

SYNTHESIS OF (1→3)-C AND HOMO(1→3)-C-LINKED IMINO-DISACCHARIDES STARTING FROM LEVOGLUCOSENONE AND ISOLEVOGLUCOSENONE

Christian Marquis,^{a,b)} Francesca Cardona,^{a,c)} Inmaculada Robina,^{d)} Gaby Wurth^{a,e)}, and Pierre Vogel^{a,*}

^{a)} Section de Chimie de l'Université de Lausanne, BCH, CH-1015 Lausanne-Dorigny, Switzerland, Fax +41 21 692 39 75; e-mail: pierre.vogel@ico.unil.ch

^{d)} Departamento de Química Orgánica, Universidad de Sevilla, Apartado 557, E - 41071 Sevilla, Spain

Dedicated to Professor James P. Kutney on the occasion of his 70th birthday

Abstract - The reaction of 2,5-(benzyloxycarbonyl)imino-2,5-dideoxy-3,4-*O*-isopropylidene-L-ribose ((-)-**15**) with levoglucosenone (**5**) in the presence of Et₂AlI gave a 3,4-dideoxy-D-*glycero*-hex-3-enopyranos-2-ulose derivative ((-)-**16**) that was converted into the (1→3)-C-linked imino-disaccharide: methyl 3,4-dideoxy-3-[(1'S)-2',5'-dideoxy-2',5'-imino-D-*ribitol*-1'-C-yl)-α-D-*lyxo*-hexopyranoside ((+)-**22**). The addition of benzyl alcohol to isolevoglucosenone (**3**), followed by cross-aldol condensation with 3,6-[*tert*-butoxycarbonyl]imino-2,3,6-trideoxy-4,5-*O*-isopropylidene-L-*arabino*-hexose ((+)-**30**) generated, after water elimination, a single enone ((+)-**31**) that was converted into a homo-(1→3)-C-linked imino-disaccharide: 3-deoxy-3-(1',2',3',6'-tetra-deoxy-3',6'-imino-L-*arabino*-hexitol-1'-C-yl)-β-D-galactofuranose (**44**).

^{b)} Actual address: Calbiochem-Novabiochem AG, Weidenmattenweg 44, CH - 4448 Läufelfingen, Switzerland

^{c)} Actual address: Dipartimento de Chimica Organica "Ugo Schiff", Università di Firenze, via G. Capponi 9, I - 50121 Firenze, Italy

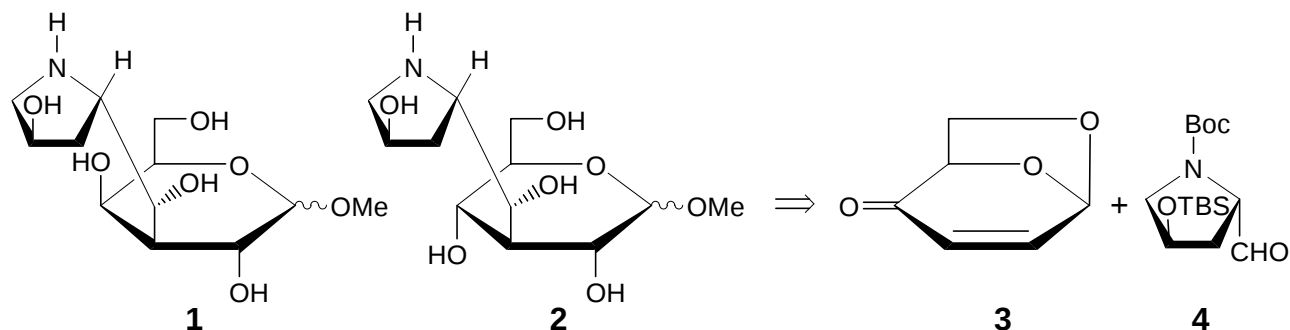
^{e)} Exchange student from the Albert-Ludwigs-Universität, Freiburg im Breisgau, Germany

INTRODUCTION

Carbohydrate mimics are potentially useful molecular tools for biology¹ and may become leads for drug discovery.² In particular, C-linked disaccharides and oligosaccharides containing them offer the advantage of being resistant to acidic and enzymatic hydrolysis.³ They are potential inhibitors of glycosidases and glycosyltransferases.^{4,5} They represent non-hydrolyzable sugar epitopes.⁶ Inhibitors of glycosidases and glycosyltransferases are potential antibacterial, antiviral, antimetastatic, antidiabetes, antihyperglycemic, antiadhesive, or immunostimulatory agents.⁷ A new class of selective glycosidase inhibitors has emerged, namely C-linked imino-disaccharides (aza-C-disaccharides),^{8,9} which contains not only the steric and charge information of the glycosyl moiety liberated during the enzyme-catalyzed hydrolysis, but also that of the "aglycone". 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 CH₂ unit) was prepared by Johnson and co-workers.¹⁰ Other examples of "linear" C-linked imino-disaccharides were obtained by the groups of Martin¹¹ and van Boom.¹² We have prepared the first examples of "branched" imino-C-disaccharides.^{8,13} Further examples were reported by Johnson and co-workers⁹ and by our group.^{14,15} Brandi and co-workers¹⁶ have obtained the first examples of (1→2)-linked pseudo imino-C-disaccharides in which a 2,3-dihydropyrrolidine or a 2-hydropyrrolidine is linked at C-2 of D-glucose *via* a single C-C bond.

In a recent note^{14a} we have shown that methyl 3-deoxy-3-[(1'*R*)-2',3',5'-trideoxy-2',5'-imino-L-*erythro*-pentitol-1'-C-yl]-D-galacto- (**1**) and -D-glucopyranosides (**2**) can be derived readily from the aldol type condensate of the 1,4-adduct of benzyl alcohol to isolevoglucosenone (**3**)¹⁷ and aldehyde (**4**) (Scheme 1).

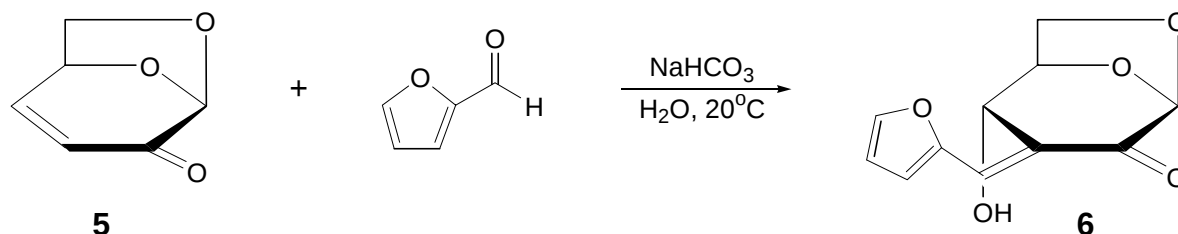
Scheme 1



Since levoglucosenone (**5**) is more readily available¹⁸ than isolevoglucosenone (**3**) we have explored the possibility to use it to construct (1→3)-C-linked imino-disaccharides following our approach.^{14,19} As we shall see, isolevoglucosenone is more successful than levoglucosenone in the sequence of reactions: 1,4-addition to the enone $\Rightarrow$ enolate intermediate + aldehyde $\Rightarrow$ cross aldolization. Levoglucosenone has been used as starting material in the synthesis of a large number of compounds of biological interest

including the pheromone serricornine,²⁰ methyl dihydroepijasmonate,^{21a} D-altrose,^{21b} C-disaccharides²² and thio-linked disaccharides.²³ Isobe and co-workers²⁴ have reported that levoglucosenone can be condensed with furfural giving enone (**6**).

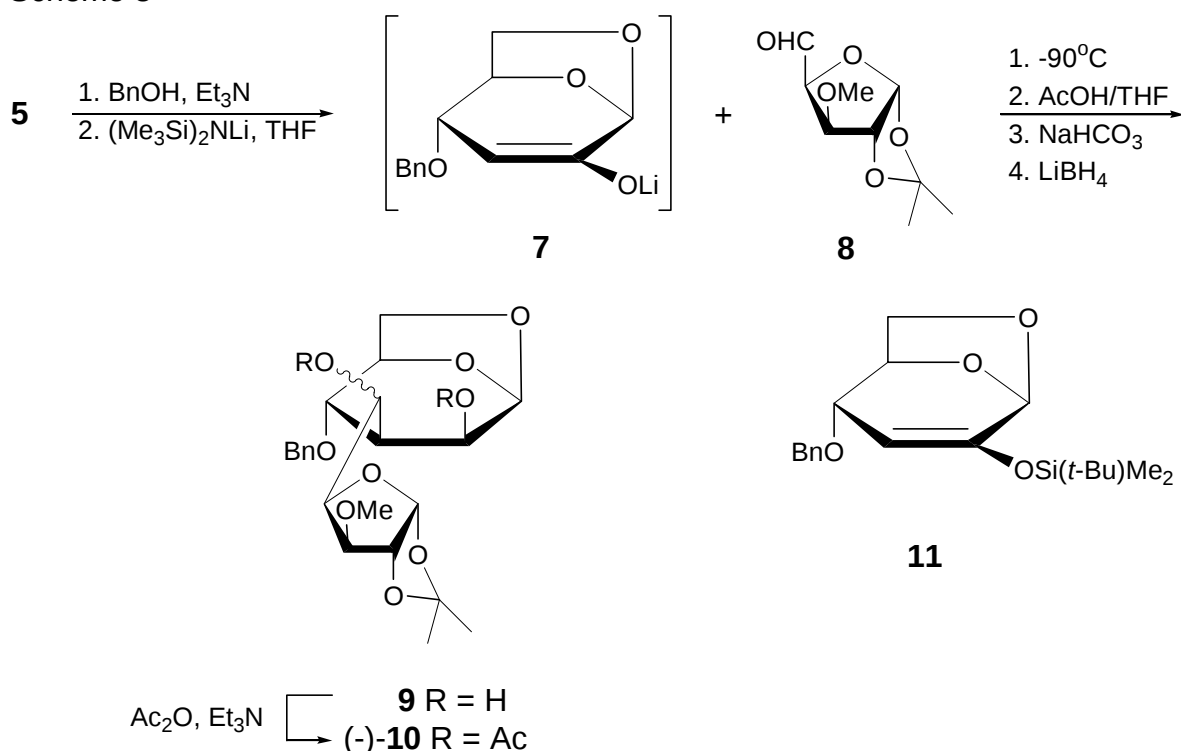
Scheme 2



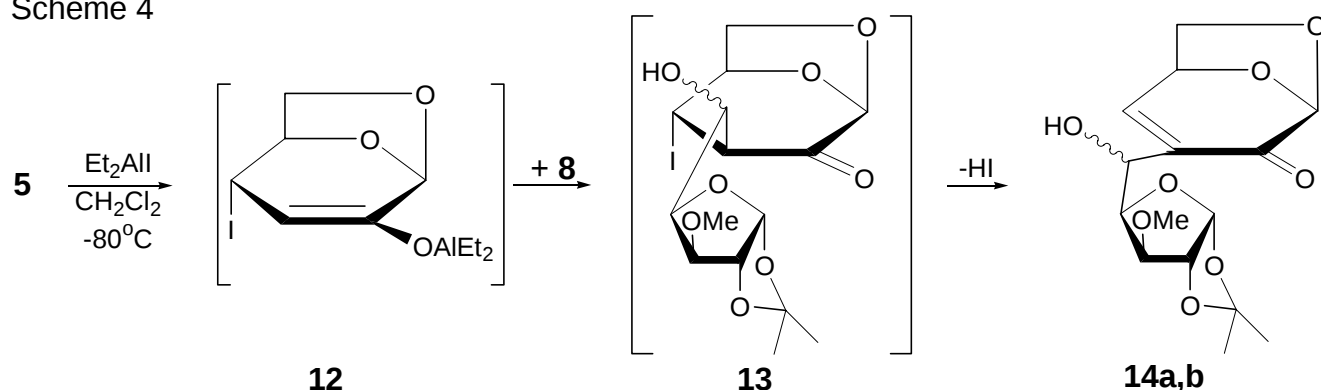
Exploratory studies.

In one of our exploratory experiments we condensed the lithium enolate (**7**) (derived from the adduct of benzyl alcohol to **5**²⁵) with the commercially available aldehyde (**8**). This produced a mixture of unstable products that could not be isolated. Thus the lithium aldolate intermediate was neutralized and the aldol was directly reduced with LiBH_4 at -95°C . After acetylation, diacetate (**10**) was obtained with a yield that never surpassed 8% (Scheme 3). Attempts to carry out Mukaiyama cross-aldol reaction²⁶ with enoxy silane (**11**) and aldehyde (**8**) all failed. Finally, we found that the addition of Et_2AlI (1M in hexane) to a 1:1 mixture of **5** and **8** (CH_2Cl_2 , -80°C) gave a 7:3 mixture of aldols that were not isolated but reduced directly with LiBH_4 to furnish a 7:3 mixture of allylic alcohols (**14a**) and (**14b**) in 58% yield (Scheme 4).

