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Conversion of Conjugated Enones into Enantiomerically Pure β-Hydroxy Ketones or 1,3-Diols – Samarium(II) Bromide Reductions of Protected α,β-Dihydroxy Ketones

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Dedicated to Professor Rolf Huisgen on the occasion of his 90th birthday

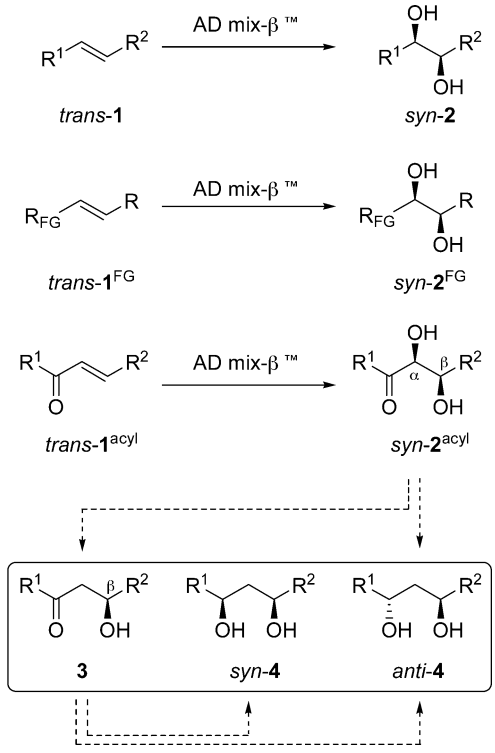
Keywords: Asymmetric dihydroxylation / Defunctionalization / Diastereoselectivity / Reduction / Samarium reagents

Asymmetric dihydroxylations of α,β-unsaturated ketones in the presence of Sharpless' AD mix-β™ delivered α,β-dihydroxy ketones or, if phenylboronic acid was present, the corresponding phenylboronates. The C^{α}–O bonds of these species were removed at –78 °C – in the former case after acetonide formation, in the latter case directly – in an unprecedented manner, namely by treatment with a suspension of Sm^{II} bromide in THF/MeOH. The resulting monohydroxy ketones could be reduced if so desired to give *syn*- or *anti*-configured 1,3-diols. The same diols were produced in one-pot reductions of the α,β-dihydroxy ketone diacetonides with Sm^{II} bromide at 0 °C. When the α,β-dihydroxy ketone phenylboronates were treated likewise, the phenylboronates of the 1,3-diols were obtained. Diastereocontrol in the one-pot reductions varied from perfect to nearly absent.

Introduction

The asymmetric dihydroxylation ("AD") reaction from a starting olefin – preferably one with a disubstituted *trans*-configured C=C bond (*trans*-**1**) – establishes a glycol moiety with *syn*-oriented OH groups at stereocenters of known absolute configurations (Scheme 1).[1] AD reactions of the olefins *trans*-$\mathbf{1}^{FG}$, containing another functional group ("FG"), lead to *functionalized* glycols *syn*-$\mathbf{2}^{FG}$ in essentially enantiomerically pure state.[2] Glycols of this kind, as well as simple glycols, are versatile building blocks for fine chemicals, pharmaceuticals, and agrochemicals.[3] AD reactions of the α,β-unsaturated *ketones* ("conjugated enones") *trans*-$\mathbf{1}^{acyl}$ furnish the *syn*-configured α,β-dihydroxy ketones *syn*-$\mathbf{2}^{acyl}$.[4–8] In addition to a certain interest in these compounds in their own right, Körber and Risch from our group showed that they also constitute novel precursors of the enantiomerically pure 1,3-diols **4**, via the intermediate β-hydroxy ketones **3**.[9] 1,3-Diols with *syn* or *anti* configurations are important structural motifs in natural products.[10]

The Körber/Risch link between conjugated enones, α,β-dihydroxy ketones (or their protected forms), β-hydroxy ketones, and 1,3-diols, starting from the octenone *trans*-$\mathbf{1}^{acyl}$**b**, is demonstrated in Scheme 2. The α,β-dihydroxy ketone *syn*-$\mathbf{2}^{acyl}$**b**, obtained with 100% *ee*, could be defunc-



Scheme 1. Asymmetric Sharpless dihydroxylations ("AD reactions") of 1,2-disubstituted ethylenes and their adaptation to syntheses of β-hydroxy ketones (**3**) and 1,3-diols (*syn*- and *anti*-**4**).

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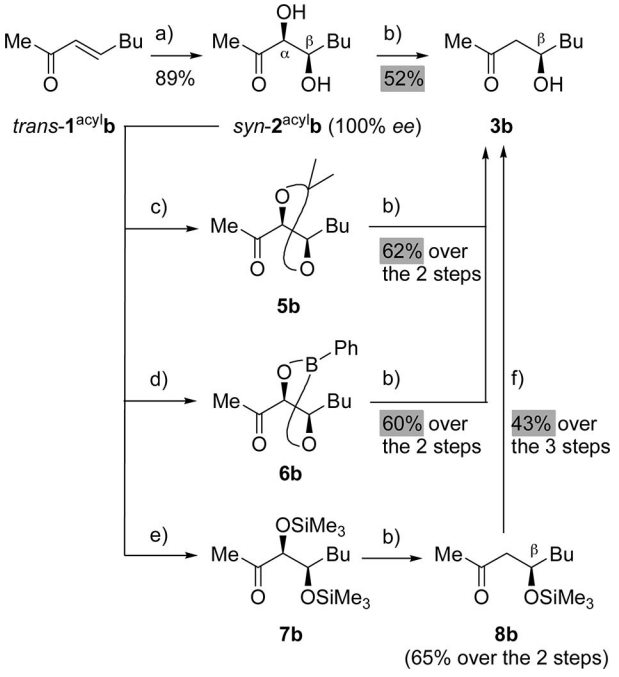
tionalized at C_α by treatment with samarium(II) iodide[11] (2.1 equiv., –78 °C to room temp.) to give the β-hydroxy ketone **3b** in 52% yield.[12,13] When the α,β-dihydroxy ketone **2b** was protected as the acetonide **5b** prior to the same samarium(II)-mediated defunctionalization, the overall yield of the β-hydroxy ketone **3b** was raised to 62%.[14,15] It turned out to be almost as high (60%) when the phenylboronate **6b** was used as an intermediate. Glycol derivatization and subsequent defunctionalization proceeded best via the bis(trimethylsilyl ether) **7b** of the dihydroxy ketone **2b**:[16] the β-siloxy ketone **8b** was isolated in 65% yield over the two steps. However, its desilylation gave the β-hydroxy ketone **3b** in only 66% yield. This lowered the overall yield to 43% and made the sequence unattractive.



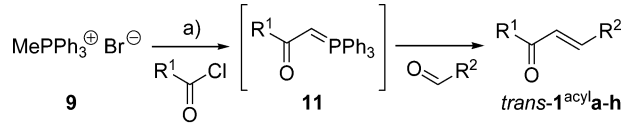
Scheme 2. SmI_2-mediated α-defunctionalizations of the α,β-dihydroxy ketone *syn*-**2**^{acyl}**b** and its derivatives.[9] *Reagents and conditions:* a) $K_2OsO_2(OH)_4$ (1 mol-%), $(DHQD)_2PHAL$ (5 mol-%), $K_3Fe(CN)_6$ (3.0 equiv.), $NaHCO_3$ (3.0 equiv.), K_2CO_3 (3.0 equiv.), *t*BuOH/H_2O (1:1, v/v), 0 °C, 60 h. b) SmI_2 (2.1 equiv.), THF, –78 °C, addition of substrate in THF/MeOH (2:1, v/v), 50 min; –78 °C→room temp., 30 min. c) Pyridinium *p*-toluenesulfonate (10 mol-%), 2,2-dimethoxypropane, room temp., 24 h; *p*-toluenesulfonic acid (3 mol-%), 22 h; 95%. d) Phenylboronic acid (1.1 equiv.), CH_2Cl_2, room temp., 24 h; 93%. e) NEt_3 (8 equiv.), Me_3SiCl (4 equiv.), CH_2Cl_2, 0 °C, 3 h; 91%. f) $Bu_4NF{\cdot}3H_2O$ (3.6 equiv.), THF, room temp., 6 h.

Bearing in mind the findings of Scheme 2, we explored the Körber/Risch synthesis of β-hydroxy ketones in more detail. Specifically, we wondered whether it would be possible to shorten the route from three to two steps by adopting the asymmetric osmylation procedure established by Muñiz and Hövelmann[17] in 2005 from a racemic osmylation variant described by Narasaka et al. in 1988.[18] In both cases boronic esters were obtained directly from the olefins simply through their dihydroxylation in the presence of phenylboronic acid. In the hands of Keck and Wager, β-hydroxy ketones akin to those resulting from Körber's and Risch's reductions had given 1,3-diols on treatment with SmI_2.[19] As a consequence, "one-pot" over-reductions of our acetonides and phenylboronates beyond the β-hydroxy ketone stage by treatment with excess Sm^{II} (i.e., leading to the desired 1,3-diols directly) seemed feasible and were therefore considered worthwhile to study.

Results and Discussion

The substrates we used in our study were the conjugated enones *trans*-**1**^{acyl} (Table 1). They are either available commercially (*trans*-**1**^{acyl}**a**, *trans*-**1**^{acyl}**b**) or were obtained (*trans*-**1**^{acyl}**c**–**h**) with perfect *trans* selectivity through Wittig reactions between the stabilized ylides **11** and the aldehydes **12**, bearing unbranched, β-branched, or α-branched alkyl substituents. The ylides **11** were generated in situ from methyltriphenylphosphonium bromide (**9**), butyllithium (2 equiv.), and the acyl chlorides **10**.[20]

Table 1. Synthesis of the *trans*-configured enones *trans*-**1**^{acyl}**c**–**h**.[a]

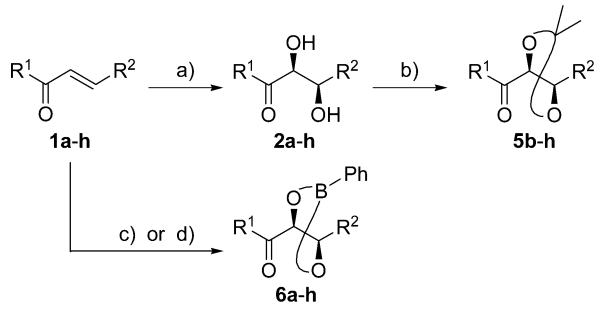


R^1	R^2	*trans*-**1**^{acyl}**a**–**h**	Yield [%]
Me	Me	**a**	[b]
Me	Bu	**b**	[b]
Bu	Me	**c**	62
Bu	Bu	**d**	73
Bu	*i*Bu	**e**	72
Bu	*i*Pr	**f**	81
*i*Bu	Bu	**g**	70
*i*Bu	*i*Bu	**h**	71

[a] *Reagents and conditions*: **9** (2.0 equiv.), BuLi (2.2 equiv.), THF, 0 °C, 30 min; addition of **10**, 0 °C→room temp., 3 h; addition of **12** (5.0 equiv.), room temp., 3 d. [b] Purchased commercially.

Analogously with the precedents of Körber and Risch,[9] the AD reactions of the enones *trans*-**1**^{acyl}**a** and *trans*-**1**^{acyl}**c**–**h** in the presence of AD mix-β™ typically proceeded in 60–70% yields (Table 2). Most substrates reacted with >99% *ee*s, the exceptions being the enones *trans*-**1**^{acyl}**a** (→ 92% *ee*) and *trans*-**1**^{acyl}**f** (→ 94% *ee*). The absolute configurations of the resulting dihydroxy ketones **2a**–**h** were not established but were assumed to be in line with the "Sharpless mnemonic".[3c,21] Protection of the dihydroxy ketones **2a**–**h** provided the corresponding acetonides **5b**–**h** in good to almost quantitative yields after purification by chromatography on silica gel.[22] Only the acetonide **5a** was too volatile to be isolable.

Table 2. AD reactions of the enones *trans*-**1**^{acyl}**a**–**h** under Sharpless' conditions[1] (top row; followed by acetonide formation) or Muñiz's conditions[17] (bottom row).[a]

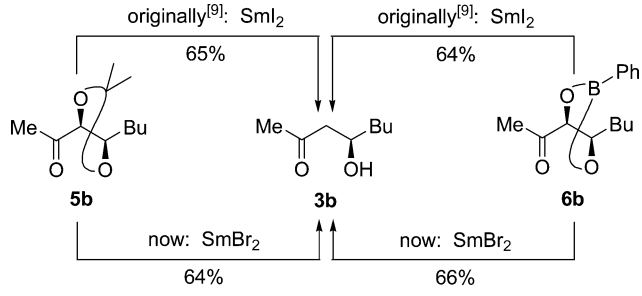


R^1	R^2	**1**, **2**, **5**, **6**	**2**		**5**	**6**			
						Procedure c		Procedure d	
			Yield [%]	*ee*[a] [%]	Yield [%]	Yield [%]	*ee*[b] [%]	Yield [%]	*ee*[b] [%]
Me	Me	**a**	51	92	[c]	61	92	63	92
Me	Bu	**b**	68[d]	>99[e]	84[f]	70	97	72	97
Bu	Me	**c**	67	>99	98	71	>99	70	98
Bu	Bu	**d**	61	>99	89	64	98	65	98
Bu	*i*Bu	**e**	63	>99	94	62	99	67	97
Bu	*i*Pr	**f**	75	94	92	75	97	82	94
*i*Bu	Bu	**g**	65	>99	98	64	99	69	96
*i*Bu	*i*Bu	**h**	69	>99	87	72	>99	74	94

[a] *Reagents and conditions*: a) AD mix-β™ [i.e., $K_2OsO_2(OH)_4$ (1 mol-%), $(DHQD)_2PHAL$ (5 mol-%), $K_3Fe(CN)_6$ (3.0 equiv.), K_2CO_3 (3.0 equiv.)], *t*BuOH/H_2O (1:1, v/v), 0 °C, 3 d. b) $Me_2C(OMe)_2$ (as a solvent), *p*TsOH (3 mol-%), room temp., 12 h. c) Same as (a) except for the additional presence of $PhB(OH)_2$ (1.2 equiv.). d) Same as (c) but at room temp., 1 d. [b] Determined by GC or HPLC analysis variously of the corresponding diol (**6b**) or of its bis(trimethylsilyl ether) (**6a**, **6c**), bis(4-nitrobenzoate) (**6d**), bis(trifluoroacetate) (**6e**, **h**), or bis(dimethylphenylsilyl ether) (**6f**, **6g**). [c] Product too volatile for isolation. [d] 89% yield.[9] [e] 100% *ee*.[9] [f] 95% yield.[9]

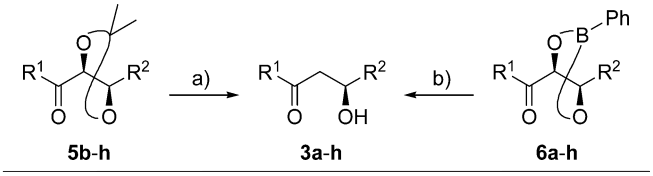
In contrast with the two-step synthesis of the phenylboronate **6b** from the enone *trans*-**1**^{acyl}**b** by Körber and Risch,[9] we gained access to the same ester **6b**, and also to its congeners **6a** and **6c**–**h** from the underlying enones *trans*-**1**^{acyl}**a** and *trans*-**1**^{acyl}**c**–**h**, in single-step manner when we adopted Muñiz's AD procedure in the presence of $PhB(OH)_2$.[17] Yields were 61 to 82%. Enantiopurities ranged from 97 to over 99% *ee* at 0 °C (3 d reaction time) and from 94 to 98% *ee* at room temperature (as in the original procedure;[17] 1 d reaction time) with the single exception of the boronate **6a**, which gave 92% *ee*. Of course, the absolute configurations of the boronates **6** should equal those of the underlying dihydroxy ketones **2**, which were assumed to have followed the AD reaction's standard course (vide supra).

Exploratory defunctionalizations of the acetonide **5b** and of the corresponding boronate **6b** with samarium(II) *bromide* (3.2 equiv.) furnished the β-hydroxy ketone **3b** in 64% and 66% yields, respectively (Scheme 3). Samarium(II) bromide (E_0^{THF} = –2.07 V) is a more powerful reductant than samarium(II) iodide (E_0^{THF} = –1.55 V).[23] From the same substrates **5b** and **6b** the latter reagent gave virtually identical amounts of **3b** (65% and 64%, respectively).[9] Because we found samarium(II) bromide to be much less sensitive in solution than samarium(II) iodide – upon exposure to air the solution turns not quite as readily from blue (Sm^{2+}) to yellow (Sm^{3+}) – we chose exclusively the former reagent[24] for reducing our sets of dihydroxy ketone acetonides **5b**–**h** and phenylboronates **6b**–**h** (Table 3). Defunctionalizations of α-oxygenated ketones by use of $SmBr_2$ have not previously been described in the literature. The β-hydroxy ketones **3b** and **3d**–**h** were obtained in 67 ± 4% yields. In contrast, the β-hydroxy ketone **3c** was inaccessible from either of the two precursors – for no obvious reason. Considering the boronate pathway, we shortened the step requirement for converting the enones **1** into the enantiomerically pure β-hydroxy ketones **3** from three (via the dihydroxy ketones **2** and their acetonides **5**) to two (via the dihydroxy ketone boronates **6**).



Scheme 3. Use of $SmBr_2$ instead of SmI_2 for the reduction of the protected α,β-dihydroxy ketones **5b** and **6b** to the β-hydroxy ketone **3b** had almost no effect on the yields.

Table 3. Synthesis of the enantiomerically pure β-hydroxy ketones **3b** and **3d**–**h** by $SmBr_2$-mediated C–O bond cleavage in the acetonides **5b** and **5d**–**h** and the phenylboronates **6b** and **6d**–**h**.[a]



R^1	R^2		**3** from **5** Yield [%]	**3** from **6** Yield [%]
Me	Me	**a**	[b]	[c]
Me	Bu	**b**	64	66
Bu	Me	**c**	[d]	[d]
Bu	Bu	**d**	66	68
Bu	*i*Bu	**e**	63	70
Bu	*i*Pr	**f**	70	69
*i*Bu	Bu	**g**	67	71
*i*Bu	*i*Bu	**h**	66	65

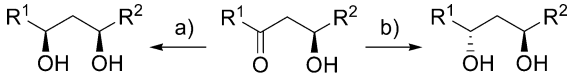
[a] *Reagents and conditions:* a) $SmBr_2$ (3.2 equiv.), THF, –78 °C; addition of **5b**–**h** in THF/MeOH (2:1, v/v), 90 min. b) Same as (a) but with **6a**–**h**. [b] Compound **5a** was inaccessible from **2a** as in Table 2. [c] Partial decomposition; 12% **6a** reisolated. [d] Decomposition; no **5c** or **6c** reisolated.

The β-hydroxy ketones **3b** and **3d**–**h** having been made available with ≥97% *ee*s, the goal of attaining isomerically pure 1,3-diols is in principle accomplished. This is because there are pertinent reduction protocols for β-hydroxy ketones from the Narasaka[25] and the Evans groups;[26]

they are very reliable and lead to *syn*- and *anti*-configured 1,3-diols, respectively. Diastereocontrol is perfect in the former case and high in the latter one. Not surprisingly, these protocols also fulfilled their respective tasks when applied to our β-hydroxy ketones **3b** and **3e** (Scheme 3).

