(Alkoxyalkyl)boronic Ester Intermediates for Asymmetric Synthesis

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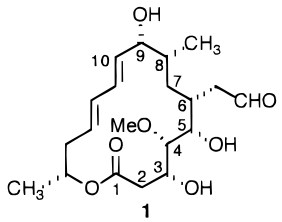
The use of boronic ester chemistry in the construction of synthetic intermediates containing two or three chiral centers corresponding to steric relationships in the macrolide leuconolide has been explored. A four-carbon chain with a substituent at each carbon has been built from each end, and the effects of different chiral directors and masking groups have been compared. Exceptionally facile debenzylation of a benzyloxy group separated by four carbon atoms from a boronic ester function has been observed and may account for the failure of earlier attempts to synthesize sugars via analogous chemistry. A novel method of reducing α-chloro boronic esters to alkylboronic esters with sodium hydride in DMSO has been found.

Introduction

Chain extension of boronic esters of chiral 1,2-diols (1,3,2-dioxaborolanes) to the homologous α-halo boronic esters provides an efficient, highly stereoselective approach to asymmetric synthesis.[1,2] It was shown previously that benzyloxy or (*p*-methoxybenzyl)oxy substituents are compatible with this process, though there appeared to be a limit to the number or perhaps the spacing of these substituents.[3,4]

The present investigation was undertaken with the antibiotic aglycone leuconolide[5,6] (**1**) in mind as a target



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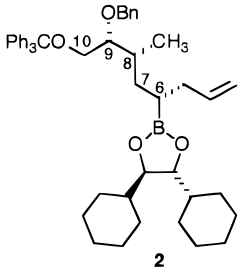

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and has proceeded as far as the C(6)−C(10) segment represented by **2**. Further progress toward this target does not appear feasible until methods are developed for connecting boronic esters of the general size and steric properties of **2** to other similar fragments. However, the present study has uncovered and solved some of the general problems in applying the boronic ester chain extension method to functionalized systems of intermediate complexity and has provided insight into the nature of the difficulties encountered previously[3] with increasing chain length and numbers of alkoxy substituents.

Results

Substituted butylboronic esters having the stereochemistry of the C(7)−C(10) segment of leuconolide (**1**) have been constructed from both directions. Opposite chiral directors are required. Otherwise, the essential difference is whether the methyl group at C(8) or the benzyloxy group at C(9) is installed first, and consideration must be given to what groups might be incorporated at C(7) and C(10) for purposes of subsequent connections.

Both routes begin from a (halomethyl)boronic ester, which is converted to an (alkoxymethyl)boronic ester before the first chain extension. The discovery of an efficient preparation of diisopropyl (bromomethyl)boronate via addition of butyllithium to a solution of dibromomethane and triisopropyl borate[7] has greatly simplified the bulk preparation of starting materials.[8] Three different chiral directors and two cleavable alkoxy substituents have been tested in this work.

Routes from C(7). The correct absolute configuration may be provided by the use of either "(*R*)-pinanediol" or a C_2-symmetrical (*S*,*S*)-diol as chiral director.[1,9] Both were tested, but the most extensive work was done with boronic esters of the (*S*,*S*)-diol, 1,2-diisopropylethanediol,[10] abbreviated here to "(*S*,*S*)-DIPED". In order to introduce the chiral director as late

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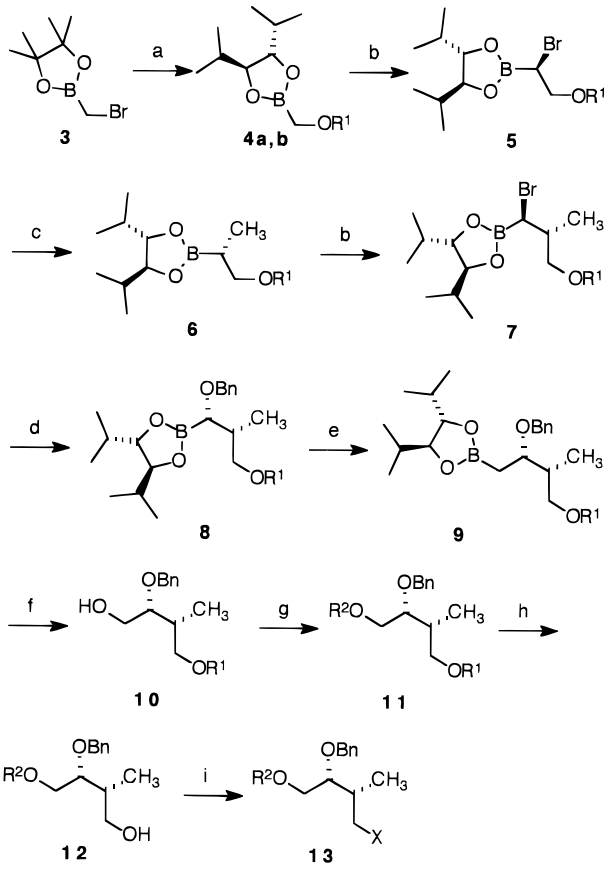
Scheme 1. Series a and b Intermediates[a]



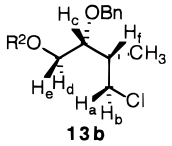
[a] Series **a**: R^1 = *p*-methoxybenzyl, R^2 = trityl. Series **b**: R^1 = trityl, R^2 = *p*-methoxybenzyl. Key: (a) $NaOR^1$ in DMSO;[8] transesterify with corresponding diol. (b) CH_2Br_2 + **4** in THF, −78 °C, add LDA; $ZnCl_2$.[3] (c) CH_3MgCl. (d) $LiOCH_2Ph$. (e) $ClCH_2I$, BuLi.[7] (f) H_2O_2, OH^-. (g) R^2Cl, base. (h) (**a**) DDQ or (**b**) HCO_2H. (i) (**a**) $MeSO_2Cl/Et_3N$, NaI, or (**b**) $(COCl)_2$/DMF.

as possible, pinacol (bromomethyl)boronate was first converted to pinacol [((*p*-methoxybenzyl)oxy)methyl]-boronate (series **a**) (Scheme 1) or pinacol [(trityloxy)-methyl]boronate[8] (series **b**) and subsequently transesterified with (*S*,*S*)-DIPED to form the (alkoxymethyl)-boronic ester (**4**).

The reaction of bromo boronic ester **5a** with methylmagnesium chloride resulted in formation of a small amount (5−10%) of the cleavage product, (*S*,*S*)-DIPED methylboronate, and the analogue **5b** yielded a somewhat larger amount (10−15%) of the methylboronate, with the remainder of the product being mainly **6** in each case. Chain extension of **6** to **8** proceeded efficiently in both series. In order to avoid contamination of **8** by its butoxy analogue, accidentally derived from partially oxidized butyllithium, it was found preferable to use sodium benzyl oxide prepared from sodium hydride and benzyl alcohol in DMSO for the conversion of **7b** to **8b**. The last extension to **9** with (chloromethyl)-lithium was nearly quantitative. (Bromomethyl)lithium proved less effective for conversion of **8** to **9**, and similar inefficiency of (bromomethyl)lithium with alkoxy-substituted boronic esters has been reported previously.[7]

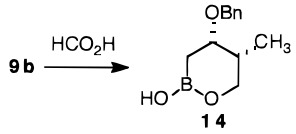
Deboronation of the final boronic esters in the sequence (**9**) with hydrogen peroxide to form the corresponding alcohols (**10**) was routine and nearly quantitative. At this point a differentially protected pair of hydroxyl functions at opposite ends of the butane chain was desired. Where the first group R^1 was *p*-methoxybenzyl, the hydroxyl R^2 was tritylated with trityl chloride to form **11a**, which with DDQ was deprotected to alcohol **12a** and converted via the unstable mesylate to iodo compound **13a**. Where R^1 was trityl, R^2 = *p*-methoxybenzyl was prepared via treatment of **10** with sodium hydride followed by *p*-methoxybenzyl chloride to form **11b**. Cleavage of R^1 = trityl by formic acid[11] readily yielded alcohol **12b**, together with a small amount of its formate ester. After chromatography, **12b** with oxalyl chloride/DMF[12] yielded chloride **13b**, which was characterized by elemental analyses, ^1H, ^{13}C and 2D COSY NMR. The last few steps were all efficient, and the overall yield of **13b** from **4b** was 40−45%.

The ^1H NMR spectrum of **13b** was too complicated to allow interpretation of the five protons (CH_aH_bCl, CH_c-OBn, and OCH_dH_e), which all overlapped in the 3.48−3.81 ppm region. This problem was solved by other NMR experiments. First, homodecoupling by irradiation of H_f at δ 2.22 caused the doublet at δ 1.01 (CH_3)



to collapse to a singlet, the multiplet at δ 3.48−3.54 to become a less complicated multiplet, the multiplet at δ 3.59−3.67 to collapse to a broad singlet and a set of less complicated multiplets, and the multiplet at δ 3.76−3.81 to collapse to a broad singlet. The unchanged peaks had to be H_d and H_e (two sets of doublet of doublets at δ 3.51 and 3.65). Second, the 2D COSY experiment shows that region 1 (δ 3.48−3.54) is coupled with region 2 (δ 3.59−3.67 ppm) and region 2 (δ 3.59−3.67) is coupled with region 3 (δ 3.76−3.81). The above data prove H_aH_b is in regions 2 and 3, H_c is in region 1 and H_dH_e is in regions 1 and 2.

Detritylation of (*S*,*S*)-DIPED (2*S*,3*R*)-[(2-(benzyloxy)-3-methyl-4-(triphenylmethoxy)butyl]boronate (**9b**) with formic acid[11] followed by workup under basic conditions apparently resulted in cyclization to a six-membered 1,2-oxaborin (**14**), which was characterized only by 200



and 500 MHz ^1H NMR.[15] A small proportion of the alcohol initially formed was esterified under the reaction conditions to the formate ester (**9**, R^1 = CHO). Attempted reactions of pinacol and pinanediol with (4*R*,5*R*)-2-oxy-4-(benzyloxy)-5-methyl-1,2-oxaborin (**14**) to break the B−O bond were unsuccessful.

(11) Bessodes, M.; Komiotis, D.; Antonakis, K. *Tetrahedron Lett.* **1986**, *27*, 579−580.
(12) Ireland, R. E.; Norbeck, D. W.; Mandel, G. S.; Mandel, N. S. *J. Am. Chem. Soc.* **1985**, *107*, 3285−3294.
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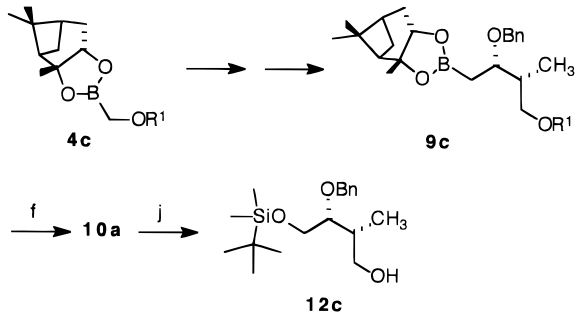
(14) Hydrogenation to DICHED: (a) Hoffmann, R. W.; Ditrich, K.; Köster, G.; Stürmer, R. *Chem. Ber.* **1989**, *122*, 1783. (b) Matteson, D. S.; Man, H.-W. *J. Org. Chem.* **1993**, *58*, 6545−6547.

Scheme 2. Series c Intermediates[a]



[a] Series **c**: R^1 = *p*-methoxybenzyl; R^2 = *tert*-$BuMe_2Si$; (*R*)-pinanediol esters. Key: (f) and preceding steps, same as series **a** and **b**. (j) *tert*-$BuMe_2SiCl$; DDQ.

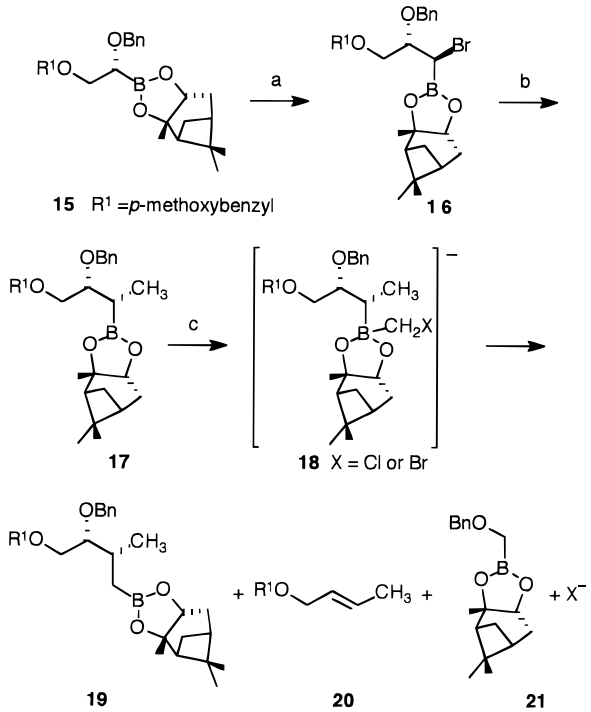
An analogous series of intermediates was made with the pinanediol boronic ester series **c** (Scheme 2). A close analogy to the route as far as (*R*)-pinanediol [(1*R*)-1-bromo-2-[(*p*-methoxybenzyl)oxy]ethyl]boronate (**5c**) via (*R*)-pinanediol [((*p*-methoxybenzyl)oxy)methyl]boronate (**4c**) had already been established,[4] with (*S*)-pinanediol (chloromethyl)boronate used in place of the bromomethyl ester **3** and the enantiomer ***ent*-4c** prepared in place of **4c**. Subsequent compounds in this series were obtained up through the monosilylated alcohol **12c**. The structures are not illustrated in detail because all of the steps were essentially the same as with series **a**. The ultimate product was the *p*-methoxybenzyl-substituted alcohol identical with **10a**, which was silylated and treated with DDQ to yield the TBDMSO-substituted alcohol **12c**. A sample of **12c** was also converted to the iodo derivative **13c** (same as **13a** with TBDMS in place of trityl), but this compound was unstable to storage and was characterized only by ^{1}H NMR.

