24. Synthesis of Polypropionate Fragments Containing Tertiary-Alcohol Moieties. Cross-Aldolisations with Lithium Enolates of 7-Oxabicyclo[2.2.1]heptan-2-one Derivatives[1])

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The *Diels-Alder* adduct of 2,4-dimethylfuran to 1-cyanovinyl (1′*R*)-camphanate ((+)-(1*R*,2*S*,4*R*)-2-*exo*-cyano-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl (1′*R*)-camphanate ((+)-**1**)) was converted into (+)-2,7-dideoxy-2,4-di-*C*-methyl-L-*glycero*- ((+)-**6**) and -D-*glycero*-L-*altro*-heptono-1,4-lactone ((+)-**7**), into (−)-(3*R*,4*R*,5*R*,6*S*)-3,4:5,7-bis(isopropylidenedioxy)-4,6-dimethylheptan-2-one ((−)-**22**), and into (+)-(2*R*,3*R*,4*R*,5*S*,6*S*)-3,4:5,6-bis(isopropylidenedioxy)-2,4-dimethylheptanal ((+)-**34**). Condensation of (+)-**34** with the lithium enolate of (−)-(1*R*,4*R*,5*S*,6*R*)-6-*exo*-[(*tert*-butyl)dimethylsilyloxy]-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptan-2-one ((−)-**38**; derived from (+)-**1**) gave a 3:2 mixture of aldols (+)-**39** and (+)-**40** (mismatched pairs of a α-methyl-substituted aldehyde and (*E*)-enolate) whereas the reaction of (±)-**34** with (±)-**38** gave a 10:1 mixture of aldols (±)-**41** and (±)-**39**. A single aldol, (−)-**44**, was obtained on condensing (+)-**34** with the lithium enolate of (+)-(1*S*,4*S*,5*S*,6*S*)-5-*exo*-(benzyloxy)-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptan-2-one ((+)-**43**; derived from (−)-(1*S*,2*R*,4*S*)-2-*exo*-cyano-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl (1′*S*)-camphanate ((−)-**3**)). All these cross-aldolisations are highly *exo*-face selective for the bicyclic ketones. The best stereochemical matching is obtained when the lithium enolates and α-methyl-substituted aldehydes can realize a 'chelated transition state' that obeys the *Cram* and *Felkin-Anh* models (steric effects). Polypropionate fragments containing eleven contiguous stereogenic centres and tertiary-alcohol moieties are thus prepared with high stereoselectivity in a convergent fashion. The chiral auxiliaries ((1*R*)- and (1*S*)-camphanic acid) are recovered at the beginning of the syntheses.

A large variety of natural products of biological interest contain polypropionate fragments (chain with alternating OH and Me substituents) and analogues involving tertiary-alcoholic centres [2]. Several methods and strategies have been developed to provide access to these systems which possess a high density of stereochemical information [3]. The control of the stereochemistry can rely on pericyclic reactions such as the *Claisen* rearrangement [4] or the *Lewis*-acid-promoted hetero-*Diels-Alder* addition [5], on aldol reactions [6] involving imide enolates [7] [8], boron enolates [9], tin(II) enolates [10], or zirconium enolates [11], on additions of crotyl boronates to aldehydes [12], on conjugate additions to butenolides [13], on additions of vinyloxiranes [14], or on using carbohydrates as starting materials [15]. Other approaches imply two directional chain elongations and a 'desymmetrization' process [16]. Bicyclic π systems that display high facial selectivity in their reactions for steric reasons have also been used as starting materials [3a] [17–22]. Recently, we have shown [1] [23] that the ZnI_2-catalyzed *Diels-Alder* addition

[1]) For a preliminary report, see [1]. Part of the Ph.D. thesis of *Ph. K.*, Ecole Polytechnique Fédérale de Lausanne, 1994.

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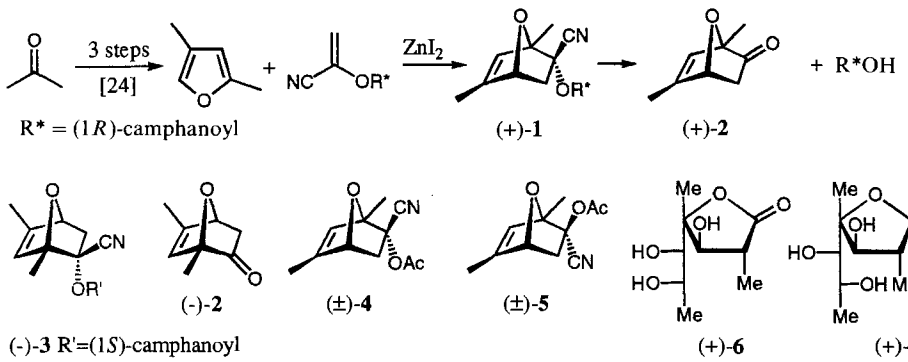
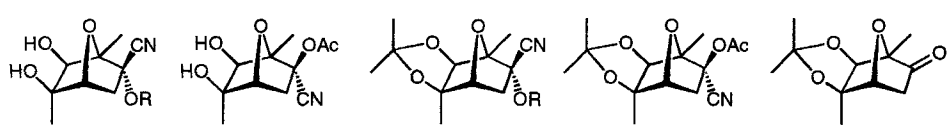
Scheme 1



of 2,4-dimethylfuran to 1-cyanovinyl (1*R*)-camphanate leads to high yield of optically pure adduct (+)-**1**, the saponification of which furnishes enone (+)-**2** and allows one to recover the chiral auxiliary ((1*R*)-camphanic acid; *Scheme 1*). Starting with 1-cyanovinyl (1*S*)-camphanate leads to the diastereoisomeric adduct (−)-**3** and enantiomeric enone (−)-**2** with the same ease[3]).

We report here on the transformation of (+)-**1** and of the racemic *Diels-Alder* adduct (±)-**4** and (±)-**5** of 1-cyanovinyl acetate to 2,4-dimethylfuran into enantiomerically pure and racemic polypropionate fragments, respectively, containing a tertiary-alcohol centre and their use in the elaboration of long-chain systems containing up to eleven contiguous stereogenic centres. The conversion of (+)-**1** into doubly branched heptono-1,4-lactones (+)-**6** and (+)-**7** is also presented.

Results and Discussion. – Double hydroxylation of (+)-**1**, (±)-**4**, and (±)-**5** (*N*-methylmorpholine *N*-oxide monohydrate, 0.01 equiv. of OsO_4) gave the diols (−)-**8** (85%), (±)-**9**, and (±)-**10** (89%), respectively, which were protected as the corresponding acetonides (−)-**11** (95%), (±)-**12**, and (±)-**13** (97%) by treatment with 2,2-dimethoxypropane (acetone, toluene-4-sulfonic acid (TsOH) as catalyst, 20°). The expected [25] [26] *exo*-face selectivity of the double hydroxylation was confirmed by the ^{1}H-NMR NOESY spectrum of (−)-**11** which showed NOE's between H_{endo}–C(3) (δ(H) 2.10 ppm, *d*, ^2J = 15.1 Hz) and Me_{endo}–C(5) (δ(H) 1.47 ppm). A NOE between the latter and H–C(6) (δ(H) 4.25 ppm, *s*) was also observed. The *endo* relative configuration at C(2) was established by the observation of a NOE between the signals of Me–C(5) and

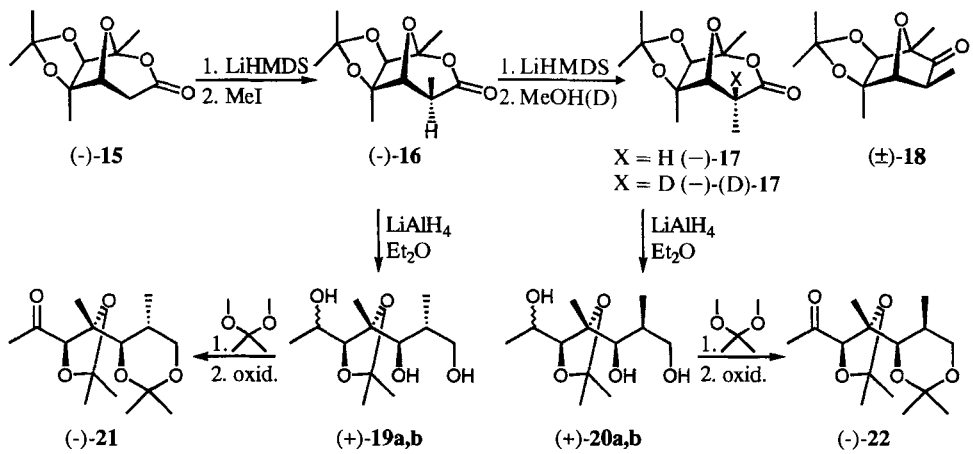


[3]) We call chirons (+)-**1**, (+)-**2**, (−)-**2**, and (−)-**3** 'naked sugars of the second generation'.

$Me_2C(7')$ (δ(H) 1.10, 0.99 ppm) of the camphanoyloxy substituent. Saponification of (−)-**11** followed by treatment with formaline (40% aqueous formaldehyde solution) provided ketone (+)-**14** (99%) and 91% of (1*R*)-camphanic acid (recovery of the chiral auxiliary). Under similar conditions, (±)-**12** and (±)-**13** gave (±)-**14** (99%).

Baeyer-Villiger oxidation [27] of (+)-**14** (3-$ClC_6H_4CO_3H$, $NaHCO_3$, CH_2Cl_2) afforded (−)-**15** (92%) with high regioselectivity, as expected [28]. Deprotonation of uronolactone (−)-**15** with $(Me_3Si)_2NLi$ (LiHMDS; 1.0 equiv.) in THF (−65°) followed by the addition of MeI (−65 to −20°) yielded the *exo*-α-methyl-lactone (−)-**16** (92%; *Scheme 2*). The

Scheme 2



isomeric *endo*-α-methyl-lactone (−)-**17** was not visible in the 250-MHz ^{1}H-NMR spectrum of the crude reaction mixture. Treatment of (−)-**16** with $(Me_3Si)_2NLi$ (1.2 equiv.) in THF at −50° followed by quenching of the enolate with MeOH led to a 88:12 mixture of (−)-**17** and (−)-**16** from which pure (−)-**17** (77%) could be isolated by flash chromatography and recrystallization. Methylation of ketone (±)-**14** as above led to a mixture from which (±)-**18** could be isolated in 55% yield only, together with unreacted starting material (26%).

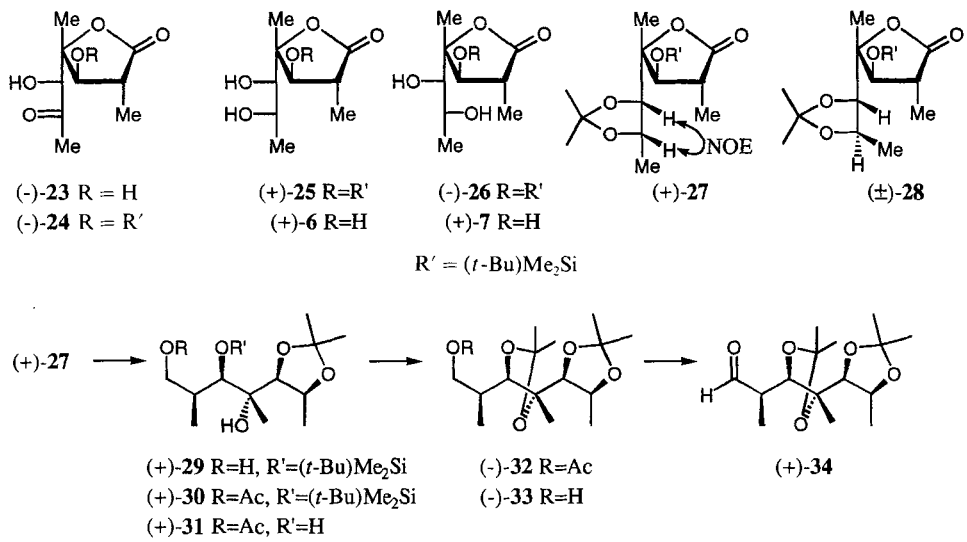
The *exo* relative configuration of the Me group at C(4) in (−)-**16** and at C(3) in (±)-**18** was given by the absence of coupling constant between the bridgehead proton H–C(5) and H–C(4) in (−)-**16** and H–C(4) and H–C(3) in (±)-**18** [29]. In contrast, (−)-**17** showed a vicinal coupling constant $^3J(H_{exo}–C(4),H–C(5)) = 4.8$ Hz in its ^{1}H-NMR spectrum. In the case of (−)-**15**, $^3J(H_{exo}–C(4),H–C(5)) = 6.0$ Hz and $^3J(H_{endo}–C(4),H–C(5)) = 0$ Hz were measured. Furthermore, the NOESY ^{1}H-NMR spectrum of (−)-**16** showed a NOE between the signals of H_{endo}–C(4) and Me–C(6), effect not visible in the NOESY spectrum of (−)-**17**. When the quenching of the lithium enolate of (−)-**16** was done with CD_3OD, complete deuteration of H–C(4) was observed (disappearance of the *qd* at δ(H) 3.04 ppm, $^3J = 7.6, 4.8$ Hz).

Reduction of the doubly branched uronolactones (−)-**16** and (−)-**17** with $LiAlH_4$ in Et_2O (0–20°) afforded triol mixtures (+)-**19a,b** and (+)-**20a,b**, respectively, the treatment of which with 2,2-dimethoxypropane and $SnCl_2$ in dioxane [30] followed by oxidation with *N*-methylmorpholine *N*-oxide in the presence of a catalytic amount of tetrapropylammonium perruthenate [31] furnished ketones (−)-**21** (73%, based on (−)-**16**) and

(−)-**22** (68%, based on (−)-**17**), respectively, two polypropionate synthons with four contiguous stereogenic atoms and a tertiary-alcohol centre (*Scheme 2*). In principle, these synthons can be engaged in the construction of more elaborate systems *via* cross-aldolisations at the methyl-ketone end.

Attempts to methanolyze uronolactones (−)-**16** and (−)-**17** under basic conditions ($NaHCO_3$/MeOH, K_2CO_3/MeOH, DBU/MeCN/MeOH, DBN/MeCN, CsF/MeOH) were not met with success. Complex mixtures were formed, and in the case the (−)-**17**, fast isomerization into (−)-**16** was observed. However, acidic hydrolysis of (−)-**17** (1N HCl, 60°, 24 h) gave crystalline dihydroxy-γ-lactone (−)-**23**, which was partially protected by silylation with (t-Bu)$Me_2SiOSO_2CF_3$ and 2,6-lutidine (CH_2Cl_2) [32] affording (−)-**24** (82%; *Scheme 3*). Reduction of ketone (−)-**24** with $NaBH_4$ (MeOH, −78°) [33] led to a

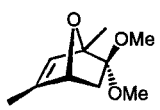
Scheme 3



1:1 mixture of diols (+)-**25** (49%) and (−)-**26** (44%) that were separated by flash chromatography on silica gel. Reduction of (−)-**24** with *L-Selectride* (Li(*sec*-Bu)$_3$BH) in THF at −78° gave a 9:1 mixture of (+)-**25** and (−)-**26**. Deprotection with 40% HF solution [34] afforded (+)-2,7-dideoxy-2,4-di-*C*-methyl-L-*glycero*-L-*altro*-heptono-1,4-lactone ((+)-**6**) and (+)-2,7-dideoxy-2,4-di-*C*-methyl-D-*glycero*-L-*altro*-heptono-1,4-lactone ((+)-**7**), respectively, nearly quantitatively. Treatment of the 9:1 mixture of (+)-**25** and (−)-**26** with 2,2-dimethoxypropane and TsOH (catalyst) gave pure acetonide (+)-**27** in 80% yield. Racemic (+)-**6** and (±)-**7** were prepared in a similar fashion starting with (±)-**14**. The relative configurations of (+)-**6** and (+)-**7** were established by the 360-MHz ^{1}H-NMR spectra of the acetonides (+)-**27** and (+)-**28** (the latter obtained by treatment of (±)-**26** with 2,2-dimethoxypropane and TsOH). While there was a significant NOE between H−C(5) and H−C(6) in (±)-**27**, no NOE was observed between these protons in the isomer (±)-**28**.

Reduction of (+)-**27** with $LiBH_4$ in THF (20°) [33] afforded diol (+)-**29** (75%; *Scheme 3*). Monoacetylation of the primary alcohol with Ac_2O/pyridine gave (+)-**30** (93%). Treatment with Bu_4NF provided the corresponding diol (+)-**31** (91%) which was protected as an acetonide (2,2-dimethoxypropane, TsOH) giving the bis-acetonide (−)-**32** (52%). Methanolysis of the acetate (MeOH, anh. K_2CO_3) gave the primary alcohol (−)-**33** (90%) the oxidation [31] of which furnished aldehyde (+)-**34** (89%), a polypropionate fragment containing five contiguous stereogenic centres and a tertiary-alcohol moiety. This compound is a valuable synthon that can be used directly in cross-aldolisations leading long-chain polypropionate system as illustrated below.

Lithium enolates of 7-oxabicyclo[2.2.1]heptan-2-one derivatives add to electrophilic agents exclusively onto their *exo*-face for steric reasons [23] [25]. It is thus expected that their reactions with asymmetric aldehydes might be highly stereoselective when there is 'matching' between the configurations of the reactants [35]. The 7-oxabicyclo-[2.2.1]heptan-2-one derivatives (−)-**38** and (±)-**38** were used to study the diastereoselectivity of their cross-aldolisations with aldehydes (+)-**34** and (±)-**34**. The former were derived from (+)-**2** and (±)-**2**, respectively, following a method developed by *Sevin et al.* [23]. Treatment of (−)-**2** in trimethyl orthoformate with montmorillonite gave the corresponding dimethyl acetal **35** which was submitted to hydroboration with $BH_3 \cdot Me_2S$ followed by an oxidative workup with $NaBO_3 \cdot 4\,H_2O$. This led to *exo*-alcohol (−)-**36** [23] [36] ($^3J(H_{exo}–C(5),H–C(4)) = 5.8$ Hz [29]) which was protected as the corresponding silyl ether (−)-**37** (96%) on treatment with (*t*-Bu)$Me_2SiOSO_2CF_3$/2,6-lutidine in CH_2Cl_2 at 0°. Hydrolysis of the acetal (*Amberlite IR 120*, acetone, 20°) afforded (−)-**38** (86%).



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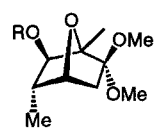
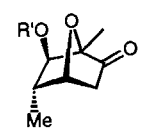


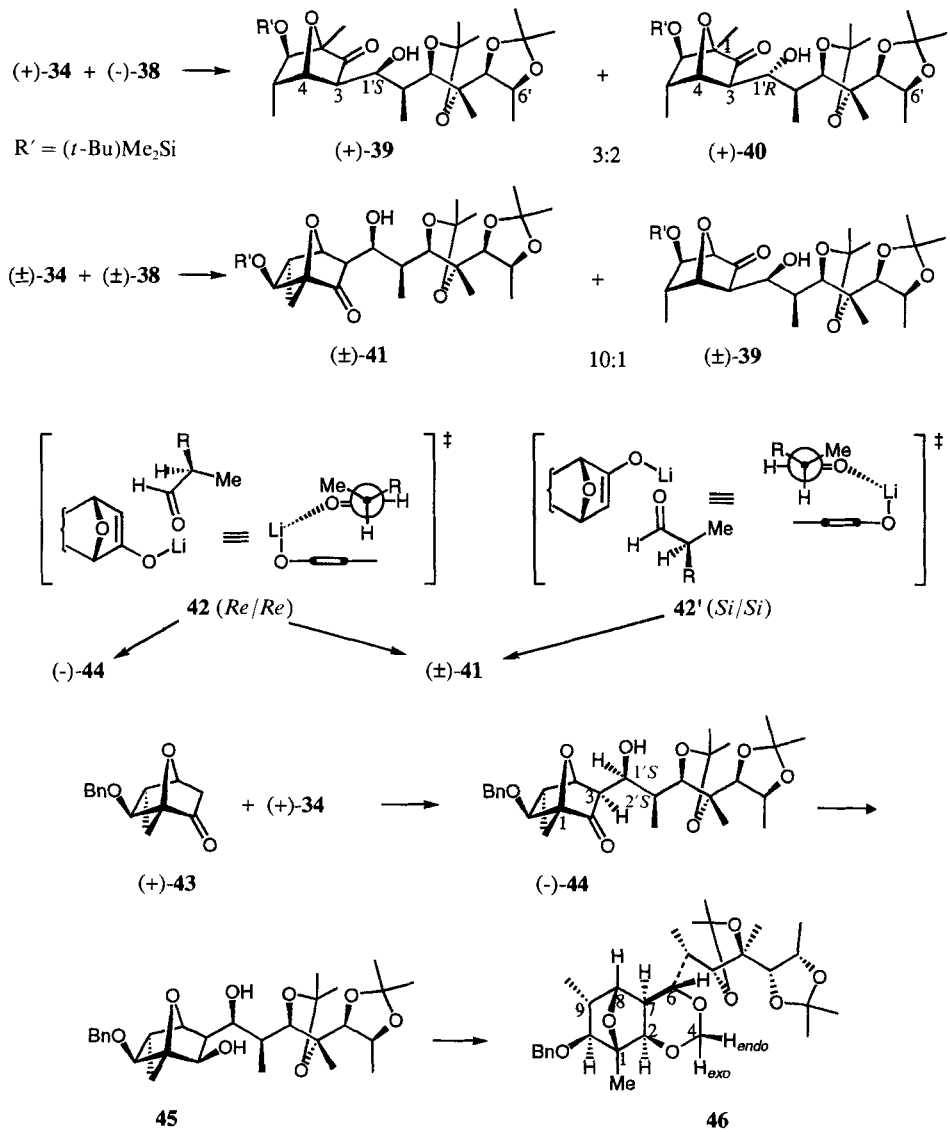
(-)-**36** R=H
(-)-**37** R′ = (*t*-Bu)Me_2Si



(-)-**38** R′ = (*t*-Bu)Me_2Si

When (−)-**38** was deprotonated with $(Me_3Si)_2NLi$ in THF at −78°, followed by the addition of aldehyde (+)-**34** (−95°, 30 min), a 3:2 mixture of aldols (+)-**39** and (+)-**40** was formed in 45 and 30% yield, respectively, and separated by flash column chromatography on silica gel (*Scheme 4*). There is obviously a stereochemical mismatching between (+)-**34** and (−)-**38** since the reaction of the lithium enolate of (±)-**38** with (±)-**34** led to a 10:1 mixture of aldols (±)-**41** and (±)-**39**. The major product (±)-**41** was obtained pure in 60% yield after chromatographic separation. These results can be interpreted in terms of a cyclic transition state [35a] of type **42** and **42′** corresponding to the like mode [35b] of cross-aldolisation which obey the *Cram* [37a] and *Felkin-Anh* rules [37b] and which are realized only for the reaction of the racemic (±)-**38** and not for the mismatched pair (±)-**34** and (−)-**38** [38]. This interpretation was not contradicted by the following experiment. The reaction of the lithium enolate of the bicyclic ketone (+)-**43** (enantiomeric with (−)-**38**, the *exo* OH group being protected as a benzyl ether instead of a silyl ether) [23] with (+)-**34** gave one major aldol (−)-**44** isolated in 57% yield. The 360-MHz ^{1}H-NMR

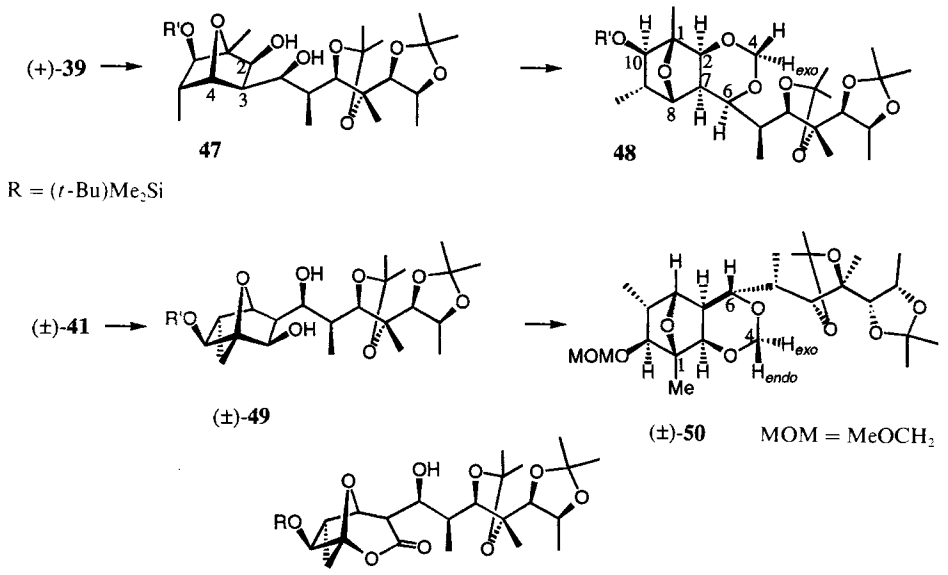
Scheme 4



spectrum of the crude reaction mixture suggested that isomeric aldols were formed in less than 5% yield.

