetimidate **26** (50 mg, 0.08 mmol) was dissolved in 1,2-dichlorobenzene (5 mL). The solution was heated to 176 °C for 29 h and cooled to RT. The reaction mixture was loaded directly on a column

(20 g silica gel) which was conditioned with petroleum ether. Chromatography (petroleum ether to petroleum ether/EtOAc 95:5) gave a mixture of starting material **26** and product **29** (41:59), whereas the product **29** was a 55:45-diastereomeric mixture. The diastereomers could not be separated by MPLC, but the product **29** was furnished as an analytically pure colorless solid foam with dr 55:45 (10 mg, 0.016 mmol, 20%); starting material **26** was recovered (7 mg, 11 μmol, 14%). R_f=0.45 (petroleum ether/EtOAc 90:10); diastereomer A: ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.00 (s, 6H, OCH_3), 3.78 (m, 1H, 1′-H), 4.81 (dd, ^3J=17.1, ^2J=2.0 Hz, 1H, 3′-H$_Z$), 4.90 (dd, ^3J=10.6, ^2J=2.0 Hz, 1H, 3′-H$_E$), 5.30 (ddd, ^3J=17.1, ^3J=10.6, ^3J=5.0 Hz, 1H, 2′-H), 5.44 (s, 2H, 4″-H, 5″-H), 5.89 (d, ^3J=7.4 Hz, 1H, NH), 7.26–7.35 ppm (m, 20H, arom CH); ^{13}C NMR (126 MHz, $CDCl_3$): δ=51.8 (OCH_3), 78.7 (C-4″, C-5″), 83.3 (CPh_2OCH_3), 113.3 (C-3′), 127.7, 127.7, 127.9, 128.0, 128.3, 129.6 (arom. CH), 132.2 (C-2′), 140.3, 140.6 (arom. C_{ipso}), 156.8 ppm (q, $^3J_{C,F}$=38 Hz, C-1), C-1′ and C-2 were not detected; diastereomer B: ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.02 (s, 6H, OCH_3), 3.78 (m, 1H, 1′-H), 4.78 (dd, ^3J=17.1, ^2J=2.0 Hz, 1H, 3′-H$_Z$), 4.93 (dd, ^3J=10.6, ^2J=2.0 Hz, 1H, 3′-H$_E$), 5.42 (s, 2H, 4″-H, 5″-H), 5.49 (ddd, ^3J=17.1, ^3J=10.6, ^3J=4.8 Hz, 1H, 2′-H), 5.85 (d, ^3J=7.9 Hz, 1H, NH), 7.26–7.35 ppm (m, 20H, arom. CH); ^{13}C NMR (126 MHz, $CDCl_3$): δ=51.8 (OCH_3), 78.7 (C-4″, C-5″), 83.2 (CPh_2OCH_3), 112.6 (C-3′), 127.5, 127.6, 127.9, 128.0, 128.4, 129.5 (arom. CH), 132.7 (C-2′), 140.3, 140.4 (arom. C_{ipso}), 156.7 ppm (q, $^3J_{C,F}$=38 Hz, C-1), C-1′ and C-2 were not detected; IR (film, ATR): $\tilde{\nu}$=3440 (N-H-ν); 3090, 3060, 3025 (arom. C-H-ν); 2970, 2940, 2910 (aliph. C-H-ν); 2835 (OCH_3, C-H-ν); 1730 (CONH, amide I); 1640 (olef. C=C-ν); 1600, 1580, 1495 (arom. C=C-ν); 1535 (CONH, amide II); 1450; 1380; 1335; 1240, 1210, 1175 (C-F); 1070 (C-O-C); 1035; 760 (Ph, C-H-$\delta_{out\ of\ plane}$); 700 cm^{-1} (Ph, Ring-δ); MS (FAB, matrix: NBA+NaI): m/z (%): 638 (25) [M+Na$^+$], 358 (14), 197 (100) [CPh_2OMe^+], 167 (6) [Ph_2CH^+], 105 (12) [$PhCO^+$], 77 (5) [Ph$^+$]; HRMS (FAB, matrix: NBA+NaI): m/z: calcd for $C_{35}H_{33}BF_3NNaO_5$: 638.2302, found: 638.2308.

Determination of configuration

Ozonolysis and reduction with $LiAlH_4$ (General procedure F): Into a flask equipped with Teflon stop cock and gas inlet frit (quickfit with Teflon gasket), the homoallyl alcohol (about 0.1 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to −78°C: A O_3/O_2 mixture was bubbled through the solution until it shows a persisting blue color. Excess O_3 was expelled by a stream of O_2. To the reaction mixture was added Me_2S (1 mL), it was allowed to warm to room temperature, concentrated under reduced pressure and dried under high vacuum. The residue was dissolved in THF (10 mL) and cooled to −78°C. $LiAlH_4$ (100 mg, 2.64 mmol) was added and the reaction mixture was allowed to warm to RT. After 1 h Et_2O (10 mL) was added and cooled to 0°C. Successively H_2O (121 μL), 15% aqueous NaOH solution (121 μL) and H_2O (358 μL) were carefully added and stirred (about 30 min) until a precipitate formed that can be readily filtered through a pad of Celite; the filter cake was washed thoroughly with Et_2O. The filtrate was concentrated under reduced pressure and dried in high vacuum.

(1*S*)-1-Phenylpropane-1,3-diol (33): According to GP F, homoallyl alcohol **31a** (25 mg, 0.11 mmol; synthesis: see below) was used. Chromatography (0.7 g silica gel, petroleum ether/EtOAc 50:50) gave a colorless spectroscopically pure oil of diol **33** (6.0 mg, 0.04 mmol, 37%). The analytical data were in full agreement to those previously reported.[30] R_f=0.13 (petroleum ether/EtOAc 50:50), 0.27 (petroleum ether/EtOAc 25:75); $[\alpha]_D^{20}$=−70 (c=0.12 in $CHCl_3$), ref.: [30] $[\alpha]_D^{22}$ (**33**)=−71 (c=1.02 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.93 (dddd, ^2J=14.6, ^3J=5.5, ^3J=4.7, ^3J=4.0 Hz, 1H, 2-H$_a$), 2.03 (dddd, ^2J=14.6, ^3J=8.5, ^3J=6.5, ^3J=5.4 Hz, 1H, 2-H$_b$), 2.44 (brs, 1H, 3-OH), 2.86 (brs, 1H, 1-OH), 3.82–3.89 (m, 2H, 3-H), 4.96 (dd, ^3J=8.5, ^3J=4.0 Hz, 1H, 1-H), 7.25–7.38 ppm (m, 5H, arom. CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=40.5 (C-2), 61.5 (C-3), 74.4 (C-1), 125.6, 127.6, 128.5 (arom. CH), 144.3 ppm (arom. C_{ipso}); IR (solution in $CDCl_3$): $\tilde{\nu}$=3600 (O-H-ν); 3500 (br, O-H-ν); 3065, 3045, 3010 (arom. C-H-ν); 2920, 2860 (aliph. C-H-ν); 1480 (arom. C=C-ν); 1440 (aliph. C-H-δ); 1410 (O-H-δ); 1035 cm^{-1} (C-OH); MS (EI, 70 eV): m/z (%): 152 (33) [M^+], 107 (100) [PhCHOH$^+$], 77 (24) [Ph$^+$]; HRMS (EI, 70 eV): m/z: calcd for $C_9H_{12}O_2$: 152.0837, found: 152.0837.

(1*S*)-1-Phenylpropane-1,3-diol (33): Allylboronate **21** (78 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (73 μL) and PhCHO (21 μL, 22 mg, 0.20 mmol) was added. After 16 h the reaction mixture was concentrated under reduced pressure and dried under high vacuum. According to GP F, the residue was used for ozonolysis and reduction. Chromatography (5.8 g silica gel, petroleum ether/EtOAc 50:50) gave a colorless slightly impure oil (49% **33**, 11 mg, 0.07 mmol). The analytical data are in full agreement to those previously reported.[30] $[\alpha]_D^{20}$=−64 (c=0.22 in $CHCl_3$); for further characterisation see above.

Modification of side chain

(3*S*,4′*R*,5′*R*)-*tert*-Butyldimethylsilyl-3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-4-penten-1-yl ether (35): Alcohol **34**[15a] (768 mg, 1.40 mmol) and imidazole (105 mg, 1.54 mmol) were dissolved in CH_2Cl_2 (1.40 mL) and TBSCl (222 mg) was added wereupon a colorless solid precipitated. The reaction mixture was stirred over night, diluted with Et_2O, and H_2O was added until the solid was dissolved completely. The aqueous phase was extracted thrice with Et_2O. The combined organic phase was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography (65 g silica gel, petroleum ether/EtOAc 98:2) gave a spectroscopically pure colorless solid foam of ether **35** (911 mg, 1.38 mmol, 98%), MPLC (petroleum ether/EtOAc 99:1) furnished an analytically pure sample. R_f=0.08 (petroleum ether/EtOAc 98:2), 0.44 (petroleum ether/EtOAc 95:5); softening range: 46–52°C; $[\alpha]_D^{20}$=−96 (c=1.12 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=−0.07, −0.05 [2s, 6H, Si(CH_3)$_2$], 0.82 [s, 9H, C(CH_3)$_3$], 1.24 (dddd, ^2J=13.5, ^3J=9.5, ^3J=7.0, ^3J=5.5 Hz, 1H, 2-H$_a$), 1.39 (dddd, ^2J=13.5, ^3J=7.8, ^3J=7.5, ^3J=4.9 Hz, 1H, 2-H$_b$), 1.46 (ddddd, ^3J=9.5, ^3J=8.2, ^3J=4.9, ^3J=1.3, ^3J=1.1 Hz, 1H, 3-H), 3.00 (s, 6H, OCH_3), 3.32 (ddd, ^2J=10.0, ^3J=7.5, ^3J=7.0 Hz, 1H, 1-H$_a$), 3.34 (ddd, ^2J=10.0, ^3J=7.8, ^3J=5.5 Hz, 1H, 1-H$_b$), 4.69 (ddd, ^3J=17.1, ^2J=2.0, ^4J=1.3 Hz, 1H, 5-H$_Z$), 4.75 (ddd, ^3J=10.3, ^2J=2.0, ^4J=1.1 Hz, 1H, 5-H$_E$), 5.29 (s, 2H, 4′-H, 5′-H), 5.44 (ddd, ^3J=17.1, ^3J=10.3, ^3J=8.2 Hz, 1H, 4-H), 7.23–7.34 ppm (m, 20H, arom. CH); ^{13}C NMR (126 MHz, $CDCl_3$): δ=−5.3, −5.3 [Si(CH_3)$_2$], 18.3 [C(CH$_3$)$_3$], 25.2 (br, C-3), 26.0 [C(CH_3)$_3$], 31.5 (C-2), 51.7 (OCH_3), 61.8 (C-1), 77.7 (C-4′, C-5′), 83.4 (CPh_2OCH_3), 113.1 (C-5), 127.2, 127.3, 127.5, 127.8, 128.5, 129.7 (arom. CH), 138.6 (C-4), 141.3, 141.4 ppm (arom. C_{ipso}); IR (KBr): $\tilde{\nu}$=3420 (br); 3070, 3040, 3005 (arom. C-H-ν); 2930, 2910, 2830 (aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1620 (olef. C=C-ν); 1590, 1570, 1480 (arom. C=C-ν); 1460; 1450; 1435; 1370; 1340; 1240; 1185; 1075; 1060 (C-O-C); 1020; 1000; 950; 885; 815, 795, 755 (TBS); 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 (Ph, ring-δ); 615; 590 cm^{-1}; MS (FAB, matrix: NBA+NaI): m/z (%): 685 (5) [M+Na$^+$], 197 (100) [CPh_2OMe^+], 167 (12) [Ph_2CH^+], 105 (9) [$PhCO^+$], 73 (11) [$MeSi(O)CH_2^+$]; elemental analysis calcd (%) for $C_{41}H_{51}BO_5Si$ (662.7): C 74.30, H 7.76, found: C 74.25, H 7.75.

