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Insertion of chiral carbenoids into pinanediol boronic esters

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Dedicated to Professor *Hagga* Schmalz, an inspiring teacher and academic role model

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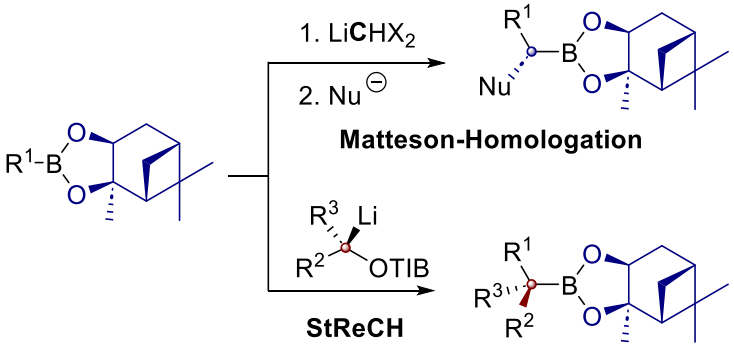
Abstract

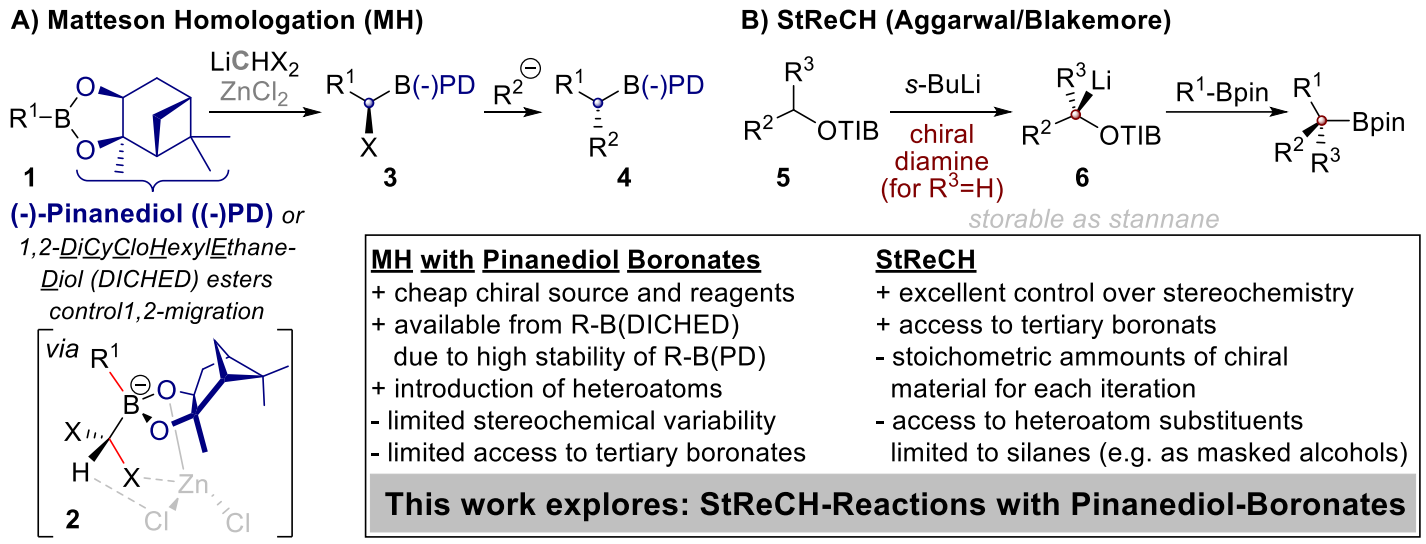
The stereochemical outcome of the Matteson homologation is determined by the substrate, more specifically the chiral diol boronic ester. This can limit stereodiversity in iterative syntheses. Stereospecific reagent-controlled homologations (StReCH) employ chiral carbenoids, which have to be prepared in equimolar amounts for each homologation. This allows for maximum stereodiversity as well as the generation of chiral, tertiary boronic esters. Combining both methods can thus be of benefit in iterative synthesis. Therefore, the combination of chiral carbenoids with chiral pinanediol boronic esters was explored in order to make the epimer inaccessible to conventional Matteson Homologations, as well as α-chiral tertiary boronic esters. This approach afforded products with a yield of up to 90% and excellent stereochemical fidelity.



Keywords: Matteson homologation, boronate homologation, stereodivergent synthesis

Introduction

Boronic ester homologations are powerful tools for the iterative assembly of products containing multiple stereocenters. Scheme 1 shows different variants of this reaction. The first reaction, shown in Scheme 1A is the classic Matteson homologation.[1–8] In it a chiral boronic ester containing a C2-symmetric chiral diol such as DiCycloHexylEthaneDiol (DICHED) or pinanediol (**1**) reacts with lithiated dichloromethane (DCM). In the resulting ate-complex (**2**) the chiral diol (supported by $ZnCl_2$) directs stereoselective 1,2-migration to an α-halo boronic ester of type **3**. It undergoes substitution under inversion with various nucleophiles.



Scheme 1. Boronate homologations with different stereselective mechanisms: (A) The Matteson homologation (MH) relies on stereoselective 1,2-migration directed by a chiral auxiliary. (B) Stereospecific Reagent Controlled Homologations (StReCH) rely on chiral carbenoids prepared by stereoselective lithiation (Aggarwal) or from chiral sulfoxides (Blakemore). (C) Converting MH products into iodides allows for Curtin-Hammett controlled substitution leading to stereodivergent products (Hirschhäuser). (D) N-Tosyl-amino acid derived auxiliaries allow for Curtin-Hammett controlled insertion with fantastic substrate scopes (Dong). (E) Fu´s nickel catalyst allowed for enantioconvergent substitution. (F) Jacobsen´s Li-isothiourea boronate catalyst allows for stereoselective insertion.

Aggarwal and Blakemore introduced boronate homologations with chiral carbenoids (**6**, Scheme 1B). As all steps after stereoselective carbenoid generation (e.g. by Hoppe lithiation[9–11] of **5** (R^3=H)) are stereospecific, Blakemore[12] coined the acronym StReCH (Stereospecific Reagent-Controlled Homologation) for this type of reaction.[13–17] Each reaction has its own strengths and limitations. The Matteson homologation allows for introducing heteroatom substituents. In addition, the chiral director offers high efficiency in iterative sequences, as it can direct the stereochemical outcome of multiple reactions. However, changing the chiral director can be challenging,[18–20] which limits stereochemical variability in iterative sequences.[4,5,7,21] While this limitation can be overcome by modifying synthetic strategies,[22–37] methods for preparing homologation products with stereodivergent outcomes directly would be preferable. Several approaches to such *epi*-Matteson products have been reported. Carreaux et al. inserted lithiated acetals (LiCHOMe and LiCHOEt) into pinanediol boronates. Thus by omitting the substitution under inversion *epi*-Matteson products were obtained.[38] Kazmaier et al inserted lithiated dihaloalkanes into DICHED boronic esters. Subsequent substitution with a hydride source resulted in *epi*-Matteson products. Substitution with a suitable carbon nucleophile even led to formation of tertiary boronic esters.[39] This report is particularly interesting because a similar approach with pinanediol boronic esters of type **1** only had very limited success.[40] We recently reported a mechanistically different variation of the Matteson sequence, in which a fast equilibrium between epimeric α-iodo boronic esters was exploited to achieve Curtin-Hammett control in the substitution step (Scheme 1C). This reaction required pinanediol boronic esters, as DICHED boronic esters can undergo ring expansive rearrangements (v.i.).[41] This process delivered *epi*-Matteson products with primary alkyl- and aryl-Grignard reagents.[42] In another recent report Dong and coworkers exploit a Curtin-Hammett controlled insertion of configurationally unstable carbenoids into oxazaborolidines.[43] While Aggarwal and coworkers had reported a mechanistically related, enantioconvergent insertion into an α-chiral pinnacol boronate,[44] it must be stressed that this reaction delivers only little stereoselectivity with diol based boronic esters of type **1** or their DICHED congeners. Key to the success of Dong and coworkers was the design of their tosyl-amino acid derived auxiliaries, in which the orientation of the tosyl-group effectively shields the adjacent boron center. This allowed for a very impressive substrate scope, including several heteroatom substituents. Furthermore, these chiral auxiliaries can be cleaved, and thus replaced, much more easily than pinanediol. Finally, two catalytic versions of the Matteson homologation should be mentioned. While Fu and coworkers targeted the substitution step (Scheme 1E),[45] Jacobsen et al. achieved a catalyst directed homologation (Scheme 1F).[46–48]

Despite these impressive advances, Matteson homologations with pinanediol boronic esters still have some important advantages. Pinanediol can be made in one step from pinene, both enantiomers of which are cheaply available.[49] Furthermore, transesterification from DICHED-boronic esters is very easy, which allows for a swift exchange of chiral directors once per sequence.[22,50,51] This is due to the rigid structure of pinanediol, which forms boronic esters without ring strain or an entropy penalty due to loss of rotational freedom. The resulting stability of pinanediol boronates makes them very easy to work with, but also almost impossible to hydrolyze.[21] Therefore the exploration of methods that allow for access to stereodivergent homologation products from pinanediol boronic esters remains worthwhile. StReCH reactions could complement this reactivity nicely. While it might seem excessive to conduct a reaction that requires stoichiometric amounts of chiral diamine[52,53] while a chiral auxiliary is present, such a combination might well be interesting in an iterative sequence. When the chiral director is used for installing multiple stereocenters, a StReCH might be used to incorporate a complementary stereocenter or a carbon atom with two substituents. Thus, the strength of Matteson homologations and StReCH reactions could be exploited at different points of a homologation sequence. Sequences based on StReCH reactions are somewhat limited when it comes to the incorporation of heteroatom

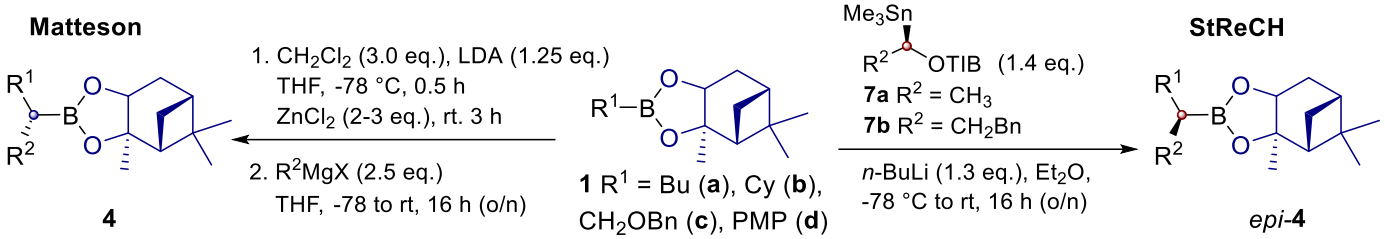
substituents. Currently such examples are limited to the introduction of silyl substituted carbenoids, in which a silyl group can serve as a masked alcohol.[54–56]

Therefore, we set out to investigate the application of Aggarwal's StReCH protocols for the insertion of chiral carbenoids into pinanediol boronates. The carbenoids employed were trapped as stannanes, which can be converted back to the carbenoid *via* tin-lithium exchange.[14,57,58] This approach offers access to both *epi*-Matteson products and tertiary boronic esters with a diastereomeric ratio of up to 99:1.

