(2*R*,3*R*)-1,4-Dimethoxy-1,1,4,4-tetraphenyl-2,3-butanediol: Chiral Auxiliary and Efficient Protecting Group for Boronic Acids

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(2*R*,3*R*)-1,4-Dimethoxy-1,1,4,4-tetraphenyl-2,3-butanediol (**1**) has been used as an efficient chiral auxiliary in the cyclopropanation of alkenylboronic esters. The stability of the obtained cyclopropylboronic esters allowed the chromatographic separation of the diastereoisomers. Furthermore, it enabled a variety of transformations in the side-chain, including oxidation, reduction, and reactions under acidic, basic, or radical conditions, that finally led to boron containing functionalized bicyclopropanes, e.g., **12** and **18**. The absolute configurations of these building blocks were established by X-ray crystallography (compound **10**) and by chemical correlation. The Matteson homologation led to a known advanced intermediate of the oligocyclopropane FR-900848.

Introduction

Cyclopropylboronic esters have frequently been reported to be ideal building blocks for cyclopropane chemistry. Especially the broad synthetic potential of the boron moiety has been noted, although the focus has been on Suzuki couplings[1] and transformations to cyclopropanols.[2] The use of chiral auxiliaries, first reported by Imai et al.,[2b] finally led directly[2d] or indirectly[2e] to enantiomerically pure 1,2-*trans*-disubstituted cyclopropanes. *cis*-Cyclopropylboronic esters were reported only recently, thus closing a gap.[2f] Despite the dramatic developments since the first successful reports about the synthesis of these intermediates,[1−3] most investigations have usually been limited to simple model compounds. This changed with the introduction of the new chiral auxiliary **1**.[4,1g] Due to the high stability of the boronic esters, it was not only possible to separate the diastereomeric cyclopropylboronic esters **2** for the first time,[2d] but also to perform simple deprotections in the side-chain.[1g,2f] An example is the simple desilylation[5] of alkenylboronic ester **3**—obtained in one step by direct hydroboration of the corresponding protected propargyl alcohol in 91% yield—giving alcohol **4** in high yield (Figure 1).[1g,6] This sequence has been performed on a multigram scale (30 g). In view of the high interest in oligocyclopropanes in general,[7] and in natural products such as the antifungal compound FR-900848[8] or the cholesteryl ester transfer protein inhibitor U-106305[9] in particular, we thought to extend our method to bicyclopropanes. For a selective and general approach, the diol **1** (or its enantiomer) should guarantee two features: (a)

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(6) On a large scale a regioisomer **4a** (see Supporting Information) could be isolated in 1% yield, proving that the hydroboration giving alkenylboronic ester **3** was not completely regioselective.

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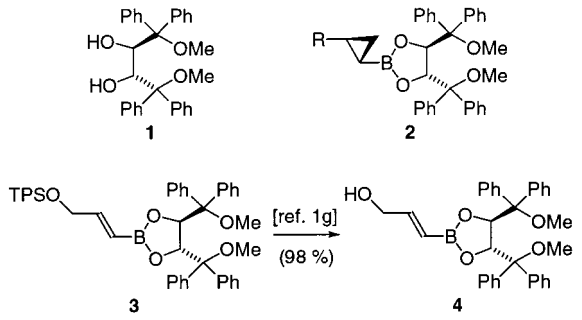
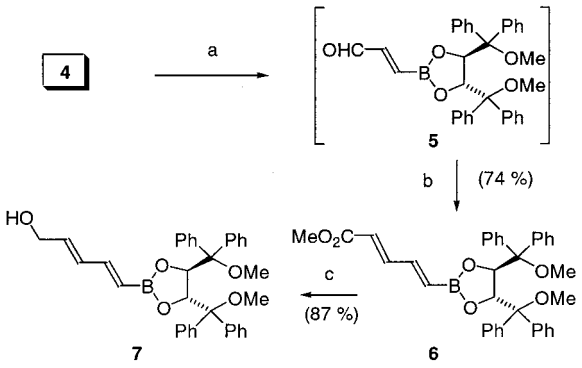


Figure 1. Transformations in the side-chain of cyclopropylboronic esters.

Scheme 1[a]



[a] Reagents: (a) cat. TPAP, NMO, CH_2Cl_2; (b) NaH, THF, $MeO_2CCH_2P(=O)(OMe)_2$; (c) DIBAL-H, THF, −78 °C to room temperature.

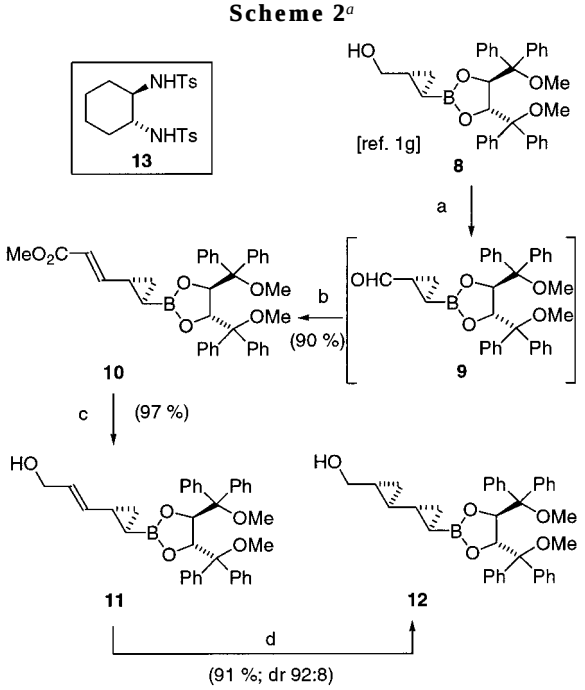
The chiral auxiliary should lead to high diastereomeric ratios in the cyclopropanation step and (b) it should fulfill all requirements of a good protecting group for boronic acids. It is already known that the introduction of diol **1** and the cleavage of boronic esters such as **2** is possible, and in this contribution we intend to answer the question about the limits of possible transformations without interfering with the boron moiety.

Results and Discussion

First of all, we examined simple chain-elongations starting with alkenylboronic ester **4** (Scheme 1). Oxidation, either using the Dess−Martin conditions[10] (64%) or, in this case preferentially, with the Ley reagent,[11] led to smooth formation of aldehyde **5**. No side-product was detected. Horner−Wadsworth−Emmons reaction[12] gave a clean transformation to diene **6** in 74% overall yield. The selectivity of the reduction is remarkable: Although prolonged reaction time with an excess of DIBAL-H is inadvisable since formation of diol **1** would be detected, the carboxylic ester reacts much faster than this boronic ester. By thoroughly following the reaction by TLC, we found that alcohol **7** was the only product obtained. First attempts to perform selective cyclopropanations failed. Only complex, inseparable mixtures of mono- and dicyclopropanated diastereoisomers were detected. In view of some recent work on Diels−Alder reactions of boron-containing dienes,[13] compounds **6** and **7** could be of considerable interest.

