

# **Stereoselective Synthesis of 8-Oxabicyclo[3.2.1]octane-2,3,4,6,7-pentols and Total Asymmetric Synthesis of 2,6-Anhydrohepturonic Acid Derivatives and of $\beta$ -C-manno-Pyranosides Suitable for the Construction of (1 $\rightarrow$ 3)-C,C-Linked Trisaccharides**

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Dedicated to Prof. *Edgar Heilbronner* on the occasion of his 80th birthday

Enantiomerically pure (+)-(1*S*,4*S*,5*S*,6*S*)-6-*endo*-(benzyloxy)-5-*exo*-[[(*tert*-butyl)dimethylsilyl]oxy]-7-oxabicyclo[2.2.1]heptan-2-one ((+)-**5**) and its enantiomer (–)-**5**, obtained readily from the *Diels-Alder* addition of furan to 1-cyanovinyl acetate, can be converted with high stereoselectivity into 8-oxabicyclo[3.2.1]octane-2,3,4,6,7-pentol derivatives (see **23**–**28** in *Scheme 2*). A precursor of them, (1*R*,2*S*,4*R*,5*S*,6*S*,7*R*,8*R*)-7-*endo*-(benzyloxy)-8-*exo*-hydroxy-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]non-5-*endo*-yl benzoate ((–)-**19**), is transformed into (1*R*,2*R*,5*S*,6*S*,7*R*,8*S*)-6-*exo*,8-*endo*-bis(acetyloxy)-2-*endo*-(benzyloxy)-4-oxo-3,9-dioxabicyclo[3.3.1]non-7-*endo*-yl benzoate ((–)-**43**) (see *Scheme 5*). The latter is the precursor of several protected 2,6-anhydrohepturonic acid derivatives such as the diethyl dithioacetal (–)-**57** of methyl 3,5-di-*O*-acetyl-2,6-anhydro-4-*O*-benzoyl-D-glycero-D-galacto-hepturonate (see *Schemes 7* and *8*). Hydrolysis of (–)-**57** provides methyl 3,5-di-*O*-acetyl-2,6-anhydro-4-*O*-benzoyl-D-glycero-D-galacto-hepturonate **48** that undergoes highly diastereoselective *Nozaki-Oshima* condensation with the aluminium enolate resulting from the conjugate addition of Me<sub>2</sub>AlSPh to (1*S*,5*S*,6*S*,7*S*)-7-*endo*-(benzyloxy)-6-*exo*-[[(*tert*-butyl)dimethylsilyl]oxy]-8-oxabicyclo[3.2.1]oct-3-en-2-one ((–)-**13**) derived from (+)-**5** (*Scheme 12*). This generates a  $\beta$ -C-mannopyranoside, *i.e.*, methyl (7*S*)-3,5-di-*O*-acetyl-2,6-anhydro-4-*O*-benzoyl-7-*C*-[(1*R*,2*S*,3*R*,4*S*,5*R*,6*S*,7*R*)-6-*endo*-(benzyloxy)-7-*exo*-[[(*tert*-butyl)dimethylsilyl]oxy]-4-*endo*-hydroxy-2-*exo*-(phenylthio)-8-oxabicyclo[3.2.1]oct-3-*endo*-yl]-L-glycero-D-manno-heptonate ((–)-**70**; see *Scheme 12*), that is converted into the diethyl dithioacetal (–)-**75** of methyl 3-*O*-acetyl-2,6-anhydro-4,5-dideoxy-4-*C*-[[methyl (7*S*)-3,5,7-tri-*O*-acetyl-2,6-anhydro-4-*O*-benzoyl-L-glycero-D-manno-heptonate]-7-*C*-yl]-5-*C*-(phenylsulfonyl)-L-glycero-D-galacto-hepturonate (**76**; see *Scheme 13*). Repeating the *Nozaki-Oshima* condensation to enone (–)-**13** and the aldehyde resulting from hydrolysis of (–)-**75**, a (1  $\rightarrow$  3)-C,C-linked trisaccharide precursor (–)-**77** is obtained.

**Introduction.** – Carbohydrate mimics are potentially useful molecular tools for biology [2] and may become leads for drug discovery [3]. In particular, C-linked disaccharides and oligosaccharides offer the advantage of being resistant to acidic and enzymatic hydrolysis [4]. They are potential inhibitors of glycosidases and glycosyl-transferases [5][6]. They represent non-hydrolyzable epitopes [7]. Since the first synthesis of  $\beta$ -D-Glcp-CH<sub>2</sub>(1  $\rightarrow$  6)-D-Glcp by *Rouzaud* and *Sinay* [8], several approaches to C-disaccharides and C-linked oligosaccharides have been reported [4][9][10]. Although several proposals have appeared for the preparation of  $\beta$ -C-manno-hexopyranosides [11], only three examples of C-disaccharides involving  $\beta$ -C-

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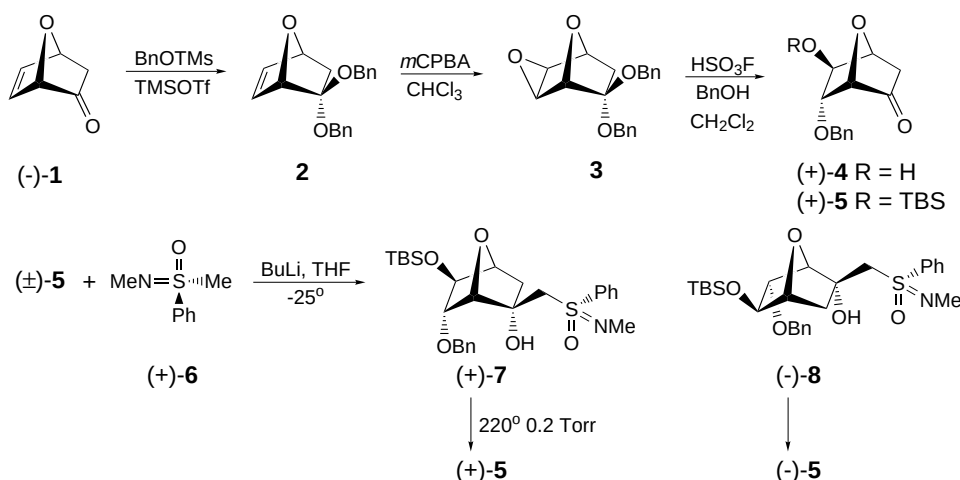
mannosides are known ( $\beta$ -D-Manp-CH<sub>2</sub>(1  $\rightarrow$  1)- $\beta$ -D-Glc [11],  $\beta$ -D-Manp-CH<sub>2</sub>(1  $\rightarrow$  4)-D-Glc-OMe [12], and  $\beta$ -D-Manp-CH<sub>2</sub>(1  $\rightarrow$  6)-D-Glc [9a]).

In 1993, we demonstrated [13] that enantiomerically pure 2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl acetate, a 'naked sugar of the first generation' [14], can be converted into enantiomerically pure 8-oxabicyclo[3.2.1]oct-6-en-2-one (both enantiomeric forms) and that the latter can be converted with high stereoselectivity into  $\beta$ -C-pyranosides either of *gulo*-hexuronic acid or of *altro*-hexodialdose. In a preliminary communication [1], we have announced that (–)-7-oxabicyclo[2.2.1]hept-5-en-2-one ((–)-**1**), another 'naked sugar of the first generation' [14] can be converted into (–)-6-*exo*-[[(*tert*-butyl)dimethylsilyl]oxy]-7-*endo*-(benzyloxy)-8-oxabicyclo[3.2.1]oct-3-en-2-one ((–)-**13**) and methyl 3,5-di-*O*-acetyl-2,6-anhydro-4-*O*-benzoyl-D-*glycero*-D-*galacto*-hepturonate, two new compounds that were condensed under *Oshima-Nozaki* conditions [15] to give a single aldol. This aldol could be transformed into a  $\beta$ -D-ManAp-CH(OAc)(1  $\rightarrow$  3)- $\alpha$ -L-GulAp-CH(SET)<sub>2</sub> derivative. We describe here the details of this chemistry that realizes a new approach to the total synthesis of  $\beta$ -C-manno-pyranosides. We show also how these C-disaccharides can be used in the construction of (1  $\rightarrow$  3)-C,C-trisaccharides.

**Stereoselective Synthesis of 8-Oxabicyclo[3.2.1]octane-2,3,4,6,7-pentol Derivatives.** – We had shown earlier that 7-oxabicyclo[2.2.1]hept-5-en-2-one ((+)- or (–)-**1**) can be converted in 3 steps into the 5-*exo*,6-*endo*-dihydroxy-7-oxabicyclo[2.2.1]heptan-2-one derivative **4** in 65% overall yield [16]. A procedure has now been developed to obtain ( $\pm$ )-**4** from ( $\pm$ )-**1** without isolation and purification of intermediates **2** and **3**. Silylation of ( $\pm$ )-**4** with (*t*-Bu)Me<sub>2</sub>SiCl and 1*H*-imidazole in DMF provided ( $\pm$ )-**5** in 96% yield. Although both enantiomeric forms of **5** are available with the same ease starting from the 'naked sugars of the first generation' (+)- and (–)-**1** [14][17], we applied the resolution method of *Johnson* and *Zeller* [18] to ketone ( $\pm$ )-**5**. Thus, after treatment with the reagent (+)-**6**, the diastereoisomeric sulfoximides (+)-**7** and (–)-**8** were separated in 42 and 44% yield, respectively, with diastereoisomer excesses better than 99% (<sup>1</sup>H-NMR, <sup>13</sup>C-satellites). Their thermolysis (220°) delivered enantiomerically pure ketones (+)- and (–)-**5**, respectively, both in 88% yield (*Scheme 1*).

Ring enlargement of ( $\pm$ )-**5** was accomplished applying the method of *Saegusa* and coworkers [19]. Enol ethers ( $\pm$ )-**9** and ( $\pm$ )-**10** were prepared (*Scheme 2*) and submitted to the *Simmons-Smith* [20] cyclopropanation under the conditions recommended by *Denmark* and coworkers [21]. This led to the unstable products ( $\pm$ )-**11** and ( $\pm$ )-**12**, respectively. Oxidation of ( $\pm$ )-**11** with FeCl<sub>3</sub> gave enone ( $\pm$ )-**13** in 15–40% yield (based on ketone ( $\pm$ )-**5**). Better reproductibility was observed with the oxidation of ( $\pm$ )-**12** that furnished ( $\pm$ )-**13** in 57% yield. Similarly, (–)-**13** was obtained from (+)-**5** (see *Exper. Part*).

Reduction of enone ( $\pm$ )-**13** under *Luche*'s conditions [22] gave *endo*-alcohol ( $\pm$ )-**14** that was esterified into ( $\pm$ )-**15** with benzoyl chloride in pyridine (*Scheme 2*). Epoxidation of ( $\pm$ )-**15** with 3-chloroperbenzoic acid (*m*CPBA) was a slow reaction (11 days at 25°), affording epoxy derivative ( $\pm$ )-**16** in mediocre yield (50%). An alternative route to ( $\pm$ )-**16** from ( $\pm$ )-**13** (66% overall yield) was opened by epoxidizing enone ( $\pm$ )-**13** with *tert*-butyl hydroperoxide in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) [23]. This provided epoxy ketone ( $\pm$ )-**17** in 99% yield that was

Scheme 1<sup>2)</sup>

reduced with  $\text{NaBH}_4$  stereoselectively into *endo*-alcohol  $(\pm)\text{-}18$  in 91% yield. Benzoylation of  $(\pm)\text{-}18$  furnished  $(\pm)\text{-}16$ . Selective deprotection of the silyl ether moiety of the latter with tetrabutylammonium fluoride provided alcohol  $(\pm)\text{-}19$ . Analogously,  $(-)\text{-}19$  was prepared from  $(-)\text{-}13$  via  $(+)\text{-}17$ ,  $(-)\text{-}18$ , and  $(-)\text{-}16$ .

The structure of compounds **9–19** were given by their  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra and confirmed by their 2D-NOESY  $^1\text{H}$ -NMR data. In particular for **19**, a vicinal coupling constant  $^3J(5,6) = 5.1$  Hz confirmed the *endo* relative configuration of the benzoate. The smaller vicinal coupling constants  $^3J(1,2) = 1.3$  Hz and  $^3J(4,5) < 0.5$  Hz demonstrated the *exo* relative configuration of the epoxide moiety. This was confirmed by the observation of an NOE between signals at  $\delta(\text{H})$  4.42 (br. d,  $^3J = 8.5$  Hz; coupling disappeared on addition of  $\text{D}_2\text{O}$  to the  $\text{CDCl}_3$  solution) and 3.18 (br. d,  $^3J = 3.9$  Hz) assigned to  $\text{H}-\text{C}(8)$  and  $\text{H}-\text{C}(2)$  of **19**.

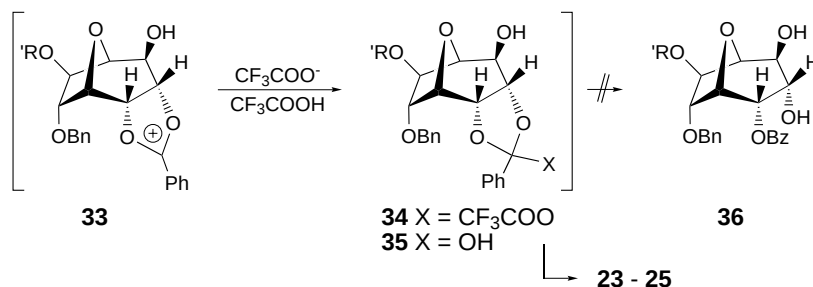
With the hope that benzyl enol ethers of type **29–31** would be intermediates for the preparation of 2,6-anhydrohepturonic acid derivatives **32** (Scheme 2) via oxidative cleavage of their alkene moieties, we converted alcohol **19** into the corresponding mesylate **20**, tosylate **21**, and nosylate **22** applying standard procedures. Attempts to induce a *syn* elimination from these sulfonates under basic conditions (DBN (1,5-diazabicyclo[4.3.0]non-5-ene), THF; DBN, MeCN,  $70^\circ$ , 10 days; CsF, DMF,  $140^\circ$ , 3 days;  $\text{Al}_2\text{O}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $20^\circ$ ; NaI, HMPA (hexamethylphosphoric triamide),  $100^\circ$ , 15 h) led only to decomposition products; no trace of enol ether **29** could be seen by  $^1\text{H}$ -NMR of the crude reaction mixtures. Since the epoxide moiety of **20–22** contributes probably to the instability of these sulfonates and of **29**, we converted **20–22** into the corresponding diols **23–25** by dissolution in  $\text{CF}_3\text{COOH}/\text{CH}_2\text{Cl}_2$  at room temperature. This acidic treatment induced smooth heterolysis of the epoxide

<sup>2)</sup> The following abbreviations are used: Bn =  $\text{PhCH}_2$ , Bz =  $\text{PhCO}$ , TMS =  $\text{Me}_3\text{Si}$ , TBS = *t*-BuMe<sub>2</sub>Si, TfO =  $\text{CF}_3\text{SO}_3$ , mCPBA = 3-chloro-4-methylbenzoic acid, LDA =  $\text{Li}(\text{i-Pr})_2\text{N}$ , DMAP = *N,N*-dimethylpyridin-4-amine, and pyr = pyridine. In the case of racemates, only one enantiomer is shown; enantiomers are characterized by the sign of optical rotation preceding their key numbers.

1) LDA, THF  $-78^{\circ}$   
 2) RCl  $-78$  to  $20^{\circ}$   
**9** R = Me<sub>3</sub>Si  
**10** R = Et<sub>3</sub>Si  
 ICH<sub>2</sub>Cl, Et<sub>2</sub>Zn  
 CH<sub>2</sub>Cl<sub>2</sub>  $-20$  to  $20^{\circ}$   
**11** R = Me<sub>3</sub>Si  
**12** R = Et<sub>3</sub>Si  
 FeCl<sub>3</sub>, pyr.  
 DMF,  $60^{\circ}$   
**(-)-13**  
*t*-BuO<sub>2</sub>H DBU  
**13**  $\xrightarrow[\text{MeOH, } 0^{\circ}]{\text{NaBH}_4, \text{CeCl}_3 \cdot 6 \text{ H}_2\text{O}}$   
 mCPBA  
 CH<sub>2</sub>Cl<sub>2</sub>  $20^{\circ}$   
 NaBH<sub>4</sub>  
 MeOH  $0^{\circ}$   
**(+)-17**  
 BzCl, pyr.  $\rightarrow$  **14** R = H  
**15** R = Bz  
 BzCl, pyr.  $\rightarrow$  **(-)-16** R = Bz  
**(-)-18** R = H  
**(-)-16**  $\xrightarrow{\text{Bu}_4\text{NF}}$   
 CF<sub>3</sub>COOH  
 CH<sub>2</sub>Cl<sub>2</sub>,  $20^{\circ}$   
 Ac<sub>2</sub>O  
 pyr.  
 DMAP  $20^{\circ}$   
**(-)-19** R' = Bz, H, R' = H  
**20** R' = MeSO<sub>2</sub> (80%)  
**23** R' = MeSO<sub>2</sub> (87%)  
**24** R' = Ts (78%)  
**25** R' = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub> (72%)  
**26** R' = MeSO<sub>2</sub> (87%)  
**27** R' = Ts (85%)  
**28** R' = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub> (95%)  
**22** R' = Bz, R' = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub> (77%)  
 base  
**29**  
 base  
**30**  
 base  
**31**  
 ?  
**32**

moiety with participation of the 5-*endo*-(benzoxyloxy) group. Intermediate cations of type **33** are expected to be formed in these reactions (*Scheme 3*). They react with the nucleophile (CF<sub>3</sub>COOH) giving the corresponding trifluoroacetates **34** that are rapidly hydrolyzed on aqueous workup giving orthoester intermediates **35**. The latter are transformed preferentially into **23–25** rather than into the isomeric products of type **36**, for thermodynamic reasons. Indeed, a 2-*endo*-benzoate moiety in **36** would suffer from *gauche* interactions with the 7-*endo*-(benzyloxy) group, a repulsive steric interaction that is more severe than that of the 4-*endo*-hydroxy group of **23–25**. Products **23–28** are the first representatives of 8-oxabicyclo[3.2.1]octane-2,3,4,6,7-pentol derivatives ever reported.

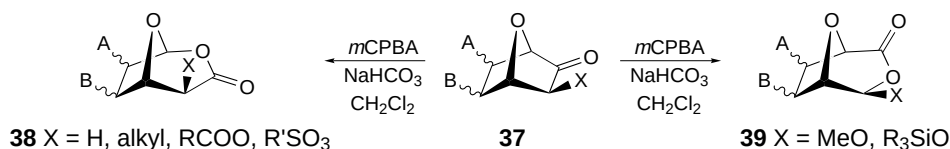
Scheme 3



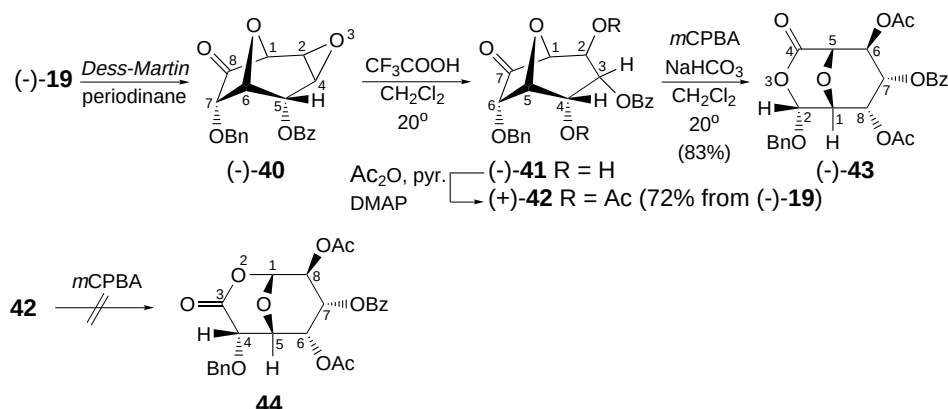
All our attempts to induce elimination of sulfonic acids from **23–25** to generate the desired benzyl enol ether derivative **30** failed. We thus protected diols **23–25** as diacetates applying standard conditions. This provided products **26–28** in good yield. None of them furnished the corresponding enol ether derivative **31** upon heating with various bases (see above, and  $t\text{-BuOK/THF}$ ). We were thus forced to explore another route to convert **19** into the desired ‘ $\beta$ -C-mannopyranosylformaldehyde’ derivatives of type **32**.

**Synthesis of 2,6-Anhydro-D-glycero-D-galacto-hepturonic Acid Derivatives.** – For 3-substituted 7-oxabicyclo[2.2.1]heptan-2-ones **37**, we had shown [24] that their *Baeyer-Villiger* oxidation gives the corresponding urono-6,1-lactones **38** due to preferred C(1) migration. This was not the case anymore for derivatives with 3-X substituents being a better releasing group than the ethereal 7-oxa bridge. Indeed when  $\text{X} = \text{MeO}$  or  $(t\text{-Bu})\text{Me}_2\text{SiO}$ , the *Baeyer-Villiger* oxidation led to the corresponding 3,8-dioxabicyclo[3.2.1]octan-2-ones **39** due to preferred C(3) migration (Scheme 4). *Ogawa* and coworkers have reported that cyclohexanones  $\alpha$ -substituted with an acyloxy group and  $\alpha'$ -substituted with a benzyloxy group undergo the *Baeyer-Villiger* oxidation with preferred migration of the (benzyloxy)alkyl group [25].

Scheme 4



We thus oxidized alcohol ( $\pm$ )-**19** into ketone ( $\pm$ )-**40** (90%) with the *Dess-Martin* periodinane [26] (Scheme 5). Oxidation of ( $\pm$ )-**19** with pyridinium chlorochromate proceeded with lower yield (27%). Treatment of ( $\pm$ )-**40** with  $\text{CF}_3\text{COOH}$  in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ$  led to diol ( $\pm$ )-**41** in 98% yield. Esterification of ( $\pm$ )-**41** with  $\text{Ac}_2\text{O}$ /pyridine and DMAP (*N,N*-dimethylpyridin-4-amine) provided ( $\pm$ )-**42** (95%). Conversion of alcohol ( $\pm$ )-**19** into ( $\pm$ )-**42** could be done without isolation and purification of ( $\pm$ )-**40** and ( $\pm$ )-**41** in 79% overall yield (Scheme 5). Subsequent *Baeyer-Villiger* oxidation of ketone ( $\pm$ )-**42** with  $m\text{CPBA}$  ( $\text{CH}_2\text{Cl}_2$ ,  $\text{NaHCO}_3$ ,  $20^\circ$ ) then afforded a single lactone ( $\pm$ )-**43**

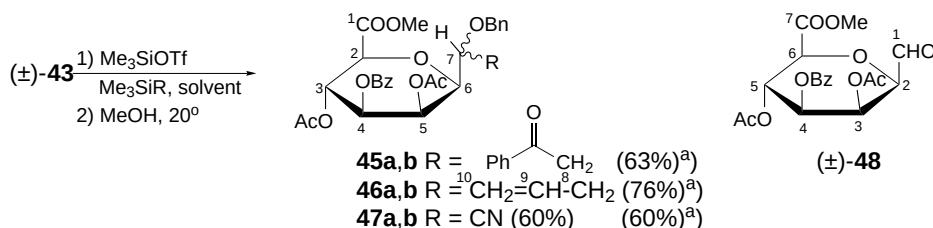
Scheme 5<sup>2)</sup>

arising from the favored (benzyloxy)alkyl-group migration. The regioisomeric lactone ( $\pm$ )-**44** that arises from the migration of the  $\sigma(\text{C}(1)–\text{C}(8))$  bond of ( $\pm$ )-**40** was not observed. Similarly, the enantiomer (–)-**19** afforded (–)-**43** via (–)-**40**, (–)-**41**, and (+)-**42**.

The  $^1\text{H-NMR}$  spectrum of ( $\pm$ )-**43** displayed a  $d$  at  $\delta(\text{H})$  4.63 ( $^3J(1,2) = 4.8$  Hz) assigned to the acetal proton  $\text{H}–\text{C}(2)$ . This assignment was confirmed by the 2D CH-COR NMR spectrum that correlated the signal at  $\delta(\text{C})$  100.7, typical of the acetal center  $\text{C}(2)$ , with the signal at  $\delta(\text{H})$  4.63 ( $\text{H}–\text{C}(2)$ ). A larger chemical shift ( $\delta(\text{H})$  5.3–5.7) would have been expected for the bridgehead proton  $\text{H}–\text{C}(1)$  of uronolactone **44** [24]. Moreover, the  $^1\text{H-NMR}$  spectrum of ( $\pm$ )-**43** showed  $^3J(1,8) = 5.9$ ,  $^3J(8,7) = 3.7$ ,  $^3J(7,6) = 3.3$ , and  $^3J(6,5) = 1.8$  Hz that are consistent with pairs of vicinal protons occupying axial/equatorial or equatorial/equatorial positions of an averaged chair conformation for the tetrahydro-2*H*-pyran ring  $\text{O}(9)–\text{C}(1)–\text{C}(8)–\text{C}(7)–\text{C}(6)–\text{C}(5)$ .

Acetals have been used as precursors for oxyalkyl-cation intermediates that can react with enoxysilanes [27][28]. The treatment of ( $\pm$ )-**43** with 1-phenyl-1-[(trimethylsilyl)oxy]ethene (trimethylsilyl enol ether of acetophenone) in the presence of trimethylsilyl triflate ( $\text{MeNO}_2$ ,  $20^\circ$ , 17 h), followed by reaction with  $\text{MeOH}$  ( $20^\circ$ , 17 h) led to a 1:1 mixture of diastereoisomeric  $\beta$ -(benzyloxy) ketones ( $\pm$ )-**45a** and ( $\pm$ )-**45b** (= **45a,b**) that could not be separated by column chromatography (Scheme 6). The reaction of ( $\pm$ )-**43** with  $\text{Me}_3\text{SiOTf}$  and allyltrimethylsilane ( $\text{MeCN}$ ,  $0^\circ$ , 1 h) followed by quenching with  $\text{MeOH}$  gave a 1:4.3 mixture of ( $\pm$ )-**46a** and ( $\pm$ )-**46b** (= **46a,b**) that could be separated by column chromatography (overall yield 76%). The reaction of ( $\pm$ )-**43** with  $\text{Me}_3\text{SiOTf}$  and trimethylsilyl cyanide, followed by quenching with  $\text{MeOH}$  gave a mixture **17a,b** from which ( $\pm$ )-**47a** and ( $\pm$ )-**47b** could be isolated in 20 and 40% yield, respectively. The relative configuration of the newly created stereogenic centers of **45a,b**–**47a,b** was not established.

Since the  $\text{C}–\text{C}$  forming reactions from acetal ( $\pm$ )-**43** were little diastereoselective (Scheme 6), we decided to transform ( $\pm$ )-**43** into the corresponding 2,6-anhydrohepturonic acid esters such as ( $\pm$ )-**48**. Attempts to generate mixtures of cyanohydrins by hydrogenolysis of **47a,b**, cyanohydrines that should eliminate  $\text{HCN}$  to give ( $\pm$ )-**48** by treatment with formaline, were not met with success. We thus chose to transform ( $\pm$ )-**43** into the corresponding uronic acid esters with the aldehyde protected as an acetal or a

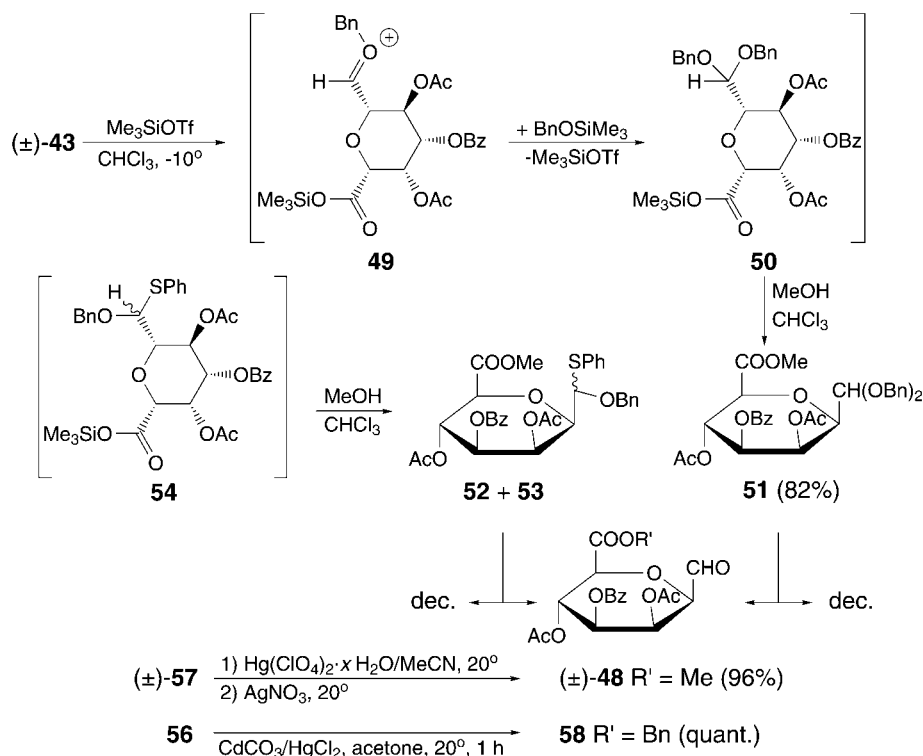
Scheme 6<sup>2)</sup>

<sup>a)</sup> The numbering in the formula refers to **46a,b** and **47a,b**.

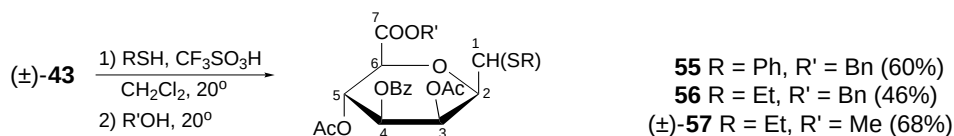
thioacetal. Good results were obtained with the following experiments. Treatment of  $(\pm)\text{-43}$  with  $\text{BnOSiMe}_3$  and  $\text{Me}_3\text{SiOTf}$  in  $\text{CHCl}_3$  at  $-10^\circ$  for 30 min, followed by quenching with MeOH ( $-10$  to  $20^\circ$ , 24 h) furnished the racemic methyl uronate dibenzyl acetal **51** in 82% yield (Scheme 7). The process implies probably the cationic intermediate **49** resulting from the Lewis acid-promoted acetal heterolysis, followed by reaction with  $\text{Me}_3\text{SiOBn}$  that gives a second intermediate **50**, which is expected to react with MeOH giving **51**. With  $\text{PhSSiMe}_3$  as nucleophile instead of  $\text{BnOSiMe}_3$ , a 1.7:1 mixture of two monothioacetals **52** and **53** was obtained in 66% yield from  $(\pm)\text{-43}$ . In this case, the hypothetical intermediate **49** reacts with  $\text{PhSSiMe}_3$  giving an other intermediate **54**, the reaction of which with MeOH gives rise to **52/53** (Scheme 7). Attempts to liberate the carbaldehyde group from dibenzyl acetal **51** (hydrogenolysis, acidic hydrolysis) or from the *O*-benzyl *S*-phenyl monothioacetals **52/53** (hydrogenolysis, treatment with  $\text{Hg}(\text{OAc})_2/\text{MeCN}$ , acidic hydrolysis) gave the desired product  $(\pm)\text{-48}$  in low yield as decomposition could not be avoided.

We thus decided to prepare the corresponding racemic dithioacetals **55–57** (Scheme 8). Treatment of  $(\pm)\text{-43}$  with an excess of thiophenol in the presence of triflic acid in anhyd.  $\text{CH}_2\text{Cl}_2$  ( $20^\circ$ , 1 h), followed by quenching with benzyl alcohol ( $20^\circ$ , 18 h) provided the racemic benzyl uronate diphenyldithioacetal **55** in 60% yield. Using  $\text{EtSH}$  instead of  $\text{PhSH}$  led to **56** in 46% yield. The same procedure using  $\text{EtSH}/\text{CF}_3\text{SO}_3\text{H}/\text{CH}_2\text{Cl}_2$  followed by quenching with MeOH provided  $(\pm)\text{-57}$  in 74% yield. The structures of **55–57** were deduced from their spectral data (see *Exper. Part*). For instance, in the case of **55**,  $^3J(2,3) = 1.1$ ,  $^3J(3,4) = 3.4$ ,  $^3J(4,5) = 10.2$ ,  $^3J(5,6) = 10.1$  Hz were measured in its  $^1\text{H-NMR}$  spectrum, establishing the  $\beta$ -C-mannopyranosyl structure [29]. Treatment of dithioacetal  $(\pm)\text{-57}$  with  $\text{Hg}(\text{ClO}_4)_2 \cdot x \text{ H}_2\text{O}$  ( $x = 3.4$ ) and then with  $\text{Ag}_2\text{CO}_3$  in MeCN gave rise to the desired aldehyde  $(\pm)\text{-48}$  in 96% yield. Similarly,  $(-)\text{-43}$  yielded optically active **48** via  $(-)\text{-57}$ . The benzyl uronate analog **58** was obtained by treatment of racemic **56** with  $\text{CdCO}_3$  and  $\text{HgCl}_2$  in acetone (Scheme 7). Aldehydes **48** and **58** were decomposed during our attempts to purify them, and were thus used as crude products in the condensations described below. They represent the first examples of 2,6-anhydrohepturonic acid derivatives, and they can be obtained in both enantiomerically pure forms starting from  $(+)\text{-5}$  and  $(-)\text{-5}$  (see above).