Results and Discussion

To better evaluate the usefulness of StReCH reactions with (-)-pinanediol boronic esters of type **1**, (+)-spartein derived carbenoids were chosen, which were conveniently stored as stannanes of type **7**. As shown in Table 1, this combination leads to *epi*-Matteson products (*epi*-**4**), i.e. the epimers of classic Matteson products of type **4**. To assess the stereofidelity of the reaction, the classic Matteson products were prepared as well, according to established protocols.[27] After a brief optimization of the StReCH protocol, similar conditions to the ones reported by Aggarwal et al.[14] emerged as suitable. Therefore 1.4 equivalents of a stannane of type **7** were reacted at -78 °C with 1.3 equivalents of *n*-BuLi for one hour to form the corresponding carbenoid of type **6**. After addition of boronic esters of type **1** and stirring at room temperature for approximately 16 h (i.e. over night), homologated pinanediol boronic esters of type *epi*-**4** were isolated. The diastereomeric ratio was determined by NMR through comparison to the corresponding Matteson products (**4**). The StReCH approach showed good yields and diastereomeric ratios with simple alkyl boronic esters. For butyl boronate **1a**, reactions with both, the methyl substituted stannane **7a** and the homobenzyl substituted stannane **7b** resulted in very good yields and diasteromeric ratios leading to **4aa** and **4ab** in 84% and 88% yield, respectively.

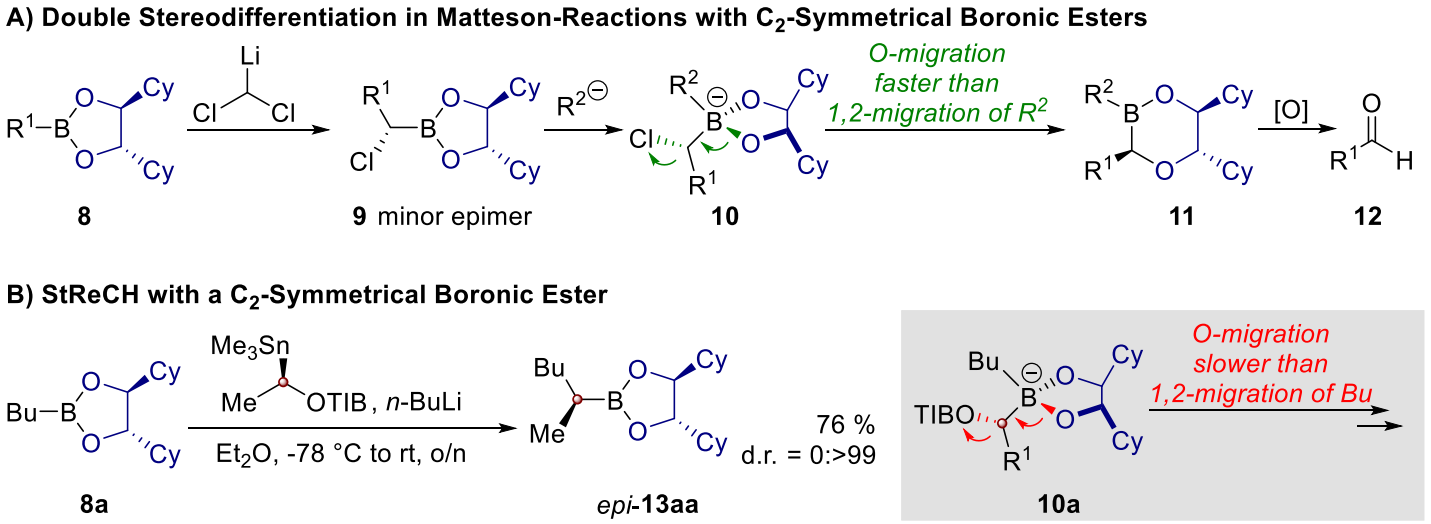
Table 1. Matteson Homologation (MH) and StReCH-Reactions with (-)-Pinanediol Boronates



Entry	Product	Matteson Product		StReCH Product	
		d.r. (**4**:*epi*-**4**)	Yield / %	d.r. (**4**:*epi*-**4**)	Yield / %
1	**4aa** R^1 = Bu, R^2 = Me	92:8[(a)]	60	0:>99	84
2	**4ab** R^1 = Bu, R^2 = CH_2Bn	90:10	67	0:>99	88
3	**4ba** R^1 = Cy, R^2 = Me	>99:0	38	0:>99	90
4	**4bb** R^1 = Cy, R^2 = CH_2Bn	>99:0	70	0:>99	67[(d)]
5	**4ca** R^1 = $BnOCH_2$, R^2 = Me	>99:0[(a)]	57	0:>99	43
6	**4cb** R^1 = $BnOCH_2$, R^2 = CH_2Bn	>99:0	12	0:>99	29
7	**4da** R^1 = *p*OMePh, R^2 = Me	-[(b)]	8	-[(b)]	66
8	**4db** R^1 = *p*OMePh, R^2 = CH_2Bn	>99:0	7[(c)(d)]	0:>99	33[(c)]

(a) MH conducted with (+)-pinanediol boronate (*ent*-***1***); (b) diastereomeric ratio could not be determined; (c) compound decomposes in the presence of air; (d) determined by internal standard.

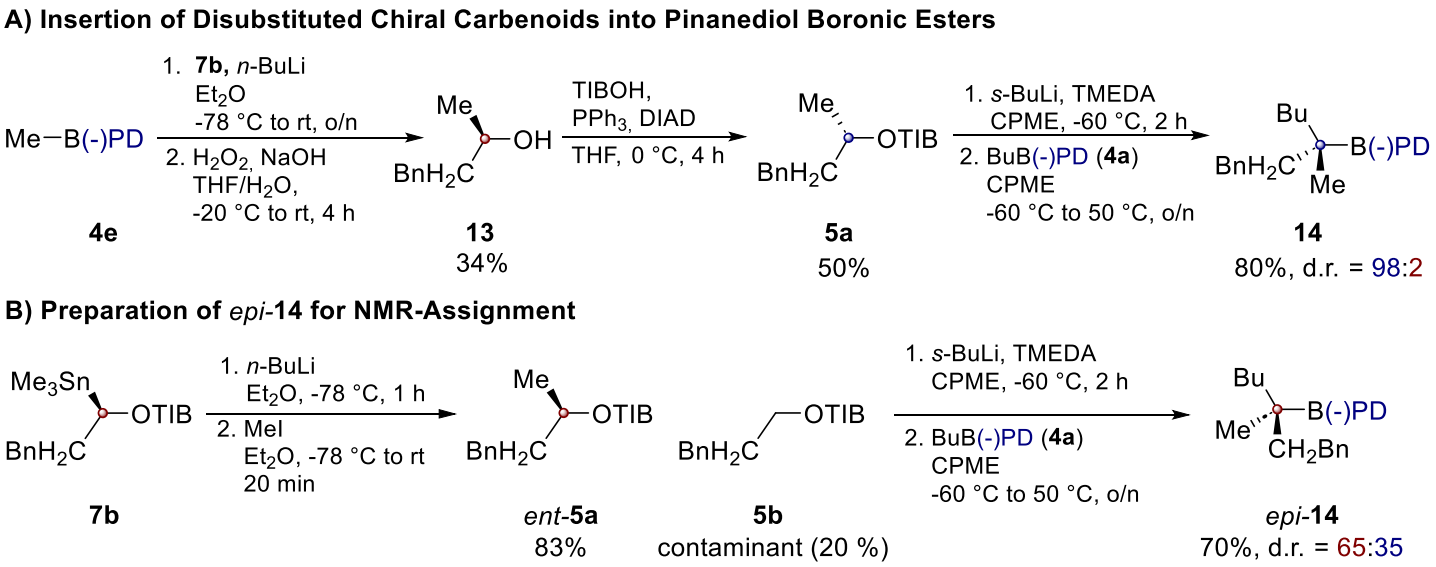
The sterically more challenged cyclohexyl boronate **4b** also showed excellent diastereomeric fidelity in both examples (**4ba** and **4bb**). While **4ba** was formed with 90% yield, reaction with the sterically more demanding carbenoid resulted in formation of **4bb** with a slightly lower yield of 67%. Next, the reaction was tested on boronic esters with useful functional groups in close proximity to the boron atom. Benzyloxy methyl boronate **1c** is a highly useful building block well established in our group.[22, 58] However, reactions with this compound can be challenging due to neighboring group participation.[59–62] Indeed standard reaction conditions that worked well for alkyl boronic esters **1a** and **1b**, did not yield the desired products even after refluxing overnight. This was attributed to a reduced migration tendency of the electron deficient CH_2OBn group. Thus modified conditions, established by Aggarwal et al. for such substrates were employed.[63] After the addition of boronic ester **1c** and allowing the reaction to warm to rt, the solvent was changed to chloroform and the reaction mixture was heated at reflux temperature overnight. The corresponding products *epi*-**4ca** and *epi*-**4cb** were obtained with excellent diastereomeric ratio albeit lower yields (43% and 29%) than their alkyl counterparts. The *p*-anisyl boronate **1d** was selected as an aromatic substrate. Aryl boronic esters are notoriously difficult substrates for Matteson homologations, although Kazmaier et al. published a specialized protocol in 2022.[66] Moreover, the *p*-anisyl group can be used as a masked carboxylic acid.[15,64] As aryl groups are often slow as migrating groups for this type of 1,2-rearrangement,[65,66] the reaction required the same migration conditions as the synthesis of β-benzyloxy boronic esters *epi*-**4ca** and *epi*-**4cb**. While *epi*-**4da** was obtained with a fair yield of 66%, the diastereomeric ratio could not be determined due to both diastereomers having indistinguishable NMR spectra (^1H and ^{13}C). That being said, it is reasonable to assume that the diastereomeric ratio is on a similar level as for the other reactions, since *epi*-**4db** was also obtained in an excellent diastereomeric ratio. The isolated yield was only 33%, as *epi*-**4db** was found to decompose in the presence of air. Based on these results it is safe to say, that chiral carbenoids can be inserted into pinanediol boronic esters of type **1** using protocols developed by the Aggarwal group for corresponding pinacol boronic esters. While this result was to be expected, attempting the same reaction with a (*S*,*S*)-DICHED (**DIC**yclo**H**exyl**E**thane-1,2-**D**iol)-boronic ester of type **8** was somewhat less predictable.



