Highly Stereoselective and Efficient Addition of Organocerium Reagents to *syn*-β-Alkyl-β-hydroxy-α-methyl Ketones by Way of Their Titanium Alkoxides − Synthesis of Complex 1,3-Diol Units with Three Stereodefined Centres

Giuseppe Bartoli,*[a] Marcella Bosco,[a] Emanuela Di Martino,[a] Enrico Marcantoni,[b] and Letizia Sambri[a]

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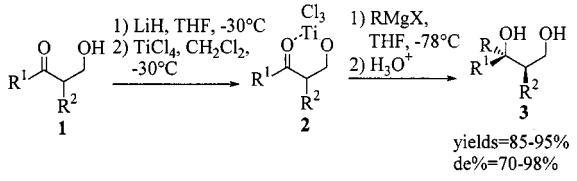
A highly efficient and stereoselective technique for additions to *syn*-β-alkyl-β-hydroxy-α-methyl ketones is now available. The methodology is based on the conversion of the starting material into a trichlorotitanium alkoxide derivative, which is able to assume a stable cyclic arrangement exhibiting high stereofacial discrimination towards nucleophilic alkyl transfer by an appropriate organometallic species. The use of Grignard reagents has serious limitations; in fact, highly hindered and basic reagents do not work well with enolizable substrates. Organocerium compounds can obviate these drawbacks, since side processes such as enolization or interaction with titanium(IV) are almost completely suppressed. The method permits the introduction of a large variety of carbon systems, including primary, secondary and tertiary alkyl chains, as well as aromatic, alkynyl and benzylic moieties, in high yields and with good stereoselectivities.

Introduction

Intense efforts have in recent years been devoted to the stereoselective synthesis of 1,3-diols, since this fragment appears in the skeleton of various biologically active natural products.[1] In this context, addition of an appropriate organometallic reagent to β-hydroxy ketones would represent one of the simpler ways to construct a stereodefined 1,3-diol unit containing a tertiary alcoholic moiety.[2] In spite of the target products' importance, however, this synthetic strategy has not up to now found significant and general solutions. *anti*-1,3-Diols were obtained by Fujisawa et al.[3] as the prevalent diastereoisomers from treatment of a β-hydroxy ketone, with a stereogenic centre in the β-position, with $MeTiCl_3$ and $MeTi(iOPr)_3$. The same organometallic reagents preferentially yielded *syn* isomers on treatment with the *O*-silyl-protected derivatives. In an analogous fashion, Ruano et al.[4] found that MeLi in the presence of $ZnBr_2$ gave prevalent *anti* addition, whereas $AlMe_3$ gave *syn* addition. However, both of these methodologies suffer from some drawbacks: (i) they were applied only to systems with a stereocenter in the β-position, (ii) the methodology was limited to the introduction of a methyl group, and (iii) diastereomeric excesses were generally only moderate to good.

The introduction of an alkyl group into *O*-protected β-hydroxy ketone systems with stereocentres in α-positions, using RLi or RMgX, was studied by Guanti et al.[5] Those authors found that the reaction proceeds with high selectivity, but often in low yields owing to the extensive occurrence of enolization processes when a saturated alkyl chain is bound to the prochiral carbonyl group. In addition, this reaction was applied only to substrates with a phenyl group on the α-stereogenic centre.

More recently we reported[6] that these limitations can be surmounted by conversion of a β-hydroxy ketone such as **1** (Scheme 1) into the corresponding titanium alkoxide **2**, followed by in situ treatment with a Grignard reagent. This methodology is capable of producing the expected diol **3** in high yields and with high diastereomeric purities. Yields are still high even when **1** is an easily enolizable ketone (R^1 = alkyl), the degree of enolization not exceeding 5% of the reaction.



Scheme 1

Given the efficiency of this simple procedure, it appeared of great synthetic interest to extend its application to more complex systems, both as it stands and with appropriate modifications. With this in mind, we experimented on β-hydroxy ketones with stereogenic centres in both the α- and the β-positions. In this work we report our studies on the stereoselective addition of RMgX and $RMgX/CeCl_3$ to *syn*-α,β-dialkyl-substituted β-hydroxy ketones.

Results and Discussion

The synthetic strategy adopted for the stereoselective addition of RMgX species to α-alkyl-β-hydroxy ketones **1** was

[a] Dipartimento di Chimica Organica "A. Mangini", Viale Risorgimento 4, 40136 Bologna, Italy
Fax: (internat.) + 39-051/644-3654
E-mail: bartoli@ms.fci.unibo.it
[b] Dipartimento Scienze Chimiche, Università di Camerino, Via S. Agostino 1, 62032 Camerino (Macerata), Italy

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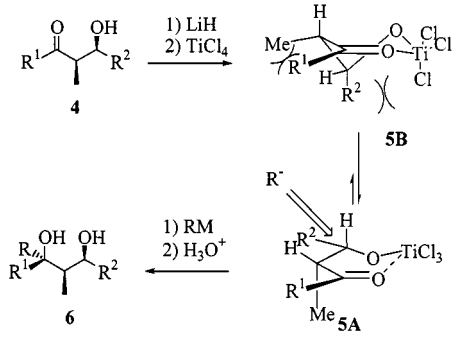
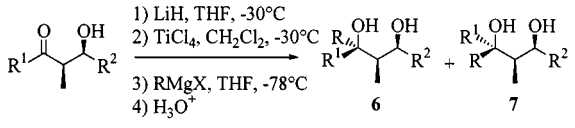
based on their conversion into the corresponding titanium alkoxides **2**. These intermediates can assume cyclic half-chair conformations, which can provide great stereofacial discrimination in the nucleophilic attack of RMgX. In the case of titanium alkoxide **5**, derived from *syn* compound **4**, two concordant effects operate,[6b,7] shifting the equilibrium completely towards conformation **5A** (Scheme 2). In fact, the more stable arrangement requires methyl and R^2 groups in axial and in equatorial dispositions, respectively, so as to minimise steric repulsions between the α-methyl group and R^1 [8] and between R^2 and the ligand at the titanium centre.[9]



Scheme 2. Pathway of alkyl addition to *syn*-α,β-dialkyl-β-hydroxy ketones **4** by way of Ti alkoxide **5**

Attack of a carbanionic species (RM) at the less hindered side of **5A** will give the diastereoisomer **6**. In our previous work[6b] on simple systems, we demonstrated that Grignard reagents do not interact with $TiCl_4$, and thus that they can be used as carbanion sources. The only liability is that these highly basic species can give competitive enolization reactions. This is possible only when R^1 is an enolizable group, the equatorial hydrogen atom at the α-stereocenter not being easily abstracted by RMgX.

We analysed various *syn*-β-alkyl-β-hydroxy-α-methyl ketones of type **4**, with enolizable and non-enolizable R^1 groups. We will first discuss the results for the latter compounds.



4a: R^1=Ph, R^2=Ph
4b: R^1=Ph, R^2=Et

Scheme 3. Addition of Grignard reagents to β-hydroxy-α-methyl ketones **4a**−**b** by way of Ti alkoxide

We applied the same procedure to ketones *syn*-**4a**−**b** (Scheme 3) as had previously been used for hydroxy ketones containing a stereocenter only in the α-position: **4a**−**b** were transformed into their corresponding Ti alkoxides by treatment with LiH in THF, followed by addition of $TiCl_4$ in CH_2Cl_2 at −30 °C. An excess of the appropriate Grignard reagent was subsequently added to the reaction mixture at −78 °C. After 30 min, the reaction mixture was allowed to come to room temperature. Conventional acidic workup gave the expected 1,3-diols **6** in high yields and with excellent diastereomeric purities. The reaction worked well with primary and secondary alkyl chains, and aromatic and alkynyl frameworks, in each case giving yields exceeding 75% (see Table 1).