Scheme 3

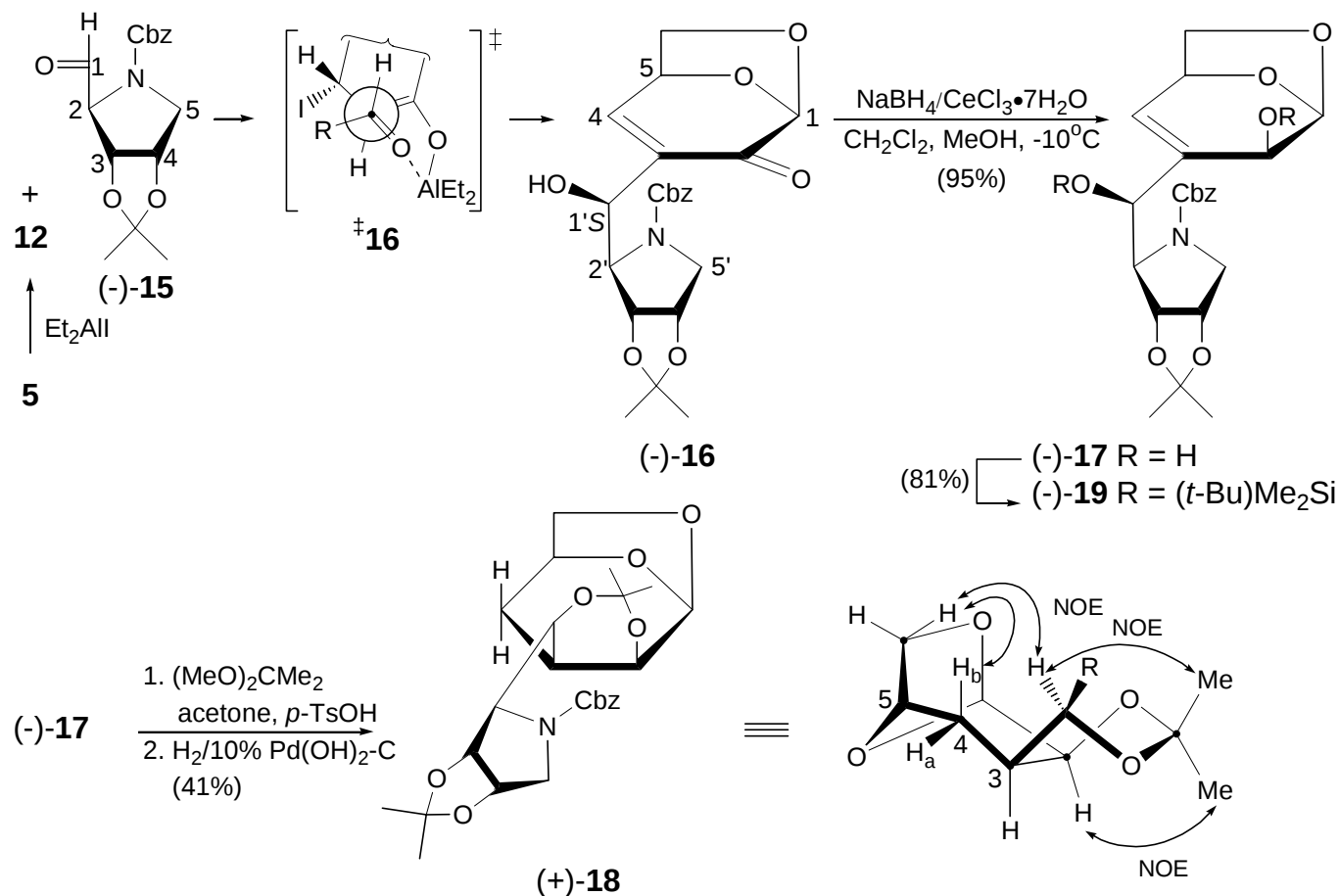


Scheme 4



Synthesis of a (1→3)-C-linked imino-disaccharide from levoglucosenone.

Under the same conditions as those of Scheme 4, the semi-protected 2,5-dideoxy-2,5-imino-L-ribose derivative ((-)-**15**)²⁷ was condensed with levoglucosenone (**5**) giving a single product ((-)-**16**) in 38% yield (Baylis-Hillmann type of condensation,²⁸ or Oshima-Nozaki type of condensation²⁹). The (1*S*)-configuration of (-)-**16** was expected for an aldol reaction occurring on the less sterically hindered face of enolate (**12**) and following the Zimmerman-Traxler model³⁰ (closed transition structure $\ddagger$ **16**).¹⁹ It was proven by the ^1H -NMR data, including the 2D-NOESY- ^1H -NMR spectrum of acetonide ((+)-**18**) obtained in the following way. Enone ((-)-**16**) was reduced selectively under Luche's conditions³¹ into diol ((-)-**17**) (95% yield). Treatment of (-)-**17** with 2,2-dimethoxypropane, acetone and *p*-toluenesulfonic

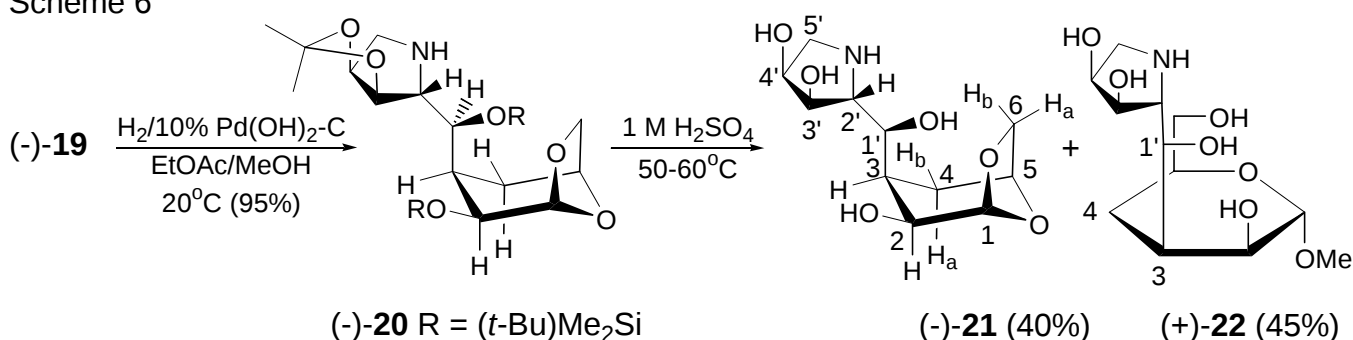


acid provided an acetonide that was hydrogenated into (+)-**18** (Scheme 5). Its ^{13}C -NMR spectrum displayed two signals for the acetonide at $\delta_{\text{H}}(\text{Me}) = 27.6$ and 27.2 ppm typical for an average twist boat conformation of the 1,3-dioxane moiety.³² This hypothesis was confirmed by the observation of typical coupling constants in the ^1H -NMR spectrum of (+)-**18** such as $^3J(\text{H-C}(1'),\text{H-C}(3)) = 11.0$ Hz, $^3J(\text{H-C}(2),\text{H-C}(3)) = 8.3$ Hz, $^3J(\text{H}_b\text{-C}(4),\text{H-C}(3)) = 9.1$ Hz, $^3J(\text{H}_a\text{-C}(4),\text{H-C}(3)) \cong 0$ Hz, $^3J(\text{H}_a\text{-C}(4),\text{H-C}(5)) = 5.2$ Hz and $^3J(\text{H}_b\text{-C}(4),\text{H-C}(5)) \approx 0$ Hz (Scheme 5).

Protection of diol ((-)-**17**) with $(t\text{-Bu})\text{Me}_2\text{SiOSO}_2\text{CF}_3$ and 2,6-lutidine (CH_2Cl_2 , -78°C) as disilyl ether ((-)-**19**) (81% yield), followed by hydrogenation ($\text{Pd}(\text{OH})_2\text{-C}$) provided (-)-**20** (95% yield). Ring opening of the anhydroaldose was a relatively difficult reaction as 1 M H_2SO_4 in methanol and heating to 50–60°C was required to observe a slow methanolysis leading to an equilibrium of (-)-**21** and (+)-**22** that were isolated in 40 and 45% yields, respectively (Scheme 6).

Attempts to run the methanolysis at lower temperature with other acids (e.g.: SOCl_2 , CuCl_2 , HCl , $p\text{-TsOH}$, amberlite-H^+) led to degradation without improving the yield for (+)-**22** (Scheme 5).

Scheme 6



The structures of (-)-**21** and (+)-**22** were deduced from their spectral data, including 2D-NOESY ^1H -NMR data. As for the hydrogenation of the ene-acetonide derived from (-)-**17** (Scheme 5), the less sterically hindered α face is favored for the alkene hydrogenation of (-)-**19**. The most probable conformation of the imino-C-disaccharide ((+)-**22**) in D_2O is shown in Figure 1. The twist boat conformation of the 4-deoxy-D-lyxo-hexopyranoside moiety is given by the observation of coupling constants $^3J(\text{H-C}(3),\text{H}_a\text{-C}(4)) = 4.3$ Hz, $^3J(\text{H-C}(3),\text{H}_e\text{-C}(4)) = 10.8$ Hz, $^3J(\text{H}_e\text{-C}(4),\text{H-C}(5)) = 3.4$ Hz and $^3J(\text{H}_a\text{-C}(4),\text{H-C}(5)) = 9.7$ Hz. As expected for numerous C-linked disaccharides^{33,34} and methyl 3-deoxy-3-C-[(1'R)-2',6',7'-trideoxy-2',6'-imino- β -D-glycero-L-manno-heptitol-1'-yl]- α - and β -D-altrofuranoside^{13a} the staggered conformation (A, Figure 1) about bond $\sigma(\text{C}(1'),\text{C}(2'))$ in which the $\sigma(\text{C}(2'),\text{C}(3'))$ and $\sigma(\text{C}(1'),\text{C}(3))$ bonds are nearly antiperiplanar is favored for (+)-**22** ($^3J(\text{H-C}(1'),\text{H-C}(2')) < 1$ Hz). The staggered conformation (B, Figure 1) about bond $\sigma(\text{C}(3),\text{C}(1'))$ in which $\sigma(\text{C}(3),\text{C}(2))$ and $\sigma(\text{C}(1'),\text{C}(2'))$ bonds are nearly antiperiplanar is indicated by $^3J(\text{H-C}(3),\text{H-C}(1')) = 9.1$ Hz. The 2D-NOESY ^1H -NMR

spectrum of (+)-**22** confirmed the proposed "average" conformation shown in Figure 1. In particular, cross-peaks were observed for signal pairs δ_{H} 3.07 ppm (H-C(2'))/1.48 ppm (Ha-C(4)). The ^1H -NMR spectrum of (+)-**22** did not vary with temperature, except for the signal assigned to H-C(1') for which δ_{H} 4.57, 4.52, 4.55, 4.55 and 4.54 ppm at 4°C, 20°C, 40°C, 60°C and 77°C, respectively. Whereas $^3J(\text{H-C}(1'),\text{H-C}(3))$ did not vary between 4° to 77°C, $^3J(\text{H-C}(1'),\text{H-C}(2'))$ remained very small ($< 1\text{Hz}$) between 4 to 40°C and was increased to 1.3 Hz and 2.9 Hz at 60°C and 77°C, respectively. This suggests that a less stable conformer than that shown in Figure 1 is present at equilibrium in water. In the case of methyl 3-deoxy-3-(1',2',6'-trideoxy-2',6'-imino-D-galactitol-1-yl)- α -D-manno-pyranoside adopted two staggered conformations about bond $\sigma(\text{C}(1'),\text{C}(2'))$ of different stabilities, and two staggered conformations about bond $\sigma(\text{C}(3),\text{C}(1'))$ of similar stability.¹⁵

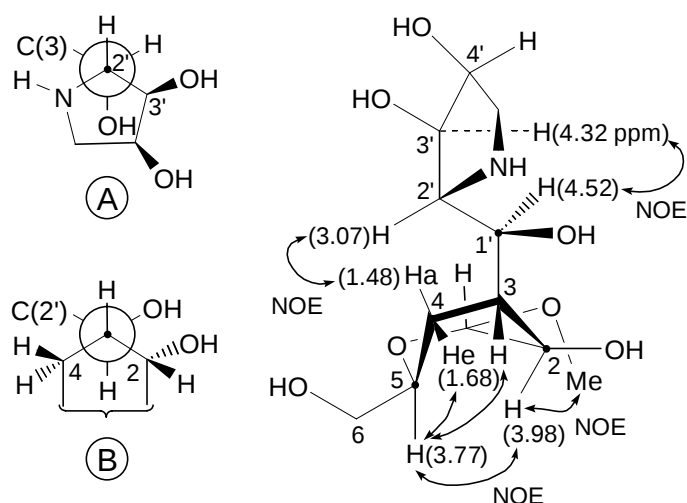
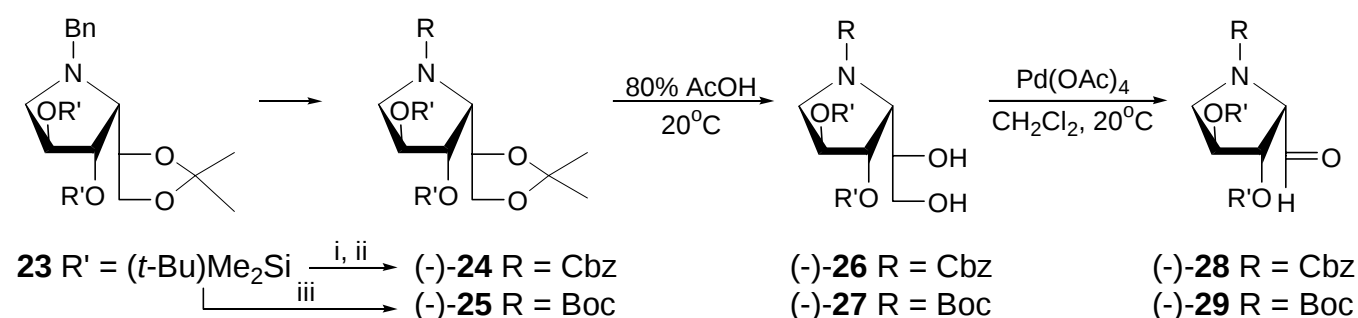


Figure 1. Possible conformation of (+)-**22** in water. The most significant NOE's are indicated.

