An Electrophilic Cleavage Procedure for the Asymmetric Dihydroxylation: Direct Enantioselective Synthesis of Cyclic Boronic Esters from Olefins**

Claas H. Hövelmann and Kilian Muñiz*[a]

Dedicated to Professor José Barluenga on the occasion of his 65th birthday.

Abstract: A variation within the osmium-catalysed asymmetric dihydroxylation (AD) of olefins is described that yields cyclic boronic esters from olefins in a straight-forward manner. This process represents the first real product alteration in asymmetric dihydroxylation, since all previous protocols lead to free diols exclusively. A protocol based on the Sharpless AD conditions (for enantioselective oxidation of prochiral olefins) was developed that gives cyclic boronic esters with excellent enantiomeric excesses (*ee*'s). Some of the *ee*'s are higher than those reported for conventional AD. The unprecedented role of phenyl boronic acid on the course of the AD reaction was investigated in detail. $PhB(OH)_2$ does not interfere with the chiral ligand, leaving the enantioselective step of olefin oxidation intact. The main role of the boronic acids—apart from protecting the diol products against potential overoxidation—relies on removing the diol entity in an electrophilic cleavage, which is in contrast to the conventional hydrolytic cleavage of the AD protocols. Thus, a mechanistically new cleavage for enantioselective dihydroxylation reactions is introduced within the present work.

Keywords: alkenes · boronic esters · dihydroxylation · osmium · oxidation

Introduction

Since its original discovery in 1980, the osmium(VIII)-catalysed Sharpless asymmetric dihydroxylation (AD reaction), which converts olefins into non-racemic vicinal diols, has developed into the most versatile oxidative catalytic process available today.[1–3] Its optimised protocol is characterised by a high substrate generality and broad functional group tolerance.[4]

The overall catalytic cycle is initiated by formation of the catalyst upon complexation of osmium tetroxide to a Cinchona alkaloid ligand L*. This chiral complex then differentiates the enantiotopic face of the olefinic substrate efficiently to generate osma(VI) glycolates with high enantiomeric excess. Reoxidation of the osmium centre is accomplished by hexacyanoferrate(III), which gives an osmium(VIII) glycolate and, upon hydrolytic cleavage, the free diol and the regenerated osmium tetroxide. This process represents the so-called first AD cycle and is characterised by formation of diols with high enantiomeric excesses (Figure 1, right). In principle, the reaction can take an alternative course at the stage of the osma(VIII) glycolate upon direct oxidation of a second olefin. This pathway is denominated the secondary cycle and proceeds through a bisglycolate ester with usually low diastereoselectivity, because the remote stereochemical information of the primary glycol entity is largely uneffective. Subsequent hydrolysis leads to liberation of a diol with lower enantiomeric excess than the one from the primary cycle. Under the optimised biphasic Sharpless AD conditions,[4] formation of a bisglycolate is prevented and the hydrolytic cleavage occurs at the stage of the monoglycolate osmium ester.

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[**] Abbreviations in this article: NMO: *N*-methyl morpholine-*N*-oxide; AD: asymmetric dihydroxylation; $(DHQD)_2PHAL$: dihydroquinidine-1,4-phthalazindiyl diether; $(DHQ)_2PHAL$: dihydroquinine-1,4-phthalazindiyl diether; $(DHQD)_2AQN$: dihydroquinidineanthraquinone-1,4-diyl diether; DHQD-PCB (4-chlorobenzoyldihydroquinidine.

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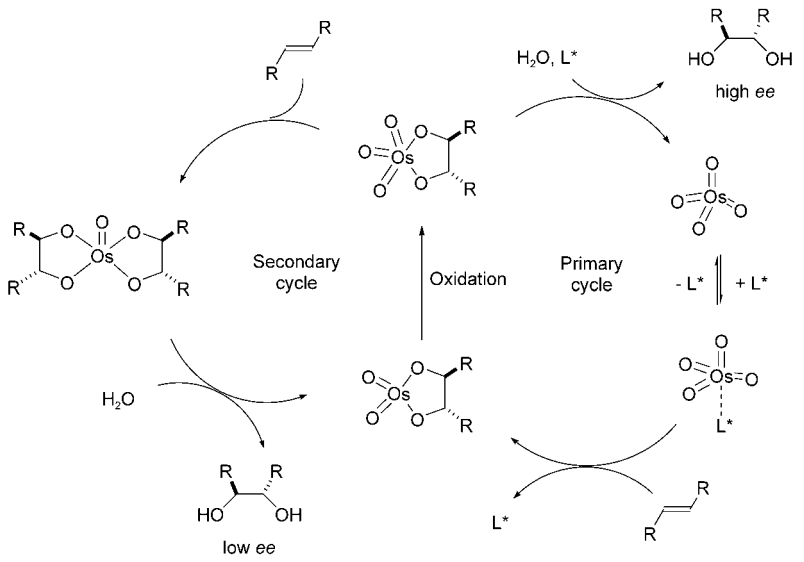


Figure 1. Current understanding of the catalytic asymmetric Sharpless dihydroxylation. L* = Cinchona alkaloid-based ligand.

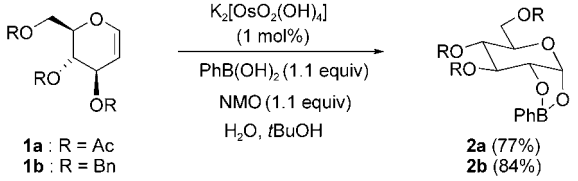
In the past, extensive investigation on the course of the primary cycle have dealt with the question on the exact mechanism for olefin oxidation with the osmium(VIII) oxidant. Here, different primary oxidation steps were debated both in experimental[5] and theoretical[6] investigations. Among rare changes on the established conditions for oxidation of the osma(VI) glycolate, development of dihydroxylation reactions under aerobic conditions or in the presence of hydrogenperoxide as terminal oxidant have emerged recently.[7] Apart from this intensive search for alternative reoxidation, further alteration in order to obtain chiral products other than free diols has remained uninvestigated. Some years ago, Narasaka and Sharpless reported use of phenyl boronic acid as turnover-generating reagent in achiral dihydroxylations under strictly anhydrous conditions (OsO_4, CH_2Cl_2, NMO) to form racemic boronic esters.[8,9]

Herein, we describe the first development of an asymmetric $PhB(OH)_2$-promoted dihydroxylation that gives rise directly to enantiomerically pure boronic esters from olefins and thereby establish a new cleavage concept for AD reactions.

