29. A Simple Procedure for the Preparation of Chiral 'Tris(hydroxymethyl)methane' Derivatives

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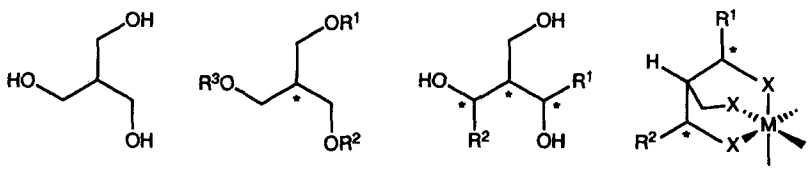
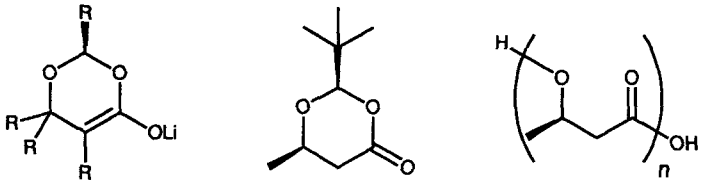
The aldol adducts **1a**–**13a** of (*R*,*R*)-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one (from 3-hydroxybutanoic acid) to aldehydes, single diastereoisomers obtained as described previously, are acetylated or benzoylated to the corresponding esters **1b**–**5b** and **6c**–**13c**, respectively, which in turn are reduced with $LiAlH_4$ to the title compounds **14**–**24**. The enantiomerically pure triols thus available may be useful as chiral building blocks, as auxiliaries for enantioselective reactions, and as center pieces for chiral dendrimers.

1. Introduction. – In connection with our interest in chiral starburst dendrimers[3]) [2] [3], we have been working on developing efficient routes to enantiomerically pure triols. The most simple structure, 'tris(hydroxymethyl)methane' **A** (C_{3v} symmetry), can be transformed into chiral structures by either introducing different substituents, R^1, R^2, and





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[2]) Postdoctoral research at ETH-Zürich from October 1990 to March 1992, financed by the *Deutsche Forschungsgemeinschaft (DFG)*, Bonn.

[3]) For a recent review article on dendrimers, see [1a]; for a 'highlight' on the subject, see [1b].

R^3 on the O-atoms[4]), see **B** [2] [4], or by introducing one or more substituents in the branches of the original structure **A**, see **C** [3]. Besides being potential central cores for chiral dendrimers, compounds of type **C** may also be welcome building blocks for more conventional target molecules, or they might serve as precursors for tripodal ligands in transition-metal complexes **D** [5] [6].

2. Preparative Results. – Our approach to the synthesis of type **C** triols uses a method by which the groups on the branches and the substitution pattern can be greatly varied. The Li enolate **E** of a 1,3-dioxan-4-one, for instance **F**, is added to an aldehyde, and the product reduced to the triol; as we will see, this is easier said than done. First, we would like to refer to the many ways of substituting and altering the structure of these chiral dioxanones: they can be prepared or derived from different 3-hydroxy-carboxylic acids (→different substituents at C(6))[5]), they may be singly[6]) or doubly[7]) substituted at C(5), and 6,6-dialkyl derivatives are available by *Michael* additions to the corresponding dioxinones [7b] [8c] [9].

For the work described here, we employed the 6-methyl-dioxanone **F** which is prepared from the inexpensive biopolymer PHB **G**[8]) [11] [12]. Aldol addition of the corresponding enolate is highly diastereoselective with aliphatic aldehydes [3]. Thus, the hydroxy-carbonyl derivatives **1a**–**5a** are obtained after purification as single diastereoisomers in yields ranging from 25 to 75% with propanal, 2-methylpropanal, cyclohexanecarboxaldehyde, 2,2-dimethylpropanal, and adamantanecarbaldehyde, respectively. The stereoselectivities (7:1 to > 99:1) increases with increasing bulk of the substituent on the aldehyde C=O group. Purification of the crude products is effected either by simple crystallization (**1a**, **2a**) or by flash chromatography followed by recrystallization. In the case of aromatic aldehydes, there is essentially no diastereoselectivity of the aldol reaction with the dioxanone **F** [3] [8b] [13]. The preference for formation of one of the isomers may even be reversed, as previously found with benzaldehyde [8b] [13], and as now confirmed with naphthalene-1- and -2-carbaldehyde, and with anthracene-9-carbaldehyde, see the products **6a**–**13a**. The yields with which the mixtures of diastereoisomers form are a bit higher (50–85%) than with aliphatic aldehydes. The separation of the diastereoisomeric pairs can be achieved either by flash chromatography (**6a**/**7a**, **10a**/**11a**), or by medium-pressure liquid chromatography (MPLC) at the stage of the benzoate esters (**12c**/**13c**). Of the two naphth-2-yl-substituted benzoates **8c** and **9c**, the former one is insoluble in most organic solvents (see structure determination below). The reactions leading to the aldol-type products[9]) **1a**–**13a** were carried out in scales of up to 70 mmol, all these compounds, as well as their esters are solid and can be recrystallized or precipitated from solutions.

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[4]) Not only is this type of compound much more difficult to prepare in nonracemic form, it also requires a strategy for a dendrimer synthesis, in which the three branches would have to be constitutionally different – a formidable task!

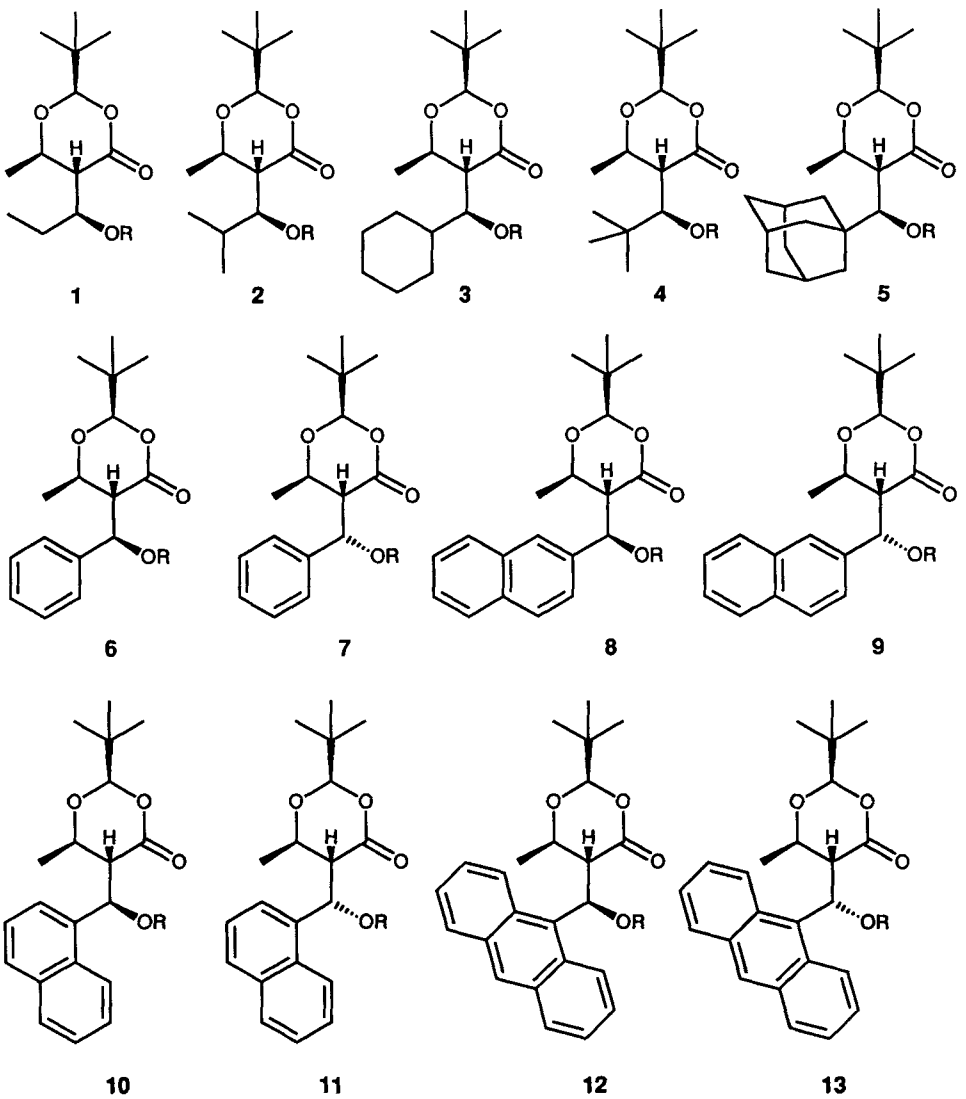
[5]) 6-Et [7a], 6-Alkyl [7b, c], 6-(CF_3) [7d], 6-(CCl_3) [7e].

[6]) By enolate alkylation [8a, b] or through 5-alkylidene derivatives [3].

[7]) Double alkylation at C(5) is possible under certain conditions [8c, d].

[8]) For review articles, see [10].

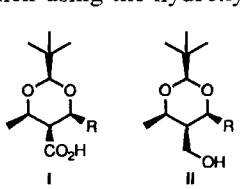
[9]) Configurationally pure but *racemic* derivatives of 3-hydroxy-2-(1′-hydroxyalkyl)alkanoic acids have been prepared by the *Fleming* aldol methodology [14].



a R = H, **b** R = CH_3CO, **c** R = PhCO

Originally, we had thought that the dioxanone aldol adducts **1a–13a** could just be treated with $LiAlH_4$ (LAH) to prepare[10]) the corresponding triols **14–24**. Experiments showed that the yields of triols were unsatisfactory (*ca.* 50%) when using the hydroxy

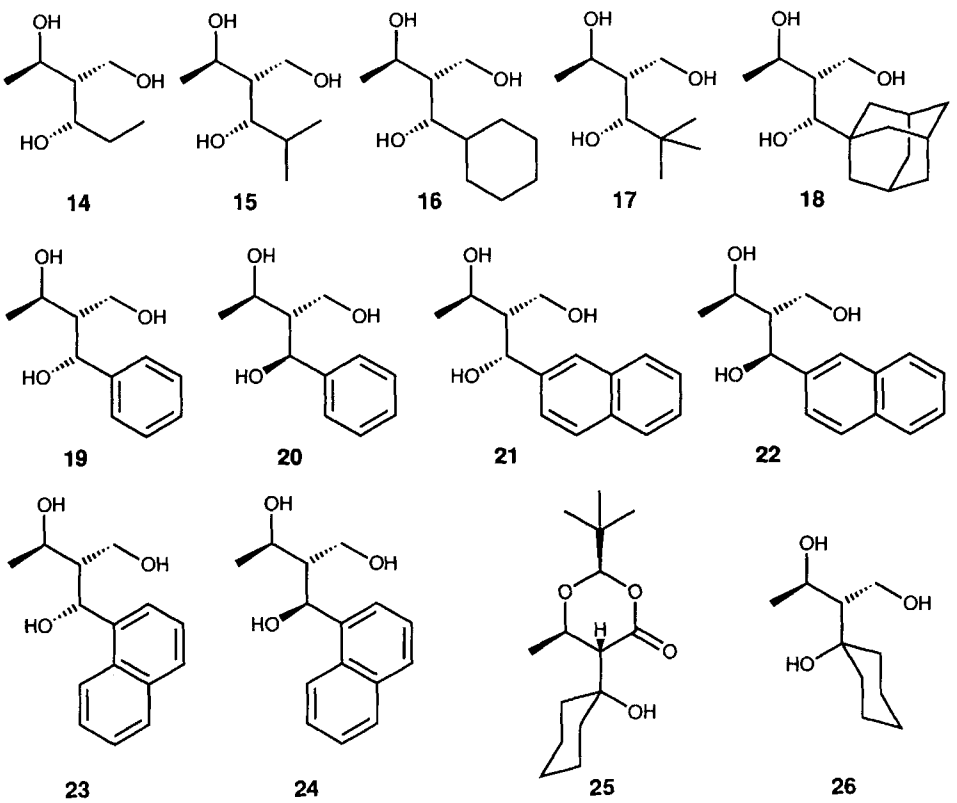
[10]) Previously, we have converted hydroxyalkylated dioxanones of this type to dioxane-carboxylic acids **i** and reduced those directly to the dioxane-5-methanols **ii** [3]. The transacetalization from the aldol adducts to the acids **i** turns out not to take place, unless R in **i** is a primary alkyl group (we tried unsuccessfully with **2a** and **6a**).



i ii

compounds directly as substrates for the reduction. We found, however, that the use of 1′-*O*-benzoates, some of which we had originally prepared as derivatives for better diastereoisomer separation, in the LAH reduction gave excellent results (**8c–11c** → **21–24**)[11]), reliably the yields are above 85%. Most of the isolated triols are oils, but can be prepared in analytically pure form by chromatography and rigorous removal of traces of solvent. As far as we know, enantiomerically pure triols of the type described here have not been prepared before.