In order to test the versatility of our method of synthesis of C(1→3) imino-disaccharide we explored the possibility to condense levoglucosenone (**5**) and isolevoglucosenone (**3**) with the semi-protected 2,5-dideoxy-2,5-imino-D-xylose derivatives ((-)-**28**) and ((-)-**29**) that were derived from the known precursor (**23**)²⁷ as shown in Scheme 7.³⁵

Scheme 7



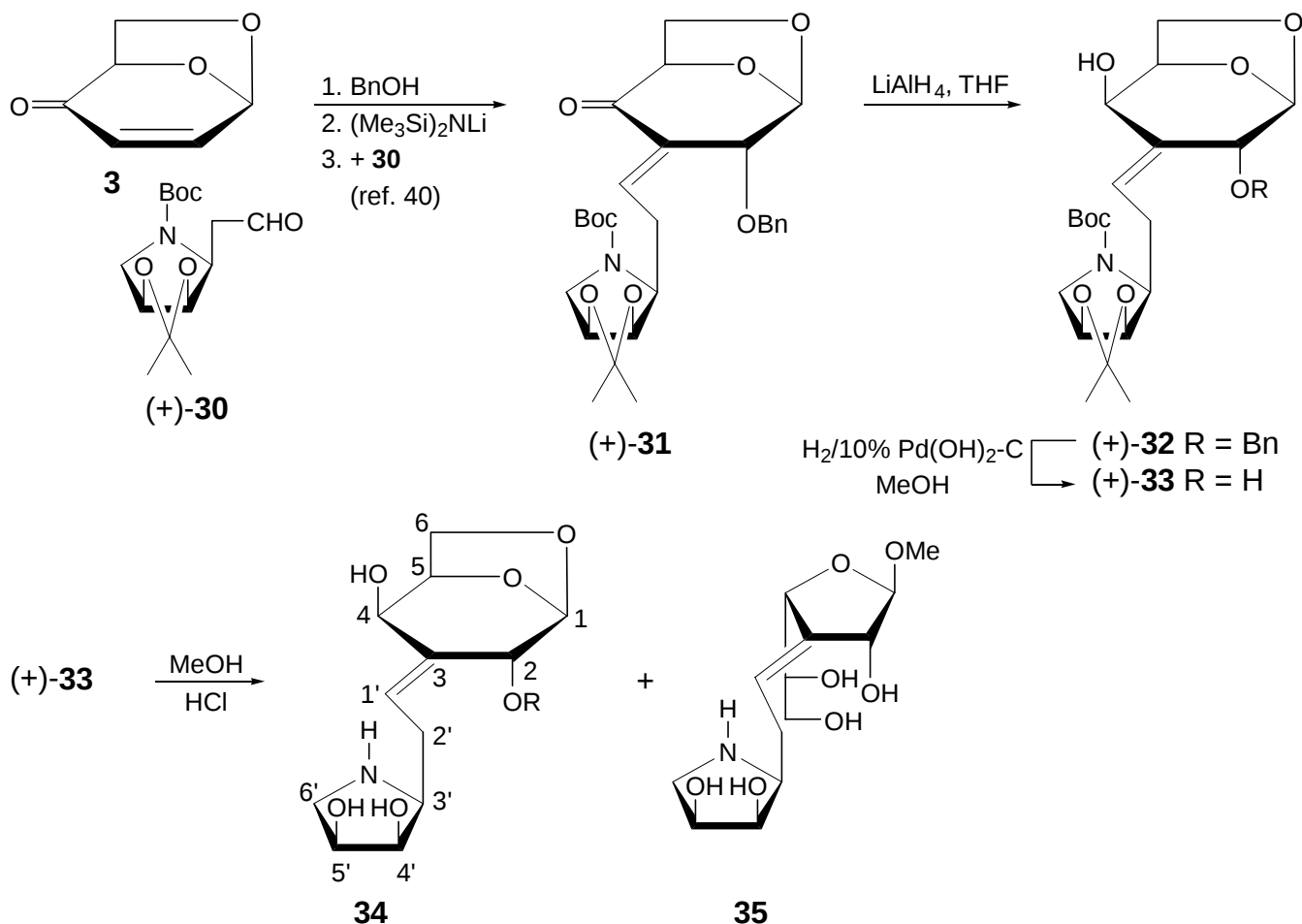
i) $\text{H}_2/10\% \text{ Pd-C}$, ii) BnOCOCI , NaHCO_3 , 50% EtOH, iii) $\text{H}_2/10\% \text{ Pd-C}$, $(\text{Boc})_2\text{O}$, MeOH

Lithium enolates derived from the products of 1,4-addition of benzyl alcohol to **3** and **5** did not add to aldehydes ((-)-**28**) and ((-)-**29**) between -100°C and 20°C (THF). Our attempts to condense **3** and **5** with (-)-**28** and (-)-**29** in the presence of Et₂AlI, with DABCO²⁸ alone or with DABCO + LiClO₄³⁶ were not met with success, only decomposition of the aldehydes was observed. These failures suggest that the 3-silyloxy substituent *syn* with respect to the formyl group of (-)-**28** and (-)-**29** retards, for steric reasons, the nucleophilic additions. This represents a limitation of our method.³⁷

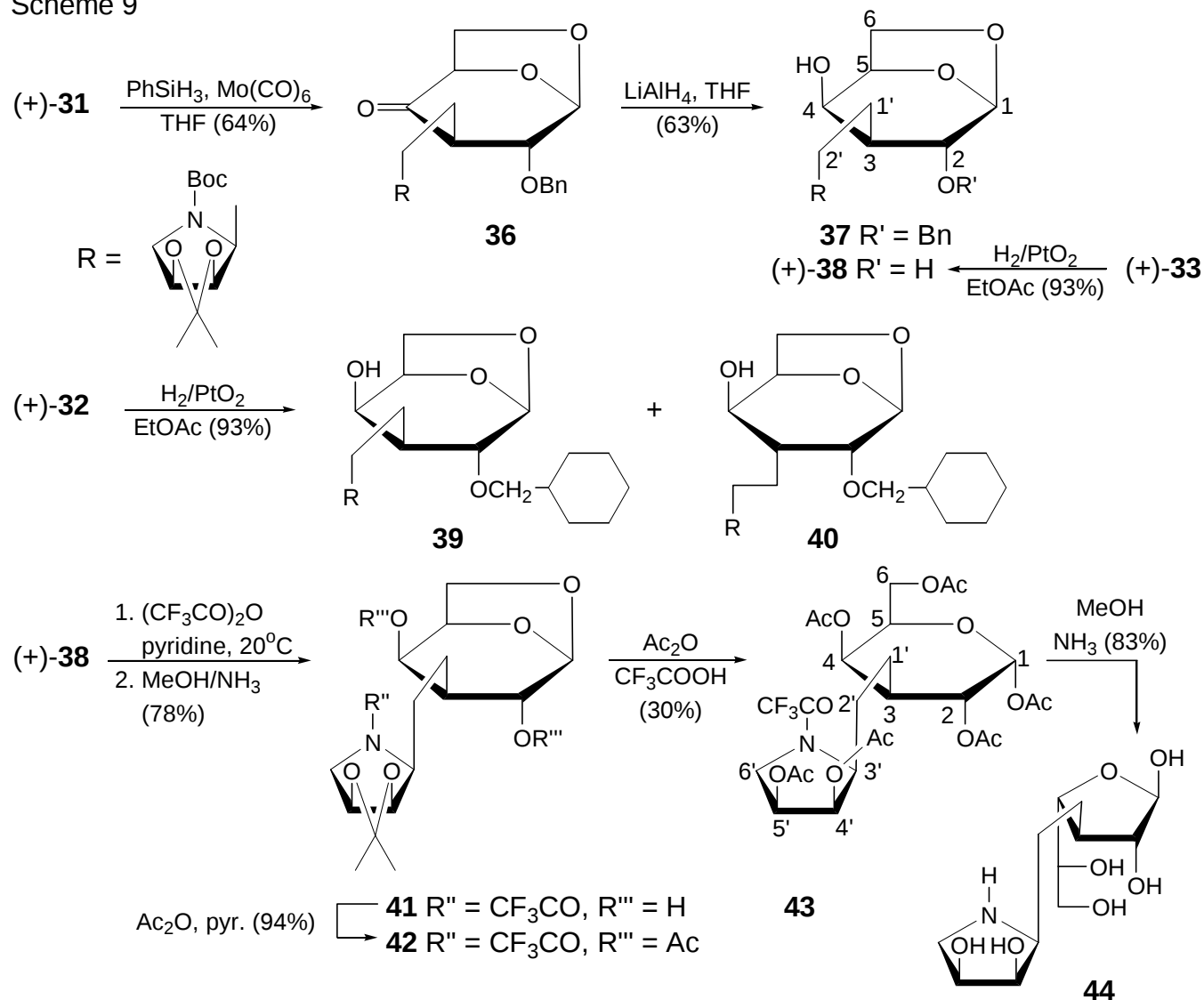
Synthesis of a homo-(1→3)-C-linked imino-disaccharide from isolevoglucosenone.

In the mechanism of the glycosidase-catalyzed hydrolysis of an *O*-disaccharide, the distance between the liberated glycosyl cation intermediate and its "aglycone" partner might be larger than that between the corresponding monosaccharides in the substrate. It is thus possible that homo-C-linked imino-disaccharides, in which iminoalditols are linked to monosaccharides through a two-carbon chain, are better glycosidase inhibitors than the corresponding C-linked imino-disaccharides in which iminoalditols are linked by one carbon linker to monosaccharides. The latter are substrate mimics rather than transition state mimics. In a preliminary note we had demonstrated that the cross-aldol reaction of aldehyde ((+)-**30**) with the 1,4-adduct of benzyl alcohol to isolevoglucosenone generates, after water elimination,

Scheme 8



a single enone ((+)-**31**) that could be reduced with LiAlH_4 into (+)-**32**.³⁹ Hydrogenolysis of (+)-**32** over 10% $\text{Pd}(\text{OH})_2\text{-C}$ provided (+)-**33**.³⁹ Acidic methanolysis of (+)-**33** furnished a 1:1 mixture of methyl (Z)-3-deoxy-3-(1',2',3',6'-tetra-deoxy-3',6'-imino-L-arabino-hexitol-1'-C-ylidene)- β -D-xylo-hexofuranoside (**35**) and (Z)-1,6-anhydro-3-deoxy-3-(1',2',3',6'-tetra-deoxy-3',6'-imino-L-arabino-hexitol-1'-C-ylidene)- β -



D-xylo-hexopyranose (**34**) (Scheme 8). All our attempts to carry out a cross-aldol reaction between the 1,4-adduct of benzyl alcohol to levoglucosenone and aldehyde (**30**) failed to give the expected aldol or the corresponding enones resulting from water, or benzyl alcohol eliminations.³⁷ This suggests again that isolevoglucosenone (**3**) is a better template than the more readily available levoglucosenone (**5**) for our syntheses of C-linked disaccharides. In order to convert enone ((+)-**31**) into a yet unknown homo-C-linked imino-disaccharide we reduced it first with PhSiH_3 in the presence of $\text{Mo}(\text{CO})_6$ (THF, reflux).⁴⁰ This furnished ketone (**36**) (64%) that was reduced on its turn with LiAlH_4 in THF giving alcohol (**37**) (63% yield). Hydrogenolysis ($\text{H}_2/10\% \text{ Pd}(\text{OH})_2\text{-C}$) of the benzyl ether of **37** delivered (+)-**38**. Alternatively, (+)-**38** was obtained in one step by hydrogenation ($\text{PtO}_2, \text{EtOAc}$)⁴¹ of allylic alcohol

((+)-**33**). The *galacto* configuration of the anhydrohexose moiety of (+)-**37** was confirmed by its NOESY 2D-¹H-NMR spectrum that showed cross-peaks for $\delta_{\text{H}} = 3.56$ ppm (H-C(2)) and $\delta_{\text{H}} = 1.60$ ppm (H-C(1')). Hydrogenation over platinum catalyst (H₂/PtO₂, EtOAc) of (+)-**32** did not hydrogenolyze its benzyl ether moiety, but generated a 1:1 mixture of cyclohexylmethyl ethers (**39**) and (**40**) that were separated in 33 and 26% yield, respectively.

The ring opening of the anhydrogalactose moiety of (+)-**38** was a difficult operation. Complex mixtures were formed on treatment of (+)-**38** with trifluoroacetic acid in MeOH at 85°C or with anhydrous MeOH saturated with HCl (65°C, 18 h). We thus applied to (+)-**38** the methodology proposed by Witczak and co-workers⁴² for the hydrolysis of anhydro-pyranoses. Exchange of the Boc protection group of (+)-**38** as a trifluoroacetamide was carried out by treatment with (CF₃CO)₂O and pyridine (20°C, 15 h), followed by methanolysis in the presence of a catalytical amount of ammonia.⁴³ This gave **41** in 78% yield (Scheme 9). Esterification of the hydroxy group under standard conditions provided **42** in 94% yield. Acetolysis of **42** with anhydride acetic and trifluoroacetic acid⁴² afforded **43** in 30% yield only. Its α -galactopyranose structure was given by its ¹H-NMR spectrum (³*J*(H-C(1),H-C(2)) = 3 Hz, ³*J*(H-C(2),H-C(3)) = 11.8 Hz). Final deprotection of **43** with MeOH/NH₃ furnished **44** in 83% yield, its β -furanose structure was indicated by its ¹³C-NMR spectrum ($\delta_{\text{C}}(1) = 98.8$ ppm) and by its ¹H-NMR spectrum (³*J*(H-C(1),H-C(2)) < 1 Hz, ³*J*(H-C(2),H-C(3)) < 1 Hz).

CONCLUSION

Enolates derived from the 1,4-additions of isolevogluconone (**3**) are more successful than the enolates derived from the 1,4-additions to levogluconone (**5**) in their aldol condensations. The reasons for this difference are not elucidated yet. Some condensations may have failed for steric reasons. Nevertheless, together with adequate sugar-derived aldehydes both enones (**3**) and (**5**) can be used as templates for the convergent construction of (1→3)-C-linked imino-disaccharides.⁴⁴ The syntheses of methyl 3,4-dideoxy-3-[(1'S)-2',5'-dideoxy-2',5'-iminoribitol-1'-C-yl]- α -D-*lyxo*-hexopyranose ((+)-**22**) and 3-deoxy-3-(1',2',3',6'-tetraideoxy-3',6'-imino-L-*arabino*-hexitol-1'-C-yl)- β -D-galactofuranose (**44**) have been presented for the first time.