Last but not least, we wondered whether Keck's observation[19] that samarium(II) iodide (3 equiv.) can reduce β-hydroxy ketones to give 1,3-diols at 0 °C in THF solutions containing MeOH (10 equiv.) made another shortcut for our diol synthesis feasible: one-pot reductions of the α,β-dihydroxy ketone acetonides **5** or boronates **6** with samarium(II) beyond the β-hydroxy ketone stage – reached by reduction with samarium(II) bromide (3.2 equiv.) at –78 °C for 90 min – to give the 1,3-diols **4** directly (Table 4). The challenge in such over-reductions was expected to be diastereocontrol. In fact, chances for diastereoselectivity to occur quite generally were scarce. This was anticipated, because *anti* selectivity appeared to be substituent-dependent and rather restricted to (β-hydroxyalkyl) *methyl* ketone reductions.[19] (β-Hydroxyalkyl) *ethyl* ketones and most (β-hydroxyalkyl) *higher alkyl* ketones were reduced less selectively or unselectively.[19]

Table 4. Representative conversions of the enantiomerically pure β-hydroxy ketones **3** into the enantiomerically pure 1,3-diols **4**.[a]



syn-**4b**,**e** **3b**,**e** *anti*-**4b**,**e**

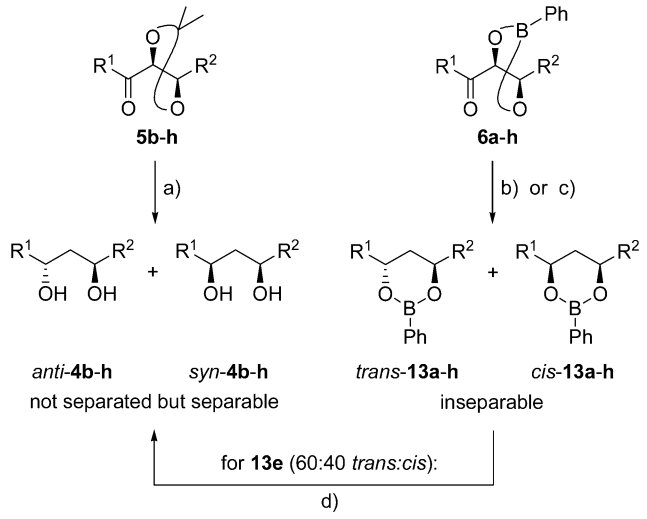
Yield *syn*-**4** [%]	R^1	R^2		Yield *anti*-**4** [%]
90[9]	Me	Bu	**b**	51[9]
75	Bu	*i*Bu	**e**	61[b]

[a] *Reagents and conditions:* a) BEt_3 (1.1 equiv.), THF/MeOH (4:1, v/v), room temp., 1 h, then –78 °C, addition of **3** in THF, 2 h, addition of $NaBH_4$ (0.8-fold molar quantity); 16 h for **4b**[9] and 18 h for **4e**. b) $Me_4NBH(OAc)_3$ (4.1 equiv.), CH_3CN/HOAc (1:1, v/v), room temp., 30 min, then –40 °C, addition of **3** in CH_3CN, 1 h, then –20 °C; 14 h for **4b**[9] and 18 h for **4e**, respectively. [b] 82:18 mixture with *syn*-**4b**.

Table 5 shows that the over-reduction of our acetonides **5** or phenylboronates **6** led to the 1,3-diols **4b**–**h**[27] (55–71%) or the corresponding dioxaborinanes **13a**–**h**[28] (52–74%) upon treatment with samarium(II) halide (4.5 equiv.) at –78 °C for 30 min and at 0 °C for 20 h. The reductions affording the boronates **13** were more efficient with samarium(II) bromide (→ 65–74% yields) as reductant than with samarium(II) iodide (→ 52–61% yields). That boronates **13** represent protected 1,3-diols was shown *pars pro toto* by the deborylation of compound **13e** with H_2O_2 (Table 5, reaction "d").[29] This liberated the underlying 1,3-diol **4e** in 80% yield.

The 1,3-diols **4b**–**h**[27] (55–71%) and the dioxaborinanes **13a**–**h**[28] were isolated as mixtures of *anti* and *syn* diastereomers and *trans* and *cis* diastereomers, respectively, which were difficultly separable and inseparable, respectively, by flash chromatography on silica gel.[22] The diastereomeric diols **4b**–**h** were distinguished (Table 6) thanks to an observation by Hoffmann et al.: in seven *anti*-configured 1,3-diols the sums of the ^{13}C NMR shifts of nuclei C^1 and C^3 were smaller by 2.7–14.5 ppm than in their *syn* isomers.[30] For the following it is helpful to recall that Hoffmann's criterion implies that 1,3-diols are hydrogen-bonded intramolecularly and accordingly contain chair-like substructures. If the underlying diol is *syn*-configured these chairs are preferentially those that accommodate both substituents "equatorially". In contrast, if the diol is *anti*-configured it consists of interconverting chairs because one substituent must be "axial" but this role is alternating between the 1- and the 3-substituent. As a consequence, C^1 and C^3 are shielded in *anti*- vs. *syn*-1,3-diols in similar manner as in *trans*- vs. *cis*-configured 1,3-dialkylcyclohexanes.[31] In an extension of this analysis – and again in accordance with observations from the Hoffmann group[30,32] – C^1 and C^3 are also shielded in the *trans*- vs. the *cis*-substituted 1,3-diol dioxaborinanes **13a**–**h** (Table 7).

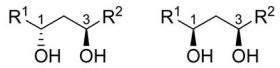
Table 5. $SmHal_2$ reductions of the acetonides **5b**–**h** and the phenylboronates **6a**–**h**: access to the enantiomerically pure 1,3-diols **4b**–**h**[27] or their dioxaborinanes **13a**–**h**[28] as mixtures of *anti* and *syn* or *trans* and *cis* diastereomers, respectively.[a]



			4		**13**			
					Procedure b		Procedure c	
R^1	R^2		Yield [%]	% *anti*	Yield [%]	% *trans*	Yield [%]	% *trans*
Me	Me	**a**	[b]		67	94	52	100
Me	Bu	**b**	68	96	65	58	58	92
Bu	Me	**c**	70	91	71	75	53	89
Bu	Bu	**d**	69	63	71	58	59	80
Bu	*i*Bu	**e**	71	71	66	60	53	66
Bu	*i*Pr	**f**	65	80	69	50	61	82
*i*Bu	Bu	**g**	67	64	65	58	52	57
*i*Bu	*i*Bu	**h**	55	58	74	58	58	58

[a] *Reagents and conditions:* a) $SmBr_2$ (4.5 equiv.) in THF, –78 °C, addition of **5b**–**h** in THF/MeOH (2:1, v/v), 30 min, then 0 °C, 20 h. b) Same as (a), but addition of **6a**–**h**. c) Same as (b), but with SmI_2 (4.5 equiv.). d) H_2O_2 (30% in H_2O, 2.0 equiv.), acetone/AcOEt (1:1, v/v), room temp, 1 d; 80% **4e** (60:40 *anti*/*syn* mixture). [b] Compound **5a** was not accessible from **2a** as in Table 2.

Table 6. ^{13}C NMR chemical shifts (ppm) of the oxygenated carbon nuclei of 1,3-diols **4b**–**h**[27] in $CDCl_3$ solution at 100.6 MHz.[a]

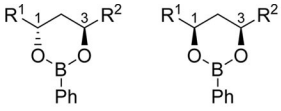


anti-**4b-h** *syn*-**4b-h**

			anti			*syn*		
R^1	R^2	**4**	δ-C^1	δ-C^3	δ-C^1 + δ-C^3	δ-C^1	δ-C^3	δ-C^1 + δ-C^3
Me	Bu	**b**	65.5	69.3	134.8	69.2	73.1	142.3
Bu	Me	**c**	69.4	65.5	134.9	73.2	69.2	142.4
Bu	Bu	**d**	69.7		139.4	73.7		147.4
Bu	*i*Bu	**e**	69.6	67.6	137.2	73.3	71.3	144.6
Bu	*i*Pr	**f**	69.5	73.9	143.4	73.4	78.1	151.5
*i*Bu	Bu	**g**	67.5	69.5	137.0	71.3	73.3	144.6
*i*Bu	*i*Bu	**h**	67.5		135.0	71.3		142.6

[a] Compound **4a** was inaccessible as in footnote [a] of Table 2.

Table 7. ^{13}C NMR chemical shifts (ppm) of the oxygenated carbon nuclei of the dioxaborinanes **13a**–**h**[28] in $CDCl_3$ solution at 100.6 MHz.



trans-**13a-h** *cis*-**13a-h**

			trans			*cis*		
R^1	R^2	**13**	δ-C^1	δ-C^3	δ-C^1 + δ-C^3	δ-C^1	δ-C^3	δ-C^1 + δ-C^3
Me	Me	**a**	64.7		129.4	68.2		136.4
Me	Bu	**b**	68.5	65.1	133.6	71.9	68.2	140.1
Bu	Me	**c**	65.1	68.5	133.6	68.3	71.9	140.2
Bu	Bu	**d**	68.9		137.8	71.9		143.8
Bu	*i*Bu	**e**	68.9	67.0	135.9	70.2	71.9	142.1
Bu	*i*Pr	**f**	68.4	72.2	140.6	70.9	75.6	146.5
*i*Bu	Bu	**g**	67.0	68.9	135.9	71.9	70.1	142.0
*i*Bu	*i*Bu	**h**	67.0		134.0	70.1		140.2

The diastereoselectivities of the one-pot reductions of Table 5 depended on the starting materials and the reductants. The acetonides **5b**–**h** reacted *anti*-selectively and their phenylboronate counterparts **6a**–**h** *trans*-selectively. The *anti* selectivities varied from 96:4 (**5b**) to 58:42 (**5h**) and the *trans* selectivities from 100:0 (**6a** + SmI_2) to 50:50 (**6f** + $SmBr_2$). The substituent size in the substrate correlates loosely and inversely with these selectivities. It is noteworthy that SmI_2 (procedure c) reduced some boronates more *trans*-selectively than $SmBr_2$ (procedure b). The reductions of the boronate **6b** are the most conspicuous example of this effect, leading to **13b** as a 92:8 *trans*/*cis* mixture when SmI_2 is used and as a 58:42 mixture with $SmBr_2$.

Conclusions

We have developed a two-step asymmetric synthesis of the β-hydroxy ketones **3** from the easily accessible starting enones **1** – which allows the pure 1,3-diols **4** of either relative configuration to be obtained enantiomerically, *syn* or *anti*, in one more step – as well as a two-step route leading preferentially to the *trans* isomers of the dioxaborinanes **13** of the same 1,3-diols. The inaugural steps were AD reactions of the enones in the presence of $PhB(OH)_2$, affording the ketones **6**, containing 1,2-diol phenylboronate moieties. These intermediates were susceptible to $SmHal_2$ reductions, which at –78 °C provided the β-hydroxy ketones **3** and at 0 °C afforded the 1,3-diol dioxaborinanes **13**. The overall sequences should have potential for natural product synthesis.

Experimental Section

General Information: All reactions were performed in oven-dried (110 °C) glassware under N_2 or argon. THF was freshly distilled from K; CH_2Cl_2 was distilled from CaH_2. Products were purified by flash chromatography[22] [column diameter (cm) × column height; volume of each collected fraction (mL)/eluents; which fractions contained the isolated product is indicated in each description as "fractions *xx*–*yy*"] on silica gel (Macherey–Nagel, 230–400 mesh). Yields refer to analytically pure samples. ^1H NMR [TMS (δ = 0.00 ppm) or $CHCl_3$ (δ = 7.26 ppm) as internal standard in $CDCl_3$]: Varian Mercury VX 300, Bruker AM 400 and DRX 500. Integrals in accordance with assignments; coupling constants in Hz. Assignments of ^1H and ^{13}C NMR resonances refer to IUPAC nomenclature except within substituents (where primed numbers are used). Combustion analyses: E. Hickl and F. Tönnies. MS: Dr. J. Wörth and C. Warth. HPLC: G. Fehrenbach (all at the Institut for Organische Chemie and Biochemie, Universität Freiburg). IR spectra: Perkin–Elmer FT-IR Paragon 1000. Optical rotations measured with a Perkin–Elmer polarimeter 341 MC at 589 nm/20 °C and calculated according to the Drude equation $\{[\alpha]_D = (\alpha_{exp} \times 100)/(c \times d)\}$; rotational values are the average of five measurements of α_{exp} in a given solution of the corresponding sample; *ee* values were determined by chiral GC or HPLC.

Preparation of THF Solutions of $SmHal_2$

SmI_2: 1,2-Diiodoethane (2.0 g) was dissolved in *tert*-butyl methyl ether (60 mL), washed with satd. aq. Na_2SO_3 (2× 30 mL), and dried with $MgSO_4$. After evaporation of the solvent the residue (0.958 mg, 3.40 mmol) was dissolved in THF (34 mL) and degassed at –78 °C. The resulting solution was cannulated onto Sm powder (40 mesh, 530 mg, 3.52 mmol, 1.05 equiv.). Through stirring at room temp. for 16 h we obtained a dark blue solution. Its concentration in SmI_2 was assumed to be 0.1 M. Because of its low stability this solution was made directly before it was used.

$SmBr_2$: 1,1,2,2-Tetrabromoethane (415 mg, 1.20 mmol, 0.5 equiv.) was dissolved in THF (24 mL) and the resulting solution was degassed at –78 °C. It was cannulated onto Sm powder (40 mesh, 360 mg, 2.40 mmol). Through stirring at room temp. for 16 h we obtained a black suspension, the concentration of which was assumed to be 0.1 M in $SmBr_2$. Because of the low stability of this solution it was prepared immediately before use.

(*E*)-Oct-2-en-4-one (1c): This compound (3.9 g, 62%) was prepared from pentanoyl chloride (4.25 mL, 6.02 g, 50.0 mmol) and acetic aldehyde (14.0 mL, 11.0 g, 250 mmol, 5 equiv.) as described for **1d**. Flash chromatography (4 × 20 cm, 50 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 3–12, 3.9 g, 62%) as

a slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.90 (t, $J_{8,7}$ = 7.3 Hz, 8-H_3), 1.32 (qt, $J_{7,8}$ = 7.5, $J_{7,6}$ = 7.4 Hz, 7-H_2), 1.58 (tt, $J_{6,7}$ = 7.5, $J_{6,5}$ = 7.4 Hz, 6-H_2), 1.88 (dd, $J_{1,2}$ = 6.8, $^4J_{1,3}$ = 1.7 Hz, 1-H_3), 2.50 (t, $J_{5,6}$ = 7.5 Hz, 5-H_2), 6.11 (dq, $J_{3,2}$ = 15.9, $^4J_{3,1}$ = 1.6 Hz, 3-H), 6.83 (dq, $J_{2,3}$ = 15.7, $J_{2,1}$ = 6.8 Hz, 2-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-8), 18.3 (C-1), 22.5 (C-7), 26.5 (C-6), 39.9 (C-5), 132.1 (C-2), 142.4 (C-3), 200.8 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3530, 3035, 2960, 2935, 2875, 1700, 1675, 1635, 1445, 1410, 1375, 1325, 1285, 1260, 1190, 1140, 1115, 1060, 970, 935, 735, 630, 530 cm^{-1}. $C_8H_{14}O$ (126.2): calcd. C 76.14, H 11.18; found C 75.9, H 11.09.

(*E*)-Undec-6-en-5-one (1d): $MePPh_3^+Br^-$ (35.7 g, 100 mmol, 2.0 equiv.) was suspended in THF (150 mL) at 0 °C. *n*BuLi (42 mL, 2.5 M, 105 mmol, 2.1 equiv.) was added over 15 min. After 30 min a solution of pentanoyl chloride (4.25 mL, 6.02 g, 50.0 mmol) in THF (40 mL) was added and the mixture was allowed to warm to room temp. After 3 h the reaction mixture was poured into H_2O (500 mL), extracted with Et_2O (5 × 80 mL), and dried with $MgSO_4$. After evaporation of the solvent, CH_2Cl_2 (80 mL) and pentanal (15.5 mL, 21.5 g, 250 mmol, 5 equiv.) were added. After 3 d the solvent was removed under reduced pressure. Flash chromatography (5 × 20 cm, 50 mL, cyclohexane/EtOAc 9:1) provided the title compound (fractions 3–10, 5.63 g, 67%) as a slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{1,2}$ = 7.3 Hz, 1-H_3), coincident with 0.91 (t, $J_{11,10}$ = 7.3 Hz, 11-H_3), 1.21–1.64 (m, 2-H_2, 3-H_2, 9-H_2, 10-H_2), 2.21 (tdd, $J_{8,9}$ = 7.2, $J_{8,7}$ = 6.9, $^4J_{8,6}$ = 0.7 Hz, 8-H_2), 2.52 (t, $J_{4,3}$ = 7.5 Hz, 4-H_2), 6.09 (dt, $J_{6,7}$ = 15.8, $^4J_{6,8}$ = 1.5 Hz, 6-H), 6.82 (dt, $J_{7,6}$ = 15.8, $J_{7,8}$ = 6.9 Hz, 7-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.90 (C-1), 13.97 (C-11), 22.3 (C-2), 22.5 (C-10), 26.6 (C-3), 30.3 (C-9), 32.2 (C-8), 39.9 (C-4), 130.42 (C-6), 147.3 (C-7), 201.1 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3740, 2960, 2930, 2870, 2360, 2340, 1700, 1675, 1630, 1510, 1465, 1460, 1410, 1380, 1185, 1145, 1100, 1060, 1020, 980, 915, 745 cm^{-1}. $C_{11}H_{20}O$ (168.3): calcd. C 78.51, H 11.98; found C 78.83, H 12.07.

(*E*)-9-Methyldec-6-en-5-one (1e): This compound (5.2 g, 62%) was prepared from pentanoyl chloride (4.25 mL, 6.02 g, 50.0 mmol) and 3-methylbutanal (26.8 mL, 21.5 g, 250 mmol, 5 equiv.) as described for **1d**. Flash chromatography (5 × 20 cm, 50 mL, cyclohexane/EtOAc 9:1) provided the title compound (fractions 4–7, 5.2 g, 62%) as a slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{1,2}$ = 7.3 Hz, 1-H_3), superimposed by 0.92 (d, $J_{9\text{-Me},9}$ = 6.7 Hz, 2 × 9-CH_3), 1.33 (qt, $J_{2,1}$ = 7.5, $J_{2,3}$ = 7.4 Hz, 2-H_2), 1.59 (tt, $J_{3,4}$ = 7.5, $J_{3,2}$ = 7.4 Hz, 3-H_2), 1.76 (qqt, $J_{9,9\text{-Me}}$ = $J_{9,10}$ = 6.8, $J_{9,8}$ = 6.7 Hz, 9-H), 2.09 (ddd, $J_{8,7}$ = 7.1, $J_{8,9}$ = 7.1, $^4J_{8,6}$ = 0.7 Hz, 8-H_2), 2.52 (t, $J_{4,3}$ = 7.4 Hz, 4-H_2), 6.07 (dt, $J_{6,7}$ = 15.8, $^4J_{6,8}$ = 1.4 Hz, 6-H) 6.79 (dt, $J_{7,6}$ = 15.7, $J_{7,8}$ = 7.4 Hz, 7-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.0 (C-1), 22.46 (2 × 9-Me*), 22.52 (C-2*), 26.6 (C-3), 28.0 (C-9), 40.0 (C-4), 41.8 (C-8), 131.5 (C-6), 146.1 (C-7), 201.0 (C=O) ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3385, 3180, 2960, 2935, 2870, 2730, 2360, 1975, 1695, 1675, 1630, 1560, 1465, 1440, 1410, 1385, 1370, 1350, 1320, 1310, 1260, 1190, 1165, 1145, 1095, 1070, 1025, 980, 930, 890, 855, 725, 695, 630, 545 cm^{-1}. $C_{11}H_{20}O$ (168.3): calcd. C 78.51, H 11.98; found C 78.20, H 12.01.