Results and Discussion

Our experimentation started from the discovery that the presence of phenyl boronic acid is compatible with the general Upjohn conditions for olefin dihydroxylation and thus does not demand anhydrous conditions at all. This process was found to be general and provided quantitative transformation of alkenes such as (*E*)-stilbene, styrene, α- and β-methyl styrene, 2-vinyl naphthalene, 1-decene, indene, and methyl and benzyl cinnamate to their corresponding cyclic boronic esters. It furthermore set the basis for the application of chiral ligands in order to render the overall process enantioselective.

Diastereoselective dihydroxylation: Under Upjohn conditions, dihydroxylation of enantiopure olefins led to boronic esters with complete diastereoselectivity. For example, oxidation of 2,3,4-triacetyl-*O*-glucal and 2,3,4-tribenzyl-*O*-glucal provided the corresponding boronic esters as single stereoisomers each and in good isolated yields (Scheme 1). These results match with those from a conventional dihydroxylation described earlier[10] and rely on an efficient stereochemical induction through the chiral glucal motif of the substrate.



Scheme 1. Diastereoselective dihydroxylation of glucals under Upjohn conditions.

This sequence represents a uniquely efficient approach toward boronic ester protection of the anomeric centre in carbohydrate chemistry. This type of ester has met with significant interest over past years in the construction of sugar-based sensors.[11]

Enantioselective dihydroxylation: To devise a highly enantioselective version of the Narasaka/Sharpless process,[8,9] it was decided to combine the standard Sharpless AD procedure[1,4] with phenyl boronic acid. Upon addition of 1.2 equivalents of $PhB(OH)_2$ to the otherwise unchanged conditions for enantioselective AD reaction, completely selective olefin oxidation and concomitant formation of cyclic boronic esters **4** took place (Scheme 2). These were the only detectable products at quantitative olefin conversion. Importantly, free diols were never observed.

A series of ten different substrates, with different aromatic, aliphatic and electron-demanding substitution patterns, was submitted to dihydroxylation in the presence of phenyl boronic acid and $(DHQD)_2PHAL$ as a chiral ligand (Table 1). All the corresponding cyclic boronic esters were isolated in high to excellent yields, showing the catalytic process to be general. In almost all cases, already the crude

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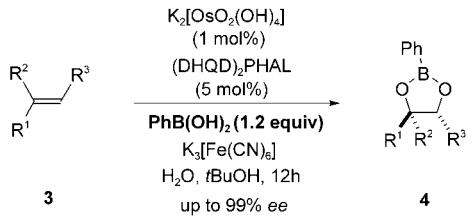

Scheme 2. Enantioselective catalytic synthesis of cyclic boronic esters from olefins.

Table 1. Boronic esters from $PhB(OH)_2$-aided catalytic olefin oxidation.

Entry	Substrate **3**	Product **4**	Yield [%][a]	*ee* [%][b]	Config.[c]
1	(*E*)-stilbene	**4a**	99	99 (99)[d]	*R*,*R*
2[e]	(*E*)-stilbene	**4a**	99	99	*S*,*S*
3	styrene	**4b**	94	96	*R*
4	α-methyl styrene	**4c**	97	94	*R*
5	β-methyl styrene	**4d**	94	98	*R*,*R*
6	methyl cinnamate	**4e**	92	98	*S*,*R*
7	benzyl cinnamate	**4f**	95	99	*S*,*R*
8	2-vinyl naphthalene	**4g**	93	98	*R*
9	1-decene	**4h**	88	82	*R*
10	indene	**4i**	98	61 (61)[d]	*R*,*S*

[a] Isolated yield at quantitative conversion. [b] Determined by HPLC after deprotection to the free diol. [c] Determined on the diol stage by comparison with literature values for optical rotation and HPLC retention times. [d] Determined on the boronic ester stage. [e] With $(DHQ)_2PHAL$ as ligand.

products from aqueous work-up were analytically pure according to ^1H and ^{13}C NMR. Complete enantioselection was observed in oxidations of (*E*)-stilbene and benzyl cinnamate. Other substrates such as styrene, α- and β-methyl styrene, methyl cinnamate and 2-vinyl naphthalene gave boronic esters with high to excellent enantiomeric excesses (*ee*'s) in the range of 95–98%. In general, enantiomeric excesses of the products were determined after deprotection of the cyclic boronic esters under standard conditions (H_2O_2, H_2O, then NaOH). Epimerisation during course of deprotection was never observed and the final vicinal diol products were isolated in over 90% chemical yield. For (*E*)-stilbene and indene oxidation, the enantiomeric excesses were determined both at the stage of the boronic esters and the free diols, respectively. Their complete agreement demonstrates the absence of any racemisation during boron removal. All obtained *ee* values and absolute configurations are in excellent agreement with those from the original Sharpless AD reactions.[12] Identical values were obtained for reactions which were carried out with commercially available AD-mix samples. For oxidations of stilbene, styrene and indene, AD mix-β gave identical values regarding yields (99, 95 and 96%, respectively) and enantiomeric excesses (99, 96 and 58%, respectively). The excellent yields of boronic esters are particularly noteworthy for substrates such as styrene, β-methyl styrene or 2-vinyl naphthalene, which tend to suffer from overoxidation under certain aqueous conditions.[13] We observed benzaldehyde and 2-naphthaldehyde formation in the range of 7–16% under standard AD reactions. This is not the case in the present protocol, which leads to protection of the chiral diol entities as boronic esters immediately after the primary oxidation step.