The triols **14–18** with aliphatic side chains are quite stable compounds, their precursors are formed with higher stereoselectivity, and their derivatives will survive conditions of catalytic hydrogenation and of dissolving metals. The triols **19–24** with aryl substituents will undergo benzylic cleavage under such conditions. We have treated both types of triols with strong base (NaH, *t*-BuOK) without observing decomposition. On the

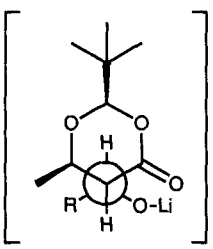


[11]) We assume that the lower yields obtained with the free hydroxy compounds (**a** series) are due to *retro*-aldol reactions during the LAH reduction. It is reasonable to expect that, in the acylated derivatives (**b** and **c** series), the dioxanone is reduced faster than the ester C=O group (lactones are generally more reactive than esters towards nucleophilic attack). Also, in the case of the naphth-1-yl derivatives **10a** and **11a**, we noticed that one of the diastereoisomers underwent epimerization during a large-scale (25 mmol) LAH reduction to give both epimers (**23**/**24**); this did not happen, when the esters **10c**, **11c** were employed under the same conditions.

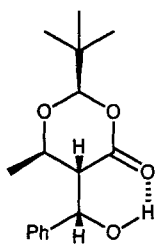
other hand, acid or *Lewis*-acid conditions are expected to cause problems (benzylic cations and their subsequent reactions, *retro-Prins* reactions, *etc.*), especially, again, with the aryl-substituted derivatives. In fact, we were not able to avoid decomposition of the anthracenyl-triols derived from **12** and **13**; they decomposed during chromatography or in $CDCl_3$ solution (at room temperature, within minutes). Thus, the aliphatic triols are likely to be more useful building blocks or auxiliaries for further use.

The triols **14**–**24** all contain one primary and two secondary OH groups, and a H-atom at the central C-atom bearing the three hydroxyalkyl branches. Other substitution patterns are accessible by our synthetic route as well. Thus, other enolates of type **E** [3] [7–9] [13] could be employed, or ketones rather than aldehydes could be used for the hydroxyalkylation of **F**. To demonstrate the last mentioned conversion, we carried out the aldol addition with cyclohexanone which gave, in good yield, the product **25** with a tertiary OH group. Protection of this OH group by esterification was not possible; there was either no reaction (under the conditions successfully applied to the analogs with secondary OH groups) or epimerization (at higher temperatures/after longer reaction times/or with stronger bases such as DMAP). Thus, the direct reduction was chosen furnishing the triol **26** (60%).

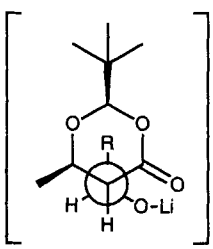
3. Structure Determination, Configurational Assignments, and Mechanistic Discussion. – We have previously assigned the configuration to dioxanone aldol adducts of some aliphatic aldehydes – formed with high diastereoselectivity – by transacetalization and NMR analysis, see the formula **i** in *Footnote 10*. According to this analysis, the primary adduct may be pictured as shown in **H** ((*Re,Re*) or *like* relative topicity). To the major product **7a** formed with benzaldehyde in low diastereoselectivity, we had assigned the (1′*S*,2*R*,5*R*,6*R*)-configuration (see **I**) on the basis of the following assumptions: *a*) a H-bridge is present between the OH and the C=O groups, *b*) the isomer **7a** (= **I**), in which H–C(1′) and H–C(5) are *cis* in the H-bonded six-membered ring, shows the



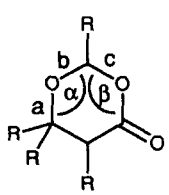
H *(Re, Re)*



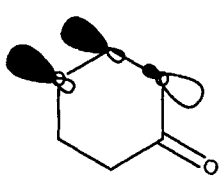
I **(7a)**



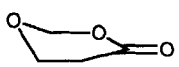
J *(Re, Si)*



K



L



M

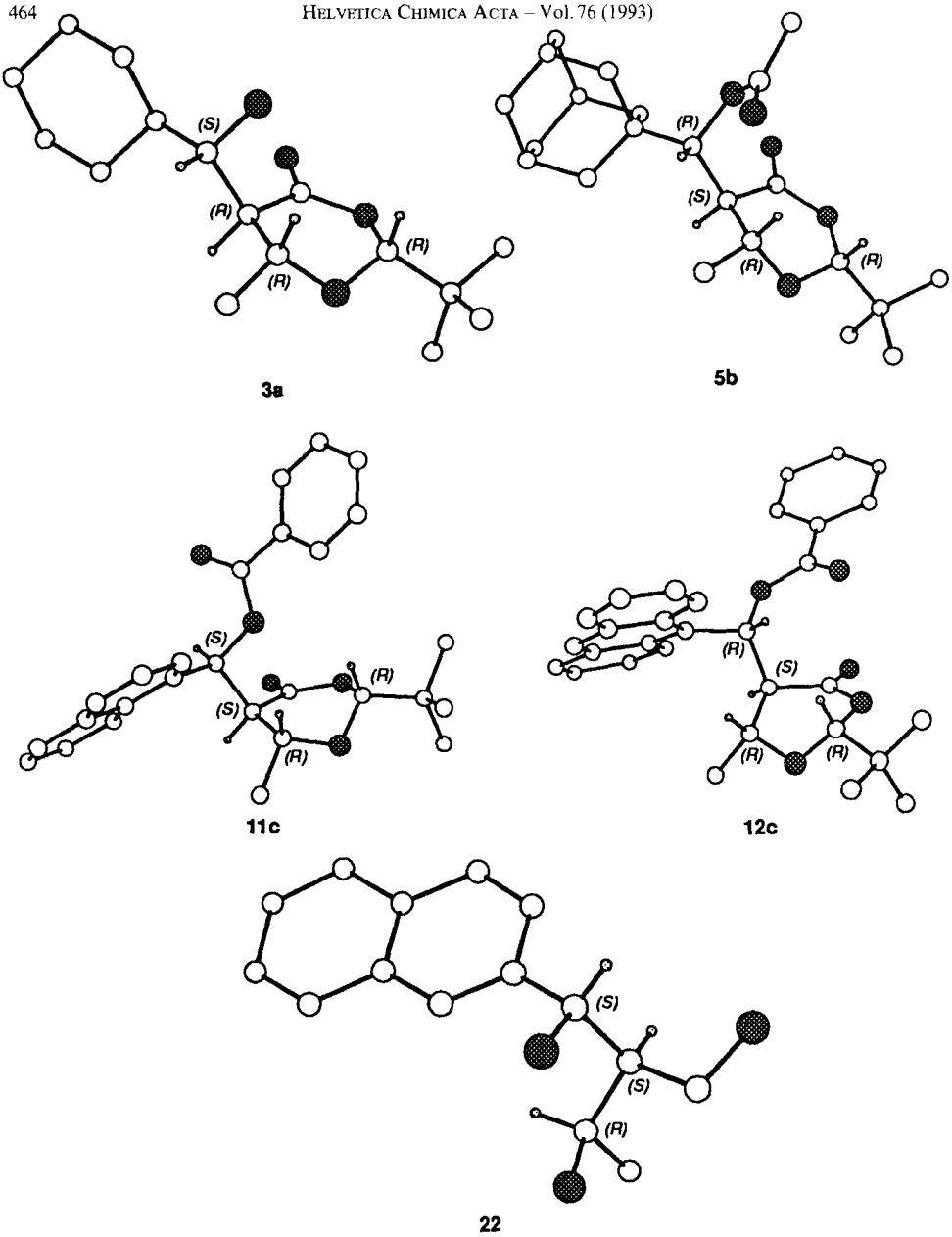


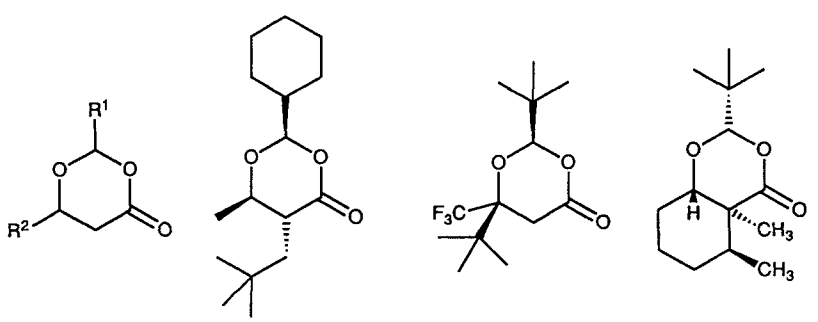
Fig. *Chem-3D presentations of the crystal structures of the dioxanone derivatives obtained with two aliphatic* (**3a**, **5b**) *and two aromatic aldehydes* (**11c**, **12c**), *as well as the structure of the triol* **22** (*from naphthalene-2-carbaldehyde*). The structures of **12c** and **22** were determined by Dr. *V. Gramlich*, *T. Bremi*, *F. Kühnle*, *S. Portmann*, and *I. Tironi*, as part of the crystallography course at ETH-Zürich, winter term 1991/92. The coordinates have been submitted for inclusion in the *Crystallographic Data Base* (Cambridge, England). The crystal data are collected in *Table 2* (*Exper. Part*). For a discussion of ring geometry and conformation of the dioxanones, see *Table 1* and text. The e.s.d.'s of bond lengths for structures **3a**, **5b**, **11c**, and **12c** range from about 0.005 to 0.008 Å, those of the angles from 0.3 to 0.5°.

smaller NMR coupling constant (3.3 *vs.* 6.3 Hz). This suggests that an (*Re,Si*) or *unlike* combination of the trigonal centers in the aldol addition is occurring with the aromatic aldehyde[12]), *cf.* **H** and **J**. Since such configurational assignments based solely on NMR measurements and assumed preferred conformations are never sure, we decided to determine the crystal structures of some of the new dioxanone aldol adducts described herein.

We succeeded in preparing suitable single crystals of the four dioxanones **3a**, **5b**, **11c**, and **12c**, as well as of the triol **22**. The X-ray crystal structures are shown in the *Figure*. The hydroxy compound **3a** is the only diastereoisomer isolated, **5b** is the acetate of the sole product formed, **11c** is the benzoate of the minor (1:2), **12c** of the major (3.6:1) adduct with naphthalene-1-carbaldehyde and anthracene-9-carbaldehyde, respectively, and **22** has been obtained from one of the isomers (**8**) formed in a 1:1 ratio with naphthalene-2-carbaldehyde.

The structures of the cyclohexyl and adamantyl derivatives confirm our previous assignments to adducts with aliphatic aldehydes [3][10]). While the enantiotopic faces of naphthalene-2-carbaldehyde are not differentiated at all, nucleophilic attack on the naphth-1-yl and anthracen-9-yl derivatives occurs preferentially with the same relative topicity as observed in the aliphatic series[13]).

Having four new dioxanone structures available, we wondered whether the geometric characteristics described for this heterocyclic system would be present in the aldol derivatives bearing bulky substituents such as adamantyl and anthracen-9-yl in the side chain. Usually, the C–O bond lengths *a*, *b*, and *c* (formula **K**) alternate, and the C–O–C bond angles α and β have typical values of *ca.* 110° ('sp^3') and 120° ('sp^2'). This is interpreted as the consequence of an anomeric effect ($n\sigma^*$ interaction, see **L** [9a]). The preferred conformation of 1,3-dioxan-4-ones is a sofa with O(1) out of the plane of the other five ring atoms, see **M**. In *Table 1*, we have collected the values for *a*, *b*, *c*, α, and β not only for the new dioxanone structures **3a**, **5b**, **11c**, and **12c**, but we included also some representatives from earlier publications and from hitherto unpublished work (**N**–**Q**). As can be



N **O** **P** **Q**

[12]) Since the reaction is carried out at −75° without any warming before workup, we are sure that the observed product configuration is subject to kinetic control.

[13]) If the assignment for the benzaldehyde adduct is correct, the primary adduct of type **J** would thus have to be less favorable as we go from Ph to naphth-2-yl, to naphth-1-yl, to anthracen-9-yl. This order makes sense, if we speculate that there may be some π-interaction between the enolate and the aromatic ring during nucleophilic attacks; as the aryl group becomes more bulky, the π-interaction is overridden by steric effects.