**Nozaki-Oshima Condensations with 8-Oxabicyclo[3.2.1]oct-3-en-2-ones.** – The addition of  $\text{Me}_2\text{AlSPh}$  to enone  $(\pm)\text{-13}$  (Scheme 2) (anh. THF,  $-78^\circ$ ) generated the

Scheme 7<sup>2)</sup>

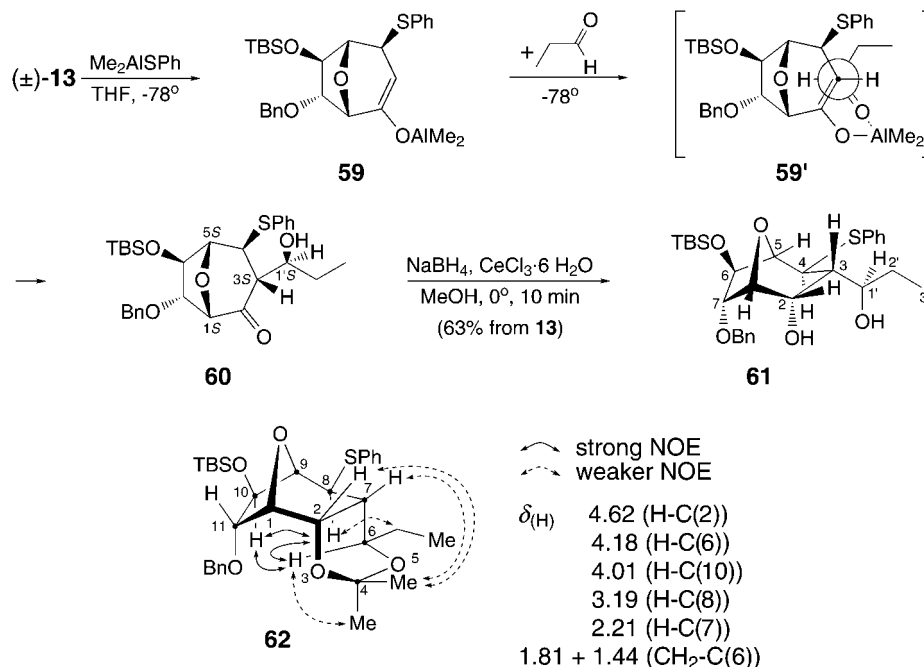
Scheme 8



enolate **59** that was trapped with propanal ( $-78^\circ$ , 12 h) giving a single racemic  $\beta$ -hydroxy ketone **60** (Scheme 9). The latter was not isolated but reduced directly under *Luche's* conditions ( $\text{NaBH}_4$ ,  $\text{CeCl}_3 \cdot 6 \text{H}_2\text{O}$ ,  $\text{MeOH}$ ) [22] giving rise to a single racemic diol **61** isolated in 63% yield based on  $(\pm)$ -**13**. Out of *sixteen* possible diastereoisomers that can be formed by this reaction cascade starting from  $(\pm)$ -**13**, only **61** was formed. This result can be interpreted in terms of steric factors. The *exo* face of the bicyclic enone  $(\pm)$ -**13** is more readily available for the conjugate addition than its *endo* face. With the phenylthio substituent of enolate **59** occupying the *exo* face, the *endo* face becomes preferred for the crossaldol reaction with propanal giving rise to  $\beta$ -hydroxy ketone **60**. The relative (1*RS*,1'*RS*)-configuration of the reduced  $\beta$ -hydroxy ketone, *i.e.*,

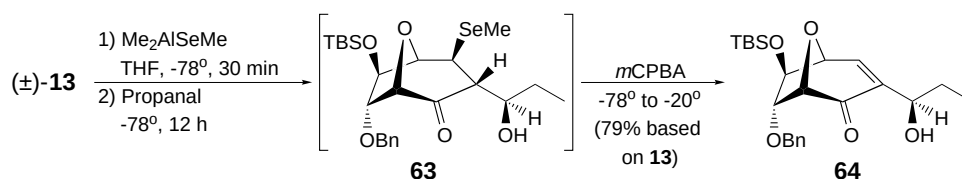


of **61**, arises from a closed transition structure [31] shown with **59'** (Scheme 9). Finally, the diastereoselective reduction of the  $\beta$ -hydroxy ketone **60** is *exo*-face selective because of the 3-*endo*-alkyl substituent. The structure of **61** was established by its NMR data and by those of its acetonide **62**, obtained from **61** in 95% yield on treatment with  $\text{Me}_2\text{C}(\text{OMe})_2/\text{acetone}$  and a catalytic amount of  $\text{TsOH}$ .

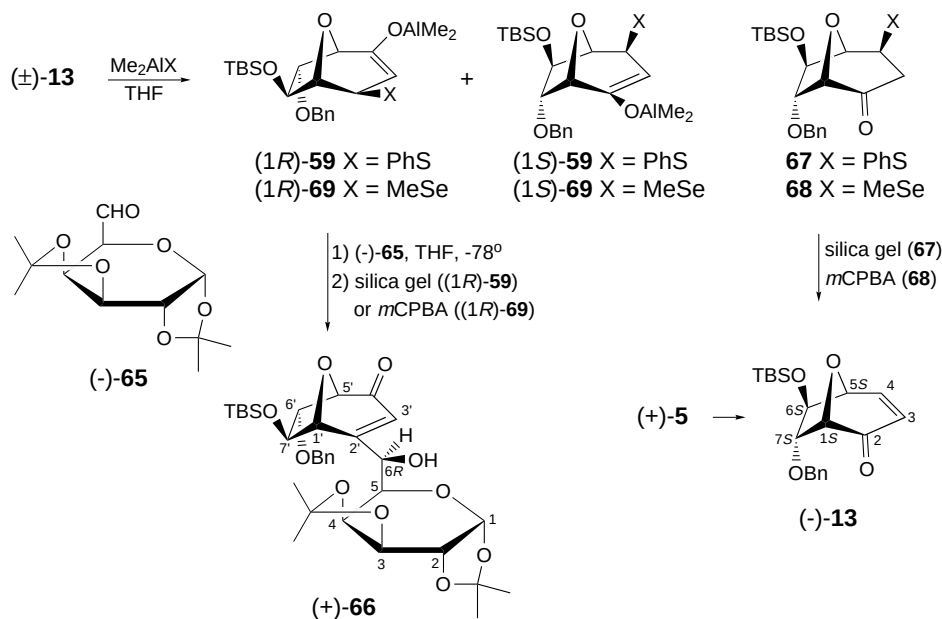
Scheme 9<sup>2)</sup>

The coupling constants measured in the  $^1\text{H}$ -NMR spectrum of **61** are consistent with an averaged boat conformation for the six-membered ring  $\text{C}(1)\text{--C}(2)\text{--C}(3)\text{--C}(4)\text{--C}(5)\text{--O}(8)$ ; typical  $^3J(1,2) = 7.6$ ,  $^3J(2,3) = 4.5$ ,  $^3J(3\text{ax},4\text{ax}) = 9.9$ , and  $^3J(4,5) < 0.5$  Hz were found. For acetonide **62**,  $^3J(1,2) = 6.7$ ,  $^3J(2,7) = 8.2$ ,  $^3J(7,8) = 3.3$ , and  $^3J(8,9) < 0.5$  Hz suggested a deformed boat conformation for its tetrahydro-2*H*-pyrane ring (flattening of the boat of **61** toward a sofa). The relatively large  $^3J(6,7)$  of 10.0 Hz demonstrated the *trans*-relationship between these two protons. The  $^{13}\text{C}$ -NMR spectrum of **62** showed two similar chemical shifts ( $\delta(\text{C})$  25.4 and 27.7) for the two Me groups of the acetonide, thus suggesting a boat or near-boat conformation of the 1,3-dioxane moiety  $\text{C}(2)\text{--C}(7)\text{--C}(6)\text{--O}(6)\text{--C}(4)\text{--O}(3)$  [32]. These assignments were confirmed by the 2D  $^1\text{H}$ -NOESY data of **62** that showed NOEs between the proton signals indicated in Scheme 9. Most significant was the large NOE cross-peak between  $\delta(\text{H})$  4.01 and 4.18 assigned to  $\text{H}\text{--C}(10)$  and  $\text{H}\text{--C}(6)$ , respectively. The signal at  $\delta(\text{H})$  3.19 assigned to  $\text{H}\text{--C}(8)$  also witnessed strong NOEs with  $\delta(\text{H})$  4.01 and 4.18.

The addition of  $\text{Me}_2\text{AlSeMe}$  to enone  $(\pm)\text{-13}$  ( $\text{THF}$ ,  $-78^\circ$ ) followed by the addition of propanal ( $\text{THF}$ ,  $-78^\circ$ ) gave a single  $\beta$ -hydroxy ketone **63** (Scheme 10) that was oxidized *in situ* with 3-chloroperbenzoic acid ( $-78$  to  $-20^\circ$ ). This provided the stable enone **64** isolated in 79% yield (from  $(\pm)\text{-13}$ ). The relative configuration at the exocyclic OH-substituted  $\text{C}(1')$  of **64** was not established unambiguously but is suggested to be (1*RS*,1'*RS*) in analogy to **61** and **62**.

Scheme 10<sup>2)</sup>

**Enantioselective Nozaki-Oshima Condensation.** – The successive addition of  $\text{Me}_2\text{AlSPh}$  to racemic  $(\pm)\text{-13}$  (THF,  $-78^\circ$ , 1 h), then of enantiomerically pure aldehyde  $(-)\text{-65}$  derived readily from D-galactose [33] (THF,  $-78^\circ$ , 16 h) led to a mixture from which unreacted enone **13** was recovered and product  $(+)\text{-66}$  isolated in 17% yield (Scheme 11). No other diastereoisomeric condensation product could be isolated by column chromatography. An analogous experiment using  $\text{Me}_2\text{AlSeMe}$  instead of  $\text{Me}_2\text{AlSPh}$ , followed by oxidative elimination ( $m\text{CPBA}$ ), led to  $(+)\text{-66}$  isolated in 27% as single product. The unreacted enone **13** was optically enriched and corresponded to  $(-)\text{-13}$  with *ca.* 30% ee for the latter experiment (comparison of  $[\alpha]_D^{25}$ ). These observations suggest a high enantioselectivity for the cross-aldol reaction of aldehyde  $(-)\text{-65}$  with the bicyclic enolates **59** and **69** derived from  $(\pm)\text{-13}$  (Scheme 11). Our results can be interpreted in terms of the formation of enolates  $(1R)\text{-59}$  (or  $(1R)\text{-69}$ ) and  $(1S)\text{-59}$  (or  $(1S)\text{-69}$ ) with selective addition of  $(1R)\text{-59}$  (or  $(1R)\text{-69}$ ) that leads to enone  $(+)\text{-66}$ . The unreacted  $(1S)\text{-59}$  is converted probably into ketone **67** that

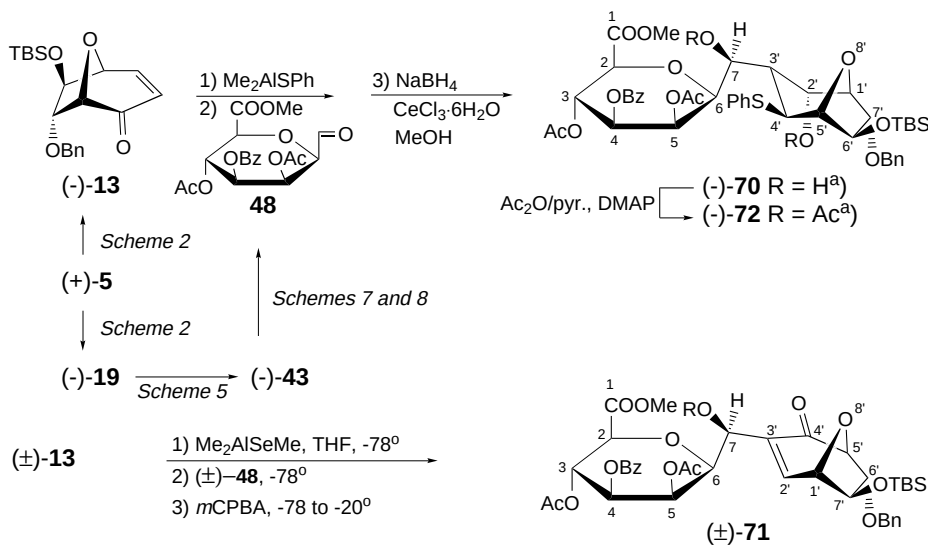
Scheme 11<sup>2)</sup>

undergoes  $\beta$ -elimination during the chromatographic (silica gel) purification giving (–)-**13**. The unreacted (1*S*)-**69** is converted into ketone **68** that undergoes oxidative elimination (*m*CPBA) also giving the enantiomerically enriched enone (–)-**13**. The (1*S*,5*S*,6*S*,7*S*) configuration of the latter was established by its independent synthesis starting from ketone (+)-**5** (*Scheme 1*). The (6*R*)-configuration at the newly created exocyclic OH-substituted stereogenic center of (+)-**66** was not established, but is proposed to result from an aldol reaction implying a closed transition structure (*Zimmerman-Traxler* model [31]), by analogy with all other related condensations involving bicyclic aluminium enolates [34].

Experiments outlined in *Scheme 11* were not optimized. They suggested, however, the possibility to prepare C-disaccharides applying the *Nozaki-Oshima* condensation to aldehydes **48** (and **58**) and bicyclic enone **13**.

**Synthesis of  $\beta$ -C(1  $\rightarrow$  3)-Linked Disaccharides.** – When racemic aluminium enolate **59**, resulting from the addition of  $\text{Me}_2\text{AlSPh}$  to ( $\pm$ )-**13** (see above, *Scheme 9*), was trapped with racemic aldehyde ( $\pm$ )-**48**, a single  $\beta$ -hydroxy ketone was formed that was not isolated but directly reduced under *Luche's* conditions [22] to afford a single diol ( $\pm$ )-**70** isolated in 56% (*Scheme 12*; yield based on dithioacetal ( $\pm$ )-**57**, see above *Scheme 7*). This result demonstrates the existence of chiral matching for the *Nozaki-Oshima* condensation of ( $\pm$ )-**13** and ( $\pm$ )-**48**. The same reaction cascade applied to enantiomerically pure enone (–)-**13** and optically active aldehyde **48** derived from thioacetal (–)-**57** afforded enantiomerically pure (–)-**70**. The 400-MHz  $^1\text{H}$ -NMR spectra of ( $\pm$ )-**70** and (–)-**70** were identical. Both (–)-**13** and (–)-**57** were derived from 7-oxanorbornanone (+)-**5** (*Schemes 1, 2, 5, and 8*).

*Scheme 12<sup>2)</sup>*

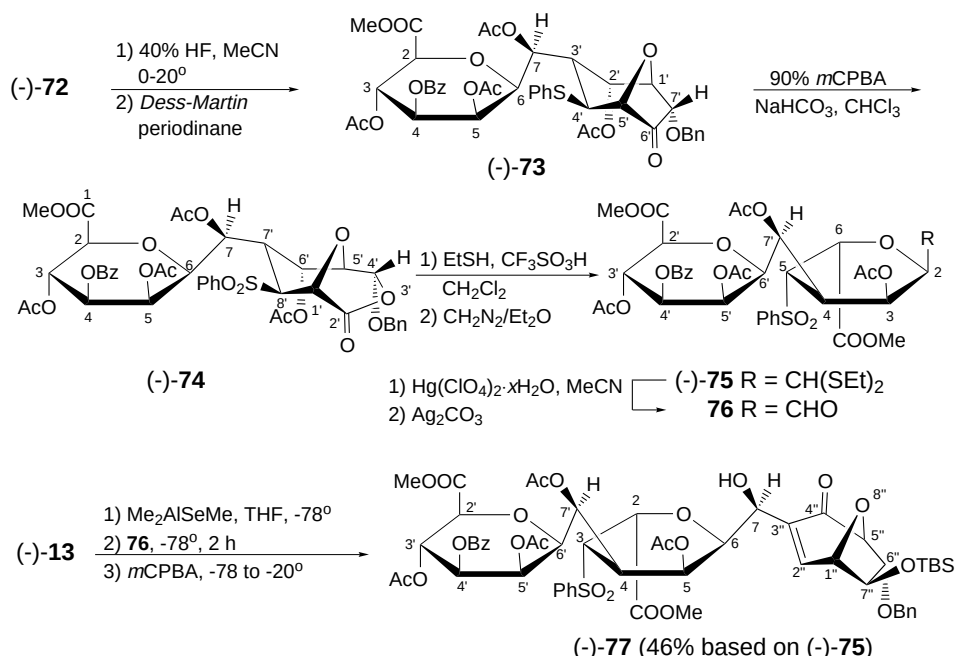


a) The numbering in the formula refers to (–)-**72**.

The addition of  $\text{Me}_2\text{AlSeMe}$  to enone ( $\pm$ )-**13**, followed by trapping of the resulting aluminium enolate with ( $\pm$ )-**48** gave also a single  $\beta$ -hydroxy ketone that was not isolated but directly oxidized with *m*CPBA affording enone ( $\pm$ )-**71** in 49% yield (from dithioacetal ( $\pm$ )-**57**; *Scheme 12*). The relative configuration of the hydroxymethano linker C(7) of ( $\pm$ )-**70** and ( $\pm$ )-**71** was not established unambiguously. The configuration proposed corresponds to that expected for a cross aldol reaction following the *Zimmerman-Traxler* model [31], as demonstrated with **62** and several other related *Nozaki-Oshima* condensations involving bicyclic enones and sugar-derived carboxaldehydes [34].

**Synthesis of a Precursor of a C,C-Trisaccharide with C(1 $\rightarrow$ 3)-Linkages.** – Desilylation of the acetate derivative (–)-**72** of (–)-**70** with 40% aqueous HF solution in MeCN (0–20°, 2 h) followed by *Dess-Martin* oxidation of the resulting alcohol provided ketone (–)-**73** quantitatively (*Scheme 13*). *Baeyer-Villiger* oxidation of (–)-**73** with 90% *m*CPBA and  $\text{NaHCO}_3$  in  $\text{CHCl}_3$  (20°, 16 h) led to (–)-**74** in quantitative yield. Concomittent oxidation of the phenylthio group to the phenylsulfonyl group could not be avoided. Importantly, the *Baeyer-Villiger* oxidation was highly regioselective, as in the case of (+)-**42**  $\rightarrow$  (–)-**43** (*Scheme 5*). Treatment of the uronolactone (–)-**74** with EtSH under acidic conditions ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CF}_3\text{SO}_2\text{H}$ ), followed by esterification of the resulting uronic acid with diazomethane gave the C-disaccharide C-glycoside derivative (–)-**75** in 61% yield (from diol (–)-**70**). Hydrolysis of the dithioacetal moiety of (–)-**75** promoted by mercuric and silver salts provided the unstable aldehyde **76** that was used without purification in the subsequent *Nozaki-Oshima* condensation implying (–)-**13** and  $\text{Me}_2\text{AlSeMe}$ . After an oxidative workup with *m*CPBA, the C,C-trisaccharide precursor (–)-**77** was isolated in 40% yield based on dithioacetal derivative (–)-**75**. The spectral data and elemental analyses (*Exper. Part*) of (–)-**73**, (–)-**74**, and (–)-**77** were in agreement with the proposed structures that were deduced from their mode of formation (see above).

**Conclusion.** – Starting from the *Diels-Alder* adduct of furan to 1-cyanovinyl acetate, enantiomerically pure 6,7-dihydroxy-8-oxabicyclo[3.2.1]oct-3-en-2-one and 8-oxabicyclo[3.2.1]octane-2,3,4,6,7-pentol derivatives were prepared for the first time. Highly stereoselective *Nozaki-Oshima* condensation and reduction cascades were found to occur with 8-oxabicyclo[3.2.1]oct-3-en-2-one and various carboxaldehyde derivatives. With enantiomerically pure aldehydes derived from sugars, highly enantioselective *Nozaki-Oshima* condensations were observed. This allows us to present a new approach to the total asymmetric synthesis of C-linked disaccharides and of C,C-linked trisaccharide precursors, thus demonstrating the possibility of iterative synthesis of oligosaccharide mimetics with C(1 $\rightarrow$ 3) linkages. Benzyl 3,5-di-*O*-acetyl-2,6-anhydro-4-*O*-benzoyl-D-glycero-D-galacto-hepturonate (**76**) was derived from (+)-(1*S*,4*S*,5*S*,6*S*)-6-endo-(benzyloxy)-5-exo-[(*tert*-butyl)dimethylsilyl]oxy]-7-oxabicyclo[2.2.1]heptan-2-one ((+)-**5**). It allows one to construct  $\beta$ -C-mannopyranosides including a disaccharide analog with a  $\beta$ -C(1 $\rightarrow$ 3) linkage. All the products described in this work can be obtained in both their enantiomeric forms as bicyclic ketones (+)- and (–)-**5** are available with the same ease [14][17]. A number of our synthetic intermediates do not have to be isolated and purified for successful further transformations.

Scheme 13<sup>2)</sup>

## Experimental Part

**General.** See [35]. The procedures described for racemic products were applied to the preparation of enantiomerically pure products. Apart from the  $[\alpha]$  values and m.p., all other data were identical for enantiomerically pure products and the corresponding racemates. <sup>1</sup>H-NMR Signal assignments were confirmed by 2D COSY and NOESY <sup>1</sup>H-NMR data. Flash chromatography (FC): silica gel (Merck No. 9385, 240–400 mesh). Electron-spray mass spectrometer: Perkin Elmer API 150 EX.

(1*S*,2*S*,4*S*,5*S*,6*S*)- and (1*R*,2*R*,4*R*,5*R*,6*R*)-6-endo-(Benzyloxy)-5-exo-[[*tert*-butyl]dimethylsilyl]oxy]-2-exo-[[*S*(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]methyl]-7-oxabicyclo[2.2.1]heptan-2-endo-ol ((+)-**7** and (–)-**8**, resp.). BuLi (1.6M in hexane; 26.9 ml, 43 mmol) was added dropwise to a stirred soln. of (+)-(*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximide (6.32 g, 37.3 mmol) in anh. THF (150 ml) cooled to –25° under Ar. After stirring at –25° for 30 min, the deep yellow soln. was cooled to –60° to which a cooled (–60°) soln. of (±)-**5** [16][36] (10.0 g, 28.7 mmol) in anh. THF (50 ml) was cannulated under stirring. The mixture was stirred and allowed to warm to –20° within ca. 3 h. Sat. aq. NH<sub>4</sub>Cl soln. (400 ml) was added and the mixture extracted with Et<sub>2</sub>O (400 ml, 5 ×). The combined org. extract was dried (MgSO<sub>4</sub>) and evaporated and the yellowish oil (18.0 g) purified by FC (10 × 31 cm, light petroleum ether/AcOEt 1:1): 6.25 g (42%) of (+)-**7** and 6.59 g (44%) of (–)-**8**, both as colorless oils.

**Data of (+)-7:** *R*<sub>f</sub> 0.60; d.e. >99%.  $[\alpha]_{589}^{25} = +51$ ,  $[\alpha]_{577}^{25} = +53$ ,  $[\alpha]_{546}^{25} = +60$ ,  $[\alpha]_{435}^{25} = +107$ ,  $[\alpha]_{405}^{25} = +130$  (*c* = 1.2, CHCl<sub>3</sub>). UV (MeCN): 272 (1900), 265 (2300), 209 (1400), 197 (15000). IR (film): 3450, 3225, 3065, 2955, 2930, 2885, 2860, 2245, 1445, 1355, 1240, 1150, 1120, 1085, 1005, 875, 840, 775, 740. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.90, 7.64–7.55, 7.40–7.30 (3*m*, 2 H, 3 H, 5 H, arom. H); 6.16 (*s*, OH–C(2)); 4.83 (br. *d*, <sup>3</sup>*J*(1,6) = 4.8, H–C(1)); 4.76, 4.62 (2*d*, <sup>2</sup>*J* = 11.4, PhCH<sub>2</sub>O); 4.16 (br. *d*, <sup>3</sup>*J*(4,3*exo*) = 6.5, H–C(4)); 4.06 (*m*, <sup>3</sup>*J*(6,1) = 4.8, <sup>3</sup>*J*(6,5) = 2.4, H–C(6)); 4.01 (*d*, <sup>3</sup>*J*(5,6) = 2.4, H–C(5)); 3.51, 3.46 (2*d*, <sup>2</sup>*J* = 14.0, CH<sub>2</sub>–C(2)); 2.70 (*s*, S=NMe); 2.07 (*dd*, <sup>3</sup>*J*(3*exo*,3*endo*) = 13.4, <sup>3</sup>*J*(3*exo*,4) = 6.5, H<sub>3*exo*</sub>–C(3)); 1.71 (*d*, <sup>3</sup>*J*(3*endo*,3*exo*) = 13.4, H<sub>3*endo*</sub>–C(3)); 0.89 (*s*, *t*-BuSi); 0.09, 0.08 (2*s*, Me<sub>2</sub>Si). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 139.1, 137.1 (2*s*, arom. C); 132.9, 129.3, 129.0, 128.4, 128.2, 127.9 (6*d*, <sup>1</sup>*J*(C,H) = 160, arom. C); 91.1 (*d*, <sup>1</sup>*J*(C,H) = 150, C(6)); 84.8 (*d*, <sup>1</sup>*J*(C,H) = 160, C(4)); 80.0 (*s*, C(2)); 79.9 (*d*, <sup>1</sup>*J*(C,H) = 144, C(5)); 76.8 (*d*, <sup>1</sup>*J*(C,H) = 160, C(1)); 72.9 (*t*, <sup>1</sup>*J*(C,H) = 141, PhCH<sub>2</sub>O); 64.3 (*t*, <sup>1</sup>*J*(C,H) = 139, CH<sub>2</sub>–C(2)); 43.4 (*t*, <sup>1</sup>*J*(C,H) = 134, C(3)); 29.1 (*q*, <sup>1</sup>*J*(C,H) = 138, S=NMe); 25.7

(*q*,  $^1J(\text{C,H}) = 125$ ,  $\text{Me}_3\text{CSi}$ ); 17.9 (*s*,  $\text{Me}_3\text{CSi}$ );  $-4.7$ ,  $-4.8$  ( $2q$ ,  $^1J(\text{C,H}) = 118$ ,  $\text{Me}_2\text{Si}$ ). CI-MS ( $\text{NH}_3$ ): 518 (27,  $[M + 1]^+$ ), 366 (11), 170 (26,  $[\text{PhS}(=\text{O})(=\text{NHMe})\text{Me}]^+$ ), 156 (53,  $[\text{PhS}(=\text{O})(=\text{NHMe})\text{H}]^+$ ), 154 (11,  $[\text{PhS}(=\text{O})(=\text{NMe})]^+$ ), 125 (27), 108 (17,  $\text{BnOH}^+$ ), 107 (36,  $\text{BnO}^+$ ), 91 (100,  $\text{C}_7\text{H}_7^+$ ), 77 (12,  $\text{C}_6\text{H}_5^+$ ). Anal. calc. for  $\text{C}_{27}\text{H}_{39}\text{NO}_5\text{SSi}$  (517.83): C 62.62, H 7.61, N 2.71, S 6.19, Si 5.42; found: C 62.68, H 7.67, N 2.68, S 6.01, Si 5.42.

Data for (+)-**8**:  $R_f$  0.42; d.e. >99%.  $[\alpha]_{\text{D}}^{25} = -17$ ,  $[\alpha]_{\text{D}}^{25} = -18$ ,  $[\alpha]_{\text{D}}^{25} = -20$ ,  $[\alpha]_{\text{D}}^{25} = -27$ ,  $[\alpha]_{\text{D}}^{25} = -30$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ ). UV (MeCN): 271 (1800), 264 (2200), 208 (14500), 200 (14000). IR (film): 3440, 3230, 3065, 2955, 2930, 2885, 2860, 2245, 1445, 1410, 1390, 1350, 1240, 1150, 1125, 1085, 1010, 870, 840, 780, 745.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.86, 7.60–7.50, 7.38–7.29 (3*m*, 2 H, 3 H, 5 H, arom. H); 5.85 (*s*, OH–C(2)); 4.78, 4.62 (2*d*,  $^2J = 11.4$ ,  $\text{PhCH}_2\text{O}$ ); 4.65 (br. *d*,  $^3J(1,6) = 4.9$ , H–C(1)); 4.19 (br. *d*,  $^3J(4,3_{\text{exo}}) = 6.5$ , H–C(4)); 4.07 (*m*,  $^3J(6,1) = 4.9$ ,  $^3J(6,5) = 2.3$ , H–C(6)); 3.99 (*d*,  $^3J(5,6) = 2.3$ , H–C(5)); 3.57, 3.47 (2*d*,  $^2J = 14.3$ ,  $\text{CH}_2$ –C(2)); 2.64 (*s*, S=NMe); 2.37 (*dd*,  $^3J(3_{\text{exo}},3_{\text{endo}}) = 13.4$ ,  $^3J(3_{\text{exo}},4) = 6.5$ ,  $\text{H}_{\text{exo}}$ –C(3)); 1.68 (*d*,  $^3J(3_{\text{exo}},3_{\text{endo}}) = 13.4$ ,  $\text{H}_{\text{endo}}$ –C(3)); 0.88 (*s*, *t*-BuSi); 0.07 (*s*,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 139.2, 136.8 (2*s*, arom. C); 132.6, 129.1, 129.0, 128.4, 128.1, 128.0 (6*d*,  $^1J(\text{C,H}) = 160$ , arom. C); 91.3 (*d*,  $^1J(\text{C,H}) = 151$ , C(6)); 84.9 (*d*,  $^1J(\text{C,H}) = 161$ , C(4)); 80.3 (*s*, C(2)); 79.8 (*d*,  $^1J(\text{C,H}) = 145$ , C(5)); 76.3 (*d*,  $^1J(\text{C,H}) = 166$ , C(1)); 73.1 (*t*,  $^1J(\text{C,H}) = 143$ ,  $\text{PhCH}_2\text{O}$ ); 63.8 (*t*,  $^1J(\text{C,H}) = 138$ ,  $\text{CH}_2$ –C(2)); 42.6 (*t*,  $^1J(\text{C,H}) = 135$ , C(3)); 29.1 (*q*,  $^1J(\text{C,H}) = 137$ , S=NMeCH<sub>3</sub>); 25.7 (*q*,  $^1J(\text{C,H}) = 125$ ,  $\text{Me}_3\text{CSi}$ ); 17.9 (*s*,  $\text{Me}_3\text{CSi}$ );  $-4.7$ ,  $-4.8$  ( $2q$ ,  $^1J(\text{C,H}) = 118$ ,  $\text{Me}_2\text{Si}$ ). CI-MS ( $\text{NH}_3$ ): 518 (44,  $[M + 1]^+$ ), 366 (23), 170 (51,  $[\text{PhS}(=\text{O})(=\text{NHMe})\text{Me}]^+$ ), 156 (47,  $[\text{PhS}(=\text{O})(=\text{NHMe})\text{H}]^+$ ), 154 (18,  $[\text{PhS}(=\text{O})(=\text{NMe})]^+$ ), 125 (27), 108 (24,  $\text{BnOH}^+$ ), 107 (28,  $\text{BnO}^+$ ), 91 (100,  $\text{C}_7\text{H}_7^+$ ), 77 (14,  $\text{C}_6\text{H}_5^+$ ). Anal. calc. for  $\text{C}_{27}\text{H}_{39}\text{NO}_5\text{SSi}$  (517.83): C 62.62, H 7.61, N 2.71, S 6.19, Si 5.42; found: C 62.59, H 7.54, N 2.60, S 6.00, Si 5.45.

(+)-(1*S*,4*S*,5*S*,6*S*)-6-endo-(Benzyloxy)-5-exo-[[*tert*-butyl]dimethylsilyl]oxy]-7-oxabicyclo[2.2.1]heptan-2-one ((+)-**5**). In a Büchi 'Kugelrohr' oven, (+)-**7** (7.63 g, 14.7 mmol) was heated to 220°/0.2 mm Torr. The same operation was repeated twice. The combined products of distillation were dissolved in heptane (20 ml). After staying at 4° overnight, 5.87 g of pure (+)-**5** was collected as colorless crystals. The mother liquor was evaporated and the residue purified by FC (7 × 25 cm, light petroleum ether/Et<sub>2</sub>O 4:1 → 3:2, then  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  9:1): 8.24 g (92%) of (+)-**5** (global yield) as white crystals and 7.42 g (99%) of (+)-(*S*)-*N,S*-dimethyl-*S*-phenylsulfoximide as yellowish oil. (+)-**5**:  $[\alpha]_{\text{D}}^{25} = 53$ ,  $[\alpha]_{\text{D}}^{25} = 56$ ,  $[\alpha]_{\text{D}}^{25} = 63$ ,  $[\alpha]_{\text{D}}^{25} = 102$ ,  $[\alpha]_{\text{D}}^{25} = 119$  ( $c = 1.3$ ,  $\text{CH}_2\text{Cl}_2$ ).

(–)-(1*R*,4*R*,5*R*,6*R*)-6-endo-(Benzyloxy)-5-exo-[[*tert*-butyl]dimethylsilyl]oxy]-7-oxabicyclo[2.2.1]heptan-2-one ((–)-**5**). As described for (+)-**5**, with (–)-**8** (1.37 g, 2.65 mmol): 0.80 g (87%) of (–)-**5** as colorless solid and 0.45 g (99%) of chiral sulfonimide as yellowish oil. (–)-**5**:  $[\alpha]_{\text{D}}^{25} = -51$ ,  $[\alpha]_{\text{D}}^{25} = -55$ ,  $[\alpha]_{\text{D}}^{25} = -62$ ,  $[\alpha]_{\text{D}}^{25} = -101$ ,  $[\alpha]_{\text{D}}^{25} = -119$  ( $c = 0.7$ ,  $\text{CH}_2\text{Cl}_2$ ).

(1*RS*,4*RS*,5*RS*,6*RS*)-6-endo-(Benzyloxy)-5-exo-[[*tert*-butyl]dimethylsilyl]oxy]-2-[(trimethylsilyl)oxy]-7-oxabicyclo[2.2.1]hept-2-ene ((±)-**9**). BuLi (1.6M in hexane; 2.6 ml, 4.16 mmol) was added dropwise under stirring to a soln. of (i-Pr)<sub>2</sub>NH (0.64 ml, 457 mg, 4.52 mmol) in anh. THF (10 ml) cooled to  $-15^\circ$  in a Schlenk tube. After stirring at  $-15^\circ$  for 15 min, the soln. was cooled to  $-78^\circ$ . A soln. of (±)-**5** (1.14 g, 3.27 mmol) in anh. THF (10 ml) cooled to  $-78^\circ$  was catalyzed into the Li(i-Pr)<sub>2</sub>N soln. under stirring. After stirring at  $-78^\circ$  for 90 min,  $\text{Me}_3\text{SiCl}$  (0.8 ml, 687 mg, 6.33 mmol) was added dropwise and the mixture stirred at  $-78^\circ$  for 2 h, then allowed to warm to  $20^\circ$ , and stirred for additional 2 h. Then the mixture was concentrated to ca. 5 ml. Pentane (12 ml) was added, the precipitate filtered off (Celite), and the solvent evaporated: 1.33 g (96%) of (±)-**9**. Yellowish solid used as such in the next step. M.p.  $45-46^\circ$ . IR (KBr): 2955, 2855, 1625, 1470, 1350, 1320, 1255, 1225, 1105, 1030, 950, 865, 775, 700, 665.  $^1\text{H-NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ ): 7.32, 7.19, 7.12 (3*m*, 2 H, 2 H, 1 H, arom. H); 4.76 (*d*,  $^3J(3,4) = 2.2$ , H–C(3)); 4.68 (*m*,  $^3J(4,3) = 2.2$ ,  $^4J(4,1) = 0.7$ , H–C(4)); 4.57 (*dd*,  $^3J(1,6) = 4.0$ ,  $^4J(1,4) = 0.7$ , H–C(1)); 4.44, 4.33 (2*d*,  $^2J = 11.4$ ,  $\text{PhCH}_2\text{O}$ ); 4.05 (*d*,  $^3J(5,6) = 0.9$ , H–C(5)); 4.01 (br. *dd*,  $^3J(6,1) = 4.0$ ,  $^3J(6,5) = 0.9$ , H–C(6)); 1.04 (*s*, *t*-BuSi); 0.16, 0.14 (2*s*,  $\text{Me}_2\text{Si}$ ); 0.12 (*s*,  $\text{Me}_3\text{Si}$ ).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.34–7.28 (*m*, 5 arom. H); 4.95 (*d*,  $^3J(3,4) = 2.2$ , H–C(3)); 4.58, 4.53 (2*d*,  $^2J = 11.3$ ,  $\text{PhCH}_2\text{O}$ ); 4.51 (*m*,  $^3J(4,3) = 2.2$ , H–C(4)); 4.50 (br. *d*,  $^3J(1,6) = 4.0$ , H–C(1)); 3.89 (br. *dd*,  $^3J(6,1) = 4.0$ ,  $^3J(6,5) = 0.7$ , H–C(6)); 3.87 (*d*,  $^3J(5,6) = 0.7$ , H–C(5)); 0.92 (*s*, *t*-BuSi); 0.20 (*s*,  $\text{Me}_3\text{Si}$ ); 0.11, 0.10 (2*s*,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 162.0 (*s*, C(3)); 137.9 (*s*, arom. C); 128.2, 127.9, 127.7 (3*d*,  $^1J(\text{C,H}) = 160$ , arom. C); 100.1 (*d*,  $^1J(\text{C,H}) = 173$ , C(3)); 86.5 (*d*,  $^1J(\text{C,H}) = 164$ , C(4)); 84.7 (*d*,  $^1J(\text{C,H}) = 152$ , C(6)); 79.5 (*d*,  $^1J(\text{C,H}) = 152$ , C(5)); 78.8 (*d*,  $^1J(\text{C,H}) = 163$ , C(1)); 72.3 (*t*,  $^1J(\text{C,H}) = 141$ ,  $\text{PhCH}_2\text{O}$ ); 25.9 (*q*,  $^1J(\text{C,H}) = 125$ ,  $\text{Me}_3\text{CSi}$ ); 18.2 (*s*,  $\text{Me}_3\text{CSi}$ );  $-0.4$  (*q*,  $^1J(\text{C,H}) = 120$ ,  $\text{Me}_3\text{Si}$ );  $-4.6$ ,  $-4.7$  ( $2q$ ,  $^1J(\text{C,H}) = 118$ ,  $\text{Me}_2\text{Si}$ ). Anal. calc. for  $\text{C}_{22}\text{H}_{36}\text{O}_4\text{Si}_2$  (420.76): C 62.80, H 8.64, Si 13.35; found: C 62.85, H 8.70, Si 13.43.