The possibility of introducing a tertiary alkyl group was also investigated. When the titanium alkoxide of **4a** was allowed to react with *t*BuMgCl under the experimental conditions reported above, the usual workup, followed by chromatographic purification, produced a 1:1 mixture of the expected diol **6af** and of the starting material **4a**. Yields of **6af** accounted for 42% of the reaction materials. Prolonged reaction times and/or the use of a larger excess of *t*BuMgCl did not change the product distribution. The occurrence of a side enolization process to give bis(alkoxide) **8a** could reasonably explain this partial conversion (Scheme 4).

Although the α-hydrogen atom of **5a** is abstracted only with difficulty, enolization can in this particular case compete with addition, since the latter is strongly disfavoured by steric hindrance. Alternatively, *t*BuMgCl can interact with Ti^{IV}: The substitution of a chlorine atom for a *tert*-butyl group in alkoxide **5a** gives a highly encumbered Ti species, which almost completely inhibits addition of sterically hindered nucleophiles.

The absence of isomerization in the recovered starting material favours the latter hypothesis, since the protonation of enolate **8a** might be expected not be stereoselective. Despite the high conversion yield (84%), and the high diastereomeric purity of the obtained diol **6af** (*de* > 98), the reaction is somewhat limited in scope, owing to the difficulty in separating the diol from the large amount of the starting β-hydroxy ketone. In fact, the diol has to be converted into the corresponding cyclic boronate **9af** by treatment of the reaction mixture with $PhB(OH)_2$ [10] (Scheme 8). The boronate can be purified easily (see Exp. Sect.) and quantitatively reconverted, by oxidative treatment, into the parent diol **6af**, thus recovered in 40% yields.[11]

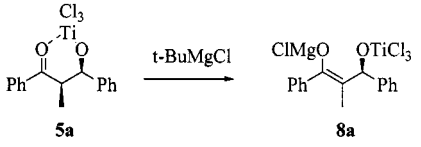
The reactivity of enolizable substrates such as **4c** and **4d** is now analysed. Results of treatment of the Ti alkoxide of **4c** with Grignard reagents depend on the nature of RMgX. With the small and basic Grignard reagent MeMgCl, the desired diol **6ca** was obtained with high diastereomeric purity (**6ca**/**7ca** = 93:7), but in moderate yield (68%) (see Table 2, Entry 1). The less basic benzylmagnesium chloride gave more satisfactory results (yield = 80%, *de* = 90, Table 2, Entry 3), comparable to those obtained in the case of non-enolizable substrates. In contrast, treatment with bulkier or more basic reagents such as PhMgBr and *i*PrMgCl did not work, with 95% and 93% unchanged starting material, respectively, being recovered after 4 h. Extended reaction times did not give any improvement; in addition, we observed a partial isomerization of *syn*-1-hydroxy-2-methyl-1-phenyl-3-pentanone (**4c**) to the *anti* isomer. Very probably, slow conversion of the kinetic enolate **10c** into the thermodynamic one **11c** can occur (Scheme 5). Protonation of **11c** would give a mixture of isomers **4c** and **12c**.

In our previous work[6b] on addition of RMgX to simple β-hydroxy ketones such as **1**, we found that the enolization process was negligible (about 5%) even with basic and

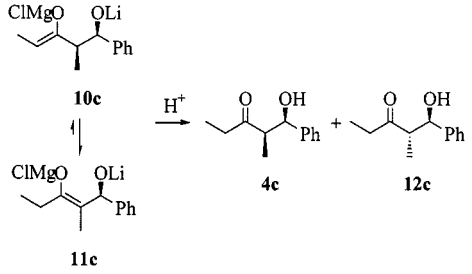
Table 1. Reaction of non-enolizable *syn*-β-hydroxy ketones **4a**−**b** with RMgCl or RMgCl−$CeCl_3$ complexes by way of their titanium alkoxides

Entry	Starting material	R^1	RM	Product	Yield (%)[a]	**6/7**
1	**4a**	Ph	MeMgCl	**6aa**	88	93:7
2	**4a**	Ph	MeMgCl−$CeCl_3$	**6aa**	92	94:6
3	**4a**	Ph	EtMgCl	**6ab**	93	95:5
4	**4a**	Ph	$PhCH_2MgCl$	**6ac**	97	> 99:1
5	**4a**	Ph	PhC≡CMgCl	**6ad**	90	85:15
6	**4a**	Ph	*i*PrMgCl	**6ae**	75	97:3
7	**4a**	Ph	*t*BuMgCl	**6af**	42[b][c] (40)[d]	> 99:1
8	**4a**	Ph	*t*BuMgCl−$CeCl_3$	**6af**	78	> 99:1
11	**4b**	Et	MeMgCl	**6ba**	90	98:2
11	**4b**	Et	*i*PrMgCl	**6be**	90	> 99:1
12	**4b**	Et	*t*BuMgCl−$CeCl_3$	**6bf**	94	> 99:1

[a] Yields of pure isolated product, after column chromatography, if not otherwise mentioned. − [b] 42% of starting material was also recovered. − [c] Estimated from ^{1}H NMR spectrum of a 1:1 mixture of **6af** and starting material **4a**. − [d] Yields in pure isolated product after purification through its boronate cyclic derivative.



Scheme 4



Scheme 5

sterically hindered reagents. The presence of an alkyl substituent in the β-position very probably makes the cyclic intermediate more rigid and more encumbered, with consequently increased discrimination towards attacking nucleophiles. In this situation, it is not surprising that a side enolization process becomes competitive.

In order to obviate this drawback, it was necessary to use less basic organometallic reagents. In this context, organocerium reagents[12] constitute an ideal tool, since they show reactivity comparable or superior to that of Grignard or lithium reagents, in association with very low basicity.[13] In addition, these compounds can easily be prepared from Grignard and lithium derivatives and they are able to transfer a large variety of carbon systems to an electrophilic centre. In other words, organocerium compounds feature the same spectrum of applicability as the parent Li and Mg species.[14] With this in mind, a suspension of PhMgBr/$CeCl_3$ in THF was added at −78 °C to a solution of the Ti alkoxide of **4c**, prepared according to the procedure reported above. The reaction mixture was left to reach −50 °C and stirred for 3 h, then quenched with aqueous HCl (1 M). The usual workup gave the expected diol **6cg** in high

Table 2. Reaction of enolizable *syn*-β-hydroxy ketones **4c**−**d** with RMgCl or RMgCl−$CeCl_3$ complexes by way of their titanium alkoxides

Entry	Starting material	R^1	RM	Product	Yield (%)[a]	**6/7P'**
1	**4c**	Ph	MeMgCl	**6ca**	68	93:7
2	**4c**	Ph	MeMgCl−$CeCl_3$	**6ca**	77	93:7
3	**4c**	Ph	$PhCH_2MgCl$	**6cc**	80	95:5
4	**4c**	Ph	$PhCH_2MgCl$−$CeCl_3$	**6cc**	85	96:4
5	**4c**	Ph	PhMgCl	**6cg**	0[b]	−
6	**4c**	Ph	PhMgCl−$CeCl_3$	**6cg**	80	> 99:1
7	**4c**	Ph	*i*PrMgCl	**6ce**	0[c]	−
8	**4c**	Ph	*i*PrMgCl−$CeCl_3$	**6ce**	60[d]	98:2
9	**4c**	Ph	*t*BuMgCl−$CeCl_3$	**6cf**	0	−
10	**4c**	Ph	PhC≡CMgCl−$CeCl_3$	**6cd**	95	92:8
11	**4d**	Et	MeMgCl−$CeCl_3$	**6da**	75	87:13
12	**4d**	Et	$PhCH_2MgCl$−$CeCl_3$	**6dc**	80	98:2
13	**4d**	Et	PhMgCl−$CeCl_3$	**6dg**	93	> 99:1
14	**4d**	Et	*i*PrMgCl−$CeCl_3$	**6de**	68	> 99:1

[a] Yield of pure isolated product, after column chromatography, if not otherwise mentioned. − [b] A 95% yield of starting material **4c** was recovered. − [c] A 93% yield of starting material **4c** was recovered. − [d] Yield of pure isolated product after purification through its boronate cyclic derivative.

yield (80%) and with excellent diastereomeric purity (**6cg**/**7cg** > 99:1, see Table 2, Entry 6).