Scheme 2. Matteson homologation and StReCH-reactions with DICHED-boronic esters.

Such C_2-symmetrical boronic esters can deliver products of exceptional diastereomeric purity under normal Matteson conditions due to an additional stereodifferentiating step depicted in Scheme 2A.[41] In the substitution

step the unwanted minor diastereomer of the homologation reaction (**9**) forms an *ate*-complex of type **10** with a Grignard reagent. In contrast to its desired epimer, one of the ring oxygen atoms in **10** preferably undergoes 1,2-migration. This leads to borinic esters of type **11**, which are easily oxidized upon aqueous workup (**12**). This mechanism reduces the amount of undesired epimers in classic Matteson sequences and is responsible for the high diastereoselectivty observed when homologating C_2-symmetrical boronic esters. As can be seen in Scheme 2B a stereochemically equivalent ate-complex is formed upon StReCH reaction of butyl DICHED boronic ester **8a**. Thus in principle a similar preference for O-migration might be expected. However, StReCH of **8a** with **7a** delivered the corresponding homologation product *epi*-**13aa**, although with a slightly diminished yield compared to the corresponding pinanediol boronic ester (66% and 84% yield, respectively). While this result is mechanistically interesting, the previously mentioned route by Kazmaier and coworkers to *epi*-Matteson products of DICHED-boronic esters, appears to be a superior method for these substrates. Their work also allowed for synthesis of tertiary DICHED-boronic esters.[39] Before their report, the synthesis of tertiary boronic esters by carbenoid insertion in high stereochemical purity has been a feat reserved for StReCH reactions.[13,57,67,68] Earlier attempts by Matteson to apply the Kazmaier approach to pinanediol boronic esters had delivered mixed results.[69] Thus we explored whether such products could be obtained by StReCH reaction.



Scheme 3. Synthesis of tertiary pinanediol boronic esters.

Therefore, the secondary triisopropylbenzoate **5a** was prepared as depicted in Scheme 3A. Stannane **7b** was lithiated and the resulting carbenoid was inserted into methylboronic ester **4e**. After oxidation with basic H_2O_2, alcohol **13** was isolated and converted into **5a** by Mitsunobu reaction. Following an established protocol,[67] **5a** was lithiated and inserted into butyl pinanediol boronic ester (**4a**, 2 equiv.), yielding the tertiary boronic ester **14** in 80% yield and a diastereomeric ratio of 98:2. To ensure that the determined diastereomeric ratio was based on a correct assignment of NMR resonances, the corresponding epimer *epi*-**14** was prepared as shown in Scheme 3B. While lithiation of **7b** and subsequent alkylation with MeI seemed to offer swift access to *ent*-**5a**, the reaction was plagued by incomplete conversion and an inability to separate *ent*-**5a** from the simple, protonated product **5b**. It is likely that the presence of this impurity led to partial isomerization of the carbenoid formed by lithiation of *ent*-**5a**, as StReCH reaction to *epi*-**14** only delivered a 65:35 diastereomeric mixture. The material thus obtained nevertheless allowed for validating the NMR assignment of both epimers of type **14**. This

confirmed that insertion of disubstituted carbenoids into pinanediol boronic esters can be conducted under comparable conditions as reported by Aggarwal and coworkers for corresponding pinacol boronates.

Conclusions

The results presented in this article demonstrate that protocols developed by Aggarwal and coworkers for StReCH reactions can be easily adapted to pinanediol boronic esters in order to generate the epimers of normal Matteson homologation products. While such reactions on their own might seem of little value, they could be employed efficiently in iterative sequences, where most stereocenters are controlled by the chiral director. Moreover, the insertion of disubstituted carbenoids provides an important extension to the normal scope of Matteson reactions using pinanediol boronic esters.

Experimental Section

General. All reactions with non-aqueous media or reagents were performed under an atmosphere of argon using dried solvents and Schlenk-line techniques. Commercially available solvents and reagents were used as obtained from *Abcr GmbH*, *Fisher Scientific*, *Carbolution GmbH*, *Fluorochem*, *Sigma Aldrich,* and *TCI* without additional purification unless stated otherwise. Deuterated NMR solvents were received from *Deutero GmbH*. Grignard reagents were titrated using salicylaldehyde phenylhydrazone, following the method presented by Love and Jones.[70] Organolithium reagents were titrated using *N*-benzylbenzamide. THF, Et_2O and dichloromethane were dried with solvent purifier *SPS 5* by *MBRAUN*. Diisopropyl amine were dried over CaH_2 and distilled under an Argon atmosphere. CPME and $CHCl_3$ were dried over 4 Å molecular sieves and stored under an Argon atmosphere. Technical grade cyclohexane was distilled at 200 mbar and 40 °C and used for flash column chromatography. For determination of yield by internal standard, a 3% v/v solution of DCM or CPME in $CDCl_3$ was used. Yields determined in that way are labeled with IS. Solvents were removed on a rotary evaporator under reduced pressure at 40 °C, if not stated otherwise. For thin-layer chromatography (TLC), *Polygram SIL G/UV254* silica plates from *Macherey-Nagel* were used. Spot visualization was performed using 254 and 365 nm or $KMnO_4$ stain. Flash-chromatography was carried out by using silica gel *MN 60 M* (0.04–0.063 mm) from *Macherey-Nagel*. High-resolution electrospray (ESI) mass spectra were measured on a *Bruker maXis 4G* spectrometer with data processing *Bruker Data Analysis* software. FT-IR spectra were measured using a *Jasco FT/IR-4600* spectrometer. NMR spectra were measured on a *Bruker AVNEO400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) spectrometer. All measurements were performed at room temperature, ^{13}C-NMR spectra were recorded with proton decoupling. Spectra are given with frequency and solvent. Chemical shifts are given in parts per million (ppm). Coupling constants *J* are given in Hertz (Hz). The undeuterated residue of the solvent served as internal reference. For the assignment of ^{1}H-NMR, following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), bs (broad singlet), dd (doublet of doublet), sxt (sextet), hpt (heptet), ddd (doublet of doublet of doublet). For the complete assignment of ^{1}H-NMR and ^{13}C-NMR signals, 2D spectra such as HSQC, HMBC and COSY were employed. In ^{13}C-NMR, the carbon atom adjacent to boron is unobservable due to carbon-boron spin-spin coupling and partially relaxed scalar coupling between boron and carbon.[71] All raw-data were processed and analyzed by using the *Bruker TopSpin 4.4.0 software*.

General procedure for the synthesis of *epi*-Matteson products of type *epi*-4 by StReCH (GP1a). Stanane **7**[24] (1.4 eq.) in Et_2O (0.15 M) was cooled to -78 °C and *n*-BuLi (1.3 eq., 2.5 M in hexane) was added dropwise. The resulting solution was stirred for 1 h at the same temperature. The boronic ester of type **1** or **8** (1.0 eq.) in Et_2O (0.15 M) was added dropwise and stirred for one additional hour at the same temperature. After that the cooling bath was removed and stirring was continued for 16 h (overnight) at room temperature. The resulting suspension was concentrated under reduced pressure (*Caution! The reaction mixture contains toxic and volatile $SnBuMe_3$*) and co-evaporated three times with toluene to remove $SnBuMe_3$. The residue was taken up in Et_2O, filtered through a plug of silica and washed with excess Et_2O. The filtrate was concentrated *in vacuo* and purified by flash column chromatography to furnish products of type *epi*-**4** or *epi*-**13**

Modified StReCH procedure for challenged migration groups (GP1b). The reaction was carried out as described in GP1a, but after addition of boronic ester **1**, stirring for 1 h at -78 °C and warming up to rt, the solvent was changed to $CHCl_3$ (0.07 M) and stirring was continued at 60 °C for 16 h (overnight).[63] Workup was conducted as described in GP1a.

General procedure for the synthesis of Matteson products of type 4 (GP2). A modified procedure by Kazmaier et al. was employed.[27] Diisopropylamine (1.35 eq.) in THF (6 M) was cooled to −78 °C and *n*-BuLi (1.25 eq., 2.5 M in hexane) was added dropwise. The resulting suspension was swiftly warmed to rt to give a fresh LDA solution. In another flask, boronic ester **1** (1.0 eq) and CH_2Cl_2 (3.0 eq.) in dry THF (0.6 M) were cooled to −78 °C, then the LDA solution was added dropwise. The reaction was stirred for an additional 0.5 h at the same temperature. Subsequently, $ZnCl_2$ (2.0−3.0 eq., 1 M in Et_2O) was added dropwise, then the reaction was warmed to rt and stirred for 3 h. Afterwards, the reaction was terminated by adding a saturated aqueous solution of NH_4Cl. The aqueous layers were extracted thrice with cyclohexane. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield the α-haloboronic ester (**3** for pinanediol, not shown for DICHED). Obtained α-haloboronic esters were used directly for the next step without further purification. The α-haloboronic ester (1.0 eq.) in THF (0.1—0.3 M) was cooled to −78 °C, then a solution of the Grignard-reagent (1.3 M in THF) was added dropwise. After 3 minutes, the cooling bath was removed and the mixture stirred at rt for 16 h (overnight). Upon completion (as monitored by TLC and/or ^{1}H-NMR), the reaction was terminated by adding a sat. aq. solution of NH_4Cl. The aq. layers were extracted three times with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography.