ACKNOWLEDGMENTS

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EXPERIMENTAL

General, see ref. 8, 40. ^1H -NMR assignments were confirmed by 2D-(COSY, NOESY)- ^1H -NMR spectra.

2-*O*-Acetyl-3-[(5'*R* or 5'*S*)-5'-*O*-acetyl-1',2'-*O*-isopropylidene-3'-*O*-methyl- α -D-xylofuranos-5'-C-yl]-1,6-anhydro-4-*O*-benzyl-3-deoxy- β -D-mannopyranose ((-)-**10**). 1.5 M BuLi in hexane (0.48 mL, 0.70 mmol) was added to a stirred solution of $(\text{Me}_3\text{Si})_2\text{NH}$ (0.1 mL) in anhydrous THF (0.4 mL) cooled to -10°C . After cooling to -25°C , (-)-1,6-anhydro-4-*O*-benzyl-3-deoxy-D-*erythro*-hexopyrano-2-ulose (adduct of benzyl alcohol to levoglucosenone,²⁵ 150 mg, 0.64 mmol) in anhydrous THF (0.45 mL) was added dropwise. After stirring at -25°C for 10 min, the mixture was cooled to -95°C and **8** (*Fluka*, 194 mg, 0.96 mmol) in anhydrous THF (0.2 mL) was added. After stirring at -95°C for 13 h, the temperature was allowed to raise to -85°C and LiBH_4 (42 mg, 1.92 mmol) was added. After stirring at -85°C for 2 h, CH_2Cl_2 (10 mL) was added and the solution washed with brine (3 mL). The organic phase was dried (MgSO_4) and the solvent evaporated. Flash chromatography on silica gel (FC) (EtOAc /light petroleum ether 3:2) afforded 70 mg (25%) of **9** as a colorless oil. It was treated with Et_3N (1 mL), anhydride acetic (0.5 mL) and CH_2Cl_2 (9 mL). After 12 h at 20°C , the mixture was washed with 1 N HCl (2 mL), then with saturated aqueous solution of NaHCO_3 (2 mL). After drying (MgSO_4) and solvent evaporation, the residue was purified by FC (EtOAc /light petroleum ether 3:2) to give 27 mg (8%, 3 steps) of (-)-**10** as a colorless oil. $[\alpha]_{\text{D}}^{25} = -110$, $[\alpha]_{\text{D}}^{25} = -113$, $[\alpha]_{\text{D}}^{25} = -122$, $[\alpha]_{\text{D}}^{25} = -137$, $[\alpha]_{\text{D}}^{25} = -168$ ($c = 0.8$, CHCl_3). UV (MeCN): $\lambda_{\text{max}} = 206$ nm ($\epsilon = 7100 \text{ M}^{-1}\text{cm}^{-1}$), 194 (13500). IR (film) ν : 2985, 2935, 2255, 1745, 1455, 1375, 1245, 1165, 1070, 1025, 915, 735 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ_{H} 7.10-7.28 (*m*, 5H, H-C arom.), 5.86 (*d*, $^3J(\text{H-C}(1'),\text{H-C}(1')) = 3.8$, H-C(1')), 5.57 (*d*, $^3J(\text{H-C}(1),\text{H-C}(2)) = 4.7$, H-C(1)), 5.48 (*dd*, $^3J(\text{H-C}(5'),\text{H-C}(4')) = 9.2$, $^3J(\text{H-C}(5'),\text{H-C}(3)) = 2.9$, H-C(5')), 4.97 (*dd*, $^3J(\text{H-C}(2),\text{H-C}(3)) = 6.6$, $^3J(\text{H-C}(2),\text{H-C}(1)) = 4.7$, H-C(2)), 4.62, 4.59 (2*d*, *AB*, $^2J_{\text{AB}} = 11.7$, $\text{C}_6\text{H}_5\text{CH}_2\text{O-}$), 4.54 (*dd*, $^3J(\text{H-C}(5),\text{Ha-C}(6)) = 6.0$, $^3J(\text{H-C}(5),\text{Hb-C}(6)) = 1.4$, H-C(5)), 4.52 (*d*, $^3J(\text{H-C}(2'),\text{H-C}(1')) = 3.8$, H-C(2')), 4.47 (*dd*, $^3J(\text{H-C}(4'),\text{H-C}(5')) = 9.2$, $^3J(\text{H-C}(4'),\text{H-C}(3')) = 3.1$, H-C(4')), 3.78 (*d*, $^3J(\text{H-C}(4),\text{H-C}(3)) = 7.4$, H-C(4)), 3.72 (*dd*, $^2J(\text{Ha-C}(6),\text{Hb-C}(6)) = 7.3$, $^3J(\text{Ha-C}(6),\text{H-C}(5)) = 6.0$, Ha-C(6)), 3.66 (*dd*, $^2J(\text{Hb-C}(6),\text{Ha-C}(6)) = 7.3$, $^3J(\text{Hb-C}(6),\text{H-C}(5)) = 1.4$, Ha-C(6)), 3.54 (*d*, $^3J(\text{H-C}(3'),\text{H-C}(4')) = 3.1$, H-C(3')), 3.31 (*s*, $\text{CH}_3\text{O-}$), 2.70 (*ddd*, $^3J(\text{H-C}(3),\text{H-C}(4)) = 7.4$, $^3J(\text{H-C}(3),\text{H-C}(2)) = 6.6$, $^3J(\text{H-C}(3),\text{H-C}(5')) = 2.9$, H-C(3)), 2.03, 2.01 (2*s*, $\text{CH}_3\text{COO-}$), 1.36, 1.30 (2*s*, Me_2C). ^{13}C -NMR (100.6 MHz, CDCl_3): δ_{C} 170.4, 168.3 (2*s*, $\text{CH}_3\text{COO-}$), 137.8 (*s*, C arom.), 128.4, 128.1, 127.8 (3*d*, $^1J(\text{C},\text{H}) = 160$, 158, 160, C arom.), 111.7 (*s*, Me_2C), 105.1 (*d*, $^1J(\text{C},\text{H}) = 183$, C(1')), 97.4 (*d*, $^1J(\text{C},\text{H}) = 183$, C(1)), 83.3 (*d*, $^1J(\text{C},\text{H}) = 150$, C(5')), 80.9 (*d*, $^1J(\text{C},\text{H}) = 164$, C(2)), 79.6 (*d*, $^1J(\text{C},\text{H}) = 198$, C(5)), 78.1 (*d*, $^1J(\text{C},\text{H}) = 149$, C(2')), 75.8 (*d*, $^1J(\text{C},\text{H}) = 154$, C(4')), 71.1 (*t*, $^1J(\text{C},\text{H}) = 142$, $\text{C}_6\text{H}_5\text{CH}_2\text{O-}$), 70.4 (*d*, $^1J(\text{C},\text{H}) = 150$, C(4)), 67.6 (*d*,

$^1J(\text{C},\text{H}) = 140$, C(3')), 66.9 (t, $^1J(\text{C},\text{H}) = 141$, C(6)), 57.5 (q, $^1J(\text{C},\text{H}) = 142$, CH₃O-), 37.8 (d, $^1J(\text{C},\text{H}) = 129$, C(3)), 26.6, 26.1 (2q, $^1J(\text{C},\text{H}) = 127$, 127, CH₃COO-), 21.1, 20.5 (2q, $^1J(\text{C},\text{H}) = 129$, 130, Me₂C). CI-MS (NH₃) m/z: 523 (13, M⁺), 465 (5), 415 (6), 325 (9), 297 (4), 250 (5), 173 (13), 115 (9), 91 (100). Anal. Calcd for C₂₆H₃₄O₁₁: C 59.76, H 6.56. Found: C 59.77, H 6.60.

65:35 Mixture of 1,6-Anhydro-3,4-dideoxy-3-[(5'*R* and 5'*S*)-1',2'-*O*-isopropylidene-3'-*O*-methyl- α -D-xylo-furanos-1'-C-yl]- β -D-glycero-hex-3-enopyranos-2-ulose ((-)-**14a,b**). 0.1 M solution of Et₂AlI in hexane (0.95 mL, 0.95 mmol) was added to a stirred mixture of levoglucosenone (**5**, 80 mg, 0.63 mmol) and **8** (256 mg, 1.27 mmol) in anhydrous CH₂Cl₂ (2 mL) cooled to -80°C for 2 h, the mixture was poured into a vigorously stirred mixture of Et₂O (5 mL) and 1 N aqueous HCl (1 mL). The mixture was extracted with Et₂O (10 mL, 4 times). The combined organic extracts were dried (MgSO₄). After solvent evaporation, flash chromatography of the residue on silica gel (EtOAc/light petroleum ether 3:7) gave 123 mg (58%) of a 65:35 mixture of **14a** + **14b**, colorless oil. [α]_D²⁵₈₉ = -211, [α]_D²⁵₇₇ = -226, [α]_D²⁵₄₆ = -276, [α]_D²⁵₃₅ = -858, [α]_D²⁵₄₀₅ = -1708 (*c* = 1.0, CHCl₃). UV (MeCN): λ_{max} = 230 (ϵ = 5500), 191 (2900). IR (film) ν : 3490, 2990, 2940, 2835, 1700, 1375, 1250, 1195, 1165, 1115, 1080, 1025, 950, 890 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃) of major diastereomer: δ_{H} 7.32 (dd, $^3J(\text{H-C}(4),\text{H-C}(5)) = 4.8$, $^4J = 1.3$, H-C(4)), 5.93 (d, $^3J(\text{H-C}(1'),\text{H-C}(2')) = 3.8$, H-C(1')), 5.35 (s, H-C(1)), 5.10 (dd, $^3J(\text{H-C}(5),\text{H-C}(4)) = 4.8$, $^3J(\text{H-C}(5),\text{H-C}(6)) = 4.7$, H-C(5)), 4.84 (m, H-C(5')), 4.52 (d, $^3J(\text{H-C}(2'),\text{H-C}(1')) = 3.8$, H-C(2')), 4.34 (dd, $^3J(\text{H-C}(4'),\text{H-C}(3')) = 5.8$, $^3J(\text{H-C}(4'),\text{H-C}(5')) = 3.2$, H-C(4')), 3.89-3.85 (m, 1H, H-C(6)), 3.78-3.74 (m, 2H, H-C(6), H-C(3')), 3.40 (s, CH₃O-), 1.45, 1.29 (2s, Me₂C).

N-Benzyloxycarbonyl-2,5-dideoxy-2,5-imino-3,4-*O*-isopropylidene-L-ribose ((-)-**15**). NaHCO₃ (0.64 g, 7.6 mmol) and Pb(OAc)₄ (2.53 g, 5.7 mmol) were added portionwise to a solution of (-)-*N*-(benzyloxycarbonyl)-1,4-dideoxy-1,4-imino-2,3-*O*-isopropylidene-D-allitol (see below, 1.3 g, 3.8 mmol) in anhydrous CH₂Cl₂ (26 mL) stirred at -78°C under Ar atmosphere. After stirring at -78°C for 50 min, the mixture was poured onto vigorously stirred ice-cold saturated solution of NaHCO₃ (50 mL). Extraction with CH₂Cl₂ (100 mL, 4 times), drying (MgSO₄), solvent evaporation and FC (EtOAc/light petroleum ether 7:3) gave 1.1 g (94%) of (-)-**15** as a colorless oil (overall yield of 33% based on D-gulonolactone,²⁷ 8 steps). [α]_D²⁵₈₉ = -64, [α]_D²⁵₇₇ = -66, [α]_D²⁵₄₆ = -77, [α]_D²⁵₃₅ = -141, [α]_D²⁵₄₀₅ = -182 (*c* = 0.8, CHCl₃). UV (MeCN): λ_{max} = 267 (ϵ = 500), 260 (600), 210 (5700). IR (film) ν : 3425, 2985, 2940, 1700, 1425, 1350, 1275, 1215, 1160, 1120, 1055, 980 cm⁻¹. ¹H-NMR (400 MHz, toluene-d₈, 110°C): δ_{H} 9.16 (s, H-C(1)), 7.19-6.96 (m, H arom.), 4.94 (s, 2H), 4.41 (br s, H-C(2)), 4.39 (d, $^3J(\text{H-C}(3),\text{H-C}(4)) = 5.9$, H-C(3)), 4.08 (dd, $^3J(\text{H-C}(4),\text{H-C}(3)) = 5.9$, $^3J(\text{H-C}(4),\text{Hb-C}(5)) = 4.9$, H-C(4)), 3.79 (d, $^2J = 12.7$, H-C(5)), 2.98 (dd, $^2J = 12.7$, $^3J(\text{Hb-C}(5),\text{H-C}(4)) = 4.9$, Hb-C(5)), 1.20, 1.03 (2s, Me₂C). ¹³C-NMR (100.6 MHz, toluene-d₈, 110°C): δ_{C} 196.4 (d, $^1J(\text{C}-\text{H}) = 179$, C(1)), 156.7 (s, BnOCON-), 128.9-127.5 (C

arom.), 112.5 (s), 79.8 (d, $^1J(\text{C},\text{H}) = 156$, C(3)), 79.3 (d, $^1J(\text{C},\text{H}) = 157$, C(4)), 72.2 (dd, $^1J(\text{C},\text{H}) = 147$, $^2J(\text{C},\text{H}) = 22$, C(2)), 67.5 (t, $^1J(\text{C},\text{H}) = 143$), 52.6 (t, $^1J(\text{C},\text{H}) = 145$, C(5)), 26.8, 24.9 (2q, $^1J(\text{C},\text{H}) = 127$, 126, Me₂C). CI-MS (NH₃) m/z: 306 (0.2, M⁺), 276 (4), 232 (9), 186 (2), 142 (3), 92 (13), 91 (100). Anal. Calcd for C₁₆H₁₉NO₅: C 62.94, H 6.27, N 4.59. Found: C 62.78, H 6.38, N 4.49.