Next, we followed the same sequence starting with the enantiomerically pure cyclopropylboronic ester **8** that we obtained by selective cyclopropanation of **4** using the Denmark conditions.[14,1g] The absolute configuration had been deduced by characteristic NMR data. At this stage we could confirm, after oxidation to aldehyde **9** and reaction with trimethyl phosphonoacetate to ester **10** (90% over two steps), the assignment (Scheme 2): The X-ray structure analysis (see supporting material) unambiguously proved our prediction. The DIBAL-H reduction to allyl alcohol **11** was again a high-yielding process. Obviously, these transformations were also possible for the diastereoisomeric series (**8a** to **11a**; see Supporting Information). Cyclopropanation led predominantly to bicyclopropane **12** (91% yield as a separable 92:8 diastereoisomeric mixture; minor diastereoisomer: **12a**) when substoichiometric amounts of bis(sulfonamide) **13** were used as a chiral ligand. A low selectivity (**12**:**12a**, 45:55) was obtained in the mismatched case utilizing enantiomer *ent*-**13**.

Scheme 2[a]



[a] Reagents: (a) cat. TPAP, NMO, CH_2Cl_2; (b) NaH, THF, $MeO_2CCH_2P(=O)(OMe)_2$; (c) DIBAL-H, THF, −78 °C to room temperature; (d) i. cat. **13**, Et_2Zn, CH_2Cl_2; ii. ZnI_2, CH_2Cl_2; iii. CH_2I_2, Et_2Zn, CH_2Cl_2.

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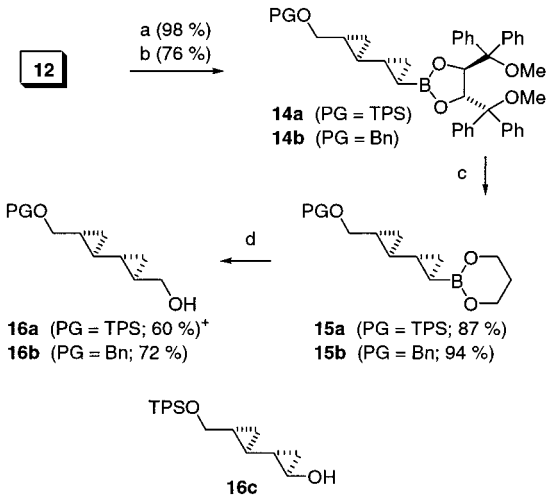
(14) Denmark, S. E.; O'Connor, S. P. *J. Org. Chem.* **1997**, *62*, 3390−3401. On a large scale we improved the yield and selectivity for the formation of cyclopropane **8**: 94% yield, dr 91:9.

Scheme 3[a]

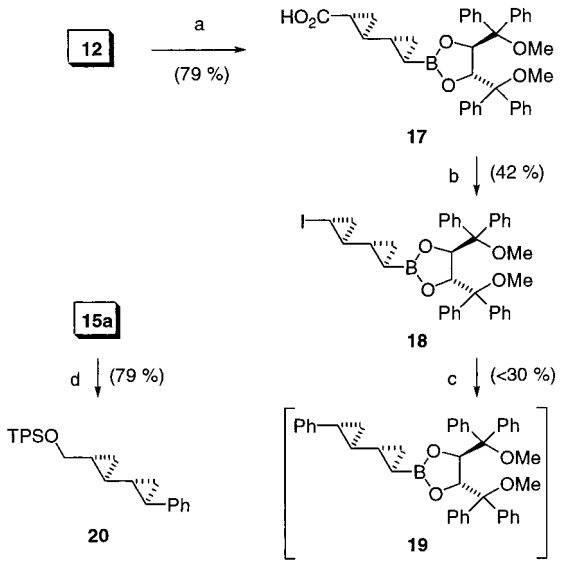


[a] Reagents: (a) TPS-Cl, imidazole, CH_2Cl_2; (b) BnBr, NaH, DMF; (c) i. $LiAlH_4$, THF, ii. NH_4Cl, iii. 1,3-propanediol; (d) i. $ClCH_2Li$, THF, −78 °C to room temperature, ii. 30% $H_2O_2/KHCO_3$. [+] Yield over two steps starting from **14a**.

Although we were confident that the assignment of the configuration for the second cyclopropane was correct, we needed some proof, especially since the NMR data were not very meaningful. We envisaged to perform a simple Matteson homologation[15] in order to synthesize a known optically pure bicyclopropane. Not surprisingly, the direct transformation of compound **12** was not successful. We did only recover the starting material. Unfortunately, all attempts to isolate the corresponding boronic acid also failed when the hydroxy group was not protected. Introduction of a silyl or a benzyl protecting group was straightforward (Scheme 3), furnishing compounds **14a** and **14b**, respectively. Again, the boronic ester remained untouched. The following transesterifications to the dioxaborinanes **15a** (87%) and **15b** (94%) were unproblematic, when using our standard procedure: formation of the corresponding alkylborohydride with $LiAlH_4$, hydrolysis with aqueous NH_4Cl, and condensation with 1,3-propanediol.[1g] Homologation with chloromethyllithium and subsequent oxidation with 30% $H_2O_2/KHCO_3$ led to the desired products **16a** (60% over two steps) and **16b** (72%; 68% over two steps), respectively. In full agreement to the observation made by Ren and Crudden,[16] we noted no sequential insertion with this reagent. In the case of the silyl-protected alcohol, we could also isolate 13% of the corresponding cyclopropanol **16c** as the only side-product. All analytical data of the known optically pure bicyclopropane **16a** were in full agreement to reported data,[8e] thus confirming that the diastereoselective cyclopropanation did not lead to the *anti* compound.[7a]

Since the oxidation to aldehydes worked well and without side-reaction at the boronic ester moiety, we were optimistic that the ruthenium-catalyzed oxidation of alcohol **12** to carboxylic acid **17** would be unproblematic. Indeed, we obtained the desired compound in 79% yield (Scheme 4). This was our starting material to test, whether the protecting group (diol **1**) would sufficiently

Scheme 4[a]



[a] Reagents: (a) $NaIO_4$, cat. $RuCl_3$; (b) 2-mercaptopyridine *N*-oxide, DCC, DMAP, cyclohexene, CHI_3, reflux; (c) $PhB(OH)_2$, $Pd(PPh_3)_4$, KO*t*Bu, DME, reflux; (d) PhI, $Pd(PPh_3)_4$, KO*t*Bu, DME, reflux.

stabilize the cyclopropylboronic ester during radical reactions. In our hands, the thermal decarboxylation of the corresponding Barton thiohydroxamic ester[17] in the presence of iodoform was the best condition. This furnished the iodocyclopropane **18**, albeit in relatively low yield (42%; ~10:1 mixture of *trans*:*cis* isomer). Nevertheless, our findings indicate that not the radical reaction itself was problematic, but the formation of some unidentified side-products during the synthesis of the Barton ester. We further speculated that the difunctionalized bicyclopropane **18** should be an ideal intermediate for a variety of consecutive transformations. A Suzuki coupling of the iodide with boronic acids followed by deprotection of our boronic ester and, for example, another Suzuki coupling with a halide, was an attractive goal. Unfortunately, we did not yet succeed to find ideal conditions for a useful protocol. Coupling with phenylboronic acid led to an inseparable mixture of three compounds. Mass spectrometry (FAB, NBA+NaI) showed the presence of some starting material **18** (*m*/*z* 693 [(M + Na)$^+$]), the corresponding reduction product (*m*/*z* 567 [(M + Na)$^+$], presumably formed after the hydrolysis of the palladium intermediate) and product **19** (*m*/*z* 643 [(M + Na)$^+$]). The phenylboronic acid was consumed (formation of product and likely benzene). Obviously the oxidative addition of palladium(0) proceeded, but was a very slow process in the presence of the bulky boronic ester. With a less bulky palladium intermediate, formed for instance during the coupling of dioxaborinane **15a** with phenyl iodide, the desired product **20** was readily formed (79%). Although these findings were not completely comparable, with the boronic esters derived from 1,3-propanediol being more reactive than the initial boronic acids,[1c] we believe that the reductive elimination was the limiting step. We are currently investigating whether, by changing the order of events, the key intermediate **12** could become a more