The relative configuration of aldol (−)-**44** was confirmed by its ^{1}H-NMR spectrum (*s* for the bridgehead H−C(4) (^3J(H−C(3),H−C(4)) ≈ 0 Hz [29])). Reduction of (−)-**44** with *L-Selectride* (THF, −78°) followed by treatment with $NaOH/H_2O_2$ (30%) at 20° afforded the corresponding *exo*-alcohol **45** (86%) which reacted with $H_2C(OMe)_2$/2,5-lutidine and $Me_3SiOSO_2CF_3$ to give the 1,3-dioxane **46** (40%; *Scheme 4*). The structure of **46** was

Scheme 5



deduced from its ^{1}H-NMR data. The structures of aldols (+)-**39** and (±)-**41** were established in a similar way after *L-Selectride* reduction (→**47** and (±)-**49**, resp.) and conversion to the corresponding 1,3-dioxanes **48** and (±)-**50** (*Scheme 5*).

The 400-MHz NOESY ^{1}H-NMR spectrum of **46** showed NOE's between proton pairs H–C(2) (3.60 ppm, *d*, ^3J = 7.2 Hz)/H_{exo}–C(4) (4.96 ppm, *d*, ^2J = 4.0 Hz), H_{endo}–C(4) (4.86 ppm, *d*, ^2J = 4.0 Hz)/H–C(6) (*ca.* 4.15 ppm), and H–C(2)/H–C(10) (2.92 ppm, *d*, ^3J = 3.8 Hz). The 400-MHz ^{1}H-NMR spectrum of **48** showed NOE's between proton pairs H–C(2) (3.79 ppm, *d*, ^3J = 6.4 Hz)/H_{exo}–C(4) (5.11 ppm, *d*, ^2J = 5.6 Hz), H_{exo}–C(4)/H–C(6), and H–C(2)/H–C(10) (3.07 ppm, *d*, ^3J = 4.7 Hz). The NOESY spectrum of (±)-**50** exhibited NOE's between proton pairs H–C(2) (3.64 ppm, *d*, ^3J = 7.4 Hz)/H_{exo}–C(4) (4.95 ppm, *d*, ^2J = 4.2 Hz), H_{endo}–C(4) (4.87 ppm)/H–C(6) (*ca.* 4.15 ppm), and H–C(2)/H–C(10) (3.12 ppm, *d*, ^3J = 3.5 Hz).

Reduction of (+)-**40** led to untractable mixtures. Its *exo* relative configuration at C(3) was established by the observation of ^3J(H–C(3),H–C(4)) ≈ 0 Hz [29], and that of the aldol C(1′) centre ('*anti*'-aldol) was deduced to be opposite of that of (+)-**39** ('*syn*'-aldol resulting from the *Si*-face attack of the enolate onto the *Re*-face of the aldehyde: unlike mode).

Baeyer-Villiger oxidation of bicyclic ketone (±)-**41** and (–)-**44** afforded the uronolactones **51** and **52** (*Scheme 5*), respectively, with high regioselectivity.

Conclusion. – The 'naked sugars of the second generation' [1] [23] have allowed the development of a convergent and highly stereoselective method for the preparation of long-chain polypropionate fragments. It is based on the cross-aldolisation of α-methyl-substituted aldehydes with lithium enolates of 7-oxabicyclo[2.2.1]heptan-2-one derivatives that are highly *exo*-face selective and follow the like mode (formation or *erythro*- or '*anti*'-aldols) [23]. The best stereochemical matching is obtained when the lithium eno-

lates and α-methyl-substituted aldehydes can realize a 'chelated transition state' that obeys the *Cram* and *Felkin-Anh* models (steric effect) [37] [38]. The method has allowed one to generate long-chain systems containing up to eleven contiguous stereogenic centres and tertiary-alcohol moieties. Polypropionate fragments with four and five contiguous stereogenic centres as well as doubly branched heptono-1,4-lactones have also been prepared with high stereoselectivity. In this approach, the chiral auxiliaries ((1*R*)- and (1*S*)-camphanic acid) are recovered at an early stage of the synthesis, and both enantiomeric forms of the polypropionate fragments are available with the same ease.

We are grateful to the *Swiss National Science Foundation*, the *Fonds Herbette*, Lausanne, and *F. Hoffmann-La Roche AG*, Basel, for financial support. We thank also Mr. *Francisco Sepulveda, Martial Rey*, and *Jean-Michel Roulet* for their technical assistance and Dr. *Anne-F. Sevin* for her advice.

Experimental Part

General. See [39]. None of the procedures was optimized. *m*-Chloroperoxybenzoic (3-$ClC_6H_4CO_3H$, 55%) was dissolved in CH_2Cl_2 and washed with sat. aq. NaCl. soln. The org. layer was dried ($MgSO_4$) and evaporated. The resulting solid contained 70% 3-$ClC_6H_3CO_4H$. Flash column chromatography (FC): *Merck* silica gel (230–400 mesh). Solvents were distilled before use. Circular dichroism (CD) spectra: *Jobin-Yvon-Mark-V* dichrograph; ($\Delta\varepsilon$) in nm. 400 MHz ^{1}H-NMR and 100.61 MHz ^{13}C-NMR Spectra: *Bruker-ARX-400 spectrometer* (*Aspect X32/3* computer, 1.5 MBYTE max. aquisition memory).

*(+)-(1*R*,2*S*,4*R*)-2-*exo*-Cyano-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl (1′R)-Camphanate* ((+)-**1**). This compound was prepared according to the procedure described for (−)-(1*S*,2*R*,4*S*)-2-*exo*-cyano-1,5-dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl (1′*S*)-camphanate ((−)-**3**) [23] using 1-cyanovinyl (1′*R*)-camphanate instead of 1-cyanovinyl (1′*S*)-camphanate. Colourless prisms. M.p. 136°. $[\alpha]_D^{25} = +92$, $[\alpha]_{578}^{25} = +96$, $[\alpha]_{546}^{25} = +111$, $[\alpha]_{546}^{25} = +202$, $[\alpha]_{365}^{25} = +350$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3700–3140, 2960, 2940, 2240, 1790, 1760, 1640, 1440, 1400, 1380, 1330, 1310, 1270, 1260, 1220, 1200, 1170, 1110, 1070, 1060, 1020, 990, 960, 930, 860, 810, 670. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.71 (*d*, $^4J = 1.6$, H–C(6)); 4.75 (*d*, $^3J = 4.7$, H–C(4)); 3.00 (*dd*, $^2J = 13.7$, $^3J = 4.7$, H_{exo}–C(3)); 2.45–2.34 (*m*, 1 H); 2.12–1.65 (*m*, CH_2(5′), H–C(6′)); 1.83 (*d*, $^4J = 1.6$, Me–C(5)); 1.82 (*s*, Me–C(1)); 1.75 (*d*, $^2J = 13.7$, H_{endo}–C(6′)); 1.12, 1.04, 0.88 (3*s*, 3 Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 177.6 (*s*, C(3′)); 166.1 (*s*, COO); 150.9 (*s*, C(5)); 127.6 (*d*, ^1J(C,H) = 177, C(6)); 117.3 (*s*, CN); 90.0 (*s*); 89.8 (*s*, C(1), C(1′)); 81.4 (*d*, ^1J(C,H) = 168, C(4)); 77.8 (*s*, C(2)); 54.7 (*s*, C(7′)); 43.9 (*t*, ^1J(C,H) = 141, C(3)); 30.2 (*t*, ^1J(C,H) = 135), 28.6 (*t*, ^1J(C,H) = 135, C(5′), C(6′)); 16.5, 16.4 (2*q*, ^1J(C,H) = 127, Me_2C(7′)); 15.1 (*q*, ^1J(C,H) = 126, *Me*–C(1)); 12.5 (*q*, ^1J(C,H) = 128, *Me*–C(5)); 9.5 (*q*, ^1J(C,H) = 127, Me–C(4′)). MS (70 eV): 345 (1, $M^{+\cdot}$), 181 (7), 149 (9), 137 (9), 135 (8), 125 (17), 109 (17), 97 (23), 96 (100), 95 (14), 83 (29), 67 (19), 55 (19). Anal. calc. for $C_{19}H_{23}NO_5$ (345.40): C 66.07, H 6.71, N 4.05; found: C 66.12, H 6.79, N 4.02.

*(+)-(1*R*,4*R*)-1,5-Dimethyl-7-oxabicyclo[2.2.1]hept-5-en-2-one* ((+)-**2**). This compound was prepared following the procedure described for (−)-**2** [23], starting with (+)-**1**. Yield 93% (recovery of 88% of (1*R*)-camphanic acid). Colourless oil. $[\alpha]_{589}^{25} = +782$, $[\alpha]_{577}^{25} = +829$ ($c = 0.91$, $CHCl_3$). CD ($c = 2.11$ mg/ml, EtOH, 25°): 342 (0), 308 (+2.4), 252 (+0.03), 224 (+1.2), 207 (0), 200 (+0.25). Anal. calc. for $C_8H_{10}O_2$ (138.17): C 69.54, H 7.29; found: C 69.43, H 7.27.

*(−)-(1*R*,2*S*,4*R*,5*S*,6*R*)-2-*exo*-Cyano-5-*exo*,6-*exo*-dihydroxy-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]hept-2-*endo*-yl (1*R*′)-Camphanate* ((−)-**8**). A soln. of 0.156M OsO_4 in CCl_4 (0.186 ml, 0.01 equiv.) was added dropwise to a stirred soln. of (+)-**1** (1.0 g, 2.9 mmol) and *N*-methylmorpholine *N*-oxide·H_2O (783 mg, 5.8 mmol) in aceton/H_2O 8:1 (40 ml) [40]. After stirring at 20° for 3 h, $CHCl_3$ (250 ml) was added and the mixture washed with 5N HCl (10 ml) and then with 45% aq. $Na_2S_2O_5$ soln. (15 ml). The two aq. layers were extracted with $CHCl_3$ (100 ml, twice) and the combined org. phases dried ($MgSO_4$) and evaporated. The residue was crystallized from AcOEt/light petroleum ether: 934 mg (85%) of colourless crystals. M.p. 173–174°. $[\alpha]_{589}^{25} = -35.4$, $[\alpha]_{577}^{25} = -38.2$, $[\alpha]_{546}^{25} = -39.0$, $[\alpha]_{435}^{25} = -54.1$, $[\alpha]_{405}^{25} = -66.0$ ($c = 0.985$, $CHCl_3$). IR (KBr): 3440, 3000, 2980, 2880, 2240, 1770, 1450, 1390, 1370, 1310, 1270, 1220, 1170, 1150, 1110, 1090, 1070, 1060, 1030, 930, 810, 795. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.24 (*d*, $^3J = 6.4$, H–C(4)); 3.87 (*d*, $^3J = 5.6$, H–C(6)); 3.31 (*d*, $^3J = 5.6$, OH–C(6)); 3.13 (*s*, OH–C(5)); 2.93 (*dd*, $^2J = 15.2$, $^3J = 6.4$, H_{exo}–C(3)); 2.42 (*ddd*, $^2J = 13.3$, $^3J = 10.7, 4.4$); 2.15–1.92 (*m*); 2.05 (*d*, $^2J = 15.2$,

H_{endo}–C(3)); 1.74 (*ddd*, ^2J = 13.2, ^3J = 9.2, 4.4, CH_2(5'), CH_2(6')); 1.65 (*s*, Me–C(5)); 1.32 (*s*, Me–C(1)); 1.13, 1.10, 0.99 (3*s*, 3 Me). ^{13}C-NMR (90.5 MHz, $CDCl_3$): 177.4 (*s*, C(3')); 165.9 (*s*, COO); 116.5 (*s*, CN); 90.6, 90.1 (2*s*, C(1), C(1')); 83.6 (*d*, ^1J(C,H) = 161, C(4)); 78.7 (*s*, C(5)); 77.6 (*s*, C(4')); 76.0 (*s*, C(2)); 75.6 (*s*, ^1J(C,H) = 153, C(6)); 54.8 (*s*, C(7')); 39.4 (*t*, ^1J(C,H) = 138, C(3)); 30.8 (*t*, ^1J(C,H) = 137), 28.8 (*t*, ^1J(C,H) = 137, C(5'), C(6')); 20.4 (*q*, ^1J(C,H) = 127, Me), 16.7 (2*q*, ^1J(C,H) = 127, 2 Me); 13.0 (*q*, ^1J(C,H) = 129, Me); 9.5 (*q*, ^1J(C,H) = 128, Me). CI-MS (NH_3): 397 (100, $[M + 18]^+$), 380 (2, $[M + 1]^+$), 216 (17), 199 (15), 109 (13), 91 (12), 83 (14), 74 (17). Anal. calc. for $C_{19}H_{25}NO_7$ (379.41): C 60.15, H 6.64, N 3.69; found: C 60.18, H 6.60, N 3.70.

*(1*RS,*2*SR,*4*RS,*5*SR,*6*RS*)-2*-exo-*Cyano-5*-exo,*6*-exo-*dihydroxy-1,5*-endo-*dimethyl-7-oxabicyclo[2.2.1]hept-2*-endo-*yl Acetate* ((±)-**9**) *and (1*RS,*2*RS,*4*RS,*5*SR,*6*RS*)-2*-endo-*Cyano-5*-exo,*6*-exo-*dihydroxy-1,5*-endo-*dimethyl-7-oxabicyclo[2.2.1]hept-2*-exo-*yl Acetate* ((±)-**10**). A mixture of 2,4-dimethylfuran (44 g, 0.46 mmol) [24], 1-cyanovinyl acetate (32.5 g, 0.293 mol), and ZnI_2 (9.35 g, 29 mmol) was stirred in the dark at 20° for 2 days. The mixture was dissolved in Et_2O and filtered through a short column of silica gel (Et_2O/light petroleum ether 1:1) to give 48.5 g (80%) of (±)-**4** [23]/(±)-**5** 1:1 which were separated by FC (silica gel). A 0.156M soln. of OsO_4 in CCl_4 (4.2 ml, 0.67 mmol) was added dropwise to a stirred soln. of (±)-**4**/(±)-**5** 1:1 (14.0 g, 67.6 mmol) and of *N*-methylmorpholine *N*-oxide·H_2O (18.3 g, 135.2 mmol) in acetone/H_2O 8:1 (240 ml). After stirring at 20° for 15 h, CH_2Cl_2 (700 ml) was added and the mixture washed with 5N HCl (100 ml; vigourous shaking for 2–3 min) and then with 45% aq. $Na_2S_2O_5$ soln. (210 ml). The two aq. phases were extracted with CH_2Cl_2 (250 ml, 4 times). The combined org. soln. was dried ($MgSO_4$) and evaporated and the residue crystallized from AcOEt/light petroleum ether: 14.5 g (89%) of (±)-**9**/(±)-**10** 1:1 that could be separated by FC (silica gel, AcOEt/light petroleum ether).

Data of (±)-**5**: Colourless crystals. M.p. 93–94°. IR (KBr): 3480, 3080, 3010, 2980, 2920, 2870, 2240, 1745, 1640, 1440, 1390, 1370, 1360, 1305, 1285, 1240, 1225, 1195, 1160, 1110, 1060, 1040, 990, 960, 920, 880, 855, 800, 790, 610. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.79 (*q*, ^4J = 1.7, H–C(6)); 4.70 (*d*, ^3J = 4.4, H–C(4)); 2.43 (*d*, ^2J = 13.3, H_{endo}–C(3)); 2.15 (*s*, AcO); 2.11 (*dd*, ^2J = 13.3, ^3J = 4.4, H_{exo}–C(3)); 1.88 (*d*, ^4J = 1.7, Me–C(5)); 1.70 (*s*, Me–C(1)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 169.6 (*s*, CO); 152.4 (*s*, C(5)); 127.9 (*d*, ^1J(C,H) = 177, C(6)); 118.0 (*s*, CN); 91.6 (*s*, C(1)); 81.3 (*d*, ^1J(C,H) = 165, C(4)); 75.1 (*s*, C(2)); 43.3 (*t*, ^1J(C,H) = 140, C(3)); 20.8 (*q*, ^1J(C,H) = 130, *Me*COO); 13.3 (*q*, ^1J(C,H) = 128), 13.0 (*q*, ^1J(C,H) = 126, 2 Me). CI-MS (NH_3): 112 (1), 109 (3), 96 (100), 81 (9), 77 (1). Anal. calc. for $C_{11}H_{13}NO_3$ (207.23): C 63.76, H 6.32, N 6.76; found: C 63.79, H 6.25, N 6.80.

Data of (±)-**9**: Colourless needles. M.p. 139–140°. IR (KBr): 3410 (br.), 2960, 2940, 2240, 1760, 1420, 1380, 1230, 1200, 1170, 1130, 1120, 1090, 1070, 1050, 1030, 1010, 990, 945, 885. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.20 (*d*, ^3J = 6.5, H–C(4)); 3.88 (*d*, ^3J = 7.5, H–C(6)); 2.97 (*d*, ^3J = 7.5, OH–C(6)); 2.91 (*dd*, ^2J = 15.2, ^3J = 6.5, H_{exo}–C(3)); 2.68 (*s*, OH–C(5)); 2.18 (*s*, Ac); 2.00 (*d*, ^2J = 15.2, H_{endo}–C(3)); 1.63 (*s*, Me–C(5)); 1.35 (*s*, Me–C(1)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 168.8 (*s*, CO); 117.0 (*s*, CN); 90.4 (*s*, C(1)); 83.3 (*d*, ^1J(C,H) = 162, C(4)); 79.1 (*s*, C(2)); 75.5 (*d*, ^1J(C,H) = 150, C(6)); 38.9 (*t*, ^1J(C,H) = 138, C(3)); 20.6 (*q*, ^1J(C,H) = 131, *Me*COO); 19.9 (*q*, ^1J(C,H) = 127, *Me*–C(5)); 12.8 (*q*, ^1J(C,H) = 129, *Me*–C(1)). CI-MS (NH_3): 242 (1, $[M + 1]^+$), 200 (6), 181 (8), 164 (4), 152 (11), 138 (23), 120 (18), 110 (90), 97 (19), 87 (40), 74 (100). Anal. calc. for $C_{11}H_{15}NO_5$ (241.25): C 54.77, H 6.27, N 5.81; found: C 54.82, H 6.30, N 5.96.

Data of (±)-**10**: Colourless needles. M.p. 154–155°. IR (KBr): 3400, 3320, 3010, 2990, 2960, 2940, 2240, 1755, 1480, 1435, 1370, 1235, 1210, 1150, 1085, 1055, 1025, 980, 965, 940, 875, 820. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.20 (*d*, ^3J = 6.2, H–C(4)); 3.96 (*s*, H–C(6)); 2.86 (br. *s*, OH); 2.72 (*d*, ^2J = 15.4, H_{endo}–C(3)); 2.61 (br. *s*, OH); 2.20 (*dd*, ^2J = 15.4, ^3J = 6.2, H_{exo}–C(3)); 2.17 (*s*, Ac); 1.56, 1.43 (2*s*, 2 Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 168.9 (*s*, CO); 116.5 (*s*, CN); 93.0 (*s*, C(1)); 83.7 (*d*, ^1J(C,H) = 161, C(4)); 78.4 (*s*, C(5)); 77.0 (*d*, ^1J(C,H) = 153, C(6)); 74.9 (*s*, C(2)); 41.7 (*t*, ^1J(C,H) = 138, C(3)); 21.1 (*q*, ^1J(C,H) = 127, *Me*–C(5)); 20.9 (*q*, ^1J(C,H) = 130, *Me*COO); 10.5 (*q*, ^1J(C,H) = 129, *Me*–C(1)). CI-MS (NH_3): 242 (0.4, $[M + 1]^+$), 199 (10), 138 (23), 121 (19), 110 (100), 83 (30), 74 (56), 71 (48). Anal. calc. for $C_{11}H_{15}NO_5$ (241.25): C 54.77, H 6.27, N 5.81; found: C 54.83, H 6.20, N 5.72.

*(1*R,*2*S,*4*R,*5*R,*6*R*)-2*-exo-*Cyano-5*-exo,*6*-exo-*(isopropylidenedioxy)-1,5*-endo-*dimethyl-7-oxabicyclo[2.2.1]hept-2*-endo-*yl (1'*R*)-Camphanate* ((−)-**11**). A mixture of (−)-**8** (400 mg, 1.05 mmol), acetone (4 ml), dimethoxypropane (0.517 ml, 4.2 mmol), and toluene-4-sulfonic acid (10 mg) was stirred at 20° for 4 days (TLC control (silica gel, AcOEt/light petroleum ether 1:1, vanilline): R_f ((−)-**8**) 0.03, R_f ((−)-**11**) 0.28). The mixture was poured in ice-water (20 ml) and extracted with CH_2Cl_2 (30 ml, 3 times), the combined org. phase washed with sat. aq. $NaHCO_3$ soln. (20 ml) and brine (20 ml), dried ($MgSO_4$), and evaporated, and the residue crystallized from AcOEt/light petroleum ether: 420 mg (95%) of colourless crystals. M.p. 159°. $[\alpha]_{589}^{25} = -42.3$, $[\alpha]_{577}^{25} = -44.9$, $[\alpha]_{546}^{25} = -46.5$, $[\alpha]_{435}^{25} = -67.0$, $[\alpha]_{405}^{25} = -80.0$ (*c* = 1.00, $CHCl_3$). IR (KBr): 2990, 2950, 2880, 1800, 1765, 1470, 1450, 1380, 1310, 1260, 1215, 1160, 1125, 1110, 1070, 1060, 1030, 1000, 870. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.26 (*d*, ^3J = 6.3, H–C(4)); 4.25 (*s*, H–C(6)); 2.83 (*dd*, ^2J = 15.1, ^3J = 6.3, H_{exo}–C(3)); 2.40 (*ddd*, ^2J = 13.3, 10.6, 4.4); 2.15–1.92 (*m*, 2 H); 2.10 (*d*, ^2J = 15.1, H_{endo}–C(3)); 1.79–1.65 (*m*, CH_2(5'), CH_2(6')); 1.68, 1.47 (2*s*, 2 Me); 1.42 (*s*, 2 Me); 1.13, 1.10, 0.99 (3*s*, 3 Me). ^{13}C-NMR (90.5 MHz, $CDCl_3$): 177.2 (*s*, C(5')); 165.9 (*s*, C(11')); 116.3 (*s*, CN);

113.3 (*s*, Me_2C); 90.0, 89.5, 89.0 (3*s*, C(1), C(5), C(1')); 85.0 (*d*, ^1J(C,H) = 160), 82.4 (*d*, ^1J(C,H) = 163, C(4), C(6)); 77.5, 77.2 (2*s*, C(2), C(4')); 54.8 (*s*, C(7')); 40.6 (*t*, ^1J(C,H) = 138, C(3)); 30.9, 28.8 (2*t*, ^1J(C,H) = 136, C(5'), C(6')); 28.5, 27.2 (2*q*, ^1J(C,H) = 126, Me_2C); 20.4 (*q*, ^1J(C,H) = 127, Me); 16.7 (2*q*, ^1J(C,H) = 127, 2 Me); 13.2 (*q*, ^1J(C,H) = 129, Me); 9.6 (*q*, ^1J(C,H) = 128, Me). CI-MS (NH_3): 437 (33, $[M + 18]^+$), 420 (2, $[M + 1]^+$), 404 (100), 362 (5), 254 (4), 222 (6), 125 (5), 114 (6), 109 (8), 97 (7), 83 (19). Anal. calc. for $C_{22}H_{29}NO_7$ (419.48): C 62.99, H 6.97, N 3.34; found: C 63.14, H 6.98, N 3.30.

*(1*RS,*2*SR,*4*RS,*5*RS,*6*RS*)-2-*exo-*Cyano-5-*exo,*6-*exo-*(isopropylidenedioxy)-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]hept-2-*endo-*yl Acetate* ((±)-**12**) *and (1*RS,*2*RS,*4*RS,*5*RS,*6*RS*)-2-*endo-*Cyano-5-*exo,*6-*exo-*(isopropylidenedioxy)-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]hept-2-*exo-*yl Acetate* ((±)-**13**). Same procedure as for (–)-**11** starting with (±)-**9** and (±)-**10**, resp. FC (silica gel, AcOEt/light petroleum ether 1:3) allowed one to separate (±)-**12** and (±)-**13** (97%).

*Data of (±)-***12**: Colourless needles. M.p. 134–135°. IR (KBr): 2980, 2940, 2240, 1760, 1460, 1440, 1370, 1240, 1230, 1195, 1150, 1120, 1070, 1050, 1000, 970, 900, 880, 870, 850, 730, 720, 610. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.27 (*s*, H–C(6)); 4.23 (*d*, ^3J = 6.1, H–C(4)); 2.77 (*dd*, ^2J = 15.1, ^3J = 6.1, H_{exo}–C(3)); 2.16 (*s*, Ac); 2.07 (*d*, ^2J = 15.1, H_{endo}–C(3)); 1.66, 1.48 (2*s*, 2 Me); 1.43 (*s*, 2 Me). ^{13}C-NMR (62.9 MHz, CD_2Cl_2): 169.3 (*s*, CO); 117.5 (*s*, CN); 113.2 (*s*, Me_2C); 89.5, 89.4 (2*s*, C(1), C(5)); 85.2 (*d*, ^1J(C,H) = 152, C(4)); 82.8 (*d*, ^1J(C,H) = 160, C(6)); 76.8 (*s*, C(2)); 40.8 (*t*, ^1J(C,H) = 138, C(3)); 28.6, 27.3 (2*q*, ^1J(C,H) = 126, Me_2C); 20.8 (*q*, ^1J(C,H) = 130, Me); 20.7 (*q*, ^1J(C,H) = 126, Me); 13.3 (*q*, ^1J(C,H) = 128, Me). CI-MS (NH_3): 299 (50, $[M + 18]^+$), 282 (5, $[M + 1]^+$), 281 (3, M^+), 266 (100), 180 (15), 164 (17), 134 (18), 121 (19), 109 (20), 99 (18), 84 (11), 82 (10). Anal. calc. for $C_{14}H_{19}NO_5$ (281.31): C 59.78, H 6.81, N 4.98; found: C 59.87, H 6.89, N 4.96.