N-Benzyloxycarbonyl-1,4-dideoxy-1,4-imino-2,3-*O*-isopropylidene-D-allitol. A mixture *N*-benzyloxycarbonyl-1,4-dideoxy-1,4-imino-2,3:5,6-di-*O*-isopropylidene-D-allitol (see below, 2.0 g, 5.3 mmol) and 4:1 AcOH/H₂O (12 mL) was stirred at 20°C for 10 h. Solvent evaporation *in vacuo* and FC (EtOAc/light petroleum ether 4:1) gave 1.22 g (68%) of a colorless solid, mp 98-99°C. $[\alpha]_{\text{D}}^{25} = -38$, $[\alpha]_{\text{D}}^{25} = -44$, $[\alpha]_{\text{D}}^{25} = -47$, $[\alpha]_{\text{D}}^{25} = -78$, $[\alpha]_{\text{D}}^{25} = -93$ ($c = 1.0$, CHCl₃). UV (MeCN): $\lambda_{\text{max}} = 263$ ($\epsilon = 1400$), 258 (1300), 212 (7800). IR (KBr) ν : 3545, 3475, 2950, 1680, 1660, 1460, 1435, 1345, 1275, 1215, 1155, 1125, 1040, 975, 870, 760, 700 cm⁻¹. ¹H-NMR (400 MHz, toluene-d₈, 110°C): δ_{H} 7.18-6.96 (H arom.), 5.02, 4.92 (2d, AB, $^2J_{\text{AB}} = 12.5$, Bn), 4.65 (d, $^3J(\text{H-C}(3),\text{H-C}(2)) = 5.7$, H-C(3)), 4.33 (dd, $^3J(\text{H-C}(2),\text{H-C}(3)) = 5.7$, $^3J(\text{H-C}(2),\text{Hb-C}(1)) = 5.1$, H-C(2)), 4.11 (br d, $^3J(\text{H-C}(4),\text{H-C}(5)) = 6.5$, H-C(4)), 3.88 (br d, $^2J = 12.7$, Ha-C(1)), 3.33-3.28 (m, 3H, H-C(5), H₂-C(6)), 3.10 (dd, $^2J = 12.7$, $^3J(\text{Hb-C}(1),\text{H-C}(2)) = 5.1$, Hb-C(1)), 1.30, 1.15 (2s, Me₂C). ¹³C-NMR (100.6 MHz, toluene-d₈, 110°C): δ_{C} 156.8 (s, BnOCO-), 129.6-125.1 (C arom.), 112.1 (s), 82.7 (d, $^1J(\text{C},\text{H}) = 160$, C(3)), 80.2 (d, $^1J(\text{C},\text{H}) = 153$, C(2)), 72.2 (t, $^1J(\text{C},\text{H}) = 141$, C(6)), 67.8 (t, $^1J(\text{C},\text{H}) = 142$), 66.9 (d, $^1J(\text{C},\text{H}) = 143$, C(4)), 63.8 (t, $^1J(\text{C},\text{H}) = 142$, C(1)), 53.3 (d, $^1J(\text{C},\text{H}) = 143$, C(5)), 27.5, 25.5 (2q, $^1J(\text{C},\text{H}) = 124$, 127, Me₂C). CI-MS (NH₃) m/z: 338 (3, M⁺), 277 (8), 276 (16), 232 (16), 142 (16), 126 (6), 92 (18), 91 (100), 90 (42), 84 (15), 83 (11). Anal. Calcd for C₁₇H₂₃NO₆: C 60.52, H 6.87, N 4.15. Found: C 60.58, H 6.81, N 4.18.

N-Benzyloxycarbonyl-1,4-dideoxy-1,4-imino-2,3:5,6-di-*O*-isopropylidene-D-allitol. NaHCO₃ (1.28 g, 15.2 mmol) and benzyl chloroformate (1.6 mL, 10.3 mmol) were added successively to a stirred solution of 1,4-dideoxy-1,4-imino-2,3:5,6-di-*O*-isopropylidene-D-allitol²⁷ (2.08 g, 8.55 mmol) in 1:1 EtOH/H₂O (52 mL). After stirring at 20°C for 40 min the mixture was poured into a saturated aqueous solution of NaHCO₃ (40 mL). Extraction with EtOAc (60 mL, 4 times), drying (MgSO₄), solvent evaporation and FC (EtOAc/light petroleum ether 1:4) afforded 2.77 g (96%) of a colorless oil. $[\alpha]_{\text{D}}^{25} = -56$, $[\alpha]_{\text{D}}^{25} = -58$, $[\alpha]_{\text{D}}^{25} = -66$, $[\alpha]_{\text{D}}^{25} = -111$, $[\alpha]_{\text{D}}^{25} = -132$ ($c = 1.2$, CHCl₃). UV (MeCN): $\lambda_{\text{max}} = 281$ ($\epsilon = 500$), 260 (700), 205 (8500). IR (film) ν : 3065, 3035, 2985, 2940, 2890, 1705, 1455, 1420, 1380, 1370, 1360, 1265, 1210, 1160, 1115, 1055, 700, 605 cm⁻¹. ¹H-NMR (400 MHz, toluene-d₈, 100°C): δ_{H} 7.19-6.96 (H arom.), 5.07, 5.01 (2d, AB, $^2J_{\text{AB}} = 12.5$, C₆H₅CH₂O-), 4.70 (d, $^3J(\text{H-C}(3),\text{H-C}(2)) = 5.9$, H-C(3)), 4.46 (dd, $^3J(\text{H-C}(2),\text{H-C}(3)) = 5.9$, $^3J(\text{H-C}(2),\text{Hb-C}(1)) = 5.0$, H-C(2)), 4.20 (br d, $^3J(\text{H-C}(4),\text{H-C}(5)) = 4.2$, H-C(4)), 4.08-4.15 (m, Ha-C(6)), 3.95 (br d, $^2J(\text{Ha-C}(1),\text{Hb-C}(1)) = 12.4$, Ha-C(1)), 3.75-3.58 (m, 2H, H-C(5), Hb-C(6)), 3.30 (dd, $^2J(\text{Hb-C}(1),\text{Ha-C}(1)) = 12.4$, $^3J(\text{Hb-C}(1),\text{H-C}(2)) = 5.0$, Hb-C(1)), 1.30, 1.26, 1.16,

1.13 (4s, 2 Me₂C). ¹³C-NMR (100.6 MHz, toluene-d₈, 100°C): δ_C 156.7 (s, BnOCO-), 129.6-125.1 (C arom.), 112.1, 110.0 (2s), 81.7 (d, ¹J(C,H) = 126, C(3)), 80.4 (d, ¹J(C,H) = 157, C(2)), 76.3 (t, ¹J(C,H) = 145, C(6)), 67.4 (d, ¹J(C,H) = 150), 67.3 (t, ¹J(C,H) = 142, C(4)), 66.9 (d, ¹J(C,H) = 148, C(5)), 53.6 (t, ¹J(C,H) = 146, C(1)), 27.4, 26.7, 25.4, 25.0 (4q, ¹J(C,H) = 124, 127, 126, 126). CI-MS (NH₃) m/z: 378 (1, M⁺), 232 (8), 101 (1), 92 (12), 91 (100). Anal. Calcd for C₂₀H₂₇NO₆: C 63.64, H 7.21, N 3.71. Found: C 63.71, H 7.18, N 3.61.

1,6-Anhydro-3-[(1'S)-N-benzyloxycarbonyl-3',4'-O-isopropylidene-2',5'-dideoxy-2',5'-imino-D-ribitol-1'-C-yl]-3,4-dideoxy-β-glycero-hex-3-enopyranos-2-ulose ((-)-**16**). A 1 M solution of Et₂AlI in hexane (2.95 mL, 2.95 mmol) was added dropwise in 4 h to a stirred solution of 2,5-(benzyloxycarbonyl)imino-2,5-dideoxy-3,4-O-isopropylidene-L-ribose ((-)-**15**),²⁷ 1 g, 3.27 mmol) and levoglucosenone (**5**) (0.21 g, 1.64 mmol) in anhydrous CH₂Cl₂ (2 mL) cooled to -35°C. After stirring at -35°C for 4 h, the mixture was poured into a vigorously stirred mixture of Et₂O (35 mL) and 1 N aqueous HCl (50 mL). Extraction with Et₂O (60 mL, 6 times), drying (MgSO₄), solvent evaporation and FC (EtOAc/light petroleum ether 3:2) gave 269 mg (38%) of (-)-**16** as a colorless solid, mp 163-164°C. [α]_D²⁵₈₉ = -129, [α]_D²⁵₇₇ = -138, [α]_D²⁵₄₆ = -170, [α]_D²⁵₃₅ = -552, [α]_D²⁵₀₅ = -1200 (c = 1.0, CHCl₃). UV (MeCN): λ_{max} = 347 (ε = 2000), 323 (2800), 208 (8900). IR (KBr) ν: 3500, 2985, 1780, 1695, 1445, 1415, 1215, 1115, 1055, 985, 730, 575 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃) 1:1 mixture of two rotamers: δ_H 7.38-7.23 (m, 6H, H-C(4), H arom.), 7.20 (dd, ³J(H-C(4),H-C(5)) = 4.9, ⁴J = 1.2, H-C(4)), 5.36 (d, AB, ²J_{AB} = 12.7, C₆H₅CH₂O-), 5.32, 5.34 (2s, H-C(1)), 5.12 (s, 2H, C₆H₅CH₂O-), 5.00 (dd, ³J(H-C(5),H-C(4)) = 4.9, ³J(H-C(5),H-C(6)) = 4.7, H-C(5)), 4.94 (dd, ³J(H-C(5),H-C(4)) = 4.7, ³J(H-C(5),H-C(6)) = 4.4, H-C(5)), 4.85 (d, AB, ²J_{AB} = 12.7, C₆H₅CH₂O-), 4.78-4.72 (m, 4H, H-C(1'), H-C(4')), 4.59 (d, ³J(H-C(3'),H-C(4')) = 5.8, H-C(3')), 4.45 (d, ³J(H-C(2'),H-C(1')) = 2.8, H-C(2')), 4.29 (d, ³J(H-C(3'),H-C(4')) = 4.1, H-C(3')), 3.92-3.87 (m, 3H, H-C(6), H-C(5')), 3.75-3.72 (m, 1H, H-C(6)), 3.62-3.59 (m, 2H, H-C(6), H-C(5')), 3.54-3.50 (m, 2H, H-C(6), H-C(5')), 1.38, 1.29, 1.29, 1.25 (4s, Me₂C). ¹³C-NMR (100.6 MHz, CDCl₃) 1:1 mixture of two rotamers: δ_C 188.8, 188.3 (2s, C(2)), 155.8, 155.5 (2s, BnOCON-), 137.2, 137.1, 136.9, 136.8 (4s, C(4), C arom.), 128.4, 128.2, 128.0, 127.2 (4d, ¹J(C-H) = 138, 137, 129, 135, C arom.), 111.5, 111.2 (2s, Me₂C), 101.1, 101.0 (2d, ¹J(C,H) = 174, C(1)), 83.3, 82.6, 79.8, 71.8, 69.7, 67.2 (6d, ¹J(C,H) = 158, 157, 159, 159, 145, 147, C(5), C(1'), C(2'), C(3'), C(4')), 66.9, 66.4, 66.2, 65.8 (2t, ¹J(C,H) = 148, 147, 154, 156, C(6), C₆H₅CH₂-), 54.6, 53.9 (2t, ¹J(C,H) = 144, C(1')), 26.8, 26.6, 26.6, 24.8 (4q, ¹J(C,H) = 128, Me₂C)). CI-MS (NH₃) m/z: 432 (0.3, [M+1]⁺), 431 (0.2, M⁺), 276 (15), 275 (8), 232 (23), 93 (12), 91 (100), 90 (72). Anal. Calcd for C₂₂H₂₅NO₈: C 61.25, H 5.84, N 3.25. Found: C 61.24, H 5.94.