This approach displayed general applicability; very good results were in fact obtained on treatment of **4c** with a large variety of RMgX/$CeCl_3$ complexes (see Table 2, Scheme 6). The highly encumbered *i*PrMgCl−$CeCl_3$ added smoothly to the carbonyl function of **4c** to give the expected diol **6ce**, in high yields and with excellent diastereomeric excess (Table 2, Entry 8). However, the reaction failed in the case of *t*BuMgCl−$CeCl_3$ complex, 93% of starting material being recovered after 4 h.

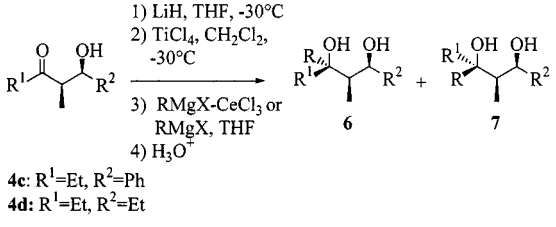
Comparison between results from treatment of **4c** with CH_3MgCl−$CeCl_3$ complex and those with MeMgCl alone allows the role of cerium chloride on the reaction outcome to be cleared up. The latter methodology gave the expected diol **6ca** in 68% yield with *de* = 86 (Table 2, Entry 1), while the former gave a 77% yield with the same *de* value (Table 2, Entry 2). In conclusion, the use of organocerium reagents had improved the efficiency of the reaction, but it had not modified the stereochemical course.

To corroborate these findings, the cerium methodology was applied to non-enolizable β-hydroxy ketones such as **4a**−**b**. Methyl group addition of MeMgCl−$CeCl_3$ complex to **4a** produced a slight improvement in yield, but a similar selectivity with respect to treatment with MeMgCl alone (see Table 1, Entries 1 and 2).

Since the organocerium reagents were prepared by mixing RMgX with dry $CeCl_3$,[15] these findings mean that it is useful to apply the organocerium methodology only when the easily available RMgX does not work well. This is the case, for example, for the introduction of a tertiary carbon chain at the prochiral sp^2 carbon atom of **4a**. The use of the *t*BuMgCl−$CeCl_3$ complex in fact produced a dramatic increase in the yield, from 42% to 78% (Table 1, Entries 7 and 8). Treatment of **4b** with *t*BuMgCl−$CeCl_3$ gave analogous, excellent results.

These findings and those reported above led us to conclude that organocerium reagents are the right choice to solve the problem of diastereoselective organometallic addition to titanium alkoxides of β-hydroxy ketones when side processes such as enolization or interactions with Ti^{IV} become important.

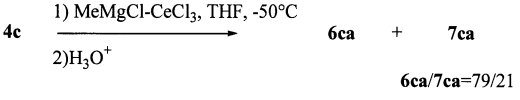
Close examination of Table 1 and 2 suggests the following further comments on the factors governing stereochemical control in system **4**. Firstly, stereoselectivity is independent of the degree of $A^{1,2}$ strain. For a given nucleophile, in fact, no significant differences are observed when



Scheme 6. Treatment of Ti alkoxides of β-hydroxy-α-methyl ketones **4c**−**d** with organocerium or Grignard reagents

the substituent at the carbonyl group is changed from an ethyl (low 1,2 strain) to a phenyl group (high 1,2 strain).[16] This means that the additional and matching effect of the β-alkyl substituent in all cases produces a complete shift of the equilibrium towards conformation **5A**. Secondly, stereoselectivity is independent of the nature of the β-substituent, very similar results being obtained for a given organometallic reagent on going from an ethyl to a phenyl group. The β-substituent very probably does not influence the stereofacial discrimination in conformer **5A**. Thirdly, sterically highly hindered organometallic reagents, such as *i*PrMgCl, *t*BuMgCl and the corresponding organocerium derivatives, are more selective then less encumbered methyl and alkynyl reagents. This is not surprising, since sensitivities towards stereofacial discrimination, and thus stereoselectivity, are expected to increase with increasing bulkiness of the entering carbon nucleophile. However, high diastereoselectivity is observed even in the most unfavourable situations.

Finally, we wish to emphasize that the conversion of compounds **4** into their titanium alkoxides is essential even when organocerium compounds are employed as carbanion sources. In fact, treatment of **4c** with an excess of MeMgCl−$CeCl_3$ gave the expected diol **6ca** in poor yield (44%) and with only moderate diastereomeric excess (see Scheme 7). On the other hand, despite the strong coordinating properties, the ability of cerium(III) compounds to form stable six-membered cyclic chelation complexes has been questioned in recent years.[6b,17]

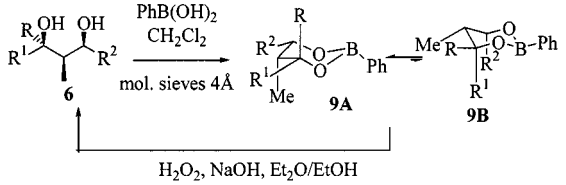


Scheme 7. Treatment of β-hydroxy-α-methyl ketone **4c** with MeMgCl−$CeCl_3$

Structural Assignment

The isomer ratios were determined by ^1H and ^{13}C NMR analysis, using long delay times. For structural assignments, a representative number of diols (**6aa**, **6ac**, **6af**, **6cc**, **6cd**, **6ce**, **6cg**, **6dc**) were converted into the corresponding boron cyclic derivatives (**9aa**, **9ac**, **9af**, **9cc**, **9cd**, **9ce**, **9cg**, **9dc**) by treatment with $PhB(OH)_2$.[10] These compounds, possessing well-defined true chair cyclic structures, permit unambiguous structural analysis. NMR NOE experiments showed that the more stable conformations of **9** in all cases require the R^1 and the R^2 groups to assume equatorial positions, and the α-methyl and R groups to assume axial ones, as shown in Scheme 8. To confirm this assignment, **9ac** and **9cc**, purified by preparative TLC, were submitted to X-ray analysis (see Exp. Sect.).

Additionally, as mentioned above in the text, the conversion of diols into the corresponding cyclic boronates was usefully exploited to separate diols **6af** and **6ce** from the starting β-hydroxy ketones, it being possible to reconvert the boronates into the diols by simple oxidation with H_2O_2 in a basic medium (NaOH 10%, Et_2O/MeOH).[11]



Scheme 8. Cyclization of 1,3-diols **6** into the corresponding phenylboronate derivatives **9**

Conclusions

A Lewis acid moiety can easily be introduced onto a β-hydroxy ketone possessing an α-stereocenter by exploiting the presence of the hydroxy function.[18] The structural modification allows the system to assume a stable cyclic arrangement offering great stereofacial discrimination potential because of an internal Lewis acid coordinating action. At the same time, strong activation of the carbonyl carbon atom towards nucleophilic attack from an appropriate organometallic reagent is produced. In the case of a simple substrate like **1**, Grignard reagents can be used as carbanion sources. In more complex and encumbered systems, such as **4**, the reactions do not work well or do not work at all with sterically highly hindered magnesium reagents, because the addition process is slow with respect to side processes with lower steric demand, such as enolization and $RMgCl-TiCl_4$ interactions. The use of organocerium compounds can actually obviate these failures, giving high addition yields without alteration of stereocontrol.

In conclusion, this work demonstrates that a high degree of compatibility can exist between a chlorotitanium(IV) Lewis acid moiety and organocerium reagents, and that, despite the complexity of the system, these two species are able to exert their assigned roles without undesired interactions. In other words, it is possible to exploit the peculiar features of organocerium compounds − that is, almost complete suppression of side processes − and at the same time to obviate their low efficiency in terms of stereochemical control by exerting this control through a Lewis acid such as $TiCl_4$, capable of forming stable complexes with bidentate compounds.[19]

Experimental Section

General: Flash chromatography was performed on Merck silica gel (0.040−0.063 nm). THF was dried by refluxing in the presence of sodium wire until the blue colour of benzophenone ketyl persisted and then distilled into a dry receiver under nitrogen. All reactions were carried out in oven-dried glassware under dry argon. − ^1H NMR, NOE and decoupling experiments were recorded at 300 MHz with a Varian Gemini instrument. − ^{13}C NMR and DEPT experiments were performed at 75 MHz with a Varian Gemini instrument. The relative proportions of the two diastereoisomers were measured by integration of some ^{13}C peaks, using appropriate long delay times. Chemical shifts are given in ppm from the Me_4Si signal. Coupling constants are given in Hertz. − Compounds **4a**−**d** were obtained with excellent diastereomeric purities (> 99%) by following the procedure reported by Masamura.[20] Spectroscopic data of known compounds **4a**,[21] **4b**[22] and **4d**[23] are identical to those reported in the literature. Spectroscopic data of unknown compound **4c** follow.

(1*R,2*R**)-1-Hydroxy-2-methyl-1-phenyl-3-pentanone (4c):** ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.01 (t, 3 H, CH_3, J_{HH} = 7.2 Hz), 1.08 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 2.30−2.55 (m, 2 H, CH_2), 2.85 (dq, 1 H, CHMe, J_{HH} = 4.1, J_{HH} = 7.1 Hz), 3.1 (br. s, 1 H, OH), 5.05 (d, 1 H, CHPh, J_{HH} = 4.1 Hz), 7.20−7.40 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.5 (CH_3), 10.5 (CH_3), 35.4 (CH_2), 52.2 (CH), 73.2 (CH), 125.9 (CH), 127.3 (CH), 128.2 (CH), 141.8 (C), 201.1 (C). − $C_{12}H_{16}O_2$: calcd. C 74.96, H 8.39; found C 74.95, H 8.40.

Alkylation of *syn*-α,β-Dialkyl-β-hydroxy Ketones to Give the Corresponding 1,3-Diols by Using RMgX (Procedure A). − General Procedure: LiH (1.3 mmol) was added to a solution of the β-hydroxy ketone (1 mmol) in dry THF at −30 °C. After 10 min, $TiCl_4$ (1.3 mmol, 1 M solution in CH_2Cl_2) was added. The reaction mixture turned orange. After 30 min, the reaction mixture was cooled to −78 °C and the appropriate Grignard reagent (6 mmol) was added (see Table 1). The mixture was stirred at this temperature for 1 h and then allowed to come to room temperature. The reaction was then quenched with aqueous HCl (1 M) and the mixture was extracted with diethyl ether, dried with $MgSO_4$ and concentrated at reduced pressure.

Alkylation of *syn*-α,β-Dialkyl-β-hydroxy Ketones to Give the Corresponding 1,3-Diols by Using $RMgX-CeCl_3$ Complexes (Procedure B). − General Procedure: LiH (1.3 mmol) was added to a solution of the β-hydroxy ketone (1 mmol) in dry THF at −30 °C. After 10 min, $TiCl_4$ (1.3 mmol, 1 M solution in CH_2Cl_2) was added. The reaction mixture turned orange. After 30 min, the reaction mixture was cooled to −78 °C and the appropriate $RMgX-CeCl_3$ complex (6 mmol), freshly prepared according to previously reported methodology,[12] was added (see Table 2). The mixture was stirred at this temperature for 1 h and then allowed to come to −50 °C and stirred for 3 h. The reaction was then quenched with aqueous HCl (1 M), and the mixture was extracted with diethyl ether, dried with $MgSO_4$ and concentrated at reduced pressure.

Purification of Reaction Products: 1,3-Diols **6** were generally obtained in pure form by subjecting the crude reaction mixture, obtained by procedure A or B, to flash chromatography on a silica gel column (petroleum ether/Et_2O, 8:2). This procedure failed in the cases of compounds **6af** and **6ce**, which were purified by way of their boron cyclic derivatives (see later in the Exp. Sect.). Yields and diastereomeric ratios are reported in Table 1 and Table 2. All diols obtained were previously unknown. Yields, ^1H and ^{13}C NMR spectroscopic data and elemental analysis follow.

(1*R,2*R**,3*S**)-2-Methyl-1,3-diphenyl-1,3-butanediol (6aa):** According to procedure A, yield 225 mg (88%); according to procedure B, yield 235 mg (92%). − ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.51 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 1.81 (s, 3 H, CH_3), 2.06 (dq, 1 H, CHMe, J_{HH} = 2.0, J_{HH} = 7.1 Hz), 3.2 (br. s, 2 H, OH), 5.54 (d, 1 H, CHPh, J_{HH} = 2.0 Hz), 7.20−7.45 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$,75 MHz): δ = 6.5 (CH_3), 29.8 (CH_3), 48.5 (CH), 73.4 (CH), 77.8 (C), 124.4 (CH), 125.5 (CH), 126.4 (CH), 126.8 (CH), 128.1 (CH), 143.4(C), 148.3 (C). − $C_{17}H_{20}O_2$: calcd. C 79.65, H 7.86, found C 79.61, H 7.89.

(1*R,2*R**,3*S**)-2-Methyl-1,3-diphenyl-1,3-pentanediol (6ab):** According to procedure A, yield 250 mg (93%). − ^1H NMR ($CDCl_3$,

300 MHz): δ = 0.52 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 0.73 (t, 3 H, CH_3, J_{HH} = 7.3 Hz), 2.05−2.20 (m, 2 H, CH and CH_2), 2.20−2.35 (m, 1 H, CH_2), 3.1 (br. s, 1 H, OH), 3.3 (br. s, 1 H, OH), 5.58 (d, 1 H, CHPh, J_{HH} = 1.7 Hz), 7.10−7.50 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 6.8 (CH_3), 8.2 (CH_3), 33.4 (CH_2), 47.8 (CH), 73.1 (CH), 80.6 (C), 125.2 (CH), 125.5 (CH), 126.3 (CH), 126.8 (CH), 128.0 (CH), 128.1 (CH), 143.4 (C), 145.4 (C). − $C_{17}H_{20}O_2$: calcd. C 79.96, H 8.20, found C 79.92, H 8.22.

(1*R,2*R**,3*S**)-2-Methyl-1,3,4-triphenyl-1,3-butanediol (6ac):** According to procedure A, yield 322 mg (97%). − ^{1}H NMR ($CDCl_3$, 300 MHz):δ = 0.54 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 2.27 (dq, 1 H, CH, J_{HH} = 7.0, J_{HH} = 1.2 Hz), 3.0 (br. s, 1 H, OH), 3.30 (d, 1 H, CH_2, J_{HH} = 13.1 Hz), 3.56 (d, 1 H, CH_2, J_{HH} = 13.1 Hz), 3.9 (br. s, 1 H, OH), 5.70 (d, 1 H, CHPh, J_{HH} = 1.2 Hz), 6.80−7.40 (m, 15 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.2 (CH_3), 46.7 (CH_2), 47.9 (CH), 72.9 (CH), 80.5 (C), 125.4 (CH), 125.6 (CH), 126.4 (CH), 126.6 (CH), 126.7 (CH), 127.8 (CH), 127.9 (CH), 128.0(CH), 130.6(CH), 135.8(C), 143.4(C), 144.7(C). − $C_{23}H_{24}O_2$: calcd. C 83.10, H 7.28, found C 83.07, H 7.31.

(1*R,2*R**,3*S**)-2-Methyl-1,3,5-triphenyl-4-pentyne-1,3-diol (6ad):** According to procedure A, yield 308 mg (90%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.60 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 2.20 (dq, 1 H, C*H*CH_3, J_{HH} = 7.1, J_{HH} = 1.6 Hz), 3.2 (br. s, 1 H, OH), 4.4 (br. s, 1 H, OH), 6.01 (d, 1 H, CHPh, J_{HH} = 1.6 Hz), 7.20−7.70 (m, 15 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 5.1 (CH_3), 51.1 (CH), 74.9 (CH), 76.6 (C), 86.1 (C), 92.8 (C), 122.5 (C), 125.4 (CH), 125.5 (CH), 126.9 (CH), 127.3 (CH), 128.0 (CH), 128.1 (CH), 128.3 (CH), 128.5 (CH), 131.7 (CH), 143.3 (C), 143.6 (C). − $C_{24}H_{22}O_2$: calcd. C 84.18, H 6.48, found C 84.15, H 6.45.

(1*R,2*R**,3*S**)-2,4-Dimethyl-1,3-diphenyl-1,3-pentanediol (6ae):** According to procedure A, yield 213 mg (75%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.58 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 0.77 (d, 3 H, CH_3, J_{HH} = 6.6 Hz), 1.01 (d, 3 H, CH_3, J_{HH} = 6.8 Hz), 2.40−2.60 (m, 2 H, $CHMe_2$ and CHMe), 3.1 (br. s, 1 H, OH), 3.2 (br. s, 1 H, OH), 5.49 (d, 1 H, CHPh, J_{HH} < 1 Hz), 7.20−7.50 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.0 (CH_3), 17.2 (CH_3), 17.7 (CH_3), 35.0 (CH), 43.8 (CH), 72.6 (CH), 82.1 (C), 125.5 (CH), 126.0 (CH), 126.5 (CH), 126.8 (CH), 127.6 (CH), 128.1 (CH), 142.2 (C), 143.6 (C). − $C_{19}H_{24}O_2$: calcd. C 80.24, H 8.51, found C 80.22, H 8.53.

(1*R,2*R**,3*R**)-1,3-Diphenyl-2,4,4-trimethyl-1,3-pentanediol (6af):** According to procedure A, yield 120 mg (40%); according to procedure B, yield 232 mg (78%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.37 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 1.02 (s, 9 H, 3 CH_3), 2.56 (dq, 1 H, CHMe, J_{HH} = 1.9, J_{HH} = 7.0 Hz), 3.4 (br. s, 2 H, OH), 5.74 (d, 1 H, CHPh, J_{HH} = 1.9 Hz), 7.00−7.50 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 8.6 (CH_3), 28.1 (CH_3), 39.4 (C), 44.2 (CH), 74.0 (CH), 83.6 (C), 125.3 (CH), 125.9 (CH), 126.8 (CH), 128.1 (CH), 128.4 (CH), 128.7(CH), 143.7(C), 146.3(C). − $C_{20}H_{26}O_2$: calcd. C 80.50, H 8.78, found C 80.47, H 8.80.

(2*R,3*S**,4*R**) 3-Methyl-2-phenyl-2,4-hexanediol (6ba):** According to procedure A, yield 187 mg (90%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.67 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 0.97 (t, 3 H, CH_3, J_{HH} = 7.4 Hz), 1.35−1.50 (m, 1 H, CH_2), 1.55−1.65 (m, 1 H, CH_2), 1.64 (s, 3 H, CH_3), 1.81 (dq, 1 H, $CHCH_3$, J_{HH} = 1.8, J_{HH} = 7.1 Hz), 3.3 (br. s, 2 H, OH), 4.24 (ddd, 1 H, CHMe, J_{HH} = 1.8, J_{HH} = 6.1, J_{HH} = 7.8 Hz), 7.20−7.45 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 6.6 (CH_3), 10.5 (CH_3), 28.3 (CH_2), 29.6 (CH_3), 44.7 (CH), 73.3 (CH), 77.8 (C), 124.4 (CH), 126.1 (CH), 128.0 (CH), 148.2 (C). − $C_{13}H_{20}O_2$: calcd. C 74.96, H 9.68, found C 74.94, H 9.70.

(3*R,4*S**,5*R**)-2,4-Dimethyl-3-phenyl-3,5-heptanediol (6be):** According to procedure A, yield 212 mg (90%). −^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.72 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 0.74 (d, 3 H, CH_3, J_{HH} = 7.7 Hz), 0.85 (d, 3 H, CH_3, J_{HH} = 6.9 Hz), 1.00 (t, 3 H, CH_3, J_{HH} = 7.4 Hz), 1.40−1.55 (m, 1 H, CH_2), 1.55−1.70 (m, 1 H, CH_2), 2.25−2.40 (m, 2 H, $CHMe_2$ and CHMe), 2.9 (br. s, 2 H, OH), 4.21 (ddd, 1 H, CHEt, J_{HH} = 1.5, J_{HH} = 6.1, J_{HH} = 7.8 Hz), 7.20−7.40 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.3 (CH_3), 10.6 (CH_3), 17.2 (CH_3), 17.6 (CH_3), 28.4 (CH_2), 35.0 (CH), 39.8 (CH), 72.8 (CH), 82.2 (C), 126.2 (CH), 126.3 (CH), 127.5 (CH), 142.6 (C). − $C_{15}H_{24}O_2$: calcd. C 76.23, H 10.23, found C 76.25, H 10.20.

(3*R,4*R**,5*S**)-2,2,4-Trimethyl-3-phenyl-3,5-heptanediol (6bf):** According to procedure B, yield 235 mg (94%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.57 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 0.92 (s, 9 H, 3 CH_3), 0.93 (t, 3 H, CH_3, J_{HH} = 7.4 Hz), 1.40−1.65 (m, 2 H, CH_2), 2.2 (br. s, 2 H, OH), 2.34 (dq, 1 H, CHMe, J_{HH} = 1.8, J_{HH} = 7.0 Hz), 4.42 (ddd, 1 H, CHEt, J_{HH} = 1.8, J_{HH} = 5.9, J_{HH} = 7.8 Hz), 7.10−7.50 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 8.5 (CH_3), 10.5 (CH_3), 28.0 (CH_3), 28.8 (CH_2), 39.2 (C), 40.6 (CH), 74.2 (CH), 83.8 (C), 125.7 (CH), 127.3 (CH), 128.4 (CH), 146.8 (C). − $C_{16}H_{26}O_2$: calcd. C 76.75, H 10.47, found C 76.72, H 10.43.

(1*R,2*R**,3*R**)-2,3-Dimethyl-1-phenyl-1,3-pentanediol (6ca):** According to procedure A, yield 140 mg (68%); according to procedure B, yield 160 mg (77%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.78 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 0.88 (t, 3 H, CH_3, J_{HH} = 7.5 Hz), 1.49 (s, 3 H, CH_3), 1.50−1.75 (m, 3 H, CHMe and CH_2), 3.0 (br. s, 2 H, OH), 5.38 (d, 1 H, CHPh, J_{HH} = 1.7 Hz), 7.20−7.45 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 5.7 (CH_3), 8.7 (CH_3), 25.5 (CH_3), 34.2 (CH_2), 44.8 (CH), 73.5 (CH), 76.4 (C), 125.6 (CH), 126.6 (CH), 128.0 (CH), 143.9 (C). − $C_{13}H_{20}O_2$: calcd. C 79.65, H 7.86, found C 79.61, H 7.89.

(1*R,2*R**,3*S**)-3-Benzyl-2-methyl-1-phenyl-1,3-pentanediol (6cc):** According to procedure A, yield 225 mg (80%); according to procedure B, yield 240 mg (85%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.84 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 0.91 (t, 3 H, CH_3, J_{HH} = 7.5 Hz), 1.25−1.40 (m, 1 H, CH_2), 1.45−1.55 (m, 1 H, CH_2), 1.83 (dq, 1 H, CH, J_{HH} = 7.0, J_{HH} = 1.3 Hz), 2.0 (br. s, 1 H, OH), 2.90 (d, 1 H, CH_2, J_{HH} = 13.5 Hz), 3.40 (d, 1 H, CH_2, J_{HH} = 13.5 Hz), 3.9 (br. s, 1 H, OH), 5.58 (d, 1 H, CHPh, J_{HH} = 1.3 Hz), 6.80−7.40 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 6.0 (CH_3), 8.8 (CH_3), 29.2 (CH_2), 41.7 (CH_2), 43.8 (CH), 72.9 (CH), 78.3 (C), 125.6 (CH), 126.6 (CH), 128.0 (CH), 128.2 (CH), 128.3 (CH), 130.5 (CH), 137.4 (C), 143.9 (C). − $C_{19}H_{24}O_2$: calcd. C 80.24, H 8.51, found C 80.27, H 8.49.

(1*R,2*R**,3*R**)-3-Ethyl-2-methyl-1,5-diphenyl-4-pentyne-1,3-diol (6cd):** According to procedure B, yield 280 mg (95%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.89 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 1.12 (t, 3 H, CH_3, J_{HH} = 7.4 Hz), 1.70−2.10 (m, 3 H, CHMe and CH_2), 2.7 (br. s, 2 H, OH), 5.90 (d, 1 H, CHPh, J_{HH} = 1.6 Hz), 7.20−7.55 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 4.7 (CH_3), 9.0 (CH_3), 33.0 (CH_2), 46.4 (CH), 75.4 (CH), 76.1 (C), 85.7 (C), 92.1 (C), 122.8 (C), 125.4 (CH), 126.8 (CH), 128.1 (CH), 128.3 (CH), 131.7 (CH), 143.6 (C). − $C_{20}H_{22}O_2$: calcd. C 81.60, H 7.53, found C 81.61, H 7.51.

(1*R,2*R**,3*S**)-3-Ethyl-2,4-dimethyl-1-phenyl-1,3-pentanediol (6ce):** According to procedure A, yield 0 mg (0%); according to procedure B, yield 142 mg (60%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.80 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 0.90 (t, 3 H, CH_3, J_{HH} = 7.7 Hz), 1.08 (d, 3 H, CH_3, J_{HH} = 6.5 Hz), 1.10 (d, 3 H, CH_3, J_{HH} =

7.3 Hz), 1.50−1.80 (m, 2 H, $CHMe_2$ and CH_2), 2.06 (dq, 1 H, CH, J_{HH} = 7.1, J_{HH} = 1.5 Hz), 2.20−2.40 (m, 1 H, CH_2), 3.1 (br. s, 2 H, OH), 5.49 (d, 1 H, CHPh, J_{HH} = 1.5 Hz), 7.20−7.40 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 6.4 (CH_3), 9.6 (CH_3), 17.4 (CH_3), 27.8 (CH_2), 35.0 (CH_3), 41.8 (CH), 52.3 (CH), 72.7 (CH), 79.4 (C), 125.5 (CH), 126.5 (CH), 128.0 (CH), 144.2 (C). − $C_{15}H_{24}O_2$: calcd. C 76.23, H 10.23, found C 76.26, H 10.21.

(1*R,2*R**,3*R**)-2-Methyl-1,3-diphenyl-1,3-pentanediol (6cg):** According to procedure A, yield 0 mg (0%); according to procedure B, yield 216 mg (80%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.63 (t, 3 H, CH_3, J_{HH} = 7.4 Hz), 1.00 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 1.65−1.85 (m, 1 H, CH_2), 1.95−2.10 (m, 1 H, CH_2), 2.17 (dq, 1 H, CH, J_{HH} = 7.1, J_{HH} = 1.1 Hz), 2.6 (br. s, 1 H, OH), 3.5 (br. s, 1 H, OH), 4.66 (d, 1 H, CHPh, J_{HH} = 1.1 Hz), 7.10−7.55 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 5.7 (CH_3), 7.8 (CH_3), 33.2 (CH_2), 48.4 (CH), 74.1 (CH), 81.0 (C), 125.1 (CH), 125.5 (CH), 126.4 (CH), 126.6 (CH), 127.9 (CH), 128.3 (CH), 143.9 (C), 146.2 (C). − $C_{18}H_{22}O_2$: calcd. C 79.96, H 8.20, found C 79.93, H 8.19.

(3*R,4*R**,5*S**)-3,4-Dimethyl-3,5-heptanediol (6da):** According to procedure B, yield 120 mg (75%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.84 (t, 3 H, CH_3, J_{HH} = 7.5 Hz), 0.91 (t, 3 H, CH_3, J_{HH} = 7.3 Hz), 0.92 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 1.28 (s, 3 H, CH_3), 1.30−1.75 (m, 5 H, CHMe and 2 CH_2), 2.5 (br. s, 2 H, OH), 4.02 (ddd, 1 H, CHEt, J_{HH} = 1.7, J_{HH} = 7.7, J_{HH} = 5.9 Hz). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 5.8 (CH_3), 8.6 (CH_3), 10.5 (CH_3), 25.3 (CH_3), 28.3 (CH_2), 33.8 (CH_2), 40.9 (CH), 73.5 (CH), 76.2 (C). − $C_9H_{20}O_2$: calcd. C 67.45, H 12.58, found C 67.43, H 12.60.

(3*R,4*S**,5*R**)-3-Benzyl-4-methyl-3,5-heptanediol (6dc):** According to procedure B, yield 190 mg (80%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.82 (t, 3 H, CH_3, J_{HH} = 7.0 Hz), 0.90 (t, 3 H, CH_3, J_{HH} = 7.4 Hz), 0.92 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 1.15−1.25 (m, 1 H), 1.30−1.45 (m, 2 H), 1.45−1.65 (m, 2 H), 2.4 (br. s, 2 H, OH), 2.62 (d, 1 H, CH_2, J_{HH} = 13.6 Hz), 3.10 (d, 1 H, CH_2, J_{HH} = 13.6 Hz), 5.58 (ddd, 1 H, CHEt, J_{HH} = 1.3, J_{HH} = 7.6, J_{HH} = 6.8 Hz), 7.10−7.30 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 6.2 (CH_3), 8.8 (CH_3), 10.7 (CH_3), 28.3 (CH_2), 29.0 (CH_2), 40.0 (CH), 41.4 (CH_2), 72.9 (CH), 78.4 (C), 126.4 (CH), 128.2 (CH), 130.5 (CH), 137.6 (C). − $C_{15}H_{24}O_2$: calcd. C 76.23, H 10.23, found C 76.21, H 10.25.

(3*R,4*S**,5*R**)-3-Ethyl-2,4-dimethyl-3,5-heptanediol (6de):** According to procedure B, yield 128 mg (68%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.89 (t, 3 H, CH_3, J_{HH} = 7.5 Hz), 0.93 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 0.95 (t, 3 H, CH_3, J_{HH} = 7.5 Hz), 0.96 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 1.04 (d, 3 H, CH_3, J_{HH} = 6.8 Hz), 1.40−1.70 (m, 4 H, 2 CH_2), 1.81 (dq, 1 H, CH, J_{HH} = 7.0, J_{HH} = 1.3 Hz), 2.10−2.25 (m, 1 H, $CHMe_2$), 2.4 (br. s, 2 H, OH), 4.05 (dt, 1 H, CHEt, J_{HH} = 1.3, J_{HH} = 7.7 Hz). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 6.5 (CH_3), 9.6 (CH_3), 10.6 (CH_3), 17.3 (CH_3), 18.0 (CH_3), 27.5 (CH_2), 28.3 (CH_2), 35.0 (CH), 37.9 (CH), 72.8 (CH), 79.3 (C). − $C_{22}H_{24}O_2$: calcd. C 82.46, H 7.55, found C 82.44, H 7.53.

(3*R,4*R**,5*S**)-4-Methyl-3-phenyl-3,5-heptanediol (6dg):** According to procedure B, yield 206 mg (93%). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.59 (t, 3 H, CH_3, J_{HH} = 7.4 Hz), 0.71 (t, 3 H, CH_3, J_{HH} = 7.5 Hz), 1.13 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 1.25−1.45 (m, 2 H), 1.55−1.75 (m, 1 H), 1.90−2.10 (m, 2 H), 2.6 (br. s, 2 H, OH), 3.35 (ddd, 1 H, CHEt, J_{HH} = 1.4, J_{HH} = 6.6, J_{HH} = 7.7 Hz), 7.20−7.40 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 6.1 (CH_3), 7.7 (CH_3), 10.1 (CH_3), 28.3 (CH_2), 33.3 (CH_2), 43.8 (CH), 74.2 (CH), 81.0 (C), 125.5 (CH), 126.1 (CH), 128.0 (CH), 146.3 (C). − $C_{18}H_{22}O_2$: calcd. C 75.63, H 9.97, found C 75.60, H 9.95.

Cyclization of 1,3-Diols 6aa, 6ac, 6af, 6bf, 6cc, 6cd, 6ce, 6cg and 6dc to the Corresponding Phenyl Boronate Derivatives 9aa, 9ac, 9af, 9bf, 9cc, 9cd, 9ce, 9cg and 9dc. − General Procedure: According to the Pelter[10] methodology, the 1,3-diol (1 mmol), dissolved in dry CH_2Cl_2 (10 mL), was added to $PhB(OH)_2$ (1.1 mmol) and molecular sieves (4 Å, 0.5 g) and the mixture was stirred for 18 h at room temperature. The solution was then filtered, concentrated and purified by chromatography through a short silica gel column to give the corresponding cyclic boronates. In all cases, almost quantitative yields were obtained (> 98%). This procedure allowed boronates to be separated from starting material, but it was unsuccessful for the separation of diastereoisomers. − To obtain pure diastereoisomers (4*R**,5*S**,6*S**)-4-benzyl-5-methyl-2,4,6-triphenyl-1,3,2-dioxaborinane (**9ac**) and (4*S**,5*R**,6*R**)-4-benzyl-4-ethyl-5-methyl-2,6-diphenyl-1,3,2-dioxaborinane (**9cc**) for X-ray analysis, an accurate preparative TLC separation was necessary, followed by crystallization from MeOH. Crystallographic data (excluding structure factors) for structures **9ac** and **9cc** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-155102 (**9ac)** and -155074 (**9cc**). Copies of the data can be obtained free of charge on applicaton to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

(4*S,5*R**,6*R**)-4,5-Dimethyl-2,4,6-triphenyl-1,3,2-dioxaborinane (9aa):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.28 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 0.92 (s, 3 H, CH_3), 2.50 (dq, 1 H, $CHCH_3$, J_{HH} = 7.0, J_{HH} = 3.0 Hz), 5.87 (d, 1 H, CHPh, J_{HH} = 3.0 Hz), 7.20−8.10 (m, 15 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.9 (CH_3), 30.9 (CH_3), 43.5 (CH), 72.7 (CH), 77.8 (C), 124.3 (CH), 125.3 (CH), 126.5 (CH), 127.0 (CH), 127.7 (CH), 128.3 (CH), 131.0 (CH), 134.1 (CH), 136.2 (C), 141.4 (C), 146.3 (C). − $C_{23}H_{23}BO_2$: calcd. C 80.72, H 6.77, found C 80.75, H 6.74.

(4*R,5*S**,6*S**)-4-Benzyl-5-methyl-2,4,6-triphenyl-1,3,2-dioxaborinane (9ac):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.33 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 2.74 (dq, 1 H, CH, J_{HH} = 7.0, J_{HH} = 3.2 Hz), 3.33 (d, 1 H, CH_2, J_{HH} = 13.2 Hz), 3.61 (d, 1 H, CH_2, J_{HH} = 13.2 Hz), 6.04 (d, 1 H, CHPh, J_{HH} = 3.2 Hz), 6.80−8.20 (m, 20 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 8.2 (CH_3), 42.1 (CH), 49.0 (CH_2), 72.8 (CH), 80.5 (C), 125.3 (CH), 126.2 (CH), 126.5 (CH), 127.0 (CH), 127.4 (CH), 127.8 (CH), 128.3 (CH), 130.7 (CH), 131.1 (CH), 134.2 (CH), 136.0 (C), 141.3 (C), 143.1 (C). − $C_{29}H_{27}BO_2$: calcd. C 83.26, H 6.51, found C 83.29, H 6.54.

(4*R,5*R**,6*R**)-4-(*tert*-Butyl)-5-methyl-2,4,6-triphenyl-1,3,2-dioxaborinane (9af):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.17 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 1.03 (s, 9 H, 3 CH_3), 2.92 (dq, 1 H, CH, J_{HH} = 7.0, J_{HH} = 3.1 Hz), 5.85 (d, 1 H, C*H*Ph, J_{HH} = 3.1 Hz), 7.00−8.10 (m, 15 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.4 (CH_3), 28.5 (CH_3), 39.4 (CH), 39.8 (C), 73.1 (CH), 84.0 (C), 124.9 (CH), 125.1 (CH), 126.2 (CH), 126.3 (CH), 126.9 (CH), 127.1 (CH), 127.7 (CH), 127.9 (CH), 128.3 (CH), 130.9 (CH), 134.1 (CH), 141.9 (C), 145.0 (C). − $C_{26}H_{29}BO_2$: calcd. C 81.26, H 7.61, found C 81.29, H 7.59.

(4*R,5*R**,6*S**)-4-(*tert*-Butyl)-6-ethyl-5-methyl-2,4-diphenyl-1,3,2-dioxaborinane (9bf):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.45 (d, 3 H, CH_3, J_{HH} = 6.9 Hz), 0.91 (s, 9 H, 3 CH_3), 1.00 (s, 3 H, CH_3, J_{HH} = 7.3 Hz), 1.40−1.50 (m, 1 H, CH_2), 1.60−1.75 (m, 1 H, CH_2), 2.58 (dq, 1 H, CH, J_{HH} = 6.9, J_{HH} = 3.0 Hz), 5.85 (m, 1 H, CHEt), 7.05−8.00 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.7 (CH_3), 10.2 (CH_3), 27.2 (CH_2), 28.4 (CH_3), 37.0

(CH), 39.8 (C), 73.6 (CH), 84.0 (C), 124.9 (CH), 126.0 (CH), 126.4 (CH), 127.0 (CH), 127.5 (CH), 127.8 (CH), 130.5 (CH), 134.0 (CH), 145.4 (C). − $C_{22}H_{29}BO_2$: calcd. C 78.58, H 8.69, found C 78.61, H 8.71.

(4*S,5*R**,6*R**)-4-Benzyl-4-ethyl-5-methyl-2,6-diphenyl-1,3,2-dioxaborinane (9cc):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.62 (d, 3 H, CH_3, J_{HH} = 7.0), 1.02 (t, 3 H, CH_3, J_{HH} = 6.6), 1.40−1.60 (m, 1 H, CH_2), 1.60−1.75 (m, 1 H, CH_2), 2.20 (dq, 1 H, CH, J_{HH} = 7.0, J_{HH} = 3.1 Hz), 3.01 (d, 1 H, CH_2, J_{HH} = 14.0 Hz), 3.42 (d, 1 H, CH_2, J_{HH} = 14.0 Hz), 5.80 (d, 1 H, CHPh, J_{HH} = 3.1 Hz), 7.20−8.00 (m, 20 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.0 (CH_3), 8.1 (CH_3), 28.0 (CH_2), 39.5 (CH), 43.5 (CH_2), 72.7 (CH), 78.4 (C), 125.4 (CH), 126.6 (CH), 127.0 (CH), 127.7 (CH), 128.2 (CH), 128.3 (CH), 130.9 (CH), 134.2 (CH), 137.4 (C), 141.9 (C). − $C_{24}H_{25}BO_2$: calcd. C 80.85, H 7.07, found C 80.81, H 7.06.

(4*R,5*R**,6*R**)-4-Ethyl-5-methyl-2,6-diphenyl-4-(2-phenylethynyl)-1,3,2-dioxaborinane (9cd):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.67 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 1.24 (t, 3 H, CH_3, J_{HH} = 7.6 Hz), 1.75−1.90 (m, 1 H, CH_2), 2.05−2.15 (m, 1 H, CH_2), 2.40 (dq, 1 H, CHMe, J_{HH} = 2.8, J_{HH} = 7.1 Hz), 6.11 (d, 1 H, CHPh, J_{HH} = 2.8 Hz), 7.20−7.55 (m, 13 H, Ph), 7.95−8.05 (m, 2 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 5.5 (CH_3), 8.7 (CH_3), 32.3 (CH_2), 42.5 (CH), 74.3 (CH), 75.4 (C), 85.3 (C), 91.4 (C), 125.3 (C), 125.4 (CH), 127.0 (CH), 127.6 (CH), 128.3 (CH), 128.5 (CH), 131.0 (CH), 131.8 (CH), 134.2 (CH), 141.4 (C). − $C_{26}H_{25}BO_2$: calcd. C 82.06, H 6.63, found C 82.07, H 6.61.

(4*S,5*R**,6*R**)-4-Ethyl-4-isopropyl-5-methyl-2,6-diphenyl-1,3,2-dioxaborinane (9ce):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.63 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 0.97 (t, 3 H, CH_3, J_{HH} = 7.7 Hz), 1.16 (d, 3 H, CH_3, J_{HH} = 7.2 Hz), 1.19 (d, 3 H, CH_3, J_{HH} = 6.9 Hz), 1.60−1.75 (m, 1 H, CH_2), 1.80−1.95 (m, 1 H, CH_2), 2.25−2.35 (m, 1 H, $CHMe_2$), 2.46 (dq, 1 H, CH, J_{HH} = 7.1, J_{HH} = 3.0 Hz), 5.59 (d, 1 H, CHPh, J_{HH} = 3.0 Hz), 7.25−7.50 (m, 8 H, Ph), 7.90−8.00 (m, 2 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.3 (CH_3), 9.3 (CH_3), 17.3 (CH_3), 18.6 (CH_3), 26.5 (CH_2), 37.3 (CH), 37.5 (CH), 72.3 (CH), 79.5 (C), 125.3 (CH), 126.8 (CH), 127.5 (CH), 128.2 (CH), 130.6 (CH), 134.0 (CH), 142.0 (C). − $C_{21}H_{27}BO_2$: calcd. C 78.21, H 8.45, found C 78.24, H 8.44.

(4*R,5*R**,6*R**)-4-Ethyl-5-methyl-2,4,6-triphenyl-1,3,2-dioxaborinane (9cg):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.77 (t, 3 H, CH_3, J_{HH} = 7.4 Hz), 0.81 (d, 3 H, CH_3, J_{HH} = 7.0 Hz), 1.70−1.90 (m, 1 H, CH_2), 2.00−2.15 (m, 1 H, CH_2), 2.55 (dq, 1 H, CH, J_{HH} = 7.0, J_{HH} = 2.7 Hz), 4.89 (d, 1 H, CHPh, J_{HH} = 2.7 Hz), 7.10−7.55 (m, 13 H, Ph), 8.00−8.15 (m, 2 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 6.5 (CH_3), 7.8 (CH_3), 32.9 (CH_2), 44.0 (CH), 73.1 (CH), 81.7 (C), 125.2 (CH), 126.8 (CH), 126.9 (CH), 127.7 (CH), 128.1 (CH), 128.5 (CH), 131.0 (CH), 134.2 (CH), 141.5 (C), 145.4 (C). − $C_{24}H_{25}BO_2$: calcd. C 80.85, H 7.07, found C 80.83, H 7.06.

(4*R,5*S**,6*R**)-4-Benzyl-4,6-diethyl-5-methyl-2-phenyl-1,3,2-dioxaborinane (9dc):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.14 (d, 3 H, CH_3, J_{HH} = 7.1 Hz), 1.24 (t, 3 H, CH_3, J_{HH} = 7.6 Hz), 1.36 (t, 3 H, CH_3, J_{HH} = 7.4 Hz), 1.70−1.95 (m, 3 H), 2.00−2.10 (m, 1 H), 2.17 (dq, 1 H, CHMe, J_{HH} = 7.1, J_{HH} = 3.1 Hz), 3.09 (d, 1 H, CH_2, J_{HH} = 14.0 Hz), 3.50 (d, 1 H, CH_2, J_{HH} = 14.0 Hz), 4.70 (ddd, 1 H, CHEt, J_{HH} = 3.1, J_{HH} = 5.5, J_{HH} = 8.3 Hz), 7.50−8.10 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 6.3 (CH_3), 8.0 (CH_3), 10.4 (CH_3), 27.1 (CH_2), 27.7 (CH_2), 36.6 (CH_2), 43.2 (CH), 73.0 (CH), 78.1 (C), 126.3 (CH), 127.5 (CH), 127.9 (CH), 130.4 (CH), 134.0 (CH), 137.5 (C). − $C_{21}H_{27}BO_2$: calcd. C 78.27, H 8.45, found C 78.30, H 8.42.

Conversion of Cyclic Boronates 9af and 9ce into the Corresponding Diols 6af and 6ce: Pure **9af** and **9ce** were reconverted into the corresponding diols **6af** and **6ce** by treatment with H_2O_2 (10%) and aqueous NaOH (10%) in an Et_2O/EtOH (1:1) solvent mixture.[11]

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