*Data of (±)-***13**: Colourless crystals. M.p. 150–151°. IR (KBr): 3500 (br.), 2995, 2940, 2240, 1760, 1460, 1435, 1370, 1240, 1215, 1180, 1090, 1060, 1030, 960, 875, 865. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.36 (*s*, H–C(6)); 4.22 (*d*, ^3J = 5.8, H–C(4)); 2.74 (*d*, ^2J = 15.1, H_{endo}–C(3)); 2.15 (*s*, Ac); 2.07 (*dd*, ^2J = 15.1, ^3J = 5.8, H_{exo}–C(3)); 1.55, 1.53, 1.48, 1.43 (4*s*, 4 Me). ^{13}C-NMR (62.9, MHz, $CDCl_3$): 168.8 (*s*, CO); 116.3 (*s*, CN); 113.5 (*s*, Me_2C); 91.5 (*s*, C(1)); 88.9 (*s*, C(5)); 85.8 (*d*, ^1J(C,H) = 157, C(4)); 82.4 (*d*, ^1J(C,H) = 162, C(6)); 73.7 (*s*, C(2)); 42.7 (*t*, ^1J(C,H) = 138, C(3)); 28.1, 27.0 (2*q*, ^1J(C,H) = 127, Me_2C); 20.9 (*q*, ^1J(C,H) = 128, Me), 20.7 (*q*, ^1J(C,H) = 130, Me); 10.7 (*q*, ^1J(C,H) = 129, *Me*–C(1)). CI-MS (NH): 299 (5, $[M + 18]^+$), 282 (2, $[M + 1]^+$), 266 (100), 121 (13), 111 (10). Anal. calc. for $C_{14}H_{19}NO_5$ (281.31): C 59.78, H 6.81, N 4.98; found: C 59.66, H 6.70, N 5.00.

*(+)-(1*R,*4*R,*5*R,*6*R*)-5-*exo,*6-*exo-*(Isopropylidenedioxy)-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**14**). A mixture of (–)-**11** (4.78 g, 11.4 mmol) and anh. K_2CO_3 (2.39 g, 17.1 mmol) in MeOH (250 ml) was stirred at 20° for 45 min. Formaline (36% aq. H_2CO soln., 5 ml, 65 mmol) was added. After stirring at 20° for 10 min, the mixture was poured into ice (400 g) and CH_2Cl_2 (600 ml) under vigourous shaking. The aq. phase was extracted with CH_2Cl_2 (250 ml, twice), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (silica gel): 2.04 g (91%) of (1*R*)-camphanic acid and 2.39 (99%) of (+)-**14** which was crystallized from light petroleum ether. Colourless needles. M.p. 48°. $[\alpha]_{589}^{25}$ = +65.3, $[\alpha]_{577}^{25}$ = +69.8, $[\alpha]_{546}^{25}$ = +85.1, $[\alpha]_{435}^{25}$ = +231.5, $[\alpha]_{405}^{25}$ = +329.1 (*c* = 1.00, $CHCl_3$). IR (KBr): 2990, 2940, 1765, 1380, 1245, 1220, 1135, 1110, 1060, 970, 870, 820, 780, 750. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.48 (*d*, ^3J = 6.2, H–C(4)); 3.82 (*s*, H–C(6)); 2.48 (*dd*, ^2J = 17.9, ^3J = 6.2, H_{exo}–C(3)); 2.14 (*d*, ^2J = 17.9, H_{endo}–C(3)); 1.51, 1.45, 1.43, 1.36 (4*s*, 4 Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 212.2 (*s*, C(2)); 114.4 (*s*, Me_2C); 90.4, 90.2 (2*s*, C(1), C(5)); 86.1 (*d*, ^1J(C,H) = 155), 81.3 (*d*, ^1J(C,H) = 163, C(4), C(6)); 39.5 (*t*, ^1J(C,H) = 135, C(3)); 28.3 (*q*, ^1J(C,H) = 125, 1C, Me_2C); 27.2 (*q*, ^1J(C,H) = 128, 1C, Me_2C); 21.2 (*q*, ^1J(C,H) = 128, Me); 10.1 (*q*, ^1J(C,H) = 129, Me). CI-MS (NH_3): 212 (18, M^+), 197 (23), 169 (10), 155 (7), 141 (20), 126 (18), 111 (100), 99 (18), 97 (10), 95 (10), 84 (45), 83 (56). Anal. calc. for $C_{11}H_{16}O_4$ (212.25): C 62.25, H 7.60; found: C 62.27, H 7.50.

*(±)-(1*RS,*4*RS,*5*RS,*6*RS*)-5-*exo,*6-*exo-*(Isopropylidenedioxy)-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one* ((±)-**14**). A mixture of (±)-**12** and (±)-**13** (2.3 g, 8.18 mmol), 5.4M MeONa in MeOH (5 ml, 27 mmol), and anh. MeOH (100 ml) was stirred at 20° for 1 h. Formaline (36% aq. H_2CO soln., 3.5 ml, 45 mmol) was added. After stirring at 20° for 15 min, the mixture was poured onto ice-H_2O (100 ml) and extracted with CH_2Cl_2 (60 ml, 4 times), the combined org. extract washed with brine (40 ml), dried ($MgSO_4$), and evaporated, and the residue crystallized from light petroleum ether: 1.7 (98%). Colourless crystals. M.p. 44°. Anal. calc. for $C_{11}H_{16}O_4$ (212.25): C 62.25, H7.60; found: C 62.29, H 7.77.

*(1*RS,*5*SR,*6*SR,*7*SR*)-6-*exo,*7-*exo-*(Isopropylidenedioxy)-1,6-*endo-*dimethyl-2,8-dioxabicyclo[3.2.1]octan-3-one* ((±)-**15**). A mixture of (±)-**14** (1.0 g, 4.71 mmol), CH_2Cl_2 (10 ml), 85% 3-$ClC_6H_4CO_3H$ (1.05 g, 5.18 mmol), and $NaHCO_3$ (800 mg, 9.4 mmol) was stirred at 20° for 5 h (TLC (silica gel, AcOEt/light petroleum ether 1:3, vanilline): R_f ((±)-**14**) 0.42, R_f ((±)-**15**) 0.33). The soln. was washed with H_2O (40 ml) and then with sat. aq. $NaHCO_3$ soln. (40 ml). The aq. phases were extracted with CH_2Cl_2 (40 ml, 3 times). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by FC (silica gel, AcOEt/light petroleum ether 1:7): 1.05 g

(98%). Colourless needles. M.p. 80–81°. IR (KBr): 3000, 2940, 1750, 1390, 1265, 1215, 1190, 1120, 1080, 1040, 980, 950, 920, 880, 860, 810, 755, 700, 620. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.44 (*dd*, ^3J = 6.0, 0.5, H–C(5)); 4.27 (*s*, H–C(7)); 2.88 (*dd*, ^2J = 18.2, ^3J = 6.0, H_{exo}–C(4)); 2.58 (*dd*, ^2J = 18.2, ^3J = 0.5, H_{endo}–C(4)); 1.64, 1.53, 1.47, 1.43 (4*s*, 4 Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 166.0 (*s*, C(3)); 113.8 (*s*, Me_2C); 112.0 (*s*, C(1)); 90.0 (*d*, ^1J(C,H) = 159, C(7)); 89.4 (*s*, C(6)); 81.6 (*d*, ^1J(C,H) = 159, C(5)); 33.9 (*t*, ^1J(C,H) = 132, C(4)); 28.1 (*q*, ^1J(C,H) = 125, 1 C, Me_2C); 27.5 (*q*, ^1J(C,H) = 126, Me_2C); 21.5 (*q*, ^1J(C,H) = 127, *Me*–C(6)); 18.7 (*q*, ^1J(C,H) = 129, *Me*–C(1)). CI-MS (NH_3): 229 (44, $[M + 1]^+$), 213 (31), 141 (10), 114 (39), 111 (47), 110 (47), 100 (30), 99 (42), 95 (17), 83 (100), 71 (27). Anal. calc. for $C_{11}H_{16}O_5$ (228.25): C 57.89, H 7.07; found: C 57.94, H 7.04.

*(–)-(1S,5R,6R,7R)-6-*exo,*7-*exo-*(Isopropylidenedioxy)-1,6-*endo-*dimethyl-2,8-dioxabicyclo[3.2.1]octan-3-one* ((–)-**15**). This compound was obtained from (+)-**14** following the procedure described for the preparation of (±)-**15**. Yield 92%. Colourless needles. M.p. 51–52°. $[\alpha]_{589}^{25} = -82.3$, $[\alpha]_{577}^{25} = -86.0$, $[\alpha]_{546}^{25} = -97.8$, $[\alpha]_{435}^{25} = -167.2$, $[\alpha]_{405}^{25} = -201.8$ (c = 1.00, $CHCl_3$). Anal. calc. for $C_{11}H_{16}O_5$ (228.25): C 57.89, H 7.07; found: C 57.88, H 6.97.

*(1RS,4RS,5SR,6SR,7SR)-6-*exo,*7-*exo-*(Isopropylidenedioxy)-1,4-*exo,*6-*endo-*trimethyl-2,8-dioxabicyclo-[3.2.1]octan-3-one* ((±)-**16**). At 0°, 1.6M BuLi in hexane (2.74 ml, 4.38 mmol) was added to a soln. of $(Me_3Si)_2NH$ (1.1 ml, 5.25 mmol) in anh. THF (20 ml). After stirring at 0° for 15 min, the soln. was cooled to –65°, and a cold (–40°) soln. of (±)-**15** (1.0 g, 4.38 mmol) in anh. THF (10 ml) was added slowly under stirring. After stirring at –65° for 1 h, MeI (1.1 ml, 17.5 mmol) was added and the mixture allowed to warm up to –20° (TCL (silica gel, AcOEt/light petroleum ether 1:3, vanilline): R_f ((±)-**15**) 0.23, R_f ((±)-**16**) 0.32). After completion of the methylation, the soln. was poured into sat. aq. NH_4Cl soln. cooled to 0° and extracted with CH_2Cl_2 (20 ml, 4 times). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue immediately filtered through a short pad of silica gel (light petroleum ether): 920 mg (86%) after crystallization from light petroleum ether. Colourless needles. M.p. 98–99°. IR (KBr): 2980, 2940, 2880, 1740, 1460, 1390, 1270, 1185, 1125, 1105, 1080, 1020, 1000, 960, 865, 760, 740. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.22 (*s*, H–C(7)); 4.10 (*d*, ^3J = 0.8, H–C(5)); 2.63 (*dq*, ^3J = 7.6, 0.8, H–C(4)); 1.63, 1.51, 1.45, 1.42 (4*s*, 4 Me); 1.44 (*d*, ^3J = 7.6, Me–C(4)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 170.2 (*s*, C(3)); 113.9 (*s*, Me_2C); 111.9 (*s*, C(1)); 89.8 (*d*, ^1J(C,H) = 160, C(5)); 89.3 (*s*, C(6)); 87.0 (*d*, ^1J(C,H) = 157, C(7)); 38.5 (*d*, ^1J(C,H) = 133, C(4)); 28.2 (*q*, ^1J(C,H) = 126, 1 C, Me_2C); 27.5 (*q*, ^1J(C,H) = 128, 1 C, Me_2C); 21.5 (*q*, ^1J(C,H) = 128, Me); 18.7 (*q*, ^1J(C,H) = 129, Me); 17.7 (*q*, ^1J(C,H) = 131, Me). CI-MS (NH_3): 243 (41, $[M + 1]^+$), 227 (17), 154 (10), 127 (18), 124 (37), 114 (58), 111 (14), 99 (44), 97 (100), 96 (42), 85 (53). Anal. calc. for $C_{12}H_{18}O_5$ (242.27): C 59.49, H 7.49; found: C 59.45, H 7.48.

*(–)-(1S,4S,5R,6R,7R)-6-*exo,*7-*exo-*(Isopropylidenedioxy)-1,4-*exo,*6-*endo-*trimethyl-2,8-dioxabicyclo-[3.2.1]octan-3-one* ((–)-**16**). Same procedure as for (±)-**16**, starting with (–)-**15**. Yield 92%. Colourless needles. M.p. 82–83°. $[\alpha]_{589}^{25} = -65.2$, $[\alpha]_{577}^{25} = -70.9$, $[\alpha]_{546}^{25} = -75.8$, $[\alpha]_{435}^{25} = -117.5$, $[\alpha]_{405}^{25} = -142.6$ (c = 1.00, $CHCl_3$). Anal. calc. for $C_{12}H_{18}O_5$ (242.27): C 59.49, H 7.49; found: C 59.58, H 7.52.

*(1RS,4SR,5SR,6SR,7SR)-6-*exo,*7-*exo-*(Isopropylidenedioxy)-1,4-*endo,*6-*endo-*trimethyl-2,8-dioxabicyclo-[3.2.1]octan-3-one* ((±)-**17**). At 0°, 1.6M BuLi in hexane /16.0 ml, 25.6 mmol) was added to a soln. of $(Me_3Si)_2NH$ (6.7 ml, 32.5 mmol) in anh. THF (100 ml). After stirring at 0° for 15 min, the soln. was cooled to –50° and a cold soln. (–50°) of (±)-**16** (5.27 g, 21.7 mmol) in anh. THF (50 ml) was added slowly. The mixture was stirred at –50° for 3 h, and MeOH (10 ml) was added (TLC (silica gel, AcOEt/light petroleum ether 1:3, vanilline): R_f ((±)-**16**) 0.37, R_f ((±)-**17**) 0.43). The mixture was then poured onto sat. aq. NH_4Cl soln. (150 ml) and CH_2Cl_2 (450 ml) cooled to 0°. The aq. layer was extracted with CH_2Cl_2 (250 ml), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue immediately filtered through a pad of silica gel (light petroleum ether) to yield (±)-**17**/(±)-**16** 88:12. FC (silica gel, AcOEt/light petroleum ether 1:5) gave 4.37 g (83%) of (±)-**17** and 165 mg (3%) of (±)-**16**. (±)-**17**: Colourless needles. M.p. 118° (AcOEt/light petroleum ether). IR (KBr): 2990, 2940, 2880, 1745, 1450, 1380, 1350, 1310, 1290, 1255, 1210, 1180, 1060, 960, 860, 815, 760. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.29 (*d*, ^3J = 4.8, H–C(5)); 4.25 (*s*, H–C(7)); 3.04 (*dq*, ^3J = 7.6, 4.8, H–C(4)); 1.60, 1.52, 1.44, 1.41 (4*s*, 4 Me); 1.31 (*d*, ^3J = 7.6, Me–C(4)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 170.7 (*s*, C(3)); 113.9 (*s*, Me_2C); 112.3 (*s*, C(1)); 91.0 (*d*, ^1J(C,H) = 159, C(7)); 90.1 (*s*, C(6)); 85.9 (*d*, ^1J(C,H) = 161, C(5)); 41.1 (*d*, ^1J(C,H) = 126, C(4)); 28.5, 27.6 (2*q*, ^1J(C,H) = 128, Me_2C); 22.7 (*q*, ^1J(C,H) = 128, *Me*–C(6)); 18.4 (*q*, ^1J(C,H) = 129, *Me*–C(1)); 11.4 (*q*, ^1J(C,H) = 129, *Me*–C(4)). CI-MS (NH_3): 243 (20, $[M + 1]^+$), 227 (17), 140 (16), 127 (24), 125 (34), 124 (17), 114 (51), 99 (47), 97 (100), 85 (62). Anal. calc. for $C_{12}H_{18}O_5$ (242.27): C 59.49, H 7.49: found: C 59.58, H 7.42.

*(1S,4R,5R,6R,7R)-6-*exo,*7-*exo-*(Isopropylidenedioxy)-1,4-*endo,*6-*endo-*trimethyl-2,8-dioxabicyclo[3.2.1]-octan-3-one* ((–)-**17**). Same procedure as for (±)-**17**, starting with (–)-**16**. Colourless needles. M.p. 71°. $[\alpha]_{589}^{25} = -52.6$, $[\alpha]_{577}^{25} = -54.9$, $[\alpha]_{546}^{25} = -62.5$, $[\alpha]_{435}^{25} = -108.7$, $[\alpha]_{405}^{25} = -132.5$ (c = 1.00, $CHCl_3$). Anal. calc. for $C_{12}H_{18}O_5$ (242.27): C 59.49, H 7.49; found: C 59.51, H 7.51.

(1RS,3SR,4RS,5RS,6RS)-5-exo,6-exo-(Isopropylidenedioxy)-1,3-exo,5-endo-trimethyl-7-oxabicyclo-[2.2.1]heptan-2-one ((±)-**18**). Same procedure as for (±)-**16**, starting with (±)-**14** (50 mg, 0.23 mmol). Yield: 13 mg (26%) of (±)-**14** and 29 mg (55%) of (±)-**18** which crystallized from light petroleum ether. Colourless prisms. M.p. 79°–80°. IR (KBr): 2980, 2920, 1760, 1460, 1375, 1360, 1250, 1200, 1070, 990, 850, 710, 640, 620. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.09 (*s*, H–C(4)); 3.84 (*s*, H–C(6)); 2.17 (*q*, ^3J = 7.3, H–C(3)); 1.53, 1.48, 1.45, 1.37 (4*s*, 4 Me); 1.25 (*d*, ^3J = 7.3, Me–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 214.9 (*s*, C(2)); 114.4 (*s*, Me_2C); 90.4, 90.1 (2*s*, C(1), C(5)); 86.9 (*d*, ^1J(C,H) = 164); 86.1 (*d*, ^1J(C,H) = 153, C(4), C(6)); 42.9 (*d*, ^1J(C,H) = 138, C(3)); 28.5, 27.2 (2*q*, ^1J(C,H) = 128, Me_2C); 21.1 (*q*, ^1J(C,H) = 127, Me); 14.4 (*q*, ^1J(C,H) = 130, Me); 10.4 (*q*, ^1J(C,H) = 129, Me). CI-MS (NH_3): 244 (4, $[M + 18]^+$), 228 (8, $M^{+\cdot}$), 211 (14), 198 (9), 169 (7), 125 (29), 123 (14), 114 (28), 111 (20), 97 (100), 83 (32). Anal. calc. for $C_{12}H_{18}O_4$ (226.28): C 63.70, H 8.02; found: C 63.69, H 8.06.

(2R,3S,4R,5S,6R and 6S)-4,5-(Isopropylidenedioxy)-2,4-dimethylheptane-1,3,6-triol ((+)-**19a** and **19b**, resp.). A sat. soln. of $LiAlH_4$ (1.5 ml; prepared from 470 mg of $LiAlH_4$ and Et_2O (12 ml) stirred at 20° for 2 h and decanted) was added to a stirred soln. of (–)-**16** (0.10 g, 0.413 mmol) in Et_2O (6 ml) cooled to 0°. After stirring at 20° for 1 h, H_2O (0.1 ml) and then Na_2SO_4 (10 g) were added. After filtration (rinsing with AcOEt), the solvent was evaporated giving 97 mg (95%) of (+)-**19a**/**19b** 5:1. FC (silica gel, AcOEt/light petroleum ether 1:1) afforded 80 mg (78%) of (+)-**19a** (6*S* or 6*R*) and 15 mg (15%) of **19b** (6*R* or 6*S*).

*Data of (+)-***19a**: Colourless oil. B.p. 200°/0.3 Torr. $[\alpha]_{589}^{25}$ = +21.3, $[\alpha]_{577}^{25}$ = +22.3, $[\alpha]_{546}^{25}$ = +25.0, $[\alpha]_{435}^{25}$ = +42.3, $[\alpha]_{405}^{25}$ = +50.6 (*c* = 1.03, $CHCl_3$). IR (film): 3300 (br.), 2970, 2920, 2860, 1450, 1370, 1250, 1210, 1190, 1090, 1070, 1060, 1050, 1020, 980, 870, 750. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.12, 4.43 (2 br. *s*, 2 OH); 4.01 (*dq*, ^3J = 8.9, 6.2, H–C(6)); 3.95 (*dd*, ^2J = 10.7, ^3J = 3.1, H–C(1)); 3.76 (*d*, ^3J = 5.4, H–C(3)); 3.71 (*dd*, ^2J = 10.7, ^3J = 6.1, H–C(1)); 3.54 (*d*, ^3J = 8.9, H–C(5)); 3.03 (br. *s*, OH); 2.17 (*dddq*, ^3J = 6.1, 3.1, 5.4, 7.2, H–C(2)); 1.45 (*s*, Me); 1.36 (*s*, 2 Me); 1.32 (*d*, ^3J = 6.2, Me(7)); 1.12 (*d*, ^3J = 7.2, Me–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 107.3 (*s*, Me_2C); 89.0 (*d*, ^1J(C,H) = 145, C(5)); 84.2 (*s*, C(4)); 77.2 (*d*, ^1J(C,H) = 139, C(3)); 67.7 (*t*, ^1J(C,H) = 141, C(1)); 65.8 (*d*, ^1J(C,H) = 143, C(6)); 34.7 (*d*, ^1J(C,H) = 128, C(2)); 28.4, 26.6, 21.1, 20.8, 17.0 (5*q*, ^1J(C,H) = 126–127, 5 Me). CI-MS (NH_3): 249 (2, $[M + 1]^+$), 191 (9), 173 (9), 159 (76), 146 (20), 115 (20), 102 (45), 101 (100), 99 (33), 98 (60), 87 (53), 85 (45), 84 (56), 71 (21). Anal. calc. for $C_{12}H_{24}O_5$ (248.16): C 58.03, H 9.75; found: C 58.13, H 9.78.

Data of **19b**: Colourless oil. IR (CH_2Cl_2): 3400 (br.), 2920, 2860, 1370, 1180, 1130, 1070, 1010, 990, 970, 910, 860, 810. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.90 (br. *s*, OH); 4.17 (br. *dq*, ^3J = 5.9, 6.6, H–C(6)); 3.79 (br. *dd*, ^2J = 11.0, ^3J = 3.1, H–C(1)); 3.77 (*d*, ^3J = 5.9, H–C(5)); 3.63 (br. *dd*, ^2J = 11.0, ^3J = 6.6, H–C(1)); 3.49 (br. *d*, ^3J = 2.0, H–C(3)); 3.13 (*s*, OH); 2.11 (*dddq*, ^3J = 3.1, 6.6, 2.0, 7.1, H–C(2)); 1.45 (*s*, Me); 1.39 (*d*, ^3J = 6.6, Me(7)); 1.36, 1.34 (2*s*, 2 Me); 1.07 (*d*, ^3J = 7.1, Me–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 106.9 (*s*, Me_2C); 87.2 (*d*, ^1J(C,H) = 141, C(5)); 83.6 (*s*, C(4)); 76.0 (*d*, ^1J(C,H) = 140, C(3)); 68.2 (*t*, ^1J(C,H) = 141, C(1)); 64.4 (*d*, ^1J(C,H) = 144, C(6)); 35.4 (*d*, ^1J(C,H) = 127, C(2)); 28.5 (*q*, ^1J(C,H) = 128, 1 C, Me_2C); 26.7 (*q*, ^1J(C,H) = 126, 1 C, Me_2C); 22.1 (*q*, ^1J(C,H) = 127, Me); 18.5 (*q*, ^1J(C,H) = 127, Me); 17.1 (*q*, ^1J(C,H) = 125, Me). CI-MS (NH_3): 249 (1, $[M + 1]^+$), 191 (5), 173 (6), 159 (20), 102 (60), 101 (39), 87 (20), 84 (100).

(2S,3S,4R,5S,6R and 6S)-4,5-(Isopropylidenedioxy)-2,4-dimethylheptane-1,3,6-triol ((+)-**20a** and (+)-**20b**). Same procedure as for (+)-**19a** and **19b** starting with (–)-**17** (0.1 mg, 0.413 mmol): 100 mg (98%) of (+)-**20a**/(+)-**20b** 1:1 which could be separated by FC (silica gel, AcOEt/light petroleum ether 1:1) giving 40 mg (39%) of (+)-**20a** and 45 mg (44%) of (+)-**20b**.

*Data of (+)-***20a** (6*R* or 6*S*): Colourless solid. M.p. 124–125°. $[\alpha]_{589}^{25}$ = +38.9, $[\alpha]_{577}^{25}$ = +43.0, $[\alpha]_{546}^{25}$ = +48.3, $[\alpha]_{435}^{25}$ = +79.6, $[\alpha]_{405}^{25}$ = +95.1 (*c* = 0.80, $CHCl_3$). IR (KBr): 3300 (br.), 2980, 2920, 1380, 1300, 1235, 1210, 1180, 1130, 1090, 1050, 1030, 980, 920, 885, 865. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.15 (br. *s*, OH); 4.05 (*dq*, ^3J = 8.9, 6.1, H–C(6)); 4.00 (*d*, ^3J = 2.7, H–C(3)); 3.82 (*dd*, ^2J = 10.4, ^3J = 2.9, H–C(1)); 3.74 (br. *s*, OH); 3.72 (*dd*, ^2J = 10.4, ^3J = 4.3, H–C(1)); 3.51 (*d*, ^3J = 8.9, H–C(5)); 2.42 (br. *s*, OH); 2.20 (*dddq*, ^3J = 2.9, 4.3, 2.7, 7.1, H–C(2)); 1.42, 1.38, 1.36 (3*s*, 3 Me); 1.33 (*d*, ^3J = 6.1, Me(7)); 1.12 (*d*, ^3J = 7.1, Me–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 107.3 (*s*, Me_2C); 89.7 (*d*, ^1J(C,H) = 145, C(5)); 83.4 (*s*, C(4)); 74.8 (*d*, ^1J(C,H) = 138, C(3)); 70.3 (*t*, ^1J(C,H) = 141, C(1)); 65.8 (*d*, ^1J(C,H) = 143, C(6)); 34.7 (*d*, ^1J(C,H) = 127, C(2)); 28.4, 26.5, 21.4, 20.8, 12.3 (5*q*, ^1J(C,H) = 126–128, 5 Me). CI-MS (NH_3): 249 (1, $[M + 1]^+$), 233 (5), 215 (5), 191 (11), 159 (69). 146 (21), 115 (20), 102 (54), 101 (100), 98 (43), 87 (64), 84 (66). Anal. calc. for $C_{12}H_{24}O_5$ (248.16): C 58.03, H 9.75; found: C 58.13, H 9.53.