1,6-Anhydro-3,4-dideoxy-3-[(1'S)-N-benzyloxycarbonyl-3',4'-O-isopropylidene-2',5'-dideoxy-2',5'-imino-D-ribitol-1'-C-yl]-D-threo-hex-3-enopyranose ((-)-**13**). A mixture of (-)-**12** (112 mg, 0.26 mmol),

CeCl₃·7 H₂O (99 mg, 0.26 mmol) and 2:1 CH₂Cl₂/MeOH (13 mL) was stirred at -10°C until complete dissolution of CeCl₃·7 H₂O. Then, NaBH₄ (10 mg, 0.26 mmol) was added. After stirring at -10°C for 20 min, acetone (1 mL), then 1 N aqueous HCl (3 mL) were added. The mixture was poured into a stirred mixture of CH₂Cl₂ (10 mL) and saturated aqueous solution of NaHCO₃ (2 mL). The organic layer was dried (MgSO₄). Solvent evaporation and FC (EtOAc/light petroleum ether 3:2) gave 107 mg (93%) of (-)-**13**, white solid, mp 196°C (decomp). [α]_D²⁵₈₉ = -3.4, [α]_D²⁵₇₇ = -6.6, [α]_D²⁵₅₄₆ = -8.4, [α]_D²⁵₄₃₅ = -10, [α]_D²⁵₄₀₅ = -13 (*c* = 1.2, CHCl₃). UV (MeCN): λ_{max} = 263 (ϵ = 1800), 203 (13400). IR (KBr) ν : 3420, 2975, 2955, 1680, 1455, 1425, 1350, 1215, 1135, 1060, 705 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ_{H} 7.37-7.28 (*m*, 5H, H arom.), 6.15 (*d*, ³*J*(H-C(4),H-C(5)) = 4.6, H-C(4)), 5.46 (*d*, ³*J*(H-C(1),H-C(2)) = 2.6, H-C(1)), 5.21, 5.13 (2*d*, AB, ²*J*_{AB} = 12.8, C₆H₅CH₂O-), 4.83-4.80 (*m*, 2H, H-C(3'), H-C(4')), 4.66 (*d*, ³*J*(H-C(1'),H-C(2')) = 2.6, H-C(1')), 4.57 (*dd*, ³*J*(H-C(5),H-C(4)) = 4.6, ³*J*(H-C(5),Ha-C(6)) = 4.4, H-C(5)), 4.43 (*br s*, H-C(2')), 4.28 (*d*, ³*J*(H-C(2),H-C(1)) = 2.6, H-C(2)), 3.85 (*d*, ³*J*(Ha-C(5'),Hb-C(5')) = 11.9, Ha-C(5')), 3.65 (*dd*, ³*J*(Hb-C(5'),Ha-C(5')) = 11.9, ³*J*(Hb-C(5'),H-C(4')) = 4.5, Hb-C(5')), 3.56 (*dd*, ³*J*(Ha-C(6),Hb-C(6)) = 6.5, ³*J*(Ha-C(6),H-C(5)) = 4.4, Ha-C(6)), 3.33 (*d*, ³*J*(Hb-C(6),Ha-C(6)) = 6.5, Hb-C(6)), 1.39, 1.31 (2*s*, Me₂C)₂). ¹³C-NMR (100.6 MHz, CDCl₃): δ_{C} 155.7 (*s*, BnOCON-), 140.2 (*s*, C arom.), 136.6 (*s*, C(3)), 128.5-126.6 ((C arom.), C(4)), 110.2 (*s*, Me₂C)₂, 101.0 (*d*, ¹*J*(C,H) = 174, C(1)), 82.8, 80.3 (2*d*, ¹*J*(C,H) = 158, 160, C(3'), C(4')), 74.6 (*d*, ¹*J*(C,H) = 138, C(2')), 70.9 (*d*, ¹*J*(C,H) = 156, C(5)), 70.6 (*d*, ¹*J*(C,H) = 150, C(2)), 69.8 (*t*, ¹*J*(C,H) = 151, C(6)), 67.0 (*d*, ¹*J*(C,H) = 147, C(1')), 66.9 (*t*, ¹*J*(C,H) = 150, C₆H₅CH₂O-), 54.9 (*t*, ¹*J*(C,H) = 146, C(5')), 26.8, 24.7 (2*q*, ¹*J*(C,H) = 128, 126, Me₂C). CI-MS (NH₃) *m/z*: 434 (0.2, [M+1]⁺), 433 (0.2, M⁺), 277 (2), 276 (4), 232 (10), 142 (8), 92 (21), 91 (100). Anal. Calcd for C₂₂H₂₇NO₈: C 60.96, H 6.28, N 3.23. Found: C 60.98, H 6.25, N 3.24.

1,6-Anhydro-3,4-dideoxy-1',4'-O-isopropylidene-3-(1'S)-N-benzyloxycarbonyl-3',4'-O-isopropylidene-2',5'-dideoxy-2',5'-imino-D-*ribitol*-1'-C-yl]- β -D-*lyxo*-pyranose ((+)-**18**). Two drops of conc. H₂SO₄ were added to a mixture of (-)-**17** (40 mg), acetone (3 mL) and 2,2-dimethoxypropane (1.5 mL). After stirring at 20°C for 5 min, Na₂CO₃ (1 g) was added. The precipitate was filtered off (Celite), the solvent was evaporated. FC (-78°C, EtOAc/light petroleum ether 3:2): 26 mg of ene-diacetonide that was dissolved in MeOH (2 mL). After degassing (vacuum line, N₂), 10% Pd(OH)₂-C (15 mg) was added and the mixture pressurized (1 atm) with H₂. After shaking at 20°C for 12 h, the mixture was filtered (Celite). The solvent was evaporated. FC (-78°C, EtOAc) afforded 13 mg (41%) of (+)-**18**, colorless oil. [α]_D²⁵₈₉ = 7.9, [α]_D²⁵₇₇ = 7.7, [α]_D²⁵₅₄₆ = 5.3, [α]_D²⁵₄₃₅ = 5.3 (*c* = 0.5, CHCl₃). UV (MeCN): λ_{max} = 195 (ϵ = 500). IR (film) ν : 3420, 2985, 2940, 1740, 1385, 1240, 1210, 1160, 1255, 1095, 1055, 905, 735 cm⁻¹. ¹H-NMR (400 MHz, toluene-*d*₈): δ_{H} 5.38 (*d*, ³*J*(H-C(1),H-C(2)) = 2.8, H-C(1)), 4.65 (*dd*, ³*J*(H-C(3'),H-C(4')) = 5.7, ³*J*(H-C(3'),H-C(2')) = 1.1, H-C(3')), 4.55 (*dd*, ³*J*(H-C(4'),H-C(3')) = 5.7, ³*J*(H-C(4'),Ha-C(5')) = 4.5, H-C(4')),

4.08 (*dd*, $^3J(\text{H-C}(1'), \text{H-C}(3)) = 11.0$, $^3J(\text{H-C}(1'), \text{H-C}(2')) = 3.0$, $\text{H-C}(1')$), 3.91 (*br ddd*, $^3J(\text{H-C}(5), \text{Ha-C}(4)) = 5.2$, $^3J(\text{H-C}(5), \text{Ha-C}(6)) = 4.9$, $^4J = 1.2$, $\text{H-C}(5)$), 3.88 (*dd*, $^3J(\text{H-C}(2), \text{H-C}(3)) = 8.3$, $^3J(\text{H-C}(2), \text{H-C}(1)) = 2.8$, $\text{H-C}(2)$), 3.39 (*ddd*, $^2J(\text{Ha-C}(6), \text{Hb-C}(6)) = 7.0$, $^3J(\text{Ha-C}(6), \text{H-C}(5)) = 4.9$, $^4J = 1.7$, $\text{Ha-C}(6)$), 3.16 (*d*, $^2J(\text{Hb-C}(6), \text{Ha-C}(6)) = 7.0$, $\text{Hb-C}(6)$), 3.12 (*br s*, $\text{H-C}(2')$), 3.02 (*dd*, $^2J(\text{Ha-C}(5'), \text{Hb-C}(5')) = 12.5$, $^3J(\text{Ha-C}(5'), \text{H-C}(4')) = 4.5$, $\text{Ha-C}(5')$), 2.87 (*d*, $^2J(\text{Hb-C}(5'), \text{Ha-C}(5')) = 12.5$, $\text{Hb-C}(5')$), 2.55 (*br ddd*, $^2J(\text{H-C}(3), \text{Hb-C}(1')) = 11.0$, $^3J(\text{H-C}(3), \text{Ha-C}(4)) = 9.1$, $^3J(\text{H-C}(3), \text{H-C}(2)) = 8.3$, $\text{H-C}(3)$), 1.78 (*ddd*, $^2J(\text{Ha-C}(4), \text{Hb-C}(4)) = 15.5$, $^3J(\text{Ha-C}(4), \text{H-C}(3)) = 9.1$, $^3J(\text{Ha-C}(4), \text{H-C}(5)) = 5.2$, $\text{Ha-C}(4)$), 1.64 (*br d*, $^2J(\text{Hb-C}(4), \text{Ha-C}(4)) = 15.5$, $\text{Ha-C}(4)$), 1.47, 1.25 (2s, Me_2C , dioxolane), 1.32, 1.29 (2s, Me_2C , dioxane). ^{13}C -NMR (100.6 MHz, CDCl_3): δ_{C} 111.0, 111.1 (2s, 2 Me_2C), 99.6 (*d*, $^1J(\text{C}, \text{H}) = 174$, $\text{C}(1)$), 85.1 (*d*, $^1J(\text{C}, \text{H}) = 157$, $\text{C}(3')$), 83.1 (*d*, $^1J(\text{C}, \text{H}) = 158$, $\text{C}(4')$), 73.1 (*d*, $^1J(\text{C}, \text{H}) = 148$, $\text{C}(1')$), 71.8 (*d*, $^1J(\text{C}, \text{H}) = 151$, $\text{C}(5)$), 69.8 (*t*, $^1J(\text{C}, \text{H}) = 150$, $\text{C}(6)$), 68.3 (*d*, $^1J(\text{C}, \text{H}) = 145$, $\text{C}(2)$), 65.3 (*d*, $^1J(\text{C}, \text{H}) = 136$, $\text{C}(2')$), 54.8 (*t*, $^1J(\text{C}, \text{H}) = 137$, $\text{C}(5')$), 31.1 (*d*, $^1J(\text{C}, \text{H}) = 134$, $\text{C}(3)$), 28.0 (*t*, $^1J(\text{C}, \text{H}) = 150$, $\text{C}(4)$), 27.2, 26.6, 26.4, 24.1 (4q, $^1J(\text{C}, \text{H}) = 126$, 2 Me_2C). ^{13}C -NMR (100.6 MHz, toluene- d_8): δ_{C} 110.1, 100.0 (2 Me_2C), 100.7 ($\text{C}(1)$), 85.6 ($\text{C}(3')$), 83.8 ($\text{C}(4')$), 73.8 ($\text{C}(1')$), 72.3 ($\text{C}(5)$), 69.4 ($\text{C}(2)$), 69.2 ($\text{C}(6)$), 65.7 ($\text{C}(2')$), 55.6 ($\text{C}(5')$), 31.5 ($\text{C}(3)$), 28.0 ($\text{C}(4)$), 27.6, 27.2 (Me_2C , dioxane), 26.9, 24.1 (Me_2C dioxolane). CI-MS (NH_3) m/z : 342 (7, $[\text{M}+1]^+$), 341 (1, 1, M^{++}), 198 (6), 143 (9), 142 (100), 141 (4), 113 (11), 85 (26), 84 (20), 83 (38).

1,6-Anhydro-2-*O*-*tert*-butyldimethylsilyl-3,4-dideoxy-3-[(1'*S*)-2',5'-dideoxy-2',5'-imino-3',4'-*O*-isopropylidene-1'-*O*-*tert*-butyldimethylsilyl-*ribose*-1'-*C*-yl]-*D*-*threo*-hex-3-enopyranose ((-)-**19**). A mixture of (-)-**13** (0.1 g, 0.24 mmol), 2,6-lutidine (0.22 mL, 1.38 mmol) and (*t*-Bu) $\text{Me}_2\text{SiOSO}_2\text{CF}_3$ (0.19 mL, 0.84 mmol) in anhydrous CH_2Cl_2 (3 mL) was made at -78°C and stirred at -78°C for 2 h. The mixture was poured onto a vigorously stirred mixture of ice-cold CH_2Cl_2 (5 mL) and 1 N aqueous HCl (2 mL). The organic layer was washed with saturated aqueous solution of NaHCO_3 (2 mL) and dried (MgSO_4). Solvent evaporation and FC (EtOAc /light petroleum ether 1:4) gave 129 mg (81%) of (-)-**19** as a colorless oil. $[\alpha]_{\text{D}}^{25} = -4.0$, $[\alpha]_{\text{D}}^{25} = -4.1$, $[\alpha]_{\text{D}}^{25} = -4.9$, $[\alpha]_{\text{D}}^{25} = -7.0$, $[\alpha]_{\text{D}}^{25} = -7.1$ ($c = 0.5$, CHCl_3). UV (MeCN): $\lambda_{\text{max}} = 260$ ($\epsilon = 1400$), 205 (13700). IR (KBr) ν : 2950, 2930, 2885, 2860, 1705, 1470, 1460, 1445, 1415, 1380, 1255, 1220, 1135, 1100, 1055, 875, 835, 775 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3) of major rotamer: δ_{H} 7.34-7.20 (*m*, 5H, H arom.), 6.05 (*d*, $^3J(\text{H-C}(4), \text{H-C}(5)) = 4.6$, $\text{H-C}(4)$), 5.57 (*d*, AB , $^2J_{\text{AB}} = 12.9$, $\text{C}_6\text{H}_5\text{CH}_2\text{O-}$), 5.40 (*d*, $^3J(\text{H-C}(1), \text{H-C}(2)) = 2.4$, $\text{H-C}(1)$), 4.93 (*d*, AB , $^2J_{\text{AB}} = 12.9$, $\text{C}_6\text{H}_5\text{CH}_2\text{O-}$), 4.71 (*dd*, $^3J(\text{H-C}(4'), \text{H-C}(3')) = 6.0$, $^3J(\text{H-C}(4'), \text{Hb-C}(5')) = 4.7$, $\text{H-C}(4')$), 4.66-4.63 (*m*, 1H, $\text{H-C}(5)$), 4.57 (*d*, $^3J(\text{H-C}(3'), \text{H-C}(4')) = 6.0$, $\text{H-C}(3')$), 4.56 (*d*, $^3J(\text{H-C}(2), \text{H-C}(1)) = 2.4$, $\text{H-C}(2)$), 4.55-4.53 (*m*, 1H, $\text{H-C}(1')$), 4.18 (*d*, $^3J(\text{H-C}(2'), \text{H-C}(1')) = 1.9$, $\text{H-C}(2')$), 3.99 (*d*, $^2J(\text{Ha-C}(5'), \text{Hb-C}(5')) = 12.2$, $\text{Ha-C}(5')$), 3.81-3.72 (*m*, 2H, $\text{H}_2\text{-C}(6)$), 3.60 (*dd*, $^2J(\text{Hb-C}(5'), \text{Ha-C}(5')) = 12.2$, $^3J(\text{Hb-C}(5'), \text{H-}$

C(4')) = 4.7, Hb-C(5')), 1.26, 1.23 (2s, Me₂C), 0.89, 0.88 (2s, 2 Me₃CSi), 0.13, 0.12, 0.06, 0.02 (4s, 2 Me₂Si). ¹³C-NMR (100.6 MHz, CDCl₃): δ_C 156.3 (s, BnOCON-), 138.6 (s, C arom.), 137.7 (s, C(3)), 128.1-127.0 ((C arom.)₅, C(4)), 111.1 (s, Me₂C), 101.5 (d, ¹J(C,H) = 160, C(1)), 83.8 (d, ¹J(C,H) = 156, C(3')), 80.4 (d, ¹J(C,H) = 158, C(4')), 73.3 (d, ¹J(C,H) = 131, C(2')), 72.8 (d, ¹J(C,H) = 144, C(1')), 71.5 (d, ¹J(C,H) = 162, C(5')), 71.2 (t, ¹J(C,H) = 151, C(6)), 67.9 (d, ¹J(C,H) = 147, C(2)), 65.9 (t, ¹J(C,H) = 146, C₆H₅CH₂O-), 54.7 (t, ¹J(C,H) = 143, C(5')), 26.6-24.8 (6s, Me₂C, Me₃CSi), 18.0, 17.8, (2s, Me₃CSi), -4.27, -4.36, -4.51, -5.18 (4q, ¹J(C,H) = 118, 2 Me₂Si₂). CI-MS (NH₃) m/z: 662 (0.2, M⁺), 386 (16), 385 (34), 92 (39), 91 (100), 85 (20), 83 (24), 74 (44), 73 (57). Anal. Calcd for C₃₄H₅₅NO₈Si₂: C 61.69, H 8.37, N 2.12. Found: C 61.70, H 8.38, N 2.03.