Table 1. *Structural Comparisons of 1,3-Dioxan-4-ones in Various Crystal Structures.*

The distances *a*, *b*, and *c* and the angles α and β are defined in **K** (see also [9a]). The values for q_2, q_3, φ, and θ are the puckering parameters as defined by *Cremer* and *Pople* [15]. The e.s.d.'s of bond lengths for structures **3a**, **5b**, **11c**, and **12c** are ranging between 0.005 and 0.008 Å

Structure	*a* [Å]	*b* [Å]	*c* [Å]	α [°]	β [°]	q_2	q_3	φ [°]	θ [°]	Ring shape	Ref.
3a	1.444	1.390	1.452	110.71	120.71	0.386	–0.341	184.01	–48.54	sofa	This paper
5b	1.430	1.362	1.460	110.92	122.49	0.361	0.346	–19.75	46.22	twisted sofa	This paper
11c	1.449	1.404	1.461	109.76	116.97	0.533	–0.242	202.40	–65.58	between sofa and boat	This paper
12c	1.430	1.387	1.447	111.80	117.90	0.558	–0.168	207.83	–73.24	twist-boat	This paper
N (R^1 = *t*-Bu, R^2 = Me, *cis*)	1.435	1.381	1.472	110.28	119.98	0.330	–0.368	174.57	–41.88	sofa	[9a]
N (R^1 = (*E*)-Styryl, R^2 = Me, *cis*)	1.450	1.386	1.467	109.97	120.37	0.346	0.371	–14.46	–43.78	sofa	[16]
N (R^1 = *t*-Bu, R^2 = CF_3, *cis*)	1.422	1.410	1.451	109.54	121.62	0.302	0.387	–6.75	37.97	sofa	[7d]
N (R^1 = *t*-Bu, R^2 = CF_3, *trans*)	1.420	1.411	1.451	112.82	115.80	0.654	0.100	48.46	81.31	between boat and twist-boat	[7d]
N (R^1 = *t*-Bu, R^2 = CCl_3 *trans*)	1.416	1.390	1.452	113.60	114.30	0.659	0.074	55.84	83.59	between boat and twist-boat	[17]
O	1.435	1.392	1.458	111.23	120.78	0.290	0.395	–9.02	36.29	sofa	[18]
P	1.425	1.406	1.448	115.46	114.95	0.661	0.071	52.16	83.87	between boat and twist-boat	[19]
Q	1.434	1.383	1.456	110.27	122.13	0.312	0.402	–35.28	37.82	twisted sofa	[16]

seen, the bond length alteration long/short/long of *a*, *b*, and *c* is observed in all twelve examples of the *Table*. Also, the difference of the angles $\alpha > \beta$ is present, except for one case. The crystals of **3a** and **5b** contain two independent molecules in the asymmetric unit (see *Table 2*). The structurally equivalent C–O bond lengths as well as the angle α (listed

Table 2. *Crystal Data of the Structures Determined*

	3a	**5b**	**11c**	**12c**	**22**
Formula	$C_{16}H_{28}O_4$	$C_{22}H_{34}O_5$	$C_{27}H_{28}O_5$	$C_{31}H_{30}O_5$	$C_{15}H_{18}O_3$
M_r	284.38	378.49	432.49	482.50	246.30
T	83 K	295 K	83 K	293 K	293 K
Crystals system	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a [Å]	11.598 (5)	6.831 (1)	10.054 (5)	9.760 (2)	7.868 (2)
b [Å]	21.716 (15)	13.009 (2)	11.134 (6)	11.500 (2)	6.237 (1)
c [Å]	13.192 (10)	24.158 (8)	20.480 (11)	23.120 (5)	13.399 (3)
α [°]	90.00	90.00	90.00	90.00	90.00
β [°]	90.00	95.90 (5)	90.00	90.00	96.58 (3)
γ [°]	90.00	90.00	90.00	90.00	90.00
V [Å^3]	3322.7	2135.3	2292.6	2595.0	656.2
Z	8	4	4	4	2
D_x [g cm^{-3}]	1.137	1.177	1.253	1.235	1.247
F [000]	1248	824	920	1024	264
Unique reflections	3053	3515	2323	1964	1714
of which $I > 6\sigma$	2462	2224	1926	1776	1677
Final *R*	0.034	0.045	0.035	0.040	0.035

in *Table 1*), obtained from the independent molecules are virtually the same (within 2 to 3 e.s.d.'s). For **3a**, the β angle calculated for the independent molecules is 120.7 and 117.2°, respectively, *i.e.* it differs by *ca.* 10 e.s.d.'s. *Table 1* also shows that the room-temperature analyses give somewhat shorter C–O distances (*ca.* 0.01 Å on average), owing to the larger librational motion of the molecules. *Table 1* also contains the puckering parameters for the twelve dioxane rings and a ring-shape assignment. While the simple *cis*-2,6-disubstituted dioxanones adopt the 'pure' sofa conformation **M**, the *trans*-isomers show a preference for a boat or twist-boat arrangement. The structures of the new aldol derivatives **11c** and **12c** with aryl substitution in the side chain have conformations between sofa and boat or twist-boat, respectively. Of the adducts to aliphatic aldehydes, the cyclohexyl-substituted compound **3a** is a 'pure' sofa, while the adamantyl analog **5b** exhibits the shape of a twisted sofa.

The structural comparison presented here for dioxanones is yet another demonstration of the fact that organic chemists should generally be much more careful taking certain conformations for 'granted', especially with heterocyclic rings, with bulky substituents, or in the presence of stereoelectronic or $A^{1,3}$ effects [16].

We are grateful for postdoctoral stipends given to *J.-M. L.* by the *Natural Sciences and Engineering Research Council of Canada* and to *W. J.* by the *Deutsche Forschungsgemeinschaft (DFG)*. *ICI* (*ICI Biological Products*, PO Box 1, GB-Billingham, Cleveland TS23 1LB) has supplied PHB, the starting material for the preparation of (*R*)-3-hydroxybutanoic acid and of the dioxanone **F**. *BASF Aktiengesellschaft* (D-Ludwigshafen) provided us with pivalaldehyde.

Experimental Part

General: Solvents used were *Fluka puriss.* grade, except for THF which was distilled over K/benzophenone. Commercially available aldehydes and acid chlorides were used as received without any further purification. The *(2R,6R)-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**F**) was prepared as described in [20]. M.p. *Büchi 510*, uncorrected. Optical rotations: *Perkin-Elmer-241* polarimeter, in 1-dm cells. IR: *Perkin-Elmer 983* or *Perkin-Elmer-297*, in cm^{-1}. NMR: *Bruker AMX400*, *Varian XL-300*, *Bruker WM 300*, or *Varian Gemini 200* spectrometers. All spectra were measured in $CDCl_3$. Chemical shifts, δ, are quoted in ppm downfield from internal TMS, coupling constants, J, in Hz. MS: *Hitachi-Perkin-Elmer RMU-6M*; *m/z* relative intensities (in %) in parentheses. Microanalyses were performed by Mikroanalytisches Laboratorium der ETH-Zürich. Medium-pressure liquid chromatography (MPLC): *Büchi* system *B-680*. TLC: glass plated *Kieselgel 60* F_{254} (*Merck*). Flash chromatography (FC); *Kieselgel 60* (*Merck*) 40–60 μm, eluant in parentheses. Abbreviations: h.v.: high vacuum, r.e.: rotary evaporator.

*(1'S,2R,5R,6R)-2-(*tert*-Butyl)-5-(1'-hydroxypropyl)-6-methyl-1,3-dioxan-4-one* (**1a**). An ice-cold soln. of 11.13 ml of $(i\text{-Pr})_2NH$ (79.4 mmol, 1.14 equiv.) in 160 ml of THF was treated with 53 ml of BuLi (79.4 mmol, 1.5M in hexane, 1.14 equiv.), kept at 0° for 15 min then cooled to −78°. To this soln. of LDA were added 12.0 g of the dioxanone **F** (69.7 mmol) in 80 ml of THF at such a rate that the temp. never exceeded −70°, then the mixture was maintained at −78° for 45 min. To the resulting enolate soln. was added 7.15 ml of propanal (99 mmol, 1.42 equiv.) in 80 ml of THF, the temp. never rising above −70°. The reaction mixture was stirred at −78° for 3 h then quenched at −78° by the addition of 200 ml of sat. aq. NH_4Cl soln. followed by 200 ml of Et_2O. The two phases were separated, and the aq. phase was extracted twice using 200 ml of Et_2O. The combined org. extracts were dried ($MgSO_4$) and the volatiles evaporated on r.e. then on h.v. pump. The crude product obtained, showing a 7:1 ratio of epimers at C(1'), was crystallized from hexanes to give 9.6 g (60%) of **1a**. The ^{1}H-NMR and ^{13}C-NMR spectra of **1a** were identical to those of the literature [3].

*(1'S,2R,5S,6R)-5-(1'-Acetoxypropyl)-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**1b**). To a soln. of 1.38 g of **1a** (6.0 mmol) in 35 ml of CH_2Cl_2 were added, successively, 2.4 ml of pyridine (29.8 mmol, 5 equiv.) and 0.65 ml of AcCl (8.9 mmol, 1.5 equiv.) at r.t. After 3 h, the mixture was poured into a separating funnel and washed three times with 10 ml of HCl 10%, once with 20 ml of H_2O, and then 20 ml of sat. aq. NaCl, soln. The org. extracts were dried ($MgSO_4$), filtered, and the volatiles were evaporated on r.e. and h.v. pump. FC (hexanes/Et_2O, 3:1), followed by recrystallization from pentane/Et_2O, gave 1.54 g (95%), of pure **1b**. M.p. 60–61°. $[\alpha]_D = -32.8$ ($c = 5.61$, $CHCl_3$). IR ($CHCl_3$): 3620*w*, 2980*s*, 2940*m*, 2880*m*, 1740*s*, 1730*s*, 1485*m*, 1460*m*, 1410*m*, 1390*m*, 1370*s*, 1350*m*, 1340*m*, 1310*w*, 1250*s*, 1155*m*, 1130*m*, 1090*m*, 1050*s*, 1030*s*, 995*s*. ^{1}H-NMR: 0.94 (*t*, J = 7.41, H–C(3')); 0.96 (*s*, *t*-Bu); 1.38 (*d*, $J = 5.92$, CH_3); 1.80–2.00 (*m*, H–C(2')); 2.09 (*s*, Ac); 2.65 (*dd*, $J = 9.76$, 2.40, H–C(5)); 3.82 (*dq*, $J = 9.76$, 6.10, H–C(6)); 4.85 (*s*, H–C(2)); 5.07 (*td*, $J = 6.06$, 2.38, H–C(1')). ^{13}C-NMR: 10.30; 20.46; 21.00; 23.80; 25.32; 35.09; 50.73; 73.03; 73.94; 108.01; 167.20; 170.37. MS: 271 (44), 255 (11), 243 (4), 229 (52), 215 (32), 201 (5), 187 (30), 173 (17), 155 (68), 142 (31), 127 (44), 109 (50), 100 (100), 82 (34), 71 (38), 57 (27), 43 (78), 29 (9). Anal. calc. for $C_{14}H_{24}O_5$: C 61.74, H 8.88; found: C 61.57, H 9.04.

*(1'S,2R,5R,6R)-2-(*tert*-Butyl)-5-(1'-hydroxy-2'-methylpropyl)-6-methyl-1,3-dioxan-4-one* (**2a**). As described for **1a**, 12.0 g of dioxanone **F** (69.7 mmol) with 11.1 ml of $(i\text{-Pr})_2NH$ (79.4 mmol, 1.14 equiv.), 52.8 ml of BuLi (79.4 mmol, 1.5M in hexane, 1.14 equiv.) and 9.0 ml of 2-methylpropanal (98.9 mmol, 1.42 equiv.). The crude product consisted of a 10:1 ratio of the C(1')-epimers. Recrystallization from hexanes gave 9.18 g (54%) of pure **2a**. The ^{1}H- and ^{13}C-NMR spectra of **2a** were identical to those of the literature [3].

*(1'S,2R,5S,6R)-5-(1'-Acetoxy-2'-methylpropyl)-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**2b**). As described for **1b**, 11.2 g of **2a** (45.8 mmol) with 18.5 ml of pyridine (229 mmol, 5 equiv.) and 4.9 ml of AcCl (68.7 mmol, 1.5 equiv.). FC (hexanes/Et_2O 2:1), followed by recrystallization from hexanes, gave 11.6 g (90%) of pure **2b**. M.p. 103–104°. $[\alpha]_D = -35.1$ ($c = 2.72$, $CHCl_3$). IR ($CHCl_3$): 3020*m*, 2980*s*, 2940*m*, 2910*m*, 2880*m*, 1740*s*, 1480*m*, 1440*w*, 1410*w*, 1390*m*, 1375*m*, 1365*m*, 1280*m*, 1240*s*. ^{1}H-NMR: 0.88 (*d*, $J = 6.63$, CH_3); 0.96 (*s*, *t*-Bu); 0.99 (*d*, $J = 6.78$, CH_3); 1.38 (*d*, $J = 6.13$, CH_3–C(6)); 2.11 (*s*, Ac); 2.51 (*m*, H–C(2')); 2.70 (*dd*, $J = 9.78$, 1.77, H–C(5)); 3.72 (*qd*, $J = 6.05$, 9.75, H–C(6)); 4.76 (*dd*, $J = 10.05$, 1.81, H–C(1')); 4.80 (*s*, H–C(2)). ^{13}C-NMR: 19.23; 20.17; 21.01; 23.89; 30.14; 35.18; 49.79; 73.48; 77.24; 108.12; 167.07; 170.83. MS: 285 (10), 243 (20), 229 (22), 201 (21), 187 (22), 169 (17), 156 (17), 141 (66), 123 (19), 114 (86), 96 (81), 87 (28), 71 (66), 57 (37), 43 (100), 28 (18). Anal. calc. for $C_{15}H_{26}O_5$: C 62.91, H 9.15; found: C 62.98, H 8.86.