(3*R*,4′*R*,5′*R*)-*tert*-Butyldimethylsilyl-3-[4′,5′-bis(methoxydiphenylmethyl)-1′,3′,2′-dioxaborolan-2′-yl]-4-penten-1-yl ether (37): The reaction was accomplished according to the synthesis of ether **35**: Alcohol **36** (1.12 g, 2.05 mmol), CH_2Cl_2 (2.05 mL), imidazole (153 mg, 2.25 mmol) and TBSCl (324 mg, 2.15 mmol) were used. Chromatography (85 g silica gel, petroleum ether/EtOAc 98:2) furnished an analytically pure colorless solid foam of ether **37** (1.38 g, 2.08 mmol, quantitative). R_f=0.11 (petroleum ether/EtOAc 98:2), 0.48 (petroleum ether/EtOAc 95:5); softening range: 42–53°C; $[\alpha]_D^{20}$=−103 (c=0.88 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=−0.05, −0.04 [2s, 6H, Si(CH_3)$_2$], 0.85 [s, 9H, C(CH_3)$_3$], 1.23–1.30 (m, 1H, 2-H$_a$), 1.40–1.44 (m, 1H, 3-H), 1.47 (dddd, ^2J=12.6, ^3J=8.5, ^3J=7.4, ^3J=5.2 Hz, 1H, 2-H$_b$), 3.00 (s, 6H, OCH_3), 3.25 (ddd, ^2J=10.0, ^3J=7.7, ^3J=7.4 Hz, 1H, 1-H$_a$), 3.32 (ddd, ^2J=10.0, ^3J=8.5, ^3J=4.7 Hz, 1H, 1-H$_b$), 4.69 (ddd, ^3J=17.1, ^2J=2.0, ^4J=1.1 Hz, 1H, 5-H$_Z$), 4.73 (ddd, ^3J=10.3, ^2J=2.0, ^4J=0.7 Hz, 1H, 5-H$_E$), 5.29 (s, 2H, 4′-H, 5′-H), 5.33 (ddd, ^3J=17.1, ^3J=10.3, ^3J=8.5 Hz, 1H, 4-H); 7.24–7.34 ppm (m, 20H, arom. CH); ^{13}C NMR (126 MHz, $CDCl_3$): δ=−5.3 [Si(CH_3)$_2$], 18.3 [C(CH$_3$)$_3$], 25.5 (br, C-3), 26.0 [C(CH_3)$_3$], 31.9 (C-2), 51.8 (OCH_3), 62.0 (C-1), 77.7 (C-4′, C-5′), 83.4 (CPh_2OCH_3), 113.4 (C-5), 127.2, 127.3, 127.5, 127.8, 128.5, 129.7 (arom. CH), 138.4 (C-4), 141.3, 141.4 ppm (arom. C_{ipso}); IR (KBr): $\tilde{\nu}$=3420 (br); 3070, 3040, 3010 (arom. C-H-ν); 2935, 2910, 2880, 2835 (aliph. C-H-ν); 2810 (OCH_3, C-H-ν); 1620 (olef. C=C-ν); 1590, 1570, 1480 (arom. C=C-ν); 1460; 1450; 1435; 1365; 1340; 1240;

1185; 1070; 1060 (C-O-C); 1020; 1000; 950; 885; 815, 795, 755 (TBS); 740 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 (Ph, ring-δ); 615; 590 cm^{-1}; MS (FAB, matrix: NBA+NaI): *m/z* (%): 685 (7) [*M*+Na^+], 197 (100) [CPh_2OMe^+], 167 (12) [Ph_2CH^+], 105 (10) [$PhCO^+$], 73 (12) [$MeSi(O)CH_2^+$]; elemental analysis calcd (%) for $C_{41}H_{51}BO_5Si$ (662.7): C 74.30, H 7.76, found: C 74.33, H 7.77.

Allyl additions

Allyl addition (General procedure D): The allylboronate (1.00 equiv) was dissolved in CH_2Cl_2 (0.5 mL per mmol of the allylboronate) and cooled to 0 °C. The aldehyde (1.20–1.50 equiv) was added and the reaction mixture was allowed to warm slowly (ice/water mixture in a Dewar pot) to RT over night. Stirring was continued at RT until complete transformation was detected by TLC. The reaction mixture was concentrated under reduced pressure, dried under high vacuum, and finally analysed by NMR spectroscopy. After concentration under reduced pressure, it was loaded on a conditioned chromatography column as a solution in the solvent for the chromatography with some silica gel; no pressure was applied during separation.

Allyl addition followed by direct $LiAlH_4$ reduction (General procedure E): The allylboronate (1.00 equiv) was dissolved in CH_2Cl_2 (0.5 mL per mmol of the allylboronate) and cooled to 0 °C. The aldehyde (1.20–1.50 equiv) was added and the reaction mixture was allowed to warm slowly (ice/water mixture in a Dewar pot) to RT over night. Stirring was continued at RT until complete transformation was detected by TLC. The reaction mixture was concentrated under reduced pressure and dried under high vacuum, and finally analysed by NMR spectroscopy. After concentration under reduced, the residue was dissolved in THF (10 mL per mmol of the allylboronate) and $LiAlH_4$ (4.00 equiv) were added. After 1 h the reaction mixture was diluted with 20 mL Et_2O and with vigorous stirring successively H_2O (46 μL per mmol $LiAlH_4$), 15% aqueous NaOH solution (46 μL per mmol $LiAlH_4$) and H_2O (136 μL per mmol $LiAlH_4$) were added carefully. After 30 min a precipitate was formed that was filtered through a pad of Celite and washed thoroughly with Et_2O. The filtrate was concentrated under reduced pressure and subjected to flash column chromatography.

(6*S*,3*Z*)-Ethyl 6-hydroxy-6-phenylhex-3-enoate (31a) and (6*R*,3*Z*)-ethyl 6-hydroxy-6-phenylhex-3-enoate (*ent*-31a): According to GP D allylboronates **15** or **16** (240 mg, 0.41 mmol, 1.00 equiv), respectively, in CH_2Cl_2 (200 μL) with benzaldehyde (62 μL, 65 mg, 0.61 mmol, 1.50 equiv) were used. The reaction mixtures were stirred at 0 °C over night and at RT for 10 h. Chromatographic purification (petroleum ether to petroleum ether/EtOAc 90:10) gave a spectroscopically pure colorless oil (**31a**: 87 mg, 0.37 mmol, 91%; Mosher ester:[41,15c] *ee* 89%; *ent*-**31a**: 85 mg, 0.36 mmol, 89%; Mosher ester: *ee* > 99%), repeated chromatography furnished an analytically pure sample. R_f (**31a**) = 0.25 (petroleum ether/EtOAc 85:15); $[\alpha]_D^{20}$ (**31a**) = −82 (*c* = 0.84 in $CHCl_3$), $[\alpha]_D^{20}$ (*ent*-**31a**) = +85 (*c* = 1.22 in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.1 Hz, 3H, 2′-H), 2.45–2.57 (m, 2H, 5-H), 2.61 (d, ^3J = 3.7 Hz, 1H, O*H*), 3.01 (ddd, ^2J = 16.6, ^3J = 7.1, ^4J = 1.5 Hz, 1H, 2-H_a), 3.08 (ddd, ^2J = 16.6, ^3J = 7.4, ^4J = 1.5 Hz, 1H, 2-H_b), 4.13 (q, ^3J = 7.1 Hz, 2H, 1′-H), 4.73 (ddd, ^3J = 7.7, ^3J = 5.2, ^3J = 3.7 Hz, 1H, 6-H), 5.63 (m, 1H, 4-H), 5.71 (dddt, ^3J = 10.8, ^3J = 7.4, ^3J = 7.1, ^4J = 1.4 Hz, 1H, 3-H), 7.25–7.37 ppm (m, 5H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (C-2′), 33.0 (C-2), 37.5 (C-5), 60.8 (C-1′), 73.3 (C-6), 124.3 (C-3), 125.7, 127.5, 128.4 (arom. *C*H), 128.9 (C-4), 144.0 (arom. C_{ipso}), 171.9 ppm (C-1); IR (solution in $CDCl_3$): $\tilde{\nu}$ = 3590 (O-H-ν); 3450 (br); 3065, 3045, 3010 (arom. C-H-ν); 2960, 2920, 2880 (aliph. C-H-ν); 2810; 1720 (C=O-ν); 1650 (olef. C=C-ν); 1595, 1575, 1485 (arom. C=C-ν); 1440 (aliph. C-H-δ); 1390 (O-H-δ); 1360; 1315; 1175 (ester, C-O); 1060; 1015 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 234 (2) [M^+], 216 (0.08) [$M-H_2O^+$], 189 (0.6) [$M-OEt^+$], 171 (6) [$M-H_2O-EtO^+$], 128 (100) [$M-PhCHO^+$], 107 (66) [$PhCHOH^+$], 77 (49) [Ph^+]; HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_{18}O_3$: 234.1256, found: 234.1257; elemental analysis calcd (%) for $C_{14}H_{18}O_3$ (234.3): C 71.77, H 7.74, found: C 71.48, H 7.88.

(6*R*,3*Z*)-Ethyl 6-hydroxy-8-phenyloct-3-enoate (31b) and (6*S*,3*Z*)-6-ethyl hydroxy-8-phenyloct-3-enoate (*ent*-31b): According to GP D allylboronates **15** or **16** (200 mg, 0.34 mmol), respectively, in CH_2Cl_2 (170 μL) with 3-phenyl propionaldehyde (54 μL, 55 mg, 0.41 mmol) were used. The reaction mixtures were stirred at 0 °C for 24 h and at RT for 48 h. Chromatography (petroleum ether/EtOAc 90:10 → 85:15) furnished a spectroscopically pure colorless oils (*ent*-**31b**: 86 mg, 0.33 mmol, 97%; HPLC: *ee* 92%), MPLC (petroleum ether/EtOAc 85:15) furnished an analytically pure sample (**31b**: 60 mg, 0.23 mmol, 67%; HPLC: *ee* 98%). R_f = 0.09 (petroleum ether/EtOAc 85:15), 0.28 (petroleum ether/EtOAc 75:25); $[\alpha]_D^{20}$ (**31b**) = −7 (*c* = 1.14 in $CHCl_3$, *ee* 98%), $[\alpha]_D^{20}$ (*ent*-**31b**) = +7 (*c* = 1.18 in $CHCl_3$, *ee* 92%); HPLC (Chiralcel OD, hexane/*i*PrOH 96:4): t_R (**31b**) = 9.2 min, t_R (*ent*-**31b**) = 6.5 min; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.1 Hz, 3H, 2′-H), 1.79 (m, 2H, 7H), 2.17 (d, ^3J = 3.4 Hz, 1H, O*H*), 2.26 (m, 2H, 5-H), 2.69 (ddd, ^2J = 13.7, ^3J = 8.9, ^3J = 7.5 Hz, 1H, 8-H_a), 2.82 (ddd, ^2J = 13.7, ^3J = 8.8, ^3J = 6.5 Hz, 1H, 8-H_b), 3.08 (ddd, ^2J = 16.5, ^3J = 7.0, ^4J = 1.4 Hz, 1H, 2-H_a), 3.15 (ddd, ^2J = 16.5, ^3J = 7.4, ^4J = 1.4 Hz, 1H, 2-H_b), 3.67 (m, 1H, 6-H), 4.13 (q, ^3J = 7.1 Hz, 2H, 1′-H), 5.65 (dtt, ^3J = 10.8, ^3J = 7.7, ^4J = 1.4 Hz, 1H, 4-H), 5.72 (dddt, ^3J = 10.8, ^3J = 7.4, ^3J = 7.0, ^4J = 1.3 Hz, 1H, 3-H), 7.16–7.21, 7.25–7.29 ppm (m, 5H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (C-2′), 32.1 (C-8), 33.0 (C-2), 35.6 (C-5), 38.6 (C-7), 60.9 (C-1′), 70.1 (C-6), 124.1 (C-3), 125.7, 128.3, 128.4 (arom. *C*H); 129.3 (C-4), 142.0 (arom. C_{ipso}), 172.0 ppm (C-1); IR (solution in $CDCl_3$): $\tilde{\nu}$ = 3430 (O-H-ν); 3065, 3040, 3005 (arom. C-H-ν); 2960, 2910, 2840 (aliph. C-H-ν); 1730 (C=O-ν); 1650 (olef. C=C-ν); 1595, 1575, 1485 (arom. C=C-ν); 1440 (aliph. C-H-δ); 1390; 1360; 1310; 1240; 1160; 1080; 1015; 915; 840; 730 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 cm^{-1} (Ph, ring-δ); MS (EI, 70 eV): *m/z* (%): 262 (3) [M^+], 244 (7) [$M-H_2O^+$], 216 (2) [$M-H_2O-C_2H_4^+$], 198 (4) [$M-2H_2O-C_2H_4^+$], 128 (100) [$M-PhCH_2CH_2CHO^+$], 117 (32) [$C_9H_9^+$], 91 (58) [$PhCH_2^+$]; elemental analysis calcd (%) for $C_{16}H_{22}O_3$ (262.3): C 73.25, H 8.48, found: C 73.06, H 8.59.

