Synthesis of C-Linked Imino Disaccharides (= Aza-*C*-disaccharides) with a Pyrrolidine-3,4-diol Moiety Attached at C(3) of Galactose *via* a Hydroxymethylene Linker and of a 7-(1,2,3-Trihydroxypropyl)-octahydroxyindolizine-1,2,6,8-tetrol[1])[2])

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The lithium enolate of (±)-6-*endo*-chloro-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one (**16**) added to furan-2-carboxaldehyde giving a single aldol **19** (*Schemes 1* and *2*) that was converted with high stereoselectivity into (±)-(1*RS*,3*SR*,4*SR*,5*RS*,6*SR*)-5-*exo*-{(*RS*)-[(*tert*-butyl)dimethylsilyloxy](furan-2-yl)methyl}-6-*endo*-(methoxymethoxy)-2-oxo-7-oxabicyclo[2.2.1]hept-3-*exo*-yl 4-bromobenzenesulfonate (**46**). Highly regioselective *Baeyer-Villiger* oxidation of **46** provided the corresponding β-DL-altrofuranurono-6,1-lactone **49**, the methanolysis of which gave (±)-methyl 1,5-anhydro-3-{(*SR*)-[(*tert*-butyl)dimethylsilyloxy](furan-2-yl)methyl}-3-deoxy-2-*O*-(methoxymethyl)-α-DL-galactofuranuronate (**51**). Reduction of **51** followed by protection furnished (±)-1,4-anhydro-3-{(*SR*)-[(*tert*-butyl)dimethylsilyloxy](furan-2-yl)methyl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-DL-galactopyranose (**54**). Clean oxidation of the furan unit in **54** was possible with dimethyldioxirane, giving the corresponding (*Z*)-4-oxoenal **59** that was converted into pyrroles such as (±)-1,4-anhydro-3-{(*SR*)-[(*tert*-butyl)dimethylsilyloxy](1-benzyl-1*H*-pyrrol-2-yl)methyl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-DL-galactopyranose (**58**; *Scheme 5*), or into pyrrolidin-3,4-diols by dihydroxylation of (±)-1,4-anhydro-3-{(1′*RS*,2′*RS*,*Z*)-1′-[(*tert*-butyl)dimethylsilyloxy]-2′,5′-bis[(methylsulfonyl)oxy]pent-3′-enyl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-DL-galactopyranose (**70**; *Schemes 6* and *7*). After adequate protection (→ **70**), selective displacement of one of the mesylate moieties with LiN_3, followed by hydrogenation of the corresponding primary azide and intramolecular substitution, led to four protected, stereoisomeric C-linked imino disaccharides (*Scheme 7*); the latter were deprotected under acidic conditions to give (±)-3-deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-α-LD-ribitol-1′-*C*-yl]-DL-galactose (**3**), (±)-3-deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-α-DL-arabinitol-1′-*C*-yl]-DL-galactose (**4**), (±)-3-deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-β-DL-ribitol-1′-*C*-yl]-DL-galactose (**5**), and (±)-3-deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-β-LD-arabinitol-1′-*C*-yl]-DL-galactose (**6**). These unprotected C-linked imino disaccharides were more stable as ammonium chlorides in H_2O. Neutralization of **4** · HCl, followed by $NaBH_4$ reduction, gave (±)-(1*RS*,2*SR*,6*SR*,7*RS*,8*RS*,8a*SR*)-1,2,3,5,6,7,8,8a-octahydro-7-[(1*SR*,2*SR*)-1,2,3-trihydroxypropyl]indolizine-1,2,6,8-tetrol (**14**), a new octahydroindolizinepolyol (*Scheme 8*). Methyl glycosides of C-linked imino disaccharides **3**–**6** were also obtained, such as (±)-methyl 3-deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-α-LD-ribitol-1′-*C*-yl]-β-DL-galactofuranoside (**7**), (±)-methyl 3-deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-β-LD-arabinitol-1′-*C*-yl]-β-DL-galactofuranoside (**8**) and -α-DL-galactopyranoside (**9**), (±)-methyl 3-deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-α-DL-arabinitol-1′-*C*-yl]-β-DL-galactofuranoside (**11**) and -α-DL-galactopyranoside (**10**), and (±)-methyl 3-deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-β-DL-ribitol-1′-*C*-yl]-β-DL-galactofuranoside (**13**) and -α-DL-galactopyranoside (**12**). All these new C-linked imino disaccharides can be obtained in their enantiomerically pure form either starting with enantiomerically pure 7-oxabicyclo[2.2.1]heptan-2-one derivatives ('naked sugars of the first generation') or using the method of *Johnson* and *Zeller* applied to the racemic protected aldol 3-*exo*-{[(*tert*-butyl)dimethylsilyloxy](furan-2-yl)methyl}-6-*endo*-chloro-5-*exo*-(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one (**22**; see *Scheme 2*). The unprotected C-linked imino disaccharides **3**–**13** and octahydroindolizinetetrol **14** were tested for their inhibitory activity toward 25 commercially available glycohydrolases. Only compound **3** which mimics the mannopyranosyl-cation intermediate during the hydrolysis of an α-mannopyranosyl-(1 → 3)-galactose has a weak, but specific α-mannosidase inhibitory activity.

[1]) For a preliminary report, see [1a, b].

[2]) According to IUPAC/IUBMB [1d], cyclic sugar derivatives in which the ring O-atom has been replaced by NH have the class name 'imino sugar' (not 'aza sugar'), hence, corresponding disaccharides are called 'imino-disaccharides (not 'aza disaccharides') and 'C-linked imino disaccharides' (not 'aza-*C*-disaccharides').

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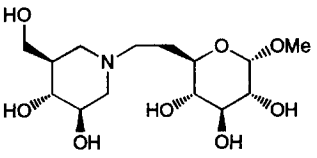
Introduction. – Glycosidases and glycosyltransferases are key enzymes in the biosynthesis and processing of glycoproteins, which are molecules involved in recognition (cell-cell, host-pathogen interactions) and in control of biological mechanisms and structures [2]. Thus, substances able to inhibit the biosynthetic pathway of glycoproteins have become important as potential antibacterial, antiviral, antimetastatic, antidiabetes, antihyperglycemic, antiadhesive, or immunostimulatory agents [3]. Deoxynojirimycin (1,5-dideoxy-1,5-imino-D-glucitol) is an α-glucosidase-I inhibitor; as a consequence it inhibits syncytia formation with HIV1 [4]. Castanospermine, another α-glucosidase inhibitor, has a synergic effect with AZT in inhibiting HIV1 and HIV2 growth [5]. It also prolongs renal allograft survival in the rat [6]. *N*-Alkylation of 1-deoxynojirimycin generates potential drugs such as *N*-butyl-1-deoxynojirimycin shown to prevent *Tay-Sachs* disease [7] or to reduce human hepatitis B [8] and HIV entry [9]. Analogues such as *N*-(7-oxadecyl)-1-deoxynojirimycin have been proposed as drug candidates to treat autoimmune diseases like rheumatoid arthritis [10]. The specific inhibition of individual N-linked glycoprotein-processing α-mannosidases by N-analogues of mannopyranose [11] and mannofuranose [12] may provide a useful anticancer strategy [13]. Swainsonine is a natural product containing a 4-amino-4-deoxy-mannofuranoside unit. It blocks *Golgi*-oligosaccharide processing (α-mannosidase-II inhibitor) and inhibits lysosomal α-mannosidase. Clinical trials have shown that it reduces solid tumors and hematological malignancies [14]. All these imino sugars[2]) often inhibit more than one enzyme *in vivo*. It is believed that selectivity would be increased if the imino sugar would include not only the steric and charge information of the glycosyl moiety which is liberated during the glycosidase-catalyzed hydrolysis but also that of the aglycon which is attached to it. Such inhibitors could be dideoxy-imino-alditols linked to other sugars through non-hydrolyzable links such as in the C-linked imino disaccharides[2]). These disaccharide mimics could also be candidates as haptens for the generation of catalytic antibodies [15]. The comparison of inhibitory activities toward glucoamylase between acarbose ($K_i \approx 10^{-12}$ M [16]) and (+)-lentiginosine ($K_i \approx 10^{-6}$ M [17]) demonstrates that inhibition is greatly enhanced if the glycosyl-cation mimic is attached to a mimic of the aglycon, the compound from which a monosaccharide is cleaved away. Recently, compound **1** which links isofagomine and methyl α-D-glucopyranoside was shown to have a potent inhibitory activity ($K_i \approx 6.3 \cdot 10^{-8}$ M) on glucoamylase [18]. *Withers* and coworkers [19] have shown that 2′-deoxy-2′-fluorocellobiose (= 2-deoxy-2-fluoro-β-D-glucopyranosyl-(1 → 4)-D-glucose) is a good and selective β-glucosidase inhibitor, much more potent and, more importantly, much more selective than 2-deoxy-2-fluoroglucose itself.



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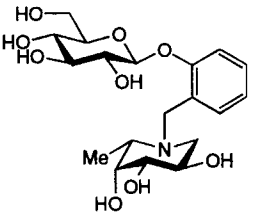

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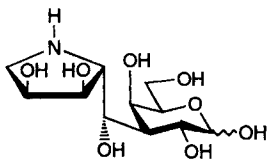
Fucosidase inhibitors can be fucosyltransferase inhibitors [20]. Compound **2** which links 1,5-dideoxy-1,5-imino-L-fucitol to D-glucose through a four-center linker was found to be a good inhibitor of α-1,3-fucosyltransferase [21]. The first example of a C-linked imino disaccharide (1,5-dideoxy-1,5-imino-D-mannitol linked at C(6) of D-galactose through a CH_2 unit) has been prepared by *Johnson* and coworkers [22]. Other examples of 'linear' C-linked imino disaccharides were obtained by *Martin* and coworkers [23]. We have prepared the first examples of C-linked imino disaccharides in which piperidinetriols are C-linked at position C(3) of hexoses [24][25]. Further examples were reported by *Johnson* and coworkers in which 1,5-dideoxy-1,5-imino-D-mannitol is β-C-linked at C(6) of D-mannose, at C(6) of D-glucose, at C(4) of D-talose, and at C(1) of D-glucose. None of these disaccharide mimics were inhibitors of α- or β-mannosidases [26]. In a preliminary study, we were more fortunate and found that the racemic disaccharide mimic **3** which connects 4-amino-1,4-anhydro-4-deoxyerythritol at C(1) to position C(3) of galactose through a CH(OH) linker was a moderate but specific inhibitor



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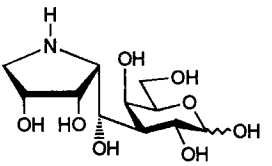

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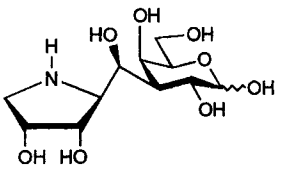

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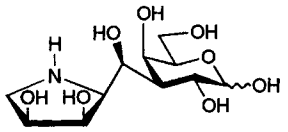

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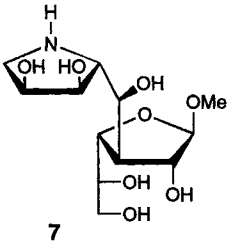

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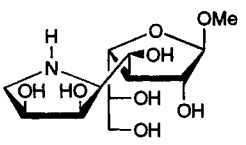

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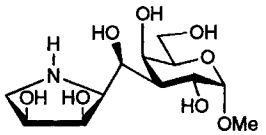

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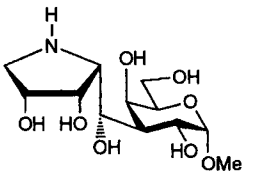

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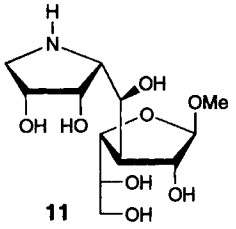

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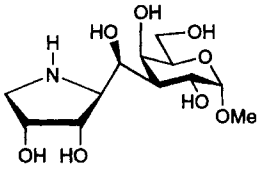

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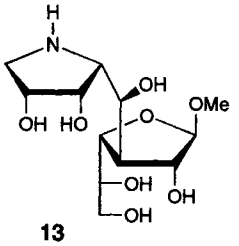

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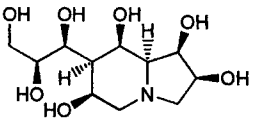

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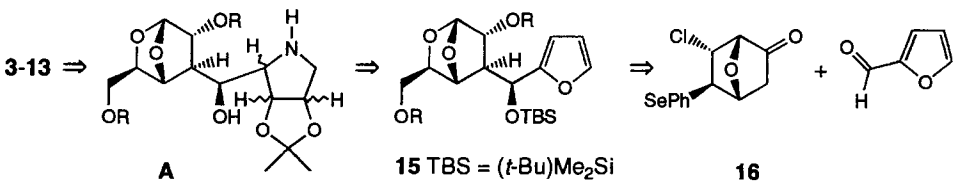
of jack-bean α-mannosidase [1a, b]. This C-linked imino disaccharide features the relative configuration of α-DL-mannose for its imino-sugar moiety. Interestingly, no commercially available glycohydrolases were inhibited at 1 mM concentration of the isomeric C-linked imino disaccharide **4**. We report here the details of the syntheses of these disaccharide mimetics together with those of the analogues **5**–**7**, **8**/**9**, **10**/**11**, and **12**/**13**, all obtained in their racemic forms[4]). We also present the synthesis of the polyhydroxylated octahydroindolizine **14**. None of these new compounds **5**–**14** did show any significant inhibitory activity toward 25 commercially available glycohydrolases.

***retro*-Synthetic Plan.** – The pyrrolidine-3,4-diol units in **3**–**13** and in the protected intermediates of type **A** will be derived from a furan moiety attached at C(3) of galactose by a C-linker as in **15** (*Scheme 1*). The galactose system will be a protected form of 1,4-anhydrogalactopyranose obtained from a 7-oxabicyclo[2.2.1]heptane derivative applying chemistry similar to that developed in our laboratory for the total synthesis of L-talose [27] from the 'naked sugars of the first generation' [28]. The CH(OH) linker between the imino sugar and galactose will result from an aldol condensation involving the 7-oxabicyclo[2.2.1]heptan-2-one derivative **16** and furan-2-carbaldehyde (= furfural).

Scheme 1

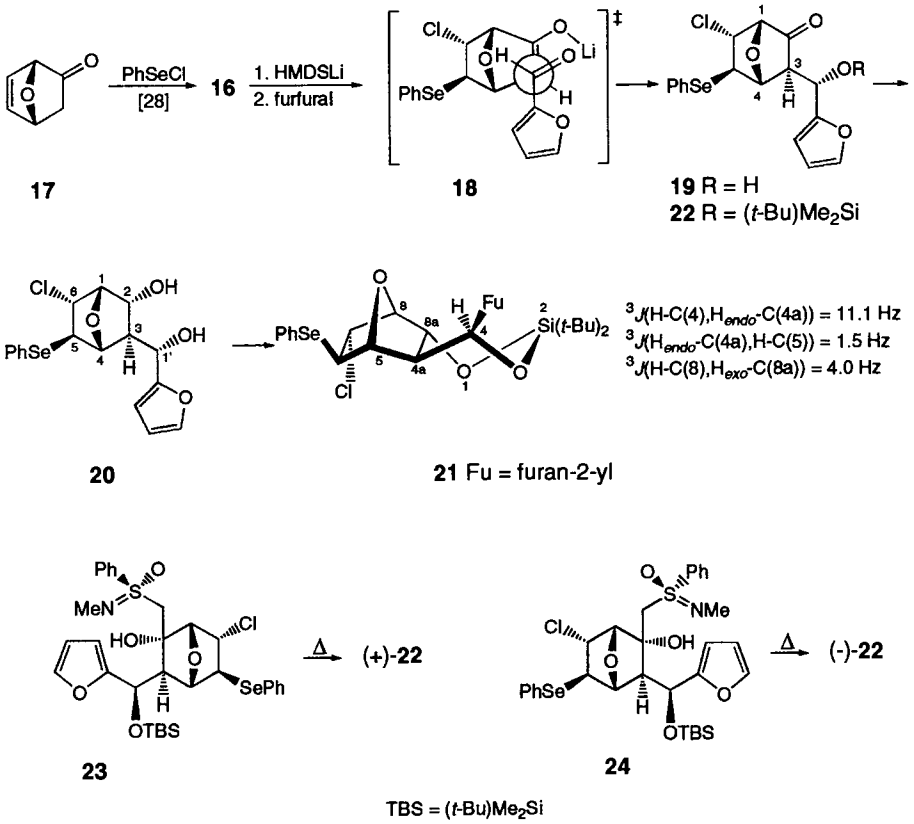


Results and Discussion. – Enone (±)-**17** added PhSeCl to give a single adduct **16** [29], the high regioselectivity of the addition being attributed to the electron-releasing effect of the homoconjugated carbonyl group [30] (*Scheme 2*). The lithium enolate of **16** (generated on treatment with $(Me_3Si)_2NLi$ in THF at −78°) reacted with furan-2-carbaldehyde at −78° to yield a single aldol **19** (95%). As expected for steric reasons (*Zimmerman-Traxler* model **18** [31], *like* mode of addition *exo*-face selective), the *anti* aldol was obtained, the relative configuration of which was established by the ^{1}H-NMR data of derivative **21** prepared in the following way. Reduction of ketone **19** with $NaBH_4$ (MeOH/THF, 0°) gave diol **20** (91%) that reacted with $(t\text{-Bu})_2Si(OTf)_2$ and 2,6-dimethylpyridine in CH_2Cl_2 (0–20°, 15 h) to provide **21** in mediocre yield (15%). Replacing CH_2Cl_2 with DMF (0°, 15 h) led to a better yield (50%).

The *exo* relative configuration of the aldol was confirmed by the vicinal coupling constant ^3J(H–C(4), H_{endo}–C(3)) ≈ 0 Hz in **19** and **20** [32]; the *endo* relative configuration of the OH group at C(2) in **20** was given by the vicinal coupling constants ^3J(H–C(1), H_{exo}–C(2)) = 4.1 and ^3J(H_{exo}–C(2), H_{endo}–C(3)) = 3.7 Hz [32]. The observation of a typical *trans*-diaxial coupling ^3J(H–C(4), H_{endo}–C(4a)) = 11.1 Hz in the perhydro-1,3-dioxa-2-silanaphthalene **21** confirmed the *anti* aldol structure **19**.

[4]) Only one enantiomer is shown in *Schemes* and *Formulae*.

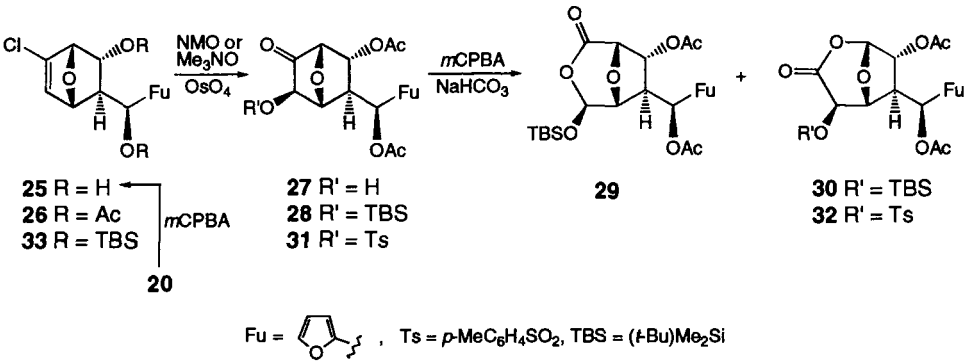
Scheme 2



Although **17** can be obtained in both its enantiomeric forms [28], we explored the possibility to resolve the racemic aldol **19**. We found that the silyl ether **22** (obtained on treating **19** with (*t*-Bu)Me_2SiCl/1*H*-imidazole in DMF (20°, 15 h, 96%)) reacted with the lithium salt of (+)-(*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximide to give a mixture of the sulfoximides [33] (92%) that were readily separated by flash chromatography (silica gel) to provide **23** and **24** in 47 and 45% yield, respectively (*Scheme 2*). Pyrolysis (150°/$3 \cdot 10^{-3}$ Torr, 5 min) gave (+)-**22** and (−)-**22**, respectively, in 52% yield. The absolute configuration of (−)-**22** was established by independent synthesis (yield 74%, 3 steps) starting from enantiomerically pure (+)-(1*R*,4*R*)-7-oxabicyclo[2.2.1]hept-5-en-2-one [28].

Oxidative elimination of the phenylseleno group of diol **20** with *meta*-chloroperbenzoic acid (*m*CPBA) afforded the corresponding chloroalkene derivative **25** (82%), the treatment of which with Ac_2O (pyridine, 4-(dimethylamino)pyridine (DMAP)) provided the diacetate **26** (92%) (*Scheme 3*). Double hydroxylation of the alkene moiety of **26** with 4-methylmorpholine 4-oxide (NMO)/OsO_4($NaHCO_3$, CCl_4/acetone/H_2O) gave the corresponding α-hydroxy ketone **27** which was not isolated but protected as a silyl ether with (*t*-Bu)Me_2SiCl/1*H*-imidazole in DMF to furnish **28** (59%). *Baeyer-Villiger* oxidation of **28**

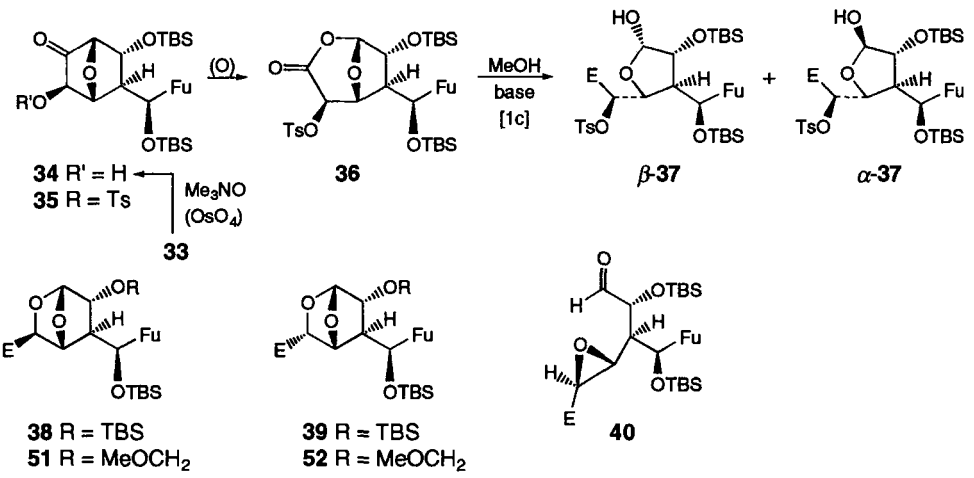
Scheme 3



with *m*CPBA ($NaHCO_3$, CH_2Cl_2) led to a 4:1 mixture of lactones **29** and **30** (76%), the major product resulting from the expected [34] insertion of an O-atom between the electron-rich (silyloxy)alkyl group and the ketone moiety. When the hydroxy ketone **27** was protected as a tosylate **31** (*p*-toluenesulfonyl chloride (TsCl), Et_3N, CH_2Cl_2), its *Baeyer-Villiger* oxidation with *m*CPBA furnished a single uronolactone **32** (54%).

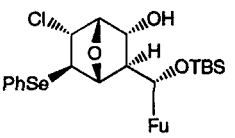
Since basic treatment of **32** led to complex mixtures of products, we protected diol **25** as bis-silyl ether **33** (83%) by treatment with (*t*-Bu)Me_2SiCl/1*H*-imidazole in DMF (*Scheme 3*). Double hydroxylation of the chloroalkene moiety of **33** with trimethylamine *N*-oxide/OsO_4 ($NaHCO_3$, CCl_4/THF/H_2O) gave **34** (86%) which was tosylated with TsCl and Et_3N to **35** (69%) (*Scheme 4*). *Baeyer-Villiger* oxidation of **35** provided uronolactone **36** (54%). Treatment of **36** with MeOH and $NaHCO_3$ (20°, 2 h) gave a 2:1 mixture of the α- and β-DL-furanose α-**37**[4]) and β-**37**[4]) [1c]. Since a S_Ni displacement of the TsO

Scheme 4

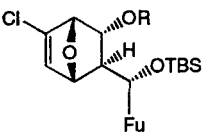


group by the β-OH group of the β-DL-furanose is expected to generate a methyl galactofuranuronate derivative, we looked for methanolysis conditions that would engender a larger proportion of β-**37** (for exper. details, see [1c]). On treatment of **36** with 1.5 equiv. of MeONa in anhydrous THF at −78°, a 1:2 mixture α-**37**/β-**37** was obtained. Finally, we found that short exposure of **36** to anhydrous K_2CO_3/MeOH (20°, 3 min) provided a 3:1 mixture β-**37**/α-**37**. When this mixture was treated under various conditions (DMF, THF/Et_3N, DBU, Li_2CO_3, K_2CO_3 + [18]-crown-6), mixtures containing the desired 1,5-anhydrogalactofuranuronate **38** and other undesired products of TsOH elimination such as the 1,5-anhydroaltrofuranuronate **39** and epoxy aldehyde **40** were obtained in mediocre yields (*Scheme 4*); the best results were found on treating a 3:1 mixture β-**37**/α-**37** in anhydrous DMF with 2.5 equiv. of K_2CO_3 (70–75°, 4 h) which led to the isolation of a 2:1 mixture of **38** and **39** (50%) and to the recovery of α-**37** (15%) [1c].

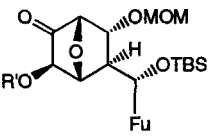
These unsatisfactory results suggested that the S_Ni displacement β-**37** → **38** is not fast enough compared with the anomerization β-**37** → α-**37**, the α-DL-anomer being more stable than the β-DL-anomer because of the bulk of the 2-(*tert*-butyl)dimethylsilyloxy group. We thus decided to replace this group by the less bulky methoxymethoxy substituent and to increase the S_Ni rate by replacing the TsO group by a better leaving group. This led us to convert the silyl-protected aldol **22** (*Scheme 2*) into alcohol **41** ($NaBH_4$, THF/MeOH; 91%) and to oxidize it with *m*CPBA (CH_2Cl_2, −78°) into the chloroalkene derivative **42** (91%) that was protected as the methoxymethyl ether **43** (84%). Double hydroxylation of **43** (as described above) gave the α-hydroxy ketone **44** which was esterified into tosylate **45** (72%), into 4-bromobenzenesulfonate **46** (77%), and into methanesulfonate **47** (78%) under standard conditions. *Baeyer-Villiger* oxidation (*m*CPBA, $NaHCO_3$, CH_2Cl_2, 0°) of **45**, **46**, and **47** provided the uronolactones **48** (77%), **49** (82%), and **50** (45%), respectively. The best yield in methyl anhydrogalactofuranuronate **51** (*Scheme 4*) was observed for the methanolysis of (brosyloxy)uronolactone **49** with 20% MeOH in anhydrous DMF containing 3 equiv. of anhydrous K_2CO_3. This



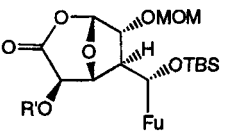
41 R = H



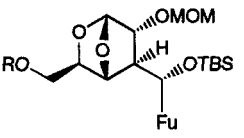
42 R = H
43 R = MOM



44 R' = H
45 R' = Ts
46 R' = Bs
47 R' = Ms



48 R' = Ts
49 R' = Bs
50 R' = Ms



53 R = H
54 R = MOM

Fu = furan-2-yl, Ts = *p*-$MeC_6H_4SO_2$, Bs = *p*-$BrC_6H_4SO_2$, Ms = $MeSO_2$,
TBS = (*t*-Bu)Me_2Si, MOM = $MeOCH_2$

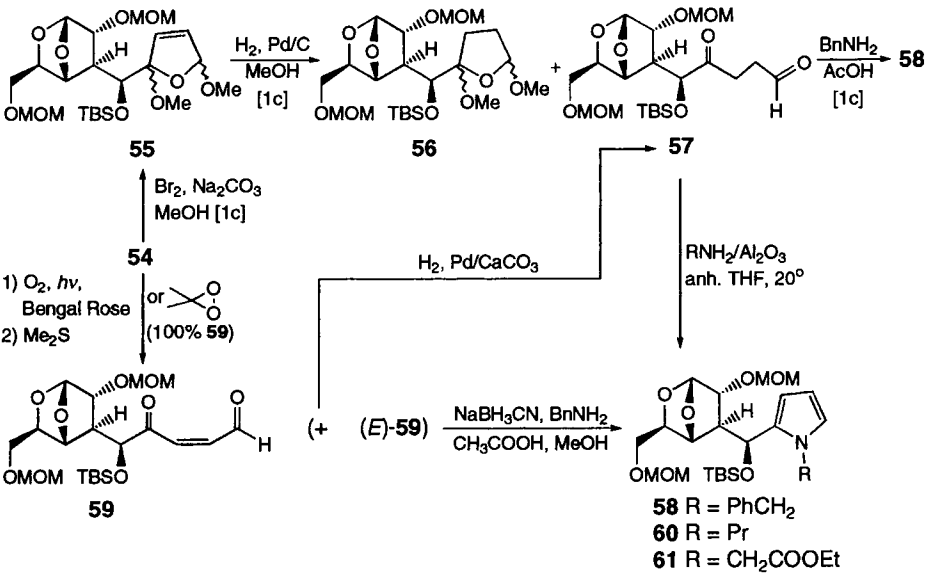
led to a 57:6 mixture of **51** and altrofuranuronate **52** (63%); a simple recrystallization provided pure **51** in 50% yield. Compound **51** was not epimerized into **52** in DMF/MeOH containing K_2CO_3 (20°, 6 h), indicating that **51** arises from the epimerization of (brosyloxy)uronolactone **49** or of an intermediate preceding the S_Ni displacement reaction. Reduction of the uronic ester **51** with $LiAlH_4$ gave alcohol **53** which was protected as methoxymethyl ether **54** (89%, 2 steps).

A procedure (see. *Exper. Part*) was worked out that allows one to convert ketone **16** (*Scheme 1*) into lactone **49** in 67% yield on a large scale (32.5 g, 8 steps). Conversion of **49** into **54** can be carried out on a 25-mmol scale (47% yield, 3 steps).

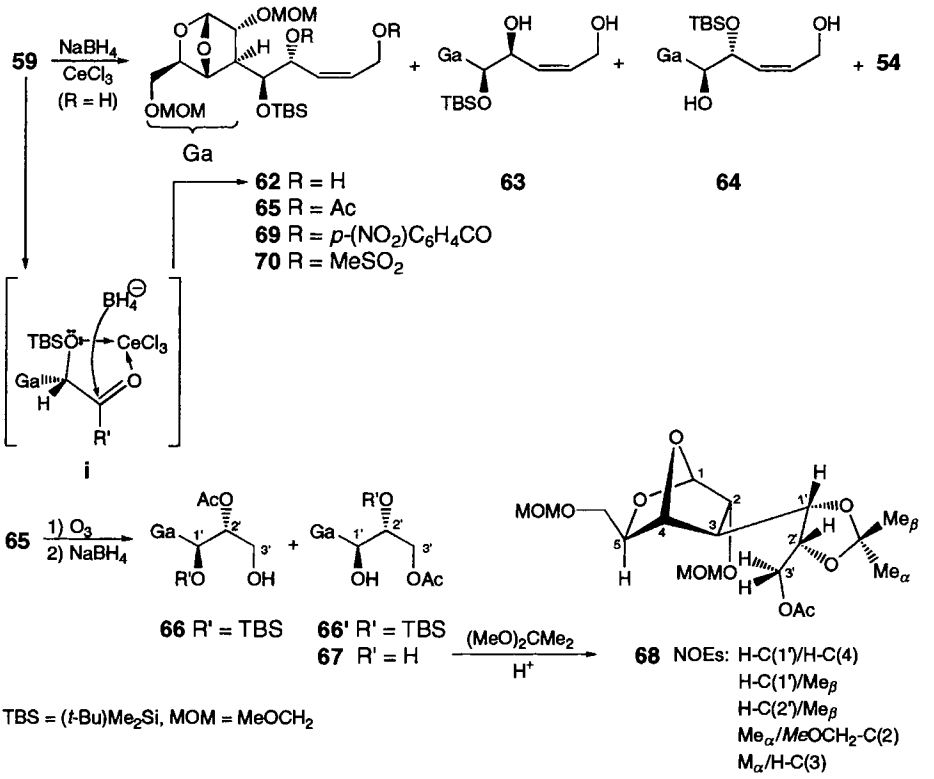
The *Clauson-Kaas* oxidation [35] of the furan moiety of **54** (Br_2, Na_2CO_3, anh. MeOH) generated the isomer mixture **55** (*Scheme 5*); the crude reaction mixture was hydrogenated (H_2, Pd/C, MeOH) and the obtained mixture **56**/**57** treated with $PhCH_2NH_2$ and AcOH [36] to provide the 1-benzyl-1*H*-pyrrole derivative **58** in trace amounts [1c]. Photooxidation (O_2, visible halogen-lamp, Bengal Rose B bound to polystyrene) of **54**, followed by reductive workup (Me_2S) gave **59** and its (*E*)-isomer which were hydrogenated (H_2, Pd/$CaCO_3$, 50 bar) into **57**. The latter was treated with $BnNH_2$ and AcOH (40°) to yield the 1*H*-pyrrole derivative **58** (45%). A somewhat better yield of **58** was obtained applying the method of *Texier-Boullet et al.* [37] ($BnNH_2$, neutral Al_2O_3, THF) to **57**. The same method allowed one to prepare the 1*H*-pyrrole derivatives **60** (39%) and **61** (35%) from **57**. Finally, a better overall yield of **58** was achieved by doubly reductive amination [38] of **59** ($NaBH_4CN$, $BnNH_2$, AcOH/MeOH). Pure (*Z*)-4-oxoenal **59** was obtained quantitatively by oxidation of furan derivative **54** with dimethyldioxirane.

Reduction of **59** under *Luche*'s conditions ($CeCl_3$, $NaBH_4$) [39] gave a *ca.* 9:1 mixture of enediols **62** and **63** (65%) together with 7–10% of **54** and variable amounts

Scheme 5



Scheme 6



of **64** resulting from the migration of the (*tert*-butyl)dimethylsilyl group in **63** (*Scheme 6*; for data of **63**, see [1c]). The relative configuration of the secondary allylic alcohol center was established in the following way. Acetylation of the mixture **62**/**63** 9:1 (Ac_2O/pyridine, DMAP) gave pure diacetate **65** (90%) which was treated with O_3 (anh. MeOH, −78°) first, then with $NaBH_4$. This led to alcohol **66** (77%). In some experiments, isomeric compound **66′** was isolated (10–15%) in which the AcO moiety, initially at C(2′), had migrated to the primary center C(3′) and the (*tert*-butyl)dimethylsilyl group, initially at C(1′), to C(2′), as suggested by its ^{1}H-NMR spectrum. Desilylation of **66** with Bu_4NF in THF liberated the diol **67** (78%) which was converted into the acetonide **68** (85%) on treatment with $Me_2C(OMe)_2$ in DMF and in the presence of pyridinium *p*-toluenesulfonate as catalyst. The structure of **68** was unequivocally established by its ^{1}H- and ^{13}C-NMR spectra and pertinent NOE data (see *Scheme 6*). The NMR data of **66** and **67** were also in agreement with the proposed structures. Thus, it was during the desilylation of **66** with Bu_4NF that the migration of the AcO group occurred. The diastereoselectivity of reduction **59** → **62** + **63** can be interpreted in terms of the *Felkin-Anh* model [41a] or in terms of the intermediacy of the cerium complex **i** which favors the *anti* mode of addition [41b].

The ^{1}H-NMR spectrum of **66′** showed a more important deshielding for the protons of the primary group CH_2(3′)–OAc (δ(H) 4.20 and 4.13) than for the protons at the secondary moieties CH(2′)–OSi (δ(H) 3.96) and

C*H*(1′)–OH (δ(H) 3.48). Confirmation for the presence of the OH–C(1′) group was given by the observation of a ^3J(H–C(1′), OH) = 9.7 Hz together with the other ^3J values (see *Exper. Part*).

The 400-MHz ^{1}H-NMR spectrum of **68** showed typical vicinal coupling constants ^3J(H–C(1′), H–C(2′)) = 7.2 Hz, consistent with a *cis* relation for these two protons, and NOEs between the signals of both H–C(1′) (δ(H) 3.88) and H–C(2′) (δ(H) 3.99) and one of the acetonide Me groups (δ 1.34 (Me_β)). NOEs between the second Me group of the acetonide moiety (δ 1.39 (Me_α)) and H–C(3) (δ 1.97) and one Me group of one of the two MOM groups (δ 3.30 (*Me*OCH$_2$–C(2)) were also observed, thus confirming structure **68**. Moreover, the ^{13}C-NMR spectrum of **68** showed signals typical for a 2,2-dimethyl-1,3-dioxolane (δ(C) 109.7 (*s*), 28.0, 27.6 (2*q*, ^1J(C,H) = 126 Hz)), not consistent with a 2,2-dimethyl-1,3-dioxane moiety adopting a chair conformation [40].

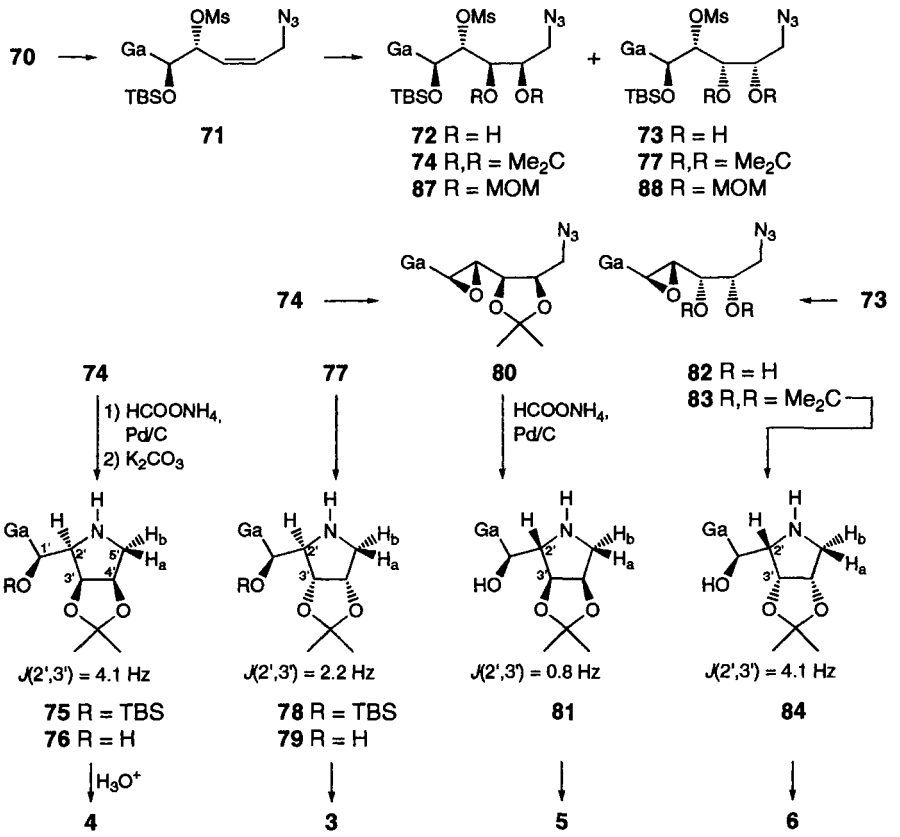
As for **66′**, the ^{1}H-NMR spectrum of diol **67** showed that protons of the primary C*H*$_2$OAc group (δ(H) 4.27 and 4.23) are more deshielded than H–C(2′) (δ(H) 3.87) and H–C(1′) (δ(H) 3.49) of the secondary moieties. The ^{13}C-NMR spectrum of **67** showed a *t* at δ(C) 66.1 with ^1J(C,H) = 150 Hz, in agreement with *C*H$_2$(3′)–OAc (*cf.* **66**: δ(*C*H$_2$(3′)–OH) 61.3 ppm, ^1J(C,H) = 141 Hz). In **68**, the protons of the primary CH$_2$(3′)–OAc group are more deshielded (δ(H) 4.22 and 4.15) than the protons at C(1′) and C(2′).

Esterification of **62** with 4-nitrobenzoyl chloride and Et$_3$N (DMAP as catalyst) provided the diester **69** (87%) (*Scheme 6*). Attempts to displace one or two ester moieties by benzylamine (DMF, 90°) led to complex product mixtures. The bis-mesylate **70** generated as an intermediate at −78° (MeSO$_2$Cl, Et$_3$N, CH$_2$Cl$_2$) reacted with LiN$_3$ (DMF, 0°) to give the unstable monoazide **71** (*Scheme 7*). The latter was treated with Me$_3$NO · 2 H$_2$O in THF/H$_2$O 4:1 in the presence of a catalytical amount of OsO$_4$ (20°). This furnished a 2:1 diol mixture **72**/**73** (55%, 3 steps)[5]) which were separated by flash column chromatography (silica gel) yielding 37 and 17% of pure **72** and **73**, respectively. The major diol **72** was protected with Me$_2$C(OMe)$_2$ (camphorsulfonic acid, 20°) and the resulting acetonide **74** (79%) reduced with HCOONH$_4$ in the presence of 10% Pd/C [43] to yield **75** (86%), after treatment with anhydrous K$_2$CO$_3$ in DMF (50°). Desilylation of **75** with Bu$_4$NF in anhydrous THF (0–20°) provided the partially protected C-linked imino disaccharide **76** (79% based on **74**). Under similar conditions, the minor diol **73** was converted into **77** (73%), **78**, and **79** (54% based on **77**). Desilylation of **74** (Bu$_4$NF, anhydrous THF), followed by treatment with DBU provided the corresponding epoxide **80** (80%). Hydrogenation of the azido moiety of **80** (HCOONH$_4$, Pd/C, MeOH) generated **81** (75%) which is the 2′-epimer of **76** (*Scheme 7*). Similarly, epoxide **82** (50%) was derived from **73** by treatment with Bu$_4$NF in anhydrous THF and then with DBU. This gave **82** which was protected as an acetonide **83**. Hydrogenation of **83** (HCOONH$_4$, Pd/C) provided **84** (63%) which is the 2′-epimer of **79**. The relative configurations of the pyrrolidines **76**, **79**, **81**, and **84** were established by their 2D NOESY ^{1}H-NMR and 2D COSY ^{1}H-NMR spectra. As expected, the vicinal coupling constants ^3J(H–C(2′), H–C(3′)) in the '*cis*' derivatives **76** and **84** are significantly larger (4.1 Hz) than those of the '*trans*' analogues **79** (2.2 Hz) and **81** (0.8 Hz).