*(1'S,2R,5R,6R)-2-(*tert*-Butyl)-5-(1'-cyclohexyl-1'-hydroxymethyl)-6-methyl-1,3-dioxan-4-one* (**3a**). As described for **1a**, 3.0 g of dioxanone **F** (17.4 mmol) with 2.78 ml of $(i\text{-Pr})_2NH$ (19.9 mmol, 1.14 equiv.), 13.2 ml of BuLi (19.9 mmol, 1.5M in hexane, 1.14 equiv.) and 3.0 ml of cyclohexanecarbaldehyde (24.7 mmol, 1.42 equiv.). The crude product contained practically one diastereoisomer. FC (hexanes/Et_2O 1:1), followed by recrystallization

from pentane, gave 3.64 g (74%) of pure **3a**. M.p. 105–106°. $[\alpha]_D = +5.3$ ($c = 3.92$, $CHCl_3$). IR ($CHCl_3$): 3620*w*, 3570*w*, 3450*w*, 3005*m*, 2980*s*, 2960*s*, 2930*s*, 2880*m*, 2860*s*, 1730*s*, 1485*m*, 1450*m*, 1410*m*, 1395*m*, 1380*m*, 1370*s*, 1350*s*, 1280*s*, 1245*s*, 1155*m*, 1110*m*, 1090*w*, 1060*w*, 1030*s*, 1000*s*, 990*m*, 975*m*, 940*w*, 925*w*, 895*w*. ^{1}H-NMR: 0.80–1.05 (*m*, 2 H); 0.97 (*s*, *t*-Bu); 1.05–1.45 (*m*, 3 H); 1.33 (*d*, $J = 6.10$, CH_3); 1.65–1.95 (*m*, 4 H); 1.95–2.10 (*m*, 3 H); 2.60 (*dd*, $J = 9.76$, 1.50, H–C(5)); 3.22 (*td*, $J = 8.69$, 1.44, H–C(1′)); 4.02 (*qd*, $J = 6.12$, 9.76, H–C(6)); 4.99 (*s*, H–C(2)). ^{13}C-NMR: 20.03, 23.89; 25.54; 25.75; 26.22, 29.67; 29.68; 35.05; 41.39; 50.81; 73.87; 76.03; 107.96; 169.19. MS: 285 (10, $[M + 1]^+$), 267 (5), 227 (45), 201 (95), 181 (30), 163 (8), 154 (18), 135 (17), 112 (18), 95 (30), 87 (100), 69 (47), 55 (15), 41 (17). Anal. calc. for $C_{16}H_{28}O_4$: C 67.57, H 9.92; found: C 67.32, H 9.86.

*(1′S,2R,5S,6R)-5-(1′-Acetoxy-1′-cyclohexylmethyl)-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**3b**). As described for **1b**, 3.25 g of **3a** (11.4 mmol) with 4.62 ml of pyridine (57.1 mmol, 5 quiv.) and 1.63 ml of AcCl (22.9 mmol, 2 equiv.). FC (hexanes/Et_2O 4:1), followed by recrystallization from hexanes, gave 2.84 g (76%) of pure **3b**. M.p. 102–102.5°. $[\alpha]_D = -2.7$ ($c = 3.59$ $CHCl_3$). IR ($CHCl_3$). 3020*m*, 2980*s*, 2960*m*, 2910*m*, 2870*m*, 2860*m*, 1735*s*, 1485*m*, 1450*m*, 1410*w*, 1390*m*, 1370*s*, 1350*s*, 1280*m*, 1250*s*, 1150*w*, 1115*w*, 1090*w*, 1030*m*, 1000*m*, 975*m*, 940*w*. ^{1}H-NMR: 0.70–1.05 (*m*, 2 H); 0.96 (*s*, *t*-Bu); 1.05–1.40 (*m*, 3 H); 1.37 (*d*, $J = 6.06$, CH_3–C(6)); 1.60–1.90 (*m*, 5 H); 2.09 (*s*, Ac); 2.10–2.30 (*m*, 1 H); 2.71 (*dd*, $J = 9.87$, 1.68, H–C(5)); 3.73 (*qd*, $J = 6.06$, 9.87, H–C(6)); 4.80 (*s*, H–C(2)); 4.84 (*dd*, $J = 10.05$, 1.67, H–C(1′)). ^{13}C-NMR: 20.17; 20.95; 23.89; 25.39; 25.61; 26.12; 29.48; 35.19; 38.94; 49.20; 73.39; 76.36; 108.09; 167.03; 170.79. MS: 325 (30), 309 (8), 295 (2), 283 (35), 269 (19), 241 (15), 227 (38), 209 (12), 196 (8), 180 (62), 163 (38), 154 (64), 136 (95), 121 (7), 112 (88), 95 (40), 81 (37), 71 (37), 57 (31), 43 (100), 29 (14). Anal. calc. for $C_{18}H_{30}O_5$: C 66.23, H 9.26; found: C 66.23, H 9.15.

*(1′R,2R,5R,6R)-2-(*tert*-Butyl)-5-(1′-hydroxy-2′,2′-dimethylpropyl)-6-methyl-1,3-dioxan-4-one* (**4a**). As described for **1a**, 3.0 g of dioxanone **F** (17.4 mmol) with 2.78 mol of $(i\text{-Pr})_2NH$ (19.9 mmol, 1.14 equiv.), 13.2 ml of BuLi (19.9 mmol, 1.5M in hexane, 1.14 equiv.) and 2.7 ml of 2,2-dimethylpropanal (24.7 mmol, 1.42 equiv.). The crude product obtained consisted of essentially one diastereoisomer. Recrystallization from pentane/Et_2O 4:1 gave 3.07 g (68%) of pure **4a**. M.p. 153–154°. $[\alpha]_D = +10.5$ ($c = 2.12$, $CHCl_3$). IR ($CHCl_3$): 3620*m*, 3450*w*, 3005*m*, 2980*s*, 2960*s*, 2910*s*, 2870*s*, 1725*s*, 1480*s*, 1460*m*, 1450*w*, 1410*m*, 1400*m*, 1370*s*, 1330*m*, 1280*m*, 1260*s*, 1240*s*, 1130*m*, 1115*m*, 1040*m*, 1030*m*, 1010*m*, 990*s*, 955*w*, 940*w*, 880*m*, 850*m*. ^{1}H-NMR: 0.92 (*s*, *t*-Bu); 0.97 (*s*, *t*-Bu); 1.48 (*d*, $J = 6.47$, CH_3); 1.84 (br. *s*, OH); 2.63 (*dd*, $J = 6.40$, 2.53, H–C(5)); 3.71 (*d*, $J = 6.41$, H–C(1′)); 3.75 (*m*, H–C(6)); 5.11 (*s*, H–C(2)). ^{13}C-NMR: 22.60; 23.86; 25.15; 35.09; 35.32; 49.66; 70.48; 84.52; 106.01; 169.72. MS: 259 (14 $[M + 1]^+$), 241 (7), 201 (81), 185 (2), 173 (30), 155 (55), 144 (3), 137 (10), 129 (75), 111 (100), 95 (4), 87 (28), 71 (36), 57 (16), 41 (12), 29 (4). Anal. calc. for $C_{14}H_{26}O_4$; C 65.09, H 10.14; found: C 64.99, H 10.14.

*(1′R,2R,5S,6R)-5-(1′-Acetoxy-2′,2′-dimethylpropyl)-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**4b**). As described for **1b**, 3.07 g of **4a** (11.9 mmol) with 4.8 ml of pyridine (59.5 mmol, 5 equiv.) and 1.7 ml of AcCl (23.8 mmol, 2 equiv.). FC (hexanes/Et_2O 2:1), followed by recrystallization from hexanes, gave 3.44 g (96%) of pure **4b**. M.p. 74–75°. $[\alpha]_D = +26.8$ ($c = 2.38$, $CHCl_3$). IR ($CHCl_3$): 3020*w*, 2980*m*, 2960*s*, 2900*w*, 2870*m*, 1740*s* 1480*m*, 1460*w*, 1450*w*, 1410*w*, 1395*w*, 1370*s*, 1330*w*, 1245*s*, 1130*m*, 1110*w*, 1090*w*, 1035*m*, 1020*m*, 990*m*. ^{1}H-NMR: 0.94 (*s*, *t*-Bu); 0.98 (*s*, *t*-Bu); 1.46 (*d*, $J = 6.44$, CH_3–C(6)); 2.09 (*s*, Ac); 2.73 (*dd*, $J = 6.51$, 2.62, H–C(5)); 3.39 (*d*, $J = 6.50$, H–C(1′); 4.85 (*s*, H–C(2)); 5.03 (*qd*, $J = 6.44$, 2.61, H–C(6)). ^{13}C-NMR: 18.69; 21.24; 23.86; 25.06; 35.10; 35.38; 47.59; 72.22; 84.52; 106.18; 168.17; 169.98. MS: 301 (29, $[M + 1]^+$), 283 (2), 257 (4), 243 (33), 213 (7), 201 (21), 183 (10), 170 (17), 157 (68), 137 (12), 128 (34), 111 (50), 97 (47), 87 (10), 69 (55), 57 (45), 43 (100), 29 (13). Anal. calc. for $C_{16}H_{28}O_5$: C 63.97, H 9.40; found: C 63.80, H 9.23.

*(1′R,2R,5R,6R)-5-[1′-(Adamant-1″-yl)-1′-hydroxymethyl]-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**5a**). As described for **1a**, 1.52 g of dioxanone **F** (8.83 mmol) with 1.41 ml of $(i\text{-Pr})_2NH$ (10.1 mmol, 1.14 equiv.), 6.71 ml of BuLi (10.1 mmol, 1.5M in hexane, 1.14 equiv.) and 2.06 g of adamantane-1-carbaldehyde (12.5 mmol, 1.42 equiv.) in THF were stirred at –78° for 4 h. The crude product contained only one diastereoisomer along with some starting dioxanone **F**. FC (hexanes/Et_2O 1:1) gave 0.79 g (26%) of pure **5a**. M.p. 168–169°. $[\alpha]_D = +12.0$ ($c = 1.19$, $CHCl_3$). IR ($CHCl_3$): 3540*w*, 3005*m*, 2980*m*, 2960*m*, 2905*s*, 2850*s*, 1720*s*, 1485*m*, 1450*m*, 1410*m*, 1390*w*, 1380*w*, 1370*m*, 1350*s*, 1280*s*, 1260*s*, 1230*s*, 1150*m*, 1070*m*, 1030*s*, 1010*s*, 990*m*, 980*m*, 940*w*, 920*w*, 890*w*. ^{1}H-NMR: 0.97 (*s*, *t*-Bu); 1.33 (*d*, $J = 6.13$, CH_3); 1.50–1.80 (*m*, 13 H); 2.04 (br. *s*, 3 H); 2.62 (*dd*, $J = 12.10$, 11.10, H–C(5)); 3.02 (*d*, $J = 12.10$, H–C(1′)); 3.93 (*qd*, $J = 6.13$, 10.20, H–C(6)); 4.97 (*s*, H–C(2)). ^{13}C-NMR: 20.04; 23.92; 28.29; 35.12; 36.94; 37.58; 38.85; 48.88; 75.30; 78.92; 108.05; 169.40. MS: 336 (3, M^+), 318 (12), 279 (14), 261 (3), 233 (9), 217 (7), 201 (40), 189 (20), 164 (5), 135 (100), 115 (14), 98 (8), 87 (43), 79 (12), 69 (17), 57 (10), 41 (7), 28 (10).

*(1′R,2R,5S,6R)-5-[1′-Acetoxy-1′-(adamant-1″-yl)methyl]-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**5b**). As described for **1b**, 0.66 g of **5a** (1.97 mmol) with 0.8 ml of pyridine (9.87 mmol, 5 quiv.) and 0.28 ml of AcCl (3.95 mmol, 2 equiv.). FC (hexanes/Et_2O 4:1), followed by a recrystallization from hexanes, gave 0.51 g (68%) of pure **5b**. M.p. 110–111°. $[\alpha]_D = +11.1$ ($c = 0.73$, $CHCl_3$). IR ($CHCl_3$): 2980*m*, 2960*m*, 2910*s*, 2870*m*, 1740*s*, 1730*s*, 1485*m*, 1450*w*, 1410*w*, 1395*w*, 1370*s*, 1350*m*, 1245*s*, 1155*m*, 1110*w*, 1030*m*, 1005*m*, 980*m*. ^{1}H-NMR: 0.94 (*s*, *t*-Bu);

1.34 (*d*, *J* = 6.17, CH_3–C(6)); 1.50–1.80 (*m*, 12 H); 2.03 (br. *s*, 3 H); 2.09 (*s*, Ac); 2.86 (*dd*, *J* = 8.53, 2.13, H–C(5)); 4.11 (*qd*, *J* = 6.15, 8.47, H–C(6)); 4.56 (br. *s*, H–C(1')); 4.85 (*s*, H–C(2)). ^{13}C-NMR: 20.71; 20.98; 23.80; 28.10; 35.09; 36.75; 37.10; 38.65; 48.78; 75.59; 79.95; 107.54; 166.59; 171.08 MS: 378 (4, M^+), 360 (12), 349 (7), 335 (20), 321 (6), 293 (10), 279 (36), 249 (2), 232 (37), 217 (3), 206 (8), 189 (35), 164 (12), 135 (100), 105 (3), 91 (7), 79 (13), 57 (9), 43 (15), 29 (2). Anal. calc. for $C_{22}H_{34}O_5$: C 69.81, H 9.05; found: C 69.25, H 9.12.

*(1'R,2R,5R,6R)- and (1'S,2R,5R,6R)-2-(*tert*-Butyl)-5-(α-hydroxybenzyl)-6-methyl-1,3-dioxan-4-one* (**6a** and **7a**, resp.). As described for **1a**, 3.0 g of dioxanone **F** (17.4 mmol) with 2.78 ml of $(i\text{-Pr})_2$NH (19.9 mmol, 1.14 equiv.), 12.4 ml of BuLi (19.9 mmol, 1.6M in hexane, 1.14, equiv.) and 12.0 ml of benzaldehyde (24.7 mmol, 1.42 equiv.). The mixture was stirred at –78° for 4 h. The ^{1}H-NMR of the crude product indicated a 2:1 ratio of the two C(1') epimers. FC (hexanes/Et_2O 2:1) gave pure 1.55 g (32%) of **6a** and 2.65 g (54%) of pure **7a**. The ^{1}H- and ^{13}C-NMR spectra of **6a** and **7a** were identical to those of the literature [8b]. The crude mixture could also be used directly for the protection step without any further purification.

*(1'R,2R,5S,6R)- and (1'S,2R,5S,6R)-5-[α-(Benzoyloxy)benzyl]-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**6c** and **7c**, resp.). The crude mixture **6a**/**7a** (2.0 g, 7.2 mmol) was dissolved in 30 ml of pyridine and then, 4.2 ml of PhCOCl (36.0 mmol) was added slowly. The mixture was stirred at r.t. for 15 min, at 60° for 30 min, then cooled to 0° and carefully diluted with 40 ml of H_2O. Acidification using 20% H_2SO_4 gave a precipitate which was filtered off and then recrystallized from hexanes to give white needles. The diastereoisomeric mixture was separated by MPLC (hexanes/Et_2O 3:1) and each diastereoisomer was recrystallized from hexanes to give 0.6 g (22% from **F**) of pure **6c**. M.p. 161–162°. $[\alpha]_D = -63.9$ (*c* = 1.52, $CHCl_3$). IR ($CHCl_3$): 3420*w*, 2980*s*, 2900*m*, 1725*s*, 1600*w*, 1580*w*, 1480*w*, 1450*m*, 1350*s*, 1270*s*, 1245*s*, 1150*m*, 1100*s*, 1090*s*, 1070*m*, 1025*s*, 1010*m*, 1000*m*, 980*s*, 940*m*, 760*m*, 715*s*, 660*m*, 595*m*. ^{1}H-NMR: 0.89 (*s*, *t*-Bu); 1.50 (*d*, *J* = 6.20, CH_3–C(6)); 3.19 (*dd*, *J* = 9.20, 3.50, H–C(5)); 3.94 (*dq*, *J* = 9.20, 6.20, H–C(6)); 4.46 (*s*, H–C(2)); 6.78 (*d*, *J* = 3.50, H–C(1')); 7.31–7.66 (*m*, 8 arom. H); 8.10–8.14 (*m*, 2 arom. H). ^{13}C-NMR: 21.58; 23.95; 35.21; 54.00; 72.47; 74.55; 108.12; 126.52; 128.79; 129.05; 129.12; 129.88; 130.08; 133.94; 137.33; 165.30; 167.90. MS: 325 (1, $[M - 57]^+$), 296 (2), 203 (9), 174 (24), 157 (5), 147 (7), 129 (35), 115 (27), 105 (100), 91 (13), 77 (53), 51 (26), 41 (25), 28 (53). Anal. calc. for $C_{23}H_{26}O_5$: C 72.23, H 6.85; found: C 72.18, H 6.95.

Pure **7c**, 1.0 g (34% from **F**). M.p. 161–162°. $[\alpha]_D = +19.2$ (*c* = 0.29, $CHCl_3$). IR ($CHCl_3$): 3440*w*, 2990*m*, 2960*m*, 2900*w*, 1730*s*, 1600*w*, 1580*w*, 1485*m*, 1450*m*, 1365*m*, 1350*s*, 1315*m*, 1285*s*, 1270*s*, 1245*s*, 1150*s*, 1105*s*, 1100*s*, 1070*m*, 1045*m*, 1030*m*, 990*s*, 965*m*, 935*m*, 755*m*, 715*s*, 600*w*. ^{1}H-NMR: 0.83 (*d*, *J* = 6.20, CH_3–C(6)); 0.97 (*s*, *t*-Bu); 3.02 (*dd*, *J* = 9.00, 3.30, H–C(5)); 4.26 (*dq*, *J* = 9.00, 6.20, H–C(6)); 5.00 (*s*, H–C(2)); 6.70 (*d*, *J* = 3.30, H–C(1')); 7.26–7.66 (*m*, 8 arom. H); 8.07–8.11 (*m*, 2 arom. H). ^{13}C-NMR: 21.66; 24.05; 35.24; 54.48; 72.32; 75.29; 108.12; 125.66; 128.74; 129.00; 129.29; 129.92; 130.01; 133.90; 137.65; 165.13; 169.06. MS: 325 (1, $[M - 57]^+$), 296 (3), 203 (4), 174 (19), 131 (15), 115 (9), 105 (100), 91 (10), 77 (35), 51 (11), 41 (14), 28 (28). Anal. calc. for $C_{23}H_{26}O_5$: C 72.23, H 6.85; found: C 72.15, H 6.91.

*(1'R,2R,5R,6R)- and (1'S,2R,5R,6R)-2-(*tert*-Butyl)-5-[1'-hydroxy-1'-(naphth-2''-yl)methyl]-6-methyl-1,3-dioxan-4-one* (**8a** and **9a**, resp.). As described for **1a**, 6.0 g of dioxanone **F** (34.8 mmol) with 5.6 ml of $(i\text{-Pr})_2$NH (39.6 mmol, 1.14 equiv.), 23.4 ml of BuLi (39.6 mmol, 1.5M in hexane, 1.14 equiv.) and 7.5 g of naphthalene-2-carbaldehyde (49.5 mmol, 1.42 equiv). The mixture was stirred at –78° for 5 h. The crude product consisted of two diastereoisomers in a 1:1 ratio. Attempts to separate the two diastereoisomers by MPLC (hexanes/Et_2O 4:1) gave 3.9 g (35%) of pure **9a**) and a mixture **8a**/**9a**. For practical reasons, it was better to directly protect the mixture before separation.

Data of **9a**: m.p. 166–167°. $[\alpha]_D = -70.0$ (*c* = 1.46, $CHCl_3$). IR ($CHCl_3$): 3390*s*, 2960*s*, 1720*s*, 1355*s*, 1280*m*, 1260*s*, 1230*m*, 1155*m*, 1085*m*, 980*m*, 800*m*, 740*s*, 540*m*. ^{1}H-NMR: 0.72 (*d*, *J* = 6.40, CH_3); 0.95 (*s*, *t*-Bu); 2.90 (*dd*, *J* = 8.00, 6.40, H–C(5)); 3.66 (*d*, *J* = 5.50, OH); 4.04 (*dq*, *J* = 8.00, 6.40, H–C(6)); 4.95 (*s*, H–C(2)); 5.61 (*dd*, *J* = 5.50, 3.30, H–C(1')); 7.39 (*dd*, *J* = 9.00, 2.50, H–C(3'')); 7.50 (*m*, 2 arom. H); 7.82 (*m*, 4 arom. H). ^{13}C-NMR: 21.05; 23.58; 34.65; 54.83; 70.63; 72.56; 107.41; 123.30; 124.19; 125.93; 126.20; 127.46; 127.78; 128.26; 132.62; 132.89; 138.14; 171.23. MS: 328 (4, M^+), 271 (6), 242 (24), 225 (28), 198 (23), 181 (42), 156 (100), 127 (68), 87 (23), 69 (29), 57 (29), 41 (23), 28 (11). Anal. calc. for $C_{20}H_{24}O_4$: C 73.15, H 7.37; found: C 73.02, H 7.40.

*(1'R,2R,5S,6R)- and (1'S,2R,5S,6R)-5-[1'-(Benzoyloxy)-1'-(naphth-2''-yl)methyl]-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**8c** and **9c**, resp.). As described for **6c** and **7c**, 3.0 g of the mixture **8a**/**9a** (9.14 mmol) in 35 ml of pyridine with 9.0 ml of PhCOCl (77.5 mmol). After acidification, the solid obtained was filtered off and washed with 300 ml of H_2O, 100 ml of sat. aq. $NaHCO_3$ soln., and 300 ml of H_2O. The solid was then washed with two portions of Et_2O (50 ml) and the solvent evaporated. The remaining solid was recrystallized from MeCN to give 1.56 g (81%) of pure **8c**. The soluble diastereoisomer **9c** was recrystallized from hexanes: 1.82 g (92%).

Data of **8c**: m.p. 184–185°. $[\alpha]_D = -74.4$ (*c* = 0.98, $CHCl_3$). IR ($CHCl_3$): 3420*w*, 2980*m*, 2930*w*, 1725*s*, 1600*w*, 1510*w*, 1485*m*, 1450*w*, 1350*m*, 1315*w*, 1265*s*, 1245*s*, 1220*m*, 1175*m*, 1150*m*, 1105*s*, 1095*s*, 1070*m*, 1035*m*, 1005*m*, 1000*m*, 980*s*, 950*m*, 870*m*, 835*m*, 755*s*, 720*m*, 705*s*. ^{1}H-NMR: 0.87 (*s*, *t*-Bu); 1.55 (*d*, *J* = 6.10, CH_3); 3.25 (*dd*,

J = 9.40, 3.50, H–C(5)); 3.93 (*dq*, J = 9.40, 6.10, H–C(6)); 4.51 (*s*, H–C(2)); 6.94 (*d*, J = 3.50, H–C(1')); 7.47–7.65 (*m*, 6 arom. H); 7.82–7.89 (*m*, 4 arom. H); 8.13–8.18 (*m*, 2 arom. H). ^{13}C-NMR: 21.08; 23.45; 34.76; 53.54; 72.14; 74.13; 107.61; 123.39; 125.14; 126.18; 126.24; 127.41; 127.96; 128.42; 129.26; 129.36; 129.50; 132.76; 132.83; 133.29; 134.13; 164.67; 167.21. MS: 432 (1, M^+), 310 (8), 253 (4), 224 (100), 207 (15), 195 (10), 179 (73), 165 (53), 152 (19), 122 (42), 105 (76), 89 (6), 77 (34), 41 (13), 28 (17). Anal. calc. for $C_{27}H_{28}O_5$: C 74.98, H 6.53; found: C 74.80, H 6.61.

Data of **9c**: m.p. 159°. $[\alpha]_D$ = +27.4 (c = 1.38, $CHCl_3$). IR ($CHCl_3$): 3420*m*, 3060*w*, 2980*m*, 2960*m*, 2900*w*, 2870*w*, 1735*s*, 1600*w*, 1560*w*, 1485*m*, 1450*m*, 1415*w*, 1355*m*, 1350*s*, 1265*s*, 1250*s*, 1220*m*, 1175*w*, 1155*m*, 1105*s*, 1095*s*, 1070*m*, 1050*w*, 1030*m*, 995*s*, 955*m*, 935*w*, 820*m*, 745*m*, 710*s*. ^{1}H-NMR: 0.81 (*d*, J = 6.20, CH_3); 0.98 (*s*, *t*-Bu); 3.14 (*dd*, J = 8.90, 3.20, H–C(5)); 4.34 (*dq*, J = 8.90, 6.20, H–C(6)); 5.05 (*s*, H–C(2)); 6.86 (*d*, J = 3.20, H–C(1')); 7.46–7.65 (*m*, 6 arom. H); 7.79–7.90 (*m*, 4 arom. H); 8.12–8.16 (*m*, 2 arom. H). ^{13}C-NMR: 21.82; 23.07; 35.27; 54.33; 72.35; 75.45; 108.17; 123.47; 124.60; 126.85; 127.02; 128.16; 128.41; 129.03; 129.35; 129.95; 130.00; 130.09;133.45; 133.94; 135.13; 165.17; 169.06. MS: 432 (2, M^+), 346 (4), 310 (1), 282 (3), 253 (2), 224 (47), 207 (7), 179 (12), 165 (14), 155 (41), 122 (5), 105 (100), 77 (15), 57 (6), 28 (10). Anal. calc. for $C_{27}H_{28}O_5$: C 74.98, H 6.53; found: C 74.92, H 6.52.

*(1'R,2R,5R,6R)- and (1'S,2R,5R,6R)-2-(*tert*-Butyl)-5-[1'-hydroxy-1'-(naphth-1''-yl)methyl]-6-methyl-1,3-dioxan-4-one* (**10a** and **11a**, resp.). As described for **1a**, 3.0 g of dioxanone **F** (17.4 mmol) with 2.8 ml of $(i\text{-Pr})_2NH$ (19.8 mmol, 1.14 equiv.), 13.2 ml of BuLi (19.8 mmol, 1.5M in hexane, 1.14 equiv.) and 3.4 ml of naphthalene-1-carbaldehyde (24.7 mmol, 1.42 equiv.). The mixture was stirred at −78° for 4 h. The crude product contained two diastereoisomers in a 2:1 ratio. FC (hexanes/Et_2O 2:1) was performed to separate the two diastereoisomers and gave 2.5 g (44%) of **10a**, 1.1 g (19%) of **11a**, and 1.2 g (21%) of **10a**/**11a**.