(6*S*,3*Z*)-Ethyl 6-hydroxy-7-(5′-methoxybenzyloxy)hept-3-enoate (31c) and (6*R*,3*Z*)-ethyl 6-hydroxy-7-(5′-methoxybenzyloxy)hept-3-enoate (*ent*-31c) According to GP D allylboronate **15** (6.51 g, 11.1 mmol) in CH_2Cl_2 (5.50 mL) with 4″-methoxybenzyloxyacetaldehyde (**42c**; 2.38 g, 13.2 mmol) was used. The reaction mixture was stirred at 0 °C for 24 h and at RT for 3 d. Chromatography (450 g silica gel, petroleum ether/EtOAc 85:15 → 75:25) furnished a spectroscopically pure colorless oil (**31c**: 3.43 g, 11.1 mmol, quant.; HPLC: *ee* 99%), MPLC (petroleum ether/EtOAc 70:30) afforded an analytically pure sample. According to GP D allylboronate **16** (3.0 g, 5.1 mmol) in CH_2Cl_2 (2.5 mL) with **42c** (1.1 g, 6.1 mmol) was used. The reaction mixture was stirred at 0 °C for 24 h and at RT for 3 d. Chromatography (220 g silica gel, petroleum ether/EtOAc 85:15 → 75:25) furnished a spectroscopically pure colorless oil (*ent*-**31c**: 1.6 g, 5.1 mmol, quant. HPLC: *ee* 87%); R_f = 0.05 (petroleum ether/EtOAc 85:15), 0.16 (petroleum ether/EtOAc 70:30); $[\alpha]_D^{20}$ (**31c**) = −6 (*c* = 1.92 in $CHCl_3$, *ee* 99%), $[\alpha]_D^{20}$ (*ent*-**31c**) = +6 (*c* = 1.94 in $CHCl_3$, *ee* 87%); HPLC (Chiralcel OD-H, hexane/*i*PrOH 90:10): t_R (**31c**) = 26.8 min, t_R (*ent*-**31c**) = 32.1 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.1 Hz, 3H, 2‴-H), 2.27 (ddd, ^3J = 7.3, ^3J = 6.4, ^3J = 1.3 Hz, 2H, 5-H), 2.49 (br s, 1H, O*H*), 3.09 (ddd, ^2J = 16.0, ^3J = 7.0, ^4J = 1.4 Hz, 1H, 2-H_a), 3.10 (ddd, ^2J = 16.0, ^3J = 7.0, ^4J = 1.4 Hz, 1H, 2-H_b), 3.36 (dd, ^2J = 9.5, ^3J = 7.0 Hz, 1H, 7-H_a), 3.47 (dd, ^2J = 9.5, ^3J = 3.7 Hz, 1H, 7-H_b), 3.80 (s, 3H, OCH_3), 3.84 (dtd, ^3J = 7.0, ^3J = 6.4, ^3J = 3.7 Hz, 1H, 6-H), 4.13 (q, ^3J = 7.1 Hz, 2H, 1‴-H), 4.48 (s, 2H, 1′-H), 5.63 (dtt, ^3J = 10.8, ^3J = 7.3, ^4J = 1.4 Hz, 1H, 4-H), 5.70 (dtt, ^3J = 10.8, ^3J = 7.0, ^4J = 1.3 Hz, 1H, 3-H), 6.88 (m, 2H, 3″-H), 7.25 ppm (m, 2H, 2″-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (C-2‴), 31.5 (C-5), 33.0 (C-2), 55.2 (OCH_3), 60.7 (C-1‴), 69.8 (C-6), 73.0 (C-1′), 73.4 (C-7), 113.8 (C-3″), 123.7 (C-3), 128.5 (C-4), 129.3 (C-2″), 130.0 (C-1″), 159.2 (C-4″), 171.8 ppm (C-1); IR (film, ATR): $\tilde{\nu}$ = 3450 (O-H-ν); 3030 (arom. C-H-ν); 2980, 2935, 2905, 2860 (aliph. C-H-ν); 2835 (OCH_3, C-H-ν); 1730 (C=O-ν); 1660 (olef. C=C-ν); 1610, 1585, 1510 (arom. C=C-ν); 1465, 1365; 1325; 1300; 1245, 1030; 1175; 1095; 945; 930; 845; 820 (1,4-disubstituted benzene ring); 755; 705 cm^{-1}; MS (ESI-1): *m/z* (%): 326 (100) [*M*+NH_4^+]; MS2 (326@16): *m/z* (%): 309 (100) [*M*+H^+]; elemental analysis calcd (%) for $C_{17}H_{24}O_5$ (308.4): C 66.21, H 7.84, found: C 66.16, H 7.93.

(6*S*,3*Z*)-6-Hydroxy-6-phenylhex-3-enoic acid dimethylamide (43a) and (6*R*,3*Z*)-6-hydroxy-6-phenylhex-3-enoic acid dimethylamide (*ent*-43a): According to GP D allylboronate **18** (284 mg, 0.48 mmol) in CH_2Cl_2 (240 μL) and benzaldehyde (69 μL, 72 mg, 0.67 mmol) was used. The reaction mixture was stirred at RT for 20 h. Chromatography (22 g silica

gel, EtOAc) gave a spectroscopically pure colorless oil (**43a**: 89 mg, 0.38 mmol, 79%; Mosher ester:[41] *ee* 94%). Following GP D, allylboronate **19** (100 mg, 0.17 mmol) in toluene (1 mL) with benzaldehyde (17 μL, 18 mg, 0.17 mmol) was used. The reaction mixture was set up at −100°C and was allowed to reach room temperature slowly. It was stirred at RT for 6 d. Chromatography (7 g silica gel, EtOAc) furnished a spectroscopically colorless oil (*ent*-**43a**: 35 mg, 0.15 mmol, 88%; Mosher ester: *ee* > 99%). To avoid long reaction times, the originally GP D should preferentially be used. R_f = 0.28 (EtOAc), 0.05 (petroleum ether/EtOAc 50:50); $[\alpha]_D^{20}$ (**43a**) = −128 (*c* = 0.20 in $CHCl_3$, *ee* 94%), $[\alpha]_D^{20}$ (*ent*-**43a**) = +132 (*c* = 0.64 in $CHCl_3$, *ee* > 99%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46–2.58 (m, 2H, 5-H), 2.92, 2.97 [2s, 6H, N(CH_3)$_2$], 3.00–3.11 (m, 2H, 2-H), 3.77 (d, ^3J = 4.2 Hz, 1H, O*H*), 4.75 (ddd, ^3J = 7.6, ^3J = 4.5, ^3J = 4.2 Hz, 1H, 6-H), 5.62 −5.70 (m, 2H, 3-H, 4-H), 7.22–7.39 ppm (m, 5H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 31.8 (C-2), 35.6, 37.3 [N(CH_3)$_2$], 37.7 (C-5), 72.9 (C-6), 124.9 (C-3), 125.6, 127.0, 128.1 (arom. *C*H), 128.9 (C-4), 144.5 (arom. C_{ipso}), 171.5 ppm (C-1); IR (solution in $CDCl_3$): $\tilde{\nu}$ = 3600 (O-H-ν); 3360 (br); 3070, 3045, 3010 (arom. C-H-ν); 2920, 2870 (aliph. C-H-ν); 1625 (C=O-ν); 1480 (arom. C=C-ν); 1440 (aliph. C-H-δ); 1390; 1250; 1130; 1040 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 233 (2) [M^+], 215 (1) [$M-H_2O^+$], 127 (87) [$M-PhCHO^+$], 107 (12) [$PhCHOH^+$], 105 (19) [$PhCO^+$], 77 (18) [Ph^+], 72 (100) [Me_2NCO^+]; HRMS (AUTO-CI): *m*/*z*: calcd for $C_{14}H_{20}NO_2$: 234.1494, found: 234.1486; elemental analysis calcd (%) for $C_{14}H_{19}NO_2$ (233.3): C 72.07, H 8.21, N 6.00, found: C 71.41, H 8.42, N 5.78.

(6*R*,3*Z*)-6-Hydroxy-8-phenyloct-3-enoic acid dimethylamide (43b), (6*S*,3*E*)-6-Hydroxy-8-phenyloct-3-enoic acid dimethylamide (46) and (6*S*,3*Z*)-6-hydroxy-8-phenyloct-3-enoic acid dimethylamide (*ent*-43b): According to GP D allylboronates **18** or **19** (200 mg, 0.34 mmol), respectively, in CH_2Cl_2 (170 μL) with 3-phenylpropionaldehyde (54 μL, 55 mg, 0.41 mmol) were used. The reaction mixtures were stirred at 0°C for 24 h and at RT for 4 d. Chromatography (14 g silica gel, petroleum ether/EtOAc 70:30 → EtOAc) yielded spectroscopically pure colorless oils [from **18** (**43b**: 58 mg, 0.22 mmol, 65%; HPLC: *ee* > 99%; **46**: 26 mg, 0.10 mmol, 29%) and **19** (*ent*-**43b**: 83 mg, 0.32 mmol, 94%; HPLC: *ee* 94%)]. R_f (**43b**) = 0.19 (EtOAc), R_f (**46**) = 0.15 (EtOAc); $[\alpha]_D^{20}$ (**43b**) = −16 (*c* = 0.90 in $CHCl_3$, *ee* > 99%), $[\alpha]_D^{20}$ (**46**) = −14 (*c* = 1.25 in $CHCl_3$), $[\alpha]_D^{20}$ (*ent*-**43b**) = +14 (*c* = 1.20 in $CHCl_3$, *ee* 94%); HPLC (Chiralcel OD-H, hexane/*i*PrOH 80:20): t_R (**43b**) = 22.4 min, t_R (*ent*-**43b**) = 19.6 min; homoallyl alcohol **43b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70–1.89 (m, 2H, 7H), 2.20–2.34 (m, 2H, 5-H), 2.70 (ddd, ^2J = 13.7, ^3J = 9.3, ^3J = 7.2 Hz, 1H, 8-H_a), 2.84 (ddd, ^2J = 13.7, ^3J = 9.5, ^3J = 5.8 Hz, 1H, 8-H_b), 2.95, 3.04 [2s, 6H, N(CH_3)$_2$], 3.08–3.21 (m, 3H, 2-H, O*H*), 3.66 (m, 1H, 6-H), 5.64–5.75 (m, 2H, 3-H, 4-H), 7.14–7.31 ppm (m, 5H, arom. C*H*); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 31.9 (C-2), 32.2 (C-8), 35.7 (C-5, NC_aH_3), 37.4 (NC_bH_3), 38.9 (C-7), 69.9 (C-6), 124.9 (C-3), 125.7, 128.3, 128.5 (arom. *C*H), 129.4 (C-4), 142.3 (arom. C_{ipso}), 171.6 ppm (C-1); IR (film, ATR): $\tilde{\nu}$ = 3400 (O-H-ν); 3085, 3060, 3025 (arom. C-H-ν); 2930, 2860 (aliph. C-H-ν); 1625 (C=O-ν); 1495 (arom. C=C-ν); 1455; 1395 (O-H-δ); 1260; 1140; 1050; 750 (Ph, C-H-$\delta_{out\ of\ plane}$); 700 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 261 (10) [M^+], 243 (10) [$M-H_2O^+$], 156 (21) [$M-PhCH_2CH_2^+$], 134 (2) [$PhCH_2CH_2CHO^+$], 127 (84) [$M-PhCH_2CH_2CHO^+$], 126 (8) [$M-PhCH_2CH_2CHOH^+$], 91 (31) [$PhCH_2^+$], 87 (16) [$MeCONMe_2^+$], 72 (100) [$OCNMe_2^+$]; MS (ESI-1): *m*/*z* (%): 262 (100) [$M+H^+$]; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{16}H_{23}NO_2$: 261.1729, found: 261.1729; elemental analysis calcd (%) for $C_{16}H_{23}NO_2$ (261.4): C 73.53, H 8.87, N 5.36, found: C 72.94, H 9.01, N 5.11; homoallyl alcohol **46**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71–1.83 (m, 2H, 7H); 2.17 (ddddt, ^2J = 13.9, ^3J = 7.9, ^3J = 7.7, ^4J = 0.9, ^5J = 0.9 Hz, 1H, 5-H_a), 2.30 (brs, 1H, O*H*), 2.31 (ddddt, ^2J = 13.9, ^3J = 6.4, ^3J = 4.2, ^4J = 1.1, ^5J = 1.0 Hz, 1H, 5-H_b), 2.68 (ddd, ^2J = 13.8, ^3J = 8.3, ^3J = 7.9 Hz, 1H, 8-H_a), 2.82 (ddd, ^2J = 13.8, ^3J = 8.0, ^3J = 7.5 Hz, 1H, 8-H_b), 2.94, 3.00 [2s, 6H, N(CH_3)$_2$], 3.10 (m, 2H, 2-H), 3.64 (dddd, ^3J = 7.9, ^3J = 6.8, ^3J = 5.8, ^3J = 4.2 Hz, 1H, 6-H), 5.53 (dddt, ^3J = 15.4, ^3J = 7.7, ^3J = 6.4, ^4J = 1.4 Hz, 1H, 4-H), 5.67 (dtdd, ^3J = 15.4, ^3J = 6.5, ^4J = 1.1, ^4J = 0.9 Hz, 1H, 3-H), 7.15–7.31 ppm (m, 5H, arom. C*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.0 (C-8), 35.5, 37.3 [br, N(CH_3)$_2$], 37.4 (C-2), 38.5 (C-7), 40.7 (C-5), 69.9 (C-6), 125.7, 128.3, 128.4 (arom. *C*H), 126.7 (C-3), 129.8 (C-4), 142.2 (arom. C_{ipso}), 171.3 ppm (C-1); IR (film, ATR): $\tilde{\nu}$ = 3395 (O-H-ν); 3085, 3060, 3025 (arom. C-H-ν); 2930, 2860 (aliph. C-H-ν); 1625 (C=O-ν); 1495 (arom. C=C-ν); 1455; 1400; 1260; 1140; 1055; 970; 750 (Ph, C-H-$\delta_{out\ of\ plane}$); 700 cm^{-1}; MS (ESI-2): *m*/*z* (%): 300 (7) [$M+K^+$], 284 (85) [$M+Na^+$], 262 (7) [$M+H^+$];