(1*RS*,4*RS*,5*RS*,6*RS*)-6-endo-(Benzyloxy)-5-exo-[[*tert*-butyl]dimethylsilyl]oxy]-2-[(triethylsilyl)oxy]-7-oxabicyclo[2.2.1]hept-2-ene ((±)-**10**). As described for (±)-**9**, with Et<sub>3</sub>SiCl instead of  $\text{Me}_3\text{SiCl}$ : 100% of (±)-**10**. The crude product was used directly in the next step.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.35–7.27 (*m*, 5 arom. H); 4.95 (*d*,  $^3J(3,4) = 2.2$ , H–C(3)); 4.61, 4.53 (2*d*,  $^2J = 11.5$ ,  $\text{PhCH}_2\text{O}$ ); 4.50 (br. *d*,  $^3J(4,3) = 2.2$ , H–C(4)); 4.49

(br. *d*,  $^3J(1,6) = 3.6$ , H–C(1)); 3.88 (br. *d*,  $^3J(6,1) = 3.6$ , H–C(6)); 3.87 (br. *s*, H–C(5)); 0.95 (*m*, (MeCH<sub>2</sub>)<sub>3</sub>Si); 0.91 (*s*, *t*-BuSi); 0.73–0.66 (*m*, (MeCH<sub>2</sub>)<sub>3</sub>Si); 0.11, 0.10 (2*s*, Me<sub>2</sub>Si). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 162.4 (*s*, C(3)); 137.9 (*s*, arom. C); 128.2, 127.8, 127.6 (3*d*,  $^1J(\text{C,H}) = 160$ , arom. C); 100.2 (*d*,  $^1J(\text{C,H}) = 170$ , C(3)); 86.5 (*d*,  $^1J(\text{C,H}) = 166$ , C(4)); 84.6 (*d*,  $^1J(\text{C,H}) = 152$ , C(6)); 79.5 (*d*,  $^1J(\text{C,H}) = 151$ , C(5)); 78.9 (*d*,  $^1J(\text{C,H}) = 163$ , C(1)); 72.3 (*t*,  $^1J(\text{C,H}) = 141$ , PhCH<sub>2</sub>O); 25.9 (*q*,  $^1J(\text{C,H}) = 125$ , Me<sub>3</sub>CSi); 18.2 (*s*, Me<sub>3</sub>CSi); 6.5 (*q*,  $^1J(\text{C,H}) = 126$ , (MeCH<sub>2</sub>)<sub>3</sub>Si); 4.4 (*t*,  $^1J(\text{C,H}) = 117$ , (MeCH<sub>2</sub>)<sub>3</sub>Si); –4.6, –4.7 (2*q*,  $^1J(\text{C,H}) = 118$ , Me<sub>2</sub>Si).

(1*RS*,2*RS*,4*SR*,5*RS*,6*RS*,7*RS*)-7-endo-(Benzoyloxy)-6-exo-[[*tert*-butyl]dimethylsilyl]oxy]-2-endo-[[*trimethylsilyl*]oxy]-8-oxatricyclo[3.2.1.0<sup>2,4</sup>]octane ((±)-**11**). Et<sub>2</sub>Zn (1*M* in hexane; 6.3 ml, 6.3 mmol) was added dropwise to a stirred soln. of ICH<sub>2</sub>Cl (0.92 ml, 2.22 g, 12.6 mmol) in anhyd. ClCH<sub>2</sub>CH<sub>2</sub>Cl (20 ml) cooled to –10° under N<sub>2</sub>. After stirring at –10° for 30 min, the mixture was cooled to –30°. A soln. of (±)-**9** (1.33 g, 3.15 mmol) in anhyd. ClCH<sub>2</sub>CH<sub>2</sub>Cl (10 ml) was added dropwise under stirring, the rate of the addition being adapted to maintain the temp. at –30°. After 1 h at –30°, the mixture was stirred at 20° for 2 h. H<sub>2</sub>O (20 ml) and sat. aq. NH<sub>4</sub>Cl soln. (20 ml) were added under stirring. The aq. layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 × 35 ml) and the combined org. extract dried (MgSO<sub>4</sub>) and evaporated: 1.33 g (97%) of crude (±)-**11**. Yellowish viscous oil, which was used directly in the next step.

(1*RS*,2*SR*,4*RS*,5*RS*,6*RS*,7*RS*)-7-endo-(Benzoyloxy)-6-exo-[[*tert*-butyl]dimethylsilyl]oxy]-2-endo-[[*triethylsilyl*]oxy]-8-oxatricyclo[3.2.1.0<sup>2,4</sup>]octane ((±)-**12**). As described for (±)-**11**, with (±)-**10** instead of (±)-**9**: 100% of (±)-**12**. Yellowish oil which was used directly in the next step.

(1*RS*,5*RS*,6*RS*,7*RS*)-7-endo-(Benzoyloxy)-6-exo-[[*tert*-butyl]dimethylsilyl]oxy]-8-oxabicyclo[3.2.1]oct-3-en-2-one ((±)-**13**). Anhyd. pyridine (14 ml, 13.8 g, 174 mmol), then (±)-**12** (14.9 g, 32.9 mmol) in anhyd. DMF (100 ml) were added to an anhyd. FeCl<sub>3</sub> (8.5 g, 52 mmol) soln. in DMF (200 ml) stirred at 0°. After stirring at 0° for 15 min, the mixture was heated to 70° for 2 h. Then AcOEt (1 l) was added and the soln. washed with 1*N* HCl (2 × 400 ml), sat. aq. NaHCO<sub>3</sub> soln. (300 ml), and brine (300 ml). The aq. phases were extracted with AcOEt (2 × 400 ml) and the combined org. extracts dried (MgSO<sub>4</sub>) and evaporated at 10<sup>–2</sup> Torr. The dark residue was purified by FC (7.5 × 23 cm, light petroleum ether/Et<sub>2</sub>O 3 : 1): 5.79 g (57% based on (±)-**5**) of (±)-**13** as yellowish oil. An anal. sample was obtained by a second FC (light petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O 14 : 19 : 1): 4.61 g (45% based on (±)-**5**) of (±)-**13**. Colorless solid. M.p. 46°. UV (MeCN): 207 (11700), 196 (11600). IR (KBr): 2935, 2920, 2860, 1700, 1260, 1095, 1050, 830, 785, 750, 700. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.36–7.26 (*m*, 5 arom. H); 7.19 (*dd*,  $^3J(4,3) = 9.9$ ,  $^3J(4,5) = 4.8$ , H–C(4)); 6.12 (*dd*,  $^3J(3,4) = 9.9$ ,  $^4J(3,1) = 1.1$ , H–C(3)); 4.83 (br. *dd*,  $^3J(1,7) = 7.0$ ,  $^4J(1,3) = 1.1$ , H–C(1)); 4.58, 4.40 (2*d*,  $^2J = 11.2$ , PhCH<sub>2</sub>O); 4.45 (br. *d*,  $^3J(5,4) = 4.8$ , H–C(5)); 4.30 (*m*,  $^3J(7,1) = 7.0$ , H–C(7)); 4.27 (br. *s*, H–C(6)); 0.90 (*s*, *t*-BuSi); 0.11, 0.10 (2*s*, Me<sub>2</sub>Si). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 194.1 (*s*, C(2)); 147.9 (*d*,  $^1J(\text{C,H}) = 163$ , C(4)); 136.8 (*s*, arom. C); 128.5, 128.4, 128.2, 128.1 (4*d*,  $^1J(\text{C,H}) = 160$ , arom. C, C(3)); 86.3 (*d*,  $^1J(\text{C,H}) = 153$ , C(7)); 83.6 (*d*,  $^1J(\text{C,H}) = 157$ , C(1)); 81.3 (*d*,  $^1J(\text{C,H}) = 158$ , C(5)); 79.6 (*d*,  $^1J(\text{C,H}) = 155$ , C(6)); 73.7 (*t*,  $^1J(\text{C,H}) = 144$ , PhCH<sub>2</sub>O); 25.7 (*q*,  $^1J(\text{C,H}) = 125$ , Me<sub>3</sub>CSi); 18.0 (*s*, Me<sub>3</sub>C); –4.9 (*q*,  $^1J(\text{C,H}) = 119$ , Me<sub>2</sub>Si). CI-MS (NH<sub>3</sub>): 360 (1, *M*<sup>+</sup>), 211 (10), 187 (7), 97 (12), 91 (100, C<sub>4</sub>H<sub>7</sub><sup>+</sup>), 75 (8), 74 (6), 73 (18). Anal. calc. for C<sub>20</sub>H<sub>28</sub>O<sub>4</sub>Si (360.57): C 66.62, H 7.84, Si 7.79; found: C 66.71, H 7.78, Si 7.69.

(1*S*,5*S*,6*S*,7*S*)-7-endo-(Benzoyloxy)-6-exo-[[*tert*-butyl]dimethylsilyl]oxy]-8-oxabicyclo[3.2.1]oct-3-en-2-one ((–)-**13**). As described for (±)-**13**, from (+)-**5**, without purification of the intermediates **10** and **11**: 58% (based on (+)-**5**) of (–)-**13**. Colorless oil.  $[\alpha]_{\text{D}}^{25} = -124$ ,  $[\alpha]_{\text{D}}^{257} = -131$ ,  $[\alpha]_{\text{D}}^{246} = -161$ ,  $[\alpha]_{\text{D}}^{235} = -461$ ,  $[\alpha]_{\text{D}}^{205} = -915$  (*c* = 0.9, CHCl<sub>3</sub>).

(1*RS*,2*SR*,5*SR*,6*SR*,7*SR*)-7-endo-(Benzoyloxy)-6-exo-[[*tert*-butyl]dimethylsilyl]oxy]-8-oxabicyclo[3.2.1]oct-3-en-2-endo-ol ((±)-**14**). CeCl<sub>3</sub> · 6H<sub>2</sub>O (443 mg, 1.25 mmol) was added portionwise to a stirred soln. of (±)-**13** (0.3 g, 0.83 mmol) in MeOH (6 ml) cooled to 0°. NaBH<sub>4</sub> (35 mg, 0.93 mmol) was then added portionwise, and the mixture was stirred at 0° for 30 min. AcOH (0.1 ml), then sat. aq. NaHCO<sub>3</sub> soln. were added. The mixture was extracted with AcOEt (50 ml, then 3 × 25 ml). The combined org. extract was dried (MgSO<sub>4</sub>) and evaporated and the residue purified by FC (3 × 13 cm, light petroleum ether/Et<sub>2</sub>O 3 : 1): 280 mg of (±)-**14**. Colorless solid. M.p. 55°. UV (MeCN): 212 (7900). IR (film): 3515, 3035, 2955, 2930, 2895, 2855, 1470, 1415, 1255, 1095, 1055, 840. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.40–7.30 (*m*, 5 arom. H); 5.91 (*ddd*,  $^3J(3,4) = 9.9$ ,  $^3J(3,2) = 1.5$ ,  $^4J(3,1) = 1.4$ , H–C(3)); 5.86 (*ddd*,  $^3J(4,3) = 9.9$ ,  $^3J(4,5) = 3.8$ ,  $^4J(4,2) = 1.3$ , H–C(4)); 4.76, 4.57 (2*d*,  $^2J = 11.5$ , PhCH<sub>2</sub>O); 4.62 (*m*,  $^3J(1,7) = 6.9$ ,  $^4J(1,3) = 1.4$ ,  $^3J(2,\text{OH}) = 11.6$ ,  $^3J(2,3) = 1.5$ ,  $^4J(2,4) = 1.3$ , H–C(1), H–C(2)); 4.44 (br. *d*,  $^3J(7,1) = 6.9$ , H–C(7)); 4.27 (br. *s*, H–C(6)); 4.10 (br. *d*,  $^3J(5,4) = 3.8$ , H–C(5)); 3.65 (*d*,  $^3J(\text{OH},2) = 11.6$ , OH–C(2)); 0.93 (*s*, *t*-BuSi); 0.14, 0.12 (2*s*, Me<sub>2</sub>Si). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 136.6 (*s*, arom. C); 132.6 (*d*,  $^1J(\text{C,H}) = 164$ , C(3)); 128.7, 128.2, 127.6 (3*d*,  $^1J(\text{C,H}) = 160$ , arom. C); 127.1 (*d*,  $^1J(\text{C,H}) = 163$ , C(4)); 93.0 (*d*,  $^1J(\text{C,H}) = 151$ , C(7)); 81.4 (*d*,  $^1J(\text{C,H}) = 149$ , C(6)); 80.3 (*d*,  $^1J(\text{C,H}) = 162$ , C(5)); 75.5 (*d*,  $^1J(\text{C,H}) = 150$ , C(1)); 73.6 (*t*,  $^1J(\text{C,H}) = 146$ , PhCH<sub>2</sub>O); 68.8 (*d*,  $^1J(\text{C,H}) = 147$ , C(2)); 25.7 (*q*,  $^1J(\text{C,H}) = 125$ ,

$\text{Me}_3\text{CSi}$ ); 17.9 (s,  $\text{Me}_3\text{CSi}$ ); –4.5, –4.8 (2q,  $^1\text{J}(\text{C},\text{H}) = 118$ ,  $\text{Me}_2\text{Si}$ ). CI-MS ( $\text{NH}_3$ ): 380 (100,  $[\text{M} + \text{NH}_4]^+$ ), 363 (15,  $[\text{M} + \text{H}]^+$ ). Anal. calc. for  $\text{C}_{20}\text{H}_{30}\text{O}_4\text{Si}$  (362.59): 66.25, H 8.36, Si 7.75; found: 66.19, H 8.47, Si 7.87.

(1RS,2SR,5SR,6SR,7SR)-7-endo-(Benzyloxy)-6-exo-[[tert-butyl]dimethylsilyl]oxy]-8-oxabicyclo[3.2.1]-oct-3-en-2-endo-yl Benzoate ((±)-**15**). A mixture of (±)-**14** (100 mg, 0.28 mmol), anh. pyridine (3 ml), and benzoyl chloride (0.1 ml, 121 mg, 0.86 mmol) was stirred at 20° for 3 h.  $\text{H}_2\text{O}$  (3 ml) was added and stirring continued for 2 h. After the addition of AcOEt (30 ml), the soln. was washed successively with 1N HCl (3 × 15 ml), sat. aq.  $\text{NaHCO}_3$  soln. (3 × 15 ml), sat. aq.  $\text{NaHCO}_3$  soln. (3 × 15 ml), and brine (15 ml). The aq. phases were extracted with AcOEt (2 × 30 ml) and the combined org. extracts dried ( $\text{MgSO}_4$ ) and evaporated. The residue was purified by FC (2 × 20 cm, light petroleum ether/AcOEt 10:1): 117 mg (89%) of (±)-**15**. Colorless solid. M.p. 71°. UV (MeCN): 228 (9600). IR (film): 2955, 2925, 2855, 1705, 1260, 1105, 1095, 980, 835, 775, 695.  $^1\text{H}$ -NMR (400 MHz,  $\text{C}_6\text{D}_6$ ): 8.09, 7.22, 7.12, 6.97 (4m, 2 H, 2 H, 4 H, 2 H, arom. H); 6.29 (m,  $^3\text{J}(2,1) = 4.7$ ,  $^3\text{J}(2,3) = 1.7$ ,  $^4\text{J}(2,4) = 2.1$ , H–C(2)); 5.81 (ddd,  $^3\text{J}(3,4) = 10.0$ ,  $^3\text{J}(3,2) = 1.7$ ,  $^4\text{J}(3,1) = 1.6$ , H–C(3)); 5.66 (ddd,  $^3\text{J}(4,3) = 10.00$ ,  $^3\text{J}(4,5) = 4.1$ ,  $^4\text{J}(4,2) = 2.1$ , H–C(4)); 5.01 (ddd,  $^3\text{J}(1,7) = 6.4$ ,  $^3\text{J}(1,2) = 4.7$ ,  $^4\text{J}(1,3) = 1.6$ , H–C(1)); 4.42 (s,  $\text{PhCH}_2\text{O}$ ); 4.38 (br. d,  $^3\text{J}(7,1) = 6.4$ , H–C(7)); 4.37 (br. s, H–C(6)); 4.18 (br. d,  $^3\text{J}(5,4) = 4.1$ , H–C(5)); 0.96 (s, *t*-BuSi); 0.05, 0.03 (2s,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ): 166.4 (s, C=O); 137.7, 129.9 (2s, arom. C); 132.9, 129.8 (2d,  $^1\text{J}(\text{C},\text{H}) = 160$ , arom. C); 129.3 (d,  $^1\text{J}(\text{C},\text{H}) = 154$ , C(4)); 128.2, 127.6, 127.5, 127.4 (4d,  $^1\text{J}(\text{C},\text{H}) = 160$ , arom. C, C(3)); 91.8 (d,  $^1\text{J}(\text{C},\text{H}) = 148$ , C(7)); 82.3 (d,  $^1\text{J}(\text{C},\text{H}) = 150$ , C(6)); 80.4 (d,  $^1\text{J}(\text{C},\text{H}) = 160$ , C(5)); 75.3 (d,  $^1\text{J}(\text{C},\text{H}) = 152$ , C(1)); 73.5 (t,  $^1\text{J}(\text{C},\text{H}) = 142$ ,  $\text{PhCH}_2\text{O}$ ); 70.3 (d,  $^1\text{J}(\text{C},\text{H}) = 158$ , C(2)); 25.7 (q,  $^1\text{J}(\text{C},\text{H}) = 125$ ,  $\text{Me}_3\text{CSi}$ ); 18.0 (s,  $\text{Me}_3\text{CSi}$ ); –4.7, –4.8 (2q,  $^1\text{J}(\text{C},\text{H}) = 118$ ,  $\text{Me}_2\text{Si}$ ). ES-MS (pos. mode): 489 (100,  $[\text{M} + \text{Na}]^+$ ), 484 (50,  $[\text{M} + \text{NH}_4]^+$ ), 467 (15,  $[\text{M} + \text{H}]^+$ ). Anal. calc. for  $\text{C}_{27}\text{H}_{34}\text{O}_5\text{Si}$  (466.70): C 69.48, H 7.36, Si 6.02; found: C 69.64, H 7.37, Si 5.98.

(1RS,2RS,4SR,5SR,6RS,7RS,8SR)-7-endo-(Benzyloxy)-8-exo-[[tert-butyl]dimethylsilyl]oxy]-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]non-5-endo-yl Benzoate ((±)-**16**). As described for (±)-**15**, with crude (±)-**18** (3.83 g, 10.1 mmol), pyridine (60 ml), and benzoyl chloride (4 ml, 4.84 g, 34.4 mmol). Purification by solvent evaporation gave 4.89 g (100%) of (±)-**16**, pure enough for the next step. An anal. sample was prepared by FC (1 × 14 cm, light petroleum ether/AcOEt 9:1 → 4:1): white solid. M.p. 99–100°. UV (MeCN): 272 (2000), 228 (14000), 200 (18500). IR (KBr): 3060, 3035, 2960, 2935, 2900, 2860, 1720, 1605, 1450, 1280, 1255, 1115, 840, 700.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ): 7.90, 7.52, 7.31–7.21 (3m, 2 H, 1 H, 7 H, arom. H); 5.32 (dd,  $^3\text{J}(5,6) = 5.2$ ,  $^4\text{J}(5,2) = 0.7$ , H–C(5)); 4.78 (ddd,  $^3\text{J}(6,7) = 6.7$ ,  $^3\text{J}(6,5) = 5.2$ ,  $^4\text{J}(6,4) = 1.6$ , H–C(6)); 4.57, 4.53 (2d,  $^2\text{J} = 11.8$ ,  $\text{PhCH}_2\text{O}$ ); 4.42 (m,  $^3\text{J}(8,7) = 1.0$ , H–C(8)); 4.27 (m,  $^3\text{J}(1,2) = 1.2$ ,  $^4\text{J}(1,7) = 1.7$ ,  $^4\text{J}(1,4) = 0.6$ , H–C(1)); 4.20 (ddd,  $^3\text{J}(7,6) = 6.7$ ,  $^3\text{J}(7,8) = 1.0$ ,  $^4\text{J}(7,1) = 1.7$ , H–C(7)); 3.42 (ddd,  $^3\text{J}(4,2) = 3.9$ ,  $^4\text{J}(4,6) = 1.6$ ,  $^4\text{J}(4,1) = 0.6$ , H–C(4)); 3.14 (ddd,  $^3\text{J}(2,4) = 3.9$ ,  $^3\text{J}(2,1) = 1.2$ ,  $^4\text{J}(2,5) = 0.7$ , H–C(2)); 0.91 (s, *t*-BuSi); 0.13, 0.12 (2s,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ): 165.7 (s, C=O); 137.5, 129.4 (2s, arom. C); 133.1, 129.8, 128.3, 128.2, 127.7, 127.4 (6d,  $^1\text{J}(\text{C},\text{H}) = 160$ , arom. C); 88.3 (d,  $^1\text{J}(\text{C},\text{H}) = 148$ , C(7)); 79.7 (d,  $^1\text{J}(\text{C},\text{H}) = 141$ , C(8)); 78.8 (d,  $^1\text{J}(\text{C},\text{H}) = 158$ , C(1)); 73.5 (t,  $^1\text{J}(\text{C},\text{H}) = 140$ ,  $\text{PhCH}_2\text{O}$ ); 73.1 (d,  $^1\text{J}(\text{C},\text{H}) = 157$ , C(6)); 67.5 (d,  $^1\text{J}(\text{C},\text{H}) = 154$ , C(5)); 52.7 (d,  $^1\text{J}(\text{C},\text{H}) = 183$ , C(4)); 49.0 (d,  $^1\text{J}(\text{C},\text{H}) = 178$ , C(2)); 25.7 (q,  $^1\text{J}(\text{C},\text{H}) = 125$ ,  $\text{Me}_3\text{CSi}$ ); 18.0 (s,  $\text{Me}_3\text{CSi}$ ); –4.6, –4.7 (2q,  $^1\text{J}(\text{C},\text{H}) = 118$ ,  $\text{Me}_2\text{Si}$ ). CI-MS ( $\text{NH}_3$ ): 483 (0.5,  $[\text{M} + 1]^+$ ), 425 (7,  $[\text{M} - \text{C}_4\text{H}_9]^+$ ), 105 (37,  $\text{Bz}^+$ ), 91 (100,  $\text{C}_7\text{H}_7^+$ ), 77 (12,  $\text{C}_6\text{H}_5^+$ ). Anal. calc. for  $\text{C}_{27}\text{H}_{34}\text{O}_6\text{Si}$  (482.70): C 67.18, H 7.11, Si 5.82; found: C 67.24, H 7.12, Si 5.82.

(1S,2S,4R,5R,6S,7S,8R)-7-endo-(Benzyloxy)-8-exo-[[tert-butyl]dimethylsilyl]oxy]-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]non-5-endo-yl Benzoate ((–)-**16**). As described for (±)-**16**, from (–)-**13** via (+)-**17** and (–)-**18**, without purification of the intermediates. White solid. M.p. 90–91°.  $[\alpha]_D^{25} = -20$ ,  $[\alpha]_{257}^{25} = -21$ ,  $[\alpha]_{256}^{25} = -24$ ,  $[\alpha]_{335}^{25} = -38$ ,  $[\alpha]_{305}^{25} = -45$  ( $c = 0.8$ ,  $\text{CH}_2\text{Cl}_2$ ).

(1RS,2SR,4SR,6RS,7RS,8SR)-7-endo-(Benzyloxy)-8-exo-[[tert-butyl]dimethylsilyl]oxy]-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]nonan-5-one ((±)-**17**). A mixture of (±)-**13** (4.0 g, 11.1 mmol), DBU (2.0 ml, 2.0 g, 13.4 mmol), and *t*-BuOOH (3M in isooctane; 7.4 ml, 22.2 mmol) in anh.  $\text{CH}_2\text{Cl}_2$  (100 ml) was stirred at 20° for 3 h. After the addition of  $\text{CHCl}_3$  (100 ml), the soln. was washed successively with 10% aq.  $\text{NaHSO}_3$  soln. (150 ml), 1N HCl (150 ml), and sat. aq.  $\text{NaHCO}_3$  soln. (150 ml). The aq. phases were extracted with  $\text{CHCl}_3$  (3 × 150 ml) and the combined org. extracts dried ( $\text{MgSO}_4$ ) and evaporated: 4.5 g (100%) of (±)-**17**. Yellowish solid pure enough for the next step. An anal. sample was obtained by FC (0.5 × 10 cm, light petroleum ether/AcOEt 9:1): colorless solid. M.p. 81–82°. UV (MeCN): 292 (850), 263 (950), 205 (8500), 195 (9800). IR (KBr): 2955, 2930, 2855, 1735, 1470, 1410, 1390, 1255, 1105, 1065, 1030, 880, 845, 790, 755, 705, 430.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ): 7.38–7.26 (m, 5 arom. H); 4.67 (br. d,  $^3\text{J}(6,7) = 7.2$ , H–C(6)); 4.53, 4.38 (2d,  $^2\text{J} = 11.1$ ,  $\text{PhCH}_2\text{O}$ ); 4.43 (m,  $^3\text{J}(1,2) = 1.7$ ,  $^4\text{J}(1,7) = 1.2$ , H–C(1)); 4.35 (br. d,  $^3\text{J}(8,7) = 1.3$ , H–C(8)); 4.21 (ddd,  $^3\text{J}(7,6) = 7.2$ ,  $^3\text{J}(7,8) = 1.3$ ,  $^4\text{J}(7,1) = 1.2$ , H–C(7)); 3.40 (dd,  $^3\text{J}(2,4) = 3.7$ ,  $^3\text{J}(2,1) = 1.7$ , H–C(2)); 3.30 (br. d,  $^3\text{J}(4,2) = 3.7$ , H–C(4)); 0.91 (s, *t*-BuSi); 0.13, 0.12 (2s,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ): 197.9 (s, C(5)); 136.3 (s, arom. C); 128.5, 128.2



(2d,  $^1J(\text{C,H}) = 160$ , arom. C); 88.6 (d,  $^1J(\text{C,H}) = 153$ , C(7)); 82.9 (d,  $^1J(\text{C,H}) = 161$ , C(6)); 79.0 (d,  $^1J(\text{C,H}) = 158$ , C(1)); 78.7 (d,  $^1J(\text{C,H}) = 146$ , C(8)); 73.3 (t,  $^1J(\text{C,H}) = 141$ ,  $\text{PhCH}_2\text{O}$ ); 52.0 (d,  $^1J(\text{C,H}) = 188$ , C(4)); 49.0 (d,  $^1J(\text{C,H}) = 183$ , C(2)); 25.6 (q,  $^1J(\text{C,H}) = 125$ ,  $\text{Me}_3\text{CSi}$ ); 18.0 (s,  $\text{Me}_3\text{CSi}$ ); -4.8, -4.9 (2q,  $^1J(\text{C,H}) = 118$ ,  $\text{Me}_2\text{Si}$ ). CI-MS ( $\text{NH}_3$ ): 394 (31,  $[\text{M} + 18]^+$ ), 319 (10,  $[\text{M} - \text{C}_4\text{H}_9]^+$ ), 185 (11), 129 (11), 108 (25,  $\text{BnOH}^+$ ), 91 (100,  $\text{C}_7\text{H}_7^+$ ). Anal. calc. for  $\text{C}_{20}\text{H}_{28}\text{O}_5\text{Si}$  (376.57): C 63.79, H 7.51, Si 7.46; found: C 63.84, H 7.46, Si 7.35.

(1S,2R,4R,6S,7S,8R)-7-endo-(Benzyloxy)-8-exo-[(tert-butyl)dimethylsilyloxy]-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]-nonan-5-one ((+)-**17**). As described for ( $\pm$ )-**17**, with (-)-**13**. Colorless oil.  $[\alpha]_{\text{D}}^{25} = 29$ ,  $[\alpha]_{\text{D}}^{357} = 31$ ,  $[\alpha]_{\text{D}}^{346} = 35$ ,  $[\alpha]_{\text{D}}^{235} = 67$ ,  $[\alpha]_{\text{D}}^{205} = 87$  ( $c = 1.1$ ,  $\text{CH}_2\text{Cl}_2$ ).

(1R,2S,2RS,4RS,5SR,6SR,7RS,8SR)-7-endo-(Benzyloxy)-8-exo-[(tert-butyl)dimethylsilyloxy]-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]nonan-5-endo-ol (( $\pm$ )-**18**). A mixture of ( $\pm$ )-**17** (4.5 g, 11.9 mmol), MeOH (200 ml), and  $\text{NaBH}_4$  (0.48 g, 12.7 mmol) was stirred at 0° for 30 min.  $\text{H}_2\text{O}$  (180 ml) and brine (180 ml) were added, and the mixture was extracted with  $\text{Et}_2\text{O}$  (500 ml, then  $4 \times 250$  ml). The combined org. extracts were dried ( $\text{MgSO}_4$ ) and evaporated: 3.83 g (85%) of ( $\pm$ )-**18**. Yellowish oil that can be used directly in the next step. An anal. sample was obtained by FC (0.5  $\times$  10 cm, light petroleum ether/AcOEt 4:1): colorless oil. UV (MeCN): 207 (8200), 196 (9000). IR (film): 3510, 2955, 2930, 2900, 2860, 1470, 1410, 1360, 1255, 1110, 1070, 860, 840, 780.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.38, 7.30 (2m, 3 H, 2 H, arom. H); 4.77, 4.55 (2d,  $^2J = 11.4$ ,  $\text{PhCH}_2\text{O}$ ); 4.46 (ddd,  $^3J(6,7) = 7.0$ ,  $^3J(6,5) = 2.5$ ,  $^4J(6,4) = 1.6$ , H-C(6)); 4.39 (br. s, H-C(8)); 4.32 (br. d,  $^3J(7,6) = 7.0$ , H-C(7)); 4.20 (m,  $^3J(1,2) = 1.0$ , H-C(1)); 4.02 (s, OH-C(5)); 4.01 (d,  $^3J(5,6) = 2.5$ , H-C(5)); 3.23 (dd,  $^3J(4,2) = 3.8$ ,  $^4J(4,6) = 1.6$ , H-C(4)); 3.06 (dd,  $^3J(2,4) = 3.8$ ,  $^3J(2,1) = 1.0$ , H-C(2)); 0.93 (s, *t*-BuSi); 0.18, 0.15 (2s,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 136.1 (s, arom. C); 128.8, 128.5, 127.7 (3d,  $^1J(\text{C,H}) = 160$ , arom. C); 90.1 (d,  $^1J(\text{C,H}) = 152$ , C(7)); 79.0 (d,  $^1J(\text{C,H}) = 156$ , C(1)); 78.8 (d,  $^1J(\text{C,H}) = 141$ , C(8)); 73.6 (t,  $^1J(\text{C,H}) = 148$ ,  $\text{PhCH}_2\text{O}$ ); 73.0 (d,  $^1J(\text{C,H}) = 156$ , C(6)); 66.4 (d,  $^1J(\text{C,H}) = 152$ , C(5)); 54.9 (d,  $^1J(\text{C,H}) = 181$ , C(4)); 49.1 (d,  $^1J(\text{C,H}) = 177$ , C(2)); 25.6 (q,  $^1J(\text{C,H}) = 125$ ,  $\text{Me}_3\text{CSi}$ ); 17.9 (s,  $\text{Me}_3\text{CSi}$ ); -4.4, -4.7 (2q,  $^1J(\text{C,H}) = 119$ ,  $\text{Me}_2\text{Si}$ ). CI-MS ( $\text{NH}_3$ ): 396 (1,  $[\text{M} + 18]^+$ ), 379 (3,  $[\text{M} + 1]^+$ ), 321 (14,  $[\text{M} - \text{C}_4\text{H}_9]^+$ ), 288 (2,  $[\text{M} - \text{Bn} + \text{H}]^+$ ), 108 (9,  $\text{BnOH}^+$ ), 91 (100,  $\text{C}_7\text{H}_7^+$ ). Anal. calc. for  $\text{C}_{20}\text{H}_{30}\text{O}_5\text{Si}$  (378.59): C 63.45, H 8.00, Si 7.42; found: C 63.31, H 7.93, Si 7.42.

(1S,2S,4S,5R,6R,7S,8R)-7-endo-(Benzyloxy)-8-exo-[(tert-butyl)dimethylsilyloxy]-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]-nonan-5-endo-ol ((-)-**18**). As described for ( $\pm$ )-**18**, with (+)-**17**. Colorless oil.  $[\alpha]_{\text{D}}^{25} = -21$ ,  $[\alpha]_{\text{D}}^{357} = -22$ ,  $[\alpha]_{\text{D}}^{346} = -25$ ,  $[\alpha]_{\text{D}}^{235} = -40$ ,  $[\alpha]_{\text{D}}^{205} = -47$  ( $c = 0.9$ ,  $\text{CH}_2\text{Cl}_2$ ).