*Data of (+)-***20b** (6*S* or 6*R*): Colourless crystals. M.p. 83–84°. $[\alpha]_{589}^{25}$ = +1.5, $[\alpha]_{577}^{25}$ = +1.7, $[\alpha]_{546}^{25}$ = +2.8, $[\alpha]_{435}^{25}$ = +6.0, $[\alpha]_{405}^{25}$ = +8.4 (*c* = 1.00, $CHCl_3$). ^{1}H-NMR (250 MHz, $CDCl_3$): 4.20 (*ddq*, ^3J = 7.3, 6.6, 2.2, H–C(6)); 4.03 (*d*, ^3J = 3.2, OH–C(3)); 3.85 (*dd*, ^3J = 4.2, 3.2, H–C(3)); 3.64 (br. *dd*, ^2J = 10.9, ^3J = 4.0, H–C(1)); 3.60 (br. *dd*, ^2J = 10.9, ^3J = 6.0, H–C(1)); 3.49 (*d*, ^3J = 2.2, H–C(5)); 3.06 (*d*, ^3J = 7.3, OH–C(6)); 2.90 (br. *s*, OH–C(1)); 2.12 (*dddq*, ^3J = 4.0, 6.0, 4.2, 6.9, H–C(2)); 1.47 (*s*, Me); 1.38 (*d*, ^3J = 6.6, Me(7)); 1.37, 1.35 (2*s*, 2 Me); 1.05 (*d*, ^3J = 6.9, Me–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 107.1 (*s*, Me_2C); 87.9 (*d*, ^1J(C,H) = 139, C(5)); 83.4

(*s*, C(4)); 72.6 (*d*, ^1J(C,H) = 139, C(3)); 68.4 (*t*, ^1J(C,H) = 143, C(1)); 64.5 (*d*, ^1J(C,H) = 145, C(6)); 35.9 (*d*, ^1J(C,H) = 131, C(2)); 28.4, 26.6, 21.9, 19.0, 13.3 (5*q*, ^1J(C,H) = 126–127, 5 Me). CI-MS (NH_3): 249 (1, $[M + 1]^+$), 173 (7), 159 (24), 102 (75), 101 (52), 99 (16), 87 (30), 85 (49), 84 (100), 71 (11). Anal. calc. for $C_{12}H_{24}O_5$ (248.16): C 58.03, H 9.75; found: C 58.03, H 9.68.

*(–)-(3*R*,4*R*,5*R*,6*R*)-3,4:5,7-Bis(isopropylidenedioxy)-4,6-dimethylheptan-2-one* ((–)-**21**). A mixture of (+)-**19a–19b** (97 mg, 0.39 mmol), 2,2-dimethoxypropane (0.13 ml), $SnCl_2$ (50 mg), and dioxane (4 ml) was stirred at 20° for 2 h. CH_2Cl_2 (25 ml) and then sat. aq. $NaHCO_3$ soln. (25 ml) were added. The aq. phase was extracted with CH_2Cl_2 (25 ml) and the combined org. extract washed with brine (10 ml), dried ($MgSO_4$), and evaporated to give 95 mg, of colourless oil which was dissolved in anh. CH_2Cl_2 (5 ml). *N*-Methylmorpholine *N*-oxide (95 mg, 0.78 mmol) was added and the mixture stirred at 20° for 5 min. Molecular sieves (4 Å, 100 mg) were added, and the soln. was stirred at 20° for 15 min. Tetrapropylammonium perruthenate (50 mg, 0.156 mmol) was added and the mixture stirred at 20° for 8 h. After filtration on *Florisil* (10 g, AcOEt/light petroleum ether 1:3), the solvent was evaporated and the residue purified by FC (silica gel, AcOEt/light petroleum ether 1:5): 86 mg (77%) of colourless oil. B.p. 155°/0.2 Torr ('Kugelrohr'). $[\alpha]_{589}^{25} = -22.6$, $[\alpha]_{577}^{25} = -23.6$, $[\alpha]_{546}^{25} = -28.4$, $[\alpha]_{435}^{25} = -63.4$, $[\alpha]_{405}^{25} = -88.0$ (c = 0.70, $CHCl_3$). IR (film): 2980, 2920, 1860, 1720, 1450, 1370, 1250, 1200, 1155, 1100, 1030, 1000, 920, 855, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.32 (*s*, H–C(3)); 3.62 (*dd*, ^2J = 10.7, ^3J = 5.1, H–C(7)); 3.55 (*d*, ^3J = 10.2, H–C(5)); 3.46 (*dd*, ^2J = 10.7, ^3J = 10.5, H–C(7)); 2.17 (*s*, Me(1)); 1.93 (*dddq*, ^3J = 10.2, 10.5, 5.1, 6.7, H–C(6)); 1.55, 1.53, 1.30, 1.28, 1.26 (5*s*, 5 Me); 0.89 (*d*, ^3J = 6.7, Me–C(6)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.1 (*s*, C(2)); 108.5, 90.6 (2*s*, 2 Me_2C); 88.0 (*d*, ^1J(C,H) = 146, C(3)); 84.5 (*s*, C(4)); 73.9 (*d*, ^1J(C,H) = 141, C(5)); 62.3 (*t*, ^1J(C,H) = 143, C(7)); 30.4 (*d*, ^1J(C,H) = 137, C(6)); 29.3, 29.0, 28.2, 26.5, 19.8, 18.1, 14.3 (7*q*, ^1J(C,H) = 127–128, (7 Me). CI-MS (NH_3): 271 (11), 229 (6), 185 (15), 157 (9), 129 (100), 111 (30), 99 (59), 97 (23), 85 (23), 71 (80). Anal. calc. for $C_{15}H_{26}O_6$ (286.18): C 62.90, H 9.16; found: C 62.99, H 9.05.

*(–)-(3*R*,4*R*,5*R*,6*S*)-3,4:5,7-Bis(isopropylidenedioxy)-4,6-dimethylheptan-2-one* ((–)-**22**). Same procedure as for (–)-**21**, starting with (+)-**20a**/(+)-**20b** 1:1 (0.1 g, 0.35 mmol). Yield 80 mg (69%). Colourless crystals. M.p. 80–81° (light petroleum ether). $[\alpha]_{589}^{25} = -19.3$, $[\alpha]_{577}^{25} = -20.0$, $[\alpha]_{546}^{25} = -24.7$, $[\alpha]_{435}^{25} = -62.8$, $[\alpha]_{405}^{25} = -91.6$ (c = 1.00, $CHCl_3$). IR (KBr): 2980, 2920, 2880, 1725, 1380, 1250, 1200, 1165, 1100, 1010, 925, 870, 850, 830. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.33 (*s*, H–C(3)); 4.07 (*dd*, ^2J = 11.5, ^3J = 2.3, H–C(7)); 3.90 (*d*, ^3J = 2.6, H–C(5)); 3.54 (*dd*, ^2J = 11.5, ^3J = 0.8, H′–C(7)); 2.21 (*s*, Me(1)); 1.75 (*dddq*, ^3J = 2.6, 2.3, 0.8, 6.9, H–C(6)); 1.62, 1.49, 1.38, 1.31, 1.26 (5*s*, 5 Me); 1.20 (*d*, ^3J = 6.9, Me–C(6)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.8 (*s*, C(2)); 108.8, 99.0 (2*s*, 2 Me_2C); 89.9 (*d*, ^1J(C,H) = 146, C(3)); 83.0 (*s*, C(4)); 70.7 (*d*, ^1J(C,H) = 139, C(5)); 68.6 (*t*, ^1J(C,H) = 143, C(7)); 29.9 (*d*, ^1J(C,H) = 128, C(6)); 29.7, 28.8, 28.1, 26.4, 21.2, 18.2, 13.9 (7*q*, ^1J(C,H) = 125–129, 7 Me). CI-MS (NH_3): 271 (11), 185 (8), 157 (13), 129 (100), 127 (10), 115 (17), 114 (13), 111 (25), 99 (48), 97 (18), 87 (27), 85 (15), 71 (48).

*(±)-2,7-Dideoxy-2,4-di-*C*-methyl-*DL*-altro-hept-6-ulosono-1,4-lactone* ((±)-**23**). A mixture of (±)-**16** (1.0 g, 4.13 mmol), dioxane (50 ml), H_2O (45 ml), and 1N HCl (5 ml) was heated to 60° for 24 h (TLC (silica gel, AcOEt/light petroleum ether 3:1, *Pancaldi*): R_f ((±)-**16**) 0.62, R_f ((±)-**23**) 0.35). After cooling to 20°, the soln. was extracted with AcOEt (200 ml). The aq. phase was extracted 4 more times with AcOEt (50 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by column chromatography (silica gel (*Lobar*), AcOEt/light petroleum ether 1:1): 762 mg (92%). Colourless prisms. M.p. 56–57° (Et_2O). IR (KBr): 3460, 2980, 2940, 1775, 1710, 1360, 1300, 1250, 1220, 1190, 1130, 1100, 1065, 1045, 1005, 950, 930, 850, 680, 630. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.18 (*dd*, ^3J = 10.8, 2.6, H–C(3)); 4.17 (*d*, ^3J = 4.2, OH–C(5)); 4.03 (*d*, ^3J = 4.2, H–C(5)); 2.82 (*d*, ^3J = 2.6, OH–C(3)); 2.66 (*dq*, ^3J = 10.8, 7.0, H–C(2)); 2.38 (*s*, Me(7)); 1.36 (*d*, ^3J = 7.0, Me–C(2)); 1.15 (*s*, Me–C(4)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 206.9 (*s*, C(6)); 175.1 (*s*, C(1)); 83.3 (*s*, C(4)); 81.9 (*d*, ^1J(C,H) = 149), 79.5 (*d*, ^1J(C,H) = 147, C(3), C(5)); 39.5 (*d*, ^1J(C,H) = 127, C(2)); 27.2, 13.9, 12.4 (3*q*, ^1J(C,H) = 127–129, 3 Me). CI-MS (NH_3): 220 (19, $[M + 18]^+$), 203 (7, $[M + 1]^+$), 129 (36), 114 (12), 111 (19), 87 (100), 74 (10). Anal. calc. for $C_9H_{14}O_5$ (202.21): C 53.46, H 6.98; found: C 53.40, H 6.86.

*(–)-2,7-Dideoxy-2,4-di-*C*-methyl-*L*-altro-hept-6-ulosono-1,4-lactone* ((–)-**23**). Same procedure as for (±)-**23**, starting with (–)-**16** (360 mg, 1.48 mmol). Yield 252 mg (79%). Colourless prisms. M.p. 64°. $[\alpha]_{589}^{25} = -112.3$, $[\alpha]_{577}^{25} = -118.9$, $[\alpha]_{546}^{25} = -141.2$, $[\alpha]_{435}^{25} = -307.9$, $[\alpha]_{405}^{25} = -418.4$ (c = 1.00, $CHCl_3$). Anal. calc. for $C_9H_{14}O_5$ (202.21): C 53.46, H 6.98; found: C 53.56, H 7.01.

*(±)-3-*O*-[(*tert*-Butyl)dimethylsilyl]-2,7-dideoxy-2,4-di-*C*-methyl-*DL*-altro-hept-6-ulosono-1,4-lactone* ((±)-**24**). At 0°, 2,6-lutidine (0.12 ml, 0.98 mmol) and then (*t*-Bu)$Me_2SiOSO_2CF_3$ (0.23 ml, 0.98 mmol) were added dropwise to a stirred soln. of (±)-**23** (100 mg, 0.49 mmol) in anh. CH_2Cl_2 (10 ml) cooled to 0°. After stirring at 0° for 30 min (TLC (silica gel, AcOEt/light petroleum ether 1:3, *Pancaldi*): R_f ((±)-**23**) 0.04, R_f ((+)-**24**) 0.36), brine (4 ml) was added and the mixture extracted with CH_2Cl_2 (20 ml, 3 times). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by FC (silica gel, AcOEt/light petroleum ether 1:3): 129 mg (82%) of colourless crystals. M.p. 53–54° (light petroleum ether). IR (KBr): 3450, 2960, 2930, 2890, 2860, 1775, 1715, 1470,

1390, 1250, 1220, 1195, 1140, 1075, 1050, 1010, 970, 950, 920, 875, 830, 780. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.25 (*d*, ^3J = 7.4, H–C(3)); 4.05 (*d*, ^3J = 5.2, H–C(5)); 3.73 (*d*, ^3J = 5.2, OH–C(5)); 2.59 (*quint.*, ^3J = 7.4, H–C(2)); 2.40 (*s*, Me(7)); 1.38 (*d*, ^3J = 7.4, Me–C(2)); 1.14 (*s*, Me–C(4)); 0.89 (*s*, *t*-BuSi); 0.13, 0.12 (2*s*, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 207.6 (*s*, C(6)); 176.1 (*s*, C(1)); 85.5 (*s*, C(4)); 81.4, 79.7 (2*d*, ^1J(C,H) = 145, C(3), C(5)); 42.8 (*d*, ^1J(C,H) = 129, C(2)); 27.9 (*q*, ^1J(C,H) = C(7)); 25.7 (*q*, ^1J(C,H) = 125, Me_3CSi); 18.1 (*s*, Me_3CSi); 14.9, 13.8 (2*q*, ^1J(C,H) = 129, 2 Me); –4.7, –4.8 (2*q*, ^1J(C,H) = 119, Me_2Si). CI-MS (NH_3): 334 (5, $[M + 18]^+$), 317 (7, $[M + 1]^+$), 259 (45), 243 (25), 217 (14), 215 (100), 185 (15), 159 (40), 157 (21), 143 (57), 131 (27), 129 (12), 125 (14), 115 (20), 111 (14), 85 (16), 75 (86), 73 (65). Anal. calc. for $C_{15}H_{28}O_5Si$ (316.47): C 56.93, H 8.92, Si 8.87; found: C 56.96, H 8.90, Si 8.85.

*(–)-3-*O*-[(*tert*-Butyl)dimethylsilyl]-2,7-dideoxy-2,4-di-*C*-methyl-*L*-altro-hept-6-ulosono-1,4-lactone* ((–)-**24**). Same procedure as for (±)-**24**, starting with (–)-**23**. Yield 82%. Colourless needles. M.p. 42–43°. $[\alpha]_{589}^{25} = -65.5$, $[\alpha]_{577}^{25} = -69.5$, $[\alpha]_{546}^{25} = -82.6$, $[\alpha]_{435}^{25} = -184.0$, $[\alpha]_{405}^{25} = -252.9$ (c = 1.00, $CHCl_3$). Anal. calc. for $C_{15}H_{28}O_5Si$ (316.47): C 56.93, H 8.92, Si 8.87; found: C 56.92, H 8.82, Si 8.86.

*(±)-3-*O*-[(*tert*-Butyl)dimethylsilyl]-2,7-dideoxy-2,4-di-*C*-methyl-*DL*-glycero-DL-altro-heptono-1,4-lactone* ((±)-**25**) *and (±)-3-*O*-[(*tert*-Butyl)dimethylsilyl]-2,7-dideoxy-2,4-di-*C*-methyl-*LD*-glycero-DL-altro-heptono-1,4-lactone* ((±)-**26**). $NaBH_4$ (10 mg, 0.26 mmol) was added portionwise to a soln. of (±)-**24** (50 mg), 0.16 mmol) in anh. MeOH (2 ml) cooled to –78° (TLC (AcOEt/light petroleum ether 1:3, *Pancaldi*): R_f((±)-**24**) 0.36, R_f((±)-**25**) ≈ 0.09, R_f((+)-**26**) 0.16). After completion of the reduction, a sat. aq. NH_4Cl soln. was added, the mixture allowed to warm up to 20° and extracted with AcOEt (10 ml, twice), and the combined org. extract dried ($MgSO_4$) and evaporated: (±)-**25**/(±)-**26** 1:1 (50 mg) separation by FC (silica gel) gave 25 mg (49%) of (±)-**25** and 22 mg (44%) of (±)-**26**.

*Data of (±)-***25**: White solid. M.p. 60–62°. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.32 (*d*, ^3J = 7.4, H–C(3)); 3.92 (*ddq*, ^3J = 6.3, 6.0, 5.2, H–C(6)); 3.55 (*dd*, ^3J = 6.0, 5.7, H–C(5)); 2.70 (*d*, ^3J = 5.7 OH–C(5)); 2.60 (*dq*, ^3J = 7.4, 7.5, H–C(2)); 2.31 (*d*, ^3J = 5.2, OH–C(6)); 1.40 (*s*, Me–C(4)); 1.33 (*d*, ^3J = 7.5, Me–C(2)); 1.29 (*d*, ^3J = 6.3, Me(7)); 0.90 (*s*, *t*-BuSi); 0.12, 0.11 (2*s*, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 176,8 (*s*, C(1)); 88.9 (*s*, C(4)); 78.7 (*d*, ^1J(C,H) = 144), 77.4 (*d*, ^1J(C,H) = 145), 67.7 (*d*, ^1J(C,H) = 143, C(3), C(5), C(6)); 43.3 (*d*, ^1J(C,H) = 128, C(2)); 25.7 (*q*, ^1J(C,H) = 125, Me_3CSi); 19.7 (*q*, ^1J(C,H) = 126, Me); 18.0 (*s*, Me_3CSi); 17.4, 13.6 (2*q*, ^1J(C,H) = 128, 2 Me); –3.9, –4.8 (2*q*, ^1J(C,H) = 118, Me_2Si). CI-MS (NH_3): 336 (73, $[M + 18]^+$), 319 (30, $[M + 1]^+$), 199 (5), 143 (11), 75 (29), 73 (25).

*Data of (±)-***26**: White amorphous solid. IR (KBr): 3520, 3380, 2930, 2860, 1755, 1250, 1240, 1100, 1040, 950, 830, 770. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.20 (*d*, ^3J = 7.6, H–C(3)); 4.02 (*ddq*, ^3J = 6.0, 5.2, 2.1, H–C(6)); 3.33 (*dd*, ^3J = 7.1, 2.1, H–C(5)); 3.07 (*d*, ^3J = 7.1, OH–C(5)); 2.62 (*dq*, ^3J = 7.6, 7.2, H–C(2)); 2.27 (*d*, ^3J = 5.2, OH–C(6)); 1.36 (*s*, Me–C(4)); 1.33 (*d*, ^3J = 7.2, Me–C(2)); 1.30 (*d*, ^3J = 6.0, Me(7)); 0.90 (*s*, *t*-BuSi); 0.12, 0.11 (2*s*, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 176.7 (*s*, C(1)); 88.8 (*s*, C(4)); 77.5 (2*d*, ^1J(C,H) = 144), 65.5 (*d*, ^1J(C,H) = 143, C(3), C(5), C(6)); 43.0 (*d*, ^1J(C,H) = 128, C(2)); 25.7 (*q*, ^1J(C,H) = 126, Me_3CSi); 21.6 (*q*, ^1J(C,H) = 127, Me); 18.0 (*s*, Me_3CSi); 16.7, 13.5 (2*q*, ^1J(C,H) = 128–129, 2 Me); –4.2, –4.8 (2*q*, ^1J(C,H) = 119, Me_2Si). CI-MS (NH_3): 336 (32, $[M + 18]^+$), 319 (17, $[M + 1]^+$), 217 (10), 159 (18), 143 (10), 131 (15), 85 (18), 77 (11), 75 (100), 73 (72). Anal. calc. for $C_{15}H_{30}O_5Si$ (318.49): C 56.57, H 9.49, Si 8.82; found: C 56.45, H 9.50, Si 8.86.

*(+)-3-*O*-[(*tert*-Butyl)dimethyl]-2,7-dideoxy-2,4-di-*C*-methyl-*L*-glycero-L-altro-heptono-1,4-lactone* ((+)-**25**) *and (–)-3-*O*-[(*tert*-Butyl)dimethylsilyl]-2,7-dideoxy-2,4-di-*C*-methyl-*D*-glycero-L-altro-heptono-1,4-lactone* ((–)-**26**). Same procedure as for (±)-**25** and (±)-**26**, starting with (–)-**24**.

*Data of (+)-***25**: White solid. $[\alpha]_{589}^{25} = +1.6$, $[\alpha]_{577}^{25} = +1.8$, $[\alpha]_{546}^{25} = +9.7$, $[\alpha]_{435}^{25} = +34.2$, $[\alpha]_{405}^{25} = +35.6$ (c = 0.50, $CHCl_3$).

*Data of (–)-***26**: Colourless crystals. M.p. 69–70°. $[\alpha]_{589}^{25} = -3.2$, $[\alpha]_{577}^{25} = -3.0$, $[\alpha]_{546}^{25} = +4.2$, $[\alpha]_{435}^{25} = +25.0$, $[\alpha]_{405}^{25} = +25.2$ (c = 0.50, $CHCl_3$).

*(–)-5,6-Di-O-acetyl-3-*O*-[(*tert*-butyl)dimethylsilyl]-2,7-dideoxy-2,4-di-*C*-methyl-*L*-glycero-L-altro-heptono-1,4-lactone.* Obtained by acetylation (Ac_2O, pyridine, 20°, 24 h) of (+)-**25**. Colourless oil. $[\alpha]_{589}^{25} = +28.2$, $[\alpha]_{577}^{25} = +28.0$, $[\alpha]_{546}^{25} = +40.0$, $[\alpha]_{435}^{25} = +85.8$, $[\alpha]_{405}^{25} = +99.0$ (c = 0.50, $CHCl_3$). IR (CH_2Cl_2): 2950, 2920, 2880, 2850, 1770, 1740, 1365, 1220, 1130, 1080, 1040, 1020, 950, 830. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.21 (*d*, ^3J = 2.8, H–C(5)); 5.08 (*dq*, ^3J = 2.8, 6.4, H–C(6)); 4.30 (*d*, ^3J = 8.4, H–C(3)); 2.59 (*dq*, ^3J = 8.4, 7.3, H–C(2)); 2.17, 2.03 (2*s*, 2 Ac); 1.34 (*d*, ^3J = 7.3, Me–C(2)); 1.29 (*d*, ^3J = 6.4, H–C(7)); 1.26 (*s*, Me–C(4)); 0.90 (*s*, *t*-BuSi); 0.16, 0.15 (2*s*, Me_2Si). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 175.3 (*s*, C(1)); 170.1, 169.9 (2*s*, 2 MeCOO); 86.7 (*s*, C(4)); 77.2 (*d*, ^1J(C,H) = 158), 75.4 (*d*, ^1J(C,H) = 146), 68.8 (*d*, ^1J(C,H) = 146, C(3), C(5), C(6)); 42.0 (*d*, ^1J(C,H) = 129, C(2)); 25.6 (*q*, ^1J(C,H) = 125, Me_3CSi); 21.0, 20.5 (2*q*, ^1J(C,H) = 130, *Me*COO); 17.9 (*s*, Me_3CSi)); 17.2 (*q*, ^1J(C,H) = 129, Me); 15.7, 13.3 (2*q*, ^1J(C,H) = 128, 2 Me); –4.3 (*q*, ^1J(C,H) = 119, MeSi); –4.9 (*q*, ^1J(C,H) = 119, MeSi). CI-MS (NH_3): 420 (3, $[M + 18]^+$), 403 (1, $[M + 1]^+$), 345 (100), 243 (20), 151 (12), 143 (28), 117 (74), 86 (17), 85 (22), 84 (29), 75 (53), 74 (41).

*(+)-5,6-Di-*O*-acetyl-3-*O*-[(*tert*-butyl)dimethylsilyl]-2,7-dideoxy-2,4-di-*C*-methyl-*D*-glycero-*L*-altro-heptono-1,4-lactone*. Obtained by acetylation (Ac_2O/pyridine, 20°, 24 h) of (−)-**26**. Colourless oil. $[\alpha]_{589}^{25} = -18.0$, $[\alpha]_{577}^{25} = -19.6$, $[\alpha]_{546}^{25} = -13.8$, $[\alpha]_{435}^{25} = -4.5$, $[\alpha]_{405}^{25} = -8.7$ ($c = 0.45$, $CHCl_3$). IR (CH_2Cl_2): 2940, 2920, 2850, 1770, 1740, 1370, 1370, 1210, 1185, 1130, 1100, 1070, 1040, 1000, 975, 950, 905, 870, 830. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.48 (*dq*, $^3J = 2.7$, 6.6, H–C(6)); 5.02 (*d*, $^3J = 2.7$, H–C(5)); 4.25 (*d*, $^3J = 8.1$, H–C(3)); 2.57 (*dq*, $^3J = 8.1$, 7.2, H–C(2)); 2.21, 2.07 (2*s*, 2 Ac); 1.33 (*d*, $^3J = 7.2$, Me–C(2)); 1.27 (*s*, Me–C(4)); 1.21 (*d*, $^3J = 6.6$, Me(7)); 0.91 (*s*, *t*-BuSi); 0.14, 0.13 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 175.3 (*s*, C(1)); 170.2, 170.0 (2*s*, 2 Me*C*OO); 86.7 (*s*, C(4)); 77.1 (*d*, ^1J(C,H) = 142), 75.3 (*s*, ^1J(C,H) = 147), 68.8 (*d*, ^1J(C,H) = 146, C(3), C(5), C(6)); 41.9 (*d*, ^1J(C,H) = 128, C(2)); 25.6 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 21.1, 20.6 (2*q*, ^1J(C,H) = 130, 2 *Me*COO); 17.9 (*s*, Me_3*C*Si); 17.2, 15.6 (2*q*, ^1J(C,H) = 129, 2 Me); 13.3 (*q*, ^1J(C,H) = 129, Me); −4.3, −4.9 (2*q*, ^1J(C,H) = 115, Me_2Si). CI-MS (NH_3): 420 (5, $[M + 18]^+$), 403 (6, $[M + 1]^+$), 345 (100), 285 (9), 279 (13), 243 (80), 225 (15), 199 (15), 151 (12), 149 (13), 143 (28), 123 (21), 117 (95), 115 (23), 85 (25), 75 (71), 73 (54).