(3*R*)-5-Phenylpentan-1,3-diol (47): According to GP F homoallyl alcohol **46** (18 mg, ≈0.07 mmol) was used. Chromatography (2 g silica gel, petroleum ether/EtOAc 40:60) gave cololurless spectroscopically pure oil of diol **47** (7.0 mg, 0.04 mmol, ≈56%). The analytical data are in full agreement to those previously reported:[42] R_f (**47**) = 0.14 (petroleum ether/EtOAc 40:60); $[\alpha]_D^{20}$ = −18 (*c* = 0.35 in $CHCl_3$), $[\alpha]_D^{24}$ = −13 (*c* = 0.35 in EtOH), ref.:[42] $[\alpha]_D^{24}$ = −10.2 (*c* = 1.32 in EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70–1.87 (m, 4H, 2-H, 4-H), 2.37, 2.54 (2brs, 2H, O*H*), 2.69 (ddd, ^2J = 13.7, ^3J = 8.8, ^3J = 6.9 Hz, 1H, 5-H_a), 2.79 (ddd, ^2J = 13.7, ^3J = 9.2, ^3J = 6.5 Hz, 1H, 5-H_b), 3.79–3.94 (m, 3H, 1-H, 3-H), 7.16–7.32 ppm (m, 5H, arom. C*H*); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 29.7 (C-5), 38.4, 39.4 (C-2, C-4), 61.8 (C-1), 71.6 (C-3), 125.9, 128.4, 128.4 (arom. *C*H), 141.9 ppm (arom. C_{ipso}); IR (film, ATR): $\tilde{\nu}$ = 3340 (br, O-H-ν); 3085, 3060, 3025 (arom. C-H-ν); 2935, 2860 (aliph. C-H-ν); 1605, 1585, 1495 (arom. C=C-ν); 1455; 1055 (C-O-ν); 745 (C-H-$\delta_{out\ of\ plane}$); 700 cm^{-1} (Ph, ring-δ).

(6*S*,3*Z*)-6-Hydroxy-7-(4″-methoxybenzyloxy)hept-3-enoic acid dimethylamide (43c) and (6*R*,3*Z*)-6-hydroxy-7-(4″-methoxybenzyloxy)hept-3-enoic acid dimethylamide (*ent*-43c): According to GP D allylboronates **18** or **19** (200 mg, 0.34 mmol), respectively, in CH_2Cl_2 (170 μL) with **42c** (73 mg, 0.41 mmol) were used. The reaction mixtures were stirred at 0°C for 24 h and at RT for 24 h. Chromatography (16 g silica gel, petroleum ether/EtOAc 60:40 → EtOAc) furnished analytically pure colorless oils (**43c**: 90 mg, 0.29 mmol, 86%; HPLC: *ee* > 99%; *ent*-**43c**: 94 mg, 0.31 mmol, 90%; HPLC: *ee* 96%); R_f = 0.15 (EtOAc); $[\alpha]_D^{20}$ (**43c**) = −25 (*c* = 1.80 in $CHCl_3$, *ee* > 99%), $[\alpha]_D^{20}$ (*ent*-**43c**) = +24 (*c* = 1.86 in $CHCl_3$, *ee* 96%); HPLC (Chiralcel OD-H, hexane/*i*PrOH 80:20): t_R (**43c**) = 27.0 min, t_R (*ent*-**43c**) = 31.9 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (ddd, ^3J = 7.4, ^3J = 6.3, ^3J = 1.3 Hz, 2H, 5-H), 2.93, 3.00 [2s, 6H, N(CH_3)$_2$], 3.11 (ddd, ^2J = 9.3, ^3J = 6.9, ^4J = 1.4 Hz, 1H, 2-H_a), 3.12 (ddd, ^2J = 9.3, ^3J = 6.9, ^4J = 1.4 Hz, 1H, 2-H_b), 3.19 (brs, 1H, O*H*), 3.40 (dd, ^2J = 9.5, ^3J = 6.4 Hz, 1H, 7-H_a), 3.46 (dd, ^2J = 9.5, ^3J = 4.5 Hz, 1H, 7-H_b), 3.80 (s, 3H, OCH_3), 3.84 (dtd, ^3J = 6.4, ^3J = 6.3, ^3J = 4.5 Hz, 1H, 6-H), 4.48 (s, 2H, 1′-H), 5.64 (dtt, ^3J = 10.9, ^3J = 7.4, ^4J = 1.4 Hz, 1H, 4-H), 5.70 (dtt, ^3J = 10.9, ^3J = 6.9, ^4J = 1.3 Hz, 1H, 3-H), 6.87 (m, 2H, 3″-H), 7.25 ppm (m, 2H, 2″-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 31.8 (C-2), 32.0 (C-5), 35.5, 37.2 [N-(CH_3)$_2$], 55.1 (OCH_3), 69.6 (C-6), 72.9 (C-1′), 73.5 (C-7), 113.6 (C-3″), 124.7 (C-3), 128.3 (C-4), 129.2 (C-2″), 130.0 (C-1″), 159.1 (C-4″), 171.3 ppm (C-1); IR (film, ATR): $\tilde{\nu}$ = 3410 (O-H-ν); 3025 (arom. C-H-ν); 2930, 2910, 2860 (aliph. C-H-ν); 2840 (OCH_3, C-H-ν); 1625 (C=O-ν); 1615, 1585, 1510 (arom. C=C-ν); 1465, 1395; 1300; 1245; 1030; 1175; 1085; 820 (1,4-disubstituted benzene ring); 710 cm^{-1}; MS (ESI-2): *m*/*z* (%): 346 (76) [$M+K^+$], 330 (100) [$M+Na^+$], 308 (59) [$M+H^+$]; elemental analysis calcd (%) for $C_{17}H_{25}NO_4$ (307.4): C 66.43, H 8.20, N 4.56, found: C 66.32, H 8.22, N 4.55.

(1*S*,3*Z*)-6-(*tert*-Butyldimethylsilyloxy)-1-phenylhex-3-en-1-ol (44a) and (1*R*,3*Z*)-6-(*tert*-butyldimethylsilyloxy)-1-phenylhex-3-en-1-ol (*ent*-44a): According to GP E allylboronates **35** or **37** (200 mg, 0.30 mmol), respectively, in CH_2Cl_2 (150 μL) with benzaldehyde (42 mg, 0.39 mmol) were used. The reaction mixtures were stirred at 0°C for 24 h and at RT for 48 h. For the reduction THF (10 mL) and $LiAlH_4$ (60 mg, 1.58 mmol) were utilized, for the work up H_2O (69 μL), 15% aqueous NaOH solution (69 μL) and H_2O (205 μL) were added. Chromatography (15 g silica gel, petroleum ether/EtOAc 96:4) furnished analytically pure colorless oils (**44a**: 74 mg, 0.24 mmol, 80%; HPLC: *ee* 87%; *ent*-**44a**: 71 mg, 0.23 mmol, 77%; HPLC: *ee* 96%); R_f = 0.11 (petroleum ether/EtOAc 95:5), 0.43 (petroleum ether/EtOAc 85:15); $[\alpha]_D^{20}$ (**44a**) = −55 (*c* = 1.36 in $CHCl_3$, *ee* 87%), $[\alpha]_D^{20}$ (*ent*-**44a**) = +58 (*c* = 1.36 in $CHCl_3$, *ee* 96%), HPLC (Chiralcel OD, hexane/*i*PrOH 99.4:0.6): t_R (**44a**) = 9.4 min, t_R (*ent*-**44a**) = 7.4 min; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.06 [s, 6H, Si(CH_3)$_2$], 0.90 [s, 9H, C(CH_3)$_3$], 2.24 (ddddd, ^2J = 14.1, ^3J = 7.2, ^3J = 6.7, ^3J = 6.5, ^4J = 1.5 Hz, 1H, 5-H_a), 2.33 (ddddd, ^2J = 14.1, ^3J = 7.2, ^3J = 6.7, ^3J = 6.4, ^4J = 1.5 Hz, 1H, 5-H_b), 2.45 (d, ^3J = 3.4 Hz, 1H, O*H*), 2.47 (dddd, ^2J = 14.2, ^3J = 6.8, ^3J = 5.0, ^4J = 1.4 Hz, 1H, 2-H_a), 2.56 (dddd, ^2J = 14.2, ^3J = 7.9, ^3J = 6.8, ^4J = 1.4 Hz, 1H, 2-H_b), 3.59 (dt, ^2J = 9.9, ^3J = 6.7, ^3J = 6.7 Hz, 1H, 6-

H_a), 3.61 (ddd, $^2J=9.9$, $^3J=6.5$, $^3J=6.4$ Hz, 1H, 6-H_b), 4.69 (ddd, $^3J=7.9$, $^3J=5.0$, $^3J=3.4$ Hz, 1H, 1-H), 5.50 (dtt, $^3J=10.9$, $^3J=6.8$, $^4J=1.5$ Hz, 1H, 3-H), 5.57 (dtt, $^3J=10.9$, $^3J=7.2$, $^4J=1.4$ Hz, 1H, 4-H), 7.24–7.27, 7.31–7.37 ppm (m, 5H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=-5.3$ [Si-(CH_3)$_2$], 18.4 [C(CH_3)$_3$], 26.0 [C(CH_3)$_3$], 31.0 (C-5), 37.5 (C-2), 62.7 (C-6), 73.6 (C-1), 125.8, 127.3, 128.3 (arom. *C*H), 126.7 (C-3), 129.9 (C-4), 144.2 ppm (arom. C_{ipso}); IR (film, ATR): $\tilde{\nu}=3380$ (O-H-ν); 3070, 3040, 3005 (arom. C-H-ν), 2935, 2905, 2865, 2835 (aliph. C-H-ν); 1645 (olef. C=C-ν); 1595, 1575, 1480 (arom. C=C-ν); 1460, 1450, 1440 (aliph. C-H-δ); 1390; 1375; 1350; 1240; 1080; 1035; 910; 820, 790, 755 (TBS); 755 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 cm^{-1} (Ph, ring-δ); MS (EI, 70 eV): *m*/*z* (%): 306 (0.06) [M^+], 288 (0.4) [$M-H_2O^+$], 157 (61) [$PhC_6H_8^+$], 143 (22) [$C_{11}H_{11}^+$], 107 (30) [$PhCHOH^+$], 105 (37) [$PhCO^+$], 75 (100) [Me_2SiOH^+], 73 (42) [$MeSi(O)CH_2^+$]; elemental analysis calcd (%) for $C_{18}H_{30}O_2Si$ (306.5): C 70.53, H 9.87, found: C 70.30, H 9.83.

(3*R*,5*Z*)-8-(*tert*-Butyldimethylsilyloxy)-1-phenyloct-5-en-3-ol (44b) and (3*S*,5*Z*)-8-(*tert*-butyldimethylsilyloxy)-1-phenyloct-5-en-3-ol (*ent*-44b): According to GP E allylboronates **35** or **37** (200 mg, 0.30 mmol), respectively, in CH_2Cl_2 (150 μL) with 3-phenylpropionaldehyde (48 μL, 49 mg, 0.36 mmol) were used. The reaction mixtures were stirred at 0 °C for 24 h and at RT for 24 h. For the reduction THF (5 mL) and $LiAlH_4$ (69 mg, 1.81 mmol), for the work up H_2O (83 μL), 15% aqueous NaOH solution (83 μL) and H_2O (246 μL) was used. Chromatography (16 g silica gel, petroleum ether/EtOAc 95:5) furnished spectroscopically pure colorless oils (*ent*-**44b**: 93 mg, 0.28 mmol, 92%; HPLC: *ee* 92%), MPLC (petroleum ether/EtOAc 95:5) yielded an analytically pure sample (**44b**: 53 mg, 0.16 mmol, 52%; HPLC: *ee* 99%). $R_f=0.08$ (petroleum ether/EtOAc 95:5), 0.39 (petroleum ether/EtOAc 85:15); $[\alpha]_D^{20}$ (**44b**) = +3 ($c=1.06$ in $CHCl_3$, *ee* 99%), $[\alpha]_D^{20}$ (*ent*-**44b**) = −3 ($c=1.30$ in $CHCl_3$, *ee* 92%); HPLC (Chiralcel OD, hexane/*i*PrOH 98:2): t_R (**44b**) = 8.0 min, t_R (*ent*-**44b**) = 4.7 min; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.06$ [s, 6H, Si(CH_3)$_2$], 0.90 [s, 9H, C(CH_3)$_3$], 1.27–1.38 (m, 2H, 7H), 2.15 (d, $^3J=4.4$ Hz, 1H, O*H*), 2.25 (m, 2H, 5-H), 2.28 (m, 1H, 2-H_a), 2.36 (m, 1H, 2-H_b), 2.68 (ddd, $^2J=13.7$, $^3J=9.2$, $^3J=7.3$ Hz, 1H, 8-H_a), 2.81 (ddd, $^2J=13.7$, $^3J=9.0$, $^3J=6.4$ Hz, 1H, 8-H_b), 3.59–3.69 (m, 3H, 1-H, 6-H), 5.46 (dtt, $^3J=10.9$, $^3J=6.8$, $^4J=1.4$ Hz, 1H, 4-H), 5.51 (dtt, $^3J=10.9$, $^3J=6.8$, $^4J=1.3$ Hz, 1H, 3-H), 7.16–7.21, 7.25–7.29 ppm (m, 5H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=-5.4$, −5.3 [Si(CH_3)$_2$], 18.4 [C(CH_3)$_3$], 26.0 [C(CH_3)$_3$], 30.9 (C-2), 32.1 (C-8), 35.5 (C-5), 38.6 (C-7), 62.7 (C-1), 70.4 (C-6), 127.0 (C-3), 125.7, 128.3, 128.4 (arom. *C*H), 129.9 (C-4); 142.2 ppm (arom. C_{ipso}); IR (film): $\tilde{\nu}=3570$ (O-H-ν); 3370 (br, O-H-ν); 3070, 3040, 3005 (arom. C-H-ν), 2930, 2905, 2880, 2835 (aliph. C-H-ν); 1640 (olef. C=C-ν); 1595, 1575, 1485 (arom. C=C-ν); 1460, 1450, 1440; 1375; 1350; 1240, 1080 (TBS); 910; 815, 790, 755 (TBS); 755 (Ph, C-H-$\delta_{out\ of\ plane}$); 675 cm^{-1} (Ph, ring-δ); MS (EI, 70 eV): *m*/*z* (%): 334 (0.8) [M^+], 185 (90) [$M-C_{10}H_{13}O^+$], 143 (62) [$C_{11}H_{11}^+$], 117 (60) [$C_9H_9^+$], 105 (93) [$PhCO^+$], 91 (100) [$C_7H_7^+$], 75 (93) [$HOSiMe_2^+$], 73 (40) [$MeSi(O)CH_2^+$]; elemental analysis calcd (%) for $C_{20}H_{34}O_2Si$ (334.6): C 71.80, H 10.24, found: C 71.60, H 10.28.

(2*S*,4*Z*)-7-(*tert*-Butyldimethylsilyloxy)-1-(4″-methoxybenzyloxy)hept-4-en-2-ol (44c) and (2*R*,4*Z*)-7-(*tert*-butyldimethylsilyloxy)-1-(4″-methoxybenzyloxy)hept-4-en-2-ol (*ent*-44c): According to GP E allylboronates **35** or **37** (200 mg, 0.30 mmol), respectively, in CH_2Cl_2 (151 μL) with **42c** (65 mg, 0.36 mmol) were used. The reaction mixtures were stirred at 0 °C for 24 h and at RT for 5 d. For the reduction THF (3 mL) and $LiAlH_4$ (46 mg, 1.21 mmol), for the work up H_2O (55 μL), 15% aqueous NaOH solution (55 μL) and H_2O (164 μL) was used respectively. Chromatography (16 g silica gel, petroleum ether/EtOAc 90:10) furnished spectroscopically pure colorless oils (**44c**: 105 mg, 0.28 mmol, 91%; ^{1}H NMR:[15a] *ee* > 95%; *ent*-**44c**: 106 mg, 0.28 mmol, 92%; ^{1}H NMR:[15a] *ee* > 95%), MPLC (petroleum ether/EtOAc 82:18) yielded an analytically pure sample. $R_f=0.16$ (petroleum ether/EtOAc 85:15), 0.42 (petroleum ether/EtOAc 75:25); $[\alpha]_D^{20}$ (**44c**) = −4 ($c=2.08$ in $CHCl_3$, *ee* > 95%), $[\alpha]_D^{20}$ (*ent*-**44c**) = +5 ($c=2.12$ in $CHCl_3$, *ee* > 95%); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.05$ [s, 6H, Si(CH_3)$_2$], 0.89 [s, 9H, C(CH_3)$_3$], 2.18–2.35 (m, 4H, 3-H, 6-H), 2.56 (br s, 1H, O*H*), 3.35 (dd, $^2J=9.5$, $^3J=7.2$ Hz, 1H, 1-H_a), 3.47 (dd, $^2J=9.5$, $^3J=3.7$ Hz, 1H, 1-H_b), 3.62 (t, $^3J=6.7$ Hz, 2H, 7-H), 3.80 (s, 3H, OCH_3), 3.82 (dddd, $^3J=9.9$, $^3J=7.2$, $^3J=6.2$, $^3J=3.7$ Hz, 1H, 2-H), 4.48 (s, 2H, 1′-H), 5.46–5.56 (m, 2H, 4-H, 5-H), 6.88 (m, 2H, 3″-H), 7.25 ppm (m, 2H, 2″-H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta=-5.3$, −5.3 [Si-(CH_3)$_2$], 18.4 [C(CH_3)$_3$], 25.9 [C(CH_3)$_3$], 31.0, 31.5 (C-2, C-5), 55.2 (OCH_3), 62.7 (C-7), 70.1 (C-2), 73.0 (C-1′), 73.6 (C-1), 113.8 (C-3″), 126.5 (C-5), 128.9 (C-4), 129.3 (C-2″), 130.0 (C-1″), 159.2 ppm (C-4″); IR (film, ATR): $\tilde{\nu}=3450$ (O-H-ν); 3010 (arom. C-H-ν); 2955, 2930, 2900, 2855 (aliph. C-H-ν); 2840 (OCH_3, C-H-ν); 1655 (olef. C=C-ν); 1615, 1585, 1515 (arom. C=C-ν); 1470; 1465; 1360; 1300; 1250 (TBS); 1175; 1090 (TBS); 1035; 1005; 935; 830, 815, 755 cm^{-1} (TBS); MS (ESI-2): *m*/*z* (%): 419 (58) [M+K$^+$], 403 (100) [M+Na$^+$], 398 (42) [M+NH_4^+]; 381 (47) [M+H$^+$]; elemental analysis calcd (%) for $C_{21}H_{36}O_4Si$ (380.6): C 66.27, H 9.53, found: C 66.22, H 9.49.

(1*S*,3*Z*)-1-Phenylhex-3-en-1-ol (45a) and (1*R*,3*Z*)-1-phenylhex-3-en-1-ol (*ent*-45a): According to GP D allylboronate **39** (196 mg, 0.37 mmol, 1.00 equiv) in CH_2Cl_2 (184 μL) with benzaldehyde (45 μL, 47 mg, 0.44 mmol, 1.20 equiv) was used. Analogously, allylboronate **41** (193 mg, 0.36 mmol, 1.00 equiv) in CH_2Cl_2 (181 μL) with benzaldehyde (44 μL, 46 mg, 0.44 mmol, 1.20 equiv) was subjected to the reaction conditions. The reaction mixtures were stirred at 0 °C for 24 h and at RT for 24 h. Chromatography (16 g silica gel, petroleum ether/EtOAc 95:5 → 85:15) furnished spectroscopically pure colorless oils (**45a**: 54 mg, 0.31 mmol, 83%; HPLC: 99%, GC: > 99%; *ent*-**45a**: 44 mg, 0.25 mmol, 69%; HPLC: > 99%). Analytical data are in agreement with those reported in the literature.[32] $R_f=0.10$ (petroleum ether/EtOAc 95:5); $[\alpha]_D^{20}$ (**45a**) = −58 ($c=1.80$ in $CHCl_3$, *ee* > 99%), $[\alpha]_D^{20}$ (*ent*-**45a**) = +65 ($c=0.76$ in $CHCl_3$, *ee* > 99%), ref.:[32] $[\alpha]_D^{25}$ (*ent*-**45a**) = +63 ($c=0.82$ in $CHCl_3$, *ee* > 99%); HPLC (Chiralcel OD, hexane/*i*PrOH 99.4:0.6): t_R (**45a**) = 12.5 min, t_R (*ent*-**45a**) = 9.4 min; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.91$ (t, $^3J=7.5$ Hz, 3H, 6-H), 2.01 (dqdd, $^2J=14.6$, $^3J=7.5$, $^3J=7.3$, $^4J=1.6$ Hz, 1H, 5-H_a), 2.03 (dqdd, $^2J=14.6$, $^3J=7.5$, $^3J=7.3$, $^4J=1.6$ Hz, 1H, 5-H_b), 2.12 (d, $^3J=2.6$ Hz, 1H, O*H*), 2.45 (dddd, $^2J=14.3$, $^3J=6.9$, $^3J=5.4$, $^4J=1.6$ Hz, 1H, 2-H_a), 2.55 (dddd, $^2J=14.3$, $^3J=6.9$, $^3J=7.8$, $^4J=1.6$, 1H, 2-H_b), 4.67 (ddd, $^3J=7.8$, $^3J=5.4$, $^3J=2.6$ Hz, 1H, 1-H), 5.34 (dtt, $^3J=10.8$, $^3J=6.9$, $^4J=1.6$ Hz, 1H, 3-H), 5.54 (dtt, $^3J=10.8$, $^3J=7.3$, $^4J=1.6$ Hz, 1H, 4-H), 7.23–7.27, 7.31–7.36 ppm (m, 5H, arom. C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=14.1$ (C-6), 20.6 (C-5), 37.1 (C-2), 73.9 (C-1), 124.0 (C-3), 125.8, 127.4, 128.3 (arom. *C*H), 135.2 (C-4), 144.1 ppm (arom. C_{ipso}); IR (film): $\tilde{\nu}=3530$ (O-H-ν); 3360 (br); 3070, 3040, 3010 (arom. C-H-ν); 2990, 2940, 2910, 2850 (aliph. C-H-ν); 1645 (olef. C=C-ν); 1590, 1480 (arom. C=C-ν); 1440; 1030; 735 (Ph, C-H-$\delta_{out\ of\ plane}$); 680 cm^{-1} (Ph, ring-δ); MS (CI, NH_3): *m*/*z* (%): 194 (26) [M+NH_4^+], 176 (100) [M^+]; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{12}H_{16}O$: 176.1201, found: 176.1202; elemental analysis calcd (%) for $C_{12}H_{16}O$ (176.3): C 81.77, H 9.15, found: C 81.05, H 9.10.

(3*R*,5*Z*)-1-Phenyloct-5-en-3-ol (45b) and (3*S*,5*Z*)-1-phenyloct-5-en-3-ol (*ent*-45b): According to GP D allylboronates **39** or **41** (200 mg, 0.38 mmol), respectively, in CH_2Cl_2 (189 μL) with 3-Phenylpropionaldehyde (60 μL, 61 mg, 0.45 mmol) were used. The reaction mixtures were stirred at 0 °C for 24 h and at RT for 4 d. Chromatography (14 g silica gel, petroleum ether/EtOAc 95:5 → 90:10) and MPLC (petroleum ether/EtOAc 95:5) furnished spectroscopically pure colorless oils (**45b**: 70 mg, 0.34 mmol, 91%; HPLC: *ee* 84%; *ent*-**45b**: 70 mg, 0.34 mmol, 91%; HPLC: *ee* 95%); the analytical data are in agreement with those previously reported.[43] $R_f=0.08$ (petroleum ether/EtOAc 95:5), 0.30 (petroleum ether/EtOAc 85:15); $[\alpha]_D^{20}$ (**45b**) = +9 ($c=0.88$ in $CHCl_3$, *ee* 84%), $[\alpha]_D^{20}$ (*ent*-**45b**) = −12 ($c=0.96$ in $CHCl_3$, *ee* 95%), ref.:[43] $[\alpha]_D^{20}$ (*ent*-**45b**) = −27 ($c=1.00$ in $CHCl_3$, *ee* > 99%); HPLC (Chiralcel OD, hexane/*i*PrOH 95:5): t_R (**45b**) = 16.0 min, t_R (*ent*-**45b**) = 24.7 min; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.96$ (t, $^3J=7.5$ Hz, 3H, 8-H), 1.70 (br s, 1H, O*H*), 1.79 (m, 2H, 2-H), 2.07 (qddt, $^3J=7.5$, $^3J=7.2$, $^4J=1.6$, $^5J=0.7$ Hz, 2H, 7-H), 2.24 (m, 2H, 4-H), 2.68 (ddd, $^2J=13.8$, $^3J=9.2$, $^3J=7.3$ Hz, 1H, 1-H_a), 2.81 (ddd, $^2J=13.8$, $^3J=8.8$, $^3J=6.9$ Hz, 1H, 1-H_b), 3.64 (dddd, $^3J=7.6$, $^3J=6.8$, $^3J=5.6$, $^3J=4.8$ Hz, 1H, 3-H), 5.36 (dtt, $^3J=10.9$, $^3J=7.3$, $^4J=1.6$ Hz, 1H, 5-H), 5.57 (dtt, $^3J=10.9$, $^3J=7.2$, $^4J=1.4$ Hz, 1H, 6-H), 7.15–7.31 ppm (m, 5H, arom. C*H*); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta=14.2$ (C-8), 20.7 (C-7), 32.1 (C-1), 35.3 (C-4), 38.4 (C-2), 70.6 (C-3), 124.2 (C-5), 125.7, 128.3, 128.4 (arom. *C*H), 135.3 (C-6), 142.1 ppm (arom. C_{ipso}); IR (film): $\tilde{\nu}=3565$ (O-H-ν); 3350 (br, O-H-ν); 3085, 3065, 3025, 3010 (arom. C-H-ν), 2960, 2930, 2875 (aliph. C-H-ν); 1655 (olef. C=C-ν); 1605, 1585, 1495 (arom. C=C-ν); 1455; 1070; 1050;

1030; 745 (Ph, C-H-$\delta_{out\ of\ plane}$); 720; 695 cm^{-1} (Ph, ring-δ); MS (CI, CH_4): *m/z* (%): 205 (6) [$M+H^+$], 187 (100) [$M-OH^+$].

(2*S*,4*Z*)-1-(4′-Methoxybenzyloxy)hept-4-en-2-ol (45c) and (2*R*,4*Z*)-1-(4′-methoxybenzyloxy)hept-4-en-2-ol (*ent*-45c) According to GP D allylboronates **39** or **41** (200 mg, 0.38 mmol), respectively, in CH_2Cl_2 (188 μL) with **42c** (135 mg, 0.75 mmol) were used. The reaction mixtures were stirred at 0 °C for 24 h and at RT for 24 h. Chromatography (16 g silica gel, petroleum ether/EtOAc 90:10) furnished spectroscopically pure colorless oils (*ent*-**45c**: 84 mg, 0.34 mmol, 89%; HPLC: *ee* 89%), MPLC (petroleum ether/EtOAc 85:15) yielded the corresponding analytically pure samples (**45c**: 83 mg, 0.33 mmol, 88%; HPLC: *ee* 94%). R_f = 0.27 (petroleum ether/EtOAc 80:20), 0.45 (petroleum ether/EtOAc 70:30; $[\alpha]_D^{20}$ (**45c**) = +2 (*c* = 1.66 in $CHCl_3$, *ee* 94%), $[\alpha]_D^{20}$ (*ent*-**45c**) = −3 (*c* = 1.64 in $CHCl_3$, *ee* 89%); HPLC (Chiralcel OD-H, hexane/*i*PrOH 99.6:0.4): t_R (**45c**) = 112.6 min, t_R (*ent*-**45c**) = 100.8 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.5 Hz, 3H, 7-H), 2.05 (qddt, ^3J = 7.5, ^3J = 7.2, ^3J = 1.5, ^4J = 0.7 Hz, 2H, 6-H), 2.23 (ddddt, ^2J = 14.4, ^3J = 7.4, ^3J = 6.5, ^3J = 1.5, ^3J = 0.7 Hz, 1H, 3-H_a), 2.26 (ddddt, ^2J = 14.4, ^3J = 7.4, ^3J = 6.5, ^3J = 1.5, ^3J = 0.7 Hz, 1H, 3-H_b), 2.41 (brs, 1H, O*H*), 3.34 (dd, ^2J = 9.5, ^3J = 7.4 Hz, 1H, 1-H_a), 3.49 (dd, ^2J = 9.5, ^3J = 3.3 Hz, 1H, 1-H_b), 3.80 (s, 3H, OCH_3), 3.81 (dtd, ^3J = 7.4, ^3J = 6.5, ^3J = 3.3 Hz, 1H, 2-H), 4.48 (s, 2H, 1′-H), 5.49 (dtt, ^3J = 10.8, ^3J = 7.4, ^4J = 1.5 Hz, 1H, 4-H), 5.53 (dtt, ^3J = 10.8, ^3J = 7.2, ^4J = 1.5 Hz, 1H, 5-H), 6.88 (m, 2H, 3″-H), 7.26 ppm (m, 2H, 2″-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (C-7), 20.6 (C-6), 31.1 (C-3), 55.2 (OCH_3), 70.2 (C-2), 73.0 (C-1′), 73.6 (C-1), 113.8 (C-3″), 123.9 (C-4), 129.3 (C-2″), 130.0 (C-1″), 134.4 (C-5), 159.2 ppm (C-4″); IR (film, ATR): $\tilde{\nu}$ = 3440 (O-H-ν); 3005 (arom. C-H-ν); 2960, 2935, 2905, 2870 (aliph. C-H-ν); 2835 (OCH_3, C-H-ν); 1655 (olef. C=C-ν); 1610, 1585, 1515 (arom. C=C-ν); 1465; 1300; 1245; 1175; 1100; 1035; 820 (1,4-disubstituted benzene ring); 720 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 250 (6) [M^+], 121 (100) [$C_8H_9O^+$]; HRMS (EI, 70 eV): *m/z*: calcd for $C_{15}H_{22}O_3$: 250.1569, found: 250.1569; elemental analysis calcd (%) for $C_{15}H_{22}O_3$ (250.3): C 71.97, H 8.86, found: C 71.63, H 8.85.

Allyl additions to 2,3-O-isopropylidene-D-glyceraldehyde (42d)

(6*S*,4′*R*,3*Z*)- and (6*R*,4′*R*,3*Z*)-ethyl 6-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-6-hydroxyhex-3-enoate (31d and *epi*-31d): According to GP D allylboronate **15** (232 mg, 0.39 mmol) was treated with a solution of (*R*)-aldehyde **42d** (72 mg, 0.55 mmol) in CH_2Cl_2 (≈200 μL). The reaction mixture was stirred at RT for 30 h. Chromatography (petroleum ether/EtOAc 85:15 → 80:20) gave a spectroscopically pure colorless oil [88 mg, 0.34 mmol, 86%; ^{1}H NMR: dr (**31d**/*epi*-**31d**) 97:3], one additional chromatography (10 g silica gel, petroleum ether/EtOAc 85:15) furnished an analytically pure sample. According to GP D allylboronate **16** (233 mg, 0.40 mmol) was treated with a solution of (*R*)-aldehyde **42d** (72 mg, 0.55 mmol) in CH_2Cl_2 (≈200 μL). The reaction mixture was stirred at RT for 22 h. Chromatography (petroleum ether/EtOAc 85:15) gave a spectroscopically pure colorless oil [91 mg, 0.35 mmol, 89%; ^{1}H NMR: dr (**31d**/*epi*-**31d**) 30:70], further chromatography furnished an analytically pure sample. According to GP D allylboronate *ent*-**15** (300 mg, 0.51 mmol) was treated with a solution of (*R*)-aldehyde **42d** (187 mg, 1.44 mmol) in CH_2Cl_2 (≈450 μL). The reaction mixture was stirred at 0 °C for 24 h and at RT for 3 d and 19 h. Chromatography (petroleum ether/EtOAc 85:15 → 75:25) gave a spectroscopically pure colorless oil [121 mg, 0.47 mmol, 92%; ^{1}H NMR: dr (**31d**/*epi*-**31d**) 35:65]. According to GP D allylboronate *ent*-**16** (300 mg, 0.51 mmol) was treated with a solution of (*R*)-aldehyde **42d** (187 mg, 1.44 mmol) in CH_2Cl_2 (≈450 μL). The reaction mixture was stirred at 0 °C for 24 h and at RT for 3 d and 19 h. Chromatography (petroleum ether/EtOAc 85:15 → 75:25) furnished a spectroscopically pure colorless oil [120 mg, 0.47 mmol, 91%; ^{1}H NMR: dr (**31d**/*epi*-**31d**) > 99:1]. R_f (**31d**) = R_f (*epi*-**31d**) = 0.07 (petroleum ether/EtOAc 80:20); $[\alpha]_D^{20}$ = −5 [*c* = 0.96 in $CHCl_3$, dr (**31d**/*epi*-**31d**) 97:3], $[\alpha]_D^{20}$ = −5 [*c* = 1.44 in $CHCl_3$, dr (**31d**/*epi*-**31d**) > 99:1], $[\alpha]_D^{20}$ = +14 [*c* = 1.22 in $CHCl_3$, dr (**31d**/*epi*-**31d**) 35:65]; *epi*-**31d**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 3H, 2″-H), 1.36, 1.42 (2s, 6H, 2′-CH_3), 2.22–2.29 (m, 1H, 5-H_a), 2.34–2.40 (m, 1H, 5-H_b), 2.75 (brs, 1H, O*H*), 3.05–3.17 (m, 2H, 2-H), 3.70 (ddd, ^3J = 8.2, ^3J = 5.8, ^3J = 4.1 Hz, 1H, 6-H), 3.95 (dd, ^2J = 7.5, ^3J = 5.9 Hz, 1H, 5′-H_a), 3.99 (ddd, ^3J = 6.0, ^3J = 5.9, ^3J = 5.8 Hz, 1H, 4′-H), 4.05 (dd, ^2J = 7.5, ^3J = 6.0 Hz, 1H, 5′-H_b), 4.15 (q, ^3J = 7.1 Hz, 2H, 1″-H), 5.71 ppm (m, 2H, 3-H, 4-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (C-2″), 25.2, 26.6 (2′-CH_3), 31.5 (C-5), 33.0 (C-2), 61.0 (C-1″), 65.9 (C-5′), 71.1 (C-6), 78.1 (C-4′), 109.1 (C-2′), 124.3 (C-3), 128.9 (C-4), 172.1 ppm (C-1); IR (solution in $CDCl_3$): $\tilde{\nu}$ = 3565 (O-H-ν); 3450 (br); 3010 (olef. C-H-ν); 2970, 2920, 2870 (aliph. C-H-ν); 1720 (C=O-ν); 1650 (olef. C=C-ν); 1440; 1370, 1360 (CH_3, C-H-δ_s); 1315; 1240; 1200; 1165; 1145; 1050; 1015; 830 cm^{-1}; MS (AUTO-CI): *m/z* (%): 259 (100) [$M+H^+$], 243 (54) [$M-CH_3^+$]; HRMS (AUTO-CI): *m/z*: calcd for $C_{13}H_{23}O_5$: 259.1545, found: 259.1547; elemental analysis calcd (%) for $C_{13}H_{22}O_5$ (258.3): C 60.45, H 8.58, found: C 60.33, H 8.64; *epi*-**31d**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 3H, 2′-H), 1.36, 1.44 (2s, 6H, 2′-CH_3), 2.24–2.32 (m, 2H, 5-H), 2.54 (d, ^3J = 4.9 Hz, 1H, O*H*), 3.06–3.17 (m, 2H, 2-H), 3.59 (m, 1H, 6-H), 3.78 (dd, ^3J = 7.9, ^3J = 6.5 Hz, 1H, 5′-H_a), 4.00–4.07 (m, 2H, 4′-H, 5′-H_b), 4.14 (q, ^3J = 7.1 Hz, 2H, 1″-H), 5.65–5.76 ppm (m, 2H, 3-H, 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-2″), 25.1, 26.4 (2′-CH_3), 31.8 (C-5), 32.9 (C-2), 60.7 (C-1″), 65.8 (C-5′), 71.2 (C-6), 78.1 (C-4′), 109.3 (C-2′), 123.9 (C-3), 128.4 (C-4), 171.8 ppm (C-1); IR (solution in $CDCl_3$): $\tilde{\nu}$ = 3565 (O-H-ν); 3450 (br); 3010 (olef. C-H-ν); 2970, 2920, 2890, 2870 (aliph. C-H-ν); 1720 (C=O-ν); 1650 (olef. C=C-ν); 1590; 1440; 1370, 1360 (CH_3, C-H-δ_s); 1315; 1240; 1200; 1170; 1140; 1050; 1015; 835 cm^{-1}; MS (CI, CH_4): *m/z* (%): 259 (100) [$M+H^+$], 243 (65) [$M-CH_3^+$]; HRMS (AUTO-CI): *m/z*: calcd for $C_{13}H_{23}O_5$: 259.1545, found: 259.1545; elemental analysis calcd (%) for $C_{13}H_{22}O_5$ (258.3): C 60.45, H 8.58, found: C 60.10, H 8.59.

(6*S*,4′*R*,3*Z*)-6-(2′,2′-Dimethyl-1′,3′-dioxolan-4′-yl)-6-hydroxyhex-3-enoic acid dimethylamide (43d): According to GP D allylboronate **18** (152 mg, 0.26 mmol) was treated with (*R*)-aldehyde **42d** (47 mg, 0.36 mmol) in CH_2Cl_2 (≈150 μL). The reaction mixture was stirred at RT for 43 h. Chromatography (EtOAc) gave a spectroscopically pure colorless oil [42 mg, 0.16 mmol, 63%; ^{1}H NMR: dr (**43d**/*epi*-**43d**) > 99:1]; R_f = 0.19 (EtOAc); $[\alpha]_D^{20}$ = −24 [*c* = 0.32, $CHCl_3$, dr (**43d**/*epi*-**43d**) > 99:1], ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36, 1.42 (2s, 6H, 2′-CH_3), 2.31 (dddd, ^2J = 14.0, ^3J = 8.9, ^3J = 8.5, ^3J = 1.3 Hz, 1H, 5-H_a), 2.45 (dddd, ^2J = 14.0, ^3J = 6.8, ^3J = 3.2, ^3J = 1.3 Hz, 1H, 5-H_b), 2.95, 3.07 [2s, 6H, N(CH_3)$_2$], 3.15 (dd, ^3J = 7.5, ^4J = 1.3 Hz, 2H, 2-H), 3.60 (dddd, ^3J = 8.5, ^3J = 7.2, ^3J = 4.2, ^3J = 3.2 Hz, 1H, 6-H), 3.87 (d, ^3J = 4.2 Hz, 1H, O*H*), 3.93–3.99, 4.1 (2m, 3H, 4′-H, 5′-H), 5.68 (dtt, ^3J = 10.8, ^3J = 7.6, ^3J = 1.3 Hz, 1H, 3-H), 5.76 ppm (dddt, ^3J = 10.8, ^3J = 8.9, ^3J = 6.8, ^3J = 1.3 Hz, 1H, 4-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.3, 26.7 (2′-CH_3), 31.6 (C-2), 31.9 (C-5), 35.8, 37.5 [N(CH_3)$_2$], 67.0 (C-5′), 71.7 (C-6), 78.4 (C-4′), 109.1 (C-2′), 124.9 (C-3), 129.5 (C-4), 171.7 ppm (C-1); IR (solution in $CDCl_3$): $\tilde{\nu}$ = 3580 (O-H-ν); 3340 (br); 3005 (olef. C-H-ν); 2970, 2920, 2870 (aliph. C-H-ν); 1625 (C=O-ν, olef. C=C-ν); 1485; 1475; 1440; 1430; 1390; 1370, 1360 (CH_3, C-H-δ_s); 1245; 1200; 1140; 1050; 830 cm^{-1}; MS (CI, CH_4): *m/z* (%): 258 (100) [$M+H^+$], 242 (19) [$M-CH_3^+$]; HRMS (AUTO-CI): *m/z*: calcd for $C_{13}H_{24}NO_4$: 258.1705, found: 258.1708.

(6*R*,4′*R*,3*Z*)-6-(2′,2′-Dimethyl-1′,3′-dioxolan-4′-yl)-6-hydroxyhex-3-enoic acid dimethylamide (*epi*-43d): According to GP D allylboronate **19** (142 mg, 0.24 mmol) was treated with (*R*)-aldehyde **42d** (44 mg, 0.34 mmol) in CH_2Cl_2 (≈150 μL). The reaction mixture was stirred at RT for 18 h. Chromatography (EtOAc) yielded a spectroscopically pure colorless oil [47 mg, 0.18 mmol, 75%; ^{1}H NMR: dr (**43d**/*epi*-**43d**) 27:73]; R_f = 0.15 (EtOAc); $[\alpha]_D^{20}$ = +28 [*c* = 0.18, $CHCl_3$, dr (**43d**/*epi*-**43d**) 13:87 (enriched fraction)]; ^{1}H NMR (500 MHz, $CDCl_3$), δ = 1.37, 1.45 (2s, 6H, 2′-CH_3), 2.22–2.27 (m, 1H, 5-H_a), 2.30–2.36 (m, 1H, 5-H_b), 2.95, 3.04 [2s, 6H, N(CH_3)$_2$], 3.02 (d, ^3J = 5.5 Hz, 1H, O*H*), 3.14–3.16 (m, 2H, 2-H), 3.60 −3.64 (m, 1H, 6-H), 3.82 (dd, ^2J = 8.1, ^3J = 6.7 Hz, 1H, 5′-H_a), 4.02 (dd, ^2J = 8.1, ^3J = 6.7 Hz, 1H, 5′-H_b), 4.10 (ddd, ^3J = 6.7, ^3J = 6.7, ^3J = 5.0 Hz, 1H, 4′-H), 5.66–5.77 ppm (m, 2H, 3-H, 4-H); ^{13}C NMR (126 MHz, $CDCl_3$), δ = 25.2, 26.5 (2′-CH_3), 31.8 (C-5), 32.1 (C-2), 35.6, 37.4 [N(CH_3)$_2$], 65.9 (C-5′), 71.1 (C-6), 78.2 (C-4′), 109.3 (C-2′), 125.0 (C-3), 128.5 (C-4), 171.3 ppm (C-1); IR (solution in $CDCl_3$): $\tilde{\nu}$ = 3570 (O-H-ν); 3340 (br); 3010 (olef. C-H-ν); 2970, 2920, 2870 (aliph. C-H-ν); 1625 (C=O-ν, olef. C=C-ν); 1480; 1440; 1390; 1370, 1360 (CH_3, C-H-δ_s); 1245; 1200; 1140; 1050; 835 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 242 (8) [$M-CH_3^+$], 199 (12) [$M-C_3H_6O^+$], 156 (59) [$M-C_5H_9O_2^+$], 127 (37) [$C_7H_{15}NO^+$], 101 (10) [$C_5H_9O_2^+$], 72 (100) [Me_2NCO^+]; HRMS (AUTO-CI): *m/z*: calcd for $C_{13}H_{24}NO_4$: 258.1705, found: 258.1707.

(1*S*,4′*R*,3*Z*)-6-(*tert*-Butyldimethylsilyloxy)-1-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-3-hexen-1-ol (44 d): According to GP E allylboronate **35** (200 mg, 0.30 mmol) in CH_2Cl_2 (≈200 μL) was treated with (*R*)-aldehyde **42 d** (59 mg, 0.45 mmol) in CH_2Cl_2 (≈50 μL). The reaction mixture was stirred at 0 °C for 24 h and at RT for 48 h. For the reduction THF (10 mL) and $LiAlH_4$ (106 mg, 2.79 mmol), for the workup H_2O (128 μL), 15 % aqueous NaOH solution (128 μL) and H_2O (380 μL) were used. Chromatography (petroleum ether/EtOAc 90:10) furnished a spectroscopically pure colorless oil [81 mg, 0.25 mmol, 81 %; ^{13}C NMR: dr (**44 d**/*epi*-**44 d**) 89:11]. R_f (**44 d**) = 0.15 (petroleum ether/EtOAc 85:15), 0.44 (petroleum ether/EtOAc 70:30); $[\alpha]_D^{20} = +3$ [c = 1.26, $CHCl_3$, dr (**44 d**/*epi*-**44 d**) 89:11]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 [s, 6H, Si(CH_3)$_2$], 0.89 [s, 9H, C(CH_3)$_3$], 1.36, 1.42 [2s, 6H, C(CH_3)$_2$], 2.18–2.40 (m, 4H, 2-H, 5-H), 2.56 (d, ^3J = 3.7 Hz, 1H, O*H*), 3.61–3.69 (m, 3H, 1-H, 6-H), 3.94 (dd, ^2J = 6.6, ^3J = 5.4 Hz, 1H, 5′-H$_a$), 3.98 (ddd, ^3J = 5.8, ^3J = 5.6, ^3J = 5.4 Hz, 1H, 4′-H), 4.03 (dd, ^2J = 6.6, ^3J = 5.6 Hz, 1H, 5′-H$_b$), 5.51–5.62 ppm (m, 2H, 3-H, 4-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = −5.4, −5.4 [Si(CH_3)$_2$], 18.4 [C(CH$_3$)$_3$], 25.3, 26.6 [C(CH_3)$_2$], 26.0 [C(CH_3)$_3$], 30.9, 31.3 (C-2, C-5), 62.7 (C-6), 65.9 (C-5′), 71.3 (C-1), 78.1 (C-4′), 109.0 (C-2′), 126.4 (C-4), 130.1 ppm (C-3); IR (film, ATR): $\tilde{\nu}$ = 3470 (br, O-H-ν); 3010 (olef. C-H-ν); 2985, 2955, 2930, 2885, 2860 (aliph. C-H-ν); 1655 (olef. C=C-ν); 1470; 1465; 1380, 1370 (CH_3, C-H-δ$_s$); 1255 (TBS); 1215; 1155; 1095 (TBS); 1065; 930; 830, 805, 775 cm^{-1} (TBS); MS (EI, 70 eV): *m*/*z* (%): 330 (0.01) [M^+], 315 (7) [$M-CH_3^+$], 273 (1) [$M-CMe_3^+$], 215 (22) [M−TBS$^+$]; HRMS (CI, CH_4): *m*/*z*: calcd for $C_{17}H_{35}O_4Si$: 331.2299, found: 331.2305.

(1*R*,4′*R*,3*Z*)-6-(*tert*-Butyldimethylsilyloxy)-1-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)hex-3-en-1-ol (*epi*-44 d): According to GP E allylboronate **37** (200 mg, 0.30 mmol) in CH_2Cl_2 (≈200 μL) was treated with (*R*)-aldehyde **42 d** (59 mg, 0.45 mmol) in CH_2Cl_2 (≈50 μL). The reaction mixture was stirred at 0 °C for 24 h and at RT for 48 h. For the reduction THF (10 mL) and $LiAlH_4$ (46 mg, 1.21 mmol), for the workup H_2O (56 μL), 15 % aqueous NaOH solution (56 μL) and H_2O (164 μL) were used. Chromatography (18 g silica gel, petroleum ether/EtOAc 90:10) gave a spectroscopically pure colorless oil [90 mg, 0.27 mmol, 90 %; ^{13}C NMR: dr (**44 d**/*epi*-**44 d**) 29:71]. R_f (*epi*-**44 d**) = 0.15 (petroleum ether/EtOAc 85:15), 0.44 (petroleum ether/EtOAc 70:30); $[\alpha]_D^{20} = +9$ (c = 1.80, $CHCl_3$, dr (**44 d**/*epi*-**44 d**) 29:71]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 [s, 6H, Si-(CH_3)$_2$], 0.89 [s, 9H, C(CH_3)$_3$], 1.37, 1.43 [2s, 6H, C(CH_3)$_2$], 2.22–2.35 (m, 4H, 2-H, 5-H), 2.38 (d, ^3J = 5.3 Hz, 1H, O*H*), 3.56 (dddd, ^3J = 7.4, ^3J = 5.3, ^3J = 5.3, ^3J = 5.3 Hz, 1H, 1-H), 3.63 (m, 2H, 6-H), 3.76 (dd, ^2J = 7.7, ^3J = 6.4 Hz, 1H, 5′-H$_a$), 4.00 (dd, ^2J = 7.7, ^3J = 6.5 Hz, 1H, 5′-H$_b$), 4.05 (ddd, ^3J = 6.5, ^3J = 6.4, ^3J = 5.3 Hz, 1H, 4′-H), 5.50–5.62 ppm (m, 2H, 3-H, 4-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = −5.3, −5.3 [Si(CH_3)$_2$], 18.4 [C-(CH$_3$)$_3$], 25.3, 26.6 [C(CH_3)$_2$], 25.9 [C(CH_3)$_3$], 31.1, 31.8 (C-2, C-5), 62.7 (C-6), 66.6 (C-5′), 71.7 (C-1), 78.3 (C-4′), 109.3 (C-2′), 126.3 (C-4), 129.2 ppm (C-3); IR (film, ATR): $\tilde{\nu}$ = 3475 (O-H-ν); 3000 (C-H-ν); 2985, 2955, 2930, 2885, 2860 (aliph. C-H-ν); 1655 (olef. C=C-ν); 1470, 1465; 1380, 1370 (CH_3, C-H-δ$_s$); 1255 (TBS); 1215; 1155; 1095 (TBS); 1065; 930; 830, 805, 775 cm^{-1} (TBS); MS (EI, 70 eV): *m*/*z* (%): 330 (0.07) [M^+], 315 (3) [$M-Me^+$], 273 (11) [$M-CMe_3^+$], 215 (42) [M−TBS$^+$]; MS (CI, CH_4): *m*/*z* (%): 331 (90) [M+H$^+$], 315 (49) [$M-Me^+$], 273 (100) [$M-CMe_3^+$], 215 (78) [M−TBS$^+$]; HRMS (CI, CH_4): *m*/*z*: calcd for $C_{17}H_{35}O_4Si$: 331.2299, found: 331.2303.