As expected, use of $(DHQ)_2PHAL$ led to enantiocomplimentary induction (Table 1, entry 2). Oxidations of (*E*)-stilbene employing other ligands such as $(DHQD)_2AQN$ and DHQD-PCB gave 99 and 95% *ee*, respectively, and isolated chemical yields of more than 95%. Apparently, the presence of phenyl boronic acid does not affect the crucial step of enantioselective olefin functionalisation with the OsO_4–Cinchona alkaloid complex. In view of the high ratio for phenyl boronic acid:Cinchona alkaloid of 24:1, complete removal of the stereoinducing Lewis basic ligand as the primary source of chiral information through deleterious complexation to the Lewis acidic boron centre was an evident possibility. Otherwise, even low concentrations of free Cinchona alkaloid would still lead to a kinetically favoured enantioselective pathway, since the AD reaction benefits from a highly ligand-accelerated catalysis.[14] Thus, already at the outset of the present investigation there had been a reasonable chance to maintain asymmetric induction under the given conditions. Even so, ^1H and ^{11}B NMR spectroscopic control experiments included titration of a solution of DHQD-PCB with phenyl boronic acid; these experiments revealed no detectable complexation at all of the basic quinuclidine unit of the chiral ligand to the

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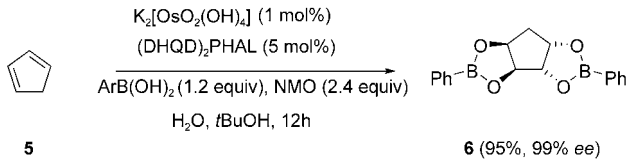
Lewis acidic boron reagent within NMR timescale. This characterises the boron centre an oxophilic, but not azaphilic Lewis acid.

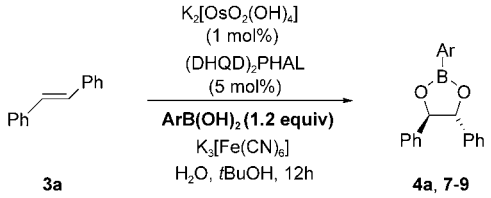
Asymmetric dihydroxylation of cyclopentadiene was carried out under Upjohn conditions due to the problematic base conditions of the original AD procedure (Scheme 3).



Scheme 3. Enantioselective dihydroxylation of cyclopentadiene. Assumed absolute *S*,*S*,*S*,*S* configuration made on the basis of the regular face selectivity of the AD.[1]

This reaction gave a single compound (>96% purity) and the potentially formed *meso*-derivative was not observed in the 300 MHz ^{1}H NMR spectrum. The only product was the chiral bis-boronic ester which was isolated in >99% *ee*. This result matches earlier elegant work from Sharpless on per-dihydroxylation of polyalkenes.[15] In addition, the stereochemistry of the second step of oxidation is consistent with the Kishi rules on dihydroxylation of cyclic allylic ethers and esters.[16]

Substituted aryl boronic acids are compatible with this new AD protocol (Scheme 4, Table 2). For the case of (*E*)-stilbene as standard AD substrate, no electronic effect regarding the substituent was detected and dihydroxylation under the usual conditions consistently gave the respective aryl boronic esters with essentially complete enantioselection (99% *ee*). The example of 4-biphenyl boronic acid (entry 4) is particularly noteworthy, since it allows for direct access to the respective chiral boronic esters, which are important derivatives for determination of absolute configuration of diols by means of circular dichroism spectroscopic analysis.[17]



Scheme 4. Dihydroxylation in the presence of substituted aryl boronic acids.

Table 2. Catalytic asymmetric synthesis of aryl boronic esters.

Entry	Ar	Product	Yield [%][a]	*ee* [%][b]
1	Ph	**4a**	99	99
2	4-F-Ph	**7**	97	99
3	4-MeO-Ph	**8**	95	99
4	4-Ph-Ph	**9**	98	99

[a] Isolated yield at quantitative conversion. [b] Determined by HPLC after deprotection to free 1,2-diphenyl ethanediol.

Mechanistic discussion: It has been a common feature in all dihydroxylation protocols established so far[1,3] that removal of the diol entity from the intermediate osma(VI) glycolate represents the decisive step for catalyst regeneration. This is usually accomplished through the hydrolytic cleavage of the osmium–oxygen bonds (Figure 2, left). Regarding the aryl boronic acid variants, already the earlier anhydrous conditions in the racemic protocol[8,9] pose the underlying mechanistic question on diol removal in the intermediary step prior to catalyst regeneration. Surprisingly, the importance of the exact working mode of diol removal by the phenyl boronic acid had not been clarified in these earlier protocols[5] and has remained largely unappreciated.

Given the inherent properties of phenyl boronic acid, it appears reasonable to assume cleavage by the unique electrophilic character of the boron centre (Figure 2, right). The role of boronic acid in this cleavage does not rely on a simple proton effect as revealed by control experiments with Brønsted acids such as acetic acid or toluene sulfonic acid. These additives gave significantly lower conversion.

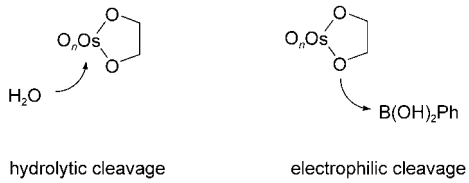


Figure 2. Hydrolytic cleavage versus electrophilic cleavage of osma glycolates.

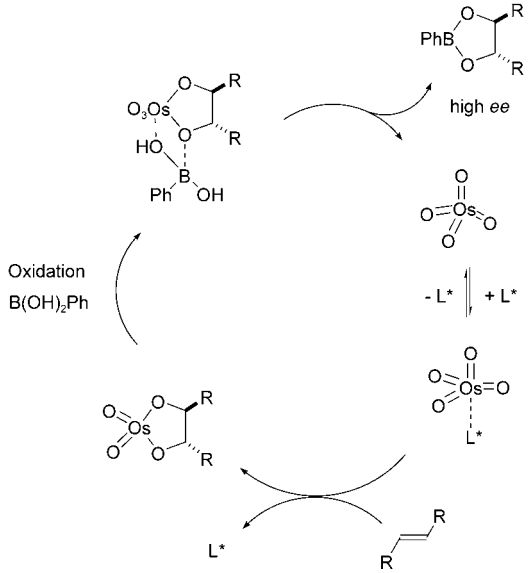


Figure 3. Catalytic cycle for phenyl boronic acid-initiated turnover in enantioselective olefin dihydroxylation.

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The resulting overall catalytic cycle is depicted in Figure 3. The stereochemically decisive initial stages are unchanged with respect to the parent Sharpless process. Thus ligation of the chiral Cinchona alkaloid ligand to osmium tetroxide furnishes the asymmetric catalyst for differentiation of the prochiral olefin faces. Asymmetric dihydroxylation and dissociation of the ligand then leads to the glycolate osmium(VI) ester, which is reoxidised to the corresponding glycolate osmium(VIII) ester. At this stage, the osmium–diolate entity is cleaved by the above-mentioned electrophilic cleavage (Figure 3). In such a scenario, initial interaction between the electrophilic boron centre and the basic oxygen atom of the glycol entity weakens the osmium–oxygen bond and ultimately leads to transesterification from osmium to boron. This releases boronic esters with high enantiomeric excess and regenerates the osmium tetroxide catalyst.