(*E*)-2-Methylnon-3-en-5-one (1f): This compound (6.3 g, 81%) was prepared from pentanoyl chloride (4.26 mL, 6.03 g, 50.0 mmol) and isobutyraldehyde (22.8 mL, 18.0 g, 250 mmol, 5 equiv.) as described for **1d**. Flash chromatography (4 × 20 cm, 50 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 5–16, 6.3 g, 81%) as a slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.92 (t, $J_{9,8}$ = 7.3 Hz, 9-H_3), 1.07 (d, $J_{2\text{-Me},2}$ = 6.8 Hz, 2-CH_3), coincident with 1.07 (d, $J_{1,2}$ = 6.8 Hz, 1-H_3), 1.34 (tq, $J_{8,7}$ = 7.5, $J_{8,9}$ = 7.4 Hz, 8-H_2), 1.59 (tt, $J_{7,6}$ = 7.6, $J_{7,8}$ = 7.5 Hz, 7-H_2), 2.46 (m_c, 2-H), 2.54 (t, $J_{6,7}$ = 7.5 Hz, 6-H_2), 6.04 (dd, $J_{4,3}$ = 16.0, $^4J_{4,2}$ = 1.5 Hz, 4-H), 6.78 (dd, $J_{3,4}$ = 16.0, $J_{3,2}$ = 6.6 Hz, 3-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.0 (C-9), 21.4 (2 × 2-Me), 22.5 (C-8), 26.5 (C-2), 31.2 (C-7), 40.0 (C-6), 127.6 (C-4), 153.3 (C-3), 201.4 (C=O) ppm. IR (film): $\tilde{\nu}$ = 2960, 2935, 2875, 1695, 1675, 1630, 1465, 1365, 1265, 1190, 1130, 1065, 985, 915, 745, 465 cm^{-1}. $C_{10}H_{18}O$ (154.2): calcd. C 77.87, H 11.76; found C 77.58, H 11.65.

(*E*)-2-Methyldec-5-en-4-one (1g): This compound (5.8 g, 69%) was prepared from 3-methylbutanoyl chloride (4.26 mL, 6.03 g, 50.0 mmol) and pentanal (15.5 mL, 21.5 g, 250 mmol, 5 equiv.) as described for **1d**. Flash chromatography (5 × 20 cm, 50 mL, cyclohexane/EtOAc 9:1) provided the title compound (fractions 4–12, 5.8 g, 69%) as a slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.88 (t, $J_{10,9}$ = 7.6 Hz, 10-H_3), superimposed by 0.89 (d, $J_{2\text{-Me},2}$ = 6.8 Hz, 2 × 2-CH_3), 1.25–1.46 (m, 8-H_2, 9-H_2), 2.05–2.21 (m, 2-H, 7-H_2), 2.36 (d, $J_{3,2}$ = 7.0 Hz, 3-H_2), 6.05 (dt, $J_{5,6}$ = 15.7, $^4J_{5,7}$ = 1.4 Hz, 5-H), 6.77 (dt, $J_{6,5}$ = 15.8, $J_{6,7}$ = 6.9 Hz, 6-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.8 (C-10), 22.3 (2 × 2-Me), 22.7 (C-9), 25.2 (C-2), 30.3 (C-8), 32.2 (C-7), 49.1 (C-3), 130.8 (C-5), 147.4 (C-6), 200.6 (C=O) ppm. IR (film): $\tilde{\nu}$ = 2960, 2930, 2870, 2360, 1695, 1675, 1630, 1505, 1465, 1405, 1365, 1335, 1295, 1250, 1200, 1170, 1150, 1105, 1060, 1020, 980, 915, 745, 670 cm^{-1}. $C_{11}H_{20}O$ (168.3): calcd. C 78.51, H 11.98; found C 78.17, H 11.95.

(*E*)-2,8-Dimethyl-non-5-en-4-one (1h): This compound (5.1 g, 61%) was prepared from 3-methylbutanoyl chloride (4.26 mL, 6.03 g, 50.0 mmol) and 3-methylbutanal (26.8 mL, 21.5 g, 250 mmol, 5 equiv.) as described for **1d**. Flash chromatography (5 × 20 cm, 50 mL, cyclohexane/EtOAc 9:1) provided the title compound (fractions 4–12, 5.1 g, 61%) as a slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.85 (d, $J_{8\text{-Me},8}$ = 6.9 Hz, 2 × 8-CH_3), superimposed by 0.86 (d, $J_{2\text{-Me},2}$ = 6.6 Hz, 2 × 2-CH_3), 1.69 (qqt., $J_{2,1}$ = 6.7, $J_{2,2\text{-Me}}$ = 6.7, $J_{2,3}$ = 6.7 Hz, 2-H), 1.99–2.14 (m, 7-H_2, 8-H), 2.32 (d, $J_{3,2}$ = 6.9 Hz, 3-H_2), 6.00 (dt, $J_{5,6}$ = 15.8, $^4J_{5,7}$ = 1.4 Hz, 5-H), 6.71 (dt, $J_{6,5}$ = 15.3, $J_{6,7}$ = 7.7 Hz, 6-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.5 (2 × 2-Me), 22.8 (2 × 8-Me), 25.3 (C-2), 27.0 (C-8), 41.8 (C-7), 49.2 (C-3), 131.9 (C-5), 146.2 (C-6), 200.6 (C=O) ppm. IR (film): $\tilde{\nu}$ = 2960, 2930, 2870, 2365, 1695, 1670, 1630, 1465, 1385, 1365, 1300, 1195, 1170, 1015, 980 cm^{-1}. $C_{11}H_{20}O$ (168.3): calcd. C 78.51, H 11.98; found C 78.22, H 12.15.

(3*S*,4*R*)-3,4-Dihydroxypentan-2-one (2a): (*E*)-Pent-3-en-2-one (0.84 g, 10 mmol) was added at 0 °C to a stirred mixture of $K_2OsO_2(OH)_4$ (36.8 mg, 1 mol-%), $(DHQD)_2PHAL$ (390 mg, 5 mol-%), K_2CO_3 (4.15 g, 30.0 mmol, 3.0 equiv.), and $K_3Fe(CN)_6$ (9.88 g, 30.0 mmol, 3.0 equiv.) in *t*BuOH (50 mL)/H_2O (50 mL). After 3 d, satd. aq. Na_2SO_3 (50 mL) was added. After extraction with EtOAc (4 × 30 mL), drying over $MgSO_4$, and evaporation of the solvent the crude title compound was obtained. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 1:1) provided the title compound (fractions 18–25, 606 mg, 5.13 mmol, 51%) as a colorless oil. $[\alpha]_D^{20}$ = +44.0 (*c* = 1.0, $CHCl_3$); the *ee* was 92% according to chiral GC (CP-Chirasil-Dex CB, 25 m × 0.25 mm, Cat. No. CP 7502, 80 °C, 10 min, then 1 °C min^{-1} → 170 °C, 60 kPa H_2) with the bis(trimethylsilyl ether) of the title compound; $t_{ret(3S,4R)}$ = 9.71 min, $t_{ret(3R,4S)}$ = 10.66 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 1.35 (d, $J_{5,4}$ = 6.4 Hz, 5-H_3), 1.86 (d, $J_{4\text{-OH},4}$ = 9.6 Hz, 4-OH), 2.28 (s, 1-H_3), 3.68 (d, $J_{3\text{-OH},3}$ = 4.2 Hz, 3-OH), 4.00 (dd, $J_{3,3\text{-OH}}$ = 4.1, $J_{3,4}$ = 2.0 Hz, 3-H), 4.21 (m_c, 4-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 20.4 (C-5), 25.5 (C-1), 68.1 (C-4), 80.5 (C-3), 208.0 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3405, 2980, 2930, 1715, 1360, 1245, 1140, 1080, 1010, 915, 745, 665 cm^{-1}.

(3*S*,4*R*)-3,4-Dihydroxyoctan-2-one (2b): This compound (1.09 g, 68%) was prepared from (*E*)-oct-3-en-2-one (**1b**, 1.26 g, 10 mmol) as described for **2a**. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 2:1) provided the title compound (fractions 16–26, 1.09 g, 6.8 mmol, 68%) as a colorless oil. $[\alpha]_D^{20}$ = +40.1 (*c* = 1.0, $CHCl_3$); the *ee* was >99% according to chiral GC (CP-Chirasil-Dex CB, 25 m × 0.25 mm, Cat. No. CP 7502, 80 °C, 10 min, then 5 °C min^{-1} → 170 °C, 100 kPa H_2); $t_{ret(3S,4R)}$ = 20.60 min, $t_{ret(3R,4S)}$ = 21.25 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.94 (t, $J_{8,7}$ = 7.0 Hz, 8-H_3), 1.32–1.52 (m, 6-H_2, 7-H_2), 1.63–1.71 (m, 4-OH, 5-H_2), 2.29 (s, 1-H_3), 3.69 (d, $J_{3,4}$ = 4.0 Hz, 3-H), 3.99 (m_c, 4-H), 4.08 (br. d, $J_{3\text{-OH},3}$ = 4.0 Hz, 3-OH) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 (C-8), 22.7 (C-7), 25.3 (C-1), 28.1 (C-6), 34.2 (C-5), 72.0 (C-4), 79.3 (C-3), 208.2 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3410, 2960, 2935, 2870, 2400, 2245, 1715, 1380, 1360, 1260, 1135, 1110, 910, 740, 685, 665, 650 cm^{-1}.

(2*R*,3*S*)-2,3-Dihydroxyoctan-4-one (2c): This compound (1.07 g, 67%) was prepared from (*E*)-oct-2-en-4-one (**1c**, 1.26 g, 10 mmol) as described for **2a**. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 10–23, 1.07 g, 6.68 mmol, 67%) as a colorless oil. $[\alpha]_D^{20}$ = +48.56 (*c* = 1.0, $CHCl_3$); the *ee* was >99% according to chiral GC (CP-Chirasil-Dex CB, 25 m × 0.25 mm, Cat. No. CP 7502, 80 °C, isothermal, 60 kPa H_2) with the bis(trimethylsilyl ether) of the title compound; $t_{ret(2R,3S)}$ = 49.35 min, $t_{ret(2S,3R)}$ = 50.32 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{8,7}$ = 7.3 Hz, 8-H_3), 1.22–1.36 (m, 7-H_2), partially superimposed by 1.35 (d, $J_{1,2}$ = 6.5 Hz, 1-H_3), 1.54–1.70 (m, 2-OH, 6-H_2), AB signal (δ_A = 2.50, δ_B = 2.60, J_{AB} = 17.1 Hz, A part additionally split by $J^1_{A,6}$ = 7.7 Hz, $J^2_{A,6}$ = 7.1 Hz, B part additionally split by $J^1_{B,6}$ = 8.0 Hz, $J^2_{B,6}$ = 7.0 Hz, 5-H_2), 3.71 (d, $J_{3,2}$ = 4.2 Hz, 3-H), 3.99 (br. d, $J_{3\text{-OH},3}$ = 4.0 Hz, 3-OH), 4.20 (m_c, 2-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-8), 20.5 (C-1), 22.4 (C-7), 25.6 (C-6), 37.9 (C-5), 68.1 (C-2), 80.0 (C-3), 210.5 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3420, 2960, 2935, 2875, 2345, 2250, 1715, 1460, 1380, 1260, 1130, 1095, 1040, 1005, 910, 740, 665, 655 cm^{-1}. $C_8H_{16}O_3$ (160.2): calcd. C 59.97, H 10.07; found C 59.81, H 10.33.

(6*S*,7*R*)-6,7-Dihydroxyundecan-5-one (2d): This compound (1.23 g, 61%) was prepared from (*E*)-undec-6-en-5-one (**1d**, 1.68 g, 10.0 mmol) as described for **2a**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 5:1) provided the title compound (fractions 12–24, 1.23 g, 6.10 mmol, 61%) as a colorless oil. $[\alpha]_D^{20}$ = +30.04 (*c* = 1.0, $CHCl_3$); the *ee* was >99% according to chiral HPLC [OD-H, heptane/propan-2-ol 9:1, v:v; 0.8 mL min^{-1}; 260 nm] with the bis(4-nitrobenzoate) of the title compound; $t_{ret(6S,7R)}$ = 20.67 min, $t_{ret(6R,7S)}$ = 25.20 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.92 (t, $J_{11,10}$ = 7.3 Hz, 11-H_3), partially superimposed by 0.93 (t, $J_{1,2}$ = 7.0 Hz, 1-H_3), 1.28–1.58 (m, 7-OH, 8-H_2, 9-H_2, 10-H_2), 1.58–1.70 (m, 2-H_2, 3-H_2), AB signal (δ_A = 2.50, δ_B = 2.61, J_{AB} = 17.0 Hz, A part additionally split by $J^1_{A,3}$ = 8.0 Hz and $J^2_{A,3}$ = 6.8 Hz, B part additionally split by $J^1_{B,3}$ = 7.42 Hz and $J^2_{B,3}$ = 7.44 Hz, 4-H_2), 3.73 (d, $J_{6,7}$ = 4.0 Hz, 6-H), 3.97 (m_c, 7-H), 4.07 (br. d, $J_{6\text{-OH},6}$ = 4.1 Hz, 6-OH) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-1), 14.1 (C-11), 22.4 (C-2), 22.7 (C-10), 25.6 (C-3), 28.2 (C-9), 34.3 (C-8), 37.7 (C-4), 72.1 (C-7), 78.8 (C-6), 210.7 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3575, 3460, 2960, 2935, 2875, 1710, 1665, 1380, 1240, 1125, 1095, 1065, 1040 cm^{-1}. $C_{11}H_{22}O_3$ (202.3): calcd. C 65.31, H 10.96; found C 65.34, H 11.18.

(6*S*,7*R*)-6,7-Dihydroxy-9-methyldecan-5-one (2e): This compound (1.27 g, 63%) was prepared from (*E*)-9-methyldec-6-en-5-one (**1e**, 1.68 g, 10.0 mmol) as described from **2a**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 5:1) provided the title compound (fractions 9–15, 1.27 g, 6.28 mmol, 63%) as a colorless oil. $[\alpha]_D^{20}$ = +36.24 (*c* = 1.0, $CHCl_3$); the *ee* was >99% according to chiral GC (CP-Chirasil-Dex CB, 25 m × 0.25 mm, Cat. No. CP 7502, 90 °C, isothermal, 60 kPa H_2) with the bis(trifluoroacetate) of the title compound; $t_{ret(6S,7R)}$ = 9.17 min, $t_{ret(6R,7S)}$ = 8.94 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.92 (t, $J_{1,2}$ = 7.3 Hz, 1-H_3), 0.93 (d, $J_{10,9}$ = 6.6 Hz, 10-H_3), partially superimposed by 0.97 (d, $J_{9\text{-Me},9}$ = 6.6 Hz, 9-CH_3), 1.28–1.47 (m, 7-OH, 8-H_2), 1.57–1.67 (m, 2-H_2, 3-H_2), 1.78 (m_c, 9-H), AB signal (δ_A = 2.50, δ_B = 2.61, J_{AB} = 17.0 Hz, A part additionally split by $J^1_{A,3}$ = 7.9 Hz and $J^2_{A,3}$ = 7.0 Hz, B part additionally split by $J^1_{B,3}$ = 7.8 Hz and $J^2_{B,3}$ = 7.2 Hz, 4-H_2), 3.72 (d, $J_{6,7}$ = 4.0 Hz, 6-H), 4.01–4.03 (m, 6-OH), 4.07 (m_c, 7-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.3 (C-1), 22.6 (9-Me*), 22.7 (C-10*), 23.3 (C-2), 24.5 (C-9**), 24.7 (C-3**), 43.5 (C-4), 46.9 (C-8), 70.0 (C-7), 79.5 (C-6), 210.1 (C=O) ppm (*/** assignment interchangeable). IR (film): $\tilde{\nu}$ = 3420, 2955, 2875, 2350, 1705, 1395, 1140, 1085, 915, 745, 655 cm^{-1}. $C_{11}H_{22}O_3$ (202.3): calcd. C 65.31, H 10.96; found C 65.30, H 11.31.

(3*R*,4*S*)-3,4-Dihydroxy-2-methylnonan-5-one (2f): This compound (1.41 g, 75%) was prepared from (*E*)-2-methylnon-3-en-5-one (**1f**, 1.54 g, 10.0 mmol) as described for **2a**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 5–10, 1.41 g, 7.49 mmol, 75%) as a colorless oil. $[\alpha]_D^{20}$ = +41.9 (*c* = 1.0, $CHCl_3$); the *ee* was 94% according to chiral HPLC (IA, *n*-heptane, 0.8 mL min^{-1}, 265 nm) with the bis(dimethylphenylsilyl ether) of the title compound; $t_{ret(3R,4S)}$ = 8.37 min, $t_{ret(3S,4R)}$ = 9.86 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{9,8}$ = 7.3 Hz, 8-H_3), 1.00 (d, $J_{1,2}$ = 6.7 Hz, 1-H_3), 1.06 (d, $J_{2\text{-Me},2}$ = 6.6 Hz, 2-CH_3), 1.34 (m_c, 4-OH, 8-H_2), 1.54–1.69 (7-H_2), 1.84–1.96 (m, 2-H), AB signal (δ_A = 2.48, δ_B = 2.59, J_{AB} = 16.8 Hz, A part additionally split by $J^1_{A,7}$ = 7.9 Hz, $J^2_{A,7}$ = 7.9 Hz, B part additionally split by $J^1_{B,7}$ = 7.8 Hz, $J^2_{B,7}$ = 7.3 Hz, 6-H_2), 3.52 (m_c, 3-H), 3.73 (d, $J_{3\text{-OH},3}$ = 3.8 Hz, 3-OH), 4.22 (d, $J_{4,3}$ = 4.1 Hz, 4-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-9), 19.2 (2-Me*), 19.3 (C-1*), 22.4 (C-8), 25.7 (C-7), 32.0 (C-2), 37.4 (C-6), 77.3 (C-3), 77.5 (C-4), 211.0 (C=O) ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3430, 2960, 2935, 2875, 2400, 2250, 1705, 1470, 1395, 1260, 1130, 1100, 1085, 1025, 910, 745, 655, 650 cm^{-1}. $C_{10}H_{20}O_3$ (188.3): calcd. C 63.80, H 10.71; found C 63.74, H 11.01.