(1*S*,4′*R*,3*Z*)-1-(2′,2′-Dimethyl-1′,3′-dioxolan-4′-yl)hex-3-en-1-ol (45 d): According to GP E allylboronate **39** (200 mg, 0.38 mmol) in CH_2Cl_2 (≈200 μL) was treated with (*R*)-aldehyde **42 d** (73 mg, 0.56 mmol)in CH_2Cl_2 (≈50 μL). The reaction mixture was stirred at 0 °C for 24 h and at RT for 48 h. For the reduction THF (4 mL) and $LiAlH_4$ (57 mg, 1.50 mmol), for the work up H_2O (69 μL), 15 % aqueous NaOH solution (69 μL) und H_2O (205 μL) were used. Chromatography (petroleum ether/EtOAc 90:10) furnisged a slightly impure colorless oil [52 mg, 0.26 mmol, 69 %; ^{1}H NMR: dr (**45 d**/*epi*-**45 d**) 96:4]. R_f = 0.12 (petroleum ether/EtOAc 85:15), 0.54 (petroleum ether/EtOAc 70:30); $[\alpha]_D^{20} = +14$ [c = 1.65, $CHCl_3$, dr (**45 d**/*epi*-**45 d** 96:4]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.5 Hz, 3H, 6-H), 1.37 (s, 3H, 2′-CH_{a3}), 1.43 (s, 3H, 2′-CH_{b3}), 2.01 (d, ^3J = 3.2 Hz, 1H, O*H*), 2.07 (qddddd, ^3J = 7.5, ^3J = 7.3, ^4J = 1.6, ^5J = 0.8, ^5J = 0.7 Hz, 2H, 5-H), 2.23 (ddddt, ^3J = 14.5, ^3J = 7.6, ^3J = 7.5, ^4J = 1.5, ^5J = 0.7 Hz, 1H, 2-H$_a$), 2.27 (ddddt, ^3J = 14.5, ^3J = 5.5, ^3J = 7.5, ^4J = 1.5, ^3J = 0.8 Hz, 1H, 2-H$_b$), 3.75 (dddd, ^3J = 7.6, ^3J = 5.5, ^3J = 4.9, ^3J = 3.2 Hz, 1H, 1-H), 3.94 (dd, ^2J = 7.4, ^3J = 6.2 Hz, 1H, 5′-H$_a$), 4.00 (dd, ^2J = 7.4, ^3J = 6.2 Hz, 1H, 5′-H$_b$), 4.03 (ddd, ^3J = 6.2, ^3J = 6.2, ^3J = 4.9 Hz, 1H, 4′-H), 5.38 (dtt, ^3J = 10.8, ^3J = 7.5, ^4J = 1.6 Hz, 1H, 3-H), 5.58 ppm (dtt, ^3J = 10.8, ^3J = 7.3, $^4J_{4,2}$ = 1.5 Hz, 1H, 4-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.2 (C-6), 20.6 (C-5), 25.2 (2′-C_aH$_3$), 26.5 (2′-C_bH$_3$), 30.9 (C-2), 65.1 (C-5′), 71.0 (C-1), 78.1 (C-4′), 109.0 (C-2′), 123.5 (C-3), 135.4 ppm (C-4); IR (film): $\tilde{\nu}$ = 3465 (O-H-ν); 3000 (olef. C-H-ν); 2985, 2965, 2935, 2875 (aliph. C-H-ν); 1655 (olef. C=C-ν); 1455; 1380, 1370 (CH_3, C-H-δ$_s$); 1250; 1210; 1155; 1060; 850 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 200 (5) [M^+], 185 (29) [$M-CH_3^+$], 182 (4) [$M-H_2O^+$], 142 (8) [$M-C_3H_6O^+$], 131 (23) [$C_6H_{11}O_3^+$], 101 (100) [$C_5H_9O_2^+$], 59 (73) [$C_3H_7O^+$], 43 (90) [$C_2H_3O^+$]; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{11}H_{20}O_3$: 200.1413, found: 200.1413.

(1*R*,4′*R*,3*Z*)-1-(2′,2′-Dimethyl-1′,3′-dioxolan-4′-yl)-3-hexen-1-ol (*epi*-45 d): According to GP E allylboronate **41** (200 mg, 0.38 mmol) in CH_2Cl_2 (≈200 μL) was treated with a solution of (*R*)-aldehyde **42 d** (73 mg, 0.56 mmol) in CH_2Cl_2 (≈50 μL). The reaction mixture was stirred at 0 °C for 24 h and at RT for 48 h. For the reduction THF (4 mL) and $LiAlH_4$ (57 mg, 1.50 mmol), for the workup H_2O (69 μL), 15 % aqueous NaOH solution (69 μL) and H_2O (205 μL) were used. Chromatography (petroleum ether/EtOAc 90:10) furnished a slightly impure colorless oil [54 mg, 0.27 mmol, 72 %; ^{1}H NMR: dr (**45 d**/*epi*-**45 d**) 30:70]; R_f (*epi*-**45 d**) = 0.17 (petroleum ether/EtOAc 85:15), 0.59 (petroleum ether/EtOAc 70:30); $[\alpha]_D^{20} = +9$ [c = 1.04, $CHCl_3$, dr (**45 d**/*epi*-**45 d**) 30:70]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.5 Hz, 3H, 6-H), 1.37 (s, 3H, 2′-CH_{a3}), 1.44 (s, 3H, 2′-CH_{b3}), 2.06 (m, 2H, 5-H), 2.27 (d, ^3J = 5.4 Hz, 1H, O*H*), 2.16–2.31 (m, 2H, 2-H), 3.55 (dddd, ^3J = 7.1, ^3J = 5.6, ^3J = 5.5, ^3J = 5.4 Hz, 1H, 1-H), 3.76 (dd, ^2J = 7.4, ^3J = 6.2 Hz, 1H, 5′-H$_a$), 3.97–4.07 (m, 2H, 5′-H$_b$, 4′-H), 5.40 (dtt, ^3J = 10.8, ^3J = 7.3, ^4J = 1.5 Hz, 1H, 3-H), 5.54 ppm (dtt, ^3J = 10.8, ^3J = 7.2, ^4J = 1.5 Hz, 1H, 4-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (C-6), 20.6 (C-5), 25.3 (2′-C_aH$_3$), 26.6 (2′-C_bH$_3$), 31.6 (C-2), 66.1 (C-5′), 71.8 (C-1), 78.3 (C-4′), 109.3 (C-2′), 123.6 (C-3), 134.7 ppm (C-4); IR (film): $\tilde{\nu}$ = 3465 (O-H-ν); 3000 (olef. C-H-ν); 2985, 2965, 2935, 2875 (aliph. C-H-ν); 1655 (olef. C=C-ν); 1455; 1380, 1370 (CH_3, C-H-δ$_s$); 1250; 1210; 1155; 1060; 855; 700 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 200 (5) [M^+], 185 (29) [$M-CH_3^+$], 182 (3) [$M-H_2O^+$], 142 (8) [$M-C_3H_6O^+$], 131 (61) [$C_6H_{11}O_3^+$], 101 (93) [$C_5H_9O_2^+$], 59 (100) [$C_3H_7O^+$], 43 (93) [$C_2H_3O^+$]; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{11}H_{20}O_3$: 200.1413, found: 200.1413.

(6*R*,4′*R*,3*Z*)-6-Benzoyloxy-6-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-hex-3-enoic acid dimethylamide (48) and (6*S*,4′*R*,3*Z*)-6-benzoyloxy-6-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)hex-3-enoic acid dimethylamide (*epi*-48): The mixture of diastereomers **43 d**/*epi*-**43 d** ≈24:76 (50 mg, 0.19 mmol) was dissolved in CH_2Cl_2 (583 μL) and pyridine (583 μL) was added. Benzoyl chloride (25 μL, 0.214 mmol) was added three times for completion of the reaction, whereas a colorless solid precipitated. Chromatography (6 g silica gel, EtOAc) yielded a spectroscopically pure colorless oil (0.17 mmol, 63 mg, 90 %; ^{1}H NMR: dr (**48**/*epi*-**48**) 28:72). The two diastereomers were almost completely separated by means of MPLC: Analytical data for **48** [25 mg, 0.07 mmol, 36 %; ^{1}H NMR: dr (**48**/*epi*-**48**) 6:94]; R_f = 0.27 (EtOAc); $[\alpha]_D^{20} = +11$ [c = 1.15, $CHCl_3$, dr (**48**/*epi*-**48**) 6:94]; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36, 1.48 (2s, 6H, 2′-CH_3), 2.58 (m, 2H, 5-H), 2.92, 2.98 [2s, 6H, N(CH_3)$_2$], 3.13 (ddd, ^2J = 16.6, ^3J = 6.7, ^3J = 1.9 Hz, 1H, 2-H$_a$), 3.20 (ddd, ^2J = 16.6, ^3J = 7.1, ^3J = 1.9 Hz, 1H, 2-H$_b$), 3.81 (dd, ^2J = 8.5, ^3J = 6.3 Hz, 1H, 5′-H$_a$), 4.05 (dd, ^2J = 8.5, ^3J = 6.8 Hz, 1H, 5′-H$_b$), 4.34 (ddd, ^3J = 6.8, ^3J = 6.3, ^3J = 3.9 Hz, 1H, 4′-H), 5.17 (td, ^3J = 6.8, ^3J = 3.9, 1H, 6-H), 5.63 (dtt, ^3J = 10.8, ^3J = 7.5, ^3J = 1.9 Hz, 1H, 4-H), 5.77 (dddt, ^3J = 10.8, ^3J = 7.1, ^3J = 6.7, ^4J = 1.5 Hz, 1H, 3-H), 7.43–7.46, 7.55–7.59, 8.05–8.07 ppm (3m, 5H, arom C*H*), ^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.3, 26.4 (2′-CH_3), 29.2 (C-5), 32.4 (C-2), 35.5, 37.2 [N-(CH_3)$_2$], 65.6 (C-5′), 72.9 (C-6), 75.7 (C-4′), 109.5 (C-2′), 126.0 (C-4), 126.2 (C-3), 128.4, 129.7, 133.1 (arom. *C*H), 130.1 (arom. C_{ipso}), 166.1 (Ph*C*O), 170.9 ppm (C-1); IR (film, ATR): $\tilde{\nu}$ = 3030 (arom. C-H-ν); 2985, 2935, 2885 (aliph. C-H-ν); 1715 (C=O-ν, ester); 1645 (C=O-ν, amide); 1490; 1450; 1395; 1380, 1370 (CH_3, C-H-δ$_s$); 1270; 1215; 1110; 1065 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 361 (2) [M^+], 346 (10) [$M-CH_3^+$], 303 (6) [$M-C_3H_6O^+$], 240 (52) [$M-PhCO_2^+$], 239 (14) [$M-PhCO_2H^+$], 105 (100) [PhCO$^+$]; elemental analysis calcd (%) for $C_{20}H_{27}NO_5$ (361.4): C 66.46, H 7.53, N 3.88, found: C 66.26, H 7.61, N 3.76. Analytical data for *epi*-**48** [7 mg, 0.02 mmol, 10 %; ^{1}H NMR: dr (**48**/*epi*-**48**) > 99:1]; R_f = 0.27

(EtOAc); $[\alpha]_D^{20} = +35$ [$c = 0.10$, $CHCl_3$, dr (**48**/*epi*-**48**) > 99:1]; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.36$, 1.39 (2s, 6H, 2′-CH_3), 2.58 (m, 2H, 5-H), 2.90, 2.94 [2s, 6H, $N(CH_3)_2$], 3.12 (m, 2H, 2-H), 3.93 (dd, $^2J = 8.5$, $^3J = 5.9$ Hz, 1H, 5′-H_a), 4.09 (dd, $^2J = 8.5$, $^3J = 6.5$ Hz, 1H, 5′-H_b), 4.30 (ddd, $^3J = 6.5$, $^3J = 6.2$, $^3J = 5.9$ Hz, 1H, 4′-H), 5.23 (m, 1H, 6-H), 5.65 (dtt, $^3J = 10.9$, $^3J = 7.4$, $^4J = 1.8$ Hz, 1H, 4-H), 5.77 (dtt, $^3J = 10.9$, $^3J = 6.9$, $^4J = 1.5$ Hz, 1H, 3-H), 7.43–7.46, 7.55–7.59, 8.01–8.03 ppm (3m, 5H, arom C*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 25.3$, 26.6 (2′-*C*H_3), 29.1 (C-5), 32.5 (C-2), 35.5, 37.2 [$N(CH_3)_2$], 66.4 (C-5′), 73.9 (C-6), 75.9 (C-4′), 109.7 (C-2′), 125.9 (C-4), 126.1 (C-3), 128.4, 129.7, 133.2 (arom. *C*H), 130.0 (arom. C_{ipso}), 165.8 (Ph*C*O), 170.9 ppm (C-1); IR (solution in $CDCl_3$): $\tilde{\nu} =$ 3050, 3010 (arom. C-H-ν); 2970, 2920, 2870 (aliph. C-H-ν); 1710 (C=O-ν, ester); 1630 (C=O-ν); 1590; 1575; 1480; 1440; 1390; 1370, 1360 (CH_3, C-H-δ_s); 1300; 1260; 1200; 1165; 1100; 1055 cm^{-1}; MS (CI, CH_4): *m*/*z* (%): 362 (33) [$M+H^+$], 346 (16) [$M-CH_3^+$], 240 (100) [$M-PhCO_2^+$], 105 (50) [$PhCO^+$]; HRMS (AUTO-CI, 70 eV): *m*/*z*: calcd for $C_{20}H_{28}NO_5$: 362.1967, found: 362.1951; elemental analysis calcd (%) for $C_{20}H_{27}NO_5$ (361.4): C 66.46, H 7.53, N 3.88, found: C 67.08, H 7.79, N 3.70.

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