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Selective 1,3-cycloboronation of enantiopure 1,1,4,4-tetrasubstituted butanetetraols: versatile preparation, structural characterization, and properties of chiral cyclic boron-containing bifunctional Lewis acids

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ABSTRACT

The selective cycloboronation of enantiopure 1,1,4,4-tetrasubstituted butanetetraols was investigated, and a general preparation of chiral cyclic boron-containing bifunctional Lewis acids was discovered. Compounds (2*R*,3*R*)- or (2*S*,3*S*)-1,1,4,4-tetrasubstituted butanetetraols were reacted with $ArB(OH)_2$ at reflux in toluene, or THF, or under solvent-free condition to furnish tricoordinated, chiral bicyclo[4.4.0]diboronic esters in high yield via selective 1,3-cycloboronation. Structural characterization and properties of the novel chiral boron compounds are also reported.

1. Introduction

Enantiopure tartaric acid derivatives, especially those possessing a C_2 symmetric axis, have been extensively applied to supramolecular chemistry[1] and asymmetric synthesis.[2] As far as the cycloboronation products of chiral tartaric acids are concerned, they have been used in asymmetric allylations of aldehydes;[3] asymmetric cyclopropanations of olefins;[4] asymmetric hydroborations of alkynes;[5] asymmetric additions of imines;[6] diastereo- and enantioselective crotylations of α-ketoesters;[7] asymmetric reductions;[8] asymmetric nitrile oxide cycloadditions to optically active vinylboronic esters,[9] asymmetric aldol reactions,[10] asymmetric Diels–Alder reactions,[11] asymmetric epoxidations,[12] etc. It has been noted that the cycloboron compounds utilized in the reactions are all tricoordinated, and have been used as chiral Lewis acid catalysts in many catalytic asymmetric reactions. However, most of them are not stable to hydrolysis, and are even highly moisture sensitive. It appears that the convenient preparation of tricoordinated, hydrolytically stable chiral boron compounds is of practical importance for widening their application and scope in asymmetric synthesis.

A short time ago, our group prepared tetracoordinated chiral spiroboric esters containing a tartaric acid ester moiety,[13] which have an O_3BN framework, and are highly stable to hydrolysis and racemization under ambient conditions. We examined their reaction chemistry,[14–16] and in the reaction with phenylmagnesium bromide, unexpectedly obtained a tricoordinated, hydrolytically stable chiral bicyclodiboronic acid ester 3,5,5,8,10,10-hexaphenyl-2,4,7,9-tetraoxa-3,8-diborobicyclo[4.4.0]decane (1*R*,6*R*)-**A** (Scheme 1).[17] Unfortunately, under similar conditions to the above, the reactions did not provide bicyclization products when PhMgBr was replaced by other Grignard reagents, such as 4-methylphenylmagnesium bromide, 2-methylphenylmagnesium bromide, 2,4,6-trimethylphenylmagnesium bromide (mesitylmagnesium bromide, MesMgBr), benzylmagnesium bromide, *n*-butylmagnesium bromide, and cyclohexylmagnesium bromide and in the reaction of the spiroboric ester with MesMgBr, highly substituted diethyl γ,γ-dimesityl-γ-hydroxy-β-oxobutanoate was isolated.[18] It appears that the reaction of the spiroboric esters containing a tartaric acid ester moiety with Grignard reagents is complicated. To investigate the chemistry of this class of structurally novel chiral boron compounds, other accesses to the hexasubstituted bicyclo[4.4.0]diboronic esters were explored. Herein, we report the convenient preparation and structural characterization of a series of novel chiral bicyclodiboronic acid esters.

2. Results and discussion

2.1. Preparation of bicyclo[4.4.0]diboronic esters

As an improvement for the aforementioned spiroboric ester method, the preparation of bicyclo[4.4.0]diboronic ester (1*R*,6*R*)-**A** via arylation of phenylboronic acid or a trialkyl borate-protected tartaric acid ester was attempted.

Diethyl (2*R*,3*R*)-tartrate was allowed to react with phenylboronic acid in toluene under azeotropic dehydrate conditions for 3 h to afford a homogeneous solution of (4*R*,5*R*)-2-phenyl-4,5-bis(ethoxycarbonyl)-1,3,2-dioxaborolane (4*R*,5*R*-**PBDB**). The solvent was removed through rotary evaporation and the residue

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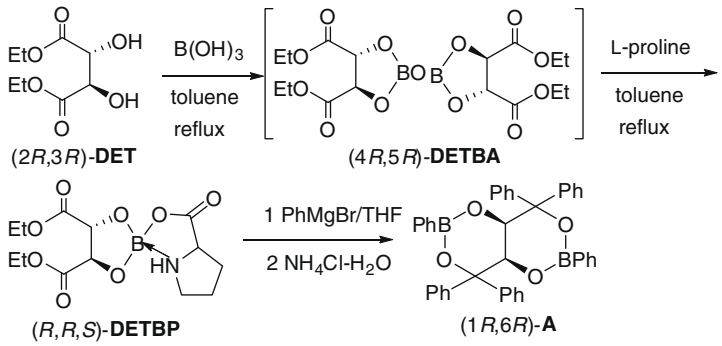
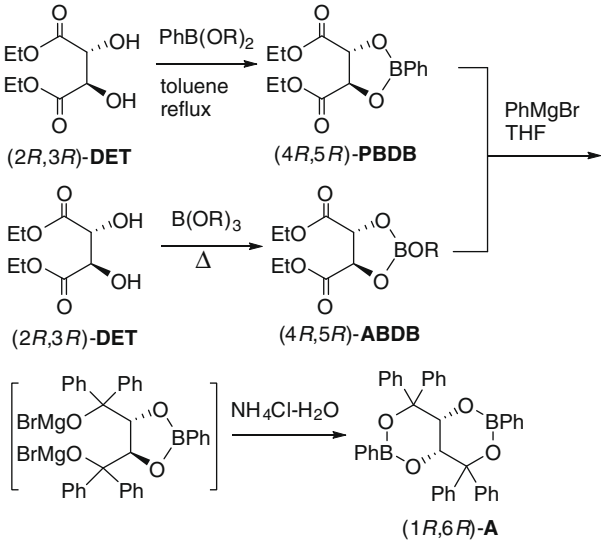


Scheme 1. Preparation of hexaphenylbicyclo[4.4.0]diboronic ester (1*R*,6*R*)-**A** via phenylation of chelated chiral boronic ester.

was dissolved with anhydrous THF. The solution was then added dropwise to a freshly prepared PhMgBr THF solution at 0 °C in a near 1:5 molar ratio; after complete addition, the mixture was stirred at the same temperature for 1 h, followed by warming to ambient temperature, then refluxed with heating for 1.5 h, cooled, worked up with saturated aqueous NH_4Cl. A white solid was obtained from the organic phase, which was recrystallized from EtOH to give pure (1*R*,6*R*)-**A**. X-ray crystallographic analysis proved that it was identical to the product obtained from the reaction of the spiroboric esters with PhMgBr.

Arylation of tartaric esters protected by trialkyl borates with PhMgBr furnished nearly the same results as above. Diethyl (2*R*,3*R*)-tartrate was cycloborated with a trialkyl borate, such as *n*-butyl borate, with heating under solvent-free conditions. After the alcohol liberated in the reaction was completely removed, liquid (4*R*,5*R*)-2-alkoxyl-4,5-bis(ethoxycarbonyl)-1,3,2-dioxaborolane (4*R*,5*R*)-**ABDB** was formed almost quantitatively. The anhydrous THF solution of (4*R*,5*R*)-**ABDB** was added dropwise to a freshly prepared PhMgBr THF solution in about 1:6 molar ratio at 0 °C and treated according to the same procedure as the above to furnish white crystals of (1*R*,6*R*)-**A**.

Preparation of (1*R*,6*R*)-**A** via phenylation of the boron-protected tartaric esters with PhMgBr is outlined in Scheme 2. Compound (1*S*,6*S*)-**B** can also be prepared from diethyl (2*S*,3*S*)-tartrate via a similar procedure to (1*R*,6*R*)-**A**.



Scheme 2. Preparation of (1*R*,6*R*)-**A** via phenylation of boron-protected (4*R*,5*R*)-tartaric ester. R = H or alkyl containing 1–4 carbon atoms.

Since we have been able to conveniently prepare (2*R*,3*R*)- and (2*S*,3*S*)-1,1,4,4-tetrasubstituted butanetetraols (**TSTOL**)[19] from enantiopure dialkyl tartrates via simple procedures, we attempted to prepare bicyclodiboronic esters via direct selective 1,3-cyclocondensation of (2*R*,3*R*)- or (2*S*,3*S*)-1,1,4,4-tetraphenylbutanetetraol (**TPTOL**)[19] with arylboronic acids in THF or toluene under reflux condition. Fortunately, in most cases, the desired products were obtained in high yield. When a 1:2 mixture of (2*R*,3*R*)-**TPTOL** with an arylboronic acid, such as phenylboronic acid, 4-bromophenylboronic acid, 3,5-dibromophenylboronic acid, 3,5-difluorophenylboronic acid, 2-methylphenylboronic acid, 3-methylphenylboronic acid, 4-methylphenylboronic acid, 3-methoxyphenylboronic acid, or 1-naphthylboronic acid, was refluxed in THF for 1-2 h, solid (1*R*,6*R*)-hexasubstituted bicyclo[4.4.0]diboronic esters (1*R*,6*R*)-**A** and **C**–**J** were obtained in over 90% yield (Scheme 3). Under similar conditions, the reaction of (2*S*,3*S*)-**TPTOL** with phenylboronic acid furnished bicyclodiboronic ester (1*S*,6*S*)-**B** in high yield. Nevertheless, condensation reactions between certain arylboronic acids and tetrasubstituted butanetetraols, such as 4-acetylphenylboronic acid and 1,1,4,4-tetraphenylbutanetetraol or phenylboronic acid and 1,1,4,4-tetra(*n*-butyl)-butanetetraol, did not occur in refluxing THF or toluene; however, under solvent-free conditions, they readily underwent the 1,3-selective cyclocondensation. For instance, 4-acetylphenylboronic acid was allowed to grind discontinuously with 1,1,4,4-tetraphenylbutanetetraol for 3 h to afford the desired bicyclodiboronic ester (1*R*,6*R*)-**K** in 91% yield. A similar solvent-free reaction of (2*R*,3*R*)-1,1,4,4-tetra(*n*-butyl)butanetetraol with phenylboronic acid also gave bicyclodiboronic ester (1*R*,6*R*)-**L** in good yield. In fact, the solvent-free reaction is more efficient than that in solution for the preparation of bicyclodiboronic esters from 1,1,4,4-tetrasubstituted butanetetraols.

Preparation of the bicyclodiboronic esters via selective 1,3-cyclocondensation of (2*R*,3*R*)- and (2*S*,3*S*)-1,1,4,4-tetrasubstituted butanetetraols with $ArB(OH)_2$ is summarized in Scheme 3.

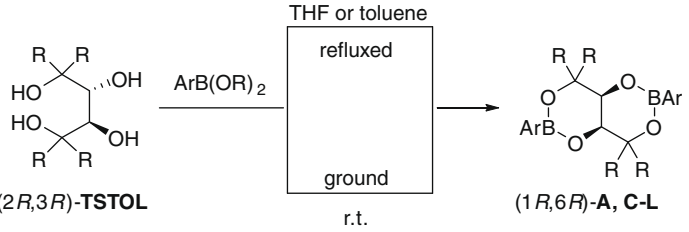
In addition, bicyclo[4.4.0]diboronic ester (1*R*,6*R*)-**K** was reduced by $LiAlH_4$, BH_3·L, or $NaBH_4$/MeOH according to conventional procedures to afford (1*R*,6*R*)-**M** (Scheme 4) in over 90% yield, mp 268–270 °C, $[\alpha]_D^{25} = +9.4$ (*c* 0.5, THF), meaning that bicyclo[4.4.0] diboronic esters could undergo functional group transformation without destroying the bicyclic framework.

The yields and physical properties of the newly synthesized chiral bicyclo[4.4.0]diboronic esters are shown in Table 1.

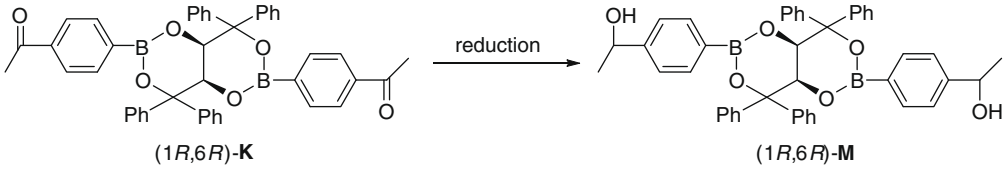
The successful preparation of the bicyclo[4.4.0]diboronic esters reveals that a highly regioselective 1,3-cyclocondensation occurs readily between the 1,1,4,4-tetrasubstituted butanetetraols and $ArB(OH)_2$.

2.2. Properties of chiral bicyclo[4.4.0]diboronic esters

All of the bicyclo[4.4.0]diboronic esters prepared are thermodynamically stable, white solids with high melting points. They are not decomposed by water and acidic or alkalic aqueous solution

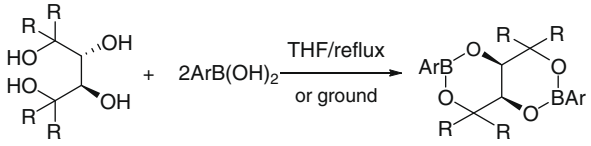


Scheme 3. Preparation of chiral hexasubstituted bicyclo[4.4.0]diboronic esters via reaction of chiral 1,1,4,4-tetrasubstituted butanetetraol with $ArB(OH)_2$. R = Ph Ar = C_6H_4 **A**, 4-BrC_6H_4 **C**, 3,5-$Br_2C_6H_3$ **D**, 3,5-$F_2C_6H_3$ **E**, 2-MeC_6H_4 **F**, 3-MeC_6H_4 **G**, 4-MeC_6H_4 **H**, 3-$MeOC_6H_4$ **I**, 1-$C_{10}H_7$ **J**, 4-$MeCOC_6H_4$ **K**. R = Bu, Ar = Ph **L**.



Scheme 4. Functional group transformation of bicyclo[4.4.0]diboronic ester (1*R*,6*R*)-**K**.

Table 1
Synthesis and physical properties of chiral hexasubstituted bicyclo[4.4.0]diboronic esters[a]



Entry	Compd	Ar	R	Yield (%)	Mp[b] (°C)	$[\alpha]_D$[c]	Chem. shift of the framework H[d]
1	(1*R*,6*R*)-**A**	C_6H_5	Ph	94	262–264	−6.0 (*c* 0.2, $CHCl_3$)	5.05 s[e]
2	(1*S*,6*S*)-**B**	C_6H_5	Ph	67	263–264	+5.9 (*c* 0.4, $CHCl_3$)	5.05 s
3	(1*R*,6*R*)-**C**	4-BrC_6H_4	Ph	86	270–271	+12.5 (*c* 1.2, THF)	5.04 s
4	(1*R*,6*R*)-**D**	3,5-$Br_2C_6H_3$	Ph	94	274–376	−20.0 (*c* 1.2, THF)	5.03 s
5	(1*R*,6*R*)-**E**	3,5-$F_2C_6H_3$	Ph	92	238–240	−18.3 (*c* 0.24, THF)	5.08 s
6	(1*R*,6*R*)-**F**	2-MeC_6H_4	Ph	82	238–239	+34.6 (*c* 1.3, THF)	5.14 s
7	(1*R*,6*R*)-**G**	3-MeC_6H_4	Ph	89	217–218	+15.6 (*c* 0.4, $CHCl_3$)	5.03 s
8	(1*R*,6*R*)-**H**	4-MeC_6H_4	Ph	91	245–247	+12.3 (*c* 1.3, THF)	5.01 s
9	(1*R*,6*R*)-**I**	3-$MeOC_6H_4$	Ph	94	177–179	−17.5 (*c* 1.6, THF)	5.08 s
10	(1*R*,6*R*)-**J**	1-$C_{10}H_7$	Ph	91	241–243	+49.5 (*c* 1.8, THF)	5.38 s
11	(1*R*,6*R*)-**K**	4-$MeCOC_6H_4$	Ph	91	300–302	+12.6 (*c* 1.2, THF)	5.11 s
12	(1*R*,6*R*)-**L**	C_6H_5	*n*-Bu	52	240–242	+10.8 (*c* 1.1, THF)	4.22 s

[a] All reactions were performed in refluxing THF for 2 h in a 2:1 molar ratio of $ArB(OH)_2$ and the tetraol except entries 11 and 12. (*R*,*R*)-**K** and(*R*,*R*)-**L** were prepared with discontinuous grinding at ambient temperature for several hours. (*S*,*S*)-**B** were prepared by (2*S*,3*S*)-1,1,4,4-tetraphenyltetraol according to a similar procedure to (*R*,*R*)-**A**. When (*R*,*R*)-**A** and (*S*,*S*)-**B** were prepared by phenylation of boron-protected dialkyl tartrate with PhMgBr and then treated with aq NH_4Cl, the desired products were obtained in medium yield.

[b] Melting points are uncorrected.

[c] *t* = 20–25 °C.

[d] The chemical shift of the protons at C(1) and C(6), ppm; $CDCl_3$ was used as solvent.

[e] The ^{11}B NMR spectra of (*R*,*R*)-**A** and (*S*,*S*)-**B** were determined, 27 ppm (300 MHz, $CDCl_3$, $F_3B{-}OEt_2$ = 0).

at ambient temperature. This high stability toward acidolysis and alkaline hydrolysis can be attributed to the hindered effect of the substituents and structural symmetry of the molecules. However, the bicyclic structure of these boron compounds could be destroyed by potassium fluorohydride or hydrofluoric acid.

The spectroscopic properties of all the bicyclodiboronic esters are similar. The solid IR spectra of them show strong B–O bond asymmetric stretching vibration for classical boronic esters at near 1330 cm^{-1}, and no O–H bond absorption was observed. The ^{11}B NMR spectra presented a singlet at near 27 ppm, meaning that both the boron atoms are equivalent. For all the compounds, the two protons bound to the stereogenic carbons exhibit a singlet resonance, which is located at 5.07 ± 0.07 ppm for the tetraaryltetraol derivatives except at 5.38 ppm for 1-naphthylboronic acid derivative (1*R*,6*R*)-**J** and at 4.22 ppm for (1*R*,6*R*)-**L** generated from 1,1,4,4-tetraalkylbutanetetraol, indicating that the protons at the stereogenic carbons are in the same environment, and their chemical shift is mainly influenced by the electronic property of the substituents at the vicinal carbons. In the ^{13}C NMR spectra, there are two singlet resonances at 81.5 ± 0.05 ppm and 70.0 ± 0.04 ppm for the four framework carbons; corresponding to the quarternary carbons [C(5) and C(10) in the bicycle] and the tertiary carbons [(C(1) and C(6) in the bicycle], respectively. The simplification of the bicycle framework resonances reveals their structural symmetry.

2.3. Crystal structure of bicyclo[4.4.0]diboronic esters

The composition and symmetric structure of bicyclo[4.4.0]diboronic esters have been proved by the X-ray crystallographic analyses. The crystal structure of (1*R*,6*R*)-**A**[20] and (1*R*,6*R*)-**I**,[21] which possess same and different substituents at the boron atoms and the carbon atoms of the bicyclic framework, respectively, is shown in Figure 1, and the crystallographic parameters are listed in Table 2.

It can be seen that for the tetraaryltetraol-derived bicyclodiboronic esters, the substituent in the aromatic ring determines the cell system and space group of the crystal. The bond distances and bond angles for the bicyclic framework show that all the B–O bond distances are near 1.36 Å, the C–O bond distances are near 1.43 Å. For the C–C bonds the distances are near 1.53 Å for (1*R*, 6*R*)-A, while the substituent in the aromatic ring leads to their inequivalence for (1*R*, 6*R*)-1. The opposite bonds and angles in the bicycle, for the diboronic esters, are nearly equal.

3. Conclusion

In conclusion, a series of hydrolytically stable tricoordinated chiral bicyclo[4.4.0]diboronic esters have been conveniently synthesized in high yield. Enantiopure 1,1,4,4-tetrasubstituted butanetetraols, which are generated from arylation or alkylation of (2*R*,3*R*)- and (2*S*,3*S*)-tartaric esters, react with arylboronic acids in THF or toluene at reflux conditions, or both reactants react under solvent-free conditions for several hours at ambient temperature to furnish hexasubstituted chiral bicyclo[4.4.0]diboronic esters in high yield via selective 1,3-cyclocondensation. For (1*R*,6*R*)- and (1*S*,6*S*)-hexaphenyl-substituted chiral bicyclodiboronic esters, (1*R*,6*R*)-**A** and (1*S*,6*S*)-**B** can also be prepared in moderate yield through phenylation of boron-protected enantiopure tartaric ester with PhMgBr and sequential acidolysis. All of the bicyclo[4.4.0]diboronic esters are stable to both common acidolysis and alkaline hydrolysis at ambient temperature.

4. Experimental

4.1. General

Enantiopure 1,1,4,4-tetrasubstituted butanetetraol: (2*R*,3*R*)-1,1,4,4-tetraphenylbutanetetraol, (2*S*,3*S*)-1,1,4,4-tetraphenylbutanetetraol, and (2*R*,3*R*)-1,1,4,4-tetra(*n*-butyl)butanetetraol were synthesized from diethyl (2*R*,3*R*)- or (2*S*,3*S*)-tartrate and PhMgBr or *n*-BuMgBr in THF in a conventional Grignard reaction procedure. The aromatic boronic acids were prepared through the reaction of tributyl borate with the corresponding ArMgBr according to the known methods. All reactions employing organometallic compounds were carried out under an argon atmosphere.

IR spectra were recorded on a *Nicolet 170 SX FT-IR* spectrophotometer, in KBr, ν in cm^{-1}. NMR spectra were recorded at 300 MHz for ^{1}H, 75 MHz for ^{13}C, and 32 MHz for ^{11}B, on a Varian Unity 300 spectrometer *Varian Mercury VS 300*; δ in (ppm) relative to TMS. Elemental analyses were determined on a *Perkin–Elmer 240 B* analyzer. Optical rotations: *Perkin–Elmer 241 Mc* polarimeter. Mp: *VEB Wagetechnik Rapio PHMK 05*; uncorrected.

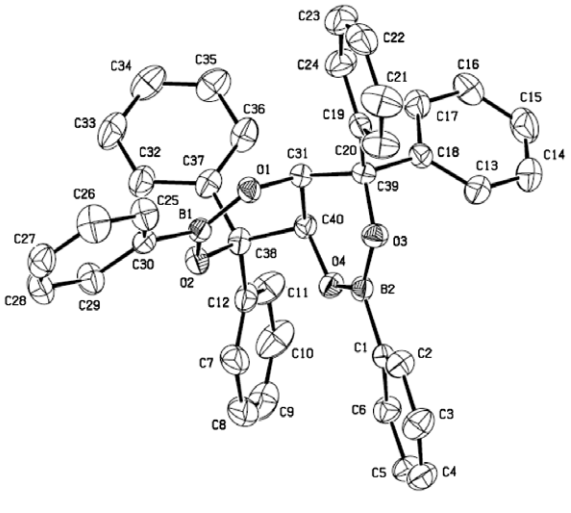
4.2. Synthesis of enantiopure bicyclo[4.4.0]diboronic esters

4.2.1. Synthesis of (1*R*,6*R*)-A or (1*S*,6*S*)-B from phenylboronic acid-protected diethyl (2*R*,3*R*)- or (2*S*,2*S*)-tartrate

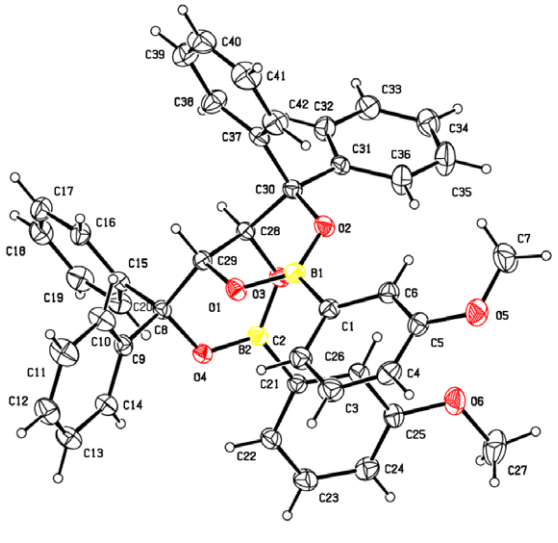
Phenylmagnesium bromide, which was prepared from Mg turnings (0.523 g, 21.78 mmol) and phenyl bromide (2.08 mL, 19.8 mmol) in anhydrous THF (20 mL) via a conventional manner, was cooled to 0 °C, followed by carefully adding dropwise the THF solution of the condensate of diethyl (2*R*,3*R*)- or (2*S*,2*S*)-tartrate (0.824 g, 4 mmol) with phenylboronic acid (0.49 g, 4 mmol). The mixture was stirred at 0 °C for 1 h, followed by warming to room temperature, and then heated at reflux and maintained for 1.5 h. After cooling to rt, 20 mL of saturated aqueous NH_4Cl was added with stirring. The organic layer was separated, and the aqueous layer was extracted with ether (3 × 15 mL). A yellow, viscous residue was obtained after the concentration of the combined extracts. Excess phenyl bromide was removed by azeotropic distillation in water, and the resulting solid residue was dissolved in hot ether, decolorized with activated charcoal, evaporated, and then the residue was recrystallized from EtOH to give white crystals of (1*R*,6*R*)-**A** or (1*S*,6*S*)-**B** in ca. 50% yield.

4.2.2. Preparation of (1*R*,6*R*)-A or (1*S*,6*S*)-B from alkyl borate-protected diethyl (2*R*,3*R*)- tartrate

A mixture of diethyl (2*R*,3*R*)- or (2*S*,3*S*)-tartrate (0.83 g, 4 mmol) with tributyl borate (0.95 g,. 4 mmol) was heated to ca. 140 °C, and



(1*R*,6*R*)-**A**



(1*R*,6*R*)-**I**

Figure 1. Crystal and molecular structure for (1*R*,6*R*)-**A** and (1*R*,6*R*)-**I**.

Table 2
Crystallographic data for (1*R*,6*R*)-**A**[20] and (1*R*,6*R*)-**I**[21]

*For (1R,6R)-**A***
Experiment formula, $C_{40}H_{32}B_2O_4$, M_w = 598.25, cell system, triclinic; space group, *P*1; cell three-dimensional size, *a* = 9.6051(13) Å, *b* = 9.9781(13) Å, *c* = 10.4687(14) Å; α = 111.552(2)°, β = 90.165(2)°, γ = 108.708(2)°; *V* = 875.5(2) Å^3; *Z* = 1; *F*(0 0 0) = 340; λ = 0.71073; −12 < *h* < 12; −12 < *k* < 10; −13 < *l* < 13; absolute structure Flack = 0.0(13); GOF = 1.066; *T* = 273(2) K; μ(Mo Kα) = 0.078 mm^{-1}; *R*(reflections) = 0.0773 (3688); wR_2 (reflections) = 0.1654 (4840).
*For (1R,6R)-**I***
Experiment formula, $C_{42}H_{36}B_2O_6$, *M*w = 658.33; cell system, monoclinic; space group, *P*2(1); cell three-dimensional size, *a* = 9.4467(10); *b* = 19.702(2); *c* = 9.6622(11); β = 98.899(2); *V* = 1776.6(3) Å^3; *Z* = 2; *F*(0 0 0) = 692; *T* = 273(2) K; λ = 0.71073; −9 < *h* < 11; −24 < *k* < 24; −10 < *l* < 12; absolute structure Flack = −0.2(7); GOF = 1.011; *T* = 273(2) K; μ(Mo Kα) = 0.080 mm^{-1}; *R*(reflections) = 0.0367 (5371); wR_2 (reflections) = 0.0847 (7213).

the temperature maintained until *n*-butanol had been completely liberated; liquid (4*R*,5*R*)- or (4*S*,5*S*)-2-ethoxyl-4,5-bis(ethoxycarbonyl)-1,3,2-dioxaborolane was obtained almost quantitatively. To it was added anhydrous THF, after which it was dissolved, and the THF solution was added dropwise to a PhMgBr THF solution freshly prepared from Mg turnings (0.63 g, 26 mmol) and phenyl bromide (2.5 mL, 23.8 mmol). After the reaction and treatment according to the same procedure as above, white crystals of (1*R*,6*R*)-**A** or (1*S*,6*S*)-**B** were obtained in medium yield.

4.2.3. A representative procedure for the preparation of chiral bicyclic diboronic ester from enantiopure 1,1,4,4-tetrasubstituted butanetetraols

4.2.3.1. Method A. 3-Methoxyphenylboronic acid (1.140 g, 1 mmol) was mixed with (2*R*,3*R*)-1,1,4,4-tetraphenylbutanetetraol (0.213 g, 0.5 mmol) in THF (6 mL). The mixture was refluxed with stirring for 3 h, and then cooled to room temperature. To it was added saturated aq NH_4Cl with stirring. The mixture was extracted with Et_2O (10 mL × 3), the extracts combined, dried over anhydrous sodium sulfate, evaporated, and then recrystallized in ethanol to furnish white crystals of (1*R*,6*R*)-5,5,10,10-tetraphenyl-3,8-bis(3-methoxyphenyl)-2,4,7,9-tetraoxa-3,8-diborobicyclo[4.4.0]-decane [(1*R*,6*R*)-**I**, 0.309 g], 94% yield; mp 177–179 °C; $[\alpha]_D^{20}$ = −17.5 (*c* 0.16, THF).

4.2.3.2. Method B. 4-Acetylphenylboronic acid (0.082 g, 0.5 mmol) was mixed with (2*R*,3*R*)-1,1,4,4-tetraphenyl-butanetetraol (0.106 g, 0.25 mmol) in a carnelian mortar and ground at ambient temperature for 2 h, after which it was recrystallized in ethanol to afford white crystals of (1*R*,6*R*)-5,5,10,10-tetraphenyl-3,8-bis(4-acetylphenyl)-2,4,7,9-tetraoxa-3,8-diborobicyclo[4.4.0]decane [(1*R*,6*R*)-**K**, 0.309 g], 91% yield; mp 300–302 °C; $[\alpha]_D^{20}$ = +12.6 (*c* 0.12, THF).

4.2.4. Data of chiral bicyclic diboronic esters

4.2.4.1. (1*R*,6*R*)-3,5,5,8,10,10-hexaphenyl-2,4,7,9-tetraoxa-3,8-diborobicyclo[4.4.0]decane (1*R*,6*R*)-A. Yield, 94%; mp 264–265 °C; $[\alpha]_D^{20}$ = −5.5 (*c* 0.3, $CHCl_3$); IR (KBr, cm^{-1}): *v* 3019, 2947, 1601, 1437, 1328; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.82-7.22 (m, 30H, Ar-H), 5.05 (s, 2H,C-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.8, 142.7, 134.6, 131.5, 129.3, 128.3, 128.2, 127.9, 127.5, 126.7, 125.5, 81.3, 69.7. ^{11}B NMR ($CDCl_3$, 32 MHz, F_3B–OEt_2 = 0): δ +27.0. ESI-MS (*m*/*z*): 600, 511, 487, 423, 339, 255, 227. HRMS (EI, *m*/*z*): 616.28440; Calcd for $C_{40}H_{36}B_2NO_4$, 616.28382.

4.2.5. (1*S*,6*S*)-B {(1*R*,6*R*)-3,5,5,8,10,10-hexaphenyl-2,4,7,9-tetraoxa-3,8-diborobicyclo[4.4.0]decane}

Yield, 75%; mp 263–264 °C; $[\alpha]_D^{20}$ = +5.9 (*c* 0.4, $CHCl_3$); IR (KBr, cm^{-1}): *v* 3019, 2947, 1601, 1437, 1328; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.81–7.27 (m, 30H, Ar-H), 5.05 (s, 2H, C–H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.8, 142.7, 134.6, 131.5, 129.3, 128.3, 128.2, 127.9, 127.5, 126.7, 125.5, 81.3, 69.7. ^{11}B NMR ($CDCl_3$, 32 MHz, F_3B–OEt_2 = 0): δ +27.0.

4.2.6. (1*R*,6*R*)-C {(1*R*,6*R*)-5,5,10,10-Tetraphenyl-3,8-bis(4-bromophenyl)-2,4,7,9-tetraoxa-3,8-diboro-bicyclo[4.4.0]decane}

Yield, 86%; mp 270–271 °C; $[\alpha]_D^{20}$ = +12.5 (*c* 0.12, THF); IR (KBr, cm^{-1}): *v* 2954, 1588, 1396, 1364, 1297, 1010, 701; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.64–7.26 (m, 30H, Ar-H), 5.04 (s, 2H, C–H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.4, 142.3, 136.1, 131.1, 129.3, 128.4, 128.2, 127.6, 126.5, 125.2, 81.3, 69.7. ESI-MS (*m*/*z*): 787 (M_{756}+31), 722, 626, 623,356. HRMS (EI, *m*/*z*): Calcd for $C_{40}H_{34}B_2Br_2NO_4$, 774.10322. Found: 774.10483.

4.2.7. (1*R*,6*R*)-5,5,10,10-Tetraphenyl-3,8-bis(3,5-dibromophenyl)-2,4,7,9-tetraoxa-3,8-di-borobicyclo[4.4.0]decane (1*R*,6*R*)-D

Yield, 94%; mp 274–276 °C; $[\alpha]_D^{20}$ = −20 (*c* 0.12, THF); IR (KBr, cm^{-1}): 2430, 1654, 1384, 839, 697, 622. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.80–7.26 (m, 26H, Ar-H), 5.03 (s, 2H, C–H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.2, 142.9, 136.7, 135.5, 129.9, 128.9, 128.6, 127.8, 126.6, 125.5, 123.4, 81.9, 70.0. ESI-MS (*m*/*z*): 945 (M_{914}+31), 701, 669, 645, 365, 339. Calcd for $C_{40}H_{28}B_2Br_4O_4$, 914.

4.2.8. (1*R*,6*R*)-5,5,10,10-Tetraphenyl-3,8-bis(3,5-difluorophenyl)-2,4,7,9-tetraoxa-3,8-di-borobicyclo[4.4.0]decane (1*R*,6*R*)-E

Yield, 92%; mp 238–240 °C; $[\alpha]_D^{20}$ = −18.3 (*c* 0.24, THF); IR (KBr, cm^{-1}): 3090, 2968, 1588, 1430, 1384, 1250, 1167, 985, 871, 698, 622. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56–6.82 (m, 26H, Ar-H), 5.08 (s, 2H, C–H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.8, 162.2, 143.1, 141.8, 129.4, 128.5, 128.3, 127.8, 126.4, 125.2, 116.5, 106.9, 81.5, 69.9. ESI-MS (*m*/*z*): 691 (M_{668}+23), 579, 547, 457, 357, 243, 217. Calcd for $C_{40}H_{28}B_2F_4O_4$: 668.

4.2.9. (1*R*,6*R*)-5,5,10,10-Tetraphenyl-3,8-bis(2-methylphenyl)-2,4,7,9-tetraoxa-3,8-diboro-bicyclo[4.4.0]decane (1*R*,6*R*)-F

Yield, 82%; mp 238–239 °C; $[\alpha]_D^{20}$ = +34.6 (*c* 0.13, THF); IR (KBr, cm^{-1}): 3062, 2950, 1598, 1450, 1384, 1317, 1277, 698, 625. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.98–7.03 (m, 28H, Ar-H), 5.14 (s, 2H, C–H); 2.15(s, 3H, Ar-C–H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.7, 145.4, 144.0, 143.0, 135.9, 131.0, 130.3, 129,3, 128.2, 128.1, 127.2, 126.2, 125.1, 125.0, 81.5, 69.7, 22.9. ESI-MS (*m*/*z*): 657 (M_{626}+31), 547, 525, 393, 365, 316. Calcd for $C_{42}H_{36}B_2O_4$, 626.

4.2.10. (1*R*,6*R*)-5,5,10,10-Tetraphenyl-3,8-bis(3-methylphenyl)-2,4,7,9-tetraoxa-3,8-diboro-bicyclo[4.4.0]decane (1*R*,6*R*)-G

Yield, 89%; mp 217–218 °C; $[\alpha]_D^{20}$ = −12.6 (*c* 0.12, THF); IR (KBr, cm^{-1}): 3028, 2952, 1604, 1581, 1492, 1449, 1383, 1208, 1130, 823, 750, 696, 623; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65–7.24 (m, 28H, Ar-H), 5.03 (s, 2H, C–H), 2.33 (s, 3H, Ar-C–H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.7, 142.6, 137.4, 137.1, 135.2, 132.2, 131.6, 129.2, 128.9, 128.5, 128.2, 128.1, 127.8, 127.5, 127.1, 126.9, 126.0, 125.5, 81.1, 69.6, 21.7. HRMS (EI, *m*/*z*): Calcd for $C_{42}H_{40}B_2NO_4$, 644.31517; found: 644.31589.

4.2.11. (1*R*,6*R*)-5,5,10,10-tetraphenyl-3,8-bis(4-methylphenyl)-2,4,7,9-tetraoxa-3,8-diboro-bicyclo[4.4.0]decane (1*R*,6*R*)-H

Yield, 91%; mp 245–247 °C; $[\alpha]_D^{20}$ = +12.3 (*c* 0.13, THF); IR (KBr, cm^{-1}): 3028, 2953, 1612, 1494, 1450, 1332, 1298, 1183, 1139, 701,

654, 623. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.70–7.10 (m, 28H, Ar-H), 5.01 (s, 2H, C–H), 2.32 (s, 3H, Ar-C–H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.8, 142.7, 141.5, 134.6, 129.2, 128.6, 128.1, 128.0, 127.3, 126.7, 125.4, 81.0, 69.6, 21.9. ESI-MS (m/z): 657 (M_{626}+31), 561, 525, 393, 316. Calcd for $C_{42}H_{36}B_2O_4$: 626.

4.2.12. (1*R*,6*R*)-5,5,10,10-Tetraphenyl-3,8-bis(3-methoxyphenyl)-2,4,7,9-tetraoxa-3,8-diboro-bicyclo[4.4.0]decane (1*R*,6*R*)-I

Yield, 94%; mp 177–179 °C; $[\alpha]_D^{20} = -17.5$ (c 0.16, THF); IR (KBr, cm^{-1}): 3062, 2953, 1575, 1487, 1450, 1384, 1334, 1295, 1232, 1047, 746, 701, 621. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65–6.96 (m, 28H, Ar-H), 5.08 (s, 2H, C–H), 3.75 (s, 3H, O–C–H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.1, 143.6, 142.6, 129.3, 129.0, 128.3, 128.1, 127.4, 126.9, 126.7, 125.5, 118.8, 117.7, 81.2, 69.7, 55.3. ESI-MS (EI, m/z): 689 (M_{658}^++31), 573, 541, 437, 393, 365, 325, 255, 237. Calcd for $C_{42}H_{36}B_2O_6$: 658.

4.2.13. (1*R*,6*R*)-5,5,10,10-Tetraphenyl-3,8-bis(1-naphthyl)-2,4,7,9-tetraoxa-3,8-diboro-bicyclo[4.4.0]decane (1*R*,6*R*)-J

Yield, 91%; mp 241–245 °C; $[\alpha]_D^{20} = +49.5$ (c 0.18, THF); IR (KBr, cm^{-1}): 3059, 1713, 1575, 1508, 1450, 1384, 1309, 1252, 1210, 779, 697, 623. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.36–7.02 (m, 34H, Ar-H), 5.38 (s, 2H, C–H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.8, 143.0, 137.1, 135.7, 134.9, 133.4, 132.0, 129.4, 128.6, 128.5, 128.4, 128.3, 127.4, 126.7, 126.3, 126.2, 125.3, 125.2, 81.7, 70.4. ESI-MS (m/z): 729 (M_{698}^++31), 717, 652, 451, 437, 409, 377, 341, 281, 255. Calcd for $C_{48}H_{36}B_2O_4$: 698.

4.2.14. {(1*R*,6*R*)-5,5,10,10-Tetraphenyl-3,8-bis(4-acetylphenyl)-2,4,7,9-tetraoxa-3,8-diboro-bicyclo[4.4.0]decane (1*R*,6*R*)-K

Yield, 91%; mp 295–299 °C; $[\alpha]_D^{20} = +12.6$ (c 0.12, THF) IR (KBr, cm^{-1}): 3024, 1686, 1632, 1384, 1329, 1268, 704, 653, 623; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.93–7.30 (m, 28H, Ar-H), 5.11 (s, 2H, C–H), 2.57 (s, 6H, C–H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 198.7, 143.3, 142.2, 139.3, 134.7, 129.4, 128.4, 128.3, 127.7, 127.5, 126.5, 125.3, 81.5, 69.8, 27.0. ESI-MS (m/z): 700 (M_{682}+18), 699, 585, 553, 443. Calcd for $C_{44}H_{36}B_2O_6$: 682.

4.2.15. {(1*R*,6*R*)-5,5,10,10-Tetra(*n*-butyl)-3,8-diphenyl-2,4,7,9-tetraoxa-3,8-diborobicyclo-[4.4.0]decane (1*R*,6*R*)-L

Yield, 52%; mp 240–242 °C; $[\alpha]_D^{20} = +10.8$ (c 0.11, THF); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76 (d, J = 6.6 Hz, 4H, Ar-H), 7.36–7.25 (m, 6H, Ar-H), 4.22 (s, 2H), 2.04–1.94 (m, 4H), 1.59–1.25 (m, 20H), 1.04–0.93 (m, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 133.8, 130.5, 127.3, 77.5, 68.1, 36.2, 33.0, 25.5, 25.1, 23.2, 23.1.

4.2.16. {(1*R*,6*R*)-5,5,10,10-Tetraphenyl-3,8-bis(4–hydroxyethylphenyl)-2,4,7,9-tetraoxa-3,8-diborobicyclo[4.4.0]decane} (1*R*,6*R*)-M

Yield, 98%; mp 268–270 °C. $[\alpha]_D^{20} = +9.4$ (c 0.5, THF); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, J = 6.6 Hz, 4H, Ar-H), 7.60 (d, J = 6.6 Hz, 4H, Ar-H); 7.41–7.27 (m, 24H, Ar-H), 5.04 (s, 2H, 2C–H), 4.85 (q, J = 6.6 Hz, 2H), 1.44 (d, J = 6.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.2, 143.7, 142.6, 134.9, 129.3, 128.3, 128.2, 127.5, 126.7, 125.5, 124.9, 81.2, 70.8, 70.7, 69.7, 25.4.

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19. A representative procedure for the direct preparation of chiral 1,1,4,4-tetrasubstituted butanetetraols (**TSTOL**) from enantiopure dialkyl tartrates: 1-phenylmagnesium bromide, which was prepared from Mg turnings (6.65 g, 277 mmol) and 1-bromobenzene (35 mL, ca. 251 mmol) in THF (100 mL) according to conventional procedure, was cooled to 0 °C, followed by adding dropwise the solution of diethyl (2*S*,3*S*)-tartrate (6.18 g, 30 mmol) in 10 mL anhydrous THF with vigorous stirring. After complete addition, the reaction solution was warmed to room temperature, continued to stir for one hour, and then heated and refluxed for another 2 h, cooled to rt, 200 mL of cooled saturated aqueous NH_4Cl was added with stirring. The organic layer was separated, and the aqueous layer extracted with diethyl ether (3 × 15 mL). The organic phases were combined and dried over anhydrous Na_2SO_4. A yellow, viscous residue was obtained after concentration of the organic solution. The residue was purified through column chromatography on silica gel to give white crystals of (2*S*,3*S*)-1,1,4,4-tetraphenylbutanetetraol (**TPTOL**), 48% yield, mp 149–150 °C; $[\alpha]_D^{25} = -156.6$ (c 1.1, $CHCl_3$); IR (KBr): 3437, 3058, 2916, 1598, 1492, 1447, 1062, 698; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37–7.13 (m, 20H, Ar-H), 4.63 (d, 2H, J = 4.8 Hz, OH, disappeared after adding D_2O), 4.42 (d, 2H, J = 4.5 Hz, CH), 3.69 (d, 2H, J = 4.8 Hz, OH, disappeared after adding D_2O). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.8, 142.7, 134.6, 131.5, 129.3, 128.3, 128.2, 127.9, 127.5, 126.7, 125.5, 81.1, 69.7.
20. The data can be obtained (CCDC 299938), free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
21. The crystallographic data can be obtained (CCDC 687725), free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).