The high enantiomeric excesses obtained by our procedure are the consequences of a well-balanced electrophilic character of the boronic acid. While it is completely cooperative with the stereoinducing ligand, it renders the rate for this cleavage process sufficiently fast in order to overcome the competitive hydrolytic cleavage. This is further strengthened by the observation that the hydrolysis-aiding methyl sulfonamide effect[1,4] is completely absent in the presence of phenyl boronic acid. For example, a qualitative comparison on the respective rates (and enantiomeric excesses) for boronic acid promoted asymmetric dihydroxylation of stilbene (Table 1, entry 7) are essentially identical for reactions with and without methyl sulfonamide addition. Therefore, product formation ocurrs exclusively through the electrophilic cleavage pathway and boronic esters are the only products from this new AD version.

Moreover, since the rate of the electrophilic cleavage process at least equals the one from sulfonamide-based AD protocols, any occurrence of secondary cycle catalysis is efficiently surpressed. Thus, the highly enantioselective osmium tetroxide Cinchona alkaloid catalyst from the Sharpless AD process constantly dominates the catalysis.

Finally, formation of boronic esters does not proceed through the alternative pathway of diol condensation with $ArB(OH)_2$.[18] A control experiment showed that reaction of free stilbene diol with $PhB(OH)_2$ in $MeOD/D_2O$ (1:1, v/v) is comparably slow at room temperature and gives only an incomplete yield, even after a prolonged reaction time of 24 h.

In summary, we have described a new electrophilic cleavage concept for the Sharpless asymmetric dihydroxylation reaction. This has resulted in the development of a one-step synthesis of enantiopure boronic esters through the asymmetric dihydroxylation of olefins in the presence of phenylboronic acid. This new procedure is noteworthy, since it is more convenient than the previous racemic protocol (osmate instead of OsO_4 as osmium source, cheap re-oxidant instead of anhydrous NMO) and combines the power of the AD with the advantage of boronic ester protection.

Experimental Section

General: Potassium osmate $K_2[OsO_2(OH)_4]$ was purchased from Aldrich and stored under argon. Methyl cinnamate, benzyl cinnamate, indene, 2-formyl naphthaldehyde, $(DHQD)_2PHAL$, $(DHQ)_2PHAL$, $(DHQD)_2AQN$ and DHQ-PCB were purchased from Fluka. Phenyl boronic acid, styrene, stilbene, α-methyl styrene and β-methyl styrene and 1-decene were purchased from Aldrich. 2-Vinyl naphthalin was synthesised following a literature Wittig procedure.[19]

All other solvents were reagent grade and used as received. Column chromatography was performed with silica gel (Merck, type 60, 0.063–0.2 mm and Machery Nagel, type 60, 0.015–0.025 mm). Optical rotations were measured on a Perkin–Elmer 341 polarimeter. Concentrations are given in g per 100 mL in dichloromethane. NMR spectra were recorded on Bruker DPX 300 MHz and Bruker DRX 500 MHz spectrometers. All chemical shifts in the NMR experiments are reported as ppm downfield from TMS. The following calibrations were used: $CDCl_3$ $\delta = 7.26$ and 77.00 ppm, C_6D_6 $\delta = 7.16$ and 128.00 ppm. Multiplicities are given by the common abbreviations (s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet; ps for pseudo). IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer. MS and HRMS experiments were performed on a Kratos MS 50 within the service centres at the Kekulé-Department, Bonn. HPLC determinations were carried out on a Knauer Wellchrome (injection valve A0258, pump K-100, solvent organizer K-1500, UV-detector K-2600). The reported values refer to 254 nm detection wavelength.

General synthetic procedure for dihydroxylation under Upjohn conditions (Procedure A): A solution of $K_2[OsO_2(OH)_4]$ (3.2 mg, 0.01 mmol) and phenyl boronic acid (146 mg, 1.2 mmol) in *tert*-butanol and water (10 mL, 1:1, v/v) was stirred at room temperature. NMO was added as a 1.2 M solution in water (1.0 mL) and the resulting solution was stirred. The substrate (1.0 mmol) was added in one portion and the solution was sealed and stirred for 12 h at room temperature. It was worked up by addition of an aqueous solution of sodium thiosulfate and extracted with dichloromethane. The organic phase was separated, dried over $MgSO_4$ and evaporated to dryness to leave the crude products.

Where appropriate, column chromatography (silica gel, hexane/ethyl acetate, 4:1, v/v) gave the analytically pure products as described below.

General synthetic procedure for dihydroxylation under Sharpless AD conditions (Procedure B): A solution of $K_2[OsO_2(OH)_4]$ (3.2 mg, 0.01 mmol), potassium carbonate (410 mg), potassium hexacyanoferrate(III) (980 mg), phenyl boronic acid (146 mg, 1.2 mmol) and the Cinchona alkaloid ligand (0.05 mmol) in *tert*-butanol and water (10 mL, 1:1, v/v) was stirred at room temperature. The substrate (1.0 mmol) was added in one portion and the solution was sealed and stirred for 12 h at room temperature. It was worked up by addition of an aqueous solution of sodium thiosulfate and extracted with water and dichloromethane. The organic phase was separated, dried over $MgSO_4$ and evaporated to dryness to leave the crude products.

Where appropriate, column chromatography (silica gel, hexane/ethyl acetate, 4:1, v/v) gave the analytically pure products as described below.

General procedure for cleavage of boronic esters: The boronic ester (1 mmol) was dissolved in ethyl acetate/acetone (10 mL 1:1, v/v) and a solution of H_2O_2 (35% in H_2O, 2 equiv, 0.17 mL) was added upon stirring. The resulting solution was stirred for a period of 3–4 h at room temperature. The remaining H_2O_2 was reduced upon addition of an aqueous solution of $Na_2S_2O_3$ at room temperature. The reaction mixture was extracted twice with ethyl acetate (2×20 mL), the organic layers were separated, washed with an aqueous solution of NaOH (1 M, 10 mL), dried over $MgSO_4$ and filtered. The solvents were removed under reduced pressure. If required, the colourless solids were purified by column chromatography (silicagel, hexanes/ethyl acetate, 3:1, v/v) to give the analytically pure diols.

Dioxoborolane 2a from oxidation of triacetyl glucal: This compound was synthesised according to the general procedure A from 2,3,4-tribenzyl-*O*-glucal (272 mg, 1 mmol). After column chromatography (silica gel, ethyl acetate), **2a** was obtained as a white solid (302 mg, 0.77 mmol, 77%).

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$[\alpha]_D^{20} = -22.3$ ($c = 0.2$ in acetone); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.97$ (s, 3H; C(O)CH_3), 2.00 (s, 3H; C(O)CH_3), 2.02 (s, 3H; C(O)CH_3), 4.14–4.20 (m, 2H; CH_2OAc), 4.29–4.36 (m, 1H; C*H*OAc), 4.77 (dd, $J = 3.2$, 6.2 Hz, 1H; C*H*OAc), 5.12–5.21 (m, 1H; C*H*OAc), 5.26–5.29 (m, 1H; C*H*OB), 6.39 (dd, $J = 1.2$, 6.1 Hz, 1H; C*H*OB), 7.30–7.38 (m, 3H; CH_{Ar}), 7.64–7.68 ppm (m, 2H; CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.58$, 20.70, 20.82, 63.29, 67.45, 67.60, 70.51, 73.90, 97.90, 128.02, 132.35, 135.18, 162.32, 169.28, 169.59, 170.65 ppm; MS (70 eV): *m*/*z* (%): 392 (100), [M^+],346 (22), 276 (9); HRMS: calcd for $C_{18}H_{21}{}^{10}BO_9$: 391.1313; found: 391.1312.

Dioxoborolane 2b from oxidation of tribenzyl glucal: This compound was synthesised according to the general procedure A from 2,3,4-tribenzyl-*O*-glucal (416 mg, 1 mmol). After column chromatography (silica gel, ethyl acetate), **2b** was obtained as a white to light purple solid (450 mg, 0.84 mmol, 84%). $[\alpha]_D^{20} = -34.9$ ($c = 0.1$ in acetone); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.64$ (d, $J = 2.4$ Hz, 1H; C*H*OBn), 3.71–3.75 (m, 2H; OC*H*CH$_2$OBn, OCHC*H*OBn), 3.88 (dd, $J = 4.1$, 4.9 Hz, 1H; OCHC*H*OBn), 4.39 (d, $J = 11.3$ Hz, 1H; PhCH*H*O), 4.47 (d, $J = 12.1$ Hz, 1H; C*H*OBn), 4.50 (d, $J = 10.0$ Hz, 1H; PhCH*H*O), 4.53 (d, $J = 10.0$ Hz, 1H; PhCH*H*O), 4.55 (d, $J = 12.1$ Hz, 1H; PhCH*H*O), 4.56 (d, $J = 11.3$ Hz, 1H; PhCH*H*O)H), , 4.65 (d, $J = 12.1$ Hz, 1H; PhCH*H*O), 4.77 (m, 1H; C*H*OB), 6.02 (d, $J = 6.2$ Hz, 1H; C*H*OB), 7.77–7.83 (m, 17H; CH_{Ar}), 8.19 (d, $J = 1.5$ Hz, 2H; CH_{Ar}), 8.22 ppm (d, $J = 1.4$ Hz, 1H; CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 69.06$, 70.29, 72.12, 72.78, 73.25, 74.45, 76.81, 79.86, 98.84, 127.48, 127.50, 127.63, 127.71, 127.88, 128.12, 128.19, 128.31, 131.83, 134.95, 135.47, 137.64, 137.81 ppm; MS (70 eV): *m*/*z* (%): 536 (100), [M^+],446 (12), 356 (14); HRMS: calcd for $C_{33}H_{33}{}^{10}BO_6$: 535.2405; found: 535.2513.

(*R*,*R*)-2,4,5-Triphenyl-1,3,2-dioxaborolane (4a):[20] This compound was synthesised according to the general procedure B from stilbene (180 mg, 1 mmol). Yield: 300 mg (1.00 mmol, 99%). $[\alpha]_D^{20} = -70$ ($c = 0.5$ in chloroform); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 5.35$ (s, 2H; C*H*OB), 7.37–7.55 (m, 13H; CH_{Ar}), 8.00 ppm (m, 2H; CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 86.96$, 125.85, 127.96, 128.39, 128.82, 131.84, 135.23, 140.39 ppm; IR (KBr): $\tilde{\nu} = 3460$, 3095, 3045, 2917, 2395, 2340, 1597, 1451, 1390, 1340, 1318, 1220, 1215, 1105, 1060, 1000, 780, 775, 695, 650, 640, 510 cm^{-1}; MS (70 eV): *m*/*z* (%): 300 (100), [M^+], 222 (20), 194 (40), 178 (5), 167 (18), 151 (10), 107 (22), 90 (45); HRMS: calcd for $C_{20}H_{17}{}^{10}BO_2$: 299.1358; found: 299.1330; HPLC data for determination of enantiomeric excess: CHIRALCEL OD-H, *n*-hexane/2-propanol, 95:5 (v/v), 0.3 mL min^{-1}, retention times: 13.7 min [(*R*,*R*)], 15.5 min [(*S*,*S*)]. Determination of enantiomeric excess was carried out at the stage of the free (*R*,*R*)- and (*S*,*S*)-1,2-diphenylethylenediol: CHIRALCEL OB-H, *n*-hexane/2-propanol, 90:10 (v/v), 1.0 mL min^{-1}, retention times: 13.0 min [(*R*,*R*)], 17.6 min [(*S*,*S*)].

(*R*)-2,4-Diphenyl-1,3,2-dioxaborolane (4b):[21] This compound was synthesised according to the general procedure B from styrene (0.12 mL, 1 mmol). Yield: 211 mg (0.94 mmol, 94%). $[\alpha]_D^{20} = -43.1$ ($c = 0.5$ in acetone); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.09$ (dd, $J = 7.5$, 9.0 Hz, 1H; C*H*HOB), 4.62 (dd, $J = 8.3$, 9.0 Hz, 1H; CH*H*OB), 5.47 (dd, $J = 7.5$, 8.3 Hz, 1H; C*H*OB), 7.19–7.43 (m, 8H; CH_{Ar}), 7.80–7.83 ppm (m, 2H; CH_{Ar}); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 73.34$, 78.89, 125.56, 127.86, 128.15, 128.72, 131.63, 135.00, 141.12 ppm; MS (70 eV): *m*/*z* (%): 224 (100) [M^+], 151 (18), 147 (44),107 (9), 90 (48); HRMS: calcd for $C_{14}H_{13}{}^{10}BO_2$: 223.1045; found: 223.1056. Determination of enantiomeric excess was carried out at the stage of free 1-phenylethylenediol: CHIRALCEL OB-H, *n*-hexane/2-propanol, 90:10 (v/v), 0.5 mL min^{-1}, retention times: 16.0 min [(*R*)], 20.2 min [(*S*)].

(*R*)-4-Methyl-2,4-diphenyl-1,3,2-dioxaborolane (4c): This compound was synthesised according to the general procedure B from α-methyl styrol (0.13 mL, 1 mmol). Yield: 230 mg (0.97 mmol, 97%). $[\alpha]_D^{20} = -154$ ($c = 0.5$ in acetone); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.66$ (s, 3H; CH_3), 4.29 (s, 2H; CH_2OB), 7.16–7.41 (m, 8H; CH_{Ar}), 7.87–7.90 ppm (m, 2H; CH_{Ar}); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 29.58$, 78.78, 83.39, 124.15, 127.17, 127.81, 128.40, 131.50, 134.91, 146.01 ppm; IR (KBr): $\tilde{\nu} = 3445$, 3090, 3060, 3045, 2985, 2940, 2920, 2370, 2340, 1600, 1495, 1435, 1385, 1360, 1240, 1220, 1085, 1010, 750, 690, 640 cm^{-1}; MS (70 eV): *m*/*z* (%): 238 (5) [M^+], 223 (100), 162 (5), 147 (5), 119 (11), 104 (26), 91 (16), 77 (10); HRMS: calcd for $C_{15}H_{15}{}^{10}BO_2$: 236.1121; found: 236.1121. Determination of enantiomeric excess was carried out at the stage of the bisbenzoate of the free 2-phenylpropylenediol: CHIRALCEL OB-H, *n*-hexane/2-propanol, 97:3 (v/v), 1.0 mL min^{-1}, retention times: 25.6 min [(*S*)], 27.2 min [(*R*)].

(*R*,*R*)-5-Methyl-2,4-diphenyl-1,3,2-dioxaborolane (4d): This compound was synthesised according to the general procedure B from β-methyl styrol (0.13 mL, 1 mmol). Yield: 224 mg (0.94 mmol, 94%). $[\alpha]_D^{20} = -75$ ($c = 0.5$ in acetone); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.42$ (d, $J = 6.2$ Hz, 3H; CH_3), 4.34 (dq, $J = 6.2$, 7.5 Hz, 1H; CH$_3$C*H*OB), 4.91 (d, $J = 7.5$ Hz, 1H; PhC*H*OB), 7.12–7.43 (m, 8H; CH_{Ar}), 7.77–7.81 ppm (m, 2H; CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 21.17$, 81.72, 86.10, 125.63, 127.86, 128.23, 128.73, 131.58, 134.98, 140.60 ppm; IR (KBr): $\tilde{\nu} = 3450$, 3050, 3015, 3025, 3015, 1760, 1730, 1600, 1500, 1440, 1400, 1380, 1360, 1290, 1205, 1100, 1020, 780, 695, 680, 650 cm^{-1}; MS (70 eV): *m*/*z* (%): 238 (100) [M^+], 223 (12), 194 (55), 105 (33), 90 (100); HRMS: calcd for $C_{15}H_{15}{}^{11}BO_2$: 238.1165; found: 238.1156. Determination of enantiomeric excess was carried out at the stage of free 1-phenylpropylenediol: CHIRALPAK AD, *n*-hexane/2-propanol, 90:10 (v/v), 0.5 mL min^{-1}, retention times: 18.1 min [(*S*,*S*)], 21.6 min [(*R*,*R*)].

(*S*,*R*)-4-(Methoxycarbonyl)-2,5-diphenyl-1,3,2-dioxaborolane (4e): This compound was synthesised according to the general procedure B from methyl cinnamate (162 mg, 1 mmol). Yield: 260 mg (0.92 mmol, 92%). $[\alpha]_D^{20} = -47.4$ ($c = 0.5$ in acetone); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.70$ (s, 3H; CO_2C*H*$_3$), 4.69 (d, $J = 6.0$ Hz, 1H; PhC*H*OB), 5.44 (d, $J = 6.0$ Hz, 1H; MeO$_2$CC*H*OB), 7.17–7.37 (m, 8H; CH_{Ar}), 7.77–7.81 ppm (m, 2H; CH_{Ar}); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 52.69$, 81.82, 82.48, 125.30, 127.92, 128.50, 128.82, 132.04, 135.22, 140.31, 170.96 ppm; IR (KBr): $\tilde{\nu} = 3475$, 3051, 3022, 2950, 2895, 2397, 2362, 1752, 1740, 1600, 1502, 1425, 1403, 1205, 1100, 1020, 997, 782, 695, 652 cm^{-1}; MS (70 eV): *m*/*z* (%): 282 (2) [M^+], 223 (6), 205 (32), 176 (70), 105 (33), 59 (100); HRMS: calcd for $C_{16}H_{15}{}^{10}BO_4$: 281.1097; found: 281.1087. Determination of enantiomeric excess was carried out at the stage of free methyl 3-phenyl-2,3-dihydroxy propionate: CHIRALCEL OB-H, *n*-hexane/2-propanol, 95:5 (v/v), 0.7 mL min^{-1}, retention times: 41.6 min [(*R*,*S*)], 46.8 min [(*S*,*R*)].

(*S*,*R*)-4-(Benzyloxycarbonyl)-2,5-diphenyl-1,3,2-dioxaborolane (4f): This compound was synthesised according to the general procedure B from benzyl cinnamate (238 mg, 1 mmol). Yield: 339 mg (0.95 mmol, 95%). $[\alpha]_D^{20} = -32$ ($c = 0.5$ in acetone); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.73$ (d, $J = 6.2$ Hz, 1H; PhC*H*OB), 5.18 (dd, $J = 12.2$, 29.8 Hz, 2H; PhCH_2O_2C), 5.42 (d, $J = 6.2$ Hz, 1H; BnO$_2$CC*H*OB), 7.12–7.37 (m, 8H; CH_{Ar}), 7.81–7.84 ppm (m, 2H; CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 31.06$, 67.16, 81.71, 82.34, 125.24, 127.80, 128.21, 128.36, 128.44, 128.53, 128.67, 131.90, 135.13, 140.11, 170.09 ppm; IR (KBr): $\tilde{\nu} = 3485$, 3057, 3018, 2963, 2395, 2355, 1760, 1598, 1495, 1452, 1440, 1400, 1365, 1280, 1200, 1105, 1025, 1000, 770, 705, 680, 660, 525 cm^{-1}; MS (70 eV): *m*/*z* (%): 335 (7) [M^+], 238 (21), 224 (81), 205 (15), 176 (100), 105 (38), 59 (96); HRMS: calcd for $C_{22}H_{19}{}^{10}BO_4$: 357.1413; found: 357.1401. Determination of enantiomeric excess was carried out at the stage of the bisbenzoate from the free benzyl 3-phenyl-2,3-dihydroxy propionate: CHIRALCEL OB-H, *n*-hexane/2-propanol, 97:3 (v/v), 0.8 mL min^{-1}, retention times: 21.0 min [(*S*,*R*)], 24.5 min [(*R*,*S*)].

(*R*)-4-(2′-Naphthyl)-2-phenyl-1,3,2-dioxaborolane (4g): This compound was synthesised according to the general procedure B from 2-vinyl naphthalene (154 mg, 1 mmol). Yield: 255 mg (0.93 mmol, 93%). $[\alpha]_D^{20} = -68.3$ ($c = 0.5$ in acetone); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.32$ (dd, $J = 7.7$, 9.0 Hz, 1H; C*H*HOB), 4.83 (dd, $J = 8.2$, 9.0 Hz, 1H; CH*H*OB), 5.79 (dd, $J = 7.7$, 8.2 Hz, 1H; C*H*OB), 7.44–7.60 (m, 6H; CH_{Ar}), 7.84–7.93 (m, 4H; CH_{Ar}), 8.00–8.04 ppm (m, 2H; CH_{Ar}); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 73.24$, 79.07, 123.16, 124.70, 126.18, 126.40, 127.72, 127.94, 127.97, 128.82, 131.69, 133.19, 135.06, 135.61, 138.35 ppm; MS (70 eV): *m*/*z* (%): 274 (16) [M^+], 156 (80), 127 (100), 77 (21); HRMS: calcd for $C_{18}H_{15}{}^{11}BO_2$: 274.1165; found: 274.1161. Determination of enantiomeric excess was carried out at the stage of free 1-(2-naphthyl)ethylenediol: CHIRALCEL OD, *n*-hexane/2-propanol, 90:10 (v/v), 1.0 mL min^{-1}, retention times: 12.6 min [(*R*)], 15.7 min [(*S*)].

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(*R*)-4-*n*-Octyl-2-phenyl-1,3,2-dioxaborolane (4h): This compound was synthesised according to the general procedure B from decene (0.2 mL, 1 mmol). Yield: 229 mg (0.88 mmol, 88 %). $[\alpha]_D^{20} = -39$ ($c = 0.5$ in acetone); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.89$ (t, $J = 6.9$ Hz, 3H; CH_3), 1.29–1.56 (m, 12H; CH_2), 1.58–1.68 (m, 1H; C*H*H), 1.70–1.75 (m, 1H; CH*H*), 3.95 (dd, $J = 7.1$, 8.8 Hz, 1H; CH*H*OB), 4.42 (dd, $J = 7.7$, 8.8 Hz, 1H; C*H*HOB), 4.57 (ddd, $J = 6.0$, 7.1, 7.7 Hz, 1H; C*H*OB), 7.35–7.40 (m, 2H; CH_{Ar}), 7.45–7.50 (m, 1H; CH_{Ar}), 7.81–7.83 ppm (m, 2H; CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 14.06$, 22.63, 24.95, 29.21, 29.47, 29.50, 31.84, 36.17, 71.20, 77.57, 127.76, 131.33, 134.80, 162.36 ppm; IR (KBr): $\tilde{\nu} = 3445$, 3080, 3070, 3030, 2960, 2905, 2395, 2340, 1610, 1505, 1425, 1405, 1385, 1350, 1305, 1220, 1095, 1015, 980, 970, 860, 760, 700, 650, 640 cm^{-1}; MS (70 eV): *m*/*z* (%): 260 (20) [M^+], 231 (5), 203 (5), 175 (10), 147 (100), 118 (36), 105 (17), 91 (20), 69 (10), 55 (11); HRMS: calcd for $C_{16}H_{25}{}^{11}BO_2$: 259.1984; found: 259.1985. Determination of enantiomeric excess was carried out at the stage of the bisbenzoate from the free decane-1,2-diol: CHIRALCEL OB-H, *n*-hexane/2-propanol, 95:5 (v/v), 0.7 mL min^{-1}, retention times: 13.6 min [(*S*)], 17.1 min [(*R*)].

(8*R*,4*S*)-2-(*B*-Phenyl)bora-1,3-dioxo-6,7-benzo-bicyclo[3.3.2]octane (4i):[8] This compound was synthesised according to the general procedure B from indene (0.12 mL, 1 mmol). Yield: 232 mg (0.98 mmol, 98 %). $[\alpha]_D^{20} = +3.2$ ($c = 0.5$ in acetone); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.21$ (dd, $J = 0.5$, 16.9 Hz, 1H; C*H*HCHOB), 3.36 (dd, $J = 0.5$, 6.7 Hz, 1H; CH*H*CHOB), 5.28 (ddd, $J = 6.6$, 6.7, 16.9 Hz, 1H; CHHC*H*OB), 5.81 (d, $J = 6.6$ Hz, 1H; C*H*OB), 7.15–7.28 (m, 5H; CH_{Ar}), 7.33–7.38 (m, 1H; CH_{Ar}), 7.47–7.50 (m, 1H; CH_{Ar}), 7.70–7.73 ppm (m, 2H; CH_{Ar}); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 39.84$, 80.91, 85.01, 125.41, 126.16, 127.43, 127.72, 129.58, 131.35, 134.82, 140.41, 140.74 ppm; IR (KBr): $\tilde{\nu} = 3515$, 3420, 3095, 3060, 3035, 2940, 2920, 2830, 1597, 1415, 1390, 1370, 1290, 1195, 1090, 1085, 1005, 980, 755, 695, 620 cm^{-1}. Determination of enantiomeric excess was carried out at the stage of free indenediol: CHIRALCEL OB-H, *n*-hexane/2-propanol, 90:10 (v/v), 0.7 mL min^{-1}, retention times: 12.6 min [(*R*,*S*)], 15.8 min [(*S*,*R*)].

Cyclopentane-1,2:3,4-tetrayl-1,2:3,4-bis(phenylboronate) (6):[9] This compound was synthesised from cyclopentadiene (66 mg, 1 mmol) according to Procedure A with $(DHQD)_2PHAL$ as chiral ligand. Yield: 291 mg (95 mmol, 95 %). $[\alpha]_D^{20} = -25$ ($c = 0.5$ in dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.51$ (pst, $J = 6.3$ Hz, 2H; CH_2), 5.03 (d, $J = 6.3$ Hz, 2H; C*H*OB), 5.17 (psq, $J = 5.8$ Hz, 2H; CH_2C*H*OB), 7.36–7.43 (m, 4H; CH_{Ar}), 7.50–7.56 (m, 2H; CH_{Ar}), 7.79–7.85 ppm (m, 4H; CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 40.17$, 79.02, 86.09, 127.56, 130.16, 131.11, 132.92, 134.63, 157.81.

(*R*,*R*)-2-(4′-Fluorophenyl)-4,5-diphenyl-1,3,2-dioxaborolane (7): This compound was synthesised according to the general procedure B from stilbene (180 mg, 1 mmol) with 4′-fluorophenyl boronic acid (168 mg, 1.2 mmol) instead of phenyl boronic acid. Yield: 302 mg (0.97 mmol, 97 %). $[\alpha]_D^{20} = -61.7$ ($c = 0.5$ in acetone); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 5.26$ (s, 2H; C*H*OB), 7.02–7.18 (m, 2H; CH_{ArF}), 7.26–7.36 (m, 10H; CH_{Ar}), 7.88–7.93 ppm (m, 2H; CH_{ArF}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 87.01$, 115.08, 115.28, 125.84, 128.45, 128.84, 137.51 (d, ^2J(C,F) = 8.4 Hz), 140.21, 166.73 ppm; ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): $\delta = -107.82$; IR (KBr): $\tilde{\nu} = 3425$, 3055, 3015, 2930, 1600, 1505, 1470, 1400, 1380, 1360, 1300, 1215, 1195, 1145, 1090, 1080, 980, 825, 775, 695, 650, 580, 520 ppm; MS (70 eV): *m*/*z* (%): 318 (71) [M^+], 240 (49), 311 (36), 180 (31), 165 (35), 135 (15),105 (42), 90 (100), 77 (28); HRMS: calcd for $C_{20}H_{16}{}^{11}BFO_2$: 318.1227; found: 318.1234. HPLC data for determination of enantiomeric excess at the stage of the free (*R*,*R*)- and (*S*,*S*)-1,2-diphenylethylenediol: CHIRALCEL OB-H, *n*-hexane/2-propanol, 90:10 (v/v), 1.0 mL min^{-1}, retention times: 13.0 min [(*R*,*R*)], 17.6 min [(*S*,*S*)].

(*R*,*R*)-2-(4′-Methoxyphenyl)-4,5-diphenyl-1,3,2-dioxaborolane (8): Synthesised according to the general procedure B from stilbene (180 mg, 1 mmol) with 4′-methoxyphenyl boronic acid (182 mg, 1.2 mmol) instead of phenyl boronic acid. Yield: 314 mg (0.95 mmol, 95 %). $[\alpha]_D^{20} = -80.1$ ($c = 0.5$ in acetone); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.70$ (s, 3H, OCH_3), 5.18 (s, 2H; C*H*OB), 6.85 (d, $J = 8.7$ Hz, 2H; CH_{ArOMe}), 7.18–7.29 (m, 10H; CH_{Ar}), 7.84 ppm (d, $J = 8.7$ Hz, 2H; CH_{ArOMe}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.03$, 86.80, 113.58, 125.81, 128.26, 128.72, 136.99, 140.46, 162.61 ppm; MS (70 eV): *m*/*z* (%): 330 (33) [M^+], 209 (32), 197 (30), 191 (15), 165 (10), 147 (11), 105 (45), 90 (26), 77 (26), 59 (100); HRMS: calcd for $C_{21}H_{19}{}^{11}BO_3$: 330.1427; found: 330.1422. HPLC data for determination of enantiomeric excess at the stage of the free (*R*,*R*)- and (*S*,*S*)-1,2-diphenylethylenediol: CHIRALCEL OB-H, *n*-hexane/2-propanol, 90:10 (v/v), 1.0 mL min^{-1}, retention times: 13.0 min [(*R*,*R*)], 17.6 min [(*S*,*S*)].

(*R*,*R*)-2-(4′-Biphenylyl)-4,5-diphenyl-1,3,2-dioxaborolane (9): This compound was synthesised according to the general procedure B from stilbene (180 mg, 1 mmol) with 4′-biphenylyl boronic acid (237 mg, 1.2 mmol) instead of phenyl boronic acid. Yield: 369 mg (0.98 mmol, 98 %). $[\alpha]_D^{20} = -133$ ($c = 0.7$ in acetone); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.65$ (s, 2H; C*H*OB), 7.04–7.17 (m, 4H; CH_{Ar}), 7.27–7.42 (m, 9H; CH_{Ar}), 7.53–7.87 ppm (m, 6H; CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 79.15$, 125.89, 126.71, 126.96, 127.28, 127.71, 127.96, 128.17, 128.87, 135.30, 140.89, 143.79 ppm; MS (70 eV): *m*/*z* (%): 377 (100) [M^++1], 222 (9), 178 (4), 167 (12), 151 (5), 107 (18), 90 (25); HRMS: calcd for $C_{26}H_{21}{}^{11}BO_2$: 376.1635; found: 376.1632. HPLC data for determination of enantiomeric excess at the stage of the free (*R*,*R*)- and (*S*,*S*)-1,2-diphenylethylenediol: CHIRALCEL OB-H, *n*-hexane/2-propanol, 90:10 (v/v), 1.0 mL min^{-1}, retention times: 13.0 min [(*R*,*R*)], 17.6 min [(*S*,*S*)].

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