*(+)-2,7-Dideoxy-2,4-di-*C*-methyl-*L*-glycero-*L*-altro-heptono-1,4-lactone* ((+)-**6**). At 0°, 40% aq. HF soln. (0.4 ml) was added dropwise to a stirred soln. of (+)-**25** (40 mg, 0.129 mmol), THF (1 ml), and MeCN (2 ml). After stirring at 0° for 1 h and then at 20° for 30 min, the solvent was evaporated at 0.1 Torr and the residue purified by FC (silica gel, CH_2Cl_2/MeOH 8:1): 25 mg (96%) of viscous oil. $[\alpha]_{589}^{25} = +8.6$, $[\alpha]_{577}^{25} = +6.6$, $[\alpha]_{546}^{25} = +16.0$, $[\alpha]_{435}^{25} = +43.4$, $[\alpha]_{405}^{25} = +46.0$ ($c = 0.50$, MeOH). IR (CH_2Cl_2): 3750, 3450 (br.), 2920, 2890, 2640, 1770, 1380, 1190, 1110, 1040, 940. ^{1}H-NMR (400 MHz, CD_3OD): 4.31 (*d*, $^3J = 9.3$, H–C(3)); 3.89 (*dq*, $^3J = 6.2$, 6.3 H–C(6)); 3.53 (*d*, $^3J = 6.2$, H–C(5)); 2.68 (*dq*, $^3J = 9.3$, 7.1, H–C(2)); 1.44 (*s*, Me–C(4)); 1.31 (*d*, $^3J = 6.3$, Me(7)); 1.29 (*d*, $^3J = 7.1$, Me–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 178.8 (*s*, C(1)); 89.9 (*s*, C(4)); 79.4 (*d*, ^1J(C,H) = 140), 75.7 (*d*, ^1J(C,H) = 148), 68.7 (*d*, ^1J(C,H) = 142, C(3), C(5), C(6)); 43.4 (*d*, ^1J(C,H) = 131, C(2)); 20.2 (*q*, ^1J(C,H) = 126, Me); 18.0, 12.9 (2*q*, ^1J(C,H) = 128, 2 Me). CI-MS (NH_3): 222 (100, $[M + 18]^+$), 205 (9, $[M + 1]^+$), 129 (6), 87 (12).

*(+)-2,7-Dideoxy-2,4-di-*C*-methyl-*D*-glycero-*L*-altro-heptono-1,4-lactone* ((+)-**7**). Same procedure as for (+)-**6**, starting with (−)-**26**. Colourless crystals. M.p. 129–130°. $[\alpha]_{589}^{25} = +14.1$, $[\alpha]_{577}^{25} = +13.5$, $[\alpha]_{546}^{25} = +19.2$, $[\alpha]_{435}^{25} = +37.1$, $[\alpha]_{405}^{25} = +40.0$ ($c = 1.00$, MeOH). IR (KBr): 3500, 3430, 2990, 2940, 2900, 2880, 1720, 1450, 1380, 1295, 1240, 1220, 1110, 1060, 1030, 990, 945, 860, 810, 790, 735, 690, 660. ^{1}H-NMR (400 MHz, CD_3OD): 4.39 (*q*, $^3J = 10.4$, H–C(3)); 4.02 (*dq*, $^3J = 1.8$, 6.4, H–C(6)); 3.53 (*d*, $^3J = 1.8$, H–C(5)); 2.76 (*dq*, $^3J = 10.4$, 7.0, H–C(2)); 1.39 (*s*, Me–C(4)); 1.33 (*d*, $^3J = 6.4$, Me(7)); 1.30 (*d*, $^3J = 7.0$, Me–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 178.6 (*s*, C(1)); 90.0 (*s*, C(4)); 77.6 (*d*, ^1J(C,H) = 137), 74.1 (*d*, ^1J(C,H) = 149), 67.8 (*d*, ^1J(C,H) = 142, C(3), C(5), C(6)); 42.1 (*d*, ^1J(C,H) = 127, C(2)); 20.6 (*q*, ^1J(C,H) = 126, Me); 17.4, 13.0 (2*q*, ^1J(C,H) = 128, 2 Me). Anal. calc. for $C_9H_{16}O_5$ (204.23): C 52.93, H 7.90; found: C 52.83, H 7.82.

*(±)-3-*O*-[(*tert*)-Butyl)dimethylsilyl]-2,7-dideoxy-5,6-*O*-(isopropylidenedioxy)-2,4-di-*C*-methyl-*DL*-glycero-DL-altro-heptono-1,4-lactone* ((±)-**27**). A mixture of (±)-**25** (50 mg, 0.157 mmol), 2,2-dimethoxypropane (4 ml), and toluene-4-sulfonic acid (10 mg) was stirred at 20° for 3 days. The mixture was poured onto a mixture of ice (5 g) and CH_2Cl_2 (30 ml), the aq. phase extracted with CH_2Cl_2 (15 ml, twice), and the combined org. extract washed with a sat. aq. $NaHCO_3$ soln. (10 ml), dried ($MgSO_4$), and evaporated. FC (silica gel, Et_2O/light petroleum ether 1:4) yielded 50 mg (88%) of colourless needles. M.p. 66–67°. IR (KBr): 2950, 2940, 2920, 2860, 1780, 1250, 1210, 1140, 1075, 1055, 1040, 855, 830, 775. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.39 (*dq*, $^3J = 6.4$, 6.7, H–C(6)); 4.03 (*d*, $^3J = 7.3$, H–C(3)); 3.95 (*d*, $^3J = 6.4$, H–C(5)); 2.58 (*dq*, $^3J = 7.3$, 7.2, H–C(2)); 1.49, 1.43 (2*s*, 2 Me); 1.38 (*d*, $^3J = 6.7$, Me(7)); 1.35 (*s*, Me); 1.33 (*d*, $^3J = 7.2$, Me–C(2)); 0.91 (*s*, *t*-BuSi); 0.12 (*s*, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 173.9 (*s*, C(1)); 107.9 (*s*, Me_2C); 86.6 (*s*, C(4)); 81.6 (*d*, ^1J(C,H) = 145), 80.4 (*d*, ^1J(C,H) = 144), 73.7 (*d*, ^1J(C,H) = 146, C(3), C(5), C(6)); 42.9 (*d*, ^1J(C,H) = 129, C(2)); 29.7 (*q*, ^1J(C,H) = 128, Me); 27.4 (*q*, ^1J(C,H) = 128, Me); 25.7 (*q*, ^1J(C,H) = 126, *Me*CSi); 25.1 (*q*, ^1J(C,H) = 127, Me); 18.0 (*s*, Me_3*C*Si); 16.7 (*q*, ^1J(C,H) = 128, Me); 13.7 (*q*, ^1J(C,H) = 129, Me); −4.1, −4.9 (2*q*, ^1J(C,H) = 120, Me_2Si). CI-MS (NH_3): 359 (6, M^+), 343 (41), 301 (16), 243 (100), 217 (15), 199 (37), 187 (17), 171 (27), 159 (11), 143 (75), 115 (91), 99 (15), 97 (11), 85 (24), 75 (87), 73 (78). Anal. calc. for $C_{18}H_{34}O_5Si$ (358.56): C 60.30, H 9.56, Si 7.83; found: C 60.12, H 9.47, Si 7.92.

*(±)-3-*O*-[(*tert*)-Butyl)dimethylsilyl]-2,7-dideoxy-5,6-*O*-(isopropylidenedioxy)-2,4-di-*C*-methyl-*DL*-glycero-LD-altro-heptono-1,4-lactone* ((±)-**28**). Same procedure as for (±)-**27**, starting with (±)-**26**. Colourless crystals. M.p. 67°. IR (KBr): 2980, 2950, 2930, 2880, 2850, 1775, 1450, 1380, 1310, 1250, 1250, 1210, 1170, 1140, 1090, 1075, 1050, 1000, 955. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.10 (*d*, $^3J = 7.6$, H–C(3)); 4.04 (*dq*, $^3J = 7.9$, 6.0, H–C(6)); 3.61 (*d*, $^3J = 7.9$, H–C(5)); 2.61 (*dq*, $^3J = 7.6$, 7.4 H–C(2)); 1.40 (*s*, 2 Me); 1.36 (*d*, $^3J = 6.0$, Me(7)); 1.34 (*s*, Me–C(4)); 1.34 (*d*, $^3J = 7.4$, Me–C(2)); 0.90 (*s*, *t*-BuSi); 0.13 (*s*, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 176.1 (*s*, C(1)); 108.8 (*s*, Me_2C); 85.7 (*s*, C(4)); 86.2 (*d*, ^1J(C,H) = 147), 79.2 (*d*, ^1J(C,H) = 145), 73.1 (*d*, ^1J(C,H) = 146, C(3), C(5), C(6)); 43.0 (*d*, ^1J(C,H) = 128, C(2)); 27.2 (*q*, ^1J(C,H) = 128, 1C, Me_2C); 26.9 (*q*, ^1J(C,H) = 126, 1C, Me_2C); 25.7

(*q*, ^1J(C,H) = 126, Me_3CSi); 19.6 (*q*, ^1J(C,H) = 128, Me); 18.0 (*s*, Me_3CSi); 16.1 (*q*, ^1J(C,H) = 130, Me); 13.6 (*q*, ^1J(C,H) = 128, Me); −4.0, −5.0 (2*q*, ^1J(C,H) = 120, Me_2Si). CI-MS (NH_3): 359 (6, $M^{+\cdot}$), 343 (36), 301 (16), 243 (100), 215 (10), 199 (22), 187 (14), 171 (26), 159 (12), 157 (15), 143 (58), 117 (21), 115 (63), 111 (16), 99 (13), 85 (20), 75 (67), 73 (56). Anal. calc. for $C_{18}H_{34}O_5Si$ (358.56): C 60.30, H 9.56, Si 7.83; found: C 60.21, H 9.65, Si 7.74.

*(+)-3-*O*-[(*tert*-Butyl)dimethylsilyl]-2,7-dideoxy-5,6-*O*-(isopropylidenedioxy)-2,4-di-*C*-methyl-*L*-glycero-*L*-altro-heptono-1,4-lactone* ((+)-**27**). A 1M *L-Selectride* (lithium tri(*sec*-butyl)borohydride) soln. in anh. THF (6 ml, 6 mmol) was added dropwise to a stirred soln. of (−)-**24** (1.0 g, 3.16 mmol) in anh. THF (100 ml). After stirring at −78° for 1 h, sat. aq. NH_4Cl soln. (40 ml) was added and the mixture extracted with AcOEt (100 ml, twice). The combined org. extract was dried ($MgSO_4$) and evaporated. The residue ((+)-**25**/(−)-**26** 9:1) was taken with 2,2-dimethoxypropane (30 ml), and toluene-4-sulfonic acid (40 mg) was added. After stirring at 20° for 3 h, the soln. was poured into a mixture of ice (40 g) and CH_2Cl_2 (100 ml). The aq. phase was extracted with CH_2Cl_2 (40 ml, twice), the combined org. extract washed with brine (20 ml), dried ($MgSO_4$), and evaporated, and the residue purified by FC (silica gel, Et_2O/light petroleum ether 1:4): 906 mg (80%) of colourless needles. M.p. 55–56°. $[\alpha]_{589}^{25}$ = +7.7, $[\alpha]_{577}^{25}$ = +8.0, $[\alpha]_{546}^{25}$ = +8.8, $[\alpha]_{435}^{25}$ = +11.1, $[\alpha]_{405}^{25}$ = +11.2 (*c* = 1.015, $CHCl_3$). Anal. calc. for $C_{18}H_{34}O_5Si$ (358.56): C 60.30, H 9.56, Si 7.83; found: C 60.22, H 9.57, Si 7.91.

*(±)-(2*RS*,3*SR*,4*RS*,5*RS*,6*RS*)-3-[(*tert*-Butyl)dimethylsilyloxy]-5,6-(isopropylidenedioxy)-2,4-dimethylheptane-1,4-diol* ((±)-**29**). A mixture of (±)-**27** (100 mg, 0.28 mmol), $LiBH_4$ (12 mg, 0.56 mmol), and anh. THF (5 ml) was stirred at 20° for 24 h. The mixture was poured onto ice-cold half-sat. aq. NH_4Cl soln. (2 ml) and stirred for 30 min. The mixture was extracted with AcOEt (4 ml, twice). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by FC (silica gel, AcOEt/light petroleum ether 1:3): 78 mg (77%) of colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.35 (*dq*, ^3J = 6.0, 6.7 H–C(6)); 4.17 (*d*, ^3J = 6.0, H–C(5)); 3.78 (*d*, ^3J = 2.0, H–C(3)); 3.56 (*dd*, ^2J = 10.5, ^3J = 5.5, H–C(1)); 3.44 (*dd*, ^2J = 10.5, ^3J = 8.7, H′–C(1)); 2.50 (br. *s*, OH); 2.19 (*m*, H–C(2)); 2.04 (br. *s*, OH); 1.47 (*s*, Me); 1.40 (*d*, ^3J = 6.7, Me(7)); 1.33, 1.30 (2*s*, 2 Me); 0.94 (*d*, ^3J = 7.2, Me–C(2)); 0.93 (*s*, *t*-BuSi); 0.13, 0.12 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 107.2 (*s*, Me_2C); 75.7 (*s*, C(4)); 78.2 (*d*, ^1J(C,H) = 146), 76.7 (*d*, ^1J(C,H) = 144), 74.5 (*d*, ^1J(C,H) = 144, C(3), C(5), C(6)); 66.3 (*t*, ^1J(C,H) = 144, C(1)); 37.0 (*d*, ^1J(C,H) = 124, C(2)); 28.0 (*q*, ^1J(C,H) = 127, 1 C, Me_2C); 26.2 (*q*, ^1J(C,H) = 125, Me_3CSi); 25.5 (*q*, ^1J(C,H) = 126, 1C, Me_2C); 21.6 (*q*, ^1J(C,H) = 127, Me); 18.6 (*s*, Me_3CSi); 17.6 (*q*, ^1J(C,H) = 127, Me); 12.1 (*q*, ^1J(C,H) = 126, Me); −3.3, −4.3 (2*q*, ^1J(C,H) = Me_2Si). CI-MS (NH_3): 363 (19, $[M + 1]^+$), 347 (7), 305 (27), 287 (26), 247 (25), 229 (75), 203 (58), 189 (22), 173 (24), 159 (21), 145 (23), 115 (53), 89 (46), 75 (100), 73 (83).

*(2*S*,3*R*,4*S*,5*S*,6*S*)-3-[(*tert*-Butyl)dimethylsilyloxy]-5,6-(isopropylidenedioxy)-2,4-dimethylheptane-1,4-diol* ((+)-**29**). Same procedure as for (±)-**29**, starting with (+)-**27**. Colourless needles. M.p. 68–69°. $[\alpha]_{589}^{25}$ = +2.6, $[\alpha]_{577}^{25}$ = +2.9, $[\alpha]_{546}^{25}$ = +3.2, $[\alpha]_{435}^{25}$ = +6.3, $[\alpha]_{405}^{25}$ = +8.1 (*c* = 1.015, $CHCl_3$). IR (KBr): 3400 (br.), 2980, 2940, 2920, 2840, 1460, 1360, 1250, 1210, 1100, 1070, 1050, 1010, 955, 900, 865, 850, 760, 660. Anal. calc. for $C_{18}H_{38}O_5Si$ (362.59): C 59.63, H 10.56, Si 7.75; found: C 59.61, H 10.52, Si 7.72.

*(±)-(2*RS*,3*SR*,4*RS*,5*RS*,6*RS*)-3-[(*tert*-Butyl)dimethylsilyloxy]-4-hydroxy-5,6-(isopropylidenedioxy)-2,4-dimethylhept-1-yl Acetate* ((±)-**30**). A mixture of (±)-**29** (750 mg, 2.07 mmol), Ac_2O (10 ml), and pyridine (1 ml) was stirred at 20° for 1 h. After addition of toluene (50 ml), the solvent was evaporated, the residue taken with toluene (10 ml), and the solvent evaporated (twice). The residue was purified by FC (silica gel, AcOEt/light petroleum ether 1:3) yielding an oil that was bulb-to-bulb distilled: 781 mg (93%) of colourless oil. B.p. 165°/0.2 Torr. IR (film): 3500, 2980, 2940, 2920, 2880, 2820, 1735, 1460, 1370, 1250–1210, 1060–1025, 850, 830, 770. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.33 (*dq*, ^3J = 5.9, 6.7, H–C(6)); 4.14 (*d*, ^3J = 5.9, H–C(5)); 4.00 (*dd*, ^2J = 10.8, ^3J = 6.2, H–C(1)); 3.85 (*dd*, ^2J = 10.8, ^3J = 9.1, H–C(1)); 3.66 (*d*, ^3J = 1.5, H–C(3)); 2.41 (*m*, H–C(2)); 2.32 (*s*, OH–C(4)); 2.06 (*s*, Ac); 1.47 (*s*, Me); 1.38 (*d*, ^3J = 6.7, Me(7)); 1.32, 1.28 (2*s*, 2 Me); 0.94 (*d*, ^3J = 6.9, Me–C(2)); 0.94 (*s*, *t*-BuSi); 0.13, 0.12 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.9 (*s*, CO); 107.3 (*s*, Me_2C); 77.7 (*d*, ^1J(C,H) = 147), 76.9 (*d*, ^1J(C,H) = 148), 74.8 (*d*, ^1J(C,H) = 144, C(3), C(5), C(6)); 75.4 (*s*, C(4)); 67.8 (*t*, ^1J(C,H) = 150, C(1)); 33.0 (*d*, ^1J(C,H) = 129, C(2)); 28.1 (*q*, ^1J(C,H) = 130, 1 C, Me_2C); 26.1 (*q*, ^1J(C,H) = 125, Me_3CSi); 25.5 (*q*, ^1J(C,H) = 126, 1C, Me_2C); 21.4 (*q*, ^1J(C,H) = 127, Me); 21.0 (*q*, ^1J(C,H) = 129, Me); 18.6 (*s*, Me_3CSi); 17.7, 11.5 (2*q*, ^1J(C,H) = 127, 2 Me); −3.5, −4.4 (2*q*, ^1J(C,H) = 118, Me_2Si). CI-MS (NH_3): 422 (21, $[M + 18]^+$), 405 (41, $[M + 1]^+$), 389 (15), 347 (42), 273 (31), 245 (22), 229 (82), 213 (25), 185 (99), 171 (72), 159 (44), 115 (45), 75 (81), 73 (100).

*(+)-(2*S*,3*R*,4*S*,5*S*,6*S*)-3-[(*tert*-Butyl)dimethylsilyloxy]-4-hydroxy-5,6-(isopropylidenedioxy)-2,4-dimethylhept-1-yl Acetate* ((±)-**30**). Same procedure as for (±)-**30**, starting with (+)-**29** (577 mg): 598 mg (93%) of colourless oil. B.p. 175°/0.3 Torr. $[\alpha]_{589}^{25}$ = 0, $[\alpha]_{577}^{25}$ = 0, $[\alpha]_{546}^{25}$ = 0, $[\alpha]_{435}^{25}$ = 0, $[\alpha]_{405}^{25}$ = 0 (*c* = 1.03, $CHCl_3$). Anal. calc. for $C_{20}H_{40}O_6Si$ (404.62): C 59.37, H 9.96, Si 6.94; found: C 59.42, H 10.03, Si 6.90.

*(±)-(2*RS*,3*SR*,4*SR*,5*RS*,6*RS*)-3,4-Dihydroxy-5,6-(isopropylidenedioxy)-2,4-dimethylhept-1-yl Acetate* ((±)-**31**). At 0°, 1M Bu_4NF in THF (2.25 ml, 2.25 mmol) was added dropwise (in 15 min) to a stirred soln. of (±)-**30**

(760 mg, 1.88 mmol) in anh. THF (20 ml) cooled to 0°. After stirring at 0° for 1 h, half-sat. aq. NH_4Cl soln. (40 ml) was added and the mixture extracted with AcOEt (50 ml). The org. extract was washed with brine (10 ml), the combined aq. phase extracted with AcOEt (25 ml), the combined org. extract dried ($MgSO_4$) and evaporated and the residue purified by FC (silica gel, AcOEt/light petroleum ether 1:1) and bulb-to-bulb distillation: 520 mg (95%) of colourless oil. B.p. 200°/0.25 Torr. IR (film): 3470, 2970, 2920, 1720, 1450, 1370, 1230, 1025, 910, 855. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.39 (*dq*, ^3J = 6.0, 6.7, H–C(6)); 4.13 (*dd*, ^2J = 10.9, ^3J = 7.3, H–C(1)); 4.06 (*d*, ^3J = 6.0, H–C(5)); 3.98 (*dd*, ^2J = 10.9, ^3J = 5.8, H–C(1)); 3.58 (*d*, ^3J = 2.3, H–C(3)); 2.57 (br. *s*, OH); 2.34 (br. *s*, OH); 2.28 (*m*, H–C(2)); 2.06 (*s*, Ac); 1.47 (*s*, Me); 1.41 (*d*, ^3J = 6.7, Me(7)); 1.34, 1.33 (2*s*, 2 Me); 1.01 (*d*, ^3J = 6.9, Me–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.4 (*s*, CO); 107.2 (*s*, Me_2C); 80.2 (*d*, ^1J(C,H) = 145), 75.3 (*d*, ^1J(C,H) = 141), 74.2 (*d*, ^1J(C,H) = 146, C(3), C(5), C(6)); 75.1 (*s*, C(4)); 68.4 (*t*, ^1J(C,H) = 148, C(1)); 33.2 (*d*, ^1J(C,H) = 128, C(2)); 27.8 (*q*, ^1J(C,H) = 128, 1C, Me_2C); 25.4 (*q*, ^1J(C,H) = 126, 1 C, Me_2C); 21.0 (*q*, ^1J(C,H) = 130, Me); 20.9 (*q*, ^1J(C,H) = 126, Me); 17.2, 11.6 (2*q*, ^1J(C,H) = 127, 2 Me). CI-MS $(NH)_3$: 308 (10, $[M + 18]^+$), 291 (34, $]M + 1]^+$), 257 (15), 250 (23), 233 (100), 175 (13), 159 (12), 155 (17), 115 (77), 102 (22), 101 (25), 84 (45). Anal. calc. for $C_{14}H_{26}O_6$ (290.36): C 57.91, H 9.03; found: C 57.99, H 9.02.

(+)-(2S,3R,4R,5S,6S)-3,4-Dihydroxy-5,6-(isopropylidenedioxy)-2,4-dimethylhept-1-yl Acetate ((+)-**31**). Same procedure as for (±)-**31**, starting with (+)-**30**. Colourless oil. B.p. 195°/0.6 Torr. $[\alpha]_{589}^{25}$ = +4.8, $[\alpha]_{577}^{25}$ = +5.2, $[\alpha]_{546}^{25}$ = +6.0, $[\alpha]_{435}^{25}$ = +10.4, $[\alpha]_{405}^{25}$ = +12.8 (*c* = 1.0, $CHCl_3$). Anal. calc. for $C_{14}H_{26}O_6$ (290.36): C 57.91, H 9.03; found: C 57.99, H 8.95.

(±)-(2RS,3SR,4SR,5RS,6RS)-3,4:5,6-Bis(isopropylidenedioxy)-2,4-dimethylhept-1-yl Acetate ((±)-**32**). A mixture of (±)-**31** (0.5 g, 1.72 mmol), 2,2-dimethoxypropane (0.2 ml), acetone (5 ml), and toluene-4-sulfonic acid (20 mg) was stirred at 20° for 2 days (TLC (silica gel, AcOEt/light petroleum ether 1:3): R_f ((±)-**31**) 0.18, R_f ((±)-**32**) 0.55). The mixture was poured onto brine (50 ml) and extracted with Et_2O (60 ml, twice). The combined org. extract was dried ($MgSO_4$) and evaporated. FC (silica gel, AcOEt/light petroleum ether 1:3) followed by bulb-to-bulb distillation gave 340 mg (60%) of colourless oil. B.p. 165°/0.3 Torr. IR (film): 2980, 2925, 1735, 1450, 1370, 1235, 1230, 1220, 1210, 1190, 1170, 1100, 1070, 1030, 980, 930, 850. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.35 (*dq*, ^3J = 6.7, 6.4, H–C(6)); 4.20 (*dd*, ^2J = 11.0, ^3J = 3.9, H–C(1)); 4.12 (*dd*, ^2J = 11.0, ^3J = 5.2, H–C(1)); 4.11 (*d*, ^3J = 6.4, H–C(5)); 3.57 (*d*, ^3J = 9.3, H–C(3)); 2.20 (*m*, H–C(2)); 2.08 (*s*, Ac); 1.44, 1.37 (2*s*, 2 Me); 1.36 (*d*, ^3J = 6.7, Me(7)); 1.35, 1,34, 1.30 (3*s*, 3 Me); 1.11 (*d*, ^3J = 6.7, Me–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.1 (*s*, CO); 107.7, 106.3 (2*s*, 2 Me_2C); 81.8 (*s*, C(4)); 86.2 (*d*, ^1J(C,H) = 144), 75.7 (*d*, ^1J(C,H) = 145), 75.1 (*d*, ^1J(C,H) = 148, C(3), C(5), C(6)); 66.6 (*t*, ^1J(C,H) = 148, C(1)); 31.7 (*d*, ^1J(C,H) = 130, C(2)); 28.5, 27.7 (2*q*, ^1J(C,H) = 127, Me_2C); 26.3, 25.3 (2*q*, ^1J(C,H) = 126, Me_2C); 20.9 (*q*, ^1J(C,H) = 129, Me); 20.4, 17.9, 15.3 (3*q*, ^1J(C,H) = 127, 3 Me). CI-MS (NH_3): 348 (3, $[M + 18]^+$), 331 (30, $[M + 1]^+$), 315 (26), 273 (45), 215 (72), 157 (100), 154 (54), 137 (22), 115 (29), 112 (26), 97 (58), 84 (42). Anal. calc. for $C_{17}H_{30}O_6$ (330.43): C 61.80, H 9.15; found: C 61.83, H 9.18.

(−)-(2S,3R,4R,5S,6S)-3,4:5,6-Bis(isopropylidenedioxy)-2,4-dimethylhept-1-yl Acetate ((±)-**32**). Same procedure as for (±)-**32**, starting with (+)-**31** (275 mg). Yield 163 mg (52%). Colourless oil. B.p. 180°/0.25 Torr. $[\alpha]_{589}^{25}$ = −29.6, $[\alpha]_{577}^{25}$ = −30.9, $[\alpha]_{546}^{25}$ = −34.9, $[\alpha]_{435}^{25}$ = −57.1, $[\alpha]_{405}^{25}$ = −67.1 (*c* = 1.04, $CHCl_3$). Anal. calc. for $C_{17}H_{30}O_6$ (330.43): C 61.80, H 9.15; found: C 61.82, H 9.15.

(±)-(2RS,3SR,4SR,5RS,6RS)-3,4:5,6-Bis(isopropylidenedioxy)-2,4-dimethylheptan-1-ol ((±)-**33**). A mixture of (±)-**32** (320 mg, 0.97 mmol), anh. K_2CO_3 (134 mg, 0.97 mmol), and anh. MeOH (15 ml) was stirred at 20° for 12 h. The mixture was filtered through a pad of basic Al_2O_3 (AcOEt), the filtrate evaporated, and the residue purified by FC (silica gel, AcOEt/light petroleum ether 1:3) and then by bulb-to-bulb distillation: 248 mg (89%) of colourless oil. B.p. 100°/1 Torr. IR (film): 3440 (br.), 2980, 2920, 2870, 1450, 1370, 1250, 1210, 1185, 1160, 1100, 1070, 1040, 1020, 990, 970, 920, 850, 815, 800. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.39 (*dq*, ^3J = 6.4, 6.7, H–C(6)); 4.15 (*d*, ^3J = 6.4, H–C(5)); 3.63 (*dd*, ^3J = 5.2, 5.3, CH_2(1)); 3.55 (*d*, ^3J = 9.2, H–C(3)); 2.42 (*t*, ^3J = 5.3, OH–C(1)); 2.09 (*m*, H–C(2)); 1.48, 1.46 (2*s*, 2 Me); 1.40 (*d*, ^3J = 6.7, Me(7)); 1.38, 1.35, 1.34 (3*s*, 3 Me); 1.10 (*d*, ^3J = 6.8, Me–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 107.8, 106.1 (2*s*, 2 Me_2C); 87.8 (*d*, ^1J(C,H) = 143, C(6)); 82.0 (*s*, C(4)); 75.6 (*s*, ^1J(C,H) = 145), 75.3 (*d*, ^1J(C,H) = 147, C(3), C(5)); 66.1 (*t*, ^1J(C,H) = 142, C(1)); 34.9 (*d*, ^1J(C,H) = 128, C(2)); 28.5, 27.6, 26.3, 25.4 (4*q*, ^1J(C,H) = 126, 2 Me_2C); 20.5, 18.0, 15.5 (3*q*, ^1J(C,H) = 127, 3 Me). CI-MS (NH_3): 273 (7), 173 (78), 155 (28), 130 (12), 115 (100), 99 (71), 97 (44), 85 (53). Anal. calc. for $C_{15}H_{28}O_5$ (288.39): C 62.47, H 9.79; found: C 62.66, H 9.84.

(−)-(2S,3R,4R,5S,6S)-3,4:5,6-Bis(isopropylidenedioxy)-2,4-dimethylheptan-1-ol ((−)-**33**). Same procedure as for (±)-**33**, starting with (−)-**32** (120 mg, 0.36 mmol). Yield 94 mg (90%). Colourless oil. B.p. 150°/0.4 Torr. $[\alpha]_{589}^{25}$ = −20.7, $[\alpha]_{577}^{25}$ = −21.4, $[\alpha]_{546}^{25}$ = −23.9, $[\alpha]_{435}^{25}$ = −37.7, $[\alpha]_{405}^{25}$ = −43.3 (*c* = 0.70, $CHCl_3$). Anal. calc. for $C_{15}H_{28}O_5$ (288.39): C 62.47, H 9.79; found: C 62.47, H 9.73.

(±)-(2RS,3RS,4RS,5SR,6SR)-3,4:5,6-Bis(isopropylidenedioxy)-2,4-dimethylheptanal ((±)-**34**). A mixture of (±)-**33** (70 mg, 0.243 mmol), *N*-methylmorpholine *N*-oxide (49 mg, 0.365 mmol) and anh. CH_2Cl_2 (7 ml) was

stirred under Ar at 20° for 5 min. Finely ground 4-Å molecular sieves (65 mg) was added and the mixture stirred at 20° for 15 min. Tetrapropylammonium perruthenate (8.3 mg, 0.024 mmol) was added. After stirring at 20° for 15 min (TLC (silica gel, AcOEt/light petroleum ether 1:3): R_f ((±)-**33**) 0.31, R_f ((±)-**34**) 0.60), the black mixture was poured onto a pad of *Florisil*, rinsing with AcOEt/light petroleum ether 1:3 (20 ml): 60 mg (86%) of colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.72 (*d*, ^3J = 1.6, H–C(1)); 4.40 (*dq*, ^3J = 6.6, 6.7, H–C(6)); 3.97 (*d*, ^3J = 6.6, H–C(5)); 3.91 (*d*, ^3J = 9.8, H–C(3)); 2.98 (*ddq*, ^3J = 1.6, 7.1, H–C(2)); 1.40 (*d*, ^3J = 6.7, Me(7)); 1.38, 1.36, 1.34, 1.32, 1.31 (5*s*, 5 Me); 1.19 (*d*, ^3J = 7.1, Me–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 202.0 (*d*, ^1J(C,H) = 176, C(1)); 107.6, 106.9 (2*s*, Me_2C); 82.0 (*s*, C(4)); 84.7, 75.7, 74.5 (3*d*, ^1J(C,H) = 145, C(3), C(5), C(6)); 45.4 (*d*, ^1J(C,H) = 129, C(2)); 28.4, 26.9, 26.3, 25.1 (4*q*, ^1J(C,H) = 127, 2 Me_2C); 21.0, 16.9, 13.4, (3*q*, ^1J(C,H)= 128–130, 3 Me). CI-MS (NH_3): 271 (10), 171 (86), 153 (17), 115 (23), 99 (35), 85 (100), 71 (24).

*(+)-(2*R*,3*R*,4*R*,5*S*,6*S*)-3,4:5,6-Bis(isopropylidenedioxy)-2,4-dimethylheptanal* ((+)-**34**). Same procedure as for (±)-**34**, starting with (−)-**33** (80 mg, 0.277 mmol): 70 mg (89%) of colourless prisms. M.p. 71–73° (Et_2O/light petroleum ether). $[\alpha]_{589}^{25}$ = +5.8, $[\alpha]_{577}^{25}$ = +5.9, $[\alpha]_{546}^{25}$ = +7.0, $[\alpha]_{435}^{25}$ = +19.5, $[\alpha]_{405}^{25}$ = +28.6 (*c* = 1.00, $CHCl_3$). IR (KBr): 2980, 2920, 2890, 1720, 1710, 1460, 1450, 1375, 1250, 1210, 1100, 1050, 1030, 985, 930, 910, 820, 800. Anal. calc. for $C_{15}H_{26}O_5$ (286.37): C 62.91, H 9.15; found: C 62.85, H 9.04.

*(−)-(1*R*,4*R*,5*S*,6*R*)-6-*exo-*Hydroxy-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal* ((−)-**36**). Same procedure as for the preparation of (+)-**36** [23], starting with (+)-**2**. Colourless needles. M.p. 107–108° (Et_2O/light petroleum ether). $[\alpha]_{589}^{25}$ = −31.9, $[\alpha]_{577}^{25}$ = −33.5, $[\alpha]_{546}^{25}$ = −38.1, $[\alpha]_{435}^{25}$ = −67.3, $[\alpha]_{405}^{25}$ = −82.3 (*c* = 1.00, $CHCl_3$). Anal. calc. for $C_{10}H_{18}O_4$ (202.25): C 59.39, H 8.97; found: C 59.29, H 8.97.

*(±)-(1*RS*,4*RS*,5*SR*,6*RS*)-6-*exo-*[(*tert*-Butyl)dimethylsilyloxy]-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal* ((±)-**37**). At 0°, 2,6-lutidine (1.15 ml, 9.9 mmol) and then (*t*-Bu)$Me_2SiOSO_2CF_3$ (1.25 ml, 5.53 mmol) were added dropwise to a stirred soln. of (±)-**36** [23] (1.00 g, 4.94 mmol) in anh. CH_2Cl_2 (50 ml). After stirring at 0° for 15–25 min, the mixture was poured onto ice-cold brine (15 ml) and extracted with CH_2Cl_2 (50 ml, 3 times). The combined org. phase was dried ($MgSO_4$) and evaporated and the residue purified by FC (silica gel, Et_2O/light petroleum ether 2:7): 1.49 g (95%) of colourless needles. M.p. 61° (light petroleum ether). IR (KBr): 3000, 2960, 2920, 2855, 1460, 1450, 1380, 1370, 1250, 1110, 1070, 1040, 1010, 970, 940, 875, 835, 800, 775, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.25 (*dd*, ^3J = 6.0, 5.8, H–C(4)); 3.74 (*d*, ^3J = 2.9, H–C(6)); 3.23, 3.20 (2*s*, 2 MeO); 2.12 (*dddq*, ^3J = 5.8, 2.9, 7.2, ^4J = 1.1, H–C(5)); 2.00 (*ddd*, ^2J = 12.8, ^3J = 6.0, ^4J = 1.1, H_{exo}–C(3)); 1.73 (*d*, ^2J = 12.8, H_{endo}–C(3)); 1.38 (*s*, Me–C(1)); 1.08 (*d*, ^3J = 7.2, Me–C(5)); 0.92 (*s*, *t*-Bu); 0.10, 0.09 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 107.8 (*s*, C(2)); 91.7 (*s*, C(1)); 78.9 (*d*, ^1J(C,H) = 151), 78.6 (*d*, ^1J(C,H) = 157, C(4), C(6)); 50.4 (*q*, ^1J(C,H) = 142, MeO); 48.6 (*d* and *q*, ^1J(C,H) = 142, C(5), MeO); 36.5 (*t*, ^1J(C,H) = 132, C(3)); 25.9 (*q*, ^1J(C,H) = 125, *t*-Bu); 18.1 (*s*, Me_3CSi); 13.4 (*q*, ^1J(C,H) = 128, Me); 13.0 (*q*, ^1J(C,H) = 125, Me); −4.1, −4.6 (2*q*, ^1J(C,H) = 118, Me_2Si). CI-MS (NH_3): 316 (11, M^+), 285 (39), 259 (15), 199 (11), 129 (100), 112 (14), 89 (18), 75 (46), 73 (68). Anal. calc. for $C_{16}H_{32}O_4Si$ (316.52): C 60.72, H 10.19, Si 8.87; found: C 60.65, H 10.04, Si 8.93.

*(−)-(1*R*,4*R*,5*S*,6*R*)-6-*exo-*[(*tert*-Butyl)dimethylsilyloxy]-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one Dimethyl Acetal* ((−)-**37**). Same procedure as for (±)-**37**, starting with (−)-**36** (1.0 g, 4.94 mmol). Yield 1.51 g (96%). Colourless needles. M.p. 80–81° (Et_2O/light petroleum ether). $[\alpha]_{589}^{25}$ = −12.0, $[\alpha]_{577}^{25}$ = −12.4, $[\alpha]_{546}^{25}$ = −14.3, $[\alpha]_{435}^{25}$ = −26.1, $[\alpha]_{405}^{25}$ = −32.6 (*c* = 1.00, $CHCl_3$). Anal. calc. for $C_{16}H_{32}O_4Si$ (316.52): C 60.72, H 10.19, Si 8.87; found: C 60.74, H 10.28, Si 8.90.

*(±)-(1*RS*,4*RS*,5*SR*,6*RS*)-6-*exo-*[(*tert*-Butyl)dimethylsilyloxy]-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one* ((±)-**38**). A mixture of (±)-**37** (1.0 g, 3.16 mmol), *Amberlite IR 120* (950 mg), and acetone (100 ml) was stirred at 20° for 6–7 h (TLC (silica gel, CH_2Cl_2/Et_2O/light petroleum ether 3:1:4)). The precipitate was filtered off and the soln. immediately filtered though a pad of silica gel (Et_2O/light petroleum ether). The solvent was evaporated and the residue purified by bulb-to-bulb distillation: 720 mg (84%) of colourless oil. B.p. 80°/1 Torr. IR (film): 2950, 2920, 2880, 2850, 1760, 1460, 1405, 1375, 1250, 1140, 1125, 1105, 1070, 1040, 1000, 965, 895, 870, 830, 800, 770. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.67 (*dd*, ^3J = 5.6, 5.7, H–C(4)); 3.36 (*d*, ^3J = 3.2, H–C(6)); 2.36 (*ddd*, ^2J = 17.6, ^3J = 5.7, ^4J = 1.6, H_{exo}–C(3)); 2.32 (*dddq*, ^3J = 3.2, 5.6, ^4J = 1.6, ^3J = 7.4, H–C(5)); 2.26 (*d*, ^2J = 17.6, H_{endo}–C(3)); 1.32 (*s*, Me–C(1)); 1.06 (*d*, ^3J = 7.4, Me–C(5)); 0.91 (*s*,*t*-BuSi); 0.07, 0.06 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 213.9 (*s*, C(2)); 91.3 (*s*, C(1)); 79.9 (*d*, ^1J(C,H) = 143), 77.7 (*d*, ^1J(C,H) = 148, C(4), C(6)); 48.1 (*d*, ^1J(C,H) = 135, C(5)); 38.8 (*t*, ^1J(C,H) = 134, C(3)); 25.7 (*q*, ^1J(C,H) = 125, *t*-BuSi); 18.1 (*s*, Me_3CSi); 13.8 (*q*, ^1J(C,H) = 126, Me); 10.7 (*q*, ^1J(C,H) = 128, Me); −4.5, −4.8 (2*q*, ^1J(C,H) = 118, Me_2Si). CI-MS (NH_3): 271 (16, M^+), 214 (12), 213 (69), 199 (17), 195 (17), 185 (12), 97 (9), 83 (19), 75 (57), 73 (100). Anal. calc. for $C_{14}H_{26}O_3Si$ (270.45): C 62.18, H 9.69, Si 10.39; found: C 62.33, H 9.52, Si 10.50.

*(−)-(1*R*,4*R*,5*S*,6*R*)-6-*exo-*[(*tert*-Butyl)dimethylsilyloxy]-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-one* ((−)-**38**). Same procedure as for (±)-**38**, starting with (−)-**37** (2.5 g). Yield 2.1 g (98%). Colourless oil. B.p.

145°/0.2 Torr. $[\alpha]_{589}^{25} = -1.6$, $[\alpha]_{577}^{25} = -2.0$, $[\alpha]_{546}^{25} = -2.8$, $[\alpha]_{435}^{25} = -6.2$, $[\alpha]_{405}^{25} = -8.6$ ($c = 1.015$, $CHCl_3$). Anal. calc. for $C_{14}H_{26}O_3Si$ (270.45): C 62.18, H 9.69, Si 10.39; found: C 62.03, H 9.59, Si 10.56.

*(1R,3S,4S,5S,6R)-6-*exo-*[(*tert*-Butyl)dimethylsilyloxy]-3-*exo-*[(1'S,2'S,3'R,4'R,5'S,6'S)-1'-hydroxy-3',4':5',6'-bis(isopropylidenedioxy)-2',4'-dimethylhept-1'-yl]-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptan-2-one* ((±)-**39**) *and (1R,3S,4S,5S,6R)-6-*exo-*[(*tert*-Butyl)dimethylsilyloxy]-3-*exo-*[(1'R,2'S,3'R,4'R,5'S,6'S)-1'-hydroxy-3',4':5',6'-bis(isopropylidenedioxy)-2',4'-dimethylhept-1'-yl]-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**40**). At 0°, 1.6M BuLi in hexane (0.11 ml, 0.176 mmol) was added dropwise to a stirred soln. of $(Me_3Si)_2NH$ (40 µl, 0.24 mmol) in anh. THF (0.6 ml). After stirring at 0° for 15 min, the soln. was cooled to −78°. A soln. of (−)-**38** (40 mg, 0.15 mmol) in anh. THF (1.4 ml) was added dropwise in 2.5 h. After stirring at −78° for 30 min, the soln. was cooled to −95° and a soln. of (+)-**34** (35 mg, 0.12 mmol) in anh. THF (0.4 ml) added slowly. After stirring at −95° for 15 min, 10% AcOH in MeOH (3 ml) was added and the mixture allowed to warm up to 20° slowly. CH_2Cl_2 (20 ml) was added and the soln. washed with sat.-aq. NH_4Cl soln. (5 ml). The aq. phase was extracted with CH_2Cl_2 (10 ml) and the combined extract dried ($MgSO_4$) and evaporated; (+)-**39**/(+)-**40** 3:2. Separation by FC (silica gel, AcOEt/light petroleum ether 1:8) gave 30 mg (45%) of (+)-**39**, 20 mg (30%) of (+)-**40**, 6 mg of (−)-**38** (15%), and 3 mg of (+)-**34** (9%).

*Data of (+)-***39**: Colourless needles. M.p. 155° (Et_2O/light petroleum ether). $[\alpha]_{589}^{25} = +25.4$, $[\alpha]_{577}^{25} = +27.6$, $[\alpha]_{546}^{25} = +32.2$, $[\alpha]_{435}^{25} = +62.4$, $[\alpha]_{405}^{25} = +82.4$ ($c = 0.50$, $CHCl_3$). IR (CH_2Cl_2): 2920, 2880, 2850, 1750, 1370, 1130, 1080, 920, 830. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.74 (*d*, $^3J = 5.8$, H−C(4)); 4.37 (*dq*, $^3J = 6.5$, 6.2, H−C(6')); 4.25 (*ddd*, $^3J = 7.4$, 2.3, 5.2, H−C(1')); 4.11 (*d*, $^3J = 6.5$, H−C(5')); 3.78 (*d*, $^3J = 7.7$, H−C(3')); 3.39 (*d*, $^3J = 3.4$, H−C(6)); 2.37 (*d*, $^3J = 7.4$, H−C(3)); 2.36 (*ddq*, $^3J = 5.8$, 3.4, 7.3, H−C(5)); 2.29 (*ddq*, $^3J = 2.3$, 7.7, 6.5, H−C(2')); 2.25 (*d*, ^3J = OH−C(1')); 1.48, 1.41 (2*s*, 2 Me); 1.40 (*d*, $^3J = 6.2$, Me(7')); 1.37, 1.35, 1.32, 1.31 (4*s*, 4 Me); 1.11 (*d*, $^3J = 7.3$, Me−C(5)); 1.10 (*d*, $^3J = 6.5$, Me−C(2')); 0.91 (*s*, *t*-BuSi); 0.07, 0.06 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 212.6 (*s*, C(2)); 107.6, 106.1 (2*s*, 2 Me_2C); 91.2 (*s*, C(1)); 86.1 (*d*, ^1J(C,H) = 142, C(6')); 82.3 (*s*, C(4')); 80.1 (*d*, ^1J(C,H) = 159), 77.2 (*d*, ^1J(C,H) = 158), 75.5 (*d*, ^1J(C,H) = 143), 75.0 (*d*, ^1J(C,H) = 145), 71.1 (*d*, ^1J(C,H) = 150, C(4), C(6), C(1'), C(3'), C(5')); 50.9, 47.9 (2*d*, ^1J(C,H) = 134, C(3), C(5)); 35.3 (*d*, ^1J(C,H) = 130, C(2')); 28.6, 27.4, 26.5, 25.2 (4*q*, ^1J(C,H) = 126, 2 Me_2C); 25.7 (*q*, ^1J(C,H) = 125, Me_3CSi); 20.7 (*q*, ^1J(C,H) = 127, Me); 18.1 (*s*, Me_3CSi); 17.8, 13.7, 11.0, 10.0 (4*q*, ^1J(C,H) = 127, 4 Me); −4.4, −4.8 (2*q*, ^1J(C,H) = 118, Me_2Si). CI-MS (NH_3): 557 (1, $[M + 1]^+$), 542 (4), 442 (11), 441 (11), 213 (12), 185 (11), 171 (20), 115 (22), 113 (23), 99 (23), 85 (45), 75 (66), 73 (100). Anal. calc. for $C_{29}H_{52}O_8Si$ (556.34): C 62.55, H 9.42, Si 5.03; found: C 62.45, H 9.48, Si 4.97.

*Data of (+)-***40**: Colourless crystals. M.p. 113–114° (Et_2O/light petroleum ether). $[\alpha]_{589}^{25} = +15.8$, $[\alpha]_{577}^{25} = +17.0$, $[\alpha]_{546}^{25} = +20.5$, $[\alpha]_{435}^{25} = +52.4$, $[\alpha]_{405}^{25} = +78.8$ ($c = 0.40$, $CHCl_3$). IR (KBr): 2950, 2920, 1740, 1250, 1080, 1040, 1030, 870, 860, 800. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.56 (*d*, $^3J = 5.8$, H−C(4)); 4.37 (*dq*, $^3J = 6.7$, 6.6, H−C(6')); 4.17 (*d*, $^3J = 6.7$, H−C(5')); 3.86 (*ddd*, ^1J(C,H) = 6.3, 5.0, 3.4, H−C(1')); 3.80 (*d*, $^3J = 2.8$, H−C(3')); 3.39 (*d*, $^3J = 3.3$, H−C(6)); 3.30 (*d*, $^3J = 3.4$, OH−C(1')); 2.48 (*ddq*, $^3J = 5.0$, 2.8, 6.9, H−C(2')); 2.43 (*d*, $^3J = 6.3$, H−C(3)); 2.33 (*ddq*, $^3J = 5.8$, 3.3, 7.2, H−C(5)); 1.46, 1.39 (2*s*, 2 Me); 1.39 (*d*, $^3J = 6.6$, Me(7')); 1.36, 1.35, 1.34, 1.33 (4*s*, 4 Me); 1.13 (*d*, $^3J = 6.9$, Me−C(2')); 1.07 (*d*, $^3J = 7.2$, Me−C(5)); 0.91 (*s*, *t*-BuSi); 0.07, 0.06 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 214.6 (*s*, C(2)); 107.7, 107.0 (2*s*, 2 Me_2C); 91.8 (*s*, C(1)); 84.1 (*d*, ^1J(C,H) = 141, C(6')); 82.6 (*s*, C(4')); 81.6 (*d*, ^1J(C,H) = 160), 79.8 (*d*, ^1J(C,H) = 141), 75.8 (*d*, ^1J(C,H) = 144), 75.7 (*d*, ^1J(C,H) = 140), 75.2 (*d*, ^1J(C,H) = 145, C(4), C(6), C(1'), C(3'), C(5')); 49.7 (*d*, ^1J(C,H) = 133), 48.2 (*d*, ^1J(C,H) = 131, C(3), C(5)); 35.2 (*d*, ^1J(C,H) = 132, C(2')); 28.6, 27.6, 26.5, 25.1 (4*q*, ^1J(C,H) = 127–128, 2 Me_2C); 25.7 (*q*, ^1J(C,H) = 125, Me_3CSi); 20.6 (*q*, ^1J(C,H) = 128, Me); 18.0 (*s*, Me_3CSi); 17.9 13.5, 11.7, 10.6 (4*q*, ^1J(C,H) = 127, 4 Me); −4.5, −4.8 (2*q*, ^1J(C,H) = 118, Me_2Si). CI-MS (NH_3): 557 (1, $[M + 1]^+$), 542 (2), 442 (2), 383 (9), 355 (10), 213 (23), 195 (11), 185 (11), 171 (39), 113 (29), 99 (15), 97 (16), 95 (13), 83 (18), 75 (68), 73 (100).