(1R,2SR,4RS,5SR,6SR,7RS,8RS)-7-endo-(Benzyloxy)-8-exo-hydroxy-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]non-5-endo-yl Benzoate (( $\pm$ )-**19**). A mixture of ( $\pm$ )-**18** (4.89 g, 10.1 mmol), anh. THF (170 ml), and  $\text{Bu}_4\text{NF}$  (1M in THF; 12.6 ml, 12.6 mmol) was stirred at 0° for 3.5 h. After the addition of  $\text{H}_2\text{O}$  (600 ml), the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 500$  ml, then  $4 \times 250$  ml). The combined org. extract was dried ( $\text{MgSO}_4$ ) and evaporated and the residue crystallized from  $\text{Et}_2\text{O}$  (-20°, 24 h): 1.90 g of white crystals. The mother liquor was evaporated and the residue purified by FC (4.5  $\times$  18 cm, light petroleum ether/AcOEt 2:3): 0.79 g of colorless crystals. Global yield: 2.69 g (66% based on ( $\pm$ )-**13**) of ( $\pm$ )-**19**. M.p. 122–123°. UV (MeCN): 280 (1050), 272 (1250), 268 (1200), 228 (9400). IR (KBr): 3315, 2965, 2390, 1720, 1715, 1450, 1280, 1270, 1120, 1035, 860, 710.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.92, 7.54, 7.31 (3m, 2 H, 1 H, 7 H, arom. H); 5.31 (d,  $^3J(5,6) = 5.1$ , H-C(5)); 4.80 (ddd,  $^3J(6,7) = 6.8$ ,  $^3J(6,5) = 5.1$ ,  $^4J(6,4) = 1.7$ , H-C(6)); 4.70, 4.58 (2d,  $^2J = 11.8$ ,  $\text{PhCH}_2\text{O}$ ); 4.42 (br. d,  $^3J(8,\text{OH}) = 8.5$ , H-C(8)); 4.39 (m,  $^4J(1,7) = 1.7$ , H-C(1)); 4.17 (br. dd,  $^3J(7,6) = 6.8$ ,  $^4J(7,1) = 1.7$ , H-C(7)); 3.45 (dd,  $^3J(4,2) = 3.9$ ,  $^4J(4,6) = 1.7$ , H-C(4)); 3.18 (br. d,  $^3J(2,4) = 3.9$ , H-C(2)); 2.08 (d,  $^3J(\text{OH},8) = 8.5$ , OH-C(8)).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 165.7 (s, C=O); 137.4, 129.4 (2s, arom. C); 133.2, 129.8, 128.4, 128.3, 127.8, 127.4 (6d,  $^1J(\text{C,H}) = 160$ , arom. C); 87.4 (d,  $^1J(\text{C,H}) = 149$ , C(7)); 78.8 (d,  $^1J(\text{C,H}) = 164$ , C(1)); 78.4 (d,  $^1J(\text{C,H}) = 150$ , C(8)); 73.4 (d,  $^1J(\text{C,H}) = 159$ , C(6)); 73.4 (t,  $^1J(\text{C,H}) = 141$ ,  $\text{PhCH}_2\text{O}$ ); 67.4 (d,  $^1J(\text{C,H}) = 152$ , C(5)); 53.0 (d,  $^1J(\text{C,H}) = 184$ , C(4)); 48.8 (d,  $^1J(\text{C,H}) = 179$ , C(2)). CI-MS ( $\text{NH}_3$ ): 369 (2,  $[\text{M} + 1]^+$ ), 263 (7,  $[\text{M} - \text{Bz}]^+$ ), 105 (100,  $\text{Bz}^+$ ), 91 (66,  $\text{C}_7\text{H}_7^+$ ), 81 (11,  $\text{C}_5\text{H}_5\text{O}^+$ ), 77 (20,  $\text{C}_6\text{H}_5^+$ ). Anal. calc. for  $\text{C}_{21}\text{H}_{20}\text{O}_6$  (368.38): C 68.46, H 5.48; found: C 68.53, H 5.54.

(1R,2S,4R,5S,6S,7R,8R)-7-endo-(Benzyloxy)-8-exo-hydroxy-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]non-5-endo-yl Benzoate ((-)-**19**). As described for ( $\pm$ )-**19**, with (-)-**18**. Yield 75% based on (-)-**13**. White solid. M.p. 95–96°.  $[\alpha]_{\text{D}}^{25} = -46$ ,  $[\alpha]_{\text{D}}^{357} = -48$ ,  $[\alpha]_{\text{D}}^{346} = -55$ ,  $[\alpha]_{\text{D}}^{235} = -91$ ,  $[\alpha]_{\text{D}}^{205} = -109$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ ).

(1R,2RS,4SR,5RS,6RS,7RS,8SR)-7-endo-(Benzyloxy)-8-exo-[(methylsulfonyl)oxy]-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]non-5-endo-yl Benzoate (**20**). A mixture of ( $\pm$ )-**19** (150 mg, 0.41 mmol), anh.  $\text{CH}_2\text{Cl}_2$  (3 ml),  $\text{MeSO}_2\text{Cl}$  (40  $\mu\text{l}$ , 0.52 mmol), and  $\text{Et}_3\text{N}$  (85  $\mu\text{l}$ , 0.61 mmol) was stirred at 20° for 30 min. After the addition of  $\text{CH}_2\text{Cl}_2$  (30 ml), the soln. was washed successively with 1N HCl (25 ml) and sat. aq.  $\text{NaHCO}_3$  soln. (25 ml). The aq. phases were extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 30$  ml) and the combined org. extracts dried ( $\text{MgSO}_4$ ) and evaporated. The residue was purified by FC (1  $\times$  15 cm, light petroleum ether/AcOEt 1:1): 143 mg of **20** (79%). Colorless solid. M.p. 113–114°. UV (MeCN): 272 (1500), 229 (12000), 200 (13500). IR (KBr): 3435, 3060, 3030,

2935, 2865, 1715, 1455, 1370, 1280, 1180, 1120, 955, 710, 530, 510.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.91, 7.55, 7.35–7.23 (3m, 2 H, 1 H, 7 H, arom. H); 5.32 (d,  $^3J(5,6) = 5.2$ , H–C(5)); 5.27 (s, H–C(8)); 4.82 (ddd,  $^3J(6,7) = 6.8$ ,  $^3J(6,5) = 5.2$ ,  $^4J(6,4) = 1.6$ , H–C(6)); 4.73, 4.59 (2d,  $^2J = 11.8$ ,  $\text{PhCH}_2\text{O}$ ); 4.66 (br. s, H–C(1)); 4.48 (br. d,  $^3J(7,6) = 6.8$ , H–C(7)); 3.47 (dd,  $^3J(4,2) = 3.8$ ,  $^4J(4,6) = 1.6$ , H–C(4)); 3.26 (br. d,  $^3J(2,4) = 3.8$ , H–C(2)); 3.07 (s,  $\text{MeSO}_2$ ).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 165.6 (s, C=O), 136.8, 129.2, (2s, arom. C); 133.3, 129.8, 128.4, 128.0, 127.7 (5d,  $^1J(\text{C,H}) = 160$ , arom. C); 84.2 (d,  $^1J(\text{C,H}) = 151$ , C(7)); 83.2 (d,  $^1J(\text{C,H}) = 155$ , C(8)); 76.6 (d,  $^1J(\text{C,H}) = 164$ , C(1)); 73.6 (t,  $^1J(\text{C,H}) = 141$ ,  $\text{PhCH}_2\text{O}$ ); 73.0 (d,  $^1J(\text{C,H}) = 159$ , C(6)); 66.9 (d,  $^1J(\text{C,H}) = 154$ , C(5)); 52.6 (d,  $^1J(\text{C,H}) = 186$ , C(4)); 48.1 (d,  $^1J(\text{C,H}) = 181$ , C(2)); 38.7 (q,  $^1J(\text{C,H}) = 140$ ,  $\text{MeSO}_2$ ). CI-MS ( $\text{NH}_3$ ): 447 (13,  $[\text{M} + \text{H}]^+$ ), 367 (1,  $[\text{M} - \text{Ms}]^+$ ), 341 (32,  $[\text{M} - \text{Bz}]^+$ ), 261 (6,  $[\text{M} - \text{Bn} - \text{OMs} + \text{H}]^+$ ), 235 (5,  $[\text{M} - \text{Bn} - \text{OBz} + \text{H}]^+$ ), 122 (5,  $\text{BzOH}^+$ ), 105 (82,  $\text{Bz}^+$ ), 91 (100,  $\text{C}_7\text{H}_7^+$ ), 77 (24,  $\text{C}_6\text{H}_5^+$ ). Anal. calc. for  $\text{C}_{22}\text{H}_{22}\text{O}_8\text{S}$  (446.51): C 59.13, H 4.98, S 7.18; found: C 59.31, H 4.99, S 7.12.

(1RS,2RS,4SR,5RS,6RS,7RS,8SR)-7-endo-(Benzyloxy)-8-exo-[[4-methylphenyl)sulfonyl]oxy]-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]non-5-endo-yl Benzoate (**21**). As described for **20**, with ( $\pm$ )-**19** (150 mg, 0.41 mmol), TsCl (170 mg, 0.89 mmol), and  $\text{Et}_3\text{N}$  (280  $\mu\text{l}$ , 2.01 mmol). FC (2  $\times$  15 cm; light petroleum ether/AcOEt 3:1): 189 mg (89%) of **21**. Colorless solid. M.p. 142–143°. UV (MeCN): 272 (2600), 263 (2700), 227 (23000), 200 (22500). IR (KBr): 3035, 2970, 2880, 1710, 1595, 1455, 1370, 1270, 1180, 1140, 1115, 985, 965, 790, 720.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.86, 7.52, 7.39, 7.31–7.21, 7.12 (5m, 4 H, H, 2 H, 5 H, 2 H, arom. H); 5.27 (d,  $^3J(5,6) = 5.3$ , H–C(5)); 5.07 (m,  $^3J(8,7) = 1.2$ , H–C(8)); 4.74 (ddd,  $^3J(6,7) = 6.9$ ,  $^3J(6,5) = 5.3$ ,  $^4J(6,4) = 1.6$ , H–C(6)); 4.47, 4.39 (2d,  $^2J = 11.7$ ,  $\text{PhCH}_2\text{O}$ ); 4.43 (m,  $^4J(1,7) = 1.5$ , H–C(1)); 4.40 (ddd,  $^3J(7,6) = 6.9$ ,  $^3J(7,8) = 1.2$ ,  $^4J(7,1) = 1.5$ , H–C(7)); 3.40 (dd,  $^3J(4,2) = 3.7$ ,  $^4J(4,6) = 1.6$ , H–C(4)); 3.13 (br. d,  $^3J(2,4) = 3.7$ , H–C(2)); 2.47 (s,  $\text{MeC}_6\text{H}_4$ ).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 165.6 (s, C=O); 145.7, 136.7, 133.2, 129.2 (4s, arom. C); 133.2, 130.2, 129.8, 128.3, 127.9, 127.8, 127.4 (7d,  $^1J(\text{C,H}) = 160$ , arom. C); 84.8 (d,  $^1J(\text{C,H}) = 154$ , C(8)); 84.6 (d,  $^1J(\text{C,H}) = 149$ , C(7)); 76.3 (d,  $^1J(\text{C,H}) = 160$ , C(1)); 73.3 (t,  $^1J(\text{C,H}) = 143$ ,  $\text{PhCH}_2\text{O}$ ); 72.7 (d,  $^1J(\text{C,H}) = 159$ , C(6)); 66.9 (d,  $^1J(\text{C,H}) = 151$ , C(5)); 52.4 (d,  $^1J(\text{C,H}) = 185$ , C(4)); 48.2 (d,  $^1J(\text{C,H}) = 180$ , C(2)); 21.7 (q,  $^1J(\text{C,H}) = 127$ ,  $\text{MeC}_6\text{H}_4$ ). CI-MS ( $\text{NH}_3$ ): 523 (1,  $[\text{M} + \text{H}]^+$ ), 417 (7,  $[\text{M} - \text{Bz}]^+$ ), 155 (5,  $\text{Ts}^+$ ), 122 (12,  $\text{BzOH}^+$ ), 105 (82,  $\text{Bz}^+$ ), 91 (100,  $\text{C}_7\text{H}_7^+$ ), 77 (18,  $\text{C}_6\text{H}_5^+$ ). Anal. calc. for  $\text{C}_{28}\text{H}_{26}\text{O}_8\text{S}$  (522.61): C 64.35, H 5.02, S 6.13; found: C 64.36, H 5.06, S 6.02.

(1RS,2RS,4SR,5RS,6RS,7RS,8SR)-7-endo-(Benzyloxy)-8-exo-[[4-nitrophenyl)sulfonyl]oxy]-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]non-5-endo-yl Benzoate (**22**). As described for **20**, with ( $\pm$ )-**19** (150 mg, 0.41 mmol), 4-nitrobenzenesulfonyl chloride (0.2 g, 0.90 mmol), and  $\text{Et}_3\text{N}$  (280  $\mu\text{l}$ , 2.01 mmol). FC (2  $\times$  15 cm, light petroleum ether/AcOEt 7:3): 174 mg (77%) of **22**. Yellowish solid. M.p. 162–163°. UV (MeCN): 231 (20500), 200 (25500). IR (KBr): 3110, 3070, 2940, 2875, 1720, 1605, 1535, 1450, 1370, 1350, 1270, 1190, 1120, 1095, 960, 865, 840, 740, 715, 615.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 8.41, 8.13, 7.89, 7.54, 7.33–7.23, 7.15 (6m, 2 H, 2 H, 2 H, H, 5 H, 2 H, arom. H); 5.30 (d,  $^3J(5,6) = 5.2$ , H–C(5)); 5.23 (m,  $^3J(8,7) = 1.2$ , H–C(8)); 4.78 (ddd,  $^3J(6,7) = 6.8$ ,  $^3J(6,5) = 5.2$ ,  $^4J(6,4) = 1.6$ , H–C(6)); 4.57, 4.51 (2d,  $^2J = 11.8$ ,  $\text{PhCH}_2\text{O}$ ); 4.54 (m,  $^4J(1,7) = 1.3$ , H–C(1)); 4.43 (ddd,  $^3J(7,6) = 6.8$ ,  $^3J(7,8) = 1.2$ ,  $^4J(7,1) = 1.3$ , H–C(7)); 3.45 (dd,  $^3J(4,2) = 3.7$ ,  $^4J(4,6) = 1.6$ , H–C(4)); 3.21 (br. d,  $^3J(2,4) = 3.7$ , H–C(2)).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 165.6 (s, C=O); 151.0, 141.8, 136.5, 129.1 (4s, arom. C); 133.4, 129.8, 128.5, 128.4, 128.1, 127.4 (6d,  $^1J(\text{C,H}) = 160$ , arom. C); 129.2, 124.7 (2d,  $^1J(\text{C,H}) = 170$ , arom. C); 85.7 (d,  $^1J(\text{C,H}) = 155$ , C(8)); 84.3 (d,  $^1J(\text{C,H}) = 148$ , C(7)); 76.3 (d,  $^1J(\text{C,H}) = 163$ , C(1)); 73.6 (t,  $^1J(\text{C,H}) = 140$ ,  $\text{PhCH}_2\text{O}$ ); 72.9 (d,  $^1J(\text{C,H}) = 154$ , C(6)); 66.8 (d,  $^1J(\text{C,H}) = 152$ , C(5)); 52.4 (d,  $^1J(\text{C,H}) = 183$ , C(4)); 48.0 (d,  $^1J(\text{C,H}) = 179$ , C(2)). CI-MS ( $\text{NH}_3$ ): 571 (59,  $[\text{M} + 18]^+$ ), 554 (100,  $[\text{M} + 1]^+$ ), 481 (5,  $[\text{M} - \text{Bn} + \text{H} + 18]^+$ ), 465 (6,  $[\text{M} - \text{BzH} + 18]^+$ ), 448 (9,  $[\text{M} - \text{Bz}]^+$ ), 351 (2,  $[\text{M} - \text{ONs}]^+$ ), 122 (9,  $\text{BzOH}^+$ ), 108 (31,  $\text{BnOH}^+$ ), 105 (91,  $\text{Bz}^+$ ), 91 (85,  $\text{C}_7\text{H}_7^+$ ), 77 (13,  $\text{C}_6\text{H}_5^+$ ). Anal. calc. for  $\text{C}_{27}\text{H}_{23}\text{NO}_{10}\text{S}$  (553.57): C 58.58, H 4.20, N 2.53, S 5.79; found: C 58.41, H 4.31, N 2.48, S 5.73.

(1RS,2SR,3SR,4SR,5SR,6RS,7SR)-6-endo-(Benzyloxy)-2-exo,4-endo-dihydroxy-7-exo-[(methylsulfonyl)oxy]-8-oxabicyclo[3.2.1]oct-3-endo-yl Benzoate (**23**). To a soln. of **20** (122 mg, 0.27 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 ml),  $\text{CF}_3\text{COOH}$  (210  $\mu\text{l}$ , 2.74 mmol) was added, and the mixture was stirred at r.t. for 20 min. After dilution with sat.  $\text{NaHSO}_3$  soln. (20 ml), the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (6  $\times$  20 ml). The combined org. layers were dried ( $\text{MgSO}_4$ ) and evaporated. FC (light petroleum ether/AcOEt 1:2) afforded **23** (102 mg, 80%). White solid. M.p. 99–100°. UV (MeCN): 273 (2000), 229 (12500), 199 (19000). IR (KBr): 3421, 3014, 2856, 1700, 1352, 1276, 1174, 1127, 1115, 961, 710.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 8.05, 7.53, 7.35, 7.29 (4m, 2 H, 1 H, 5 H, 2 H, arom. H); 5.63 (d,  $^3J(7,6) = 2.9$ , H–C(7)); 5.51 (br. d,  $^3J(3,4) = 5.6$ , H–C(3)); 4.85, 4.79 (2d,  $^2J = 11.2$ ,  $\text{PhOCH}_2$ ); 4.63 (br. dd,  $^3J(6,5) = 6.7$ ,  $^3J(6,7) = 2.9$ , H–C(6)); 4.55 (dd,  $^3J(5,6) = 6.7$ ,  $^3J(5,4) = 5.0$ , H–C(5)); 4.38 (ddd,  $^3J(4,\text{OH}) = 11.6$ ,  $^3J(4,3) = 5.6$ ,  $^3J(4,5) = 5.0$ , H–C(4)); 4.32 (br. s, H–C(1)); 4.10 (br. s, H–C(2)); 3.19 (br. d,  $^3J(\text{OH},4) = 11.6$ , OH–C(4)); 3.03 (s,  $\text{MeSO}_2$ ); 2.85 (br. s, OH–C(2)).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 165.5 (s, C=O); 136.1, 128.9 (2s, arom. C); 133.6, 129.9, 128.8, 128.6, 128.5, 128.2 (6d,  $^1J(\text{C,H}) = 160$ , arom. C); 86.6 (d,  $^1J(\text{C,H}) = 150$ , C(6)); 82.8 (d,  $^1J(\text{C,H}) = 159$ , C(1)); 81.7 (d,  $^1J(\text{C,H}) = 154$ , C(7)); 74.7 (t,  $^1J(\text{C,H}) = 143$ ,

PhCH<sub>2</sub>O); 74.0 (*d*, <sup>1</sup>J(C,H)=155, C(5)); 71.4 (*d*, <sup>1</sup>J(C,H)=156, C(3)); 68.9 (*d*, <sup>1</sup>J(C,H)=147, C(2)); 66.2 (*d*, <sup>1</sup>J(C,H)=147, C(4)); 38.4 (*q*, <sup>1</sup>J(C,H)=139, MeSO<sub>2</sub>). CI-MS (NH<sub>3</sub>): 482 (15, [*M*+18]<sup>+</sup>), 465 (10, [*M*+1]<sup>+</sup>), 447 (16, [*M*–OH]<sup>+</sup>), 359 (16, [*M*–Bz]<sup>+</sup>), 263 (16, [*M*–Bz–MsOH]<sup>+</sup>), 105 (100, Bz<sup>+</sup>), 91 (93, C<sub>7</sub>H<sub>7</sub><sup>+</sup>), 77 (26, C<sub>6</sub>H<sub>5</sub><sup>+</sup>). Anal. calc. for C<sub>22</sub>H<sub>24</sub>O<sub>9</sub>S (464.53): C 56.88, H 5.21, S 6.90; found: C 56.76, H 5.32, S 6.85.

(1*RS*,2*SR*,3*SR*,4*SR*,5*SR*,6*RS*,7*SR*)-6-endo-(Benzyloxy)-2-exo,4-endo-dihydroxy-7-exo-[(4-methylphenyl)sulfonyl]oxy]-8-oxabicyclo[3.2.1]oct-3-endo-yl Benzoate (**24**). As described for **23**, starting from **21** (115 mg, 0.22 mmol). FC (1 × 13 cm, light petroleum ether/AcOEt 1:1): 93 mg (78%) of **24**. White solid. M.p. 143–145°. UV (MeCN): 273 (2800), 266 (2900), 226 (23500), 201 (24000). IR (KBr): 3455 (br.), 3065, 2915, 1725, 1600, 1450, 1365, 1265, 1180, 1115, 1095, 1075, 970, 840, 715. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.90, 7.63, 7.55, 7.35, 7.19, 7.06 (6*m*, 2 H, 2 H, 1 H, 3 H, 4 H, 2 H, arom. H); 5.38 (br. *d*, <sup>3</sup>J(3,4)=5.4, H–C(3)); 5.21 (*d*, <sup>3</sup>J(7,6)=3.2, H–C(7)); 4.58 (br. *dd*, <sup>3</sup>J(6,5)=6.8, <sup>3</sup>J(6,7)=3.2, H–C(6)); 4.56, 4.46 (2*d*, <sup>2</sup>J=11.0, PhCH<sub>2</sub>O); 4.50 (*dd*, <sup>3</sup>J(5,6)=6.8, <sup>3</sup>J(5,4)=5.0, H–C(5)); 4.33 (*ddd*, <sup>3</sup>J(4,OH)=12.0, <sup>3</sup>J(4,3)=5.4, <sup>3</sup>J(4,5)=5.0, H–C(4)); 4.23 (br. *s*, H–C(1)); 3.90 (br. *d*, <sup>3</sup>J(2,OH)=8.4, H–C(2)); 3.11 (*d*, <sup>3</sup>J(OH,4)=12.0, OH–C(4)); 2.69 (*d*, <sup>3</sup>J(OH,2)=8.4, OH–C(2)); 2.36 (*s*, MeC<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 165.3 (*s*, C=O); 136.1, 133.3, 128.9 (3*s*, arom. C); 133.4, 130.1, 129.9, 128.7, 128.5, 127.9, 127.8 (7*d*, <sup>1</sup>J(C,H)=160, arom. C); 86.5 (*d*, <sup>1</sup>J(C,H)=152, C(6)); 82.9 (*d*, <sup>1</sup>J(C,H)=153, C(7)); 82.7 (*d*, <sup>1</sup>J(C,H)=163, C(1)); 74.3 (*t*, <sup>1</sup>J(C,H)=144, PhCH<sub>2</sub>O); 73.9 (*d*, <sup>1</sup>J(C,H)=157, C(5)); 71.7 (*d*, <sup>1</sup>J(C,H)=158, C(3)); 68.8 (*d*, <sup>1</sup>J(C,H)=146, C(2)); 66.1 (*d*, <sup>1</sup>J(C,H)=143, C(4)); 21.7 (*q*, <sup>1</sup>J(C,H)=128, MeC<sub>6</sub>H<sub>4</sub>). CI-MS (NH<sub>3</sub>): 540 (1, *M*<sup>+</sup>), 523 (2, [*M*–OH]<sup>+</sup>), 435 (13, [*M*–Bz]<sup>+</sup>), 236 (3, [*M*–TsOH–Bz]<sup>+</sup>), 155 (3, Ts<sup>+</sup>), 122 (6, BzOH<sup>+</sup>), 105 (92, Bz<sup>+</sup>), 91 (100, C<sub>7</sub>H<sub>7</sub><sup>+</sup>), 77 (32, C<sub>6</sub>H<sub>5</sub><sup>+</sup>). Anal. calc. for C<sub>28</sub>H<sub>28</sub>O<sub>9</sub>S (540.63): C 62.20, H 5.23, S 5.93; C 62.10, H 5.08, S 5.93.

(1*RS*,2*SR*,3*SR*,4*SR*,5*SR*,6*RS*,7*SR*)-6-endo-(Benzyloxy)-2-exo,4-endo-dihydroxy-7-exo-[(4-nitrophenyl)sulfonyl]oxy]-8-oxabicyclo[3.2.1]oct-3-endo-yl Benzoate (**25**). As described for **23**, with **22** (127 mg, 0.23 mmol): 95 mg (72%) of **25**. Colorless solid. M.p. 147°. UV (MeCN): 232 (17000), 200 (22500). IR (KBr): 3520, 3420, 3105, 3065, 2950, 2915, 1715, 1535, 1375, 1350, 1275, 1255, 1190, 1115, 1100, 1075, 965, 850, 725, 610. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 8.04, 7.91, 7.84, 7.53, 7.38, 7.21, 7.12 (7*m*, 2 H, 2 H, 2 H, 1 H, 3 H, 2 H, 2 H, arom. H); 5.37 (*dm*, <sup>3</sup>J(3,4)=5.5, H–C(3)); 5.19 (*d*, <sup>3</sup>J(7,6)=3.2, H–C(7)); 4.67, 4.51 (2*d*, <sup>2</sup>J=10.6, PhCH<sub>2</sub>O); 4.61 (*ddm*, <sup>3</sup>J(6,5)=6.6, <sup>3</sup>J(6,7)=3.2, H–C(6)); 4.57 (*dd*, <sup>3</sup>J(5,6)=6.6, <sup>3</sup>J(5,4)=4.8, H–C(5)); 4.36 (*ddd*, <sup>3</sup>J(4,OH)=11.9, <sup>3</sup>J(4,3)=5.5, <sup>3</sup>J(4,5)=4.8, H–C(4)); 4.33 (br. *s*, H–C(1)); 4.02 (br. *d*, <sup>3</sup>J(2,OH)=8.3, H–C(2)); 2.96 (*d*, <sup>3</sup>J(OH,4)=11.9, OH–C(4)); 2.57 (br. *d*, <sup>3</sup>J(OH,2)=8.3, OH–C(2)). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 165 (*s*, C=O); 150.8, 140.8, 135.9, 128.6 (4*s*, arom. C); 133.8, 129.8, 128.9, 128.8, 128.5, 128.1 (6*d*, <sup>1</sup>J(C,H)=160, arom. C); 129.2, 124.4 (2*d*, <sup>1</sup>J(C,H)=173, arom. C); 86.4 (*d*, <sup>1</sup>J(C,H)=146, C(6)); 84.2 (*d*, <sup>1</sup>J(C,H)=155, C(7)); 82.2 (*d*, <sup>1</sup>J(C,H)=160, C(1)); 75.0 (*t*, <sup>1</sup>J(C,H)=143, PhCH<sub>2</sub>O); 73.8 (*d*, <sup>1</sup>J(C,H)=157, C(5)); 71.7 (*d*, <sup>1</sup>J(C,H)=158, C(3)); 68.6 (*d*, <sup>1</sup>J(C,H)=151, C(2)); 66.0 (*d*, <sup>1</sup>J(C,H)=145, C(4)). CI-MS (NH<sub>3</sub>): 589 (19, [*M*+18]<sup>+</sup>), 572 (2, [*M*+H]<sup>+</sup>), 554 (2, [*M*–OH]<sup>+</sup>), 466 (6, [*M*–Bz]<sup>+</sup>), 386 (15, [*M*–Ns+H]<sup>+</sup>), 369 (11, [*M*–ONs]<sup>+</sup>), 311 (12, [*M*–C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>–OBz–OH]<sup>+</sup>), 296 (12, [*M*–Bn–Ns+2 H]<sup>+</sup>), 282 (19, [*M*–Bz–Ns+2 H]<sup>+</sup>), 279 (14, [*M*–Bn–ONs+H]<sup>+</sup>), 108 (17, BnOH<sup>+</sup>), 105 (100, Bz<sup>+</sup>), 91 (92, C<sub>7</sub>H<sub>7</sub><sup>+</sup>), 77 (15, C<sub>6</sub>H<sub>5</sub><sup>+</sup>). Anal. calc. for C<sub>27</sub>H<sub>25</sub>NO<sub>11</sub>S (571.60): C 56.73, H 4.42, N 2.45, S 5.61; found: C 56.81, H 4.51, N 2.39, S 5.64.

(1*RS*,2*SR*,3*SR*,4*SR*,5*RS*,6*RS*,7*SR*)-2-exo,4-endo-Bis(acetyloxy)-6-endo-(benzyloxy)-7-exo-[(methylsulfonyl)oxy]-8-oxabicyclo[3.2.1]oct-3-endo-yl Benzoate (**26**). DMAP (2 mg) was added to a stirred mixture of **23** (70 mg, 0.151 mmol), Ac<sub>2</sub>O (0.8 ml), and pyridine (0.8 ml) cooled to 0°. After stirring at 0° for 30 min, stirring was continued at 20° for 4 h. The solvent was evaporated and the residue purified by FC (1 × 15 cm, light petroleum ether/AcOEt 3:2): 72 mg (87%) of **26**. White solid. M.p. 172–175°. UV (MeCN): 274 (2600), 230 (15500), 199 (25000). IR (KBr): 3020, 2950, 1740, 1600, 1500, 1460, 1360, 1270, 1235, 1220, 1175, 1120, 1055, 965, 715. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 8.10, 7.49, 7.26, 7.18 (4*m*, 2 H, 1 H, 2 H, 5 H, arom. H); 5.78 (*d*, <sup>3</sup>J(7,6)=3.4, H–C(7)); 5.61 (*m*, <sup>3</sup>J(3,4)=5.1, <sup>3</sup>J(3,2)=1.7, H–C(3)); 5.53 (*dd*, <sup>3</sup>J(4,3)=5.1, <sup>3</sup>J(4,5)=4.8, H–C(4)); 5.10 (*dd*, <sup>3</sup>J(2,3)=1.7, <sup>3</sup>J(2,1)=1.7, H–C(2)); 4.65, 4.58 (2*d*, <sup>2</sup>J=11.2, PhCH<sub>2</sub>O); 4.60 (br. *dd*, <sup>3</sup>J(5,6)=6.3, <sup>3</sup>J(5,4)=4.8, H–C(5)); 4.56 (br. *dd*, <sup>3</sup>J(6,5)=6.3, <sup>3</sup>J(6,7)=3.4, H–C(6)); 4.46 (*m*, <sup>3</sup>J(1,2)=1.7, H–C(1)); 3.05 (*s*, MeSO<sub>2</sub>); 2.18, 1.92 (2*s*, 2 Ac). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 169.6, 169.4, 165.3 (3*s*, C=O); 136.8, 128.8 (2*s*, arom. C); 133.4, 130.1, 128.3, 128.2, 127.7, 127.3 (6*d*, <sup>1</sup>J(C,H)=160, arom. C); 85.9 (*d*, <sup>1</sup>J(C,H)=149, C(6)); 82.8 (*d*, <sup>1</sup>J(C,H)=155, C(7)); 80.4 (*d*, <sup>1</sup>J(C,H)=161, C(1)); 73.7 (*t*, <sup>1</sup>J(C,H)=140, PhCH<sub>2</sub>O); 73.5 (*d*, <sup>1</sup>J(C,H)=155, C(5)); 70.4 (*d*, <sup>1</sup>J(C,H)=153, C(2)); 67.0 (*d*, <sup>1</sup>J(C,H)=159, C(3)); 66.5 (*d*, <sup>1</sup>J(C,H)=148, C(4)); 38.3 (*q*, <sup>1</sup>J(C,H)=139, MeSO<sub>2</sub>); 20.8, 20.5 (2*q*, <sup>1</sup>J(C,H)=130, 2 MeCO<sub>2</sub>). CI-MS (NH<sub>3</sub>): 548 (1, *M*<sup>+</sup>), 505 (1, [*M*–Ac]<sup>+</sup>), 443 (9, [*M*–Bz]<sup>+</sup>), 122 (9, BzOH<sup>+</sup>), 105 (100, Bz<sup>+</sup>), 91 (99, C<sub>7</sub>H<sub>7</sub><sup>+</sup>), 77 (22, C<sub>6</sub>H<sub>5</sub><sup>+</sup>). Anal. calc. for C<sub>26</sub>H<sub>28</sub>O<sub>11</sub>S (548.61): C 56.62, H 5.15, S 5.85; found: C 56.91, H 5.10, S 5.71.

(1*RS*,2*SR*,3*SR*,4*SR*,5*RS*,6*RS*,7*SR*)-2-exo,4-endo-Bis(acetyloxy)-6-endo-(benzyloxy)-7-exo-[[4-methylphenyl)sulfonyl]oxy]-8-oxabicyclo[3.2.1]oct-3-endo-yl Benzoate (**27**). As described for **26**, with **24** (75 mg, 0.139 mmol): 74 mg (85%) of **27**. Colorless solid. M.p. 156–158°. UV (MeCN): 272 (2800), 265 (2900), 227 (18500), 198 (29500). IR (KBr): 3070, 2960, 1735, 1600, 1450, 1370, 1270, 1225, 1175, 1100, 1050, 995, 720, 555. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.96, 7.75, 7.49, 7.23–7.06 (4*m*, 2 H, 2 H, 1 H, 9 H, arom. H); 5.52 (*m*, <sup>3</sup>*J*(3,4) = 5.1, <sup>3</sup>*J*(3,2) = 1.8, H–C(3)); 5.46 (*dd*, <sup>3</sup>*J*(4,3) = 5.1, <sup>3</sup>*J*(4,5) = 4.8, H–C(4)); 5.41 (*d*, <sup>3</sup>*J*(7,6) = 3.5, H–C(7)); 4.93 (*dd*, <sup>3</sup>*J*(2,3) = 1.8, <sup>3</sup>*J*(2,1) = 1.8, H–C(2)); 4.54 (*dd*, <sup>3</sup>*J*(5,6) = 6.3, <sup>3</sup>*J*(5,4) = 4.8, H–C(5)); 4.49, 4.31 (2*d*, <sup>2</sup>*J* = 11.2, PhCH<sub>2</sub>O); 4.47 (*dd*, <sup>3</sup>*J*(6,5) = 6.3, <sup>3</sup>*J*(6,7) = 3.5, H–C(6)); 4.36 (*m*, <sup>3</sup>*J*(1,2) = 1.8, H–C(1)); 2.37 (*s*, MeC<sub>6</sub>H<sub>4</sub>), 2.17, 1.90 (2*s*, 2 Ac). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 169.6, 139.1, 165.1 (3*s*, 3 C=O); 145.3, 137.0, 132.5, 128.8 (4*s*, arom. C); 133.2, 130.1, 130.0, 128.2, 128.1, 128.0, 127.6, 127.1 (8*d*, <sup>1</sup>*J*(C,H) = 160, arom. C); 85.7 (*d*, <sup>1</sup>*J*(C,H) = 147, C(6)); 83.4 (*d*, <sup>1</sup>*J*(C,H) = 155, C(7)); 80.4 (*d*, <sup>1</sup>*J*(C,H) = 161, C(1)); 73.5 (*t*, <sup>1</sup>*J*(C,H) = 142, PhCH<sub>2</sub>O); 73.2 (*d*, <sup>1</sup>*J*(C,H) = 158, C(5)); 70.0 (*d*, <sup>1</sup>*J*(C,H) = 152, C(2)); 67.1 (*d*, <sup>1</sup>*J*(C,H) = 158, C(3)); 66.6 (*d*, <sup>1</sup>*J*(C,H) = 148, C(4)); 21.7 (*q*, <sup>1</sup>*J*(C,H) = 127, MeC<sub>6</sub>H<sub>4</sub>); 20.9, 20.6 (2*q*, <sup>1</sup>*J*(C,H) = 130, 2 MeCO). CI-MS (NH<sub>3</sub>): 642 (1, [*M* + 18]<sup>+</sup>), 624 (1, *M*<sup>+</sup>), 519 (19, [*M* – Bz]<sup>+</sup>), 155 (6, Ts<sup>+</sup>), 122 (13, BzOH<sup>+</sup>), 105 (86, Bz<sup>+</sup>), 91 (100, C<sub>7</sub>H<sub>7</sub><sup>+</sup>), 77 (19, C<sub>6</sub>H<sub>5</sub><sup>+</sup>). Anal. calc. for C<sub>32</sub>H<sub>32</sub>O<sub>11</sub>S (624.71): C 61.52, H 5.17, S 5.13; found: C 61.64, H 5.19, S 5.18.