(5*S*,6*R*)-5,6-Dihydroxy-2-methyldecan-4-one (2g): This compound (1.31 g, 65%) was prepared from (*E*)-2-methyldec-5-en-4-one (**1g**, 1.68 g, 10.0 mmol) as described for **2a**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 8–10, 1.31 g, 6.48 mmol, 65%) as a colorless oil. $[\alpha]_D^{20}$ = +30.3 (*c* = 1.0, $CHCl_3$); the *ee* was >99% according to chiral HPLC (OD-H, heptane; 0.8 mL min^{-1}; 265 nm) with the bis(dimethylphenylsilyl ether) of the title compound; $t_{ret(5S,6R)}$ = 10.26 min, $t_{ret(5R,6S)}$ = 11.46 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.92 (t, $J_{10,9}$ = 6.4 Hz, 10-H_3), partially superimposed by 0.93 (d, $J_{1,2}$ = 7.3 Hz, 1-H_3), partially superimposed by 0.95 (d, $J_{2\text{-Me},2}$ = 6.7 Hz, 2-CH_3), 1.31–1.51 (m, 6-OH, 8-H_2, 9-H_2), 1.61–1.69 (m, 7-H_2), 2.26 (m_c, 2-H), AB signal (δ_A = 2.38, δ_B = 2.48, J_{AB} = 16.6 Hz, A part additionally split by $J_{A,2}$ = 7.0 Hz, A part additionally split by $J_{B,2}$ = 6.7 Hz, 3-H_2), 3.73 (d, $J_{5,6}$ = 4.1 Hz, 5-H), 3.90–4.03 (m, 5-OH, 6-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 (C-10), 22.6 (C-1*), 22.7 (2-Me*), 24.5 (C-2), 27.0 (C-9), 28.2 (C-8), 34.3 (C-7), 46.8 (C-3), 71.9 (C-6), 79.1 (C-5), 210.2 (C=O) ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3410, 2955, 2930, 2870, 2405, 2250, 1700, 1465, 1395, 1135, 1090, 1015, 910, 745, 665, 655 cm^{-1}. $C_{11}H_{22}O_3$ (202.3): calcd. C 65.31, H 10.96; found C 65.36, H 11.24.

(5*S*,6*R*)-5,6-Dihydroxy-2,8-dimethylnonan-4-one (2h): This compound (1.39 g, 69%) was prepared from (*E*)-2,8-dimethylnon-5-en-4-one (**1h**, 1.68 g, 10.0 mmol) as described for **2a**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 5:1) provided the title compound (fractions 15–24, 1.39 g, 6.87 mmol, 69%) as a colorless oil. $[a]_D^{20}$ = +20.5 (*c* = 1.0, $CHCl_3$); the *ee* was >99% according to chiral GC (CP-Chirasil-Dex CB, 25 m × 0.25 mm, Cat. No. CP 7502, 85 °C, isothermal, 60 kPa H_2) with the bis(trifluoroacetate) of the title compound; $t_{ret(5S,6R)}$ = 8.58 min, $t_{ret(5R,6S)}$ = 8.37 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.94 (d, $J_{9,8}$ = 6.6 Hz, 9-H_3), partially superimposed by 0.97 (br. d, $J_{8\text{-Me},8}$ = 6.6 Hz, 8-CH_3), partially superimposed by 0.97 (d, $J_{2\text{-Me},2}$ = 6.5 Hz, 2-CH_3), partially superimposed by 0.98 (d, $J_{1,2}$ = 6.8 Hz, 1-H_3), 1.36–1.47 (m, 6-OH, 7-H_2), 1.81 (m_c, 8-H), 2.24 (m_c, 2-H), AB signal (δ_A = 2.40, δ_B = 2.50, J_{AB} = 16.5 Hz, A part additionally split by $J_{A,2}$ = 7.0 Hz, B part additionally split by $J_{B,2}$ = 6.7 Hz, 3-H_2), 3.75 (d, $J_{5,6}$ = 4.1 Hz, 5-H), 3.98 (br. d, $J_{5\text{-OH},5}$ = 4.1 Hz, 5-OH), 4.07 (m_c, 6-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.3 (C-1*), 22.4 (2-Me*), 23.2 (8-Me and C-9), 24.7 (C-2), 25.6 (C-8), 37.7 (C-7), 43.5 (C-3), 70.1 (C-6), 79.2 (C-5), 210.6 (C=O) ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3440, 2955, 2870, 2245, 1705, 1390, 1145, 915, 845, 745, 655 cm^{-1}. $C_{11}H_{22}O_3$ (202.3): calcd. C 65.31, H 10.96; found C 65.12, H 11.35.

(*R*)-4-Hydroxyoctan-2-one (3b): A degassed solution of the boronate **6b** (187 mg, 0.76 mmol) in THF (8 mL) and MeOH (4 mL) was slowly added at –78 °C to a freshly prepared suspension of $SmBr_2$ (0.1 M in THF, 24 mL, 2.4 mmol, 3.2 equiv.). After 90 min the mixture was allowed to warm to room temp. After addition of satd. aq. $NaHCO_3$ (20 mL) and HCl (1 M, 50 mL) the mixture was extracted with EtOAc (3 × 20 mL) and dried with $MgSO_4$. After the addition of silica gel (1 g) the solvent was removed under reduced pressure. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 16–28, 72 mg, 0.50 mmol, 66%) as a colorless oil. From the starting acetonide **5b** the same conditions provided **3b** in 64% yield. $[a]_D^{20}$ = –24.0 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{8,7}$ = 7.0 Hz, 8-H_3), 1.26–1.52 (m, 5-H_2, 6-H_2, 7-H_2), 2.18 (s, 1-H_3), AB signal (δ_A = 2.53, δ_B = 2.63, J_{AB} = 17.7 Hz, A part additionally split by $J_{A,4}$ = 3.1 Hz, B part additionally split by $J_{B,4}$ = 8.8 Hz, 3-H_2), 2.91 (d, $J_{OH,4}$ = 3.5 Hz, OH), 4.03 (m_c, 4-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 (C-8), 22.7 (C-7), 27.7 (C-6), 30.8 (C-1), 36.2 (C-5), 50.0 (C-3), 67.6 (C-4), 210.1 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3490, 2960, 2930, 2360, 1715, 1360, 1220, 1170, 1085, 915, 770, 745, 670 cm^{-1}.

(*R*)-7-Hydroxyundecan-5-one (3d): This compound (96.3 mg, 68%) was prepared from the boronate **6d** (219 mg, 0.760 mmol) as described for **3b**. Flash chromatography (1 × 20 cm, 3 mL, cyclohexane/EtOAc 8:1) provided the title compound (fractions 7–12, 96.3 mg, 0.517 mmol, 68%) as a colorless oil. From the starting acetonide **5d** the same conditions provided **3d** in 66% yield. $[a]_D^{20}$ = –34.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.89 (t, $J_{1,2}$ = 7.3 Hz, 1-H_3), coincident with 0.89 (t, $J_{11,10}$ = 7.3 Hz, 11-H_3), 1.23–1.44 (m, 2-H_2, 8-H_2, 9-H_2, 10-H_2), 1.54 (tt, $J_{3,2}$ = 7.5, $J_{3,4}$ = 7.5 Hz, 3-H_2), 2.40 (t, $J_{4,3}$ = 7.4 Hz, 4-H_2), AB signal (δ_A = 2.48, δ_B = 2.57, J_{AB} = 17.2 Hz, A part additionally split by $J_{A,7}$ = 3.1 Hz, B part additionally split by $J_{B,7}$ = 8.4 Hz, 6-H_2), 3.03 (d, $J_{OH,7}$ = 3.5 Hz, OH), 4.00 (m_c, 7-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-1), 14.1 (C-11), 22.4 (C-2), 22.7 (C-10), 25.8 (C-3), 27.7 (C-9), 36.2 (C-8), 43.5 (C-4), 49.0 (C-6), 67.7 (C-7), 217.7 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3455, 2960, 2935, 2875, 2360, 2250, 1710, 1465, 1410, 1380, 1220, 1125, 1030, 915, 745, 655 cm^{-1}.

(*R*)-7-Hydroxy-9-methyldecan-5-one (3e): This compound (99 mg, 70%) was prepared from the boronate **6e** (219 mg, 0.760 mmol) as described for **3b**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 8–14, 99 mg, 0.53 mmol, 70%) as a colorless oil. From the starting acetonide **5e** the same conditions provided **3e** in 63% yield. $[a]_D^{20}$ = –78.9 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.89 (t, $J_{1,2}$ = 6.3 Hz, 1-H_3), superimposed by 0.90 (d, $J_{10,9}$ = 5.7 Hz, 10-H_3), coincident with 0.90 (d, $J_{9\text{-Me},9}$ = 5.7 Hz, 9-CH_3), 1.10 (m_c, 9-H), 1.30 (tq $J_{2,1}$ = 7.5 Hz, $J_{2,3}$ = 7.4 Hz, 2-H_2), 1.40–1.47 (m, 8-H^1), 1.55 (tt, $J_{3,2}$ = 7.5, $J_{3,4}$ = 7.5 Hz, 3-H_2), 1.77 (m_c, 8-H^2), 2.41 (t, $J_{4,3}$ = 7.5 Hz, 4-H_2), AB signal (δ_A = 2.47, δ_B = 2.56, J_{AB} = 17.9 Hz, A part additionally split by $J_{A,7}$ = 3.1 Hz, B part additionally split by $J_{B,7}$ = 8.8 Hz, 6-H_2), 3.03 (d, $J_{OH,7}$ = 3.4 Hz, OH), 4.10 (m_c, 7-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-1), 22.1 (C-2), 22.4 (C-10), 23.4 (9-Me), 24.4 (C-9), 25.8 (C-3), 43.5 (C-4), 45.6 (C-8), 49.5 (C-6), 65.8 (C-7), 212.7 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3450, 2955, 2935, 2870, 2360, 2345, 2250, 1705, 1465, 1410, 1385, 1370, 1305, 1215, 1170, 1135, 1100, 1070, 1045, 910, 845, 740, 665, 650, 555 cm^{-1}. $C_{11}H_{22}O_2$ (186.3): calcd. C 70.92, H 11.90; found C 70.62, H 12.19.

(*S*)-3-Hydroxy-2-methylnonan-5-one (3f): This compound (90 mg, 69%) was prepared from the boronate **6f** (208 mg, 0.76 mmol) as described for **3b**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 2:1) provided the title compound (fractions 16–28, 90 mg, 0.52 mmol, 69%) as a colorless oil. From the starting acetonide **5f** the same conditions provided **3f** in 70% yield. $[a]_D^{20}$ = –136 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.89 (t, $J_{9,8}$ = 7.3 Hz, 9-H_3), partially superimposed by 0.89 (d, $J_{2\text{-Me},2}$ = 6.9 Hz, 2-CH_3), partially superimposed by 0.92 (d, $J_{1,2}$ = 6.9 Hz, 1-H_3), 1.30 (tq $J_{8,9}$ = 7.5, $J_{8,7}$ = 7.4 Hz, 8-H_2), 1.55 (tt, $J_{7,8}$ = 7.5, $J_{7,6}$ = 7.4 Hz, 7-H_2), 1.65 (m_c, 2-H), 2.43 (t, $J_{6,7}$ = 7.4 Hz, 6-H_2), AB signal (δ_A = 2.48, δ_B = 2.57, J_{AB} = 17.0 Hz, A part additionally split by $J_{A,3}$ = 2.8 Hz, B part additionally split by $J_{B,3}$ = 8.3 Hz, 4-H_2), 3.04 (d, $J_{OH,3}$ = 3.4 Hz, OH), 3.79 (m_c, 3-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-9), 17.8 (C-1*), 18.4 (2-Me*), 22.3 (C-8), 25.8 (C-7), 33.1 (C-2), 43.5 (C-6), 46.0 (C-4), 72.4 (C-3), 212.9 (C=O) ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3475, 2960, 2935, 2875, 2360, 2250, 1705, 1465, 1410, 1380, 1260, 1220, 1170, 1130, 1035, 1000, 915, 770, 745, 670, 650, 565 cm^{-1}.

(*R*)-6-Hydroxy-2-methyldecan-4-one (3g): This compound (101 mg, 71%) was prepared from the boronate **6g** (219 mg, 0.76 mmol) as described for **3b**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 26–32, 101 mg, 0.542 mmol, 71%) as a colorless oil. From the starting acetonide **5g** the same conditions provided **3g** in 67% yield. $[a]_D^{20}$ = –111 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.89 (t, $J_{10,9}$ = 7.1 Hz, 10-H_3), superimposed by 0.91 (d, $J_{1,2}$ = 6.6 Hz, 1-H_3), coincident with 0.91 (d, $J_{2\text{-Me},2}$ = 6.6 Hz, 2-CH_3), 1.24–1.52 (m, 7-H_2, 8-H_2, 9-H_2), 2.13 (m_c, 2-H), 2.28 (d, $J_{3,2}$ = 7.03 Hz, 3-H_2), AB signal (δ_A = 2.46, δ_B = 2.56, J_{AB} = 17.6 Hz, A part additionally split by $J_{A,6}$ = 3.0 Hz, B part additionally split by $J_{B,6}$ = 8.9 Hz, 5-H_2), 3.01 (d, $J_{OH,6}$ = 3.5 Hz, OH), 4.00 (m_c, 6-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 (C-10), 22.6 (C-1 and 2-Me), 22.7 (C-9), 24.6 (C-2), 27.7 (C-8), 36.2 (C-7), 49.6 (C-5), 52.7 (C-3), 67.7 (C-6), 212.3 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3450, 2960, 2935, 2870, 2365, 2250, 1705, 1465, 1405, 1370, 1295, 1220, 1170, 1125, 1100, 1030, 915, 740, 665, 650 cm^{-1}. $C_{11}H_{22}O_2$ (186.3): calcd. C 70.92, H 11.90; found C 70.82, H 12.08.

(*R*)-6-Hydroxy-2,8-dimethylnonan-4-one (3h): This compound (92 mg, 65%) was prepared from the boronate **6h** (219 mg,

0.76 mmol) as described for **3b**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 4–28, 92 mg, 0.49 mmol, 65%) as a colorless oil. From the starting acetonide **5h** the same conditions provided **3h** in 66% yield. $[\alpha]_D^{20}$ = –26.9 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.90 (d, $J_{1,2}$ = 6.6 Hz, 1-H_3), coincident with 0.90 (d, $J_{2\text{-Me},2}$ = 6.6 Hz, 2-CH_3), coincident with 0.90 (d, $J_{9,8}$ = 6.6 Hz, 9-H_3), coincident with 0.90 (d, $J_{8\text{-Me},8}$ = 6.6 Hz, 8-CH_3), 1.11 (m_c, 8-H), 1.44 (m, 2-H), 1.77 (m_c, 7-H^1), 2.12 (m_c, 7-H^2), 2.28 (d, $J_{3,2}$ = 7.1 Hz, 3-H_2), AB signal (δ_A = 2.45, δ_B = 2.53, J_{AB} = 17.6 Hz, A part additionally split by $J_{A,6}$ = 3.2 Hz, B part additionally split by $J_{B,6}$ = 8.6 Hz, 5-H_2), 3.00 (d, $J_{OH,6}$ = 3.1 Hz, OH), 4.10 (m_c, 6-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.1 (C-1*), 22.6 (2-Me*), 23.4 (C-9*), 24.5 (8-Me*), 24.7 (C-2), 27.0 (C-8), 45.6 (C-7), 50.1 (C-5), 52.7 (C-3), 65.8 (C-6), 212.4 (C=O) ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3450, 2955, 2935, 2870, 2360, 2345, 2250, 1705, 1460, 1380, 1370, 1305, 1220, 1165, 1135, 1105, 1070, 1045, 910, 845, 740, 660, 650, 555 cm^{-1}.

(2*R*,4*R*)-Octane-2,4-diol [*anti*-4b;[27] in a mixture (96:4) with (2*S*,4*R*)-octane-2,4-diol (*syn*-4b)]:[27] A degassed solution of acetonide **5b** (152 mg, 0.760 mmol) in THF (1.2 mL) and MeOH (0.6 mL) was added at –78 °C to a freshly prepared $SmBr_2$ suspension (0.1 M in THF, 34 mL, 3.4 mmol, 4.5 equiv.). After 30 min at this temperature the mixture was warmed to 0 °C and stirred at this temperature for 20 h. After addition of satd. aq. $NaHCO_3$ (20 mL) and HCl (1 M, 50 mL) the mixture was extracted with EtOAc (4 × 20 mL) and dried with $MgSO_4$. Removal of the solvent under reduced pressure and flash chromatography (2 × 20 cm, 20 mL, cyclohexane/EtOAc 2:1) provided the title compound (fractions 16–24, 76.0 mg, 0.52 mmol, 68%) as a colorless oil. $[\alpha]_D^{20}$ = –26.3 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.89 [t, $J_{8,7}$ = 6.6 Hz, 8-H_3 (*anti* and *syn*)], 1.18 [d, $J_{1,2}$ = 6.2 Hz, 1-H_3 (*syn*)], 1.21 [d, $J_{1,2}$ = 6.3 Hz, 1-H_3 (*anti*)], 1.23–1.54 [m, 5-H_2, 6-H_2, 7-H_2 (*anti* and *syn*)], 1.57 [dd, $J_{3,2}$ = 5.6, $J_{3,4}$ = 5.6 Hz, 3-H_2 (*anti* and *syn*)], 2.06 [br. s, 2-OH and 4-OH (*syn*)], 2.82 [br. s, 2-OH (*anti*)], partially superimposed by 2.91 [br. s, 4-OH (*anti*)], 3.79–3.86 [m, 4-H (*syn*)], 3.88–3.94 [m, 4-H (*anti*)], 3.98–4.05 [m, 2-H (*syn*)], 4.10–4.17 [m, 2-H (*anti*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 [C-8 (*anti* and *syn*)], 22.8 [C-7 (*anti* and *syn*)], 23.6 [C-1 (*anti*)], 24.2 [C-1 (*syn*)], 27.6 [C-6 (*syn*)], 28.0 [C-6 (*anti*)], 37.2 [C-5 (*anti*)], 38.0 [C-5 (*syn*)], 44.1 [C-3 (*anti*)], 44.7 [C-3 (*syn*)], 65.5 [C-2 (*anti*)], 69.2 [C-2 (*syn*)], 69.3 [C-4 (*anti*)], 73.1 [C-4 (*syn*)] ppm. IR (film): $\tilde{\nu}$ = 3355, 2960, 2930, 2870, 2360, 2250, 1460, 1380, 1145, 1120, 1070, 910, 830, 740, 665, 650 cm^{-1}.

(2*R*,4*R*)-Octane-2,4-diol [*anti*-4c;[27] as a mixture (91:9) with (2*R*,4*S*)-octane-2,4-diol (*syn*-4c)]: This compound (77.5 mg, 70%) was prepared from the acetonide **5c** (152 mg, 0.760 mmol) as described for **4b**. Flash chromatography (2 × 20 cm, 20 mL, cyclohexane/EtOAc 1:1) provided the title compound (fractions 10–17, 77.5 mg, 0.530 mmol, 70%) as a colorless oil. $[\alpha]_D^{20}$ = –33.6 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.89 [t, $J_{8,7}$ = 7.1 Hz, 8-H_3 (*anti* and *syn*)], 1.19 [d, $J_{1,2}$ = 6.2 Hz, 1-H_3 (*syn*)], 1.22 [d, $J_{1,2}$ = 6.3 Hz, 1-H_3 (*anti*)], 1.23–1.56 [m, 5-H_2, 6-H_2, 7-H_2 (*anti* and *syn*)], 1.58 [dd, $J_{3,2}$ = 5.6, $J_{3,4}$ = 5.6 Hz, 3-H_2 (*anti* and *syn*)], 1.90 [br. s, 2-OH and 4-OH (*syn*)], 2.64 [br. s, 2-OH (*anti*)], partially superimposed by 2.72 [br. s, 4-OH (*anti*)], 3.79–3.86 [m, 4-H (*syn*)], 3.88–3.94 [m, 4-H (*anti*)], 3.98–4.07 [m, 2-H (*syn*)], 4.09–4.18 [m, 2-H (*anti*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 [C-8 (*syn* and *anti*)], 22.8 [C-7 (*syn* and *anti*)], 23.6 [C-1 (*anti*)], 24.3 [C-1 (*syn*)], 27.6 [C-6 (*syn*)], 28.0 [C-6 (*anti*)], 37.2 [C-5 (*anti*)], 38.0 [C-5 (*syn*)], 44.1 [C-3 (*anti*)], 44.7 [C-3 (*syn*)], 65.5 [C-2 (*anti*)], 69.2 [C-2 (*syn*)], 69.4 [C-4 (*anti*)], 73.2 [C-4 (*syn*)] ppm. IR (film): $\tilde{\nu}$ = 3355, 2965, 2930, 2870, 2245, 1460, 1380, 1110, 910, 740, 650 cm^{-1}.