1,6-Anhydro-2-*O*-[*tert*-butyldimethylsilyl]-3,4-dideoxy-3-[(1*S*)-1'-*O*-[*tert*-butyldimethylsilyl]-2',5'-dideoxy-2',5'-imino-3',4'-*O*-isopropylidene-*ribitol*-1'-C-yl]-β-*D*-lyxo-hexopyranose ((-)-**20**). A mixture of 10% Pd(OH)₂-C (45 mg), (-)-**19** (111 mg, 0.17 mmol), EtOAc (4 mL) and MeOH (4 mL) was degassed and then pressurized with H₂. After shaking at 20°C for 3 days, the precipitate was filtered off (Celite) and the solvent evaporated, giving 90 mg (95%) of (-)-**20** as a colorless oil. [α]_D²⁵₈₉ = -38, [α]_D²⁵₇₇ = -40, [α]_D²⁵₅₄₆ = -45, [α]_D²⁵₄₃₅ = -76, [α]_D²⁵₄₀₅ = -90 (*c* = 1.0, CHCl₃). UV (MeCN): λ_{max} = 228 (ε = 800). IR (film) ν: 2955, 2930, 2890, 2855, 1470, 1435, 1380, 1370, 1250, 1210, 1160, 1110, 855, 835, 775 cm⁻¹. ¹H-NMR (400 MHz, C₆D₆, 60°C): δ_H 5.50 (d, ³J(H-C(1),H-C(2)) = 1.5, H-C(1)), 4.49 (ddd, ³J(H-C(4'),H-C(3')) = 6.2, ³J(H-C(4'),Hb-C(5')) = 4.4, ³J(H-C(4'),Ha-C(5')) = 2.2, H-C(4')), 4.45 (dd, ³J(H-C(3'),H-C(4')) = 6.2, ³J(H-C(3'),H-C(2')) = 2.6, H-C(3')), 4.15-4.16 (*m*, 1H, H-C(5)), 3.95 (d, ³J(H-C(1'),H-C(2')) = 9.4, H-C(1')), 3.90 (dd, ³J(H-C(2),H-C(3)) = 9.1, ³J(H-C(2),H-C(1)) = 1.5, H-C(2)), 3.58 (dd, ²J(Ha-C(6),Hb-C(6)) = 6.8, ³J(Ha-C(6),H-C(5)) = 0.9, Ha-C(6)), 3.53 (ddd, ²J(Hb-C(6),Ha-C(6)) = 6.8, ³J(Hb-C(6),H-C(5)) = 5.0, ⁴J = 1.4, Hb-C(6)), 3.11 (dd, ³J(H-C(2'),H-C(1')) = 9.4, ³J(H-C(2'),H-C(3')) = 2.6, H-C(2')), 2.92 (dd, ²J(Ha-C(5'),Hb-C(5')) = 12.4, ³J(Ha-C(5'),H-C(4')) = 2.2, Ha-C(5')), 2.86 (dd, ²J(Hb-C(5'),Ha-C(5')) = 12.4, ³J(Hb-C(5'),H-C(4')) = 4.4, Hb-C(5')), 2.20 (ddd, ³J(H-C(3),Ha-C(4)) = 12.0, ³J(H-C(3),H-C(2)) = 9.1, ³J(H-C(3),Hb-C(4)) = 5.1, H-C(3)), 2.13 (dddd, ²J(Ha-C(4),Hb-C(4)) = 12.1, ³J(Ha-C(4),H-C(3)) = 12.0, ³J(Ha-C(4),H-C(5)) = 3.4, ⁴J = 1.3, Ha-C(4)), 1.44-1.39 (*m*, 1H, Hb-C(4)), 1.42, 1.20 (2s, Me₂C), 1.05, 0.98 (2s, 2 Me₃CSi), 0.24, 0.23, 0.19, 0.15 (4s, 2 Me₂Si). ¹³C-NMR (100.6 MHz, C₆D₆, 60°C): δ_C 112.2 (s, Me₂C), 103.1 (d, ¹J(C,H) = 169, C(1)), 83.8 (d, ¹J(C,H) = 152, C(3')), 82.1 (d, ¹J(C,H) = 153, C(4')), 73.6 (d, ¹J(C,H) = 152, C(5)), 72.9 (d, ¹J(C,H) = 143, C(2)), 70.6 (d, ¹J(C,H) = 125, C(1')), 69.4 (d, ¹J(C,H) = 124, C(2')), 68.7 (t, ¹J(C,H) = 142, C(6)), 52.3 (t, ¹J(C,H) = 138, C(5')), 40.3 (d, ¹J(C,H) = 126, C(3)), 27.7 (t, ¹J(C,H) = 120, C(4)), 27.1, 26.6, 26.1, 24.8 (4q, ¹J(C,H) = 126, Me₂C, 2 Me₃CSi), 19.1, 18.4 (2s, Me₂CSi), -2.8, -3.2, -3.8, -3.9 (4q, ¹J(C,H) = 118, 2 Me₂Si). CI-MS (NH₃) m/z: 530 (1, M⁺), 475 (17), 142 (100), 76 (21), 75 (44), 74 (55), 73 (82). Anal.

Calcd for C₂₆H₅₁NO₆Si₂: C 58.94, H 9.70, N 2.64. Found: C 58.80, H 9.57, N 2.67.

1,6-Anhydro-3,4-dideoxy-3-[(1'S)-2',5'-dideoxy-2',5'-imino-D-*ribitol*-1'-C-yl]-β-D-*lyxo*-hexopyranose ((-)-**21**) and methyl 3,4-dideoxy-3-[(1'S)-2',5'-dideoxy-2',5'-imino-D-*ribitol*-1'-C-yl]-α-D-*lyxo*-hexopyranoside ((+)-**22**). A mixture of (-)-**20** (92 mg, 0.17 mmol) and 1 M H₂SO₄ in MeOH (4 mL) was stirred at 50°C for 10 h. Amberlite (OH⁻) (2 g) was added and the solution collected. The resin was washed with MeOH (20 mL), then with water (60 mL). The combined solutions were concentrated under vacuum. FC (*i*-PropOH/5% aqueous NH₄ 5:2) separated (-)-**21** and (+)-**22** that were purified by chromatography on Dowex (1x8 OH⁻, elution with H₂O). Lyophilisation gave 23 mg (40%) of (-)-**21** and 25 mg (45%) of (+)-**22**.

Data of (-)-**21**: white solid. $[\alpha]_{589}^{25} = -5.2$, $[\alpha]_{577}^{25} = -7.7$, $[\alpha]_{546}^{25} = -9.2$, $[\alpha]_{435}^{25} = -8.7$, $[\alpha]_{405}^{25} = -10$ (*c* = 0.6, H₂O). IR (KBr) ν : 3385, 1635, 1400, 1195, 1105, 1020, 620 cm⁻¹. ¹H-NMR (400 MHz, D₂O/CD₃OD 4:1, 50°C): δ_{H} 5.42 (*d*, ³*J*(H-C(1),H-C(2)) = 1.8, H-C(1)), 4.76 (*br ddd*, ³*J*(H-C(5),Hb-C(4)) = 6.3, ³*J*(H-C(5),H-C(6)) = 4.6, ³*J*(H-C(5),Ha-C(4)) = 4.1, H-C(5)), 4.42 (*ddd*, ³*J*(H-C(4'),H-C(3')) = 4.2, ³*J*(H-C(4'),Ha-C(5')) = 3.9, ³*J*(H-C(4'),Hb-C(5')) = 1.9, H-C(4')), 4.25 (*dd*, ³*J*(H-C(3'),H-C(2')) = 8.4, ³*J*(H-C(3'),H-C(4')) = 4.2, H-C(3')), 4.11 (*dd*, ³*J*(H-C(1'),H-C(2')) = 7.1, ³*J*(H-C(1'),H-C(3)) = 3.6, H-C(1')), 3.96 (*dd*, ²*J*(Ha-C(6),Hb-C(6)) = 7.4, ⁴*J* = 0.8, Ha-C(6)), 3.85 (*ddd*, ²*J*(Hb-C(6),Ha-C(6)) = 7.4, ³*J*(Hb-C(6),H-C(5)) = 5.1, ⁴*J* = 1.2, Hb-C(6)), 3.66 (*dd*, ³*J*(H-C(2'),H-C(3')) = 8.4, ³*J*(H-C(2'),H-C(1')) = 7.1, H-C(2')), 3.60 (*dd*, ²*J*(H-C(2),H-C(3)) = 9.7, ³*J*(H-C(2),H-C(1)) = 1.8, H-C(2)), 3.53 (*dd*, ²*J*(Hb-C(5'),Ha-C(5')) = 13.0, ³*J*(Ha-C(5'),H-C(4')) = 3.9, Ha-C(5')), 3.43 (*dd*, ²*J*(Hb-C(5'),Ha-C(5')) = 13.0, ³*J*(Hb-C(5'),H-C(4')) = 1.9, Hb-C(5')), 2.07 (*dddd*, ³*J*(H-C(3),Ha-C(4)) = 11.3, ³*J*(H-C(3),H-C(2)) = 9.7, ³*J*(H-C(3),Hb-C(4)) = 6.5, ³*J*(H-C(3),H-C(1')) = 3.6, H-C(3)), 1.87 (*br ddd*, ²*J*(Ha-C(4),Hb-C(4)) = 13.6, ³*J*(Ha-C(4),H-C(3)) = 11.3, ³*J*(Ha-C(4),H-C(5)) = 4.1, Ha-C(4)), 1.82 (*br dddd*, ²*J*(Hb-C(4),Ha-C(4)) = 13.6, ³*J*(Hb-C(4),H-C(5)) = 6.3, ³*J*(Hb-C(4),H-C(3)) = 6.5, ⁴*J* = 1.9, Hb-C(4)). ¹³C-NMR (100.6 MHz, D₂O/CD₃OD 9:1): δ_{C} 103.0 (*d*, ¹*J*(C,H) = 174, C(1)), 74.3 (*d*, ¹*J*(C,H) = 153, C(5)), 73.7 (*d*, ¹*J*(C,H) = 125, C(3')), 70.8 (*d*, ¹*J*(C,H) = 153, C(4')), 69.3 (*d*, ¹*J*(C,H) = 151, C(2)), 69.1 (*t*, ¹*J*(C,H) = 145, C(6)), 68.9 (*d*, ¹*J*(C,H) = 141, C(1')), 63.4 (*d*, ¹*J*(C,H) = 143, C(2')), 50.4 (*t*, ¹*J*(C,H) = 145, C(5')), 39.1 (*d*, ¹*J*(C,H) = 123, C(3)), 28.0 (*t*, ¹*J*(C,H) = 127, C(4)). CI-MS (NH₃) *m/z*: 262 (100, *M*⁺), 219 (19), 199 (18), 177 (32), 159 (12), 123 (18), 102 (55).