Acidic hydrolysis (3N HCl/H$_2$O, 20°, 3 h) of **76**, **79**, **81**, and **84** led to the unprotected C-linked imino disaccharides **4**, **3**, **5**, and **6**, respectively, which are mixtures of α-DL- and β-DL-pyranoses and furanoses, their proportion varying with time, concentration, and temperature. The acidic aqueous solutions of **3**, **4**, **5**, and **6** are stable at 0° (pH 1) for one week. When an aqueous solution of **4** · HCl was neutralized to pH 8, indolizinium salt

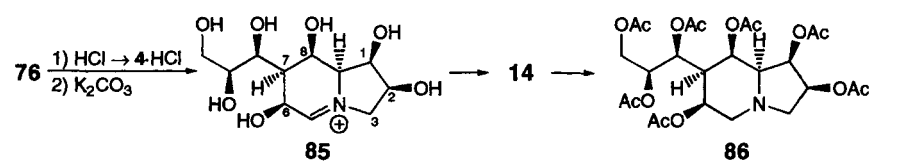
[5]) Under the conditions of asymmetric dihydroxylation [42], only slow decomposition was observed.

Scheme 7



for Ga, see *Scheme 6*; TBS = (*t*-Bu)Me_2Si, MOM = $MeOCH_2$

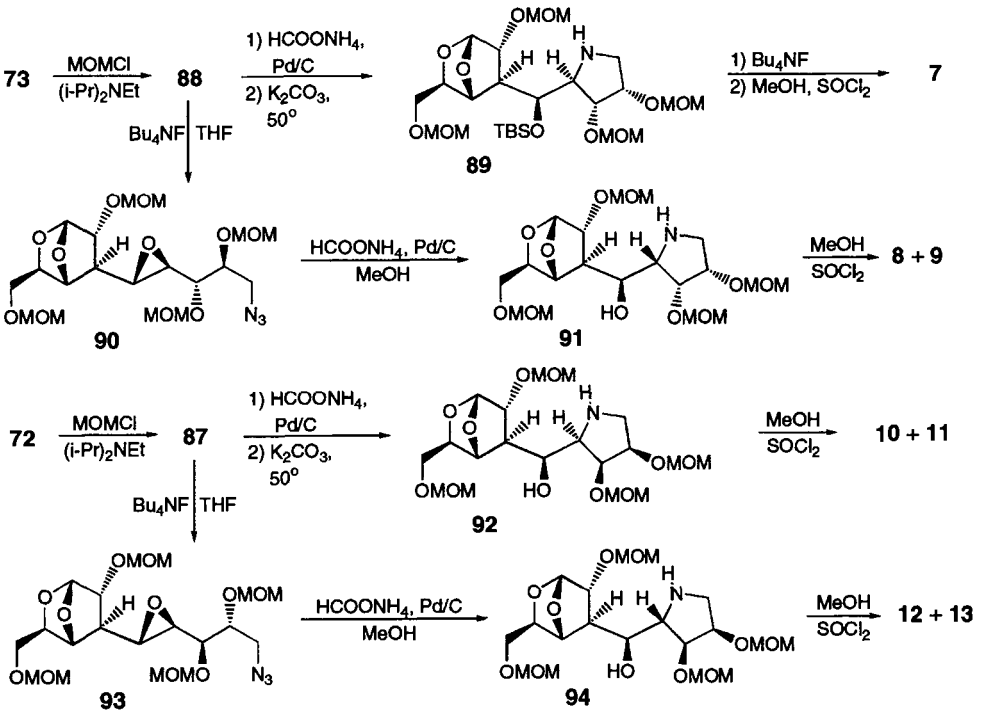
Scheme 8



85 was formed exclusively (*Scheme 8*), as indicated by its ^{1}H-NMR spectrum. After the addition of $NaBH_4$ (20°) and allowing to react for 1 h, 1N HCl was added (pH 2) and the product purified on *Dowex* exchange resin, giving octahydroindolizinetetrol **14** in 64% yield. This compound was fully characterized as its polyacetate **86** (54%) obtained on treatment with Ac_2O/pyridine and DMAP as catalyst.

Attempts to engender methyl pyranosides or furanosides of the C-linked imino disaccharides **3**–**6** under usual conditions (anh. MeOH, acid catalyst) all failed. We thus decided to replace the acetonide protective groups of the pyrrolidine-3,4-diol moieties in

Scheme 9



TBS = (*t*-Bu)Me_2Si, MOM = $MeOCH_2$

the precursors **74** and **77** by methoxymethyl groups, *i.e.*, **87** and **88** (*Scheme 7*) were prepared on treating diols **72** and **73** with $MeOCH_2Cl$ and $(i\text{-}Pr)_2NEt$, respectively (*Scheme 9*). Reduction of the azido group in **88** ($HCOONH_4$, Pd/C, MeOH), followed by treatment with K_2CO_3 (50°), gave **89** (63%). Desilylation (Bu_4NF, THF), followed by methanolysis and *Fischer*'s glycosidation (MeOH, $SOCl_2$, 20°, 15 h), led to methyl β-DL-furanoside **7**, isolated in 63% yield. This compound contained *ca.* 30% of methyl α-DL-furanoside and methyl α- and β-DL-pyranosides (by ^{1}H-NMR). On treating **88** with Bu_4NF (THF), epoxide **90** was obtained in 96% yield. Hydrogenation of the azide ($HCOONH_4$, Pd/C, MeOH) provided pyrrolidine **91** (65%) which, on treatment with MeOH and $SOCl_2$, furnished a 1:1 mixture of methyl β-DL-galactofuranoside **8** and methyl α-DL-galactopyranoside **9**. Under similar conditions (*Scheme 9*), **87** was converted into pyrrolidine **92** (80%), which, upon acidic treatment ($MeOH/SOCl_2$), provided a 3:2 mixture of methyl β-DL-galactofuranoside **10** and methyl α-DL-galactopyranoside **11**. Treatment of **87** with Bu_4NF in THF led to epoxide **93** (96%) which was converted into pyrrolidine **94** (74%). Methanolysis of **94** furnished a 6:3:1 mixture (87%) of methyl β-DL-galactofuranoside **13**, methyl α-DL-galactopyranoside **12**, and methyl α-DL-galactofuranoside (anomer of **13**). The relative configuratons of pyrrolidines **89**, **91**, **92**, and **94** were confirmed by their 2D NOESY and 2D COSY ^{1}H-NMR spectra.

Glycohydrolase Inhibition Assays. – At 1 mM concentration (solutions buffered just before use), the C-linked imino disaccharides **4**–**13** and the octahydroindolizinetetrol derivative **14** did not inhibit the following enzymes under standard conditions and optimal pH [12][44]: α-glucosidases (maltases) from yeast or rice; α-glucosidase (isomaltase) from baker's yeast; amyloglucosidases from *Aspergillus niger* or *Rhizopus* mold; β-glucosidases from almonds or *Caldocellum saccharolyticum*; α-galactosidases from coffee beans, *Aspergillus niger*, or *Escherichia coli*; β-galactosidases from *E. coli*, bovine liver, *Aspergillus niger*, *Aspergillus orizae*, or jack beans; α-mannosidases from jack beans or almonds; β-mannosidase from *Helix pomatia*; β-D-xylosidase from *Aspergillus niger*; α-L-fucosidases from bovine epididymis or human placenta; α-*N*-acetylgalactosaminidase from chicken liver; β-*N*-acetylglucosaminidases from jack beans, bovine epididymis A, or bovine epididymis B. Except for a 43 and 27% inhibition of jack bean and almond α-mannosidases, respectively, at 1 mM concentration, **3** did not inhibit the other 23 glycosidases. Compared with other pyrrolidinepolyols [45], **3** is a moderate α-mannosidase inhibitor, but on the contrary to the simpler analogues, it is much more specific.

The somewhat deceiving inhibitory activities found for the racemic C-linked imino disaccharide **3** are probably due to the fact that the α-mannosidases tested are not tuned up for the cleavage of α-mannofuranosyl- or α-mannopyranosyl-(1 → 3)-galactose but for α-mannofuranosyl- or α-mannopyranosyl-(1 → *n*) of other hexoses, with $n = 2, 3, 4$, or 6. C-Linked imino disaccharides having a pyrrolidine-3,4-diol moiety attached by its C(2) to position C(1), C(2), C(3), C(4), or C(6) of various hexoses *via* a CH_2 or CH(X) linker have to be prepared and tested to define whether the C-linked imino disaccharides can be useful tools for glycobiology and eventually useful leads for new drug discovery.

Conclusion. – A linear approach to the total synthesis of imino disaccharides linking pyrrolidine-3,4-diols to C(3) of galactose *via* a hydroxymethylene linker was developed starting from furan and furan-2-carbaldehyde. It features the highly stereoselective cross-aldol condensation of furan-2-carbaldehyde with a 7-oxabicyclo[2.2.1]heptan-2-one derivative than can be obtained in both its enantiomerically pure forms. The 7-oxabicyclo[2.2.1]heptan-2-one moiety of the aldol was converted into a 1,4-anhydrogalactopyranose derivative C-branched at C(3). The furan unit could then be oxidized cleanly by dimethyldioxirane, giving a (*Z*)-4-oxoenal system that was converted into pyrroles and pyrrolidine-3,4-diols applying standard reactions. Conditions were found allowing the transformation of these intermediates into non-protected C-linked imino disaccharides **3**–**6** and methyl-glycoside forms **7**–**13**. Only the disaccharide **3** ((±)-3-deoxy-[(1′*RS*)-2′,5′-dideoxy-2′,5′-imino-α-LD-ribitol-1′-*C*-yl]-α-DL-galactose) which mimics the intermediate mannopyranosyl cation, generated during the hydrolysis of a α-DL-mannopyranosyl-(1 → 3)-DL-galactose, showed weak, but specific α-mannosidase inhibitory activity. Interestingly, when the DL-galactose unit of the C-linked imino disaccharide **3** was conformationally blocked in its methyl β-DL-galactofuranoside derivative **10**, the α-mannosidase inhibitory activity was completely suppressed. As expected, the structure and conformation of the 'aglycon' part of the disaccharide mimetic plays a crucial role on the enzymatic inhibiting properties of the C-linked imino disaccharide.

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Experimental Part

General. Most procedures were not optimized. All solvents were distilled prior to use: THF and Et_2O from Na and benzophenone; DMF, CH_2Cl_2, and toluene from P_2O_5; Et_3N, $(i\text{-}Pr)_2NEt$, and pyridine from CaH_2; MeOH from Mg. Solns. after reactions and extractions were evaporated in a rotatory evaporator under reduced pressure. Liquid/solid flash chromatography (FC): columns of silica gel (0.040–0.63 μm, *Merck* No. *9385* silica gel *60*, 240–400 mesh) or *Lobar* columns (*Merck* SiO_2 or *RP-8*). Thin-layer chromatography (TLC) for reaction monitoring: *Merck* silica gel *60* F_{254} plates; detection by UV light. *Pancaldi* reagent ($(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O), or $KMnO_4$. Reagents were from *Fluka* or *Aldrich* and used without purification. M.p.: uncorrected; *Tottoli* (*Büchi SMP-20*) apparatus. Optical rotations: *Jasco-DIP-370* polarimeter. UV/VIS Spectra: *Kontron-Uvikon-811* or *Hewlett-Packard-HP8450A* spectrometer; λ in nm (ε [$dm^3\ mol^{-1}\ cm^{-1}$]). IR Spectra: *Perkin-Elmer-1420* or *Beckman-IR4230* spectrometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR Spectra: *Bruker-AC-250*, *Bruker-DPX-400*, or *Bruker-ARX-400* spectrometer, δ(H) in ppm rel. to internal Me_4Si (= 0.00 ppm) or to the solvent's residual ^{1}H-signal ($CHCl_3$, δ(H) 7.27; C_6HD_5, δ(H) 7.16; CHD_2COCD_3, δ(H) 1.95; CD_2HCN, δ(H) 2.50; CHD_2SOCD_3, δ(H) 2.50; CHD_2OD, δ(H) 3.31) as internal reference; in D_2O, internal reference $Me_3SiCH_2CH_2CH_2SO_3Na$ ($\delta(Me_3Si)$ 0), all ^{1}H-signal assignments were confirmed by double irradiation experiments or by 2D COSY-DQF or COSY-45 spectra. ^{13}C-NMR Spectra: same instruments as above (62.9 MHz, 100.61 MHz); δ(C) in ppm rel. to internal Me_4Si (= 0.00 ppm) or to the solvent's C-signal ($CDCl_3$, δ(C) 77.0; C_6D_6, δ(C) 128.4; $(CD_3)_2CO$, δ(C) 29.8; CD_3CN, δ(C) 1.3; $(CD_3)_2SO$, δ(C) 39.5; CD_3OD, δ(C) 49.2) as internal reference; coupling constants J in Hz (±0.5 Hz). MS: *Nermag R-10-10C*, chemical ionization (NH_3) mode; m/z (amu) (% rel. base peak (100%)). Elemental analysis: *Ilse Beetz*, D-96301 Kronach, Germany.

Enzymatic Assays. See [17][43].

*(±)-3-Deoxy-3-[(1′SR)-2′,5′-dideoxy-2′,5′-imino-α-*LD*-ribitol-1′-*C*-yl]-α-*DL*-galactose Deuteriumchloride* (**3** · DCl). In a 5-mm NMR tube, **79** (27 mg, 0.067 mmol) was dissolved in 3M DCl in D_2O (0.8 ml). After a few min at 20°, **3** · DCl was formed as 28:22:20:29:11 mixture of anomers. The soln. was stable at 0° for one week. ^{1}H-NMR (400 MHz, D_2O/DCl): 5.37 (*s*, 0.19 H), 5.33 (*d*, $^3J(1,2)$ = 1.8, 0.28 H), 5.29 (*d*, $^3J(1,2)$ = 4.5, 0.22 H), 5.26 (*d*, $^3J(1,2)$ = 3.5, 0.11 H), 4.72 (*d*, $^3J(1,2)$ = 7.8, 0.20 H, H–C(1)); 4.67–4.63 (*m*, 0.22 H), 4.58–4.54 (*m*, 0.61 H), 4.53–4.47 (*m*, 2 H, H–C(4′), H–C(3′), H–C(2)); 4.34–4.32 (*m*, 0.29 H), 4.28–4.16 (*m*, 0.86 H), 4.14–3.98 (*m*, 0.57 H, H–C(1′), H–C(4)); 3.95–3.88 (*m*, 0.76 H), 4.87–4.63 (*m*, 3.8 H, H–C(4), H–C(5), H–C(2), 2 H–C(6)); 3.58–3.39 (*m*, 3 H, 2 H–C(5′), H–C(2)); 2.78–2.71 (*m*, 0.11 H), 2.60–2.50 (*m*, 0.5 H), 2.21–2.15 (*m*, 0.40 H, H–C(3)). ^{13}C-NMR (100.6 MHz, D_2O/DCl): 102.8, 102.0, 97.7, 97.4, 95.7 (C(1)); 79.9, 79.3, 78.0, 77.2, 76.9, 76.8, 73.0, 71.8, 71.5, 71.1, 70.7, 70.5, 70.3, 70.2, 70.0, 68.3, 67.8, 67.5 (*d*, C(2), C(4), C(5), C(1′), C(3′), C(4′)); 63.7–63.4 (*t*, C(6)); 62.7–61.4 (*d*, C(2′)); 50.5 (*t*, C(5′)); 49.9–49.6 (*d*, C(3)).

*(±)-3-Deoxy-3-[(1′SR)-2′,5′-dideoxy-2′,5′-imino-α-*DL*-arabinitol-1′-*C*-yl]-*DL*-galactose Deuteriumchloride* (**4** · DCl). In a 5-mm NMR tube, **76** (32 mg, 0.079 mmol) was dissolved in 3M DCl in D_2O (0.8 ml). After 3 h at 20°, **4** · DCl was formed as a 44:44:12 mixture of α-DL-pyranose, α-DL-furanose, and β-DL-pyranose. The soln. is stable at 0° for one week. ^{1}H-NMR (400 MHz, D_2O/DCl): 5.27 (*d*, $^3J(1,2)$ = 2.5, 0.44 H), 5.26 (*d*, $^3J(1,2)$ = 4.3, 0.44 H), 4.72 (*d*, $^3J(1,2)$ = 8.0, 0.12 H, H–C(1)); 4.64–4.54 (*m*, 1 H, H–C(4′)); 4.53–4.45 (*m*, 1 H, H–C(3′)); 3.40–3.26 (*m*, 2 H, H–C(1′), H–C(2)); 4.23 (*dd*, ^3J = 8.2, 2.2, 0.4 H), 4.13 (*dd*, ^3J = 8.4, 3.1, 0.4 H, H–C(4)); 3.94–3.87 (*m*, 1 H, H–C(2′)); 3.86–3.62 (*m*, 4 H, H–C(5), CH_2(6), H_a–C(5′)); 3.30–3.22 (*m*, 1 H, H_b–C(5′)); 2.45–2.38 (*m*, 1 H, H–C(3)). ^{13}C-NMR (100.6 MHz, D_2O/DCl): 102.8, 95.6 (2*d*, C(1)); 78.9, 78.5, 78.1, 75.8, 71.3, 70.9, 70.1 (*d*, C(2), C(4), C(5), C(1′), C(3′), C(4′)); 69.3, 68.9 (*t*, C(6)); 64.2, 63.5 (*d*, C(2′)); 48.9 (*d*, C(3)); 47.9 (*t*, C(5′)); 44.9 (*d*, C(3)).

*(±)-3-Deoxy-3-[(1′SR)-2′,5′-dideoxy-2′,5′-imino-β-*DL*-ribitol-1′-*C*-yl]-*DL*-galactose Deuteriumchloride* (**5** · DCl). In a 5-mm NMR tube, **81** (37 mg, 0.091 mmol) was dissolved in 3M DCl in D_2O (0.8 ml). After 3 h at 20°, **5** · DCl was formed as a 33:33:17:17 mixture of anomers. The soln. was stable at 0° for one week. ^{1}H-NMR (D_2O/DCl, 400 MHz): 5.48 (*s*, 0.17 H), 5.28 (*d*, $^3J(1,2)$ = 3.0, 0.33 H), 5.27 (*d*, $^3J(1,2)$ = 5.0, 0.33 H), 4.69 (*d*, $^3J(1,2)$ = 8.0, 0.17 H, H–C(1)); 4.45–4.42 (*m*, 1 H, H–C(4′)); 4.42–4.28 (*m*, 2 H, H–C(3′), H–C(2)); 4.23–4.05 (*m*, 2 H, H–C(1′), H–C(4)); 3.88–3.66 (*m*, 4 H, H–C(2′), H–C(5), 2 H–C(6)); 3.66–3.40 (*m*, 2 H, CH_2(5′)); 2.55–2.48, 2.12–2.06 (2 *m*, 1 H, H–C(3)). ^{13}C-NMR (100.6 MHz, D_2O/DCl): 102.7 (*d*, J = 171), 101.1 (*d*, J = 173), 98.0 (*d*, J = 164), 95.7 (*d*, J = 174, C(1)); 79.1, 78.6, 78.2, 76.4, 75.8, 73.1, 72.7, 71.4, 71.1, 70.0, 69.8, 68.8, 68.6, 65.9, 65.4, 64.9, 64.0 (*d*, C(2), C(4), C(5), C(1′), C(3′), C(4′)); 63.5, 62.9, 61.9, 61.5 (*t*, C(6)); 58.2 (*d*, C(2′)); 51.0, 50.6, 50.5, 50.4, (*t*, C(5′)); 49.9, 47.5, 46.5, 45.8 (*d*, C(3)).

*(±)-3-Deoxy-3-[(1′SR)-2′,5′-dideoxy-2′,5′-imino-β-*LD*-arabinitol-1′-*C*-yl]-*DL*-galactose Deuteriumchloride* (**6** · DCl). In a 5-mm NMR tube, **84** (40 mg, 0.098 mmol) was dissolved in 3M DCl in D_2O (0.8 ml). After 3 h at 20°, **6** · DCl was formed as a 40:45:15 mixture of α-DL-pyranose, α-DL-furanose, and β-DL-pyranose. The soln. was

stable at 0° for one week. ^{1}H-NMR (400 MHz, D_2O/DCl): 5.28–5.24 (*m*, 0.85 H), 4.72 (*d*, $^3J(1,2)$ = 8.0, 0.15 H, H–C(1)); 4.62–4.53 (*m*, 1 H, H–C(4′)); 4.45–4.37 (*m*, 1.4 H, H–C(3′), H–C(2)); 3.34–3.28 (*m*, 1.6 H, H–C(1′), H–C(2)); 4.12–4.05 (*m*, 1 H, H–C(6), H–C(4)); 3.95 (*dd*, ^3J = 9.4, 3.0, 0.4 H), 3.86 (*dd*, ^3J = 9.8, 3.0, 0.4 H, H–C(2′)); 3.34–3.10 (*m*, 4.2 H, H–C(2), H–C(5), CH_2(6), H_a–C(5′)); 3.27–3.18 (*m*, 1 H, H_b–C(5′)); 2.50–2.42 (*m*, 1 H, H–C(3)). ^{13}C-NMR (100.6 MHz, D_2O/DCl): 102.6 (*d*, *J* = 172), 95.7 (*d*, *J* = 174, C(1)); , 78.7, 78.2, 75.6, 72.3, 71.3, 70.7, 70.5, 70.4, 70.0, 69.9, 69.4 (*d*, C(2), C(4), C(5), C(1′), C(3′), C(4′)); 65.2, 65.0 (*t*, C(6)); 63.4, 63.2 (*d*, C(2′)); 49.3 (*d*, C(3)); 47.0 (*t*, C(5′)); 45.6 (*d*, C(3)).

*(±)-Methyl 3-Deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-*α*-*LD*-ribitol-1′-C-yl]-*β*-*DL*-galactofuranoside* (**7**) *and Isomers.* A mixture of anhydro sugar **89** (30 mg, 0.053 mmol), anh. THF (2 ml), and 1M Bu_4NF in THF (0.106 ml, 0.106 mmol) was stirred at 20° for 5 min under Ar. The solvent was evaporated, the residue taken up with anh. MeOH (1 ml) under Ar, and freshly distilled $SOCl_2$ (40 µl, 0.42 mmol) was added. After stirring at 20° for 15 h, the solvent was evaporated and the residue purified on a column of *Dowex 50Wx8* resin (MeOH, then H_2O, then 1M aq. NH_3; *Pancaldi*). Lyophilization yielded 33 mg (63%) of **7** and isomers as a colorless powder, the ^{1}H- and ^{13}C-NMR of which [46] showing that **7** is contaminated by less than 30% of α-DL-furanoside, α-DL- and β-DL-pyranosides. IR (KBr): 3405, 2930, 1640, 1420, 1035. ^{1}H-NMR (400 MHz, D_2O, 310 K; data of **7**): 4.93 (*d*, $^3J(1,2)$ = 1.7, H–C(1)); 4.30 (*dd*, $^3J(2,3)$ = 4.5, $^3J(2,1)$ = 1.7, H–C(2)); 4.23–4.18 (*m*, H–C(4′), H–C(3′)); 4.10 (*dd*, $^3J(4,3)$ = 7.7, $^3J(4,5)$ = 2.0, H–C(4)); 3.89–3.72 (*m*, H–C(1′), H–C(5)); 3.72–3.68 (*m*, CH_2(6)); 3.38 (*s*, MeO); 3.30 (*dd*, $^3J(2′,1′)$ = 5.2, $^3J(2′,3′)$ = 4.6, H–C(2′)); 3.21 (*dd*, ^2J = 12.2, ^3J(5′a,4′) = 4.4, H_a–C(5′)); 3.02 (*dd*, ^2J = 12.2, ^3J(5′b,4′) = 3.8, H_b–C(5′)); 2.43 (*ddd*, $^3J(3,4)$ = 7.7, $^3J(3,1′)$ = 5.6, $^3J(3,2)$ = 4.5, H–C(3)). ^{13}C-NMR (100.6 MHz, D_2O, 310 K; data of **7**): 110.1 (*d*, *J* = 170, C(1)); 80.1 (*d*, *J* = 143, C(4)); 76.0 (*d*, *J* = 151, C(2)); 72.8 (*d*, *J* = 142, C(3′)); 71.7 (*d*, *J* = 152, C(4′)); 71.2 (*d*, *J* = 145, C(5)); 69.7 (*d*, *J* = 142, C(1′)); 64.8 (*d*, *J* = 139, C(2′)); 63.8 (*t*, *J* = 138, C(6)); 55.7 (*q*, *J* = 144, MeO); 50.6 (*t*, *J* = 143, C(5′)); 50.5 (*d*, *J* = 131, C(3)[6]). Anal. calc. for $C_{12}H_{23}NO_8$ (309.315): C 46.60, H 7.50, N 4.53; found: C 45.42, H 7.20, N 4.21.

*1:1 Mixture of (±)-Methyl 3-Deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-β-*LD*-arabinitol-1′-C-yl]-β-*DL*-galactofuranoside* (**8**) *and (±)-Methyl 3-Deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-β-*LD*-arabinitol-1′-C-yl]-α-*DL*-galactopyranoside* (**9**). Freshly distilled $SOCl_2$ (40 µl, 0.42 mmol) was added to a stirred soln. of **91** (21 mg, 0.05 mmol) in anh. MeOH (1 ml) under Ar. After stirring at 20° for 15 h, the solvent was evaporated and the residue purified on a column of *Dowex50Wx8* resin (MeOH, then H_2O, then 1M aq. NH_3; *Pancaldi*). Lyophilization yielded 12 mg (82%) of **8**/**9** 1:1. Colorless powder. IR (KBr): 3385, 1635, 1420, 1125, 620. ^{1}H-NMR (400 MHz, D_2O, 310 K): 4.88 (*d*, 0.5 H, $^3J(1,2)$ = 2.0, 0.5 H, H–C(1)fur); 4.81 (*d*, $^3J(1,2)$ = 4.6, 0.5 H, H–C(1)pyr); 4.39–4.31 (*m*, 1.5 H, H–C(4′), H–C(2)fur); 4.27–4.21 (*m*, 1.5 H, H–C(3′), H–C(2)fur); 4.08–4.05 (*m*, 1 H, H–C(4)); 4.00–3.97 (*m*, 1 H, H–C(1′)); 3.74–3.58 (*m*, 3 H, H–C(5′), CH_2(6)); 3.45–3.41 (*m*, 1 H, H–C(2′)); 3.45, 3.41 (*s*, 3 H, MeO); 3.33–3.29 (*m*, 1 H, H–C(5′)); 3.01–2.93 (*m*, 1 H, H–C(5′)); 2.36–2.32 (*m*, 1 H, H–C(3)). ^{13}C-NMR (100.6 MHz, D_2O, 310 K): 110.3 (*d*, *J* = 169, C(1)fur); 103.6 (*d*, *J* = 173, C(1)pyr); 80.0, 79.5 (*d*, *J* = 148, C(4)); 75.7 (*d*, *J* = 149, C(2)fur); 74.0 (*d*, *J* = 143), 72.0, 71.9 (*d*, *J* = 150), 71.5, 71.3 (*d*, *J* = 149), 70.5 (*d*, *J* = 145, C(3′), C(4′), C(5)); 70.2 (*d*, *J* = 142, C(2)pyr); 67.1, 66.7 (*d*, *J* = 146, C(1′)); 64.4, 64.3 (*d*, *J* = 141, C(2′)); 63.7, 63.0 (*t*, *J* = 145, C(6)); 55.9, 55.7 (*q*, *J* = 140, MeO); 50.5 (*d*, *J* = 129, C(3)fur); 48.3, 48.2 (*t*, *J* = 144, C(5′)), 45.2 (*d*, *J* = 169, C(3)pyr). CI-MS (NH_3): 310 (18, $[M + 1]^+$), 309 (10, M^+), 278 (21), 170 (5), 132 (8), 102 (100), 85 (25). Anal. calc. for $C_{12}H_{23}NO_8$ (309.315): C 46.60, H 7.50, N 4.53; found: C 46.54, H 4.47, N 4.46.

*3:2 Mixture of (±)-Methyl 3-Deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-α-*DL*-arabinitol-1′-C-yl]-β-*DL*-galactofuranoside* (**11**) *and Methyl (±)-3-Deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-α-*DL*-arabinitol-1′-C-yl]-α-*DL*-galactopyranoside* (**10**). As described for **8**/**9**, with **92** (156 mg, 0.34 mmol), MeOH (6 ml), and $SOCl_2$ (240 µl). 86 mg (81%) of **10**/**11** 2:3. Colorless powder. IR (KBr): 3405, 2940, 1640, 1420, 1035. ^{1}H-NMR (400 MHz, D_2O, 310 K): 4.97 (*d*, $^3J(1,2)$ = 0.8, 0.6 H, H–C(1)fur); 4.90 (*d*, $^3J(1,2)$ = 4.5, 0.4 H, H–C(1)pyr); 4.46–4.33 (*m*, 3 H, H–C(3′), H–C(4′), H–C(2)); 4.18 (*dd*, ^3J = 9.1, 1.6, 0.6 H, H–C(4)fur); 4.15–4.05 (*m*, 1 H, H–C(4)pyr, H–C(1′)fur); 4.01 (*dd*, ^3J = 8.9, 2.4, 0.4 H, H–C(1′)pyr); 3.80–3.78 (*m*, 0.4 H, H–C(5)pyr); 3.79–3.76 (*m*, 2 H, H–C(6)); 3.70–3.65 (*m*, 0.6 H, H–C(5)fur); 3.94–3.89 (*m*, 0.4 H, H–C(1′)); 3.80 (*dd*, 1 H, ^3J = 5.6, 4.2, H–C(1′)fur); 3.55 (*dd*, ^3J = 9.7, 3.2, 1 H, H–C(2′)pyr); 3.51, 3.44 (2*s*, 3 H, MeO–C(1)); 3.44–3.30 (*m*, 1.4 H, H–C(5′), H–C(2′)pyr); 2.91–2.86 (*m*, 1 H, H–C(5′)); 2.45–2.40 (*m*, 1 H, H–C(3)). ^{13}C-NMR (100.6 MHz, D_2O, 310 K): 109.5 (*d*, *J* = 171, C(1)fur); 102.7 (*d*, *J* = 174, C(1)pyr); 78.9, 78.6 (*d*, *J* = 146, C(4)); 74.8 (*d*, *J* = 148, C(2)fur); 72.3 (*d*, *J* = 147, C(5)pyr); 71.5, 71.3, 71.0, 70.8 (*d*, *J* = 148, C(3′), C(4′)); 70.1 (*d*, *J* = 141,

[6]) For methyl galactosides in D_2O: δ(C) 100.1 for α-pyranoside, δ(C) 104.6 for β-pyranoside, δ(C) 103.8 for α-furanoside and δ(C) 109.9 for β-furanoside [46]. NOE's were observed between signals at 4.92 and 2.43 ppm in the ^{1}H-NMR spectrum. The product of peracetylation of **7** showed δ(C) 106.9 ppm for C(1), confirming the β-DL-furanoside structure.

C(5)fur); 69.8 (*d*, *J* = 147, C(2)pyr); 65.7, 65.4 (*d*, *J* = 145, C(1′)); 63.0 (*t*, *J* = 139, C(6)); 62.3, 62.0 (*d*, *J* = 146, C(2′)); 55.1, 54.8 (*q*, *J* = 144, MeO); 49.0 (*d*, *J* = 129, C(3)fur); 48.2 (*t*, *J* = 143, C(5′)); 44.7 (*d*, *J* = 130, C(3)pyr). CI-MS (NH_3): 310 (2, $[M + 1]^+$), 309 (2, $[M + 1]^+$), 278 (11), 248 (3), 216 (5), 169 (5), 102 (100), 84 (24). Anal. calc. for $C_{12}H_{23}NO_8$ (309.315): C 46.60, H 7.50, N 4.53; found: C 46.73, H 7.42, N 4.51.

*2:1 Mixture of (±)-Methyl 3-Deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-β-*DL*-ribitol-1′-C-yl]-β-*DL*-galactofuranoside* (**13**) *and (±)-Methyl 3-Deoxy-3-[(1′*SR*)-2′,5′-dideoxy-2′,5′-imino-β-*DL*-ribitol-1′-C-yl]-α-*DL*-galactopyranoside* (**12**). As described for **8**/**9**, with **94** (140 mg, 0.31 mmol), MeOH (6 ml), and $SOCl_2$ (240 µl): 83 mg (87%) of **13**/**12** 2:1 contaminated by *ca.* 10% of α-DL-galactofuranoside. Colorless powder. IR (KBr): 3405, 2935, 1635, 1420, 1195, 1035, 620. ^{1}H-NMR (400 MHz, D_2O, 310 K): 4.90 (*d*, ^3J(1,2) = 1.8, 0.6 H, H–C(1)fur); 4.84 (*d*, ^3J(1,2) = 4.3, 0.3 H, H–C(1)pyr), 4.83 (br. *s*, 0.1 H, H–C(1)fur); 4.28 (*dd*, ^3J = 9.4, 4.5, 0.3 H, H–C(2)pyr); 4.25 (*dd*, ^3J = 4.5, 1.8, 0.6 H, H–C(2)fur), 4.20–4.14 (*m*, 1.1 H, H–C(4′), H–C(2)); 4.05 (*dd*, ^3J(4,3) = 7.8, ^3J(4,5) = 2.5, 0.6 H, H–C(4)fur); 4.02–3.95 (*m*, 1.4 H, H–C(3′), H–C(4)pyr); 3.94–3.89 (*m*, 0.4 H, H–C(1′)); 3.80 (*dd*, ^3J = 5.6, 4.2, 1 H, H–C(1′)fur); 3.73 (*ddd*, ^3J = 7.2, 5.0, 2.6, 1 H, H–C(5)fur); 3.68–3.58 (*m*, 2.4 H, H–C(6), H–C(5)); 3.41 (*s*, 0.9 H, 3.37 (*s*, 1.8 H, 3.35 (*s*, 0.3 H, MeO–C(1)); 3.35–3.20 (*m*, 1.4 H, H–C(5′), H–C(2′)); 3.07 (*dd*, ^3J = 7.8, 4.0, 0.6 H, H–C(2′)fur); 2.97 (*dd*, ^2J = 12.7, 0.3 H, ^3J(5′b,4′) = 3.0), 2.90 (*dd*, ^2J = 12.6, ^3J(5′b,4′) = 3.2, 0.6 H), 2.83 (*dd*, ^2J = 12.6, ^3J(5′b,4′) = 3.4, 0.1 H, H_b–C(5′)); 2.40–2.30 (*m*, 1 H, H–C(3)). ^{13}C-NMR (100.6 MHz, D_2O, 310 K): 110.0 (*d*, *J* = 174, C(1)fur); 103.5 (*d*, *J* = 170, C(1)pyr); 80.5, 80.2 (*d*, *J* = 149, C(4)); 76.2 (*d*, *J* = 149, C(2)fur); 73.8, 73.5 (*d*, *J* = 148), 73.1 (*d*, *J* = 150), 71.6, 71.4, 71.1 (*d*, *J* = 149, C(3′), C(4′), C(5)); 70.7 (*d*, *J* = 147, C(2)pyr); 68.3, 67.3 (*d*, *J* = 144, C(1′)); 64.7, 64.5 (*d*, *J* = 143, C(2′)); 63.8, 63.3 (*t*, *J* = 145, C(6)); 55.9, 55.5 (*q*, *J* = 144, MeO); 51.5, (*d*, *J* = 131, C(3)fur); 51.2, 51.1 (*t*, *J* = 143, C(5′)); 47.6 (*d*, *J* = 131, C(3)pyr). CI-MS (NH_3): 310 (3, $[M + 1]^+$), 309 (2, M^+), 278 (9), 157 (8), 131 (11), 102 (100), 95 (33), 84 (88). Anal. calc. for $C_{12}H_{23}NO_8$ (309.315): C 46.60, H 7.50, N 4.53; found: C 44.66, H 7.26, N 4.35.

*(±)-(1*RS*,3*RS*,4*SR*,5*SR*,6*SR*)-6-*endo-*Chloro-3-*exo-*[(*RS*)-(furan-2-yl)hydroxymethyl]-5-*exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-one* (**19**). To anh. THF (70 ml) and $Me_3SiNHSiMe_3$ (10.8 ml, 51.7 mmol) in a flame-dried flask at −10° under Ar, 1.6M BuLi in hexane (29.8 ml, 47.7 mmol) was added slowly keeping the temp. at −5°. After stirring at −5° for 15 min, the soln. was cooled to −78° and ketone **16** [29] (12 g, 39.8 mmol) in anh. THF (85 ml) was added within 1 h. After stirring at −78° for 15 min, a soln. of anh. furan-2-carbaldehyde (4.94 ml, 59.7 mmol) in THF (25 ml) was added slowly (30 min). After stirring at −78° for 90 min, AcOH (4.08 ml, 79.6 mmol) in MeOH (10 ml) was added slowly, and the cooling bath was removed. Once at 20°, the mixture was poured into a vigourously stirred mixture of sat. aq. $NaHCO_3$ soln. (200 ml) and CH_2Cl_2 (100 ml). The aq. phase was extracted with CH_2Cl_2 (100 ml, twice), the combined org. extract dried ($MgSO_4$) and evaporated, and the yellowish solid (16.45 g) recrystallized from $CHCl_3$: 15.02 g (95%) of **19**. Colorless solid. M.p. 138–129°. UV (MeCN): 218 (8700). IR (KBr): 3495, 3020, 1760, 1575, 1400, 1210, 1180, 1120, 1065, 1025, 910, 800, 725. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.52–7.49 (*m*, 2 arom. H); 7.36–7.27 (*m*, 3 arom. H, H–C(5″), $CHCl_3$); 6.33 (*dd*, ^3J(4″,3″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.31 (*d*, ^3J(3″,4″) = 3.2, H–C(3″)); 4.91 (*dd*, ^3J(1′,3) = 9.5, ^3J(1′, OH–C(1′)) = 2.0, H–C(1′)); 4.56 (*dd*, ^3J(1,6) = 6.0, ^4J(1,4) = 0.8, H–C(1)); 4.42 (br. *s*, H–C(4)); 4.24 (*ddd*, ^3J(6,1) = 6.0, ^3J(6,5) = 3.0, ^3J(6,4) = 1.0, H–C(6)); 3.57 (*d*, ^3J(5,6) = 3.0, H–C(5)); 3.22 (*d*, ^3J(OH–C(1′),1′) = 2.0, OH–C(1′)); 2.75 (*d*, ^3J(3,1′) = 9.5, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 206.0 (*s*, C=O); 152.0 (*s*, C(2″)); 142.9 (*d*, *J* = 203, C(5″)); 134.1 (*d*, *J* = 165, 2 arom. C); 129.5 (*d*, *J* = 161, 2 arom. C); 128.3 (*d*, *J* = 161, arom. C); 128.2 (*s*, arom. C); 110.3 (*d*, *J* = 181), 108.6 (*d*, *J* = 174, C(3″), C(4″)); 84.6 (*d*, *J* = 167), 83.2 (*d*, *J* = 167, C(1), C(4)); 66.9 (*d*, *J* = 144, C(1′)); 56.8 (*d*, *J* = 166, C(6)); 55.8 (*d*, *J* = 138, C(3)); 50.7 (*d*, *J* = 154, C(5)). CI-MS (NH_3): 398 (8, $[M + 1]^+$), 360 (2), 302 (15), 265 (12), 225 (20), 195 (30), 158 (35), 138 (20), 96 (76), 92 (100). Anal. calc. for $C_{17}H_{15}ClO_4Se$ (397.716): C 51.34, H 3.80, Cl 8.91, Se 19.85; found: C 51.28, H 3.83, Cl 8.91, Se 19.79.

*(±)-(1*RS*,2*SR*,3*RS*,4*SR*,5*SR*,6*SR*)-6-*endo-*Chloro-3-*exo-*[(*RS*)-(furan-2-yl)hydroxymethyl]-5-*exo-*(phenylseleno)-7-oxabicyclo[2.2.1]heptan-2-*endo-*ol* (**20**). $NaBH_4$ (1.83 g, 48.3 mmol) was added portionwise to a stirred soln. of **19** (9.60 g, 24.1 mmol) in MeOH/THF 1:1 (300 ml) at 0°. After stirring at 0° for 5 min, 1N aq. HCl was added until pH 5. The mixture was then poured onto ice-cold H_2O (250 ml) and CH_2Cl_2 (250 ml). The aq. phase was extracted with CH_2Cl_2 (100 ml, twice), the combined org. extract dried ($MgSO_4$) and evaporated, and the colorless solid recrystallized from AcOEt and light petroleum ether: 8.78 g (91%) of **20**. Colorless crystals. M.p. 129–131°. UV (MeCN): 217 (8730). IR (KBr): 3250, 3110, 2990, 2910, 1575, 1475, 1430, 1235, 1070, 1020, 955, 915, 810, 750, 730. ^{1}H-NMR (400 MHz, (D_6)DMSO): 7.54 (*d*, ^3J(5″,4″) = 1.8, H–C(5″)); 7.37–7.33 (*m*, 2 H), 7.32–7.25 (*m*, 3 H, arom. H); 6.45 (*dd*, ^3J(4″,3″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.22 (*d*, ^3J(3″,4″) = 3.2, H–C(3″)); 5.49 (*d*, ^3J(OH–C(1′),1′) = 5.1, OH–C(1′)); 5.03 (*d*, ^3J(OH–C(2),2) = 4.5, OH–C(2)); 4.40 (*dd*, ^3J(1,6) = 4.8, ^3J(1,2) = 4.1, H–C(1)); 4.29 (*ddd*, ^3J(2,OH–C(2)) = 4.5, ^3J(2,1) = 4.1, ^3J(2,3) = 3.7, H–C(2)); 4.26 (*dd*, ^3J(1′,3) = 9.7, ^3J(1′, OH–C(1′)) = 5.1, H–C(1′)); 4.13 (*dd*, ^3J(6,1) = 4.8, ^3J(6,5) = 4.3,

H–C(6)); 3.94 (br. *s*, H–C(4)); 3.60 (*d*, $^3J(6,5)$ = 4.3, H–C(5)); 2.21 (*dd*, $^3J(3,1')$ = 9.7, $^3J(3,2)$ = 3.7, H–C(3)). ^{13}C-NMR (100.6 MHz, (D$_6$)DMSO): 156.2 (*s*, C(2'')); 142.1 (*d*, *J* = 203, C(5'')); 131.9 (*d*, *J* = 166, 2 arom. C); 129.6 (*s*, arom. C); 129.5 (*d*, *J* = 160, 2 arom. C); 127.2 (*d*, *J* = 155, arom. C); 110.1 (*d*, *J* = 175), 106.6 (*d*, *J* = 170, C(3''), C(4'')); 86.6 (*d*, *J* = 161), 79.0 (*d*, *J* = 161, C(1), C(4)); 76.4 (*d*, *J* = 144, C(2)); 67.6 (*d*, *J* = 141, C(1')); 60.3 (*d*, *J* = 160, C(6)); 56.4 (*d*, *J* = 134, C(3)); 51.2 (*d*, *J* = 148, C(5)). CI-MS (NH_3): 418 (1, $[M + 1 + 18]^+$), 402 (7, $[M + 2]^+$), 400 (18, $M^{+\cdot}$), 398 (21), 330 (2), 284 (5), 225 (9), 158 (22), 122 (34), 97 (50), 78 (100). Anal. calc. for $C_{17}H_{17}ClO_4Se$ (399.732): C 51.08, H 4.28, Cl 8.86, Se 19.75; found: C 51.20, H 4.35, Cl 8.77, Se 19.73.