Data of **10a**: recrystallized from hexanes/Et_2O. M.p. 151–152°. $[\alpha]_D$ = +27.4 (c = 3.45, $CHCl_3$). IR ($CHCl_3$): 3600*w*, 3450*m*, 3005*s*, 2980*s*, 2960*s*, 2940*m*, 2890*m*, 2870*m*, 1730*s*, 1700*s*, 1600*w*, 1510*w*, 1480*m*, 1460*w*, 1410*m*, 1380*m*, 1370*s*, 1350*s*, 1340*s*, 1280*s*, 1250*s*, 1230*s*, 1150*m*, 1110*m*, 1080*m*, 1050*m*, 1030*s*, 995*s*, 955*w*, 940*w*, 925*w*, 860*w*. ^{1}H-NMR: 0.74 (*d*, J = 6.07, CH_3); 0.94 (*s*, *t*-Bu); 3.08 (*dd*, J = 9.08, 6.85, H–C(5)); 3.81 (*qd*, J = 6.08, 9.08, H–C(6)); 4.09 (*d*, J = 2.56, OH); 4.92 (*s*, H–C(2)); 5.53 (*dd*, J = 6.83, 2.46, H–C(1')); 7.43–7.60 (*m*, 3 arom. H); 7.64 (*d*, J = 7.04, 1 arom. H); 7.81–7.91 (*m*, 2 arom. H); 8.20 (*d*, J = 7.87, 1 arom. H). ^{13}C-NMR: 20.81; 23.79; 35.12; 54.38; 71.44; 73.48; 107.89; 123.18; 125.21; 125.76; 126.44; 129.25; 130.71; 133.95; 135.42; 170.85. MS: 328 (10, M^+), 225 (7), 199 (12), 181 (15), 173 (17), 156 (100), 128 (63), 115 (15), 87 (41), 77 (6), 69 (72), 57 (48), 41 (24), 29 (13). Anal. calc. for $C_{20}H_{24}O_4$: C 73.15, H 7.37; found: C 73.13, H 7.36.

Data of **11a**: recrystallized from hexanes/Et_2O. M.p. 189–190°. $[\alpha]_D$ = −37.9 (c = 1.23, $CHCl_3$). IR ($CHCl_3$): 3600*m*, 3440*w*, 3050*w*, 3020*w*, 3005*m*, 2980*m*, 2960*m*, 2930*m*, 2900*m*, 2970*w*, 1725*s*, 1595*w*, 1510*w*, 1480*m*, 1460*w*, 1410*m*, 1380*m*, 1365*m*, 1350*s*, 1280*s*, 1250*s*, 1225*s*, 1165*w*, 1050*s*, 1115*m*, 1080*m*, 1070*m*, 1020*s*, 1000*s*, 975*s*, 930*w*, 920*w*. ^{1}H-NMR: 0.31 (*d*, J = 6.12, CH_3); 0.97 (*s*, *t*-Bu); 2.62 (*dd*, J = 4.34, 1.15, OH); 3.02 (*ddd*, J = 8.72, 2.64, 0.99, H–C(5)); 4.18 (*qd*, J = 6.15, 8.73, H–C(6)); 5.10 (*s*, H–C(2)); 6.33 (*dd*, J = 3.30, 3.29, H–C(1')); 7.40–7.60 (*m*, 3 arom. H); 7.70–7.90 (*m*, 3 arom. H); 8.00–8.10 (*m*, 1 arom. H). ^{13}C-NMR: 21.24; 23.89; 34.90; 53.35; 70.21; 70.44; 107.47; 122.27; 122.78; 125.21; 126.05; 126.86; 128.64; 129.07; 129.32; 133.50; 136.28; 171.60. MS: 328 (22, M^+), 271 (7), 242 (70), 225 (68), 207 (23), 196 (46), 181 (80), 156 (100), 128 (72), 115 (21), 101 (6), 87 (32), 77 (10), 69 (74), 57 (57), 41 (23), 29 (12). Anal. calc. for $C_{20}H_{24}O_4$: C 73.15, H 7.37; found: C 72.96, H 7.30.

*(1'R,2R,5S,6R)- and (1'S,2R,5S,6R)-5-[1'-(Benzoyloxy)-1'-(naphth-1''-yl)methyl]-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**10c** and **11c**, resp.). As described for **6c** and **7c**, 1.22 g of the mixture **10a**/**11a** (3.72 mmol) in 16 ml of pyridine with 3.7 ml of PhCOCl (31.9 mmol). After acidification, the soln. was extracted using 3 portions of CH_2Cl_2 (50 ml) and the volatiles evaporated on r.e., affording a yellow solid. FC (hexanes/Et_2O 4:1) gave 0.72 g (45%) of **10c**, and 0.68 g (42%) of **11c**.

Data of **10c**: recrystallized from hexanes/Et_2O. M.p. 140–141°. $[\alpha]_D$ = −77.5 (c = 1.42, $CHCl_3$). IR ($CHCl_3$): 3005*w*, 2980*m*, 2960*m*, 2940*w*, 2905*w*, 2880*w*, 1790*w*, 1740*s*, 1730*s*, 1600*m*, 1510*w*, 1485*m*, 1450*m*, 1370*m*, 1350*m*, 1315*m*, 1270*s*, 1250*s*, 1180*m*, 1155*m*, 1105*s*, 1095*s*, 1070*m*, 1035*m*, 1000*m*, 975*m*. ^{1}H-NMR: 0.92 (*s*, *t*-Bu); 1.53 (*d*, J = 6.17, CH_3); 3.27 (*dd*, J = 8.46, 3.36, H–C(5)); 4.06 (*dq*, J = 8.44, 6.17, H–C(6)); 4.86 (*s*, H–C(2)); 7.03 (*d*, J = 3.28, H–C(1')); 7.41–7.71 (*m*, 7 arom. H); 7.80–7.93 (*m*, 2 arom. H); 8.02–8.19 (*m*, 3 arom. H). ^{13}C-NMR: 21.20; 23.79; 35.09; 53.28; 71.80; 74.00; 107.70; 122.07; 125.08; 125.73; 126.73; 128.72; 129.19; 129.35; 129.42; 129.65; 129.90; 130.58; 132.62; 133.69; 133.85; 165.12; 166.54. MS: 432 (6, M^+), 310 (3), 262 (3), 226 (16), 198 (32), 182 (11), 149 (6), 122 (45), 105 (100), 77 (33), 51 (12), 28 (20). Anal. calc. for $C_{27}H_{28}O_5$: C 74.98, H 6.53; found: C 74.88, H 6.57.

Data of **11c**: recrystallized from hexanes/Et_2O. M.p. 200–201°. $[\alpha]_D$ = +118.4 (c = 2.12, $CHCl_3$). IR ($CHCl_3$): 3020*w*, 2980*w*, 2960*w*, 1740*s*, 1600*w*, 1510*w*, 1485*m*, 1450*m*, 1410*m*, 1380*w*, 1365*m*, 1345*m*, 1310*w*, 1270*s*, 1250*s*, 1180*w*, 1155*m*, 1105*m*, 1095*m*, 1070*m*, 1060*w*, 1030*m*, 1020*w*, 1000*m*, 970*m*, 935*w*. ^{1}H-NMR: 0.47 (*d*, J = 6.08,

CH_3); 0.99 (*s*, *t*-Bu); 3.26 (*dd*, *J* = 8.91, 2.84, H–C(5)); 4.36 (*dq*, *J* = 8.92, 6.10, H–C(6)); 5.15 (*s*, H–C(2)); 7.38–7.70 (*m*, H–C(1'), 7 arom. H); 7.82–7.94 (*m*, 2 arom. H); 8.10–8.26 (*m*, 3 arom. H). ^{13}C-NMR: 21.24; 23.89; 35.06; 52.02; 71.97; 73.03; 107.93; 122.05; 122.43; 125.01; 126.33; 127.22; 128.68; 129.09; 129.16; 129.29; 129.67; 132.75; 133.56; 133.76; 164.48; 169.24. MS: 432 (26, M^+), 346 (24), 310 (9), 253 (6), 224 (23), 207 (12), 181 (12), 165 (17), 155 (35), 105 (100), 77 (18), 57 (6), 28 (12). Anal. calc. for $C_{27}H_{28}O_5$: C 74.98, H 6.53; found: C 74.55, H 6.23.

*(1'R,2R,5R,6R)- and (1'S,2R,5R,6R)-5-[1'-(Anthracen-9''-yl)-1'-hydroxymethyl]-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**12a** and **13a**, resp.). As described for **1a**, 6.0 g of dioxanone **F** (34.8 mmol) with 5.6 ml of $(i\text{-Pr})_2NH$ (39.6 mmol, 1.14 equiv.), 26.4 ml of BuLi (39.6 mmol, 1.5M in hexane, 1.14 equiv.) and 10.2 g of anthracene-9-carbaldehyde (49.5 mmol, 1.42 equiv.). The mixture was stirred at −78° for 4 h. The crude product contained two diastereoisomers in a 3.6:1 ratio. Separation of the diastereoisomers by MPLC (hexanes/Et_2O 2:1) was performed on 1.9 g of the diastereoisomeric mixture and gave 1.0 g (64%) of **12a** and 0.3 g (19%) of **13a**.

Data of **12a**: m.p. 182–184°. $[\alpha]_D$ = +68.8 (*c* = 1.14, $CHCl_3$). IR ($CHCl_3$): 3390*s*, 2980*m*, 2950*m*, 2900*m*, 1725*s*, 1715*s*, 1620*w*, 1520*w*, 1480*m*, 1410*m*, 1380*m*, 1370*s*, 1350*s*, 1285*s*, 1260*s*, 1225*m*, 1155*s*, 1120*m*, 1090*s*, 1030*m*, 1000*m*, 980*s*, 890*m*, 845*m*, 795*m*. ^{1}H-NMR: 0.32 (*d*, *J* = 5.90, CH_3); 1.00 (*s*, *t*-Bu); 3.18 (*dd*, *J* = 8.80, 3.50, H–C(5)); 3.24 (*s*, OH); 4.68 (*qd*, *J* = 5.90, 8.80, H–C(6)); 5.22 (*s*, H–C(2)); 7.06 (*d*, *J* = 3.50, H–C(1')); 7.29–7.58 (*m*, 4 arom. H); 7.96 (*d*, 2 arom. H); 8.37 (*s*, 2 arom. H); 9.49 (*s*, 1 arom. H). MS: 378 (1, M^+), 229 (1), 206 (100), 178 (78), 151 (14), 115 (11), 87 (15), 69 (37), 57 (27), 41 (12).

Data of **13a**: m.p. 182–184°. $[\alpha]_D$ = +77.7 (*c* = 1.23, $CHCl_3$). ^{1}H-NMR: −0.05 (*d*, *J* = 5.90, CH_3); 0.98 (*s*, *t*-Bu); 3.41 (*dq*, *J* = 7.50, 5.90, H–C(6)); 3.69 (*dd*, *J* = 11.20, 7.50, H–C(5)); 5.00 (*s*, H–C(2)); 6.50 (*d*, *J* = 11.20, H–C(1')); 7.40–8.80 (*m*, 9 arom. H).

*(1'R,2R,5S,6R)- and (1'S,2R,5S,6R)-5-[1'-(Anthracen-9''-yl)-1'-(benzoyloxy)methyl]-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one* (**12c** and **13c**, resp.). As described for **6c** and **7c**, 3.0 g of the mixture **12a**/**13a** (7.9 mmol) in 33 ml of pyridine with 4.6 ml of PhCOCl (39.4 mmol). After acidification, the soln. was extracted with 3 portions of CH_2Cl_2 (50 ml), and the volatiles were evaporated on r.e., leading to a yellow solid. FC (CH_2Cl_2) was performed to eliminate the contaminating anthracene-9-carbaldehyde, and then the mixture of the two diastereoisomers was separated by MPLC (hexanes/Et_2O 3:1) to give 2.15 g of **12c** and 0.55 g of **13c**.

Data of **12c**: m.p. 157°. $[\alpha]_D$ = +5.3 (*c* = 1.71, $CHCl_3$). IR ($CHCl_3$): 3450*w*, 2980*m*, 2960*m*, 2880*w*, 1735*s*, 1620*w*, 1600*w*, 1580*w*, 1525*w*, 1480*m*, 1450*m*, 1420*w*, 1370*m*, 1355*m*, 1340*m*, 1280*s*, 1225*s*, 1175*m*, 1160*m*, 1100*s*, 1090*s*, 1070*m*, 1030*m*, 1025*s*, 995*s*, 890*m*, 790*w*, 740*s*, 705*s*. ^{1}H-NMR: 0.36 (*d*, *J* = 6.00, CH_3); 1.00 (*s*, *t*-Bu); 3.71 (*dq*, *J* = 6.00, 6.00, H–C(6)); 4.00 (*dd*, *J* = 11.00, 6.00, H–C(5)); 5.26 (*s*, H–C(2)); 7.27–7.82 (*m*, 8 arom. H); 8.04–8.14 (*m*, 4 arom. H); 8.54 (*s*, 1 arom. H); 8.64 (*s*, 1 arom. H); 9.04 (*s*, 1 arom. H). ^{13}C-NMR: 21.06; 23.59; 34.94; 52.74; 69.18; 73.08; 106.68; 124.88; 126.07; 126.74; 126.95; 127.36; 128.13; 129.27; 129.47; 129.72; 129.97; 130.10; 132.96; 165.85; 167.51. MS: 482 (16, M^+), 274 (16), 257 (8), 231 (15), 215 (21), 202 (9), 178 (9), 105 (100), 77 (18), 57 (8), 41 (6). Anal. calc. for $C_{31}H_{30}O_5$: C 77.16, H 6.27; found: C 76.92, H 6.34.

Data of **13c**: m.p. 154–159°. $[\alpha]_D$ = +125.6 (*c* = 1.09, $CHCl_3$). IR ($CHCl_3$): 3490*s*, 2980*m*, 2960*m*, 2900*w*, 1720*s*, 1620*w*, 1520*w*, 1480*m*, 1460*w*, 1445*m*, 1410*m*, 1380*m*, 1370*s*, 1355*s*, 1285*s*, 1260*s*, 1230*s*, 1155*s*, 1125*m*, 1090*s*, 1070*m*, 1030*m*, 1000*m*, 980*s*, 960*w*, 925*w*, 890*s*, 860*w*, 845*m*, 800*m*, 770*m*, 740*s*, 725*w*, 710*m*. ^{1}H-NMR: 0.33 (*d*, *J* = 6.00, CH_3); 1.00 (*s*, *t*-Bu); 2.98 (*d*, *J* = 5.00, H–C(1')); 3.19 (*dd*, *J* = 10.00, 3.00, H–C(5)); 4.68 (*dq*, *J* = 10.00, 5.00, H–C(6)); 5.21 (*s*, H–C(2)); 7.06–7.14 (*m*, arom. H); 7.25 (*s*, arom. H); 7.40–7.61 (*m*, arom. H); 8.00 (*d*, arom. H); 8.41 (*s*, arom. H). MS: 483 (0.04, $[M + 1]^+$), 378 (0.6), 248 (0.3), 229 (0.5), 215 (2), 178 (79), 151 (19), 126 (6), 98 (13), 87 (38), 69 (72), 57 (88), 41 (100), 28 (64).

(2R,3S,4S)-3-(Hydroxymethyl)hexane-2,4-diol (**14**). To 0.47 g of LAH (12.4 mmol, 5 equiv.) in 20 ml of Et_2O was added 0.68 g of **1b** in 5 ml of ether. The mixture was stirred at r.t. for 15 min then at reflux for 14 h. After cooling to 0°, 0.47 ml of H_2O, 0.47 ml of 15% NaOH and 1.4 ml of H_2O were added consecutively, and the resulting mixture was stirred vigorously, until a white precipitate formed. Addition of $MgSO_4$, filtration, and evaporation of the volatiles on r.e. yielded a colourless liquid. FC (Et_2O), followed by distillation on a Kugelrohr apparatus, gave 0.35 g (96%) of pure **14**. B.p. 110° (0.5 mm Hg). $[\alpha]_D$ = −5.7 (*c* = 0.21, $CHCl_3$). IR ($CHCl_3$): 3620*s*, 3520*s*, 2970*s*, 2960*m*, 2900*m*, 2880*m*, 2250*w*, 1600*w*, 1460*w*, 1420*m*, 1155*m*, 1120*m*, 1080*s*, 1040*m*, 975*m*. ^{1}H-NMR: 0.98 (*t*, *J* = 7.37, H–C(6)); 1.30 (*m*, H–C(3)); 1.34 (*d*, *J* = 6.45, H–C(1)); 1.55–1.75 (*m*, H–C(5)); 2.14 (br. *s*, OH); 3.26 (br. *s*, OH); 3.32 (br. *s*, OH); 3.84 (*m*, H–C(4)); 4.05 (*dd*, *AB* system, *J* = 11.90, 3.12, H–C(1')); 4.09 (*dd*, *AB* system, *J* = 11.76, 2.93, H–C(1')); 4.21 (*quint.*, *J* = 6.23, H–C(2)). ^{13}C-NMR: 10.45; 21.88; 28.61; 48.45; 59.75; 70.75; 76.59. MS: 149 (18, $M + 1]^+$), 131 (6), 119 (72), 113 (26), 101 (11), 86 (15), 72 (31), 57 (100), 43 (21), 29 (9). Anal. calc. for $C_7H_{16}O_3$: C 56.73, H 10.88; found: C 56.44, H 10.85.

(2R,3S,4S)-3-(Hydroxymethyl)-5-methylhexane-2,4-diol (**15**). As described for **14**, 8.2 g of **2b** (28.6 mmol) with 5.4 g of LAH (143 mmol, 5 equiv.). FC (Et_2O) gave 4.06 g (87%) of pure **15**. M.p. 12°. $[\alpha]_D$ = −4.1 (*c* = 2.82, $CHCl_3$). IR ($CHCl_3$): 3620*m*, 3450*s*, 3005*s*, 2970*s*, 2930*s*, 2910*s*, 2880*s*, 1470*m*, 1450*m*, 1415*s*, 1390*s*, 1235*s*, 1155*m*,

1125*m*, 1070*s*, 1050*s*, 1010*m*, 990*m*, 980*m*, 960*m*, 930*m*, 905*m*, 875*w*. ^{1}H-NMR: 0.88 (*d*, *J* = 6.73, CH_3); 1.02 (*d*, *J* = 6.57, CH_3); 1.33 (*d*, *J* = 6.40, H–C(1)); 1.46 (*m*, H–C(3)); 1.90 (*qq*, *J* = 6.70, 6.62, H–C(5)); 3.37 (br. *s*, OH); 3.50 (*dd*, *J* = 8.13, 3.23, H–C(4)); 3.53 (br. *s*, 2 OH); 4.01 (*dd*, *AB* system, *J* = 11.72, 3.11, H–C(1′)); 4.11 (*dd*, *AB* system, *J* = 11.74, 3.15, H–C(1′)); 4.18 (*qd*, *J* = 6.41, 6.32, H–C(2)). ^{13}C-NMR: 18.76; 19.39; 21.86; 31.76; 46.20; 59.94; 70.60; 80.45. MS: 163 (33, $[M + 1]^+$), 145 (7), 127 (36), 119 (25), 101 (37), 83 (11), 72 (41), 57 (100), 43 (35), 29 (6). Anal. calc. for $C_8H_{18}O_3$: C 59.23, H 11.18; found: C 59.29, H 11.01.

(1S,2S,3R)-1-Cyclohexyl-2-(hydroxymethyl)butane-1,3-diol (**16**). As described for **14**, 2.6 g of **3b** (8.1 mmol) with 1.54 g of LAH (40.5 mmol, 5 equiv.). FC (Et_2O) gave 1.40 g (85%) of pure **16**. $[\alpha]_D = -5.7$ (*c* = 2.59, $CHCl_3$). IR ($CHCl_3$): 3620*m*, 3490*s*, 3005*s*, 2930*s*, 2860*s*, 1450*s*, 1415*m*, 1380*m*, 1350*w*, 1315*w*, 1240*w*, 1190*w*, 1150*w*, 1120*m*, 1080*m*, 1065*s*, 1045*s*, 1010*w*, 985*m*, 970*m*, 940*w*, 910*w*, 890*w*. ^{1}H-NMR: 0.86–1.08 (*m*, 2 H); 1.10–1.39 (*m*, 4 H); 1.32 (*d*, *J* = 6.41, H–C(4)); 1.45 (*m*, H–C(2)); 1.52–1.88 (*m*, 4 H); 2.04 (br. *d*, *J* = 12.86, 1 H); 3.29 (*d*, *J* = 5.98, 1 H); 3.47–3.86 (*m*, 2 OH); 4.00 (br. *d*, *AB* system, *J* = 11.73, H–C(1′)); 4.10 (br. *d*, *AB* system, *J* = 11.55, H–C(1′)); 4.18 (*m*, H–C(3)). ^{13}C-NMR: 21.85; 25.93; 26.06; 26.41; 29.13; 29.52; 41.34; 45.68; 60.02; 70.66; 79.46. MS: 203 (30, $M + 1]^+$), 185 (22), 167 (29), 153 (3), 140 (5), 119 (46), 95 (64), 83 (41), 72 (65), 57 (100), 41 (28), 28 (23). Anal. calc. for $C_{11}H_{22}O_3$: C 65.31, H 10.96; found: C 65.26, H 10.81.

(2R,3S,4R)-3-(Hydroxymethyl)-5,5-dimethylhexane-2,4-diol (**17**). As described for **14**, 3.38 g of **4b** (11.7 mmol) with 2.14 g of LAH (56.3 mmol, 5 equiv.). FC (Et_2O) gave 1.68 g (82%) of pure **17**. M.p. 66–66.5°. $[\alpha]_D = +12.6$ (*c* = 4.01, $CHCl_3$). IR ($CHCl_3$): 3620*m*, 3480*s*, 3005*s*, 2960*s*, 2910*s*, 2870*s*, 1480*s*, 1470*s*, 1410*s*, 1400*s*, 1380*s*, 1370*s*, 1315*m*, 1240*s*, 1195*m*, 1130*s*, 1060*s*, 1020*m*, 1000*m*, 980*m*, 935*w*, 920*m*, 900*w*. ^{1}H-NMR: 0.95 (*s*, *t*-Bu); 1.33 (*d*, *J* = 6.42, H–C(1)); 1.56 (*m*, H–C(3)); 3.24 (*d*, *J* = 4.26, H–C(4)); 3.42 (*d*, *J* = 5.30, OH); 3.49 (br. *t*, *J* = 5.73, OH); 3.59 (*dd*, *J* = 4.24, 2.17, OH); 4.01 (br. *q*, *J* = 6.48, H–C(2)); 4.09 (*m*, H–C(1′)). ^{13}C-NMR: 21.75; 26.03; 36.00; 45.13; 61.15; 72.39; 82.09. MS: 177 (65, $[M + 1]^+$), 159 (14), 141 (56), 119 (11), 114 (2), 101 (21), 87 (12), 71 (24), 57 (100), 43 (22), 29 (10). Anal. calc. for $C_9H_{20}O_3$: C 61.33, H 11.44; found: C 61.59, H 11.15.

(1R,2S,3R)-1-(Adamant-1′-yl)-2-(hydroxymethyl)butane-1,3-diol (**18**). As described for **14**, 76.4 mg of **5b** (0.20 mmol) with 38 mg of LAH (1.0 mmol, 5 equiv.). FC (Et_2O) gave 43 mg (85%) of pure **18**. M.p. 109–110°. $[\alpha]_D = +14.6$ (*c* = 1.12, $CHCl_3$). IR ($CHCl_3$): 3619*m*, 3474*m*, 3007*m*, 2975*m*, 2905*s*, 2850*s*, 1451*m*, 1410*m*, 1261*m*, 1135*m*, 938*w*, 922*w*, 880*w*. ^{1}*H-NMR*: 1.32 (*d*, *J* = 6.40, H–C(4)); 1.48–1.80 (*m*, 13 H); 2.01 (br. *s*, 3 H); 2.78 (*d*, *J* = 4.09, H–C(1)); 3.17 (*d*, *J* = 5.09, OH); 3.25 (br. *s*, OH); 3.39 (*d*, *J* = 1.67, OH); 3.89–4.14 (*m*, H–C(3), H–C(1′)). ^{13}C-NMR: 21.72; 28.26; 37.10; 37.71; 38.20; 43.93; 61.60; 72.38; 82.68. MS: 255 (4, $[M + 1]^+$), 236 (21), 218 (10), 205 (54), 192 (94), 165 (21), 149 (5), 135 (100), 119 (12), 107 (6), 93 (13), 79 (12), 57 (7). Anal. calc. for $C_{15}H_{26}O_3$: C 70.83, H 10.30; found: C 70.73, H 10.17.

(1R,2S,3R)-2-(Hydroxymethyl)-1-phenylbutane-1,3-diol (**19**). As described for **14**, 2.3 g of **6c** (8.26 mmol) with 1.41 g of LAH (37.2 mmol, 4.5 equiv.). FC (AcOEt) gave 1.13 g (96%) of pure **19**. B.p. 185–205° (0.1 mm Hg). $[\alpha]_D = -48.2$ (*c* = 2.15, $CHCl_3$). IR ($CHCl_3$): 3610*m*, 3430*s*,3000*m*, 2980*m*, 2900*m*, 1600*w*, 1490*w*, 1450*m*, 1420*m*, 1230*m*, 1205*m*, 1090*s*, 1070*s*, 1030*s*, 990*m*, 920*w*, 890*w*, 855*w*, 695*s*. ^{1}H-NMR: 1.15 (*d*, *J* = 6.80, H–C(4)); 1.66 (*m*, H–C(2)); 3.58 (*dd*, *AB* system, *J* = 11.20, 4.30, H–C(1′)); 3.90 (*dd*, *AB* system, *J* = 11.20, 5.60, H–C(1′)); 4.17 (*dq*, *J* = 2.50, 6.80, H–C(3)); 5.07 (*d*, *J* = 6.20, H–C(1)); 7.15–7.40 (*m*, 5 arom. H). ^{13}C-NMR: 20.91; 51.21; 60.16; 66.85; 73.65; 126.12; 127.46; 128.46; 143.06. MS: 196 (0.2, M^+), 178 (2), 160 (2), 147 (3), 134 (7), 117 (6), 107 (100), 92 (8), 79 (34), 57 (17), 43 (9), 28 (6). Anal. calc. for $C_{11}H_{16}O_3$: C 67.32, H 8.22; found: C 67.09, H 8.21.

(1S,2S,3R)-2-(Hydroxymethyl)-1-phenylbutane-1,3-diol (**20**). As described for **14**, 2.3 g of **7c** (8.26 mmol) with 1.41 g of LAH (37.2 mmol, 4.5 equiv.). FC (AcOEt) gave 1.05 g (89%) of pure **20**. B.p. > 150° (0.01 mm Hg). [α]D = −44.7 (*c* = 1.17, $CHCl_3$). IR ($CHCl_3$): 3610*m*, 3440*s*, 3080*w*, 3060*w*, 3020*s*, 3010*s*, 2980*s*, 2920*m*, 2900*m*, 1600*w*, 1490*w*, 1450*s*, 1410*s*, 1380*m*, 1280*m*, 1230*m*, 1200*m*, 1085*s*, 1070*s*, 1060*s*, 1030*s*, 985*m*, 920*w*, 910*w*, 885*w*, 850*w*, 840*w*, 695*s*. ^{1}H-NMR: 1.11 (*d*, *J* = 6.60, H–C(4)); 1.65 (*m*, H–C(2)); 3.54 (*dd*, *AB* system, *J* = 11.50, 4.50, H–C(1′)); 3.90 (*dd*, *AB* system, *J* = 11.50, 6.00, H–C(1′)); 4.14, (*dq*, *J* = 2.00, 6.60, H–C(3)); 5.04 (*d*, *J* = 5.80, H–C(1)); 7.21–7.30 (*m*, 5 arom. H). ^{13}C-NMR: 20.70; 50.92; 60.12; 66.71; 73.55; 125.79; 127.15; 128.14; 142.77. MS: 196 (0.2, M^+), 178 (2), 160 (2), 147 (3), 134 (7), 117 (21), 107 (100), 91 (9), 79 (38), 57 (16), 43 (12). Anal. calc. for $C_{11}H_{16}O_3$: C 67.32, H 8.22; found: C 67.42, H 8.22.

(1R,2S,3R)-2-(Hydroxymethyl)-1-(naphth-2′-yl)butane-1,3-diol (**21**). As described for **14**, 7.9 g of **8c** (18.3 mmol) with 5.2 g of LAH (140 mmol, 7.5 equiv.). FC (AcOEt) gave 3.87 g (86%) of pure **21** as a viscous oil. $[\alpha]_D = +34.7$ (*c* = 2.23, $CHCl_3$). IR ($CHCl_3$): 3600*m*, 3400*s*, 3060*m*, 3000*s*, 2980*s*, 2920*m*, 2900*m*, 1630*w*, 1600*w*, 1510*m*, 1420*s*, 1380*s*, 1270*m*, 1240*m*, 1120*s*, 1060*s*, 1020*m*, 950*w*, 920*m*, 900*m*, 860*s*, 820*s*. ^{1}H-NMR: 1.35 (*d*, *J* = 6.41, H–C(4)); 1.65–1.75 (*m*, H–C(2)); 2.70 (*d*, *J* = 4.25, OH); 2.88 (br. *s*, OH); 3.56 (*d*, *J* = 4.00, OH); 3.85–4.20 (*m*, H–C(1′), H–C(3)); 5.29 (*t*, *J* = 4.00, H–C(1)); 7.40–7.55 (*m*, 3 arom. H); 7.75–7.90 (*m*, 4 arom. H). ^{13}C-NMR: 22.20; 51.43; 59.82; 69.79; 76.30; 123.95; 124.79; 125.96; 126.30; 127.69; 128.00; 128.35; 132.91;

133.27; 140.43. MS: 246 (27, M^+), 228 (19), 210 (3), 197 (12), 181 (28), 165 (52), 156 (100), 141 (17), 129 (92), 115 (7), 101 (5), 87 (3), 77 (10), 63 (7), 57 (12), 43 (18), 28 (37). Anal. calc. for $C_{15}H_{18}O_3$: C 73.15, H 7.37; found: C 72.87, H 7.42.

(1S,2S,3R)-2-(Hydroxymethyl)-1-(naphth-2'-yl)butane-1,3-diol (**22**). As described for **14**, 7.9 g of **9c** (18.3 mmol) with 5.2 g of LAH (140 mmol, 7.5 equiv.). FC (AcOEt) gave 3.7 g (81%) of pure **22**. M.p. 89–90°. $[\alpha]_D = -44.0$ ($c = 1.51$, $CHCl_3$). IR ($CHCl_3$): 3610*s*, 3450*s*, 3060*m*, 3005*s*, 2980*s*, 2930*m*, 2900*m*, 1630*w*, 1600*w*, 1415*s*, 1380*m*, 1360*m*, 1270*m*, 1230*m*, 1170*w*, 1125*s*, 1080*s*, 1060*s*, 1035*s*, 990*m*, 950*w*, 925*w*, 900*m*, 860*s*, 825*s*. ^{1}H-NMR: 1.24 (*d*, $J = 6.60$, H–C(4)); 1.80 (*m*, H–C(2)); 2.67 (br. *s*, OH); 3.15 (br. *s*, OH); 3.70 (br. *s*, OH); 3.69–3.80 (*m*, *AB* system, H–C(1')); 4.10 (*dd*, *AB* system, $J = 11.53, 4.50$, H–C(1')); 4.29 (*m*, H–C(3)); 5.36 (br. *s*, H–C(1)); 7.40–7.52 (*m*, 3 arom. H); 7.76–7.89 (*m*, 4 arom. H). ^{13}C-NMR: 21.30; 50.85; 61.41; 67.30; 74.98; 123.98; 124.88; 125.94; 126.28; 127.67; 128.00; 128.32; 132.88; 133.24; 140.39. MS: 246 (26, M^+), 228 (44), 210 (12), 197 (17), 184 (16), 167 (40), 156 (100), 141 (13), 129 (73), 77 (7), 57 (8), 43 (12), 29 (7). Anal. calc. for $C_{15}H_{18}O_3$: C 73.15, H 7.37; found: C 72.90, H 7.45.

(1R,2S,3R)-2-(Hydroxymethyl)-1-(naphth-1'-yl)butane-1,3-diol (**23**). As described for **14**, 2.33 g of **10c** (7.08 mmol) with 1.35 g of LAH (35.4 mmol, 5 equiv.). FC (Et_2O) gave 1.41 g (81%) of pure **23** as a glass solid. M.p. 45–46°. $[\alpha]_D = +74.6$ ($c = 1.22$, $CHCl_3$). IR ($CHCl_3$): 3600*m*, 3400*s*, 3040*w*, 3000*s*, 2980*s*, 2920*m*, 2900*m*, 1600*w*, 1510*m*, 1420*m*, 1400*m*, 1380*m*, 1070*s*, 1010*m*, 990*m*, 945*w*, 920*m*, 880*w*, 860*w*. ^{1}H-NMR: 1.36 (*d*, $J = 6.41$, H–C(4)); 1.75–1.85 (*m*, H–C(2)); 2.01 (br. *s*, OH); 3.09 (br. *s*, OH); 3.27 (br. *d*, $J = 3.00$, OH); 3.80–4.00 (*m*, H–C(1')); 4.19 (*m*, H–C(3)); 5.80 (*m*, H–C(1)); 7.38–7.50 (*m*, 3 arom. H); 7.65–7.90 (*m*, 4 arom. H). ^{13}C-NMR: 22.05; 50.20; 59.89; 69.70; 73.28; 122.82; 123.79; 125.37; 125.57; 126.15; 128.09; 129.10; 130.03; 133.85; 138.45. MS: 246 (41, M^+), 228 (4), 210 (2), 198 (7), 181 (16), 165 (40), 156 (100), 141 (12), 129 (65), 115 (4), 102 (3), 87 (2), 77 (5), 63 (3), 57 (6), 43 (9), 28 (18). Anal. calc. for $C_{15}H_{18}O_3$: C 73.15, H 7.37; found: C 73.18, H 7.31.

(1S,2S,3R)-2-(Hydroxymethyl)-1-(naphth-1'-yl)butane-1,3-diol (**24**). As described for **14**, 1.09 g of **11c** (3.32 mmol) with 0.63 g of LAH (16.6 mmol, 5 equiv.). FC (Et_2O) gave 0.70 g (85%) of pure **24**. M.p. 54–55°. $[\alpha]_D = -82.6$ ($c = 1.76$, $CHCl_3$). IR ($CHCl_3$): 3610*s*, 3400*s*, 3050*m*, 3000*s*, 2980*s*, 2930*s*, 2800*s*, 1600*w*, 1510*m*, 1450*m*, 1420*s*, 1400*s*, 1380*s*, 1350*m*, 1250*s*, 1170*s*, 1090*s*, 1080*s*, 1040*s*, 1020*m*, 990*m*, 920*w*, 890*w*, 870*w*, 860*w*. ^{1}H-NMR: 1.10 (*d*, $J = 6.70$, H–C(4)); 1.95 (*m*, H–C(2)); 2.01 (br. *s*, OH); 2.96 (br. *s*, OH); 3.65 (br. *s*, OH); 3.89 (*dd*, *AB* system, $J = 11.39, 3.20$, H–C(1')); 4.10–4.40 (*m*, H–C(1'), H–C(3)); 6.00 (*dd*, $J = 3.43, 3.34$, H–C(1)); 7.40–7.50 (*m*, 3 arom. H); 7.65–8.00 (*m*, 4 arom. H). ^{13}C-NMR: 21.17; 49.46; 61.03; 66.85; 71.87; 123.00; 123.76; 125.31; 125.57; 126.18; 128.03; 129.02; 129.97; 133.85; 138.39. MS: 246 (44, M^+), 228 (12), 210 (2), 197 (8), 181 (10), 165 (35), 156 (100), 141 (10), 129 (62), 115 (3), 102 (2), 87 (1), 77 (5), 57 (7), 43 (9), 28 (6). Anal. calc. for $C_{15}H_{18}O_3$: C 73.15, H 7.37; found: C 73.05, H 7.51.

*(2R,5S,6R)-2-(*tert*-Butyl)-5-(1'-hydroxycyclohexyl)-6-methyl-1,3-dioxan-4-one* (**25**). As described for **1a**, 3.0 g of dioxanone **F** (17.4 mmol) with 2.78 ml of $(i\text{-Pr})_2NH$ (19.9 mmol, 1.14 equiv.), 12.4 ml of BuLi (19.9 mmol, 1.6M, 1.14 equiv.), and 2.56 ml of cyclohexanone (24.7 mmol, 1.42 equiv.). FC (1:1 hexanes/Et_2O) gave 3.79 g (81%) of **25**. Recrystallization from pentane/Et_2O gave colorless crystals. M.p. 99–100°. $[\alpha]_D = -23.6$ ($c = 3.34$, $CHCl_3$). IR ($CHCl_3$): 3600*wm*, 3490*m*, 3005*m*, 2980*s*, 2940*s*, 2870*s*, 1710*s*, 1485*m*, 1450*m*, 1410*m*, 1390*w*, 1380*m*, 1370*m*, 1350*s*, 1320*m*, 1280*s*, 1250*s*, 1180*s*, 1150*s*, 1120*m*, 1105*w*, 1080*m*, 1030*m*, 1000*s*, 980*s*. ^{1}H-NMR: 0.96 (*s*, *t*-Bu); 1.10–1.30 (*m*, 1 H), 1.39 (*d*, $J = 6.11$, CH_3), 1.50–1.80 (*m*, 9 H), 2.56 (*d*, $J = 7.91$, H–C(5)); 3.19 (*d*, $J = 1.16$, OH); 4.02 (*qd*, $J = 6.07, 7.87$, H–C(6)); 4.91 (*s*, H–C(2)). ^{13}C-NMR: 21.46; 23.31; 23.81; 25.34; 34.51; 34.99; 36.19; 59.20; 72.41; 72.58; 107.28; 171.18. MS: 270 (19, M^+), 253 (3), 234 (6), 227 (11), 213 (27), 195 (1), 185 (6), 167 (100), 149 (17), 140 (25), 121 (12), 111 (6), 99 (60), 87 (34), 69 (78), 55 (33), 41 (36). Anal. calc. for $C_{15}H_{26}O_4$: C 66.64, H 9.69; found: C 66.62, H 9.83.

(2S,3R)-2-(1'-Hydroxycyclohexyl)butane-1,3-diol (**26**). As described for **14**, 2.74 g of **25** (10.1 mmol) with 1.92 g of LAH (50.7 mmol, 5 equiv.). FC (Et_2O), followed by distillation on a *Kugelrohr* apparatus, gave 1.12 g (60%) of pure **26**. B.p. 120–140° (0.1 mm Hg). $[\alpha]_D = -4.0$ ($c = 2.12$, $CHCl_3$). IR ($CHCl_3$): 3490*s*, 3007*s*, 2937*s*, 2862*s*, 1612*w*, 1486*w*, 1448*m*, 1406*m*, 1351*w*, 1301*w*, 1264*m*, 1162*m*, 1082*s*, 1062*s*, 1017*m*, 967*s*, 924*w*, 853*w*, 841*w*. ^{1}H-NMR: 1.16 (*m*, H–C(2)); 1.21–1.40 (*m*, 1 H); 1.34 (*d*, $J = 6.52$, H–C(4)); 1.40–1.78 (*m*, 7 H); 1.84–1.98 (*m*, 2 H); 3.29–3.44 (br. *m*, 2 OH); 3.63 (*d*, $J = 4.70$, OH); 4.10–4.28 (*m*, H–C(1)); 4.56 (br. *m*, H–C(3)). ^{13}C-NMR: 21.98; 22.06; 25.74; 36.09; 36.77; 49.20; 59.69; 67.85; 75.68. MS: 188 (23, M^+), 171 (5), 153 (49), 145 (8), 134 (25), 126 (28), 119 (2), 108 (20), 99 (100), 81 (45), 70 (17), 55 (37), 43 (15), 29 (5). Anal. calc. for $C_{10}H_{20}O_3$: C 63.80, H 10.71; found: C 63.54, H 10.49.

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