(2*R*)-Hex-2-yl-(-)-pinanediol boronic ester (*epi*-4aa). According to **GP1a**, butyl-(-)-pinanediol boronic ester **1a** (100 mg, 0.42 mmol), **7a** (207 mg, 0.59 mmol) and *n*-BuLi (0.22 mL, 0.55 mmol) were reacted to furnish *epi*-**4aa** as a colorless oil (68 mg, 0.26 mmol), as well as a mixture (74 mg) of EtOTIB (0.10 mmol) and *epi*-**4aa** (0.09 mmol). Total yield 84% (*ent*-**4aa**:*epi*-**4aa** < 1:99). R_f = 0.33 (CyH:Et_2O = 98:2). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.25 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.37 – 2.30 (m, 1H), 2.24 – 2.18 (m, 1H), 2.05 (t, *J* = 5.6 Hz, 1H), 1.92 – 1.88 (m, 1H), 1.82 – 1.80 (m, 1H), 1.50 – 1.44 (m, 1H), 1.37 (s, 3H), 1.34 – 1.23 (m, 8H), 1.11 (d, *J* = 10.8 Hz, 1H), 1.08 – 1.02 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.88 (t, *J* = 6.6 Hz, 3H), 0.84 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 85.3, 77.7, 54.4, 39.7, 38.3, 35.8, 33.2, 31.4, 28.9, 27.2, 26.6, 24.2, 23.1, 15.9, 14.3 ppm. IR: $\tilde{\nu}$ = 2987 (w) C-H, 2916 (s) C-H, 2871 (s) C-H, 1386 (s) B-O, 1375 (s) B-O, 1278 (m) C-O, 1235 (m) C-O, 1030 (m) B-C cm^{-1}. HRMS (ESI): found: 265.2335, 287.2155, calculated *m/z* for $C_{16}H_{30}BO_2^+$: 265.2336, $C_{16}H_{29}BO_2Na^+$: 287.2156.

(3*R*)-1-Phenyl-hept-3-yl-(-)-pinanediol boronic ester (*epi*-4ab). According to **GP1a**, butyl-(-)-pinanediol boronic ester **1a** (100 mg, 0.42 mmol), **7b** (260 mg, 0.59 mmol) and *n*-BuLi (0.22 mL, 0.55 mmol) were reacted to furnish *epi*-**4ab** as a colorless oil (46 mg, 0.13 mmol), as well as a mixture (91 mg) of $BnCH_2OTIB$ (0.24 mmol) and *epi*-**4ab** (0.24 mmol). Total yield of 88% (**4aa**:*epi*-**4aa** <1:99). R_f = 0.33 (CyH:Et_2O = 98:2). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.25 (m, 2H, superimposed by $CHCl_3$), 7.19 – 7.14 (m, 3H), 4.29 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.69 – 2.55

(m, 2H), 2.40 – 2.33 (m, 1H), 2.27 – 2.20 (m, 1H), 2.08 (t, *J* = 5.5, 1H), 1.94 – 1.90 (m, 1H), 1.87 – 1.82 (m, 1H), 1.80 – 1.62 (m, 2H), 1.51 – 1.44 (m, 2H), 1.39 (s, 3H), 1.34 -1.23 (m, 7H), 1.17 (d, *J* = 10.8 Hz, 1H), 1.13 – 1.07 (m, 1H), 0.90 – 0.86 (m, 6H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 143.3, 128.5, 128.4, 125.7, 85.5, 77.7, 51.4, 39.7, 38.3, 35.9, 35.9, 33.7, 31.6, 31.2, 29.0, 27.2, 26.8, 24.2, 23.1, 14.2 ppm. IR**:** $\tilde{\nu}$ = 2917 (s) C-H, 2870 (s) C-H, 1559 (w) C-Ar, 1386 (s) B-O, 1375 (s) B-O, 1363 (s) B-O, 1339 (m), 1278 (m) C-O, 1252 (w), 1236 (m) C-O, 1028 (m) B-C cm^{-1}. HRMS (ESI): found: 355.2805, 372.3071, 377.2625, calculated *m*/*z* for $C_{23}H_{36}BO_2^+$: 355.2807, $C_{23}H_{39}BO_2N^+$: 372.3071 $C_{23}H_{35}BO_2Na^+$: 377.2626.

(*S*)-1-Cyclohexyl-ethyl-(-)-pinanediol boronic ester (*epi*-4ba). According to **GP1a**, cyclohexyl-(-)-pinanediol boronic ester (100 mg, 0.38 mmol), **7a** (186 mg, 0.53 mmol), *n*-BuLi (0.20 mL, 0.50 mmol) was reacted to furnish the desired product as a 13:10:77 mixture (101 mg) of EtOTIB (0.05 mmol), starting material (0.04 mmol) and ***epi*-4ba** (0.34 mmol, 90%, **4ba**:*epi*-**4ba** = 0:99). R_f = 0.35 (CyH:Et_2O = 98:2). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.26 (dd, *J* = 8.8, 2.1 Hz, 1H), 2.38 – 2.31 (m, 1H), 2.24 – 2.18 (m, 1H), 2.05 (t, *J* = 5.5 Hz, 1H), 1.93 – 1.88 (m, 1H), 1.85 – 1.80 (m, 1H), 1.76 – 1.61 (m, 5H), 1.38 – 0.94 (m, 17H, superimposed by contaminants), 0.84 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 85.3, 77.6, 54.4, 40.8, 39.7, 38.3, 35.9, 32.8, 32.0, 29.0, 27.2, 27.0, 26.91, 26.9, 26.7, 24.2, 13.0 ppm. HRMS (ESI): found: 291.2493, 308.2763, 313.2316, calculated *m*/*z* for $C_{18}H_{32}BO_2^+$: 291.2493 $C_{18}H_{35}BO_2N^+$: 308.2759 $C_{18}H_{31}BO_2Na^+$: 313.2313.

(*S*)-1-Cyclohexyl-3-phenyl-propyl-(-)-pinanediol boronic ester (*epi*-4bb). According to **GP1a**, cyclohexyl-(-)-pinanediol boronic ester (100 mg, 0.38 mmol), **7b** (234 mg, 0.53 mmol), *n*-BuLi (0.20 mL, 0.50 mmol) was reacted to furnish the desired product as an inseparable mixture (115 mg) with unknown contaminants. The yield was determined after addition of an internal standard (0.25 mmol, 67%^{IS}, **4bb:***epi*-**4bb** = 0:99). R_f = 0.29 (CyH:Et_2O = 98:2). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.24 (m, 2H, superimposed with $CHCl_3$), 7.19 – 7.14 (m, 3H), 4.31 (dd, *J* = 8.9, 2.2 Hz, 1H), 2.70 – 2.63 (m, 1H), 2.55 – 2.48 (m, 1H), 2.42 – 2.35 (m, 1H), 2.28 – 2.21 (m, 1H), 2.09 (t, *J* = 5.6 Hz, 1H), 1.95 – 1.91 (m, 1H), 1.88 – 1.84 (m, 1H), 1.81 – 1.61 (m, 7H), 1.49 – 1.41 (m, 1H), 1.40 (s, 3H), 1.30 (s, 3H), 1.27 – 0.95 (m, 7H, superimposed with contaminants), 0.86 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 143.4, 128.5, 128.4, 125.7, 85.5, 77.6, 51.4, 40.1, 39.7, 38.3, 36.4, 36.0, 33.1, 32.6, 31.4, 29.1, 27.2, 27.0, 26.9, 26.9, 24.2 ppm. HRMS (ESI): found: 381.2962, 398.3228, 403.2782, calculated *m*/*z* for $C_{25}H_{38}BO_2^+$: 381.2964, $C_{25}H_{41}BO_2N^+$: 398.3229, $C_{25}H_{37}BO_2Na^+$: 403.2783.

(2*S*)-1-Benzyloxy-prop-2-yl-(-)-pinanediol boronic ester (*epi*-4ca). According to **GP1b**, (benzyloxy)methyl-(-)-pinanediolboronic ester (150 mg, 0.5 mmol), **7a** (244 mg, 0.70 mmol), *n*-BuLi (0.28 mL, 0.65 mmol) was reacted to furnish the desired product as a colorless oil (71 mg, 0.22 mmol, 43%, *ent*-**4ca**:*epi*-**4ca** = 0:99). R_f = 0.15 (CyH:EtOAc = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.30 (m, 4H), 7.27 – 7.24 (m, 1H, superimposed with $CHCl_3$), 4.51 (dd, *J* = 12.2, 18.7 Hz, 2H), 4.26 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.59 (dd, *J* = 8.9, 5.9 Hz, 1H), 3.49 (dd, *J* = 8.8, 8.0 Hz, 1H), 2.36 – 2.29 (m, 1H), 2.21 – 2.14 (m, 1H), 2.04 (t, *J* = 5.5 Hz, 1H), 1.91 – 1.86 (m, 1H), 1.85 – 1.80 (m, 1H), 1.52 – 1.47 (m, 1H), 1.37 (s, 3H), 1.28 (s, 3H), 1.14 (d, *J* = 10.9 Hz, 1H), 1.07 (d, *J* = 7.4 Hz, 3H), 0.84 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 139.1, 128.4, 127.6, 127.4, 85.7, 77.8, 73.7, 72.9, 51.4, 39.6, 38.3, 35.7, 28.8, 27.2, 26.5, 24.1, 12.9 ppm. IR: $\tilde{\nu}$ = 2981 (s) C-H, 2915 (s) C-H, 2871 (s) C-H, 1540 (w) C-Ar, 1365 (s) B-O, 1279 (m) C-O, 1237 (s) C-O, 1076 (s) B-C, 1028 (s) B-C cm^{-1}. HRMS (ESI): found: 346.2551, 351.2104, calculated *m*/*z* for $C_{20}H_{33}BO_2N^+$: 346.2552, $C_{20}H_{29}BO_2Na^+$: 351.2104.