Data of (+)-**22**: slightly yellowish oil. $[\alpha]_{589}^{25} = 39$, $[\alpha]_{577}^{25} = 42$, $[\alpha]_{546}^{25} = 65$, $[\alpha]_{435}^{25} = 101$, $[\alpha]_{405}^{25} = 100$ (*c* = 0.6, H₂O). IR (film) ν : 3075, 2015, 1765, 1410 cm⁻¹. ¹H-NMR (400 MHz, D₂O/CD₃OD 4:1, 40°C): δ_{H} 4.86 (*s*, H-C(1)), 4.52 (*br d*, ³*J*(H-C(1'),H-C(3)) = 9.1, H-C(1')), 4.32 (*dd*, ³*J*(H-C(3'),H-C(2')) = 6.0, ³*J*(H-C(3'),H-C(4')) = 4.3 H-C(3')), 4.22 (*ddd*, ³*J*(H-C(4'),H-C(3')) = 4.3, ³*J*(H-C(4'),Hb-C(5')) = 3.4,

$^3J(\text{H-C}(4'), \text{Ha-C}(5')) = 2.1$, $\text{H-C}(4')$), 3.98 (br d , $^3J(\text{H-C}(2), \text{H-C}(3)) = 4.4$, $\text{H-C}(2)$), 3.77 (dddd, $^3J(\text{H-C}(5), \text{Hb-C}(4)) = 9.7$, $^3J(\text{H-C}(5), \text{Hb-C}(6)) = 6.6$, $^3J(\text{H-C}(5), \text{Ha-C}(6)) = 4.1$, $^3J(\text{H-C}(5), \text{Ha-C}(4)) = 3.4$, $\text{H-C}(5)$), 3.63 (dd , $^2J(\text{Ha-C}(6), \text{Hb-C}(6)) = 11.6$, $^3J(\text{Ha-C}(6), \text{H-C}(5)) = 4.1$, $\text{Ha-C}(6)$), 3.54 (dd , $^2J(\text{Hb-C}(6), \text{Ha-C}(6)) = 11.6$, $^3J(\text{Hb-C}(6), \text{H-C}(5)) = 6.6$, $\text{Hb-C}(6)$), 3.43 (s , $\text{H}_3\text{CO-}$), 3.07 (d , $^2J(\text{H-C}(2'), \text{H-C}(3')) = 6.0$, $\text{Ha-C}(2')$), 2.95 (dd , $^2J(\text{Ha-C}(5'), \text{Hb-C}(5')) = 12.6$, $^3J(\text{Ha-C}(5'), \text{H-C}(4')) = 2.1$, $\text{Ha-C}(5')$), 2.80 (m , $\text{H-C}(3)$), 2.83 (dd , $^2J(\text{Hb-C}(5'), \text{Ha-C}(5')) = 12.6$, $^3J(\text{Hb-C}(5'), \text{H-C}(4')) = 3.4$, $\text{Hb-C}(5')$), 1.68 (ddd , $^2J(\text{Ha-C}(4), \text{Hb-C}(4)) = 14.0$, $^3J(\text{Ha-C}(4), \text{H-C}(3)) = 10.8$, $^3J(\text{Ha-C}(4), \text{H-C}(5)) = 3.4$, $\text{Ha-C}(4)$), 1.48 (ddd , $^2J(\text{Hb-C}(4), \text{Ha-C}(4)) = 14.0$, $^3J(\text{Hb-C}(4), \text{H-C}(5)) = 9.7$, $^3J(\text{Hb-C}(4), \text{H-C}(3)) = 4.3$, $\text{Hb-C}(4)$). $^{13}\text{C-NMR}$ (100.6 MHz, $\text{D}_2\text{O}/\text{CD}_3\text{OD}$ 9:1): δ_{C} 109.6 (d , $^1J(\text{C}, \text{H}) = 172$, $\text{C}(1)$), 83.0, 75.9, 74.1, 73.7, 71.1 (d , $^1J(\text{C}, \text{H}) = 148$, 147, 155, 152, 142, $\text{C}(2)$, $\text{C}(5)$, $\text{C}(1')$, $\text{C}(3')$, $\text{C}(4')$), 66.9 (t , $^1J(\text{C}, \text{H}) = 142$, $\text{C}(6)$), 61.5 (d , $^1J(\text{C}, \text{H}) = 136$, $\text{C}(2')$), 55.6 (q , $^1J(\text{C}, \text{H}) = 144$, $\text{CH}_3\text{O-}$), 52.1 (t , $^1J(\text{C}, \text{H}) = 141$, $\text{C}(5')$), 39.5 (d , $^1J(\text{C}, \text{H}) = 129$, $\text{C}(3)$), 27.8 (t , $^1J(\text{C}, \text{H}) = 124$, $\text{C}(4)$). CI-MS (NH_3) m/z : 293 (1, M^+), 217 (7), 191 (9), 163 (20), 130 (38), 121 (25), 109 (65), 95 (100), 81 (88). Anal. Calcd for $\text{C}_{12}\text{H}_{23}\text{NO}_7$: C 49.14, H 7.90. Found: C 49.00, H 8.14.

(-)-*N*-Benzyloxycarbonyl-2,3-di-*O*-[*tert*-butyldimethylsilyl]-1,4-dideoxy-1,4-imino-5,6-*O*-isopropylidene-D-glucitol ((-)-**24**). A mixture of *N*-benzyl-2,3-di-*O*-[*tert*-butyldimethyl]-1,4-dideoxy-1,4-imino-5,6-*O*-isopropylidene-D-glucitol (**23**,³⁵ 605 mg, 1.16 mmol), 10% Pd-C (100 mg) and THF (20 mL) was degassed and pressurized with H_2 (1 atm). After shaking at 20°C for 2 days, the precipitate was filtered off (Celite) and the solvent evaporated *in vacuo* to dryness. The residue was taken in 1:1 EtOH/ H_2O (25 mL). NaHCO_3 (175 mg), then benzyl chloroformate (170 mg, 1.39 mmol) were added. The mixture was stirred at 20°C for 1 h and a saturated aqueous solution of NaHCO_3 (20 mL) was added. Extraction with EtOAc (15 mL, 4 times), drying (MgSO_4), solvent evaporation and FC (EtOAc/light petroleum ether 1:10) afforded 974 mg (84%) of (-)-**24** as a colorless oil. $[\alpha]_{\text{D}}^{25} = -9$, $[\alpha]_{\text{D}}^{25} = -56$, $[\alpha]_{\text{D}}^{25} = -95$, $[\alpha]_{\text{D}}^{25} = -99$, $[\alpha]_{\text{D}}^{25} = -146$ ($c = 0.9$, CHCl_3). UV (MeCN): $\lambda_{\text{max}} = 205$ nm ($\epsilon = 7900$). IR (film) ν : 2935, 2960, 1710, 1465, 1405, 1350, 1255, 1210, 1125, 1065, 1040, 1010, 920 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, toluene- d_8 , 373 K): δ_{H} 7.37 (m , 5H), 5.21 (s , 2H), 4.51 (dd , $^3J = 8.2$, 7.4, $\text{Ha-C}(6)$), 4.41 (m , $\text{Hb-C}(6) + \text{H-C}(3)$), 4.28 (m , $\text{H-C}(5) + \text{H-C}(4)$), 4.15 (br s , $\text{H-C}(2)$), 3.86 and 3.72 ($2d$, $^2J = 12.0$, $\text{H}_2\text{C}(1)$), 1.49 and 1.52 ($2s$, Me_2C), 1.11 and 1.02 ($2s$, 2 t -Bu), 0.33, 0.29, 0.21, 0.18 ($4s$, 2 Me_2Si). $^{13}\text{C-NMR}$ (100.6 MHz, toluene- d_8 , 373 K): δ_{C} 161 (s , CO), 132 (C arom.), 112 (s), 83.0, 80.4, 80.1 ($3d$), 74.1, 71.8 ($2t$), 68.5 (d), 58.9 (t), 31.4 and 30.8 ($2q$), 30.7 and 30.4 ($2q$, 2 t -BuSi), 24.8 (s), -0.04, -0.09 ($2q$, 2 Me_2Si). CI-MS (NH_3) m/z : 566 (40, M^+), 450 (24), 330 (35), 91 (100). Anal. Calcd for $\text{C}_{29}\text{H}_{51}\text{NO}_6\text{Si}_2$: C 61.54, H 9.08, N 2.47, Si 9.92. Found: C 61.66, H 9.00, N 2.39, Si 9.02.

(-)-*N*-[*tert*-Butylcarbonyl]-2,3-di-*O*-[*tert*-butyldimethylsilyl]-1,4-dideoxy-1,4-imino-5,6-*O*-isopropylidene-

dene-D-glucitol ((-)-**25**). A mixture of *N*-benzyl-2,3-di-*O*-[*tert*-butyldimethyl]-1,4-dideoxy-1,4-imino-5,6-*O*-isopropylidene-D-glucitol (**23**,²⁷ 997 mg, 1.91 mmol), MeOH (40 mL), di-*tert*-butyl dicarbonate ((*t*-BuOCO)₂O, 0.96 g, 3.7 mmol) and 10% Pd(OH)₂ on charcoal (0.54 g) was degassed and pressurized (1 atm) with H₂. After shaking at 20°C for 48 h, the precipitate was filtered off (Celite) and the solvent evaporated. FC (EtOAc/light petroleum ether 1:10) gave 985 mg (97%) of (-)-**25** as an amorphous solid. [α]₅₈₉²⁵ = -19, [α]₅₇₇²⁵ = -20, [α]₅₄₆²⁵ = -25, [α]₄₃₅²⁵ = -37, [α]₄₀₅²⁵ = -43 (*c* = 0.9, CHCl₃). ¹H-NMR (400 MHz, toluene-d₈, 373 K): δ _H 4.65 (*dd*, ²*J* = 8.0, ³*J*(Ha-C(6),H-5) = 5.9, Ha-C(6)), 4.49 (*m*, 2H, Hb-C(6) + H-C(3)), 4.36 (*dd*, ³*J* = 8.6, 5.9, H-C(5)), 4.33 (*d*, ³*J*(H-C(4),H-C(5)) = 8.5, ³*J*(H-C(3),H-C(4)) = 4.7, H-C(4)), 4.22 (*m*, H-C(2)), 3.92 (*d*, ²*J* = 11.0, Ha-C(1)), 3.73 (*dd*, ²*J* = 11.0, ³*J*(Hb-C(1),H-C(2)) = 3.4, Hb-C(1)), 1.67 (*s*, *t*-Bu), 1.62 and 1.58 (2*s*, Me₂Si), 1.18 and 1.13 (2*s*, 2 *t*-BuSi), 0.40, 0.37, 0.30 and 0.29 (4*s*, 2 Me₂Si). ¹³C-NMR (100.6 MHz, toluene-d₈, 373 K): δ _C 157.1 (*s*), 108.6 (*s*), 84.4 (*s*), 78.6 (*d*, ¹*J*(C,H) = 152), 75.9 (*d*, ¹*J*(C,H) = 150), 75.3 (*d*, ¹*J*(C,H) = 149), 68.9 (*t*, ¹*J*(C,H) = 150), 62.9 (*d*, ¹*J*(C,H) = 142), 53.9 (*t*, ¹*J*(C,H) = 144), 28.4 (*q*, ¹*J*(C,H) = 130), 26.7 and 26.0 (2*q*, ¹*J*(C,H) = 126), 25.8 and 25.6 (2*q*, ¹*J*(C,H) = 125), 19.9 and 19.7 (2*s*), 5.0 and 4.8 (2*q*, ¹*J*(C,H) = 117). CI-MS (NH₃) *m/z*: 532 (1.1, *M*⁺•), 360 (100), 330 (28).

(-)-*N*-Benzyloxycarbonyl-2,3-di-*O*-[*tert*-butyldimethylsilyl]-1,4-dideoxy-1,4-imino-D-glucitol ((-)-**26**). A mixture of (-)-**24** (453 mg, 0.80 mmol) and 80% aqueous trifluoroacetic acid was stirred at 25°C overnight. Solvent evaporation to dryness and then FC (EtOAc/light petroleum ether 1:4) gave 345 mg (82%) of (-)-**26** as a colorless oil. [α]₅₈₉²⁵ = -19, [α]₅₇₇²⁵ = -21, [α]₅₄₆²⁵ = -23, [α]₄₃₅²⁵ = -40, [α]₄₀₅²⁵ = -47 (*c* = 0.9, CHCl₃). UV (MeCN): λ_{max} = 197 nm (ϵ = 9000). IR (film) ν : 3445, 3035, 2950, 2890, 1685, 1465, 1410, 1355, 1255, 1195, 1125, 835 cm⁻¹. ¹H-NMR (400 MHz, toluene-d₈, 373 K): δ _H 7.31 (*m*, 5 H arom.), 5.22 (*AB*, 2H, ²*J* $\cong$ 11), 4.39 (*m*, H-C(3)), 4.30 (*dd*, ³*J* = 6.5, 5.9, H-C(4)), 4.15 (*m*, H-C(2)), 4.04 (*m*, H-C(5)), 3.85 (*m*, 2H, H₂C(6)), 3.79 (*br d*, ²*J* = 12.0, Ha-C(1)), 3.58 (*dd*, ²*J* = 12.0, ³*J*(Hb-C(1),H-C(2)) = 3.4, Hb-C(1)), 1.09 and 1.02 (2*s*, 2 *t*-BuSi), 0.32, 0.28, 0.21 and 0.16 (4*s*, 2 Me₂Si). ¹³C-NMR (100.6 MHz, toluene-d₈, 373 K): δ _C 155.4 (*s*), 128.3 (C arom.), 78.4 (*d*), 76.1 (*d*), 70.5 (*d*), 67.5 (*t*), 63.9 (*t*), 63.2 (*d*), 53.2 (*t*), 25.7 and 25.5 (2*q*), 17.9 (*s*), -5.0 and -5.1 (2*q*). CI-MS (NH₃) *m/z*: 526 (40, *M*⁺•), 121 (39), 91 (100). Anal. Calcd for C₂₆H₄₇O₆NSi₂: C 59.38, H 9.00, N 2.66, Si 10.68. Found: C 59.37, H 8.99, N 2.69, Si 10.72.

(-)-*N*-[*tert*-Butyloxycarbonyl]-2,3-di-*O*-[*tert*-butyldimethylsilyl]-1,4-dideoxy-1,4-imino-D-glucitol ((-)-**27**). Same procedure as for the preparation of (-)-**26**, starting from (-)-**25** (0.9 g, 1.69 mmol). FC (EtOAc/light petroleum ether 1:6): 723 mg (87%) of (-)-**27**, colorless oil. [α]₅₈₉²⁵ = -16, [α]₅₇₇²⁵ = -17, [α]₅₄₆²⁵ = -20, [α]₄₃₅²⁵ = -32, [α]₄₀₅²⁵ = -38 (*c* = 0.8, CHCl₃). UV (MeCN): λ_{max} = 196 nm (ϵ = 5500). IR (film) ν : 3445, 3055, 2930, 1555, 1470, 1395, 1255, 1205, 1040, 920, 880 cm⁻¹. ¹H-NMR (400 MHz, toluene-d₈,

373 K): δ_{H} 4.42 (*dd*, $^3J(\text{H-C}(2),\text{H-C}(3)) = 2.6$, $^3J(\text{H-C}(3),\text{H-C}(4)) = 5.4$, H-C(3)), 5.29 (*dd*, $^3J(\text{H-C}(3),\text{H-C}(4)) = 5.4$, $^3J(\text{H-C}(4),\text{H-C}(5)) = 6.4$, H-C(4)), 4.19 (*m*, H-C(2)), 4.06 (*m*, H-C(5)), 3.90 (*m*, AB, 2H, $^2J \approx 11$, H₂C(6)), 3.77 (*br d*, $^2J = 11.8$, