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 β-C-*manno*-Pyranosides Suitable for the Construction of (1 → 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.$0^{2,4}$]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_2AlSPh 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 β-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 → 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 glycosyltransferases [5][6]. They represent non-hydrolyzable epitopes [7]. Since the first synthesis of β-D-Glc*p*-CH_2(1 → 6)-D-Glc*p* by *Rouzaud* and *Sinaÿ* [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 β-C-*manno*-hexopyranosides [11], only three examples of C-disaccharides involving β-C-

[1]) Taken from the Ph.D. Thesis of *Patrick Gerber* [1]. Current address: *Serono Pharmaceutical Research Institute*, Plan-les-Ouates, Geneva, Switzerland.

mannosides are known (β-D-Man*p*-$CH_2(1\rightarrow1)$-β-D-Glc [11], β-D-Man*p*-$CH_2(1\rightarrow4)$-D-Glc-OMe [12], and β-D-Man*p*-$CH_2(1\rightarrow6)$-D-Glc [9a]).

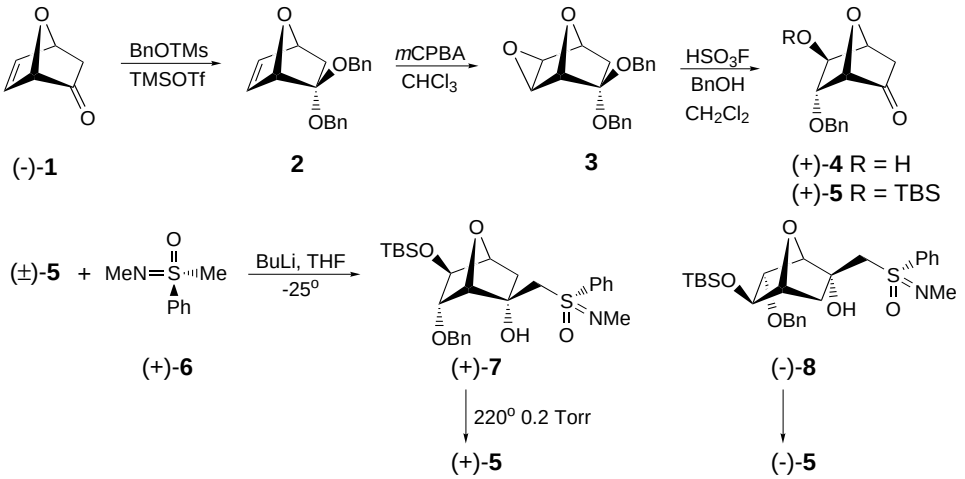
In 1993, we demonstrated [13] that enantiomerically pure 2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl acetate, a 'naked sugar of the first generation' [14], can be converted into enantiomerically pure 8-oxabicyclo[3.2.1]oct-6-en-2-one (both enantiomeric forms) and that the latter can be converted with high stereoselectivity into β-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 β-D-ManA*p*-CH(OAc)$(1\rightarrow3)$-α-L-GulA*p*-$CH(SEt)_2$ derivative. We describe here the details of this chemistry that realizes a new approach to the total synthesis of β-C-*manno*-pyranosides. We show also how these C-disaccharides can be used in the construction of $(1\rightarrow3)$-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 (±)-**4** from (±)-**1** without isolation and purification of intermediates **2** and **3**. Silylation of (±)-**4** with (*t*-Bu)Me_2SiCl and 1*H*-imidazole in DMF provided (±)-**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 (±)-**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% (^{1}H-NMR, ^{13}C-satellites). Their thermolysis (220°) delivered enantiomerically pure ketones (+)- and (−)-**5**, respectively, both in 88% yield (*Scheme 1*).

Ring enlargement of (±)-**5** was accomplished applying the method of *Saegusa* and coworkers [19]. Enol ethers (±)-**9** and (±)-**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 (±)-**11** and (±)-**12**, respectively. Oxidation of (±)-**11** with $FeCl_3$ gave enone (±)-**13** in 15–40% yield (based on ketone (±)-**5**). Better reproductibility was observed with the oxidation of (±)-**12** that furnished (±)-**13** in 57% yield. Similarly, (−)-**13** was obtained from (+)-**5** (see *Exper. Part*).

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

Scheme 1[2])



reduced with $NaBH_4$ stereoselectively into *endo*-alcohol (±)-**18** in 91% yield. Benzoylation of (±)-**18** furnished (±)-**16**. Selective deprotection of the silyl ether moiety of the latter with tetrabutylammonium fluoride provided alcohol (±)-**19**. Analogously, (−)-**19** was prepared from (−)-**13** *via* (+)-**17**, (−)-**18**, and (−)-**16**).

The structure of compounds **9**–**19** were given by their ^{1}H- and ^{13}C-NMR spectra and confirmed by their 2D-NOESY ^{1}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 δ(H) 4.42 (br. *d*, $^3J = 8.5$ Hz; coupling disappeared on addition of D_2O to the $CDCl_3$ solution) and 3.18 (br. *d*, $^3J = 3.9$ Hz) assigned to H–C(8) and H–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°, 10 days; CsF, DMF, 140°, 3 days; Al_2O_3, CH_2Cl_2, 20°; NaI, HMPA (hexamethylphosphoric triamide), 100°, 15 h) led only to decomposition products; no trace of enol ether **29** could be seen by ^{1}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 CF_3COOH/CH_2Cl_2 at room temperature. This acidic treatment induced smooth heterolysis of the epoxide

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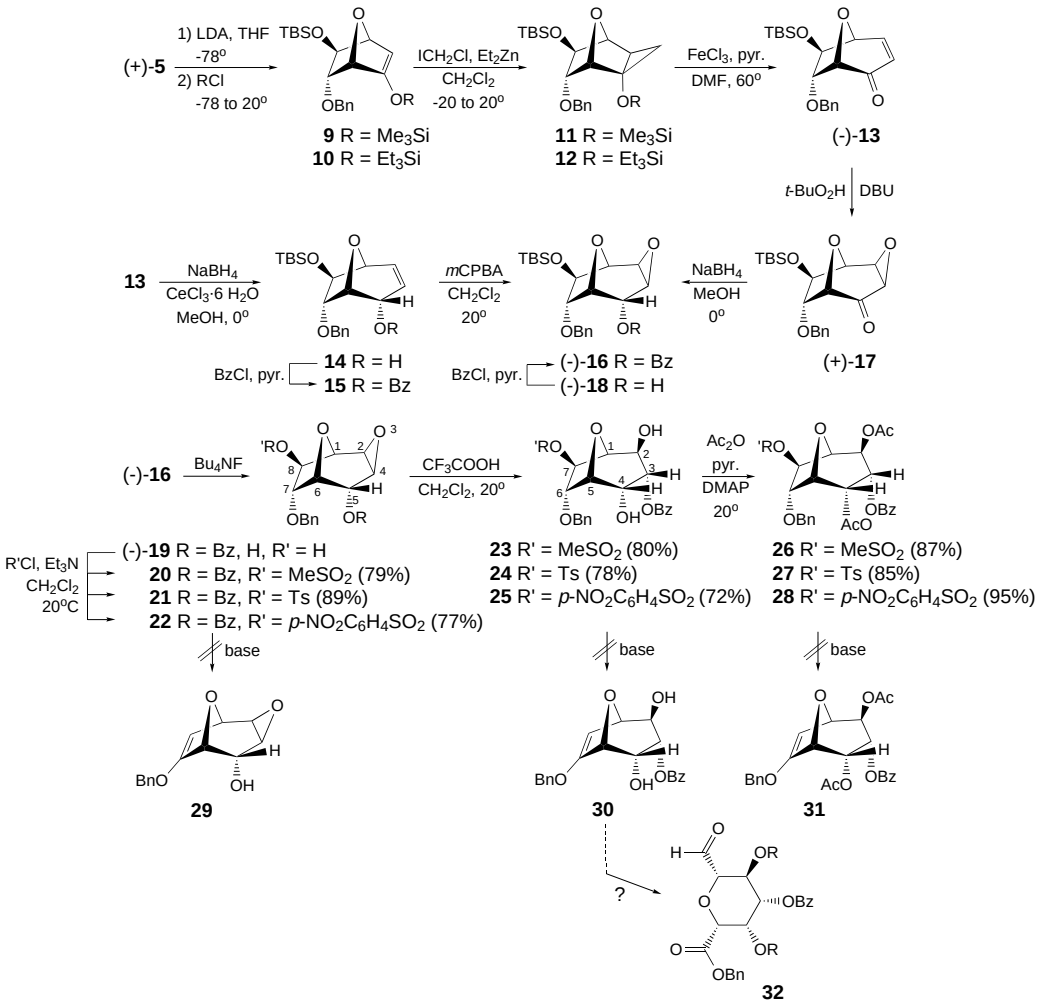
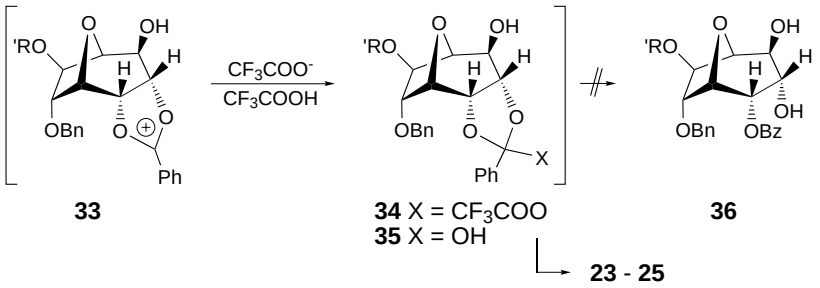
[2]) The following abbreviations are used: Bn = $PhCH_2$, Bz = PhCO, TMS = Me_3Si, TBS = *t*-$BuMe_2Si$, TfO = CF_3SO_3, *m*CPBA = 3-$ClC_6H_4CO_3H$, LDA = $Li(i\text{-}Pr)_2N$, DMAP = *N*,*N*-dimethylpyridin-4-amine, and pyr = pyridine. In the case of racemates, only one enantiomer is shown; enantiomers are characterized by the sign of optical rotation preceding their key numbers.

Scheme 2[2])



moiety with participation of the 5-*endo*-(benzoyloxy) group. Intermediate cations of type **33** are expected to be formed in these reactions (*Scheme 3*). They react with the nucleophile (CF_3COOH) 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.

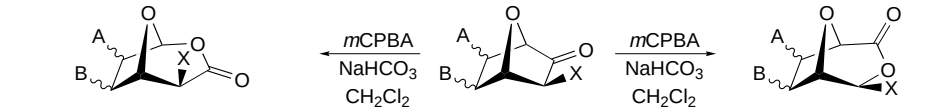
Scheme 3



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*-BuOK/THF). We were thus forced to explore another route to convert **19** into the desired '*β*-C-mannopyranosylformaldehyde' derivatives of type **32**.

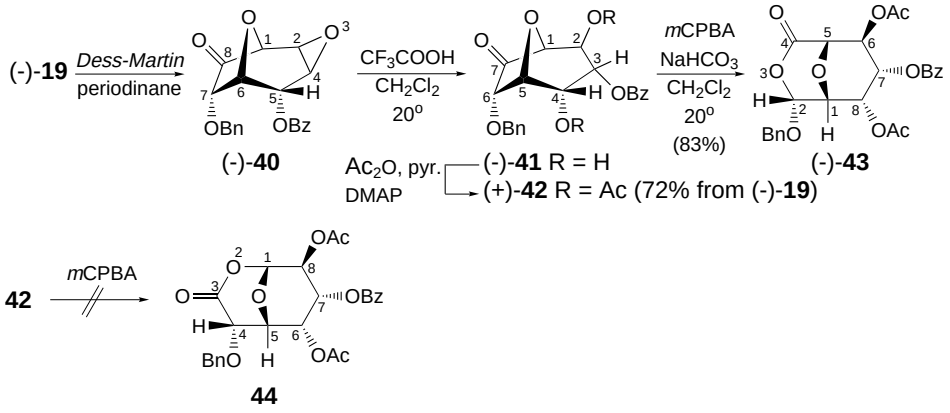
Synthesis of 2,6-Anhydro-D-*glycero*-D-*galacto*-hepturonic Acid Derivatives. – For 3-substituted 7-oxabicyclo[2.2.1]heptan-2-ones **37**, we had shown [24] that their *Baeyer-Villiger* oxidation gives the corresponding urono-6,1-lactones **38** due to preferred C(1) migration. This was not the case anymore for derivatives with 3-X substituents being a better releasing group than the ethereal 7-oxa bridge. Indeed when X = MeO or (*t*-Bu)Me_2SiO, the *Bayer-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 *α*-substituted with an acyloxy group and *α′*-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 (±)-**19** into ketone (±)-**40** (90%) with the *Dess-Martin* periodinane [26] (*Scheme 5*). Oxidation of (±)-**19** with pyridinium chlorochromate proceeded with lower yield (27%). Treatment of (±)-**40** with CF_3COOH in CH_2Cl_2 at 20° led to diol (±)-**41** in 98% yield. Esterification of (±)-**41** with Ac_2O/pyridine and DMAP (*N*,*N*-dimethylpyridin-4-amine) provided (±)-**42** (95%). Conversion of alcohol (±)-**19** into (±)-**42** could be done without isolation and purification of (±)-**40** and (±)-**41** in 79% overall yield (*Scheme 5*). Subsequent *Baeyer-Villiger* oxidation of ketone (±)-**42** with *m*CPBA (CH_2Cl_2, $NaHCO_3$, 20°) then afforded a single lactone (±)-**43**

Scheme 5[2])



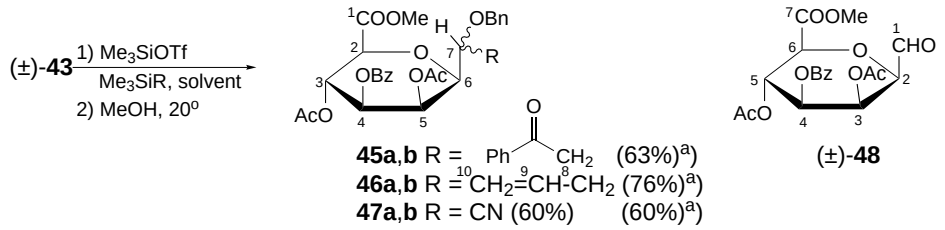
arising from the favored (benzyloxy)alkyl-group migration. The regioisomeric lactone (±)-**44** that arises from the migration of the σ(C(1)–C(8)) bond of (±)-**40** was not observed. Similarly, the enantiomer (–)-**19** afforded (–)-**43** *via* (–)-**40**, (–)-**41**, and (+)-**42**.

The ^{1}H-NMR spectrum of (±)-**43** displayed a *d* at δ(H) 4.63 (^3J(1,2) = 4.8 Hz) assigned to the acetal proton H–C(2). This assignment was confirmed by the 2D CH-COR NMR spectrum that correlated the signal at δ(C) 100.7, typical of the acetal center C(2), with the signal at δ(H) 4.63 (H–C(2)). A larger chemical shift (δ(H) 5.3–5.7) would have been expected for the bridgehead proton H–C(1) of uronolactone **44** [24]. Moreover, the ^{1}H-NMR spectrum of (±)-**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 O(9)–C(1)–C(8)–C(7)–C(6)–C(5)).

Acetals have been used as precursors for oxyalkyl-cation intermediates that can react with enoxysilanes [27][28]. The treatment of (±)-**43** with 1-phenyl-1-[(trimethylsilyl)oxy]ethene (trimethylsilyl enol ether of acetophenone) in the presence of trimethylsilyl triflate ($MeNO_2$, 20°, 17 h), followed by reaction with MeOH (20°, 17 h) led to a 1:1 mixture of diastereoisomeric β-(benzyloxy) ketones (±)-**45a** and (±)-**45b** (=**45a**,**b**) that could not be separated by column chromatography (*Scheme 6*). The reaction of (±)-**43** with Me_3SiOTf and allyltrimethylsilane (MeCN, 0°, 1 h) followed by quenching with MeOH gave a 1:4.3 mixture of (±)-**46a** and (±)-**46b** (=**46a**,**b**) that could be separated by column chromatography (overall yield 76%). The reaction of (±)-**43** with Me_3SiOTf and trimethylsilyl cyanide, followed by quenching with MeOH gave a mixture **17a**,**b** from which (±)-**47a** and (±)-**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 C–C forming reactions from acetal (±)-**43** were little diastereoselective (*Scheme 6*), we decided to transform (±)-**43** into the corresponding 2,6-anhydrohepturonic acid esters such as (±)-**48**. Attempts to generate mixtures of cyanohydrins by hydrogenolysis of **47a**,**b**, cyanohydrines that should eliminate HCN to give (±)-**48** by treatment with formaline, were not met with success. We thus chose to transform (±)-**43** into the corresponding uronic acid esters with the aldehyde protected as an acetal or a

Scheme 6[2])



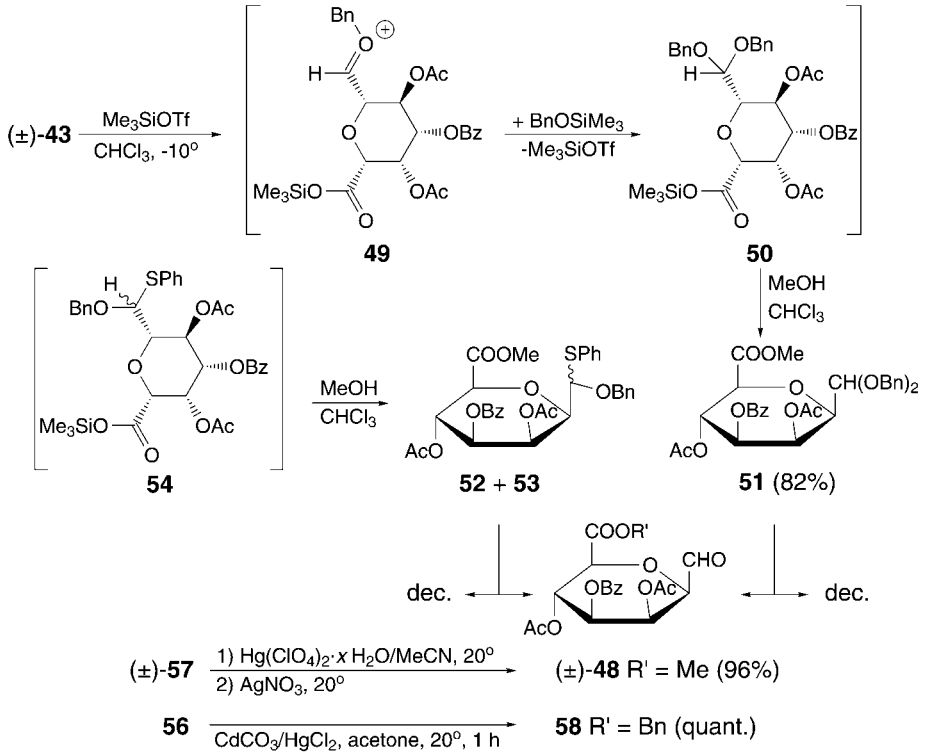
[a]) The numbering in the formula refers to **46a**,**b** and **47a**,**b**.

thioacetal. Good results were obtained with the following experiments. Treatment of (±)-**43** with $BnOSiMe_3$ and Me_3SiOTf in $CHCl_3$ at $-10°$ for 30 min, followed by quenching with MeOH (-10 to $20°$, 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 Me_3SiOBn that gives a second intermediate **50**, which is expected to react with MeOH giving **51**. With $PhSSiMe_3$ as nucleophile instead of $BnOSiMe_3$, a 1.7:1 mixture of two monothioacetals **52** and **53** was obtained in 66% yield from (±)-**43**. In this case, the hypothetical intermediate **49** reacts with $PhSSiMe_3$ 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 $Hg(OAc)_2$/MeCN, acidic hydrolysis) gave the desired product (±)-**48** in low yield as decomposition could not be aboided.

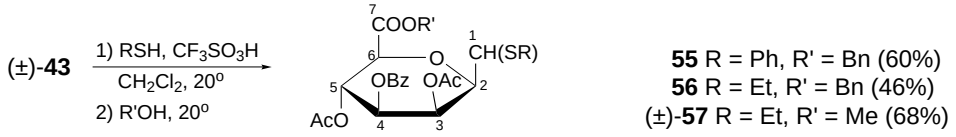
We thus decided to prepare the corresponding racemic dithioacetals **55**–**57** (*Scheme 8*). Treatment of (±)-**43** with an excess of thiophenol in the presence of triflic acid in anh. CH_2Cl_2 (20°, 1 h), followed by quenching with benzyl alcohol (20°, 18 h) provided the racemic benzyl uronate diphenyldithioacetal **55** in 60% yield. Using EtSH instead of PhSH led to **56** in 46% yield. The same procedure using $EtSH/CF_3SO_3H/CH_2Cl_2$ followed by quenching with MeOH provided (±)-**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}H-NMR spectrum, establishing the β-C-mannopyranosyl structure [29]. Treatment of dithioacetal (±)-**57** with $Hg(ClO_4)2 \cdot x\ H_2O$ (2.2 equiv., $x = 3.4$) and then with Ag_2CO_3 in MeCN gave rise to the desired aldehyde (±)-**48** in 96% yield. Similarly, (−)-**43** yielded optically active **48** *via* (−)-**57**. The benzyl uronate analog **58** was obtained by treatment of racemic **56** with $CdCO_3$ and $HgCl_2$ 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 (+)-**5** and (−)-**5** (see above).

***Nozaki-Oshima* Condensations with 8-Oxabicyclo[3.2.1]oct-3-en-2-ones.** – The addition of Me_2AlSPh to enone (±)-**13** (*Scheme 2*) (anh. THF, $-78°$) generated the

Scheme 7[2])



Scheme 8

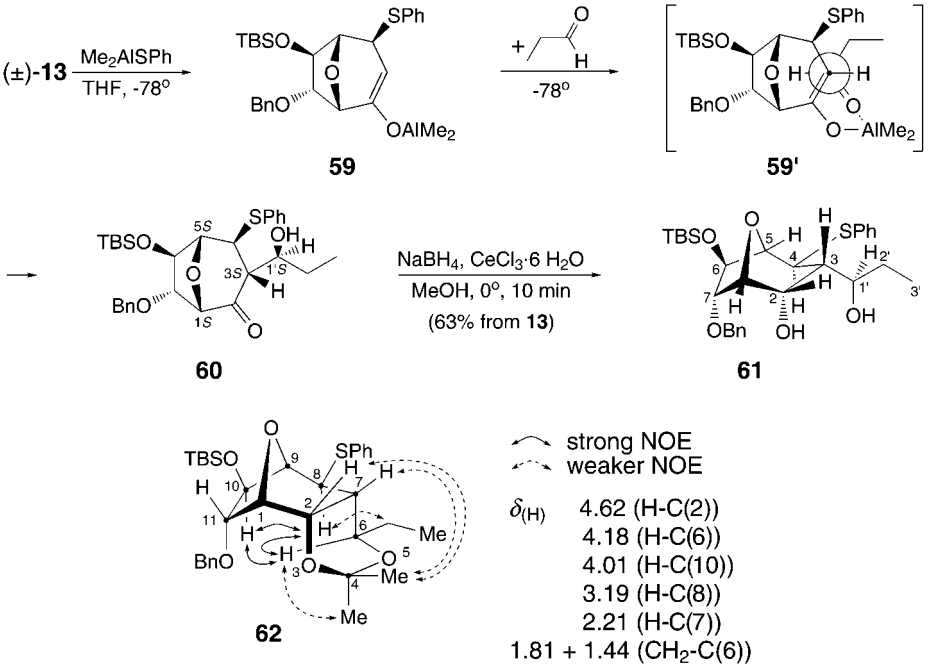


(+)-**5** *Scheme 2* (-)-**19** *Scheme 5* (-)-**43** → (-)-**57** → opt.active **48** (not isolated)

enolate **59** that was trapped with propanal (−78°, 12 h) giving a single racemic β-hydroxy ketone **60** (*Scheme 9*). The latter was not isolated but reduced directly under *Luche*'s conditions ($NaBH_4$, $CeCl_3 \cdot 6\ H_2O$, MeOH) [22] giving rise to a single racemic diol **61** isolated in 63% yield based on (±)-**13**. Out of *sixteen* possible diastereoisomers that can be formed by this reaction cascade starting from (±)-**13**, only **61** was formed. This result can be interpreted in terms of steric factors. The *exo* face of the bicyclic enone (±)-**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 β-hydroxy ketone **60**. The relative (1*RS*,1′*RS*)-configuration of the reduced β-hydroxy ketone, *i.e.*,

of **61**, arises from a closed transition structure [31] shown with **59′** (*Scheme 9*). Finally, the diastereoselective reduction of the β-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 $Me_2C(OMe)_2$/acetone and a catalytic amount of TsOH.

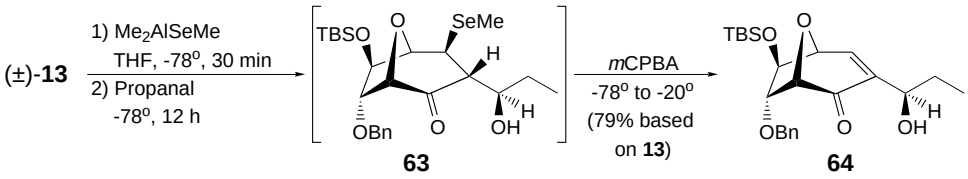
Scheme 9[2])



The coupling constants measured in the ^{1}H-NMR spectrum of **61** are consistent with an averaged boat conformation for the six-membered ring C(1)–C(2)–C(3)–C(4)–C(5)–O(8); typical $^3J(1,2) = 7.6$, $^3J(2,3) = 4.5$, $^3J(3ax,4ax) = 9.9$, 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}C-NMR spectrum of **62** showed two similar chemical shifts (δ(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 C(2)–C(7)–C(6)–O(6)–C(4)–O(3) [32]. These assignments were confirmed by the 2D ^{1}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 δ(H) 4.01 and 4.18 assigned to H–C(10) and H–C(6), respectively. The signal at δ(H) 3.19 assigned to H–C(8) also witnessed strong NOEs with δ(H) 4.01 and 4.18.

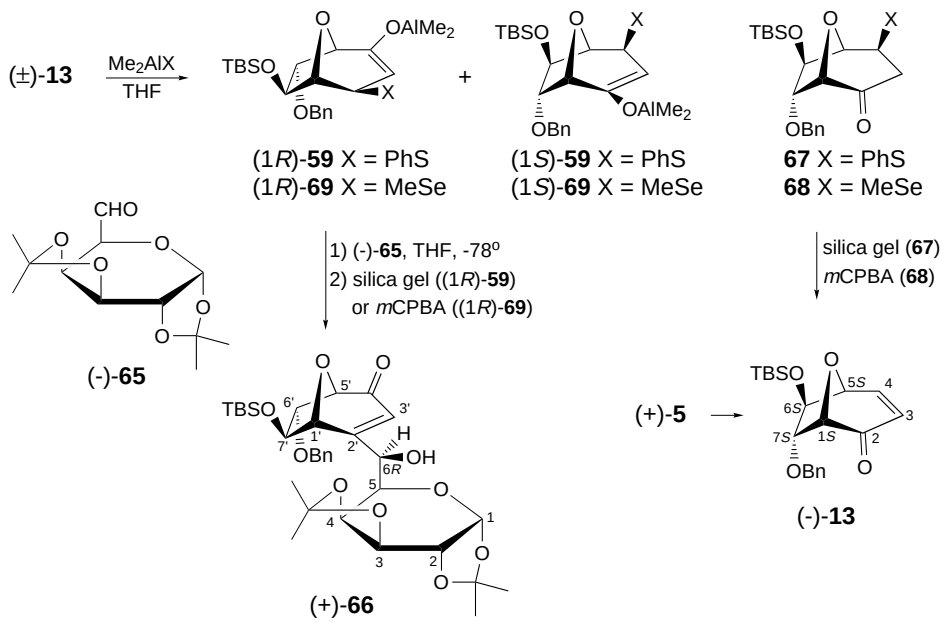
The addition of $Me_2AlSeMe$ to enone (±)-**13** (THF, −78°) followed by the addition of propanal (THF, −78°) gave a single β-hydroxy ketone **63** (*Scheme 10*) that was oxidized *in situ* with 3-chloroperbenzoic acid (−78 to −20°). This provided the stable enone **64** isolated in 79% yield (from (±)-**13**). The relative configuration at the exocyclic OH-substituted 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[2])



Enantioselective *Nozaki-Oshima* Condensation. – The successive addition of Me_2AlSPh to racemic (±)-**13** (THF, −78°, 1 h), then of enantiomerically pure aldehyde (−)-**65** derived readily from D-galactose [33] (THF, −78°, 16 h) led to a mixture from which unreacted enone **13** was recovered and product (+)-**66** isolated in 17% yield (*Scheme 11*). No other diastereoisomeric condensation product could be isolated by column chromatography. An analogous experiment using $Me_2AlSeMe$ instead of Me_2AlSPh, followed by oxidative elimination (*m*CPBA), led to (+)-**66** isolated in 27% as single product. The unreacted enone **13** was optically enriched and corresponded to (−)-**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 (−)-**65** with the bicyclic enolates **59** and **69** derived from (±)-**13** (*Scheme 11*). Our results can be interpreted in terms of the formation of enolates (1*R*)-**59** (or (1*R*)-**69**) and (1*S*)-**59** (or (1*S*)-**69**) with selective addition of (1*R*)-**59** (or (1*R*)-**69**) that leads to enone (+)-**66**. The unreacted (1*S*)-**59** is converted probably into ketone **67** that

Scheme 11[2])

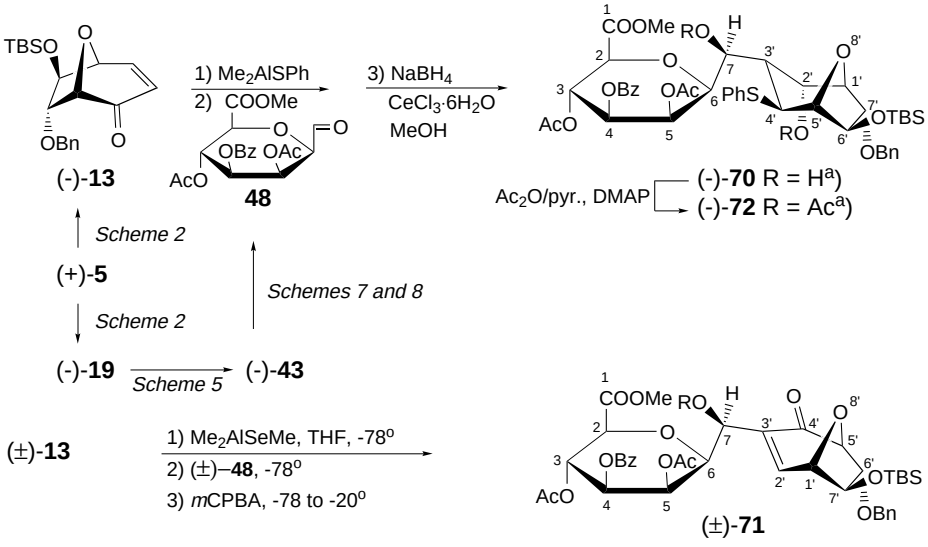


undergoes β-elimination during the chromatographic (silica gel) purification giving (−)-**13**. The unreacted (1*S*)-**69** is converted into ketone **68** that undergoes oxidative elimination (*m*CPBA) also giving the enantiomerically enriched enone (−)-**13**. The (1*S*,5*S*,6*S*,7*S*) configuration 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 β-C(1 → 3)-Linked Disaccharides. – When racemic aluminium enolate **59**, resulting from the addition of Me_2AlSPh to (±)-**13** (see above, *Scheme 9*), was trapped with racemic aldehyde (±)-**48**, a single β-hydroxy ketone was formed that was not isolated but directly reduced under *Luche*'s conditions [22] to afford a single diol (±)-**70** isolated in 56% (*Scheme 12*; yield based on dithioacetal (±)-**57**, see above *Scheme 7*). This result demonstrates the existence of chiral matching for the *Nozaki-Oshima* condensation of (±)-**13** and (±)-**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}H-NMR spectra of (±)-**70** and (−)-**70** were identical. Both (−)-**13** and (−)-**57** were derived from 7-oxanorbornanone (+)-**5** (*Schemes 1*, *2*, *5*, and *8*).

Scheme 12[2])



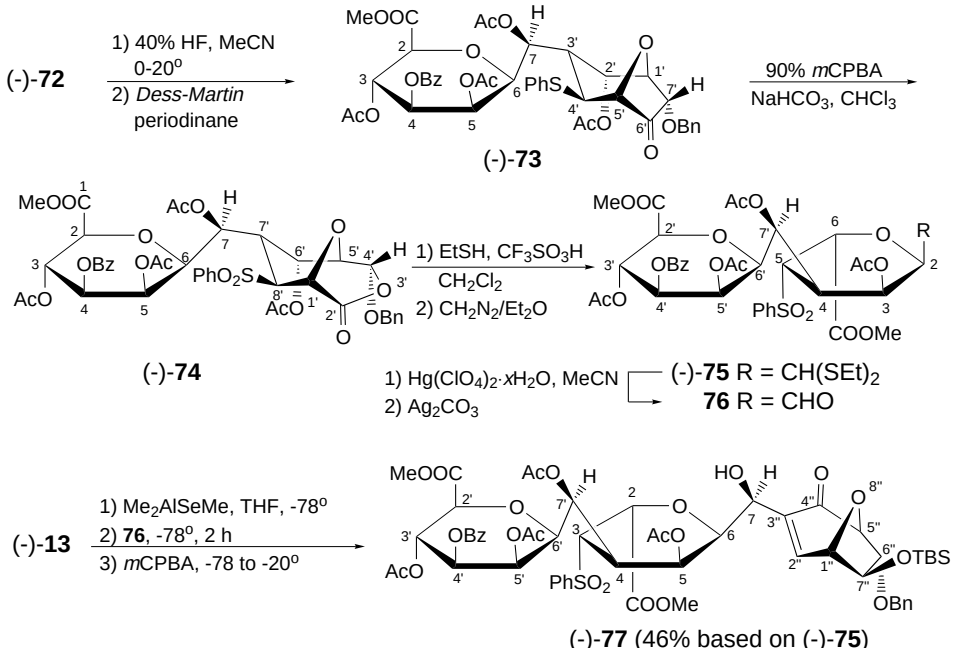
[a]) The numbering in the formula refers to (−)-**72**.

The addition of $Me_2AlSeMe$ to enone (±)-**13**, followed by trapping of the resulting aluminium enolate with (±)-**48** gave also a single β-hydroxy ketone that was not isolated but directly oxidized with *m*CPBA affording enone (±)-**71** in 49% yield (from dithioacetal (±)-**57**; *Scheme 12*). The relative configuration of the hydroxymethano linker C(7) of (±)-**70** and (±)-**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→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 $NaHCO_3$ in $CHCl_3$ (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** → (−)-**43** (*Scheme 5*). Treatment of the uronolactone (−)-**74** with EtSH under acidic conditions (CH_2Cl_2, CF_3SO_2H), 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 $Me_2AlSeMe$. 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→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 β-C-mannopyranosides including a disaccharide analog with a β-C(1→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[2])



Experimental Part

General. See [35]. The procedures described for racemic products were applied to the preparation of enantiomerically pure products. Apart from the [α] values and m.p., all other data were identical for enantiomerically pure products and the corresponding racemates. ^{1}H-NMR Signal assignments were confirmed by 2D COSY and NOESY ^{1}H-NMR data. Flash chromatography (FC): silica gel (*Merck* No. 9385, 240–400 mesh). Electron-spray mass spectromer: *Perkin Elmer AP1 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 canulated under stirring. The mixture was stirred and allowed to warm to −20° within *ca*. 3 h. Sat. aq. NH_4Cl soln. (400 ml) was added and the mixture extracted with Et_2O (400 ml, 5 ×). The combined org. extract was dried ($MgSO_4$) 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_f 0.60; d.e. >99%. $[\alpha]_{589}^{25} = +51$, $[\alpha]_{577}^{25} = +53$, $[\alpha]_{546}^{25} = +60$, $[\alpha]_{435}^{25} = +107$, $[\alpha]_{405}^{25} = +130$ ($c = 1.2$, $CHCl_3$). 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. ^{1}H-NMR (400 MHz, $CDCl_3$): 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*, $^3J(1,6) = 4.8$, H−C(1)); 4.76, 4.62 (2*d*, $^2J = 11.4$, PhCH_2O); 4.16 (br. *d*, $^3J(4,3exo) = 6.5$, H−C(4)); 4.06 (*m*, $^3J(6,1) = 4.8$, $^3J(6,5) = 2.4$, H−C(6)); 4.01 (*d*, $^3J(5,6) = 2.4$, H−C(5)); 3.51, 3.46 (2*d*, $^2J = 14.0$, CH_2−C(2)); 2.70 (*s*, S=NMe); 2.07 (*dd*, $^3J(3exo,3endo) = 13.4$, $^3J(3exo,4) = 6.5$, H_{exo}−C(3)); 1.71 (*d*, $^3J(3endo,3exo) = 13.4$, H_{endo}−C(3)); 0.89 (*s*, *t*-BuSi); 0.09, 0.08 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 139.1, 137.1 (2*s*, arom. C); 132.9, 129.3, 129.0, 128.4, 128.2, 127.9 (6*d*, $^1J(C,H) = 160$, arom. C); 91.1 (*d*, $^1J(C,H) = 150$, C(6)); 84.8 (*d*, $^1J(C,H) = 160$, C(4)); 80.0 (*s*, C(2)); 79.9 (*d*, $^1J(C,H) = 144$, C(5)); 76.8 (*d*, $^1J(C,H) = 160$, C(1)); 72.9 (*t*, $^1J(C,H) = 141$, PhCH_2O); 64.3 (*t*, $^1J(C,H) = 139$, CH_2−C(2)); 43.4 (*t*, $^1J(C,H) = 134$, C(3)); 29.1 (*q*, $^1J(C,H) = 138$, S=NMe); 25.7

(*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.7, −4.8 (2*q*, ^1J(C,H) = 118, Me$_2$Si). CI-MS (NH_3): 518 (27, $[M+1]^+$), 366 (11), 170 (26, $[PhS(=O)(=NHMe)Me]^+$), 156 (53, $[PhS(=O)(=NHMe)H]^+$), 154 (11, $[PhS(=O)(=NMe)]^+$), 125 (27), 108 (17, $BnOH^+$), 107 (36, BnO^+), 91 (100, $C_7H_7^+$), 77 (12, $C_6H_5^+$). Anal. calc. for $C_{27}H_{39}NO_5SSi$ (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%. $[\alpha]_D^{25} = -17$, $[\alpha]_{577}^{25} = -18$, $[\alpha]_{546}^{25} = -20$, $[\alpha]_{435}^{25} = -27$, $[\alpha]_{405}^{25} = -30$ (*c* = 1.0, CH_2Cl_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}H-NMR (400 MHz, $CDCl_3$): 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, PhCH_2O); 4.65 (br. *d*, ^3J(1,6) = 4.9, H−C(1)); 4.19 (br. *d*, ^3J(4,3*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, CH_2−C(2)); 2.64 (*s*, S=NMe); 2.37 (*dd*, ^3J(3*exo*,3*endo*) = 13.4, ^3J(3*exo*,4) = 6.5, H_{exo}−C(3)); 1.68 (*d*, ^3J(3*exo*,3*endo*) = 13.4, H_{endo}−C(3)); 0.88 (*s*, *t*-BuSi); 0.07 (*s*, Me$_2$Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 139.2, 136.8 (2*s*, arom. C); 132.6, 129.1, 129.0, 128.4, 128.1, 128.0 (6*d*, ^1J(C,H) = 160, arom. C); 91.3 (*d*, ^1J(C,H) = 151, C(6)); 84.9 (*d*, ^1J(C,H) = 161, C(4)); 80.3 (*s*, C(2)); 79.8 (*d*, ^1J(C,H) = 145, C(5)); 76.3 (*d*, ^1J(C,H) = 166, C(1)); 73.1 (*t*, ^1J(C,H) = 143, Ph*C*H$_2$O); 63.8 (*t*, ^1J(C,H) = 138, *C*H$_2$−C(2)); 42.6 (*t*, ^1J(C,H) = 135, C(3)); 29.1 (*q*, ^1J(C,H) = 137, S=NMe*C*H$_3$); 25.7 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si)); −4.7, −4.8 (2*q*, ^1J(C,H) = 118, Me$_2$Si). CI-MS (NH_3): 518 (44, $[M+1]^+$), 366 (23), 170 (51, $[PhS(=O)(=NHMe)Me]^+$), 156 (47, $[PhS(=O)(=NHMe)H]^+$), 154 (18, $[PhS(=O)(=NMe)]^+$), 125 (27), 108 (24, $BnOH^+$), 107 (28, BnO^+), 91 (100, $C_7H_7^+$), 77 (14, $C_6H_5^+$). Anal. calc. for $C_{27}H_{39}NO_5SSi$ (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_2O 4:1 → 3:2, then CH_2Cl_2/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**: $[\alpha]_D^{25} = 53$, $[\alpha]_{577}^{25} = 56$, $[\alpha]_{546}^{25} = 63$, $[\alpha]_{435}^{25} = 102$, $[\alpha]_{405}^{25} = 119$ (*c* = 1.3, CH_2Cl_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**: $[\alpha]_D^{25} = -51$, $[\alpha]_{577}^{25} = -55$, $[\alpha]_{546}^{25} = -62$, $[\alpha]_{435}^{25} = -101$, $[\alpha]_{405}^{25} = -119$ (*c* = 0.7, CH_2Cl_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)$_2$NH (0.64 ml, 457 mg, 4.52 mmol) in anh. THF (10 ml) cooled to −15° in a *Schlenk* tube. After stirring at −15° for 15 min, the soln. was cooled to −78°. A soln. of (±)-**5** (1.14 g, 3.27 mmol) in anh. THF (10 ml) cooled to −78° was canulated into the Li(i-Pr)$_2$N soln. under stirring. After stirring at −78° for 90 min, Me_3SiCl (0.8 ml, 687 mg, 6.33 mmol) was added dropwise and the mixture stirred at −78° for 2 h, then allowed to warm to 20°, 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°. IR (KBr): 2955, 2855, 1625, 1470, 1350, 1320, 1255, 1225, 1105, 1030, 950, 865, 775, 700, 665. ^{1}H-NMR (400 MHz, C_6D_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, PhCH_2O); 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*, Me$_2$Si); 0.12 (*s*, Me$_3$Si). ^{1}H-NMR (400 MHz, $CDCl_3$): 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, PhCH_2O); 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*, Me$_3$Si); 0.11, 0.10 (2*s*, Me$_2$Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 162.0 (*s*, C(3)); 137.9 (*s*, arom. C); 128.2, 127.9, 127.7 (3*d*, ^1J(C,H) = 160, arom. C); 100.1 (*d*, ^1J(C,H) = 173, C(3)); 86.5 (*d*, ^1J(C,H) = 164, C(4)); 84.7 (*d*, ^1J(C,H) = 152, C(6)); 79.5 (*d*, ^1J(C,H) = 152, C(5)); 78.8 (*d*, ^1J(C,H) = 163, C(1)); 72.3 (*t*, ^1J(C,H) = 141, Ph*C*H$_2$O); 25.9 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 18.2 (*s*, Me$_3$*C*Si); −0.4 (*q*, ^1J(C,H) = 120, Me$_3$Si); −4.6, −4.7 (2*q*, ^1J(C,H) = 118, Me$_2$Si). Anal. calc. for $C_{22}H_{36}O_4Si_2$ (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_3SiCl instead of Me_3SiCl: 100% of (±)-**10**. The crude product was used directly in the next step. ^{1}H-NMR (400 MHz, $CDCl_3$): 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, PhCH_2O); 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*, (*Me*CH_2)$_3$Si); 0.91 (*s*, *t*-BuSi); 0.73–0.66 (*m*, (MeCH_2)$_3$Si); 0.11, 0.10 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 162.4 (*s*, C(3)); 137.9 (*s*, arom. C); 128.2, 127.8, 127.6 (3*d*, ^1J(C,H) = 160, arom. C); 100.2 (*d*, ^1J(C,H) = 170, C(3)); 86.5 (*d*, ^1J(C,H) = 166, C(4)); 84.6 (*d*, ^1J(C,H) = 152, C(6)); 79.5 (*d*, ^1J(C,H) = 151, C(5)); 78.9 (*d*, ^1J(C,H) = 163, C(1)); 72.3 (*t*, ^1J(C,H) = 141, PhCH_2O); 25.9 (*q*, ^1J(C,H) = 125, Me_3CSi); 18.2 (*s*, Me_3CSi); 6.5 (*q*, ^1J(C,H) = 126, (*Me*CH_2)$_3$Si); 4.4 (*t*, ^1J(C,H) = 117, (MeCH_2)$_3$Si); –4.6, –4.7 (2*q*, ^1J(C,H) = 118, Me_2Si).

*(1*RS*,2*RS*,4*SR*,5*RS*,6*RS*,7*RS*)-7-*endo-*(Benzyloxy)-6-*exo-*[[(*tert-*butyl)dimethylsilyl]oxy]-2-*endo-*[(trimethylsilyl)oxy]-8-oxatricyclo[3.2.1.0^{2,4}]octane* ((±)-**11**). Et_2Zn (1M in hexane; 6.3 ml, 6.3 mmol) was added dropwise to a stirred soln. of ICH_2Cl (0.92 ml, 2.22 g, 12.6 mmol) in anh. $ClCH_2CH_2Cl$ (20 ml) cooled to –10° under N_2. After stirring at –10° for 30 min, the mixture was cooled to –30°. A soln. of (±)-**9** (1.33 g, 3.15 mmol) in anh. $ClCH_2CH_2Cl$ (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_2O (20 ml) and sat. aq. NH_4Cl soln. (20 ml) were added under stirring. The aq. layer was extracted with CH_2Cl_2 (4 × 35 ml) and the combined org. extract dried ($MgSO_4$) 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-*(Benzyloxy)-6-*exo-*[[(*tert-*butyl)dimethylsilyl]oxy]-2-*endo-*[(triethylsilyl)oxy]-8-oxatricyclo[3.2.1.0^{2,4}]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-*(Benzyloxy)-6-*exo-*[[(*tert-*butyl)dimethylsilyl]oxy]-8-oxabicyclo[3.2.1]oct-3-en-2-one* ((±)-**13**). Anh. pyridine (14 ml, 13.8 g, 174 mmol), then (±)-**12** (14.9 g, 32.9 mmol) in anh. DMF (100 ml) were added to an anh. $FeCl_3$ (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 1N HCl (2 × 400 ml), sat. aq. $NaHCO_3$ soln. (300 ml), and brine (300 ml). The aq. phases were extracted with AcOEt (2 × 400 ml) and the combined org. extracts dried ($MgSO_4$) and evaporated at 10^{-2} Torr. The dark residue was purified by FC (7.5 × 23 cm, light petroleum ether/Et_2O 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_2Cl_2/Et_2O 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. ^{1}H-NMR (400 MHz, $CDCl_3$): 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_2O); 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_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 194.1 (*s*, C(2)); 147.9 (*d*, ^1J(C,H) = 163, C(4)); 136.8 (*s*, arom. C); 128.5, 128.4, 128.2, 128.1 (4*d*, ^1J(C,H) = 160, arom. C, C(3)); 86.3 (*d*, ^1J(C,H) = 153, C(7)); 83.6 (*d*, ^1J(C,H) = 157, C(1)); 81.3 (*d*, ^1J(C,H) = 158, C(5)); 79.6 (*d*, ^1J(C,H) = 155, C(6)); 73.7 (*t*, ^1J(C,H) = 144, PhCH_2O); 25.7 (*q*, ^1J(C,H) = 125, Me_3CSi); 18.0 (*s*, Me_3C); –4.9 (*q*, ^1J(C,H) = 119, Me_2Si). CI-MS (NH_3): 360 (1, M^+), 211 (10), 187 (7), 97 (12), 91 (100, $C_7H_7^+$), 75 (8), 74 (6), 73 (18). Anal. calc. for $C_{20}H_{28}O_4Si$ (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-*(Benzyloxy)-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. $[\alpha]_D^{25} = -124$, $[\alpha]_{577}^{25} = -131$, $[\alpha]_{546}^{25} = -161$, $[\alpha]_{435}^{25} = -461$, $[\alpha]_{405}^{25} = -915$ ($c = 0.9$, $CHCl_3$).

*(1*RS*,2*SR*,5*SR*,6*SR*,7*SR*)-7-*endo-*(Benzyloxy)-6-*exo-*[[(*tert-*butyl)dimethylsilyl]oxy]-8-oxabicyclo[3.2.1]-oct-3-en-2-*endo-*ol* ((±)-**14**). $CeCl_3 \cdot 6H_2O$ (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°. $NaBH_4$ (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. $NaHCO_3$ soln. were added. The mixture was extracted with AcOEt (50 ml, then 3 × 25 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by FC (3 × 13 cm, light petroleum ether/Et_2O 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. ^{1}H-NMR (400 MHz, $CDCl_3$): 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_2O); 4.62 (*m*, $^3J(1,7) = 6.9$, $^4J(1,3) = 1.4$, ^3J(2,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(OH,2) = 11.6, OH–C(2)); 0.93 (*s*, *t*-BuSi); 0.14, 0.12 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 136.6 (*s*, arom. C); 132.6 (*d*, ^1J(C,H) = 164, C(3)); 128.7, 128.2, 127.6 (3*d*, ^1J(C,H) = 160, arom. C); 127.1 (*d*, ^1J(C,H) = 163, C(4)); 93.0 (*d*, ^1J(C,H) = 151, C(7)); 81.4 (*d*, ^1J(C,H) = 149, C(6)); 80.3 (*d*, ^1J(C,H) = 162, C(5)); 75.5 (*d*, ^1J(C,H) = 150, C(1)); 73.6 (*t*, ^1J(C,H) = 146, PhCH_2O); 68.8 (*d*, ^1J(C,H) = 147, C(2)); 25.7 (*q*, ^1J(C,H) = 125,

Me$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.5, −4.8 (2*q*, ^1J(C,H) = 118, Me$_2$Si). CI-MS (NH_3): 380 (100, $[M+NH_4]^+$), 363 (15, $[M+H]^+$). Anal. calc. for $C_{20}H_{30}O_4Si$ (362.59): 66.25, H 8.36, Si 7.75; found: 66.19, H 8.47, Si 7.87.

*(1*RS*,2*SR*,5*SR*,6*SR*,7*SR*)-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. H_2O (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. $NaHCO_3$ soln. (3 × 15 ml), sat. aq. $NaHCO_3$ soln. (3 × 15 ml), and brine (15 ml). The aq. phases were extracted with AcOEt (2 × 30 ml) and the combined org. extracts dried ($MgSO_4$) 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}H-NMR (400 MHz, C_6D_6): 8.09, 7.22, 7.12, 6.97 (4*m*, 2 H, 2 H, 4 H, 2 H, arom. H); 6.29 (*m*, ^3J(2,1) = 4.7, ^3J(2,3) = 1.7, ^4J(2,4) = 2.1, H−C(2)); 5.81 (*ddd*, ^3J(3,4) = 10.0, ^3J(3,2) = 1.7, ^4J(3,1) = 1.6, H−C(3)); 5.66 (*ddd*, ^3J(4,3) = 10.00, ^3J(4,5) = 4.1, ^4J(4,2) = 2.1, H−C(4)); 5.01 (*ddd*, ^3J(1,7) = 6.4, ^3J(1,2) = 4.7, ^4J(1,3) = 1.6, H−C(1)); 4.42 (*s*, PhCH_2O); 4.38 (br. *d*, ^3J(7,1) = 6.4, H−C(7)); 4.37 (br. *s*, H−C(6)); 4.18 (br. *d*, ^3J(5,4) = 4.1, H−C(5)); 0.96 (*s*, *t*-BuSi); 0.05, 0.03 (2*s*, Me$_2$Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 166.4 (*s*, C=O); 137.7, 129.9 (2*s*, arom. C); 132.9, 129.8 (2*d*, ^1J(C,H) = 160, arom. C); 129.3 (*d*, ^1J(C,H) = 154, C(4)); 128.2, 127.6, 127.5, 127.4 (4*d*, ^1J(C,H) = 160, arom. C, C(3)); 91.8 (*d*, ^1J(C,H) = 148, C(7)); 82.3 (*d*, ^1J(C,H) = 150, C(6)); 80.4 (*d*, ^1J(C,H) = 160, C(5)); 75.3 (*d*, ^1J(C,H) = 152, C(1)); 73.5 (*t*, ^1J(C,H) = 142, Ph*C*H$_2$O); 70.3 (*d*, ^1J(C,H) = 158, C(2)); 25.7 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.7, −4.8 (2*q*, ^1J(C,H) = 118, Me$_2$Si). ES-MS (pos. mode): 489 (100, $[M+Na]^+$), 484 (50, $[M+NH_4]^+$), 467 (15, $[M+H]^+$). Anal. calc. for $C_{27}H_{34}O_5Si$ (466.70): C 69.48, H 7.36, Si 6.02; found: C 69.64, H 7.37, Si 5.98.

*(1*RS*,2*RS*,4*SR*,5*SR*,6*RS*,7*RS*,8*SR*)-7-*endo-*(Benzyloxy)-8-*exo-*{[(*tert-*butyl)dimethylsilyl]oxy}-3,9-dioxatricyclo[4.2.1.0^{2,4}]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}H-NMR (400 MHz, $CDCl_3$): 7.90, 7.52, 7.31–7.21 (3*m*, 2 H, 1 H, 7 H, arom. H); 5.32 (*dd*, ^3J(5,6) = 5.2, ^4J(5,2) = 0.7, H−C(5)); 4.78 (*ddd*, ^3J(6,7) = 6.7, ^3J(6,5) = 5.2, ^4J(6,4) = 1.6, H−C(6)); 4.57, 4.53 (2*d*, ^2J = 11.8, PhCH_2O); 4.42 (*m*, ^3J(8,7) = 1.0, H−C(8)); 4.27 (*m*, ^3J(1,2) = 1.2, ^4J(1,7) = 1.7, ^4J(1,4) = 0.6, H−C(1)); 4.20 (*ddd*, ^3J(7,6) = 6.7, ^3J(7,8) = 1.0, ^4J(7,1) = 1.7, H−C(7)); 3.42 (*ddd*, ^3J(4,2) = 3.9, ^4J(4,6) = 1.6, ^4J(4,1) = 0.6, H−C(4)); 3.14 (*ddd*, ^3J(2,4) = 3.9, ^3J(2,1) = 1.2, ^4J(2,5) = 0.7, H−C(2)); 0.91 (*s*, *t*-BuSi); 0.13, 0.12 (2*s*, Me$_2$Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 165.7 (*s*, C=O); 137.5, 129.4 (2*s*, arom. C); 133.1, 129.8, 128.3, 128.2, 127.7, 127.4 (6*d*, ^1J(C,H) = 160, arom. C); 88.3 (*d*, ^1J(C,H) = 148, C(7)); 79.7 (*d*, ^1J(C,H) = 141, C(8)); 78.8 (*d*, ^1J(C,H) = 158, C(1)); 73.5 (*t*, ^1J(C,H) = 140, Ph*C*H$_2$O); 73.1 (*d*, ^1J(C,H) = 157, C(6)); 67.5 (*d*, ^1J(C,H) = 154, C(5)); 52.7 (*d*, ^1J(C,H) = 183, C(4)); 49.0 (*d*, ^1J(C,H) = 178, C(2)); 25.7 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.6, −4.7 (2*q*, ^1J(C,H) = 118, Me$_2$Si). CI-MS (NH_3): 483 (0.5, $[M+1]^+$), 425 (7, $[M-C_4H_9]^+$), 105 (37, Bz^+), 91 (100, $C_7H_7^+$), 77 (12, $C_6H_5^+$). Anal. calc. for $C_{27}H_{34}O_6Si$ (482.70): C 67.18, H 7.11, Si 5.82; found: C 67.24, H 7.12, Si 5.82.

*(1*S*,2*S*,4*R*,5*R*,6*S*,7*S*,8*R*)-7-*endo-*(Benzyloxy)-8-*exo-*{[(*tert-*butyl)dimethylsilyl]oxy}-3,9-dioxatricyclo[4.2.1.0^{2,4}]-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°. $[\alpha]_D^{25} = -20$, $[\alpha]_{577}^{25} = -21$, $[\alpha]_{546}^{25} = -24$, $[\alpha]_{435}^{25} = -38$, $[\alpha]_{405}^{25} = -45$ (c = 0.8, CH_2Cl_2).

*(1*RS*,2*SR*,4*SR*,6*RS*,7*RS*,8*SR*)-7-*endo-*(Benzyloxy)-8-*exo-*{[(*tert-*butyl)dimethylsilyl]oxy}-3,9-dioxatricyclo[4.2.1.0^{2,4}]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. CH_2Cl_2 (100 ml) was stirred at 20° for 3 h. After the addition of $CHCl_3$ (100 ml), the soln. was washed successively with 10% aq. $NaHSO_3$ soln. (150 ml), 1N HCl (150 ml), and sat. aq. $NaHCO_3$ soln. (150 ml). The aq. phases were extracted with $CHCl_3$ (3 × 150 ml) and the combined org. extracts dried ($MgSO_4$) 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}H-NMR (400 MHz, $CDCl_3$): 7.38–7.26 (*m*, 5 arom. H); 4.67 (br. *d*, ^3J(6,7) = 7.2, H−C(6)); 4.53, 4.38 (2*d*, ^2J = 11.1, PhCH_2O); 4.43 (*m*, ^3J(1,2) = 1.7, ^4J(1,7) = 1.2, H−C(1)); 4.35 (br. *d*, ^3J(8,7) = 1.3, H−C(8)); 4.21 (*ddd*, ^3J(7,6) = 7.2, ^3J(7,8) = 1.3, ^4J(7,1) = 1.2, H−C(7)); 3.40 (*dd*, ^3J(2,4) = 3.7, ^3J(2,1) = 1.7, H−C(2)); 3.30 (br. *d*, ^3J(4,2) = 3.7, H−C(4)); 0.91 (*s*, *t*-BuSi); 0.13, 0.12 (2*s*, Me$_2$Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 197.9 (*s*, C(5)); 136.3 (*s*, arom. C); 128.5, 128.2

(2*d*, ^1J(C,H) = 160, arom. C); 88.6 (*d*, ^1J(C,H) = 153, C(7)); 82.9 (*d*, ^1J(C,H) = 161, C(6)); 79.0 (*d*, ^1J(C,H) = 158, C(1)); 78.7 (*d*, ^1J(C,H) = 146, C(8)); 73.3 (*t*, ^1J(C,H) = 141, Ph*C*H$_2$O); 52.0 (*d*, ^1J(C,H) = 188, C(4)); 49.0 (*d*, ^1J(C,H) = 183, C(2)); 25.6 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); −4.8, −4.9 (2*q*, ^1J(C,H) = 118, Me$_2$Si). CI-MS (NH$_3$): 394 (31, $[M+18]^+$), 319 (10, $[M-C_4H_9]^+$), 185 (11), 129 (11), 108 (25, BnOH$^+$), 91 (100, $C_7H_7^+$). Anal. calc. for $C_{20}H_{28}O_5Si$ (376.57): C 63.79, H 7.51, Si 7.46; found: C 63.84, H 7.46, Si 7.35.

*(1*S*,2*R*,4*R*,6*S*,7*S*,8*R*)-7-*endo*-(Benzyloxy)-8-*exo*-[[(*tert*-*butyl*)*dimethylsilyl*]*oxy*]-3,9-*dioxatricyclo*[4.2.1.0^{2,4}]-*nonan*-5-*one* ((+)-**17**). As described for (±)-**17**, with (−)-**13**. Colorless oil. $[\alpha]_D^{25} = 29$, $[\alpha]_{577}^{25} = 31$, $[\alpha]_{546}^{25} = 35$, $[\alpha]_{435}^{25} = 67$, $[\alpha]_{405}^{25} = 87$ ($c = 1.1$, CH_2Cl_2).

*(1*RS*,2*RS*,4*RS*,5*SR*,6*SR*,7*RS*,8*SR*)-7-*endo*-(Benzyloxy)-8-*exo*-[[(*tert*-*butyl*)*dimethylsilyl*]*oxy*]-3,9-*dioxatricyclo*[4.2.1.0^{2,4}]*nonan*-5-*endo*-*ol* ((±)-**18**). A mixture of (±)-**17** (4.5 g, 11.9 mmol), MeOH (200 ml), and $NaBH_4$ (0.48 g, 12.7 mmol) was stirred at 0° for 30 min. H_2O (180 ml) and brine (180 ml) were added, and the mixture was extracted with Et_2O (500 ml, then 4 × 250 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated: 3.83 g (85%) of (±)-**18**. Yellowish oil that can be used directly in the next step. An anal. sample was obtained by FC (0.5 × 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}H-NMR (400 MHz, $CDCl_3$): 7.38, 7.30 (2*m*, 3 H, 2 H, arom. H); 4.77, 4.55 (2*d*, $^2J = 11.4$, PhC*H*$_2$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 (2*s*, Me$_2$Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 136.1 (*s*, arom. C); 128.8, 128.5, 127.7 (3*d*, ^1J(C,H) = 160, arom. C); 90.1 (*d*, ^1J(C,H) = 152, C(7)); 79.0 (*d*, ^1J(C,H) = 156, C(1)); 78.8 (*d*, ^1J(C,H) = 141, C(8)); 73.6 (*t*, ^1J(C,H) = 148, Ph*C*H$_2$O); 73.0 (*d*, ^1J(C,H) = 156, C(6)); 66.4 (*d*, ^1J(C,H) = 152, C(5)); 54.9 (*d*, ^1J(C,H) = 181, C(4)); 49.1 (*d*, ^1J(C,H) = 177, C(2)); 25.6 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); −4.4, −4.7 (2*q*, ^1J(C,H) = 119, Me$_2$Si). CI-MS (NH$_3$): 396 (1, $[M+18]^+$), 379 (3, $[M+1]^+$), 321 (14, $[M-C_4H_9]^+$), 288 (2, $[M-Bn+H]^+$), 108 (9, BnOH$^+$), 91 (100, $C_7H_7^+$). Anal. calc. for $C_{20}H_{30}O_5Si$ (378.59): C 63.45, H 8.00, Si 7.42; found: C 63.31, H 7.93, Si 7.42.

*(1*S*,2*S*,4*S*,5*R*,6*R*,7*S*,8*R*)-7-*endo*-(Benzyloxy)-8-*exo*-[[(*tert*-*butyl*)*dimethylsilyl*]*oxy*]-3,9-*dioxatricyclo*[4.2.1.0^{2,4}]-*nonan*-5-*endo*-*ol* ((−)-**18**). As described for (±)-**18**, with (+)-**17**. Colorless oil. $[\alpha]_D^{25} = -21$, $[\alpha]_{577}^{25} = -22$, $[\alpha]_{546}^{25} = -25$, $[\alpha]_{435}^{25} = -40$, $[\alpha]_{405}^{25} = -47$ ($c = 0.9$, CH_2Cl_2).

*(1*RS*,2*SR*,4*RS*,5*SR*,6*SR*,7*RS*,8*RS*)-7-*endo*-(Benzyloxy)-8-*exo*-*hydroxy*-3,9-*dioxatricyclo*[4.2.1.0^{2,4}]*non*-5-*endo*-*yl Benzoate* ((±)-**19**). A mixture of (±)-**16** (4.89 g, 10.1 mmol), anh. THF (170 ml), and Bu_4NF (1M in THF; 12.6 ml, 12.6 mmol) was stirred at 0° for 3.5 h. After the addition of H_2O (600 ml), the mixture was extracted with CH_2Cl_2 (2 × 500 ml, then 4 × 250 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue crystallized from Et_2O (−20°, 24 h): 1.90 g of white crystals. The mother liquor was evaporated and the residue purified by FC (4.5 × 18 cm, light petroleum ether/AcOEt 2:3): 0.79 g of colorless crystals. Global yield: 2.69 g (66% based on (±)-**13**) of (±)-**16**. 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}H-NMR (400 MHz, $CDCl_3$): 7.92, 7.54, 7.31 (3*m*, 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 (2*d*, $^2J = 11.8$, PhC*H*$_2$O); 4.42 (br. *d*, $^3J(8,OH) = 8.5$, 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*, $^3J(OH,8) = 8.5$, OH−C(8)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 165.7 (*s*, C=O); 137.4, 129.4 (2*s*, arom. C); 133.2, 129.8, 128.4, 128.3, 127.8, 127.4 (6*d*, ^1J(C,H) = 160, arom. C); 87.4 (*d*, ^1J(C,H) = 149, C(7)); 78.8 (*d*, ^1J(C,H) = 164, C(1)); 78.4 (*d*, ^1J(C,H) = 150, C(8)); 73.4 (*d*, ^1J(C,H) = 159, C(6)); 73.4 (*t*, ^1J(C,H) = 141, Ph*C*H$_2$O); 67.4 (*d*, ^1J(C,H) = 152, C(5)); 53.0 (*d*, ^1J(C,H) = 184, C(4)); 48.8 (*d*, ^1J(C,H) = 179, C(2)). CI-MS (NH$_3$): 369 (2, $[M+1]^+$), 263 (7, $[M-Bz]^+$), 105 (100, Bz$^+$), 91 (66, $C_7H_7^+$), 81 (11, $C_5H_5O^+$), 77 (20, $C_6H_5^+$). Anal. calc. for $C_{21}H_{20}O_6$ (368.38): C 68.46, H 5.48; found: C 68.53, H 5.54.

*(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^{2,4}]*non*-5-*endo*-*yl Benzoate* ((−)-**19**). As described for (±)-**19**, with (−)-**16**. Yield 75% based on (−)-**13**. White solid. M.p. 95–96°. $[\alpha]_D^{25} = -46$, $[\alpha]_{577}^{25} = -48$, $[\alpha]_{546}^{25} = -55$, $[\alpha]_{435}^{25} = -91$, $[\alpha]_{405}^{25} = -109$ ($c = 1.0$, CH_2Cl_2).

*(1*RS*,2*RS*,4*SR*,5*RS*,6*RS*,7*RS*,8*SR*)-7-*endo*-(Benzyloxy)-8-*exo*-[(*methylsulfonyl*)*oxy*]-3,9-*dioxatricyclo*-[4.2.1.0^{2,4}]*non*-5-*endo*-*yl Benzoate* (**20**). A mixture of (±)-**19** (150 mg, 0.41 mmol), anh. CH_2Cl_2 (3 ml), $MeSO_2Cl$ (40 µl, 0.52 mmol), and Et_3N (85 µl, 0.61 mmol) was stirred at 20° for 30 min. After the addition of CH_2Cl_2 (30 ml), the soln. was washed successively with 1N HCl (25 ml) and sat. aq. $NaHCO_3$ soln. (25 ml). The aq. phases were extracted with CH_2Cl_2 (2 × 30 ml) and the combined org. extracts dried ($MgSO_4$) and evaporated. The residue was purified by FC (1 × 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}H-NMR (400 MHz, $CDCl_3$): 7.91, 7.55, 7.35–7.23 (3*m*, 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 (2*d*, $^2J = 11.8$, PhCH_2O); 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*, $MeSO_2$). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 165.6 (*s*, C=O), 136.8, 129.2, (2*s*, arom. C); 133.3, 129.8, 128.4, 128.0, 127.7 (5*d*, ^1J(C,H) = 160, arom. C); 84.2 (*d*, ^1J(C,H) = 151, C(7)); 83.2 (*d*, ^1J(C,H) = 155, C(8)); 76.6 (*d*, ^1J(C,H) = 164, C(1)); 73.6 (*t*, ^1J(C,H) = 141, Ph*C*H$_2$O); 73.0 (*d*, ^1J(C,H) = 159, C(6)); 66.9 (*d*, ^1J(C,H) = 154, C(5)); 52.6 (*d*, ^1J(C,H) = 186, C(4)); 48.1 (*d*, ^1J(C,H) = 181, C(2)); 38.7 (*q*, ^1J(C,H) = 140, $MeSO_2$). CI-MS (NH_3): 447 (13, $[M+H]^+$), 367 (1, $[M-Ms]^+$), 341 (32, $[M-Bz]^+$), 261 (6, $[M-Bn-OMs+H]^+$), 235 (5, $[M-Bn-OBz+H]^+$), 122 (5, $BzOH^+$), 105 (82, Bz^+), 91 (100, $C_7H_7^+$), 77 (24, $C_6H_5^+$). Anal. calc. for $C_{22}H_{22}O_8S$ (446.51): C 59.13, H 4.98, S 7.18; found: C 59.31, H 4.99, S 7.12.

*(1*RS*,2*RS*,4*SR*,5*RS*,6*RS*,7*RS*,8*SR*)-7*-endo-*(Benzyloxy)-8*-exo-*{[(4-methylphenyl)sulfonyl]oxy}-3,9-dioxatricyclo[4.2.1.0^{2,4}]non-5*-endo-*yl Benzoate* (**21**). As described for **20**, with (±)-**19** (150 mg, 0.41 mmol), TsCl (170 mg, 0.89 mmol), and Et_3N (280 µl, 2.01 mmol). FC (2 × 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}H-NMR (400 MHz, $CDCl_3$): 7.86, 7.52, 7.39, 7.31–7.21, 7.12 (5*m*, 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 (2*d*, $^2J = 11.7$, PhCH_2O); 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*, *Me*C$_6$H$_4$). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 165.6 (*s*, C=O); 145.7, 136.7, 133.2, 129.2 (4*s*, arom. C); 133.2, 130.2, 129.8, 128.3, 127.9, 127.8, 127.4 (7*d*, ^1J(C,H) = 160, arom. C); 84.8 (*d*, ^1J(C,H) = 154, C(8)); 84.6 (*d*, ^1J(C,H) = 149, C(7)); 76.3 (*d*, ^1J(C,H) = 160, C(1)); 73.3 (*t*, ^1J(C,H) = 143, Ph*C*H$_2$O); 72.7 (*d*, ^1J(C,H) = 159, C(6)); 66.9 (*d*, ^1J(C,H) = 151, C(5)); 52.4 (*d*, ^1J(C,H) = 185, C(4)); 48.2 (*d*, ^1J(C,H) = 180, C(2)); 21.7 (*q*, ^1J(C,H) = 127, *Me*C$_6$H$_4$). CI-MS (NH_3): 523 (1, $[M+H]^+$), 417 (7, $[M-Bz]^+$), 155 (5, Ts^+), 122 (12, $BzOH^+$), 105 (82, Bz^+), 91 (100, $C_7H_7^+$), 77 (18, $C_6H_5^+$). Anal. calc. for $C_{28}H_{26}O_8S$ (522.61): C 64.35, H 5.02, S 6.13; found: C 64.36, H 5.06, S 6.02.

*(1*RS*,2*RS*,4*SR*,5*RS*,6*RS*,7*RS*,8*SR*)-7*-endo-*(Benzyloxy)-8*-exo-*{[(4-nitrophenyl)sulfonyl]oxy}-3,9-dioxatricyclo[4.2.1.0^{2,4}]non-5*-endo-*yl Benzoate* (**22**). As described for **20**, with (±)-**19** (150 mg, 0.41 mmol), 4-nitrobenzenesulfonyl chloride (0.2 g, 0.90 mmol), and Et_3N (280 µl, 2.01 mmol). FC (2 × 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}H-NMR (400 MHz, $CDCl_3$): 8.41, 8.13, 7.89, 7.54, 7.33–7.23, 7.15 (6*m*, 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(1)); 4.57, 4.51 (2*d*, $^2J = 11.8$, PhCH_2O); 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}C-NMR (100.6 MHz, $CDCl_3$): 165.6 (*s*, C=O); 151.0, 141.8, 136.5, 129.1 (4*s*, arom. C); 133.4, 129.8, 128.5, 128.4, 128.1, 127.4 (6*d*, ^1J(C,H) = 160, arom. C); 129.2, 124.7 (2*d*, ^1J(C,H) = 170, arom. C); 85.7 (*d*, ^1J(C,H) = 155, C(8)); 84.3 (*d*, ^1J(C,H) = 148, C(7)); 76.3 (*d*, ^1J(C,H) = 163, C(1)); 73.6 (*t*, ^1J(C,H) = 140, Ph*C*H$_2$O); 72.9 (*d*, ^1J(C,H) = 154, C(6)); 66.8 (*d*, ^1J(C,H) = 152, C(5)); 52.4 (*d*, ^1J(C,H) = 183, C(4)); 48.0 (*d*, ^1J(C,H) = 179, C(2)). CI-MS (NH_3): 571 (59, $[M+18]^+$), 554 (100, $[M+1]^+$), 481 (5, $[M-Bn+H+18]^+$), 465 (6, $[M-BzH+18]^+$), 448 (9, $[M-Bz]^+$), 351 (2, $[M-ONs]^+$), 122 (9, $BzOH^+$), 108 (31, $BnOH^+$), 105 (91, Bz^+), 91 (85, $C_7H_7^+$), 77 (13, $C_6H_5^+$). Anal. calc. for $C_{27}H_{23}NO_{10}S$ (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.

*(1*RS*,2*SR*,3*SR*,4*SR*,5*SR*,6*RS*,7*SR*)-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 CH_2Cl_2 (3 ml), CF_3COOH (210 µl, 2.74 mmol) was added, and the mixture was stirred at r.t. for 20 min. After dilution with sat. $NaHSO_3$ soln. (20 ml), the mixture was extracted with CH_2Cl_2 (6 × 20 ml). The combined org. layers were dried ($MgSO_4$) 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}H-NMR (400 MHz, $CDCl_3$): 8.05, 7.53, 7.35, 7.29 (4*m*, 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 (2*d*, $^2J = 11.2$, PhOCH_2); 4.63 (br. *dd*, $^3J(6,5) = 6.7$, $^3J(6,7) = 2.9$, H–C(7)); 4.55 (*dd*, $^3J(5,6) = 6.7$, $^3J(5,4) = 5.0$, H–C(5)); 4.38 (*ddd*, $^3J(4,OH) = 11.6$, $^3J(4,3) = 5.6$, $^3J(4,5) = 5.0$, H–C(4)); 4.32 (br. *s*, H–C(1)); 4.10 (br. *s*, H–C(2)); 3.19 (br. *d*, $^3J(OH,4) = 11.6$, OH–C(4)); 3.03 (*s*, $MeSO_2$); 2.85 (br. *s*, OH–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 165.5 (*s*, C=O); 136.1, 128.9 (2*s*, arom. C); 133.6, 129.9, 128.8, 128.6, 128.5, 128.2 (6*d*, ^1J(C,H) = 160, arom. C); 86.6 (*d*, ^1J(C,H) = 150, C(6)); 82.8 (*d*, ^1J(C,H) = 159, C(1)); 81.7 (*d*, ^1J(C,H) = 154, C(7)); 74.7 (*t*, ^1J(C,H) = 143,

PhCH$_2$O); 74.0 (*d*, ^1J(C,H) = 155, C(5)); 71.4 (*d*, ^1J(C,H) = 156, C(3)); 68.9 (*d*, ^1J(C,H) = 147, C(2)); 66.2 (*d*, ^1J(C,H) = 147, C(4)); 38.4 (*q*, ^1J(C,H) = 139, MeSO$_2$). CI-MS (NH$_3$): 482 (15, [*M* + 18]$^+$), 465 (10, [*M* + 1]$^+$), 447 (16, [*M* − OH]$^+$), 359 (16, [*M* − Bz]$^+$), 263 (16, [*M* − Bz − MsOH]$^+$), 105 (100, Bz$^+$), 91 (93, C$_7$H$_7^+$), 77 (26, C$_6$H$_5^+$). Anal. calc. for C$_{22}$H$_{24}$O$_9$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. ^{1}H-NMR (400 MHz, CDCl$_3$): 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*, ^3J(3,4) = 5.4, H−C(3)); 5.21 (*d*, ^3J(7,6) = 3.2, H−C(7)); 4.58 (br. *dd*, ^3J(6,5) = 6.8, ^3J(6,7) = 3.2, H−C(6)); 4.56, 4.46 (2*d*, ^2J = 11.0, PhC*H*$_2$O); 4.50 (*dd*, ^3J(5,6) = 6.8, ^3J(5,4) = 5.0, H−C(5)); 4.33 (*ddd*, ^3J(4,OH) = 12.0, ^3J(4,3) = 5.4, ^3J(4,5) = 5.0, H−C(4)); 4.23 (br. *s*, H−C(1)); 3.90 (br. *d*, ^3J(2,OH) = 8.4, H−C(2)); 3.11 (*d*, ^3J(OH,4) = 12.0, OH−C(4)); 2.69 (*d*, ^3J(OH,2) = 8.4, OH−C(2)); 2.36 (*s*, *Me*C$_6$H$_4$). ^{13}C-NMR (100.6 MHz, CDCl$_3$): 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*, ^1J(C,H) = 160, arom. C); 86.5 (*d*, ^1J(C,H) = 152, C(6)); 82.9 (*d*, ^1J(C,H) = 153, C(7)); 82.7 (*d*, ^1J(C,H) = 163, C(1)); 74.3 (*t*, ^1J(C,H) = 144, PhC*H*$_2$O); 73.9 (*d*, ^1J(C,H) = 157, C(5)); 71.7 (*d*, ^1J(C,H) = 158, C(3)); 68.8 (*d*, ^1J(C,H) = 146, C(2)); 66.1 (*d*, ^1J(C,H) = 143, C(4)); 21.7 (*q*, ^1J(C,H) = 128, *Me*C$_6$H$_4$). CI-MS (NH$_3$): 540 (1, *M*$^+$), 523 (2, [*M* − OH]$^+$), 435 (13, [*M* − Bz]$^+$), 236 (3, *M* − TsOH − Bz]$^+$), 155 (3, Ts$^+$), 122 (6, BzOH$^+$), 105 (92, Bz$^+$), 91 (100, C$_7$H$_7^+$), 77 (32, C$_6$H$_5^+$). Anal. calc. for C$_{28}$H$_{28}$O$_9$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. ^{1}H-NMR (400 MHz, CDCl$_3$): 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*, ^3J(3,4) = 5.5, H−C(3)); 5.19 (*d*, ^3J(7,6) = 3.2, H−C(7)); 4.67, 4.51 (2*d*, ^2J = 10.6, PhC*H*$_2$O); 4.61 (*ddm*, ^3J(6,5) = 6.6, ^3J(6,7) = 3.2, H−C(6)); 4.57 (*dd*, ^3J(5,6) = 6.6, ^3J(5,4) = 4.8, H−C(5)); 4.36 (*ddd*, ^3J(4,OH) = 11.9, ^3J(4,3) = 5.5, ^3J(4,5) = 4.8, H−C(4)); 4.33 (br. *s*, H−C(1)); 4.02 (br. *d*, ^3J(2,OH) = 8.3, H−C(2)); 2.96 (*d*, ^3J(OH,4) = 11.9, OH−C(4)); 2.57 (br. *d*, ^3J(OH,2) = 8.3, OH−C(2)). ^{13}C-NMR (100.6 MHz, CDCl$_3$): 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*, ^1J(C,H) = 160, arom. C); 129.2, 124.4 (2*d*, ^1J(C,H) = 173, arom. C); 86.4 (*d*, ^1J(C,H) = 146, C(6)); 84.2 (*d*, ^1J(C,H) = 155, C(7)); 82.2 (*d*, ^1J(C,H) = 160, C(1)); 75.0 (*t*, ^1J(C,H) = 143, PhC*H*$_2$O); 73.8 (*d*, ^1J(C,H) = 157, C(5)); 71.7 (*d*, ^1J(C,H) = 158, C(3)); 68.6 (*d*, ^1J(C,H) = 151, C(2)); 66.0 (*d*, ^1J(C,H) = 145, C(4)). CI-MS (NH$_3$): 589 (19, [*M* + 18]$^+$), 572 (2, [*M* + H]$^+$), 554 (2, [*M* − OH]$^+$), 466 (6, [*M* − Bz]$^+$), 386 (15, [*M* − Ns + H]$^+$), 369 (11, [*M* − ONs]$^+$), 311 (12, [*M* − C$_6$H$_4$NO$_2$ − OBz − OH]$^+$), 296 (12, [*M* − Bn − Ns + 2 H]$^+$), 282 (19, [*M* − Bz − Ns + 2 H]$^+$), 279 (14, [*M* − Bn − ONs + H]$^+$), 108 (17, BnOH$^+$), 105 (100, Bz$^+$), 91 (92, C$_7$H$_7^+$), 77 (15, C$_6$H$_5^+$). Anal. calc. for C$_{27}$H$_{25}$NO$_{11}$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$_2$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. ^{1}H-NMR (400 MHz, CDCl$_3$): 8.10, 7.49, 7.26, 7.18 (4*m*, 2 H, 1 H, 2 H, 5 H, arom. H); 5.78 (*d*, ^3J(7,6) = 3.4, H−C(7)); 5.61 (*m*, ^3J(3,4) = 5.1, ^3J(3,2) = 1.7, H−C(3)); 5.53 (*dd*, ^3J(4,3) = 5.1, ^3J(4,5) = 4.8, H−C(4)); 5.10 (*dd*, ^3J(2,3) = 1.7, ^3J(2,1) = 1.7, H−C(2)); 4.65, 4.58 (2*d*, ^2J = 11.2, PhC*H*$_2$O); 4.60 (br. *dd*, ^3J(5,6) = 6.3, ^3J(5,4) = 4.8, H−C(5)); 4.56 (br. *dd*, ^3J(6,5) = 6.3, ^3J(6,7) = 3.4, H−C(6)); 4.46 (*m*, ^3J(1,2) = 1.7, H−C(1)); 3.05 (*s*, MeSO$_2$); 2.18, 1.92 (2*s*, 2 Ac). ^{13}C-NMR (100.6 MHz, CDCl$_3$): 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*, ^1J(C,H) = 160, arom. C); 85.9 (*d*, ^1J(C,H) = 149, C(6)); 82.8 (*d*, ^1J(C,H) = 155, C(7)); 80.4 (*d*, ^1J(C,H) = 161, C(1)); 73.7 (*t*, ^1J(C,H) = 140, PhC*H*$_2$O); 73.5 (*d*, ^1J(C,H) = 155, C(5)); 70.4 (*d*, ^1J(C,H) = 153, C(2)); 67.0 (*d*, ^1J(C,H) = 159, C(3)); 66.5 (*d*, ^1J(C,H) = 148, C(4)); 38.3 (*q*, ^1J(C,H) = 139, MeSO$_2$); 20.8, 20.5 (2*q*, ^1J(C,H) = 130, 2 *Me*CO$_3$). CI-MS (NH$_3$): 548 (1, *M*$^+$), 505 (1, [*M* − Ac]$^+$), 443 (9, [*M* − Bz]$^+$), 122 (9, BzOH$^+$), 105 (100, Bz$^+$), 91 (99, C$_7$H$_7^+$), 77 (22, C$_6$H$_5^+$). Anal. calc. for C$_{26}$H$_{28}$O$_{11}$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. ^{1}H-NMR (400 MHz, $CDCl_3$): 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*, $^3J(3,4) = 5.1$, $^3J(3,2) = 1.8$, H–C(3)); 5.46 (*dd*, $^3J(4,3) = 5.1$, $^3J(4,5) = 4.8$, H–C(4)); 5.41 (*d*, $^3J(7,6) = 3.5$, H–C(7)); 4.93 (*dd*, $^3J(2,3) = 1.8$, $^3J(2,1) = 1.8$, H–C(2)); 4.54 (*dd*, $^3J(5,6) = 6.3$, $^3J(5,4) = 4.8$, H–C(5)); 4.49, 4.31 (2*d*, $^2J = 11.2$, PhCH_2O); 4.47 (*dd*, $^3J(6,5) = 6.3$, $^3J(6,7) = 3.5$, H–C(6)); 4.36 (*m*, $^3J(1,2) = 1.8$, H–C(1)); 2.37 (*s*, *Me*C_6H_4), 2.17, 1.90 (2*s*, 2 Ac). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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*, $^1J(C,H) = 160$, arom. C); 85.7 (*d*, $^1J(C,H) = 147$, C(6)); 83.4 (*d*, $^1J(C,H) = 155$, C(7)); 80.4 (*d*, $^1J(C,H) = 161$, C(1)); 73.5 (*t*, $^1J(C,H) = 142$, Ph*C*H_2O); 73.2 (*d*, $^1J(C,H) = 158$, C(5)); 70.0 (*d*, $^1J(C,H) = 152$, C(2)); 67.1 (*d*, $^1J(C,H) = 158$, C(3)); 66.6 (*d*, $^1J(C,H) = 148$, C(4)); 21.7 (*q*, $^1J(C,H) = 127$, *Me*C_6H_4); 20.9, 20.6 (2*q*, $^1J(C,H) = 130$, 2 *Me*CO). CI-MS (NH_3): 642 (1, $[M+18]^+$), 624 (1, M^+), 519 (19, $[M-Bz]^+$), 155 (6, Ts^+), 122 (13, $BzOH^+$), 105 (86, Bz^+), 91 (100, $C_7H_7^+$), 77 (19, $C_6H_5^+$). Anal. calc. for $C_{32}H_{32}O_{11}S$ (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. ^{1}H-NMR (400 MHz, $CDCl_3$): 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*, $^3J(3,4) = 5.2$, $^3J(3,2) = 1.8$, $^4J(3,5) = 1.5$, $^4J(3,1) = 1.5$, H–C(3)); 5.49 (*d*, $^3J(7,6) = 3.8$, H–C(7)); 5.48 (*dd*, $^3J(4,3) = 5.2$, $^3J(4,5) = 5.0$, H–C(4)); 4.96 (*dd*, $^3J(2,1) = 1.9$, $^3J(2,3) = 1.8$, H–C(2)); 4.57 (*m*, $^3J(5,6) = 6.3$, $^3J(5,4) = 5.0$, $^4J(5,3) = 1.5$, H–C(5)); 4.56, 4.30 (2*d*, $^2J = 10.8$, PhCH_2O); 4.48 (*dd*, $^3J(6,5) = 6.3$, $^3J(6,7) = 3.8$, H–C(6)); 4.38 (*m*, $^3J(1,2) = 1.9$, $^4J(1,3) = 1.5$, H–C(1)); 2.17, 1.92 (2*s*, 2 Ac). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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*, $^1J(C,H) = 160$, arom. C); 129.3, 124.5 (2*d*, $^1J(C,H) = 170$, arom. C); 85.8 (*d*, $^1J(C,H) = 147$, C(6)); 84.7 (*d*, $^1J(C,H) = 156$, C(7)); 79.9 (*d*, $^1J(C,H) = 161$, C(1)); 73.9 (*t*, $^1J(C,H) = 140$, Ph*C*H_2); 73.3 (*d*, $^1J(C,H) = 156$, C(5)); 69.9 (*d*, $^1J(C,H) = 152$, C(2)); 67.2 (*d*, $^1J(C,H) = 159$, C(3)); 66.4 (*d*, $^1J(C,H) = 147$, C(4)); 20.8, 20.6 (2*q*, $^1J(C,H) = 130$, *Me*CO). CI-MS (NH_3): 655 (1, M^+), 550 (5, $[M-Bz]^+$), 122 (5, $BzOH^+$), 105 (95, Bz^+), 91 (100, $C_7H_7^+$), 77 (22, $C_6H_5^+$). Anal. calc. for $C_{31}H_{29}NO_{13}S$ (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^{2,4}]non-5*-endo-*yl Benzoate* ((±)-**40**). A mixture of (±)-**19** (2.66 g, 7.2 mmol), anh. CH_2Cl_2 (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_2O (400 ml), the soln. was washed successively with sat. aq. $NaHCO_3$ soln. (400 ml) containing $Na_2S_2O_3$ (19 g, 120 mmol), sat. aq. $NaHCO_3$ soln. (400 ml), and H_2O (400 ml). The aq. phases were extracted with Et_2O (2 × 300 ml). The combined org. extracts were dried ($MgSO_4$) 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_2Cl_2/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. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.97, 7.55, 7.35–7.17 (3*m*, 2 H, 1 H, 7 H, arom. H); 5.50 (*dd*, $^3J(5,6) = 6.0$, $^4J(5,2) = 0.6$, H–C(5)); 5.03 (*ddd*, $^3J(6,7) = 7.6$, $^3J(6,5) = 6.0$, $^4J(6,4) = 1.6$, H–C(6)); 4.81, 4.65 (2*d*, $^2J = 11.8$, PhCH_2O); 4.42 (br. *dd*, $^3J(1,2) = 1.7$, $^4J(1,7) = 1.8$, H–C(1)); 4.34 (*dd*, $^3J(7,6) = 7.6$, $^3J(7,1) = 1.8$, H–C(7)); 3.44 (br. *dd*, $^3J(4,2) = 3.8$, $^4J(4,6) = 1.6$, H–C(4)); 3.28 (*ddd*, $^3J(2,4) = 3.8$, $^3J(2,1) = 1.7$, $^4J(2,5) = 0.6$, H–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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*, $^1J(C,H) = 160$, arom. C); 78.5 (*d*, $^1J(C,H) = 144$, C(7)); 73.9 (*t*, $^1J(C,H) = 146$, Ph*C*H_2O); 72.8 (*d*, $^1J(C,H) = 166$, C(1)); 70.2 (*d*, $^1J(C,H) = 164$, C(6)); 65.4 (*d*, $^1J(C,H) = 153$, C(5)); 51.1 (*d*, $^1J(C,H) = 180$, C(4)); 46.6 (*d*, $^1J(C,H) = 186$, C(2)). CI-MS (NH_3): 385 (1, $[M+H+18]^+$), 367 (1, $[M+H]^+$), 279 (7, $[M-Bz+18]^+$), 122 (10, $BzOH^+$), 105 (100, Bz^+), 91 (73, $C_7H_7^+$), 77 (28, $C_6H_5^+$). Anal. calc. for $C_{21}H_{18}O_6$ (366.39): C 68.84, H 4.96; found: C 68.81, H 5.03.

*(1*S*,2*S*,4*R*,5*S*,6*R*,7*S*)-7*-endo-*(Benzyloxy)-8-oxo-3,9-dioxatricyclo[4.2.1.0^{2,4}]non-5*-endo-*yl Benzoate* ((−)-**40**). As described for (±)-**40**, with (−)-**19**. White solid. M.p. 122–124°. $[\alpha]_D^{25} = -152$, $[\alpha]_{577}^{25} = -160$, $[\alpha]_{546}^{25} = -185$, $[\alpha]_{435}^{25} = -355$, $[\alpha]_{405}^{25} = -364$ ($c = 1.0$, CH_2Cl_2).

*(1*RS*,2*RS*,3*SR*,4*SR*,5*SR*,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_2Cl_2 (120 ml), and CF_3COOH (5.5 ml, 8.2 g, 72 mmol) was stirred at 20° for 1 h. After the addition of sat. aq. $NaHCO_3$ soln. (120 ml), the mixture was extracted with CH_2Cl_2 (6 × 100 ml). The combined org. extracts were dried ($MgSO_4$) and

evaporated: 2.69 g (96%) of (±)-**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, 1720, 1690, 1600, 1455, 1405, 1270, 1100, 1070, 670. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.07, 7.53, 7.34 (3*m*, 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 (2*d*, $^2J=11.5$, 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*, $^3J(4,OH)=11.9$, $^3J(4,3)=5.0$, $^3J(4,5)=4.9$, 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*, $^3J(2,OH)=8.1$, $^3J(2,1)=2.5$, $^3J(2,3)=2.0$, H–C(2)); 3.05 (*d*, $^3J(OH,4)=11.9$, OH–C(4)); 2.96 (*d*, $^3J(OH,2)=8.1$, OH–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 207.3 (*s*, C(7)); 165.6 (*s*, C=O); 136.0, 128.6 (2*s*, arom. C); 133.5, 130.3, 128.7, 128.3, 128.0 (5*d*, $^1J(C,H)=160$, arom. C); 80.8 (*d*, $^1J(C,H)=139$, C(6)); 79.0 (*d*, $^1J(C,H)=161$, C(1)); 74.7 (*t*, $^1J(C,H)=143$, PhCH_2O); 73.4 (*d*, $^1J(C,H)=158$, C(5)); 71.4 (*d*, $^1J(C,H)=158$, C(3)); 68.9 (*d*, $^1J(C,H)=153$, C(2)); 65.8 (*d*, $^1J(C,H)=147$, C(4)). CI-MS (NH_3): 385 (3, $[M+1]^+$), 279 (13, $[M-Bz]^+$), 105 (74, Bz^+), 91 (100, $C_7H_7^+$), 77 (20, $C_6H_5^+$). Anal. calc. for $C_{21}H_{20}O_7$ (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 (±)-**41**, with (−)-**40**. White foam. $[\alpha]_D^{25}=-41$, $[\alpha]_{577}^{25}=-42$, $[\alpha]_{546}^{25}=-46$, $[\alpha]_{435}^{25}=-54$, $[\alpha]_{405}^{25}=-40$ ($c=1.1$, CH_2Cl_2).

*(1*RS*,2*RS*,3*SR*,4*SR*,5*SR*,6*RS*)-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 the preparation of **26**, with (±)-**41** (2.65 g, 6.89 mmol). FC (5 × 18 cm, light petroleum ether/AcOEt 3:2): 2.68 g (79% based on (±)-**19**) of (±)-**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}H-NMR (400 MHz, $CDCl_3$): 8.08, 7.50, 7.33, 7.18 (4*m*, 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 (2*d*, $^2J=11.5$, PhCH_2O); 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 (2*s*, 2 Ac). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 205.5 (*s*, C(7)); 169.7, 169.3, 165.3 (3*s*, C=O); 136.7, 128.4 (2*s*, arom. C); 133.3, 130.5, 128.1, 127.7, 127.1 (5*d*, $^1J(C,H)=160$, arom. C); 81.1 (*d*, $^1J(C,H)=140$, C(6)); 76.9 (*d*, $^1J(C,H)=163$, C(1)); 73.7 (*t*, $^1J(C,H)=141$, PhCH_2O); 72.7 (*d*, $^1J(C,H)=160$, C(5)); 69.9 (*d*, $^1J(C,H)=155$, C(2)); 67.1 (*d*, $^1J(C,H)=159$, C(3)); 66.2 (*d*, $^1J(C,H)=147$, C(4)); 20.8, 20.5 (2*q*, $^1J(C,H)=130$, 2 *Me*CO). CI-MS (NH_3): 486 (5, $[M+18]^+$), 469 (5, $[M+1]^+$), 363 (3, $[M-Bz]^+$), 347 (2, $[M-BzO]^+$), 289 (3, $[M-BzO-AcO+H]^+$), 247 (3, $[M-BzO-AcO-Ac+2H]^+$), 180 (13), 138 (10), 105 (85, Bz^+), 91 (100, $C_7H_7^+$), 77 (20, $C_6H_5^+$). Anal. calc. for $C_{25}H_{24}O_9$ (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 (±)-**42**, with (−)-**41**. Yield 72% based on (−)-**19**. Colorless oil. $[\alpha]_D^{25}=3.7$, $[\alpha]_{577}^{25}=4.7$, $[\alpha]_{546}^{25}=7.3$, $[\alpha]_{435}^{25}=40$, $[\alpha]_{405}^{25}=76$ ($c=1.3$, CH_2Cl_2).

*(1*RS*,2*RS*,5*SR*,6*SR*,7*RS*,8*SR*)-6*-exo,*8*-endo-*Bis(acetyloxy)-2*-endo-*(benzyloxy)-4-oxo-3,9-dioxabicyclo[3.3.1]-non-7*-endo-*yl Benzoate* ((±)-**43**). A dried soln. of 70% 3-chloroperbenzoic acid (3.22 g, 13.1 mmol; *Fluka*) was made by dissolving *m*CPBA in CH_2Cl_2 (200 ml) and drying with $MgSO_4$. After filtration, 175 ml of this soln. were used to dissolved (±)-**42** (2.68 g, 5.72 mmol). $NaHCO_3$ (0.96 g, 11.4 mmol) was added and the mixture stirred at 20° for 12 h. Then 0.5M aq. $Na_2S_2O_3$ (50 ml) was added slowly under vigourous stirring. After 1 h, AcOEt (400 ml) was added and the soln. washed successively with 0.5M aq. $Na_2S_2O_3$ (150 ml), sat. aq. $NaHCO_3$ soln. (200 ml), and brine (200 ml). The aq. layers were extracted with AcOEt (2 × 200 ml) and the org. extracts dried ($MgSO_4$) and evaporated. The residue was purified by FC (5 cm × 17 cm, light petroleum ether/AcOEt 3:2): 2.3 g (83%) of (±)-**43**. Colorless oil that crystallized slowly. Washing of the crystals with Et_2O 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}H-NMR (400 MHz, $CDCl_3$): 8.10, 7.55, 7.43, 7.19, 7.01 (5*m*, 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 (2*d*, $^2J=11.3$, PhCH_2O); 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 (2*s*, Ac). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.0, 169.0, 165.1, 165.0 (4*s*, C(4), 3 C=O); 135.5, 128.7 (2*s*, arom. C); 133.5, 130.1, 128.4, 128.2, 128.0, 127.6 (6*d*, $^1J(C,H)=160$, arom. C); 100.7 (*d*, $^1J(C,H)=174$, C(2)); 72.0 (*t*, $^1J(C,H)=143$, PhCH_2O); 70.5 (*d*, $^1J(C,H)=156$, C(6)); 70.0 (*d*, $^1J(C,H)=159$, C(5)); 66.7 (*d*, $^1J(C,H)=159$, C(7)); 66.1 (*d*, $^1J(C,H)=148$, C(8)); 65.2 (*d*, $^1J(C,H)=154$, C(1)); 20.7, 20.3 (2*q*, $^1J(C,H)=130$, 2 *Me*CO). CI-MS (NH_3): 502 (77, $[M+18]^+$), 485 (26, $[M+H]^+$), 363 (11, $[M-BzO]^+$), 108 (21, $BnOH^+$), 105 (87), 91 (100), 77 (12). Anal. calc. for $C_{25}H_{24}O_{10}$ (484.49): C 61.97, H 5.00; found: C 61.82, H 5.10.

*(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**). As described for (±)-**43**, with (+)-**42**. White foam. Yield 84%. $[\alpha]_D^{25} = -75$, $[\alpha]_{577}^{25} = -78$, $[\alpha]_{546}^{25} = -89$, $[\alpha]_{435}^{25} = -145$, $[\alpha]_{405}^{25} = -169$ ($c = 1.3$, CH_2Cl_2).

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-gluco-*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. $MeNO_2$ (0.7 ml), and $Me_3SiOSO_2CF_3$ (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. $NaHCO_3$ soln. (5 ml) was added and the mixture extracted with CH_2Cl_2 (5 ml, 4 times). The combined org. extracts were dried ($MgSO_4$) and evaporated. FC (1 × 15 cm, CH_2Cl_2/Et_2O 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**). $Me_3SiOSO_2CF_3$ (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. $NaHCO_3$ soln. (5 ml) was added and the mixture extracted with CH_2Cl_2 (4 × 5 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated: 58 mg of (±)-**46a**/(±)-**46b** 4.3 :1. FC (2 × 15 cm, light petroleum ether/CH_2Cl_2/Et_2O 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. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.94, 7.56, 7.41, 7.30 (4*m*, 2 H, 1 H, 2 H, 5 H, arom. H); 5.90 (*dddd*, ^3J(9,10*cis*) = 16.8, ^3J(9,10*trans*) = 10.5, ^3J(9,8b) = 8.6, ^3J(9,8a) = 5.9, H−C(9)); 5.88 (*d*, ^3J(5,4) = 3.4, H−C(5)); 5.56 (*dd*, ^3J(3,4) = 10.1, ^3J(3,2) = 10.0, H−C(3)); 5.32 (*dd*, ^3J(4,3) = 10.1, ^3J(4,5) = 3.4, H−C(4)); 5.18 (br. *d*, ^3J(10*cis*,9) = 16.8, H_{cis}−C(10)); 5.17 (br. *d*, ^3J(10*trans*,9) = 10.5, H_{trans}−C(10)); 4.56, 4.33 (2*d*, ^2J = 10.8, PhCH_2O); 4.02 (*d*, ^3J(2,3) = 10.0, H−C(2)); 3.79 (*s*, COOMe); 3.67 (*m*, ^3J(7,8b) = 3.3, H−C(6), H−C(7)); 2.68 (*m*, ^2J(8a,8b) = 14.5, ^3J(8a,9) = 5.9, H_a−C(8)); 2.41 (br. *ddd*, ^2J(8b,8a) = 14.5, ^3J(8b,9) = 8.6, ^3J(8b,7) = 3.3, H_b−C(8)); 2.06, 1.97 (2*s*, 2 Ac). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.8, 169.7, 167.7, 165.2 (4*s*, 4 C=O); 137.2 (*s*, arom. C); 133.3, 133.1 (2*d*, ^1J(C,H) = 161, 155, C(9), arom. C); 129.6 (*d*, ^1J(C,H) = 160, arom. C); 129.1 (*s*, arom. C); 128.6, 128.5, 128.4, 127.9 (4*d*, ^1J(C,H) = 160, arom. C); 118.5 (*t*, ^1J(C,H) = 155, C(10)); 77.3 (*d*, ^1J(C,H) = 138, C(7)); 76.9 (*d*, ^1J(C,H) = 155, C(2)); 73.6 (*d*, ^1J(C,H) = 145, C(6)); 72.6 (*d*, ^1J(C,H) = 147, C(4)); 71.4 (*t*, ^1J(C,H) = 145, PhCH_2O); 67.1, 67.0 (2*d*, ^1J(C,H) = 155, C(3), C(5)); 52.8 (*q*, ^1J(C,H) = 148, COO*Me*); 33.4 (*t*, ^1J(C,H) = 129, C(8)); 20.8, 20.6 (2*q*, ^1J(C,H) = 130, 2 *Me*CO). CI-MS (NH_3): 558 (100, $[M + NH_4]^+$). Anal. calc. for $C_{29}H_{32}O_{10}$ (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. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.94, 7.58, 7.44, 7.39 – 7.26 (4*m*, 2 H, 1 H, 2 H, 5 H, arom. H); 5.90 (*dddd*, ^3J(9,10*cis*) = 17.2, ^3J(9,10*trans*) = 10.1, ^3J(9,8b) = 7.9, ^3J(9,8a) = 6.1, H−C(9)); 5.69 (br. *d*, ^3J(5,4) = 3.4, H−C(5)); 5.62 (*dd*, ^3J(3,4) = 10.1, ^3J(3,2) = 10.0, H−C(3)); 5.28 (*dd*, ^3J(4,3) = 10.1, ^3J(4,5) = 3.4, H−C(4)); 5.15 (br. *d*, ^3J(10*cis*,9) = 17.2, H_{cis}−C(10)); 5.13 (br. *d*, ^3J(10*trans*,9) = 10.1, H_{trans}−C(10)); 4.80, 4.65 (2*d*, ^2J = 11.4, PhCH_2O); 4.08 (*d*, ^3J(2,3) = 10.0, H−C(2)); 3.80 (*s*, COOMe); 3.79 (br. *d*, ^3J(6,7) = 8.0, H−C(6)); 3.70 (*ddd*, ^3J(7,6) = 8.0, ^3J(7,8b) = 6.8, ^3J(7,8a) = 3.6, H−C(7)); 2.39 (*m*, ^2J(8a,8b) = 14.7, ^3J(8a,9) = 6.1, ^3J(8a,7) = 3.6, H_a−C(8)); 2.16 (br. *ddd*, ^2J(8b,8a) = 14.7, ^3J(8b,9) = 7.9, ^3J(8b,7) = 6.8, H_b−C(8)); 2.12, 1.99 (2*s*, 2 Ac). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.0, 169.7, 167.7, 165.4 (4*s*, 4 C=O); 138.5, 129.0 (2*s*, arom. C); 133.5, 133.3 (2*d*, ^1J(C,H) = 162, 155, C(9), arom. C); 129.6, 128.5, 128.3, 127.9, 127.6 (5*d*, ^1J(C,H) = 160, arom. C); 118.2 (*t*, ^1J(C,H) = 156, C(10)); 80.5 (*d*, ^1J(C,H) = 141, C(6)); 77.6 (*d*, ^1J(C,H) = 138, C(7)); 76.5 (*d*, ^1J(C,H) = 151, C(2)); 74.0 (*t*, ^1J(C,H) = 142, PhCH_2O); 72.6 (*d*, ^1J(C,H) = 148, C(4)); 67.5 (*d*, ^1J(C,H) = 153, C(5)); 66.6 (*d*, ^1J(C,H) = 156, C(3)); 52.7 (*q*, ^1J(C,H) = 148, COO*Me*); 35.0 (*t*, ^1J(C,H) = 128, C(8)); 20.7, 20.6 (2*q*, ^1J(C,H) = 130, 2 *Me*CO). CI-MS (NH_3): 558 (100, $[M + 18]^+$), 540 (2, M^+), 481 (6, $[M - Ac]^+$), 433 (7, $[M - OBn]^+$), 105 (52), 91 (78), 77 (9). Anal. calc. for $C_{29}H_{32}O_{10}$ (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_3SiCN instead of $PhCH(OSiMe_3)CH_2$. FC (1 × 16 cm, light petroleum ether/CH_2Cl_2/Et_2O 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. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.91, 7.58, 7.43, 7.36 – 7.28 (4*m*, 2 H, 1 H, 2 H, 5 H, arom. H); 5.75 (*dd*, ^3J(5,4) = 3.3, ^3J(5,6) = 1.1, H−C(5)); 5.51 (*dd*, ^3J(3,4) = 10.2, ^3J(3,2) = 10.0, H−C(3)); 5.29 (*dd*, ^3J(4,3) = 10.2, ^3J(4,5) = 3.3, H−C(4)); 4.84, 4.53 (2*d*, ^2J = 11.9, PhCH_2O); 4.18 (*d*, ^3J(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*, COO*Me*); 1.99, 1.84 (2*s*, 2 *Me*CO). CI-MS (NH_3): 543 (100, $[M+18]^+$), 526 (2, $[M+H]^+$), 525 (1, M^+), 499 (2, $[M-CN]^+$), 436 (11), 426 (4), 359 (4), 105 (35), 91 (23), 77 (10).

Data for (±)-**47b**: R_f 0.27. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 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_2O); 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_3): 543 (100, $[M+18]^+$), 499 (1, $[M-CN]^+$), 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 $Hg(ClO_4)_2 \cdot (H_2O)_{3.4}$ (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, $CHCl_3$ (100 ml) was added, followed by Ag_2CO_3 (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_2Cl_2/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_2O were eliminated (if required) by azeotropic distillation with anh. toluene. ^{1}H-NMR (400 MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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*, $^1J(C,H) = 148$, COO*Me*); 20.5, 20.4 (2*q*, $^1J(C,H) = 130$, 2 *Me*CO). CI-MS (NH_3): 426 (0.1, $[M+18]^+$), 379 (0.2, $[M-CHO]^+$), 349 (0.6, $[M-AcO]^+$), 287 (4, $[M-BzO]^+$), 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**). $Me_3SiOSO_2CF_3$ (25 µl) was added to a soln. of (±)-**43** (100 mg, 0.21 mmol) and $PhCH_2OSiMe_3$ (80 µl, 75 mg, 0.41 mmol) in anh. $CHCl_3$ (3.5 ml) cooled to –10°. The soln. became dark yellow. After stirring at –10° for 75 min, anh. MeOH (0.2 ml) was added and the mixture stirred at 20° for 12 h. A sat. aq. $NaHCO_3$ soln. (5 ml) was added to the colorless soln., the mixture extracted with CH_2Cl_2 (4 × 5 ml), the combined org. extract dried ($MgSO_4$) 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. ^{1}H-NMR (400 MHz, $CDCl_3$): 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_2O); 4.77 (*d*, $^3J(1,2) = 7.1$, H–C(1)); 4.65, 4.45 (2*d*, $^2J = 11.6$, PhCH_2O); 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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_2O); 67.6 (*d*, $^1J(C,H) = 156$, C(3)); 66.6 (*d*, $^1J(C,H) = 155$, C(5)); 52.7 (*q*, $^1J(C,H) = 148$, COO*Me*); 20.6 (*q*, $^1J(C,H) = 130$, 2 *Me*CO). CI-MS (NH_3): 626 (54, $[M+18]^+$), 499 (20, $[M-OBn]^+$), 367 (9), 366 (8), 108 (17), 105 (49), 91 (100), 77 (12). Anal. calc. for $C_{33}H_{34}O_{11}$ (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 $PhSSiMe_3$ (200 µl, 190 mg, 1.05 mmol) instead of $BnOSiMe_3$. 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_2Cl_2/Et_2O 57:3:40): 18 mg (14%) of **52** as colorless oil.

Data for **52**: R_f 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. ^{1}H-NMR (400 MHz, $CDCl_3$): 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_2O); 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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(C,H) = 156, C(1)); 76.7 (*d*, ^1J(C,H) = 147, C(6)); 76.1 (*d*, ^1J(C,H) = 144, C(2)); 72.4 (*d*, ^1J(C,H) = 148, C(4)); 69.3 (*t*, ^1J(C,H) = 143, Ph*C*H$_2$O); 67.4 (*d*, ^1J(C,H) = 157, C(3)); 66.7 (*d*, ^1J(C,H) = 156, C(5)); 52.9 (*q*, ^1J(C,H) = 148, COO*Me*); 20.6, 20.5 (2*q*, ^1J(C,H) = 130, 2 *Me*CO). CI-MS (NH_3): 626 (29, $[M+18]^+$), 499 (21, $[M-SPh]^+$), 110 (8), 109 (10), 108 (9), 105 (27), 91 (100), 77 (14). Anal. calc. for $C_{32}H_{32}O_{10}S$ (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}H-NMR (400 MHz, $CDCl_3$): 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*, ^2J = 11.9, PhC*H*$_2$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*, 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}C-NMR (100.6 MHz, $CDCl_3$): 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(C,H) = 160, arom. C); 85.9 (*d*, ^1J(C,H) = 158, C(1)); 78.5 (*d*, ^1J(C,H) = 155, C(2)); 76.5 (*d*, ^1J(C,H) = 147, C(6)); 72.6 (*d*, ^1J(C,H) = 147, C(4)); 70.5 (*t*, ^1J(C,H) = 143, Ph*C*H$_2$O); 67.8 (*d*, ^1J(C,H) = 152, C(3)); 66.5 (*d*, ^1J(C,H) = 156, C(5)); 52.7 (*q*, ^1J(C,H) = 148, COO*Me*); 20.6 (*q*, ^1J(C,H) = 130, 2 *Me*CO). CI-MS (NH_3): 626 (53, $[M+18]^+$), 499 (23, $[M-PhS]^+$), 367 (6), 110 (8), 109 (11), 108 (13), 105 (109), 91 (100), 77 (9). Anal. calc. for $C_{32}H_{32}O_{10}S$ (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-hepturonate* (**55**). CF_3SO_3H (50 mg), then PhSH (50 µl, 55 mg, 0.50 mmol) were added to a soln. of (±)-**43** (13 mg, 0.027 mmol) in anh. CH_2Cl_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 × 16 cm, light petroleum ether/CH_2Cl_2/Et_2O 40 : 57 : 3): 11 mg (60%) of **55**. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 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*, ^2J = 12.1, PhC*H*$_2$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}C-NMR (100.6 MHz, $CDCl_3$): 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×), 128.6 (2×), 128.5, 128.3 (12*d*, ^1J(C,H) = 160, arom. C); 78.3 (*d*, ^1J(C,H) = 148, C(2)); 76.8 (*d*, ^1J(C,H) = 153, C(6)); 72.8 (*d*, ^1J(C,H) = 147, C(4)); 67.8 (*d*, ^1J(C,H) = 155, C(3)); 67.6 (*t*, ^1J(C,H) = 149, Ph*C*H$_2$O); 66.3 (*d*, ^1J(C,H) = 156, C(5)); 59.4 (*d*, ^1J(C,H) = 154, C(1)); 20.6, 20.4 (2*q*, ^1J(C,H) = 130, *Me*CO). CI-MS (NH_3): 577 (2, $[M-SPh]^+$), 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-hepturonate* (**56**). A mixture of (±)-**43** (103 mg, 0.21 mmol), anh. CH_2Cl_2 (20 ml), CF_3SO_3H (10 µl, 17 mg, 0.11 mmol), and 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. $NaHCO_3$ soln. (10 ml) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated. FC (1.5 × 15 cm, light petroleum ether/AcOEt 3 : 2, then light petroleum ether/CH_2Cl_2/Et_2O 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}H-NMR (400 MHz, $CDCl_3$): 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*, PhC*H*$_2$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 MeC*H*$_2$S); 2.13, 1.73 (2*s*, 2 Ac); 1.23, 1.22 (2*t*, ^3J = 7.4, 2 *Me*CH$_2$S). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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(C,H) = 160, arom. C); 80.9 (*d*, ^1J(C,H) = 144, C(2)); 76.7 (*d*, ^1J(C,H) = 147, C(6)); 72.8 (*d*, ^1J(C,H) = 147, C(4)); 68.1 (*d*, ^1J(C,H) = 154, C(3)); 67.6 (*t*, ^1J(C,H) = 149, Ph*C*H$_2$O); 66.4 (*d*, ^1J(C,H) = 156, C(5)); 49.6 (*d*, ^1J(C,H) = 152, C(1)); 26.6, 24.4 (2*t*, ^1J(C,H) = 140, 2 MeC*H*$_2$S); 20.7, 20.4 (2*q*, ^1J(C,H) = 130, 2 *Me*CO); 14.3 (*q*, ^1J(C,H) = 128, 2 MeC*H*$_2$S). CI-MS (NH_3): 608 (6, $[M+18]^+$), 590 (2, M^+), 529 (26, $[M-SEt]^+$), 409 (14, $[M-Bn-Et_2S]^+$), 408 (12, $[M-SEt-OBz]^+$), 135 (30), 105 (82), 91 (100), 77 (15). Anal. calc. for $C_{29}H_{34}O_9S_2$ (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-hepturonate* ((±)-**57**). EtSH (0.4 ml, 340 mg, 5.41 mmol) then CF_3SO_3H (60 µl, 100 mg, 0.69 mmol) were added to a stirred soln. of (±)-**43** (0.2 g, 0.42 mmol) in anh. CH_2Cl_2 (16 ml). After stirring at 20° for 25 min, anh. MeOH (1.5 ml) was added, and stirring was continued for 16 h at 20°. A sat. aq. $NaHCO_3$ soln. (20 ml) was added, the aq. layer extracted with CH_2Cl_2 (3 × 20 ml), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue submitted to FC (3 × 13 cm, light petroleum ether/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. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.92, 7.57, 7.44 (3*m*, 2 H, 1 H, 2 H, arom. H); 6.01 (*dd*, $^3J(3,4)=3.4$, $^3J(3,2)=1.0$, H–C(3)); 5.57 (*dd*, $^3J(5,4)=10.1$, $^3J(5,6)=10.0$, H–C(5)); 5.32 (*dd*, $^3J(4,5)=10.1$, $^3J(4,3)=3.4$, H–C(4)); 4.10 (*d*, $^3J(6,5)=10.0$, H–C(6)); 3.98 (*d*, $^3J(1,2)=9.5$, H–C(1)); 3.78 (*s*, COOMe); 3.77 (*dd*, $^3J(2,1)=9.5$, $^3J(2,3)=1.0$, H–C(2)); 2.81–2.56 (*m*, $^3J=7.4$, 2 Me*C*H$_2$S); 2.13, 1.99 (2*s*, 2 Ac); 1.27, 1.22 (2*t*, $^3J=7.4$, 2 *Me*CH$_2$S). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.7, 169.5, 167.4, 165.4 (4*s*, 4 C=O); 133.4, 129.6, 128.5 (3*d*, ^1J(C,H) = 160, arom. C); 129.1 (*s*, arom. C); 80.7 (*d*, ^1J(C,H) = 139, C(2)); 76.8 (*d*, ^1J(C,H) = 147, C(6)); 72.7 (*d*, ^1J(C,H) = 147, C(4)); 68.0 (*d*, ^1J(C,H) = 153, C(3)); 66.6 (*d*, ^1J(C,H) = 155, C(5)); 52.8 (*q*, ^1J(C,H) = 148, COO*Me*); 49.8 (*d*, ^1J(C,H) = 150, C(1)); 26.3, 24.3 (2*t*, ^1J(C,H) = 140, 2 Me*C*H$_2$S); 20.8, 20.6 (2*q*, ^1J(C,H) = 130, 2 *Me*CO); 14.4 (*q*, ^1J(C,H) = 128, 2 *Me*CH$_2$S). CI-MS (NH_3): 514 (4, M^+), 453 (5, $[M-\mathrm{SEt}]^+$), 333 (24, $[M-\mathrm{OBz}-\mathrm{EtS}+\mathrm{H}]^+$), 303 (8, $[M-\mathrm{OBz}-\mathrm{Et_2S}]^+$), 287 (9), 271 (14), 229 (16), 135 (41), 105 (100), 77 (34). Anal. calc. for $C_{23}H_{30}O_9S_2$ (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. $[\alpha]_D^{25}=-87$, $[\alpha]_{577}^{25}=-89$, $[\alpha]_{546}^{25}=-103$, $[\alpha]_{435}^{25}=-182$, $[\alpha]_{405}^{25}=-222$ ($c=0.9$, $CHCl_3$).

Benzyl 3,5-Di-O-*acetyl-2,6-anhydro-4*-O-*benzoyl*-DL-glycero-DL-galacto-*hepturonate* (**58**). $CdCO_3$ (50 mg, 0.29 mmol) was suspended in a soln. of $HgCl_2$ (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 $CdCO_3$ (rinsing with acetone), the filtrate was evaporated, the viscous residue extracted with CH_2Cl_2 (4 × 1 ml), and the combined extract washed with a KI (0.2 g) soln., $Na_2S_2O_4\cdot H_2O$ (0.2 g) in H_2O (5 ml), and then H_2O (10 ml). The aq. layers were extracted with CH_2Cl_2 (2 × 5 ml) and the org. extracts dried ($MgSO_4$) and evaporated: 21 mg (100%) of **58**. Yellowish foam. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.62 (*s*, H–C(1)); 7.92, 7.57, 7.44–7.35 (3*m*, 2 H, 1 H, 7 H, arom. H); 5.97 (*dd*, $^3J(3,4)=3.4$, $^3J(3,2)=1.5$, H–C(3)); 5.67 (*dd*, $^3J(5,4)=10.1$, $^3J(5,6)=10.0$, H–C(5)); 5.32 (*dd*, $^3J(4,5)=10.1$, $^3J(4,3)=3.4$, H–C(4)); 5.26, 5.21 (2*d*, $^2J=12.0$, PhC*H*$_2$O); 4.24 (*d*, $^3J(2,3)=1.5$, H–C(2)); 4.23 (*d*, $^3J(6,5)=10.0$, H–C(6)); 2.06, 1.73 (2*s*, 2 Ac).

*(1*RS*,2*SR*,3*RS*,4*SR*,5*RS*,6*RS*,7*SR*)-7-*endo*-*(Benzyloxy)-6*-exo-*{[(*tert*-butyl)dimethylsilyl]oxy}-3*-endo-*[(1*RS*)-1-hydroxypropyl]-4*-exo-*(phenylthio)-8-oxabicyclo[3.2.1]octan-2*-endo-*ol* (**61**). At –78° 0.7M Me_2AlSPh in CH_2Cl_2 (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 $CHCl_3$ (–10°) and the soln. washed immediately with ice-cold 1N HCl (20 ml) and then with sat. aq. $NaHCO_3$ soln. (20 ml). The aq. layers were extracted with $CHCl_3$ (3 × 20 ml) and the combined org. extracts dried ($MgSO_4$) and evaporated. The residue **60** was taken in MeOH (10 ml) and cooled to 0°. $CeCl\cdot 6H_2O$ (200 mg, 0.56 mmol), then $NaBH_4$ (20 mg, 0.53 mmol) were added portionwise. After stirring at 0° for 10 min, AcOEt (50 ml), then sat. aq. NH_4Cl soln. (25 ml) and H_2O (until dissolution of salts) were added. The aq. layer was extracted with AcOEt (4 × 25 ml), and the combined org. extract dried ($MgSO_4$) and evaporated. FC (2 × 15 cm, light petroleum ether/Et_2O 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. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.53, 7.41–7.23 (2*m*, 2 H, 8 H, arom. H); 4.88 (br. *s*, OH–C(2)); 4.75, 4.57 (2*d*, $^2J=11.4$, PhC*H*$_2$O); 4.71 (*dd*, $^3J(2,1)=7.6$, $^3J(2,3)=4.5$, H–C(2)); 4.30 (br. *d*, $^3J(6,7)=4.4$, H–C(6)); 4.25 (br. *s*, H–C(5)); 4.21 (*dd*, $^3J(1,2)=7.6$, $^3J(1,7)=5.7$, H–C(1)); 4.16 (*m*, $^3J(1,3)=3.8$, H–C(1′)); 4.10 (*dd*, $^3J(7,1)=5.7$, $^3J(7,6)=4.4$, H–C(7)); 3.69 (br. *d*, $^3J(4,3)=9.9$, H–C(4)); 3.57 (br. *s*, OH–C(1′)); 1.75 (*m*, ^3J(2′a,3′) = 7.4, H_a–C(2′)); 1.65 (*ddd*, $^3J(3,4)=9.9$, $^3J(3,2)=4.5$, $^3J(3,1')=3.8$, H–C(3)); 1.56 (*m*, ^3J(2′b,3) = 7.4, H_b–C(2′)); 1.03 (*dd*, ^3J(3′,2′a) = 7.4, ^3J(3′,2′b) = 7.4, H–C(3′)); 0.82 (*s*, *t*-BuSi); –0.02, –0.16 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 136.4, 134.3 (2*s*, arom. C); 133.4, 129.1, 128.8, 128.5, 128.0, 127.6 (6*d*, ^1J(C,H) = 160, arom. C); 90.3 (*d*, ^1J(C,H) = 151, C(7)); 89.1 (*d*, ^1J(C,H) = 158, C(5)); 82.4 (*d*, ^1J(C,H) = 146, C(6)); 74.2 (*t*, ^1J(C,H) = 144, PhC*H*$_2$O); 73.1 (*d*, ^1J(C,H) = 155, C(1)); 72.3 (*d*, ^1J(C,H) = 146, C(1′)); 70.5 (*d*, ^1J(C,H) = 152, C(2)); 49.0 (*d*, ^1J(C,H) = 144, C(4)); 41.5 (*d*, ^1J(C,H) = 128, C(3)); 28.5 (*t*, ^1J(C,H) = 125, C(2′)); 25.6 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 17.7 (*s*, Me$_3$*C*Si); 10.8 (*q*, ^1J(C,H) = 126, C(3′)); –4.9, –5.0 (2*q*, ^1J(C,H) = 119, Me_2Si). APCI-MS (pos. mode): 531 (100, $[M+\mathrm{H}]^+$), 513 (100, $[M-\mathrm{OH}]^+$), 495 (50, $[M-\mathrm{H_2O}-\mathrm{OH}]^+$), 381 (50, $[M-\mathrm{H_2O}-(t\text{-Bu})\mathrm{SiO}]^+$). APCI-MS (neg. mode): 529 (100, $[M-\mathrm{H}]^-$). Anal. calc. for $C_{29}H_{42}O_5SSi$ (530.87): C 65.61, H 7.97, S 6.04; found: C 65.65, H 7.94, S 5.98.

*(1*RS*,2*SR*,6*RS*,7*RS*,8*SR*,9*RS*,10*RS*,11*SR*)-11-(Benzyloxy)-10-{[(*tert*-butyl)dimethylsilyl]oxy}-6-ethyl-4,4-dimethyl-8-(phenylthio)-3,5,12-trioxatricyclo[7.2.1.0^{2,7}]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_2O (10 mg) was stirred at 20° for 1 h. A sat. aq. $NaHCO_3$ soln. (5 ml) was added and the mixture extracted with $CHCl_3$ (4 × 5 ml). The

combined org. extracts were dried ($MgSO_4$) and evaporated. FC (1×10 cm, light petroleum ether/Et_2O 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}H-NMR (400 MHz, $CDCl_3$): 7.47, 7.31 (2*m*, 2 H, 8 H, arom. H); 4.75, 4.50 (2*d*, ^2J = 12.1, PhCH_2O); 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, H_b–C(15)); 1.44 (*ddq*, ^2J(15a,15b) = 14.8, ^3J(15a,16) = 8.0, ^3J(15a,16) = 7.4, H_a–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 (2*s*, Me_2Si). ES-MS (pos. mode): 593 (100, $[M+Na]^+$), 571 (20, $[M+H]^+$), 513 (35, $[M-$acetone$+H]^+$). Anal. calc. for $C_{32}H_{46}O_5SSi$ (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-[(1*SR*)-1-hydroxypropyl]-8-oxabicyclo[3.2.1]oct-3-en-2-one* (**64**). At –78° 0.5M Me_2AlSeMe in toluene (1.6 ml, 0.8 mmol) was added to a stirred soln. of (±)-**13** (0.2 g, 0.55 mmol) in anh. THF (2 ml). After stirring at –78° for 30 min, propanal (0.2 ml, 160 mg, 2.75 mmol) was added dropwise. After stirring at –78° for 12 h, 100% *m*CPBA (275 mg, 1.6 mmol) was added. After stirring at –78° for 1 h, the mixture was allowed to warm up to –20° within *ca*. 3 h. $CHCl_3$ (20 ml) was added, and the soln. was washed successively with 1N HCl (10 ml), 0.5M aq. $Na_2S_2O_3$ soln. (10 ml), and sat. aq. $NaHCO_3$ soln. (10 ml). The aq. layers were extracted with $CHCl_3$ (3×10 ml) and the combined org. extracts dried ($MgSO_4$) and evaporated. FC (2×13 cm, light petroleum ether/Et_2O 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}H-NMR (400 MHz, $CDCl_3$): 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 (2*d*, ^2J = 11.2, PhCH_2O); 4.51 (br. *d*, ^3J(5,4) = 4.9, H–C(5)); 4.35 (*m*, ^3J(1′,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(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 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 195.0 (*s*, C(2)); 141.6 (*d*, ^1J(C,H) = 159, C(4)); 140.8 (*s*, C(3)); 136.8 (*s*, arom. C); 128.4, 128.1, 128.0 (3*d*, ^1J(C,H) = 160, arom. C); 86.1 (*d*, ^1J(C,H) = 153, C(7)); 83.1 (*d*, ^1J(C,H) = 159, C(1)); 81.6 (*d*, ^1J(C,H) = 157, C(5)); 79.4 (*d*, ^1J(C,H) = 150, C(6)); 73.6 (*t*, ^1J(C,H) = 142, PhCH_2O); 70.6 (*d*, ^1J(C,H) = 143, C(1′)); 28.7 (*t*, ^1J(C,H) = 127, C(2′)); 25.7 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 18.1 (*s*, Me_3*C*Si); 9.6 (*q*, ^1J(C,H) = 126, C(3′)); –4.9 (*q*, ^1J(C,H) = 119, Me_2Si). CI-MS (NH_3): 436 (100, $[M+18]^+$), 418 (43, M^+), 401 (80, $[M-OH]^+$), 269 (20, $[M-C_3H_7O-Bn+H]^+$), 264 (32), 245 (14), 207 (35), 155 (54) 108 (37), 91 (86). Anal. calc. for $C_{23}H_{34}O_5Si$ (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-α-*D-galacto-*pyranose* ((+)-**66**). At –78°, 0.5M Me_2AlSeMe in toluene (0.7 ml, 0.35 mmol) was added dropwise to a stirred soln. of (±)-**13** (0.1 g, 0.277 mmol) in anh. THF (1 ml). After stirring at –78° for 1 h, a soln. of 1,2:3,4-di-*O*-isopropylidene-α-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°. After stirring at –78° for 16 h, 100% *m*CPBA (135 mg, 0.78 mmol) was added. After stirring at –78° for 1 h, the mixture was allowed to warm up to –20° with in 90 min under stirring. $CHCl_3$ (5 ml) was added, and the soln. was immediately washed successively with ice-cold 1N HCl (5 ml), 0.5M aq. $Na_2S_2O_3$ (5 ml), and sat. aq. $NaHCO_3$ soln. (5 ml). The aq. layers were extracted with $CHCl_3$ (3×5 ml) and the combined org. extracts dried ($MgSO_4$) and evaporated. FC (1.5×14 cm, light petroleum ether/Et_2O 1:1) gave 45 mg (27%) of (+)-**66**. Colorless foam. $[\alpha]_D^{25} = 9.6$, $[\alpha]_{577}^{25} = 8.8$, $[\alpha]_{546}^{25} = 13$, $[\alpha]_{435}^{25} = 187$, $[\alpha]_{405}^{25} = 544$ ($c = 0.13$, CH_2Cl_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}H-NMR (400 MHz, $CDCl_3$): 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,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 (2*d*, ^2J = 10.9, PhCH_2O); 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(OH,6) = 8.6, OH–C(6)); 1.62, 1.46, 1.33, 1.16 (4*s*, 2 Me_2C); 0.92 (*s*, Me_3CSi); 0.12, 0.11 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 194.7 (*s*, C(4′)); 144.3 (*d*, ^1J(C,H) = 163, C(2′)); 138.1, 136.6 (2*s*, C(3′), arom. C); 128.7, 128.1, 128.0 (3*d*, ^1J(C,H) = 160, arom. C); 109.0, 108.8 (2*s*, 2 Me_2*C*); 96.7 (*d*, ^1J(C,H) = 181, C(1)); 86.5 (*d*, ^1J(C,H) = 153, C(6′)); 83.0 (*d*, ^1J(C,H) = 160, C(5′)); 81.6 (*d*, ^1J(C,H) = 161, C(1′)); 79.8 (*d*, ^1J(C,H) = 150, C(7′)); 74.0 (*t*, ^1J(C,H) = 142, PhCH_2O); 71.5 (*d*, ^1J(C,H) = 151, C(4)); 70.5, 70.4, 70.2 (3*d*, ^1J(C,H) = 150, C(6), C(3), C(2)); 65.5 (*d*, ^1J(C,H) = 141, C(5)); 26.0, 25.7, 25.1, 23.6 (4*q*, ^1J(C,H) = 126,

2 *Me*$_2$C); 25.7 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 18.1 (*s*, Me$_3$*C*); −4.9 (*q*, ^1J(C,H) = 119, Me$_2$Si). CI-MS (NH_3): 636 (44, $[M+18]^+$), 619 (100, $[M+H]^+$), 601 (7, $[M-OH]^+$), 469 (12, $[M-H_2O-(t\text{-Bu})Me_2SiO]^+$), 445 (16, $[M-C(CH_3)_2-(t\text{-Bu})Me_2SiO]^+$), 355 (80), 276 (26), 207 (15), 91 (87). Anal. calc. for $C_{32}H_{46}O_{10}Si$ (618.79): C 62.10, H 7.51, Si 4.54; found: C 62.18, H 7.65, Si 4.63.

*Methyl (7*RS*)-3,5-Di*-O*-acetyl-2,6-anhydro-4*-O*-benzoyl-7*-C*-[(1*SR*,2*RS*,3*SR*,4*RS*,5*SR*,6*RS*,7*SR*)-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°, 0.7M Me_2AlSPh in CH_2Cl_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° for 45 min, crude (±)-**48** (48 mg) in soln. in anh. THF (0.5 ml) was added dropwise. After stirring at −78° for 1 h, the mixture was poured into ice-cold 1N aq. HCl (10 ml) under vigourous stirring. The mixture was extracted with $CHCl_3$ (15 ml, then 3 × 10 ml). The combined org. extract was washed with sat. aq. $NaHCO_3$ soln. (10 ml), dried ($MgSO_4$), and evaporated and the residue taken up in MeOH (4 ml). After cooling to 0°, $CeCl_3 \cdot 6H_2O$ (65 mg, 0.183 mmol), then $NaBH_4$ (5 mg, 0.13 mmol) were added portionwise under vigourous stirring. After 15 min at 0° the mixture was poured into sat. aq. NH_4Cl soln. (10 ml), H_2O (5 ml) and AcOEt (20 ml) under stirring. The aq. layer was extracted with AcOEt (4 × 10 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated. FC (1 × 15 cm, light petroleum ether/Et_2O/MeOH 40:60:1): 60 mg (56% based on (±)-**57** of (±)-**70**). Colorless solid. M.p. 192–194°. 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}H-NMR (400 MHz, $CDCl_3$): 7.95, 7.59–7.28 (2*m*, 2 H, 13 H, arom. H); 5.98 (br. *d*, ^3J(5,4) = 3.4, H−C(5)); 5.64 (*dd*, ^3J(3,4) = 10.2, ^3J(3,2) = 10.0, H−C(3)); 5.39 (*dd*, ^3J(4,3) = 10.2, ^3J(4,5) = 3.4, H−C(4)); 5.22 (br. *s*, OH); 4.76, 4.57 (2*d*, ^2J = 11.4, PhC*H*$_2$O); 4.68 (*dd*, ^3J(4′,5′) = 7.9, ^3J(4′,3′) = 4.4, H−C(4′)); 4.43 (*m*, ^3J(7,6) = 9.5, ^3J(7,3′) = 3.8, H−C(7)); 4.30 (*d*, ^3J(7′,6′) = 4.3, H−C(7′)); 4.29 (*s*, H−C(1′)); 4.20 (*dd*, ^3J(5′,4′) = 7.9, ^3J(5′,6′) = 5.3, H−C(5′)); 4.08 (*dd*, ^3J(6′,5′) = 5.3, ^3J(6′,7′) = 4.3, H−C(6′)); 4.07 (br. *s*, OH); 4.05 (*d*, ^3J(2,3) = 10.0, H−C(2)); 3.88 (br. *d*, ^3J(6,7) = 9.5, H−C(6)); 3.80 (*s*, COOMe); 3.64 (*d*, ^3J(2′,3′) = 10.7, H−C(2′)); 2.15, 1.98 (2*s*, 2 Ac); 2.00 (*ddd*, ^3J(3′,2′) = 10.7, ^3J(3′,4′) = 4.4, ^3J(3′,7) = 3.8, H−C(3′)); 0.84 (*s*, *t*-BuSi); 0.01, −0.10 (2*s*, Me$_2$Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.9, 169.6, 167.5, 165.5 (4*s*, 4 C=O); 136.2, 133.2, 129.2 (3*s*, arom. C); 134.1, 133.3, 129.7, 129.0, 128.8, 128.7, 128.5, 128.1, 127.9 (9*d*, ^1J(C,H) = 160, arom. C); 90.2 (*d*, ^1J(C,H) = 150, C(6′)); 88.8 (*d*, ^1J(C,H) = 158, C(1′)); 82.8 (*d*, ^1J(C,H) = 144, C(7′)); 77.8 (*d*, ^1J(C,H) = 142, C(6)); 77.3 (*d*, ^1J(C,H) = 145, C(2)); 74.4 (*t*, ^1J(C,H) = 144, PhC*H*$_2$O); 72.7 (*d*, ^1J(C,H) = 149, C(4)); 72.5 (*d*, ^1J(C,H) = 155, C(5′)); 71.1 (*d*, ^1J(C,H) = 149, C(4′)); 67.9 (*d*, ^1J(C,H) = 148, C(7)); 67.5 (*d*, ^1J(C,H) = 157, C(5)); 67.1 (*d*, ^1J(C,H) = 155, C(3)); 52.8 (*q*, ^1J(C,H) = 148, COO*Me*); 47.6 (*d*, ^1J(C,H) = 143, C(2′)); 37.5 (*d*, ^1J(C,H) = 132, C(3′)); 25.6 (*q*, ^1J(C,H) = 148, *Me*$_3$CSi); 20.7, 20.6 (2*q*, ^1J(C,H) = 130, 2 *Me*CO); 17.8 (*s*, Me$_3$*C*Si); −4.8, −4.9 (2*q*, ^1J(C,H) = 119, Me$_2$Si). CI-MS (NH_3): 881 (9, $[M+1]^+$), 676 (3, $[M-(t\text{-Bu})Me_2Si-Bn+2H]^+$), 626 (4, $[M-BzOH-(t\text{-Bu})Me_2SiOH]^+$), 550 (2, $[M-Bz-(t\text{-Bu})Me_2Si-PhSH]^+$), 510 (3, $[M-AcO-Bn-Bz-(t\text{-Bu})Me_2Si]^+$), 468 (3, $[M-Ac-AcO-Bn-Bz-(t\text{-Bu})Me_2Si]^+$), 281 (10), 207 (18), 110 (11), 108 (6), 105 (10), 91 (16), 77 (9). Anal. calc. for $C_{45}H_{56}O_{14}SSi$ (881.17): C 61.33, H 6.42; found: C 61.41, H 6.46.

*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**). As described for (±)-**70**, from (−)-**57** (source of optically active **48**) and (−)-**13**. Yield 44% based on (−)-**57**. White foam. $[\alpha]_D^{25} = -26$, $[\alpha]_{577}^{25} = -28$, $[\alpha]_{546}^{25} = -32$, $[\alpha]_{435}^{25} = -51$, $[\alpha]_{405}^{25} = -61$ (*c* = 0.5, CH_2Cl_2).

*Methyl (7*RS*)-3,5-Di*-O*-acetyl-2,6-anhydro-4*-O*-benzoyl-7*-C*-[(1*RS*,5*RS*,6*RS*,7*RS*)-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°, 0.5M $Me_2AlSeMe$ 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° 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° for 18 h, 100% *m*CPBA (112 mg, 0.65 mmol) was added. The mixture was stirred at −78° for 1 h and allowed to warm to −20° within *ca.* 4 h. After dilution with cold $CHCl_3$ (−20°, 15 ml), the mixture was washed successively with ice-cold 1N aq. HCl (10 ml), 0.5M aq. $Na_2S_2O_3$ (10 ml), and sat. aq. $NaHCO_3$ soln. (10 ml). The aq. layers were extracted with $CHCl_3$ (3 × 10 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated. FC (1.5 × 12 cm, light petroleum ether/Et_2O 3:7): 77 mg (52% based on (±)-**57**) of (±)-**71**. Colorless foam. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.90, 7.57, 7.43, 7.33 (4*m*, 2 H, 1 H, 2 H, 5 H, arom. H); 7.13 (*dd*, ^3J(2′,1′) = 4.9, ^4J(2′,7) = 1.1, H−C(2′)); 5.73 (*d*, ^3J(5,4) = 3.3, H−C(5)); 5.52 (*dd*, ^3J(3,4) = 10.0, ^3J(3,2) = 10.0, H−C(3)); 4.86 (*dd*, ^3J(4,3) = 10.0, ^3J(4,5) = 3.3, H−C(4)); 4.77 (*d*, ^3J(5′,6′) = 7.1, H−C(5′)); 4.76 (*dd*, ^3J(7,6) = 5.3, ^4J(7,2′) = 1.1, H−C(7)); 4.56 (*s*, PhC*H*$_2$O); 4.49 (*d*, ^3J(1′,2′) = 4.9, H−C(1′)); 4.40 (*s*, H−C(7′)); 4.27 (*d*, ^3J(6′,5′) = 7.1, H−C(6′)); 3.96 (*d*, ^3J(2,3) = 10.0, H−C(2)); 3.79 (*d*, ^3J(6,7) = 5.3, H−C(6)); 3.77 (*s*, COOMe); 2.09, 1.98 (2*s*, 2 Ac); 0.87 (*s*, *t*-

BuSi); 0.09 (*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 194.9 (*s*, C(4′)); 169.7, 169.6, 167.7, 164.8 (4*s*, 4 C=O); 145.7 (*d*, ^1J(C,H) = 164, C(2′)); 136.8, 129.2 (2*s*, arom. C); 135.2 (*s*, C(3′)); 133.3, 129.6, 128.6, 128.5, 128.4, 128.1 (6*d*, ^1J(C,H) = 160, arom. C); 85.5 (*d*, ^1J(C,H) = 153, C(6′)); 83.0 (*d*, ^1J(C,H) = 160, C(5′)); 81.9 (*d*, ^1J(C,H) = 163, C(1′)); 78.8 (*d*, ^1J(C,H) = 152, C(7′)); 76.9, 76.7 (2*d*, ^1J(C,H) = 145, C(2), C(6)); 73.3 (*t*, ^1J(C,H) = 144, PhCH_2O); 72.5 (*d*, ^1J(C,H) = 148, C(4)); 69.1 (*d*, ^1J(C,H) = 152, C(7)); 66.7, 66.6 (2*d*, ^1J(C,H) = 155, C(3), C(5)); 52.7 (*q*, ^1J(C,H) = 148, COO*Me*); 25.7 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 20.9, 20.6 (2*q*, ^1J(C,H) = 130, 2 *Me*CO); 18.0 (*s*, Me_3*C*Si); −5.0, −5.1 (2*q*, ^1J(C,H) = 119, Me_2Si). CI-MS (NH_3): 768 (24, M^+), 619 (21, $[M - AcO - Bn + H]^+$), 595 (42, $[M - AcO - TBS + H]^+$), 505 (20), 207 (21), 105 (92), 91 (100), 77 (38).

*Methyl (7*RS*)-3,5,7-Tri*-O-*acetyl-7*-C-*[(1*SR,*2*RS,*3*SR,*4*RS,*5*SR,*6*SR,*7*RS*)-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_2O (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^{-1} Torr, the residue taken up in CH_2Cl_2 (10 ml) and the soln. washed with 1N aq. HCl (5 ml) and sat. aq. $NaHCO_3$ soln. (5 ml). The aq. layers were extracted with CH_2Cl_2 (4 × 10 ml) and the combined org. extracts dried ($MgSO_4$) 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_2O 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. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.91, 7.56, 7.42, 7.31 (4*m*, 2 H, 1 H, 4 H, 8 H, arom. H); 5.76 (*dd*, ^3J(7,6) = 9.5, ^3J(7,3′) = 5.7, H−C(7)); 5.58 (br. *d*, ^3J(5,4) = 3.4, H−C(5)); 5.56 (*dd*, ^3J(3,4) = 10.1, ^3J(3,2) = 10.0, H−C(3)); 5.51 (*dd*, ^3J(2′,1′) = 8.0, ^3J(2′,3′) = 4.4, H−C(2′)); 5.32 (*dd*, ^3J(4,3) = 10.1, ^3J(4,5) = 3.4, H−C(4)); 4.45 (br. *dd*, ^3J(1′,2′) = 8.0, ^3J(1′,7′) = 5.4, H−C(1′)); 4.43, 4.40 (2*d*, ^2J = 11.0, PhCH_2O); 4.23 (*dd*, ^3J(6′,7′) = 6.0, ^3J(6′,5′) = 1.8, H−C(6′)); 4.16 (*m*, ^3J(5′,6′) = 1.8, H−C(5′)); 4.13 (*d*, ^3J(2,3) = 10.0, H−C(2)); 4.04 (br. *d*, ^3J(6,7) = 9.5, H−C(6)); 3.82 (*dd*, ^3J(7′,6′) = 6.0, ^3J(7′,1′) = 5.4, H−C(7′)); 3.68 (*s*, COOMe); 3.23 (*d*, ^3J(4′,3′) = 10.2, H−C(4′)); 2.33 (*ddd*, ^3J(3′,4′) = 10.2, ^3J(3′,7) = 5.7, ^3J(3′,2′) = 4.4, H−C(3′)); 2.11, 1.96, 1.95, 1.72 (4*s*, 4 Ac); 0.81 (*s*, *t*-BuSi); 0.00, −0.08 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.0, 170.5, 169.6, 169.2, 167.3, 165.4 (6*s*, 6 C=O); 137.2, 133.0, 129.0 (3*s*, arom. C); 133.5, 133.1, 129.6, 129.2, 128.6, 128.5, 128.2, 127.9, 127.8 (9*d*, ^1J(C,H) = 160, arom. C); 88.6 (*d*, ^1J(C,H) = 148, C(7′)); 87.5 (*d*, ^1J(C,H) = 159, C(5′)); 80.5 (*d*, ^1J(C,H) = 147, C(6′)); 76.5 (*d*, ^1J(C,H) = 154, C(2)); 75.9 (*d*, ^1J(C,H) = 145, C(6)); 74.3 (*t*, ^1J(C,H) = 142, PhCH_2O); 72.3 (*d*, ^1J(C,H) = 145, C(4)); 72.1 (*d*, ^1J(C,H) = 155, C(1′)); 67.5 (*d*, ^1J(C,H) = 149, C(7)); 66.9 (*d*, ^1J(C,H) = 156, C(2′)); 66.6, 66.4 (2*d*, ^1J(C,H) = 155, C(3), C(5)); 52.7 (*q*, ^1J(C,H) = 148, COO*Me*); 47.9 (*d*, ^1J(C,H) = 143, C(4′)); 39.2 (*d*, ^1J(C,H) = 129, C(3′)); 25.6 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 21.2, 20.8, 20.6, 20.5 (4*q*, ^1J(C,H) = 130, 4 *Me*CO); 17.9 (*s*, Me_3*C*Si); −4.7, −5.0 (2*q*, ^1J(C,H) = 118, Me_2Si). CI-MS (NH_3): 908 (13, $[M - C_4H_9 + H]^+$), 110 (28), 105 (52), 91 (100), 77 (23). Anal. calc. for $C_{49}H_{60}O_{16}SSi$ (965.25): C 60.97, H 6.28; found: C 61.06, H 6.34.

*Methyl (7*S*)-3,5,7-Tri*-O-*acetyl-7*-C-*[(1*R,*2*S,*3*R,*4*S,*5*R,*6*R,*7*S*)-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. $[\alpha]_D^{25}$ = −1.7, $[\alpha]_{577}^{25}$ = −2.0, $[\alpha]_{546}^{25}$ = −1.5, $[\alpha]_{435}^{25}$ = 0.3, $[\alpha]_{405}^{25}$ = 2.1 (*c* = 0.9, CH_2Cl_2).

*Methyl (7*RS*)-3,5,7-Tri*-O-*acetyl-7*-C-*[(1*SR,*2*RS,*3*SR,*4*RS,*5*SR,*7*RS*)-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. $NaHCO_3$ soln. (10 ml) was added and the mixture extracted with AcOEt (30 ml, then 4 × 5 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated giving 87 mg of yellowish foamy alcohol that was taken up in anh. CH_2Cl_2 (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. $NaHCO_3$ soln. containing $Na_2S_2O_3$ (240 mg, 10 ml), then with H_2O (10 ml). The aq. layers were extracted with AcOEt (4 × 10 ml). The combined org. extracts were dried ($MgSO_4$) 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_2O 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. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.91, 7.56, 7.43, 7.33 (4*m*, 2 H, 1 H, 4 H, 8 H, arom. H); 5.77 (*dd*, ^3J(7,6) = 9.5, ^3J(7,3′) = 4.6, H−C(7)); 5.64 (*dd*, ^3J(2′,1′) = 7.6, ^3J(2′,3′) = 3.5, H−C(2′)); 5.58 (*dd*, ^3J(3,4) = 10.1, ^3J(3,2) = 10.0, H−C(3)); 5.54 (*dd*, ^3J(5,4) = 3.4, ^3J(5,6) = 1.0, H−C(5)); 5.32 (*dd*, ^3J(4,3) = 10.1, ^3J(4,5) = 3.4, H−C(4)); 4.72 (*ddd*, ^3J(1′,2′) = 7.6, ^3J(1′,7′) = 6.3, ^4J(1′,5′) = 1.9, H−C(1′)); 4.63, 4.57 (2*d*, ^2J = 11.6, PhCH_2O); 4.38 (*m*, ^4J(5′,1′) = 1.9, ^4J(5′,7′) = 1.4, H−C(5′)); 4.26 (*dd*, ^3J(7′,1′) = 6.3, ^4J(7′,5′) = 1.4, H−C(7′)); 4.11 (*d*, ^3J(2,3) = 10.0, H−C(2)); 3.96 (*dd*, ^3J(6,7) = 9.5, ^3J(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 (4*s*, 4 Ac). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 209.6 (*s*, C(6')); 170.8, 170.4, 169.6, 169.1, 167.2, 165.4 (6*s*, 6 C=O); 136.3, 132.5, 128.9 (3*s*, arom. C); 133.5, 132.1, 129.6, 129.3, 128.6, 128.4, 128.3, 127.7 (8*d*, ^1J(C,H) = 160, arom. C); 81.8, 81.7 (2*d*, ^1J(C,H) = 147, 157, C(5'), C(7')); 76.7 (*d*, ^1J(C,H) = 150, C(2)); 75.5 (*d*, ^1J(C,H) = 140, C(6)); 74.3 (*d*, ^1J(C,H) = 162, C(1')); 73.9 (*t*, ^1J(C,H) = 143, Ph*C*H_2O); 72.2 (*d*, ^1J(C,H) = 148, C(4)); 67.0 (*d*, ^1J(C,H) = 152, C(7)); 66.5 (*d*, ^1J(C,H) = 155, C(3)); 66.2 (*d*, ^1J(C,H) = 155, C(5)); 66.1 (*d*, ^1J(C,H) = 155, C(2')); 52.8 (*q*, ^1J(C,H) = 148, COO*Me*); 44.4 (*d*, ^1J(C,H) = 145, C(4')); 39.2 (*d*, ^1J(C,H) = 131, C(3')); 21.0, 20.7, 20.6 (3*q*, ^1J(C,H) = 130, 4 *Me*CO). CI-MS (NH_3): 866 (1, $[M+18]^+$), 849 (2, $[M+H]^+$), 789 (0.5, $[M-AcO]^+$), 731 (0.5, $[M-2AcO+H]^+$), 619 (2, $[M-BnO-BzOH]^+$), 531 (5), 109 (13), 105 (67), 91 (100), 77 (20). Anal. calc. for $C_{43}H_{44}O_{16}S$ (848.94). C 60.84, H 5.22; found: C 60.88, H 5.29.

*Methyl (7*S*)-3,5,7-Tri*-O-*acetyl-7*-C-*[(1*R*,2*S*,3*R*,4*S*,5*R*,7*S*)-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 (±)-**73**, with (–)-**72**. Colorless oil. $[\alpha]_D^{25}=-19$, $[\alpha]_{577}^{25}=-19$, $[\alpha]_{546}^{25}=-24$, $[\alpha]_{435}^{25}=-31$, $[\alpha]_{405}^{25}=-28$ ($c=0.6$, CH_2Cl_2).

*Methyl (7*RS*)-3,5,7-Tri*-O-*acetyl-7*-C-*[(1*SR*,4*SR*,5*SR*,6*RS*,7*SR*,8*RS*)-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 (±)-**73** (89 mg, 0.105 mmol), $NaHCO_3$ (10 mg), 90% *m*CPBA (74 mg, 0.39 mg), and anh. $CHCl_3$ (4 ml) was stirred at 20° for 16 h. AcOEt (25 ml) was added and the soln. washed with 0.5M aq. $Na_2S_2O_3$ (15 ml), then with sat. aq. $NaHCO_3$ soln. (15 ml). The aq. layers were extracted with AcOEt (4 × 15 ml) and the combined org. extracts dried ($MgSO_4$) and evaporated; 90 mg (96%) of (±)-**74**. Yellowish foam, which was used in the next step. An anal. sample was obtained by FC (1 × 12 cm, light petroleum ether/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}H-NMR (400 MHz, $CDCl_3$): 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*, $^2J=11.7$, Ph*C*H_2O); 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 (4*s*, 4 Ac). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.2, 169.5, 169.0, 168.9, 167.6, 167.0, 165.4 (7*s*, 6 C=O, C(2')); 136.9, 135.0, 129.0 (3*s*, arom. C); 134.4, 133.4, 129.7, 129.5, 129.4, 128.7, 128.6, 128.5, 128.2 (9*d*, ^1J(C,H) = 160, arom. C); 100.6 (*d*, ^1J(C,H) = 177, C(4')); 76.7 (*d*, ^1J(C,H) = 150, C(2)); 75.4 (*d*, ^1J(C,H) = 144, C(6)); 72.1 (*d*, ^1J(C,H) = 146, C(4)); 71.8 (*t*, ^1J(C,H) = 144, Ph*C*H_2O); 70.2 (*d*, ^1J(C,H) = 154, C(5')); 69.9 (*d*, ^1J(C,H) = 153, C(1')); 68.2 (*d*, ^1J(C,H) = 152, C(7)); 66.3 (*d*, ^1J(C,H) = 155, C(5)); 66.2 (*d*, ^1J(C,H) = 155, C(3)); 63.7 (*d*, ^1J(C,H) = 154, C(6')); 62.2 (*d*, ^1J(C,H) = 144, C(8')); 52.9 (*q*, ^1J(C,H) = 148, COO*Me*); 34.4 (*d*, ^1J(C,H) = 132, C(7')); 21.1, 20.6 (2*q*, ^1J(C,H) = 130, 4 *Me*CO). CI-MS (NH_3): 914 (2, $[M+18]^+$), 896 (1, M^+), 717 (1, $[M-AcO-Bz+H]^+$), 577 (1, $[M-AcO-Bz-PhSO_2+2H]^+$), 471 (2), 122 (11), 108 (14), 105 (67), 91 (100), 77 (34). Anal. calc. for $C_{43}H_{44}O_{19}S$ (896.94): C 57.59, H 4.94, S 3.57; found: C 57.47, H 4.88, S 3.49.

*Methyl (7*S*)-3,5,7-Tri*-O-*acetyl-7*-C-*[(1*R*,4*R*,5*R*,6*S*,7*R*,8*S*)-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 (±)-**74**, with (–)-**73**. White foam. $[\alpha]_D^{25}=-62$, $[\alpha]_{577}^{25}=-66$, $[\alpha]_{546}^{25}=-74$, $[\alpha]_{435}^{25}=-122$, $[\alpha]_{405}^{25}=-144$ ($c=0.3$, CH_2Cl_2).

Diethyl Dithioacetal of Methyl 3-O-*Acetyl-2,6-anhydro-4,5-dideoxy-5*-C-*(phenylsulfonyl)-4*-C-*[[methyl (7*RS*)-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 CF_3SO_3H (15 µl) were added successively to a stirred soln. of crude (±)-**74** (90 mg, 0.10 mmol) in anh. CH_2Cl_2 (5 ml). After stirring at 20° for 15 min, a soln. of diazomethane in Et_2O was added until persistence of the yellow color. A drop of AcOH was added, then a sat. aq. $NaHCO_3$ soln. (15 ml). The mixture was extracted with AcOEt (25 ml, then 4 × 15 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated. FC (1 × 15 cm, light petroleum ether/AcOEt 1:1) gave 57 mg (61% based on (±)-**70**) of (±)-**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}H-NMR (400 MHz, $CDCl_3$): 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 (2*s*, 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_2S); 1.99, 1.99, 1.95, 1.92 (4*s*, 4 Ac); 1.27, 1.22 (2*t*, $^3J=7.4$, 2 *Me*CH_2S). ^{1}H-NMR (400 MHz, C_6D_6): 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_2S); 1.72, 1.71, 1.68, 1.62 (4*s*, 4 Ac); 1.19, 1.14 (2*t*, $^3J=7.4$, 2 *Me*CH_2S). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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(C,H) = 160, arom. C); 77.8 (*d*, ^1J(C,H) = 147, C(2)); 76.2 (*d*, ^1J(C,H) = 151, C(2′)); 74.3 (*d*, ^1J(C,H) = 144, C(6′)); 71.9 (*d*, ^1J(C,H) = 149, C(4′)); 69.9 (*d*, ^1J(C,H) = 147, C(6)); 68.9 (*d*, ^1J(C,H) = 151, C(7′)); 66.5 (*d*, ^1J(C,H) = 157, C(3′)); 65.9 (*d*, ^1J(C,H) = 156, C(5′)); 64.8 (*d*, ^1J(C,H) = 157, C(3)); 59.7 (*d*, ^1J(C,H) = 139, C(5)); 52.8 (*q*, ^1J(C,H) = 148, 2 COOMe); 52.0 (*d*, ^1J(C,H) = 151, C(1)); 37.3 (*d*, ^1J(C,H) = 131, C(4)); 25.2, 24.1 (2*t*, ^1J(C,H) = 139, 2 Me*C*H_2S); 21.4, 20.7, 20.6, 20.5 (4*q*, ^1J(C,H) = 130, 4 *Me*CO); 14.6, 14.3 (2*q*, ^1J(C,H) = 128, 2 *Me*CH_2S). CI-MS (NH_3): 944 (0.5, $[M+18]^+$), 926 (0.4, M^+), 865 (1, $[M-SEt]^+$), 849 (1, $[M-Ph]^+$), 745 (13, $[M-Ph-Bz+H]^+$), 663 (9, $[M-PhSO_2-BzOH]^+$), 603 (6, $[M-PhSO_2-BzOH-AcOH]^+$), 559 (5), 135 (14), 105 (100), 77 (31).

*Diethyl Dithioacetal 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* ((−)-**75**). As described for (±)-**75**, with (−)-**74**. Yield 48% based on (−)-**70**. White foam. $[\alpha]_D^{25}=-39$, $[\alpha]_{577}^{25}=-40$, $[\alpha]_{546}^{25}=-49$, $[\alpha]_{435}^{25}=-81$, $[\alpha]_{405}^{25}=-95$ ($c=0.7$, CH_2Cl_2).

*Methyl 3-*O*-Acetyl-2,6-anhydro-4,5-dideoxy-4-*C*-{[methyl (7*RS*)-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), anh. MeCN (2.3 ml), and $Hg(ClO_4)_2\cdot H_2O$ (35 mg, 0.076 mmol) was stirred at 20° for 30 min. $CHCl_3$ (25 ml) and Ag_2CO_3 (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 $CHCl_3$/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. ^{1}H-NMR (400 MHz, $CDCl_3$): 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 (7*RS*)-5-*O*-Acetyl-2,6-anhydro-7-*C*-[(1*RS*,5*RS*,6*RS*,7*RS*)-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 (7*RS*)-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-gluco-heptonate* ((±)-**77**). At −78°, 0.5M $Me_2AlSeMe$ in toluene (0.25 ml) was added dropwise to a stirred soln. of (±)-**13** (36 mg, 0.10 mmol) in anh. THF (1 ml). After stirring at −78° for 45 min, a soln. of (±)-**76** (27 mg, 0.033 mmol) in anh. 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. $CHCl_3$ (10 ml) was added and the soln. washed successively with 1N HCl (10 ml), 0.5M aq. $Na_2S_2O_3$ (10 ml), and sat. aq. $NaHCO_3$ soln. (10 ml). The aq. layers were extracted with $CHCl_3$ (4 × 10 ml) and the combined org. extracts dried ($MgSO_4$) 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. ^{1}H-NMR (400 MHz, 55°, C_6D_6): 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_2O); 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_2Si). ^{13}C-NMR (100.6 MHz, 55°,

C_6D_6): 194.5 (*s*, C(4″)); 171.4, 170.5, 169.8, 169.4, 169.3, 168.1, 165.7 (7*s*, 7 C=O); 147.1 (*d*, ^1J(C,H) = 167, C(2″)); 137.7, 137.3, 133.9, 130.2 (4*s*, 3 arom. C, C(3″)); 134.4, 133.3, 130.0, 129.7, 129.6, 129.5, 129.3, 128.9, 128.6 (9*d*, ^1J(C,H) = 160, arom. C); 88.5 (*d*, ^1J(C,H) = 152, C(6″)); 83.8 (*d*, ^1J(C,H) = 159, C(5″)); 82.2 (*d*, ^1J(C,H) = 163, C(1″)); 79.8 (*d*, ^1J(C,H) = 154, C(7″)); 78.0 (*d*, ^1J(C,H) = 145, C(6′)); 76.7 (*d*, ^1J(C,H) = 151, C(2′)); 76.0 (*d*, ^1J(C,H) = 149, C(6)); 74.9 (*t*, ^1J(C,H) = 141, Ph*C*H$_2$O); 74.0 (*d*, ^1J(C,H) = 148, C(4′)); 70.3 (*d*, ^1J(C,H) = 148, C(7)); 70.2 (*d*, ^1J(C,H) = 142, C(2)); 67.3 (*d*, ^1J(C,H) = 155, C(7′)); 67.1 (*d*, ^1J(C,H) = 155, C(5′)); 67.0 (*d*, ^1J(C,H) = 155, C(3′)); 63.9 (*d*, ^1J(C,H) = 156, C(5)); 61.3 (*d*, ^1J(C,H) = 143, C(3)); 52.4, 52.0 (2*q*, ^1J(C,H) = 148, 2 COO*Me*); 39.9 (*d*, ^1J(C,H) = 132, C(4)); 26.0 (*q*, ^1J(C,H) = 125, *Me*$_3$CSi); 21.7, 21.6, 20.5, 20.2 (4*q*, ^1J(C,H) = 130, 4 *Me*CO); 18.2 (*s*, Me$_3$*C*Si); −4.6, −4.7 (2*q*, ^1J(C,H) = 119, 2 Me$_2$Si). CI-MS (NH_3): 1198 (5, $[M+18]^+$), 1180 (3, M^+), 1031 (2, $[M-\text{Bn}-\text{OAc}+\text{H}]^+$), 1007 (2, $[M-\text{OAc}-(t\text{-Bu})\text{Me}_2\text{Si}+\text{H}]^+$), 917 (4, $[M-\text{Bn}-\text{OAc}-(t\text{-Bu})\text{Me}_2\text{Si}+2\,\text{H}]^+$), 207 (9), 125 (12), 105 (82), 91 (100), 77 (18). Anal. calc. for $C_{57}H_{68}O_{23}SSi$ (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 (7*S*)-5*-O-*Acetyl-2,6-anhydro-7*-C-*[(1*S*,5*S*,6*S*,7*S*)-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 (7*S*)-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-gluco-*heptonate* ((−)-**77**). As described for (±)-**77**, with (−)-**13**. Yield 46% based on (−)-**75**, enantiomerically pure **76** was not fully characterized. (−)-**77**: Colorless oil. $[\alpha]_D^{25} = -65$, $[\alpha]_{577}^{25} = -67$, $[\alpha]_{546}^{25} = -80$, $[\alpha]_{435}^{25} = -19$, $[\alpha]_{405}^{25} = -32$ ($c = 0.3$, CH_2Cl_2).

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