*(±)-(4*RS,*4a*RS,*5*SR,*6*SR,*7*SR,*8*RS,*8a*SR*)-2,2-Di(*tert*-*butyl*)-7-chloro-4-(furan-2-yl)-4a,5,6,7,8,8a-hexahydro-6-(phenylseleno)-5,8-epoxy-4*H*-1,3,2-benzodioxasiline* (**21**). Under Ar 2,6-dimethylpyridine (46 µl, 0.4 mmol) and (*t*-Bu)$_2$Si(OSO$_2$CF$_3$)$_2$ (79 µl, 0.24 mmol) were added to a soln. of **20** (32 mg, 0.08 mmol) in anh. DMF (0.3 ml) at 0°. After stirring at 20° for 15 h, the mixture was poured into brine (10 ml) and extracted with CH_2Cl_2 (10 ml, 3 times). The combined org. phase was dried ($MgSO_4$) and evaporated, and the residue purified by FC (SiO_2, 230–400 mesh, AcOEt/CH_2Cl_2/light petroleum ether 1:1:8): 22 mg (51%) of **21**. Colorless oil. UV (MeCN): 220 (12500). IR (film): 3580, 2930, 2855, 1475, 1395, 1330, 1240, 1215, 1095, 1005, 825. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.49–7.45 (*m*, 2 arom. H); 7.33 (*dd*, $^3J(5',4')$ = 1.8, $^3J(3',5')$ = 0.8, H–C(5')); 7.30–7.25 (*m*, 3 arom. H, $CHCl_3$); 6.33 (*d*, $^3J(4',3')$ = 3.3, $^3J(4',5')$ = 1.8, H–C(4')); 6.21 (*dm*, $^3J(3',4')$ = 3.3, H–C(3')); 5.03 (*d*, $^3J(4,4a)$ = 11.1, H–C(4)); 4.62 (*dd*, $^3J(7,8)$ = 5.5, $^3J(8,8a)$ = 4.0, H–C(8)); 4.44–4.41 (*m*, H–C(7), H–C(8a)); 4.33 (br. *s*, H–C(5)); 3.62 (*d*, $^3J(6,7)$ = 2.1, H–C(6)); 2.42 (*ddd*, $^3J(4,4a)$ = 11.1, $^3J(4a,8a)$ = 8.8, $^3J(4a,5)$ = 1.5, H–C(4a)); 1.10, 1.05 (2*s*, 18 H, 2 *t*-BuSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 154.7 (*s*, C(2')); 142.3 (*d*, *J* = 202, C(5')); 133.1 (*d*, *J* = 163, 2 arom. C); 129.5 (*s*, arom. C); 129.3 (*d*, *J* = 167, 2 arom. C); 127.6 (*d*, *J* = 167, arom. C); 110.1 (*d*, *J* = 175), 106.7 (*d*, *J* = 175, C(3'), C(4')); 83.2 (*d*, *J* = 166), 81.4 (*d*, *J* = 150), 78.6 (*d*, *J* = 163); 74.0 (*d*, *J* = 146, C(8), C(8a), C(5), C(4)); 60.7 (*d*, *J* = 163), 56.2 (*d*, *J* = 153), 53.2 (*d*, *J* = 132, C(4a), C(6)); 27.5, 27.2 (2*q*, *J* = 126, 2 *Me*$_3$CSi); 20.8, 20.3, (2*s*, 2 Me$_3$*C*Si). CI-MS (NH_3): 542 (2, $[M + 1]^+$), 541 (1, $M^{+\cdot}$), 540 (3, $[M - 1]^+$), 387 (2), 326 (19), 297 (75), 259 (18), 223 (23), 147 (15), 78 (100). Anal. calc. for $C_{25}H_{34}ClO_4SeSi$ (541.042): C 55.50, H 6.33, Cl 6.55; found: C 55.59, H 6.44, Cl 6.59.

*(±)-(1*RS,*3*RS,*4*SR,*5*SR,*6*SR*)-3-*exo-*{(*RS*)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-*2*-*yl*)*methyl*}-*6*-*endo*-*chloro*-*5*-*exo*-(*phenylseleno*)-*7*-*oxabicyclo*[*2.2.1*]*heptan*-*2*-*one* (**22**). A mixture of **19** (1.0 g, 2.51 mmol), anh. DMF (4 ml), (*t*-Bu)Me$_2$SiCl (416 mg, 2.65 mmol), and 1*H*-imidazole (603 mg, 10.04 mmol) was stirred at 20° for 2 h. More (*t*-Bu)Me$_2$SiCl (341 mg, 2.5 mmol) was added and the mixture stirred at 20° for 2 h. The mixture was poured onto AcOEt (20 ml) and 1N aq. HCl (20 ml), the org. layer washed successively with 5% aq. Na_2CO_3 soln. (10 ml) and brine (10 ml), dried ($MgSO_4$), and evaporated, and the residue purified by FC (SiO_2, EtOAc/CH_2Cl_2/light petroleum ether 1:1:18): 1.23 g (96%) of **22**. Colorless oil that crystallized at 4°. M.p. 68–70°. UV (MeCN): 219 (11050). IR (KBr): 2945, 2855, 1770, 1470, 1340, 1250, 1140, 1090, 1000, 900, 870, 830, 800, 770, 730, 690. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.58–7.48 (*m*, 2 arom. H); 7.38–7.30 (*m*, 3 arom. H, H–C(5'')); 6.30 (*dd*, $^3J(3'',4'')$ = 3.2, $^3J(4'',5'')$ = 1.8, H–C(4'')); 6.20 (*d*, $^3J(3'',4'')$ = 3.2, H–C(3'')); 5.00 (*d*, $^3J(1',3)$ = 6.5, H–C(1')); 4.65 (br. *s*, H–C(4)); 4.35 (*d*, $^3J(1,6)$ = 5.7, H–C(1)); 4.18 (*ddd*, $^3J(1,6)$ = 5.7, $^3J(5,6)$ = 3.1, $^4J(4,6)$ = 1.0, H–C(6)); 3.48 (*d*, $^3J(5,6)$ = 3.1, H–C(5)); 2.62 (*d*, $^3J(3,1')$ = 6.6, H–C(3)); 0.84 (*s*, *t*-Bu); 0.03, –0.10 (*s*, Me$_2$Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 202.6 (*s*, C(2)); 153.1 (*s*, C(2'')); 142.1 (*d*, *J* = 203, C(5'')); 133.9 (*d*, *J* = 161, 2 arom. C); 129.5 (*d*, *J* = 160, 2 arom. C); 128.7 (*s*, arom. C); 128.2 (*d*, *J* = 161, arom. C); 110.1 (*d*, *J* = 176), 107.5 (*d*, *J* = 175, C(3''), C(4'')); 84.2 (*d*, *J* = 173), 82.8 (*d*, *J* = 171, C(1), C(4)); 67.1 (*d*, *J* = 145, C(1')); 58.6 (*d*, *J* = 134, C(3)); 57.2 (*d*, *J* = 170, C(6)); 51.2 (*d*, *J* = 154, C(5)); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$CSi); –5.2, –5.3 (2*q*, *J* = 118, Me$_2$Si). CI-MS (NH_3): 311 (90, $[M^+ - 201]^+$), 285 (7), 259 (7), 237 (100), 196 (11), 147 (20), 73 (41). Anal. calc. for $C_{23}H_{29}ClO_4SeSi$ (511.980): C 53.96, H 5.71, Cl 6.92, Se 15.42, Si 5.49; found: C 53.95, H 5.79, Cl 6.91, Se 15.47, Si 5.46.

*(+)-(1*R,*3*R,*4*S,*5*S,*6*S*)-3-*exo-*{(R)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-*2*-*yl*)*methyl*}-*6*-*endo*-*chloro*-*5*-*exo*-(*phenylseleno*)-*7*-*oxabicyclo*[*2.2.1*]*heptan*-*2*-*one* ((+)-**22**). For 5 min, **23** (100 mg) was heated to 150° in a 'Kugelrohr' apparatus under reduced pressure ($3 \cdot 10^{-1}$ Torr). The resulting oil was purified by FC (SiO_2, AcOEt/CH_2Cl_2/light petroleum ether 1:1:8): 38 mg (52%) (+)-**22**. Colorless oil that crystallized at +4°. $[\alpha]_{589}^{25}$ = +64 (*c* = 0.75, $CHCl_3$).

*(–)-(1*S,*3*S,*4*R,*5*R,*6*R*)-3-*exo-*{(S)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-*2*-*yl*)*methyl*}-*6*-*endo*-*chloro*-*5*-*exo*-(*phenylseleno*)-*7*-*oxabicyclo*[*2.2.1*]*heptan*-*2*-*one* ((–)-**22**). As described for (+)-**22**, with **24**. Also from (+)-**17** [28], following the procedures **16** → **19** and **19** → (–)-**22**. $[\alpha]_{589}^{25}$ = –57 (*c* = 0.61, $CHCl_3$).

*(S)-*S*-{{(1*S,*2*S,*3*R,*4*S,*5*S,*6*S*)-3-*exo-*{(R)-[(*tert*-*Butyl*)*dimethylsilyloxy*]*furan*-*2*-*yl*)*methyl*}-*6*-*endo*-*chloro*-*2*-*endo*-*hydroxy*-*5*-*exo*-(*phenylseleno*)-*7*-*oxabicyclo*[*2.2.1*]*hept*-*2*-*exo*-*yl*}*methyl*}-N-*methyl*-S-*phenylsulfoximide* (**23**) *and* *(S)-*S*-{{(1*R,*2*R,*3*S,*4*R,*5*R,*6*R*)-3-*exo-*{(S)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-*2*-*yl*)*methyl*}-*6*-*endo*-

chloro-2-endo-*hydroxy-5*-exo-*{phenylseleno}-7-oxabicyclo[2.2.1]hept-2*-exo-*yl}methyl}*-N-*methyl*-S-*phenylsulfoximide* (**24**). At −20°, 1.6M BuLi in hexane (4.06 ml, 6.49 mmol) was added dropwise to a stirred soln. of (*S*)-*N*-methyl-*S*-phenylsulfoximide [33] (1.0 g, 5.90 mmol) in anh. THF (9 ml) cooled to −20°. After cooling to −78°, **22** (1.51 g, 2.95 mmol) in anh. THF (9 ml) was added dropwise. After reacting at −78° for 2 h, sat. aq. NH_4Cl soln. (1 ml) was added, the mixture poured into sat. aq. $NaHCO_3$ soln. (50 ml) and extracted with CH_2Cl_2 (50 ml, 3 times), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue purified and separated by FC (SiO_2, 230–400 mesh, AcOEt/CH_2Cl_2/light petroleum ether 1:1:8; R_f (**22**) 0.71, R_f (**23**) 0.46, R_f (**24**) 0.21 (UV)): 946 mg (47%) of **23** and 905 mg (45%) of **24**.

Data of **23**: M.p. 78–80°. UV (MeCN): 215 (31000). IR (film): 3380, 2930, 1445, 1150, 1080, 840, 740. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.97–7.87 (*m*, 2 arom. H); 7.70–7.50 (*m*, 3 arom. H); 7.40–7.30 (*m*, 2 arom. H), H–C(5″)); 7.25–7.10 (*m*, 3 arom. H); 6.22 (*dd*, $^3J(3'',4'') = 3.2$, $^3J(4'',5'') = 1.8$, H–C(4″)); 6.08 (*dd*, $^3J(3'',4'') = 3.2$, $^4J(3'',5'') = 0.8$, H–C(3″)); 5.40 (*dd*, $^3J(1,6) = 4.8$, $^4J(1,4) = 1.2$, H–C(1)); 4.49 (*d*, $^3J(1',3) = 10.6$, H–C(1′)); 4.09 (*dd*, $^3J(5,6) = 5.6$, $^3J(1,6) = 4.8$, H–C(6)); 4.05 (*d*, $^2J = 13.7$, CH_a–S); 3.81 (br. *s*, H–C(4)); 3.50 (*d*, $^3J(5,6) = 5.6$, H–C(5)); 3.41 (*d*, $^2J = 13.7$, CH_b–S); 2.68 (*s*, MeN); 2.61 (*d*, $^3J(3,1') = 10.6$, H–C(3)); 0.64 (*s*, 9 H, *t*-BuSi); −0.45, −0.46 (2*s*, 6 H, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 153.7 (*s*, C(2″)); 142.1 (*d*, *J* = 203, C(5″)); 139.0 (*s*, arom. C); 133.8 (*d*, *J* = 163, 2 arom. C); 133.3 (*d*, *J* = 166, arom. C); 129.6 (*d*, *J* = 163, 2 arom. C); 129.2 (*s*, arom. C); 129.0 (*d*, *J* = 165, 2 arom. C); 127.6 (*d*, *J* = 160, 2 arom. C); 110.2 (*d*, *J* = 176), 108.9 (*d*, *J* = 173, C(3″), C(4″)); 87.1 (*d*, *J* = 164, C(1), C(4)); 83.5 (*s*, C(2)); 81.5 (*d*, *J* = 159, C(1), C(4)); 67.6 (*d*, *J* = 142), 63.5 (*d*, *J* = 138), 60.1 (*d*, *J* = 158, C(1′), C(5), C(6)); 60.0 (*t*, *J* = 142, CH_2S); 52.0 (*d*, *J* = 152, C(3)); 28.8 (*q*, *J* = 138, MeN); 25.7 (*q*, *J* = 125, Me_3CSi); 18.8 (*s*, Me_3CSi); −5.2, −5.7 (2*q*, *J* = 119, Me_2Si). CI-MS (NH_3): 683 (56, $[M + 1]^+$), 682 (50, $M^{+\cdot}$), 625 (3), 525 (12), 489 (14), 357 (6), 211 (29), 156 (41), 125 (28), 107 (27), 94 (24), 78 (100). Anal. calc. for $C_{31}H_{41}ClO_5NSSeSi$ (682.234): C 54.58, H 6.06; found: C 54.55, H 6.18.

Data of **24**: M.p. 85–88°. UV (MeCN). 215 (30200). IR (KBr): 3490, 2930, 2850, 1580, 1480, 1445, 1250, 1200, 1140, 1090, 1050, 1000, 925, 840, 740, 695. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.91–7.87 (*m*, 2 arom. H); 7.65–7.55 (*m*, 3 arom. H); 7.34–7.19 (*m*, 4 arom. H, H–C(5″), $CDCl_3$); 6.21 (*dd*, $^3J(3'',4'') = 3.2$, $^3J(4'',5'') = 1.8$, H–C(4″)); 6.11 (*dd*, $^3J(3'',4'') = 3.2$, $^4J(3'',5'') = 0.6$, H–C(3″)); 4.76 (*dd*, $^3J(1,6) = 4.9$, $^4J(1,4) = 0.9$, H–C(1)); 4.52 (*d*, $^3J(1',3) = 10.5$, H–C(1′)); 4.22 (*d*, $^2J = 14.2$, CH_aS); 4.00 (*dd*, $^3J(5,6) = 5.4$, $^3J(1,6) = 4.9$, H–C(6)); 3.77 (br. *s*, H–C(4)); 3.67 (*d*, $^2J = 14.2$, CH_bS); 3.49 (*d*, 1 H, $^3J(5,6) = 5.4$, H–C(5)); 2.73 (*s*, MeN); 2.62 (*d*, $^3J(3,1') = 10.5$, H–C(3)); 0.69 (*s*, *t*-BuSi); −0.19, −0.43 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 153.5 (*s*, C(2″)); 142.2 (*d*, *J* = 203, C(5″)); 139.4 (*s*, arom. C); 133.8 (*d*, *J* = 166), 133.3 (*d*, *J* = 166, 4 arom. C); 129.7 (*d*, *J* = 163, 2 arom. C); 129.2 (*d*, *J* = 162, arom. C); 129.1 (*d*, *J* = 161, 2 arom. C); 127.7 (*d*, *J* = 162, arom. C), 110.3 (*d*, *J* = 179), 109.0 (*d*, *J* = 175, C(3″), C(4″)); 86.8 (*d*, *J* = 163, C(1), C(4)); 82.9 (*s*, C(2)); 81.3 (*d*, *J* = 163, C(1), C(4)); 67.3 (*d*, *J* = 143), 63.5 (*d*, *J* = 138, C(1′), C(5), C(6)); 60.3 (*t*, *J* = 140, CH_2S); 60.0 (*d*, *J* = 158, C(1′), C(5), C(6)); 52.2 (*d*, *J* = 153, C(3)); 29.5 (*q*, *J* = 138, MeN); 25.5 (*q*, *J* = 125, Me_3CSi); 17.7 (*s*, Me_3CSi); −5.2, −5.4, (2*q*, *J* = 118, Me_2Si)). CI-MS (NH_3): 683 (7, $[M + 1]^+$), 682 (5, $M^{+\cdot}$), 624 (1), 527 (2), 278 (3), 268 (4), 203 (8), 156 (20), 125 (26), 107 (23), 94 (23), 78 (100). Anal. calc. for $C_{31}H_{41}ClNO_5SSeSi$ (682.234): C 54.58, H 6.06; found: C 54.57, H 5.97.

*(±)-(1*RS,*2*SR,*3*RS,*4*SR*)-6-Chloro-3*-exo-*[(*RS*)-*(furan-2-yl)hydroxymethyl]-7-oxabicyclo[2.2.1]hept-5-en-2*-endo-*ol* (**25**). A soln. of *m*CPBA (*Fluka*; 55%; 9.59 g, 30.6 mmol) in CH_2Cl_2 (150 ml) was dried ($MgSO_4$), filtered, and added dropwise to a stirred soln. of **20** (9.40 g, 23.5 mmol) in THF (150 ml) at −78°. The mixture was stirred overnight after removal of the cooling bath. The yellow soln. was poured into a stirred mixture of CH_2Cl_2 (150 ml) and sat. aq. $NaHCO_3$ soln. (200 ml). The aq. layer was extracted with CH_2Cl_2 (150 ml, twice), the combined org. extract dried ($MgSO_4$) and evaporated, and the yellow solid (10.9 g) purified by FC (SiO_2, AcOEt/light petroleum ether 1:2 until extractiion of $(PhSe)_2$, then AcOEt (500 ml), yielding a colorless oil that was crystallized from AcOEt/light petroleum ether): 4.68 g (82%) of **25**. Colorless solid. M.p. 119–120°. UV (MeCN): 220 (6400). IR (KBr): 3480, 2960, 1580, 1500, 1430, 1325, 1290, 1240, 1140, 1100, 1070, 1000, 955, 920, 880, 865, 830, 810, 790, 740, 640. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.41 (*dd*, $^3J(4'',5'') = 2.2$, $^4J(3'',5'') = 0.6$, H–C(5″)); 6.37 (*d*, 1 H, $^3J(4,5) = 2.2$, H–C(5)); 6.36 (*dd*, $^3J(3'',4'') = 3.3$, $^3J(4'',5'') = 2.2$, H–C(4″)); 6.32 (*dm*, $^3J(3'',4'') = 3.3$, H–C(3″)); 4.72 (*d*, $^3J(1,2) = 4.4$, H–C(1)); 4.70 (*dd*, $^3J(1',3) = 8.9$, $^3J(1'$, OH–C(1′)) = 4.4, H–C(1′)); 4.67 (*ddd*, $^3J((2,OH–C(2)) = 4.6$, $^3J(2,1) = 4.4$, $^3J(2,3) = 2.0$, H–C(2)); 4.50 (*d*, $^3J(4,5) = 2.2$, H–C(4)); 3.10 (*d*, ^3J(OH–C(1′),1′) = 4.4, OH–C(1′)); 2.98 (*d*, ^3J(OH–C(2),2) = 4.6, OH–C(2)); 2.02 (*dd*, $^3J(3,1') = 8.9$, $^3J(3,2) = 2.0$, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 154.7 (*s*, C(2″)); 142.6 (*d*, *J* = 203, C(5″)); 137.9 (*s*, C(6)); 130.3 (*d*, *J* = 180), 120.3 (*d*, *J* = 186, C(3″), C(4″)); 107.5 (*d*, *J* = 175, C(5)); 83.1 (*d*, *J* = 167), 83.0 (*d*, *J* = 165), C(1), C(4)); 72.7 (*d*, *J* = 154, C(2)); 69.1 (*d*, *J* = 144, C(1′)); 53.6 (*d*, *J* = 138, C(3)). CI-MS (NH_3): 260 (13, $[M + 18]^+$), 242 (3, $M^{+\cdot}$), 221 (21), 209 (29), 169 (68), 155 (12), 137 (36), 115 (69), 95 (81), 86 (100). Anal. calc. for $C_{11}H_{11}ClO_4$ (242.658): C 54.44, H 4.57, Cl 14.61; found: C 54.46, H 4.47, Cl 14.50.

*(±)-(1*RS,*2*SR,*3*RS,*4*SR*)-3*-exo-*[(*RS*)-Acetoxy(furan-2-yl)methyl]-6-chloro-7-oxabicyclo[2.2.1]hept-5-en-2*-endo-*yl Acetate* (**26**). A mixture of **25** (2.00 g, 8.24 mmol), anh. pyridine (15 ml), Ac_2O (5 ml), and 4-(dimethylamino)pyridine (50 mg) was stirred at 20° for 15 h. The solvent was evaporated at 0.1 mbar yielding 3.08 g of a brownish oil that was purified by filtration on a pad of silica gel (230–400 mesh, AcOEt/light petroleum ether 1:1; R_f (**26**) 0.6, *Pancaldi*): 2.47 g (92%) of oily **26**. The oil crystallized at −20° and was recrystallized from Et_2O/light petroleum ether. Colorless crystals. M.p. 68–70°. UV (MeCN): 220 (5900). IR (KBr): 3120, 1740, 1590, 1500, 1430, 1365, 1235, 1150, 1080, 1050, 1010, 970, 940, 875, 810, 775, 745, 675, 645. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.41 (*dd*, ^3J((4″,5″) = 1.8, ^4J(3″,5″) = 0.8, H–C(5″)); 6.43 (*d*, ^3J(3″,4″) = 3.2, ^4J(3″,5″) = 1.0, H–C(3″)); 6.37 (*dd*, ^3J(4″,5″) = 1.8, ^3J(3″,4″) = 3.2, H–C(4″)); 6.36 (*d*, ^3J(4,5) = 2.0, H–C(5)); 5.90 (*d*, ^3J(1′,3) = 10.0, H–C(1′)); 5.14 (*dd*, ^3J(1,2) = 4.3, ^3J(2,3) = 2.2, H–C(2)); 4.95 (*dd*, ^3J(1,2) = 4.3, ^4J(1,4) = 1.0, H–C(1)); 4.55 (*dd*, ^3J(4,5) = 2.0, ^4J(1,4) = 1.0, H–C(4)); 2.46 (*dd*, ^3J(3,1′) = 10.0, ^3J(3,2) = 2.2, H–C(3)); 2.06, 2.05 (2*s*, 2 Ac). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.4, 170.0 (2*s*, 2 MeCO); 150.6 (*s*, C(2″)); 143.0 (*d*, *J* = 202, C(5″)); 137.8 (*s*, C(6)); 130.3 (*d*, *J* = 181, C(5)); 110.4 (*d*, *J* = 176), 110.1 (*d*, *J* = 176, C(3″), C(4″)); 82.1 (*d*, *J* = 168), 81.5 (*d*, *J* = 173, C(1), C(4)); 73.1 (*d*, *J* = 160, C(2)); 68.9 (*d*, *J* = 149, C(1′)); 49.2 (*d*, *J* = 140, C(3)); 21.0, 20.5 (2*q*, *J* = 129, 2 *Me*C(O)). CI-MS (NH_3): 344 (1, $[M + 18]^+$), 326 (1, M^+), 331 (15), 224 (27), 207 (13), 189 (11), 182 (24), 165 (32), 122 (83), 94 (100). Anal. calc. for $C_{15}H_{15}ClO_6$ (326.732): C 54.14, H 4.63, Cl 10.85; found: C 55.18, H 4.74, Cl 10.83.

*(±)-(1*RS,*2*SR,*3*RS,*4*SR,*5*SR*)-3*-exo-*[(*RS*)-Acetoxy(furan-2-yl)methyl]-5*-exo-*{[(*tert*-butyl)dimethylsilyloxy]-6-oxo-7-oxabicyclo[2.2.1]hept-2*-endo-*yl Acetate* (**28**). $NaHCO_3$ (103 mg, 1.22 mmol), 0.156M OsO_4 soln. in CCl_4 (39 µl, 0.0061 mmol), and 4-methylmorpholine 4-oxide monohydrate (165 mg, 1.22 mmol) were added successively to a soln. of **26** (200 mg, 0.61 mmol) in acetone/H_2O 8:1 (4 ml) stirred at 0°. After stirring at 0° for 4 h, the brownish soln. became yellowish. It was poured into a vigourously stirred mixture of CH_2Cl_2 (20 ml) and 10% aq. $NaHSO_3$ soln. (20 ml). After stirring for 2 min and decantation, the aq. layer was extracted with CH_2Cl_2 (2 × 20 ml). The combined org. extracts were dried ($MgSO_4$) and concentrated to 1 ml. After the addition of DMF (1 ml), the solvent was evaporated (25°/10^{-3} Torr). (*t*-Bu)Me_2SiCl (185 mg, 1.22 mmol) and 1*H*-imidazole (167 mg, 2.45 mmol) were added under Ar, and the mixture was stirred at 20° for 15 h. The yellow soln. was poured into a stirred mixture of AcOEt (20 ml) and 1N aq. HCl (20 ml). The aq. layer was extracted with AcOEt (2 × 10 ml), the combined org. extract washed successively with 5% aq. Na_2CO_3 soln. (30 ml) and brine (30 ml), dried ($MgSO_4$) and evaporated, and the viscous oil (470 mg) purified by FC (SiO_2, AcOEt/light petroleum ether 1:3; R_f (**28**) 0.47, *Pancaldi*): 158 mg (59%) of **28**. Colorless oil that solidified at 4°. M.p. 108–109°. UV (MeCN): 215 (8100). IR (KBr): 2940, 2850, 1770, 1730, 1365, 1220, 1190, 1110, 1025, 985, 950, 915, 875, 830, 800, 775, 750, 670, 635. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.40 (*dd*, ^3J(4″,5″) = 2.0, ^4J(3″,5″) = 0.6, H–C(5″)); 6.48 (*dm*, ^3J((3″,4″) = 3.2, H–C(3″)); 6.39 (*dd*, ^3J(3″,4″) = 3.2, ^3J(4″,5″) = 2.0, H–C(4″)); 5.96 (*d*, ^3J(1′,3) = 10.0, H–C(1′)); 5.12 (*ddd*, ^3J(2,1) = 5.5, ^3J(2,3) = 2.8, ^4J(2,4) = 1.2, H–C(2)); 4.51 (*dm*, ^3J(1,2) = 5.5, H–C(1)); 4.08 (br. *s*, H–C(4)); 3.74 (*s*, H–C(3)); 2.64 (*ddm*, ^3J(3,1′) = 10.0, ^3J(3,2) = 2.8, H–C(5)); 2.07, 2.05 (2*s*, 2 MeCO); 0.86 (*s*, *t*-BuSi); 0.09, 0.08 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 206.0 (*s*, C(6)); 170.1, 169.4 (2*s*, 2 MeCO); 150.1 (*s*, C(2″)); 143.1 (*d*, *J* = 205, C(5″)); 110.7 (*d*, *J* = 175), 110.6 (*d*, *J* = 175, C(3″), C(4″)); 84.8 (*d*, *J* = 164), 79.2 (*d*, *J* = 171), 74.0 (*d*, *J* = 145), 72.2 (*d*, *J* = 159, C(1), C(2), C(4), C(5)); 68.0 (*d*, *J* = 150, C(1′)); 49.0 (*d*, *J* = 136, C(3)); 25.7 (*q*, *J* = 125, Me_3CSi); 20.9, 20.6 (2*q*, *J* = 130, 2 *Me*CO); 18.3 (*s*, Me_3CSi); −4.8, −5.1 (2*q*, *J* = 120, Me_2Si). CI-MS (NH_3): 456 (23, $[M + 18]^+$), 439 (30, $[M + 1]^+$), 396 (20), 379 (69), 319 (44), 291 (100), 279 (73), 261 (72), 233 (32), 187 (19), 157 (29), 117 (12), 75 (82). Anal. calc. for $C_{21}H_{30}O_8Si$ (438.549): C 57.51, H 6.90, Si 6.40; found: C 57.63, H 6.95, Si 6.45.

*(±)-(1*RS,*2*SR,*3*RS,*4*SR,*5*SR*)-3*-exo-*[(*RS*)-Acetoxy(furan-2-yl)methyl]-5*-exo-*[(*tert*-butyl)dimethylsilyloxy]-7-oxo-6,8-dioxabicyclo[3.2.1]oct-2*-endo-*yl Acetate* (= 7-exo-*[Acetoxy(furan-2-yl)methyl]-2*-exo-*[(*tert*-butyl)dimethylsilyloxy]-4-oxo-3,8-dioxabicyclo[3.2.1]oct-6-yl Acetate*; **29**) *and (±)-3-[(*RS*)-Acetoxy(furan-2-yl)methyl]-2-*O*-acetyl-5-O-[(*tert*-butyl)dimethylsilyl]-3-deoxy-β-*DL*-altrofuranurono-6,1-lactone* (**30**). *m*CPBA (*Fluka*; 80%; 64 mg, 0.296 mmol) and $NaHCO_3$ (38 mg, 0.456 mmol) were added to a stirred soln. of **28** (100 mg, 0.228 mmol) in CH_2Cl_2 (2 ml) at 0°. After stirring at 0° for 7 h, the mixture was poured into ice-cold, sat. aq. $NaHSO_3$ soln. (20 ml) and CH_2Cl_2 (20 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 20 ml), the combined org. phase washed with sat. aq. $NaHCO_3$ soln. (10 ml) and brine (10 ml), dried ($MgSO_4$), and evaporated and the yellowish solid (143 mg) purified by FC (SiO_2, AcOEt/light petroleum ether 1:3; R_f (**29**, **30**) 0.5, *Pancaldi*): 79 mg (76%) of a unseparable 4:1 mixture **29**/**30**. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.46–7.43 (*m*, 1 H, H–C(5″)); 6.50–6.45 (*m*, 1 H, H–C(4″)); 6.38–6.34 (*m*, 1 H, H–C(3″)); 6.03 (*d*, ^3J(1′,3) = 8.9, 0.8 H, H–C(1′) of **29**); 5.97 (*d*, ^3J(1,2) = 4.0, 0.2 H, H–C(1) of **30**); 5.95 (*d*, ^3J(1′,3) = 9.5, 0.2 H, H–C(1′) of **30**); 5.42 (*s*, 0.8 H, H–C(5) of **29**); 5.32 (*dd*, ^3J(2,1) = 6.8, ^3J(2,3) = 4.9, 0.8 H, H–C(2) of **29**); 5.03 (*dd*, ^3J(2,3) = 4.2, ^3J((2,1) = 4.0, 0.2 H, H–C(2) of **30**); 4.81 (*dm*, ^3J(1,7) = 6.8, 0.8 H, H–C(1) of **29**); 4.25 (*dd*, ^3J(4,3) = 2.0, ^3J(4,5) = 0.7, 0.2 H,

H–C(4) of **30**); 4.02 (*d*, $^3J(4,5)$ = 0.7, 0.2 H, H–C(5) of **30**); 3.92 (*dd*, $^3J(4,3)$ = 1.8, 0.8 H, H–C(4) of **29**); 2.94 (*ddd*, $^3J(3,1')$ = 8.9, $^3J(3,2)$ = 4.9, $^3J(3,4)$ = 1.8, 0.8 H, H–C(3) of **29**); 2.94 (*ddd*, $^3J(3,1')$ = 9.5, $^3J(3,2)$ = 4.2, $^3J(3,4)$ = 2.0, 0.2 H, H–C(3) of **30**); 2.08, 2.06, (2*s*, 6 H, 2 MeCO); 0.86, 0.84 (2*s*, 2 *t*-BuSi); 0.16, 0.15, 0.09, 0.09 (4*s*, 2 Me_2Si).

*(±)-(1*RS,2SR,3RS,4SR,5SR*)-3-*exo-*[(*RS*)-Acetoxy(furan-2-yl)methyl]-6-oxo-5-*exo-*[(*p-*tolylsulfonyl)-oxy]-7-oxabicyclo[2.2.1]hept-2-*endo-*yl Acetate* (**31**). $NaHCO_3$ (51 mg, 0.612 mmol), 0.156M OsO_4 in CCl_4 (20 µl, 0.003 mmol), and trimethylamine *N*-oxide dihydrate (68 mg, 0.612 mmol) were added to a stirred soln. of **26** (100 mg, 0.306 mmol) in THF/H_2O 4:1 (1 ml). After stirring at 20° for 3 h, the mixture was poured into a vigourously stirred mixture of CH_2Cl_2 (20 ml) and 1N aq. HCl (20 ml). The org. phase was washed with 10% aq. $NaHSO_3$ soln. (20 ml). The aq. layer from the latter process was extracted with CH_2Cl_2 (2 × 20 ml). The combined org. extract was dried ($MgSO_4$) and evaporated. The residue was dissolved in anh. CH_2Cl_2 (1 ml) and cooled to 0°. TsCl (70 mg, 0.367 mmol) was added, followed by Et_3N (51 µl, 0.367 mmol) dropwise. After stirring at 0° for 4 h, the mixture was poured onto an ice-cold and vigourously stirred mixture of CH_2Cl_2 (20 ml) and 10% aq. HCl soln. The org. layer was washed successively with 5% aq. Na_2CO_3 soln. (10 ml) and brine (10 ml), dried ($MgSO_4$), and evaporated, and the viscous, yellow oil (110 mg) purified by FC (SiO_2, AcOEt/CH_2Cl_2/light petroleum ether 1:3:16; R_f (**31**) 0.4, *Pancaldi*): 68 mg (46%) of **31**. Colorless solid. M.p. 113–115°. UV (MeCN): 240 (9200). IR (KBr): 2970, 1780, 1590, 1500, 1360, 1170, 1150, 1090, 1010, 1000, 955, 910, 865, 810, 775, 750, 670, 650. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.76 (*d*, ^3J = 8.4, 2 arom. H); 7.44 (*dd*, $^3J(4'',5'')$ = 1.8, $^4J(3'',5'')$ = 0.7, H–C(5'')); 7.34 (*d*, ^3J = 8.4, 2 arom. H); 6.44 (*dm*, $^3J(3'',4'')$ = 3.3, H–C(3'')); 6.40 (*dd*, $^3J(4'',5'')$ = 1.8, $^3J(3'',4'')$ = 3.3, H–C(4'')); 5.90 (*d*, $^3J(1',3)$ = 9.8, H–C(1')); 5.12 (*ddd*, $^3J(2,1)$ = 5.6, $^3J(2,3)$ = 2.7, $^4J(2,4)$ = 1.0, H–C(2)); 4.55 (*s*, H–C(5)); 4.54 (*dd*, $^3J(1,2)$ = 5.6, $^4J(1,4)$ = 0.7, H–C(1)); 4.42 (br. *s*, H–C(4)); 2.70 (*dd*, $^3J(3,1')$ = 9.8, $^3J(3,2)$ = 2.7, H–C(3)); 2.45 (*s*, MeC_6H_4); 2.07, 2.02 (2*s*, 2 MeCO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.3 (*s*, C(6)); 170.1, 169.3 (2*s*, 2 MeCO); 149.3, 145.5 (2*s*, C(2''), C_{ipso}); 143.5 (*d*, *J* = 202, C(5'')); 132.9 (*s*, C_p); 130.0 (*d*, *J* = 162), 127.9 (*d*, *J* = 166, 4 arom. C); 110.8, 110.6 (2*d*, *J* = 176, C(3''), C(4'')); 82.0 (*d*, *J* = 167), 79.2 (*d*, *J* = 178), 76.2 (*d*, *J* = 160), 71.1 (*d*, *J* = 162), 67.4 (*d*, *J* = 149, C(1'), C(1), C(2), C(4), C(5)); 49.0 (*d*, *J* = 137, C(3)); 21.7 (*q*, *J* = 127), 20.9 (*q*, *J* = 130), 20.5 (*q*, *J* = 130, MeC_6H_4, 2 MeCO). CI-MS (NH_3): 678 (1, $M^{+\cdot}$), 435, (8), 359 (10), 331 (15), 308 (3), 265 (11), 204 (59), 139 (50), 97 (76), 91 (94), 81 (100). Anal. calc. for $C_{22}H_{22}O_{10}S$ (478.472): C 55.22, H 4.63, S 6.70; found: C 55.32, H 4.53, S 6.65.

*(±)-3-[(*RS*)-Acetoxy(furan-2-yl)methyl]-2-*O*-acetyl-3-deoxy-5-*O*-(*p-*tolylsulfonyl)-β-*DL*-altrofuranurono-6,1-lactone* (**32**). A mixture of **31** (50 mg, 0.104 mmol), *m*CPBA (*Fluka*; 80%; 25 mg, 0.114 mmol), $NaHCO_3$ (16 mg, 0.208 mmol), and CH_2Cl_2 (2 ml) was stirred at 0° for 2 h. The mixture was poured into ice-cold 10% aq. $NaHSO_3$ soln. (10 ml) and CH_2Cl_2 (10 ml), the aq. layer extracted with CH_2Cl_2 (2 × 10 ml), the combined org. phase washed with sat. aq. $NaHCO_3$ soln. (10 ml) and brine (10 ml), dried ($MgSO_4$), and evaporated, and the yellowish oil (75 mg) purified by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**32**) 0.42, UV): 28 mg (54%) of **32**. Colorless oil that solidified slowly. M.p. 133–134°. UV (MeCN): 239 (10100). IR (KBr): 1760, 1740, 1590, 1498, 1425, 1370, 1230, 1200, 1170, 1140, 1120, 1080, 1040, 1010, 990, 950, 920, 890, 875, 845, 810, 775, 740, 675. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.78 (*d*, ^3J = 8.4, 2 arom. H); 7.47 (*dd*, $^3J(4'',5'')$ = 1.8, $^4J(3'',5'')$ = 0.6, H–C(5'')); 7.36 (*d*, ^3J = 8.4, 2 arom. H); 6.49 (*dm*, $^3J((3'',4'')$ = 3.4, H–C(3'')); 6.42 (*dd*, $^3J((4'',5'')$ = 1.8, $^3J(3'',4'')$ = 3.4, H–C(4'')); 6.00 (*d*, $^3J(1',3)$ = 8.6, H–C(1')); 5.98 (*d*, $^3J(1,2)$ = 3.2, H–C(1)); 5.05 (*dd*, $^3J(2,3)$ = 4.6, $^3J(2,1)$ = 3.2, H–C(2)); 4.79 (*d*, $^3J(4,5)$ = 0.8, H–C(5)); 4.62 (*dd*, $^3J(4,3)$ = 1.9, $^3J(4,5)$ = 0.8, H–C(4)); 2.79 (*ddd*, $^3J(3,1')$ = 8.6, $^3J(3,2)$ = 4.6, $^3J(3,4)$ = 1.9, H–C(3)); 2.46 (*s*, MeC_6H_4); 2.09, 2.07 (2*s*, 2 MeCO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.8, 159.7, 148.7, 145.7 (4*s*, C(6), C(2''), C_{ipso}, 2 MeCO); 143.6 (*d*, *J* = 205, C(5'')); 132.5 (*s*, C_p); 129.9 (*d*, *J* = 176), 128.1 (*d*, *J* = 180, 4 arom. C); 111.1 (*d*, *J* = 176), 110.6 (*d*, *J* = 170, C(3''), C(4'')); 99.9 (*d*, *J* = 191), 80.2 (*d*, *J* = 165), 75.7 (*d*, *J* = 152), 75.6 (*d*, *J* = 165, C(1), C(2), C(4), C(5)); 67.5 (*d*, *J* = 149, C(1')); 44.9 (*d*, *J* = 135, C(3)); 21.7 (*q*, *J* = 127), 20.7 (*q*, *J* = 130), 20.2 (*q*, *J* = 130, MeC_6H_4, 2 *Me*CO). CI-MS (NH_3): 512 (1, $[M + 18]^+$), 494 (4, $M^{+\cdot}$), 451 (10), 435 (5), 351 (7), 305 (3), 263 (7), 221 (5), 205 (7), 192 (16), 163 (44), 125 (52), 91 (100). Anal. calc. for $C_{22}H_{22}O_{11}S$ (494.471): C 53.44, H 4.48, S 6.48; found: C 53.50, H 4.43, S 6.50.

*(±)-(1*RS,2SR,3RS,4SR*)-2-*endo-*[(*tert-*Butyl)dimethylsilyloxy]-3-*exo-*{(*RS*)-[(*tert-*butyl)dimethylsilyloxy]-(furan-2-yl)methyl}-6-chloro-7-oxabicyclo[2.2.1]hept-5-ene* (= *6-*endo-*[(*tert-*Butyl)dimethylsilyloxy]-5-*exo-*{[(*tert-*butyl)dimethylsilyloxy](furan-2-yl)methyl}-2-chloro-7-oxabicyclo[2.2.1]hept-2-ene* (**33**). A mixture of **25** (2.00 g, 8.24 mmol), anh. DMF (25 ml), (*t*-Bu)Me_2SiCl (4.96 g, 32.9 mmol), and 1*H*-imidazole (4.48 g, 66.0 mmol was stirred at 60° under Ar for 15 h. The mixture was poured into 1N aq. HCl (150 ml) and extracted with AcOEt (2 × 100 ml). The combined org. extract was washed with 5% aq. Na_2CO_3 soln. and brine (100 ml), dried ($MgSO_4$), and evaporated yielding 3.73 g of a yellow oil that solidified at 4°. Recrystallization from AcOEt/light petroleum ether provided 3.22 g (83%) of **33**. Colorless crystals. M.p. 62–64°. UV (MeCN): 224 (6370). IR (KBr): 2945, 2845, 1590, 1460, 1380, 1230, 1145, 1115, 1075, 1020, 1010, 960, 940, 885, 855, 835, 770, 750, 660, 620.

^{1}H-NMR (250 MHz, $CDCl_3$): 7.37 (*dd*, ^3J(4″,5″) = 1.8, ^4J(3″,5″) = 0.9, H–C(5″)); 6.32 (*dd*, ^3J(3″,4″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.27 (*d*, ^3J(4,5) = 2.0, H–C(5)); 6.22 (*dm*, ^3J(3″,4″) = 3.2, H–C(3″)); 4.79 (*d*, ^3J(1′,3) = 7.6, H–C(1′)); 4.58 (*dd*, ^3J(4,5) = 2.0, ^4J(1,4) = 0.8, H–C(4)); 4.51 (*dm*, ^3J(1,2) = 4.4, H–C(1)); 4.44 (*dd*, ^3J(2,1) = 4.4, ^3J(2,3) = 2.0, H–C(2)); 1.98 (*dd*, ^3J(3,1′) = 7.6, ^3J(3,2) = 2.0, H–C(3)); 0.89, 0.87 (2*s*, 2 *t*-BuSi); 0.15, 0.14, −0.10, −0.30 (4*s*, 4 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 155.3 (*s*, C(2″)); 141.7 (*d*, *J* = 202, C(5″)); 138.3 (*s*, C(6)); 129.9 (*d*, *J* = 160, C(5)); 110.0 (*d*, *J* = 164), 107.4 (*d*, *J* = 174), C(3″), C(4″)); 83.5 (*d*, *J* = 167), 82.6 (*d*, *J* = 165, C(1), C(4)); 71.9 (*d*, *J* = 152, C(2)); 70.1 (*d*, *J* = 140, C(1′)); 55.1 (*d*, *J* = 140, C(3)); 25.7 (2*q*, *J* = 126, 2 *Me*$_3$CSi); 18.4, 17.9 (2*s*, 2 Me$_3$*C*Si); −4.5, −4.7, −4.8 (3*q*, *J* = 118, 4 MeSi). CI-MS (NH_3): 353 (2, $[M-117]^+$), 311 (100), 285 (6), 259 (3), 237 (93), 196 (23), 147 (15), 73 (78). Anal. calc. for $C_{23}H_{39}ClO_4Si_2$ (471.186): C 58.63, H 8.34, Cl 7.52, Si 11.92; found: C 58.69, H 8.42, Cl 7.52, Si 11.86.

*(±)-(1*RS,*3*SR,*4*SR,*5*RS,*6*SR*)-6*-endo-*[(*tert-*Butyl)dimethylsilyloxy]-5*-exo-*{(*RS*)-[(*tert-*butyl)dimethylsilyloxy](furan-2-yl)methyl}-3*-exo-*hydroxy-7-oxabicyclo[2.2.1]heptan-2-one* (**34**). A mixture of **33** (711 mg, 1.51 mmol), THF/H_2O 4:1 (5 ml), $NaHCO_3$ (252 mg, 3.02 mmol), 0.156M OsO_4 in CCl_4 (97 µl, 0.015 mmol), and trimethylamine *N*-oxide dihydrate (337 mg, 3.02 mmol) was stirred at 20° for 3 h. The mixture was poured into a vigourously stirred mixture of CH_2Cl_2 (100 ml) and 1N aq. HCl (100 ml), The aq. layer was extracted with CH_2Cl_2 (50 ml; twice), the combined org. extract washed with 10% aq. $NaHSO_3$ soln. (100 ml) and brine (100 ml), dried ($MgSO_4$), and evaporated, and the yellow oil (680 mg) purified by FC (SiO_2, AcOEt/CH_2Cl_2/light petroleum ether 1:3:16; R_f (**34**) 0.25, *Pancaldi*): 605 mg (86%) of **34**. Yellowish oil that solidified at 4°. M.p. 58–63°. UV (MeCN): 224 (5600). IR (film): 3415, 2930, 2855, 1780, 1470, 1360, 1255, 1115, 1005, 925, 840, 780, 735. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.38 (*dd*, ^3J(4″,5″) = 1.8, ^4J(3″,5″) = 0.7, H–C(5″)); 6.34 (*dd*, ^3J(3″,4″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.27 (*dm*, ^3J(3″,4″) = 3.2, H–C(3″)); 4.66 (*d*, ^3J(1′,3) = 9.2, H–C(1′)); 4.43 (*dm*, ^3J(1,6)) = 5.3, H–C(6)); 4.32 (*dm*, ^3J(1,6) = 5.3, H–C(1)); 4.19 (br. *s*, H–C(4)); 3.78 (*d*, ^3J(3, OH–C(3)) = 4.7, H–C(3)); 2.49 (*d*, ^3J(OH–C(3), 3) = 4.7, OH–C(3)); 2.32 (*dd*, ^3J(1′,5) = 9.2, ^3J(5,6) = 1.5, H–C(5)); 0.85, 0.83 (2*s*, 2 *t*-BuSi); 0.13, 0.11, −0.01, −0.08 (4*s*, 2 Me$_2$Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 207.4 (*s*, C(2)); 154.2 (*s*, C(2″)); 142.2 (*d*, *J* = 203, C(5″)); 110.2 (*d*, *J* = 180), 108.3 (*d*, *J* = 174, C(3″), C(4″)); 84.6 (*d*, *J* = 156), 82.3 (*d*, *J* = 167), 72.7 (*d*, *J* = 153), 71.9 (*d*, *J* = 155), 68.8 (*d*, *J* = 155, C(1), C(4), C(1′), C(3), C(6)); 56.2 (*d*, *J* = 137, C(5)); 25.9, 25.5 (2*q*, *J* = 125, 2 *Me*$_3$CSi); 18.3, 17.6 (2*s*, 2 Me$_3$*C*Si); −4.7, −4.8, −5.0 (4*q*, *J* = 119, 2 Me$_2$Si). CI-MS (NH_3): 468 (1, $M^{+\cdot}$), 393 (1), 287 (5), 275 (25), 251 (7), 211 (26), 147 (4), 123 (8), 75 (100). Anal. calc. for $C_{23}H_{40}O_6Si_2$ (468.739): C 58.93, H 8.60, Si 11.98; found: C 59.00, H 8.57, Si 11.92.

*(±)-(1*RS,*3*SR,*4*SR,*5*RS,*6*SR*)-6*-endo-*[(*tert-*Butyl)dimethylsilyloxy]-5*-exo-*{(*RS*)-[(*tert-*butyl)dimethylsilyloxy](furan-2-yl)methyl}-2*-oxo-*7-oxabicyclo[2.2.1]hept-3*-exo-*yl 4-Methylbenzenesulfonate* (= *5*-endo-*[(*tert-*Butyl)dimethylsilyloxy]-6*-exo-*{[(*tert-*butyl)dimethylsilyloxy](furan-2-yl)methyl}-3-oxo-7-oxabicyclo[2.2.1]hept-2*-exo-*yl 4-Methylbenzenesulfonate*; **35**). To a mixture of **34** (1.74 g, 3.71 mmol), anh. CH_2Cl_2 (20 ml), and TsCl (849 mg, 4.45 mmol) at 0° under Ar, Et_3N (0.62 ml, 4.45 mmol) was added dropwise within 5 min. After 2 h at 0° and 1 h at 20°, the mixture was poured into an ice-cold, vigourously stirred mixture of CH_2Cl_2 (100 ml) and 10% aq. HCl soln. (100 ml). The aq. layer was extracted with CH_2Cl_2 (2 × 50 ml), the combined org. extract washed with ice-cold 5% aq. Na_2CO_3 soln. (50 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated, and the viscous oil (2.05 g) purified by FC (SiO_2, AcOEt/CH_2Cl_2/light petroleum ether 1:3:16; R_f (TsCl), 0.35, R_f (**35**) 0.3, UV): 1.71 g (74%) of **35** as a colorless oil that solidified at 4° (m.p. 68–71°). Recrystallization from CH_2Cl_2/light petroleum ether yielded 1.59 g (69%) of colorless crystals. M.p. 77–79°. UV (MeCN): 223 (9300). IR (KBr): 2920, 2350, 2785, 1590, 1495, 1465, 1385, 1245, 1185, 1170, 1140, 1100, 1090, 1080, 1025, 990, 965, 920, 895, 830, 780, 750, 660. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.76 (*d*, ^3J = 8.4, 2 arom. H); 7.41 (*dd*, ^3J(4″,5″) = 1.8, ^4J(3″,5″) = 0.8, H–C(5″)); 7.32 (*d*, ^3J = 8.4, 2arom. H); 6.36 (*dd*, ^3J(3″,4″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.25 (*dm*, ^3J(3″,4″) = 3.2, H–C(3″)); 4.65 (*d*, ^3J(1′,5) = 8.6, H–C(1′)); 4.46 (br. *s*, H–C(3)); 4.41 (*ddd*, ^3J(1,6) = 5.3, ^3J(5,6) = 1.7, ^4J(4,6) = 1.6, H–C(6)); 4.34 (br. *s*, H–C(4)); 4.27 (*dd*, ^3J(1,6) = 5.3, *J*(1,4) = 1.3, H–C(1)); 2.45 (*s*, *Me*C$_6$H$_4$); 2.31 (*dd*, ^3J(1′,5) = 8.6, ^3J(5,6) = 1.7, H–C(5)); 0.85, 0.78 (2*s*, 2 *t*-BuSi); 0.09, 0.06, −0.01, −0.08 (4*s*, 2 Me$_2$Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.4 (*s*, C(2)); 153.8, 145.1 (2*s*, C(2″), C_{ipso}); 142.3 (*d*, *J* = 202, C(5″)); 133.7 (*s*, C_p); 129.8 (*d*, *J* = 162), 128.0 (*d*, *J* = 166, 4 arom. C); 110.2 (*d*, *J* = 173), 108.3 (*d*, *J* = 175, C(3″), C(4″)); 82.7 (*d*, *J* = 165), 81.8 (*d*, *J* = 168), 76.8 (*d*, *J* = 158), 71.4 (*d*, *J* = 156), 68.5 (*d*, *J* = 140, C(1), C(4), C(1′), C(3), C(6)); 56.1 (*d*, *J* = 137, C(5)); 25.8, 25.4 (2*q*, *J* = 125, 2 *Me*$_3$CSi); 21.7 (*q*, *J* = 127, *Me*C$_6$H$_4$); 18.3, 17.6 (2*s*, 2 Me$_3$*C*Si); −4.8, −4.9, −5.0 (3*q*, *J* = 118, 2 Me$_2$Si). CI-MS (NH_3): 565 (5, $[M-57]^+$), 441 (6), 405 (3), 393 (5), 367 (5), 275 (19), 229 (20), 211 (100), 155 (5), 91 (17), 75 (45), 73 (46). Anal. calc. for $C_{30}H_{47}O_8SSi_2$ (623.934): C 57.75, H 7.59, S 5.14, Si 9.00; found: C 57.88, H 7.45, S 5.02, Si 9.06.

*(±)-2-*O*-[(*tert-*Butyl)dimethylsilyl]-3-{(*RS*)-[(*tert-*butyl)dimethylsilyloxy](furan-2-yl)methyl}-3-deoxy-5-*O*-(p-tolylsulfonyl)-β-*DL*-altrofuranurono-6,1-lactone* (**36**). A mixture of **35** (100 mg, 0.16 mmol), CH_2Cl_2 (6 ml),

*m*CPBA (*Fluka*; 80%; 45 mg, 0.21 mmol), and $NaHCO_3$ (27 mg, 0.32 mmol) was stirred at 0° for 4.5 h. The mixture was poured into 10% aq. $NaHSO_3$ soln. and extracted with CH_2Cl_2 (3 × 40 ml). The combined org. extract was washed with sat. aq. $NaHCO_3$ soln. (50 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated, and the yellow oil (108 mg) purified by FC (SiO_2, AcOEt/light petroleum ether 1:3; R_f (**36**) 0.65, UV): 76 mg (74%) of **36**. Viscous, yellowish oil that solidified at 4°. M.p. 79–80°. UV (MeCN): 223 (8600). IR (KBr): 2920, 2850, 1755, 1590, 1460, 1350, 1250, 1200, 1170, 1140, 1090, 1010, 1000, 965, 920, 830, 780, 735, 655. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.83 (*d*, ^3J = 8.4, 2 arom. H); 7.38 (*dd*, $^3J(4'',5'')$ = 1.8, $^4J(3'',5'')$ = 0.7, H–C(5'')); 7.25 (*d*, ^3J = 8.4, 2 arom. H); 6.35 (*dd*, $^3J(3'',4'')$ = 3.2, $J(4'',5'')$ = 1.8, H–C(4'')); 6.29 (*dm*, $^3J(3'',4'')$ = 3.2, H–C(3'')); 5.55 (*d*, $^3J(1,2)$ = 3.7, H–C(1)); 4.90 (*d*, $^3J(1',3)$ = 5.1, H–C(1')); 4.75 (*dm*, $^3J(4,3)$ = 1.8, H–C(4)); 4.69 (*dm*, $^3J(4,5)$ = 0.7, H–C(4)); 4.36 (*ddd*, $^3J(2,3)$ = 4.3, $^3J(2,1)$ = 3.7, $^4J(2,4)$ = 1.3, H–C(2)); 2.45 (*s*, MeC_6H_4); 2.20 (*ddd*, $^3J(3,1')$ = 5.1, $^3J(3,2)$ = 4.3, $^3J(3,4)$ = 1.8, H–C(3)); 0.90, 0.83 (2*s*, 2 *t*-BuSi); 0.061, 0.058, 0.021, −0.058 (4*s*, 2 Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 160.6 (*s*, C(6)); 153.3 (*s*, C(2'')); 145.3 (*s*, C_{ipso}); 142.4 (*d*, *J* = 203, C(5'')); 132.8 (*s*, C_p); 129.8 (*d*, *J* = 165), 128.2 (*d*, *J* = 165, 4 arom. C); 110.2 (*d*, *J* = 179), 108.3 (*d*, *J* = 175, C(3''), C(4'')); 101.9 (*d*, *J* = 191, C(1)); 80.5 (*d*, *J* = 165), 76.8 (*d*, *J* = 152), 74.4 (*d*, *J* = 149), 67.9 (*d*, *J* = 142, C(2), C(4), C(5), C(1')); 52.3 (*d*, *J* = 126, C(3)); 25.7, 25.5 (2*q*, *J* = 125, 2 Me_3CSi); 21.7 (*q*, *J* = 127, MeC_6H_4); 18.0, 17.8 (2*s*, 2 Me_3*C*Si); −4.80, −5.01, −5.07, −5.30 (4*q*, *J* = 118, 2 Me_2Si): CI-MS (NH_3): 656 (1, $[M + 18]^+$), 581 (22), 494 (2), 411 (22), 381 (9), 323 (6), 237 (15), 229 (26), 211 (41), 155 (14), 81 (15), 75 (90), 73 (100). Anal. calc. for $C_{30}H_{46}O_6Si_2S$ (638.925): C 56.40, H 7.26, S 8.79, Si 5.02; found: C 56.51, H 7.31, S 8.78, Si 4.99.

*(±)-(1*RS,*2*SR,*3*SR,*4*SR,*5*SR,*6*SR*)-3*-exo-*{(*RS*)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-2-*yl*)*methyl*}-6-endo-*chloro*-5-exo-*(*phenylseleno*)-7-*oxabicyclo*[2.2.1]*heptan*-2-endo-*ol* (**41**). $NaBH_4$ (274 mg, 7.2 mmol) was added portionwise to a stirred soln. of **22** (1.84 g, 3.6 mmol) in MeOH/THF 1:1 (20 ml) at 0°. After stirring at 0° for 5 min, 1N aq. HCl was added until pH 5 and the mixture poured into H_2O (70 ml) and CH_2Cl_2 (50 ml) and extracted with CH_2Cl_2 (2 × 100 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by FC (SiO_2, AcOEt/CH_2Cl_2/light petroleum ether 1:1:8; R_f (**41**) 0.4, UV): 1.68 g (91%) of **41**. Colorless solid. M.p. 74–75°. UV (MeCN): 217 (11200). IR (KBr): 3480, 2930, 2365, 1475, 1255, 1105, 1005, 850, 810, 775, 730, 690, 545. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41–7.38 (*m*, 2 arom. H); 7.33 (*d*, $^3J(4'',5'')$ = 1.8, H–C(5'')); 7.29–7.21 (*m*, 3 arom. H, $CHCl_3$); 6.29 (*dd*, $^3J(3'',4'')$ = 3.2, $^3J(4'',5)$ = 1.8, H–C(4'')); 6.17 (*d*, $^3J(3'',4'')$ = 3.2, H–C(3'')); 4.55 (*d*, $^3J(1',3)$ = 9.4, H–C(1')); 4.49 (*dd*, $^3J(1,6)$ = 4.8, $^3J(1,2)$ = 4.4, H–C(1)); 4.39 (*ddd*, ^3J(2, OH–C(2)) = 7.7, ^3J(2,3) = 4.5, $^3J(2,1)$ = 4.4, H–C(2)); 4.24 (*ddd*, $^3J(1,6)$ = 4.8, $^3J(5,6)$ = 4.3, $^4J(4,6)$ = 0.7, H–C(6)); 4.14 (br. *s*, H–C(4)); 3.50 (*d*, $^3J(5,6)$ = 4.3, H–C(5)); 2.50 (*d*, ^3J(OH–C(2), 2) = 7.7, OH–C(2)); 2.28 (*dd*, $^3J(3,1')$ = 9.4, $^3J(3,2)$ = 4.5, H–C(3)); 0.86 (*s*, *t*-BuSi); 0.04, −0.18 (2*s*, 2 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 154.3 (*s*, C(2'')); 142.1 (*d*, *J* = 203, C(5'')); 133.5 (*d*, *J* = 163), 129.3 (*d*, *J* = 163, 4 arom. C); 129.1 (*s*, arom. C); 127.7 (*d*, *J* = 162, arom. C); 110.1 (*d*, *J* = 186), 107.8 (*d*, *J* = 174, C(3''), C(4'')); 86.5 (*d*, *J* = 173), 79.2 (*d*, *J* = 152), 78.4 (*d*, *J* = 161), 69.9 (*d*, *J* = 144), 61.6 (*d*, *J* = 162, C(1), C(4), C(2), C(1'), C(6)); 57.9 (*d*, *J* = 135, C(3)); 52.7 (*d*, *J* = 147, C(5)); 25.6 (*q*, *J* = 125, Me_3CSi); 18.0 (*s*, Me_3CSi); −5.1, −5.4 (2*q*, *J* = 118, (Me_2Si). CI-MS (NH_3): 532 (1, $[M + 18]^+$), 457 (1), 421 (1), 401 (2), 383 (15), 314 (7), 264 (3), 189 (20), 171 (20), 123 (90), 92 (10), 75 (100). Anal. calc. for $C_{23}H_{31}ClO_4SeSi$ (523.996): C 53.75, H 6.08, Cl 6.90, Se 15.36, Si 5.46; found: C 53.70, H 6.12, Cl 56.90, Se 15.42, Si 5.51.

*(±)-(1*RS,*2*SR,*3*SR,*4*SR*)-3*-exo-*{(*RS*)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-2-*yl*)*methyl*}-6-*chloro*-7-*oxabicyclo*[2.2.1]*hept*-5-*en*-2-endo-*ol* (**42**). A dried ($MgSO_4$) soln. of *m*CPBA (*Fluka*, 55%; 1.04 g, 3.34 mmol) in CH_2Cl_2 (11 ml) was added dropwise to a stirred soln. of **41** (1.56 g, 3.03 mmol) in THF (11 ml) cooled to −78°. After stirring at −78° for 30 min, the cooling bath was removed. After 2.5 h, the yellow soln. was poured onto a stirred mixture of CH_2Cl_2 (50 ml) and 10% aq $NaHSO_3$ soln. (50 ml). The aq. layer was extracted with CH_2Cl_2 (2 × 30 ml), the combined org. extract washed with ice-cold sat. aq. $NaHCO_3$ soln. (50 ml), dried ($MgSO_4$), and evaporated, and the residue purified by FC (SiO_2, AcOEt/CH_2Cl_2/light petroleum ether 1:3:16, without preabsorption; R_f (**42**) 0.27, *Pancaldi*): 1.01 g (91%) of **42**. Colorless oil. UV (MeCN): 214 (5500). IR (film): 3455, 2930, 2855, 1595, 1470, 1255, 1150, 1100, 1010, 875, 840, 780, 740, 630. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39 (*dd*, $^3J(4'',5'')$ = 1.8, $^4J(3'',5'')$ = 0.5, H–C(5'')); 6.34 (*dd*, $^3J(4'',5'')$ = 3.2, $^3J(3'',4'')$ = 1.8, H–C(4'')); 6.33 (*d*, $^3J(4,5)$ = 2.1, H–C(5)); 6.26 (*dm*, $^3J(3'',4'')$ = 3.2, H–C(3'')); 4.72 (*d*, $^3J(1,2)$ = 4.4, $^4J(1,4)$ = 0.9, H–C(1)); 4.56 (*d*, $^3J(1',3)$ = 10.2, H–C(1')); 4.48 (*dd*, $^3J(2,1)$ = 4.4, $^3J(2,3)$ = 2.1, ^3J(2,OH–C(2)) = 6.1, H–C(2)); 4.38 (*dd*, $^3J(4,5)$ = 2.1, $^4J(1,4)$ = 0.9, H–C(4)); 2.02 (*dd*, $^3J(3,1')$ = 10.2, $^3J(3,2)$ = 2.1, H–C(3)); 1.80 (*d*, ^3J(OH–C(2), 2) = 6.1, OH–C(2)); 0.87 (*s*, *t*-BuSi); 0.06, −0.19 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 154.7 (*s*, C(2'')); 142.2 (*d*, *J* = 203, C(5'')); 137.5 (*s*, C(6)); 130.6 (*d*, *J* = 180, C(5)); 110.2 (*d*, *J* = 179), 107.8 (*d*, *J* = 174, C(3''), C(4'')); 83.2 (*d*, *J* = 168), 82.4 (*d*, *J* = 166, C(1), C(4)); 73.9 (*d*, *J* = 155), 69.9 (*d*, *J* = 142, C(1'), C(2)); 55.7 (*d*, *J* = 138, C(3)); 25.7 (*q*, *J* = 125, (Me_3CSi); 18.0 (*s*, Me_3*C*Si); −5.0, −5.3 (2*q*, *J* = 118, Me_2Si).

CI-MS (NH_3): 299 (2, $[M-57]^+$), 197 (31), 171 (69), 149 (4), 123 (28), 97 (20), 75 (100). Anal. calc. for $C_{17}H_{25}ClO_4Si$ (356.922): C 57.21, H 7.06; found: C 57.30, H 6.95.

*(±)-(1*RS,*2*SR,*3*RS,*4*SR*)-3*-exo-*{(*RS*)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-2-*yl*)*methyl*}-6-*chloro*-2-endo-(*methoxymethoxy*)-7-*oxabicyclo*[2.2.1]*hept*-5-*ene* (= 5-exo-{[(tert-*Butyl*)*dimethylsilyloxy*](*furan*-2-*yl*)*methyl*}-2-*chloro*-6-endo-(*methoxymethoxy*)-7-*oxabicyclo*[2.2.1]*hept*-2-*ene*; **43**). Bu_4NI (104 mg, 0.28 mmol) and $MeOCH_2Cl$ (1.07 ml, 14.0 mmol) were added to a soln. of **42** (1.00 g, 2.80 mmol) in anh. $(i\text{-}Pr)_2NEt$ (4 ml) and CH_2Cl_2 (4 ml) at 0°. After stirring at 0° for 30 min and at 20° for 2 h, the soln. was cooled to 0°, and $MeOCH_2Cl$ (1.07 ml, 14.0 mmol) was added. After stirring at 0° for 30 min and at 20° for 2 h, the mixture was poured into 1N aq. HCl (50 ml) and extracted with CH_2Cl_2 (3 × 50 ml). The combined org. extract was dried ($MgSO_4$) and evaporated, and the residue (1.11 g) purified by FC (SiO_2, AcOEt/CH_2Cl_2/light petroleum ether 1:1:18, without preabsorption; R_f (**43**) 0.37, *Pancaldi*): 943 mg (84%) of **43**. Colorless oil that solidified at 4°. M.p. 48–50°. UV (MeCN): 213 (15800). IR (KBr): 2950, 2900, 2855, 2365, 2340, 1595, 1465, 1360, 1260, 1155, 1110, 1055, 960, 925, 840, 775, 760, 605. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38 (*dd*, $^3J(4'',5'') = 1.8$, $^4J(3'',5'') = 0.6$, H–C(5'')); 6.33 (*dd*, $^3J(3'',4'') = 3.2$, $^3J(4'',5'') = 1.8$, H–C(4'')); 6.28 (*d*, $^3J(4,5) = 2.1$, H–C(5)); 6.25 (*dm*, $^3J(3'',4'') = 3.2$, H–C(3'')); 4.80, 4.61 (2*d*, $^2J = 6.6$, $MeOCH_2$); 4.73 (*dm*, $^3J(1,2) = 4.2$, H–C(1)); 4.58 (*d*, $^3J(1',3) = 9.8$, H–C(1')); 4.39 (*d*, $^3J(4,5) = 2.1$, $^4J(4,1) = 0.9$, H–C(4)); 4.33 (*dd*, $^3J(2,1) = 4.2$, $^3J(2,3) = 2.1$, H–C(2)); 3.42 (*s*, $MeOCH_2$); 2.13 (*dd*, $^3J(3,1') = 9.8$, $^3J(3,2) = 2.1$, H–C(3)); 0.85 (*s*, *t*-BuSi); 0.04, –0.15 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 155.0 (*s*, C(2'')); 142.0 (*d*, $J = 203$, C(5'')); 138.2 (*s*, C(6)); 110.1 (*d*, $J = 180$, C(5)); 107.8, 107.6 (2*d*, $J = 174$, C(3''), C(4'')); 96.2 (*t*, $J = 163$, $MeOCH_2$); 82.7 (*d*, $J = 174$), 82.5 (*d*, $J = 165$), 77.6 (*d*, $J = 154$), 69.9 (*d*, $J = 142$, C(1), C(4), C(2), C(1')); 55.9 (*q*, $J = 142$, $MeOCH_2$); 53.5 (*d*, $J = 140$, C(3)); 25.8 (*q*, $J = 125$, Me_3CSi); 18.1 (*s*, *t*-BuSi); –5.0, –5.2 (2*q*, $J = 119$, Me_2Si). CI-MS (NH_3): 419 (3, $[M+1+18]^+$), 241 (2), 211 (74), 167 (100), 89 (41), 73 (33). Anal. calc. for $C_{19}H_{29}ClO_5Si$ (400.975): C 56.91, H 7.29; found: C 57.05, H 7.32.

*(±)-(1*RS,*3*SR,*4*SR,*5*RS,*6*SR*)-5*-exo-*{(*RS*)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-2-*yl*)*methyl*}-6-endo-(*methoxymethoxy*)-2-*oxo*-7-*oxabicyclo*[2.2.1]*hept*-3-exo-*yl* 4-*Methylbenzenesulfonate* (= 6-exo-{[(tert-*Butyl*)*dimethylsilyloxy*](*furan*-2-*yl*)*methyl*}-5-endo-(*methoxymethoxy*)-3-*oxo*-7-*oxabicyclo*[2.2.1]*hept*-2-exo-*yl* 4-*Methylbenzenesulfonate* **45**). $NaHCO_3$ (275 mg, 4.5 mmol), 0.67M OsO_4 in CCl_4 (90 µl, 0.075 mmol), and trimethylamine *N*-oxide dihydrate (0.5 g, 4.5 mmol) were added successively to a stirred soln. of **43** (903 mg, 2.25 mmol) in THF/H_2O 4:1 (10 ml) at 20°. After stirring at 20° for 3 h, the yellow soln. was poured into 1N aq. HCl (50 ml) and extracted with CH_2Cl_2 (50 ml, twice). The combined org. extract was washed with 10% aq. $NaHSO_3$ soln. (50 ml) and brine (100 ml), dried ($MgSO_4$), and evaporated: 950 mg of a clear yellow oil, the crude α-hydroxy ketone **44**. To a soln. of this oil in anh. CH_2Cl_2 (12 ml) at 0°, TsCl (472 mg, 2.62 mmol) and then Et_3N (0.47 ml, 3.57 mmol) were added within 5 min. After stirring at 0° for 30 min and then at 20° for 3 h, the mixture was poured into a vigourously stirred, ice-cold CH_2Cl_2/10% aq. HCl soln. 1:1 (100 ml). The aq. layer was extracted with CH_2Cl_2 (2 × 30 ml), the combined org. extract washed successively by ice-cold 10% aq. Na_2CO_3 soln. (50 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated, and the viscous yellow oil (877 mg) purified by FC (SiO_2, AcOEt/CH_2Cl_2/light petroleum ether 1:1:8; R_f (TsCl) 0.63, R_f (**45**) 0.35, UV): 877 mg (72%) of **45**. Viscous, colorless oil that solidified at 4°. M.p. 82–83° (Et_2O/light petroleum ether). UV (MeCN): 221 (20600). IR (KBr): 2950, 1795, 1375, 1180, 1115, 1050, 995, 880, 840, 780, 670, 555. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.75 (*d*, $^3J = 8.4$, 2 arom. H); 7.42 (*dd*, $^3J(4'',5'') = 1.8$, $^4J(3'',5'') = 0.8$, H–C(5'')); 7.32 (*d*, $^3J = 8.4$, 2 arom. H); 6.37 (*dd*, $^3J(3'',4'') = 3.2$, $^3J(4'',5'') = 1.8$, H–C(4'')); 6.25 (*dm*, $^3J(3'',4'') = 3.2$, H–C(3'')); 4.68 (*d*, $^2J = 6.8$, 1 H, $MeOCH_2$); 4.61 (*d*, $^3J(1',3) = 9.3$, H–C(1')); 4.50 (*d*, $^2J = 6.8$, 1 H, $MeOCH_2$); 4.43 (br. *s*, H–C(3)); 4.42 (*d*, $^3J(1,6) = 5.4$, H–C(1)); 4.29 (br. *s*, H–C(4)); 4.22 (*ddd*, $^3J(1,6) = 5.4$, $^3J(5,6) = 2.5$, $^4J(4,6) = 1.2$, H–C(6)); 3.32 (*s*, $MeOCH_2$); 2.45 (*s*, MeC_6H_4); 2.39 (*dd*, $^3J(1,5) = 9.3$, $^3J(5,6) = 2.5$, H–C(5)); 0.84 (*s*, *t*-BuSi); 0.03, –0.17 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 200.2 (*s*, C(2)); 153.6 (2*s*, C(2'')); 145.2 (*s*, C_{ipso}); 142.5 (*d*, $J = 203$, C(5'')); 133.0 (*s*, C_p); 129.9 (*d*, $J = 162$), 128.0 (*d*, $J = 167$, 4 arom. C); 110.2 (*d*, $J = 176$), 108.5 (*d*, $J = 173$, C(3''), C(4'')); 96.4 (*t*, $J = 164$, $MeOCH_2$); 82.3 (*d*, $J = 165$), 80.8 (*d*, $J = 171$), 76.9 (*d*, $J = 157$), 76.8 (*d*, $J = 156$), 68.3 (*d*, $J = 143$, C(1), C(4), C(1'), C(3), C(6)); 56.2 (*q*, $J = 143$, $MeOCH_2$); 53.5 (*d*, $J = 136$, C(5)); 25.7 (*q*, $J = 125$, Me_3CSi); 21.7 (*q*, $J = 127$, MeC_6H_4); 18.0 (*s*, Me_3CSi); –5.2 (*q*, $J = 118$, Me_2Si). CI-MS (NH_3): 570 (100, $[M+18]^+$), 463 (2), 401 (3), 389 (4), 211 (8), 205 (9), 147 (6), 91 (19). Anal. calc. for $C_{26}H_{36}O_9SSi$ (552.715): C 56.50, H 6.57; found: C 56.62, H 6.67.

*(±)-(1*RS,*3*SR,*4*SR,*5*RS,*6*SR*)-5*-exo-*{(*RS*)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-2-*yl*)*methyl*}6-endo-(*methoxymethoxy*)-2-*oxo*-7-*oxabicyclo*[2.2.1]*hept*-3-exo-*yl* 4-*Bromobenzenesulfonate* (**46**; *cf.* **45** for systematic numbering). 4-Bromobenzenesulfonyl chloride (363 mg, 1.38 mmol) and then Et_3N (0.27 ml, 1.88 mmol) were added within 5 min to a stirred soln. of **44** (500 mg, 1.25 mmol) in anh. CH_2Cl_2 (5 ml; see above) at 0° under Ar. After stirring at 0° for 30 min and then at 20° for 3 h, the mixture was poured into vigourously stirred CH_2Cl_2/

1N aq. HCl 1:1 (50 ml). The aq. layer was extracted with CH_2Cl_2 (3 × 25 ml), the combined org. extract washed with ice-cold 5% aq. Na_2CO_3 soln. (25 ml) and brine (25 ml), dried ($MgSO_4$), and evaporated and the viscous, yellow oil (750 mg) purified by FC (SiO_2, AcOEt/CH_2Cl_2/light petroleum ether 1:1:8; R_f (**46**) 0.35, UV): 617 mg (77%) of **46**. Viscous, colorless oil that solidified at 4°. M.p. 92–93° (Et_2O/light petroleum ether). UV (MeCN): 235 (20500). IR (KBr): 2955, 2360, 1770, 1575, 1470, 1385, 1255, 1195, 1110, 1060, 980, 845, 780, 740, 605, 550. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.74–7.71 (*m*, 2 arom. H); 7.68–7.65 (*m*, 2 arom. H); 7.42 (*dd*, ^3J(4″,5″) = 1.8, ^4J(3″,5″) = 0.7, H–C(5″)); 6.39 (*dd*, ^3J(3″,4″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.27 (*dm*, ^3J(3″,4″) = 3.2, H–C(3″)); 4.68 (*d*, ^2J = 6.8, 1 H, MeOCH_2); 4.59 (*d*, ^3J(1′,5) = 9.4, H–C(1′)); 4.56 (*d*, ^2J = 06.8, 1 H, MeOCH_2); 4.45 (*s*, H–C(3)); 4.43 (*d*, ^3J(1,6) = 6.2, H–C(1)); 4.23 (br. *s*, H–C(4)); 4.22 (*ddd*, ^3J(1,6) = 6.2, ^3J(5,6) = 1.8, ^4J(4,6) = 1.0, H–C(6)); 3.32 (*s*, *Me*OCH_2); 2.39 (*dd*, ^3J(1′,5) = 9.4, ^3J(5,6) = 1.8, H–C(5)); 0.84 (*s*, *t*-BuSi); 0.03, −0.18 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.9 (*s*, C(2)); 153.4 (*s*, C(2″)); 142.5 (*d*, *J* = 203, C(5″)); 135.1 (*s*, C_{ipso}); 132.6 (*d*, *J* = 171, 2 arom. C); 129.4 (*s*, C_p); 129.3 (*d*, *J* = 170, 2 arom. C); 110.3 (*d*, *J* = 176), 108.6 (*d*, *J* = 171, C(3″), C(4″)); 96.3 (*t*, *J* = 164, MeO*C*H_2); 82.1 (*d*, *J* = 166), 80.8 (*d*, *J* = 171), 77.2 (*d*, *J* = 154), 76.6 (*d*, *J* = 156), 68.2 (*d*, *J* = 143, C(1), C(4), C(1′), C(3), C(6)); 56.2 (*q*, *J* = 144, *Me*OCH_2); 53.5 (*d*, *J* = 137, C(5)); 25.6 (*q*, *J* = 125, Me_3CSi); 18.0 (*s*, Me_3*C*Si); −5.2 (*q*, *J* = 118, Me_2Si). CI-MS (NH_3): 637 (75, $[M + 2 + 18]^+$), 636 (91, $[M + 1 + 18]^+$), 635 (100, $[M + 18]^+$), 560 (3), 454 (7), 401 (12), 370 (2), 251 (8), 211 (21), 205 (23), 147 (10), 106 (27), 81 (41). Anal. calc. for $C_{25}H_{33}BrO_9SSi$ (617.584): C 48.62, H 5.39; found: C 48.53, H 5.36.

*(±)-(1*RS,*3*SR,*4*SR,*5*RS,*6*SR*)-5*-exo-*{(*RS*)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-2-*yl*)*methyl*}-6-endo-(*methoxymethoxy*)-2-*oxo*-7-*oxabicyclo*[2.2.1]*hept*-3-exo-*yl Methanesulfonate* (**47**; *cf.* **45** for systematic numbering). Methanesulfonyl chloride (76 µl, 0.97 mmol) and then Et_3N (170 µl, 1.21 mmol) were added slowly (1 min) to a stirred soln. of crude hydroxy ketone **44** (324 mg, 0.81 mmol) in anh. CH_2Cl_2 (1 ml; see above) cooled to −10° und Ar. After stirring at −10° for 30 min, the mixture was poured into ice-cold brine (20 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. extract was dried ($MgSO_4$) and evaporated, and the viscous, yellow oil (350 mg) purified by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**47**) 0.58, *Pancaldi*): 302 mg (78%) of **47**. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41 (*dd*, ^3J(4″,5″) = 1.8, ^4J(3″,5″) = 0.9, H–C(5″)); 6.36 (*dd*, ^3J(3″,4″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.31 (*dm*, ^3J(3″,4″) = 3.2, H–C(3″)); 4.72 (*d*, ^2J = 6.8, 1 H, MeOCH_2); 4.64 (*d*, ^3J(1′,5) = 9.3, H–C(1′)); 4.54 (*d*, ^2J = 6.8, 1 H, MeOCH_2); 4.50 (*d*, ^3J(1,6) = 5.1, H–C(1)); 4.34 (*m*, H–C(4)); 4.29 (*ddd*, ^3J(1,6) = 5.1, ^3J(5,6) = 2.1, ^4J(4,6) = 1.2, H–C(6)); 3.36 (*s*, *Me*OCH_2); 3.16 (*s*, $MeSO_2$); 2.46 (*dd*, ^3J(1′,5) = 9.3, ^3J(5,6) = 2.1, H–C(5)); 0.86 (*s*, *t*-BuSi); −0.04, −0.16 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 201.7 (*s*, C(2)); 153.4 (*s*, C(2″)); 142.6 (*d*, *J* = 203, C(5″)); 110.3 (*d*, *J* = 172), 108.6 (*d*, *J* = 177, C(3″), C(4″)); 96.4 (*t*, *J* = 164, MeO*C*H_2); 82.6 (*d*, *J* = 158), 81.0 (*d*, *J* = 167), 77.1 (*d*, *J* = 158), 76.7 (*d*, *J* = 156), 68.2 (*d*, *J* = 137, C(1), C(4), C(1′), C(3), C(6)); 56.2 (*q*, *J* = 142, *Me*OCH_2); 53.7 (*d*, *J* = 136, C(5)); 39.3 (*q*, *J* = 137, $MeSO_2$); 25.6 (*q*, *J* = 125, Me_3CSi); 18.0 (*s*, Mc_3CSi); −5.2 (*q*, *J* = 118, Me_2Si).

*(±)-3-{(*RS*)-[(*tert*-*Butyl*)*dimethylsilyloxy*](*furan*-2-*yl*)*methyl*}-3-*deoxy*-2-O-(*methoxymethyl*)-5-O-(*p*-*toluylsulfonyl*)-β-DL-*altrofuranurono*-6,1-*lactone* (**48**). *m*CPBA (*Fluka*; 80%; 520 mg, 2.39 mmol) and then $NaHCO_3$ (264 mg, 3.18 mmol) were added to a stirred soln. of **45** (877 mg, 1.59 mmol) in CH_2Cl_2 (15 ml) at 0°. After stirring at 0° for 2 h, the mixture was poured into sat. aq. $NaHSO_3$ soln. (50 ml) and extracted with CH_2Cl_2 (3 × 50 ml). The combined org. extract was washed with sat. aq. $NaHCO_3$ soln. (70 ml) and brine (70 ml), dried ($MgSO_4$), and evaporated, and the yellowish oil purified by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**48**) 0.35, UV): 611 mg (77%) of **48**. Colorless solid. M.p. 74–76°. UV (MeCN): 222 (20600). IR (KBr): 2955, 2365, 1770, 1600, 1375, 1250, 1180, 1055, 980, 840, 550. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.80 (*d*, ^3J = 8.3, 2 arom. H); 7.41 (*dd*, ^3J(4″,5″) = 1.8, ^4J(3″,5″) = 0.8, H–C(5″)); 7.35 (*d*, ^3J = 8.3, 2 arom. H); 6.37 (*dd*, ^3J(3″,4″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.31 (*dm*, ^3J(3″,4″) = 3.2, H–C(3″)); 5.78 (*d*, ^3J(1,2) = 3.5, H–C(1)); 4.89 (*d*, ^3J(1′,3) = 6.2, H–C(1′)); 4.67 (*d*, ^3J(4,5) = 1.2, H–C(5)); 4.65 (*dd*, ^3J(4,3) = 2.1, ^3J(4,5) = 1.2, H–C(4)); 4.60 (*d*, ^2J = 7.0, 1 H, MeOCH_2); 4.52 (*d*, ^2J = 7.0, 1 H, MeOCH_2); 4.11 (*dd*, ^3J(2,3) = 4.9, ^3J(2,1) = 3.5, H–C(2)); 3.36 (*s*, *Me*OCH_2); 2.45 (*s*, *Me*C_6H_4); 2.32 (*ddd*, ^3J(3,1′) = 6.2, ^3J(3,2) = 4.9, ^3J(3,4) = 2.1, H–C(3)); 0.88 (*s*, *t*-BuSi); 0.07, −0.12, (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 160.3 (*s*, C(6)); 153.2 (*s*, C(2″)); 145.4 (*s*, C_{ipso}); 142.5 (*d*, *J* = 203, C(5″)); 132.7 (*s*, C_p); 129.8 (*d*, *J* = 163), 128.2 (*d*, *J* = 166, 4 arom. C); 110.3 (*d*, *J* = 179), 108.3 (*d*, *J* = 175, C(3″), C(4″)); 102.0 (*d*, *J* = 185, C(1)); 97.3 (*t*, *J* = 165, MeOCH_2), 80.6 (*d*, *J* = 147), 79.9 (*d*, *J* = 163), 76.5 (*d*, *J* = 152), 68.1 (*d*, *J* = 142, C(2), C(4), C(1′), C(5)); 56.5 (*q*, *J* = 142, *Me*OCH_2); 49.2 (*d*, *J* = 134, C(3)); 25.6 (*q*, *J* = 126, Me_3CSi); 21.7 (*q*, *J* = 127, *Me*C_6H_4); 18.0 (*s*, Me_3CSi); −5.1, −5.3 (2*q*, *J* = 119, Me_2Si). CI-MS (NH_3): 587 (97, $[M + 1 + 18]^+$), 586 (100, $[M + 18]^+$), 507 (5), 480 (5), 416 (3), 337 (2), 279 (3), 229 (16), 135 (14), 91 (30). Anal. calc. for $C_{26}H_{36}O_{10}SSi$ (568.714): C 54.91, H 6.38; found: C 55.00, H 6.45.

*(±)-5-O-[(4-Bromophenyl)sulfonyl]-3-{(RS)-[(tert-Butyl)dimethylsilyloxy](furan-2-yl)methyl}-3-deoxy-2-O-(methoxymethyl)-β-*DL*-altrofuranurono-6,1-lactone* (**49**). As described for **48**, with **46**, (460 mg, 0.74 mmol). FC (SiO_2, AcOEt/CH_2Cl_2/light petroleum ether 1:1:8; R_f (**49**) 0.22, UV) yielded 386 mg (82%) of **49**. Colorless solid. M.p. 102–104°. UV (MeCN): 232 (18600). IR (KBr): 2955, 1790, 1385, 1115, 845, 785, 605. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.80–7.71 (*m*, 2 arom. H); 7.72–7.68 (*m*, 2 arom. H); 7.41 (*dd*, ^3J(4″,5″) = 1.8, ^4J(3″,5″) = 0.8, H–C(5″)); 6.37 (*dd*, ^3J(3″,4″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.31 (*dm*, ^3J(3″,4″) = 3.2, H–C(3″)), 5.79 (*d*, ^3J(1,2) = 3.6, H–C(1)); 4.89 (*d*, ^3J(1′,3) = 6.2, H–C(1′)); 4.71 (*d*, ^3J(4,5) = 1.0, H–C(5)); 4.63 (*dd*, ^3J(4,3) = 2.0, ^3J(4,5) = 1.0, H–C(4)); 4.61 (*d*, ^2J = 7.1, 1 H), 4.53 (*d*, ^2J = 7.1, 1 H, MeOCH_2); 4.11 (*dd*, 1 H, ^3J(2,3) = 4.9, ^3J(2,1) = 3.6, H–C(2)); 3.37 (*s*, *Me*OCH$_2$); 2.33 (*ddd*, ^3J(3,1′) = 6.2, ^3J(3,2) = 4.9, ^3J(3,4) = 2.0, H–C(3)); 0.88 (*s*, *t*-BuSi); 0.07, –0.11 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 160.2 (*s*, C(6)); 153.1 (*s*, C(2″)); 142.6 (*d*, *J* = 203, C(5″)); 134.8 (*s*, arom. C); 132.5 (*d*, *J* = 177, 2 arom. C); 129.7 (*s*, arom. C); 129.6 (*d*, *J* = 176, 2 arom. C); 110.3 (*d*, *J* = 176), 108.4 (*d*, *J* = 177, C(3″), C(4″)); 102.0 (*d*, *J* = 188, C(1)); 97.3 (*t*, *J* = 164, MeO*C*H); 80.5 (*d*, *J* = 149), 79.9 (*d*, *J* = 163), 76.8 (*d*, *J* = 146), 68.0 (*d*, *J* = 143, C(2), C(4), C(1′), C(5)); 56.5 (*q*, *J* = 143, *Me*OCH$_2$); 49.2 (*d*, *J* = 134, C(3)); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me$_3$*C*Si); –5.1, –5.3 (2 *q*, *J* = 119, Me_2Si). CI-MS (NH_3): 653 (93, $[M + 2 + 18]^+$), 652 (100, $[M + 1 + 18]^+$), 651 (86, $[M + 18]^+$), 572 (11), 417 (7), 338 (5), 295 (15), 211 (73), 135 (32), 106 (39), 81 (48), 75 (60). Anal. calc. for $C_{25}H_{33}BrO_{10}SSi$ (633.598): C 47.39, H 5.25; found: C 47.35, H 5.14.

*(±)-3-{(RS)-[(tert-Butyl)dimethylsilyloxy](furan-2-yl)methyl}-3-deoxy-5-O-(methylsulfonyl)-2-O-(methoxymethyl)-β-*DL*-altrofuranurono-6,1-lactone* (**50**). As described for **48**, with **47** (300 mg, 0.63 mmol). FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**50**) 0.45, *Pancaldi*) yielded 140 mg (45%) of **50**. Colorless oil. IR (film): 2930, 2855, 1755, 1440, 1370, 1260, 1210, 1180, 1155, 1110, 1055, 965, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39 (*dd*, ^3J(4″,5″) = 1.8, ^4J(3″,5″) = 0.7, H–C(5″)); 6.34 (*dd*, ^3J(3″,4″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.31 (*dm*, ^3J(3″,4″) = 3.2, H–C(3″)); 5.82 (*d*, ^3J(1,2) = 3.6, H–C(1)); 4.91 (*d*, ^3J(1′,3) = 6.1, H–C(1′)); 4.84 (br. *s*, H–C(5)); 4.63 (*d*, ^2J = 7.0, 1 H, MeOCH_2); 4.59 (br. *s*, H–C(4)); 4.55 (*d*, ^2J = 7.0, 1 H, MeOCH_2); 4.16 (*dd*, ^3J(2,3) = 4.4, ^3J(2,1) = 3.6, H–C(2)); 3.40 (*s*, *Me*OCH$_2$); 3.21 (*s*, MeSO$_2$); 2.36 (*ddd*, ^3J((3,1′) = 6.1, ^3J(3,2) = 4.4, ^3J(3,4) = 2.1, H–C(3)); 0.87 (*s*, *t*-BuSi); 0.06, –0.13 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 161.7 (*s*, C(6)); 153.1 (*s*, C(2″)); 142.6 (*d*, *J* = 203, C(5″)); 110.2 (*d*, *J* = 176), 108.4 (*d*, *J* = 181, C(3″), C(4″)); 102.3 (*d*, *J* = 188, C(1)); 97.3 (*t*, *J* = 164, MeO*C*H$_2$); 80.4 (*d*, *J* = 162), 80.3 (*d*, *J* = 164), 77.1 (*d*, *J* = 153), 67.9 (*d*, *J* = 143, C(2), C(4), C(1′), C(5)); 56.5 (*q*, *J* = 142, *Me*OCH$_2$); 49.3 (*d*, *J* = 134, C(3)); 39.2 (*q*, *J* = 140, MeSO$_2$); 25.5 (*q*, *J* = 125, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); –5.1, –5.3 (2 *q*, *J* = 119, Me_2Si). CI-MS (NH_3): 510 (1, $[M + 18]^+$), 435 (2), 431 (12), 405 (5), 373 (4), 299 (5), 249 (12), 185 (13), 153 (29), 135 (35), 89 (52), 81 (73), 75 (87), 73 (100). Anal. calc. for $C_{20}H_{32}O_{10}SSi$ (492.66): C 48.76, H 6.55; found: C 48.86, H 6.53.

*(±)-Methyl 1,5-Anhydro-3-{(SR)-[(tert-butyl)dimethylsilyloxy](furan-2-yl)methyl}-3-deoxy-2-O-(methoxymethyl)-α-*DL*-galactofuranuronate* (**51**) *and (±)-Methyl 1,5-Anhydro-3-{(SR)-[(tert-butyl)dimethylsilyloxy](furan-2-yl)methyl}-3-deoxy-2-O-(methoxymethyl)-α-*DL*-altrofuranuronate* (**52**). In a flame-dried flask, K_2CO_3 (1.88 g, 13.61 mmol) was dried in a flame *in vacuo*. After pressurizing with Ar, **49** (2.80 g, 4.54 mmol), anh. DMF (28 ml), and anh. MeOH (14 ml) were added. After vigourous stirring at 20° for 10 min, more DMF (42 ml) was added and the soln. stirred at 20° for 90 min. The solvent was evaporated at 35°, the residue taken up with AcOEt (300 ml), the soln. washed with brine (100 ml), dried ($MgSO_4$) and evaporated, and the viscous, yellow oil (**51**/**52** 9:1, 1.95 g) purified by FC (SiO_2, 230–400 mesh, AcOEt/light petroleum ether 1:2; R_f (**51**) 0.45, *Pancaldi*), yielding 1.42 g (63%) of **51** as a yellow solid that was recrystallized from Et_2O/light petroleum ether: 1.14 g (50%) of colorless solid. The mother-liquor contained **51**/**52** 1:1 which were separated by successive FC and recrystallizations.

Data of **51**: M.p. 72–73°. UV (MeCN): 215 (10900). IR (KBr). 2955, 1730, 1280, 1060, 845, 745. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40 (*dd*, ^3J(4″,5″) = 1.7, ^4J(3″,5″) = 0.7, H–C(5″)); 6.35 (*dd*, ^3J(3″,4″) = 3.2, ^3J(4″,5″) = 1.8, H–C(4″)); 6.28 (*dm*, ^3J(3″,4″) = 3.2, H–C(3″)); 5.74 (*d*, ^3J(1,2) = 2.3, H–C(1)); 4.77 (*d*, ^2J = 6.8, 1 H), 4.63 (*d*, ^2J = 6.8, 1 H, MeOCH_2); 4.55 (*d*, ^3J(1′,3) = 9.3, H–C(1′)); 4.51 (*s*, H–C(4)); 4.26 (*s*, H–C(5)); 3.92 (*dd*, ^3J(2,3) = 2.7, ^3J(2,1) = 2.3, H–C(2)); 3.73 (*s*, COOMe); 3.43 (*s*, *Me*OCH$_2$); 2.23 (*dd*, ^3J(3,1′) = 9.3, ^3J(3,2) = 2.7, H–C(3)); 0.84 (*s*, *t*-BuSi); 0.02, –0.18 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.0 (*s*, C(6)); 154.1 (*s*, C(2″)); 142.3 (*d*, *J* = 203, C(5″)); 110.2 (*d*, *J* = 175), 108.2 (*d*, *J* = 174, C(3″), C(4″)); 101.7 (*d*, *J* = 183, C(1)); 96.6 (*t*, *J* = 164, MeO*C*H$_2$); 82.0 (*d*, *J* = 147), 81.7 (*d*, *J* = 167), 76.8 (*d*, *J* = 155), 68.8 (*d*, *J* = 142, C(2), C(4), C(5), C(1′)); 55.9 (*q*, *J* = 143, *Me*OCH$_2$); 53.1 (*d*, *J* = 137, C(3)); 52.5 (*q J* = 148, COO*Me*); 25.7 (*q*, *J* = 125, *Me*$_3$CSi); 18.1 (*s*, Me$_3$*C*Si); –5.1, –5.2 (2 *q*, *J* = 119, Me_2Si). CI-MS (NH_3): 446 (33, $[M + 18]^+$), 385 (5), 368 (11), 340 (4), 310 (12), 300 (7), 282 (9), 266 (7), 252 (10), 235 (15), 211 (100), 147 (13), 89 (43), 81 (39), 75 (48), 73 (81). Anal. calc. for $C_{20}H_{32}O_8Si$ (428.554): C 56.05, H 7.52; found: C 56.15, H 7.45.

Data of **52**: M.p. 85–87°. UV (MeCN): 215 (10300). IR (KBr): 2930, 1765, 1730, 1470, 1440, 1250, 1220, 1150, 1125, 1055, 840, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38 (*dd*, ^3J(4″,5″) = 1.8, ^4J(3″,5″) = 0.8, H–C(5″));

6.34 (*dd*, ^3J(3'',4) = 3.2, ^3J(4'',5'') = 1.8, H–C(4'')); 6.27 (*dm*, ^3J(3'',4'') = 3.2, H–C(3'')); 5.63 (*d*, ^3J(1,2) = 2.2, H–C(1)); 4.78 (*d*, ^2J = 6.8, 1 H), 4.68 (*d*, ^2J = 6.8, 1 H, MeOCH_2); 4.58 (*d*, ^3J(1',3) = 9.2, H–C(1')); 4.55 (*d*, ^3J(4,5) = 4.0, H–C(4)); 4.41 (*d*, ^3J(4,5) = 4.0, H–C(5)); 3.90 (*dd*, ^3J(2,3) = 3.0, ^3J(2,1) = 2.2, H–C(2)); 3.77 (*s*, COOMe); 3.47 (*s*, *Me*OCH_2); 2.17 (*dd*, ^3J(3,1') = 9.2, ^3J(3,2) = 3.0, H–C(3)); 0.84 (*s*, *t*-BuSi); 0.02, −0.16 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 168.5 (*s*, C(6)); 154.3 (*s*, C(2'')); 142.0 (*d*, *J* = 202, C(5'')); 110.2 (*d*, *J* = 175), 107.9 (*d*, *J* = 174, C(3''), C(4'')); 102.7 (*d*, *J* = 183, C(1)); 96.3 (*t*, *J* = 164, MeO*C*H_2); 82.0 (*d*, *J* = 147), 80.3 (*d*, *J* = 167); 77.5 (*d*, *J* = 152), 68.8 (*d*, *J* = 142, C(2), C(4), C(5), C(1')); 55.8 (*q*, *J* = 142, *Me*OCH_2); 52.0 (*q*, *J* = 148, COOMe); 49.1 (*d*, *J* = 137, C(3)); 25.6 (*q*, *J* = 125, *Me*$_3$CSi); 18.0 (*s*, Me_3*C*Si); −5.2, −5.3 (2 *q*, *J* = 119, Me_2Si). CI-MS (NH_3): 371 (10, $[M - 57]^+$), 339 (11), 309 (40), 291 (23), 277 (15), 265 (15), 263 (18), 251 (14), 242 (19), 241 (81), 235 (59), 211 (28), 203 (34), 81 (56), 75 (66), 73 (100). Anal. calc. for $C_{20}H_{32}O_8Si$ (428.554): C 56.05, H 7.53; found: C 56.12, H 7.50.

*(±)-1,4-Anhydro-3-{(*SR*)-[(*tert*-butyl)dimethylsilyloxy](furan-2-yl)methyl}-3-deoxy-2-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**53**). 1M $LiAlH_4$ in Et_2O (1 ml, 1.02 mmol) was added dropwise to a stirred soln. of **51** (204 mg, 0.51 mmol) in anh. THF (2 ml) cooled to 0°. After stirring at 0° for 3 min, a few drops of MeOH were added, and the mixture was poured into 1N aq. HCl (20 ml) and extracted with AcOEt (3 × 20 ml). The combined extracts were washed with sat. aq. $NaHCO_3$ soln. (50 ml), and dried ($MgSO_4$). Solvent evaporation gave 200 mg of light-yellow oil that was purified by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**53**) 0.25, *Pancaldi*): 171 mg (94%) of **53**. Colorless oil. UV (MeCN): 213 (8300). IR (film): 3470, 2950, 2930, 2890, 2855, 1470, 1360, 1250, 1225, 1155, 1120, 1085, 1055, 1010, 965, 880, 840, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38 (*dd*, ^3J(4'',5'') = 1.8, ^4J(3'',5'') = 0.7, H–C(5'')); 6.33 (*dd*, ^3J(3'',4'') = 3.2, ^3J(4'',5'') = 1.8, H–C(4'')); 6.27 (*dm*, ^3J(3'',4'') = 3.2, H–C(3'')); 5.60 (*d*, ^3J(1,2) = 2.4, H–C(1)); 4.81 (*d*, ^2J = 6.7, 1 H), 4.64 (*d*, ^2J = 6.7, 1 H, MeOCH_2); 4.52 (*d*, ^3J(1',3) = 9.7, H–C(1')); 4.14 (br. *s*, H–C(4)); 3.95 (*dd*, ^3J(2,3) = 2.5, ^3J(2,1) = 2.4, H–C(2)); 3.85 (*t*, ^3J(5,6) = 5.1, H–C(5)); 3.55–3.45 (*m*, 2 H–C(6)); 3.42 (*s*, *Me*OCH_2); 2.16 (*dd*, ^3J(3,1') = 9.7, ^3J(3,2) = 2.5, H–C(3)); 1.95 (*t*, ^3J(OH–C(6),6) = 5.9, OH–C(6)); 0.84 (*s*, *t*-BuSi); 0.09, −0.18 (2*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 154.4 (*s*, C(2'')); 142.2 (*d*, *J* = 202, C(5'')); 110.2 (*d*, *J* = 175), 108.1 (*d*, *J* = 174, C(3''), C(4'')); 100.7 (*d*, *J* = 181, C(1)); 96.2 (*t*, *J* = 164, MeO*C*H_2); 81.8 (*d*, *J* = 147), 79.6 (*d*, *J* = 162), 79.2 (*d*, *J* = 151), 68.8 (*d*, *J* = 152, C(2), C(4), C(5), C(1')); 63.6 (*t*, *J* = 153, C(6)); 55.7 (*q*, *J* = 1.42, *Me*OCH_2); 53.5 (*d*, *J* = 137, C(3)); 25.7 (*q*, *J* = 125, *Me*$_3$CSi); 18.1 (*s*, Me_3*C*Si); −5.2 (*q*, *J* = 118, Me_2Si). CI-MS (NH_3): 311 (3, $[M - 89]^+$), 283 (3), 265 (2), 251 (8), 237 (5), 211 (100), 177 (7), 135 (19), 107 (22), 89 (30), 81 (43), 73 (78). Anal. calc. for $C_{19}H_{32}O_7Si$ (400.544): C 56.97, H 8.05; found: C 56.97, H 7.99.

*(±)-1,4-Anhydro-3-{(*SR*)-[(*tert*-butyl)dimethylsilyloxy](furan-2-yl)methyl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**54**). Methoxymethyl chloride (291 µl, 3.12 mmol) and Bu_4NI (29 mg, 0.08 mmol) were added to a stirred soln. of **53** (313 mg, 0.78 mmol) in anh. CH_2Cl_2 (1 ml) and (i-Pr)$_2$NEt (1 ml) at 0°. After stirring at 0° for 15 min and then at 20° for 3.5 h, the soln. was poured into 1N aq. HCl (20 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. extract was dried ($MgSO_4$) and evaporated, and the light-yellow oil (350 mg) purified by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**54**) 0.51, *Pancaldi*): 319 mg (96%) of **54**. Colorless oil that solidified at 4°. M.p. 74–75°. UV (MeCN): 215 (9900). IR (KBr): 2960, 2850, 1475, 1250, 1155, 1110, 1060, 1030, 840, 775, 750. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38 (*dd*, ^3J(4'',5'') = 1.8, H–C(5'')); 6.33 (*dd*, ^3J(3'',4'') = 3.2, ^3J(4'',5'') = 1.8, H–C(4'')); 6.27 (*dd*, ^3J(3'',4'') = 3.2, H–C(3'')); 5.53 (*d*, ^3J(1,2) = 2.5, H–C(1)); 4.80 (*d*, ^2J = 6.7, 1 H), 4.63 (*d*, ^2J = 6.7, 1 H, MeOCH_2); 4.56 (*s*, 2 H, MeOCH_2); 4.53 (*d*, ^3J(1',3) = 9.7, H–C(1')); 4.15 (*s*, H–C(4)); 3.93 (*dd*, ^3J(2,1) = 2.5, ^3J(2,3) = 2.4, H–C(2)); 3.91 (*dd*, ^3J(5,6a) = 7.8, ^3J(5,6b) = 5.4, H–C(5)); 3.41 (*s*, 1 *Me*OCH_2); 3.40 (*dd*, ^2J = 10.2, ^3J(6a,5) = 7.8, H_a–C(6)); 3.34 (*dd*, ^2J = 10.2, ^3J(6b,5) = 5.4, H_b–C(6)); 3.23 (*s*, 1 *Me*OCH_2); 2.17 (*dd*, ^3J(3,1') = 9.7, ^3J(3,2) = 2.4, H–C(3)); 0.84 (*s*, *t*-BuSi); 0.09, −0.18 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 154.5 (*s*, C(2'')); 142.1 (*d*, *J* = 202, C(5'')); 110.1 (*d*, *J* = 166), 107.9 (*d*, *J* = 174, C(3''), C(4'')); 100.7 (*d*, *J* = 180, C(1)); 96.8, 96.2 (2*t*, *J* = 164, MeO*C*H_2); 81.9 (*d*, *J* = 153), 79.7 (*d*, *J* = 163), 77.7 (*d*, *J* = 148), 69.0 (*d*, *J* = 140, C(2), C(4), C(5), C(1')); 68.3 (*t*, *J* = 142, C(6)); 55.7, 55.1 (2*q*, *J* = 142, *Me*OCH_2); 53.3 (*d*, *J* = 137, C(3)); 25.7 (*q*, *J* = 125, *Me*$_3$CSi); 18.1 (*s*, Me_3*C*Si); −5.2 (*q*, *J* = 119, Me_2Si). CI-MS (NH_3): 445 (1, $[M + 1]^+$), 355 (1), 311 (3), 281 (9), 263 (5), 251 (5), 237 (5), 211 (100), 111 (21), 73 (65). Anal. calc. for $C_{21}H_{36}O_8Si$ (444.597): C 56.73, H 8.16; found: C 56.88, H 8.01.

Preparation of **54** *in Multigram Batches Starting with 7-Oxatrinorbornanone* **16**. In a flame-dried 1-l flask under Ar, anh. THF (170 ml) and $(Me_3Si)_2NH$ (27 ml, 129 mmol) were mixed, cooled to −10°, and treated dropwise with 1.6M BuLi in hexane (74.5 ml, 119 mmol) under stirring and maintaining the temp. below 0°. After stirring at −10° for 15 min, the soln. was cooled to −78°, and a soln. of ketone **16** (30 g, 99 mmol) in anh. THF (220 ml) was added dropwise under stirring within *ca.* 30 min. Freshly distilled furan-2-carbaldehyde (12.4 ml, 149 mmol) dissolved in anh. THF (60 ml) was added dropwise within *ca.* 30 min. The mixture was stirred for

90 min at −78°, and AcOH (10 ml, 200 mmol) in MeOH (25 ml) was added dropwise under stirring at −78°. The cooling bath was removed and the mixture allowed to reach 20°. The mixture was poured into sat. aq. $NaHCO_3$ soln. (400 ml) and CH_2Cl_2 (400 ml) under vigorous stirring. The aq. phase was extracted with CH_2Cl_2 (2 × 200 ml), the combined org. extract dried ($MgSO_4$) and evaporated, and the yellowish solid (41 g) recrystallized from $CHCl_3$ to remove the excess of furan-2-carbaldehyde: 37.5 g (95%) of aldol **19** as colorless crystals. To a soln. of **19** (29.1 g, 73 mmol) in anh. DMF (120 ml), (*t*-Bu)Me_2SiCl (11 g, 77 mmol) was added, followed by 1*H*-imidazole (20 g, 291 mmol). After stirring at 20° for 2 h, more (*t*-Bu)Me_2SiCl (11 g) was added and the mixture stirred for another 2 h at 20°. The mixture was poured onto AcOEt (500 ml) and 1N aq. HCl (300 ml) and shaken vigorously. The aq. phase was extracted with AcOEt (300 ml), the combined org. extract washed wth 5% aq. Na_2CO_3 soln. (300 ml), dried ($MgSO_4$), and evaporated, and the residue dried at 10^{-1} Torr: silyl ether **22** (38.5 g) as a colorless oil. A soln. of **22** (38.5 g) in THF/MeOH 1:1 (400 ml) was cooled to 0°. $NaBH_4$ (5.3 g, 140 mmol) was added portionwise under stirring. After stirring at 20° for 5 min, 10% aq. HCl soln. was added until pH 2–3, and the mixture was poured onto vigorously stirred CH_2Cl_2 (600 ml) and H_2O (600 ml). The aq. layer was extracted with CH_2Cl_2 (200 ml), the combined org. extracts were washed with 5% aq. Na_2CO_3 soln. (400 ml), dried ($MgSO_4$), and evaporated, and the residue was dried at 10^{-1} Torr: 37.9 g of alcohol **41** as a colorless solid. It was dissolved (37.9 g) in THF (225 ml), and the soln. was cooled to −78°. *m*CPBA (*Fluka*; 70%; 17.0 g, 73.6 mmol) dissolved in CH_2Cl_2 (225 ml) (decanted and the org. soln. dried ($MgSO_4$)) was added dropwise. After stirring at −78° for 30 min, the cooling bath was removed and the mixture allowed to reach 20° and stirred at 20° for 2.5 h. The yellow soln. was poured into a vigorously stirred mixture of CH_2Cl_2 (500 ml) and 10% aq. $NaHSO_3$ soln. (500 ml). The aq. layer was extracted with CH_2Cl_2 (500 ml), the combined org. extract poured carefully under stirring onto sat. aq. $NaHCO_3$ soln. (400 ml), and the aq. phase extracted with CH_2Cl_2 (200 ml). The combined org. extract was dried ($MgSO_4$) and evaporated: 34.5 g of a viscous, yellow oil. The product was filtered through silica gel (400 g, 25 × 8 cm; AcOEt/CH_2Cl_2/light petroleum ether 1:3:16). The 2nd fraction contained the chloroalkene derivative **42** (23 g) as a yellowish oil. A soln. of **42** (23 g) in anh. (i-Pr)$_2$NEt (120 ml) was cooled to 0°. After the addition of $MeOCH_2Cl$ (24 ml, 316 mmol), the mixture was stirred at 0° for 30 min and then at 20° for 2 h. After cooling to 0°, $MeOCH_2Cl$ (5 ml, 65 mmol) was added. The mixture was stirred at 0° for 30 min and then at 20° for 2 h. The mixture was poured carefully into ice-cold 1N aq. HCl (500 ml) and extracted with AcOEt (500 ml). The combined org. phase was washed with sat. aq. $NaHCO_3$ soln. (300 ml), dried ($MgSO_4$), and evaporated, and the residue dried at 20°/10^{-1} Torr: 25.3 g of alkene **43** as a light-yellow oil. To a soln. of **43** (25.3 g) in THF/H_2O 4:1 (250 ml, 20°), $NaHCO_3$ (10.6 g, 126 mmol), 0.1M OsO_4 in CCl_4 (6.3 ml, 0.63 mmol), and trimethylamine *N*-oxide dihydrate (14.0 g, 126 mmol) were added successively. After stirring at 20° for 5 h, the mixture was poured into ice-cold 1N aq. HCl (250 ml) and extracted with CH_2Cl_2 (250 ml, twice). The combined org. extract was washed with 10% aq. $NaHSO_3$ soln. (300 ml) and brine (300 ml), dried ($MgSO_4$), and evaporated at 20°: 28.9 g of α-hydroxy ketone **44** as a yellow oil. A soln. of **44** (28.9 g) in CH_2Cl_2 (170 ml) was cooled to 0°. 4-Bromobenzenesulfonyl chloride (13.2 g, 51.4 mmol) and then Et_3N (13.2 mg, 77.0 mmol) were added successively within 5 min. After stirring at 0° for 30 min, then at 20° for 3 h, the mixture was poured into CH_2Cl_2 (200 ml) and ice-cold 1N aq. HCl (500 ml). The aq. phase was extracted with CH_2Cl_2 (300 ml, twice). The combined org. extract was washed with ice-cold, sat. aq. $NaHCO_3$ soln. (500 ml), dried ($MgSO_4$), and evaporated yielding 39.0 g of a brownish solid that was filtered as a soln. in AcOEt/CH_2Cl_2/light petroleum ether 1:1:8 on silica gel (400 g). The main fraction yielded 32.3 g of brosylate **46** as light-yellow crystals. A soln. of **46** (32.3 g) in CH_2Cl_2 (400 ml) was cooled to 0°. *m*CPBA (70%; 13.3 g, 61.1 mmol) and then $NaHCO_3$ (6.4 g, 83.3 mmol) were added, and the mixture was stirred at 0° for 1 h, then poured into ice-cold, sat. aq. $NaHSO_3$ soln. (500 ml), and extracted with CH_2Cl_2 (400 ml, 3 times). The combined org. extract was carefully poured into ice-cold sat. aq. $NaHCO_3$ soln. (500 ml) and the aq. layer decanted and extracted with CH_2Cl_2 (200 ml). The combined org. extract was dried ($MgSO_4$) and evaporated giving 32.5 g of lactone **49** as colorless crystals (overall yield: 70% based on aldol **19**, 7 steps; 67% based on ketone **16**, 8 steps). The conversions of lactone **49** into methyl galactouronate **51** can be carried as described for the synthesis of **51**, starting with 16 g (25 mmol) of **49**. Yield: 53% of **51**. Reduction of **51** (10 g, 22.8 mmol) into alcohol **53** required 0.8 equiv. of $LiAlH_4$. The crude alcohol **53** (8.7 g) was dissolved in (i-Pr)$_2$NEt (25 ml), the soln. cooled to 0°, and $MeOCH_2Cl$ (9 ml, 60 mmol) added. After stirring at 0° for 15 min and then at 20° for 1 h, the soln. was cooled to 0°, and more $MeOCH_2Cl$ (5 ml, 34 mmol) was added. The mixture was stirred at 0° for 30 min and then at 20° for 1 h. The mixture was poured carefully into ice-cold 1N aq. HCl (100 ml) and extracted with AcOEt (100 ml, 3 times). The combined org. extract was dried ($MgSO_4$) and evaporated to give 9.0 g (overall yield 89%) of 1,4-anhydrogalactopyranose **54** as a yellowish oil that solidified at 4°, pure enough for the subsequent transformations.

*(±)-1,4-Anhydro-3-{(*SR*)-[(*tert*-butyl)dimethylsilyloxy](1-benzyl-1*H*-pyrrol-2-yl)methyl}-3-deoxy-2,6-bis-O-(methoxymethyl)-α-*DL*-galactopyranose* (**58**). A soln. of **59** (120 mg, 0.26 mmol) in anh. MeOH (0.2 ml) and

then $NaBH_3CN$ (36 mg, 0.53 mmol) were added to a stirred soln. of $BnNH_2$ (32 µl, 0.26 mmol) and AcOH (16 µl, 0.26) in anh. MeOH (2 ml) at −78° under Ar. After stirring at −78° for 30 min and then at 20° for 30 min, the soln. was poured into 5% aq. Na_2CO_3 soln. (25 ml) and extracted with CH_2Cl_2 (3 × 25 ml). The combined org. extract was dried ($MgSO_4$) and evaporated. FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**58**) 0.6, UV) yielded 84 mg (60%) of **58**. Yellowish oil. UV (MeCN): 200 (12400). IR (film): 3155, 2910, 2870, 1560, 1490, 1420, 1280, 1185, 1105, 1070, 865, 795, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.22 (*m*, $CHCl_3$, 3 arom. H); 6.93 (*d*, ^3J = 7.4, 2 arom. H); 6.63 (*dd*, $^3J(4'',5'')$ = 2.7, $^4J(3'',5'')$ = 1.8, H–C(5'')); 6.11 (*dd*, $^3J(3'',4'')$ = 3.5, $^3J(4'',5'')$ = 2.7, H–C(4'')); 6.10 (*dd*, $^3J(3'',4'')$ = 3.5, $^4J(3'',5'')$ = 1.8, H–C(3'')); 5.52 (*d*, ^2J = 16.9, 1 H, PhCH_2); 5.48 (*d*, $^3J(1,2)$ = 2.4, H–C(1)); 5.14 (*d*, ^2J = 16.9, 1 H, PhCH_2); 4.74 (*d*, ^2J = 6.6, 1 H), 4.58 (*d*, ^2J = 6.6, 1 H); 4.55 (*s*, 2 H, 2 MeOCH_2); 4.52 (*d*, $^3J(1',3)$ = 11.2, H–C(1')); 4.00 (br. *s*, H–C(4)); 3.80 (*dd*, $^3J(2,1)$ = 2.4, $^3J(2,3)$ = 2.0, H–C(2)); 3.34 (*s*, 1 *Me*OCH$_2$); 3.29 (*s*, 1 *Me*OCH$_2$); 3.40–3.15 (*m*, H–C(5), 2 H–C(6)); 1.82 (*dd*, $^3J(3,1')$ = 11.2, $^3J(3,2)$ = 2.0, H–C(3)); 0.87 (*s*, *t*-BuSi); 0.02, −0.22 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 139.0 (*s*, arom. C); 128.9 (*d*, *J* = 159), 127.7 (*d*, *J* = 151, arom. C, C(5'')); 127.3 (*s*, C(2'')); 125.9 (*d*, *J* = 157), 123.7 (*d*, *J* = 179, arom. C, C(5'')); 110.3 (*d*, *J* = 163), 107.5 (*d*, *J* = 163, C(3''), C(4'')); 83.0 (*d*, *J* = 188, C(1)); 96.5, 96.2 (2 *t*, *J* = 163, MeOCH_2), 83.1 (*d*, *J* = 152), 80.2 (*d*, *J* = 156), 77.2 (*d*, *J* = 148), 71.0 (*d*, *J* = 146, C(2), C(4), C(5), C(1')); 67.9 (*t*, *J* = 143, C(6)); 55.7, 55.2 (2 *q*, *J* = 142, *Me*OCH$_2$); 53.3 (*d*, *J* = 136, C(3)); 48.8 (*t*, *J* = 137, PhCH_2); 25.8 (*q*, *J* = 125, Me_3CSi); 18.1 (*s*, Me_3CSi); −5.2, −5.4 (2*q*, *J* = 118, Me_2Si). CI-MS (NH_3): 533 (1, $M^{+\cdot}$), 476 (4), 402 (3), 300 (100), 170 (7), 160 (19), 152 (6), 91 (57), 73 (37). Anal. calc. for $C_{28}H_{43}O_7NSi$ (533.738): C 63.01, H 8.12, N 2.62; found: C 63.02, H 8.06, N 2.57.

*(±)-1,4-Anhydro-3-{(1'*SR*,Z)-1'-[(*tert*-butyl)dimethylsilyloxy]-2',5'-dioxopent-3'-enyl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**59**). A mixture of **54** (1.07 g, 2.41 mmol) and 0.1M dimethyldioxirane in acetone (60 ml) was stirred at 20° for 6–8 h (TLC (AcOEt/light petroleum ether 1:2): R_f (**54**) 0.51). Solvent evaporation yielded 1.11 g (100%) of **59**. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 10.22 (*d*, $^3J(5',4')$ = 7.1, H–C(5')); 7.38 (*d*, $^3J(3',4')$ = 12.0, H–C(3')); 6.31 (*dd*, $^3J(4',3')$ = 12.0, $^3J(4',5')$ = 7.1, H–C(4')); 5.49 (*d*, $^3J(1,2)$ = 2.4, H–C(1)); 4.71 (*d*, ^2J = 6.8, 1 H), 4.66 (*d*, ^2J = 6.8, 1 H), 4.61 (*s*, 2 H, 2 MeOCH_2); 4.57 (*s*, H–C(4)); 4.16 (*d*, $^3J(1',3)$ = 7.8, H–C(1')); 3.94 (*dd*, $^3J(2,3)$ = 2.7, $^3J(2,1)$ = 2.4, H–C(2)); 3.91 (*dd*, $^3J(5,6a)$ = 8.2, $^3J(5,6b)$ = 5.2, H–C(5)); 3.45 (*dd*, ^2J = 10.2, $^3J(6b,5)$ = 5.2, H_b–C(6)); 3.41 (*s*, 1 *Me*OCH$_2$); 3.35 (*dd*, ^2J = 10.2, $^3J(6a,5)$ = 8.2, H_a–C(6)); 3.34 (*s*, 1 *Me*OCH$_2$); 1.95 (*dd*, $^3J(3,1')$ = 7.8, $^3J(3,2)$ = 2.7, H–C(3)); 0.93 (*s*, *t*-BuSi); 0.13, 0.06 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 201.2 (*s*, C(2')); 192.3 (*s*, C(5')); 139.7 (*d*, *J* = 163), 136.0 (*d*, *J* = 162, C(3'), C(4')); 110.1 (*d*, *J* = 181, C(1)); 96.6, 96.5 (2*t*, *J* = 163, MeOCH_2); 80.3 (*d*, *J* = 154), 78.2 (*d*, *J* = 164), 77.9 (*d*, *J* = 165), 77.6 (*d*, *J* = 160, C(2), C(4), C(1'), C(5)); 67.5 (*t*, *J* = 144, C(6)); 55.6, 54.9 (*q*, *J* = 143, 2 *Me*OCH$_2$); 51.5 (*d*, *J* = 136, C(3)); 25.4 (*q*, *J* = 125, Me_3CSi); 17.7 (*s*, Me_3CSi); −5.2, −5.3 (2*q*, *J* = 118, Me_2Si).

*(±)-1,4-Anhydro-3-{(*SR*)-[(*tert*-butyl)dimethylsilyloxy][1-propyl-1*H*-pyrrol-2-yl]methyl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**60**). A mixture of **54** (198 mg, 0.44 mmol), Bengal Rose B (on polystyrene 0.3 mmol/g, 15 mg, 0.004 mmol), and anh. CH_2Cl_2 (2 ml) was cooled to −78° under Ar and irradiated (500 W, halogen lamp) for 2 h while dry O_2 was bubbled through the soln. The gas flow was stopped, Me_2S (0.32 ml, 4.40 mmol) added, and the mixture allowed to warm up to 20° within 15 min. The solvent was evaporated and the residue taken in AcOEt (20 ml) and filtered. The filtrate was washed with brine (20 ml, twice), dried ($MgSO_4$), and evaporated giving 212 mg of a bright yellow oil (**59**/(*E*)-**59**) that was taken up in AcOEt (4 ml). After addition of 5% $PdCaCO_3$ (93 mg, 0.044 mmol) and pressurization with H_2 (50 bar), the mixture was shaken at 20° for 30 min. The catalyst was filtered off (*Celite*) and rinsed (AcOH, 3 × 10 ml). The solvent was evaporated yielding 201 mg of **57** as slightly yellow oil of 80% purity. Crude **57** (50 mg, 0.10 mmol) was taken up with anh. THF (0.2 ml), propylamine (0.2 ml, 2.42 mmol) and Al_2O_3 (neutral, *Fluka 06300*, 60 mg) were added, and the mixture was stirred at 20° for 15 h. The solid was filtered off and rinsed with CH_2Cl_2. The solvent was evaporated and the residue purified by FC (SiO_2, AcOEt/light petroleum 1:2; R_f (**60**) 0.75, *Pancaldi*): 23 mg (39%) of **60**. Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.64 (*dd*, $^3J(4'',5'')$ = 2.2, $^4J(3'',5'')$ = 1.7, H–C(5'')); 6.05 (*dd*, $^3J(3'',4'')$ = 3.6, $^3J(4'',5'')$ = 2.2, H–C(4'')); 6.00 (*dd*, $^3J(3'',4'')$ = 3.6, $^4J(3'',5'')$ = 1.7, H–C(3'')); 5.58 (*d*, $^3J(1,2)$ = 2.3, H–C(1)); 4.80 (*d*, ^2J = 6.7, 1 H), 4.67 (*d*, ^2J = 6.7, 1 H, MeOCH_2); 4.55 (*d*, $^3J(1',3)$ = 10.8, H–C(1')); 4.52 (*s*, MeOCH_2); 4.10 (br. *s*, H–C(4)); 3.92 (*dd*, $^3J(2,1)$ = 2.3, $^3J(2,3)$ = 2.2, H–C(2)); 3.89 (*dd*, $^3J(5,6a)$ = 7.3, $^3J(5,6b)$ = 5.5, H–C(5)); 3.44 (*s*, *Me*OCH$_2$); 3.43–3.40 (*m*, ^2J = 7.6, CH_2N); 3.38 (*dd*, ^2J = 10.2, $^3J(6b,5)$ = 5.5, H_b–C(6)); 3.23 (*dd*, ^2J = 10.2, $^3J(6a,5)$ = 7.3, H_a–C(6)); 3.21 (*s*, 1 *Me*OCH$_2$); 2.13 (*dd*, $^3J(3,1')$ = 10.8, $^3J(3,2)$ = 2.2, H–C(3)); 1.80–1.76 (*m*, MeCH_2CH$_2$); 0.96 (*t*, ^3J = 7.4, *Me*CH$_2$OH$_2$); 0.85 (*s*, *t*-BuSi); −0.11, −0.23 (2*s*, Me_2Si).

*(±)-1,4-Anhydro-3-{(*SR*)-[(*tert*-butyl)dimethylsilyloxy][1-(ethoxycarbonylmethyl)-1*H*-pyrrol-2-yl]methyl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**61**). As described for **60**, with crude **57** (50 mg, *ca.*

0.1 mmol), using ethyl glycinate hydrochloride (500 mg, 3.58 mmol) instead of propylamine, and Et_3N (500 µl, 3.58 mmol). FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**61**) 0.42, *Pancaldi*): 22 mg (35%) of **61**. Slightly yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.58 (*dd*, $^3J(4'',5'') = 2.5$, $^4J(3'',5'') = 1.7$, H–C(5'')); 6.09 (*dd*, $^3J(3'',4'') = 3.5$, $^3J(4'',5'') = 2.5$, H–C(4'')); 6.04 (*dd*, $^3J(3'',4'') = 3.5$, $^4J(3'',5'') = 1.7$, H–C(3'')); 5.57 (*d*, $^3J(1,2) = 2.3$, H–C(1)); 5.07 (*d*, $^2J = 17.8$, 1 H, CH_2COOEt); 4.78, 4.67 (2*d*, $^2J = 6.7$, 2 H, MeOCH_2); 4.64 (*d*, $^2J = 17.8$, 1 H, CH_2COOEt); 4.57, 4.55 (2*d*, $^2J = 6.6$, 2 H, MeOCH_2); 4.51 (*d*, $^3J(1',3) = 11.2$, H–C(1')); 4.22, 4.18 (2 *dq*, $^2J = 14.0$, $^3J = 7.1$, MeCH_2O); 4.11 (br. *s*, H–C(4)); 3.85 (*dd*, $^3J(2,1) = 2.3$, $^3J(2,3) = 2.1$, H–C(2)); 3.81 (*t*, $^3J = 6.2$, H–C(5)); 3.42 (*s*, 1 *Me*OCH$_2$); 3.37 (*dd*, $^2J = 9.8$, ^3J(6a,5) = 6.2, H_a–C(6)); 3.29 (*dd*, $^2J = 9.8$, ^3J(6b,5) = 6.2, H_b–C(6)); 3.25 (*s*, 1 *Me*OCH$_2$); 1.95 (*dd*, $^3J(3,1') = 11.2$, $^3J(3,2) = 2.1$, H–C(3)); 1.29 (*t*, $^3J = 7.1$, *Me*CH_2O); 0.84 (*s*, *t*-BuSi); 0.03, –0.24 (2*s*, Me_2Si).

*(±)-1,4-Anhydro-3-{(1'*SR,RS,Z*)-1'-[(*tert*-butyl)dimethylsilyloxy]-2',5'-dihydroxypent-3'-enyl}-3-deoxy-2,6-bis*-O-*(methoxymethyl)*-α-DL-*galactopyranose* (**62**). A mixture of **54** (1.07 g, 2.41 mmol) and 0.1M dimethyldioxirane in acetone (60 ml, 0.6 mmol) was stirred at 20° for 6–8 h. After solvent evaporation, the residue (**59**) was taken up in anh. MeOH (5 ml) and the soln. added to a stirred soln. of $CeCl_3$ (461 mg, 4.82 mmol) in anh. MeOH (5 ml) at 0° under Ar. $NaBH_4$ (182 mg, 4.82 mmol) was added portionwise. After stirring at 0° for 5 min, the colorless soln. was poured into ice-cold 1N aq. HCl (50 ml) and extracted with CH_2Cl_2 (3 × 50 ml). The combined org. extract was washed with 5% aq. Na_2CO_3 soln. (50 ml), dried ($MgSO_4$), and evaporated, and the oil (1.01 g) purified by FC (SiO_2, AcOEt/light petroleum ether 2:1; R_f (**62**) 0.2, *Pancaldi*): 75 mg (7%) of **54**, followed by 677 mg (61%) of **62** as a colorless oil which contained less than 10% of the isomer **63** (see *Scheme 6*). IR (film): 3395, 2925, 1630, 1255, 1150, 1040, 940, 835. ^{1}H-NMR (400 MHz, $CDCl_3$; data of **62**): 5.87 (*ddd*, $^3J(4',3') = 11.5$, $^3J(4',5'a) = 7.4$, $^3J(4',5'b) = 6.3$, H–C(4')); 5.59 (*ddt*, $^3J(3',4') = 11.5$, $^3J(3',2') = 8.0$, $^4J(3',5') = 0.8$, H–C(3')); 5.50 (*d*, $^3J(1,2) = 2.2$, H–C(1)); 4.71 (*d*, $^2J = 6.8$, 1 H), 4.66 (*d*, $^2J = 6.8$, 1 H), 4.62 (*s*, 2 H, 2 MeOCH_2); 4.59 (br. *s*, H–C(4)); 4.41 (*dd*, $^3J(2',3') = 8.0$, $^3J(2',1') = 5.5$, H–C(2')); 4.27 (*ddd*, $^2J = 13.4$, $^3J(5'a,4') = 7.4$, $^4J(5'a,3') = 0.8$, H_a–C(5')); 4.17 (*ddd*, $^2J = 13.4$, $^3J(5'b,4') = 6.3$, $^4J(5'b,3') = 0.8$, H_b–C(5')); 3.99 (*dd*, $^3J(2,3) = 3.0$, $^3J(2,1) = 2.2$, H–C(2)); 3.90 (*dd*, ^3J(5,6b) = 8.3, ^3J(5,6a) = 5.2, H–C(5)); 3.79 (*dd*, $^3J(1',2') = 5.5$, $^3J(1',3) = 4.3$, H–C(1')); 3.44 (*dd*, $^2J = 10.0$, ^3J(6a,5) = 5.2, H_a–C(6)); 3.43 (*s*, 1 *Me*OCH$_2$); 3.37 (*dd*, $^2J = 10.0$, ^3J(6b,5) = 8.3, H_b–C(6)); 3.36 (*s*, 1 *Me*OCH$_2$); 1.90 (*dd*, $^3J(3,1') = 4.3$, $^3J(3,2) = 3.0$, H–C(3)); 0.93 (*s*, 9 H, *t*-BuSi); 0.15, 0.14 (2 *s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 132.0 (*d*, *J* = 154), 131.1 (*d*, *J* = 153, C(3'), C(4')); 100.0 (*d*, *J* = 182, C(1)); 96.7, 96.4 (2*t*, *J* = 163, MeOCH_2); 81.2 (*d*, *J* = 150), 80.5 (*d*, *J* = 165), 78.4 (*d*, *J* = 154), 75.1 (*d*, *J* = 142), 69.3 (*d*, *J* = 136, C(2), C(4), C(5), C(1'), C(2')); 67.6 (*t*, *J* = 144, C(6)); 58.3 (*t*, *J* = 143, C(5')); 55.8, 55.1 (2 *q*, *J* = 142, *Me*OCH$_2$); 49.4 (*d*, *J* = 132, C(3)); 25.7 (*q*, *J* = 125, *Me*$_3$CSi); 17.9 (*s*, Me_3*C*Si); –4.3, –4.5 (2*q*, *J* = 118, Me_2Si). CI-MS (NH_3): 347 (5, [*M* – 117]$^+$), 313 (2), 283 (4), 271 (4), 214 (8), 199 (7), 171 (6), 111 (13), 89 (19), 81 (38), 75 (100), 73 (93). Anal. calc. for $C_{21}H_{40}O_9Si$ (464.628): C 54.29, H 8.68; found: C 54.18, H 8.58.

*(±)-1,4-Anhydro-3-{(1'*SR,2'RS,Z*)-2'-[(*tert*-butyl)dimethylsilyloxy]-1',5'-dihydroxypent-3'-enyl}-3-deoxy-2,6-bis*-O-*(methoxymethyl)*-α-DL-*galactopyranose* (**64**). The above FC afforded as a 3rd fraction **64** (40–80 mg, 4–8%). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.83 (*dddd*, $^3J(4',3') = 11.2$, $^3J(4',5'a) = 7.2$, $^3J(4',5'b) = 6.1$, $^4J(2',4') = 0.9$, H–C(4')); 5.54 (*ddt*, $^3J(3',4') = 11.2$, $^3J(3',2') = 8.9$, $^4J(3',5') = 1.1$, H–C(3')); 5.52 (*d*, $^3J(1,2) = 2.4$, H–C(1)); 4.76 (*s*, MeOCH_2); 4.77 (br. *s*, H–C(4)); 4.62 (*d*, $^2J = 3.9$), 4.60 (*d*, $^2J = 3.9$, MeOCH_2); 4.56 (*ddd*, $^3J(2',3') = 8.9$, $^3J(2',1') = 6.2$, $^4J(2',4') = 0.9$, H–C(2')); 4.21 (*ddd*, $^2J = 13.0$, $^3J(5'a,4') = 7.2$, $^4J(5'a,3') = 1.1$, H_a–C(5')); 4.13 (*ddd*, $^2J = 13.0$, $^3J(5'b,4') = 6.1$, $^4J(5'b,3') = 1.1$, H_b–C(5')); 4.05 (*dd*, $^3J(2,3) = 2.9$, $^3J(2,1) = 2.4$, H–C(2)); 3.93 (*dd*, ^3J(5,6b) = 8.5, ^3J(5,6a) = 5.0, H–C(5)); 3.54 (*dd*, $^3J(1',3) = 8.3$, $^3J(1',2') = 6.2$, H–C(1')); 3.45 (*dd*, $^2J = 9.9$, ^3J(6a,5) = 5.0, H_a–C(6)); 3.43, 3.36 (2*s*, 2 *Me*OCH$_2$); 3.35 (*dd*, $^2J = 9.9$, ^3J(6b,5) = 8.5, H_b–C(6)); 1.81 (*dd*, $^3J(3,1') = 8.3$, $^3J(3,2) = 2.9$, H–C(3)); 0.90 (*s*, *t*-BuSi); 0.09, 0.05 (2*s*, Me_2Si).

*(±)-1,4-Anhydro-3-{(1'*SR,2'RS,Z*)-2',5'-diacetoxy-1'-[(*tert*-butyl)dimethylsilyloxy]pent-3'-enyl}-3-deoxy-2,6-bis*-O-*(methoxymethyl)*-α-DL-*galactopyranose* (**65**). A mixture of diol **62**/**63** (*ca.* 9:1; 50 mg, 0.107 mmol), pyridine (0.5 ml), Ac_2O (0.5 ml), and DMAP (10 mg, 0.081 mmol) was allowed to stand at 20° for 15 h. After solvent evaporation, the reside was separated by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**65**) 0.29, *Pancaldi*): 53 mg (90%) of pure **65**. Colorless oil. IR (film): 2930, 1740, 1470, 1370, 1230, 1155, 1040, 840, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.74 (*dt*, $^3J(4',3') = 11.1$, $^3J(4',5') = 6.4$, H–C(4')); 5.54 (*ddt*, $^3J(3',4') = 11.1$, $^3J(3',2') = 9.1$, $^4J(3',5') = 1.6$, H–C(3')); 5.47 (*d*, ^3J((1,2) = 2.2, H–C(1)); 5.41 (*dd*, $^3J(2',3') = 9.1$, $^3J(2',1') = 5.8$, H–C(2')); 4.75 (*dd*, $^3J(5',4') = 6.4$, $^4J(3',5') = 1.6$, 2 H–C(5')); 4.71 (*d*, $^2J = 6.8$), 4.66 (*d*, $^2J = 6.8$), 4.61 (*s*, 2 H, 2 MeOCH_2); 4.49 (br. *s*, H–C(4)); 3.96 (*dd*, $^3J(2,3) = 2.7$, $^3J(2,1) = 2.2$, H–C(2)); 3.90 (*dd*, $^3J(1',2') = 5.8$, $^3J(1',3) = 3.8$, H–C(1')); 3.88 (*dd*, ^3J(5,6a) = 8.3, ^3J(5,6b) = 5.2, H–C(5)); 3.43 (*dd*, $^2J = 9.9$, ^3J(6b,5) = 5.2, H_b–C(6)); 3.42 (*s*, 1 *Me*OCH$_2$); 3.37 (*dd*, $^2J = 9.9$, ^3J(6a,5) = 8.3, H_a–C(6)); 3.35 (*s*, 1 *Me*OCH$_2$); 2.06, 2.05 (2*s*,

2 Ac); 1.84 (*dd*, $^3J(3,1') = 3.8$, $^3J(3,2) = 2.7$, H–C(3)); 0.88 (*s*, *t*-BuSi); 0.13, 0.11 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.6, 169.7 (2*s*, 2 CO); 129.7 (*d*, $J = 153$), 127.7 (*d*, $J = 159$, C(3′), C(4′)); 100.4 (*d*, $J = 181$, C(1)); 97.1, 96.6 (2*t*, $J = 164$, $MeOCH_2$); 81.3 (*d*, $J = 144$), 80.8 (*d*, $J = 166$), 78.4 (*d*, $J = 155$), 72.7 (*d*, $J = 142$), 71.6 (*d*, $J = 148$, C(2), C(4), C(5), C(1′), C(2′)); 67.6 (*t*, $J = 143$, C(6)); 60.8 (*t*, $J = 149$, C(5′)); 55.9, 55.2 (2 *q*, $J = 143$, $MeOCH_2$); 49.1 (*d*, $J = 136$, C(3)); 25.7 (*q*, $J = 125$, Me_3CSi); 21.2, 20.8 (2 *q*, $J = 129$, *Me*CO); 17.9 (*s*, Me_3CSi); −4.3, −4.2 (2 *q*, $J = 118$, Me_2Si). CI-MS (NH_3): 566 (1, $[M + 18]^+$), 517 (2), 413 (1), 325 (9), 265 (9), 197 (19), 155 (11), 117 (91), 81 (42), 75 (81), 73 (100). Anal. calc. for $C_{25}H_{44}O_{11}Si$ (548.703): C 54.73, H 8.08; found: C 54.71, H 8.05.

*(±)-3-{*DL-erythro-*2′-Acetoxy-1′-[(*tert*-butyl)dimethylsilyloxy]-3′-hydroxypropyl}-1,4-anhydro-3-deoxy-2,6-bis-*O-*(methoxymethyl)-α-*DL-*galactopyranose* (**66**). Ozone was bubbled through a soln. of **65** (53 mg, 0.096 mmol) in MeOH (1 ml) at −78°. After disappearance of **65** (TLC (AcOEt/light petroleum ether 1:2): R_f (**65**) 0.29), $NaBH_4$ (16 mg, 0.428 mmol) was added and the mixture stirred at 0° for 5 min. The mixture was poured into sat. aq. NH_4Cl soln. (20 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. phase was washed with 5% aq. Na_2CO_3 soln., dried ($MgSO_4$), and evaported, and the residue purified by FC (SiO_2, AcOEt/light petroleum ether 1:1; R_f (**66**) 0.43, *Pancaldi*): 36 mg (77%) of **66**. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.49 (*d*, $^3J(1,2) = 2.2$, H–C(1)); 4.94 (*ddd*, $^3J(2',3'a) = 5.7$, $^3J(2',1') = 4.6$, $^3J(2',3'b) = 4.0$, H–C(2′)); 4.70 (*d*, $^2J = 6.9$, 1 H), 4.65 (*d*, $^2J = 6.9$, 1 H), 4.62 (*s*, 2 H, 2 MeOCH_2); 4.58 (br. *s*, 1 H, H–C(4)); 3.99 (*dd*, $^3J(1',3) = 5.9$, $^3J(1',2') = 4.6$, H–C(1′)); 3.92 (*dd*, $^3J(5,6a) = 8.3$, $^3J(5,6b) = 5.2$, H–C(5)); 3.90 (*dd*, $^2J = 11.2$, $^3J(3'b,2') = 4.0$, H_a–C(3′)); 3.88 (*dd*, $^3J(2,3) = 3.3$, $^3J(2,1) = 2.2$, H–C(2)); 3.81 (*dd*, $^2J = 11.2$, $^3J(3'b,2') = 5.7$, H_b–C(3′)); 3.44 (*dd*, $^2J = 9.9$, $^3J(6b,5) = 5.2$, H_b–C(6)); 3.43 (*s*, 1 *Me*OCH_2); 3.38 (*dd*, $^2J = 9.9$, $^3J(6a,5) = 8.3$, H_a–C(6)); 3.37 (*s*, 1 *Me*OCH_2); 2.12 (*s*, Ac); 1.94 (*dd*, $^3J(3,1') = 5.9$, $^3J(3,2) = 3.3$, H–C(3)); 0.91 (*s*, *t*-BuSi); 0.16, 0.13 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.3 (*s*, CO); 100.2 (*d*, $J = 174$, C(1)); 97.0, 96.6 (2*t*, $J = 161$, $MeOCH_2$); 81.8 (*d*, $J = 146$), 80.6 (*d*, $J = 170$), 78.3 (*d*, $J = 154$), 76.1 (*d*, $J = 144$), 70.7 (*d*, $J = 142$, C(2), C(4), C(5), C(1′), C(2′)); 67.7 (*t*, $J = 144$, C(6)); 61.3 (*t*, $J = 141$, C(3′)); 56.0, 55.3 (2*q*, $J = 141$, *Me*OCH_2); 49.3 (*d*, $J = 130$, C(3)); 25.7 (*q*, $J = 126$, Me_3CSi); 21.2 (*q*, $J = 129$, *Me*CO); 17.9 (*s*, Me_3CSi); −4.6 (*q*, $J = 118$, Me_2Si).

*(±)-3-{*DL-erythro-*3′-Acetoxy-2′-[(*tert*-butyl)dimethylsilyloxy]-1′-hydroxypropyl}-1,5-anhydro-3-deoxy-2,6-bis-*O-*(methoxymethyl)-α-*DL-*galactofuranose* (**66′**). In some experiments, the above FC provided as a 2nd fraction **66′** (10–15%). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.54 (*d*, $^3J(1,2) = 2.4$, H–C(1)); 4.78, 4.75 (2*d*, $^2J = 6.9$, 2 H); 4.60 (*s*, 2 H); 4.45 (br. *s*, H–C(4)); 4.20 (*dd*, $^2J = 11.1$, $^3J(2',3') = 6.6$, H_a–C(3′)); 4.13 (*dd*, $^2J = 11.1$, $^3J = 5.8$, H_b–C(3′)); 4.02 (*dd*, $^3J(2,3) = 2.5$, $^3J(1,2)$, H–C(2)); 3.96 (*ddd*, $^3J(2',3') = 6.6$, 5.8, $^3J(1',2') = 1.6$, H–C(2′)); 3.90 (*dd*, $^3J(5,6) = 8.5$, 4.9, H–C(5)); 3.49 (*dd*, $^2J = 9.8$, $^3J(5,6) = 4.9$, H_b–C(6)); 3.48 (*ddd*, $^3J(1',3) = 10.7$, $^3J(1',OH) = 9.7$, $^3J(1',2') = 1.6$, H–C(1′)); 3.43 (*s*, 3 H); 3.36 (*dd*, $^2J = 9.8$, $^3J(5,6) = 8.5$, H_a–C(6)); 3.35 (*s*, 3 H); 2.65 (*d*, $^3J = 9.7$, OH–C(1′)); 2.08 (*s*, 3 H); 1.88 (*dd*, $^3J(1',3) = 10.7$, $^3J(2,3) = 2.5$, H–C(3)); 0.92 (*s*, *t*-BuSi); 0.15, 0.11 (2*s*, Me_2Si).

*(±)-3-[*DL-erythro-*3′-Acetoxy-1′,2′-dihydroxypropyl]-1,4-anhydro-3-deoxy-2,6-bis-*O-*(methoxymethyl)-α-*DL-*galactopyranose* (**67**). At 0°, 1M Bu_4NF in THF (0.112 ml, 0.112 mmol) was added to a soln. of **66** (36 mg, 0.075 mmol) in anh. THF (0.5 ml) under stirring. After 5 min at 0°, the mixture was poured into sat. aq. NH_4Cl soln. (20 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. extract was dried ($MgSO_4$) and evaporated, and the residue purified by FC (SiO_2, AcOEt/MeOH 98:2; R_f (**67**) 0.17, *Pancaldi*): 22 mg (78%) of **67**. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.55 (*d*, $^3J(1,2) = 2.4$, H–C(1)); 4.79 (*d*, $^2J = 6.9$, 1 H), 4.76 (*d*, $^2J = 6.9$, 1 H), 4.62 (*s*, 2 H, 2 MeOCH_2); 4.44 (br. *s*, H–C(4)); 4.27 (*dd*, $^2J = 11.6$, $^3J(3'a,2') = 7.0$, H_a–C(3′)); 4.23 (*dd*, $^2J = 11.6$, $^3J(3'b,2') = 5.1$, H_b–C(3′)); 4.02 (*dd*, $^3J(2,3) = 2.7$, $^3J(2,1) = 2.4$, H–C(2)); 3.98 (*dd*, $^3J(5,6a) = 8.3$, $^3J(5,6b) = 4.9$, H–C(5)); 3.87 (*ddm*, $^3J(2',3'a) = 7.0$, $^3J(2',3'b) = 5.1$, H–C(2′)); 3.49 (*dm*, $^3J(1',3) = 9.8$, H–C(1′)); 3.48 (*dd*, $^2J = 10.1$, $^3J(6b,5) = 4.9$, H_b–C(6)); 3.45 (*s*, 1 *Me*OCH_2); 3.38 (*dd*, $^2J = 10.1$, $^3J(6a,5) = 8.3$, H_a–C(6)); 3.37 (*s*, 1 *Me*OCH_2); 2.59 (*d*, $^3J = 5.7$, OH–C(1′)); 2.12 (*s*, Ac); 2.04 (*dd*, $^3J(3,1') = 9.8$, $^3J(3,2) = 2.7$, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.4 (*s*, CO); 100.0 (*d*, $J = 180$, C(1)); 97.0, 96.6 (2*t*, $J = 168$, $MeOCH_2$); 82.7 (*d*, $J = 149$), 79.9 (*d*, $J = 162$), 78.0 (*d*, $J = 154$), 71.3 (*d*, $J = 145$), 69.7 (*d*, $J = 142$, C(2), C(4), C(5), C(1′), C(2′)), 67.7 (*t*, $J = 144$, C(6)); 66.1 (*t*, $J = 150$, C(3′)); 55.8, 55.3 (2*q*, $J = 142$, *Me*OCH_2); 49.3 (*d*, $J = 136$, C(3)); 20.9 (*q*, $J = 130$, *Me*CO).

*(±)-3-[*DL-erythro-*3′-Acetoxy-1′,2′-(isopropylidenedioxy)propyl]-1,4-anhydro-3-deoxy-2,6-bis-*O-*(methoxymethyl)-α-*DL-*galactopyranose* (**68**). A mixture of **67** (22 mg, 0.066 mmol), DMF (0.5 ml), $Me_2C(OMe)_2$ (0.5 ml), and pyridinium *p*-toluenesulfonate (0.01 mmol) was allowed to stand at 20° for 24 h. Solvent evaporation and purification by FC (SiO_2, AcOEt/light petroleum ether 2:1; R_f (**68**) 0.66, *Pancaldi*) gave 23 mg (85%) of **68**. Colorless oil. UV (MeCN): 200 (450). IR (film): 2935, 1745, 1455, 1370, 1225, 1155, 1045, 915, 865. ^{1}H-NMR (400 MHz, C_6D_6): 5.58 (*d*, $^3J(1,2) = 2.2$, H–C(1)); 4.63 (*d*, $^2J = 6.8$, 1 H, MeOCH_2); 4.62 (br. *s*, H–C(4)); 4.52

(*d*, ^2J = 6.8, 1 H); 4.40 (*s*, 2 H, 2 MeOCH_2); 4.22 (*dd*, ^2J = 11.7, ^3J(3'a,2') = 5.4, H_a–C(3')); 4.14 (*dd*, ^2J = 11.7, ^3J(3'b,2') = 4.7, H_b–C(3')); 4.07 (*dd*, ^3J(5,6a) = 8.7, ^3J(5,6b) = 4.8, H–C(5)); 4.04 (*dd*, ^3J(2,3) = 3.1, ^3J(2,1) = 2.2, H–C(2)); 3.99 (*ddd*, ^3J(2',1') = 7.2, ^3J(2',3'a) = 5.4, ^3J(2',3'b) = 4.7, H–C(2')); 3.88 (*dd*, ^3J(1',2') = 7.2, ^3J(1',3) = 7.0, H–C(1')); 3.59 (*dd*, ^2J = 10.0, ^3J(6b,5) = 4.8, H_b–C(6)); 3.51 (*dd*, ^2J = 10.0, ^3J(6a,5) = 8.7, H_a–C(6)); 3.30, 3.12 (2 *s*, 2 *Me*OCH_2); 1.97 (*dd*, ^3J(3,1') = 7.0, ^3J(3,2) = 3.1, H–C(3)); 1.71 (*s*, Ac); 1.39, 1.34 (2*s*, Me_2C). ^{13}C-NMR (100.6 MHz, C_6D_6): 170.3 (*s*, CO); 109.7 (*s*, Me_2C); 101.2 (*d*, *J* = 172, C(1)); 97.3, 97.2 (2*t*, *J* = 163, MeO*C*H_2); 82.6 (*d*, *J* = 151), 80.1 (*d*, *J* = 165), 79.4 (*d*, *J* = 146), 79.2 (*d*, *J* = 155), 78.4 (*d*, *J* = 149, C(2), C(4), C(5), C(1'), C(2')); 68.8 (*t*, *J* = 143), 65.1 (*t*, *J* = 144, C(6), C(3')); 56.0, 55.4 (2 *q*, *J* = 142, *Me*OCH_2); 50.8 (*d*, *J* = 134, C(3)); 28.0, 27.6 (2*q*, *J* = 126, Me_2C); 20.7 (*q*, *J* = 129, *Me*CO). CI-MS (NH_3): 391 (2, $[M-15]^+$, 317 (3), 173 (13), 136 (13), 115 (100), 81 (22). Anal. calc. for $C_{18}H_{30}O_{10}$ (406.428): C 53.19, H 7.44; found: C 53.24, H 7.44.

*(±)-1,4-Anhydro-3-{(1'*SR,*2'*RS,Z*)-[1'-[(*tert*-*butyl*)*dimethylsilyloxy*]-*2',5'-bis*(*4-nitrobenzoyloxy*)]*pent-3'-enyl*}*-3-deoxy-2,6-bis*-O-(*methoxymethyl*)-α-DL-*galactopyranose* (**69**). A mixture of diol **62** (20 mg, 0.043 mmol; containing *ca.* 10% of **63**), anh. CH_2Cl_2 (0.5 ml), Et_3N (21 µl, 0.150 mmol), 4-nitrobenzoyl chloride (24 mg, 0.130 mmol), and DMAP (3 mg, 0.004 mmol) was stirred at 20° under Ar for 30 min. The mixture was poured into 1N aq. HCl (25 ml) and extracted with CH_2Cl_2 (3 × 25 ml). The combined org. extract was washed with a sat. aq. Na_2CO_3 soln., dried ($MgSO_4$), and evaporated. The residue was separated by FC (SiO_2, AcOEt/light petroleum ether 1:3; R_f (**69**) 0.65, UV): 30 mg (91%) of pure **69**. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.31–8.18 (*m*, 8 arom. H); 5.98 (*ddd*, ^3J(4',3') = 11.0, ^3J(4',5'a) = 6.8, ^3J(4',5'b) = 6.4, H–C(4')); 5.91 (*dd*, ^3J(2',3') = 9.4, ^3J(2',1') = 4.9, H–C(2')); 5.84 (*ddt*, ^3J(3',4') = 11.0, ^3J(3',2') = 9.4, ^4J(3',5') = 1.0, H–C(3')); 5.50 (*d*, ^3J(1,2) = 2.2, H–C(1)); 5.16 (*ddd*, ^2J = 13.3, ^3J(5'b,4') = 6.4, ^4J(5'b,3') = 1.0, H_b–C(5')); 5.10 (*ddd*, ^2J = 13.3, ^3J(5'a,4') = 6.8, ^4J(5'a,3') = 1.0, H_a–C(5')); 4.77, 4.69 (2*d*, ^2J = 6.8, 2 H, MeOCH_2); 4.62 (br. *s*, H–C(4)); 4.59 (*s*, 2 H, MeOCH_2); 4.11 (*dd*, ^3J(1',2') = 4.9, ^3J(1',3) = 4.7, H–C(1')); 4.06 (*dd*, ^3J(2,3) = 3.5, ^3J(2,1) = 2.2, H–C(2)); 3.92 (*dd*, ^3J(5,6b) = 8.5, ^3J(5,6a) = 4.9, H–C(5)); 3.44 (*s*, 1 *Me*OCH_2); 3.39 (*dd*, ^2J = 9.9, ^3J(6a,5) = 4.9, H_a–C(6)); 3.36 (*dd*, ^2J = 9.9, ^3J(6b,5) = 8.5, H_b–C(6)); 3.32 (*s*, 1 *Me*OCH_2); 1.98 (*dd*, ^3J(3,1') = 4.7, ^3J(3,2) = 3.5, H–C(3)); 0.89 (*s*, *t*-BuSi); 0.14, 0.11 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 164.4, 163.7 (2*s*, CO); 150.6, 135.4, 135.2 (3*s*, arom. C); 130.7 (*d*, *J* = 169), 129.5 (*d*, *J* = 164), 128.5 (*d*, *J* = 162), 123.6, 123.5 (2 *d*, *J* = 172, arom. C, C(3'), C(4')); 100.3 (*d*, *J* = 181, C(1)); 97.2, 96.6 (2*t*, *J* = 163, MeO*C*H_2); 81.4 (*d*, *J* = 164), 80.5 (*d*, *J* = 165), 78.5 (*d*, *J* = 153), 72.8 (*d*, *J* = 143), 72.3 (*d*, *J* = 150, C(2), C(4), C(5), C(1'), C(2')); 67.6 (*t*, *J* = 144, C(6)); 61.4 (*t*, *J* = 150, C(5')); 56.0, 55.3 (2*q*, *J* = 144, *Me*OCH_2); 49.7 (*d*, *J* = 131, C(3)); 25.7 (*q*, *J* = 125, *Me*$_3$CSi); 17.9 (*s*, Me_3CSi); −4.2, −4.4 (2*q*, *J* = 119, Me_2Si).

*(±)-1,4-Anhydro-3-{(1'*SR,*2'*RS,Z*)-[1'-[(*tert*-*butyl*)*dimethylsilyloxy*]-*2',5'-bis*[(*methylsulfonyl*)*oxy*]]*pent-3'-enyl*}*-3-deoxy-2,6-bis*-O-(*methoxymethyl*)-α-DL-*galactopyranose* (**70**). Et_3N (81 µl, 0.58 mmol) and then $MeSO_2Cl$ (39 µl, 0.50 mmol) were added dropwise to a stirred soln. of diol **62** (77 mg, 0.17 mmol; containing *ca.* 10% of **63**) in anh. CH_2Cl_2 (1 ml) cooled to −78°. After stirring at −78° for 5 min, the mixture was poured into ice-cold, sat. aq. $NaHCO_3$ soln. and extracted quickly with ice-cold CH_2Cl_2 (3 × 30 ml). The combined org. extract was dried ($MgSO_4$) and evaporated: 82 mg of crude **70**. Yellowish oil. Data of **70**: ^{1}H-NMR (400 MHz, $CDCl_3$): 5.98 (*ddd*, ^3J(4',3') = 10.9, ^3J(4',5'a) = 7.8, ^3J(4',5'b) = 5.7, H–C(4')); 5.83 (*ddt*, ^3J(3',4') = 10.9, ^3J(3',2') = 9.6, ^4J(3',5') = 0.8, H–C(3')); 5.51 (*d*, ^3J(1,2) = 2.1, H–C(1)); 5.19 (*dd*, ^3J(2',3') = 9.6, ^3J(2',1') = 5.4, H–C(2')); 4.96 (*ddd*, ^2J = 12.9, ^3J(5'a,4') = 7.8, ^4J(5'a,3') = 0.8, H_a–C(5')); 4.84 (*ddd*, ^2J = 12.9, ^3J(5'b,4') = 5.7, ^4J(5'b,3') = 0.8, H_b–C(5')); 4.70 (*d*, ^2J = 6.8, 1 H), 4.67 (*d*, ^2J = 6.8, 1 H), 4.62 (*s*, 2 H, 2 MeOCH_2); 4.51 (br. *s*, H–C(4)); 4.04 (*dd*, ^3J(1',2') = 5.4, ^3J(1',3) = 3.8, H–C(1')); 3.98 (*dd*, ^3J(2,3) = 2.5, ^3J(2,1) = 2.1, H–C(2)); 3.91 (*dd*, ^3J(5,6b) = 8.0, ^3J(5,6a) = 5.0, H–C(5)); 3.45 (*dd*, ^2J = 9.8, ^3J(6a,5) = 5.0, H_a–C(6)); 3.44 (*s*, 1 *Me*OCH_2); 3.38 (*dd*, ^2J = 9.8, ^3J(6b,5) = 8.0, H_b–C(6)); 3.37 (*s*, 1 *Me*OCH_2); 3.06, 3.04 (2*s*, 2 $MeSO_2$); 1.88 (*dd*, ^3J(3,1') = 3.8, ^3J(3,2) = 2.5, H–C(3)); 0.91 (*s*, *t*-BuSi); 0.13, 0.09 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 129.6 (*d*, *J* = 163), 128.5 (*d*, *J* = 162, C(3'), C(4')); 101.2 (*d*, *J* = 182, C(1)); 97.0, 96.6 (2*t*, *J* = 163, MeO*C*H_2); 80.8 (*d*, *J* = 147), 80.7 (*d*, *J* = 147), 78.5 (*d*, *J* = 157), 76.7 (*d*, *J* = 141, C(2), C(4), C(1'), C(2')); 67.5 (*t*, *J* = 144, C(6)); 65.4 (*t*, *J* = 151, C(5')); 56.0, 55.2, (2*q*, *J* = 142, *Me*OCH_2); 48.8 (*d*, *J* = 131, C(5)); 39.3, 39.2 (2*q*, *J* = 150, $MeSO_2$); 37.7 (*d*, *J* = 135, C(3)); 25.7 (*q*, *J* = 125, *Me*$_3$CSi); 17.8 (*s*, Me_3*C*Si); −4.2, −4.7 (2*q*, *J* = 119, Me_2Si).

*(±)-1,4-Anhydro-3-{(1'*SR,*2'*RS,Z*)-*5'-azido-1'-*[(*tert*-*butyl*)*dimethylsilyloxy*]-*2'-*[(*methylsulfonyl*)*oxy*]*pent-3'-enyl*}*-3-deoxy-2,6-bis*-O-(*methoxymethyl*)-α-DL-*galactopyranose* (**71**). To crude **70** (see above; 82 mg, *ca.* 0.132 mmol) in anh. DMF (0.15 ml) at 0°, a soln. of LiN_3 (19 mg, 0.40 mmol) in anh. DMF (0.1 ml) was added dropwise and the mixture stirred at 0° for 30 min. The solvent was evaporated and the residue taken up in CH_2Cl_2 (10 ml). The soln. was poured into ice-cold, sat. aq. $NaHCO_3$ soln. (30 ml), the aq. phase extracted with CH_2Cl_2 (2 × 30 ml), and the combined org. extract dried ($MgSO_4$) and evaporated: 72 mg of **71** as yellowish oil, pure

enough for the next transformations. An anal. sample was obtained on purification by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**71**) 0.45, *Pancaldi*). UV (MeCN): 208 (2050). IR (film): 2930, 2100, 1470, 1360, 1255, 1175, 1150, 1115, 1055, 920, 840, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.90 (*ddd*, $^3J(4',3')$ = 11.4, $^3J(4',5'a)$ = 7.9, $^3J(4',5'b)$ = 5.9, H–C(4')); 5.78 (*ddt*, $^3J(3',4')$ = 11.4, $^3J(3',2')$ = 9.8, $^4J(3',5')$ = 1.0, H–C(3')); 5.50 (*d*, $^3J(1,2)$ = 2.2, H–C(1)); 5.19 (*dd*, $^3J(2',3')$ = 9.8, $^3J(2',1')$ = 5.4, H–C(2')); 4.69 (*d*, ^2J = 6.8, 1 H), 4.65 (*d*, ^2J = 6.8, 1 H), 4.62 (*s*, 2 H, 2 MeOCH_2); 4.49 (br. *s*, H–C(4)); 4.14 (*ddd*, ^2J = 14.5, $^3J(5'a,4')$ = 7.9, $^4J(5'a,3')$ = 1.0, H_a–C(5')); 4.03 (*dd*, $^3J(1',2')$ = 5.4, $^3J(1',3)$ = 4.0, H–C(1')); 3.99 (*dd*, $^3J(2,3)$ = 2.9, $^3J(2,1)$ = 2.2, H–C(2)); 3.92 (*ddd*, ^2J = 14.5, $^3J(5'b,4')$ = 5.9, $^4J(5'b,3')$ = 1.0, H_b–C(5')); 3.91 (*dd*, $^3J(5,6b)$ = 8.2, $^3J(5,6a)$ = 5.0, H–C(5)); 3.44 (*s*, 1 *Me*OCH$_2$); 3.43 (*dd*, ^2J = 10.0, $^3J(6a,5)$ = 5.0, H_a–C(6)); 3.37 (*dd*, ^2J = 10.0, $^3J(6b,5)$ = 8.2, H_b–C(6)); 3.36 (*s*, 1 *Me*OCH$_2$); 3.02 (*s*, MeSO$_2$); 1.90 (*dd*, $^3J(3,1')$ = 4.0, $^3J(3,2)$ = 2.9, H–C(3)); 0.91 (*s*, *t*-BuSi); 0.17, 0.14 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 131.1 (*d*, *J* = 160), 127.2 (*d*, *J* = 161, C(3'), C(4')); 100.4 (*d*, *J* = 182, C(1)); 97.1, 96.6 (2*t*, *J* = 163, MeO*C*H$_2$); 81.0 (*d*, *J* = 152), 80.9 (*d*, *J* = 150), 78.5 (*d*, *J* = 152), 77.4 (*d*, *J* = 139), 73.1 (*d*, *J* = 142, C(2), C(4), C(1'), C(2'), C(5)); 67.6 (*t*, *J* = 144, C(6)); 56.0, 55.3 (2*q*, *J* = 142, *Me*OCH$_2$); 48.7 (*d*, *J* = 130, C(3)); 47.7 (*t*, *J* = 145, C(5')); 39.5 (*q*, *J* = 139, MeSO$_2$); 25.8 (*q*, *J* = 125, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); –4.1, –4.6 (2*q*, *J* = 119, Me_2Si). CI-MS (NH_3): 585 (3, $[M + 18]^+$), 429 (3), 347 (4), 271 (12), 225 (6), 213 (6), 197 (12), 153 (41), 89 (40), 81 (40), 75 (97), 73 (100). Anal. calc. for $C_{22}H_{41}O_{10}N_3SSi$ (567.731): C 46.54, H 7.28, N 7.40; found: C 46.64, H 7.32, N 7.32.

*(±)-1,4-Anhydro-3-{(1'*SR*)-5'-azido-1'-*O*-[(*tert*-butyl)dimethylsilyl]-5'-deoxy-2'-*O*-(methylsulfonyl)*-DL-*ribitol-1'-C-yl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL-*galactopyranose* (**72**) *and (±)-1,4-Anhydro-3-{(1'*SR*)-5'-azido-1'-*O*-[(*tert*-butyl)dimethylsilyl]-5'-deoxy-2'-*O*-(methylsulfonyl)-*LD-*arabinitol-1'-C-yl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL-*galactopyranose* (**73**). A mixture of crude **71** (72 mg, *ca.* 0.13 mmol), THF/H_2O 4:1 (0.2 ml), $Me_3NO_2H_2O$ (37 mg, 0.33 mmol), and 0.1M OsO_4 in CCl_4 (83 µl, 0.008 mmol) was stirred at 20° for 20 h. The brown soln. was poured into 5% aq. $NaHSO_3$ soln. (20 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. extract was dried ($MgSO_4$) and evaporated, and the residue separated by FC (SiO_2, AcOEt/light petroleum ether 1:1; R_f (**72**) 0.30, R_f (**73**) 0.11, *Pancaldi*): 38 mg (37%) of **72** and 17 mg (17%) of **73** (overall yield 54%, based on **62**).

Data of **72**: Colorless oil. UV (MeCN): 212 (600), 195 (820). IR (film): 3455, 2935, 2105, 1640, 1470, 1350, 1260, 1175, 1155, 1055, 940, 840, 780, 740, 705. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.53 (*d*, $^3J(1,2)$ = 2.3, H–C(1)); 4.78 (*dd*, $^3J(2',3')$ = 7.0, $^3J(2',1')$ = 4.1, H–C(2')); 4.71 (*d*, ^2J = 6.9, 1 H), 4.68 (*d*, ^2J = 6.9, 1 H), 4.63 (*s*, 2 H, 2 MeOCH_2); 4.59 (br. *s*, H–C(4)); 4.29 (*dd*, $^3J(1',3)$ = 6.2, $^3J(1',2')$ = 4.1, H–C(1')); 4.08 (*ddd*, $^3J(3',2')$ = 7.0, $^3J(3',4')$ = 5.9, $^3J(3',OH–C(3'))$ = 3.9, H–C(3')); 3.96 (*dd*, $^3J(2,3)$ = 3.0, $^3J(2,1)$ = 2.3, H–C(2)); 3.95 (*dd*, $^3J(5,6b)$ = 8.1, $^3J(5,6a)$ = 5.2, H–C(5)); 3.92 (*dddd*, $^3J(4',5'a)$ = 6.7, $^3J(4',OH–C(4'))$ = 6.5, $^3J(4',3')$ = 5.9, $^3J(4'5'b)$ = 3.7, H–C(4')); 3.63 (*d*, $^3J(OH–C(3'),3')$ = 3.9, OH–C(3')); 3.60 (*dd*, ^2J = 12.7, $^3J(5'b,4')$ = 3.7, H_b–C(5')); 3.55 (*dd*, ^2J = 12.7, $^3J(5'a,4')$ = 6.7, H_a–C(5')); 3.46 (*dd*, ^2J = 10.0, $^3J(6a,5)$ = 5.2, H_a–C(6)); 3.44 (*s*, 1 *Me*OCH$_2$); 3.40 (*dd*, ^2J = 10.0, $^3J(6b,5)$ = 8.1, H_b–C(6)); 3.37 (*s*, 1 *Me*OCH$_2$); 3.14 (*s*, MeSO$_2$); 2.56 (*d*, $^3J(OH–C(4'),4')$ = 6.5, OH–C(4')); 2.14 (*dd*, $^3J(3,1')$ = 6.2, $^3J(3,2)$ = 3.0, H–C(3)); 0.92 (*s*, 9 H, *t*-BuSi); 0.24, 0.17 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 100.3 (*d*, *J* = 174, C(1)); 97.2, 96.8 (2*t*, *J* = 163, MeO*C*H$_2$); 81.9 (*d*, *J* = 138), 81.0 (*d*, *J* = 154), 79.1 (*d*, *J* = 149), 78.2 (*d*, *J* = 156), 73.3 (*d*, *J* = 142), 71.7 (*d*, *J* = 148), 71.5 (*d*, *J* = 146, C(2), C(4), C(5), C(1'), C(2'), C(3'), C(4')); 67.9 (*t*, *J* = 143, C(6)); 56.1, 55.4 (2*q*, *J* = 143, *Me*OCH$_2$); 53.2 (*t*, *J* = 143, C(5')); 48.6 (*d*, *J* = 133, C(3)); 38.8 (*q*, *J* = 139, MeSO$_2$); 25.8 (*q*, *J* = 120, *Me*$_3$CSi); 17.9 (*s*, Me$_3$*C*Si); –4.4, –4.7 (2*q*, *J* = 120, Me_2Si). CI-MS (NH_3): 619 (57, $[M + 18]^+$), 562 (5), 424 (5), 347 (5), 306 (11), 228 (11), 158 (7), 129 (24), 92 (48), 75 (100). Anal. calc. for $C_{22}H_{43}N_3O_{12}SSi$ (601.745): C 43.91, H 7.20, N 6.98; found: C 44.12, H 7.20, N 6.78.

Data of **73**: Colorless oil. UV (MeCN): 212 (670), 196 (900). IR (film): 3410, 2930, 2140, 1725, 1640, 1355, 1175, 1090, 1045, 940, 895, 835, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.54 (*d*, $^3J(1,2)$ = 2.3, H–C(1)); 5.04 (*d*, $^3J(2',1')$ = 5.1, H–C(2')); 4.74 (*d*, ^2J = 6.9, 1 H), 4.72 (*d*, ^2J = 6.9, 1 H), 4.62 (*s*, 2 H, 2 MeOCH_2); 4.56 (br. *s*, H–C(4)); 4.15 (*dd*, $^3J(1',3)$ = 6.4, $^3J(1',2')$ = 5.1, H–C(1')); 4.09 (*dd*, $^3J(2,3)$ = 3.0, $^3J(2,1)$ = 2.3, H–C(2)); 4.07 (*dd*, $^3J(3',4')$ = 8.9, $J(3',OH–C(3'))$ = 6.7, H–C(3')); 3.96 (*dd*, $^3J(5,6b)$ = 8.3, $^3J(5,6a)$ = 5.1, H–C(5)); 3.75 (*dddd*, $^3J(4',3')$ = 8.9, $^3J(4',OH–C(4'))$ = 6.2, $^3J(4',5'a)$ = 5.4, $^3J(4',5'b)$ = 2.9, H–C(4')); 3.65 (*dd*, ^2J = 12.6, $^3J(5'b,4')$ = 2.9, H_b–C(5')); 3.58 (*d*, $^3J(OH–C(3'),3')$ = 6.7, OH–C(3')); 3.52 (*dd*, ^2J = 12.6, $^3J(5'a,4')$ = 5.4, H_a–C(5')); 3.46 (*dd*, ^2J = 10.0, $^3J(6a,5)$ = 5.1, H_a–C(6)); 3.44 (*s*, 1 *Me*OCH$_2$); 3.38 (*dd*, ^2J = 10.0, $^3J(6b,5)$ = 8.3, H_b–C(6)); 3.37 (*s*, 1 *Me*OCH$_2$); 3.19 (*s*, MeSO$_2$); 2.79 (*d*, $^3J(OH–C(4'),4')$ = 6.2, OH–C(4')); 2.41 (*dd*, $^3J(3,1')$ = 6.4, $^3J(3,2)$ = 3.0, H–C(3)); 0.85 (*s*, *t*-BuSi); 0.18, 0.14 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 100.0 (*d*, *J* = 149, C(1)); 97.0, 96.7 (2*t*, *J* = 166, MeO*C*H$_2$); 82.2 (*d*, *J* = 140), 82.1 (*d*, *J* = 147), 77.9 (*d*, *J* = 153), 77.7 (*d*, *J* = 136), 71.8 (*d*, *J* = 140), 69.9 (*d*, *J* = 146), 68.0 (*d*, *J* = 137, C(2), C(4), C(5), C(1'), C(2'), C(3'), C(4')); 67.8 (*t*, *J* = 143, C(6)); 56.2, 55.4 (2*q*, *J* = 142, *Me*OCH$_2$); 53.8 (*t*, *J* = 142, C(5')); 47.7 (*d*, *J* = 133,

C(3)); 38.2 (*q*, J = 139, $MeSO_2$); 25.7 (*q*, J = 125, Me_3CSi); 17.9 (*s*, Me_3CSi); −4.5, −4.9 (2*q*, J = 118 Me_2Si). CI-MS (NH_3): 619 (57, $[M + 18]^+$), 532 (4), 454 (4), 306 (9), 244 (6), 129 (17), 92 (47), 75 (100). Anal. calc. for $C_{22}H_{43}N_3O_{12}SSi$ (601.745): C 43.91, H 7.20, N 6.98, S 5.33; found: C 44.05, H 7.35, N 6.88, S 5.27.

*(±)-1,4-Anhydro-3-{(1'SR)-5'-azido-1'-O-[(*tert*-butyl)dimethylsilyl]-3',4'-O-isopropylidene-5'-deoxy-2'-O-(methylsulfonyl)*-DL-*ribitol-1'-C-yl}-3-deoxy-2,6-bis-*O-*(methoxymethyl)*-α-DL-*galactopyranose* (**74**). A mixture of **72** (93 mg, 0.15 mmol), $Me_2C(OMe)_2$ (0.7 ml) and camphorsulfonic acid (7 mg, 0.03 mmol) was stirred at 20° for 45 min. More camphorsulfonic acid was added (7 mg) and the mixtue stirred another 45 min at 20°. Addition of camphorsulfonic acid was repeated with stirring at 20° for 45 min until complete disappearance of **72** (TLC (AcOEt/light petroleum ether 1:1): R_f (**74**) 0.5, R_f (**72**) 0.32, *Pancaldi*). The mixture was poured into sat. aq. $NaHCO_3$ soln. (25 ml) and extracted with CH_2Cl_2 (25 ml, 3 times). The combined org. phase was dried ($MgSO_4$) and evaporated, and the residue purified by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**74**) 0.23): 71 mg (79%) of **74**. Colorless oil. UV (MeCN): 193 (2000). IR (film): 3420, 2930, 2100, 1725, 1470, 1360, 1260, 1220, 1175, 1055, 950, 835, 780, 735. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.53 (*d*, $^3J(1,2)$ = 2.1, H−C(1)); 4.94 (*dd*, $^3J(2',3')$ = 5.7, $^3J(2',1')$ = 2.9, H−C(2')); 4.70 (*d*, ^2J = 6.8, 1 H), 4.64 (*d*, ^2J = 6.8, 1 H), 4.63 (*s*, 2 H, 2 $MeOCH_2$); 4.58 (br. *s*, H−C(4)); 4.45–4.34 (*m*, H−C(3'), H−C(4)); 4.11 (*dd*, $^3J(1',3)$ = 8.5, $^3J(1',2')$ = 2.9, H−C(1')); 3.92 (*dd*, $^3J(5,6b)$ = 8.1, $^3J(5,6a)$ = 5.1, H−C(5)); 3.86 (*dd*, $^3J(2,3)$ = 2.8, $^3J(2,1)$ = 2.1, H−C(2)); 3.50–3.35 (*m*, 2 H−C(6), 2 H−C(5')); 3.42, 3.37 (2*s*, 2 *Me*OCH_2); 3.15 (*s*, $MeSO_2$); 1.97 (*dd*, $^3J(3,1')$ = 8.5, $^3J(3,2)$ = 2.8, H−C(3)); 1.53, 1.38 (2*s*, Me_2C); 0.93 (*s*, *t*-BuSi); 0.19, 0.15 (2*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 108.7 (*s*, Me_2C); 100.5 (*d*, J = 181, C(1)); 96.9, 96.6 (2*t*, J = 164, $MeOCH_2$); 82.4 (*d*, J = 144), 79.7 (*d*, J = 164), 79.4 (*d*, J = 148), 78.1 (*d*, J = 153), 76.3 (*d*, J = 151), 74.1 (*d*, J = 146), 71.1 (*d*, J = 148, C(2), C(4), C(5), C(1'), C(2'), C(3'), C(4')); 67.6 (*t*, J = 144, C(6)); 56.0, 55.3 (2*q*, J = 142, *Me*OCH_2); 51.4 (*t*, J = 144, C(5')); 50.9 (*d*, J = 133, C(3)); 39.2 (*q*, J = 140, $MeSO_2$); 27.7 (*q*, J = 127, *Me*C); 25.8 (*q*, J = 125, Me_3CSi); 25.3 (*q*, J = 130, *Me*C); 18.1 (*s*, Me_3CSi); −4.2, −4.3 (2*q*, J = 119, Me_2Si). CI-MS (NH_3): 659 (1, $[M + 18]^+$), 626 (2), 614 (2), 568 (19), 556 (8), 460 (7), 384 (2), 346 (5), 301 (6), 272 (10), 225 (7), 153 (32), 75 (100). Anal. calc. for $C_{25}H_{47}N_3O_{12}SSi$ (641.810): C 46.79, H 7.38, N 6.55; found: C 46.81, H 7.28, N 6.41.

*(±)-1,4-Anhydro-3-{(1'SR)-1'-O-[(*tert*-butyl)dimethylsilyl]-2',5'-dideoxy-2',5'-imino-3',4'-O-isopropylidene-*α*-DL-arabinitol-1'-C-yl}-3-deoxy-2,6-bis-*O-*(methoxymethyl)*-α-DL-*galactofuranose* (**75**). $HCOONH_4$ (30 mg, 0.22 mmol) and then 10% Pd/C (8.2 mg, 0.008 mmol) were added to a stirred soln. of **74** (25 mg, 0.042 mmol) in anh. MeOH (0.6 ml). After stirring at 20° for 90 min, the catalyst was filtered off over *Celite* (rinsing with AcOEt, 3 × 10 ml) and the filtrate evaporated. To the residue in anh. DMF (0.3 ml) under Ar, anh. K_2CO_3 (5 mg, 0.078 mmol) was added and the mixture stirred at 60° for 15 h. The suspension was evaporated at (1 Torr) and the residue purified by FC (SiO_2, AcOEt/MeOH 98:2; R_f (**75**) 0.25, *Pancaldi*): 14 mg (86%). Colorless oil. UV (MeCN): 195 (1360). IR (film): 3425, 2930, 2855, 1630, 1380, 1255, 1205, 1040, 835, 665. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.49 (*d*, $^3J(1,2)$ = 2.2, H−C(1)); 4.71, 4.67 (2*d*, ^2J = 6.8, 2 H, $MeOCH_2$); 4.65–4.55 (*m*, 5 H, H−C(3'), H−C(4'), H−C(4), $MeOCH_2$); 4.37 (*dd*, $^3J(2,3)$ = 2.3, $^3J(2,1)$ = 2.2, H−C(2)); 4.13 (*dd*, $^3J(1'3)$ = 7.6, $^3J(1',2')$ = 3.2, H−C(1')); 3.94 (*dd*, $^3J(5,6b)$ = 8.0, $^3J(5,6a)$ = 5.4, H−C(5)); 3.44 (*dd*, ^2J = 10.0, $^3J(6a,5)$ = 5.4, H_a−C(6)); 3.41 (*s*, 1 *Me*OCH_2); 3.38 (*dd*, ^2J = 10.0, $^3J(6b,5)$ = 8.0, H_b−C(6)); 3.36 (*s*, 1 *Me*OCH_2); 3.05 (*d*, ^2J = 12.6, H_a−C(5')); 2.68 (*dd*, $^3J(2',3')$ = 8.7, $^3J(2',1')$ = 3.2, H−C(2')); 2.62 (*dd*, ^2J = 12.6, $^3J(5'b,4')$ = 3.6, H_b−C(5')); 2.05 (*dd*, $^3J(3,1')$ = 7.6, $^3J(3,2)$ = 2.3, H−C(3)); 1.47, 1.30 (2*s*, Me_2C); 0.89 (*s*, *t*-BuSi); 0.13, 0.12 (2*s*, MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 110.1 (*s*, Me_2C); 100.2 (*d*, J = 178, C(1)); 96.9, 96.6 (2*t*, J = 163, $MeOCH_2$); 80.7 (*d*, J = 158), 80.4 (*d*, J = 153), 80.2 (*d*, J = 165), 79.0 (*d*, J = 149), 78.9 (*d*, J = 154), 70.2 (*d*, J = 143, C(2), C(4), C(1'), C(2'), C(3'), C(4')); 67.7 (*t*, J = 158, C(6)); 66.8 (*d*, J = 134, C(5)); 55.7, 55.2 (2*q*, J = 142, *Me*OCH_2); 53.6 (*t*, J = 143, C(5')); 51.3 (*d*, J = 132, C(3)); 26.0 (*q*, J = 130, *t*-BuSi); 25.9 (*q*, J = 123), 23.9 (*q*, J = 124), (Me_2C); 18.2 (*s*, *t*-BuSi); −4.5, −4.6 (2*q*, J = 119, Me_2Si). CI-MS (NH_3): 521 (100, $[M + 2]^+$), 520 (89, $[M + 1]^+$), 462 (21), 360 (8), 312 (5), 288 (29), 243 (5), 142 (87), 75 (40). Anal. calc. for $C_{24}H_{45}NO_9Si$ (519.708): C 55.46, H 8.77; found: C 55.56, H 8.61.

*(±)-1,4-Anhydro-3-deoxy-3-[(1'SR)-2',5'-dideoxy-2',5'-imino-3',4'-O-isopropylidene-*α*-DL-arabinitol-1'-C-yl]-2,6-bis-*O-*(methoxymethyl)*-α-DL-*galactopyranose* (**76**). A mixture of **75** (22 mg, 0.048 mmol), anh. THF (0.8 ml), and 1M Bu_4NF in THF (97 µl, 0.096 mmol) was allowed to stand at 20° for 1 h. After evaporation, the residue was purified by FC (SiO_2, AcOEt/MeOH 9:1; R_f (**76**) 0.18, *Pancaldi*): 17 mg (92%) of **76**. Colorless oil. UV (MeCN): 193 (320). IR (film): 3500, 2935, 1640, 1445, 1380, 1270, 1210, 1155, 1115, 1045, 980, 915, 875. ^{1}H-NMR (365 K, 400 MHz, C_6D_6): 5.54 (*d*, $^3J(1,2)$ = 2.3, H−C(1)); 4.79 (br. *s*, H−C(4)); 4.74 (*d*, ^2J = 6.5, 1 H), 4.64 (*d*, ^2J = 6.5, 1 H), 4.49 (*s*, 2 H, 2 $MeOCH_2$); 4.48 (*dd*, $^3J(3',4')$ = 5.4, $^3J(3',2')$ = 4.3, H−C(3')); 4.27 (*dd*, $^3J(4',3')$ = 5.4, $^3J(4',5'a)$ = 4.3, H−C(4')); 4.21 (*dd*, $^3J(2,3)$ = 2.8, $^3J(2,1)$ = 2.3, H−C(2)); 4.08 (*dd*, $^3J(5,6b)$ = 8.1, $^3J(5,6a)$ = 5.0, H−C(5)); 4.02 (*dd*, $^3J(1',3)$ = 8.3, $^3J(1',2')$ = 5.8, H−C(1')); 3.59 (*dd*, ^2J = 10.2, $^3J(6a,5)$ = 5.0, H_a−C(6)); 3.54 (*dd*, ^2J = 10.2, $^3J(6b,5)$ = 8.1, H_b−C(6)); 3.33, 3.19

(2*s*, 2 *Me*OCH$_2$); 3.05 (*d*, ^2J = 13.1, H$_b$–C(5')); 2.74 (*dd*, ^3J(2',1') = 5.8, ^3J(2',3') = 4.3, H–C(2')); 2.45 (*dd*, ^2J = 13.1, ^3J(5'a,4') = 4.3, H$_a$–C(5')); 2.15 (*dd*, ^3J(3,1') = 8.3, ^3J(3,2) = 2.8, H–C(3)); 1.36, 1.12 (2*s*, Me$_2$C). ^{13}C-NMR (100.6 MHz, C$_6$D$_6$): 111.4 (*s*, Me$_2$*C*); 101.4 (*d*, *J* = 181, C(1)); 97.6, 97.3 (2*t*, *J* = 162, 2 MeO*C*H$_2$); 84,0 (*d*, *J* = 147), 82.6 (*d*, *J* = 148), 82.4 (*d*, *J* = 156), 80.7 (*d*, *J* = 155), 79.0 (*d*, *J* = 155), 72.1 (*d*, *J* = 151, C(2), C(4), C(5), C(1'), C(3'), C(4')); 69.9 (*t*, *J* = 145, C(6)); 69.5 (*d*, *J* = 139, C(2')); 55.9, 55.5 (2*q*, *J* = 142, 2 *Me*OCH$_2$); 53.0 (*t*, *J* = 142, C(5')); 52.9 (*d*, *J* = 134, C(3)); 26.1 (*q*, *J* = 125), 24.0 (*q*, *J* = 125, Me$_2$C). CI-MS (NH$_3$): 406 (100, [*M* + 1]$^+$), 360 (15), 280 (18), 142 (43), 126 (6), 84 (9). Anal. calc. for C$_{18}$H$_{31}$NO$_9$ (405.544): C 54.32, H 7.71, N 3.45; found: C 54.17, H 7.79, N 3.50.

*(±)-1,4-Anhydro-3-{(1'*SR*)-5'-azido-1'-O-[(*tert*-butyl)dimethylsilyl]-5'-deoxy-3',4'-O-isopropylidene-2'-O-(methylsulfonyl)-*L*D-arabinitol-1'-C-yl}-3-deoxy-2,6-bis-O-(methoxymethyl)-α-*D*L-galactopyranose* (**77**). As described for **74**, with **73** (60 mg, 0.10 mmol), TLC control (AcOEt/light petroleum ether 1:1): R_f (**77**) 0.5, R_f (**73**) 0.18): 44 mg (68%) of **77**. Colorless oil. UV (MeCN): 194 (1480). IR (film): 3420, 2930, 2105, 1630, 1465, 1355, 1175, 1155, 1090, 1055, 950, 835. ^{1}H-NMR (400 MHz, CDCl$_3$): 5.52 (*d*, ^3J(1,2) = 2.3, H–C(1)); 4.76–4.59 (*m*, 7 H, H–C(2'), H–C(3'), H–C(4), 2 MeOC*H*$_2$); 4.45–4.34 (*m*, H–C(4')); 3.96 (*dd*, ^3J(1',3) = 10.2, ^3J(1',2') = 3.2, H–C(1')); 3.93 (*dd*, ^3J(5,6b) = 7.2, ^3J(5,6a) = 5.6, H–C(5)); 3.72 (*dd*, ^2J = 12.6, ^3J(5',4') = 7.5, H$_a$–C(5')); 3.61 (*dd*, ^3J(2,3) = 2.7, ^3J(2,1) = 2.3, H–C(2)); 3.49–3.35 (*m*, 9 H, 2 H–C(6), 2 H–C(5'), 2 *Me*OCH$_2$); 3.14 (*s*, MeSO$_2$); 2.16 (*dd*, ^3J(3,1') = 10.2, ^3J(3,2) = 2.7, H–C(3)); 1.51, 1.37 (2*s*, Me$_2$C); 0.90 (*s*, *t*-BuSi); 0.22, 0.15 (2*s*, Me$_2$Si). ^{13}C-NMR (100.6 MHz, CDCl$_3$): 109.8 (*s*, Me$_2$*C*); 100.8 (*d*, *J* = 182, C(1)); 96.9, 96.3 (2*t*, *J* = 162, MeO*C*H$_2$); 84.0 (*d*, *J* = 152), 79.1 (*d*, *J* = 136), 78.1 (*d*, *J* = 145), 77.8 (*d*, *J* = 158), 75.4 (*d*, *J* = 162), 72.3 (*d*, *J* = 147), 72.2 (*d*, *J* = 159, C(2), C(4), C(5), C(1'), C(2'), C(3'), C(4')); 67.9 (*t*, *J* = 144, C(6)); 56.0, 55.2 (2*q*, *J* = 142, *Me*OCH$_2$); 50.9 (*d*, *J* = 136, C(3)); 50.0 (*t*, *J* = 143, C(5')); 39.9 (*q*, *J* = 139, MeSO$_2$); 26.5 (*q*, *J* = 130, *Me*$_3$CSi); 25.7 (*q*, *J* = 125), 25.3 (*q*, *J* = 130, *Me*$_2$C); 17.8 (*s*, Me$_3$*C*Si); –4.4, –4.5 (2*q*, *J* = 119, Me$_2$Si). CI-MS (NH$_3$): 641 (1, $M^{+\cdot}$), 626 (2, [*M* – 15]$^+$), 614 (1), 598 (3), 582 (4), 568 (24), 556 (10), 480 (3), 284 (43), 153 (38), 73 (100). Anal. calc. for C$_{25}$H$_{47}$N$_3$O$_{12}$SSi (641.810): C 46.79, H 7.38, N 6.55; found: C 46.64, H 7.53, N 6.31.

*(±)-1,4-Anhydro-3-{(1'*SR*)-1'-O-[(*tert*-butyl)dimethylsilyl]-2',5'-dideoxy-2',5'-imino-3',4'-O-(isopropylidene-α-*L*D-ribitol-1'-C-yl}-3-deoxy-2,6-bis-O-(methoxymethyl)-α-*D*L-galactopyranose* (**78**). As described for **75**, with **77** (33 mg, 0.051 mmol), TLC control (AcOEt/MeOH 4:1); R_f (**77**) 0.22, *Pancaldi*): 15 mg (57%) of **78**. Colorless oil. UV (MeCN): 196 (200). IR (film): 3350, 2930, 2100, 1630, 1470, 1370, 1255, 1210, 1155, 1115, 1085, 1045, 940, 920, 835, 755. ^{1}H-NMR (400 MHz, CDCl$_3$): 5.50 (*d*, ^3J(1,2) = 2.2, H–C(1)); 4.78 (*dd*, ^3J(3',4') = 5.9, ^3J(3',2') = 1.5, H–C(3')); 4.71 (*d*, ^2J = 6.8, 1 H), 4.65 (*d*, ^2J = 6.8, 1 H, MeOC*H*$_2$); 4.63 (*ddd*, ^3J(4',3') = 5.9, ^3J(4',5'b) = 4.4, ^3J(4'5'a) = 1.5, H–C(4')); 4.62 (*d*, ^2J = 6.5, 1 H), 4.60 (*d*, ^2J = 6.5, 1 H, MeOC*H*$_2$); 4.55 (br. *s*, H–C(4)); 4.27 (*dd*, ^3J(2,3) = 3.1, ^3J(2,1) = 2.2, H–C(2)); 3.94 (*dd*, ^3J(5,6b) = 8.0, ^3J(5,6a) = 5.3, H–C(5)); 3.70 (*dd*, ^3J(1',2') = 7.4, ^3J(1',3) = 4.5, H–C(1')); 3.44 (*dd*, ^2J = 10.0, ^3J(6a,5) = 5.3, H$_a$–C(6)); 3.42 (*s*, 1 *Me*OCH$_2$); 3.38 (*dd*, ^2J = 10.0, ^3J(6b,5) = 8.0, H$_b$–C(6)); 3.36 (*s*, 1 *Me*OCH$_2$); 3.23 (*dd*, ^3J(2',1') = 7.4, ^3J(2',3') = 1.5, H–C(2')); 2.98 (*dd*, ^2J = 13.2, ^3J(5'a,4') = 1.5, H$_a$–C(5')); 2.90 (*dd*, ^2J = 13.2, ^3J(5'b,4') = 4.4, H$_b$–C(5')); 2.06 (*dd*, ^3J(3,1') = 4.5, ^3J(3,2) = 3.1, H–C(3)); 1.47, 1.31 (2*s*, 6 H, *Me*$_2$C); 0.92 (*s*, 9 H, *t*-BuSi); 0.11, 0.10 (2*s*, Me$_2$Si). ^{13}C-NMR (100.6 MHz, CDCl$_3$): 111.2 (*s*, Me$_2$*C*); 101.4 (*d*, *J* = 179, C(1)); 97.0, 96.6 (2*t*, *J* = 163, MeO*C*H$_2$); 82.9 (*d*, *J* = 154), 81.7 (*d*, *J* = 152), 81.3 (*d*, *J* = 138), 80.1 (*d*, *J* = 160), 78.6 (*d*, *J* = 139), 71.1 (*d*, *J* = 138), 68.1 (*d*, *J* = 158, C(2), C(4), C(5), C(1'), C(2'), C(3'), C(4')); 67.7 (*t*, *J* = 144, C(6)); 55.8, 55.3 (2*q*, *J* = 143, *Me*OCH$_2$); 52.7 (*t*, *J* = 142, C(5')); 51.5 (*d*, *J* = 132, C(3)); 26.5 (*q*, *J* = 126, *Me*C); 25.9 (*q*, *J* = 125, *Me*$_3$CSi); 24.1 (*q*, *J* = 126, *Me*C); 18.1 (*s*, Me$_3$*C*Si); –3.7, –4.4 (2*q*, *J* = 118, Me$_2$Si). CI-MS (NH$_3$): 521 (31, [*M* + 2]$^+$), 520 (44, [*M* + 1]$^+$), 474 (5), 312 (10), 142 (100), 126 (28), 91 (19), 75 (30). Anal. calc. for C$_{24}$H$_{45}$NO$_9$Si (519.708): C 55.46, H 8.77; found: C 55.43, H 8.69.

*(±)-1,4-Anhydro-3-deoxy-3[(1'*SR*)-2',5'-dideoxy-2',5'-imino-3',4'-O-isopropylidene-α-*L*D-ribitol-1'-C-yl]-2,6-bis-O-(methoxymethyl)-α-*D*L-galactopyranose* (**79**). As described for **76**, with **78** (15 mg, 0.029 mmol), TLC control (AcOEt/MeOH 9:1): R_f (**79**) 0.20, *Pancaldi*): 12 mg, (95%) of **79**. Colorless oil. UV (MeCN): 198 (1000). IR (film): 3415, 2935, 1640, 1455, 1375, 1210, 1155, 1115, 1045, 965, 915, 870, 800, 735. ^{1}H-NMR (400 MHz, CDCl$_3$): 5.54 (*d*, ^3J(1,2) = 2.4, H–C(1)); 4.81 (*dd*, ^3J(3',4') = 5.9, ^3J(3',2') = 2.2, H–C(3')); 4.78, 4.75 (2*d*, ^2J = 6.9, 2 H, MeOC*H*$_2$); 4.72 (*ddd*, ^3J(4',3') = 5.9, ^3J(4',5'a) = 4.2, ^3J(4',5'b) = 1.9, H–C(4')); 4.68 (br. *s*, H–C(4)); 4.62 (*s*, 2 H, MeOC*H*$_2$); 4.06 (*dd*, ^3J(2,3) = 2.6, ^3J(2,1) = 2.4, H–C(2)); 3.99 (*dd*, ^3J(5,6b) = 7.9, ^3J(5,6a) = 5.3, H–C(5)); 3.53 (*dd*, ^3J(1',3) = 8.0, ^3J(1',2') = 6.9, H–C(1')); 3.52 (*dd*, ^2J = 10.2, ^3J(6a,5) = 5.3, H$_a$–C(6)); 3.44 (*s*, 1 *Me*OCH$_2$); 3.39 (*dd*, ^2J = 10.2, ^3J(6b,5) = 7.9, H$_b$–C(6)); 3.36 (*s*, 1 *Me*OCH$_2$); 3.15 (*dd*, ^3J(2',1') = 6.9, ^3J(2',3') = 2.2, H–C(2')); 3.08 (*dd*, ^2J = 13.2, ^3J(5'b,4') = 1.9, H$_b$–C(5')); 3.03 (*dd*, ^2J = 13.2, ^3J(5'a,4') = 4.2, H$_a$–C(5')); 1.98 (*dd*, ^3J(3,1') = 8.0, ^3J(3,2) = 2.6, H–C(3)); 1.48, 1.33 (2*s*, Me$_2$C). ^{13}C-NMR (100.6 MHz, CDCl$_3$): 111.5 (*s*, Me$_2$*C*); 100.0 (*d*, *J* = 181, C(1)); 97.0, 96.6 (2*t*, *J* = 160, MeO*C*H$_2$); 82.0 (*d*, *J* = 155), 81.6

(*d*, *J* = 154), 81.5 (*d*, *J* = 155), 81.2 (*d*, *J* = 163), 78.0 (*d*, *J* = 156), 70.4 (*d*, *J* = 134), 68.7 (*d*, *J* = 138, C(2), C(4), C(5), C(1'), C(2'), C(3'), C(4')); 67.7 (*t*, *J* = 144, C(6)); 55.8, 55.3 (2*q*, *J* = 143, *Me*OCH$_2$); 52.5 (*t*, *J* = 139, C(5')); 50.8 (*d*, *J* = 132, C(3)); 26.6, 24.3 (2*q*, *J* = 130, Me$_2$C). CI-MS (NH$_3$): 423 (1, $[M + 18]^+$), 407 (17, $[M + 2]^+$), 406 (32, $[M + 1]^+$), 339 (6), 280 (10), 213 (10), 142 (100), 126 (40), 94 (35). Anal. calc. for $C_{18}H_{31}NO_9$ (405.544): C 54.32, H 7.71, N 3.45; found: C 54.20, H 7.82, N 3.29.

*(±)-1,4-Anhydro-3-[(1'*SR*)-1',2'-anhydro-5'-azido-5'-deoxy-3',4'-*O*-isopropylidene-*DL*-arabinitol-1'-C-yl]-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**80**). At 0°, 1M Bu$_4$NF in THF (0.165 ml, 0.16 mmol) was added dropwise to a stirred soln. of **74** (71 mg, 0.11 mmol) in anh. THF under Ar. After 10 min at 0°, DBU (33 µl, 0.30 mmol) was added and the mixture stirred at 20° for 5 h. The mixture was poured into ice-cold 1N aq. HCl (20 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. extracts was dried ($MgSO_4$) and evaporated, and the residue purified by FC (SiO_2, AcOEt/light petroleum ether 1:1; R_f (**80**) 0.32, *Pancaldi*): 39 mg (80%) of **80**. Colorless oil. UV (MeCN): 210 (3100). IR (film): 3425, 2960, 2105, 1450, 1370, 1260, 1220, 1150, 1040. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.57 (*d*, ^3J(1,2) = 2.3, H–C(1)); 4.75 (*d*, ^2J = 6.7, 1 H), 4.65 (*d*, ^2J = 6.7, 1 H), 4.61 (*s*, 2 H, MeO$_2$CH_2); 4.56 (br. *s*, H–C(4)); 4.30 (*ddd*, ^3J(4',3') = 6.6, ^3J(4',5'a) = 5.9, ^3J(4',5'b) = 5.6, H–C(4')); 4.12 (*dd*, ^3J(3',2') = 7.1, ^3J(3',4') = 6.6, H–C(3')); 4.11 (*dd*, ^3J(2,3) = 2.6, ^3J(2,1) = 2.3, H–C(2)); 3.92 (*dd*, ^3J(5,6b) = 8.6, ^3J(5,6a) = 4.9, H–C(5)); 3.55 (*dd*, ^2J = 12.6, ^3J(5'a,4') = 5.9, H$_a$–C(5')); 3.48 (*dd*, ^2J = 10.0, ^3J(6a,5) = 4.9, H$_a$–C(6)); 3.46 (*dd*, ^2J = 12.6, ^3J(5'b,4') = 5.6, H$_b$–C(5')); 3.42 (*s*, 1 *Me*OCH$_2$); 3.38 (*dd*, ^2J = 10.0, ^3J(6b,5) = 8.6, H$_b$–C(6)); 3.36 (*s*, 1 *Me*OCH$_2$); 3.15 (*dd*, ^3J(2',3') = 7.1, ^3J(2',1') = 4.1, H–C(2')); 3.08 (*dd*, ^3J(1',3) = 9.2, ^3J(1',2') = 4.1, H–C(1')); 1.76 (*dd*, ^3J(3,1') = 9.2, ^3J(3,2) = 2.6, H–C(3)); 1.53, 1.37 (2*s*, Me$_2$C). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 109.9 (*s*, Me$_2$*C*); 100.1 (*d*, *J* = 182, C(1)); 96.7, 96.5 (2*t*, *J* = 161, MeO*C*H$_2$); 83.0 (*d*, *J* = 153), 80.6 (*d*, *J* = 158), 77.8 (*d*, *J* = 164), 75.9 (*d*, *J* = 148), 75.4 (*d*, *J* = 148, C(2), C(4), C(5), C(3'), C(4')); 67.4 (*t*, *J* = 144, C(6)); 57.3 (*d*, *J* = 175), 56.0 (*d*, *J* = 176, C(1'), C(2')); 55.8, 53.3 (2*q*, *J* = 142, *Me*OCH$_2$); 50.8 (*t*, *J* = 146, C(5')); 45.8 (*d*, *J* = 139, C(3)); 27.7, 25.3 (2*q*, *J* = 125, *Me*$_2$C). CI-MS (NH$_3$): 431 (1, $M^{+\cdot}$), 416 (2), 258 (15), 298 (5), 269 (8), 169 (16), 142 (22), 123 (100), 111 (12), 95 (36), 81 (47), 71 (18). Anal. calc. for $C_{18}H_{29}N_3O_9$ (431.442): C 50.11, H 6.78, N 9.74; found: C 50.15, H 6.80, N 9.77.

*(±)-1,4-Anhydro-3-deoxy-3-[(1'*SR*)-2',5'-dideoxy-2',5'-imino-3',4'-*O*-isopropylidene-β-*DL*-ribitol-1'-C-yl]-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**81**). A mixture of **80** (28 mg, 0.066 mmol), anh. MeOH (1 ml), $HCOONH_4$ (23 mg, 0.33 mmol), and 10% Pd/C (14 mg, 0.013 mmol) was stirred at 20° for 20 h. After filtration over *Celite* and rinsing with AcOEt (3 × 10 ml), the solvent was evaporated and the residue purifid by FC (SiO_2, CH_2Cl_2/MeOH 95:5; R_f (**81**) 0.20, *Pancaldi*): 18 mg (75%) of **81**. Colorless oil. UV (MeCN): 193 (500). IR (film): 3500, 2935, 1440, 1375, 1210, 1150, 1115, 1040, 915, 875, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.54 (*d*, ^3J(1,2) = 2.4, H–C(1)); 4.76 (*d*, ^2J = 5.5, 1 H, MeO*CH*$_2$); 4.75 (*dd*, ^3J(4',3') = 5.6, ^3J(4',5'a) = 4.2, H–C(4')); 4.74 (*d*, ^2J = 5.5, 1 H), 4.63, 4.61 (2*d*, ^2J = 6.6, 2 H, MeO*CH*$_2$); 4.59 (*d*, ^3J(3',4') = 5.6, H–C(3')); 4.49 (br. *s*, H–C(4)); 4.04 (*dd*, ^3J(2,3) = 2.9, ^3J(2,1) = 2.4, H–C(2)); 3.97 (*dd*, ^3J(5,6b) = 8.2, ^3J(5,6a) = 5.2, H–C(5)); 3.47 (*dd*, ^2J = 9.9, ^3J(6a,5) = 5.2, H$_a$–C(6)); 3.45 (*dd*, ^3J(1',3) = 6.9, ^3J(1',2') = 6.5, H–C(1')); 3.44 (*s*, 1 *Me*OCH$_2$); 3.40 (*dd*, ^2J = 9.9, ^3J(6b,5) = 8.2, H$_b$–C(6)); 3.36 (*s*, 1 *Me*OCH$_2$); 3.16 (*dm*, ^3J(2',1') = 6.5, H–C(2')); 3.07 (*d*, ^2J = 13.4, H$_b$–C(5')); 2.89 (*dd*, ^2J = 13.4, ^3J(5'a,4') = 4.2, H$_a$–C(5')); 1.94 (*dd*, 1 H, ^3J(3,1') = 6.9, ^3J(3,2) = 2.9, H–C(3)); 1.47, 1.32 (2*s*, 6 H, Me$_2$C). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 111.1 (*s*, Me$_2$*C*); 100.1 (*d*, *J* = 180, C(1)); 97.0, 96.7 (2*t*, *J* = 164, MeO*CH*$_2$); 84.5 (*d*, *J* = 155), 82.6 (*d*, *J* = 153), 81.8 (*d*, *J* = 151), 80.6 (*d*, *J* = 160), 78.4 (*d*, *J* = 155), 70.1 (*d*, *J* = 167), 67.5 (*d*, *J* = 154, C(2), C(4), C(5), C(1'), C(2'), C(3'), C(4')); 67.7 (*t*, *J* = 144, C(6)); 55.8, 55.3 (2*q*, *J* = 143, *Me*OCH$_2$); 52.9 (*t*, *J* = 138, C(5')); 50.0 (*d*, *J* = 131, C(3)); 26.4, 24.0 (2*q*, *J* = 127, Me$_2$C). CI-MS (NH$_3$): 406 (5, $[M + 1]^+$), 390 (3), 374 (4), 360 (32), 298 (10), 238 (6), 142 (100), 126 (36), 84 (26). Anal. calc. for $C_{18}H_{31}NO_9$ (405.544): C 53.32, H 7.71; found: C 53.71, H 7.45.

*(±)-1,4-Anhydro-3-[(1'*SR*)-1',2'-anhydro-5'-azido-5'-deoxy-*LD*-ribitol-1'-C-yl]-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**82**). At 0°; 1M Bu$_4$NF in THF (111 µl, 0.11 mmol) was added dropwise to a stirred soln. of **73** (45 mg, 0.075 mmol) in anh. THF (0.75 ml). After stirring at 20° for 10 min (TLC control (AcOEt/light petroleum ether 1:1): R_f (**73**) 0.18) and complete disappearance of **73**, DBU (22 µl, 0.150 mmol) was added and the mixture stirred at 20° for 30 min. The mixture was poured into ice-cold 1N aq. HCl (20 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. extract was dried ($MgSO_4$) and evaporated, and the residue purified by FC (SiO_2, AcOEt/light petroleum ether 4:1; R_f (**82**) 0.29, *Pancaldi*): 21 mg (71%) of **82**. Colorless oil. UV (MeCN): 213 (510). IR (film): 3400, 2110, 1645, 1445, 1270, 1150, 1045, 865, 795. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.59 (*d*, ^3J(1,2) = 2.4, H–C(1)); 4.72 (*d*, ^2J = 6.8, 1 H), 4.69 (*d*, ^2J = 6.8, 1 H), 4.65, 4.63 (2*d*, ^2J = 6.6, 2 MeO*CH*$_2$); 4.61 (br. *s*, H–C(4)); 4.13 (*dd*, ^3J(2,3) = 2.5, ^3J(2,1) = 2.4, H–C(2)); 3.99 (*ddd*, ^3J(4',5'b) = 6.1, ^3J(4',3') = 4.8, ^3J(4',5'a) = 4.7, H–C(4')); 3.96 (*dd*, ^3J(5,6b) = 8.3, ^3J(5,6a) = 4.7, H–C(5)); 3.61 (*dd*, ^3J(3',2') = 7.9, ^3J(3',4') = 4.8, H–C(3')); 3.50 (*dd*, ^2J = 10.4, ^3J(5'a,4') = 4.7, H$_a$–C(5')); 3.44–3.36 (*m*, CH$_2$(6), H$_b$–C(5'), 2 *Me*OCH$_2$); 3.20 (*dd*, ^3J(2',3') = 7.9, ^3J(2',1) = 4.0, H–C(2')); 3.06 (*dd*, ^3J(1',3) = 9.4, ^3J(1',2') = 4.0,

H–C(1')); 1.79 (*dd*, $^3J(3,1') = 9.4$, $^3J(3,2) = 2.5$, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 100.0 (*d*, $J = 181$, C(1)); 96.9, 96.7 (2*t*, $J = 164$, MeOCH_2); 83.2 (*d*, $J = 144$), 80.7 (*d*, $J = 158$), 78.0 (*d*, $J = 135$), 72.7 (*d*, $J = 144$), 69.5 (*d*, $J = 143$, C(2), C(4), C(5), C(3'), C(4')); 68.3 (*t*, $J = 144$, C(6)); 57.5 (*d*, $J = 172$), 56.4 (*d*, $J = 173$, C(1'), C(2')); 55.8, 55.5 (2*q*, $J = 143$, *Me*OCH$_2$); 52.8 (*t*, $J = 143$, C(5')); 45.6 (*d*, $J = 136$, C(3)). CI-MS (NH_3): 273 (2, $[M - 118]^+$), 213 (2), 169 (12), 123 (100), 111 (9), 95 (35), 81 (33), 72 (14). Anal. calc. for $C_{15}H_{25}N_3O_9$ (391.377): C 46.03, H 6.44, N 10.74; found: C 46.18, H 6.51, N 10.62.

*(±)-1,4-Anhydro-3-[(1'*SR*)-1',2'-anhydro-5'-azido-5'-deoxy-3',4'-*O*-isopropylidene-*LD*-ribitol-1'-C-yl]-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**83**). A mixture of **82** (21 mg, 0.054 mmol), $Me_2C(OMe)_2$ (0.3 ml), and camphorsulfonic acid (2.5 mg, 0.011 mmol) was stirred at 20° for 30 min; TLC control (AcOEt petroleum ether 4:1): R_f (**82**) 0.29, R_f (**83**) 0.63, *Pancaldi*). After disappearance of **82**, the mixture was poured into ice-cold, sat. aq. $NaHCO_3$ soln. (25 ml) and extracted wtih CH_2Cl_2 (3 × 25 ml). The combined org. extract was dried ($MgSO_4$) and evaporated, and the residue purified by FC (SiO_2, AcOEt/light petroleum ether 2:1; R_f (**83**) 0.45): 19 mg (70%) of **83**. Colorless oil. UV (MeCN): 209 (1400). IR (film): 3460, 2935, 2100, 1455, 1370, 1220, 1150, 1040, 865, 795, 735. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.64 (*d*, $^3J(1,2) = 2.2$, H–C(1)); 4.78, 4.74 (2*d*, $^2J = 6.5$, 2 H), 4.71 (*s*, 2 MeOCH_2); 4.70 (br. *s*, H–C(4)); 4.49 (*ddd*, $^3J(4',5'a) = 6.5$, $^3J(4',3') = 6.1$, $^3J(4',5'b) = 4.3$, H–C(4')); 4.16 (*dd*, $^3J(2,3) = 2.4$, $^3J(2,1) = 2.2$, H–C(2)); 4.06 (*dd*, $^3J(5,6b) = 7.6$, $^3J(5,6a) = 5.2$, H–C(5)); 3.96 (*dd*, $^3J(3',2') = 8.7$, $^3J(3',4') = 6.1$, H–C(3')); 3.73 (*dd*, $^2J = 12.7$, $^3J(5'b,4') = 4.3$, H_b–C(5')); 3.69 (*dd*, $^2J = 12.7$, $^3J(5'a,4') = 6.5$, H_a–C(5')); 3.59 (*dd*, $^2J = 9.8$, $^3J(6a,5) = 5.2$, H_a–C(6)); 3.54 (*dd*, $^2J = 9.8$, $^3J(6b,5) = 7.6$, H_b–C(6)); 3.53, 3.48 (2*s*, 2 *Me*OCH$_2$); 3.25 (*dd*, $^3J(2',3') = 8.7$, $^3J(2',1') = 3.9$, H–C(2')); 3.20 (*dd*, $^3J(1',3) = 8.9$, $^3J(1',2') = 3.9$, H–C(1')); 1.85 (*dd*, $^3J(3,1') = 8.9$, $^3J(3,2) = 2.4$, H–C(3)); 1.71, 1.54 (2*s*, Me_2C). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 110.0 (*s*, Me_2C); 100.1 (*d*, $J = 188$, C(1)); 96.7, 96.5 (2*t*, $J = 166$, MeOCH_2); 83.0 (*d*, $J = 150$), 80.6 (*d*, $J = 161$), 77.9 (*d*, $J = 154$), 76.5 (*d*, $J = 149$), 74.4 (*d*, $J = 148$, C(2), C(4), C(5), C(3'), C(4')); 67.8 (*t*, $J = 143$, C(6)); 57.6 (*d*, $J = 174$, C(1'), C(2')); 55.8, 53.3 (2 *q*, $J = 142$, *Me*OCH$_2$); 54.0 (*d*, $J = 178$, C(1'), C(2')); 50.3 (*t*, $J = 142$, C(5')); 45.4 (*d*, $J = 135$, C(3)); 27.6 (*q*, $J = 128$), 25.0 (*q*, $J = 128$, Me_2C). CI-MS (NH_3): 416 (4, $[M - 15]^+$), 328 (2), 298 (2), 269 (6), 213 (2), 169 (14), 123 (100), 101 (19), 95 (24), 81 (26). Anal. calc. for $C_{18}H_{29}N_3O_9$ (431.442): C 50.11, H 6.78, N 9.74; found: C 50.21, H 6.87, N 9.74.