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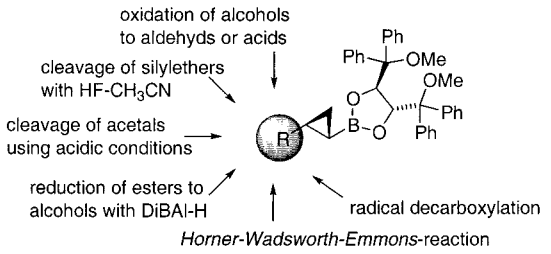

Figure 2. Diol **1**: Chiral auxiliary and protecting group for boronic acids.

general building block for the synthesis of bicyclopropanes.

Conclusion

We demonstrated that diol **1** qualifies as an efficient protecting group for boronic acids. Highly stable dienyl- and bicyclopropylboronic esters have been synthesized from readily available alkenylboronic ester **4** by a variety of transformations (Figure 2) in the side-chain of the boronic ester. Deprotection was achieved with $LiAlH_4$, followed by aqueous workup and condensation with 1,3-propanediol. The 1,3,2-dioxaborinanes were successfully used for CC-bond forming reactions such as the Suzuki coupling or the Matteson homologation. This last reaction also allowed the unambiguous assignment of the absolute configuration of the synthesized bicyclopropanes by comparison of our results with literature data.

Experimental Section

General. All reagents were used as purchased from commercial suppliers without further purification. The reactions were carried out using standard Schlenk techniques under a dry nitrogen atmosphere. Glassware was oven-dried at 150 °C overnight. Solvents were dried and purified by conventional methods prior to use; diethyl ether and THF were freshly distilled from sodium/benzophenone. Flash-column chromatography: Merck silica gel 60, 0.040−0.063 mm (230−400 mesh). TLC: Precoated sheets, Alugram SIL G/UV_{254} Macherey-Nagel; detection by UV extinction or by cerium molybdenium solution [phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), concentrated H_2SO_4 (60 mL), H_2O (940 mL)]. Preparative MPLC: Packed column (49 × 500 mm), LiChroprep, Si60 (15−25 μm), and UV detector (259 nm). ^1H and ^{13}C signals were assigned by means of C−H and H−H COSY spectra. Microanalysis: Performed at the Institut für Organische Chemie, Stuttgart.

Preparation of (4*R*,5*R*)-2-[(1*E*,3*E*)-4-Methoxycarbonyl-1,3-butadien-1-yl]-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane 6. To a stirred solution of alkenylboronic ester **4** (3.05 g, 5.86 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added *N*-methylmorpholine *N*-oxide (872 mg, 6.45 mmol), 4 Å molecular sieves (5.0 g), and tetra-*n*-propylammonium perruthenate (103 mg, 0.29 mmol). Stirring was continued at room temperature for 12 h (TLC indicated complete consumption of the starting material). Filtration through Celite and silica gel (CH_2Cl_2) followed by evaporation of the solvent under reduced pressure gave the crude aldehyde **5** which was directly used without further purification.

Trimethyl phosphonoacetate (1.17 g, 6.45 mmol) was added to a suspension of NaH (258 mg, 6.45 mmol, 60% in paraffin) in THF (50 mL) at 0 °C. After 1 h the mixture was treated with a solution of aldehyde **5** in THF (10 mL). Stirring was continued for 12 h at room temperature. The crude product was obtained after addition of saturated aqueous NH_4Cl solution, extraction of the aqueous layer with Et_2O, washing of the combined organic layer with brine, drying over anhydrous $MgSO_4$, and evaporation of the solvent. Flash-column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (85:15), yielded a colorless foam (2.50 g, 4.35 mmol, 74%).

Softening range = 80−86 °C; $[\alpha]^{20}_D = +15$ (*c* 0.3, $CHCl_3$); IR (film) 3080, 1719 cm^{-1}; MS [FAB, NBA+NaI] *m*/*z* 597 (15) [$(M + Na)^+$], 197 (65) [$(Ph_2COCH_3)^+$], 176 (100); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.98 (s, 6 H, OCH_3), 3.69 (s, 3 H, CO_2CH_3), 5.35 (s, 2 H, 4-H/5-H), 5.83 (dd, J = 17.6, 0.8 Hz, 1 H, 1′-H), 6.13 (dd, J = 15.4, 0.8 Hz, 1 H, 4′-H), 6.88 (ddd, J = 17.6, 11.0, 0.8 Hz, 1 H, 2′-H), 7.36 (ddd, J = 15.4, 11.0, 0.8 Hz, 1 H, 3′-H), 7.24−7.32 (m, 20 H, Ar-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 51.7 (CO_2CH_3), 51.8 (OCH_3), 77.8 (C-4/C-5), 83.3 (CPh_2OCH_3), 123.6 (C-4′), 127.3, 127.4, 127.6, 127.9, 128.4, 129.7, 140.9, 141.1 (Ar−C), 145.4 (C-3′), 145.6 (C-2′), 167.1 (CO_2CH_3), (C-1′ not detected). Anal. Calcd for $C_{36}H_{35}BO_6$ (574.47): C, 75.27; H, 6.14. Found: C, 75.22; H, 6.28.

Preparation of (4*R*,5*R*)-2-[(1*E*,3*E*)-5-Hydroxy-1,3-pentadien-1-yl]-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane 7. DIBAL-H (4.2 mL of a 1 M solution in hexane, 4.2 mmol) was added to a stirred solution of ester **6** (804 mg, 1.40 mmol) in THF (14 mL) at −78 °C. The reaction mixture was slowly (over 2 h) warmed to room temperature; at this point TLC indicated complete consumption of the starting material. Addition of H_2O (0.5 mL), NaOH (1 mL of a 2 M solution in H_2O), and again H_2O (0.5 mL) led to a precipitate that was separated by filtration. The solid was thoroughly washed with Et_2O. The crude product was obtained after evaporation of the solvent under reduced pressure. Flash-column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (95:5 to 80:20), yielded a colorless foam (660 mg, 1.21 mmol, 87%).

Softening range = 92−100 °C; $[\alpha]^{20}_D = +43$ (*c* 0.5, $CHCl_3$); IR (film) 3400, 3058 cm^{-1}; MS [FAB, NBA+NaI] *m*/*z* 569 (12) [$(M + Na)^+$], 197 (100) [$(Ph_2COCH_3)^+$]; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.35 (br s, 1 H, O*H*), 2.92 (s, 6 H, OCH_3), 4.06 (d, J = 5.4 Hz, 2 H, 5′-H), 5.09 (d, J = 17.7 Hz, 1 H, 1′-H), 5.27 (s, 2 H, 4-H/5-H), 5.75 (dt, J = 15.3, 5.4 Hz, 1 H, 4′-H), 6.06 (dd, J = 15.3, 10.5 Hz, 1 H, 3′-H), 6.50 (dd, J = 17.7, 10.5 Hz, 1 H, 2′-H), 7.17−7.33 (m, 20 H, Ar−H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 51.8 (OCH_3), 63.0 (C-5′), 77.7 (C-4/C-5), 83.4 (CPh_2OCH_3), ∼121 (br, C-1′), 127.3, 127.5, 127.6, 127.8, 128.5, 129.7 (Ar-*C*), 132.7 (C-3′), 135.5 (C-4′), 141.0, 141.4 (Ar-*C*), 148.3 (C-2′). Anal. Calcd for $C_{35}H_{35}BO_5$ (546.46): C, 76.93; H, 6.46. Found: C, 76.47; H, 6.59.

(1′*R*,2′*R*,4*R*,5*R*)-2-{2-[(*E*)-2-Methoxycarbonylethenyl]-cyclopropyl}-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane 10. The same procedure was followed as described above for the synthesis of diene **6**. Starting from cyclopropylboronic ester **8** (19.76 g, 36.99 mmol), we obtained the product **10** as a colorless foam (19.56 g, 33.2 mmol, 90%). Recrystallization from petroleum ether/diethyl ether at −20 °C yielded colorless crystals, suitable for X-ray analysis.

Mp = 157 °C; $[\alpha]^{20}_D = -83.0$ (*c* 0.96, $CHCl_3$); IR (film) 3058, 1720 cm^{-1}; MS [EI, 70 eV] *m*/*z* 588 (<0.1) [M^+], 556 (1.5) [$(M - CH_3OH)^+$], 197 (100) [$(Ph_2COCH_3)^+$]; ^1H NMR ($CDCl_3$, 500 MHz) δ -0.19 (ddd, J = 10.2, 7.1, 5.1 Hz, 1 H, 1′-H), 0.47 (ddd, J = 7.5, 7.1, 3.7 Hz, 1 H, 3′-H_{trans}), 0.62 (ddd, J = 10.2, 4.9, 3.7 Hz, 1 H, 3′-H_{cis}), 1.46 (dddd, J = 10.0, 7.5, 5.1, 4.9 Hz, 1 H, 2′-H), 2.99 (s, 6 H, CPh_2OCH_3), 3.66 (s, 3 H, CO_2CH_3), 5.29 (s, 2 H, 4-H/5-H), 5.78 (d, J = 15.4 Hz, 1 H, 2″-H), 6.19 (dd, J = 15.4, 10.0 Hz, 1 H, 1″-H), 7.25−7.32 (m, 20 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ ∼4 (br, C-1′), 14.1 (C-3′), 21.1 (C-2′), 51.3 (CPh_2OCH_3), 51.8 (CO_2CH_3), 77.7 (C-4/C-5), 83.3 (CPh_2OCH_3), 117.7 (C-2″), 127.4, 127.4, 127.6, 127.9, 128.4, 129.7, 141.0, 141.1 (Ar-*C*), 153.9 (C-1″), 167.0 (CO_2CH_3). Anal. Calcd for $C_{37}H_{37}BO_6$ (588.50): C, 75.51; H, 6.34. Found: C, 75.66; H, 6.52.

Preparation of (1′*R*,2′*R*,4*R*,5*R*)-2-{2-[(*E*)-2-Hydroxymethylethenyl]cyclopropyl}-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane 11. The same procedure was followed as described above for the synthesis of alcohol **7**. Starting from cyclopropylboronic ester **10** (1.40 g, 2.38 mmol), we obtained the product **10** as a colorless foam (1.29 g, 2.31 mmol, 97%).

Softening range = 83−87 °C; $[\alpha]^{21}_D = -83.5$ (*c* 0.82, $CHCl_3$); IR (film) 3392 cm^{-1}; MS [EI, 70 eV] *m*/*z* 560 (<0.1) [M^+], 528 (1.5) [$(M - CH_3OH)^+$], 197 (100) [$(Ph_2COCH_3)^+$]; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.44(ddd, *J* = 10.1, 6.6, 5.3 Hz, 1 H, 1′-H), 0.32 (ddd, *J* = 7.8, 6.6, 3.5 Hz, 1 H, 3′-H_{trans}), 0.41 (ddd, *J* = 10.1, 5.1, 3.5 Hz, 1 H, 3′-H_{cis}), 1.22 (t, *J* = 7.0 Hz, 1 H, O*H*), 1.35 (dddd, *J* = 8.9, 7.8, 5.3, 5.1 Hz, 1 H, 2′-H), 3.01 (s, 6 H, CPh_2OCH_3), 3.98−4.03 (m, 2 H, CH_2OH), 5.02 (ddt, *J* = 15.2, 8.9, 1.3 Hz, 1 H, 1″-H), 5.28 (s, 2 H, 4-H/5-H), 5.62 (dt, *J* = 15.2, 6.2 Hz, 1 H, 2″-H), 7.25−7.32 (m, 20 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ ∼2.2 (br, C-1′), 12.6 (C-3′), 20.5 (C-2′), 51.7 (CPh_2OCH_3), 63.6 (CH_2OH), 77.5 (C-4/C-5), 83.2 (CPh_2OCH_3), 126.5, 127.2, 127.5, 127.8, 128.4, 128.7 (Ar-*C*), 126.5 (C-1″), 137.0 (C-2″), 141.1, 141.2 (Ar-*C*). Anal. Calcd for $C_{36}H_{37}BO_5$ (560.49): C, 77.14; H, 6.65. Found: C, 77.18; H, 6.76.

Preparation of (4R,5*R*,1′*R*,2′*R*,1″*S*,2″R)-2-{2-[2-Hydroxymethylcyclopropyl]cyclopropyl}-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane 12 and (4R,5*R*,1′*R*,2′*R*,1″*R*,2″S)-2-{2-[2-Hydroxymethylcyclopropyl]-cyclopropyl}-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane 12a. To a stirred solution of alkenylboronic ester **11** (6.74 g, 12.0 mmol) and bis(sulfonamide) **13** (509 mg, 1.21 mmol) in CH_2Cl_2 (36 mL) was added diethyl zinc (12.0 mL of a 1 M solution in hexane) at 0 °C. After 10 min, the mixture was transferred to a second flask containing freshly prepared ZnI_2 (from 6.22 g iodine and 12.3 mL of diethyl zinc solution [1 M in hexane]) in CH_2Cl_2 (120 mL). The suspension was stirred for 5 min at 0 °C, and was then added to a third flask with a preformed reagent [2.03 mL (24.1 mmol) CH_2I_2 dissolved in CH_2Cl_2 (265 mL) and treated with diethyl zinc solution (12.0 mL of a 1 M solution in hexane) at 0 °C] for the cyclopropanation. Stirring was continued for 12 h at room temperature. After quenching the reaction with saturated aqueous NH_4Cl (120 mL), the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was purified by flash-column chromatography (petroleum ether/ethyl acetate 80:20). Yield: 6.29 g (11.0 mmol, 91%), dr **12**:**12a**, 92:8; with bis(sulfonamid) *ent*-**13** (instead of **13**), a diastereomeric ratio of dr **12**:**12a**, 45:55 was obtained. The desired diastereomer **12** could be isolated and further purified by MPLC (petroleum ether/ethyl acetate 80:20). The first eluted minor diastereomer **12a** could not be fully purified; the ^{13}C NMR data were obtained from the mixture (^1H NMR data were ambiguous).