*(1RS,3SR,4SR,5SR,6RS)-6-*exo-*[(*tert*-Butyl)dimethylsilyloxy]-3-*exo-*[(1'RS,2'RS,3'SR,4'SR,5'RS,6'RS)-1'-hydroxy-3',4':5',6'-bis(isopropylidenedioxy)-2',4'-dimethylhept-1'-yl]-1,5-*endo*-dimethyl-7-oxabicyclo-[2.2.1]heptan-2-one* ((±)-**41**). Same procedure as for (+)-**39** and (+)-**40**, starting with (±)-**38** (20 mg, 0.074 mmol) and (±)-**34** (21 mg, 0.074 mmol). FC (silica gel, CH_2Cl_2/Et_2O/light petroleum ether 3:1:7) gave 25 mg (60%) of (±)-**41** and 1.5 mg (3.5%) of (±)-**39**. (±)-**41**: Colourless crystals. M.p. 148–150°. IR (KBr): 3520, 2970, 2940, 2920, 2880, 2850, 1730, 1460, 1400, 1375, 1360, 1250, 1210, 1085, 1050, 990, 865, 835, 770, 660. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.37 (*dq*, $^3J = 6.5$, 6.7, H−C(6')); 4.36 (*d*, $^3J = 5.5$, H−C(4)); 4.32 (br. *dd*, $^3J = 1.9$, H−C(1')); 4.13 (*d*, $^3J = 6.5$, H−C(5')); 3.85 (*d*, $^3J = 10.0$, H−C(3')); 3.42 (*d*, $^3J = 3.9$, H−C(6)); 2.93 (br. *s*, OH−C(1')); 2.33 (*d*, $^3J = 9.8$, H−C(3)); 2.29 (*ddq*, $^3J = 5.5$, 3.9, 7.3, H−C(5)); 2.12 (*ddq*, $^3J = 1.9$, 10.0, 6.8, H−C(2')); 1.46, 1.43 (2*s*, 2 Me); 1.39 (*d*, $^3J = 6.7$, Me(7')); 1.37, 1.34, 1.33, 1.30 (4*s*, 4 Me); 1.12 (*d*, $^3J = 7.3$, Me−C(5)); 1.03 (*d*, $^3J = 6.8$, Me−C(2')); 0.91 (*s*, *t*-BuSi); 0.07, 0.06 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 216.9 (*s*, C(2)); 108.0, 105.8 (2*s*, 2 Me_2C); 90.9 (*s*, C(1)); 85.7 (*d*, ^1J(C,H) = 147, C(6')); 82.1 (*s*, C(4')); 79.4 (*d*, ^1J(C,H) = 141), 79.1 (*d*,

^1J(C,H) = 159), 76.7 (*d*, ^1J(C,H) = 143), 75.6 (*d*, ^1J(C,H) = 145), 69.0 (*d*, ^1J(C,H) = 150, C(4), C(6), C(1'), C(3'), C(5')); 49.6 (*d*, ^1J(C,H) = 135), 48.2 (*d*, ^1J(C,H) = 139, C(3), C(5)); 35.6 (*d*, ^1J(C,H) = 125, C(2')); 28.6, 27.2, 26.4, 25.2 (4*q*, ^1J(C,H) ≅ 125, Me_2C); 25.7 (*q*, ^1J(C,H) = 125, Me_3CSi); 20.5 (*q*, ^1J(C,H) = 131, Me); 18.1 (*s*, Me_3CSi); 17.9, 13.4, 10.6, 9.9 (4*q*, ^1J(C,H) = 125–128, 4 Me); −4.4, −4.8 (2*q*, ^1J(C,H) = 119, Me_2Si). CI-MS (NH_3): 557 (100, $[M + 1]^+$), 499 (37), 481 (20), 442 (28), 383 (17), 271 (52), 229 (17), 213 (23), 171 (63), 73 (78). Anal. calc. for $C_{29}H_{52}O_8Si$ (556.34): C 62.55, H 9.42, Si 5.03; found: C 62.42, H 9.43, Si 5.02.

*(1S,3R,4R,5R,6S)-6-*exo*-(Benzyloxy)-3-*exo*-[(1'S,2'S,3'R,4'R,5'S,6'S)-1'-hydroxy-3',4':5',6'-bis(isopropylidenedioxy)-2',4'-dimethylhept-1'-yl]-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptan-2-one* ((−)-**44**). Same procedure as for the preparation of (+)-**39** and (+)-**40**, starting with (+)-(1*S*,4*S*,5*S*,6*S*)-5-*exo*-(benzyloxy)-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptan-2-one ((+)-**43**) [23] (17.2 mg, 0.07 mmol) and (+)-**34** (20 mg, 0.07 mmol). FC (silica gel, AcOEt/light petroleum ether 1:8) gave (−)-**44** (21 mg, 57%), (+)-**43** (4 mg, 20%), and (+)-**34** (3 mg, 15%). (−)-**44**: Colourless oil. $[\alpha]_{589}^{25} = -47.8$, $[\alpha]_{577}^{25} = -51.0$, $[\alpha]_{546}^{25} = -58.6$, $[\alpha]_{435}^{25} = -115.4$, $[\alpha]_{405}^{25} = -153.2$ (*c* = 0.50, $CHCl_3$). IR (CH_2Cl_2): 2920, 2880, 1740, 1370, 1070, 995, 855. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.28 (*m*, Ph); 4.56 (*s*, PhCH_2); 4.40 (*d*, ^3J = 5.9, H–C(4)); 4.37 (*dq*, ^3J = 6.5, 6.7, H–C(6')); 4.35 (*ddd*, ^3J = 9.8, 1.9, 1.4, H–C(1')); 4.13 (*d*, ^3J = 6.5, H–C(5')); 3.85 (*d*, ^3J = 10.1, H–C(3')); 3.21 (*d*, ^3J = 3.9, H–C(6)); 2.86 (*dd*, ^3J = 1.4, ^4J = 1.3, OH–C(1')); 2.46 (*ddq*, ^3J = 5.9, 3.9, 7.3, H–C(5)); 2.33 (*d*, ^3J = H–C(3)); 2.12 (*dddq*, ^3J = 1.9, 10.1, 6.8, ^4J = 1.3, H–C(2')); 1.46, 1.45, 1.43 (3*s*, 3 Me); 1.39 (*d*, ^3J = 6.7, H–C(7')); 1.37, 1.35, 1.33 (3*s*, 3 Me); 1.07 (*d*, ^3J = 7.3, Me–C(5)); 1.02 (*d*, ^1J = 6.8, Me–C(2')); assignments confirmed by 2D NOESY. ^{13}C-NMR (100.6 MHz, $CDCl_3$): 216.2 (*s*, C(2)); 137.5 (*s*, arom. C); 128.5 (*d*, ^1J(C,H) = 160); 128.0 (*d*, ^1J(C,H) = 161); 127.7 (*d*, ^1J(C,H) = 158); 108.0, 105.8 (2*s*, 2 Me_2C); 90.5 (*s*, C(1)); 82.1 (*s*, C(4')); 72.4 (*t*, ^1J(C,H) = 142, PhCH_2); 85.7 (*d*, ^1J(C,H) = 147), 84.8 (*d*, ^1J(C,H) = 143), 79.1 (*d*, ^1J(C,H) = 161), 75.6 (*d*, ^1J(C,H) = 144), 75.0 (*d*, ^1J(C,H) = 149), 68.8 (*d*, ^1J(C,H) = 150, C(4), C(6), C(1'), C(3'), C(5'), C(6')); 49.6, 46.0 (2*d*, ^1J(C,H) = 133), 34.6 (*d*, ^1J(C,H) = 127, C(3), C(5), C(2')); 28.6, 27.1, 26.4, 25.2 (4*q*, ^1J(C,H) = 126, 2 Me_2C); 20.5 (*q*, ^1J(C,H) = 129); 17.9 (*q*, ^1J(C,H) = 127); 14.1 (*q*, ^1J(C,H) = 126); 10.5 (*q*, ^1J(C,H) = 129); 9.9 (*q*, ^1J(C,H) = 127). CI-MS (NH_3): 532 (1, $M^{+\cdot}$), 517 (1), 475 (1), 417 (8), 339 (2), 331 (2), 325 (2), 249 (2), 171 (7), 155 (5), 125 (8), 115 (13), 99 (11), 91 (100).

*(1R,2R,3S,4R,5R,6S)-6-*exo*-(Benzyloxy)-3-*exo*-[(1'S,2'S,3'R,4'R,5'S,6'S)-1'-hydroxy-3',4':5',6'-bis(isopropylidenedioxy)-2',4'-dimethylhept-1'-yl]-1,5-*endo*-dimethyl-7-oxabicyclo-[2.2.1]heptan-2-*exo*-ol* (**45**). A soln. of *L-Selectride* (1M in THF, 0.1 ml) was added dropwise to a stirred soln. of (−)-**44** (10 mg, 0.019 mmol) in anh. THF (0.5 ml). After stirring at −78° for 3 h, the mixture was stirred at 20° for 1.5 h, and 3N NaOH (0.2 ml), then 30% H_2O_2 soln. (0.2 ml) were added. After stirring at 20° for 12 h, the mixture was extracted with AcOEt (10 ml, twice). The combined org. extract was washed with brine (3 ml), dried ($MgSO_4$), and evaporated and the residue purified by FC (silica gel, AcOEt/light petroleum ether 1:3): 9 mg (86%) of colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.27 (*m*, Ph); 4.58, 4.52 (2*d*, ^2J = 12.0, PhCH_2); 4.39 (*dq*, ^3J = 6.6, 6.7, H–C(6')); 4.21 (br. *dd*, ^3J = 10.7, 1.5, H–C(1')); 4.15 (*d*, ^3J = 6.6, H–C(5')); 4.06 (*d*, ^3J = 5.1, H–C(4)); 3.88 (*d*, ^3J = 9.3, H–C(3')); 3.79 (*dd*, ^3J = 6.8, 7.2, H–C(2)); 2.95 (*d*, ^3J = 4.4, H–C(6)); 2.91 (*s*, OH–C(1')); 2.36 (*d*, ^3J = 7.2, OH–C(2)); 2.31 (*dd*, ^3J = 10.7, 6.8, H–C(3)); 2.13–1.97 (*m*, H–C(5), H–C(2')); 1.51, 1.47, 1.45 (3*s*, 3 Me); 1.41 (*d*, ^3J = 6.7, H–C(7')); 1.38, 1.36, 1.33 (3*s*, 3 Me); 1.07 (*d*, ^3J = 6.8); 1.06 (*d*, ^3J = 7.1, Me–C(5), Me–C(2')); assignments confirmed by NOESY. ^{13}C-NMR (100.6 MHz, $CDCl_3$): 138.1 (*s*); 128.4, 127.6 (2*d*, ^1J(C,H) = 160); 127.5 (*d*, ^1J(C,H) = 158); 107.9, 105.9 (2*s*); 90.7 (*s*, C(1)); 82.2 (*s*, C(4')); 71.7 (*t*, ^1J(C,H) = 140, PhCH_2); 86.7 (*d*, ^1J(C,H) = 143), 86.5 (*d*, ^1J(C,H) = 145), 79.1 (*d*, ^1J(C,H) = 157), 76.7 (*d*, ^1J(C,H) = 149, 75.6 (*d*, ^1J(C,H) = 144), 75.0 (*d*, ^1J(C,H) = 146), 68.8 (*d*, ^1J(C,H) = 145, C(2), C(4), C(6), C(1'), C(3'), C(5'), C(6')); 46.3 (*d*, ^1J(C,H) = 129), 45.9 (*d*, ^1J(C,H) = 131, C(3), C(5)); 34.5 (*d*, ^1J(C,H) = 127, C(2')); 28.6, 27.2 26.4, 25.2 (4*q*, ^1J(C,H) = 127, 4 Me_2C); 20.7 (*q*, ^1J(C,H) = 126); 17.8 (*q*, ^1J(C,H) = 127); 13.9 (*q*, ^1J(C,H) = 125); 11.6 (*q*, ^1J(C,H) = 128); 9.7 (*q*, ^1J(C,H) = 129).

*(1S,2R,6S,7S,8R,9R,10S)-10-*exo*-(Benzyloxy)-6-[(1'S,2'R,3'R,4'S,5'S)-2',3':4',5'-bis(isopropylidenedioxy)-1',3'-dimethylhex-1'-yl]-1,9-*endo*-dimethyl-3,5,11-trioxabicyclo[6.2.1.0^{2,7}]undecane* (**46**). At 0°, 2,6-lutidine (10 µl), then $Me_3SiOSO_2CF_3$ (25 µl) were added to a stirred soln. of **45** (8 mg, 0.015 mmol) in $(MeO)_2CH_2$ (0.5 ml). After stirring at 0° for 10 min (yellow soln.), H_2O (1 ml) was added, the mixture extracted with CH_2Cl_2 (5 ml, twice), and the combined extract dried ($MgSO_4$). FC (silica gel, AcOEt/light petroleum ether 1:8) gave 3 mg (36%) of colourless oil. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.38–7.28 (*m*, Ph); 4.96 (*d*, ^2J = 4.0, H_{exo}–C(4)); 4.86 (*d*, ^2J = 4.0, H_{endo}–C(4)); 4.59, 4.51 (2*d*, ^2J = 12.4, PhCH_2); 4.38 (*dq*, ^3J = 6.6, 6.7, H–C(5')); 4.16–4.07 (*m*, H–C(6), H–C(2'), H–C(4')); 3.78 (*d*, ^3J = 9.5, H–C(8)); 3.60 (*d*, ^3J = 7.2, H–C(2)); 2.92 (*d*, ^3J = 3.8, H–C(10)); 2.39 (*dd*, ^3J = 7.1, 10.0, H–C(7)); 2.37–2.26 (*m*, H–C(9)); 2.18–2.10 (*m*, H–C(1')); 1.54, 1.46, 1.43 (3*s*, 3 Me); 1.40 (*d*, ^3J = 6.7, H–C(6')); 1.37, 1.34, 1.32 (3*s*, 3 Me); 1.10 (*d*, ^3J = 6.7, Me–C(9)); 1.05 (*d*, ^3J = 7.6, Me–C(1')); assignments confirmed by NOESY.

*(1S,2S,3R,4S,5S,6R)-6-*exo*-[(*tert*-Butyl)dimethylsilyloxy]-3-*exo*-[(1'S,2'S,3'R,4'R,5'S,6'S)-1'-hydroxy-3',4':5',6'-bis(isopropylidenedioxy)-2',4'-dimethylhept-1'-yl]-1,5-*endo*-dimethyl-7-oxabicyclo[2.2.1]heptan-2-*exo*-*

ol (**47**). Same procedure as for **45**, starting with (+)-**39** (10 mg, 0.018 mmol). FC (silica gel, AcOEt/light petroleum ether 1:3) gave 7 mg (70%) of colourless oil. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.41 (*dq*, ^3J = 6.6, 6.7, H–C(6′)); 4.41 (*d*, ^3J = 5.2, H–C(4)); 4.17 (*ddd*, ^3J = 5.8, ^3J = 2.7, 6.8, H–C(1′)); 4.15 (*d*, ^3J = 6.6, H–C(5′)); 3.79 (*d*, ^3J = 8.0, H–C(3′)); 3.58 (*dd*, ^3J = 7.2, 10.8, H–C(2)); 3.12 (*d*, ^3J = 3.9, H–C(6)); 3.00 (*d*, ^3J = 10.8, OH–C(2)); 2.40 (*ddq*, ^3J = 2.7, 8.0, 6.8, H–C(2′)); 2.22 (*dd*, ^3J = 7.2, 5.8, H–C(3)); 2.10 (*d*, ^3J = 6.8, OH–C(1′)); 2.06 (*ddq*, ^3J = 3.9, 5.2, 7.2, H–C(5)); 1.51, 1.43 (2*s*, 2 Me); 1.42 (*d*, ^3J = 6.7, Me(7′)); 1.37, 1.35, 1.34, 1.33 (4*s*, 4 Me); 1.11 (*d*, ^3J = 6.8, Me–C(2′)); 1.04 (*d*, ^3J = 7.2, Me–C(5)); 0.92 (*s*, *t*-Bu); 0.07 (*s*, Me_2Si).

*(1S,2S,6S,7R,9S,10R)-10-*exo-*[(*tert-*Butyl)dimethylsilyloxy]-6-[(1′S,2′R,3′R,4′S,5′S)-2′,3′:4′,5′-bis(isopropylidenedioxy)-1′,3′-dimethylhex-1′-yl]-1,9-*endo-*dimethyl-3,5,11-trioxatricyclo[6.2.1.0^{2,7}]undecane* (**48**). Same procedure as for **46**, starting with **47** (7 mg, 0.012 mmol). Yield: 4 mg (56%). Colourless oil. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.11 (*d*, ^2J = 5.6, H_{exo}–C(4)); 4.65 (*d*, ^2J = 5.6, H_{endo}–C(4)); 4.54 (*d*, ^3J = 4.9, H–C(8)); 4.41 (*dq*, ^3J = 6.8, 6.7, H–C(5′)); 4.14 (*d*, ^3J = 6.8, H–C(4′)); 3.98 (*dd*, ^3J = 5.0, 3.5, H–C(6)); 3.79 (*d*, ^3J = 6.4, H–C(2)); 3.74 (*d*, ^3J = 6.9, H–C(2′)); 3.07 (*d*, ^3J = 4.7, H–C(10)); 2.31 (*ddq*, ^3J = 3.5, 6.9, 6.4, H–C(1′)); 2.08–1.96 (*m*, H–C(9), H–C(7)); 1.47 (*s*, Me); 1.43 (*d*, ^3J = 6.7, Me(6′)); 1.40, 1.39, 1.38, 1.34, 1.31 (5*s*, 5 Me); 1.21 (*d*, ^3J = 6.4, Me–C(1′)); 1.05 (*q*, ^3J = 7.1, Me–C(9)); 0.91 (*s*, *t*-BuSi); 0.06 (*s*, Me_2Si); assignments confirmed by 2D NOESY. ^{13}C-NMR (100.6 MHz, $CDCl_3$): 107.3, 106.2 (2*s*, 2 Me_2C); 90.9 (*s*, C(1)); 90.8 (*t*, ^1J(C,H) = 163, C(4)); 82.4 (*s*, C(3′)); 84.9 (*d*, ^1J(C,H) = 143), 80.3 (*d*, ^1J(C,H) = 150), 77.8 (*d*, ^1J(C,H) = 155), 77.5 (*d*, ^1J(C,H) = 142), 75.8 (*d*, ^1J(C,H) = 149), 74.9 (*d*, ^1J(C,H) = 146), 74.8 (*d*, ^1J(C,H) = 145, C(2), C(6), C(8), C(10), C(2′), C(4′), C(5′)); 49.2 (*d*, ^1J(C,H) = 133), 38.0, 34.3 (2*d*, ^1J(C,H) = 125, C(7), C(9), C(1′)); 28.6, 27.4, 26.5, 25.1 (4*q*, ^1J(C,H) = 126, 2 *Me*$_2$C); 25.8 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 21.2 (*q*, ^1J(C,H) = 129); 18.0 (*s*); 17.4, 13.1, 12.7, 11.9 (4*q*, ^1J(C,H) = 127, 4 Me); –4.2, –4.7 (2*q*, ^1J(C,H) = 118, Me_2Si). CI-MS (NH_3): 571 (1, $[M + 1]^+$), 570 (1, $M^{+\cdot}$), 445 (18), 441 (8), 367 (10), 265 (6), 254 (10), 197 (12), 185 (12), 123 (24), 115 (55), 85 (57), 75 (63), 73 (100).

*(1RS,2RS,3SR,4RS,5RS,6SR)-6-*exo-*[(*tert-*Butyl)dimethylsilyloxy]-3-*exo-*[(1′SR,2′SR,3′RS,4′RS,5′SR,6′SR)-1′-hydroxy-3′,4′:5′,6′-bis(isopropylidenedioxy)-2,4-dimethylhept-1′-yl]-1,5-*endo-*dimethyl-7-oxabicyclo[2.2.1]heptan-2-*exo-*ol* ((-**49**). Same procedure as for **45** starting with (±)-**41** (12 mg, 0.022 mmol). Yield: 10 mg (83%). Colourless oil. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.38 (*dq*, ^3J = 6.8, 6.7, H–C(6′)); 4.23–4.10 (*m*, H–C(1′), H–C(5′)); 3.99 (*d*, ^3J = 4.9, H–C(4)); 3.89 (*d*, ^3J = 9.0, H–C(3′)); 3.74 (*dd*, ^3J = 6.7, 8.3, H–C(2)); 3.14 (*d*, ^3J = 4.6, H–C(6)); 2.94 (br. *s*, OH–C(1′)); 2.31 (*d*, ^3J = 8.3, OH–C(2)); 2.30 (*dd*, ^3J = 10.8, 6.7, H–C(3)); 2.13–1.87 (*m*, H–C(5), H–C(2′)); 1.51, 1.45 (2*s*, 2 Me); 1.41 (*d*, ^3J = 6.7, Me(7′)); 1.38, 1.36, 1.34, 1.33 (4*s*, 4 Me); 1.08 (*d*, ^3J = 6.8), 1.06 (*d*, ^3J = 7.1, Me–C(5), Me–C(2′)); 0.92 (*s*, *t*-Bu); 0.07 (*s*, Me_2Si).

*(1RS,2SR,6RS,7RS,8SR,9SR,10RS)-6-[(1′RS,2′SR,3′SR,4′RS,5′RS)-2′,3′:4′,5′-Bis(isopropylidenedioxy)-1′,3′-dimethylhex-1′-yl]-10-*exo-*(methoxymethoxy)-1,9-*endo-*dimethyl-3,5,11-trioxatricyclo[6.2.1.0^{2,7}]undecane* ((±)-**50**). Same procedure as for **46**, starting with (±)-**49**) (10 mg, 0.018 mmol). Yield 4.5 mg (50%). Colourless oil. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.95 (*d*, ^2J = 4.2, H_{exo}–C(4)); 4.87 (*d*, ^2J = 4.2, H_{endo}–C(4)); 4.69, 4.61 (2*d*, ^2J = 6.9, MeOCH_2); 4.39 (*dq*, ^3J = 6.2, 6.7, H–C(5′)); 4.16–4.10 (*m*, H–C(6), H–C(2′), H–C(4′)); 3.79 (*d*, ^3J = 9.7, H–C(8)); 3.64 (*d*, ^3J = 7.4, H–C(2)); 3.38 (*s*, MeO); 3.12 (*d*, ^3J = 3.5, H–C(10)); 2.43 (*dd*, ^3J = 7.4, 10.0, H–C(7)); 2.13—2.00 (*m*, H–C(9), H–C(1′)); 1.54, 1.43, 1.41 (3*s*, 3 Me); 1.40 (*d*, ^3J = 6.7, Me(6′)); 1.37, 1.34, 1.32 (3*s*, 3 Me); 1.12 (*d*, ^3J = 6.8, Me–C(9)); 1.05 (*d*, ^3J = 7.3, Me–C(1′)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 108.0, 105.7 (2*s*); 95.6 (*t*, ^1J(C,H) = 163), 90.1 (*t*, ^1J(C,H) = 164, C(4), MeO*C*H$_2$); 90.1 (*s*, C(1)); 82.1 (*s*, C(3′)), 85.6 (*d*, ^1J(C,H) = 142), 85.3 (*d*, ^1J(C,H) = 140), 79.3 (*d*, ^1J(C,H) = 155), 77.2 (*d*, ^1J(C,H) = 147), 75.8 (*d*, ^1J(C,H) = 146), 75.1 (*d*, ^1J(C,H) = 146), 70.8 (*d*, ^1J(C,H) = 146, C(2), C(6), C(8), C(10), C(2′), C(4′), C(5′)); 55.4 (*q*, ^1J(C,H) = 142, MeO); 46.0 (*d*, ^1J(C,H) = 133), 40.0 (*d*, ^1J(C,H) = 134), 34.6 (*d*, ^1J(C,H) = 128, C(7), C(9), C(2′)); 28.6, 27.5, 26.4, 25.6 (4*q*, ^1J(C,H) = 127, 2 *Me*$_2$C); 20.6, 17.9, 13.8, 11.2 (4*q*, ^1J(C,H) = 126–128, 5 Me). CI-MS (NH_3): 500 (3, $M^{+\cdot}$), 485 (3), 385 (48), 355 (2), 325 (3), 243 (6), 181 (13), 115 (24), 99 (18), 97 (27), 84 (100), 71 (25).

*(1RS,4RS,5RS,6RS,7SR)-7-*exo-*[(*tert-*Butyl)dimethylsilyloxy]-4-*exo-*[(1′SR,2′SR,3′RS,4′RS,5′SR,6′SR)-1′-hydroxy-3′,4′:5′,6′-bis(isopropylidenedioxy)-2′,4′-dimethylhept-1′-yl]-1,6-*endo-*dimethyl-2,8-dioxabicyclo[3.2.1]octan-3-one* (**51**). A mixture of $NaHCO_3$ (40 mg), 3-$ClC_6H_4CO_3H$ (85%, *Aldrich*; 40 mg), (±)-**41** (50 mg, 0.09 mmol), and CH_2Cl_2 (7 ml) was stirred at 20° for 5 h. The mixture was poured onto a half-sat aq. $NaHCO_3$ soln. (20 ml) and extracted with CH_2Cl_2 (20 ml, 3 times). The combined extract was dried ($MgSO_4$) and evaporated. FC (silica gel, Et_2O/light petroleum ether 1:2) gave 46 mg (89%) of colourless oil. IR (KBr): 2990, 2950, 2940, 2860, 1710, 1380, 1260, 1220, 1130, 1100, 1070, 1040, 1000, 860, 840, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.53 (*d*, ^3J = 7.9, H–C(5)); 4.41 (*ddd*, ^3J = 9.5, 2.0, 1.5, H–C(1′)); 4.37 (*dq*, ^3J = 6.4, 6.7, H–C(6′)); 4.15 (*d*, ^3J = 6.4, H–C(5′)); 3.93 (*d*, ^3J = 9.9, H–C(3′)); 3.84 (*d*, ^3J = 4.0, H–C(7)); 3.74 (*d*, ^3J = 1.5, OH–C(1′)); 2.55 (*d*, ^3J = 9.5, H–C(4)); 2.35 (*ddq*, ^3J = 7.9, 4.0, 7.5, H–C(6)); 2.20 (*ddq*, ^3J = 9.9, ^2J = 2.0, ^3J = 6.7, H–C(2′)); 1.56, 1.47, 1.46 (3*s*, 3 Me); 1.38 (*d*, ^3J = 6.7, Me(7′)); 1.37, 1.36, 1.33 (3*s*, 3 Me); 1.18 (*d*, ^3J = 7.5, Me–C(6)); 1.02 (*d*, ^3J = 6.7, Me–C(2′)); 0.91 (*s*, *t*-BuSi); 0.10 (*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.9 (*s*, C(3)); 114.0 (*s*, C(1)); 108.0, 105.8 (2*s*); 82.0 (*s*,

C(4')); 85.9 (*d*, ^1J(C,H) = 143), 84.0 (*d*, ^1J(C,H) = 143), 76.4 (*d*, ^1J(C,H) = 155), 75.6, 75.1 (2*d*, ^1J(C,H) = 145), 68.2 (*d*, ^1J(C,H) = 151, C(5), C(7), C(1'), C(3'), C(5'), C(6')); 46.2 (*d*, ^1J(C,H) = 134), 44.7 (*d*, ^1J(C,H) = 130, C(4), C(6)); 33.6 (*d*, ^1J(C,H) = 129, C(2')); 28.6, 27.5, 26.4, 25.1 (4*q*, ^1J(C,H) = 126, 2 *Me*$_2$C); 25.6 (*q*, ^1J(C,H) = 125, Me_3CSi); 20.3 (*q*, ^1J(C,H) = 127); 19.4 (*q*, ^1J(C,H) = 129); 18.1 (*q*, ^1J(C,H) = 128); 17.8 (*s*, Me_3CSi); 13.2 (*q*, ^1J(C,H) = 126); 9.7 (*q*, ^1J(C,H) = 127); −4.4, −4.8 (2*q*, ^1J(C,H) = 119, Me_2Si). CI-MS (NH_3): 573 (100, $[M + 1]^+$), 457 (48), 439 (27), 399 (19), 287 (31), 229 (26), 171 (33), 73 (40).

*(1R,4R,5R,6R,7S)-7-*exo*-[(Benzyloxy)-4-*exo*-[(1'S,2'S,3'R,4'R,5'S,6'S)-1'-hydroxy-3',4':5',6'-bis(isopropylidenedioxy)-2',4'-dimethylhept-1'-yl]-1,6-*endo*-dimethyl-2,8-dioxabicyclo[3.2.1]octan-3-one* (**52**). Same procedure as for **51**, starting with (−)-**44** (9 mg, 0.017 mmol). FC (silica gel, AcOEt/light petroleum ether 1:5) gave 8 mg (86%) of colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41–7.30 (*m*, arom. H); 4.65 (*d*, ^3J = 12.0, 1 H, PhCH_2); 4.59 (*d*, ^3J = 12.0, 1 H, PhCH_2); 4.54 (*d*, ^3J = 7.9, H–C(5)); 4.41 (br. *dd*, ^3J = 9.5, 1.9, H–C(1')); 4.37 (*dq*, ^3J = 6.4, 6.7, H–C(6')); 4.15 (*d*, ^3J = 6.4, H–C(5')); 3.93 (*d*, ^3J = 10.0, H–C(3')); 3.27 (br. *s*, OH–C(1')); 3.66 (*d*, ^3J = 4.3, H–C(7)); 2.55 (*d*, ^3J = 9.5, H–C(4)); 2.52 (*ddq*, ^3J = 7.9, 4.3, 7.5, H–C(6)); 2.19 (br. *ddq*, ^3J = 10.0, 1.9, 6.7, H–C(2')); 1.71, 1.48, 1.47 (3*s*, 3 Me); 1.38 (*d*, ^3J = 6.7, H–C(7')); 1.38, 1.36, 1.31 (3*s*, 3 Me); 1.12 (*d*, ^3J = 7.5, Me–C(6)); 1.02 (*d*, ^3J = 6.7, Me–C(2')). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 171.6 (*s*, C(3)); 137.2 (*s*); 128.6, 128.2 (2*d*, ^1J(C,H) = 160); 127.7 (*d*, ^1J(C,H) = 158), 113.2 (*s*, C(1')); 108.0, 105.8 (*s*, 2 Me_2C); 82.0 (*s*, C(4')); 72.6 (*t*, ^1J(C,H) = 142, PhCH_2); 89.5 (*d*, ^1J(C,H) = 148), 85.8 (*d*, ^1J(C,H) = 149), 76.4 (*d*, ^1J(C,H) = 157), 75.6 (*d*, ^1J(C,H) = 143), 75.1 (*d*, ^1J(C,H) = 145), 68.2 (*d*, ^1J(C,H) = 147, C(5), C(7), C(1'), C(3'), C(5'), C(6')); 44.6 (*d*, ^1J(C,H) = 133), 43.8 (*d*, ^1J(C,H) = 135), 33.6 (*d*, ^1J(C,H) = 128, C(4), C(6), C(2')); 28.6, 27.5, 26.4, 25.2 (4*q*, ^1J(C,H) = 126, 4 Me); 20.3 (*q*, ^1J(C,H) = 127); 19.2 (*q*, ^1J(C,H) = 129); 18.1 (*q*, ^1J(C,H) = 126); 13.8 (*q*, ^1J(C,H) = 126); 9.7 (*q*, ^1J(C,H) = 128).

REFERENCES

[1] P. Kernen, P. Vogel, *Tetrahedron Lett.* **1993,** *324,* 2473.

[2] See *e.g.* a) the macrolide antibiotics: K. L. Rinehart, L. S. Shield, Jr., *Fortschr. Chem. Org. Naturst.* **1976,** *33,* 23; P. A. Bartlett, *Tetrahedron* **1980,** *36,* 2; I. Paterson, M. M. Mansuri, *ibid.* **1985,** *41,* 3569; T. L. B. Boivin, *ibid.* **1987,** *43,* 3309; R. W. Hoffmann, *Angew. Chem. Int. Ed.* **1987,** *26,* 489; J. Mulzer, *ibid.* **1991,** *30,* 1452; R. Stürmer, K. Ritter, R. W. Hoffmann, *Angew. Chem. Int. Ed.* **1993,** *32,* 101, and ref. cit. therein; b) swinholides; S. Tsukamoto, M. Ishibashi, T. Sasaki, J. i. Kobayashi, *J. Chem. Soc., Perkin Trans. 1* **1991,** 3185; c) tylonolides: J. A. Marshall, T. D. Crute, III, J. D. Hsi, *J. Org. Chem.* **1992,** *57,* 115; d) rapamycin: K. C. Nicolaou, T. K. Chakraborty, A. D. Piscopio, N. Nimowa, P. Bertinato, *J. Am. Chem. Soc.* **1993,** *115,* 4419; D. Romo, S. D. Meyer, D. D. Johnson, S. L. Schreiber, *ibid.* **1993,** *115,* 7906; C. M. Hayward, D. Yokannes, S. Danishefsky, *ibid.* **1993,** *115,* 9345: e) FK-506: M. K. Rosen, S. L. Schreiber, *Angew. Chem. Int. Ed.* **1992,** *31,* 384; f) rifamycins: M. Miyashita, K. Yoshihara, K. Kawamine, M. Hoshino, H. Irie, *Tetrahedron Lett.* **1993,** *34,* 6285; g) etheromycin: I. Paterson, R. D. Tillyer, G. R. Ryan, *ibid.* **1993,** *34,* 4389; h) streptovaricins: W. R. Roush, A. D. Palkowitz, *J. Org. Chem.* **1989,** *54,* 3009; Z. Wang, S. L. Schreiber, *Tetrahedron Lett.* **1990,** *31,* 31; h) ionomycin: D. A. Evans, R. L. Dow, T. L. Shih, J. D. Takacs, R. Zahler, *J. Am. Chem. Soc.* **1990,** *112,* 5290, and ref. cit. in these papers; i) oligomycins: H. Laatsch, M. Kellner, G. Wolf, Y. S. Lee, F. Hansske, S. Konetschung-Rapp, U. Pessara, W. Scheuer, H. Stockinger, *J. Antibiot.* **1993,** *46,* 1334; j) sekothrixide: Y. J. Kim, K. Furinata, A. Shimazu, K. Furihata, H. Seto, *ibid.* **1991,** *44,* 1280; k) sporeamicin C: A. Morishita, S. Murofushi, K. Ishizawa, N. Mutoh, S. Yaginuma, *ibid.* **1992,** *45,* 1011; l) discodermolide: S. P. Gunasekera, M. Gunasekera, R. E. Longley, G. K. Schulte, *J. Org. Chem.* **1991,** *56,* 1346; J. B. Nerenberg, D. T. Hung, P. K. Somers, S. L. Schreiber, *J. Am. Chem. Soc.* **1993,** *115,* 12621; D. L. Clark, C. H. Heathcock, *J. Org. Chem.* **1993,** *58,* 5878; m) denticulatins: I. Paterson, M. V. Perkino, *Tetrahedron Lett.* **1992,** *33,* 801, and ref cit. in these papers; n) onchitriols: J. Rodriguez, R. Riguera, C. Debitus, *J. Org. Chem.* **1992,** *57,* 4624.

[3] For recent reviews see *e.g.*: a) M. Lautens, *Synlett* **1993,** 177; b) I. Paterson, *Pure Appl. Chem.* **1992,** *64,* 1821; c) S. Martin, D. E. Guinn, *Synthesis* **1991,** 245.

[4] F. E. Ziegler, A. Kneisky, J. K. Thottatkil, R. T. Wester, *J. Am. Chem. Soc.* **1988,** *110,* 5434; F. E. Ziegler, W. T. Cain, A. Kneisley, E. P. Stirchak, R. T. Wester, *ibid.* **1988,** *110,* 5442; F. E. Ziegler, M. R. Becker, *J. Org. Chem.* **1990,** *55,* 2800.

[5] D. C. Myles, S. J. Danishefsky, G. Schulte, *J. Org. Chem.* **1990,** *55,* 1636; Q. Gao, K. Ishihara, T. Maruyama, M. Mouri, H. Yamamoto, *Tetrahedron* **1994,** *50,* 979; M. D. Bednarski, J. P. Lyssikatos, in 'Comprehensive Organic Synthesis', Eds B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, Vol. 2., Chapt. 2.5, p. 661.

[6] C.C. Heathcock, 'Asymmetric Synthesis', Academic Press, New York, 1984, Vol. 3, Chapt. 2; *ibid.* D.A. Evans, *ibid.* Vol. 3, Chapt. 1; M. Born, C. Tamm, *Synthesis* **1991,** 435; *Helv. Chim. Acta* **1990,** *73,* 2242; I. Paterson, S. Bower, R.D. Tillyer, *Tetrahedron Lett.* **1993,** *34,* 4393; C.H. Heathcock, in 'Comprehensive Organic Synthesis', Eds. B.M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, Vol. 2, Chapt. 1.5, p. 133, Chapt. 1.6, p. 181; T.-H. Chan, *ibid.* Vol. 2, Chapt. 2.3, p. 595; C. Gennari, *ibid.* Vol. 2, Chapt. 2.4, p. 629.

[7] D.A. Evans, M.D. Enuis, D.J. Mathre, *J. Am. Chem. Soc.* **1982,** *104,* 1737; D.A. Evans, R.L. Dew, *Tetrahedron Lett.* **1986,** *27,* 1007; D.A. Evans, S.W. Kalder, T.K. Jones, J. Clardy, T.J. Stout, *J. Am. Chem. Soc.* **1990,** *112,* 7001; D.A. Evans, G.S. Sheppard, *J. Org. Chem.* **1990,** *55,* 5192; D.A. Evans, H.P. Ng, *Tetrahedron Lett.* **1993,** *34,* 2229.

[8] T. Nakata, M. Fukui, T. Oishi, *Tetrahedron Lett.* **1988,** *29,* 2219.

[9] B.M. Kim, S.F. Williams, S. Masamune, in 'Comprehensive Organic Synthesis', Eds. B.M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, Vol. 2, Chapt. 1.7, p. 239; W.R. Roush, A.D. Palkowitz, *J. Org. Chem.* **1989,** *54,* 3009; D.A. Evans, D.L. Rieger, M.T. Bilodeau, F. Urpi, *J. Am. Chem. Soc.* **1991,** *113,* 1047; M.R. Johnson, T. Nakata, Y. Kishi, *Tetrahedron Lett.* **1979,** 4343; M.R. Johnson, Y. Kishi, *ibid.* **1979,** 4347; Y. Kishi, *Pure Appl. Chem.* **1981,** *53,* 1163; H. Nagaoka, G. Schmid, H. Iio, Y. Kishi, *Tetrahedron Lett.* **1981,** *22,* 899; K.J. Hale, G.S. Bhatia, S.A. Peak, S. Manaviazar, *ibid.* **1993,** *34,* 5343; I. Paterson, J. Channon, *ibid.* **1992,** *33,* 797; I. Paterson, J.D. Smith, *ibid.* **1993,** *34,* 5351; I. Paterson, R.D. Tillyer, *J. Org. Chem.* **1993,** *58,* 4182.

[10] S. Masamune, B. Imperiali, D.S. Garrey, *J. Am. Chem. Soc.* **1982,** *104,* 5528; I. Paterson, M.V. Perkins, *Tetrahedron Lett.* **1992,** *33,* 801; I. Paterson, A. Lister, R.D. Norcross, *ibid.* **1992,** *33,* 1767; I. Paterson, J.A. Channon, *ibid.* **1992,** *33,* 797; D.A. Evans, J.S. Clark, R. Metternich, V.J. Nozack, G.S. Sheppard, *J. Am. Chem. Soc.* **1990,** *112,* 866; I. Paterson, R.D. Tillyer, *Tetrahedron Lett.* **1992,** *33,* 4233; D.A. Evans, H.P. Ng, J.S. Claux, D.L. Rieger, *Tetrahedron* **1992,** *48,* 2127.

[11] M. Braun, H. Sacha, *Angew. Chem. Int. Ed.* **1991,** *30,* 1318; see also: I. Paterson, in 'Comprehensive Organic Synthesis', Eds. B.M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, Chapt. 1.9, p. 301.

[12] W.R. Roush, A.D. Palkowitz, K. Ando, *J. Am. Chem. Soc.* **1990,** *112,* 6348; J.D. White, W.J. Porter, T. Tiller, *Synlett* **1993,** 535; W.R. Roush, in 'Comprehensive Organic Synthesis', Eds. B.M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, Chapt. 1.1, p. 1; I. Fleming, *ibid.* Vol. 2, Chapt. 2.2, p. 563.

[13] S. Hanessian, P.J. Murray, *Tetrahedron* **1987,** *43,* 5055; S. Hanessian, N.G. Cooke, B. De Hoff, Y. Sahito, *J. Am. Chem. Soc.* **1990,** *112,* 5276; G. Stork, S.D. Rychnowsky, *ibid.* **1987,** *109,* 1564, 1565.

[14] J.A. Marshall, J.D. Trometer, B.E. Blough, T.D. Crute, *J. Org. Chem.* **1988,** *53,* 4174; J.A. Marshall, J.D. Trometer, *Tetrahedron* **1989,** *45,* 391; J.A. Marshall, B.E. Blough, *J. Org. Chem.* **1990,** *55,* 1540; J.A. Marshall, B.E. Blough, *ibid.* **1991,** *56,* 2225; M. Mirashita, K. Yoshihara, K. Kawamine, M. Hoshino, H. Irie, *Tetrahedron Lett.* **1993,** *34,* 6285; see also: R. Tirado, J.A. Prieto, *J. Org. Chem.* **1993,** *58,* 5666.

[15] See *e.g.*: M. Miljkocic, M. Gliorijevic, T. Satoh, D. Miljkovic, *J. Org. Chem.* **1974,** *39,* 1379; S. Hanessian, G. Rancourt, *Can J. Chem.* **1977,** *55,* 1111; S. Hanessian, J.R. Pougny, I. Boessenkool, *Tetrahedron Lett.* **1984,** *40,* 1289; K.C. Nicolaou, S.P. Seitz, M.R. Pavia, *J. Am. Chem. Soc.* **1981,** *103,* 1222, 1224; K. Tatsua, Y. Amemiya, Y. Kamemura, H. Takahashi, M. Kinoshita, *Tetrahedron Lett.* **1982,** *23,* 3375; K.C. Nicolaou, S.P. Seitz, M.R. Pavia, *J. Am. Chem. Soc.* **1982,** *104,* 5781; R.E. Ireland, J.P. Daub, G.S. Mandel, N.S. Mandel, *J. Org. Chem.* **1983,** *48,* 1312; M. Wakata, M. Takao, Y. Ikeyama, T. Sakai, K. Tatsua, M. Kinoshita, *Bull. Chem. Soc. Jpn.* **1981,** *54,* 1749; B. Fraser-Reid, L. Magdzinski, B. Molino, *J. Am. Chem. Soc.* **1984,** *106,* 731; M. Nakata, M. Kinoshita, S. Ohba, Y. Saito, *Tetrahedron Lett.* **1983,** *23,* 4199; E.J. Corey, L.O. Weigl, A.R. Chamberlin, B. Lipschutz, *J. Am. Chem. Soc.* **1980,** *102,* 1439; E.J. Corey, L.O. Weigl, A.R. Chamberlin, M. Cho, D.H. Hua, *ibid.* **1980,** *102,* 6613; M.J. Fisher, C.D. Myres, J. Joglar, S.H. Chen, S.J. Danishefsky, *J. Org. Chem.* **1991,** *56,* 5826; S.H. Chen, R.F. Horvath, J. Joglar, M.J. Fisher, S.J. Danishefsky, *ibid.* **1991,** *56,* 5834; H. Tone, T. Nishi, Y. Oikawa, M. Hitoka, O. Yonemitsu, *Tetrahedron Lett.* **1987,** *28,* 4569; J. Mulzer, H.M. Kirstein, J. Buschmann, C. Lehmann, P. Luger, *J. Am. Chem. Soc.* **1991,** *113,* 910; M.J. Fisher, C.D. Myres, J. Joglar, S.H. Chen, S.J. Danishefsky, *J. Org. Chem.* **1991,** *56,* 5826; S.H. Chen, R.F. Horvath, J. Joglar, M.J. Fisher, S.J. Danishefsky, *ibid.* **1991,** *56,* 5834; M. Nakata, N. Akiyama, J.-i. Kamata, K. Kojima, H. Masuda, M. Kinoshita, K. Tatsuta, *Tetrahedron* **1990,** *46,* 4629; A.F. Suiridov, V.S. Borodkin, M.S. Ermolenko, D.V. Yashunsky, N.K. Kochetkov, *ibid.* **1991,** *47,* 2291, 2317; J.E. Eshelman, J.L. Epps, J. Kallmerten, *Tetrahedron Lett.* **1993,** *34,* 749; N. Sin, J. Kallmerten, *ibid.* **1993,** *34,* 753.

[16] T.R. Hoye, D.R. Peck, T.A. Swanson, *J. Am. Chem. Soc.* **1984,** *106,* 2738; S.L. Schreiber, T. Samakia, E.D. Uehling, *J. Org. Chem.* **1989,** *54,* 15; T. Harada, Y. Kagamihara, S. Tanaka, K. Sakamoto, A. Ohu, *ibid.* **1992,** *57,* 1637; Y.-b. Zhao, N.E. Pratt, M.J. Heeg, K.F. Albizati, *ibid.* **1993,** *58,* 1300.

[17] S. Masamune, H. Yamamoto, S. Kamata, A. Fukuzawa, *J. Am. Chem. Soc.* **1975,** *97,* 3513; S. Masamune, C.U. Kim, K.E. Wilson, G.O. Spessard, P.E. Georghiou, G.S. Bates, *ibid.* **1975,** *97,* 3512.
[18] P.A. Grieco, J. Inanaga, N.-H. Lin, T. Yanami, *J. Am. Chem. Soc.* **1982,** *104,* 5781.
[19] J.D. White, Y. Fukuyama, *J. Am. Chem. Soc.* **1979,** *101,* 226.
[20] M. Lautens, P. Chiu, *Tetrahedron Lett.* **1993,** *34,* 773; M. Lautens, P. Chiu, J.T. Colucci, *Angew. Chem. Int. Ed.* **1993,** *32,* 281.
[21] O. Arjona, A. Martin-Domenech, J. Plumet, *J. Org. Chem.* **1993,** *58,* 7929.
[22] M. Lautens, C. Gajda, P. Chiu, *J. Chem. Soc., Chem. Commun.* **1993,** 1193.
[23] A.F. Sevin, P. Vogel, *J. Org. Chem.* **1994,** *59,* 5920.
[24] T. Morel, P.E. Verkade, *Recl. Trav. Chim. Pays-Bas* **1949,** *68,* 619; *ibid.* **1951,** *70,* 35.
[25] a) P. Vogel, D. Fattori, F. Gasparini, C. Le Drian, *Synlett* **1990,** 173; P. Vogel, *Bull. Soc. Chim. Belg.* **1990,** *99,* 395; b) S. Jeganathan, P. Vogel, *J. Org. Chem.* **1991,** *56,* 5143; c) Y. Chen, P. Vogel, *ibid.* **1994,** *59,* 2487.
[26] R.R. Schmidt, C. Beitzke, A.K. Forrest, *J. Chem. Soc., Chem. Commun.* **1982,** 909.
[27] G.R. Krow, *Tetrahedron* **1981,** *37,* 2697.
[28] G. Arvai, D. Fattori, P. Vogel, *Tetrahedron* **1992,** *48,* 10621.
[29] D. Gagnaire, E. Payo-Subiza, *Bull. Soc. Chim. Fr.* **1963,** 2627; K.C. Ramey, D.C. Lini, *J. Magn. Reson.* **1970,** *3,* 94; W.L. Nelson, D.R. Allen, *J. Heterocycl. Chem.* **1972,** *9,* 561; F. Kienzle, *Helv. Chim. Acta* **1975,** *58,* 1180; C. Mahaim, P. Vogel, *ibid.* **1982,** *65,* 866.
[30] G.J.F. Chittenden, *Carbohydr. Res.* **1980,** *87,* 219.
[31] W.P. Griffith, S.V. Ley, G.P. Whitcombe, A.D. White, *J. Chem. Soc., Chem. Commun.* **1987,** 1625.
[32] E.J. Corey, H. Cho, C. Rücker, D. Hua, *Tetrahedron Lett.* **1981** *22,* 3455.
[33] J. Seyden-Penne, in 'Reductions by the Alumino- and Borohydrides in Organic Synthesis', VCH Publishers, Inc., Weinheim, 1991.
[34] E.W. Collington, H. Finch, I.J. Smith, *Tetrahedron Lett.* **1985,** *26,* 681; R.F. Newton, D.P. Reynolds, M.A.W. Finch, D.R. Kelly, S.M. Roberts, *ibid.* **1979,** 3981.
[35] a) C.T. Buse, C.H. Heathcock, *J. Am. Chem. Soc.* **1977,** *99,* 8109; C.H. Heathcock, C.T. Buse, W.A. Kleschick, M.C. Pirrung, J.E. Sohn, J. Lampe, *J. Org. Chem.* **1980,** *45,* 1066; b) D. Seebach, V. Prelog, *Angew. Chem. Int. Ed.* **1982,** *21,* 654; c) F.A. Corey, M.E. Kuehne, *J. Org. Chem.* **1982,** *47,* 3811; d) D. Schinzer, *Synthesis* **1989,** 179; e) see also: E. Juaristi, A.K. Beck, J. Hansen, T. Matt, T. Mukhopadhyay, M. Simson, D. Seebach, *ibid.* **1993,** 1271.
[36] H.C. Brown, J.H. Kawakami, *J. Am. Chem. Soc.* **1970,** *92,* 1990; Y.F. Shealy, J.D. Clayton, *ibid* **1969,** *91,* 3075; H.-J. Trede, E.F. Jenny, K. Heusler, *Tetrahedron Lett.* **1973,** 3425; A. Chollet, C. Mahaim, C. Foetisch, M. Hardy, P. Vogel, *Helv. Chim. Acta* **1977** *60,* 59.
[37] a) D.J. Cram, F.A. Abd Elhafez, *J. Am. Chem. Soc.* **1952,** *74,* 5828; E.L. Eliel, in 'Asymmetric Synthesis', Ed. J.D. Morrison, Academic Press, Inc., New York, 1983, Vol. 2., Chapt. 5, pp. 125–155; b) M. Chérest, H. Felkin, *Tetrahedron Lett.* **1968,** 2205; M. Chérest, H. Felkin, N. Prudent, *ibid.* **1968,** 2199; M. Chérest, N. Prudent, *Tetrahedron* **1980,** *36,* 1599; N.T. Anh, O. Eisenstein, *Nouv. J. Chim.* **1976,** *1,* 61.
[38] W.R. Roush, *J. Org. Chem.* **1991,** *56,* 4151, and ref. cit. therein.
[39] F. Gasparini, P. Vogel, *J. Org. Chem.* **1990,** *55,* 2451; J. Wagner, E. Vieira, P. Vogel, *Helv. Chim. Acta* **1988,** *71,* 624.
[40] E. Vieira, P. Vogel, *Helv. Chim. Acta* **1982,** *65,* 1700.