(1*RS*,2*SR*,3*SR*,4*SR*,5*RS*,6*RS*,7*SR*)-2-exo,4-endo-Bis(acetyloxy)-6-endo-(benzyloxy)-7-exo-[[4-nitrophenyl)sulfonyl]oxy]-8-oxabicyclo[3.2.1]oct-3-endo-yl Benzoate (**28**). As described for **26**, with **25** (75 mg, 0.131 mmol): 82 mg (95%) of **28**. White solid. M.p. 192–194°. UV (MeCN): 232 (18000), 202 (19500). IR (KBr): 3110, 3070, 3035, 3960, 1745, 1725, 1535, 1375, 1275, 1235, 1185, 1055, 715. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 8.11, 7.99, 7.52, 7.26, 7.18, 7.07 (6*m*, 2 H, 4 H, 1 H, 1 H, 4 H, 2 H, arom. H); 5.54 (*dddd*, <sup>3</sup>*J*(3,4) = 5.2, <sup>3</sup>*J*(3,2) = 1.8, <sup>4</sup>*J*(3,5) = 1.5, <sup>4</sup>*J*(3,1) = 1.5, H–C(3)); 5.49 (*d*, <sup>3</sup>*J*(7,6) = 3.8, H–C(7)); 5.48 (*dd*, <sup>3</sup>*J*(4,3) = 5.2, <sup>3</sup>*J*(4,5) = 5.0, H–C(4)); 4.96 (*dd*, <sup>3</sup>*J*(2,1) = 1.9, <sup>3</sup>*J*(2,3) = 1.8, H–C(2)); 4.57 (*m*, <sup>3</sup>*J*(5,6) = 6.3, <sup>3</sup>*J*(5,4) = 5.0, <sup>4</sup>*J*(5,3) = 1.5, H–C(5)); 4.56, 4.30 (2*d*, <sup>2</sup>*J* = 10.8, PhCH<sub>2</sub>O); 4.48 (*dd*, <sup>3</sup>*J*(6,5) = 6.3, <sup>3</sup>*J*(6,7) = 3.8, H–C(6)); 4.38 (*m*, <sup>3</sup>*J*(1,2) = 1.9, <sup>4</sup>*J*(1,3) = 1.5, H–C(1)); 2.17, 1.92 (2*s*, 2 Ac). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 169.4, 169.2, 165.0 (3*s*, C=O); 150.8, 141.2, 136.6, 128.7 (4*s*, arom. C); 133.6, 130.1, 128.3, 128.1, 127.3 (5*d*, <sup>1</sup>*J*(C,H) = 160, arom. C); 129.3, 124.5 (2*d*, <sup>1</sup>*J*(C,H) = 170, arom. C); 85.8 (*d*, <sup>1</sup>*J*(C,H) = 147, C(6)); 84.7 (*d*, <sup>1</sup>*J*(C,H) = 156, C(7)); 79.9 (*d*, <sup>1</sup>*J*(C,H) = 161, C(1)); 73.9 (*t*, <sup>1</sup>*J*(C,H) = 140, PhCH<sub>2</sub>O); 73.3 (*d*, <sup>1</sup>*J*(C,H) = 156, C(5)); 69.9 (*d*, <sup>1</sup>*J*(C,H) = 152, C(2)); 67.2 (*d*, <sup>1</sup>*J*(C,H) = 159, C(3)); 66.4 (*d*, <sup>1</sup>*J*(C,H) = 147, C(4)); 20.8, 20.6 (2*q*, <sup>1</sup>*J*(C,H) = 130, MeCO). CI-MS (NH<sub>3</sub>): 655 (1, *M*<sup>+</sup>), 550 (5, [*M* – Bz]<sup>+</sup>), 122 (5, BzOH<sup>+</sup>), 105 (95, Bz<sup>+</sup>), 91 (100, C<sub>7</sub>H<sub>7</sub><sup>+</sup>), 77 (22, C<sub>6</sub>H<sub>5</sub><sup>+</sup>). Anal. calc. for C<sub>31</sub>H<sub>29</sub>NO<sub>13</sub>S (655.68): C 56.78, H 4.47, N 2.14, S 4.89; found: C 56.89, H 4.36, N 2.22, S 4.90.

(1*RS*,2*RS*,4*SR*,5*RS*,6*SR*,7*RS*)-7-endo-(Benzyloxy)-8-oxo-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]non-5-endo-yl Benzoate ((±)-**40**). A mixture of (±)-**19** (2.66 g, 7.2 mmol), anh. CH<sub>2</sub>Cl<sub>2</sub> (150 ml), and 1,1,1-tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (5.15 g, 12.1 mmol) was stirred at 20° for 4 h. After the addition of Et<sub>2</sub>O (400 ml), the soln. was washed successively with sat. aq. NaHCO<sub>3</sub> soln. (400 ml) containing Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (19 g, 120 mmol), sat. aq. NaHCO<sub>3</sub> soln. (400 ml), and H<sub>2</sub>O (400 ml). The aq. phases were extracted with Et<sub>2</sub>O (2 × 300 ml). The combined org. extracts were dried (MgSO<sub>4</sub>) and evaporated: 2.62 g (100%) of (±)-**40**. Yellowish, viscous oil, which was used as such in the next step. An anal. sample was obtained by FC (1 × 12 cm, CH<sub>2</sub>Cl<sub>2</sub>/AcOEt 95 : 5): colorless solid. M.p. 119–120°. UV (MeCN): 274 (1700), 229 (12500), 202 (12000). IR (KBr): 3035, 2945, 2870, 1775, 1725, 1600, 1455, 1310, 1265, 1115, 1065, 1030, 860, 745, 720, 695. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.97, 7.55, 7.35–7.17 (3*m*, 2 H, 1 H, 7 H, arom. H); 5.50 (*dd*, <sup>3</sup>*J*(5,6) = 6.0, <sup>4</sup>*J*(5,2) = 0.6, H–C(5)); 5.03 (*ddd*, <sup>3</sup>*J*(6,7) = 7.6, <sup>3</sup>*J*(6,5) = 6.0, <sup>4</sup>*J*(6,4) = 1.6, H–C(6)); 4.81, 4.65 (2*d*, <sup>2</sup>*J* = 11.8, PhCH<sub>2</sub>O); 4.42 (br. *dd*, <sup>3</sup>*J*(1,2) = 1.7, <sup>4</sup>*J*(1,7) = 1.8, H–C(1)); 4.34 (*dd*, <sup>3</sup>*J*(7,6) = 7.6, <sup>3</sup>*J*(7,1) = 1.8, H–C(7)); 3.44 (br. *dd*, <sup>3</sup>*J*(4,2) = 3.8, <sup>4</sup>*J*(4,6) = 1.6, H–C(4)); 3.28 (*ddd*, <sup>3</sup>*J*(2,4) = 3.8, <sup>3</sup>*J*(2,1) = 1.7, <sup>4</sup>*J*(2,5) = 0.6, H–C(2)). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 207.5 (*s*, C(8)); 165.7 (*s*, C=O); 136.3, 129.0 (2*s*, arom. C); 133.4, 129.9, 128.4, 128.1, 128.0 (5*d*, <sup>1</sup>*J*(C,H) = 160, arom. C); 78.5 (*d*, <sup>1</sup>*J*(C,H) = 144, C(7)); 73.9 (*t*, <sup>1</sup>*J*(C,H) = 146, PhCH<sub>2</sub>O); 72.8 (*d*, <sup>1</sup>*J*(C,H) = 166, C(1)); 70.2 (*d*, <sup>1</sup>*J*(C,H) = 164, C(6)); 65.4 (*d*, <sup>1</sup>*J*(C,H) = 153, C(5)); 51.1 (*d*, <sup>1</sup>*J*(C,H) = 180, C(4)); 46.6 (*d*, <sup>1</sup>*J*(C,H) = 186, C(2)). CI-MS (NH<sub>3</sub>): 385 (1, [*M* + H + 18]<sup>+</sup>), 367 (1, [*M* + H]<sup>+</sup>), 279 (7, [*M* – Bz + 18]<sup>+</sup>), 122 (10, BzOH<sup>+</sup>), 105 (100, Bz<sup>+</sup>), 91 (73, C<sub>7</sub>H<sub>7</sub><sup>+</sup>), 77 (28, C<sub>6</sub>H<sub>5</sub><sup>+</sup>). Anal. calc. for C<sub>21</sub>H<sub>18</sub>O<sub>6</sub> (366.39): C 68.84, H 4.96; found: C 68.81, H 5.03.

(1*S*,2*S*,4*RS*,5*S*,6*RS*,7*S*)-7-endo-(Benzyloxy)-8-oxo-3,9-dioxatricyclo[4.2.1.0<sup>2,4</sup>]non-5-endo-yl Benzoate ((–)-**40**). As described for (±)-**40**, with (–)-**19**. White solid. M.p. 122–124°. [*α*]<sub>D</sub><sup>25</sup> = –152, [*α*]<sub>D</sub><sup>25</sup> = –160, [*α*]<sub>D</sub><sup>25</sup> = –185, [*α*]<sub>D</sub><sup>25</sup> = –355, [*α*]<sub>D</sub><sup>25</sup> = –364 (*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

(1*RS*,2*RS*,3*SR*,4*SR*,5*RS*,6*RS*)-6-endo-(Benzyloxy)-2-exo,4-endo-dihydroxy-7-oxo-8-oxabicyclo[3.2.1]oct-3-endo-yl Benzoate ((±)-**41**). A mixture of (±)-**40** (2.62 g, 7.15 mmol), CH<sub>2</sub>Cl<sub>2</sub> (120 ml), and CF<sub>3</sub>COOH (5.5 ml, 8.2 g, 72 mmol) was stirred at 20° for 1 h. After the addition of sat. aq. NaHCO<sub>3</sub> soln. (120 ml), the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (6 × 100 ml). The combined org. extracts were dried (MgSO<sub>4</sub>) and

evaporated: 2.69 g (96%) of ( $\pm$ )-**41**. Yellowish, viscous oil, which was used as such in the next step. An anal. sample was obtained by FC (light petroleum ether/AcOEt 2:3): white solid. M.p. 138–139°. UV (MeCN): 229 (10400), 268 (1300), 274 (1350), 281 (1200). IR (KBr): 3510, 3430, 2950, 2875, 2365, 1770, 1690, 1600, 1455, 1405, 1270, 1100, 1070, 670.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 8.07, 7.53, 7.34 (3m, 2 H, 1 H, 7 H, arom. H); 5.49 (m,  $^3J(3,4) = 5.0$ ,  $^3J(3,2) = 2.0$ ,  $^4J(3,1) = 1.8$ , H–C(3)); 5.00, 4.92 (2d,  $^2J = 11.5$ ,  $\text{PhCH}_2$ ); 4.80 (br. dd,  $^3J(5,6) = 7.4$ ,  $^3J(5,4) = 4.9$ , H–C(5)); 4.55 (m,  $^3J(6,5) = 7.4$ ,  $^4J(6,1) = 1.7$ , H–C(6)); 4.54 (br. ddd,  $^3J(4,\text{OH}) = 11.9$ ,  $^3J(4,3) = 5.0$ ,  $^3J(4,5) = 4.9$ , H–C(4)); 4.17 (ddd,  $^3J(1,2) = 2.5$ ,  $^4J(1,3) = 1.8$ ,  $^4J(1,6) = 1.7$ , H–C(1)); 4.10 (br. ddd,  $^3J(2,\text{OH}) = 8.1$ ,  $^3J(2,1) = 2.5$ ,  $^3J(2,3) = 2.0$ , H–C(2)); 3.05 (d,  $^3J(\text{OH},4) = 11.9$ , OH–C(4)); 2.96 (d,  $^3J(\text{OH},2) = 8.1$ , OH–C(2)).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 207.3 (s, C(7)); 165.6 (s, C=O); 136.0, 128.6 (2s, arom. C); 133.5, 130.3, 128.7, 128.3, 128.0 (5d,  $^1J(\text{C,H}) = 160$ , arom. C); 80.8 (d,  $^1J(\text{C,H}) = 139$ , C(6)); 79.0 (d,  $^1J(\text{C,H}) = 161$ , C(1)); 74.7 (t,  $^1J(\text{C,H}) = 143$ ,  $\text{PhCH}_2\text{O}$ ); 73.4 (d,  $^1J(\text{C,H}) = 158$ , C(5)); 71.4 (d,  $^1J(\text{C,H}) = 158$ , C(3)); 68.9 (d,  $^1J(\text{C,H}) = 153$ , C(2)); 65.8 (d,  $^1J(\text{C,H}) = 147$ , C(4)). CI-MS ( $\text{NH}_3$ ): 385 (3,  $[M+1]^+$ ), 279 (13,  $[M-\text{Bz}]^+$ ), 105 (74,  $\text{Bz}^+$ ), 91 (100,  $\text{C}_7\text{H}_7^+$ ), 77 (20,  $\text{C}_6\text{H}_5^+$ ). Anal. calc. for  $\text{C}_{21}\text{H}_{20}\text{O}_7$  (384.41): C 65.61, H 5.25; found: C 65.67, H 5.30.

(1*S*,2*S*,3*R*,4*R*,5*R*,6*S*)-6-endo-(Benzyloxy)-2-exo,4-endo-dihydroxy-7-oxo-8-oxabicyclo[3.2.1]oct-3-endo-yl Benzoate ((–)-**41**). As described for ( $\pm$ )-**41**, with (–)-**40**. White foam.  $[\alpha]_{\text{D}}^{25} = -41$ ,  $[\alpha]_{\text{D}}^{35} = -42$ ,  $[\alpha]_{\text{D}}^{546} = -46$ ,  $[\alpha]_{\text{D}}^{25} = -54$ ,  $[\alpha]_{\text{D}}^{25} = -40$  ( $c = 1.1$ ,  $\text{CH}_2\text{Cl}_2$ ).

(1*R*,2*S*,3*R*,5*R*,6*S*)-2-exo,4-endo-Bis(acetyloxy)-6-endo-(benzyloxy)-7-oxo-8-oxabicyclo[3.2.1]oct-3-endo-yl Benzoate (( $\pm$ )-**42**). As described for the preparation of **26**, with ( $\pm$ )-**41** (2.65 g, 6.89 mmol). FC ( $5 \times 18$  cm, light petroleum ether/AcOEt 3:2): 2.68 g (79% based on ( $\pm$ )-**19**) of ( $\pm$ )-**42**. White foam. UV (MeCN): 274 (1950), 230 (15200), 201 (17200). IR (KBr): 3070, 3035, 2980, 2870, 1750, 1730, 1600, 1455, 1370, 1270, 1220, 1095, 1055, 715.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 8.08, 7.50, 7.33, 7.18 (4m, 2 H, 1 H, 2 H, 5 H, arom. H); 5.66 (dd,  $^3J(4,5) = 4.6$ ,  $^3J(4,3) = 4.6$ , H–C(4)); 5.62 (m,  $^3J(3,4) = 4.6$ ,  $^3J(3,2) = 2.1$ , H–C(3)); 5.05 (dd,  $^3J(2,3) = 2.1$ ,  $^3J(2,1) = 2.0$ , H–C(2)); 4.86 (br. dd,  $^3J(5,6) = 7.0$ ,  $^3J(5,4) = 4.6$ , H–C(5)); 4.73, 4.69 (2d,  $^2J = 11.5$ ,  $\text{PhCH}_2\text{O}$ ); 4.56 (dd,  $^3J(6,5) = 7.0$ ,  $^4J(6,1) = 1.2$ , H–C(6)); 4.41 (m,  $^3J(1,2) = 2.0$ ,  $^3J(1,6) = 1.2$ , H–C(1)); 2.21, 1.93 (2s, 2 Ac).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 205.5 (s, C(7)); 169.7, 169.3, 165.3 (3s, C=O); 136.7, 128.4 (2s, arom. C); 133.3, 130.5, 128.1, 127.7, 127.1 (5d,  $^1J(\text{C,H}) = 160$ , arom. C); 81.1 (d,  $^1J(\text{C,H}) = 140$ , C(6)); 76.9 (d,  $^1J(\text{C,H}) = 163$ , C(1)); 73.7 (t,  $^1J(\text{C,H}) = 141$ ,  $\text{PhCH}_2\text{O}$ ); 72.7 (d,  $^1J(\text{C,H}) = 160$ , C(5)); 69.9 (d,  $^1J(\text{C,H}) = 155$ , C(2)); 67.1 (d,  $^1J(\text{C,H}) = 159$ , C(3)); 66.2 (d,  $^1J(\text{C,H}) = 147$ , C(4)); 20.8, 20.5 (2q,  $^1J(\text{C,H}) = 130$ , 2 MeCO). CI-MS ( $\text{NH}_3$ ): 486 (5,  $[M+18]^+$ ), 469 (5,  $[M+1]^+$ ), 363 (3,  $[M-\text{Bz}]^+$ ), 347 (2,  $[M-\text{BzO}]^+$ ), 289 (3,  $[M-\text{BzO}-\text{AcO}+\text{H}]^+$ ), 247 (3,  $[M-\text{BzO}-\text{AcO}-\text{Ac}+2\text{H}]^+$ ), 180 (13), 138 (10), 105 (85,  $\text{Bz}^+$ ), 91 (100,  $\text{C}_7\text{H}_7^+$ ), 77 (20,  $\text{C}_6\text{H}_5^+$ ). Anal. calc. for  $\text{C}_{25}\text{H}_{24}\text{O}_9$  (468.49): C 64.09, H 5.17; found: C 63.21, H 5.16.

(1*S*,2*S*,3*R*,4*R*,5*R*,6*S*)-2-exo,4-endo-Bis(acetyloxy)-6-endo-(benzyloxy)-7-oxo-8-oxabicyclo[3.2.1]oct-3-endo-yl Benzoate ((+)-**42**). As described for ( $\pm$ )-**42**, with (–)-**41**. Yield 72% based on (–)-**19**. Colorless oil.  $[\alpha]_{\text{D}}^{25} = 3.7$ ,  $[\alpha]_{\text{D}}^{35} = 4.7$ ,  $[\alpha]_{\text{D}}^{25} = 7.3$ ,  $[\alpha]_{\text{D}}^{25} = 40$ ,  $[\alpha]_{\text{D}}^{25} = 76$  ( $c = 1.3$ ,  $\text{CH}_2\text{Cl}_2$ ).

(1*R*,2*S*,3*R*,5*R*,6*S*,7*R*,8*S*)-6-exo,8-endo-Bis(acetyloxy)-2-endo-(benzyloxy)-4-oxo-3,9-dioxabicyclo[3.3.1]non-7-endo-yl Benzoate (( $\pm$ )-**43**). A dried soln. of 70% 3-chloroperbenzoic acid (3.22 g, 13.1 mmol; Fluka) was made by dissolving *m*CPBA in  $\text{CH}_2\text{Cl}_2$  (200 ml) and drying with  $\text{MgSO}_4$ . After filtration, 175 ml of this soln. were used to dissolve ( $\pm$ )-**42** (2.68 g, 5.72 mmol).  $\text{NaHCO}_3$  (0.96 g, 11.4 mmol) was added and the mixture stirred at 20° for 12 h. Then 0.5M aq.  $\text{Na}_2\text{S}_2\text{O}_3$  (50 ml) was added slowly under vigorous stirring. After 1 h, AcOEt (400 ml) was added and the soln. washed successively with 0.5M aq.  $\text{Na}_2\text{S}_2\text{O}_3$  (150 ml), sat. aq.  $\text{NaHCO}_3$  soln. (200 ml), and brine (200 ml). The aq. layers were extracted with AcOEt ( $2 \times 200$  ml) and the org. extracts dried ( $\text{MgSO}_4$ ) and evaporated. The residue was purified by FC (5 cm  $\times$  17 cm, light petroleum ether/AcOEt 3:2): 2.3 g (83%) of ( $\pm$ )-**43**. Colorless oil that crystallized slowly. Washing of the crystals with  $\text{Et}_2\text{O}$  gave 1.5 g of colorless crystals. M.p. 130–131°. UV (MeCN): 281 (1100), 273 (1300), 267 (1200), 263 (1200), 230 (11900), 202 (11400). IR (KBr): 3065, 3035, 2965, 2910, 1755, 1740, 1730, 1265, 1240, 1225, 1210, 1145, 1105, 1045, 715.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 8.10, 7.55, 7.43, 7.19, 7.01 (5m, 10 arom. H); 5.91 (d,  $^3J(2,1) = 4.8$ , H–C(2)); 5.62 (dd,  $^3J(7,8) = 3.7$ ,  $^3J(7,6) = 3.3$ , H–C(7)); 5.56 (dd,  $^3J(8,1) = 5.9$ ,  $^3J(8,7) = 3.7$ , H–C(8)); 5.34 (dd,  $^3J(6,7) = 3.3$ ,  $^3J(6,5) = 1.8$ , H–C(6)); 4.91, 4.53 (2d,  $^2J = 11.3$ ,  $\text{PhCH}_2\text{O}$ ); 4.64 (d,  $^3J(5,6) = 1.8$ , H–C(5)); 4.63 (dd,  $^3J(1,8) = 5.9$ ,  $^3J(1,2) = 4.8$ , H–C(1)); 2.18, 1.76 (2s, Ac).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 170.0, 169.0, 165.1, 165.0 (4s, C(4), 3 C=O); 135.5, 128.7 (2s, arom. C); 133.5, 130.1, 128.4, 128.2, 128.0, 127.6 (6d,  $^1J(\text{C,H}) = 160$ , arom. C); 100.7 (d,  $^1J(\text{C,H}) = 174$ , C(2)); 72.0 (t,  $^1J(\text{C,H}) = 143$ ,  $\text{PhCH}_2\text{O}$ ); 70.5 (d,  $^1J(\text{C,H}) = 156$ , C(6)); 70.0 (d,  $^1J(\text{C,H}) = 159$ , C(5)); 66.7 (d,  $^1J(\text{C,H}) = 159$ , C(7)); 66.1 (d,  $^1J(\text{C,H}) = 148$ , C(8)); 65.2 (d,  $^1J(\text{C,H}) = 154$ , C(1)); 20.7, 20.3 (2q,  $^1J(\text{C,H}) = 130$ , 2 MeCO). CI-MS ( $\text{NH}_3$ ): 502 (77,  $[M+18]^+$ ), 485 (26,  $[M+\text{H}]^+$ ), 363 (11,  $[M-\text{BzO}]^+$ ), 108 (21,  $\text{BnOH}^+$ ), 105 (87), 91 (100), 77 (12). Anal. calc. for  $\text{C}_{25}\text{H}_{24}\text{O}_{10}$  (484.49): C 61.97, H 5.00; found: C 61.82, H 5.10.

(1R,2R,5S,6S,7R,8S)-6-exo,8-endo-Bis(acetyloxy)-2-endo-(benzyloxy)-4-oxo-3,9-dioxabicyclo[3.3.1]non-7-endo-yl Benzoate ((-)-**43**). As described for (±)-**43**, with (+)-**42**. White foam. Yield 84%.  $[\alpha]_D^{25} = -75$ ,  $[\alpha]_{377}^{25} = -78$ ,  $[\alpha]_{546}^{25} = -89$ ,  $[\alpha]_{435}^{25} = -145$ ,  $[\alpha]_{405}^{25} = -169$  ( $c = 1.3$ , CH<sub>2</sub>Cl<sub>2</sub>).

Mixture of Methyl 5,7-Di-O-acetyl-4,8-anhydro-6-O-benzoyl-3-O-benzyl-2-deoxy-1-C-phenyl-DL-erythro-LD-manno- and -DL-erythro-LD-glucos-nonuronate (**45a,b**). A mixture of (±)-**43** (20 mg, 0.04 mmol), 1-phenyl-1-[(trimethylsilyl)oxy]ethene (40 µl, 37 mg, 0.19 mmol), anh. MeNO<sub>2</sub> (0.7 ml), and Me<sub>3</sub>SiOSO<sub>2</sub>CF<sub>3</sub> (added the latest, 100 mg) was stirred at 20° for 1 h. After the addition of anh. MeOH (0.1 ml), the mixture was stirred at 20° for 17 h. A sat. aq. NaHCO<sub>3</sub> soln. (5 ml) was added and the mixture extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 ml, 4 times). The combined org. extracts were dried (MgSO<sub>4</sub>) and evaporated. FC (1 × 15 cm, CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O 95:5) gave 16 mg (63%) of (±)-**45a**/(±)-**45b** 1:1. Colorless oil.

Mixture of Methyl 3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-7-O-benzyl-8,9,10-trideoxy-LD-erythro-DL-manno-dec-9-enonate and -DL-threo-DL-manno-dec-9-enonate (**46a,b**). Me<sub>3</sub>SiOSO<sub>2</sub>CF<sub>3</sub> (100 mg) was added to a stirred soln. of (±)-**43** (54 mg, 0.111 mmol) and 3-(trimethylsilyl)prop-2-ene (69 mg, 0.604 mmol) in anh. MeCN (1.5 ml) cooled to 0°. After stirring at 0° for 1 h, anh. MeOH (0.1 ml) was added and the mixture stirred at 20° for 18 h. A sat. aq. NaHCO<sub>3</sub> soln. (5 ml) was added and the mixture extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 × 5 ml). The combined org. extracts were dried (MgSO<sub>4</sub>) and evaporated: 58 mg of (±)-**46a**/(±)-**46b** 4.3:1. FC (2 × 15 cm, light petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O 40:57:3): 8 mg (13%) of (±)-**46a** and 38 mg (63%) of (±)-**46b**.

Data for (±)-**46a**:  $R_f$  0.16. Colorless oil. UV (MeCN): 229 (21200), 209 (15900). IR (film): 3060, 3035, 2985, 2955, 1755, 1740, 1725, 1455, 1370, 1275, 1220, 1120, 1090, 1055, 715, 695. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.94, 7.56, 7.41, 7.30 (4m, 2 H, 1 H, 2 H, 5 H, arom. H); 5.90 (dddd, <sup>3</sup>J(9,10cis) = 16.8, <sup>3</sup>J(9,10trans) = 10.5, <sup>3</sup>J(9,8b) = 8.6, <sup>3</sup>J(9,8a) = 5.9, H-C(9)); 5.88 (d, <sup>3</sup>J(5,4) = 3.4, H-C(5)); 5.56 (dd, <sup>3</sup>J(3,4) = 10.1, <sup>3</sup>J(3,2) = 10.0, H-C(3)); 5.32 (dd, <sup>3</sup>J(4,3) = 10.1, <sup>3</sup>J(4,5) = 3.4, H-C(4)); 5.18 (br. d, <sup>3</sup>J(10cis,9) = 16.8, H<sub>cis</sub>-C(10)); 5.17 (br. d, <sup>3</sup>J(10trans,9) = 10.5, H<sub>trans</sub>-C(10)); 4.56, 4.33 (2d, <sup>2</sup>J = 10.8, PhCH<sub>2</sub>O); 4.02 (d, <sup>3</sup>J(2,3) = 10.0, H-C(2)); 3.79 (s, COOMe); 3.67 (m, <sup>3</sup>J(7,8b) = 3.3, H-C(6), H-C(7)); 2.68 (m, <sup>2</sup>J(8a,8b) = 14.5, <sup>3</sup>J(8a,9) = 5.9, H<sub>a</sub>-C(8)); 2.41 (br. ddd, <sup>3</sup>J(8b,8a) = 14.5, <sup>3</sup>J(8b,9) = 8.6, <sup>3</sup>J(8b,7) = 3.3, H<sub>b</sub>-C(8)); 2.06, 1.97 (2s, 2 Ac). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 169.8, 169.7, 167.7, 165.2 (4s, 4 C=O); 137.2 (s, arom. C); 133.3, 133.1 (2d, <sup>1</sup>J(C,H) = 161, 155, C(9), arom. C); 129.6 (d, <sup>1</sup>J(C,H) = 160, arom. C); 129.1 (s, arom. C); 128.6, 128.5, 128.4, 127.9 (4d, <sup>1</sup>J(C,H) = 160, arom. C); 118.5 (t, <sup>1</sup>J(C,H) = 155, C(10)); 77.3 (d, <sup>1</sup>J(C,H) = 138, C(7)); 76.9 (d, <sup>1</sup>J(C,H) = 155, C(2)); 73.6 (d, <sup>1</sup>J(C,H) = 145, C(6)); 72.6 (d, <sup>1</sup>J(C,H) = 147, C(4)); 71.4 (t, <sup>1</sup>J(C,H) = 145, PhCH<sub>2</sub>O); 67.1, 67.0 (2d, <sup>1</sup>J(C,H) = 155, C(3), C(5)); 52.8 (q, <sup>1</sup>J(C,H) = 148, COOMe); 33.4 (t, <sup>1</sup>J(C,H) = 129, C(8)); 20.8, 20.6 (2q, <sup>1</sup>J(C,H) = 130, 2 MeCO). CI-MS (NH<sub>3</sub>): 558 (100, [M + NH<sub>4</sub>]<sup>+</sup>). Anal. calc. for C<sub>29</sub>H<sub>32</sub>O<sub>10</sub> (540.61): C 64.43, H 5.98; found: C 64.42, H 6.05.

Data for (±)-**46b**:  $R_f$  0.12. Colorless solid. M.p. 116–118°. UV (MeCN): 280 (1150), 272 (1400), 267 (1350), 228 (12800), 201 (11300). IR (KBr): 3070, 3035, 2980, 2955, 2920, 1760, 1740, 1725, 1640, 1455, 1370, 1275, 1235, 1120, 1095, 715. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.94, 7.58, 7.44, 7.39–7.26 (4m, 2 H, 1 H, 2 H, 5 H, arom. H); 5.90 (dddd, <sup>3</sup>J(9,10cis) = 17.2, <sup>3</sup>J(9,10trans) = 10.1, <sup>3</sup>J(9,8b) = 7.9, <sup>3</sup>J(9,8a) = 6.1, H-C(9)); 5.69 (br. d, <sup>3</sup>J(5,4) = 3.4, H-C(5)); 5.62 (dd, <sup>3</sup>J(3,4) = 10.1, <sup>3</sup>J(3,2) = 10.0, H-C(3)); 5.28 (dd, <sup>3</sup>J(4,3) = 10.1, <sup>3</sup>J(4,5) = 3.4, H-C(4)); 5.15 (br. d, <sup>3</sup>J(10cis,9) = 17.2, H<sub>cis</sub>-C(10)); 5.13 (br. d, <sup>3</sup>J(10trans,9) = 10.1, H<sub>trans</sub>-C(10)); 4.80, 4.65 (2d, <sup>2</sup>J = 11.4, PhCH<sub>2</sub>O); 4.08 (d, <sup>3</sup>J(2,3) = 10.0, H-C(2)); 3.80 (s, COOMe); 3.79 (br. d, <sup>3</sup>J(6,7) = 8.0, H-C(6)); 3.70 (ddd, <sup>3</sup>J(7,6) = 8.0, <sup>3</sup>J(7,8b) = 6.8, <sup>3</sup>J(7,8a) = 3.6, H-C(7)); 2.39 (m, <sup>2</sup>J(8a,8b) = 14.7, <sup>3</sup>J(8a,9) = 6.1, <sup>3</sup>J(8a,7) = 3.6, H<sub>a</sub>-C(8)); 2.16 (br. ddd, <sup>3</sup>J(8b,8a) = 14.7, <sup>3</sup>J(8b,9) = 7.9, <sup>3</sup>J(8b,7) = 6.8, H<sub>b</sub>-C(8)); 2.12, 1.99 (2s, 2 Ac). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 170.0, 169.7, 167.7, 165.4 (4s, 4 C=O); 138.5, 129.0 (2s, arom. C); 133.5, 133.3 (2d, <sup>1</sup>J(C,H) = 162, 155, C(9), arom. C); 129.6, 128.5, 128.3, 127.9, 127.6 (5d, <sup>1</sup>J(C,H) = 160, arom. C); 118.2 (t, <sup>1</sup>J(C,H) = 156, C(10)); 80.5 (d, <sup>1</sup>J(C,H) = 141, C(6)); 77.6 (d, <sup>1</sup>J(C,H) = 138, C(7)); 76.5 (d, <sup>1</sup>J(C,H) = 151, C(2)); 74.0 (t, <sup>1</sup>J(C,H) = 142, PhCH<sub>2</sub>O); 72.6 (d, <sup>1</sup>J(C,H) = 148, C(4)); 67.5 (d, <sup>1</sup>J(C,H) = 153, C(5)); 66.6 (d, <sup>1</sup>J(C,H) = 156, C(3)); 52.7 (q, <sup>1</sup>J(C,H) = 148, COOMe); 35.0 (t, <sup>1</sup>J(C,H) = 128, C(8)); 20.7, 20.6 (2q, <sup>1</sup>J(C,H) = 130, 2 MeCO). CI-MS (NH<sub>3</sub>): 558 (100, [M + 18]<sup>+</sup>), 540 (2, M<sup>+</sup>), 481 (6, [M - Ac]<sup>+</sup>), 433 (7, [M - OBn]<sup>+</sup>), 105 (52), 91 (78), 77 (9). Anal. calc. for C<sub>29</sub>H<sub>32</sub>O<sub>10</sub> (540.61): C 64.43, H 5.98; found: C 64.36, H 5.91.

Mixture of Methyl 3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-7-O-benzyl-7-C-cyano-LD-erythro-DL-manno-heptonate and -DL-threo-DL-manno-heptonate (**47a,b**). As described for **45a,b** with (±)-**43** (18 mg, 0.037 mmol) and Me<sub>3</sub>SiCN instead of PhCH(OSiMe<sub>3</sub>)CH<sub>2</sub>. FC (1 × 16 cm, light petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O 20:76:4): 2 mg (10%) of pure (±)-**47a** ( $R_f$  0.38) and 6 mg (±)-**47b**/(±)-**47a** 4:1.

Data for (±)-**47a**:  $R_f$  0.38. Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.91, 7.58, 7.43, 7.36–7.28 (4m, 2 H, 1 H, 2 H, 5 H, arom. H); 5.75 (dd, <sup>3</sup>J(5,4) = 3.3, <sup>3</sup>J(5,6) = 1.1, H-C(5)); 5.51 (dd, <sup>3</sup>J(3,4) = 10.2, <sup>3</sup>J(3,2) = 10.0, H-C(3)); 5.29 (dd, <sup>3</sup>J(4,3) = 10.2, <sup>3</sup>J(4,5) = 3.3, H-C(4)); 4.84, 4.53 (2d, <sup>2</sup>J = 11.9, PhCH<sub>2</sub>O); 4.18 (d, <sup>3</sup>J(7,6) =

9.1, H–C(7)); 4.14 (*d*,  $^3J(2,3) = 10.0$ , H–C(2)); 4.08 (*dd*,  $^3J(6,7) = 9.1$ ,  $^3J(6,5) = 1.1$ , H–C(6)); 3.78 (*s*, COOMe); 1.99, 1.84 (2*s*, 2 MeCO). CI-MS (NH<sub>3</sub>): 543 (100, [M + 18]<sup>+</sup>), 526 (2, [M + H]<sup>+</sup>), 525 (1, M<sup>+</sup>), 499 (2, [M – CN]<sup>+</sup>), 436 (11), 426 (4), 359 (4), 105 (35), 91 (23), 77 (10).

*Data for (±)-47b*: *R*<sub>f</sub> 0.27. Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.93, 7.58, 7.46–7.32 (3*m*, 2 H, 1 H, 7 H, arom. H); 5.90 (*dd*,  $^3J(5,4) = 3.3$ ,  $^3J(5,6) = 1.1$ , H–C(5)); 5.67 (*dd*,  $^3J(3,4) = 10.2$ ,  $^3J(3,2) = 10.0$ , H–C(3)); 5.30 (*dd*,  $^3J(4,3) = 10.2$ ,  $^3J(4,5) = 3.3$ , H–C(4)); 4.89, 4.56 (2*s*,  $^2J = 11.9$ , PhCH<sub>2</sub>O); 4.47 (*d*,  $^3J(7,6) = 6.2$ , H–C(7)); 4.08 (*d*,  $^3J(2,3) = 10.0$ , H–C(2)); 3.96 (*dd*,  $^3J(6,7) = 6.2$ ,  $^3J(6,5) = 1.1$ , H–C(6)); 3.79 (*s*, COOMe); 2.19, 1.98 (2*s*, 2 Ac). CI-MS (NH<sub>3</sub>): 543 (100, [M + 18]<sup>+</sup>), 499 (1, [M – CN]<sup>+</sup>), 436 (10), 426 (5), 359 (4), 105 (38), 91 (21), 77 (10).

*Methyl 3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-DL-glycero-DL-galacto-hepturonate ((±)-48)*. A soln. of Hg(ClO<sub>4</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>3.4</sub> (125 mg, 0.272 mmol) in MeCN (1 ml) was added dropwise to a stirred soln. of (±)-**57** in MeCN (6.5 ml). After stirring at 20° for 45 min, CHCl<sub>3</sub> (100 ml) was added, followed by Ag<sub>2</sub>CO<sub>3</sub> (630 mg). After stirring at 20° for 15 min, the precipitate was filtered off (*Celite*) and the solvent evaporated. The residue was taken up in CH<sub>2</sub>Cl<sub>2</sub>/light petroleum ether, the precipitate filtered off (*Celite*), and the filtrate evaporated. The latter operation was repeated four more times, giving 48 mg (98%) of crude (±)-**48**, which was used as such in the next step. Traces of H<sub>2</sub>O were eliminated (if required) by azeotropic distillation with anhyd. toluene. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 9.61 (*s*, H–C(1)); 7.93, 7.58, 7.44 (3*m*, 2 H, 1 H, 2 H, arom. H); 5.99 (*dd*,  $^3J(3,4) = 3.4$ ,  $^3J(3,2) = 1.5$ , H–C(3)); 5.66 (*dd*,  $^3J(5,4) = 10.1$ ,  $^3J(5,6) = 9.9$ , H–C(5)); 5.36 (*dd*,  $^3J(4,5) = 10.1$ ,  $^3J(4,3) = 3.4$ , H–C(4)); 4.26 (*d*,  $^3J(2,3) = 1.5$ , H–C(2)); 4.20 (*d*,  $^3J(6,5) = 9.9$ , H–C(6)); 3.83 (*s*, COOMe); 2.07, 2.00 (2*s*, 2 Ac). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 195.9 (*d*,  $^1J(C,H) = 187$ , C(1)); 169.5, 169.3, 167.0, 165.3 (4*s*, 4 C=O); 133.6, 129.7, 128.6 (3*d*,  $^1J(C,H) = 160$ , arom. C); 128.7 (*s*, arom. C); 80.7 (*d*,  $^1J(C,H) = 141$ , C(2)); 76.6 (*d*,  $^1J(C,H) = 154$ , C(6)); 71.7 (*d*,  $^1J(C,H) = 148$ , C(4)); 67.3 (*d*,  $^1J(C,H) = 156$ , C(3)); 66.3 (*d*,  $^1J(C,H) = 156$ , C(5)); 53.0 (*q*,  $^1J(C,H) = 148$ , COOMe); 20.5, 20.4 (2*q*,  $^1J(C,H) = 130$ , 2 MeCO). CI-MS (NH<sub>3</sub>): 426 (0.1, [M + 18]<sup>+</sup>), 379 (0.2, [M – CHO]<sup>+</sup>), 349 (0.6, [M – AcO]<sup>+</sup>), 287 (4, [M – BzO]<sup>+</sup>), 229 (6), 201 (41), 105 (100), 77 (22).

*Dibenzyl Acetal of Methyl 3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-DL-glycero-DL-galacto-hepturonate (51)*. Me<sub>3</sub>SiOSO<sub>2</sub>CF<sub>3</sub> (25 μl) was added to a soln. of (±)-**43** (100 mg, 0.21 mmol) and PhCH<sub>2</sub>OSiMe<sub>3</sub> (80 μl, 75 mg, 0.41 mmol) in anhyd. CHCl<sub>3</sub> (3.5 ml) cooled to –10°. The soln. became dark yellow. After stirring at –10° for 75 min, anhyd. MeOH (0.2 ml) was added and the mixture stirred at 20° for 12 h. A sat. aq. NaHCO<sub>3</sub> soln. (5 ml) was added to the colorless soln., the mixture extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 × 5 ml), the combined org. extract dried (MgSO<sub>4</sub>) and evaporated and the yellowish oily residue crystallized from heptane and a few drops of AcOEt: 103 mg (82%) of pure **51**. Colorless crystals. M.p. 122–123°. UV (MeCN): 280 (1700), 272 (1900), 263 (2050), 229 (13800), 199 (23000). IR (KBr): 3065, 3030, 2950, 1755, 1720, 1600, 1455, 1375, 1285, 1235, 1120, 1060, 720. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.92, 7.56, 7.45–7.21 (3*m*, 2 H, 1 H, 12 H, arom. H); 5.81 (*dd*,  $^3J(3,4) = 3.4$ ,  $^3J(3,2) = 1.1$ , H–C(3)); 5.54 (*dd*,  $^3J(5,4) = 10.1$ ,  $^3J(5,6) = 10.0$ , H–C(5)); 5.28 (*dd*,  $^3J(4,5) = 10.1$ ,  $^3J(4,3) = 3.4$ , H–C(4)); 4.79, 4.70 (2*d*,  $^2J = 11.8$ , PhCH<sub>2</sub>O); 4.77 (*d*,  $^3J(1,2) = 7.1$ , H–C(1)); 4.65, 4.45 (2*d*,  $^2J = 11.6$ , PhCH<sub>2</sub>O); 3.93 (*d*,  $^3J(6,5) = 10.0$ , H–C(6)); 3.85 (*dd*,  $^3J(2,1) = 7.1$ ,  $^3J(2,3) = 1.1$ , H–C(2)); 3.78 (*s*, COOMe); 1.97, 1.90 (2*s*, 2 Ac). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 169.6, 169.5, 167.4, 165.3 (4*s*, 4 C=O); 138.0, 136.2, 129.1 (3*s*, arom. C); 133.4, 129.6, 129.0, 128.5, 128.4, 128.1, 127.7 (7*d*,  $^1J(C,H) = 160$ , arom. C); 97.5 (*d*,  $^1J(C,H) = 166$ , C(1)); 77.8 (*d*,  $^1J(C,H) = 141$ , C(2)); 76.6 (*d*,  $^1J(C,H) = 148$ , C(6)); 72.3 (*d*,  $^1J(C,H) = 147$ , C(4)); 68.8, 68.7 (2*t*,  $^1J(C,H) = 144$ , 2 PhCH<sub>2</sub>O); 67.6 (*d*,  $^1J(C,H) = 156$ , C(3)); 66.6 (*d*,  $^1J(C,H) = 155$ , C(5)); 52.7 (*q*,  $^1J(C,H) = 148$ , COOMe); 20.6 (*q*,  $^1J(C,H) = 130$ , 2 MeCO). CI-MS (NH<sub>3</sub>): 626 (54, [M + 18]<sup>+</sup>), 499 (20, [M – OBn]<sup>+</sup>), 367 (9), 366 (8), 108 (17), 105 (49), 91 (100), 77 (12). Anal. calc. for C<sub>33</sub>H<sub>34</sub>O<sub>11</sub> (606.67): C 65.33, H 5.66; found: C 65.36, H 5.76.

*O-Benzyl S-Phenyl Monothioacetal of Methyl 3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-DL-glycero-DL-galacto-hepturonate (52 and 53)*. As described for **51**, with (±)-**43** (106 mg, 0.22 mmol) and PhSSiMe<sub>3</sub> (200 μl, 190 mg, 1.05 mmol) instead of BnOSiMe<sub>3</sub>. The crude oil containing **52/53** 1:3.3 was crystallized from AcOEt/pentane yielding 91 mg (68%) of **53** as colorless crystals. The mother liquor was evaporated and purified by FC (1 × 12 cm, light petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O 57:3:40): 18 mg (14%) of **52** as colorless oil.

*Data for 52*: *R*<sub>f</sub> 0.35. UV (MeCN): 271 (11600), 218 (20800). IR (film): 3065, 3035, 2985, 2955, 1755, 1740, 1725, 1455, 1370, 1275, 1220, 1110, 1090, 1055, 695. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.89, 7.55, 7.43–7.34, 7.29 (4*m*, 2 H, 3 H, 5 H, 5 H, arom. H); 5.73 (*dd*,  $^3J(3,4) = 3.4$ ,  $^3J(3,2) = 1.1$ , H–C(3)); 5.51 (*dd*,  $^3J(5,4) = 10.1$ ,  $^3J(5,6) = 10.0$ , H–C(5)); 5.12 (*dd*,  $^3J(4,5) = 10.1$ ,  $^3J(4,3) = 3.4$ , H–C(4)); 4.89, 4.77 (2*d*,  $^2J = 11.3$ , PhCH<sub>2</sub>O); 4.71 (*d*,  $^3J(1,2) = 8.8$ , H–C(1)); 3.84 (*s*, COOMe); 3.75 (*d*,  $^3J(6,5) = 10.0$ , H–C(6)); 3.31 (*dd*,  $^3J(2,1) = 8.8$ ,  $^3J(2,3) = 1.1$ , H–C(2)); 1.94, 1.84 (2*s*, 2 MeCO). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 169.5, 167.3, 165.3 (3*s*, 4 C=O); 135.7, 133.3, 129.7, 129.6, 128.9, 128.8, 128.5, 128.4, 128.2 (9*d*,  $^1J(C,H) = 160$ , arom. C); 135.6, 130.0, 129.1 (3*s*,

arom. C); 83.2 (*d*,  $^1J(\text{C,H}) = 156$ , C(1)); 76.7 (*d*,  $^1J(\text{C,H}) = 147$ , C(6)); 76.1 (*d*,  $^1J(\text{C,H}) = 144$ , C(2)); 72.4 (*d*,  $^1J(\text{C,H}) = 148$ , C(4)); 69.3 (*t*,  $^1J(\text{C,H}) = 143$ ,  $\text{PhCH}_2\text{O}$ ); 67.4 (*d*,  $^1J(\text{C,H}) = 157$ , C(3)); 66.7 (*d*,  $^1J(\text{C,H}) = 156$ , C(5)); 52.9 (*q*,  $^1J(\text{C,H}) = 148$ ,  $\text{COOMe}$ ); 20.6, 20.5 (2*q*,  $^1J(\text{C,H}) = 130$ , 2 *MeCO*). CI-MS ( $\text{NH}_3$ ): 626 (29,  $[M + 18]^+$ ), 499 (21,  $[M - \text{SPh}]^+$ ), 110 (8), 109 (10), 108 (9), 105 (27), 91 (100), 77 (14). Anal. calc. for  $\text{C}_{32}\text{H}_{32}\text{O}_{10}\text{S}$  (608.71): C 63.14, H 5.31; found: C 62.93, H 5.50.

Data for **53**:  $R_f$  0.30. UV (MeCN): 272 (11000), 218 (19600), 202 (22800). IR (film): 3075, 2985, 2955, 2890, 1755, 1740, 1725, 1275, 1220, 1110, 1090, 1055, 715.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.94, 7.55, 7.45–7.29 (3*m*, 2 H, 3 H, 10 H, arom. H); 6.08 (*dd*,  $^3J(3,4) = 3.4$ ,  $^3J(3,2) = 0.8$ , H–C(3)); 5.55 (*dd*,  $^3J(5,4) = 10.2$ ,  $^3J(5,6) = 10.0$ , H–C(5)); 5.17 (*dd*,  $^3J(4,5) = 10.2$ ,  $^3J(4,3) = 3.4$ , H–C(4)); 5.05, 4.79 (2*d*,  $^3J = 11.9$ ,  $\text{PhCH}_2\text{O}$ ); 4.92 (*d*,  $^3J(1,2) = 8.4$ , H–C(1)); 4.00 (*d*,  $^3J(6,5) = 10.0$ , H–C(6)); 3.79 (*s*,  $\text{COOMe}$ ); 3.76 (*dd*,  $^3J(2,1) = 8.4$ ,  $^3J(2,3) = 0.8$ , H–C(2)); 1.98, 1.96 (2*s*, 2 *MeCO*).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 169.7, 169.5, 167.5, 165.3 (4*s*, 4 C=O); 137.0, 131.0, 129.2 (3*s*, arom. C); 134.0, 133.4, 129.6, 129.2, 128.5, 128.45, 128.4, 128.0, 127.9 (9*d*,  $^1J(\text{C,H}) = 160$ , arom. C); 85.9 (*d*,  $^1J(\text{C,H}) = 158$ , C(1)); 78.5 (*d*,  $^1J(\text{C,H}) = 155$ , C(2)); 76.5 (*d*,  $^1J(\text{C,H}) = 147$ , C(6)); 72.6 (*d*,  $^1J(\text{C,H}) = 147$ , C(4)); 70.5 (*t*,  $^1J(\text{C,H}) = 143$ ,  $\text{PhCH}_2\text{O}$ ); 67.8 (*d*,  $^1J(\text{C,H}) = 152$ , C(3)); 66.5 (*d*,  $^1J(\text{C,H}) = 156$ , C(5)); 52.7 (*q*,  $^1J(\text{C,H}) = 148$ ,  $\text{COOMe}$ ); 20.6 (*q*,  $^1J(\text{C,H}) = 130$ , 2 *MeCO*). CI-MS ( $\text{NH}_3$ ): 626 (53,  $[M + 18]^+$ ), 499 (23,  $[M - \text{PhS}]^+$ ), 367 (6), 110 (8), 109 (11), 108 (13), 105 (109), 91 (100), 77 (9). Anal. calc. for  $\text{C}_{32}\text{H}_{32}\text{O}_{10}\text{S}$  (608.71): C 63.14, H 5.31, S 5.27; found: C 62.38, H 5.44, S 5.31.

*Diphenyl Dithioacetal of Benzyl 3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-DL-glycero-DL-galacto-hepturate (55)*.  $\text{CF}_3\text{SO}_3\text{H}$  (50 mg), then  $\text{PhSH}$  (50  $\mu\text{l}$ , 55 mg, 0.50 mmol) were added to a soln. of ( $\pm$ )-**43** (13 mg, 0.027 mmol) in anh.  $\text{CH}_2\text{Cl}_2$  (0.5 ml). After 1 h at 20°, benzyl alcohol (100 mg) was added and the mixture stirred at 20° for 17 h. After the addition of silica gel (100 mg) and evaporation, the residue was purified by FC (1  $\times$  16 cm, light petroleum ether/ $\text{CH}_2\text{Cl}_2$ / $\text{Et}_2\text{O}$  40 : 57 : 3): 11 mg (60%) of **55**. Colorless oil.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.92, 7.56, 7.48–7.28 (3*m*, 2 H, 3 H, 15 H, arom. H); 6.11 (*dd*,  $^3J(3,4) = 3.4$ ,  $^3J(3,2) = 1.1$ , H–C(3)); 5.62 (*dd*,  $^3J(5,4) = 10.2$ ,  $^3J(5,6) = 10.1$ , H–C(5)); 5.25, 5.19 (2*d*,  $^3J = 12.1$ ,  $\text{PhCH}_2\text{O}$ ); 5.21 (*dd*,  $^3J(4,5) = 10.2$ ,  $^3J(4,3) = 3.4$ , H–C(4)); 4.52 (*d*,  $^3J(1,2) = 9.1$ , H–C(1)); 4.01 (*d*,  $^3J(6,5) = 10.1$ , H–C(6)); 3.66 (*dd*,  $^3J(2,1) = 9.1$ ,  $^3J(2,3) = 1.1$ , H–C(2)); 1.95, 1.72 (2*s*, 2 Ac).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 169.5, 169.4, 166.6, 165.4 (4*s*, 4 C=O); 134.9, 133.0, 132.3, 129.0 (4*s*, arom. H); 134.7, 133.4, 132.9, 129.7, 129.1, 128.9, 128.7 (2  $\times$ ), 128.6 (2  $\times$ ), 128.5, 128.3 (12*d*,  $^1J(\text{C,H}) = 160$ , arom. C); 78.3 (*d*,  $^1J(\text{C,H}) = 148$ , C(2)); 76.8 (*d*,  $^1J(\text{C,H}) = 153$ , C(6)); 72.8 (*d*,  $^1J(\text{C,H}) = 147$ , C(4)); 67.8 (*d*,  $^1J(\text{C,H}) = 155$ , C(3)); 67.6 (*t*,  $^1J(\text{C,H}) = 149$ ,  $\text{PhCH}_2\text{O}$ ); 66.3 (*d*,  $^1J(\text{C,H}) = 156$ , C(5)); 59.4 (*d*,  $^1J(\text{C,H}) = 154$ , C(1)); 20.6, 20.4 (2*q*,  $^1J(\text{C,H}) = 130$ , *MeCO*). CI-MS ( $\text{NH}_3$ ): 577 (2,  $[M - \text{SPh}]^+$ ), 457 (2), 110 (69), 109 (25), 105 (100), 91 (74), 77 (19).

*Diethyl Dithioacetal of Benzyl 3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-DL-glycero-DL-galacto-hepturate (56)*. A mixture of ( $\pm$ )-**43** (103 mg, 0.21 mmol), anh.  $\text{CH}_2\text{Cl}_2$  (20 ml),  $\text{CF}_3\text{SO}_3\text{H}$  (10  $\mu\text{l}$ , 17 mg, 0.11 mmol), and  $\text{EtSH}$  (0.2 ml, 170 mg, 2.70 mmol) was stirred at 20° for 4 h. Benzyl alcohol (0.11 ml, 1.06 mmol) was added and the mixture stirred at 20° for 16 h. A sat. aq.  $\text{NaHCO}_3$  soln. (10 ml) was added, and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  10 ml). The combined org. extracts were dried ( $\text{MgSO}_4$ ) and evaporated. FC (1.5  $\times$  15 cm, light petroleum ether/ $\text{AcOEt}$  3 : 2, then light petroleum ether/ $\text{CH}_2\text{Cl}_2$ / $\text{Et}_2\text{O}$  40 : 57 : 3) gave 57 mg (46%) of **56**. Colorless crystals. M.p. 149–150°. UV (MeCN): 280 (1300), 272 (1600), 229 (14000), 200 (16000). IR (KBr): 2965, 1750, 1725, 1285, 1230, 1125, 710.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.92, 7.56, 7.44–7.33 (3*m*, 2 H, 1 H, 7 H, arom. H); 5.99 (*dd*,  $^3J(3,4) = 3.4$ ,  $^3J(3,2) = 0.9$ , H–C(3)); 5.59 (*dd*,  $^3J(5,4) = 10.1$ ,  $^3J(5,6) = 10.0$ , H–C(5)); 5.28 (*dd*,  $^3J(4,5) = 10.1$ ,  $^3J(4,3) = 3.4$ , H–C(4)); 5.20 (*s*,  $\text{PhCH}_2\text{O}$ ); 4.14 (*d*,  $^3J(6,5) = 10.0$ , H–C(6)); 3.96 (*d*,  $^3J(1,2) = 9.4$ , H–C(1)); 3.80 (*dd*,  $^3J(2,1) = 9.4$ ,  $^3J(2,3) = 0.9$ , H–C(2)); 2.82–2.56 (*m*,  $^3J = 7.4$ , 2  $\text{MeCH}_2\text{S}$ ); 2.13, 1.73 (2*s*, 2 Ac); 1.23, 1.22 (2*t*,  $^3J = 7.4$ , 2  $\text{MeCH}_2\text{S}$ ).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 169.6, 169.4, 166.8, 165.4 (4*s*, 4 C=O); 134.8, 129.1 (2*s*, arom. C); 133.3, 129.6, 128.8, 128.6, 128.5 (5*d*,  $^1J(\text{C,H}) = 160$ , arom. C); 80.9 (*d*,  $^1J(\text{C,H}) = 144$ , C(2)); 76.7 (*d*,  $^1J(\text{C,H}) = 147$ , C(6)); 72.8 (*d*,  $^1J(\text{C,H}) = 147$ , C(4)); 68.1 (*d*,  $^1J(\text{C,H}) = 154$ , C(3)); 67.6 (*t*,  $^1J(\text{C,H}) = 149$ ,  $\text{PhCH}_2\text{O}$ ); 66.4 (*d*,  $^1J(\text{C,H}) = 156$ , C(5)); 49.6 (*d*,  $^1J(\text{C,H}) = 152$ , C(1)); 26.6, 24.4 (2*t*,  $^1J(\text{C,H}) = 140$ , 2  $\text{MeCH}_2\text{S}$ ); 20.7, 20.4 (2*q*,  $^1J(\text{C,H}) = 130$ , 2 *MeCO*); 14.3 (*q*,  $^1J(\text{C,H}) = 128$ , 2  $\text{MeCH}_2\text{S}$ ). CI-MS ( $\text{NH}_3$ ): 608 (6,  $[M + 18]^+$ ), 590 (2,  $M^+$ ), 529 (26,  $[M - \text{SEt}]^+$ ), 409 (14,  $[M - \text{Bn} - \text{Et}_2\text{S}]^+$ ), 408 (12,  $[M - \text{SEt} - \text{OBz}]^+$ ), 135 (30), 105 (82), 91 (100), 77 (15). Anal. calc. for  $\text{C}_{29}\text{H}_{34}\text{O}_9\text{S}_2$  (590.77): C 58.96, H 5.81, S 10.86; found: C 58.88, H 5.71, S 10.81.

*Diethyl Dithioacetal of Methyl 3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-DL-glycero-DL-galacto-hepturate (( $\pm$ )-57)*.  $\text{EtSH}$  (0.4 ml, 340 mg, 5.41 mmol) then  $\text{CF}_3\text{SO}_3\text{H}$  (60  $\mu\text{l}$ , 100 mg, 0.69 mmol) were added to a stirred soln. of ( $\pm$ )-**43** (0.2 g, 0.42 mmol) in anh.  $\text{CH}_2\text{Cl}_2$  (16 ml). After stirring at 20° for 25 min, anh.  $\text{MeOH}$  (1.5 ml) was added, and stirring was continued for 16 h at 20°. A sat. aq.  $\text{NaHCO}_3$  soln. (20 ml) was added, the aq. layer extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  20 ml), the combined org. extract dried ( $\text{MgSO}_4$ ) and evaporated, and the residue submitted to FC (3  $\times$  13 cm, light petroleum ether/ $\text{AcOEt}$  4 : 1 (500 ml), then 3 : 1): 159 mg (74%) of **57**.



White solid. M.p. 145–146°. UV (MeCN): 280 (1100), 273 (1300), 228 (12300), 201 (9700). IR (KBr): 2970, 2930, 1755, 1725, 1455, 1375, 1290, 1235, 1125, 720. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.92, 7.57, 7.44 (3m, 2 H, 1 H, 2 H, arom. H); 6.01 (dd, <sup>3</sup>J(3,4) = 3.4, <sup>3</sup>J(3,2) = 1.0, H–C(3)); 5.57 (dd, <sup>3</sup>J(5,4) = 10.1, <sup>3</sup>J(5,6) = 10.0, H–C(5)); 5.32 (dd, <sup>3</sup>J(4,5) = 10.1, <sup>3</sup>J(4,3) = 3.4, H–C(4)); 4.10 (d, <sup>3</sup>J(6,5) = 10.0, H–C(6)); 3.98 (d, <sup>3</sup>J(1,2) = 9.5, H–C(1)); 3.78 (s, COOMe); 3.77 (dd, <sup>3</sup>J(2,1) = 9.5, <sup>3</sup>J(2,3) = 1.0, H–C(2)); 2.81–2.56 (m, <sup>3</sup>J = 7.4, 2 MeCH<sub>2</sub>S); 2.13, 1.99 (2s, 2 Ac); 1.27, 1.22 (2t, <sup>3</sup>J = 7.4, 2 MeCH<sub>2</sub>S). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 169.7, 169.5, 167.4, 165.4 (4s, 4 C=O); 133.4, 129.6, 128.5 (3d, <sup>1</sup>J(C,H) = 160, arom. C); 129.1 (s, arom. C); 80.7 (d, <sup>1</sup>J(C,H) = 139, C(2)); 76.8 (d, <sup>1</sup>J(C,H) = 147, C(6)); 72.7 (d, <sup>1</sup>J(C,H) = 147, C(4)); 68.0 (d, <sup>1</sup>J(C,H) = 153, C(3)); 66.6 (d, <sup>1</sup>J(C,H) = 155, C(5)); 52.8 (q, <sup>1</sup>J(C,H) = 148, COOMe); 49.8 (d, <sup>1</sup>J(C,H) = 150, C(1)); 26.3, 24.3 (2t, <sup>1</sup>J(C,H) = 140, 2 MeCH<sub>2</sub>S); 20.8, 20.6 (2q, <sup>1</sup>J(C,H) = 130, 2 MeCO); 14.4 (q, <sup>1</sup>J(C,H) = 128, 2 MeCH<sub>2</sub>S). CI-MS (NH<sub>3</sub>): 514 (4, M<sup>+</sup>), 453 (5, [M – SEt]<sup>+</sup>), 333 (24, [M – OBz – EtS + H]<sup>+</sup>), 303 (8, [M – OBz – Et<sub>2</sub>S]<sup>+</sup>), 287 (9), 271 (14), 229 (16), 135 (41), 105 (100), 77 (34). Anal. calc. for C<sub>23</sub>H<sub>30</sub>O<sub>9</sub>S<sub>2</sub> (514.67): C 53.67, H 5.89, S 12.46; found: C 53.71, H 5.86, S 12.50.

*Diethyl Dithioacetal of Methyl 3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-D-glycero-D-galacto-hepturonate* ((–)-**57**). As described for (±)-**57**, with (–)-**43**. Yield 68%. White foam. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –87, [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –89, [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –103, [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –182, [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –222 (c = 0.9, CHCl<sub>3</sub>).

*Benzyl 3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-DL-glycero-DL-galacto-hepturonate* (**58**). CdCO<sub>3</sub> (50 mg, 0.29 mmol) was suspended in a soln. of HgCl<sub>2</sub> (170 mg, 0.63 mmol) in acetone (0.5 ml). After stirring at 20° for 1 h, a soln. of **56** (25 mg, 0.042 mmol) in acetone (0.25 ml) was added and stirring continued for 6 h. After filtration over a bed of CdCO<sub>3</sub> (rinsing with acetone), the filtrate was evaporated, the viscous residue extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 × 1 ml), and the combined extract washed with a KI (0.2 g) soln., Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> · H<sub>2</sub>O (0.2 g) in H<sub>2</sub>O (5 ml), and then H<sub>2</sub>O (10 ml). The aq. layers were extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 5 ml) and the org. extracts dried (MgSO<sub>4</sub>) and evaporated: 21 mg (100%) of **58**. Yellowish foam. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 9.62 (s, H–C(1)); 7.92, 7.57, 7.44–7.35 (3m, 2 H, 1 H, 7 H, arom. H); 5.97 (dd, <sup>3</sup>J(3,4) = 3.4, <sup>3</sup>J(3,2) = 1.5, H–C(3)); 5.67 (dd, <sup>3</sup>J(5,4) = 10.1, <sup>3</sup>J(5,6) = 10.0, H–C(5)); 5.32 (dd, <sup>3</sup>J(4,5) = 10.1, <sup>3</sup>J(4,3) = 3.4, H–C(4)); 5.26, 5.21 (2d, <sup>2</sup>J = 12.0, PhCH<sub>2</sub>O); 4.24 (d, <sup>3</sup>J(2,3) = 1.5, H–C(2)); 4.23 (d, <sup>3</sup>J(6,5) = 10.0, H–C(6)); 2.06, 1.73 (2s, 2 Ac).

(1RS,2SR,3RS,4SR,5RS,6RS,7SR)–7-endo-(Benzylxy)–6-exo-[[tert-butyl]dimethylsilyl]oxy]–3-endo-[[1RS)–1-hydroxypropyl]–4-exo-(phenylthio)–8-oxabicyclo[3.2.1]octan-2-endo-ol (**61**). At –78° 0.7M Me<sub>2</sub>AlSPH in CH<sub>2</sub>Cl<sub>2</sub> (1.2 ml, 0.84 mmol) was added to a stirred soln. of (±)-**13** (0.2 g, 0.56 mmol) in anh. THF (3 ml). After stirring at –78° for 45 min, propanal (0.2 ml, 160 mg, 2.75 mmol) was added dropwise and the mixture stirred at –78° for 12 h. The mixture was poured into cold CHCl<sub>3</sub> (–10°) and the soln. washed immediately with ice-cold 1N HCl (20 ml) and then with sat. aq. NaHCO<sub>3</sub> soln. (20 ml). The aq. layers were extracted with CHCl<sub>3</sub> (3 × 20 ml) and the combined org. extracts dried (MgSO<sub>4</sub>) and evaporated. The residue **60** was taken in MeOH (10 ml) and cooled to 0°. CeCl · 6H<sub>2</sub>O (200 mg, 0.56 mmol), then NaBH<sub>4</sub> (20 mg, 0.53 mmol) were added portionwise. After stirring at 0° for 10 min, AcOEt (50 ml), then sat. aq. NH<sub>4</sub>Cl soln. (25 ml) and H<sub>2</sub>O (until dissolution of salts) were added. The aq. layer was extracted with AcOEt (4 × 25 ml), and the combined org. extract dried (MgSO<sub>4</sub>) and evaporated. FC (2 × 15 cm, light petroleum ether/Et<sub>2</sub>O 3:2) gave 187 mg (63%) of **61**. Colorless oil. UV (MeCN): 260 (6000), 210 (14500). IR (film): 3420, 2955, 2930, 2855, 1470, 1255, 1115, 1045, 840, 780, 750, 695. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.53, 7.41–7.23 (2m, 2 H, 8 H, arom. H); 4.88 (br. s, OH–C(2)); 4.75, 4.57 (2d, <sup>2</sup>J = 11.4, PhCH<sub>2</sub>O); 4.71 (dd, <sup>3</sup>J(2,1) = 7.6, <sup>3</sup>J(2,3) = 4.5, H–C(2)); 4.30 (br. d, <sup>3</sup>J(6,7) = 4.4, H–C(6)); 4.25 (br. s, H–C(5)); 4.21 (dd, <sup>3</sup>J(1,2) = 7.6, <sup>3</sup>J(1,7) = 5.7, H–C(1)); 4.16 (m, <sup>3</sup>J(1,3) = 3.8, H–C(1')); 4.10 (dd, <sup>3</sup>J(7,1) = 5.7, <sup>3</sup>J(7,6) = 4.4, H–C(7)); 3.69 (br. d, <sup>3</sup>J(4,3) = 9.9, H–C(4)); 3.57 (br. s, OH–C(1')); 1.75 (m, <sup>3</sup>J(2'a,3') = 7.4, H<sub>a</sub>–C(2')); 1.65 (ddd, <sup>3</sup>J(3,4) = 9.9, <sup>3</sup>J(3,2) = 4.5, <sup>3</sup>J(3,1') = 3.8, H–C(3)); 1.56 (m, <sup>3</sup>J(2'b,3) = 7.4, H<sub>b</sub>–C(2')); 1.03 (dd, <sup>3</sup>J(3',2'a) = 7.4, <sup>3</sup>J(3',2'b) = 7.4, H–C(3')); 0.82 (s, t-BuSi); –0.02, –0.16 (2s, Me<sub>2</sub>Si). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 136.4, 134.3 (2s, arom. C); 133.4, 129.1, 128.8, 128.5, 128.0, 127.6 (6d, <sup>1</sup>J(C,H) = 160, arom. C); 90.3 (d, <sup>1</sup>J(C,H) = 151, C(7)); 89.1 (d, <sup>1</sup>J(C,H) = 158, C(5)); 82.4 (d, <sup>1</sup>J(C,H) = 146, C(6)); 74.2 (t, <sup>1</sup>J(C,H) = 144, PhCH<sub>2</sub>O); 73.1 (d, <sup>1</sup>J(C,H) = 155, C(1)); 72.3 (d, <sup>1</sup>J(C,H) = 146, C(1')); 70.5 (d, <sup>1</sup>J(C,H) = 152, C(2)); 49.0 (d, <sup>1</sup>J(C,H) = 144, C(4)); 41.5 (d, <sup>1</sup>J(C,H) = 128, C(3)); 28.5 (t, <sup>1</sup>J(C,H) = 125, C(2')); 25.6 (q, <sup>1</sup>J(C,H) = 125, Me<sub>3</sub>CSi); 17.7 (s, Me<sub>3</sub>CSi); 10.8 (q, <sup>1</sup>J(C,H) = 126, C(3')); –4.9, –5.0 (2q, <sup>1</sup>J(C,H) = 119, Me<sub>2</sub>Si). APCI-MS (pos. mode): 531 (100, [M + H]<sup>+</sup>), 513 (100, [M – OH]<sup>+</sup>), 495 (50, [M – H<sub>2</sub>O – OH]<sup>+</sup>), 381 (50, [M – H<sub>2</sub>O – (t-Bu)SiO]<sup>+</sup>). APCI-MS (neg. mode): 529 (100, [M – H]<sup>–</sup>). Anal. calc. for C<sub>29</sub>H<sub>42</sub>O<sub>5</sub>SSi (530.87): C 65.61, H 7.97, S 6.04; found: C 65.65, H 7.94, S 5.98.

(1RS,2SR,6RS,7RS,8SR,9RS,10RS,11SR)–11-(Benzylxy)–10-[[tert-butyl]dimethylsilyl]oxy]–6-ethyl-4,4-dimethyl-8-(phenylthio)–3,5,12-trioxatricyclo[7.2.1.0<sup>2,7</sup>]dodecane (**62**). A mixture of **61** (12.0 mg, 22.6 μmol), acetone (0.5 ml), 2,2-dimethoxypropane (0.5 ml), and pyridinium *p*-toluenesulfonate · H<sub>2</sub>O (10 mg) was stirred at 20° for 1 h. A sat. aq. NaHCO<sub>3</sub> soln. (5 ml) was added and the mixture extracted with CHCl<sub>3</sub> (4 × 5 ml). The

combined org. extracts were dried ( $\text{MgSO}_4$ ) and evaporated. FC ( $1 \times 10$  cm, light petroleum ether/ $\text{Et}_2\text{O}$  7:3) gave 12.2 mg (95%) of **62**. Colorless oil. UV (MeCN): 260 (5100), 207 (15000). IR (film): 3065, 3030, 2985, 2955, 2930, 2880, 2855, 1475, 1465, 1380, 1255, 1225, 1105, 1050, 835, 780, 695.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.47, 7.31 (2m, 2 H, 8 H, arom. H); 4.75, 4.50 (2d,  $^2J = 12.1$ ,  $\text{PhCH}_2\text{O}$ ); 4.62 (dd,  $^3J(2,7) = 8.2$ ,  $^3J(2,1) = 6.7$ , H-C(2)); 4.54 (dd,  $^3J(1,2) = 6.7$ ,  $^3J(1,11) = 6.2$ , H-C(1)); 4.18 (ddd,  $^3J(6,7) = 10.0$ ,  $^3J(6,15a) = 8.0$ ,  $^3J(6,15b) = 2.8$ , H-C(6)); 4.08 (dd,  $^3J(11,1) = 6.2$ ,  $^3J(11,10) = 4.1$ , H-C(11)); 4.01 (br. d,  $^3J(10,11) = 4.1$ , H-C(10)); 3.88 (br. s, H-C(9)); 3.19 (br. d,  $^3J(8,7) = 3.3$ , H-C(8)); 2.21 (ddd,  $^3J(7,6) = 10.0$ ,  $^3J(7,2) = 8.2$ ,  $^3J(7,8) = 3.3$ , H-C(7)); 1.81 (ddq,  $^2J(15b,15a) = 14.8$ ,  $^3J(15b,16) = 7.4$ ,  $^3J(15b,6) = 2.8$ ,  $\text{H}_b\text{-C}(15)$ ); 1.44 (ddq,  $^2J(15a,15b) = 14.8$ ,  $^3J(15a,16) = 8.0$ ,  $^3J(15a,16) = 7.4$ ,  $\text{H}_a\text{-C}(15)$ ); 1.36 (s, Me(14)); 1.20 (s, Me(13)); 0.98 (dd,  $^3J(16,15a) = 7.4$ ,  $^3J(16,15b) = 7.4$ , Me(16)); 0.78 (s, *t*-BuSi); -0.06, -0.13 (2s,  $\text{Me}_2\text{Si}$ ). ES-MS (pos. mode): 593 (100,  $[\text{M} + \text{Na}]^+$ ), 571 (20,  $[\text{M} + \text{H}]^+$ ), 513 (35,  $[\text{M} - \text{acetone} + \text{H}]^+$ ). Anal. calc. for  $\text{C}_{32}\text{H}_{46}\text{O}_5\text{SSi}$  (570.94): C 67.31, H 8.14; found: C 67.48, H 8.17.

(1*RS*,5*RS*,6*RS*,7*RS*)-7-endo-(Benzyloxy)-6-exo-[[*tert*-butyl]dimethylsilyl]oxy]-3-[(*ISR*)-1-hydroxypropyl]-8-oxabicyclo[3.2.1]oct-3-en-2-one (**64**). At  $-78^\circ$  0.5M  $\text{Me}_2\text{AlSeMe}$  in toluene (1.6 ml, 0.8 mmol) was added to a stirred soln. of ( $\pm$ )-**13** (0.2 g, 0.55 mmol) in anh. THF (2 ml). After stirring at  $-78^\circ$  for 30 min, propanal (0.2 ml, 160 mg, 2.75 mmol) was added dropwise. After stirring at  $-78^\circ$  for 12 h, 100% *m*CPBA (275 mg, 1.6 mmol) was added. After stirring at  $-78^\circ$  for 1 h, the mixture was allowed to warm up to  $-20^\circ$  within ca. 3 h.  $\text{CHCl}_3$  (20 ml) was added, and the soln. was washed successively with 1N HCl (10 ml), 0.5M aq.  $\text{Na}_2\text{S}_2\text{O}_3$  soln. (10 ml), and sat. aq.  $\text{NaHCO}_3$  soln. (10 ml). The aq. layers were extracted with  $\text{CHCl}_3$  ( $3 \times 10$  ml) and the combined org. extracts dried ( $\text{MgSO}_4$ ) and evaporated. FC ( $2 \times 13$  cm, light petroleum ether/ $\text{Et}_2\text{O}$  3:2) gave 182 mg (79%) of **64**. Colorless oil. UV (MeCN): 240 (5400), 205 (11000), 193 (15000). IR (film): 3460 (br.), 3065, 3035, 2955, 2930, 2885, 2860, 1695, 1465, 1360, 1255, 1115, 1065, 840.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.35–7.24 (m, 5 arom. H); 7.04 (dd,  $^3J(4,5) = 4.9$ ,  $^4J(4,1') = 1.1$ , H-C(4)); 4.78 (d,  $^3J(1,7) = 7.0$ , H-C(1)); 4.54, 4.41 (2d,  $^2J = 11.2$ ,  $\text{PhCH}_2\text{O}$ ); 4.51 (br. d,  $^3J(5,4) = 4.9$ , H-C(5)); 4.35 (m,  $^3J(1',\text{OH}) = 5.9$ ,  $^4J(1',4) = 1.1$ , H-C(1')); 4.27 (br. d,  $^3J(7,1) = 7.0$ , H-C(7)); 4.24 (br. s, H-C(6)); 2.27 (d,  $^3J(\text{OH},1') = 5.9$ , OH-C(1')); 1.69–1.52 (m,  $^3J(2',3') = 7.4$ , 2 H-C(2')); 0.90 (s, *t*-BuSi); 0.87 (t,  $^3J(3',2') = 7.4$ , Me(3')); 0.11, 0.10 (2s,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 195.0 (s, C(2)); 141.6 (d,  $^1J(\text{C,H}) = 159$ , C(4)); 140.8 (s, C(3)); 136.8 (s, arom. C); 128.4, 128.1, 128.0 (3d,  $^1J(\text{C,H}) = 160$ , arom. C); 86.1 (d,  $^1J(\text{C,H}) = 153$ , C(7)); 83.1 (d,  $^1J(\text{C,H}) = 159$ , C(1)); 81.6 (d,  $^1J(\text{C,H}) = 157$ , C(5)); 79.4 (d,  $^1J(\text{C,H}) = 150$ , C(6)); 73.6 (t,  $^1J(\text{C,H}) = 142$ ,  $\text{PhCH}_2\text{O}$ ); 70.6 (d,  $^1J(\text{C,H}) = 143$ , C(1')); 28.7 (t,  $^1J(\text{C,H}) = 127$ , C(2')); 25.7 (q,  $^1J(\text{C,H}) = 125$ ,  $\text{Me}_3\text{CSi}$ ); 18.1 (s,  $\text{Me}_3\text{CSi}$ ); 9.6 (q,  $^1J(\text{C,H}) = 126$ , C(3')); -4.9 (q,  $^1J(\text{C,H}) = 119$ ,  $\text{Me}_2\text{Si}$ ). CI-MS ( $\text{NH}_3$ ): 436 (100,  $[\text{M} + 18]^+$ ), 418 (43,  $\text{M}^+$ ), 401 (80,  $[\text{M} - \text{OH}]^+$ ), 269 (20,  $[\text{M} - \text{C}_3\text{H}_7\text{O} - \text{Bn} + \text{H}]^+$ ), 264 (32), 245 (14), 207 (35), 155 (54), 108 (37), 91 (86). Anal. calc. for  $\text{C}_{23}\text{H}_{34}\text{O}_5\text{Si}$  (418.66): C 65.98, H 8.20, Si 6.71; found: C 65.80, H 8.19, Si 6.69.

(6*R*)-6-[(1*R*,5*R*,6*R*,7*R*)-6-endo-(Benzyloxy)-7-exo-[[*tert*-butyl]dimethylsilyl]oxy]-4-oxo-8-oxabicyclo[3.2.1]oct-2-en-3-yl]-1,2:3,4-di-*O*-isopropylidene- $\alpha$ -D-galacto-pyranose ((+)-**66**). At  $-78^\circ$ , 0.5M  $\text{Me}_2\text{AlSeMe}$  in toluene (0.7 ml, 0.35 mmol) was added dropwise to a stirred soln. of ( $\pm$ )-**13** (0.1 g, 0.277 mmol) in anh. THF (1 ml). After stirring at  $-78^\circ$  for 1 h, a soln. of 1,2:3,4-di-*O*-isopropylidene- $\alpha$ -D-galactohexodialdo-1,5-pyranose ((-)-**65**; 40 mg, 0.15 mmol) in anh. THF (0.3 ml) was added dropwise maintaining the temp. below  $-70^\circ$ . After stirring at  $-78^\circ$  for 16 h, 100% *m*CPBA (135 mg, 0.78 mmol) was added. After stirring at  $-78^\circ$  for 1 h, the mixture was allowed to warm up to  $-20^\circ$  with in 90 min under stirring.  $\text{CHCl}_3$  (5 ml) was added, and the soln. was immediately washed successively with ice-cold 1N HCl (5 ml), 0.5M aq.  $\text{Na}_2\text{S}_2\text{O}_3$  (5 ml), and sat. aq.  $\text{NaHCO}_3$  soln. (5 ml). The aq. layers were extracted with  $\text{CHCl}_3$  ( $3 \times 5$  ml) and the combined org. extracts dried ( $\text{MgSO}_4$ ) and evaporated. FC ( $1.5 \times 14$  cm, light petroleum ether/ $\text{Et}_2\text{O}$  1:1) gave 45 mg (27%) of (+)-**66**. Colorless foam.  $[\alpha]_D^{25} = 9.6$ ,  $[\alpha]_{577}^{25} = 8.8$ ,  $[\alpha]_{536}^{25} = 13$ ,  $[\alpha]_{435}^{25} = 187$ ,  $[\alpha]_{405}^{25} = 544$  ( $c = 0.13$ ,  $\text{CH}_2\text{Cl}_2$ ). UV (MeCN): 237 (6100), 206 (12500), 195 (15000). IR (film): 3510, 2985, 2930, 2860, 1695, 1465, 1385, 1255, 1215, 1115, 1065, 1010, 840.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.38 (dd,  $^3J(2',1') = 5.1$ ,  $^4J(2',6) = 1.7$ , H-C(2')); 7.36–7.21 (m, 5 arom. H); 5.57 (d,  $^3J(1,2) = 5.0$ , H-C(1)); 4.75 (d,  $^3J(5',6') = 7.0$ , H-C(5')); 4.72 (m,  $^3J(6,\text{OH}) = 8.6$ ,  $^3J(6,5) = 5.2$ ,  $^4J(6,2') = 1.7$ , H-C(6)); 4.57 (br. d,  $^3J(1',2') = 5.1$ , H-C(1')); 4.54, 4.38 (2d,  $^2J = 10.9$ ,  $\text{PhCH}_2\text{O}$ ); 4.30 (br. d,  $^3J(6',5') = 7.0$ , H-C(6')); 4.27 (dd,  $^3J(5,6) = 5.2$ ,  $^3J(5,4) = 1.7$ , H-C(5)); 4.23 (dd,  $^3J(4,3) = 8.0$ ,  $^3J(4,5) = 1.7$ , H-C(4)); 4.20 (dd,  $^3J(2,1) = 5.0$ ,  $^3J(2,3) = 2.3$ , H-C(2)); 4.19 (br. s, H-C(7)); 4.02 (dd,  $^3J(3,4) = 8.0$ ,  $^3J(3,2) = 2.3$ , H-C(3)); 3.73 (d,  $^3J(\text{OH},6) = 8.6$ , OH-C(6)); 1.62, 1.46, 1.33, 1.16 (4s, 2  $\text{Me}_2\text{C}$ ); 0.92 (s,  $\text{Me}_3\text{CSi}$ ); 0.12, 0.11 (2s,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 194.7 (s, C(4')); 144.3 (d,  $^1J(\text{C,H}) = 163$ , C(2')); 138.1, 136.6 (2s, C(3')), 128.7, 128.1, 128.0 (3d,  $^1J(\text{C,H}) = 160$ , arom. C); 109.0, 108.8 (2s, 2  $\text{Me}_2\text{C}$ ); 96.7 (d,  $^1J(\text{C,H}) = 181$ , C(1)); 86.5 (d,  $^1J(\text{C,H}) = 153$ , C(6')); 83.0 (d,  $^1J(\text{C,H}) = 160$ , C(5')); 81.6 (d,  $^1J(\text{C,H}) = 161$ , C(1')); 79.8 (d,  $^1J(\text{C,H}) = 150$ , C(7)); 74.0 (t,  $^1J(\text{C,H}) = 142$ ,  $\text{PhCH}_2\text{O}$ ); 71.5 (d,  $^1J(\text{C,H}) = 151$ , C(4)); 70.5, 70.4, 70.2 (3d,  $^1J(\text{C,H}) = 150$ , C(6), C(3), C(2)); 65.5 (d,  $^1J(\text{C,H}) = 141$ , C(5)); 26.0, 25.7, 25.1, 23.6 (4q,  $^1J(\text{C,H}) = 126$ ,

2  $\text{Me}_2\text{C}$ ); 25.7 ( $q$ ,  $^1\text{J}(\text{C},\text{H}) = 125$ ,  $\text{Me}_2\text{CSi}$ ); 18.1 ( $s$ ,  $\text{Me}_3\text{C}$ );  $-4.9$  ( $q$ ,  $^1\text{J}(\text{C},\text{H}) = 119$ ,  $\text{Me}_2\text{Si}$ ). CI-MS ( $\text{NH}_3$ ): 636 (44,  $[\text{M} + 18]^+$ ), 619 (100,  $[\text{M} + \text{H}]^+$ ), 601 (7,  $[\text{M} - \text{OH}]^+$ ), 469 (12,  $[\text{M} - \text{H}_2\text{O} - (t\text{-Bu})\text{Me}_2\text{SiO}]^+$ ), 445 (16,  $[\text{M} - \text{C}(\text{CH}_3)_2 - (t\text{-Bu})\text{Me}_2\text{SiO}]^+$ ), 355 (80), 276 (26), 207 (15), 91 (87). Anal. calc. for  $\text{C}_{32}\text{H}_{46}\text{O}_{10}\text{Si}$  (618.79): C 62.10, H 7.51, Si 4.54; found: C 62.18, H 7.65, Si 4.63.

*Methyl (7RS)-3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-7-C-[(1SR,2RS,3SR,4RS,5SR,6RS,7SR)-6-endo-(benzyloxy)-7-exo-[(tert-butyl)dimethylsilyl]oxy]-4-endo-hydroxy-2-exo-(phenylthio)-8-oxabicyclo[3.2.1]oct-3-endo-yl]-DL-glycero-LD-manno-heptonate ((±)-70)*. At  $-78^\circ$ , 0.7M  $\text{Me}_2\text{AlSPh}$  in  $\text{CH}_2\text{Cl}_2$  (0.26 ml, 0.18 mmol) was added dropwise to a stirred soln. of (±)-**13** (64 mg, 0.177 mmol) in anh. THF (1 ml). After stirring at  $-78^\circ$  for 45 min, crude (±)-**48** (48 mg) in soln. in anh. THF (0.5 ml) was added dropwise. After stirring at  $-78^\circ$  for 1 h, the mixture was poured into ice-cold 1N aq. HCl (10 ml) under vigorous stirring. The mixture was extracted with  $\text{CHCl}_3$  (15 ml, then  $3 \times 10$  ml). The combined org. extract was washed with sat. aq.  $\text{NaHCO}_3$  soln. (10 ml), dried ( $\text{MgSO}_4$ ), and evaporated and the residue taken up in MeOH (4 ml). After cooling to  $0^\circ$ ,  $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$  (65 mg, 0.183 mmol), then  $\text{NaBH}_4$  (5 mg, 0.13 mmol) were added portionwise under vigorous stirring. After 15 min at  $0^\circ$  the mixture was poured into sat. aq.  $\text{NH}_4\text{Cl}$  soln. (10 ml),  $\text{H}_2\text{O}$  (5 ml) and AcOEt (20 ml) under stirring. The aq. layer was extracted with AcOEt ( $4 \times 10$  ml). The combined org. extracts were dried ( $\text{MgSO}_4$ ) and evaporated. FC ( $1 \times 15$  cm, light petroleum ether/Et<sub>2</sub>O/MeOH 40:60:1): 60 mg (56% based on (±)-**57** of (±)-**70**). Colorless solid. M.p.  $192-194^\circ$ . UV (MeCN): 257 (6800), 224 (18500), 216 (19000), 198 (39500). IR (film): 3455, 3060, 2955, 2930, 2855, 1755, 1735, 1600, 1585, 1440, 1375, 1275, 1235, 1105, 840, 715.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.95, 7.59–7.28 (2m, 2 H, 13 H, arom. H); 5.98 (br. d,  $^3\text{J}(5,4) = 3.4$ , H–C(5)); 5.64 (dd,  $^3\text{J}(3,4) = 10.2$ ,  $^3\text{J}(3,2) = 10.0$ , H–C(3)); 5.39 (dd,  $^3\text{J}(4,3) = 10.2$ ,  $^3\text{J}(4,5) = 3.4$ , H–C(4)); 5.22 (br. s, OH); 4.76, 4.57 (2d,  $^2\text{J} = 11.4$ ,  $\text{PhCH}_2\text{O}$ ); 4.68 (dd,  $^3\text{J}(4',5') = 7.9$ ,  $^3\text{J}(4',3') = 4.4$ , H–C(4')); 4.43 (m,  $^3\text{J}(7,6) = 9.5$ ,  $^3\text{J}(7,3) = 3.8$ , H–C(7)); 4.30 (d,  $^3\text{J}(7',6') = 4.3$ , H–C(7')); 4.29 (s, H–C(1')); 4.20 (dd,  $^3\text{J}(5',4') = 7.9$ ,  $^3\text{J}(5',6') = 5.3$ , H–C(5')); 4.08 (dd,  $^3\text{J}(6',5') = 5.3$ ,  $^3\text{J}(6',7') = 4.3$ , H–C(6')); 4.07 (br. s, OH); 4.05 (d,  $^3\text{J}(2,3) = 10.0$ , H–C(2)); 3.88 (br. d,  $^3\text{J}(6,7) = 9.5$ , H–C(6)); 3.80 (s, COOMe); 3.64 (d,  $^3\text{J}(2',3') = 10.7$ , H–C(2')); 2.15, 1.98 (2s, 2 Ac); 2.00 (ddd,  $^3\text{J}(3',2') = 10.7$ ,  $^3\text{J}(3',4') = 4.4$ ,  $^3\text{J}(3',7) = 3.8$ , H–C(3')); 0.84 (s,  $t\text{-BuSi}$ ); 0.01,  $-0.10$  (2s,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ): 169.9, 169.6, 167.5, 165.5 (4s, 4 C=O); 136.2, 133.2, 129.2 (3s, arom. C); 134.1, 133.3, 129.7, 129.0, 128.8, 128.7, 128.5, 128.1, 127.9 (9d,  $^1\text{J}(\text{C},\text{H}) = 160$ , arom. C); 90.2 (d,  $^1\text{J}(\text{C},\text{H}) = 150$ , C(6')); 88.8 (d,  $^1\text{J}(\text{C},\text{H}) = 158$ , C(1')); 82.8 (d,  $^1\text{J}(\text{C},\text{H}) = 144$ , C(7')); 77.8 (d,  $^1\text{J}(\text{C},\text{H}) = 142$ , C(6)); 77.3 (d,  $^1\text{J}(\text{C},\text{H}) = 145$ , C(2)); 74.4 (t,  $^1\text{J}(\text{C},\text{H}) = 144$ ,  $\text{PhCH}_2\text{O}$ ); 72.7 (d,  $^1\text{J}(\text{C},\text{H}) = 149$ , C(4)); 72.5 (d,  $^1\text{J}(\text{C},\text{H}) = 155$ , C(5')); 71.1 (d,  $^1\text{J}(\text{C},\text{H}) = 149$ , C(4')); 67.9 (d,  $^1\text{J}(\text{C},\text{H}) = 148$ , C(7)); 67.5 (d,  $^1\text{J}(\text{C},\text{H}) = 157$ , C(5)); 67.1 (d,  $^1\text{J}(\text{C},\text{H}) = 155$ , C(3)); 52.8 (q,  $^1\text{J}(\text{C},\text{H}) = 148$ , COOMe); 47.6 (d,  $^1\text{J}(\text{C},\text{H}) = 143$ , C(2)); 37.5 (d,  $^1\text{J}(\text{C},\text{H}) = 132$ , C(3')); 25.6 (q,  $^1\text{J}(\text{C},\text{H}) = 148$ ,  $\text{Me}_2\text{CSi}$ ); 20.7, 20.6 (2q,  $^1\text{J}(\text{C},\text{H}) = 130$ , 2 MeCO); 17.8 (s,  $\text{Me}_3\text{CSi}$ );  $-4.8$ ,  $-4.9$  (2q,  $^1\text{J}(\text{C},\text{H}) = 119$ ,  $\text{Me}_2\text{Si}$ ). CI-MS ( $\text{NH}_3$ ): 881 (9,  $[\text{M} + 1]^+$ ), 676 (3,  $[\text{M} - (t\text{-Bu})\text{Me}_2\text{Si} - \text{Bn} + 2\text{H}]^+$ ), 626 (4,  $[\text{M} - \text{BzOH} - (t\text{-Bu})\text{Me}_2\text{SiOH}]^+$ ), 550 (2,  $[\text{M} - \text{Bz} - (t\text{-Bu})\text{Me}_2\text{Si} - \text{PhSH}]^+$ ), 510 (3,  $[\text{M} - \text{AcO} - \text{Bn} - \text{Bz} - (t\text{-Bu})\text{Me}_2\text{Si}]^+$ ), 468 (3,  $[\text{M} - \text{Ac} - \text{AcO} - \text{Bn} - \text{Bz} - (t\text{-Bu})\text{Me}_2\text{Si}]^+$ ), 281 (10), 207 (18), 110 (11), 108 (6), 105 (10), 91 (16), 77 (9). Anal. calc. for  $\text{C}_{45}\text{H}_{56}\text{O}_{14}\text{SSi}$  (881.17): C 61.33, H 6.42; found: C 61.41, H 6.46.

*Methyl (7S)-3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-7-C-[(1R,2S,3R,4S,5R,6S,7R)-6-endo-(benzyloxy)-7-exo-[(tert-butyl)dimethylsilyl]oxy]-4-endo-hydroxy-2-exo-(phenylthio)-8-oxabicyclo[3.2.1]oct-3-endo-yl]-L-glycero-D-manno-heptonate ((-)-70)*. As described for (±)-**70**, from (–)-**57** (source of optically active **48**) and (–)-**13**. Yield 44% based on (–)-**57**. White foam.  $[\alpha]_D^{25} = -26$ ,  $[\alpha]_{377}^{25} = -28$ ,  $[\alpha]_{346}^{25} = -32$ ,  $[\alpha]_{435}^{25} = -51$ ,  $[\alpha]_{405}^{25} = -61$  ( $c = 0.5$ ,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (7RS)-3,5-Di-O-acetyl-2,6-anhydro-4-O-benzoyl-7-C-[(1RS,5RS,6RS,7RS)-6-endo-(benzyloxy)-7-exo-[(tert-butyl)dimethylsilyl]oxy]-4-oxo-8-oxabicyclo[3.2.1]oct-2-en-3-yl]-DL-glycero-LD-manno-heptonate ((±)-71)*. At  $-78^\circ$ , 0.5M  $\text{Me}_2\text{AlSeMe}$  in toluene (0.65 ml, 0.32 mmol) was added dropwise to a stirred soln. of (±)-**13** (81 mg, 0.22 mmol) in anh. THF (0.75 ml). After stirring at  $-78^\circ$  for 90 min, a soln. of (±)-**48** (61 mg, 0.149 mmol) in anh. THF (0.45 ml) was added dropwise. After stirring at  $-78^\circ$  for 18 h, 100% *m*CPBA (112 mg, 0.65 mmol) was added. The mixture was stirred at  $-78^\circ$  for 1 h and allowed to warm to  $-20^\circ$  within ca. 4 h. After dilution with cold  $\text{CHCl}_3$  ( $-20^\circ$ , 15 ml), the mixture was washed successively with ice-cold 1N aq. HCl (10 ml), 0.5M aq.  $\text{Na}_2\text{S}_2\text{O}_3$  (10 ml), and sat. aq.  $\text{NaHCO}_3$  soln. (10 ml). The aq. layers were extracted with  $\text{CHCl}_3$  ( $3 \times 10$  ml). The combined org. extracts were dried ( $\text{MgSO}_4$ ) and evaporated. FC ( $1.5 \times 12$  cm, light petroleum ether/Et<sub>2</sub>O 3:7): 77 mg (52% based on (±)-**57**) of (±)-**71**. Colorless foam.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.90, 7.57, 7.43, 7.33 (4m, 2 H, 1 H, 2 H, 5 H, arom. H); 7.13 (dd,  $^3\text{J}(2',1') = 4.9$ ,  $^4\text{J}(2',7) = 1.1$ , H–C(2')); 5.73 (d,  $^3\text{J}(5,4) = 3.3$ , H–C(5)); 5.52 (dd,  $^3\text{J}(3,4) = 10.0$ ,  $^3\text{J}(3,2) = 10.0$ , H–C(3)); 4.86 (dd,  $^3\text{J}(4,3) = 10.0$ ,  $^3\text{J}(4,5) = 3.3$ , H–C(4)); 4.77 (d,  $^3\text{J}(5',6') = 7.1$ , H–C(5')); 4.76 (dd,  $^3\text{J}(7,6) = 5.3$ ,  $^4\text{J}(7,2') = 1.1$ , H–C(7)); 4.56 (s,  $\text{PhCH}_2\text{O}$ ); 4.49 (d,  $^3\text{J}(1',2') = 4.9$ , H–C(1')); 4.40 (s, H–C(7)); 4.27 (d,  $^3\text{J}(6',5') = 7.1$ , H–C(6')); 3.96 (d,  $^3\text{J}(2,3) = 10.0$ , H–C(2)); 3.79 (d,  $^3\text{J}(6,7) = 5.3$ , H–C(6)); 3.77 (s, COOMe); 2.09, 1.98 (2s, 2 Ac); 0.87 (s,  $t$ -

BuSi); 0.09 (s, Me<sub>2</sub>Si). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 194.9 (s, C(4')); 169.7, 169.6, 167.7, 164.8 (4s, 4 C=O); 145.7 (d, <sup>1</sup>J(C,H) = 164, C(2')); 136.8, 129.2 (2s, arom. C); 135.2 (s, C(3')); 133.3, 129.6, 128.6, 128.5, 128.4, 128.1 (6d, <sup>1</sup>J(C,H) = 160, arom. C); 85.5 (d, <sup>1</sup>J(C,H) = 153, C(6')); 83.0 (d, <sup>1</sup>J(C,H) = 160, C(5')); 81.9 (d, <sup>1</sup>J(C,H) = 163, C(1')); 78.8 (d, <sup>1</sup>J(C,H) = 152, C(7)); 76.9, 76.7 (2d, <sup>1</sup>J(C,H) = 145, C(2), C(6)); 73.3 (t, <sup>1</sup>J(C,H) = 144, PhCH<sub>2</sub>O); 72.5 (d, <sup>1</sup>J(C,H) = 148, C(4)); 69.1 (d, <sup>1</sup>J(C,H) = 152, C(7)); 66.7, 66.6 (2d, <sup>1</sup>J(C,H) = 155, C(3), C(5)); 52.7 (q, <sup>1</sup>J(C,H) = 148, COOMe); 25.7 (q, <sup>1</sup>J(C,H) = 125, Me<sub>3</sub>CSi); 20.9, 20.6 (2q, <sup>1</sup>J(C,H) = 130, 2 MeCO); 18.0 (s, Me<sub>3</sub>CSi); –5.0, –5.1 (2q, <sup>1</sup>J(C,H) = 119, Me<sub>2</sub>Si). CI-MS (NH<sub>3</sub>): 768 (24, M<sup>+</sup>), 619 (21, [M – AcO – Bn + H]<sup>+</sup>), 595 (42, [M – AcO – TBS + H]<sup>+</sup>), 505 (20), 207 (21), 105 (92), 91 (100), 77 (38).

*Methyl (7RS)-3,5,7-Tri-O-acetyl-7-C-[(1SR,2RS,3SR,4RS,5SR,6SR,7RS)-2-endo-(acetyloxy)-7-endo-(benzyloxy)-6-exo-[(tert-butyl)dimethylsilyl]oxy]-4-exo-(phenylthio)-8-oxabicyclo[3.2.1]oct-3-endo-yl]-2,6-anhydro-4-O-benzoyl-DL-glycero-LD-manno-heptonate ((±)-72)*. A mixture of (±)-70 (88 mg, 0.10 mmol), Ac<sub>2</sub>O (2 ml), pyridine (2 ml), and *N,N*-dimethylpyridin-4-amine (5 mg) was stirred at 0° for 1 h. The solvent was evaporated at 20°, 10<sup>–1</sup> Torr, the residue taken up in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and the soln. washed with 1N aq. HCl (5 ml) and sat. aq. NaHCO<sub>3</sub> soln. (5 ml). The aq. layers were extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 × 10 ml) and the combined org. extracts dried (MgSO<sub>4</sub>) and evaporated: 99 mg (100%) of (±)-72, pure enough for the next step. An anal. sample was obtained by FC (1 × 12 cm, light petroleum ether/Et<sub>2</sub>O 2 : 3): colorless oil that solidified slowly in the refrigerator. UV (MeCN): 256 (6600), 197 (37000). IR (film): 3065, 2955, 2930, 2855, 1750, 1600, 1585, 1455, 1440, 1370, 1275, 1230, 1110, 1065, 1025, 840, 710. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.91, 7.56, 7.42, 7.31 (4m, 2 H, 1 H, 4 H, 8 H, arom. H); 5.76 (dd, <sup>3</sup>J(7,6) = 9.5, <sup>3</sup>J(7,3') = 5.7, H – C(7)); 5.58 (br. d, <sup>3</sup>J(5,4) = 3.4, H – C(5)); 5.56 (dd, <sup>3</sup>J(3,4) = 10.1, <sup>3</sup>J(3,2) = 10.0, H – C(3)); 5.51 (dd, <sup>3</sup>J(2',1') = 8.0, <sup>3</sup>J(2',3') = 4.4, H – C(2')); 5.32 (dd, <sup>3</sup>J(4,3) = 10.1, <sup>3</sup>J(4,5) = 3.4, H – C(4)); 4.45 (br. dd, <sup>3</sup>J(1',2') = 8.0, <sup>3</sup>J(1',7') = 5.4, H – C(1')); 4.43, 4.40 (2d, <sup>2</sup>J = 11.0, PhCH<sub>2</sub>O); 4.23 (dd, <sup>3</sup>J(6',7') = 6.0, <sup>3</sup>J(6',5') = 1.8, H – C(6')); 4.16 (m, <sup>3</sup>J(5',6') = 1.8, H – C(5')); 4.13 (d, <sup>3</sup>J(2,3) = 10.0, H – C(2)); 4.04 (br. d, <sup>3</sup>J(6,7) = 9.5, H – C(6)); 3.82 (dd, <sup>3</sup>J(7',6') = 6.0, <sup>3</sup>J(7',1') = 5.4, H – C(7')); 3.68 (s, COOMe); 3.23 (d, <sup>3</sup>J(4',3') = 10.2, H – C(4')); 2.33 (ddd, <sup>3</sup>J(3',4') = 10.2, <sup>3</sup>J(3',7') = 5.7, <sup>3</sup>J(3',2') = 4.4, H – C(3')); 2.11, 1.96, 1.95, 1.72 (4s, 4 Ac); 0.81 (s, *t*-BuSi); 0.00, –0.08 (2s, Me<sub>2</sub>Si). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 171.0, 170.5, 169.6, 169.2, 167.3, 165.4 (6s, 6 C=O); 137.2, 133.0, 129.0 (3s, arom. C); 133.5, 133.1, 129.6, 129.2, 128.6, 128.5, 128.2, 127.9, 127.8 (9d, <sup>1</sup>J(C,H) = 160, arom. C); 88.6 (d, <sup>1</sup>J(C,H) = 148, C(7)); 87.5 (d, <sup>1</sup>J(C,H) = 159, C(5')); 80.5 (d, <sup>1</sup>J(C,H) = 147, C(6')); 76.5 (d, <sup>1</sup>J(C,H) = 154, C(2)); 75.9 (d, <sup>1</sup>J(C,H) = 145, C(6)); 74.3 (t, <sup>1</sup>J(C,H) = 142, PhCH<sub>2</sub>O); 72.3 (d, <sup>1</sup>J(C,H) = 145, C(4)); 72.1 (d, <sup>1</sup>J(C,H) = 155, C(1')); 67.5 (d, <sup>1</sup>J(C,H) = 149, C(7)); 66.9 (d, <sup>1</sup>J(C,H) = 156, C(2)); 66.6, 66.4 (2d, <sup>1</sup>J(C,H) = 155, C(3), C(5)); 52.7 (q, <sup>1</sup>J(C,H) = 148, COOMe); 47.9 (d, <sup>1</sup>J(C,H) = 143, C(4')); 39.2 (d, <sup>1</sup>J(C,H) = 129, C(3')); 25.6 (q, <sup>1</sup>J(C,H) = 125, Me<sub>3</sub>CSi); 21.2, 20.8, 20.6, 20.5 (4q, <sup>1</sup>J(C,H) = 130, 4 MeCO); 17.9 (s, Me<sub>3</sub>CSi); –4.7, –5.0 (2q, <sup>1</sup>J(C,H) = 118, Me<sub>2</sub>Si). CI-MS (NH<sub>3</sub>): 908 (13, [M – C<sub>4</sub>H<sub>9</sub> + H]<sup>+</sup>), 110 (28), 105 (52), 91 (100), 77 (23). Anal. calc. for C<sub>49</sub>H<sub>60</sub>O<sub>16</sub>SSi (965.25): C 60.97, H 6.28; found: C 61.06, H 6.34.

*Methyl (7S)-3,5,7-Tri-O-acetyl-7-C-[(1R,2S,3R,4S,5R,6R,7S)-2-endo-(acetyloxy)-7-endo-(benzyloxy)-6-exo-[(tert-butyl)dimethylsilyl]oxy]-4-exo-(phenylthio)-8-oxabicyclo[3.2.1]oct-3-endo-yl]-2,6-anhydro-4-O-benzoyl-L-glycero-D-manno-heptonate ((–)-72)*. As described for (±)-72, from (–)-70. Colorless oil. [α]<sub>D</sub><sup>25</sup> = –1.7, [α]<sub>D</sub><sup>25</sup><sub>777</sub> = –2.0, [α]<sub>D</sub><sup>25</sup><sub>546</sub> = –1.5, [α]<sub>D</sub><sup>25</sup><sub>435</sub> = 0.3, [α]<sub>D</sub><sup>25</sup><sub>405</sub> = 2.1 (c = 0.9, CH<sub>2</sub>Cl<sub>2</sub>).

*Methyl (7RS)-3,5,7-Tri-O-acetyl-7-C-[(1SR,2RS,3SR,4RS,5SR,7RS)-2-endo-(acetyloxy)-7-endo-(benzyloxy)-6-oxo-4-exo-(phenylthio)-8-oxabicyclo[3.2.1]oct-3-endo-yl]-2,6-anhydro-4-O-benzoyl-DL-glycero-LD-manno-heptonate ((±)-73)*. A mixture of (±)-72 (99 mg, 0.102 mmol), MeCN (7 ml), and 40% aq. HF soln. (0.35 ml) was stirred at 0° for 15 min, then at 20° for 2 h. A sat. aq. NaHCO<sub>3</sub> soln. (10 ml) was added and the mixture extracted with AcOEt (30 ml, then 4 × 5 ml). The combined org. extracts were dried (MgSO<sub>4</sub>) and evaporated giving 87 mg of yellowish foamy alcohol that was taken up in anh. CH<sub>2</sub>Cl<sub>2</sub> (3.5 ml) containing 1,1,1-tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (64 mg, 0.15 mmol). After stirring at 20° for 45 min, AcOEt (15 ml) was added. The soln. was washed with sat. aq. NaHCO<sub>3</sub> soln. containing Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (240 mg, 10 ml), then with H<sub>2</sub>O (10 ml). The aq. layers were extracted with AcOEt (4 × 10 ml). The combined org. extracts were dried (MgSO<sub>4</sub>) and evaporated: 89 mg (quant.) of (±)-73. Yellowish foam, which was used as such in the next step. An anal. sample was obtained by FC (1 × 12 cm, light petroleum ether/Et<sub>2</sub>O 15 : 35): colorless oil that solidified in the refrigerator. UV (MeCN): 217 (18000), 201 (21500). IR (film): 3065, 2955, 2875, 1755, 1750, 1730, 1600, 1585, 1455, 1440, 1370, 1270, 1225, 1115, 1025, 960, 715. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.91, 7.56, 7.43, 7.33 (4m, 2 H, 1 H, 4 H, 8 H, arom. H); 5.77 (dd, <sup>3</sup>J(7,6) = 9.5, <sup>3</sup>J(7,3') = 4.6, H – C(7)); 5.64 (dd, <sup>3</sup>J(2',1') = 7.6, <sup>3</sup>J(2',3') = 3.5, H – C(2')); 5.58 (dd, <sup>3</sup>J(3,4) = 10.1, <sup>3</sup>J(3,2) = 10.0, H – C(3)); 5.54 (dd, <sup>3</sup>J(5,4) = 3.4, <sup>3</sup>J(5,6) = 1.0, H – C(5)); 5.32 (dd, <sup>3</sup>J(4,3) = 10.1, <sup>3</sup>J(4,5) = 3.4, H – C(4)); 4.72 (ddd, <sup>3</sup>J(1',2') = 7.6, <sup>3</sup>J(1',7') = 6.3, <sup>4</sup>J(1',5') = 1.9, H – C(1')); 4.63, 4.57 (2d, <sup>2</sup>J = 11.6, PhCH<sub>2</sub>O); 4.38 (m, <sup>4</sup>J(5',1') = 1.9, <sup>4</sup>J(5',7') = 1.4, H – C(5')); 4.26 (dd, <sup>3</sup>J(7',1') = 6.3, <sup>4</sup>J(7',5') = 1.4, H – C(7')); 4.11 (d, <sup>3</sup>J(2,3) = 10.0, H – C(2)); 3.96 (dd, <sup>3</sup>J(6,7) = 9.5, <sup>3</sup>J(6,5) =

1.0, H–C(6)); 3.73 (s, COOMe); 3.48 (br. *d*,  $^3J(4',3') = 10.9$ , H–C(4')); 2.52 (*ddd*,  $^3J(3',4') = 10.9$ ,  $^3J(3',7) = 4.6$ ,  $^3J(3',2) = 3.5$ , H–C(3')); 2.11, 1.98, 1.92, 1.83 (4s, 4 Ac).  $^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ): 209.6 (s, C(6')); 170.8, 170.4, 169.6, 169.1, 167.2, 165.4 (6s, 6 C=O); 136.3, 132.5, 128.9 (3s, arom. C); 133.5, 132.1, 129.6, 129.3, 128.6, 128.4, 128.3, 127.7 (8*d*,  $^1J(\text{C,H}) = 160$ , arom. C); 81.8, 81.7 (2*d*,  $^1J(\text{C,H}) = 147$ , 157, C(5'), C(7')); 76.7 (*d*,  $^1J(\text{C,H}) = 150$ , C(2)); 75.5 (*d*,  $^1J(\text{C,H}) = 140$ , C(6)); 74.3 (*d*,  $^1J(\text{C,H}) = 162$ , C(1')); 73.9 (*t*,  $^1J(\text{C,H}) = 143$ ,  $\text{PhCH}_2\text{O}$ ); 72.2 (*d*,  $^1J(\text{C,H}) = 148$ , C(4)); 67.0 (*d*,  $^1J(\text{C,H}) = 152$ , C(7)); 66.5 (*d*,  $^1J(\text{C,H}) = 155$ , C(3)); 66.2 (*d*,  $^1J(\text{C,H}) = 155$ , C(5)); 66.1 (*d*,  $^1J(\text{C,H}) = 155$ , C(2')); 52.8 (*q*,  $^1J(\text{C,H}) = 148$ , COOMe); 44.4 (*d*,  $^1J(\text{C,H}) = 145$ , C(4')); 39.2 (*d*,  $^1J(\text{C,H}) = 131$ , C(3')); 21.0, 20.7, 20.6 (3*q*,  $^1J(\text{C,H}) = 130$ , 4 MeCO). CI-MS ( $\text{NH}_3$ ): 866 (1,  $[M+18]^+$ ), 849 (2,  $[M+H]^+$ ), 789 (0.5,  $[M-\text{AcO}]^+$ ), 731 (0.5,  $[M-2\text{AcO}+H]^+$ ), 619 (2,  $[M-\text{BnO}-\text{BzOH}]^+$ ), 531 (5), 109 (13), 105 (67), 91 (100), 77 (20). Anal. calc. for  $\text{C}_{43}\text{H}_{44}\text{O}_{16}\text{S}$  (848.94): C 60.84, H 5.22; found: C 60.88, H 5.29.

*Methyl (7S)-3,5,7-Tri-O-acetyl-7-C-[(1R,2S,3R,4S,5R,7S)-2-endo-(acetyloxy)-7-endo-(benzyloxy)-6-oxo-4-exo-(phenylthio)-8-oxabicyclo[3.2.1]oct-3-endo-yl]-2,6-anhydro-4-O-benzoyl-L-glycero-D-manno-heptonate ((-)-73)*. As described for ( $\pm$ )-**73**, with (–)-**72**. Colorless oil.  $[\alpha]_{\text{D}}^{25} = -19$ ,  $[\alpha]_{577}^{25} = -19$ ,  $[\alpha]_{546}^{25} = -24$ ,  $[\alpha]_{335}^{25} = -31$ ,  $[\alpha]_{305}^{25} = -28$  (*c* = 0.6,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (7RS)-3,5,7-Tri-O-acetyl-7-C-[(1SR,4SR,5SR,6RS,7SR,8RS)-6-endo-(acetyloxy)-4-endo-(benzyloxy)-2-oxo-8-exo-(phenylsulfonyl)-3,9-dioxabicyclo[3.3.1]non-7-endo-yl]-2,6-anhydro-4-O-benzoyl-DL-glycero-LD-manno-heptonate ((±)-74)*. A mixture of ( $\pm$ )-**73** (89 mg, 0.105 mmol),  $\text{NaHCO}_3$  (10 mg), 90% *m*CPBA (74 mg, 0.39 mg), and anhyd.  $\text{CHCl}_3$  (4 ml) was stirred at 20° for 16 h.  $\text{AcOEt}$  (25 ml) was added and the soln. washed with 0.5M aq.  $\text{Na}_2\text{S}_2\text{O}_3$  (15 ml), then with sat. aq.  $\text{NaHCO}_3$  soln. (15 ml). The aq. layers were extracted with  $\text{AcOEt}$  (4 × 15 ml) and the combined org. extracts dried ( $\text{MgSO}_4$ ) and evaporated; 90 mg (96%) of ( $\pm$ )-**74**. Yellowish foam, which was used in the next step. An anal. sample was obtained by FC (1 × 12 cm, light petroleum ether/ $\text{AcOEt}$  4:5): colorless foam. UV (MeCN): 271 (6600), 264 (7000), 217 (32000), 196 (63000). IR (film): 2955, 2920, 1755, 1450, 1375, 1270, 1225, 1110.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ): 8.00, 7.92, 7.70, 7.65–7.54, 7.44–7.28 (5*m*, 2 H, 2 H, 1 H, 3 H, 7 H, arom. H); 6.03 (*dd*,  $^3J(7,6) = 9.3$ ,  $^3J(7,7') = 2.2$ , H–C(7)); 6.02 (*dd*,  $^3J(6',5') = 7.1$ ,  $^3J(6',7') = 2.2$ , H–C(6')); 5.63 (*dd*,  $^3J(3,4) = 10.1$ ,  $^3J(3,2) = 10.0$ , H–C(3)); 5.62 (*d*,  $^3J(4',5') = 3.7$ , H–C(4')); 5.44 (br. *d*,  $^3J(5,4) = 3.4$ , H–C(5)); 5.32 (*dd*,  $^3J(4,3) = 10.1$ ,  $^3J(4,5) = 3.4$ , H–C(4)); 5.05 (*m*,  $^4J(1',5') = 1.1$ , H–C(1')); 4.89, 4.69 (2*d*,  $^2J = 11.7$ ,  $\text{PhCH}_2\text{O}$ ); 4.23 (*ddd*,  $^3J(5',6') = 7.1$ ,  $^3J(5',4') = 3.7$ ,  $^4J(5',1') = 1.1$ , H–C(5')); 4.18 (*d*,  $^3J(2,3) = 10.0$ , H–C(2)); 4.03 (br. *d*,  $^3J(6,7) = 9.3$ , H–C(6)); 3.81 (s, COOMe); 3.74 (br. *d*,  $^3J(8',7') = 10.6$ , H–C(8')); 2.93 (*ddd*,  $^3J(7',8') = 10.6$ ,  $^3J(7',6') = 2.2$ ,  $^3J(7',7) = 2.2$ , H–C(7')); 2.15, 1.99, 1.95, 1.85 (4s, 4 Ac).  $^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ): 170.2, 169.5, 169.0, 168.9, 167.6, 167.0, 165.4 (7s, 6 C=O, C(2)); 136.9, 135.0, 129.0 (3s, arom. C); 134.4, 133.4, 129.7, 129.5, 129.4, 128.7, 128.6, 128.5, 128.2 (9*d*,  $^1J(\text{C,H}) = 160$ , arom. C); 100.6 (*d*,  $^1J(\text{C,H}) = 177$ , C(4')); 76.7 (*d*,  $^1J(\text{C,H}) = 150$ , C(2)); 75.4 (*d*,  $^1J(\text{C,H}) = 144$ , C(6)); 72.1 (*d*,  $^1J(\text{C,H}) = 146$ , C(4)); 71.8 (*t*,  $^1J(\text{C,H}) = 144$ ,  $\text{PhCH}_2\text{O}$ ); 70.2 (*d*,  $^1J(\text{C,H}) = 154$ , C(5')); 69.9 (*d*,  $^1J(\text{C,H}) = 153$ , C(1')); 68.2 (*d*,  $^1J(\text{C,H}) = 152$ , C(7)); 66.3 (*d*,  $^1J(\text{C,H}) = 155$ , C(5)); 66.2 (*d*,  $^1J(\text{C,H}) = 155$ , C(3)); 63.7 (*d*,  $^1J(\text{C,H}) = 154$ , C(6)); 62.2 (*d*,  $^1J(\text{C,H}) = 144$ , C(8')); 52.9 (*q*,  $^1J(\text{C,H}) = 148$ , COOMe); 34.4 (*d*,  $^1J(\text{C,H}) = 132$ , C(7)); 21.1, 20.6 (2*q*,  $^1J(\text{C,H}) = 130$ , 4 MeCO). CI-MS ( $\text{NH}_3$ ): 914 (2,  $[M+18]^+$ ), 896 (1,  $M^+$ ), 717 (1,  $[M-\text{AcO}-\text{Bz}+H]^+$ ), 577 (1,  $[M-\text{AcO}-\text{Bz}-\text{PhSO}_2+2H]^+$ ), 471 (2), 122 (11), 108 (14), 105 (67), 91 (100), 77 (34). Anal. calc. for  $\text{C}_{43}\text{H}_{44}\text{O}_{16}\text{S}$  (896.94): C 57.59, H 4.94, S 3.57; found: C 57.47, H 4.88, S 3.49.

*Methyl (7S)-3,5,7-Tri-O-acetyl-7-C-[(1R,4R,5R,6S,7R,8S)-6-endo-(acetyloxy)-4-endo-(benzyloxy)-2-oxo-8-exo-(phenylsulfonyl)-3,9-dioxabicyclo[3.3.1]non-7-endo-yl]-2,6-anhydro-4-O-benzoyl-L-glycero-D-manno-heptonate ((-)-74)*. As described for ( $\pm$ )-**74**, with (–)-**73**. White foam.  $[\alpha]_{\text{D}}^{25} = -62$ ,  $[\alpha]_{577}^{25} = -66$ ,  $[\alpha]_{546}^{25} = -74$ ,  $[\alpha]_{335}^{25} = -122$ ,  $[\alpha]_{305}^{25} = -144$  (*c* = 0.3,  $\text{CH}_2\text{Cl}_2$ ).

*Diethyl Dithioacetal of Methyl 3-O-Acetyl-2,6-anhydro-4,5-dideoxy-5-C-(phenylsulfonyl)-4-C-[[methyl (7RS)-3,5,7-tri-O-acetyl-2,6-anhydro-4-O-benzoyl-DL-glycero-LD-manno-heptonate]-7-C-yl]-DL-glycero-LD-galacto-hepturonate ((±)-75)*. EtSH (0.1 ml, 1.35 mmol) and  $\text{CF}_3\text{SO}_3\text{H}$  (15  $\mu\text{l}$ ) were added successively to a stirred soln. of crude ( $\pm$ )-**74** (90 mg, 0.10 mmol) in anhyd.  $\text{CH}_2\text{Cl}_2$  (5 ml). After stirring at 20° for 15 min, a soln. of diazomethane in  $\text{Et}_2\text{O}$  was added until persistence of the yellow color. A drop of  $\text{AcOH}$  was added, then a sat. aq.  $\text{NaHCO}_3$  soln. (15 ml). The mixture was extracted with  $\text{AcOEt}$  (25 ml, then 4 × 15 ml). The combined org. extracts were dried ( $\text{MgSO}_4$ ) and evaporated. FC (1 × 15 cm, light petroleum ether/ $\text{AcOEt}$  1:1) gave 57 mg (61% based on ( $\pm$ )-**70**) of ( $\pm$ )-**75**. Colorless foam. UV (MeCN): 272 (3200), 265 (3300), 260 (3400), 222 (15000), 202 (30500). IR (film): 2955, 2930, 1750, 1450, 1375, 1270, 1225, 1150, 1110, 1065, 1020.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ): 8.03, 7.89, 7.70, 7.56, 7.41 (5*m*, 2 H, 2 H, 3 H, 1 H, 2 H, arom. H); 5.86 (*dd*,  $^3J(3,4) = 3.3$ ,  $^3J(3,2) = 1.1$ , H–C(3)); 5.51 (*dd*,  $^3J(3',4') = 10.0$ ,  $^3J(3',2') = 9.9$ , H–C(3')); 5.38 (br. *d*,  $^3J(5',4') = 3.5$ , H–C(5')); 5.34 (*dd*,  $^3J(4',3') = 10.0$ ,  $^3J(4',5') = 3.5$ , H–C(4')); 5.19 (br. s, H–C(6)); 4.97 (*dd*,  $^3J(7',6') = 9.5$ ,  $^3J(7',4) = 3.2$ , H–C(7')); 4.33 (br. *d*,  $^3J(6',7') = 9.5$ , H–C(6')); 4.23 (*m*,  $^3J(5,4) = 6.5$ , H–C(5)); 4.22 (*d*,  $^3J(2',3') = 9.9$ ,

H–C(2''); 3.85, 3.78 (2s, 2 COOMe); 3.82 (*d*,  $^3J(1,2)=8.8$ , H–C(1)); 3.67 (*dd*,  $^3J(2,1)=8.8$ ,  $^3J(2,3)=1.1$ , H–C(2)); 2.97 (*ddd*,  $^3J(4,5)=6.5$ ,  $^3J(4,3)=3.3$ ,  $^3J(4,7')=3.2$ , H–C(4)); 2.77–2.58 (*m*, 4 H,  $^3J=7.4$ , 2 MeCH<sub>2</sub>S); 1.99, 1.99, 1.95, 1.92 (4s, 4 Ac); 1.27, 1.22 (2*t*,  $^3J=7.4$ , 2 MeCH<sub>2</sub>S). <sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 8.18, 7.20, 7.04 (3*m*, 4 H, 2 H, 4 H, arom. H); 6.30 (*br. d*,  $^3J(3,4)=3.1$ , H–C(3)); 5.94 (*dd*,  $^3J(3',4')=10.2$ ,  $^3J(3',2')=10.0$ , H–C(3')); 5.86 (*dd*,  $^3J(5',4')=3.4$ ,  $^3J(5',6')=0.7$ , H–C(5')); 5.55 (*dd*,  $^3J(4',3')=10.2$ ,  $^3J(4',5')=3.4$ , H–C(4')); 5.46 (*br. s*, H–C(6)); 5.42 (*dd*,  $^3J(7',6')=9.5$ ,  $^3J(7',4)=3.0$ , H–C(7')); 4.71 (*dd*,  $^3J(6',7')=9.5$ ,  $^3J(6',5')=0.7$ , H–C(6')); 4.65 (*br. d*,  $^3J(5,4)=6.7$ , H–C(5)); 4.07 (*s*, H–C(1), H–C(2)); 3.93 (*d*,  $^3J(2',3')=10.0$ , H–C(2')); 3.43 (*ddd*,  $^3J(4,5)=6.7$ ,  $^3J(4,3)=3.1$ ,  $^3J(4,7')=3.0$ , H–C(4)); 3.34, 3.20 (2*s*, 2 COOMe); 2.79–2.55 (*m*,  $^3J=7.4$ , 2 MeCH<sub>2</sub>S); 1.72, 1.71, 1.68, 1.62 (4*s*, 4 Ac); 1.19, 1.14 (2*t*,  $^3J=7.4$ , 2 MeCH<sub>2</sub>S). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 170.6, 170.1, 170.0, 169.7, 169.0, 167.2, 165.2 (7*s*, 7 C=O); 136.5, 128.9 (2*s*, arom. C); 134.3, 133.4, 130.1, 129.6, 129.5, 128.5 (6*d*,  $^1J(\text{C,H})=160$ , arom. C); 77.8 (*d*,  $^1J(\text{C,H})=147$ , C(2)); 76.2 (*d*,  $^1J(\text{C,H})=151$ , C(2')); 74.3 (*d*,  $^1J(\text{C,H})=144$ , C(6')); 71.9 (*d*,  $^1J(\text{C,H})=149$ , C(4')); 69.9 (*d*,  $^1J(\text{C,H})=147$ , C(6)); 68.9 (*d*,  $^1J(\text{C,H})=151$ , C(7')); 66.5 (*d*,  $^1J(\text{C,H})=157$ , C(3')); 65.9 (*d*,  $^1J(\text{C,H})=156$ , C(5')); 64.8 (*d*,  $^1J(\text{C,H})=157$ , C(3)); 59.7 (*d*,  $^1J(\text{C,H})=139$ , C(5)); 52.8 (*q*,  $^1J(\text{C,H})=148$ , 2 COOMe); 52.0 (*d*,  $^1J(\text{C,H})=151$ , C(1)); 37.3 (*d*,  $^1J(\text{C,H})=131$ , C(4)); 25.2, 24.1 (2*t*,  $^1J(\text{C,H})=139$ , 2 MeCH<sub>2</sub>S); 21.4, 20.7, 20.6, 20.5 (4*q*,  $^1J(\text{C,H})=130$ , 4 MeCO); 14.6, 14.3 (2*q*,  $^1J(\text{C,H})=128$ , 2 MeCH<sub>2</sub>S). CI-MS (NH<sub>3</sub>): 944 (0.5, [M+18]<sup>+</sup>), 926 (0.4, M<sup>+</sup>), 865 (1, [M–SEt]<sup>+</sup>), 849 (1, [M–Ph]<sup>+</sup>), 745 (13, [M–Ph–Bz+H]<sup>+</sup>), 663 (9, [M–PhSO<sub>2</sub>–BzOH]<sup>+</sup>), 603 (6, [M–PhSO<sub>2</sub>–BzOH–AcOH]<sup>+</sup>), 559 (5), 135 (14), 105 (100), 77 (31).

*Diethyl Dithioacetal of Methyl 3-O-Acetyl-2,6-anhydro-4,5-dideoxy-4-C-[[methyl (7S)-3,5,7-tri-O-acetyl-2,6-anhydro-4-O-benzoyl-L-glycero-D-manno-heptonate]-7-C-yl]-5-C-(phenylsulfonyl)-L-glycero-D-galacto-hepturonate ((–)-75)*. As described for (±)-75, with (–)-74. Yield 48% based on (–)-70. White foam.  $[\alpha]_{\text{D}}^{25} = -39$ ,  $[\alpha]_{\text{D}}^{35} = -40$ ,  $[\alpha]_{\text{D}}^{25} = -49$ ,  $[\alpha]_{\text{D}}^{35} = -81$ ,  $[\alpha]_{\text{D}}^{25} = -95$  (*c* = 0.7, CH<sub>2</sub>Cl<sub>2</sub>).

*Methyl 3-O-Acetyl-2,6-anhydro-4,5-dideoxy-4-C-[[methyl (7RS)-3,5,7-tri-O-acetyl-2,6-anhydro-4-O-benzoyl-DL-glycero-LD-manno-heptonate]-7-C-yl]-5-C-(phenylsulfonyl)-DL-glycero-LD-galacto-hepturonate ((±)-76)*. A mixture of (±)-75 (32 mg, 0.035 mmol), anhyd. MeCN (2.3 ml), and Hg(ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (35 mg, 0.076 mmol) was stirred at 20° for 30 min. CHCl<sub>3</sub> (25 ml) and Ag<sub>2</sub>CO<sub>3</sub> (140 mg, 0.51 mmol) were added and the mixture stirred at 20° for 15 min. The precipitate was filtered off (*Celite*) and the solvent evaporated. The residue was taken up in CHCl<sub>3</sub>/light petroleum ether 1:1 (1 ml). The precipitate was filtered off and the solvent evaporated. The latter operation was repeated 3 times giving 27 mg (94%) of crude (±)-76. Colorless foam, which was used directly in the next step. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 9.56 (*s*, H–C(1)); 8.19, 7.23, 7.04 (3*m*, 4 H, 2 H, 4 H, arom. H); 6.09 (*dd*,  $^3J(3,4)=3.0$ ,  $^3J(3,2)=2.8$ , H–C(3)); 5.93 (*dd*,  $^3J(3',4')=10.2$ ,  $^3J(3',2')=10.0$ , H–C(3')); 5.83 (*br. d*,  $^3J(5',4')=3.1$ , H–C(5')); 5.57 (*dd*,  $^3J(4',3')=10.2$ ,  $^3J(4',5')=3.1$ , H–C(4')); 5.53 (*br. s*, H–C(6)); 5.39 (*dd*,  $^3J(7',6')=9.5$ ,  $^3J(7',4)=2.8$ , H–C(7')); 4.53 (*br. d*,  $^3J(5,4)=7.1$ , H–C(5)); 4.52 (*br. d*,  $^3J(6',7')=9.5$ , H–C(6')); 3.81 (*d*,  $^3J(2',3')=10.0$ , H–C(2')); 3.78 (*d*,  $^3J(2,3)=2.8$ , H–C(2)); 3.35, 3.09 (2*s*, 2 COOMe); 3.33 (*ddd*,  $^3J(4,5)=7.1$ ,  $^3J(4,3)=3.0$ ,  $^3J(4,7')=2.8$ , H–C(4)); 1.70, 1.64, 1.46 (3*s*, 3 H, 6 H, 3 H, 4 Ac).

*Methyl (7RS)-5-O-Acetyl-2,6-anhydro-7-C-[(1RS,5RS,6RS,7RS)-6-endo-(benzyloxy)-7-exo-[(tert-butyl)dimethylsilyloxy]-4-oxo-8-oxabicyclo[3.2.1]oct-2-en-3-yl]-3,4-dideoxy-4-C-[[methyl (7RS)-3,5,7-tri-O-acetyl-2,6-anhydro-4-O-benzoyl-DL-glycero-LD-manno-heptonate]-7-C-yl]-3-C-(phenylsulfonyl)-DL-glycero-LD-glucio-heptonate ((±)-77)*. At –78°, 0.5M Me<sub>2</sub>AlSeMe in toluene (0.25 ml) was added dropwise to a stirred soln. of (±)-13 (36 mg, 0.10 mmol) in anhyd. THF (1 ml). After stirring at –78° for 45 min, a soln. of (±)-76 (27 mg, 0.033 mmol) in anhyd. THF (0.5 ml) was added dropwise. After stirring at –78° for 2 h, 100% *m*CPBA (27 mg, 0.156 mmol) was added and the mixture stirred at –78° for 45 min. The mixture was allowed to warm up to –20° within 15 min. CHCl<sub>3</sub> (10 ml) was added and the soln. washed successively with 1*N* HCl (10 ml), 0.5*M* aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10 ml), and sat. aq. NaHCO<sub>3</sub> soln. (10 ml). The aq. layers were extracted with CHCl<sub>3</sub> (4 × 10 ml) and the combined org. extracts dried (MgSO<sub>4</sub>) and evaporated. FC (1 × 14 cm, light petroleum ether/AcOEt 1:1) gave 22 mg (53% based on (±)-75) of (±)-77 as colorless foam and 26 mg (72%) of (±)-13. (±)-77: UV (MeCN): 219 (21000), 197 (39500). IR (KBr): 3480 (*br.*), 2955, 2930, 2860, 1755, 1695, 1450, 1370, 1270, 1230, 1150, 1110, 1065. <sup>1</sup>H-NMR (400 MHz, 55°, C<sub>6</sub>D<sub>6</sub>): 8.18, 8.07, 7.74, 7.44, 7.22, 7.11 (6*m*, 2 H, 2 H, 3 H, 2 H, 3 H, 3 H, arom. H); 7.28 (*dd*,  $^3J(2'',1'')=5.2$ ,  $^4J(2'',7)=2.0$ , H–C(2'')); 6.11 (*dd*,  $^3J(3',4')=10.1$ ,  $^3J(3',2')=10.0$ , H–C(3'')); 5.82 (*d*,  $^3J(5',4')=3.1$ , H–C(5'')); 5.69 (*dd*,  $^3J(4',3')=10.1$ ,  $^3J(4',5')=3.1$ , H–C(4'')); 5.25 (*d*,  $^3J(5,4)=4.7$ , H–C(5)); 5.24 (*dd*,  $^3J(7',4)=9.0$ ,  $^3J(7',6')=8.6$ , H–C(7'')); 5.17 (*br. d*,  $^3J(3,4)=3.7$ , H–C(3)); 4.86 (*m*,  $^3J(7,6)=3.5$ ,  $^4J(7,2'')=2.0$ , H–C(7)); 4.79 (*d*,  $^3J(2',3')=10.0$ , H–C(2'')); 4.78 (*br. s*, H–C(2)); 4.76 (*br. s*, H–C(7'')); 4.74 (*d*,  $^3J(5'',6'')=7.0$ , H–C(5'')); 4.58 (*d*,  $^3J(6',7')=8.6$ , H–C(6'')); 4.50 (*br. d*,  $^3J(1'',2'')=5.2$ , H–C(1'')); 4.47, 4.25 (2*d*,  $^2J=10.5$ , PhCH<sub>2</sub>O); 4.40 (*d*,  $^3J(6,7)=3.5$ , H–C(6)); 4.29 (*br. d*,  $^3J(6'',5'')=7.0$ , H–C(6'')); 4.04 (*br. s*, OH–C(7)); 3.54, 3.24 (2*s*, 2 COOMe); 2.76 (*ddd*,  $^3J(4,7')=9.0$ ,  $^3J(4,5)=4.7$ ,  $^3J(4,3)=3.7$ , H–C(4)); 1.87, 1.78, 1.76, 1.74 (4*s*, 4 Ac); 1.02 (*s*, *t*-BuSi); 0.21, 0.18 (2*s*, Me<sub>2</sub>Si). <sup>13</sup>C-NMR (100.6 MHz, 55°,

C<sub>6</sub>D<sub>6</sub>): 194.5 (s, C(4'')); 171.4, 170.5, 169.8, 169.4, 169.3, 168.1, 165.7 (7s, 7 C=O); 147.1 (d, <sup>1</sup>J(C,H) = 167, C(2'')); 137.7, 137.3, 133.9, 130.2 (4s, 3 arom. C, C(3'')); 134.4, 133.3, 130.0, 129.7, 129.6, 129.5, 129.3, 128.9, 128.6 (9d, <sup>1</sup>J(C,H) = 160, arom. C); 88.5 (d, <sup>1</sup>J(C,H) = 152, C(6'')); 83.8 (d, <sup>1</sup>J(C,H) = 159, C(5'')); 82.2 (d, <sup>1</sup>J(C,H) = 163, C(1'')); 79.8 (d, <sup>1</sup>J(C,H) = 154, C(7'')); 78.0 (d, <sup>1</sup>J(C,H) = 145, C(6'')); 76.7 (d, <sup>1</sup>J(C,H) = 151, C(2'')); 76.0 (d, <sup>1</sup>J(C,H) = 149, C(6)); 74.9 (t, <sup>1</sup>J(C,H) = 141, PhCH<sub>2</sub>O); 74.0 (d, <sup>1</sup>J(C,H) = 148, C(4'')); 70.3 (d, <sup>1</sup>J(C,H) = 148, C(7)); 70.2 (d, <sup>1</sup>J(C,H) = 142, C(2)); 67.3 (d, <sup>1</sup>J(C,H) = 155, C(7'')); 67.1 (d, <sup>1</sup>J(C,H) = 155, C(5'')); 67.0 (d, <sup>1</sup>J(C,H) = 155, C(3'')); 63.9 (d, <sup>1</sup>J(C,H) = 156, C(5)); 61.3 (d, <sup>1</sup>J(C,H) = 143, C(3)); 52.4, 52.0 (2q, <sup>1</sup>J(C,H) = 148, 2 COOMe); 39.9 (d, <sup>1</sup>J(C,H) = 132, C(4)); 26.0 (q, <sup>1</sup>J(C,H) = 125, Me<sub>3</sub>CSi); 21.7, 21.6, 20.5, 20.2 (4q, <sup>1</sup>J(C,H) = 130, 4 MeCO); 18.2 (s, Me<sub>3</sub>CSi); -4.6, -4.7 (2q, <sup>1</sup>J(C,H) = 119, 2 Me<sub>2</sub>Si). CI-MS (NH<sub>3</sub>): 1198 (5, [M + 18]<sup>+</sup>), 1180 (3, M<sup>+</sup>), 1031 (2, [M - Bn - OAc + H]<sup>+</sup>), 1007 (2, [M - OAc - (t-Bu)Me<sub>2</sub>Si + H]<sup>+</sup>), 917 (4, [M - Bn - OAc - (t-Bu)Me<sub>2</sub>Si + 2H]<sup>+</sup>), 207 (9), 125 (12), 105 (82), 91 (100), 77 (18). Anal. calc. for C<sub>57</sub>H<sub>68</sub>O<sub>23</sub>SSi (1181.41): C 57.96, H 5.80, S 2.71, Si 2.38; found: C 57.99, H 5.74, S 2.66, Si 2.49.

*Methyl (7S)-5-O-Acetyl-2,6-anhydro-7-C-[(1S,5S,6S,7S)-6-endo-(benzyloxy)-7-exo-[[tert-butyl]dimethylsilyl]oxy]-4-oxo-8-oxabicyclo[3.2.1]oct-2-en-3-yl]-3,4-dideoxy-4-C-[[methyl (7S)-3,5,7-tri-O-acetyl-2,6-anhydro-4-O-benzoyl-L-glycero-D-manno-heptonate]-7-C-yl]-3-C-(phenylsulfonyl)-L-glycero-D-glucro-heptonate ((-)-77)*. As described for (±)-77, with (-)-13. Yield 46% based on (-)-75, enantiomerically pure 76 was not fully characterized. (-)-77: Colorless oil. [α]<sub>D</sub><sup>25</sup> = -65, [α]<sub>377</sub><sup>25</sup> = -67, [α]<sub>346</sub><sup>25</sup> = -80, [α]<sub>435</sub><sup>25</sup> = -19, [α]<sub>405</sub><sup>25</sup> = -32 (c = 0.3, CH<sub>2</sub>Cl<sub>2</sub>).

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