12: Softening range = 83−86 °C; $[\alpha]^{21}_D = -127$ (*c* 0.76, $CHCl_3$); IR (film) 3384 cm^{-1}; MS [FAB, NBA+NaI] *m*/*z* 597 (10) [$(M + Na)^+$], 197 (100) [$(Ph_2COCH_3)^+$]; ^1H NMR ($CDCl_3$, 500 MHz) δ -0.77 (ddd, *J* = 9.9, 6.2, 5.7 Hz, 1 H, 1′-H), −0.06 (ddd, *J* = 7.9, 6.2, 3.4 Hz, 1 H, 3′-H_{trans}), 0.09 (ddd, *J* = 9.9, 5.4, 3.4 Hz, 1 H, 3′-H_{cis}), 0.16 (m_c, 2 H, 3″-H_a/3″H_b), 0.56 (dddd, *J* = 8.5, 5.6, 4.5, 4.5 Hz, 1 H, 1″-H), 0.69 (m_c, 1 H, 2″-H), 0.80 (dddd, *J* = 7.9, 5.7, 5.4, 4.5 Hz, 1 H, 2′-H), 1.39 (br s, 1 H, O*H*), 2.98 (s, 6 H, OCH_3), 3.29 (dd, *J* = 11.2, 7.1 Hz, 1 H, 1‴-H_a), 3.33 (dd, *J* = 11.2, 7.1 Hz, 1 H, 1‴-H_b), 5.23 (s, 2 H, 4-H/5-H), 7.21−7.32 (m, 20 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ ∼ −1.5 (br, C-1′), 7.7 (C-3″), 10.2 (C-3′), 19.09 (C-1″), 19.1 (C-2′), 19.4 (C-2″), 51.6 (OCH_3), 66.8 (C-1‴), 77.4 (C-4/C-5), 83.4 (CPh_2OCH_3), 127.2, 127.2, 127.4, 127.8, 128.4, 129.7, 141.2, 141.3 (Ar-*C*). Anal. Calcd for $C_{37}H_{39}BO_5$ (574.51): C, 77.35; H, 6.84. Found: C, 76.99; H, 6.99.

12a: ^{13}C NMR ($CDCl_3$, 125 MHz) δ ∼ −1.5 (br, C-1′), 7.9 (C-3″), 10.5 (C-3′), 19.08 (C-1″), 19.1 (C-2′), 19.2 (C-2″), 51.57 (OCH_3), 66.78 (C-1‴), 77.4 (C-4/C-5), 83.4 (CPh_2OCH_3), 127.2, 127.2, 127.45, 127.75, 128.4, 129.7, 141.2, 141.3 (Ar-*C*).

Preparation of (4*R*,5*R*,1′*R*,2′*R*,1″*S*,2″R)-2-{2-[2-(*tert*-Butyldiphenylsiloxymethyl)cyclopropyl]cyclopropyl}-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane 14a. Imidazole (97.0 mg, 1.41 mmol) and then *t*-$BuPh_2SiCl$ (373 mg, 1.36 mmol) were slowly added to a stirred solution of bicyclopropane **12** (740 mg, 1.29 mmol) in CH_2Cl_2 (5 mL) at 0 °C. A voluminous precipitate formed. After 5 h, the reaction was quenched with H_2O, the organic layer separated, and the aqueous layer extracted with pentane. After washing with brine, drying over $MgSO_4$, and evaporation of the solvents under reduced pressure, the crude product was obtained. Purification by flash-column chromatography (petroleum ether/diethyl ether, 95:5) yielded (1.04 g, 1.28 mmol, 98%) a colorless foam.

Softening range = 65−75 °C; $[\alpha]^{21}_D = -91.2$ (*c* 2.04, $CHCl_3$); IR (film) 3060, 1077 cm^{-1}; MS [FAB, NBA+NaI] *m*/*z* 835 (4) [$(M + Na)^+$], 197 (100) [$(Ph_2COCH_3)^+$]; ^1H NMR ($CDCl_3$, 500 MHz) δ -0.81 (ddd, *J* = 9.9, 6.1, 5.9 Hz, 1 H, 1′-H), −0.26 (ddd, *J* = 7.9, 6.1, 3.4 Hz, 1 H, 3′-H_{trans}), 0.07 (ddd, *J* = 9.9, 5.6, 3.4 Hz, 1 H, 3′-H_{cis}), 0.01−0.09 (m, 2 H, 3″-H_a/3″H_b), 0.53 (dddd, *J* = 8.5, 5.3, 4.5, 4.4 Hz, 1 H, 1″-H), 0.63 (m_c, 1 H, 2″-H), 0.75 (dddd, *J* = 7.9, 5.9, 5.6, 4.5 Hz, 1 H, 2′-H), 0.98 (s, 9 H, $(CH_3)_3C$), 2.98 (s, 6 H, OCH_3), 3.37 (dd, *J* = 10.7, 6.2 Hz, 1 H, 1‴-H_a), 3.46 (dd, *J* = 10.7, 5.9 Hz, 1 H, 1‴-H_b), 5.22 (s, 2 H, 4-H/5-H), 7.23−7.70 (m, 30 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ ∼ −2 (br, C-1′), 7.4 (C-3″), 9.8 (C-3′), 18.5(C-1″), 18.8 (C-2″), 19.1 ($(CH_3)_3C$), 19.2 (C-2′), 26.9 ($(CH_3)_3C$), 51.7 (OCH_3), 67.0 (C-1‴), 77.4 (C-4/C-5), 83.4 (CPh_2OCH_3), 127.2, 127.2, 127.5, 127.6, 127.7, 127.8, 128.4, 129.5, 129.6, 129.7 134.8, 135.5, 134.1, 134.1, 141.3, 141.4 (Ar-*C*). Anal. Calcd for $C_{53}H_{57}BO_5Si$ (812.91): C, 78.31; H, 7.07. Found: C, 77.92; H, 7.23.

Preparation of (4*R*,5*R*,1′*R*,2′*R*,1″*S*,2″R)-2-{2-[2-(Benzyloxymethyl)cyclopropyl]cyclopropyl}-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane 14b. NaH (251 mg, 6.26 mmol, 60% in paraffin) was slowly added to a stirred solution of bicyclopropane **12** (3.00 g, 5.22 mmol) in DMF (5 mL) at room temperature. Benzyl bromide (744 μL, 1.07 g, 6.26 mmol) was syringed into the reaction flask, and stirring was continued for 48 h. The mixture was diluted with Et_2O, the aqueous layer separated, the organic layer washed with brine and dried over $MgSO_4$, and the solvents were evaporated under reduced pressure. The crude product was purified by flash-column chromatography (petroleum ether/ethyl acetate, 95:5). Yield 2.62 g (3.94 mmol, 76%) of a colorless foam.

Softening range = 60−65 °C; $[\alpha]^{21}_D = -118$ (*c* 0.57, $CHCl_3$); IR (film) 3062, 1075 cm^{-1}; MS [FAB, NBA+NaI] *m*/*z* 687 (4) [$(M + Na)^+$], 197 (100) [$(Ph_2COCH_3)^+$]; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.75 (ddd, *J* = 9.8, 6.2, 5.8 Hz, 1 H, 1′-H), −0.07 (ddd, *J* = 7.9, 6.2, 3.5 Hz, 1 H, 3′-H_{trans}), 0.10 (ddd, *J* = 9.8, 5.4, 3.5 Hz, 1 H, 3′-H_{cis}), 0.16 (m_c, 2 H, 3″-H_a/3″H_b), 0.56 (dddd, *J* = 7.0, 6.2, 4.6, 4.5 Hz, 1 H, 1″-H), 0.71 (m_c, 1 H, 2″-H), 0.81 (dddd, *J* = 7.9, 5.8, 5.4, 4.6 Hz, 1 H, 2′-H), 2.98 (s, 6 H, OCH_3), 3.15 (dd, *J* = 10.4, 7.0 Hz, 1 H, 1‴-H_a), 3.25 (dd, *J* = 10.4, 6.6 Hz, 1 H, 1‴-H_b), 4.44 (s, 2 H, OCH_2Ph), 5.23 (s, 2 H, 4-H/5-H), 7.23−7.34 (m, 25 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ ∼ −1.5 (br, C-1′), 8.0 (C-3″), 9.7 (C-3′), 16.6 (C-2″), 19.2 (C-1″), 19.2 (C-2′), 51.7 (OCH_3), 72.2 (OCH_2Ph), 73.8 (C-1‴), 77.4 (C-4/C-5), 83.2 (CPh_2OCH_3), 127.2, 127.2, 127.4, 127.4, 127.6, 127.8, 128.3, 128.4, 129.7, 138.6, 141.2, 141.3 (Ar-*C*). Anal. Calcd for $C_{44}H_{45}BO_5$ (664.64): C, 79.51; H, 6.82. Found: C, 79.43; H, 6.87.

Preparation of (1′*R*,2′*R*,1″*S*,2″*R*)-2-{2-[2-(*tert*-Butyldiphenylsiloxymethyl)cyclopropyl]cyclopropyl}-1,3,2-dioxaborinane 15a. $LiAlH_4$ (114 mg, 3 mmol) was slowly added to a stirred solution of dioxaborolane **14a** (813 mg, 1.00 mmol) in THF (10 mL) at room temperature. After 2 h, the starting material was consumed (as judged by TLC). The reaction was carefully quenched with saturated aqueous NH_4Cl solution (10 mL) and the reaction mixture filtered through silica gel. With petroleum ether/ethyl acetate 80:20 the diol **1** was eluted first, changing the solvent system to ethyl acetate allowed the separation of the crude boronic acid. After evaporation of the solvent under reduced pressure, pentane (5 mL) and 1,3-propanediol (73 μL, 77 mg, 1.0 mmol) were added. After 12 h at room temperature, the clear solution was dried over $MgSO_4$. Evaporation of the solvents under reduced pressure and finally in a kugelrohr apparatus yielded 376 mg (0.87 mmol, 87%) of product **15a** as a colorless oil.

$[\alpha]^{21}_D = -62.0$ (*c* 0.43, $CHCl_3$); IR (film) 3025, 1095 cm^{-1}; MS [FAB, NBA+NaI] *m*/*z* 377 (4) [$(M-C_4H_9)^+$]; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.56 (ddd, *J* = 9.5, 6.2, 5.9 Hz, 1 H, 1′-H), 0.18 (m_c, 2 H, 3″-H), 0.25 (ddd, *J* = 9.5, 5.2, 3.2 Hz, 1 H,

3′-H_{cis}), 0.27 (ddd, J = 7.9, 6.2, 3.2 Hz, 1 H, 3′-H_{trans}), 0.65 (m_c, 1 H, 1″-H), 0.80 (m_c, 1 H, 2″-H), 0.93 (m_c, 1 H, 2′-H), 1.09 (s, 9 H, C(CH_3)$_3$C), 1.88 (q, J = 5.5 Hz, 2 H, 5-H), 3.39 (t, J = 5.5 Hz, 4 H, 4-H/6-H), 3.47 (dd, J = 10.7, 6.3 Hz, 2 H, 1‴-H), 7.23−7.63 (m, 10 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) $\delta \sim -4.0$ (br, C-1′), 7.7 (C-3″), 9.1 (C-3′), 18.6 (C-2′), 18.9 (C-1″), 19.2 ((CH_3)$_3$*C*), 19.3 (C-2″), 26.9 ((*C*H_3)$_3$C), 27.4 (C-5), 61.6 (C-4/C-6), 67.1 (C-1‴), 127.5, 129.4, 135.6, 134.1 (2 x) (Ar-*C*). Anal. Calcd for $C_{26}H_{35}BO_3Si$ (434.45): C, 71.88; H, 8.12. Found: C, 71.81; H, 8.08.

Preparation of (1′*R*,2′*R*,1″*S*,2″R)-2-{2-[2-(Benzyloxymethyl)cyclopropyl]cyclopropyl}-1,3,2-dioxaborinane 15b. The same procedure as described for the synthesis of dioxaborinane **15a** was followed: 3.13 g (4.71 mmol) dioxaborolane **14b** gave 1.26 g (4.40 mmol, 94%) of product **15b** as a colorless oil.

$[\alpha]^{21}_D$ = −89.1 (*c* 1.62, $CHCl_3$); IR (film) 3064, 1098 cm^{-1}; MS [EI, 70 eV] *m*/*z* 286 (1) [(M)$^+$], 91 (100) [(C_7H_7)$^+$]; ^{1}H NMR ($CDCl_3$, 500 MHz) δ -0.56 (ddd, J = 9.5, 6.2, 5.9 Hz, 1 H, 1′-H), 0.26−0.37 (m, 3 H, 3′-H_{cis}/3″-H), 0.50 (ddd, J = 7.9, 6.4, 3.2 Hz, 1 H, 3′-H_{trans}), 0.71 (m_c, 1 H, 1″-H), 0.92 (m_c, 1 H, 2″-H), 0.96 (m_c, 1 H, 2′-H), 1.91 (q, J = 5.5 Hz, 2 H, 5-H), 3.25 (dd, J = 10.4, 7.0 Hz, 1 H, 1‴-H_a), 3.36 (dd, J = 10.4, 6.6 Hz, 1 H, 1‴-H_b), 3.93 (t, J = 5.5 Hz, 4 H, 4-H/6-H), 4.53 (m, 2 H, OCH_2Ph), 7.26−7.36 (m, 5 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) $\delta \sim -4.0$ (br, C-1′), 8.5 (C-3″), 9.2 (C-3′), 17.3 (C-2″), 18.9 (C-2′), 19.9 (C-1″), 27.6 (C-5), 61.8 (C-4/C-6), 72.5 (O*C*H_2-Ph), 74.3 (C-1‴), 127.6, 127.9, 128.6, 138.9 (Ar-*C*). Anal. Calcd for $C_{17}H_{23}BO_3$ (286.17): C, 71.35; H, 8.10. Found: C, 71.31; H, 8.11.

Preparation of (1′*R*,2′*R*,1″*S*,2″R)-2-{2-[2-(*tert*-Butyldiphenylsiloxymethyl)cyclopropyl]cyclopropyl}methanol 16a. Dioxaborolane **14a** (602 mg, 0.74 mmol) was converted to dioxaborinane **15a**. The crude product and CH_2ClI (163 μL, 391 mg, 2.23 mmol) in THF (5 mL) was cooled to −78 °C. *t*-BuLi (2.84 mL of a 1.5 M solution in Et_2O, 4.26 mmol) was slowly added, and the temperature kept for 30 min before warming to room temperature. Stirring was continued for 48 h. The reaction was quenched with a mixture of a saturated $KHCO_3$ solution (10 mL) and H_2O_2 (2 mL of a 40% aqueous solution). After 1 h, the mixture was extracted with Et_2O. The organic layer was separated and dried over $MgSO_4$, and the solvents were removed under reduced pressure. The pure product **16a** was isolated after flash-column chromatography (petroleum ether/ethyl acetate 80:20) and MPLC (petroleum ether/ethyl acetate 85:15). Yield 169 mg (0.44 mmol, 60%) as a colorless oil.

$[\alpha]^{20}_D$ = −41.2 (*c* 2.82, $CHCl_3$); IR (film) 3336, 3069 cm^{-1}; MS [CI, NH_3] *m*/*z* 398 (25) [(M + NH_4)$^+$], 363 (100) [(M − OH)$^+$]; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.17−0.24 (m, 2 H, 3′-H), 0.25−0.31 (m, 2 H, 3″-H), 0.64 (m, 1H, 1″-H), 0.69 (m, 1H, 2′-H), 0.77 (m_c, 1H, 2″-H), 0.81 (m_c, 1 H, 1′-H), 1.02 (s, 9 H, C(CH_3)$_3$), 1.19 (t, J = 5.8 Hz, 1H, O*H*), 3.33−3.42 (m, 2 H, 1-H_a/1-H_b), 3.38 (dd, J = 10.7, 6.8 Hz, 1H, 1‴-H_a), 3.57 (dd, J = 10.7, 5.8 Hz, 1H, 1‴-H_b), 7.34−7.66 (m, 10 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 8.0 (C-3′), 8.2 (C-3″), 17.7 (C-1″), 18.1 (C-2′), 19.2 (*C*(CH_3)$_3$), 19.3 (C-2″), 19.7 (C-1′), 26.8 (C(*C*H_3)$_3$), 66.9 (C-1), 67.0 (C-1‴), 127.5, 129.5, 135.6, 134.0, 134.0 (Ar-*C*). Anal. Calcd for $C_{24}H_{32}O_2Si$ (380.59): C, 75.74; H, 8.47. Found: C, 75.96; H, 8.54.

Preparation of (1′*R*,2′*R*,1″*S*,2″R)-2-{2-[2-(Benzyloxymethyl)cyclopropyl]cyclopropyl}methanol 16b. The same procedure as described for the synthesis of bicyclopropane **16a** was followed: 1.21 g (4.23 mmol) dioxaborinane **15b** gave 710 mg (3.06 mmol, 72%) of slightly impure product **16b** as a colorless oil after a single chromatographic separation (silica gel, petroleum ether/ethyl acetate 80:20).

$[\alpha]^{19}_D$ = −73.4 (*c* 0.37, $CHCl_3$); IR (film) 3388, 3064 cm^{-1}; MS [FAB, NBA+NaI] *m*/*z* 255 (100) [(M + Na)$^+$]; HRMS: Calcd for $C_{15}H_{20}NaO_2$ [(M + Na)$^+$] 255.1361; found: 255.1357. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.30−0.38 (m, 4 H, 3′-H/3″-H), 0.76−0.82 (m, 2 H, 1″-H/2′-H), 0.86−0.93 (m, 1H, 1′-H/2″-H), 1.39 (br, 1H, O*H*), 3.28−3.33 (m, 2 H, 1‴-H_a/1‴-H_b or 1-H_a/1-H_b), 3.40−3.47 (m, 2 H, 1‴-H_a/1‴-H_b or 1-H_a/1-H_b), 4.53 (m, 2 H, OCH_2Ph), 7.27−7.35 (m, 5 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 8.0 (C-3′ or C-3″), 8.3 (C-3′ or C-3″), 17.0 (C-1″ or C-2′), 18.0 (C-1′ or C-2″), 19.9 (C-1″ or C-2′), 19.9 (C-1′ or C-2″), 66.8 (C-1), 72.4 (OCH_2Ph), 73.9 (C-1‴), 127.50, 127.63, 128.3, 138.5 (Ar-*C*). Anal. Calcd for $C_{15}H_{20}O_2$ (232.32): C, 77.55; H, 8.68. Found: C, 76.12; H, 8.62.

Preparation of (4R,5*R*,1′*R*,2′*R*,1″*S*,2″R)-2-{2-[2-Iodocyclopropyl]cyclopropyl}-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane 18. $RuCl_3$·3H_2O (16 mg, 61 μmol) was added to a vigorously stirred mixture of alcohol **12** (690 mg, 1.20 mmol) and $NaIO_4$ (771 mg, 3.60 mmol) in 7 mL of CCl_4/H_2O/CH_3CN (2:3:2) at room temperature. After 3 h, the starting material was consumed (as judged by TLC).). The reaction was quenched with saturated aqueous NH_4Cl solution (20 mL). Extraction with ethyl acetate, drying of the organic layer with Na_2SO_4, filtration, and evaporation of the solvents under reduced pressure furnished the crude product. Filtration through a pad of silica gel (petroleum ether to ethyl acetate) yielded a solid (556 mg, 0.95 mmol, 79%) that was directly subjected to the next transformation.

Softening range = 83−86 °C; $[\alpha]^{20}_D$ = −136 (*c* 0.40, $CHCl_3$); IR (film) 3410 (br), 1725, 1358, 1060 cm^{-1}; MS [FAB, NBA+NaI] *m*/*z* 611 (14) [(M + Na)$^+$], 197 (100) [(Ph_2COCH_3)$^+$]; ^{1}H NMR ($CDCl_3$, 500 MHz) δ -0.68 (ddd, J = 10.0, 6.4, 5.6 Hz, 1 H, 1′-H), −0.04 (ddd, J = 7.8, 6.4, 3.8 Hz, 1 H, 3′-H_{trans}), 0.15 (ddd, J = 10.0, 5.6, 3.8 Hz, 1 H, 3′-H_{cis}), 0.59 (ddd, J = 8.2, 6.6, J 4.4 Hz, 1 H, 3″-H_{trans}), 0.79 (dddd, J = 7.8, 5.6, 5.6, 4.9 Hz, 1 H, 2′-H), 1.01 (ddd, J = 9.2, 4.6, 4.4 Hz, 1 H, 3″-H_{cis}), 1.24 (ddd, J = 8.2, 4.6, 3.9 Hz, 1 H, 2″-H), 1.34 (dddd, J = 9.2, 6.6, 4.9, 3.9 Hz, 1 H, 1″-H), 2.99 (s, 6 H, OCH_3), 5.25 (s, 2 H, 4-H/5-H), 7.24−7.47 (m, 20 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) $\delta \sim -1$ (br, C-1′), 9.4 (C-3′), 13.8 (C-3″), 18.6 (C-2′), 19.0 (C-2″), 26.0 (C-1″), 51.6 (OCH_3), 77.4 (C-4/C-5), 83.2 (*C*Ph_2-OCH_3), 127.2, 127.3, 127.5, 127.8, 128.3, 129.7, 141.2, 141.2 (Ar-*C*), 180.2 (*C*OOH). Anal. Calcd for $C_{37}H_{39}BO_5$ (574.51): C, 77.35; H, 6.84. Found: C, 76.99; H, 6.99.

Protected from light, a mixture containing the carboxylic acid **17** (556 mg, 0.95 mmol), DCC (586 mg, 2.84 mmol), DMAP (231 mg, 1.89 mmol), CHI_3 (1.12 g, 2.84 mmol), 2-mercaptopyridine *N*-oxide (361 mg, 2.84 mmol), and cyclohexene (15 mL) was first stirred for 2 h at room temperature and then refluxed for 14 h. The solids were filtered off and washed with Et_2O. The organic layer was washed with saturated aqueous NH_4Cl solution, dried over $MgSO_4$, and filtered, and the solvents were removed under reduced pressure. Purification by flash-column chromatography (petroleum ether/ethyl acetate, 98:2) and MPLC (petroleum ether/ethyl acetate, 99:1) furnished 264 mg (0.39 mmol, 42%) of the slightly impure title compound **18**.

Softening range = 75−85 °C; $[\alpha]^{20}_D$ = −98.5 (*c* 0.96, $CHCl_3$); IR (film) 3059, 1076 cm^{-1}; MS [FAB, NBA+NaI] *m*/*z* 693 (10) [(M + Na)$^+$], 197 (100) [(Ph_2COCH_3)$^+$]; HRMS: calcd. for $C_{36}H_{36}BINaO_4$ [(M + Na)$^+$] 693.1646; found: 693.1646. ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.71 (ddd, J = 9.9, 6.3, 5.8 Hz, 1 H, 1′-H), −0.07 (ddd, J = 7.9, 6.3, 3.7 Hz, 1 H, 3′-H_{trans}), 0.06 (ddd, J = 9.9, 5.3, 3.7 Hz, 1 H, 3′-H_{cis}), 0.59 (ddd, J = 7.8, 6.2, 6.2 Hz, 1 H, 3″-H_{trans}), 0.65 (ddd, J = 9.2, 6.2, 4.6 Hz, 1 H, 3″-H_{cis}), 0.78 (dddd, J = 7.9, 5.8, 5.3, 4.8 Hz, 1 H, 2′-H), 1.07 (dddd, J = 9.2, 6.2, 4.8, 3.9 Hz, 1 H, 1″-H), 1.93 (ddd, J = 7.8, 4.6, 3.9 Hz, 1 H, 2″-H), 2.97 (s, 6 H, OCH_3), 5.23 (s, 2 H, 4-H/5-H), 7.21−7.29 (m, 20 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) −16.4 (C-2″), $\sim$ −2 (br, C-1′), 9.2 (C-3′), 14.3 (C-3″), 18.7 (C-2′), 25.6 (C-1″), 51.7 (OCH_3), 77.6 (C-4/C-5), 83.2 (*C*Ph_2-OCH_3), 127.2, 127.6, 127.8 (2 x), 128.4, 129.7, 141.2, 141.2 (Ar-*C*). Anal. Calcd for $C_{36}H_{36}BIO_4$ (670.38): C, 64.50; H, 5.41. Found: C, 65.49; H, 5.89.

Preparation of (1′*R*,2′*R*,1″*S*,2″*R*)-2-[2-(*tert*-Butyldiphenylsiloxymethyl)cyclopropyl]cyclopropylbenzol 20. Dioxaborinane **15a** (265 mg, 0.61 mmol) was dissolved in DME (7 mL). After addition of Pd(PPh_3)$_4$ (70 mg, 61 μmol) and KO*t*Bu (1.22 mL of a 1 *M* solution in *t*BuOH), the mixture was carefully deoxygenated by freeze technique. Phenyliodide (68.0 mL, 124 mg, 0.61 mmol) was added. After 50 h at 80 °C, the mixture was treated with H_2O and extracted with diethyl ether. The organic layer was washed with brine and dried ($MgSO_4$), the solvent removed under reduced pressure, and

the crude product purified (after filtration through silica gel) by means of MPLC (petroleum ether/ethyl acetate 95:5). The product **20** (205 mg, 0.48 mmol, 79%) was obtained as colorless oil.

$[\alpha]^{20}_D = -93.3$ (*c* 0.61, $CHCl_3$); IR (film) 2980, 1065 cm^{-1}; MS [EI, 30 eV] *m*/*z* 426 (35) [$(M)^+$], 369 (100) [$(M - C_4H_9)^+$]; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.26 (ddd, J = 8.4, 5.2, 4.9 Hz, 1 H, 3′-H_a), 0.28 (ddd, J = 8.2, 5.3, 4.9 Hz, 1 H, 3′-H_b), 0.72 (ddd, J = 8.8, 5.8, 4.9 Hz, 1 H, 3-H_{cis}), 0.77 (m_c, 1 H, 1′-H), 0.78 (ddd, J = 8.6, 5.1, 4.9 Hz, 1 H, 3-H_{trans}), 0.89 (m_c, 1 H, 2′-H), 1.03 (s, 9 H, $C(CH_3)_3$), 1.08 (dddd, J = 8.6, 5.1, 5.1, 4.6 Hz, 1 H, 2-H), 1.60 (ddd, J = 8.8, 5.1, 5.1 Hz, 1 H, 1-H), 3.42 (dd, J = 10.7, 6.7 Hz, 1 H, 1″-H_a), 3.62 (dd, J = 10.7, 5.8 Hz, 1 H, 1″-H_b), 6.98−7.66 (m, 10 H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 7.8 (C-3′), 14.1 (C-3), 18.4 (C-1′), 19.2 ($C(CH_3)_3$), 19.5 (C-2′), 22.0 (C-1), 24.8 (C-2), 26.9 ($C(CH_3)_3$), 67.1 (C-1″), 125.2, 125.6, 127.2, 127.6, 129.5, 135.6, 134.0, 134.1, 143.6 (Ar-*C*). Anal. Calcd for $C_{29}H_{34}OSi$ (426.67): C, 81.64; H, 8.03. Found: C, 81.55; H, 8.06.

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Supporting Information Available: Crystallographic data for compound **10**; NMR spectra of **7**, **16b**, and **18**; full data for **4a**, **10a**, **11a**, and **16c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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