(2*S*)-1-Benzyloxy-4-phenyl-but-2-yl-(-)-pinanediol boronic ester (*epi*-4cb). According to **GP1b**, (benzyloxy)methyl-(-)-pinanediol boronic ester (150 mg, 0.5 mmol), **7b** (307 mg, 0.70 mmol), *n*-BuLi (0.28 mL, 0.65 mmol) was reacted to furnish the desired product as a colorless oil (59 mg, 0.14 mmol, 29%, **4cb**:*epi*-**4cb** = 0:99). **R_f** = 0.11 (CyH:EtOAc = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.32 (m, 4H), 7.28 – 7.24 (m, 3H, superimposed with $CHCl_3$), 7.19 – 7.14 (m, 3H), 4.50 (dd, *J* = 12.0, 13.8 Hz, 2H), 4.28 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.60 (d, *J* = 6.8 Hz, 2H), 2.73 – 2.58 (m, 2H), 2.38 – 2.31 (m, 1H), 2.21 – 2.15 (m, 1H), 2.06 (t, *J* = 5.5 Hz, 1H), 1.91 – 1.79

(m, 4H), 1.55 – 1.48 (m, 1H), 1.38 (s, 3H), 1.29 (s, 3H), 1.21 (d, *J* = 10.8 Hz, 1H), 0.85 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): *δ* = 143.0, 139.0, 128.6, 128.4, 127.7, 127.4, 125.8, 85.8, 77.8, 73.0, 72.0, 51.4, 39.7, 38.3, 35.7, 35.6, 30.3, 28.9, 27.02, 26.6, 24.2 ppm. HRMS (ESI): found: 419.2757, 436.3024, 441.2578, calculated *m/z* for $C_{27}H_{36}BO_2^+$: 419.2757 $C_{27}H_{39}BO_2N^+$: 436.3022, $C_{27}H_{35}BO_2Na^+$: 441.2576. IR: $\tilde{\nu}$ = 2981 (s) C-H, 2915 (s) C-H, 2861 (s) C-H, 1366 (s) B-O, 1340 (s) B-O, 1279 (s) C-O, 1236 (s) C-O, 1076 (s) B-C, 1028 (s) B-C cm^{-1}.

(*S*)-1-(p-Methoxyphenyl)-ethyl-(-)-pinanediol boronic ester (*epi*-4da). According to **GP1b**, *p*-anisyl-(-)-pinanediol boronic ester (100 mg, 0.35 mmol), **7a** (171 mg, 0.49 mmol), *n*-BuLi (0.19 mL, 0.45 mmol) was reacted to furnish the desired product as a colorless oil which solidified to a resin upon standing and slowly decomposed (73 mg, 0.23 mmol, 66%). R_f = 0.11 (CyH:Et_2O = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* = 7.15 (td, *J* = 9.6, 1.9 Hz, 2H), 6.82 (td, *J* = 9.6, 2.6 Hz, 2H), 4.25 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.78 (s, 3H), 2.43 (q, *J* = 7.5 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.20 – 2.13 (m, 1H), 2.04 (t, *J* = 5.6 Hz, 1H), 1.89 – 1.84 (m, 1H), 1.81 – 1.76 (m, 1H), 1.35 (s, 3H), 1.34 (d, *J* = 7.6 Hz, 3H), 1.27 (s, 3H), 1.02 (d, *J* = 10.9 Hz, 1H), 0.82 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): *δ* = 157.4, 137.2, 128.7, 113.9, 85.8, 78.0, 55.4, 51.4, 39.6, 38.31, 36.7, 28.7, 27.2, 26.5, 24.1, 17.6 ppm. IR: $\tilde{\nu}$ = 2980 (s) C-H, 2915 (s) C-H, 1512 (s) C-Ar, 1456 (s) C-Ar, 1375 (s) B-O, 1342 (m), 1288 (s) C-O, 1241 (s) C-O, 1175 (m) B-C, 1122 (m) B-C, 1078 (m) B-C cm^{-1}. HRMS (ESI): *compound decomposed*.

(*S*)-1-(p-Methoxyphenyl)-3-phenyl-prop-1-yl-(-)-pinanediol boronic ester (*epi*-4db). According to **GP1b**, *p*-anisyl-(-)-pinanediol boronic ester (100 mg, 0.35 mmol), **7b** (215 mg, 0.49 mmol), *n*-BuLi (0.19 mL, 0.45 mmol) was reacted to furnish the desired product as a colorless oil which readily decomposed to a white soild (<63 mg, <0.16 mmol, <33%, **4db**:*epi*-**4db** = 0:99). R_f = 0.10 (CyH:Et_2O = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* = 7.24 – 7.22 (m, 2H, superimposed with $CHCl_3$), 7.17 – 7.13 (m, 5H), 6.83 (td, *J* = 9.6, 2.6 Hz, 2H), 4.25 (dd, *J* = 8.8, 2.1 Hz, 1H), 3.78 (s, 3H), 2.59 – 2.55 (m, 2H), 2.37 – 2.27 (m, 2H), 2.20 – 2.10 (m, 2H), 2.04 (t, *J* = 5.6 Hz, 1H), 2.02 – 1.94 (m, 1H), 1.87 – 1.83 (m, 1H), 1.79 – 1.74 (m, 1H), 1.33 (s, 3H), 1.26 (s, 3H), 1.00 (d, *J* = 10.9 Hz, 1H), 0.82 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): *δ* = 157.5, 142.7, 135.1, 129.4, 128.7, 128.4, 125.7, 113.9, 85.8, 78.0, 55.3, 51.4, 39.6, 38.3, 35.7, 35.5, 34.7, 28.7, 27.2, 26.6, 24.1 ppm. IR: $\tilde{\nu}$ = 2979 (s) C-H, 2916 (s) C-H, 1611 (w) C-Ar, 1512 (s) C-Ar, 1376 (s) B-O, 1288 (m) C-O, 1242 (s) C-O, 1175 (m) B-C, 1122 (m) B-C, 1079 (m) B-C, 1032 (s) B-C cm^{-1}. HRMS (ESI): *compound decomposed*.

(3*R*)-Hex-2-yl-(+)-pinanediol boronic ester (*ent*-4aa). According to **GP2**, butyl-(+)-pinanediol boronic ester (109 mg, 0.46 mmol), D*i*PA (0.10 mL, 0.64 mmol), *n*-BuLi (2.33 mL, 0.58 mmol), CH_2Br_2 (0.98 mL, 1.41 mmol), $ZnCl_2$ (0.92 mL, 0.92 mmol, 1.0 M in Et_2O) and MeMgBr (0.20 mL, 0.59 mmol, 3 M in THF)[72] were reacted to furnish the desired product as a colorless oil (72 mg, 0.28 mmol, 60%, *ent*-**4aa**:*epi*-**4aa** = 92:8). R_f = 0.30 (CyH:Et_2O = 98:2). ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* = 4.25 (dd, *J* = 8.8, 2.1 Hz, 1H), 2.37 - 2.30 (m, 1H), 2.24 - 2.18 (m, 1H), 2.05 (t, *J* = 5.6 Hz, 1H), 1.93 - 1.88 (m, 1H), 1.85 - 1.80 (m, 1H), 1.50 - 1.44 (m, 1H), 1.37 (s, 3H), 1.32 - 1.25 (m, 8H), 1.11 (d, *J* = 10.9 Hz, 1H), 1.07 - 1.02 (m, 1H), 0.99 (d, *J* = 6.3 Hz, 3H), 0.90 - 0.85 (m, 3H), 0.84 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): *δ* = 85.3, 77.7, 51.4, 39.7, 38.3, 35.8, 33.18 (epimer at 33.23ppm.), 31.43 (epimer at 31.38ppm.), 28.9, 27.2, 26.6, 24.2, 23.1, 15.9, 14.3 ppm. NMR data complies with published data.[73]

(3*S*)-1-Phenyl-hept-3-yl-(-)-pinanediol boronic ester (4ab). According to **GP2**, butyl-(-)-pinanediol boronic ester (500 mg, 2.12 mmol), D*i*PA (0.39 mL, 2.9 mmol), *n*-BuLi (1.06 mL, 2.65 mmol), CH_2Cl_2 (0.41 mL, 6.4 mmol), $ZnCl_2$ (4.2 mL, 4.2 mmol, 1.0 M in Et_2O) and freshly prepared $BnCH_2MgBr$ (2.0 mL, 5.3 mmol, 2.6 M in THF)[72] were reacted to furnish the desired product as a colorless oil (496 mg, 1.40 mmol, 67%, **4ab**:*epi*-**4ab** = 90:10). R_f = 0.25 (CyH:Et_2O = 98:2). ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* = 7.28 – 7.25 (m, 2H, superimposed with $CHCl_3$), 7.20 – 7.14 (m, 3H), 4.28 (dd, *J* = 8.8, 2.1 Hz, 1H), 2.69 – 2.56 (m, 2H), 2.40 – 2.23 (m, 1H), 2.40 – 2.33 (m, 1H), 2.27 – 2.20 (m, 1H), 2.08 (t, *J* = 5.5 Hz, 1H), 1.94 – 1.90 (m, 1H), 1.87 – 1.82 (m, 1H), 1.81 – 1.63 (m, 2H), 1.52 – 1.40 (m, 2H), 1.39 (s, 3H), 1.34 – 1.26 (m, 7H), 1.17 (d, *J* = 10.8 Hz, 1H), 1.12 – 1.05 (m, 1H), 0.90 – 0.86 (m, 6H) ppm. **^{13}C-**NMR (100 MHz, $CDCl_3$): *δ* = 143.3, 128.6, 128.3, 125.7, 85.5, 77.7, 51.4, 39.7, 38.3, 36.9, 35.8, 33.7, 31.6, 31.1, 29.0,

27.2, 26.8, 24.2, 23.1, 14.3 ppm. **IR:** $\tilde{\nu}$ = 2981 (s) C-H, 2916 (s) C-H, 2870 (s) C-H, 1604 (w) C-Ar, 1386 (s) B-O, 1279 (m) C-O, 1252 (m) C-O, 1235 (m) C-O, 1154 (w) B-C, 1122 (m) B-C, 1077 (m) B-C cm^{-1}. HRMS (ESI): found: 355.2807, 372.3073, 377.2627, calculated *m/z* for $C_{23}H_{36}BO_2^+$: 355.2807, $C_{23}H_{39}BO_2N^+$: 372.3071 $C_{23}H_{35}BO_2Na^+$: 377.2626.

(1*R*)-1-Cyclohexyl-ethyl-(-)-pinanediol boronic ester (4ba). According to **GP2**, cyclohexyl-(-)-pinanediol boronic ester (130 mg, 0.48 mmol), D*i*PA (0.09 mL, 0.67 mmol), *n*-BuLi (0.25 mL, 0.62 mmol), CH_2Cl_2 (0.10 mL, 1.5 mmol), $ZnCl_2$ (1.0 mL, 1.0 mmol, 1.0 M in Et_2O) and MeMgBr (0.16 mL, 0.48 mmol, 3.0 M in THF) was reacted to furnish the desired product as a colorless oil (52 mg, 0.18 mmol, 38%, **4ba**:*epi*-**4ba** = 0:99). R_f = 0.38 (CyH:EtOAc = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.25 (dd, *J* = 8.8, 2.1 Hz, 1H), 2.38 – 2.31 (m, 1H), 2.24 – 2.18 (m, 1H), 2.06 (t, *J* = 5.6 Hz, 1H), 1.93 – 1.88 (m, 1H), 1.85 – 1.80 (m, 1H), 1.76 – 1.60 (m, 5H), 1.73 – 0.92 (m, 17H), 0.84 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 85.3, 77.6, 51.4, 40.7, 39.7, 38.3, 35.9, 32.8, 32, 29, 27.2, 26.9, 26.9, 26.7, 24.2, 12.9 ppm. IR: $\tilde{\nu}$ = 2981 (s) C-H, 2916 (s) C-H, 2850 (s) C-H, 1375 (s) B-O, 1278 (m) C-O, 1235 (m) C-O, 1122 (m) B-C, 1078 (m) B-C cm^{-1}. HRMS (ESI): found: 291.2493, 308.2759, 313.2313, calculated *m/z* for $C_{18}H_{32}BO_2^+$: 291.2493 $C_{18}H_{35}BO_2N^+$: 308.2759 $C_{18}H_{31}BO_2Na^+$: 313.2313.

(1*R*)-1-Cyclohexyl-3-phenyl-propyl-(-)-pinanediol boronic ester (4bb). According to **GP2**, cyclohexyl-(-)-pinanediol boronic ester (130 mg, 0.48 mmol), D*i*PA (0.09 mL, 0.67 mmol), *n*-BuLi (0.25 mL, 0.62 mmol), CH_2Cl_2 (0.10 mL, 1.5 mmol), $ZnCl_2$ (1.0 mL, 1.0 mmol, 1.0 M in Et_2O) and freshly prepared $BnCH_2MgBr$ (0.50 mL, 0.48 mmol, 0.95 M in THF)[72] was reacted to furnish two fractions. First a 6:16:78 mixture (116 mg) of starting material (0.02 mmol), α-chloro boronic ester (0.05 mmol) and the product (0.25 mmol) and a pure fraction as a colorless oil (32 mg, 0.08 mmol) with a total yield of 70% (**4bb**:*epi*-**4bb** = 0:99). R_f = 0.41 (CyH:EtOAc = 96:4) ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.24 (m, 2H, superimposed with $CHCl_3$), 7.19 – 7.13 (m, 3H), 4.30 (d, *J* = 8.9, 2.2 Hz, 1H), 2.69 – 2.62 (m, 1H), 2.56 – 2.49 (m, 1H), 2.41 – 2.34 (m, 1H), 2.28 – 2.21 (m, 1H), 2.09 (t, *J* = 5.6 Hz, 1H), 1.93 – 1.91 (m, 1H), 1.88 – 1.83 (m, 1H), 1.81 – 1.61 (m, 7H), 1.48 – 1.41 (m, 1H), 1.40 (s, 3H), 1.30 (s, 3H), 1.27 – 0.97 (m, 7H), 0.86 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 143.3, 128.5, 128.3, 125.7, 85.4, 77.6, 51.4, 39.8, 39.7, 38.4, 36.2, 36, 32.9, 32.5, 31.2, 29.2, 27.3, 27.1, 26.9, 26.9, 24.2 ppm. IR: $\tilde{\nu}$ = 2981 (s) C-H, 2916 (s) C-H, 2850 (s) C-H, 1496 (w) C-Ar, 1385 (s) B-O, 1277 (m) C-O, 1235 (m) C-O, 1077 (m) B-C, 1029 (m) B-C cm^{-1}. HRMS (ESI): found: 381.2966, 398.3232, 403.2783, calculated *m/z* for $C_{25}H_{38}BO_2^+$: 381.2964, $C_{25}H_{41}BO_2N^+$: 398.3229, $C_{25}H_{37}BO_2Na^+$: 403.2783.

((*S*)-1-(Benzyloxy)propan-2-yl)-(+)-pinanediol boronic ester (*ent*-4ca). According to the procedure by Matteson et al.,[61] benzyloxymethyl-(+)-pinanediol boronic ester (1.80 g, 6.00 mmol), D*i*PA (1.24 mL, 8.99 mmol, 1.50 eq.), *n*-BuLi (2.88 mL, 7.20 mmol, 1.20 eq.), CH_2Br_2 (2.52 mL, 36.0 mmol, 6.0 eq.) and $ZnCl_2$ (18 mL, 18 mmol, 3.0 eq., 1.0 M in Et_2O) and MeMgBr (3 mL, 6.90 mmol, 1.15 eq., 2.3 M in Et_2O) were reacted. Subsequent purification by flash column chromatography (silica, CyH/Et_2O = 95:5) afforded the product **6c** as a colorless oil (1.13 g, 3.45 mmol, 57%, *ent*-**4ca**:*epi*-**4ca** = >99:0). R_f = 0.31 (CyH/Et_2O = 95:5). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.33 - 7.24 (m, 5H, superimposed on $CDCl_3$), 4.51 (d, J = 1.4 Hz, 2H), 4.26 (dd, *J* = 8.7, 1.9 Hz, 1H), 3.60 - 3.46 (m, 2H), 2.36 - 2.29 (m, 1H), 2.20 - 2.13 (m, 1H), 2.04 (t, *J* = 5.5 Hz, 1H), 1.91 - 1.81 (m, 2H), 1.53 - 1.46 (m, 1H), 1.37 (s, 3H), 1,28 (s, 3H), 1.15 (d, *J* = 10.88 Hz, 1H), 1.06 (d, *J* = 7.4 Hz, 3H), 0.84 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 139.1, 128.4, 127.7, 127.4, 85.7, 77.8, 73.8, 72.9, 51.4, 39.6, 38.3, 35.7, 28.8, 27.2, 26.5, 24.1, 12.9 ppm. IR: ṽ = 2981 (s) C-H, 2971 (s) C-H, 1453 (m) C-Ar, 1375 (s) B-O, 1365 (s) B-O, 1340 (s) B-O, 1279 (s) C-O, 1237 (s) C-O, 1094 (s) C-B, 1076 (s) C-B, 1056 (s) C-B, 1028 (s) C-B, 990 (m) cm^{-1}. HRMS (ESI): found: 329.2283, 351.2107, calculated *m/*z for $C_{20}H_{30}BO_3^+$: 329.2286, $C_{20}H_{29}BO_3Na^+$: 351.2106.

(2*S*)-1-Benzyloxy-4-phenyl-but-2-yl-(-)-pinanediol boronic ester (4cb). As described for *ent*-**4ca**, (benzyloxy)methyl-(-)-pinanediol boronic ester (150 mg, 0.50 mmol), D*i*PA (0.10 mL, 0.75 mmol, 1.50 eq.), *n*-

BuLi (0.26 mL, 0.60 mmol, 1.20 eq.), CH_2Br_2 (0.21 mL, 3.0 mmol, 6.0 eq.) and $ZnCl_2$ (1.30 mL, 1.30 mmol, 2.6 eq., 1.0 M in Et_2O) were reacted to furnish the corresponding α-bromo boronic ester that was used directly after aqueous work-up without further purification. The resulting bromide was reacted with freshly prepared $BnCH_2MgBr$ (0.50 mL, 0.65 mmol, 1.32 M in THF, 1.3 eq.)[72] to furnish the desired product as a colorless oil (25 mg, 0.06 mmol, 12%, **4cb**:*epi*-**4cb** = 99:0). R_f = 0.14 (CyH:EtOAc = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.32 (m, 4H), 7.28 – 7.25 (m, 3H, superimposed with $CHCl_3$), 7.20 – 7.15 (m, 3H), 4.50 (s, 2H), 4.28 (dd, *J* = 8.9, 1.7 Hz, 1H), 3.60 (m, 2H), 2.73 – 2.59 (m, 2H), 2.38 – 2.32 (m, 1H), 2.21 – 2.15 (m, 1H), 2.06 (t, *J* = 5.5 Hz, 1H), 1.92 – 1.80 (m, 4H), 1.57 – 1.50 (m, 1H), 1.39 (s, 3H), 1.29 (s, 3H), 1.21 (d, *J* = 10.9 Hz, 1H), 0.85 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 143, 139, 128.6, 128.4, 127.7, 127.4, 125.7, 85.7, 77.8, 73, 72, 51.4, 39.7, 38.3, 35.7, 35.5, 30.2, 28.9, 27.2, 26.6, 24.2 ppm. IR: $\tilde{\nu}$ = 2981 (s) C-H, 2916 (s) C-H, 2861 (s) C-H, 1453 (m) C-Ar, 1375 (s) B-O, 1279 (m) C-O, 1237 (m) C-O, 1076 (s) C-B, 1028 (s) C-B cm^{-1}. HRMS (ESI): found: 419.2758, 436.3023, 441.2576, calculated *m/z* for $C_{27}H_{36}BO_2^+$: 419.2757 $C_{27}H_{39}BO_2N^+$: 436.3022, $C_{27}H_{35}BO_2Na^+$: 441.2576.

(*R*)-1-(*p*-Methoxyphenyl)-ethyl-(-)-pinanediol boronic ester (4da). Following a combined procedure by Kazmaier et al.[30,27], CH_2Cl_2 (0.05 mL, 0.85 mmol, 1.7 eq.) in THF (0.5 M) was cooled to -100 °C and *n*-BuLi (0.22 mL, 0.53 mmol, 1.05 eq.) was added dropwise. After stirring 0.5 h at the same temperature, a solution of *p*-anisyl-(-)-pinanediol boronic ester (143 mg, 0.50 mmol) in THF (0.7 M) was added. The mixture was stirred for an additional 0.5 h at the same temperature, before $ZnCl_2$ (0.53 mL, 0.53 mmol, 1.05 eq., 1.0 M in Et_2O) was added dropwise. The reaction mixture was warmed to rt and stirred for 16 h (overnight) and terminated by adding sat. aq. NH_4Cl. The aqueous layer was extracted three times with CyHex. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting α-chloro boronic ester was dissolved in THF (0.25 M) and cooled to 0 °C. The solution was reacted with MeMgBr (0.22 mL, 0.65 mmol, 1.3 eq.) as described above to furnish the desired product as a 33:67 mixture (13 mg) of starting material (0.02 mmol) and the product (0.04 mmol, 8%) which slowly decomposed. R_f = 0.24 (CyH:EtOAc = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.15 (td, *J* = 9.7, 2.6 Hz, 2H), 6.82 (td, *J* = 9.7, 2.6 Hz, 2H), 4.25 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.78 (s, 3H), 2.43 (q, *J* = 7.6 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.20 – 2.14 (m, 1H), 2.05 (t, *J* = 5.6 Hz, 1H), 1.89 – 1.85 (m, 1H), 1.81 – 1.76 (m, 1H), 1.35 (s, 3H), 1.34 (d, *J* = 7.6 Hz, 3H), 1.27 (s, 3H), 1.02 (d, *J* = 10.92 Hz, 1H), 0.82 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 157.4, 137.2, 128.7, 113.9, 85.8, 78, 55.3, 51.4, 39.6, 38.3, 35.7, 28.7, 27.2, 26.5, 24.1, 17.6 ppm. IR: $\tilde{\nu}$ = 2981 (s) C-H, 2916 (s) C-H, 2861 (s) C-H, 1453 (m) C-Ar, 1340 (m) B-O, 1279 (m) C-O, 1237 (m) C-O, 1076 (s) B-C, 1028 (s) B-C cm^{-1}. HRMS (ESI): *compound decomposed*.

(*R*)-1-(*p*-Methoxyphenyl)-3-phenyl-prop-1-yl-(-)-pinanediol boronic ester (4db). As described for 4da, *p*-anisyl-(-)-pinanediol boronic ester (143 mg, 0.50 mmol), *n*-BuLi (0.22 mL, 0.53 mmol, 1.05 eq.), CH_2Cl_2 (0.05 mL, 0.85 mmol, 1.7 eq.), $ZnCl_2$ (0.53 mL, 0.53 mmol, 1.05 eq.) were reacted to the corresponding α-chloro boronic ester. After aqueous work-up, the chloride was directly used for the next reaction without further purifications. It was reacted with freshly prepared $BnCH_2MgBr$ (0.50 mL, 0.65 mmol, 1.3 eq., 1.32 M in THF)[72] to furnish the desired product as a mixture with unknown contaminants from which the yield was determined by using an internal standard (14 mg, 0.03 mmol, 7%^{IS}, **4db**:*epi*-**4db** = 0:99). The product swiftly decomposed. R_f = 0.29 (CyH:EtOAc = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.22 (m, 2H, superimposed with $CHCl_3$), 7.18 – 7.14 (m, 5H), 6.83 (td, *J* = 9.6, 2.5 Hz, 2H), 4.26 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.79 (s, 3H), 2.63 – 2.54 (m, 2H), 2.38 – 2.27 (m, 2H), 2.21 – 2.11 (m, 2H), 2.06 – 1.93 (m, 2H), 1.88 – 1.84 (m, 1H), 1.80 – 1.75 (m, 1H), 1.34 (s, 3H), 1.27 (s, 3H), 1.01 (d, *J* = 10.9 Hz, 1H), 0.82 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 157.5, 142.7, 135.1, 129.4, 128.7, 128.4, 125.7, 113.9, 85.8, 78.0, 55.3, 51.4, 39.6, 38.3, 35.7, 35.5, 34.7, 28.7, 27.2, 26.6, 24.1 ppm. IR: $\tilde{\nu}$ = 2981 (s) C-H, 2934 (m) C-H, 1508 (m) C-Ar, 1375 (w) B-O, 1278 (w) C-O, 1249 (w) C-O, 1176 (w) B-C, 1151 (w) B-C, 1076 (w) B-C cm^{-1}. HRMS (ESI): *compound decomposed*.

(S)-Hexan-2-yl-(S,S)-DICHED boronic ester (*epi*-13aa). According to **GP1a**, butyl-(-)-DICHED boronic ester **8** (123 mg, 0.42 mmol), **7b** (220 mg, 0.50 mmol) and *n*-BuLi (0.18 mL, 0.44 mmol) were reacted to furnish *epi*-**13aa** as a colorless oil (101 mg, 0.32 mmol, 76%, **13aa**:*epi*-**13aa** = <0:99). R_f = 0.68 (CyH:Et_2O:DCM = 99:0.5:0.5). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.83 – 3.82 (m, 2H), 1.78 – 1.75 (m, 6H), 1.69 – 1.66 (m, 2H), 1.61 – 1.57 (m, 2H), 1.50 – 1.42 (m, 1H), 1.32 – 1.02 (m, 16H, superimposed by TIB ester), 0.99 – 0.97 (m, 5H), 0.91 – 0.86 (m, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 83.3, 43.2, 33.2, 31.3, 28.4, 27.5, 26.6, 26.2, 26.1, 23.1, 15.9, 14.3 ppm. HRMS (ESI): *compound decomposed*.

(R)-Hexan-2-yl-(S,S)-DICHED boronic ester (13aa). According to **GP1a**, butyl-(-)-DICHED boronic ester **8** (123 mg, 0.42 mmol), **7b** (220 mg, 0.50 mmol) and *n*-BuLi (0.18 mL, 0.44 mmol) were reacted to furnish *epi*-**13aa** as a colorless oil (101 mg, 0.32 mmol, 54%, **13aa**:*epi*-**13aa** = <0:99). R_f = 0.28 (CyH:Et_2O = 98:2). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.83-3.82 (m, 2H), 1.78 - 1.75 (m, 6H), 1.69 - 1.66 (m, 2H), 1.61 - 1.57 (m, 2H), 1.50 - 1.44 (m, 1H). 1.35 - 1.02 (m, 16H), 0.99 - 0.93 (m, 5H), 0.88 (m, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 83.3, 42.2, 33.3, 31.5, 28.4, 27.5, 26.6, 26.2, 26.1, 23.1, 16.1, 14.3 ppm. IR: $\tilde{\nu}$ = 2919 (s) C-H, 1375 (s) B-O, 1360 (s) B-O, 1339 (s) B-O, 1279 (s) C-O, 1236 (s) C-O, 1226 (s) C-O, 1077 (s) B-C, 1030 (s) B-C, 1021 (s) B-C cm^{-1}. HRMS (ESI): *compound decomposed*.

(*R*)-4-Phenylbutan-2-yl-2,4,6-triisopropyl benzoate (*ent*-5a). Stannane **7b** (170 mg, 0.32 mmol, 1.0 eq.) in 2.1 mL THF (0.15 M) was cooled to -78 °C and treated with *n*-BuLi (0.13 mL, 0.34 mmol, 1.05 eq.). The mixture was stirred for 1 h at the same temperature. Then MeI (0.08 mL, 1.3 mmol, 4.0 eq.) was added and the reaction mixture was allowed to warm to rt and stirred for 20 min. The reaction mixture was concentrated under reduced pressure (Caution! Toxic and volatile $SnMe_3Bu$ and MeI). The residue was taken up with Et_2O, filtered through a pad of silica and washed with excess Et_2O and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica, CyHex/Et_2O = 96:4) furnishing a 17:83 mixture (103 mg) of $BnCH_2OTIB$ **5b** (0.05 mmol) and the title compound (0.27 mmol, 83%). R_f = 0.35 (CyH:Et_2O = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.28 (m, 2H), 7.22 – 7.18 (m, 3H), 7.02 (s, 2H), 5.30 – 5.22 (m, 1H), 2.96 – 2.84 (m, 3H), 2.81 – 2.64 (m, 2H), 2.09 – 1.98 (m, 1H), 1.93 – 1.84 (m, 1H), 1.40 (d, *J* = 6.3 Hz, 3H), 1.28 – 1.24 (m, 18H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.6, 150.2, 144.7, 141.7, 131, 128.6, 128.4, 126.1, 121, 71.7, 37.9, 34.6, 32, 31.5, 24.5, 24.3, 24.1, 20.1 ppm. Analytical data complies with published data.[67]

(*R*)-4-Phenylbutan-2-ol (13). According to **GP1a**, methyl-(-)-pinanediol boronic ester (**4e**) (180 mg, 0.93 mmol), **7b** (570 mg, 1.30 mmol), *n*-BuLi (0.51 mL, 1.2 mmol) was reacted to furnish the corresponding boronic ester, from which an analytical sample was taken, before the material was oxidized as described below. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.14 (m, 5H, superimposed with $CHCl_3$), 4.27 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.67 – 2.62 (m, 2H), 2.38 – 2.31 (m, 1H), 2.25 – 2.19 (m, 1H), 2.06 (t, *J* = 5.6 Hz, 1H), 1.93 – 1.89 (m, 1H), 1.87 – 1.76 (m, 2H), 1.65 – 1.56 (m, 1H), 1.38 (s, 3H), 1.29 (s, 3H), 1.13 (d, *J* = 10.9 Hz, 1H, superimposed with impurities), 1.05 (d, *J* = 6.92 Hz, 3H), 0.85 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 143.2, 128.6, 128.3, 125.7, 85.5, 77.7, 51.4, 39.7, 38.3, 35.8, 35.6, 35.5, 28.9, 27.2, 26.7, 24.2, 15.9 ppm. HRMS (ESI): found: 313.2337, 330.2603, 335.2157, calculated *m*/*z* for $C_{20}H_{30}BO_2^+$: 313.2337, $C_{20}H_{33}BO_2N^+$: 330.2602, $C_{20}H_{29}BO_2Na^+$: 335.2156. The crude boronic ester (117 mg, <0.33 mmol) was dissolved in 1.1 mL THF (0.3 M) and treated with 0.67 mL of a 2:1 mixture of aq. NaOH (30% w/w) and 30% aq. H_2O_2 at -20 °C. Then the mixture was stirred for 4 h at rt. The reaction was terminated by adding brine. The aqueous layer was extracted three times with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica, 2% MeOH in DCM), which furnished the product as a colorless oil (59 mg, 0.31 mmol, 34%). R_f = 0.25 (DCM:MeOH = 98:2). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.267 (m, 2H), 7.22 – 7.17 (m, 3H), 3.84 (sxt, *J* = 6.2 Hz, 1H), 2.80 – 2.64 (m, 2H), 1.81 – 1.75 (m, 2H), 1.42 (bs, 1H), 1.23 (d, *J* = 6.20 Hz,

3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 142.2, 128.5, 126.0, 67.7, 41.0, 32.3, 23.8 ppm. Analytical data complies with published data.[74]

(*S*)-4-Phenylbutan-2-yl-2,4,6-triisopropyl benzoate (5a). Following the procedure published by Aggarwal et al.[13], alcohol **13** (54 mg, 0.36 mmol), 2,4,6-triisopropylbenzoic acid (103 mg, 0.41 mmol, 1.15 eq.), PPh_3 (104 mg, 0.39 mmol, 1.10 eq.) and DIAD (80 mg, 0.39 mmol, 1.10 eq.) in 0.54 mL THF (0.67 M) were reacted. After purification by flash column chromatography (silica, Pentane/DCM = 7:3), the title compound was obtained as a colorless oil (70 mg, 0.18 mmol, 50%).R_f = 0.16 (Pentane:DCM = 7:3). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.28 (m, 2H), 7.22 – 7.18 (m, 3H), 7.02 (s, 2H), 5.30 – 5.22 (m, 1H), 2.98 – 2.84 (m, 3H), 2.81 – 2.64 (m, 2H), 2.08 – 2.00 (m, 1H), 1.98 – 1.85 (m, 1H), 1.40 (d, *J* = 6.28 Hz, 3H), 1.28 – 1.24 (m, 18H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.6, 150.2, 144.7, 141.7, 131, 128.6, 128.4, 126.1, 121, 71.7, 37.9, 34.6, 32, 31.5, 24.5, 24.3, 24.1, 20.1 ppm. Analytical data complies with published data.[75]

(3*R*)-3-Methyl-1-phenyl-hept-3-yl-(-)-pinanediol boronic ester (14). According to a procure of Aggarwal et al.[13], benzoate **5a** (70 mg, 0.18 mmol, 1.0 eq.) and TMEDA (0.17 mL, 1.10 mmol, 6.0 eq.) in CPME (1.1 mL, 0.17 M) were cooled to -60 °C, before *s*-BuLi (0.22 mL, 0.29 mmol, 1.6 eq., 1.34 M in cyclohexane/hexane) was added dropwise. The resulting mixture was stirred for 2 h at the same temperature. Afterwards, butyl-(-)-pinanediol boronic ester (**1a**) (87 mg, 0.37 mmol, 2.0 eq.) in CPME (1.1 mL, 0.17 M) was added dropwise over 10 minutes. The resulting mixture was stirred for 1 h at the same temperature before it was warmed to 50 °C and stirred for 16 h (overnight). The reaction was terminated by adding sat. aq. NH_4Cl. The aqueous layer was extracted three times with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Subsequent purification by flash column chromatography (silica, CyH/Et_2O = 96:4) resulted in a 55:45 mixture (65 mg) of butyl-(-)-pinanediol boronic ester (0.11 mmol) and the product (0.09 mmol) and the pure title compound as a colorless oil (19 mg, 0.05 mmol), thus resulting in a total yield of 80% (**14:*epi*-14** = 98:2). R_f = 0.48 (CyH:Et_2O = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.24 (m, 2H, superimposed with $CHCl_3$, Ph), 7.20 – 7.13 (m, 3H, Ph), 4.29 (dd, *J* = 8.8, 2.1 Hz, 1H, pinanyl), 2.65 – 2.51 (m, 2H, H-1), 2.40 – 2.33 (m, 1H, pinanyl), 2.25 – 2.19 (m, 1H, pinanyl), 2.08 (t, *J* = 5.5 Hz, 1H, pinanyl), 1.93 – 1.89 (m, 1H, pinanyl), 1.87 – 1.82 (m, 1H, pinanyl), 1.78 – 1.71 (td, *J* = 12.8, 5.2 Hz, 1H, H-2a), 1.53 – 1.42 (m, 2H, H-2b, H-4a), 1.38 (s, 3H, pinanyl), 1.33 – 1.23 (m, 8H, H-4b, H-5, H-6, pinanyl), 1.17 (d, *J* = 10.8 Hz, 1H, pinanyl), 1.02 (s, 3H, Me), 0.89 (t, *J* = 6.8 Hz, 3H, H-7), 0.85 (s, 3H, pinanyl) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 143.9 (C, Ph), 128.5 (CH, Ph), 128.4 (CH, Ph), 125.6 (CH, Ph), 85.6 (C, pinanyl), 77.8 (CH, pinanyl), 51.4 (CH, pinanyl), 41.9 (CH_2, C-2), 39.7 (CH, pinanyl), 39.3 (CH_2, C-4), 38.3 (C, pinanyl), 36.0 (CH_2, pinanyl), 32.7 (CH_2, C-1), 29.1 (CH_3, pinanyl), 28.2 (CH_2, C-5), 27.2 (CH_3, pinanyl), 26.8 (CH_2, pinanyl), 24.2 (CH_3, pinanyl), 23.8 (CH_2, C-6), 21.7 (CH_3, Me), 14.3 (CH_3, C-7) ppm. **IR:** $\tilde{\nu}$ = 2928 (s) C-H, 1457 (w) C-Ar, 1364 (w) B-O, 1279 (w) C-O, 1076 (w) C-B, 1029 (w) C-B cm^{-1}. HRMS (ESI): found: 369.2963, 386.3229, 391.2782, calculated *m*/*z* for $C_{24}H_{38}BO_2^+$: 369.2964, $C_{24}H_{41}BO_2N^+$: 386.3229, $C_{24}H_{37}BO_2Na^+$: 319.2784.

(3*S*)-3-Methyl-1-phenyl-hept-3-yl-(-)-pinanediol boronic ester (*epi*-14*)*. As described for **14**, benzoate *ent*-**5a** (124 mg, 0.33 mmol, 1.0 eq.), *s*-BuLi (0.39 mL, 0.52 mmol, 1.6 eq., 1.34 M in cyclohexane/hexane), TMEDA (0.29 mL, 1.95 mmol, 6.0 eq.) and butyl-(-)-pinanediol boronic ester (154 mg, 0.65 mmol, 2.0 eq.) were reacted. Subsequent purification by flash column chromatography (silica, CyH/Et_2O = 96:4) resulted in a 54:46 mixture (81 mg) of butyl-(-)-pinanediol boronic ester (0.15 mmol) and the product (0.13 mmol) and the pure title compound (28 mg, 0.08 mmol, **14:*epi*-14** = 35:65) as a colorless oil with total yield of 70%. R_f = 0.49 (CyH:Et_2O = 96:4). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.24 (m, 2H, superimposed with $CHCl_3$, Ph), 7.20 – 7.14 (m, 3H, Ph), 4.29 (dd, *J* = 8.8, 2.1 Hz, 1H, pinanyl), 2.64 – 2.51 (m, 2H, H-1), 2.41 – 2.33 (m, 1H, pinanyl), 2.26 – 2.19 (m, 1H, pinanyl), 2.08 (t, *J* = 5.6 Hz, 1H, pinanyl), 1.94 – 1.89 (m, 1H, pinanyl), 1.87 – 1.81 (m, 1H, pinanyl), 1.76 – 1.68 (m, 1H, H-2a), 1.56 – 1.43 (m, 2H, H-2b, H-4a), 1.38 (s, 3H, pinanyl), 1.33 – 1.23 (m, 8H, H-

4b, H-5, H-6, pinanyl), 1.18 (d, *J* = 10.76 Hz, 1H, pinanyl), 1.02 (s, 3H, Me), 0.90 (t, *J* = 7.0 Hz, 3H, H-7), 0.85 (s, 3H, pinanyl) ppm.^{13}C-NMR (100 MHz, $CDCl_3$): δ = 143.9 (C, Ph), 128.5 (CH, Ph), 128.4 (CH, Ph), 125.6 (CH, Ph), 85.6 (C, pinanyl), 77.8 (CH, pinanyl), 51.4 (CH, pinanyl), 41.9 (CH_2, C-2), 39.7 (CH, pinanyl), 38.9 (CH_2, C-4), 38.3 (C, pinanyl), 36.0 (CH_2, pinanyl), 32.6 (CH_2, C-1), 29.1 (CH_3, pinanyl), 28.2 (CH_2, C-5), 27.2 (CH_3, pinanyl), 26.8 (CH_2, pinanyl), 24.2 (CH_3, pinanyl), 23.8 (CH_2, C-6), 21.8 (CH_3, Me), 14.3 (CH_3, C-7) ppm. IR: $\tilde{\nu}$ = 2917 (s) C-H, 2870 (s) C-H, 1456 (m) C-Ar, 1363 (s) B-O, 1278 (m) C-O, 1236 (m) C-O, 1077 (m) C-B, 1028 (m) C-B cm^{-1}. HRMS (ESI): found: 369.2965, 386.3223, 391.2784, calculated *m/z* for $C_{24}H_{38}BO_2^+$: 369.2964, $C_{24}H_{41}BO_2N^+$: 386.3229, $C_{24}H_{37}BO_2Na^+$: 319.2784.

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Supplementary Material

Procedures for the preparation of *p*OMePh-Bpin and pOMePh-B(-)PD, copies of ^{1}H and ^{13}C NMR spectra and spectra for determination of diastereomeric ratios are available in the supplementary material file associated with this manuscript.

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