*(±)-1,4-Anhydro-3-deoxy-3[(1'*SR*)-2',5'-dideoxy-2',5'-imino-3',4'-*O*-isopropylidene-β-*LD*-arabinitol-1'-C-yl]-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**84**). As described for **81**, with **83** (22 mg, 0.051 mmol), MeOH (0.8 ml), $HCOONH_4$ 835 mg, 0.51 mmol), and 10% Pd/C (11 mg, 0.01 mmol) (R_f (**84**) 0.18): 13 mg (63%) of **84**. Colorless oil. UV (MeCN): 195 (780). IR (film): 3480, 2935, 1640, 1375, 1210, 1155, 1040, 915, 735. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.52 (*d*, $^3J(1,2) = 2,3$, H–C(1)); 4.84 (*d*, $^2J = 6.6$, 1 H, MeOCH_2); 4.73 (*dd*, $^3J(4',3') = 5.7$, $^3J(4',5'a) = 3.9$, H–C(4')); 4.68 (*dd*, $^3J(3',4') = 5.7$, $^3J(3',2') = 4.1$, H–C(3)); 4.64 (*d*, $^2J = 6.6$, 1 H), 4.61 (*s*, 2 H, 2 MeOCH_2); 4.44 (br. *s*, H–C(4)); 4.08 (*dd*, $^3J(2,3) = 2.7$, $^3J(2,1) = 2.3$, H–C(2)); 4.02 (*dd*, $^3J(5,6b) = 7.7$, $^3J(5,6a) = 5.3$, H–C(5)); 3.99 (*dd*, $^3J(1',3) = 9.1$, $^3J(1',2' = 2.5$, H–C(1')); 3.47 (*dd*, $^2J = 10.2$, $^3J(6a,5) = 5.3$, H_a–C(6)); 3.42 (*s*, *Me*OCH$_2$); 3.41 (*dd*, $^2J = 10.2$, $^3J(6b,5) = 7.7$, H_b–C(6)); 3.35 (*s*, 1 *Me*OCH$_2$); 3.20 (*d*, $^2J = 13.5$, H_b–C(5')); 2.78 (*dd*, $^3J(2',3') = 4.1$, $^3J((2',1') = 2.5$, H–C(2')); 2.69 (*dd*, $^2J = 13.5$, $^3J(5'a,4') = 3.9$, H_a–C(5')); 2.04 (*dd*, $^3J(3,1') = 9.1$, $^3J(3,2) = 2.7$, H–C(3)); 1.48, 1.33 (2*s*, Me_2C). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 111.3 (*s*, Me_2C); 100.5 (*d*, $J = 174$, C(1)); 96.7, 96.1 (2*t*, $J = 163$, MeOCH_2); 83.2 (*d*, $J = 156$), 82.1 (*d*, $J = 154$), 81.3 (*d*, $J = 143$), 79.9 (*d*, $J = 157$), 78.0 (*d*, $J = 158$, C(2), C(4), C(1'), C(3'), C(4')); 69.4 (*d*, $J = 143$, C(2')), C(5)); 67.9 (*t*, $J = 144$, C(6)); 64.1 (*d*, $J = 136$, C(2'), C(5)); 55.7, 55.3 (2*q*, $J = 144$, *Me*OCH$_2$); 52.1 (*t*, $J = 143$, C(5')); 50.6 (*d*, $J = 134$, C(3)); 25.6, 23.4 (2*q*, $J = 128$, Me_2C). CI-MS (NH_3): 406 (5, $[M + 1]^+$), 390 (4), 374 (6), 360 (46), 298 (21), 238 (7), 142 (100), 126 (52), 84 (31). Anal. calc. for $C_{18}H_{31}NO_9$ (405.544): C 54.32, H 7.71, N 3.45; found: C 54.40, H 7.84, N 3.52.

*(±)-(1*RS*,2*SR*,6*SR*,7*SR*,8*RS*,8a*SR*)-2,3,6,7,8,8a-Hexahydro-1,2,6,8-tetrahydroxy-7-[(1'*SR*,2'*SR*)-1',2',3'-trihydroxypropyl]-1*H*-indolizinium Cation* (**85**) *and (±)-(1*RS*,2*SR*,6*SR*,7*RS*,8*RS*,8a*SR*)-1,2,3,5,6,7,8,8a-Octahydro-7-[(1'*SR*,2'*SR*)-1',2',3'-trihydroxypropyl]indolizine-1,2,6,8-tetrol* (**14**). Pyrrolidine **76** (26 mg, 0.06 mmol) was dissolved in 3M DCl in D_2O (0.8 ml). After 3 h at 20°, K_2CO_3 was added until pH 8. ^{1}H-NMR of the soln.: signals of **85** (single product formed). Then, 1N aq. HCl was added until pH 2, and the soln. was filtered through a column of *Dowex50Wx8* resin (MeOH, H_2O, then 0.5M NH_3 in H_20 (*Pancaldi*). After lyophilization, 11 mg (64%) of **14** was obtained.

Data of **85**: ^{1}H-NMR (400 MHz, D_2O, 310 K): 4.81 (br. *s*, H–C(5)); 4.34 (*ddd*, $^3J(2,H_a–C(3)) = 7.6$, $^3J(2,1) = 5.4$, $^3J(2,H_b–C(3)) = 2.8$, H–C(2)); 4.18 (*dd*, $^3J(1,2) = 5.4$, $^3J(1,8a) = 3.5$, H–C(1)); 4.13 (*d*, $^3J(1',2') = 6.6$, H–C(1')); 4.08 (*dd*, $^3J(8,8a) = 9.2$, $^3J(7,8) = 2.8$, H–C(8)); 3.90 (br. *s*, H–C(6)); 3.88 (*ddd*, $^3J(2',H_b–C(3')) = 7.1$, $^3J(2',1') = 6.6$, $^3J(2',H_a–C(3')) = 3.8$, H–C(2')); 3.71 (*dd*, $^2J = 11.8$, $^3J(H_a–C(3'),2') = 3.8$, H_a–C(3')); 3.53 (*dd*, $^2J = 11.8$, $^3J(H_b–C(3'),2') = 7.1$, H_b–C(3')); 2.96 (*dd*, $^2J = 10.0$, $^3J(H_a–C(3),2) = 7.6$, H_a–C(3)); 2.70 (*dd*, $^2J = 10.0$, $^3J(H_b–C(3),2) = 2.8$, H_b–C(3)); 2.61 (*d*, $^3J(7,8) = 2.8$,

H–C(7)); 2.38 (*dd*, $^3J(8,8a) = 9.2$, $^3J(1,8a) = 3.5$, H–C(8a)). ^{13}C-NMR (100.6 MHz, D_2O, 310 K): 92.2 (*d*, $J = 167$, C(5)); 81.4 (*d*, $J = 147$, C(1')); 76.6 (*d*, $J = 160$, C(6)); 75.9 (*d*, $J = 147$, C(2')); 72.7 (*d*, $J = 145$, C(2)); 70.8 (*d*, $J = 163$, C(1)); 66.8 (*d*, $J = 160$, C(8)); 66.5 (*d*, $J = 142$, C(8a)); 65.7 (*t*, $J = 144$, C(3')); 56.3 (*t*, $J = 145$, C(3)); 52.9 (*d*, $J = 143$, C(7)).

Data of **14**: Colorless powder. IR (KBr): 3410, 1655, 1125, 1035, 670, 620. ^{1}H-NMR (400 MHz, D_2O, 310 K): 4.43 (*ddd*, $^3J(2,H_a–C(3)) = 7.8$, $^3J(2,1) = 5.9$, $^3J(2,H_b–C(3)) = 3.4$, H–C(2)); 4.25 (*dd*, $^3J(1,2) = 5.9$, $^3J(1,8a) = 4.0$, H–C(1)); 4.20–4.17 (*m*, H–C(8), H–C(6)); 4.14 (*dd*, $^3J(1',7) = 8.3$, $^3J(1',2') = 1.6$, H–C(1')); 3.87 (*ddd*, $^3J(2',H_b–C(3')) = 7.2$, $^3J(2',H_a–C(3')) = 5.1$, $^3J(2',1') = 1.6$, H–C(2')); 3.70 (*dd*, $^2J = 11.4$, $^3J(H_a–C(3'),2') = 5.1$, H_a–C(3')); 3.67 (*dd*, $^2J = 11.4$, $^3J(H_b–C(3'),2') = 7.2$, H_b–C(3')); 3.08 (*dd*, $^2J = 11.5$, $^3J(H_a–C(5),6) = 3.8$, H_a–C(5)); 2.96 (*dd*, $^2J = 11.8$, $^3J(H_a–C(3),2) = 7.8$, H_a–C(3)); 2.88 (*dd*, $^2J = 11.8$, $^3J(H_b–C(3),2) = 3.4$, H_b–C(3)); 2.82 (*dd*, $^2J = 11.5$, $^3J(H_b–C(5),6) = 6.9$, H_b–C(5)); 2.78 (*dd*, $^3J(8,8a) = 6.4$, $^3J(1,8a) = 4.0$, H–C(8a)); 2.38 (*ddd*, $^3J = 8.3$, 4.2, 3.8, H–C(7)). ^{13}C-NMR (100.6 MHz, D_2O, 310 K): 72.8 (*d*, $J = 175$, C(2')); 71.0 (*d*, $J = 171$, C(1)); 70.1 (*d*, $J = 168$, C(2)); 68.7 (*d*, $J = 153$, C(8a)); 68.6 (*d*, $J = 145$, C(1')); 66.6 (*d*, $J = 150$, C(6)); 66.3 (*d*, $J = 149$, C(8)); 64.1 (*t*, $J = 141$, C(3')); 60.2 (*t*, $J = 142$, C(3)); 57.3 (*t*, $J = 151$, C(5)); 42.6 (*d*, $J = 126$, C(7)). For elemental analysis, see **86**.

*(±)-(1*RS,*2*SR,*6*SR,*7*RS,*8*RS,*8a*SR*)-1,2,3,5,6,7,8,8a-Octahydro-7-[(1'*SR*,2'*SR*)-1',2',3'-triacetoxypropyl]-indolizine-1,2,6,8-tetrayl Tetracetate* (**86**). A mixture of **14** (4 mg, 0.014 mmol), DMAP (2 mg), pyridine (0.5 ml), and Ac_2O (0.5 ml) was allowed to stand at 20° for 24 h. The solvent was evaporated and the residue purified by FC (SiO_2, AcOEt/MeOH 98:2; R_f (**86**) 0.60, *Pancaldi*): 4.4 mg (54%) of **86**. Colorless oil. IR (film): 1745, 1435, 1375, 1230, 1035, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.51 (*dd*, $^3J = 9.1$, 2.9, H–C(1')); 5.44 (*dd*, $^3J = 6.2$, 4.5, H–C(1)); 5.34–5.27 (*m*, H–C(2), H–C(8), H–C(2')); 5.23 (*m*, H–C(6)); 4.26 (*dd*, $^2J = 11.8$, $^3J(H_a–C(3'),2') = 4.4$, H_a–C(3')); 3.87 (*dd*, $^2J = 11.8$, $^3J(H_b–C(3'),2') = 7.2$, H_b–C(3')); 3.39 (*dd*, $^2J = 12.0$, $^3J(H_a–C(5),6) = 6.6$, H_a–C(5)); 3.04 (*dd*, $^2J = 11.4$, $^3J(H_a–C(3),2) = 2.6$, H_a–C(3)); 2.66–2.54 (*m*, H–C(7), H–C(8a), H_b–C(3)); 2.38 (*dd*, $^2J = 12.0$, $^3J(H_b–C(5),6) = 4.1$, H_b–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 69.9–67.7 (7*s*, 7 CO); 71.1 (*d*, $J = 146$), 70.5 (*d*, $J = 143$), 69.6 (*d*, $J = 148$), 67.5 (*d*, $J = 150$), 66.5 (*d*, $J = 153$), 66.0 (*d*, $J = 145$), 65.7 (*d*, $J = 142$, C(1), C(2), C(6), C(8), C(8a), C(1'), C(2')); 62.8 (*t*, $J = 150$); 58.0 (*t*, $J = 143$); 54.8 (*t*, $J = 140$, C(3), C(5), C(3')); 37.7 (*d*, $J = 129$, C(7)); 21.0–20.4 (7*q*, $J = 130.7$, *Me*CO). CI-MS (NH_3): 574 (100, $[M + 1]^+$), 514 (2), 453 (4), 334 (1), 216 (1), 167 (1), 77 (2). Anal. calc. for $C_{25}H_{35}NO_{14}$ (573.548): C 52.35, H 6.15, N 2.44; found: C 52.40, H 6.02, N 2.39.

*(±)-1,4-Anhydro-3-{(1'*SR*)-5'-azido-1'-*O*-[(*tert*-butyl)dimethylsilyl]-5'-deoxy-2'-*O*-(methylsulfonyl)-3',4'-bis-*O*-(methoxymethyl)-*DL*-ribitol-1'-*C*-yl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**87**). $MeOCH_2Cl$ (0.54 ml, 7.5 mmol) was added dropwise to a stirred soln. of **72** (450 mg, 0.75 mmol) in anh. $(i\text{-}Pr)_2NEt$ (4 ml) at 0° under Ar. After stirring at 0° for 30 min, the mixture was stirred at 20° for 2 h (TLC control (AcOEt/light petroleum ether 1:1); R_f (**72**) 0.30). In the case of incomplete conversion, $MeOCH_2Cl$ (0.54 ml, 7.5 mmol) was added and the mixture stirred at 20° for 2 more h. The mixture was poured into ice-cold 1N aq. HCl (50 ml) and extracted with AcOEt (50 ml, 3 times). The combined org. extract was washed with sat. aq. $NaHCO_3$ soln. (50 ml), dried ($MgSO_4$), and evaporated, and the residue purified by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**87**) 0.35, *Pancaldi*): 351 mg (68%) of **87**. Colorless oil. IR (film): 2935, 2895, 2855, 2105, 1475, 1365, 1255, 1180, 1155, 1040, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.48 (*d*, $^3J(1,2) = 2.1$, H–C(1)); 4.77–4.71 (*m*, 6 H, H–C(2'), $MeOCH_2$); 4.62–4.57 (*m*, 3 H, $MeOCH_2$); 4.51 (br. *s*, H–C(4)); 4.17 (*dd*, $^3J(3',4') = 5.1$, $^3J(3',2') = 2.9$, H–C(3')); 4.13 (*dd*, $^3J(1',2') = 7.3$, $^3J(1',3) = 5.0$, H–C(1')); 3.99 (*dd*, $^3J(2,3) = 3.2$, $^3J(2,1) = 2.1$, H–C(2)); 3.92 (*dd*, $^3J(5,6a) = 7.9$, $^3J(5,6b) = 5.4$, H–C(5)); 3.85 (*ddd*, $^3J(4',5'b) = 5.9$, $^3J(4',3') = 5.1$, $^3J(4',5'a) = 2.9$, H–C(4')); 3.69 (*dd*, $^2J = 13.1$, $^3J(5'a,4') = 2.9$, H_a–C(5')); 3.52 (*dd*, $^2J = 13.1$, $^3J(5'b,4') = 5.9$, H_b–C(5')); 3.44–3.33 (*m*, 14 H, therein 3*s* (3.44, 3.40, 3.33, 12 H), 4 $MeOCH_2$, CH_2(6)); 3.09 (*s*, $MeSO_2$); 1.95 (*dd*, $^3J(3,1') = 5.0$, $^3J(3,2) = 3.2$, H–C(3)); 0.89 (*s*, *t*-BuSi), 0.14, 0.10 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 100.5 (*d*, $J = 182$, C(1)); 97.1, 96.4, 96.1 (3*t*, $J = 163$, 4 $MeOCH_2$); 83.9 (*d*, $J = 149$), 81.6 (*d*, $J = 153$), 80.0 (*d*, $J = 166$), 78.4 (*d*, $J = 152$), 76.6 (*d*, $J = 142$), 74.5 (*d*, $J = 143$), 70.5 (*d*, $J = 145$, C(2), C(4), C(5), C(1'), C(2'), C(3'), C(4')); 67.5 (*t*, $J = 143$, C(6)); 56.4, 56.0, 55.9, 55.1 (4*q*, $J = 142$, $MeOCH_2$); 51.7 (*t*, $J = 143$, C(5')); 49.4 (*d*, $J = 132$, C(3)); 39.1 (*q*, $J = 140$, $MeSO_2$); 26.0 (*q*, $J = 126$, Me_3CSi); 17.9 (*s*, Me_3CSi); –4.0 (2*q*, $J = 119$, Me_2Si). CI-MS (NH_3): 708 (100, $[M + 19]^+$), 665 (1), 631 (3), 605 (1), 554 (2), 496 (2), 106 (3), 90 (9), 73 (12). Anal. calc. for $C_{26}H_{51}N_3O_{14}SSi$ (689.851): C 45.27, H 7.45, N 6.09; found: C 45.27, H 7.52, N 6.05.

*(±)-1,4-Anhydro-3-{(1'*SR*)-5'-azido-1'-[(*tert*-butyl)dimethylsilyl]-5'-deoxy-3',4'-bis-*O*-(methoxymethyl)-2'-*O*-(methylsulfonyl)-*LD*-arabinitol-1'-*C*-yl}-3-deoxy-2,6-bis-*O*-(methoxymethyl)-α-*DL*-galactopyranose* (**88**). As described for **87**, with **73** (139 mg, 0.23 mmol) (TLC (AcOEt/light petroleum ether 1:1): R_f (**73**) 0.11, R_f (**88**) 0.45, *Pancaldi*). 118 mg (74%) of **88**. Colorless oil. UV (MeCN): 213 (550). IR (film): 2935, 2110, 1470, 1360, 1260, 1155, 1045, 835, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.51 (*d*, $^3J(1,2) = 2.3$, H–C(1)); 4.85 (*dd*, $^3J(2',3') = 4.4$,

$^3J(2',1') = 4.2$, H–C(2')); 4.81–4.58 (*m*, H–C(4), 4 MeOCH_2); 4.20 (*dd*, $^3J(3',4') = 5.4$, $^3J(3',2') = 4.4$, H–C(3')); 4.00 (*dd*, $^3J(1',3) = 9.1$, $^3J(1',2') = 4.2$, H–C(1')); 3.94–3.91 (*m*, H–C(5), H–C(4')); 3.76 (*dd*, $^3J(2,3) = 2.6$, $^3J(2,1) = 2.3$, H–C(2)); 3.63 (*dd*, $^2J = 13.2$, $^3J(5'a,4') = 3.5$, H_a–C(5')); 3.58 (*dd*, $^2J = 13.2$, $^3J(5'b,4') = 5.0$, H_b–C(5')); 3.45 (*dd*, $^2J = 10.2$, $^3J(6a,5) = 5.3$, H_a–C(6)); 3.43, 3.42, 3.41 (3*s*, 3 *Me*OCH_2); 3.37 (*dd*, $^2J = 10.2$, $^3J(6b,5) = 8.3$, H_b–C(6)); 3.34 (*s*, 1 *Me*OCH_2); 3.11 (*s*, $MeSO_2$); 2.15 (*dd*, $^3J(3,1') = 9.1$, $^3J(3,2) = 2.6$, H–C(3)); 0.84 (*s*, *t*-BuSi); 0.18, 0.13 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 100.6 (*d*, $J = 182$, C(1)); 98.4, 97.7, 96.9, 96.5 (4*t*, $J = 163$, MeOCH_2); 83.2 (*d*, $J = 151$), 79.9 (*d*, $J = 151$), 79.8 (*d*, $J = 150$), 77.7 (*d*, $J = 143$), 77.4 (*d*, $J = 161$), 74.6 (*d*, $J = 139$), 72.2 (*d*, $J = 141$, C(2), C(4), C(5), C(1'), C(2'), C(3'), C(4')); 67.6 (*t*, $J = 143$, C(6)); 56.6, 56.1, 55.9, 55.2 (4*q*, $J = 142$, *Me*OCH_2); 51.1 (*t*, $J = 143$, C(5')); 49.6 (*d*, $J = 139$, C(3)); 38.7 (*q*, $J = 138$, $MeSO_2$); 25.8 (*q*, $J = 125$, *Me*$_3$CSi); 17.8 (*s*, Me$_3$*C*Si); −4.2, −4.8 (2*q*, $J = 119$, Me_2Si). CI-MS (NH_3): 707 (1, $[M + 18]^+$), 530 (2), 386 (2), 271 (7), 231 (7), 197 (10), 153 (24), 73 (100). Anal. calc. for $C_{26}H_{51}N_3O_{14}SSi$ (689.851): C 45.27, H 7.45, N 6.09; found: C 45.29, H 7.30, N 6.08.

*(±)-1,4-Anhydro-3-{(1'*SR*)-1'*-O-*[(*tert-*butyl)dimethylsilyl]-2',5'-dideoxy-2',5'-imino-3',4'-bis-*O-*(methoxymethyl)-α-*LD-*ribitol-1'-*C*-yl}-3-deoxy-2,6-bis-*O-*(methoxymethyl)-α-*DL-*galactopyranose* (**89**). A mixture of **88** (58 mg, 0.084 mmol), anh. MeOH (1 ml), $HCOONH_4$ (16 mg, 0.17 mmol), and 5% Pd/C (36 mg, 0.017 mmol) was shaken vigourously at 20° for 1 h. The catalyst was filtered off and washed with AcOEt (3 × 20 ml). The solvent was evaporated and the residue taken up in anh. DMF (1 ml) under Ar. Fresh flame-dried K_2CO_3 (23 mg, 0.163 mmol) was added and the mixture heated to 50° for 13 h. The solvent was evaporated at 10^{-1} Torr and the residue purified by FC (SiO_2, CH_2Cl_2/MeOH 95:5; R_f (**89**) 0.50, *Pancaldi*): 30 mg (63%) of **89**. Colorless oil. UV (MeCN): 200 (1500). IR (film): 2930, 2355, 1470, 1255, 1215, 1040, 920, 835, 755. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.48 (*d*, $^3J(1,2) = 2.3$, H–C(1)); 4.73, 4.71 (2*s*, 4 H), 4.64–4.59 (*m*, 4 H, 4 MeOCH_2); 4.42 (br. *s*, H–C(4)); 4.16–4.08 (*m*, H–C(2), H–C(3'), H–C(4')); 3.93 (*dd*, $^3J(5,6b) = 7.6$, $^3J(5,6a) = 5.5$, H–C(5)); 3.65 (*dd*, $^3J(1',3) = 6.1$, $^3J(1',2') = 5.2$, H–C(1')); 3.46–3.35 (*m*, CH_2(6), H–C(2'), 4 *Me*OCH_2); 3.13–3.04 (*m*, CH_2(5')); 2.07 (*dd*, $^3J(3,1') = 6.1$, $^3J(3,2) = 3.1$, H–C(3)); 1.63 (br. *s*, NH); 0.91 (*s*, *t*-BuSi); 0.13, 0.11 (2*s*, Me_2Si). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 100.7 (*d*, $J = 180$, C(1)); 96.9, 96.6, 96.1, 95.9 (4*t*, $J = 163$, MeOCH_2); 81.7 (*d*, $J = 150$), 80.6 (*d*, $J = 152$), 78.2 (*d*, $J = 154$), 77.1, 76.7 (*d*, $J = 150$), 73.9 (*d*, $J = 151$, C(2), C(4), C(1'), C(2'), C(3'), C(4')); 67.9 (*t*, $J = 139$, C(6)); 65.0 (*d*, $J = 138$, C(5)); 55.9, 55.8, 55.6, 55.3 (4*q*, $J = 143$, 4 *Me*OCH_2); 50.3 (*d*, $J = 132$, C(3)); 49.0 (*t*, $J = 141$, C(5')); 26.0 (*q*, $J = 125$, *Me*$_3$CSi), 18.1 (*s*, Me$_3$*C*Si); −3.8, −4.1 (2*q*, $J = 119$, Me_2Si). CI-MS (NH_3): 568 (12, $[M + 1]^+$), 522 (30), 460 (5), 336 (4), 190 (82), 158 (13), 114 (31), 75 (100). Anal. calc. for $C_{25}H_{49}NO_{11}Si$ (567.749): C 52.89, H 8.70, N 2.47; found: C 52.95, H 8.74, N 2.48.

*(±)-1,4-Anhydro-3-[{(1'*SR*)1',2'-anhydro-5'-azido-5'-deoxy-3',4'-bis-*O-*(methoxymethyl)-*LD-*ribitol-1'-C-yl]-3-deoxy-2,6-bis-*O-*(methoxymethyl)-α-*DL-*galactopyranose* (**90**). A mixture of **88** (262 mg, 0.38 mmol), anh. THF (5 ml), and 1M Bu_4NF in THF (0.76 ml, 0.76 mmol) was stirred at 20° for 10 min. The solvent was evaporated and the residue purified by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**90**) 0.13, *Pancaldi*): 175 mg (96%) of **90**. Colorless oil. IR (film): 3455, 2940, 2105, 1635, 1445, 1150, 1110, 1040, 920, 870. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.57 (*d*, $^3J(1,2) = 2.2$, H–C(1)); 4.79 (*d*, $^2J = 6.8$, 1 H), 4.74 (*d*, $^2J = 6.8$, 1 H), 4.70 (*d*, $^2J = 6.7$, 1 H), 4.68 (*s*, 2 H), 4.63 (*d*, $^2J = 6.7$, 1 H), 4.60 (*s*, 2 H, 4 MeOCH_2); 4.54 (br. *s*, H–C(4)); 4.06 (*dd*, $^3J(2,3) = 2.5$, $^3J(2,1) = 2.2$, H–C(2)); 3.96 (*ddd*, $^3J(4',5'a) = 7.5$, $^3J(4',5'b) = 4.9$, $^3J(4',3') = 2.6$, H–C(4')); 3.94 (*dd*, $^3J(5,6b) = 7.8$, $^3J(5,6a) = 5.4$, H–C(5)); 3.62 (*dd*, $^3J(3',2') = 8.4$, $^3J(3',4') = 2.6$, H–C(3')); 3.60 (*dd*, $^2J = 11.8$, $^3J(5'a,4') = 7.5$, H–C(5')); 3.47 (*dd*, $^2J = 11.8$, $^3J(5'b,4') = 4.9$, H_b–C(5')); 3.45 (*dd*, $^2J = 9.8$, $^3J(6a,5) = 5.4$, H_a–C(6)); 3.42, 3.39, 3.37, 3.34 (4*s*, 4 *Me*OCH_2); 3.38 (*dd*, $^2J = 9.8$, $^3J(6b,5) = 7.8$, H_b–C(6)); 3.17 (*dd*, $^3J(2',3') = 8.4$, $^3J(2',1') = 3.8$, H–C(2')); 3.03 (*dd*, $^3J(1',3) = 9.7$, $^3J(1',2') = 3.8$, H–C(1')); 1.74 (*dd*, $^3J(3,1') = 9.7$, $^3J(3,2) = 2.5$, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 100.0 (*d*, $J = 181$, C(1)); 96.9, 96.5, 96.2, 95.8 (*t*, $J = 163$, 4 MeOCH_2); 82.5 (*d*, $J = 147$), 80.4 (*d*, $J = 163$), 77.8 (*d*, $J = 146$), 77.7 (*d*, $J = 150$), 73.6 (*d*, $J = 144$, C(2), C(4), C(5), C(3'), C(4')); 67.5 (*t*, $J = 144$, C(6)); 57.7 (*d*, $J = 175$), 56.3 (*d*, $J = 177$, C(1'), C(2')); 55.8, 55.7, 55.6, 55.2 (4*q*, $J = 142$, 4 *Me*OCH_2); 51.2 (*t*, $J = 143$, C(5')); 45.2 (*d*, $J = 137$, C(3)). CI-MS (NH_3): 498 (42, $[M + 19]^+$), 497 (100, $[M + 18]^+$), 454 (8), 421 (5), 395 (4), 169 (3), 123 (6), 81 (13), 74 (13). Anal. calc. for $C_{19}H_{33}N_3O_{11}$ (479.483): C 47.59, H 6.94, N 876; found C 47.43, H 7.04, N 8.73.

*(±)-1,4-Anhydro-3-deoxy-3-[(1'*SR*)-2',5'-dideoxy-2',5'-imino-3',4'-*O-*(methoxymethyl)-β-*DL-*arabinitol-1'-C-yl]-2,6-bis-*O-*(methoxymethyl)-α-*DL-*galactopyranose* (**91**). A mixture of **90** (43 mg, 0.090 mmol), anh. MeOH (1.5 ml), $HCOONH_4$ (28 mg, 0.45 mmol), and 5% Pd/C (19 mg, 0.009 mmol) was agitated vigourously at 20° for 20 h. The catalyst was filtered off (*Celite*) and rinsed with AcOEt (3 × 10 ml). The solvent was evaporated and the residue purified by FC (SiO_2, CH_2Cl_2/MeOH 95:5; R_f (**91**) 0.20, *Pancaldi*): 27 mg (65%) of **91**. Colorless oil. IR (film): 3425, 2940, 1650, 1445, 1155, 1035, 920, 805. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.52 (*d*, $^3J(1,2) = 2.3$, H–C(1)); 4.83 (*d*, $^2J = 6.7$, 1 H), 4.80 (*d*, $^2J = 6.7$, 1 H), 4.74–4.59 (*m*, 6 H, 4 MeOCH_2); 4.46 (br. *s*, H–C(4)); 4.30 (*dd*, $^3J(3',4') = 7.2$, $^3J(3',2') = 4.4$, H–C(3')); 4.17 (*ddd*, $^3J(4',3') = 7.2$, $^3J(4',5'b) = 4.3$, $^3J(4',5'a) = 3.6$,

H–C(4')); 4.07 (*dd*, $^3J(2,3) = 2.6$, $^3J(2,1') = 2.3$, H–C(2)); 3.98 (*dd*, $^3J(5,6b) = 7.7$, $^3J(5,6a) = 5.3$, H–C(5)); 3.85 (*dd*, $^3J(1',3) = 9.4$, $^3J(1',2') = 0.8$, H–C(1')); 3.47 (*dd*, $^2J = 10.1$, $^3J(6a,5) = 5.3$, H_a–C(6)); 3.41, 3.40, 3.38, 3.35 (4*s*, 4 *Me*OCH$_2$); 3.41–3.35 (*m*, H–C(2'), H_b–C(6)); 3.15 (*dd*, $^2J = 12.2$, $^3J(5'a,4') = 3.6$, H_a–C(5')); 2.93 (*dd*, $^2J = 12.2$, $^3J(5'b,H–C(4')) = 4.3$, H_b–C(5')); 1.89 (*dd*, $^3J(3,1') = 9.4$, $^3J(3,2) = 2.6$, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 100.5 (*d*, $J = 181$, C(1)); 196.7, 96.6, 96.1, 96.0 (*t*, $J = 163$, 4 MeO*C*H$_2$); 81.5 (*d*, $J = 157$), 79.9 (*d*, $J = 157$), 78.2 (*d*, $J = 166$), 78.1 (*d*, $J = 154$), 76.6 (*d*, $J = 144$), 68.3 (*d*, $J = 144$, C(2), C(4), C(5), C(1'), C(3'), C(4')); 67.5 (*t*, $J = 144$, C(6)); 59.7 (*d*, $J = 135$, C(2')); 56.1, 55.8, 55.7, 55.3 (4*q*, $J = 142$, 4 *Me*OCH$_2$); 50.2 (*d*, $J = 135$, C(3)); 49.2 (*t*, $J = 143$, C(5')). CI-MS (NH_3): 454 (14, $[M + 1]^+$), 422 (13), 408 (44), 346 (9), 286 (5), 190 (100), 158 (11), 114 (32), 81 (19). Anal. calc. for $C_{19}H_{35}NO_{11}$ (453.483): C 50.32, H 7.78; found: C 50.17, H 7.85.

*(±)-1,4-Anhydro-3-deoxy-{(1'*SR*)-2',5'-dideoxy-2',5'-imino-3',4'-bis*-O-*(methoxymethyl)*-α-DL-*arabinitol-1'*-C-*yl}-2,6-bis*-O-*(methoxymethyl)*-α-DL-*galactopyranose* (**92**). As described for **89**, with **87** (346 mg, 0.50 mmol) in anh. MeOH (6 ml); heating with K_2CO_3 in anh. DMF to 50° for 20 h. Then, addition of 1M Bu_4NF (0.8 ml, 0.8 mmol) and stirring for 20 min at 20°. FC (SiO_2, AcOEt/MeOH 9:1; R_f (**92**) 0.15, *Pancaldi*): 181 mg (80%) of **92**. Colorless oil. IR (film): 3485, 2945, 2895, 1640, 1445, 1150, 1115, 1045, 915. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.48 (*d*, $^3J(1,2) = 2.2$, H–C(1)); 4.80–4.56 (*m*, 4 MeOCH_2, H–C(4)); 4.22 (*dd*, $^3J(3',2') = 4.4$, $^3J(3',2') = 4.2$, H–C(3')); 4.22 (*ddd*, $^3J(4',5'a) = 8.0$, $^3J(4',5'b) = 7.4$, $^3J(4',3') = 4.2$, H–C(4')); 4.11 (*dd*, $^3J(2,3) = 3.5$, $^3J(2,1) = 2.2$, H–C(2)); 3.93 (*dd*, $^3J(5,6b) = 7.9$, $^3J(5,6a) = 5.1$, H–C(5)); 3.92 (*dd*, $^3J(1',2') = 8.9$, $^3J(1',3) = 4.7$, H–C(1')); 3.41–3.27 (*m*, 2 H–C(6), 4 *Me*OCH$_2$); 3.17 (*dd*, $^2J = 10.9$, $^3J(5'b,4') = 7.4$, H_b–C(5')); 3.13 (*dd*, $^3J(2',1') = 8.9$, $^3J(2',3') = 4.4$, H–C(3)); 2.94 (*dd*, $^2J = 10.9$, $^3J(5'a,4') = 8.0$, H_a–C(5')); 1.96 (*dd*, $^3J(3,1') = 4.7$, $^3J(3,2) = 3.5$, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 100.0 (*d*, $J = 181$, C(1)); 97.7, 96.7, 96.5, 96.0 (4*t*, $J = 164$, MeO*C*H$_2$); 81.0 (*d*, $J = 166$), 80.8 (*d*, $J = 148$), 78.6 (*d*, $J = 154$), 77.8 (*d*, $J = 148$), 70.6 (*d*, $J = 145$, C(2), C(4), C(5), C(1'), C(3), C(4')); 67.8 (*t*, $J = 143$, C(6)); 61.9 (*d*, $J = 135$, C(2')); 56.0, 55.7, 55.5, 55.2 (4*q*, $J = 142$, 4 *Me*OCH$_2$); 49.1 (*d*, $J = 131$, C(3)); 48.5 (*t*, $J = 138$, C(5')). CI-MS (NH_3): 454 (5, $[M + 1]^+$), 422 (14), 408 (58), 346 (12), 284 (62), 190 (100), 158 (16), 114 (41), 82 (38). Anal. calc. for $C_{19}H_{35}NO_{11}$ (453.483): C 50.32, H 7.78, N 3.09; found: C 50.27, H 7.88, N 3.11.

*(±)-1,4-Anhydro-3-[(1'*SR*)-1',2'-anhydro-5'-azido-5'-deoxy-3',4'-bis*-O-*(methoxymethyl)*-DL-*arabinitol-1'*-C-*yl]-3-deoxy-2,6-bis*-O-*(methoxymethyl)*-α-DL-*galactopyranose* (**93**). A mixture of **87** (353 mg, 0.51 mmol), anh. THF (6 ml), and 1M Bu_4NF in THF (1 ml, 1 mmol) was stirred at 20° for 10 min under Ar. The solvent was evaporated and the residue purified by FC (SiO_2, AcOEt/light petroleum ether 1:2; R_f (**93**) 0.11, *Pancaldi*): 234 mg (96%) of **93**. Colorless oil. IR (film): 3440, 2945, 2105, 1645, 1445, 1150, 1105, 1035, 920, 865. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.55 (*d*, $^3J(1,2) = 2.4$, H–C(1)); 4.91 (*d*, $^2J = 6.5$, 1 H), 4.77 (*d*, $^2J = 6.9$, 1 H), 4.73 (*d*, $^2J = 6.7$, 1 H), 4.70 (*d*, $^2J = 6.9$, 1 H), 4.65 (*d*, $^2J = 6.7$, 1 H), 4.64 (*d*, $^2J = 6.5$, 1 H), 4.58 (*s*, 2 H, 4 MeOCH_2); 4.51 (br. *s*, H–C(4)); 4.07 (*dd*, $^3J(2,3) = 2.5$, $^3J(2,1) = 2.4$, H–C(2)); 3.96 (*dd*, $^3J(5,6b) = 8.2$, $^3J(5,6a) = 5.2$, H–C(5)); 3.74 (*ddd*, $^3J(4',3') = 7.4$, $^3J(4',5'b) = 3.8$, $^3J(4',5'a) = 3.0$, H–C(4')); 3.71 (*dd*, $^3J(3',2') = 8.4$, $^3J(3',4') = 7.4$, H–C(3')); 3.64 (*dd*, $^2J = 13.2$, $^3J(5'a,4') = 3.0$, H_a–C(5')); 3.47 (*dd*, $^2J = 13.2$, $^3J(5'b,4') = 3.8$, H_b–C(5')); 3.45 (*dd*, $^2J = 9.9$, $^3J(6a,5) = 5.2$, H_a–C(6)); 3.41, 3.40, 3.38, 3.32 (4*s*, 4 *Me*OCH$_2$); 3.37 (*dd*, $^2J = 9.9$, $^3J(6b,5) = 8.2$, H_b–C(6)); 3.10 (*dd*, $^3J(2',3') = 8.4$, $^3J(2',1') = 4.1$, H–C(2')); 2.98 (*dd*, $^3J(1',3) = 9.9$, $^3J(1',2') = 4.1$, H–C(1')); 1.71 (*dd*, $^3J(3,1') = 9.9$, $^3J(3,2) = 2.5$, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 100.0 (*d*, $J = 183$, C(1)); 96.4, 96.2, 95.9 (3*t*, $J = 164$, 4 MeO*C*H$_2$); 82.2 (*d*, $J = 149$), 80.4 (*d*, $J = 163$), 77.5 (*d*, $J = 156$), 76.4 (*d*, $J = 138$), 73.6 (*d*, $J = 146$, C(2), C(4), C(5), C(3'), C(4')); 67.2 (*t*, $J = 144$, C(6)); 59.6 (*d*, $J = 172$)); 56.7 (*d*, $J = 175$, C(1'), C(2')); 55.9, 55.6, 55.1 (3*q*, $J = 142$, 4 *Me*OCH$_2$); 50.1 (*t*, $J = 143$, C(5')); 45.8 (*d*, $J = 137$, C(3)). CI-MS (NH_3): 498 (9, $[M + 19]^+$), 498 (100, $[M + 18]^+$), 454 (4), 420 (20), 394 (2), 280 (2), 169 (4), 123 (6), 81 (18). Anal. calc. for $C_{19}H_{33}N_3O_{11}$ (479.483): C 47.59, H 6.94, N 8.76; found: C 47.65, H 6.85, N 8.79.

*(±)-1,4-Anhydro-3-deoxy-3-[(1'*SR*)-2',5'-dideoxy-2',5'-imino-3',4'-bis*-O-*(methoxymethyl)*-β-DL-*ribitol-1'*-C-*yl]-2,6-bis*-O-*(methoxymethyl)*-α-DL-*galactopyranose* (**94**). A mixture of **93** (237 mg, 0.494 mmol), anh. MeOH (6 ml), $HCOONH_4$ (93 mg, 1.48 mmol), and 5% Pd/C (210 mg, 0.10 mmol) was agitated vigourously at 20° for 4 h. The catalyst was filtered off over *Celite* and rinsed with AcOEt (3 × 40 ml). The solvent was evaporated and the residue purified by FC (SiO_2, AcOEt/MeOH 9:1; R_f (**94**) 0.09, *Pancaldi*): 165 mg (74%) of **94**. Colorless oil. IR (film): 3430, 2945, 2825, 1645, 1445, 1215, 1150, 1040, 915, 875. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.48 (*d*, $^3J(1,2) = 2.3$, H–C(1)); 4.75–4.67 (*m*, 6 H), 4.59–4.56 (*m*, 2 H, 4 MeOCH_2); 4.44 (br. *s*, H–C(4)); 4.10 (*ddd*, $^3J(4',3') = 7.9$, $^3J(4',5'b) = 3.4$, $^3J(4',5'a) = 1.9$, H–C(4')); 4.03 (*dd*, $^3J(3',4') = 7.9$, $^3J(3',2') = 4.2$, H–C(3')); 3.97 (*dd*, $^3J(2,3) = 2.7$, $^3J(2,1) = 2.3$, H–C(2)); 3.88 (*dd*, $^3J(5,6b) = 8.2$, $^3J(5,6a) = 5.1$, H–C(5)); 3.46 (*dd*, $^3J(1',3) = 9.1$, $^3J(1',2') = 0.8$, H–C(1')); 3.43 (*dd*, $^2J = 10.0$, $^3J(6a,5) = 5.1$, H_a–C(6)); 3.41–3.31 (*m*, *Me*OCH$_2$, H–C(2'), H_b–C(6)); 3.16 (*dd*, $^2J = 12.6$, $^3J(5'a,4') = 1.9$, H_a–C(5')); 2.94 (*dd*, $^2J = 12.6$, $^3J(5'b,4') = 3.4$, H_b–C(5')); 1.72 (*dd*, $^3J(3,1') = 9.1$, $^3J(3,2) = 2.7$, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$):

100.2 (*d*, J = 180, C(1)); 96.7, 96.6, 95.9 (3*t*, J = 163, 4 MeO*C*H$_2$); 82.2 (*d*, J = 148), 79.5 (*d*, J = 146), 79.2 (*d*, J = 145), 78.0 (*d*, J = 160), 76.6 (*d*, J = 148), 69.5 (*d*, J = 146, C(2), C(4), C(5), C(1'), C(3'), C(4')); 67.7 (*t*, J = 144, C(6)); 61.3 (*d*, J = 139, C(2')); 55.7, 55.6, 55.2 (3*q*, J = 142, 4 *Me*OCH$_2$); 52.0 (*d*, J = 133, C(3)); 50.2 (*t*, J = 140, C(5')). CI-MS (NH_3): 454 (17, $[M + 1]^+$), 422 (6), 408 (17), 346 (14), 286 (2), 220 (9), 190 (100), 158 (12), 114 (33), 81 (19). Anal. calc. for $C_{19}H_{35}NO_{11}$ (453.483): C 50.32, H 7.78, N 3.09; found: C 50.38, H 7.78, N 3.06.

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