Routes from C(10). The synthesis starting from C(7) provides intermediates most likely to be useful if the next operations are to be carried out at the boronic ester terminus, C(10), since extra protection and deprotection steps are required in order to reach a structure having a reactive C(7) terminus such as **13**. To provide the opposite pattern of active functionality, the C(10) terminus was used as a starting point.

The first study was made with the pinanediol ester series (Scheme 3). The (1,2-dialkoxyethyl)boronic ester **15** had been synthesized previously via ***ent*-4c**,[4] the route to which was modified in the present work to utilize (*S*)-pinanediol (bromomethyl)boronate in place of the chloro analogue and sodium *p*-methoxybenzyl oxide in DMSO in place of the lithium alkoxide in THF. Conversion of **15** via bromo boronic ester **16** to the (1-methyl-2,3-dialkoxypropyl)boronic ester **17** was routine, but reaction of **17** with (chloromethyl)lithium or (bromomethyl)lithium yielded mixtures of the homologous boronic ester **19** with substantial amounts of the elimination products crotyl *p*-methoxybenzyl ether (**20**) and pinanediol [(benzyloxy)methyl]boronate (**21**).

The second study (Scheme 4) was made with (*R*,*R*)-

Scheme 3. Pinanediol Ester Series[a]



[a] (a) $LiCHBr_2$.[4] (b) CH_3MgBr. (c) ICH_2Cl or CH_2Br_2 + **17** in THF, −78 °C, add BuLi.

1,2-dicyclohexyl-1,2-ethanediol[13,14] ["(*R*,*R*)-DICHED"] boronic esters and the trityl blocking group for the terminal oxygen. (*R*,*R*)-DICHED ((trityloxy)methyl)-boronate[8] (**22**) was prepared in an analogous manner to **4**, described above. Chain extension to the (1-(benzyloxy)-2-(trityloxy)ethyl)boronic ester **23** was carried out efficiently with (dichloromethyl)lithium followed by sodium benzyl oxide. The second chain extension to chloroboronic ester **24** and *C*-methylation to **25** was carried out in the usual manner. When the direct homologation of **25** to **27** was attempted with (chloromethyl)lithium or (bromomethyl)lithium, it appeared that considerable elimination analogous to that seen in the conversion of **17** to **19** and byproducts **20** and **21** could not be avoided, but the reaction of **25** with (dichloromethyl)lithium to form **26** proved efficient.

Reduction of α-chloro boronic esters with various borohydride reagents is well-known.[4,16,17] However, observation of such reduction by sodium hydride in DMSO as a side reaction[18] prompted us to try this reagent for synthetic purposes, and it proved convenient and efficient for conversion of **26** to **27**.

Chain extension of **27** with (dichloromethyl)lithium and reaction of the resulting α-chloro boronic ester with allylmagnesium chloride yielded ~60% **2**. A major side reaction was debenzylation to benzyl chloride, which was positively identified by GC−mass spectrometry, apparently during the zinc chloride promoted rearrangement of the adduct of **27** with (dichloromethyl)-

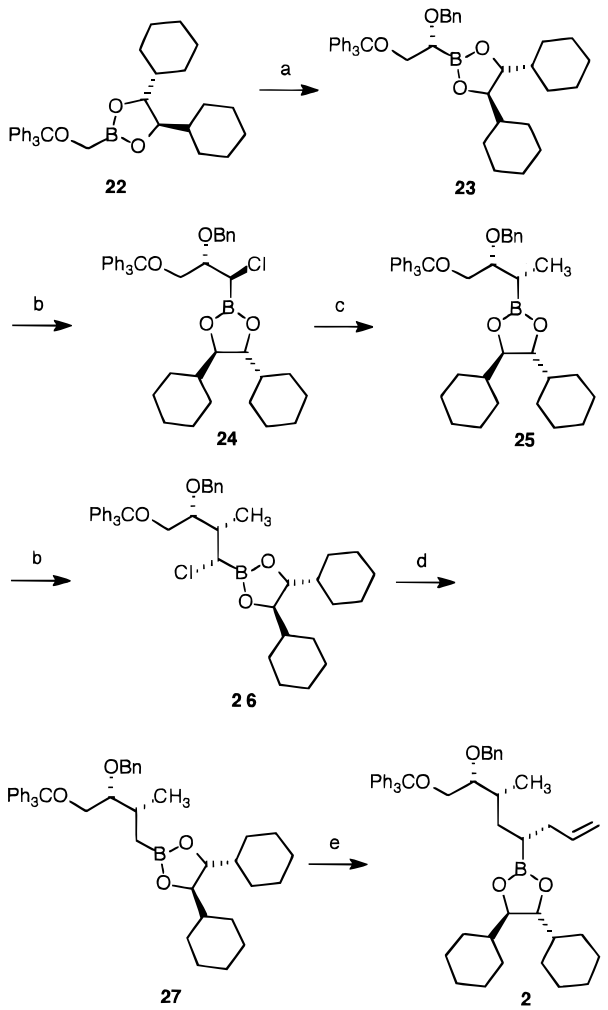
(15) The ring proton NMR signals in **14** are all well separated and can be assigned on the basis of chemical shifts and splittings. The observed couplings (in Hz) are as follows: J_{34} = 6, 5.5; J_{45} = ~3; J_{56} = 4.5, 7. These may be compared with results of a PC Model MMX calculation on (4*R*,5*R*)-2-oxy-4-methoxy-5-methyl-1,2-oxaborin (analogue of **14** having Me in place of Bn) using boron−oxygen parameters reflecting strong π-bonding.[8] The weighted average of the 5-methyl equatorial/axial conformers ($\Delta E°$ = 0.15 kcal mol^{-1}) yielded J_{34cis} = 6.2, $J_{34trans}$ = 5.1, J_{45} = 2.2, J_{56cis} = 3.1, and $J_{56trans}$ = 7.3.

(16) (a) Brown, H. C.; Naik, R. G.; Singaram, B.; Pyun, C. *Organometallics* **1985**, *4*, 1925−1929. (b) Brown, H. C.; Imai, T.; Perumal, P. T.; Singaram, B. *J. Org. Chem.* **1985**, *50*, 4032−4036.

(17) Matteson, D. S.; Beedle, E. C.; Christenson, E.; Dewey, M. A.; Peterson, M. L. *J. Labelled Compd. Radiopharm.* **1988**, *25*, 675−683.

(18) We thank Hon-Wah Man for this observation. Reaction of an α-chloro boronic ester with sodium benzyl oxide prepared from benzyl alcohol and excess sodium hydride in DMSO resulted in some replacement of Cl by H.

Scheme 4[a]

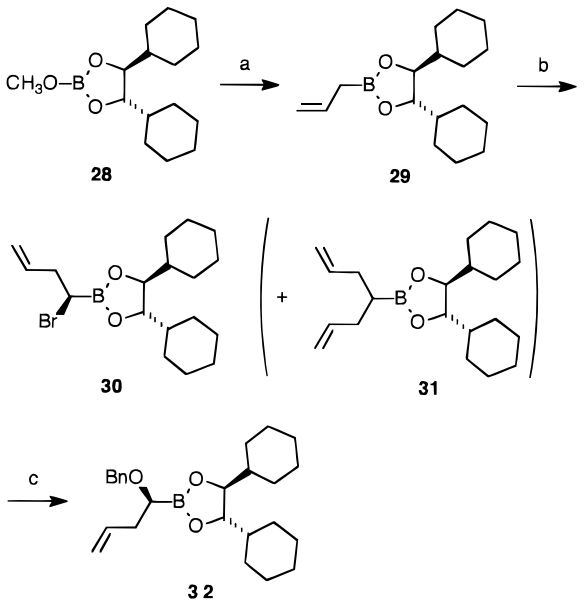


[a] Key: (a) $LiCHCl_2$, −100 °C; $ZnCl_2$, −100 → 25 °C; LiOBn. (b) $LiCHCl_2$, −100 °C; $ZnCl_2$, −100 → +25 °C. (c) CH_3MgCl. (d) NaH, DMSO. (e) $LiCHCl_2$, −100 °C; $ZnCl_2$, −100 → 25 °C; $CH_2{=}CHCH_2MgCl$.

lithium. Two attempts to carry out chain extension of **2** failed, but the amount of available compound and other resources had dwindled to the point where further work was not feasible.

Allylboronic Ester Chain Extension. This work was undertaken with the C(1)−C(6) segment of leuconolide in mind but was not completed very far (Scheme 5). (*S*,*S*)-DICHED (*R*)-[bromoallylmethyl]boronate (**30**) was prepared in a conventional manner via allylation of (*S*,*S*)-DICHED methoxyboronate (**28**) to the allylboronic ester **29** and chain extension with (dibromomethyl)lithium. Although reasonable yields of **30** were obtained, substantial amounts of the allyl transfer product **31** were also present. This kind of transfer of an allyl group from a borate intermediate to an (α-haloalkyl)boronic ester product has been reported previously in the 2,3-butanediol boronic ester series.[19] Pinanediol esters do not have this problem,[19] and it was not anticipated that the DICHED ester would behave like the relatively unhindered butanediol ester. Conversion of the crude **30** to the benzyloxy derivative **32** was carried out in the usual manner.

Scheme 5[a]



[a] Key: (a) $CH_2{=}CHCH_2MgCl$. (b) CH_2Br_2 + **29** in THF, −78 °C, add LDA; $ZnCl_2$. (c) LiOBn.

Discussion

In accord with previous work,[1−4] ^{1}H NMR data have indicated that all of the products of asymmetric reactions in the present series are formed in high enantiomeric and diastereomeric purity. No quantitative estimates of diastereomer content were attempted in the present work, but products generally appeared to be single compounds, consistent with the previous findings[1−4] of diastereomer levels below 1%. One cautionary note is the recent discovery that unhindered α-bromo boronic esters, for example, DICHED 1-bromopentylboronate, epimerize extremely easily.[20] However, the (α-bromohomoallyl)boronic ester **30** yielded benzyloxy derivative **32** which, after chromatography, showed no evidence of diastereomer above the ∼1% noise level near the C*H*OBn triplet at δ 3.42 in the 300 MHz ^{1}H NMR. The possibility that ∼10% contaminant apparent at δ ∼3.33 in another sample could have been diastereomer was not ruled out.

The chain extension of the one-carbon synthon **4a** to four-carbon synthon **9a** and the analogous conversion of **4b** to **9b** both proceeded in approximately 60% yields over all. The pinanediol series **4c** to **9c** yielded 49%, with the largest difference being in the last step, **8c** to **9c**. Because yields in these reactions are highly sensitive to experimental technique, there is no clear evidence that one route is inherently any more efficient than another.

The unexpected debenzylation of **27** to form benzyl chloride in the reaction with (dichloromethyl)lithium presumably involves 1,2-oxaborin or perhaps 1,2-oxaborolane formation somewhat analogous to the generation of oxaborin **14**. The presumed 3-chloro-1,2-oxaborin or tetrahydrofurylboronic ester from ring contraction or alternative oxaborolane was not observed, but may have been adsorbed strongly on silica. Earlier attempts to synthesize sugars via related chemistry failed inexplicably at introduction of the fifth carbon atom,[3a] and

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(20) Matteson, D. S.; Man, H.-W. *J. Org. Chem.* **1994**, *59*, 5734−5741.

similar debenzylation is a plausible explanatory hypothesis. The use of alternative masking groups in such situations remains to be investigated.

It was anticipated that the (α-bromohomoallyl)boronic ester **30** could be connected to a lithio derivative of C(7)−C(10) fragment **13a** to form a compound identical with **2** except for the opposite chirality of the DICHED. Indeed, 200 MHz ^{1}H NMR data indicated that this analogue of **2** was formed and underwent chain extension with (dibromomethyl)lithium, though further characterization of these intermediates was not accomplished. It was hoped that the resulting C(10)−C(5) fragment could be converted to an α-lithio ether,[21] which might then be joined to a C(1)−C(4) fragment in the form of an α-halo-*β*-alkoxy boronic ester. However, this approach was abandoned when we observed no coupling of model compound (1-methoxy-2-methylpropyl)lithium[21] with an appropriate, though incompletely characterized, α-halo-*β*-alkoxy boronic ester.[22] Several other attempts to extend carbon chains of boronic esters beyond the final compounds in the series reported here yielded encouraging 200 MHz ^{1}H NMR spectra, but attempts to characterize them definitively were ultimately defeated by our inability to obtain satisfactory mass spectra or sufficiently definitive NMR spectra with the equipment available to us at the time the work was done.

Conclusions

(1) Several potentially useful boronic ester synthons for differentially protected (2*R*,3*R*)-3-methyl-1,2,4-butanetriol and related compounds have been synthesized efficiently in high diastereomeric and enantiomeric purity. Because the opposite chiral directors are readily available, the (2*S*,3*S*)-enantiomers could be made equally easily.

(2) Compounds bearing benzyloxy and boronic ester groups separated by a chain of four intervening carbon atoms are unexpectedly susceptible to benzylic cleavage.

(3) Reduction of an α-chloro boronic ester, RCHClB(OR′)$_2$, with sodium hydride in dimethyl sulfoxide has provided an efficient route to an α-unsubstituted boronic ester, RCH$_2$B(OR′)$_2$.

Experimental Section

General Methods. Procedures similar to those used in this work have been described previously.[1−4] All procedures involving carbanions and other air- or moisture-sensitive intermediates were carried out under an atmosphere of argon.

Pinacol (Bromomethyl)boronate. Diisopropyl (bromomethyl)boronate[7] (226 g, 1.19 mol) and pinacol (155 g, 1.31 mol) in diethyl ether (1 L) were stirred overnight, concentrated, and distilled to yield pinacol (bromomethyl)boronate: bp 35 °C (0.3 Torr) or 72−75 °C (4.5−5 Torr); 239 g (90%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 12), 2.59 (s, 2); HRMS (M^+) calcd for $C_7H_{14}BBrO_2$, *m/e* 222.0250; found *m/e* 222.0257.

2-((*p*-Methoxybenzyl)oxy)methyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane {Pinacol [((*p*-Methoxybenzyl)oxy)-methyl]boronate}. Under argon, a solution of butyllithium in hexane (1.6 M, 194 mL, 0.31 mol) was added slowly to a solution of *p*-methoxybenzyl alcohol (43 g, 0.31 mol) and (optionally) a few crystals of 1,10-phenanthroline indicator in anhydrous THF (250 mL) stirred at 0 °C. The resulting solution of lithium *p*-methoxybenzyl oxide was stirred at 0 °C during the addition of 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [pinacol (bromomethyl)boronate] via cannula. Dimethyl sulfoxide (24.2 g, 0.31 mol) was added, and the mixture was stirred overnight at 20−25 °C. Water (150 mL) was added, followed by light petroleum ether (bp 35−60 °C), and the phases were separated. Saturated aqueous sodium chloride (100 mL) was added to the aqueous phase, which was then extracted with light petroleum ether (25−40 mL). The combined organic phase was washed with water (2 × 100 mL), dried over magnesium sulfate, filtered, and concentrated under vacuum. Distillation yielded 2-((*p*-methoxybenzyl)oxy)methyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a clear oil: bp 128−129 °C (0.25 Torr), 49−60 g (70−86%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 12), 3.24 (s, 2), 3.80 (s, 3), 4.45 (s, 2), 6.85−7.35 (m, 4). This intermediate was not further characterized but was transesterified to **4a** or **4c**.

2-(((*p*-Methoxybenzyl)oxy)methyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane {(*S,S*)-DIPED [((*p*-Methoxybenzyl)oxy)methyl]boronate} (4a). (3*S*,4*S*)-2,5-Dimethyl-3,4-hexanediol [(*S,S*)-DIPED] (36.5 g, 0.25 mol) was added to a solution of 2-(((*p*-methoxybenzyl)oxy)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69.5 g, 0.25 mol) in pentane (150 mL) and stirred 15 min (until the solid dissolved). Water (200 mL) was added, the mixture was shaken vigorously in a separatory funnel, and the phases were separated. The organic phase was washed with water (3 × 100 mL) in order to remove the pinacol and then dried over magnesium sulfate and concentrated under vacuum. The viscous oily 2-(((*p*-methoxybenzyl)oxy)methyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane was pure enough to use directly in the next step but could be distilled, bp 149−151 °C (0.35 Torr), 74 g (97%), or, for small batches, purified by chromatography on silica (230−400 mesh) with 5% ethyl acetate in light petroleum ether: 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.92 (d, J = 6.8 Hz, 12), 1.70 (m, 2), 3.32 (AB, 2), 3.79 (s, 3), 3.89 (m, 2), 4.45 (s, 2), 6.86 (d, J = 8.7 Hz, 2), 7.28 (d, J = 8.4 Hz, 2); 75 MHz ^{13}C NMR ($CDCl_3$) δ 16.73, 17.81, 32.88, 55.18, 75.20, 84.46, 113.60, 129.65, 130.32, 159.11. Anal. Calcd for $C_{17}H_{27}BO_4$: C, 66.68; H, 8.89; B, 3.53. Found: C, 66.11; H, 8.96; B, 3.14.

(1′*R*)-2-(2-((*p*-Methoxybenzyl)oxy)-1-methylethyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane {(*S,S*)-DIPED (1*R*)-[(2-((*p*-Methoxybenzyl)oxy)-1-methylethyl]boronate} (6a). In a 250-mL three-neck round bottom flask was placed 2-(((*p*-methoxybenzyl)oxy)methyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane (**4a**) (30.6 g, 0.1 mol) and dibromomethane (52.2 g, 0.3 mol) in anhydrous tetrahydrofuran (THF) (150 mL) under an argon atmosphere. This mixture was stirred vigorously at ∼78 °C while lithium diisopropylamide (0.12 mol) was added dropwise so that the internal temperature did not rise unduly. (Overheated mixtures showed evidence of decomposition by turning brown.) Powdered anhydrous (fused) zinc chloride was added (53 g, 0.49 mol), and the solution was allowed to warm to room temperature and stirred 12−16 h. The mixture was treated with petroleum ether (bp 35−60 °C) (150 mL) followed by saturated aqueous ammonium chloride (100 mL). The aqueous phase was separated together with the small amount of emulsion and, to facilitate phase separation, was treated with saturated aqueous sodium chloride (∼50 mL) and then extracted with a second portion of petroleum ether (25 mL). The combined organic phase was washed with water (2 × 100 mL) and dried over anhydrous magnesium sulfate. The solution was concentrated on a rotary evaporator and finally under higher vacuum (0.1−1 Torr). The resulting crude (1′*R*)-2-(2-((*p*-methoxybenzyl)oxy)-1-bromoethyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane (**5a**) was dissolved in THF (100 mL) and cooled to −78 °C under argon. The solution was stirred and methylmagnesium chloride in THF (3 M, 35 mL, 0.105

(21) Matteson, D. S.; Tripathy, P. B.; Sarkar, A.; Sadhu, K. M. *J. Am. Chem. Soc.* **1989**, *111*, 4399−4402.

(22) The boronic esters tested were (*S,S*)-DIPED (1*R*,2*S*)-1-bromo-2-(benzyloxy)-4-[(*p*-methoxybenzyl)oxy]butylboronate and its 1-chloro analogue. These compounds were prepared by straightforward application of known reactions and characterized only by 200 MHz ^{1}H NMR.

mol) was added dropwise. The mixture was stirred 12−15 h at 20−25 °C. Light petroleum ether (150 mL) was added, followed by 100 mL of water and a small amount of dilute hydrochloric acid to clear up any emulsion present. The phases were separated, and the aqueous phase was washed with water (2 × 50 mL), dried over magnesium sulfate, filtered, and concentrated under vacuum. Chromatography on silica gel (230−400 mesh) with 5% ethyl acetate in light petroleum ether separated a small amount of 2-methyl-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane (0.85−1.7 g, 5−10%) from the colorless oily (1′*R*)-2-(2-((*p*-methoxybenzyl)oxy)-1-methylethyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane (**6a**) (23.0−31.0 g, 69−93%): 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.89 (d, J = 6.8 Hz, 6), 0.90 (d, J = 6.8 Hz, 6), 1.06 (d, J = 7.4 Hz, 3), 1.50 (m, 1), 1.67 (m, 2), 3.43 (t, J = 8.6 Hz, 1), 3.58 (dd, J = 6.15 Hz, J = 8.9 Hz, 1), 3.80 (s, 3), 3.83 (m, 2), 4.44 (AB, J = 11.7 Hz, 2), 6.86 (d, J = 8.7 Hz, 2), 7.26 (d, J = 8.6 Hz, 2). The use of a larger than normal amount of zinc chloride (53 g, 0.39 mol, 3.9 equiv, instead of 39.4 g, 0.29 mol, 2.9 equiv) resulted in formation of less of the byproduct, 2-methyl-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane. Anal. Calcd for $C_{19}H_{31}BO_4$: C, 68.27; H, 9.35; B 3.23. Found: C, 67.98; H, 9.30; B 2.55.

(4*S*,5*S*,1′*S*,2′*R*)-2-(1′-(Benzyloxy)-3′-((*p*-methoxybenzyl)oxy)-2′-methylpropyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane {(*S*,*S*)-DIPED (1*S*,2*R*)-[(1-(Benzyloxy)-3-((*p*-methoxybenzyl)oxy)-2-methylpropyl]boronate} (8a). The reaction of (1′*R*)-2-(2-((*p*-methoxybenzyl)oxy)-1-methylethyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane (**6a**) (33.4 g, 0.1 mol) with (dibromomethyl)lithium was carried out according to the procedure described above for conversion **4a** to **5a**, except that the amount of zinc chloride used was 39.4 g (0.29 mol). The crude (1′*R*,2′*R*)-2-(1-bromo-3-((*p*-methoxybenzyl)oxy)-2-methylpropyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane (**7a**) was treated with excess lithium benzyl oxide (0.15 mol) under conditions similar to those used for the preparation of 2-((*p*-methoxybenzyl)oxy)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4a**). Chromatography and concentration yielded clear viscous liquid (1′*S*,2′*R*)-2-(1-benzyloxy)-3-((*p*-methoxybenzyl)-oxy)-2-methylpropyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane (**8a**) (29.5−34 g, 65−75%): 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.90 (d, J = 6.7 Hz, 6), 0.92 (d, J = 6.7 Hz, 6), 1.01 (d, J = 6.8 Hz, 3), 1.62 (m, 2), 2.24 (m, 1), 3.31 (d, J = 6.4 Hz, 1), 3.33 (t, J = 6.4 Hz, 1), 3.51 (dd, J = 6.0 Hz, J = 6.2 Hz, 1), 3.79 (s, 3), 3.83 (m, 2), 4.41 (s, 2), 4.52 (AB, 2), 6.81−7.32 (m, 9); HRMS $C_{27}H_{39}BO_5$ (M^+) calcd m/e 454.2890, found m/e 454.2903. Anal. Calcd for $C_{27}H_{39}BO_5$: C, 71.37; H, 8.65; B, 2.38. Found: C, 70.98; H, 8.67; B, 2.46.

(4*S*,5*S*,2′*S*,3′*R*)-2-(2′-(Benzyloxy)-4′-((*p*-methoxybenzyl)oxy)-3′-methylbutyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane {(*S*,*S*)-DIPED (2*S*,3*R*)-[(2-(Benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutyl]boronate} (9a). A solution of (1′*S*,2′*R*)-2-(1-(benzyloxy)-3-((*p*-methoxybenzyl)oxy)-2-methylpropyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane (**8a**) (22.7 g, 50 mmol) and chloroiodomethane (9.7 g, 55 mmol) in THF (50 mL) was stirred at −78 °C during the dropwise addition of butyllithium (1.6 M in hexane, 34.4 mL, 55 mmol). At the end of the addition the mixture turned into a slurry. Stirring was continued for 10−12 h at 20−25 °C. The mixture was diluted with light petroleum ether (75 mL) and extracted with water (3 × 50 mL). The organic phase was dried over magnesium sulfate, filtered, and concentrated under vacuum. The ^{1}H NMR spectrum of this crude product indicated <5% remaining unchanged (1′*S*,2′*R*)-2-(1-benzyloxy)-3-((*p*-methoxybenzyl)oxy)-2-methylpropyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane in the (2′*S*,3′*R*)-2-(2-(benzyloxy)-4-((*p*-methoxybenzyl)-oxy)-3-methylbutyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane (**9a**) (22−23 g, 95−98%): 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.91 (m, 12), 1.02 (d, J = 6.9 Hz, 3), 1.65 (m, 2), 2.25 (m, 1), 3.31−3.55 (m, 3), 3.75 (m, 2), 3.80 (s, 3), 4.41 (s, 2), 4.51 (AB, J = 11.5 Hz, 2), 6.84−7.31 (m, 9).

(2*R*,3*R*)-2-(Benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methyl-1-butanol (10a). A solution of (2′*S*,3′*R*)-2-(2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutyl)-4,5-bis(1-methylethyl)-1,3,2-dioxaborolane (**9a**) (23.4 g, 50 mmol) in THF (140 mL) was stirred in an ice bath. Water (60 mL) and aqueous sodium hydroxide (3 M, 18.6 mL, 56 mmol) were added. Hydrogen peroxide (30%, 6.3 mL, 55 mmol) was added dropwise. The mixture was stirred for an additional 2 h at 20−25 °C. Water (100 mL) was added, and the mixture was extracted with light petroleum ether (100 mL). The phases were separated, the aqueous phase was extracted with light petroleum ether (30 mL), and the combined organic phase was washed with water (2 × 50 mL) and then dried over magnesium sulfate and concentrated under vacuum. The residue was put into a sublimation apparatus and kept in an oil bath at 65−75 °C under vacuum (0.1 Torr) for 2−3 days. The (*S*,*S*)-DIPED sublimed, leaving an oily residue of ∼98% (2*R*,3*R*)-2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methyl-1-butanol (**10a**): 16.2 g (98%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.99 (d, J = 7 Hz, 2), 2.1 (m, 1), 2.5 (1, br) 3.40−3.56 (m, 5), 4.43 (s, 2), 4.55 (AB, 2), 6.85−7.34 (m, 9). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.71; H, 8.08.

(2*R*,3*R*)-2-(Benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methyl-1-(triphenylmethoxy)butane (11a). A solution of (2*R*,3*R*)-2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methyl-1-butanol (3.3 g, 10 mmol) in THF (25 mL) was treated with triphenylmethyl chloride (3.06 g, 11 mmol), triethylamine (5 mL), and 4-(dimethylamino)pyridine (0.12 g, 1 mmol) and stirred at 40 °C for 2 days. The mixture was treated with water (30 mL) and extracted with light petroleum ether (30 mL). The aqueous phase was extracted with a second portion of petroleum ether (10 mL). The combined organic phase was washed with water (2 × 10 mL), dried over magnesium sulfate, filtered, and concentrated under vacuum. The viscous liquid (2*R*,3*R*)-2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methyl-1-(triphenylmethoxy)butane (**11a**) was chromatographed on silica gel (230−400 mesh) with 5:1 hexane/ethyl acetate: 4.4 g (79%); 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.88 (d, J = 6.9 Hz, 3), 2.20 (m, 1), 3.16−3.59 (m, 5), 3.80 (s, 3); 4.38 (AB, 2), 4.63 (AB, 2), 6.84−7.53 (m, 24).

(2*S*,3*R*)-3-(Benzyloxy)-4-(triphenylmethoxy)-2-methyl-1-iodobutane (13a). (2*R*,3*R*)-2-(Benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methyl-1-(triphenylmethoxy)butane (2.79 g, 5 mmol) was oxidized with dichlorodicyanoquinone, and the resulting alcohol **12a** was treated with methanesulfonyl chloride and triethylamine according to the procedure described previously for the preparation of mesylates.[9b] The resulting mesylate was formed quantitatively but was unstable toward storage or purification. The mesylate was treated with sodium iodide (∼4 equiv) in acetone at 20−25 °C for 2 days. The organic phase was dried over magnesium sulfate, filtered, and concentrated under vacuum. The ^{1}H NMR spectrum indicated complete conversion of the mesylate to (2*S*,3*R*)-3-(benzyloxy)-4-(triphenylmethoxy)-2-methyl-1-iodobutane (**13a**): 2.65 g (95%); 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.83 (d, J = 6.7 Hz, 3), 1.90 (m, 1), 3.03−3.61 (m, 5), 4.61 (AB, 2), 7.21−7.51 (m, 20). HRMS ($C_{31}H_{31}IO_2$): calcd, m/e 562.1369; found, m/e 562.1349.

(*S*,*S*)-DIPED (1*R*)-[1-methyl-2-triphenylmethoxy)ethyl]boronate (6b). LDA (lithium diisopropylamide) (129 mL, 1.43 M, 185 mmol) was added dropwise to a well-stirred solution of (*S*,*S*)-DIPED [(triphenylmethoxy)methyl]boronate[8] (**5**) (65.99 g, 154 mmol) and dibromomethane (80.42 g, 462 mmol) in THF (600 mL) at −78 °C. After the addition, anhydrous (freshly fused) zinc chloride (63 g, 463 mmol) was added. The solution was allowed to warm to room temperature and kept for 18 h. The solution was poured into saturated ammonium chloride (500 mL) and ether/hexane (1:1, 600 mL). The organic layer was dried over magnesium sulfate and filtered through a short pad of magnesium sulfate. Removal of solvent gave a mixture of unchanged (*S*,*S*)-DIPED [(triphenylmethoxy)methyl]boronate (**4b**) (∼13%) and (*S*,*S*)-DIPED [(1*R*)-1-bromo-2-(triphenylmethoxy)ethyl]boronate (**5b**). The crude **5b** was dissolved in THF (600 mL) and cooled to −78

°C under argon. The solution was stirred, and methylmagnesium chloride (2.68 M, 57.5 mL, 154 mmol) in THF was added dropwise. The mixture was stirred 12−15 h at 20−25 °C. Ether/hexane (1:1, 600 mL) was added, followed by saturated ammonium chloride (500 mL) to clear up any emulsion present. The phases were separated, and the aqueous phase was washed with water (2 × 300 mL), dried over magnesium sulfate, filtered, and concentrated under vacuum. Chromatography on silica gel (230−400 mesh) with 10% diethyl ether in hexane separated a small amount of (*S,S*)-DIPED methylboronate (10−15%) from the colorless oily (*S,S*)-DIPED (1*R*)-[1-methyl-2-(triphenylmethoxy)ethyl]boronate (**6b**): 52.7 g (115.5 mmol, 75%); 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.89 (d, J = 6.8 Hz, 6), 0.91 (d, J = 6.8 Hz, 6), 1.05 (d, J = 7.4 Hz, 3), 1.50 (m, 1), 1.7 (m, 2), 3.11 (dd, J = 6.7 Hz, J = 8.2 Hz, 1), 3.19 (dd, J = 6.9 Hz, J = 8.2 Hz, 1), 3.85 (m, 2), 7.2−7.5 (m, 15). HRMS: Calcd for $C_{30}H_{37}BO_3$ (M^+) m/e 456.2836, found m/e 456.2794.

(*S,S*)-DIPED (1*S*,2*R*)-[(1-(Benzyloxy)-2-methyl-3-(triphenylmethoxy)propyl]boronate (8b). To a solution of (*S,S*)-DIPED (1*R*)-[1-methyl-2-(triphenylmethoxy)ethyl]boronate (**6b**) (41.33 g, 90 mmol) and methylene bromide (47.2 g, 271 mmol) in THF (300 mL) was added LDA (74 mL, 1.47 M, 108 mmol) dropwise at −78 °C. After the addition, anhydrous (fused) zinc chloride (36.7 g, 270 mmol) was added. The solution was allowed to warm to room temperature and kept for 18 h. The solution was poured into saturated ammonium chloride (300 mL, saturated) and ether/hexane (1:1, 400 mL). The organic layer was dried over magnesium sulfate, and filtered through a short pad of magnesium sulfate. Removal of solvent gave a mixture of unchanged (*S,S*)-DIPED (1*R*)-[1-methyl-2-(triphenylmethoxy)ethyl]boronate (**6b**) (5−10%) and (*S,S*)-DIPED (1*R*,2*R*)-[1-bromo-2-methyl-3-(triphenylmethoxy)-propyl]boronate (**7b**). The crude **7b** was transferred to a solution of sodium benzyl oxide in THF and DMSO at 0 °C. The sodium benzyl oxide solution had been prepared by addition of sodium hydride (4.32 g 108 mmol) (60% dispersion in mineral oil) to benzyl alcohol (10.7 g, 99 mmol) in dimethyl sulfoxide (200 mL) and THF (100 mL) at room temperature overnight. The solution was allowed to warm to room temperature and stirred for 18 h. The mixture was worked up by addition of saturated aqueous ammonium chloride (300 mL) and extraction with hexanes (2 × 300 mL). The organic solution (hexanes layer) was washed with water (6 × 300 mL) and brine (300 mL). Concentration in a rotary evaporator gave crude (*S,S*)-DIPED (1*S*,2*R*)-[1-(benzyloxy)-2-methyl-3-(triphenylmethoxy)propyl]boronate (**8b**) which contained 10% unchanged **6b**. The product was obtained by flash chromatography on silica with 1:20 ether/hexane (44 g, 76.5 mmol, 85%): 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.86 (d, J = 6.8 Hz, 6), 0.87 (d, J = 6.8 Hz, 6), 1.03 (d, J = 6.96 Hz, 3), 1.7 (m, 2), 2.26 (m, 1), 3.06 (dd, J = 6.3 Hz, J = 8.7 Hz, 1), 3.19 (dd, J = 5.2 Hz, J = 8.7 Hz, 1), 3.39 (d, J = 7.6 Hz), 3.81 (m, 2), 4.37 (AB, J = 11.85 Hz, 1), 4.52 (AB, J = 11.85 Hz, 1), 7.2−7.5 (m, 20); ^{13}C NMR ($CDCl_3$) δ 14.70, 16.90, 17.95, 32.91, 36.29, 65.34, 72.52, 84.40, 86.09, 126.68, 127.14, 127.56, 127.65, 128.05, 128.82, 139.07, 144.42.

(*S,S*)-DIPED (1*S*,2*R*)-[1-Butoxy-2-methyl-3-(triphenylmethoxy)propyl]boronate as a Byproduct. Crude (*S,S*)-DIPED (1*R*, 2*R*)-[1-bromo-2-methyl-3-(triphenylmethoxy)ethyl]-boronate (**7b**) was treated with excess lithium benzyl oxide under conditions similar to the reported procedure.[3,4] In addition to **8b** (68%), (*S,S*)-DIPED (1*S*,2*R*)-[(1-butoxy-2-methyl-3-(triphenylmethoxy)propyl]boronate (20%) was isolated by chromatography: 500 MHz ^{1}H NMR ($CDCl_3$) δ 0.83−0.88 (m, 15), 1.01 (d, J = 7 Hz, 3), 1.24 (m, 2), 1.41 (m, 2), 1.58 (m, 2), 2.18 (m, 1), 3.06 (dd, J = 6.5 Hz, J = 8.5 Hz, 1), 3.15 (dd, J = 4.5 Hz, J = 8.5 Hz, 1), 3.20 (d, J = 8.5 Hz), 3.25 (m, 1), 3.38 (m, 1), 3.80 (m, 2), 7.1−7.5 (m, 15); ^{13}C NMR ($CDCl_3$) δ 13.93, 14.57, 16.89, 17.95, 19.25, 32.09, 32.95, 36.15, 65.16, 70.80, 84.32, 86.01, 126.68, 127.56, 128.86, 144.50.

(*S,S*)-DIPED (2*S*,3*R*)-[2-(benzyloxy)-3-methyl-4-(triphenylmethoxy)butyl]boronate (9b). A solution of (*S,S*)-DIPED (1*S*,2*R*)-[1-(benzyloxy)-2-methyl-3-(triphenylmethoxy)-propyl]boronate (**8b**) (13.8 g, 24 mmol) and chloroiodomethane (4.65 g, 26 mmol) in THF (50 mL) was stirred at −78 °C during the dropwise addition of butyllithium (1.6 M in hexane, 16.5 mL, 26.4 mmol). At the end of the addition the mixture turned into a slurry. Stirring was continued for 10−12 h at 20−25 °C. The mixture was diluted with hexane (100 mL) and extracted with water (3 × 50 mL). The organic phase was dried over magnesium sulfate, filtered, and concentrated under vacuum. The ^{1}H NMR spectrum of this crude product indicated <5% remaining unchanged (*S,S*)-DIPED (1*S*,2*R*)-[1-(benzyloxy)-2-methyl-3-(triphenylmethoxy)propyl]boronate (**8b**) in the (*S,S*)-DIPED (2*S*,3*R*)-[2-(benzyloxy)-3-methyl-4-(triphenylmethoxy)butyl]boronate (**9b**) (13.75 g, 97%): 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.87−1.02 (m, 14), 1.02 (d, J = 6.9 Hz, 3), 1.6 (m, 2), 2.18 (m, 1), 3.04 (dd, J = 6.4 Hz, J = 8.8 Hz, 1), 3.12 (dd, J = 5.6 Hz, J = 8.8 Hz, 1), 3.78 (m, 2), 3.83 (m, 1), 4.39 (AB, J = 11.46 Hz, 1), 4.50 (AB, J = 11.46 Hz, 1), 7.2−7.5 (m, 20); ^{13}C NMR ($CDCl_3$) δ 12.98, 16.90, 18.00, 33.07, 38.34, 65.57, 70.85, 78.06, 84.16, 86.19, 126.77, 127.26, 127.53, 127.84, 128.76, 130.15, 139.17, 144.42.

(2*R*,3*R*)-2-(Benzyloxy)-3-methyl-4-(triphenylmethoxy)-1-butanol (10b). A solution of (*S,S*)-DIPED (2*S*,3*R*)-[2-(benzyloxy)-3-methyl-4-(triphenylmethoxy)butyl]boronate (**9b**) (11 g, 18.6 mmol) in THF (90 mL) was stirred in an ice bath. Aqueous sodium hydroxide (3 M, 6.8 mL, 20.5 mmol) was added. Hydrogen peroxide (30%, 2 mL, 25 mmol) was added dropwise. The mixture was stirred for an additional 2 h at 20−25 °C. Water (100 mL) was added, and the mixture was extracted with light petroleum ether (100 mL). The phases were separated, the aqueous phase was extracted with light petroleum ether (30 mL), and the combined organic phase was washed with water (2 × 50 mL) and then dried over magnesium sulfate and concentrated under vacuum. The residue was put into a sublimation apparatus and kept in an oil bath at 65−75 °C under vacuum (0.1 Torr) for 2−3 days. The (*S,S*)-DIPED sublimed, leaving an oily residue of (2*R*,3*R*)-2-(benzyloxy)-3-methyl-4-(triphenylmethoxy)-1-butanol (**10b**): 8.2 g (98%); 300 MHz ^{1}H NMR ($CDCl_3$) δ 1.03 (d, J = 7 Hz, 3), 1.97 (1, br), 2.14 (m, 1), 3.18 (m, 2), 3.58 (m, 3), 4.43 (AB, J = 11.3 Hz, 1), 4.47 (AB, J = 11.3 Hz, 1), 7.2−7.5 (m, 20).

(2*R*,3*R*)-2-(Benzyloxy)-1-((*p*-methoxybenzyl)oxy)-3-methyl-4-(triphenylmethoxy)butane (11b). A solution of (2*R*,3*R*)-2-(benzyloxy)-3-methyl-4-(triphenylmethoxy)-1-butanol (**10b**) (8 mmol, 3.6 g), sodium hydride (0.32 g, 8 mmol) (60% dispersion in mineral oil), dimethyl sulfoxide (20 mL), and THF (40 mL) was stirred at room temperature for 5−8 h. *p*-Methoxybenzyl chloride was added to the stirred mixture at room temperature for 4 h and treated with water (40 mL) and light petroleum ether (50 mL). The phases were separated, the aqueous phase was extracted with light petroleum ether (20 mL), and the combined organic phase was washed with water (2 × 20 mL), dried over magnesium sulfate, and concentrated under vacuum. The resulting viscous oil was chromatographed on silica gel (230−400 mesh) with 1−4% ethyl acetate in light petroleum ether. The yield of (2*R*,3*R*)-(2-(benzyloxy)-1-((*p*-methoxybenzyl)oxy)-3-methyl-4-(triphenylmethoxy)butane (**11b**) was 4.35 g (95%): 300 MHz ^{1}H NMR ($CDCl_3$) 0.98 (d, J = 7 Hz, 3), 2.13 (m, 1), 3.10 (dd, J = 5.9 Hz, J = 8.9 Hz, 1), 3.15 (dd, J = 5.5 Hz, J = 8.9 Hz, 1), 3.50−3.67 (m, 3), 3.79 (s, 3), 4.42 (s, 2), 4.43 + 4.64 (AB, J = 11.6, 2), 7.15−7.5 (m, 24). HRMS: calcd for $C_{39}H_{40}O_4$ (M^+) m/e 572.2927, found m/e 572.2874.

(2*R*,3*R*)-2-(Benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutanol (12b). A solution of (2*R*,3*R*)-2-(benzyloxy)-1-((*p*-methoxybenzyl)oxy)-3-methyl-4-(triphenylmethoxy)butane (**11b**) (5.72 g, 10 mmol) was stirred in a mixture of formic acid and diethyl ether (20 mL, 1:1) at room temperature for 1.5 h. After the end of the reaction the solution was diluted with diethyl ether (20 mL), washed with brine and saturated

aqueous sodium hydrogen carbonate until neutral, dried, and concentrated. The residue was chromatographed on silica gel (230−400 mesh) with 10% ethyl acetate in hexane. The yield of (2*R*,3*R*)-2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutanol (**12b**) was 2.97 g (90%): 300 MHz ^{1}H NMR ($CDCl_3$) 0.93 (d, J = 7 Hz, 3), 2.0 (m, 1), 2.59 (br, 1, O*H*), 3.61 (m, 5), 3.80 (s, 3, OCH_3), 4.49 (AB, 2), 4.53 + 4.74 (AB, J = 11.6, 2), 6.8−7.4 (m, 9); HRMS calcd for $C_{20}H_{26}O_4$ (M^+) m/e 330.1831, found m/e 330.1772. The residue also contained 5% (2*R*,3*R*)-2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutyl formate: HRMS calcd for $C_{21}H_{26}O_5$ (M^+) m/e 358.1780, found m/e 358.1751.

(2*S*,3*R*)-2-(Benzyloxy)-1-chloro-4-((*p*-methoxybenzyl)oxy)-3-methylbutane (13b). To a stirred solution of (0.72 mL, 8.25 mmol) of oxalyl chloride in 20 mL of dichloromethane at 0 °C was added, dropwise over 3 min, *N*,*N*-dimethylformamide (0.65 mL, 8.25 mmol). The resulting white suspension was allowed to warm to room temperature and after 10 min was recooled to 0 °C, and (2*R*,3*R*)-2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutanol (**12b**) (2.5 g, 7.5 mmol) was then added in one portion. The resulting solution was heated at reflux for 4.5 h and then cooled to room temperature, poured into 100 mL of saturated aqueous sodium chloride, and then extracted with two 200 mL portions of ether. The organic extracts were combined and dried over magnesium sulfate and concentrated under vacuum. The resulting oil was chromatographed on silica gel (230−400 mesh) with 4:6 ether/light petroleum ether to yield **13b** (2.35 g, 90%): 300 MHz ^{1}H NMR ($CDCl_3$) 1.01 (d, J = 6.8 Hz, 3), 2.22 (m, 1), 3.48−3.54 (m, 2), 3.59−3.67 (m, 2), 3.77 (m, 1), 3.80 (s, 3), 4.45 + 4.51 (AB, J = 11.7 Hz, 2), 4.51 + 4.70 (AB, J = 11.7 Hz, 2), 6.86−7.34 (m, 9); ^{13}C NMR ($CDCl_3$) δ 14.42, 37.11, 48.79, 55.25, 69.33, 72.63, 73.02, 79.50, 113.75, 127.58, 127.91, 128.31, 129.28, 130.23, 138.40, 159.18. Anal. Calcd for $C_{20}H_{25}O_3Cl$: C, 68.86; H, 7.22; Cl, 10.16. Found: C, 69.02; H, 7.22; Cl, 10.17.

(*S*,*S*)-DIPED (2*S*,3*R*)-[2-(Benzyloxy)-3-methyl-4-(formyloxy)butyl]boronate (9, R^1 = CHO) and (4*R*,5*R*)-2-Oxy-4-(benzyloxy)-5-methyl-1,2-oxaborin (14). A solution of (*S*,*S*)-DIPED (2*S*,3*R*)-[2-(benzyloxy)-3-methyl-4-(triphenylmethoxy)butyl]boronate (**9b**) (0.59 g, 1 mmol) in a mixture of formic acid and diethyl ether (2 mL, 1:1) was stirred at room temperature for 1.5 h. Brine (4 mL) was added, and the mixture was extracted with ether (4 mL). The phases were separated. The organic phase was washed with water (2 × 3 mL) and then dried over magnesium sulfate and concentrated under vacuum. The residue was stirred in a mixture of aqueous sodium hydroxide (1 M, 2 mL) and diethyl ether (2 mL) at room temperature for 3 h. The phases were separated. The ether phase contained DIPED and a 5−10% yield of (*S*,*S*)-DIPED (2*S*,3*R*)-[2-(benzyloxy)-3-methyl-4-(formyloxy)butyl]boronate (**9**, R^1 = CHO), which was separated by chromatography: 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.90−0.93 (m, 14), 0.99 (d, J = 6.9 Hz, 3), 1.65 (m, 2), 2.19 (m, 1), 3.68 (q, J = 6.27 Hz, 1) 3.84 (m, 2), 4.14 (ddd, J = 0.7, 6.5, 10.8 Hz, 1), 4.24 (ddd, J = 0.7, 5.1, 10.8 Hz, 1), 4.45 (AB, J = 11.43 Hz, 1), 4.63 (AB, J = 11.43 Hz, 1), 7.3 (m, 5), 8.05 (s, 1); HRMS calcd for $C_{21}H_{33}O_5B$ (M^+) m/e 376.2421, found m/e 376.2434. The aqueous phase, which contained most of the boron, was neutralized by HCl, extracted with ether (10 mL), and dried over magnesium sulfate. Concentration in a rotary evaporator gave (4*R*,5*R*)-2-oxy-4-(benzyloxy)-5-methyl-1,2-oxaborin (**14**): 500 MHz ^{1}H NMR ($CDCl_3$) δ 0.96 (d, J = 7 Hz, 3), 1.11 (dd, J = 5.5, 17 Hz, 1), 1.24 (dd, J = 6, 17 Hz, 1) 1.70 (1, br), 2.00 (m, 1), 3.71 (ddd, J = 5.5, 2.5, 6 Hz, 1), 3.87 (dd, J = 4.5, 11 Hz, 1), 3.96 (dd, J = 7.5, 11 Hz, 1), 4.44 (AB, J = 12 Hz, 1), 4.47 (AB, J = 12 Hz, 1), 7.2−7.4 (m, 5).

(*S*)-Pinanediol [((*p*-Methoxybenzyl)oxy)methyl]boronate (*ent*-4c). The procedure was similar to that described previously,[4] except that in place of (*S*)-pinanediol (chloromethyl)boronate and lithium *p*-methoxybenzyl oxide, (*S*)-pinanediol (bromomethyl)boronate and sodium *p*-methoxybenzyl oxide were used. Diisopropyl (bromomethyl)boronate[7] (96.4 g, 0.432 mol) and (*S*)-pinanediol in diethyl ether (200 mL) stirred overnight at 20−25 °C, and then distilled, yielded (*S*)-pinanediol (bromomethyl)boronate (113.8 g, 96.5%): bp 94 °C (0.5 Torr); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 3), 1.20 (m, 1), 1.42 (s, 3), 1.70 (s, 3), 1.84−2.47 (m, 5), 2.64 (s, 2), 4.38 (dd, J = 1.8, J = 8.8 Hz, 1) (not characterized further). *p*-Methoxybenzyl alcohol (23.3 g, 0.169 mol) was added to a stirred suspension of sodium hydride (6.74 g of 60% in mineral oil, 0.169 mol) in THF (300 mL) at 20−25 °C. Anhydrous dimethyl sulfoxide (90 mL, 0.127 mol) was added, and the mixture was stirred at 20−25 °C for 2−3 h. (*S*)-Pinanediol (bromomethyl)-boronate (46.0 g, 169 mmol) was added, resulting in an exothermic reaction and formation of a white precipitate. The mixture was stirred at 20−25 °C overnight and then treated with diethyl ether and saturated aqueous ammonium chloride. The ether phase was washed with water followed by saturated sodium chloride and then dried over sodium sulfate and concentrated. The (*S*)-pinanediol [((*p*-methoxybenzyl)oxy)-methyl]boronate was isolated by flash chromatography on silica gel with petroleum ether/diethyl ether (12:1 to 5:1): 44.5 g (80%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 3), 1.15 (m, 1), 1.28 (s, 3), 1.40 (s, 3), 1.83−2.43 (m, 5), 3.30 (s, 2), 3.80 (s, 3), 4.31 (dd, J = 1.8, J = 8.4 Hz, 1), 4.46 (s, 2), 6.87 (d, J = 8.6 Hz, 2), 7.28 (d, J = 8.6 Hz, 2). The 90 MHz ^{1}H NMR spectrum was reported previously.[4]

(*R*)-Pinanediol [((*p*-Methoxybenzyl)oxy)methyl]boronate (4c). (*R*)-Pinanediol (7.7 g, 45.3 mmol) and pinacol [((*p*-methoxybenzyl)oxy)methyl]boronate (12.6 g,45.3 mmol) in 50 mL of diethyl ether were stirred overnight at 20−25 °C. Flash chromatography on 220 g of silica gel with petroleum ether/ethyl acetate (15:1) yielded (*R*)-pinanediol [((*p*-methoxybenzyl)oxy)methyl]boronate: 12.3 g (82%); 200 MHz ^{1}H NMR ($CDCl_3$) same as (*S*)-isomer.

(*R*)-Pinanediol (1*R*)-[2-((*p*-Methoxybenzyl)oxy)-1-methylethyl]boronate (6c). Lithium diisopropylamide (1.5 M as THF complex in cyclohexane, 12.2 mL, 18.2 mmol) was added dropwise to a stirred solution of (*R*)-pinanediol [((*p*-methoxybenzyl)oxy)methyl]boronate (5.00 g, 15.12 mmol) and dibromomethane (7.65 g, 44 mmol) in THF (50 mL) at ∼78 °C. Anhydrous powdered zinc chloride (8.1 g, 59 mmol) was added. After 30 min the cooling bath was removed, and the mixture was stirred at 20−25 °C overnight. The mixture was worked up with saturated aqueous ammonium chloride and diethyl ether, and the ether phase was dried over magnesium sulfate. The solution was concentrated under reduced pressure, and the residue was found to be 95% (*R*)-pinanediol (1*R*)-[1-bromo-2-((*p*-methoxybenzyl)oxy)ethyl]boronate[8] (**5c**) and 5% unchanged [((*p*-methoxybenzyl)oxy)methyl]boronate (**4c**) by NMR analysis. This residue was dissolved in THF (35 mL) and stirred at ∼78 °C during the dropwise addition of methylmagnesium bromide in ether (5.6 mL of 3 M, 16.8 mmol). The mixture was stirred at 20−25 °C overnight and then worked up with saturated aqueous ammonium chloride and diethyl ether, and the ether phase was dried over magnesium sulfate. Concentration followed by flash chromatography on silica gel (60 g) with petroleum ether/ethyl acetate (15:1) yielded 4.0 g (74%) of (*R*)-pinanediol (1*R*)-[2-((*p*-methoxybenzyl)oxy)-1-methylethyl]boronate (**6c**): $[\alpha]^{21}_D$ ∼13.7° (*c* 0.99, $CHCl_3$); 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 3), 1.05 (d, J = 7.0 Hz, 3), 1.15 (m, 1), 1.28 (s, 3), 1.37 (s, 3), 1.47 (m, 1), 1.78−1.9 (m, 2), 2.0−2.06 (m, 1), 2.12−2.22 (m, 1), 2.26−2.38 (m, 1), 3.44 (m, 1), 3.54 (m, 1), 3.80 (s, 3), 4.26 (dd, J = 2, J = 9 Hz, 1), 4.44 (s, 2), 6.85 (d, J = 8.5 Hz, 2), 7.26 (d, J = 8.5 Hz, 2); 75.5 MHz ^{13}C NMR ($CDCl_3$) δ 12.7, 18.36 br, 23.95, 27.05, 28.64, 26.29, 35.48, 38.08, 39.47, 51.24, 55.21, 72.36, 73.28, 77.64, 85.46, 113.59, 129.03, 131.04, 158.93. Anal. Calcd for $C_{21}H_{31}BO_4$: C, 70.40; H, 8.72; B, 3.02. Found: C, 70.27; H, 8.64; B, 3.02.

(*R*)-Pinanediol (1*S*,2*R*)-[1-(Benzyloxy)-3-((*p*-methoxybenzyl)oxy)-2-methylpropyl]boronate (8c). By the procedure described in the preceding paragraph for the preparation of **5c**, (*R*)-pinanediol (1*R*)-[2-((*p*-methoxybenzyl)oxy)-1-

methylethyl]boronate (**6c**) (43.5 mmol) was converted to crude (*R*)-pinanediol (1*R*,2*R*)-[1-bromo-3-((*p*-methoxybenzyl)oxy)-2-methylpropyl]boronate (**7c**), which showed no evidence of unchanged **6c** in the ^{1}H NMR spectrum. Dimethyl sulfoxide (6.8 g, 87 mmol) followed by the crude (1*R*,2*R*)-[1-bromo-3-((*p*-methoxybenzyl)oxy)-2-methylpropyl]boronate was added to a solution of lithium benzyl oxide (87 mmol) at ~78 °C, which had been prepared by addition of butyllithium (54.4 mL of 1.6 M, 87 mmol) to benzyl alcohol (9.4 g, 87 mmol) in THF (100 mL) at ~78 °C. The mixture was stirred at 20−25 °C overnight and then worked up with saturated aqueous ammonium chloride and diethyl ether, and the ether phase was dried over magnesium sulfate. Concentration followed by flash chromatography on silica gel (60 g) with petroleum ether/ethyl acetate (15:1) yielded (*R*)-pinanediol (1*S*,2*R*)-[1-(benzyloxy)-3-((*p*-methoxybenzyl)oxy)-2-methylpropyl]boronate (17.8 g, 85%): $[\alpha]^{21}_D$ ~2.32° (*c* 0.9, $CHCl_3$); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 3), 1.00 (d, J = 7.0 Hz, 3), 1.20 (m, 1), 1.28 (s, 3), 1.34 (s, 3), 1.77−2.43 (m, 5), 3.26−3.57 (m, 4), 3.80 (s, 3), 4.28 (dd, 1), 4.44 (s, 2), 4.46, 4.64 (AB, J = 12.6 Hz, 2), 6.85 (d, 2), 7.29 (m, 7). Anal. Calcd for $C_{29}H_{39}BO_5$: C, 72.80; H, 8.22; B, 2.26. Found: C, 71.90 (low); H, 8.37; B, 2.40.

(*R*)-Pinanediol (2*S*,3*R*)-[2-(Benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutyl]boronate (9c). *n*-Butyllithium in hexane (1.6 M, 15.7 mL, 25.1 mmol) was added dropwise to a stirred solution of (*R*)-pinanediol (1*S*,2*R*)-[1-(benzyloxy)-3-((*p*-methoxybenzyl)oxy)-2-methylpropyl]boronate (**8c**) (10 g, 20.9 mmol) and chloroiodomethane (4.43 g, 25.1 mmol) in THF (160 mL) at ~78 °C. The mixture was stirred at 20−25 °C overnight and then worked up with saturated aqueous ammonium chloride and diethyl ether, and the ether phase was dried over magnesium sulfate. Concentration followed by flash chromatography on silica gel (500 g) with petroleum ether/ethyl acetate (20:1) yielded (*R*)-pinanediol (2*S*,3*R*)-[2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutyl]boronate (**9c**) (8.0 g, 78%): $[\alpha]^{21}_D$ ~4.2° (*c* 0.4, $CHCl_3$); 500 MHz ^{1}H NMR ($CDCl_3$) δ 0.81 (s, 3), 0.95 (d, J = 7.0 Hz, 3), 1.0−1.08 (m, 1), 1.14 (m, 1), 1.16−1.23 (m, 1), 1.26 (s, 3), 1.33 (s, 3), 1.76−1.88 (m, 2), 1.98−2.04 (m, 1), 2.06−2.22 (m, 2), 2.24−2.35 (m, 1), 3.33 (m, 1), 3.47 (m, 1), 3.75 (m, 1), 3.79 (s, 3), 4.23 (dd, J = 2, J = 8.8 Hz, 1), 4.40 (s, 2), 4.46, 4.55 (AB, J = 11.4 Hz, 2), 6.86 (d, 2), 7.28 (m, 7); 75.5 MHz ^{13}C NMR ($CDCl_3$) δ 12.93, 23.99, 27.06, 28.61, 26.38, 35.42, 37.88, 38.07, 39.44, 51.19, 55.21, 71.11, 72.47, 72.63, 77.63, 78.27, 85.51, 113.66, 127.17, 127.65, 128.11, 129.16, 130.85, 139.17, 158.99 (B*C* not observed). Anal. Calcd for $C_{30}H_{41}BO_5$: C, 73.17; H, 8.39; B 2.20. Found: 73.07; H, 8.49; B, 2.20.

(2*R*,3*R*)-2-(Benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutanol (10c). (*R*)-Pinanediol (1*S*,2*R*)-[1-(benzyloxy)-3-((*p*-methoxybenzyl)oxy)-2-methylpropyl]boronate (9.6 g, 20 mmol) was converted to (*R*)-pinanediol (2*S*,3*R*)-[2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutyl]boronate (**9c**), which was not purified but dissolved in THF (270 mL) and treated with hydrogen peroxide (30%, 2.5 mL) and 3 M aqueous sodium hydroxide (6.6 mL). The mixture was allowed to warm to 20−25 °C and stirred for 2 h. The mixture was worked up with water and diethyl ether. The ether phase was dried over sodium sulfate and concentrated. Flash chromatography on silica gel (400 g) with petroleum ether/ethyl acetate (4:1) yielded (2*R*,3*R*)-2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutanol (**10c**) (4.22 g, 64%): $[\alpha]^{21}_D$ +7.73° (*c* 0.9, $CHCl_3$); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.99 (d, J = 7.1 Hz, 3), 2.15 (m, 1), 3.38−3.66 (m, 5), 3.80 (s, 3), 4.43 (s, 2), 4.54, 4.57 (AB, J = 6.0 Hz, 2), 6.87 (d, 2), 7.26 (M, 7). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.01 (low); H, 8.09. A major byproduct was (2*R*)-3-((*p*-methoxybenzyl)oxy)-2-methylpropanal (0.80 g, 19%): 200 MHz ^{1}H NMR ($CDCl_3$) δ 1.12 (d, J = 7.1 Hz, 3), 2.65 (m, 1), 3.62 (d, 1), 3.64 (d, 1), 3.80 (s, 3), 4.46 (s, 2), 6.88 (d, J = 8.4 Hz, 2), 7.24 (d, J = 8.6 Hz, 2), 9.71 (s, 1). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 67.94 (low); H, 7.94.

(2*R*,3*R*)-2-(Benzyloxy)-1-{[(1,1-dimethylethyl)dimethylsilyl]oxy}-4-((*p*-methoxybenzyl)oxy)-3-methylbutane (11c). A solution of (2*R*,3*R*)-2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methylbutanol (2.57 g, 7.8 mmol), *tert*-butyldimethylsilyl chloride (1.52 g, 10.11 mmol), triethylamine (3.84 g, 38.9 mmol), and 4-(dimethylamino)pyridine (85 mg, 0.78 mmol) in THF (16 mL) was stirred overnight at 42 °C. (Higher temperatures resulted in less silylation.) The mixture was worked up with diethyl ether and water. The ether phase was dried over sodium sulfate and concentrated under vacuum. Flash chromatography on silica gel (60 g) with petroleum ether/diethyl ether (20:1) yielded (2*R*,3*R*)-2-(benzyloxy)-1-{[(1,1-dimethylethyl)dimethylsilyl]oxy}-4-((*p*-methoxybenzyl)oxy)-3-methylbutane (**11c**) (2.85 g, 85%): $[\alpha]^{21}_D$ +18.86° (*c* 1.0, $CHCl_3$); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 6), 0.90 (s, 9), 0.99 (d, J = 7 Hz, 3), 2.07 (m, 1), 3.39−3.55 + 3.65−3.82 (m, 5), 3.79 (s, 3), 4.40 (s, 2), 4.51, 4.72 (AB, J = 11.5 Hz, 2), 6.87 (d, J = 8.8 Hz, 2), 7.24 (d, J = 8.8 Hz, 2), 7.3 (m, 5). Anal. Calcd for $C_{26}H_{40}O_4Si$: C, 70.23; H, 9.07. Found: C, 70.17; H, 9.19.

(2*R*,3*R*)-2-(Benzyloxy)-1-{[dimethyl(1,1-dimethylethyl)silyl]oxy}-4-((*p*-methoxybenzyl)oxy)-3-methylbutane (11c) from 10a. A solution of (2*R*,3*R*)-2-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-3-methyl-1-butanol (**10a**) (50 mmol, 16.5 g), chloro(1,1-dimethylethyl)dimethylsilane (9.0 g, 60 mmol), triethylamine (25.3 g, 250 mmol), and 4-(dimethylamino)pyridine (0.6 g, 5 mmol) in THF (50 mL) was stirred at 45−50 °C for 5−8 h. The mixture was cooled to room temperature and treated with water (100 mL) and light petroleum ether (80 mL). The phases were separated, the aqueous phase was extracted with light petroleum ether (20 mL), and the combined organic phase was washed with water (2 × 25 mL), dried over magnesium sulfate, and concentrated under vacuum. The resulting viscous oil was chromatographed on silica gel (230−400 mesh) with 1−4% ethyl acetate in light petroleum ether. The yield of (2*R*,3*R*)-2-(benzyloxy)-1-{[dimethyl(1,1-dimethylethyl)silyl]oxy}-4-((*p*-methoxybenzyl)oxy)-3-methylbutane (**11c**) was 20.2 g (91%): 200 MHz ^{1}H NMR same as above; HRMS ($C_{26}H_{40}O_4Si$) calcd *m*/*e* 444.2696, found *m*/*e* 444.2726.

(2*R*,3*R*)-3-(Benzyloxy)-4-{[(1,1-dimethylethyl)dimethylsilyl]oxy}-2-methyl-1-butanol (12c). (2*R*,3*R*)-2-(Benzyloxy)-1-{[(1,1-dimethylethyl)dimethylsilyl]oxy}-4-((*p*-methoxybenzyl)oxy)-3-methylbutane (2.47 g, 5.76 mmol) and 2,3-dichloro-5,6-dicyano-1,4-quinone (1.57 g, 6.91 mmol) in water (30 mL) and dichloromethane (30 mL) were stirred for 1 h at 20-25 °C. The dichloromethane phase was filtered through Celite, dried over sodium sulfate, and concentrated. Flash chromatography on silica gel (60 g) with petroleum ether/diethyl ether (5:1) yielded (2*R*,3*R*)-3-(benzyloxy)-4-{[(1,1-dimethylethyl)dimethylsilyl]oxy}-2-methylbutanol (1.60 g, 85%): $[\alpha]^{21}_D$ +27.6° (*c* 0.95, $CHCl_3$); 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 6), 0.91 (s, 9), 0.97 (d, J = 7.0 Hz, 3), 1.97 (m, 1), 3.44 (m, 1), 3.60 (m, 2), 3.71, 3.81 (d of AB, J = 4.5, J = 10.9 Hz), 4.54, 4.75 (AB, J = 11.5 Hz), 7.33 (m, 5). Anal. Calcd for $C_{18}H_{32}O_3Si$: C, 66.62; H, 9.94. Found: C, 66.83; H, 10.10.

(2*S*,3*R*)-3-(Benzyloxy)-4-{[dimethyl(1,1-dimethylethyl)silyl]oxy}-2-methyl-1-iodobutane (13c). This compound was prepared from **12c** in the same manner as **13a** was prepared from **12a**. The crude yield was 95%, but **13c** was not very stable: 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 6), 0.91 (s, 9), 1.01 (d, J = 6.6 Hz, 3), 1.72 (m, 1), 3.25−3.87 (m, 5), 4.62 (AB, 2), 7.23−7.38 (m, 5).

(*S*)-Pinanediol (1*S*,2*R*)-[2-(Benzyloxy)-3-((*p*-methoxybenzyl)oxy)-1-methylpropyl]boronate (17). Crude (*S*)-pinanediol (1*S*,2*S*)-[2-(benzyloxy)-1-bromo-3-((*p*-methoxybenzyl)-oxy)propyl]boronate (**16**) was prepared from (*S*)-pinanediol (1*R*)-[1-(benzyloxy)-2-((*p*-methoxybenzyl)oxy)ethyl]boronate (**15**) (1.11 mmol) by the procedure previously described.[4] This crude material was dissolved in THF (3 mL) and stirred at −78 °C during the addition of methylmagnesium bromide in diethyl ether (0.41 mL of 3 M, 1.22 mmol). The mixture was stirred at 20−25 °C overnight and then at 45 °C for 3−4 h.

The mixture was worked up with diethyl ether and saturated aqueous ammonium chloride. The ether phase was dried over magnesium sulfate and concentrated under vacuum. Flash chromatography on silica gel (30 g) with petroleum ether/ethyl acetate (12:1) yielded (*S*)-pinanediol (1*S*,2*R*)-[2-(benzyloxy)-3-((*p*-methoxybenzyl)oxy)-1-methylpropyl]boronate (**17**) (364 mg, 69%): $[\alpha]^{21}_D$ +15.5° (*c* 0.99, $CHCl_3$); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.81 (s, 3), 0.99 (d, J = 7.3 Hz, 3), 1.14 (m, 1), 1.26 (s, 3), 1.29 (s, 3), 1.50 (m, 1), 1.70−2.39 (m, 5), 3.55 (d, 2), 3.77 (m, 1), 3.80 (s, 3), 4.22 (dd, 1), 4.43 + 4.50 (AB, J = 12 Hz, 2), 4.59 + 4.67 (AB, J = 12 Hz, 2), 6.85 (d, 2), 7.26 (m, 7); 125.7 MHz ^{13}C NMR ($CDCl_3$) δ 10.69, 19.8 br (B*C*), 23.96, 27.01, 28.52, 26.15, 35.42, 38.05, 39.37, 51.15, 55.20, 70.86, 71.67, 72.79, 77.53, 80.83, 85.36, 113.62, 127.11, 127.47, 128.09, 129.32, 130.52, 139.22, 159.0. Anal. Calcd for $C_{29}H_{39}BO_5$: C, 72.80; H, 8.22; B, 2.26. Found: C, 72.52; H, 8.28; B, 2.32%.

(*S*)-Pinanediol (2*R*,3*R*)-[3-(Benzyloxy)-4-((*p*-methoxybenzyl)oxy)-2-methylbutyl]boronate (19). Following the previously described procedure for generation of (bromomethyl)lithium,[7] *n*-butyllithium in hexane (0.625 mL of 1.6 M, 1 mmol) was added dropwise to a stirred solution of (*S*)-pinanediol (1*S*,2*R*)-[2-(benzyloxy)-3-((*p*-methoxybenzyl)oxy)-1-methylpropyl]boronate (400 mg, 0.836 mmol) and dibromomethane (174 mg, 1 mmol) in THF (5 mL) cooled with a −78 °C bath. The mixture was allowed to warm to 20−25 °C and stirred overnight. The mixture was treated with petroleum ether and saturated aqueous ammonium chloride, and the organic phase was dried over magnesium sulfate. Concentration under reduced pressure and flash chromatography on silica gel (60 g) with petroleum ether/ethyl acetate yielded (*S*)-pinanediol (2*R*,3*R*)-[3-(benzyloxy)-4-((*p*-methoxybenzyl)-oxy)-2-methylbutyl]boronate (**19**) (290 mg, 70.6%) as a colorless oil: $[\alpha]^{21}_D$ +11.4° (*c* 0.67, $CHCl_3$); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.82 (s, 3), 0.97 (d, J = 6.8 Hz, 3), 1.0−1.23 (m, 2), 1.13 (m, 1), 1.27 (s, 3), 1.32 (s, 3), 1.6−2.4 (m, 6), 3.3−3.67 (m, 3), 3.80 (s, 3), 4.22 (dd, 1), 4.45 (s, 2), 4.59 + 4.71 (AB, J = 12 Hz, 2), 6.86 (d, 2), 7.30 (m, 7); 125.7 MHz ^{13}C NMR ($CDCl_3$) δ 14.8 br (B*C*), 18.52, 23.96, 27.02, 28.58, 26.46, 31.55, 35.46, 38.03, 39.43, 51.17, 55.21, 71.09, 72.29, 72.88, 77.41, 83.48, 85.28, 113.65, 127.19, 127.69, 128.14, 129.18, 130.60, 139.26, 159.02. Anal. Calcd for $C_{30}H_{41}BO_5$: C, 73.17; H, 8.39; B, 2.20. Found: C, 73.33; H, 8.45; B, 2.20%.

(*E*)-1-(2-Butenyl) *p*-Methoxybenzyl ether (20). This compound was isolated as a byproduct from the preparation of (*S*)-pinanediol (2*R*,3*R*)-[3-(benzyloxy)-4-((*p*-methoxybenzyl)-oxy)-2-methylbutyl]boronate: 200 MHz ^{1}H NMR ($CDCl_3$) δ 1.72 (d, J = 6 Hz, 3), 3.80 (s, 3), 3.93 (d, J = 6 Hz, 2), 4.43 (s, 2), 5.78 (m, 2, C*H*═C*H*), 6.88 (d, 2), 7.27 (d, 2). A 500 MHz spectrum with decoupling of the CH_3 indicated that the C*H*═C*H* J = 15.6 Hz. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.56; H, 8.53.

(*S*)-Pinanediol [(Benzyloxy)methyl]boronate (21). This known compound[3,23] was also isolated as a byproduct from the preparation of (*S*)-pinanediol (2*R*,3*R*)-[3-(benzyloxy)-4-((*p*-methoxybenzyl)oxy)-2-methylbutyl]boronate: 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 3), 1.16 (m, 1), 1.28 (s, 3), 1.41 (s, 3), 1.65−2.4 (m, 5), 3.34 (s, 2), 4.23 (dd, 1), 4.53 (s, 2), 7.33 (m, 5), in accord with that previously reported.[3] When the reaction was run with dibromomethane, the apparent molar ratio of this elimination product to chain extension product by NMR analysis was 37:63, though the isolated yield of chain extension product was 70%, and when chloroiodomethane was used under the same conditions, the NMR analysis indicated 57% elimination.

(*R*,*R*)-DICHED (1*R*)-[(1-(Benzyloxy)-2-(triphenylmethoxy)ethyl]boronate (23). (Dichloromethyl)lithium was prepared by addition of 1-butyllithium (85.8 mL, 1.5 M, 129 mmol) slowly down the side of chilled flask to stirred dichloromethane (25.3 g, 298 mmol) in THF (150 mL) at −100 °C as previously described.[24] After 5 min, a solution of (*R*,*R*)-DICHED [(triphenylmethoxy)methyl]boronate (**22**) (50.49 g, 99 mmol) in THF (150 mL) was added via cannula. After 10 min, anhydrous zinc chloride (24.23 g, 178 mmol), which had been dried by fusion and ground in a mortar, was added to the solution. The solution was allowed to warm to room temperature and kept for 18 h to form (*R*,*R*)-DICHED (1*S*)-[1-chloro-2-(triphenylmethoxy)ethyl]boronate. [A sample of chloro compound obtained by concentration of the crude solution showed the following: 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.9−1.4 and 1.55−1.8 (m, 22), 3.40 (dd J = 5.5 and 9.0 Hz, 1), 3.53 (m, 2) 3.92−3.97 (m, 2) 7.19−7.50 (m, 15); 75 MHz ^{13}C NMR ($CDCl_3$) δ 25.82, 25.97, 26.39, 27.33, 28.21, 42.8, 65.92, 84.38, 86.68, 127.01, 127.75, 128.80, 143.87. HRMS: calcd for $C_{35}H_{42}O_3BCl$ (M^+) m/e 556.2916, found m/e 556.2946.] The solvent and the excess dichloromethane were removed under vacuum before the crude chloro compound was transferred to a solution of sodium benzyl oxide in THF and DMSO at 0 °C, which had been prepared by addition of sodium hydride (4.36 g 110 mmol) (60% dispersion in mineral oil) to benzyl alcohol (13.9 g.130 mmol) in dimethyl sulfoxide (200 mL) and THF (100 mL) at room temperature overnight. The mixture was allowed to warm to room temperature and stirred for 18 h and then worked up by addition of saturated aqueous ammonium chloride (300 mL) followed by extraction with hexanes (2 × 300 mL). The organic solution (hexanes layer) was washed with water (6 × 300 mL) and brine (300 mL). Concentration in a rotary evaporator gave crude (*R*,*R*)-DICHED (1*R*)-[(1-(benzyloxy)-2-(triphenylmethoxy)ethyl]boronate (**23**) which contain 10% unchanged starting material. The product was purified by flash chromatography on silica with 1:20 ether/hexane (85% yield): 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.80−1.42 and 1.58−1.84 (m, 22), 3.33 (dd, J = 5.5, and 9.9 Hz, 1), 3.39 (dd, J = 3.7, and 9.9 Hz, 1) 3.54 (dd, J = 3.7, and 5.5 Hz, 1) 3.89−3.93 (m, 2), 4.56 (AB, J = 12 3 Hz, 1), 4.66 (AB, J = 12.3 Hz, 1), 7.19−7.51 (m, 20); 75 MHz ^{13}C NMR ($CDCl_3$) δ 25.87, 25.97, 26.38, 27.38, 28.21, 42.79, 64.48, 72.24, 83.89, 86.44, 126.75, 127.64, 127.98, 128.07, 128.16, 128.92, 139.07, 144.20.

(*R*,*R*)-DICHED (1*S*,2*R*)-(2-(Benzyloxy)-1-methyl-3-(triphenylmethoxy)propyl)boronate (25). (Dichloromethyl)-lithium was prepared by addition of 1-butyllithium (68.5 mL, 1.5 M, 103 mmol) to dichloromethane (20.12 g, 237 mmol) in THF (150 mL) at −100 °C (as described for **23** above). After 5 min, a solution of crude (*R*,*R*)-DICHED (1*R*)-[(1-(benzyloxy)-2-(triphenylmethoxy)ethyl]boronate (**23**) (50 g, 79 mmol) was added to the solution via cannula. After 10 min, anhydrous zinc chloride (30.1 g, 221 mmol) was added. The mixture was allowed to warm to room temperature and kept for 18 h to form a solution of (*R*,*R*)-DICHED (1*S*,2*R*)-[(2-(benzyloxy)-1-chloro-3-triphenylmethoxy)propyl]boronate (**24**). The solution was cooled to 0 °C, and methylmagnesium chloride (52.6 mL, 3 M, 158 mmol) was added dropwise. The solution was allowed to warm to room temperature and kept for 36 h. Aqueous ammonium chloride (10 mL) was added to the mixture. Some gas (methane) was liberated. The solvent was removed by rotary evaporator. To the mixture was added hexane (500 mL) and aqueous ammonium chloride (100 mL). The organic solution was washed with ammonium chloride (200 mL) followed by water (3 × 200 mL) and dried over magnesium sulfate. Removal of the solvent by rotary evaporator yielded a mixture containing a small amount of (*R*,*R*)-DICHED methylboronate (∼10%) with the major product (*R*,*R*)-DICHED (1*S*,2*R*)-(2-(benzyloxy)-1-methyl-3-(triphenylmethoxy)propyl)-boronate (**25**) (46.65 g). Chromatography of **25** resulted in partial decomposition. Therefore, the crude material was used in the next step without further purification. A partially purified analytical sample was obtained by flash chromatography on silica with 1:30 ether/hexane: 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.92−1.38 and 1.48−1.8 (m, 23), 0.86 (d, J = 7.5 Hz, 3), 3.20 (dd, J = 5.7, 10 Hz, 1), 3.27 (dd, J = 3.45, 10 Hz,

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1), 3.68−3.76 (m, 3), 4.58 (AB, J = 11.9 Hz, 1), 4.75 (AB, J = 11.9 Hz, 1), 7.19−7.48 (m, 20); 75 MHz ^{13}C NMR ($CDCl_3$) δ 11.70, 25.79, 25.92, 26.39, 27.47, 28.28, 42.86, 64.93, 71.76, 81.74, 83.28, 86.50, 126.76, 126.91, 127.11, 128.03, 128.80, 139.42, 144.27; HRMS calcd for $C_{44}H_{53}O_4B$ (M^+) m/e 656.4036, found m/e 656.4068. Anal. Calcd for $C_{44}H_{53}O_4B$: C, 80.44; H, 8.14; B, 1.68. Found: C, 79.89 (low); H, 8.42; B, 1.54.

(*R*,*R*)-DICHED (2*R*,3*R*)-[(3-(Benzyloxy)-2-methyl-4-(triphenylmethoxy)butyl]boronate (27). (Dichloromethyl)lithium was prepared by addition of 1-butyllithium (65 mL, 1.5 M, 97.5 mmol) to dichloromethane (19.1 g, 225 mmol) in THF (200 mL) at −100 °C (as described for **23** above). After 5 min, a solution of crude (*R*,*R*)-DICHED (2*S*,3*R*)-(2-(benzyloxy)-1-methyl-4-(triphenylmethoxy)butyl]boronate (**25**) (49.2 g, 75 mmol) was added to the solution via cannula. After 10 min, anhydrous zinc chloride (25.8 g, 189 mmol) was added to the mixture. The mixture was allowed to warm to room temperature, kept for 18 h, and concentrated in a rotary evaporator to yield crude (*R*,*R*)-DICHED (1*S*,2*S*,3*R*)-[3-(benzyloxy)-1-chloro-2-methyl-4-(triphenylmethoxy)butyl]boronate (**26**): HRMS calcd for $C_{45}H_{54}O_4BCl$ (M^+) m/e 704.3804, found m/e 704.3826. The crude **26** was treated with DMSO (100 mL) and sodium hydride (4.5 g 112.5 mmol) (60% dispersion in mineral oil) at room temperature and stirred for 18 h. The mixture was treated with hexanes (300 mL) and was washed with ammonium chloride (300 mL) followed by water (3 × 200 mL) and dried over magnesium sulfate. Removal of the solvent by rotary evaporator yielded a mixture containing a small amount of (2*?*,3*R*)-3-(benzyloxy)-4-(triphenylmethoxy)-2-butanol[25] (∼10%), presumably from accidental oxidation of **25**, with the major product (*R*,*R*)-DICHED (2*R*,3*R*)-[3-(benzyloxy)-2-methyl-4-(triphenylmethoxy)butyl]boronate (**27**) (45.23 g). The product **27** was purified by flash chromatography on silica with 1:30 ether/hexane: 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.66−0.71 (dd, J = 9.3 Hz, 1), 0.8−1.8 (m, 23), 0.83 (d, J = 6.8 Hz, 3), 2.1 (m, 1), 3.17 (dd, J = 5.9, 10.05 Hz, 1), 3.26 (dd, J = 3, 10.05 Hz, 1), 3.38 (m, 1), 3.73−3.79 (m, 2)), 4.57 (AB, J = 11.7 Hz, 1), 4.74 (AB, J = 11.7 Hz, 1), 7.20−7.49 (m, 20); 75 MHz ^{13}C NMR ($CDCl_3$) δ 18.35, 25.86, 26.00, 26.44, 27.48, 28.49, 31.65, 42.99, 64.35, 72.35, 83.28, 83.93, 86.55, 126.82, 127.2, 127.69, 128.17, 128.78, 139.29, 144.26; HRMS calcd for $C_{45}H_{55}O_4B$ (M^+) m/e 670.4193, found m/e 670.4162. Anal. Calcd for $C_{45}H_{55}O_4B$: C, 80.55; H, 8.27; B, 1.64. Found: C, 80.43; H, 8.31; B, 1.63.

(*R*,*R*)-DICHED (1*R*,3*R*,4*R*)-[(1-Allyl-4-(benzyloxy)-3-methyl-5-(triphenylmethoxy)pentyl]boronate (2). (Dichloromethyl)lithium was prepared by addition of 1-butyllithium (6.5 mL, 1.5 M, 9.75 mmol) to dichloromethane (1.9 g, 22.5 mmol) in THF (20 mL) at −100 °C (as described for **23** above). After 5 min, a solution of (*R*,*R*)-DICHED (2*R*,3*R*)-[3-(benzyloxy)-2-methyl-4-(triphenylmethoxy)butyl]boronate (**27**) (5 g, 7.5 mmol) was added to the solution via cannula. After 10 min, anhydrous zinc chloride (2.84 g, 20.8 mmol) was added to the solution. The resulting solution of (*R*,*R*)-DICHED (1*S*,3*R*,4*R*)-[4-(benzyloxy)-1-chloro-3-methyl-5-(triphenylmethoxy)pentyl]boronate was allowed to warm to room temperature and kept for 18 h. The solution was cooled to 0 °C, and allylmagnesium chloride (7.5 mL, 2 M, 15 mmol) was added dropwise. The solution was allowed to warm to room temperature and kept for 36 h. Aqueous ammonium chloride (2 mL) was added to the mixture. The solvent was removed by rotary evaporator. To the mixture was added hexane (50 mL) and aqueous ammonium chloride (10 mL). The organic solution was washed with ammonium chloride (20 mL) followed by water (3 × 20 mL) and dried over magnesium sulfate. Removal of the solvent by rotary evaporator yielded a mixture containing the major product (*R*,*R*)-DICHED (1*R*,3*R*,4*R*)-[1-allyl-4-(benzyloxy)-3-methyl-5-(triphenylmethoxy)pentyl]boronate (**2**) together with 20−30 mol % benzyl chloride, identified by GC-MS (EI) (in CHEM SYSTEM CHEM/database. WILEY.1). A purified sample of **2** was obtained by flash chromatography on silica with 1:20 ether/hexane: 3.26 g (60%); 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.92−1.36 and 1.5−1.8 (m, 25) 0.76 (d, J = 6.8 Hz, 3), 1.92 (m, 1), 2.06 (m, 1), 2.17 (m, 1) 3.16 (dd, J = 6.03, 10.2 Hz, 1), 3.25 (dd, J = 2.46, 10.2 Hz, 1), 3.37 (m, 1), 3.77−3.81 (m, 2), 4.55 (AB, J = 11.7 Hz, 1), 4.70 (AB, J = 11.7 Hz, 1), 4.90 (dd, J = 2.13, 10.11 Hz, 1), 4.96 (dd, J = 2.13, 17.07 Hz, 1), 5.76 (ddd, J = 6.9, 10.11, 17.07 Hz, 1), 7.18−7.49 (m, 20); 75 MHz ^{13}C NMR ($CDCl_3$) δ 14.92, 25.82, 25.92, 26.41, 27.58, 28.43, 34.34, 34.52, 36.51, 43.03, 64.22, 72.16, 83.33, 83.47, 86.54, 114.79, 126.77, 127.13, 127.56, 127.64, 128.11, 128.74, 138.61, 139.30, 144.27; HRMS calcd for $C_{49}H_{61}O_4B$ $(M - 1)^+$ m/e 723.4585, found m/e 723.4565.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-methoxy-1,3,2-dioxaborolane [(*S*,*S*)-DICHED Methoxyboronate] (28). (1*S*,2*S*)-1,2-Dicyclohexylethane-1,2-diol [(*S*,*S*)-DICHED] (45.2 g, 0.2 mol) was stirred with freshly distilled trimethyl borate (20.8 g, 0.2 mol) under argon, and the methanol produced was distilled at atmospheric pressure. The product was distilled, bp 142 °C (1 Torr), 50.5 g (95%): 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.89−1.80 (m, 22), 3.59 (s, 3), 3.79 (m, 2); 75 MHz ^{13}C NMR ($CDCl_3$) δ 25.8, 25.9, 26.4, 27.2, 28.2, 52.66, 82.55; HRMS $C_{15}H_{27}BO_3$ calcd m/e 266.2053, found m/e 266.2058.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-(3-propenyl)-1,3,2-dioxaborolane [(*S*,*S*)-DICHED Allylboronate] (29). Allylmagnesium chloride (50 mL of 2 M in THF, 0.1 mol) was added dropwise to a stirred solution of (*S*,*S*)-DICHED methoxyboronate (**28**) (26.6 g, 0.1 mol) in THF (100 mL) at 0 °C. The mixture was stirred for 1 h at room temperature and treated with saturated aqueous ammonium chloride (100 mL). The mixture was extracted with petroleum ether (bp 35−60 °C) (200 mL), and the organic phase was dried over anhydrous magnesium sulfate. The solution was filtered and concentrated on a rotary evaporator. The oily product **29** was distilled, bp 145−147 °C (0.7 Torr), 26.2−27.0 g (95−98%): 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.92−1.76 (m, 24), 3.84 (m, 2), 4.89−5.03 (m, 2), 5.80−5.94 (m, 1); 75 MHz ^{13}C NMR ($CDCl_3$) δ 25.8, 25.9, 26.4, 27.3, 28.2, 42.9, 83.4, 114.7, 134.2; HRMS $C_{17}H_{29}BO_2$ calcd m/e 276.2260, found m/e 276.2255.

(2′*S*,4*S*,5*S*)-4,5-Dicyclohexyl-2-(allyl(benzyloxy)methyl)-1,3,2-dioxaborolane {(*S*,*S*)-DICHED (*S*)-[Allyl(benzyloxy)-methyl]boronate} (32). [(*S*,*S*)-DICHED (*R*)-[allylbromomethyl]boronate] (**30**) was prepared by the procedure described for preparation of **5a** (intermediate for **6a**), with (*S*,*S*)-DICHED allylboronate (**29**) (24.1 g, 0.087 mol) in place of **4a**, with appropriate amounts of dibromomethane (45.6 g, 0.26 mol), THF (125 mL), LDA (0.105 mol), and zinc chloride (22.6 g, 0.166 mol). After the mixture had warmed to room temperature overnight, it was treated with petroleum ether and saturated ammonium chloride, the organic phase was filtered through a short column of magnesium sulfate, and the solution was concentrated to yield a crude mixture of **30**, DICHED [diallylmethyl]boronate (**31**), and DICHED or its boric acid ester: 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.85−1.4 and 1.6−1.8 (m, theory 22, found 34) [**31**: 2.19 (m, 15% of 4); lit.[19] butanediol [diallylmethyl]boronate, 2.18], 2.66 (m, 2), 3.37 (t, 1) [impurities: 3.83, 3.85 (m's, 0.6)], 3.95 (m, 2) [**31**: 4.93, 4.97, 5.03 (m's, ∼15% of 4); lit.[19] analogue 4.9−5.1], 5.08−5.12 and 5.15 (m's, 2), 5.82 (m, 1) [**31**: 5.81 (m, mostly obscured by **30**); lit.[19] analogue 5.82]; HRMS (**30**) $C_{18}H_{30}BBrO_2$ calcd, m/e 368.1522; found, m/e 368.1541; HRMS (**31**) calcd for $C_{21}H_{35}BO_2$, m/e 330.2730, found, m/e 330.2728. The crude **30** was dissolved in THF (45 mL) and added dropwise to a stirred solution of lithium benzyl oxide (0.13 mol) in an 0 °C bath, which had been prepared by titrating benzyl alcohol (14.1 g) with butyllithium to the 1,10-phenanthroline endpoint in THF (90 mL) at 0 °C. Dimethyl sulfoxide (10 g, 0.13 mol was added, and the solution was kept at room temperature overnight. The

(25) 300 MHz ^{1}H NMR ($CDCl_3$): δ 1.07 (d, J = 6.4 Hz, 3), 2.6 (b), 3.19 (dd, J = 4.6, 10.17 Hz, 1), 3.31 (m, 1), 3.40 (dd, J = 3.75, 10.17 Hz, 1), 3.93 (m, 1), 4.47 (AB, J = 11.4 Hz, 1), 4.76 (AB, J = 11.4 Hz, 1) 7.20−7.49 (m, 20). ^{13}C NMR ($CDCl_3$): δ 18.77, 62.99, 67.75, 72.81, 82.96, 86.88, 127.06, 127.86, 127.94, 128.46, 128.64, 138.12, 143.82. HRMS: calcd for $C_{30}H_{30}O_3$ (M^+) m/e 438.2195, found m/e 438.2203.

mixture was worked up with water and petroleum ether, the petroleum ether phase was concentrated, and the residue of **32** was purified by chromatography on silica with 2% ethyl acetate in petroleum ether (bp 35−60 °C): 15 g (43%); 300 MHz ^{1}H NMR ($CDCl_3$) δ 0.85−1.40 and 1.57−1.79 (m, 22), 2.47 (m, 2, C═CHCH_2CH(OBn)B) [assignments based on decoupling, this frequency irradiated], 3.42 (t, 1, CH_2CH(OBn)B), 3.91 (m, 2), 4.56 (AB, 2), 5.03 (m, 1), 5.11 (m, 1), 5.89 (m, 1, C═CHCH_2), 7.25−7.38 (m, 5); 75 MHz ^{13}C NMR δ 25.86, 25.98, 26.41, 27.41, 28.27, 35.92, 42.88, 72.08, 83.76, 116.37, 127.32, 127.82, 128.18, 135.89, 139.00; HRMS $C_{25}H_{37}BO_3$ calcd, *m*/*e* 396.2836; found, *m*/*e* 396.2849.

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