(5*R*,7*R*)-Undecane-5,7-diol [*anti*-4d; as a mixture (63:37) with *meso*-undecane-5,7-diol (*syn*-4d)]: This compound (98.7 mg, 69%) was prepared from the acetonide **5d** (184 mg, 0.760 mmol) as described for **4b**. Flash chromatography (2 × 20 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 10–22, 98.7 mg, 0.520 mmol, 69%) as a colorless oil. $[\alpha]_D^{20}$ = –7.05 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.91 [t, $J_{11,10}$ = 7.0 Hz, 11-H_3 (*anti* and *syn*)], coincident with 0.91 [t, $J_{1,2}$ = 7.0 Hz, 1-H_3 (*anti* and *syn*)], 1.24–1.57 [m, 2-H_2, 3-H_2, 4-H_2, 8-H_2, 9-H_2, 10-H_2 (*anti* and *syn*)], 1.61 [dd, $J_{6,7}$ = 6.1, $J_{6,5}$ = 5.2 Hz, 6-H_2 (*anti* and *syn*)], 2.36 [br. s, 5-OH, 7-OH (*anti* and *syn*)], 3.82–3.88 [m, 5-H and 7-H (*syn*)], 3.91–3.97 [m, 5-H and 7-H (*anti*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 [C-1 and C-11 (*syn* and *anti*)], 22.9 [C-2 and C-10 (*syn* and *anti*)], 27.7 [C-3 and C-9 (*syn*)], 28.1 [C-3 and C-9 (*anti*)], 37.4 [C-4 and C-8 (*anti*)], 38.3 [C-4 and C-8 (*syn*)], 42.5 [C-6 (*syn* and *anti*)], 69.7 [C-5 and C-7 (*anti*)], 73.7 [C-5 and C-7 (*syn*)] ppm. IR (film): $\tilde{\nu}$ = 3285, 2955, 2930, 2875, 2855, 2360, 2250, 1465, 1410, 1350, 1185, 1145, 1125, 1065, 1045, 1010, 910, 830, 740, 650 cm^{-1}.

(4*R*,6*R*)-2-Methyldecane-4,6-diol [*anti*-4e;[27] as a mixture (71:29) with (4*R*,6*S*)-2-methyldecane-4,6-diol (*syn*-4e)]:[27] This compound (101.6 mg, 71%) was prepared from the acetonide **5e** (184 mg, 0.760 mmol) as described for **4b**. Flash chromatography (2 × 20 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 10–18, 101.6 mg, 0.540 mmol, 71%) as a colorless oil. $[\alpha]_D^{20}$ = –8.00 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.89 [t, $J_{10,9}$ = 7.0 Hz, 10-H_3 (*anti* and *syn*)], partially superimposed by 0.91 [d, $J_{1,2}$ = 6.6 Hz, 1-H_3 (*anti* and *syn*)], coincident with 0.91 [d, $J_{2\text{-Me},2}$ = 6.6 Hz, 2-CH_3 (*anti* and *syn*)], 1.17–1.51 [m, 3-H_2, 7-H_2, 8-H_2, 9-H_2 (*anti* and *syn*)], 1.57 [m_c, 5-H_2 (*anti* and *syn*)], 1.72 [m_c, 2-H (*anti* and *syn*)], 2.55 [br. s. 4-OH, 6-OH (*anti* and *syn*)], 3.81–3.88 [m, 6-H (*syn*)], 3.89–3.95 [m, 4-H (s*yn*) and 6-H (*anti*)], 3.99–4.04 [m, 4-H (*anti*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 [C-10 (*syn* and *anti*)], 22.2 [C-9 (*syn*)], 22.4 [C-9 (*anti*)], 22.8 [C-1 (*syn* and *anti*)], 23.3 [2-Me* (*anti*)], 23.4 [2-Me* (*syn*)], 24.4 [C-2 (*syn*)], 24.7 [C-2 (*anti*)], 27.6 [C-8 (*syn*)], 28.0 [C-8 (*anti*)], 37.3 [C-7 (*anti*)], 38.1 [C-7 (*syn*)], 42.9 [C-5 (*anti*)], 43.6 [C-5 (*syn*)], 46.7 [C-3 (*anti*)], 47.6 [C-3 (*syn*)], 67.6 [C-4 (*anti*)], 69.6 [C-6 (*anti*)], 71.3 [C-4 (*syn*)], 73.3 [C-6 (*syn*)] ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3310, 2955, 2930, 2870, 2245, 1465, 1430, 1405, 1365, 1130, 1070, 1050, 1000, 910, 835, 805, 740, 665, 650 cm^{-1}. $C_{11}H_{24}O_2$ (188.3): calcd. C 70.16, H 12.85; found C 70.45, H 12.75.

(4*S*,6*R*)-2-Methyldecane-4,6-diol (*syn*-4e):[27] A mixture of BEt_3 (1 M in THF, 0.53 mL, 0.53 mmol, 1.1 equiv.), THF (3.6 mL), and MeOH (1 mL) was stirred at room temp. for 1 h. The mixture was then cooled to –78 °C, the hydroxy ketone **3e** (93 mg, 0.50 mmol) in THF (4.4 mL) was added, and the mixture was stirred for 2 h. $NaBH_4$ (15 mg, 0.40 mmol, 0.8 equiv.) was added and the mixture was stirred overnight at –78 °C. After the addition of satd. aq. NH_4Cl (5 mL) the mixture was allowed to warm to room temp. The reaction mixture was then extracted with CH_2Cl_2 (3 × 10 mL) and dried with $MgSO_4$, and the solvent was removed under reduced pressure. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 2–4, 71 mg, 0.38 mmol, 75%) as a colorless oil. $[\alpha]_D^{20}$ = 7.60 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{10,9}$ = 7.1 Hz, 10-H_3), partially superimposed by 0.92 (d, $J_{1,2}$ = 6.6 Hz, 1-H_3), partially superimposed by 0.93 (d, $J_{2\text{-Me},2}$ = 6.7 Hz, 2-CH_3), 1.21–1.60 (m, 3-H_2, 5-H_2, 7-H_2, 8-H_2, 9-H_2), 1.68–1.81 (m, 2-H), 2.46 (d, $J_{4\text{-OH},4}$ = 4.0 Hz, 4-OH), partially superimposed by 2.51 (d, $J_{6\text{-OH},6}$ = 3.8 Hz, 6-OH), 3.90–3.97 (m, 4-H), 4.00–4.08 (m, 6-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 (C-10), 22.4 (C-9), 22.8 (C-

1*), 23.3 (2-Me*), 24.7 (C-2), 28.0 (C-8), 37.3 (C-7), 42.9 (C-5), 46.7 (C-3), 67.5 (C-4), 69.5 (C-6) ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3365, 2955, 2930, 2870, 2360, 2345, 2250, 1510, 1465, 1430, 1380, 1365, 1325, 1210, 1150, 1085, 915, 845, 745, 665, 450 cm^{-1}. HRMS (CI NH_3): calcd. for $C_{11}H_{24}O_2$ [M + H] 189.18456; found 189.18560 (–0.8 ppm).

(4*R*,6*R*)-2-Methyldecane-4,6-diol (*anti*-4e):[27] A mixture of $Me_4NBH(OAc)_3$ (526 mg, 2.00 mmol, 4 equiv.), acetonitrile (2.5 mL), and glacial acetic acid (2.5 mL) was stirred at room temp. for 30 min. After that the reaction mixture was cooled to –40 °C. The hydroxy ketone **3e** (93 mg, 0.50 mmol) in acetonitrile (1 mL) was added. The resulting mixture was stirred for 1 h at this temp. and then warmed to –20 °C and stirred overnight. After addition of satd. aq. potassium sodium tartrate (5 mL) the mixture was filtered through a pad of Celite® and the pad was washed with CH_2Cl_2 (4 × 5 mL). The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 39–48, 57 mg, 0.31 mmol, 61%) as a colorless oil. $[\alpha]_D^{20}$ = –11.7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.77 (t, $J_{10,9}$ = 7.8 Hz, 10-H_3), 0.83 (d, $J_{1,2}$ = 6.7 Hz, 1-H_3), coincident with 0.83 (d, $J_{2\text{-Me},2}$ = 6.7 Hz, 2-CH_3), 1.09–1.49 (m, 2-H, 3-H_2, 4-OH, 6-OH, 7-H_2, 8-H_2, 9-H_2), 1.70–1.80 (m, 5-H_2), 3.77–3.90 (m, 4-H, 6-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 (C-10), 22.6 (C-9), 22.8 (C-1*), 23.2 (2-Me*), 24.3 (C-2), 27.2 (C-8), 37.2 (C-7), 39.4 (C-5), 46.8 (C-3), 69.7 (C-4), 71.5 (C-6) ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3365, 2955, 2930, 2870, 2360, 2345, 2250, 1510, 1465, 1430, 1380, 1365, 1325, 1210, 1150, 1085, 915, 845, 745 cm^{-1}. $C_{11}H_{24}O_2$ (188.3): calcd. C 70.16, H 12.85; found C 70.45, H 12.75.

(4*R*,6*R*)-2-Methyldecane-4,6-diol [*anti*-4e;[27] **as a mixture (60:40) with (4*R*,6*S*)-2-methyldecane-4,6-diol (*syn*-4e)]:**[27] H_2O_2 (30%, 0.6 mL) was added at room temp. to a stirred solution of a 60:40 *trans*/*cis* mixture of the dioxaborinanes **13e** (80 mg, 0.29 mmol) in acetone (6 mL) and EtOAc (6 mL). After 2 d at this temp., peroxides were destroyed by addition of dimethylsulfide (5 mL) and satd. aq. $Na_2S_2O_3$ (10 mL). The reaction mixture was extracted with EtOAc (5 × 20 mL) and dried with $MgSO_4$. After addition of silica gel (0.5 g) the solvent was removed under reduced pressure. Flash chromatography (3 × 20 cm, 10 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 31–38, 45.5 mg, 0.242 mmol, 83%) as a colorless oil. $[\alpha]_D^{20}$ = +8.00 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.89 [t, $J_{10,9}$ = 7.0 Hz, 10-H_3 (*anti* and *syn*)], partially superimposed by 0.91 [d, $J_{1,2}$ = 6.6 Hz, 1-H_3 (*anti* and *syn*)], coincident with 0.91 [d, $J_{2\text{-Me},2}$ = 6.6 Hz, 2-CH_3 (*anti* and *syn*)], 1.17–1.51 [m, 3-H_2, 7-H_2, 8-H_2, 9-H_2 (*anti* and *syn*)], 1.57 [m_c, 5-H_2 (*anti* and *syn*)], 1.72 [m_c, 2-H (*anti* and *syn*)], 2.55 [br. s, 4-OH, 6-OH (*anti* and *syn*)], 3.81–3.88 [m, 6-H (*syn*)], 3.89–3.95 [m, 4-H (*syn*) and 6-H (*anti*)], 3.99–4.04 [m, 4-H (*anti*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 [C-10 (*syn* and *anti*)], 22.2 [C-9 (*syn*)], 22.4 [C-9 (*anti*)], 22.8 [C-1 (*syn* and *anti*)], 23.3 [2-Me (*anti*)], 23.4 [2-Me (*syn*)], 24.4 [C-2 (*syn*)], 24.7 [C-2 (*anti*)], 27.6 [C-8 (*syn*)], 28.0 [C-8 (*anti*)], 37.3 [C-7 (*anti*)], 38.1 [C-7 (*syn*)], 42.9 [C-5 (*anti*)], 43.6 [C-5 (*syn*)], 46.7 [C-3 (*anti*)], 47.6 [C-3 (*syn*)], 67.6 [C-4 (*anti*)], 69.6 [C-6 (*anti*)], 71.3 [C-4 (*syn*)], 73.3 [C-6 (*syn*)] ppm. IR (film): $\tilde{\nu}$ = 3310, 2955, 2930, 2870, 2245, 1465, 1430, 1405, 1365, 1130, 1070, 1050, 1000, 910, 835, 805, 740, 665, 650 cm^{-1}. $C_{11}H_{24}O_2$ (188.3): calcd. C 70.16, H 12.85; found C 70.45, H 12.75.

(3*S*,5*R*)-2-Methylnonane-3,5-diol [*anti*-4f; as a mixture (80:20) with (3*S*,5*S*)-2-methylnonane-3,5-diol (*syn*-4f)]: This compound (85.4 mg, 65%) was prepared from the acetonide **5f** (174 mg, 0.760 mmol) as described for **4b**. Flash chromatography (2 × 20 cm, 20 mL, cyclohexane/EtOAc 2:1) provided the title compound (fractions 10–17, 85.4 mg, 0.49 mmol, 65%) as a colorless oil. $[\alpha]_D^{20}$ = –69.5 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.88 [d, $J_{2\text{-Me},2}$ = 6.8 Hz, 2-CH_3 (*anti* and *syn*)], partially superimposed by 0.89 [t, $J_{9,8}$ = 7.5 Hz, 9-H_3 (*anti* and *syn*)], 0.93 [d, $J_{1,2}$ = 6.7 Hz, 1-H_3 (*anti* and *syn*)], 1.22–1.72 [m, 2-H, 4-H_2, 6-H_2, 7-H_2, 8-H_2 (*anti* and *syn*)], 2.81 [br. s, 3-OH and 5-OH (*anti* and *syn*)], 3.58–3.67 [m, 5-H (*syn*) and 5-H (*anti*)], 3.77–3.83 [m, 3-H (*syn*)], 3.86–3.92 [m, 3-H (*anti*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 [C-9 (*syn* and *anti*)], 17.5 [C-1 (*syn*)*], 18.1 [C-1 (*anti*)**], 18.3 [2-Me (*syn*)*], 18.7 [2-Me (*anti*)**], 22.8 [C-8 (*syn* and *anti*)], 27.6 [C-7 (*syn*)], 28.1 [C-7 (*anti*)], 33.8 [C-2 (*anti*)], 34.3 [C-2 (*syn*)], 37.2 [C-6 (*anti*)], 38.0 [C-6 (*syn*)], 39.4 [C-4 (*syn* and *anti*)], 69.5 [C-5 (*anti*)], 73.4 [C-5 (*syn*)], 73.9 [C-3 (*anti*)], 78.1 [C-3 (*syn*)] ppm (*/** assignment interchangeable). IR (film): $\tilde{\nu}$ = 3360, 2960, 2935, 2875, 2245, 1465, 1380, 1350, 1145, 1130, 1045, 960, 910, 845, 740, 685, 645 cm^{-1}.

(4*R*,6*R*)-2-Methyldecane-4,6-diol [*anti*-4g;[27] **as a mixture (64:34) with (4*S*,6*R*)-2-methyldecane-4,6-diol (*syn*-4g)]:** This compound (95.9 mg, 67%) was prepared from the acetonide **5g** (184 mg, 0.760 mmol) as described for **4b**. Flash chromatography (2 × 20 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 14–25, 95.9 mg, 0.51 mmol, 67%) as a colorless oil. $[\alpha]_D^{20}$ = –8.60 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.89 [t, $J_{10,9}$ = 6.7 Hz, 10-H_3 (*anti* and *syn*)], partially superimposed by 0.90 [d, $J_{1,2}$ = 6.6 Hz, 1-H_3 (*anti* and *syn*)], partially superimposed by 0.91 [d, $J_{2\text{-Me},2}$ = 6.7 Hz, 2-CH_3 (*anti* and *syn*)], 1.16–1.59 [m, 3-H_2, 5-H_2, 7-H_2, 8-H_2, 9-H_2 (*anti* and *syn*)], 1.66–1.79 [m, 2-H (*anti* and *syn*)], 2.59 [br. s, 4-OH (***anti***)], partially superimposed by 2.63 [br. s, 4-OH (*syn*)], 3.17 [br. s, 6-OH (*anti*)], partially superimposed by 3.20 [br. s, 6-OH (*syn*)], 3.80–3.86 [m, 6-H (*syn*)], 3.87–3.95 [m, 4-H (*syn*) and 6-H (*anti*)], 3.97–4.05 [m, 4-H (*anti*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1 [C-10 (*syn* and *anti*)], 22.2 [C-9 (*syn*)], 22.3 [C-9 (*anti*)], 22.8 [C-1 (*syn*)* and (*anti*)**], 23.3 [2-Me (*anti*)**], 23.4 [2-Me (*syn*)*], 24.4 [C-2 (*syn*)], 24.7 [C-2 (*anti*)], 27.6 [C-8 (*syn*)], 28.0 [C-8 (*anti*)], 37.3 [C-7 (*anti*)], 38.0 [C-7 (*syn*)], 42.9 [C-5 (*anti*)], 43.5 [C-5 (*syn*)], 46.7 [C-3 (*anti*)], 47.5 [C-3 (*syn*)], 67.5 [C-4 (*anti*)], 69.5 [C-6 (*anti*)], 71.3 [C-4 (*syn*)], 73.3 [C-6 (*syn*)] ppm (*/** assignment interchangeable). IR (film): $\tilde{\nu}$ = 3300, 2955, 2930, 2870, 2360, 2340, 2245, 1465, 1430, 1405, 1380, 1365, 1220, 1150, 1130, 1070, 1050, 1000, 910, 835, 805, 740, 665, 650 cm^{-1}. HRMS (CI NH_3): calcd. for $C_{11}H_{24}O_2$ [M + H] 189.18546; found 189.18530 (+0.8 ppm).

(4*R*,6*R*)-2,8-Dimethylnonane-4,6-diol [*anti*-4h; as a mixture (58:42) with *meso*-2,8-dimethylnonane-4,6-diol (*syn*-4h)]: This compound (78.7 mg, 55%) was prepared from the acetonide **5h** (184 mg, 0.760 mmol) as described for **4b**. Flash chromatography (2 × 20 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 12–19, 78.7 mg, 0.420 mmol, 55%) as a colorless oil. $[\alpha]_D^{20}$ = –20.7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.90 [d, $J_{9,8}$ = 6.6 Hz, 9-H_3 (*anti* and *syn*)], partially superimposed by 0.91 [d, $J_{8\text{-Me},8}$ = 6.6 Hz, 8-CH_3 (*anti* and *syn*)], coincident with 0.91 [d, $J_{2\text{-Me},2}$ = 6.6 Hz, 2-CH_3 (*anti* and *syn*)], partially superimposed by 0.91 [d, $J_{1,2}$ = 6.7 Hz, 1-H_3 (*anti* and *syn*)], 1.16–1.26 [m, 2-H, 8-H (*anti* and *syn*)], 1.37–1.57 [m, 3-H_2, 7-H_2 (*anti* and *syn*)], 1.66–1.80 [m, 5-H_2 (*anti* and *syn*)], 2.47 [br. s, 4-OH, 6-OH (*anti* and *syn*)], 3.90–3.96 [m, 4-H, 6-H (*syn*)], 3.99–4.05 [m, 4-H, 6-H (*anti*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.2 [C-1 and C-9 (*syn*)], 22.3 [C-1 and C-9 (*anti*)], 23.4 [2-Me and 8-Me (*anti*)], 23.4 [2-Me and 8-Me (*syn*)], 24.4 [C-2 and C-8 (*syn*)], 24.7 [C-2 and C-8 (*anti*)], 43.4 [C-5 (*anti*)], 44.1 [C-5 (*syn*)], 46.8 [C-3 and C-7 (*anti*)], 47.6, [C-3 and C-7 (*syn*)], 67.5 [C-4 and C-6 (*anti*)], 71.3 [C-

4 and C-6 (*syn*)] ppm. IR (film): ṽ = 3300, 2955, 2930, 2870, 2360, 2340, 2245, 1465, 1430, 1405, 1380, 1365, 1220, 1150, 1130, 1070, 1050, 1000, 910, 835, 805, 740 cm^{-1}. HRMS (CI NH_3): calcd. for $C_{11}H_{24}O_2$ [M + H] 189.18546; found 189.18510 (+1.9 ppm).

1-[(4*S*,5*R*)-5-Butyl-2,2-dimethyl-1,3-dioxolan-4-yl]ethanone (5b): The dihydroxy ketone **2b** (801 mg, 5.00 mmol) was dissolved in 2,2-dimethoxypropane (10 mL) and *p*TsOH (29 mg, 3 mol-%) was added. After the system had been allowed to stand for 12 h at room temp., imidazole (34 mg, 10 mol-%) was added and the solvent was removed under reduced pressure. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 8–12, 841 mg, 4.20 mmol, 84%) as a colorless oil. $[\alpha]_D^{20}$ = –24.5 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{4'',3'}$ = 7.2 Hz, 4''-H_3), 1.26–1.77 (m, 1''-H_2, 2''-H_2, 3''-H_2), partially superimposed by 1.43 and 1.45 [2 × s, 2'-$(CH_3)_2$], 2.27 (s, 2-H_3), 3.92–3.98 (m, 4'-H and 5'-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.0 (C-4''), 22.7 (C-3''), 26.36 and 26.39 [2 × (2'-Me)], 27.3 (C-2), 28.0 (C-2''), 33.4 (C-1''), 78.2 (C-5), 85.6 (C-4), 110.3 (C-2'), 208.8 (C=O) ppm. IR (film): ṽ = 2990, 2960, 2935, 2870, 2865, 1715, 1470, 1460, 1385, 1375, 1360, 1240, 1220, 1165, 1080 cm^{-1}.

1-[(4*S*,5*R*)-2,2,5-Trimethyl-1,3-dioxolan-4-yl]pentan-1-one (5c): This compound was prepared from the dihydroxy ketone **2c** (801 mg, 5.00 mmol) as described for **5b**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 3–6, 981 mg, 4.90 mmol, 98%) as a colorless oil. $[\alpha]_D^{20}$ = –141 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.92 (t, $J_{5,4}$ = 7.3 Hz, 5-H_3) 1.26–1.37 (m, 4-H_2), 1.39 (d, $J_{1'',5'}$ = 5.9 Hz, 1''-H_3), 1.43 and 1.46 [2 × s, 2'-$(CH_3)_2$], 1.53–1.63 (m, 3-H_2), 2.63 (dd, $J_{2,3}{}^1$ = 7.3, $J_{2,3}{}^2$ = 7.3 Hz, 2-H_2), 3.89 (d, $J_{4',5'}$ = 8.3 Hz, 4'-H), 4.01 (dq, $J_{5',4'}$ = 8.3, $J_{5',1''}$ = 6.0 Hz, 5'-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-5), 18.7 (C-1''), 22.4 (C-4), 25.0 (C-3), 26.4 and 27.3 (2'-Me_2), 38.4 (C-2), 74.3 (C-4'), 86.7 (C-5'), 110.0 (C-2'), 210.2 (C=O) ppm. IR (film): ṽ = 2985, 2935, 2875, 2255, 1715, 1455, 1380, 1240, 1175, 1100, 985, 910, 855, 805, 740, 650 cm^{-1}. HRMS (CI NH_3): calcd. for $C_{11}H_{20}O_3$ [M + H] 201.14907; found 201.14880 (+1.3 ppm).

1-[(4*S*,5*R*)-5-Butyl-2,2-dimethyl-1,3-dioxolan-4-yl]pentan-1-one (5d): This compound was prepared from the dihydroxy ketone **2d** (1.01 g, 5.00 mmol) as described for **5b**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 5–8, 1.08 g, 4.46 mmol, 89%) as a colorless oil. $[\alpha]_D^{20}$ = –18.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.88 (t, $J_{4'',3''}$ = 7.1 Hz, 4''-H_3), partially superimposed by 0.89 (t, $J_{5,4}$ = 7.3 Hz, 5-H_3), 1.25–1.37 (m, 1''-H^1, 2''-H_2, 3''-H_2), 1.40 and 1.42 [2 × brs, 2'-$(CH_3)_2$], 1.43–1.63 (m, 3-H_2, 4-H_2), 1.67–1.75 (m, 1''-H^2), 2.60 (t, $J_{2,3}$ = 7.3 Hz, 2-H_2), 3.88–3.94 (m, 5'-H), partially superimposed by 3.93 (d, $J_{4',5'}$ = 6.4 Hz, 4'-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-5), 14.0 (C-4''), 22.4 (C-4), 22.7 (C-3''), 25.1 (C-3), 26.4 and 27.3 (2'-Me_2), 28.0 (C-2''), 33.4 (C-1''), 38.3 (C-2), 78.3 (C-5'), 85.3 (C-4'), 110.1 (C-2'), 210.6 (C=O) ppm. IR (film): ṽ = 3030, 2960, 2935, 2875, 2860, 2365, 2255, 1715, 1465, 1400, 1380, 1370, 1240, 1170, 1090, 985, 910, 865, 810, 740, 650 cm^{-1}. HRMS (CI NH_3): calcd. for $C_{14}H_{26}O_3$ [M + H] 243.19602; found 243.19560 (+1.7 ppm).

1-[(4*S*,5*R*)-5-Isobutyl-2,2-dimethyl-1,3-dioxolan-4-yl]pentan-1-one (5e): This compound was prepared from the dihydroxy ketone **2e** (1.01 g, 5.00 mmol) as described for **5b**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 7–12, 1.14 g, 4.70 mmol, 94%) as a colorless oil. $[\alpha]_D^{20}$ = –11.9 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.89 (t, $J_{5,4}$ = 7.3 Hz, 5-H_3), partially superimposed by 0.89 (d, $J_{3'',2''}$ = 6.7 Hz, 3''-H_3), 0.92 (d, $J_{2''\text{-Me},2''}$ = 6.7 Hz, 2''-CH_3), AB signal (δ_A = 1.26, δ_B = 1.32, J_{AB} = 14.8 Hz, A part additionally split by $J_{A,2''}$ = 7.4 Hz, $J_{A,5'}$ = 7.4 Hz, B part additionally split by $J_{B,2''}$ = 7.4 Hz, $J_{B,5'}$ = 7.4 Hz, 1''-H_2), 1.40 and 1.42 [2 × brs, 2'-$(CH_3)_2$], 1.46–1.59 (m, 3-H_2, 4-H_2), 1.73–1.84 (m, 2''-H), 2.60 (t, $J_{2,3}$ = 7.3 Hz, 2-H_2), 3.89 (d, $J_{4',5'}$ = 8.0 Hz, 4'-H), 3.97 (ddd, $J_{5',4'}$ = 8.3, $J_{5',1''}{}^1$ = 8.3, $J_{5',1''}{}^2$ = 3.9 Hz, 5'-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.0 (C-5), 22.0 (C-4), 22.4 (C-3''*), 23.5 (2''-Me*), 25.1 (C-2''), 25.4 (C-3), 26.4 and 27.4 (2'-Me_2), 38.3 (C-2), 42.8 (C-1''), 76.7 (C-5'), 85.8 (C-4'), 110.2 (C-2'), 210.5 (C=O) ppm (* assignment interchangeable). IR (film): ṽ = 3030, 2960, 2935, 2875, 2860, 2365, 2255, 1715, 1465, 1400, 1380, 1370, 1240, 1170, 1090, 985, 910, 865, 810, 740, 650 cm^{-1}. $C_{14}H_{26}O_3$ (242.4): calcd. C 69.38, H 10.81; found C 69.52, H 11.09.

1-[(4*S*,5*R*)-5-Isopropyl-2,2-dimethyl-1,3-dioxolan-4-yl]pentan-1-one (5f): This compound was prepared from the dihydroxy ketone **2f** (941 mg, 5.00 mmol) as described for **5b**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 5–8, 1.05 g, 4.60 mmol, 92%) as a colorless oil. $[\alpha]_D^{20}$ = –19.5 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{5,4}$ = 7.3 Hz, 5-H_3), partially superimposed by 0.95 (d, $J_{1''\text{-Me},1''}$ = 6.9 Hz, 1''-CH_3), 0.98 (d, $J_{2'',1''}$ = 6.8 Hz, 2''-H_3), 1.26–1.39 (m, 4-H_2), partially superimposed by 1.39 and 1.44 [2 × s, 2'-$(CH_3)_2$], 1.49–1.63 (m, 3-H_2), 1.87 (m_c, 1''-H), 2.64 (dd, $J_{2,3}{}^1$ = 7.3, $J_{2,3}{}^2$ = 7.3 Hz, 2-H_2), 3.88 (dd, $J_{5',4'}$ = 7.0, $J_{5',1''}$ = 5.7 Hz, 5'-H), 4.06 (d, $J_{4',5'}$ = 7.0 Hz, 4'-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.0 (C-5), 17.6 (C-2''*), 19.1 (1''-Me*), 22.4 (C-4), 25.2 (C-1''), 26.4 (C-3), 27.1 and 31.2 (2'-Me_2), 38.4 (C-2), 82.8 (C-4'), 83.4 (C-5'), 110.1 (C-2'), 211.1 (C=O) ppm (* assignment interchangeable). IR (film): ṽ = 3035, 2960, 2935, 2255, 1720, 1465, 1380, 1370, 1240, 1210, 1170, 1070, 1015, 970, 910, 880, 810, 740, 650 cm^{-1}. $C_{13}H_{24}O_3$ (228.3): calcd. C 68.38, H 10.59; found C 68.04, H 10.71.

1-[(4*S*,5*R*)-5-Butyl-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbutan-1-one (5g): This compound was prepared from the dihydroxy ketone **2g** (1.01 g, 5.00 mmol) as described for **5b**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 5–8, 1.19 g, 4.91 mmol, 98%) as a colorless oil. $[\alpha]_D^{20}$ = –35.0 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{4'',3''}$ = 7.3 Hz, 4''-H_3), 1.22–1.40 (m, 2''-H_2, 3-H, 3''-H_2), partially superimposed by 1.39 (d, $J_{4,3}$ = 5.9 Hz, 4-H_3), coincident with 1.39 (d, $J_{3\text{-Me},3}$ = 5.9 Hz, 3-CH_3), 1.43 and 1.45 [2 × s, 2'-$(CH_3)_2$], 1.49–1.61 (m, 1''-H_2), 2.62 (d, $J_{2,3}$ = 7.3 Hz, 2-H_2), 3.89 (d, $J_{4',5'}$ = 8.3 Hz, 4'-H), 4.0 (ddd, $J_{5',1''}{}^1$ = 12.0, $J_{5',4'}$ = 8.3, $J_{5',1''}{}^2$ = 6.0 Hz, 5'-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-4''), 18.7 (C-4*), 22.3 (3-Me*), 22.4 (C-3), 25.0 (C-3''), 26.1 and 26.4 (2'-Me_2), 27.3 (C-2''), 38.4 (C-1''), 74.3 (C-5'), 77.3 (C-2), 86.7 (C-4'), 110.0 (C-2'), 210.2 (C=O) ppm (* assignment interchangeable). IR (film): ṽ = 3030, 2960, 2935, 2365, 2255, 1715, 1455, 1380, 1370, 1240, 1175, 1100, 985, 910, 855, 805, 740, 650 cm^{-1}. $C_{14}H_{26}O_3$ (242.4): calcd. C 69.38, H 10.81; found C 69.42, H 11.06.

1-[(4*S*,5*R*)-5-Isobutyl-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbutan-1-one (5h): This compound was prepared from the dihydroxy ketone **2h** (1.01 g, 5.00 mmol) as described for **5b**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 3–6, 1.05 g, 4.33 mmol, 87%) as a colorless oil. $[\alpha]_D^{20}$ = –23.0 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.92 (d, $J_{2''\text{-Me},2''}$ = 6.7 Hz, 2''-CH_3), coincident with 0.92 (d, $J_{3'',2''}$ = 6.7 Hz, 3''-H_3), 0.94 (d, $J_{4,3}$ = 6.7 Hz, 4-H_3), partially superimposed by 0.95 (d, $J_{3\text{-Me},3}$ = 6.6 Hz, 3-CH_3), 1.42 and 1.44 [2 × brs, 2'-$(CH_3)_2$], 1.47–1.61 (m, 1''-H^1 and 2''-H), 1.74–

1.87 (m, 3-H), 2.18 (m_c, 1′′-H^2), AB signal (δ_A = 2.49, δ_B = 2.52, J_{AB} = 17.3 Hz, A part additionally split by $J_{A,3}$ = 7.0 Hz, B part additionally split by $J_{B,3}$ = 6.7 Hz, 2-H_2), 3.88 (d, $J_{4',5'}$ = 8.0 Hz, 4′-H), 3.99 (ddd, $J_{5',1''}{}^1$ = 8.3, $J_{5',1''}{}^2$ = 8.3, $J_{5',4'}$ = 3.7 Hz, 5′-H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 21.9 (C-4), 22.5 (3-Me), 22.6 (C-3′′), 23.4 (2′′-Me), 23.5 (C-3), 25.3 (C-2′′), 26.3 and 27.3 (2′-Me_2), 42.7 (C-1′′), 47.4 (C-2), 76.4 (C-5′), 85.9 (C-4′), 110.1 (C-2′), 209.9 (C=O) ppm. IR (film): $\tilde{\nu}$ = 2960, 2935, 2875, 2250, 1715, 1470, 1380, 1370, 1240, 1170, 1070, 1030, 995, 915, 840, 745, 665, 655, 620 cm^{-1}. HRMS (CI NH_3): calcd. for $C_{14}H_{26}O_3$ [M + H] 243.19602; found 243.19600 (+0.1 ppm).

1-[(4*S*,5*R*)-5-Methyl-2-phenyl-1,3,2-dioxaborolan-4-yl]ethanone (6a): The enone **1a** (2.3 g, 90%, 25 mmol) was added at room temp. to a stirred mixture of $K_2OsO_2(OH)_4$ (92 mg, 1 mol-%), $(DHQD)_2$-PHAL (974 mg, 5 mol-%), K_2CO_3 (10.37 g, 75.00 mmol, 3.0 equiv.), $K_3Fe(CN)_6$ (25 g, 75 mmol, 3.0 equiv.), and phenylboronic acid (3.7 g, 30 mmol, 1.2 equiv.) in *t*BuOH (125 mL)/H_2O (125 mL). After 18 h, satd. aq. $Na_2S_2O_3$ (250 mL) was added. The reaction mixture was extracted with CH_2Cl_2 (4 × 100 mL) and dried with $MgSO_4$. After the addition of silica gel (15 g) the solvent was removed under reduced pressure. Flash chromatography (5 × 20 cm, 50 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 6–12, 3.2 g, 16 mmol, 63%) as a colorless oil. Under otherwise identical conditions but at 0 °C and with an extended reaction time of 3 d we obtained **6a** in 63% yield and with 92% *ee*. $[\alpha]_D^{20}$ = –60.7 (*c* = 1.0, $CHCl_3$); the *ee* was 92% according to chiral GC (CP-Chirasil-Dex CB, 25 m × 0.25 mm, Cat. No. CP 7502, 80 °C, 10 min, then 1 °C min^{-1} → 170 °C, 80 kPa H_2) with the bis(trimethylsilyl ether) of the diol obtained by hydrolysis of the title compound; $t_{ret(4S,5R)}$ = 10.97 min, $t_{ret(4R,5S)}$ = 12.07 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = (d, $J_{1'',5'}$ = 6.3 Hz, 1′′-H_3), 2.32 (s, 2-H_3), 4.34 (d, $J_{4',5'}$ = 6.9 Hz, 4′-H), 4.58 (qd, $J_{5',4'}$ = 6.4, $J_{5',1''}$ = 6.3 Hz, 5′-H), 7.37–7.86 (m, 5 × arom. H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.7 (C-1′′), 26.3 (C-2), 76.6 (C-5′), 88.0 (C-4′), 128.0, 132.0, and 135.0 (3 resonances for 4 nonequivalent arom. C), 208.6 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3855, 3745, 3675, 3650, 3630, 2925, 2360, 2340, 1700, 1520, 1100, 825 cm^{-1}.

1-[(4*S*,5*R*)-5-Butyl-2-phenyl-1,3,2-dioxaborolan-4-yl]ethanone (6b): This compound was prepared from the enone **1b** (1.3 g, 10 mmol) as described for **6a**. Flash chromatography (3 × 20 cm, 10 mL, cyclohexane/EtOAc 8:1) provided the title compound (fractions 17–28, 1.8 g, 7.2 mmol, 72%) as a colorless oil. Under otherwise identical conditions but at 0 °C and with an extended reaction time of 3 d we obtained **6b** in 70% yield and with 97% *ee*. $[\alpha]_D^{20}$ = –35.6 (*c* = 1.0, $CHCl_3$); the *ee* was 97% according to chiral GC (CP-Chirasil-Dex CB, 25 m × 0.25 mm, Cat. No. CP 7502, 80 °C, 10 min, then 5 °C min^{-1} → 170 °C, 100 kPa H_2) of the title compound; $t_{ret(3S,4R)}$ = 20.60 min, $t_{ret(3R,4S)}$ = 21.25 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.94 (t, $J_{4'',3''}$ = 7.0 Hz, 4′′-H_3), 1.24–1.59 (m, 2′′-H_2 and 3′′-H_2), 1.72–1.82 (m, 1′′-H_2), 2.33 (s, 2-H_3), 4.40 (d, $J_{4',5'}$ = 6.2 Hz, 4′-H), superimposed by 4.47 (td, $J_{5',4'}$ = 6.2, $J_{5',1''}$ = 6.2 Hz, 5′-H), 7.39–7.88 (m, 5 × arom. H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.0 (C-4′′), 22.5 (C-3′′), 26.2 (C-2), 26.9 (C-2′′), 36.6 (C-1′′), 80.3 (C-5′), 86.5 (C-4′), 128.0, 132.0, and 135.1 (6 × arom. C), 208.9 (C=O) ppm. IR (film): $\tilde{\nu}$ = 2960, 2935, 2875, 2860, 1720, 1605, 1500, 1465, 1460, 1440, 1405, 1380, 1360, 1305, 1205, 1100, 1070, 1035, 1030, 985 cm^{-1}.

1-[(4*S*,5*R*)-5-Methyl-2-phenyl-1,3,2-dioxaborolan-4-yl]pentan-1-one (6c): This compound was prepared from the enone **1c** (1.3 g, 10 mmol) as described for **6a**. Flash chromatography (3 × 20 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 6–24, 1.7 g, 7.0 mmol, 70%) as a colorless oil. Under otherwise identical conditions but at 0 °C and with an extended reaction time of 3 d we obtained **6c** in 71% yield and with >99% *ee*. $[\alpha]_D^{20}$ = –71.4 (*c* = 1.0, $CHCl_3$); the *ee* was 98% according to chiral GC (CP-Chirasil-Dex CB, 25 m × 0.25 mm, Cat. No. CP 7502, 80 °C, isothermal, 60 kPa H_2) with the bis(trimethylsilyl ether) of the diol obtained by hydrolysis of the title compound; $t_{ret(4S,5R)}$ = 49.35 min, $t_{ret(4R,5S)}$ = 50.32 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{5,4}$ = 7.3 Hz, 5-H_3), 1.24–1.40 (m, 4-H_2), 1.53 (d, $J_{1'',5'}$ = 6.3 Hz, 1′′-H_3), 1.55–1.67 (m, 3-H_2), 2.57–2.79 (m, 2-H_2), 4.37 (d, $J_{4',5'}$ = 6.7 Hz, 4′-H), 4.57 (dq, $J_{5',4'}$ = 6.4, $J_{5',1''}$ = 6.4 Hz, 5′-H), 7.38–7.85 (m, 5 × arom. H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-5), 22.4 (C-1′′), 22.8 (C-4), 25.0 (C-3), 38.3 (C-2), 87.8 (C-4′ and C-5′), 128.0, 132.0, and 135.0 (3 resonances for 4 nonequivalent arom. C), 210.6 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3080, 3055, 2960, 2935, 2875, 2360, 2245, 1715, 1605, 1505, 1440, 1405, 1370, 1350, 1295, 1210, 1100, 1030, 915, 745, 700 cm^{-1}. HRMS (EI 70 eV): calcd. for $C_{14}H_{19}BO_3$ $[M]^+$ 246.14273; found 246.14280 (+0.3 ppm).

1-[(4*S*,5*R*)-5-Butyl-2-phenyl-1,3,2-dioxaborolan-4-yl]pentan-1-one (6d): This compound was prepared from the enone **1d** (1.7 g, 10 mmol) as described for **6a**. Flash chromatography (3 × 20 cm, 10 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 11–29, 1.1 g, 6.5 mmol, 65%) as a colorless oil. Under otherwise identical conditions but at 0 °C and with an extended reaction time of 3 d we obtained **6d** in 64% yield and with 98% *ee*. $[\alpha]_D^{20}$ = –32.9 (*c* = 1.0, $CHCl_3$); the *ee* was 98% according to chiral HPLC [OD-H, heptane/propan-2-ol 9:1, v/v; 0.8 mL min^{-1}; 260 nm] with the bis(4-nitro benzoate) of the diol obtained by hydrolysis of the title compound; $t_{ret(4S,5R)}$ = 20.67 min, $t_{ret(4R,5S)}$ = 25.20 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.91 (t, $J_{4'',3''}$ = 7.6 Hz, 4′′-H_3), coincident with 0.93 (t, $J_{5,4}$ = 7.6 Hz, 5-H_3), 1.26–1.79 (m, 2-H_2, 2′′-H_2, 3-H_2, 3′′-H_2, 4-H_2), AB signal (δ_A = 2.62, δ_B = 2.71, J_{AB} = 17.8 Hz, A part additionally split by $J_{A,2''}{}^1$ = 7.4 Hz, $J_{A,2''}{}^2$ = 7.4 Hz, B part additionally split by $J_{B,2''}{}^1$ = 7.43 Hz, $J_{B,2''}{}^2$ = 7.43 Hz, 1′′-H_2), 4.41 (d, $J_{4',5'}$ = 5.9 Hz, 4′-H), superimposed by 4.45 (td, $J_{5',1''}$ = 5.8, $J_{5',4'}$ = 5.7 Hz, 5′-H), 7.38–7.88 (m, 5 × arom. H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-5), 14.1 (C-4′′), 22.4 (C-4), 22.5 (C-3′′), 25.0 (C-3), 26.9 (C-2′′), 36.7 (C-1′′), 38.2 (C-2), 80.4 (C-5′), 86.3 (C-4′), 128.0, 131.9, 135.1 (3 resonances for 4 nonequivalent arom. C), 210.9 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3855, 3745, 3675, 3650, 3630, 2980, 2870, 2360, 2340, 1700, 1520, 1385, 1130, 915, 825, 735 cm^{-1}. $C_{17}H_{25}BO_3$ (288.2): calcd. C 70.85, H 8.74; found C 70.67, H 9.01.

1-[(4*S*,5*R*)-5-Isobutyl-2-phenyl-1,3,2-dioxaborolan-4-yl]pentan-1-one (6e): This compound was prepared from the enone **1e** (1.7 g, 10 mmol) as described for **6a**. Flash chromatography (3 × 20 cm, 10 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 11–21, 1.9 g, 6.7 mmol, 67%) as a colorless oil. Under otherwise identical conditions but at 0 °C and with an extended reaction time of 3 d we obtained **6e** in 62% yield and with 99% *ee*. $[\alpha]_D^{20}$ = –35.0 (*c* = 1.0, $CHCl_3$), the *ee* was 97% according to chiral GC (CP-Chirasil-Dex CB, 25 m × 0.25 mm, Cat. No. CP 7502, 90 °C, isothermal, 60 kPa H_2) with the bis(trifluoroacetate) of the diol obtained by hydrolysis of the title compound; $t_{ret(4S,5R)}$ = 9.17 min, $t_{ret(4R,5S)}$ = 8.94 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.90 (t, $J_{5,4}$ = 7.3 Hz, 5-H_3), 0.99 (d, $J_{3'',2''}$ = 6.6 Hz, 3′′-H_3), coincident with 0.99 (d, $J_{2''\text{-Me},2''}$ = 6.6 Hz, 2′′-CH_3), 1.22–1.39 (m, 4-H_2), 1.50–1.74 (m, 2-H_2 and 3-H_2), 1.86–1.99 (m_c, 2′′-H), 2.55–2.77 (m_c, 1′′-H_2), 4.37 (d, $J_{4',5'}$ = 6.3 Hz, 4′-H), 4.47–4.54 (m_c, 5′-H), 7.37–7.86 (m, 5 × arom. H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9 (C-5), 22.3 (C-4), 22.4 (C-3′′*), 23.1 (2′′-Me*), 24.8 (C-2′′), 25.0 (C-3), 38.2 (C-2), 46.4 (C-1′′), 79.0 (C-5′), 86.9 (C-4′), 128.0,

131.9, and 135.0 (3 resonances for 4 nonequivalent arom. C), 210.8 (C=O) ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3585, 3745, 3675, 3650, 3630, 2980, 2870, 2360, 2340, 1700, 1520, 1140, 915, 825, 740 cm^{-1}. $C_{17}H_{25}BO_3$ (288.2): calcd. C 70.85, H 8.74; found C 70.96, H 9.01.

1-[(4*S*,5*R*)-5-Isopropyl-2-phenyl-1,3,2-dioxaborolan-4-yl]pentan-1-one (6f): This compound was prepared from the enone **1f** (1.5 g, 10 mmol) as described for **6a**. Flash chromatography (3 × 20 cm, 50 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 4–8, 2.2 g, 8.2 mmol, 82%) as a colorless oil. Under otherwise identical conditions but at 0 °C and with an extended reaction time of 3 d we obtained **6f** in 75% yield and with 97% *ee*. $[\alpha]_D^{20}$ = –66.2 (*c* = 1.0, $CHCl_3$); the *ee* was 94% according to chiral HPLC (IA, *n*-heptane, 0.8 mL min^{-1}, 265 nm) with the bis(dimethylphenylsilyl ether) of the diol obtained by hydrolysis of the title compound; $t_{ret(3R,4S)}$ = 8.37 min, $t_{ret(3S,4R)}$ = 9.86 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.90 (t, $J_{5,4}$ = 7.3 Hz, 5-H_3), 1.01 (d, $J_{1''\text{-Me},1''}$ = 6.7 Hz, 1″-CH_3), coincident with 1.01 (d, $J_{2'',1''}$ = 6.7 Hz, 2″-H_3), 1.26–1.38 (m, 4-H_2), 1.53–1.64 (m, 3-H_2), 1.86–1.96 (m, 1″-H), 2.54–2.77 (m, 2-H_2), 4.28 (dd, $J_{5',4'}$ = 5.6, $J_{5',1''}$ = 5.6 Hz, 5′-H), 4.49 (d, $J_{4',5'}$ = 5.4 Hz, 4′-H), 7.38–7.88 (m, 5 × arom. H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.0 (C-5), 16.8 (C-2″), 17.7 (1″-Me), 22.4 (C-4), 25.1 (C-3), 33.4 (C-1″), 38.2 (C-2), 84.0 (C-5′), 84.9 (C-4′), 128.0, 131.9, and 135.1 (3 resonances for 4 nonequivalent arom. C), 211.2 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3420, 3080, 3055, 3025, 2960, 2875, 2730, 2345, 2160, 1965, 1900, 1825, 1720, 1605, 1575, 1500, 1465, 1440, 1380, 1285, 1255, 1215, 1180, 1095, 1070, 1030, 1005, 995, 960, 940, 910, 855, 805, 765, 700, 655, 545, 530 cm^{-1}.

1-[(4*S*,5*R*)-5-Butyl-2-phenyl-1,3,2-dioxaborolan-4-yl]-3-methylbutan-1-one (6 g): This compound was prepared from the enone **1g** (1.7 g, 10 mmol) as described for **6a**. Flash chromatography (3 × 20 cm, 10 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 4–7, 2.0 g, 6.9 mmol, 69%) as a colorless oil. Under otherwise identical conditions but at 0 °C and with an extended reaction time of 3 d we obtained **6g** in 64% yield and with 99% *ee*. $[\alpha]_D^{20}$ = –42.3 (*c* = 1.0, $CHCl_3$); the *ee* was 96% according to chiral HPLC (OD-H, heptane; 0.8 mL min^{-1}; 265 nm) with the bis(dimethylphenylsilyl ether) of the diol obtained by hydrolysis of the title compound; $t_{ret(4S,5R)}$ = 10.26 min, $t_{ret(4R,5S)}$ = 11.46 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.91 (d, $J_{4,3}$ = 6.8 Hz, 4-H_3), superimposed by 0.92 (t, $J_{4'',3''}$ = 7.3 Hz, 4″-H_3), superimposed by 0.94 (d, $J_{3\text{-Me},3}$ = 6.8 Hz, 3-CH_3), 1.33–1.54 (m, 2″-H_2 and 3″-H_2), 1.66–1.78 (m, 1″-H_2), 2.12–2.25 (m, 3-H), AB signal (δ_A = 2.48, δ_B = 2.59, J_{AB} = 17.2 Hz, A part additionally split by $J_{A,3}$ = 6.7 Hz, B part additionally split by $J_{B,3}$ = 6.8 Hz, 2-H_2), 4.37 (d, $J_{4',5'}$ = 6.3 Hz, 4′-H), 4.43 (dt, $J_{5',4'}$ = 6.1, $J_{5',1''}$ = 6.0 Hz, 5′-H), 7.37–7.87 (m, 5 × arom. H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.0 (C-4″), 22.5 (C-4*), 22.7 (3-Me*), 22.7 (C-3″), 23.7 (C-3), 26.9 (C-2″), 36.7 (C-1″), 47.3 (C-2), 80.3 (C-5′), 86.5 (C-4′), 128.0, 131.9, and 135.1 (3 resonances for 4 nonequivalent arom. C), 210.3 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3855, 3745, 3675, 3650, 3630, 2930, 2360, 2340, 1700, 1525, 1135, 915, 825, 745 cm^{-1}. $C_{17}H_{25}BO_3$ (288.2): calcd. C 70.85, H 8.74; found C 70.60, H 9.13.

1-[(4*S*,5*R*)-5-Isobutyl-2-phenyl-1,3,2-dioxaborolan-4-yl]-3-methylbutan-1-one (6h): This compound was prepared from the enone **1h** (1.7 g, 10 mmol) as described for **6a**. Flash chromatography (3 × 20 cm, 10 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 5–8, 2.1 g, 7.4 mmol, 74%) as a colorless oil. Under otherwise identical conditions but at 0 °C and with an extended reaction time of 3 d we obtained **6h** in 72% yield and with >99% *ee*. $[\alpha]_D^{20}$ = –34.1 (*c* = 1.0, $CHCl_3$); the *ee* was 94% according to chiral GC (CP-Chirasil-Dex CB, 25 m × 0.25 mm, Cat. No. CP 7502, 85 °C, isothermal, 60 kPa H_2) with the bis(trifluoroacetate) of the diol obtained by hydrolysis of the title compound; $t_{ret(4S,5R)}$ = 8.58 min, $t_{ret(4R,5S)}$ = 8.37 min. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.91 (d, $J_{4,3}$ = 6.6 Hz, 4-H_3), 0.95 (d, $J_{3'',2''}$ = 6.6 Hz, 3″-H_3), 0.99 (d, $J_{2''\text{-Me},2''}$ = 6.8 Hz, 2″-CH_3), coincident with 0.99 (d, $J_{3\text{-Me},3}$ = 6.8 Hz, 3-CH_3), 1.49–1.73 (m, 1″-H_2), 1.86–1.99 (m, 2″-H), 2.12–2.27 (m, 3-H), AB signal (δ_A = 2.49, δ_B = 2.59, J_{AB} = 17.4, A part additionally split by $J_{A,3}$ = 7.2 Hz, B part additionally split by $J_{B,3}$ = 7.5 Hz, 2-H_2), 4.34 (d, $J_{4',5'}$ = 6.4 Hz, 4′-H), 4.47–4.54 (m, 5′-H), 7.37–7.87 (m, 5 × arom. H) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.3 (C-4), 22.7 (3-Me), 22.7 (C-3″), 23.1 (2″-Me), 23.8 (C-3), 24.8 (C-2″), 46.4 (C-1″), 47.3 (C-2), 78.9 (C-5′), 87.0 (C-4′), 128.0, 131.9, and 135.1 (3 resonances for 4 nonequivalent arom. C), 210.2 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3855, 3745, 3675, 3650, 3630, 2955, 2870, 2360, 2340, 1700, 1520, 1140, 825, 745 cm^{-1}. $C_{17}H_{25}BO_3$ (288.2): calcd. C 70.85, H 8.74; found C 70.95, H 9.00.

(4*R*,6*R*)-4,6-Dimethyl-2-phenyl-1,3,2-dioxaborinane [*trans*-13a; as a mixture (94:6) with *meso*-4,6-dimethyl-2-phenyl-1,3,2-dioxaborinane (*cis*-13a)]: A degassed solution of the boronate **6a** (155 mg, 0.760 mmol) in THF (1.2 mL) and MeOH (0.6 mL) was added at –78 °C to a freshly prepared $SmBr_2$ suspension (0.1 M in THF, 34 mL, 3.4 mmol, 4.5 equiv.). After 30 min the mixture was warmed to 0 °C and stirred at this temperature for 20 h. After addition of satd. aq. $NaHCO_3$ (20 mL) and HCl (1 M, 50 mL) the mixture was extracted with EtOAc (4 × 20 mL) and dried with $MgSO_4$. Removal of the solvent under reduced pressure and flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 30:1) provided the title compound (fractions 11–17, 96.8 mg, 0.51 mmol, 67%) as a colorless oil. An otherwise identical reduction of the boronate **6a** with SmI_2 led to 52% pure *trans*-**13a**. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ = 1.38 [d, J_{vic} = 6.4 Hz, 4-CH_3 (*trans* and *cis*) and 6-CH_3 (*trans* and *cis*)], 1.84 [dd, $J_{5,4}$ = 5.5, $J_{5,6}$ = 5.1 Hz, 5-H_2 (*trans* and *cis*)], 4.27 [m_c, 4-H and 6-H (*cis*)], 4.42 [qt, $J_{with\ CH_3}$ = 6.0, $J_{with\ CH_2}$ = 5.9 Hz, 4-H and 6-H (*trans*)], 7.33–7.43 [m, 3 arom. H (*trans* and *cis*)], 7.80–7.82 [m, 2 arom. H (*trans* and *cis*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.8 [4-Me and 6-Me (*trans*)], 23.3 [4-Me and 6-Me (*cis*)], 39.4 [C-5 (*trans*)], 42.6 [C-5 (*cis*)], 64.7 [C-4 and C-6 (*trans*)], 68.2 [C-4 and C-6 (*cis*)], 127.6, 130.5, and 133.8 [6 arom. C (*trans* and *cis*)] ppm. IR (film): $\tilde{\nu}$ = 2960, 2925, 2855, 2350, 2250, 1310, 1260, 1105, 915, 795, 745, 700, 665, 655 cm^{-1}.

(4*R*,6*R*)-6-Butyl-4-methyl-2-phenyl-1,3,2-dioxaborinane [*trans*-13b;[28] as a mixture (58:42) with (4*S*,6*R*)-6-butyl-4-methyl-2-phenyl-1,3,2-dioxaborinane (*cis*-13b)]:[28] This compound was prepared from the boronate **6b** (187 mg, 0.760 mmol) as described for **13a**. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 30:1) provided the title compound (fractions 3–28, 114 mg, 0.49 mmol, 65%) as a colorless oil. An otherwise identical reduction of the boronate **6b** with SmI_2 led to a 92:8 mixture of *trans*-**13b** and *cis*-**13b** in 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ = 0.96 [t, $J_{4',3'}$ = 7.3 Hz, 4′-H_3 (*cis*)], partially superimposed by 0.97 [t, $J_{4',3'}$ = 7.2 Hz, 4′-H_3 (*trans*)], 1.35 [d, $J_{1'',4}$ = 6.3 Hz, 1″-H_3 (*cis*)], 1.38 [d, $J_{1'',4}$ = 6.6 Hz, 1″-H_3 (*trans*)], 1.39–1.47 [m, 2′-H^1 and 3′-H_2 (*trans* and *cis*)], 1.51–1.61 [m, 1′-H^1 (*trans* and *cis*) and 2′-H^2 (*trans* and *cis*)], 1.62–1.75, [m, 1′-H^2 (*trans* and *cis*)], 1.79–1.91 [m, 5-H^1 (*trans* and *cis*), 5-H^2 (*cis*)], 1.96–2.00 [m, 5-H^2 (*trans*)], 4.08–4.13 [m, 4-H (*cis*)], 4.18–4.23 [m, 4-H (*trans*)], 4.23–4.30 [m, 6-H (*cis*)], 4.37–4.43 [m, 6-H (*trans*)], 7.33–7.43 [m, 3 arom. H (*trans* and *cis*)], 7.80–7.84 [m, 2 arom. H (*trans* and *cis*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.2 [C-4′ (*trans* and *cis*)], 22.8 [C-3′ and C-1″ (*trans*)], 22.8 [C-3′ and C-1″ (*cis*)], 27.4 [C-2′

(*cis*)], 27.9 [C-2′ (*trans*)], 36.7 [C-1′ (*trans*)], 37.1 [C-1′ (*cis*)], 37.8 [C-5 (*trans*)], 40.9 [C-5 (*cis*)], 65.1 [C-4 (*trans*)], 68.2 [C-4 (*cis*)], 68.5 [C-6 (*trans*)], 71.9 [C-6 (*cis*)], 126.4, 129.4, 132.7 (3 resonances for 4 nonequivalent arom. C) ppm. IR (film): $\tilde{\nu}$ = 3500, 3075, 3055, 3025, 2955, 2930, 2870, 1600, 1495, 1440, 1405, 1355, 1305, 1160, 1070, 1025, 915, 745, 700, 665, 650 cm^{-1}. HRMS (EI 70 eV): calcd. for $C_{14}H_{21}BO_2$ $[M]^+$ 232.16346; found 232.16351 (+0.2 ppm).

(4*R*,6*R*)-4-Butyl-6-methyl-2-phenyl-1,3,2-dioxaborinane [*trans*-13c;[28] as a 75:25 mixture with (4*S*,6*R*)-4-butyl-6-methyl-2-phenyl-1,3,2-dioxaborinane (*cis*-13c)]: This compound was prepared from the boronate **6c** (187 mg, 0.760 mmol) as described for **13a**. Flash chromatography (2 × 20 cm, 20 mL, cyclohexane/EtOAc 30:1) provided the title compound (fractions 4–21, 125 mg, 0.540 mmol, 71%) as a colorless oil. An otherwise identical reduction of the boronate **6c** with SmI_2 led to a 89:11 mixture of *trans*-**13c** and *cis*-**13c** in 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.93 [t, $J_{4',3'}$ = 7.1 Hz, 4′-H_3 (*trans*)], partially superimposed by 0.93 [t, $J_{4',3'}$ = 7.2 Hz, 4′-H_3 (*cis*)], 1.32 [d, $J_{1'',6}$ = 6.2 Hz, 1′′-H_3 (*cis*)], 1.35 [d, $J_{1'',6}$ = 6.4 Hz, 1′′-H_3 (*trans*)], partially superimposed by 1.33–1.43 [m, 2′-H^1 and 3′-H_2 (*trans* and *cis*)], 1.47–1.58 [m, 2′-H^2 (*trans* and *cis*)], 1.61–1.72, [m, 1′-H_2 (*trans* and *cis*)], 1.76–1.89 [m, 5-H^1 (*trans* and *cis*), 5-H^2 (*cis*)], 1.94–1.98 [m, 5-H^2 (*trans*)], 4.05–4.11 [m, 4-H (*cis*)], 4.14–4.20 [m, 4-H (*trans*)], partially superimposed by 4.20–4.28 [m, 6-H (*cis*)], 4.33–4.41 [m, 6-H (*trans*)], 7.30–7.41 [m, 3 arom. H (*trans* and *cis*)], 7.77–7.80 [m, 2 arom. H (*trans* and *cis*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.2 [C-4′ (*trans* and *cis*)], 22.8 [C-3′ and C-1′′ (*trans*)], 23.4 [C-3′ (*cis*)], 27.4 [C-1′′ and C-2′ (*cis*)], 27.9 [C-2′ (*trans*)], 36.7 [C-1′ (*trans*)], 37.1 [C-1′ (*cis*)], 37.8 [C-5 (*trans*)], 40.9 [C-5 (*cis*)], 65.1 [C-6 (*trans*)], 68.3 [C-6 (*cis*)], 68.5 [C-4 (*trans*)], 71.9 [C-4 (*cis*)], 127.6, 130.5, 133.8, 133.9 [3 resonances for 4 nonequivalent arom. C (*trans* and *cis*)] ppm. IR (film): $\tilde{\nu}$ = 3730, 2975, 2870, 2360, 2335, 2250, 1605, 1440, 1380, 1305, 1145, 1025, 915, 745, 700, 665, 650 cm^{-1}. HRMS (EI 70 eV): calcd. for $C_{14}H_{21}BO_2$ $[M]^+$ 232.16346; found 232.16350 (+0.2 ppm).

(4*R*,6*R*)-4,6-Dibutyl-2-phenyl-1,3,2-dioxaborinane [*trans*-13d; as a mixture (58:42) with *meso*-4,6-Dibutyl-2-phenyl-1,3,2-dioxaborinane (*cis*-13d)]: This compound was prepared from the boronate **6d** (219 mg, 0.760 mmol) as described for **13a**. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 30:1) provided the title compound (fractions 6–26, 148 mg, 0.540 mmol, 71%) as a colorless oil. An otherwise identical reduction of the boronate **6d** with SmI_2 led to a 80:20 mixture of *trans*-**13d** and *cis*-**13d** in 59% yield. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ = 0.94 [2 × t, J_{vic} = 7.3 Hz, 2 × CH_2-CH_2-CH_2-CH_3 (*cis*)], partially superimposed by 0.95 [2 × t, J_{vic} = 7.2 Hz, 2 × CH_2-CH_2-CH_2-CH_3 (*trans*)], 1.35–1.45 [m, 2 × CH_2-CH_2-CH_2-CH_3 and 2 × CH_2-CH_2-CH_2-CH_3, (*trans* and *cis*)], 1.50–1.58 [m, 1 × CH_2-CH_2-CH_2-CH_3, (*trans* and *cis*)], 1.61–1.73, [m, 1 × CH_2-CH_2-CH_2-CH_3, (*trans* and *cis*)], 1.85 [dd, $J_{5,4}$ = 5.3, $J_{5,6}$ = 5.3 Hz, 5-H_2 (*trans* and *cis*)], 4.06–4.11 [m, 4-H and 6-H (*cis*)], 4.14–4.19 [4-H and 6-H (*trans*)], 7.32–7.42 [m, 3 arom. H (*trans* and *cis*)], 7.79–7.82 [m, 2 arom. H (*trans* and *cis*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.2 [2 × CH_2-CH_2-CH_2-CH_3 (*trans* and *cis*)], 22.8 [2 × CH_2-CH_2-CH_2-CH_3 (*trans* and *cis*)], 27.4 [CH_2-CH_2-CH_2-CH_3 (*cis*)], 27.9 [CH_2-CH_2-CH_2-CH_3 (*trans*)], 36.3, [2 × CH_2-CH_2-CH_2-CH_3 (*trans*)], 36.7 [C-5 (*trans*)], 37.2 [2 × CH_2-CH_2-CH_2-CH_3 (*cis*)], 39.1 [C-5 (*cis*)], 68.9 [C-4 and C-6 (*trans*)], 71.9 [C-4 and C-6 (*cis*)], 127.5, 127.6, 130.5, 133.8, and 133.9 [6 arom. C (*trans* and *cis*)] ppm. IR (film): $\tilde{\nu}$ = 2955, 2930, 2870, 2410, 2350, 1600, 1440, 1410, 1375, 1310, 1155, 1030, 915, 745, 700, 665, 650 cm^{-1}. HRMS (EI 70 eV): calcd. for $C_{17}H_{27}BO_2$ $[M]^+$ 274.21041; found 274.21048 (+0.3 ppm).

(4*R*,6*R*)-4-Butyl-6-isobutyl-2-phenyl-1,3,2-dioxaborinane [*trans*-13e;[28] as a mixture (60:40) with (4*S*,6*R*)-4-butyl-6-isobutyl-2-phenyl-1,3,2-dioxaborinane (*cis*-13e)]:[28] This compound was prepared from the boronate **6e** (219 mg, 0.760 mmol) as described for **13a**. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 4–22, 137 mg, 0.500 mmol, 66%) as a colorless oil. An otherwise identical reduction of the boronate **6e** with SmI_2 led to a 66:34 mixture of *trans*-**13e** and *cis*-**13e** in 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.94 [d, $J_{3'',2''}$ = 7.5 Hz, 3′′-H_3 (*cis*)], partially superimposed by 0.94 [d, $J_{3'',2''}$ = 7.3 Hz, 3′′-H_3 (*trans*)], partially superimposed by 0.95 [d, $J_{2''\text{-Me},2''}$ = 7.3 Hz, 2′′-CH_3 (*cis*)], partially superimposed by 0.99 [d, $J_{2''\text{-Me},2''}$ = 6.6 Hz, 2′′-CH_3 (*trans*)], partially superimposed by 0.99 [t, $J_{4',3'}$ = 6.9 Hz, 4′-H_3 (*trans* and *cis*)], 1.26–1.47 [m, 2′-H_2, 2′′-H, and 3′-H_2, (*trans* and *cis*)], 1.51–1.74 [m, 1′-H_2 (*trans* and *cis*)], 1.78–2.06 [m, 1′′-H_2, and 5-H_2 (*trans* and *cis*)], 4.07–4.21 [m, 4-H (*cis*), 4-H (*trans*), and 6-H (*cis*)], 4.23–4.31 [m, 6-H (*trans*)], 7.31–7.42 [m, 3 arom. H (*trans* and *cis*)], 7.79–7.83 [m, 2 arom. H (*trans* and *cis*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.2 [C-4′ (*trans* and *cis*)], 22.5 [C-3′ (*trans*)], 22.8 [C-3′ (*cis*)], 22.8 [C-3′′ (*trans*)*], 23.3 [2′′-Me (*trans*)*], 23.4 [C-3′′ and 2′′-Me (*cis*)], 24.5 [C-2′′ (*cis*)], 24.8 [C-2′′ (*trans*)], 27.4 [2′-C (*cis*)], 27.9 [C-2′ (*trans*)], 36.8 [C-1′ (*trans* and *cis*)], 37.2 [C-5 (*trans*)], 39.7 [C-5 (*cis*)], 46.1 [C-1′′ (*trans*)], 46.7 [C-1′′ (*cis*)], 67.0 [C-6 (*trans*)], 68.9 [C-4 (*trans*)], 70.2 [C-6 (*cis*)], 71.9 [C-4 (*cis*)], 127.6, 127.6, 130.5, 133.8, and 133.9 [6 arom. C (*trans* and *cis*)] ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 2955, 2935, 2870, 2405, 2350, 1600, 1440, 1410, 1375, 1310, 1145, 1030, 915, 745, 700, 665, 645, 450 cm^{-1}. HRMS (EI 70 eV): calcd. for $C_{17}H_{27}BO_2$ $[M]^+$ 274.21041; found 274.21047 (+0.2 ppm).

(4*R*,6*S*)-4-Butyl-6-isopropyl-2-phenyl-1,3,2-dioxaborinane [*trans*-13f; as a mixture (50:50) with (4*S*,6*S*)-4-butyl-6-isopropyl-2-phenyl-1,3,2-dioxaborinane (*cis*-13f)]: This compound was prepared from the boronate **6f** (208 mg, 0.760 mmol) as described for **13a**. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 30:1) provided the title compound (fractions 3–26, 135 mg, 0.52 mmol, 69%) as a colorless oil; an otherwise identical reduction of the boronate **6f** with SmI_2 led to a 82:18 mixture of *trans*-**13f** and *cis*-**13f** in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.95 [t, $J_{4',3'}$ = 7.1 Hz, 4′-H_3 (*cis*)], partially superimposed by 0.96 [t, $J_{4',3'}$ = 6.9 Hz, 4′-H_3 (*trans*)], partially superimposed by 0.97 [d, $J_{1''\text{-Me},1''}$ = 6.7 Hz, 1′′-CH_3 (*cis*)], 0.99 [d, $J_{2'',1''}$ = 6.8 Hz, 2′′-H_3 (*cis*)], 1.06 [d, $J_{2'',1''}$ = 6.8 Hz, 2′′-H_3 (*trans*)], 1.09 [d, $J_{1''\text{-Me},1''}$ = 6.7 Hz, 1′′-CH_3 (*trans*)], 1.36–1.46 [m, 2′-H_2 and 3′-H_2 (*trans* and *cis*)], 1.51–1.59 [m, 1′-H^1 (*trans* and *cis*) and 1′′-H (*trans* and *cis*)], 1.61–1.84, [m, 1′H^2 (*trans* and *cis*), 5-H^1 (*cis*), 5-H^2 (*trans*)], 1.90–1.98 [m, 5-H^1 (*trans*), 5-H^2 (*cis*)], 3.81–3.88 [m, 4-H and 6-H (*cis*)], 4.05–4.12 [m, 4-H (*trans*)], 4.15–4.21 [m, 6-H (*trans*)], 7.32–7.43 [m, 3 arom. H (*trans* and *cis*)], 7.81–7.84 [m, 2 arom. H (*trans* and *cis*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.1 [C-4′ (*trans*)], 13.1 [C-4′ (*cis*)], 16.7 [1′′-Me (*trans*)*], 17.1 [C-2′′ (*trans*)*], 17.4 [C-2′′ and 1′′-Me (*cis*)], 21.6 [C-3′ (*trans*)], 21.7 [C-3′ (*cis*)], 26.3 [C-2′ (*cis*)], 26.9 [C-2′ (*trans*)], 32.3 [C-1′ (*cis*)], 32.6 [C-1′′ (*cis*)], 32.9 [C-1′′ (*trans*)], 34.8 [C-1′ (*trans*)], 35.4 [C-5 (*cis*)], 36.2 [C-5 (*trans*)], 68.4 [C-4 (*trans*)], 70.9 [C-4 (*cis*)], 72.2 [C-6 (*trans*)], 75.6 [C-6 (*cis*)], 126.4, 126.4, 129.4, 132.7, and 132.8 [6 arom. C (*trans* and *cis*)] ppm (* assignment interchangeable). IR (film): $\tilde{\nu}$ = 3670, 3075, 2960, 2930, 2870, 2360, 2240, 1710, 1600, 1440, 1405, 1375, 1310, 1145, 1030, 980, 970, 960, 910, 875, 865, 845, 810, 800, 790, 740, 700, 665, 650, 630, 620, 610 cm^{-1}. HRMS (EI 70 eV): calcd. for $C_{16}H_{25}BO_2$ $[M]^+$ 260.19476; found 260.19480 (+0.2 ppm).

(4*R*,6*R*)-4-Butyl-6-isobutyl-2-phenyl-1,3,2-dioxaborinane [*trans*-13g;[28] as a mixture (58:42) with (4*R*,6*S*)-4-butyl-6-isobutyl-2-

phenyl-1,3,2-dioxaborinane (*cis*-13g)]: This compound was prepared from the boronate **6g** (219 mg, 0.760 mmol) as described for **13a**. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 30:1) provided the title compound (fractions 4–24, 135 mg, 0.492 mmol, 65%) as a colorless oil. An identical SmI_2 reduction of the boronate **6g** led to a 57:43 mixture of *trans*-**13g** and *cis*-**13g** in 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 0.94 [d, $J_{3'',2''}$ = 7.4 Hz, 3''-H_3 (*cis*)], partially superimposed by 0.95 [d, $J_{3'',2''}$ = 7.4 Hz, 3''-H_3 (*trans*)], 0.97 [d, $J_{2''\text{-Me},2''}$ = 5.8 Hz, 2''-CH_3 (*cis*)], partially superimposed by 0.99 [d, $J_{2''\text{-Me},2''}$ = 6.6 Hz, 2''-CH_3 (*trans*)], partially superimposed by 0.99 [t, $J_{4',3'}$ = 6.9 Hz, 4'-H_3 (*cis* and *trans*)], 1.26–1.45 [m, 2'-H_2, 2''-H, and 3'-H_2 (*trans* and *cis*)], 1.52–1.72 [m, 1'-H_2 and 1''-H_2 (*trans* and *cis*)], 1.82–2.04 [m, 5-H_2 (*trans* and *cis*)], 4.07–4.21 [m, 4-H (*cis*), 4-H (*trans*) and 6-H (*cis*)], 4.24–4.31 [m, 6-H (*trans*)], 7.31–7.42 [m, 3 arom. H (*trans* and *cis*)], 7.78–7.82 [m, 2 arom. H (*trans* and *cis*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.2 [C-4' (*trans* and *cis*)], 22.5 [C-3' (*trans* and *cis*)], 22.8 [C-3'' (*trans*)*], 22.8 [C-3'' (*cis*)**], 23.3 [2''-Me (*trans*)*], 23.4 [2''-Me (*cis*)**], 24.4 [C-2'' (*cis*)], 24.8 [C-2'' (*trans*)], 27.4 [C-2' (*cis*)], 27.9 [C-2' (*trans*)], 36.8 [C-1' (*trans*)], 37.2 [C-1' (*cis*)], 39.7 [C-5 (*cis*)], 46.1 [C-5 and C-1'' (*trans*)], 46.7 [C-1'' (*cis*)], 67.0 [C-6 (*trans*)], 68.9 [C-4 (*trans*)], 70.1 [C-6 (*cis*)], 71.9 [C-4 (*cis*)], 127.5, 127.6, 130.5, 133.8, and 133.9 [6 arom. C (*trans* and *cis*)] ppm (*/** assignment interchangeable). IR (film): $\tilde{\nu}$ = 2955, 2935, 2870, 2360, 2340, 1600, 1440, 1410, 1370, 1310, 1160, 1030, 915, 805, 745, 700, 670, 650 cm^{-1}. HRMS (EI 70 eV): calcd. for $C_{17}H_{27}BO_2$ $[M]^+$ 274.21041; found 274.21048 (+0.2 ppm).

(4*R*,6*R*)-4,6-Diisobutyl-2-phenyl-1,3,2-dioxaborinane [*trans*-13h; as a mixture (58:42) with *meso*-4,6-diisobutyl-2-phenyl-1,3,2-dioxaborinane (*cis*-13h)]: This compound was prepared from the boronate **6h** (219 mg, 0.760 mmol) as described for **13a**. Flash chromatography (2 × 20 cm, 10 mL, cyclohexane/EtOAc 30:1) provided the title compound (fractions 10–29, 154 mg, 0.562 mmol, 74%) as a colorless oil. An otherwise identical reduction of the boronate **6h** with SmI_2 led to a 58:42 mixture of *trans*-**13h** and *cis*-**13h** in 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ = 0.98 [d, J_{vic} = 6.9 Hz, 1 × CH_2-CH-(CH_3)$_2$ (*cis* and *trans*)], partially superimposed by 0.99 [d, J_{vic} = 6.9 Hz, 1 × CH_2-CH-(CH_3)$_2$ (*cis* and *trans*)], partially superimposed by 1.00 [d, J_{vic} = 6.9 Hz, 1 × CH_2-CH-(CH_3)$_2$ (*cis* and *trans*)], partially superimposed by 1.00 [d, J_{vic} = 6.6 Hz, 1 × CH_2-CH-(CH_3)$_2$ (*cis* and *trans*)], 1.29–1.34 [m, 2 × CH_2-C*H*-(CH_3)$_2$ (*trans* and *cis*)], 1.53–1.68 [m, 1 × CH_2-CH-(CH_3)$_2$ (*trans* and *cis*)], 1.81–2.06, [m, 1 × CH_2-CH-(CH_3)$_2$ (*trans* and *cis*), 5-H_2 (*trans* and *cis*)], 4.16–4.22 [m, 4-H (*cis*), 6-H (*cis*)], 4.25–4.30 [m, 4-H (*trans*) and 6-H (*trans*)], 7.31–7.42 [m, 3 arom. H (*trans* and *cis*)], 7.79–7.81 [m, 2 arom. H (*trans* and *cis*)] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.5 [4 × CH_2-CH-(*C*H_3)$_2$ (*trans*)], 23.3 [4 × CH_2-CH-(*C*H_3)$_2$ (*cis*)], 23.4 [CH_2-*C*H-(CH_3)$_2$ (*trans*)], 24.4 [CH_2-*C*H-(CH_3)$_2$ (*trans*)], 24.8 [2 × CH_2-*C*H-(CH_3)$_2$ (*cis*)], 37.2 [C-5 (*trans*)], 40.2 [C-5 (*cis*)], 46.1 [2 × *C*H_2-CH-(CH_3)$_2$ (*trans*)], 46.7 [2 × *C*H_2-CH-(CH_3)$_2$ (*cis*)], 67.0 [C-4 and C-6 (*trans*)], 70.1 [C-4 and C-6 (*cis*)], 127.5, 127.6, 130.5, 133.8, and 133.9 [6 arom. C (*trans* and *cis*)] ppm. IR (film): $\tilde{\nu}$ = 2955, 2870, 2365, 2345, 1600, 1440, 1410, 1370, 1310, 1160, 1030, 915, 745, 700, 665, 645 cm^{-1}. HRMS (EI 70 eV): calcd. for $C_{17}H_{27}BO_2$ $[M]^+$ 274.21041; found 274.21050 (+0.3 ppm).

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[28] Compound *trans*-**13b** equals *trans*-**13c** and *cis*-**13b** equals *ent-cis*-**13c**; compound *trans*-**13e** equals *trans*-**13g** and *cis*-**13e** equals *ent-cis*-**13g**.

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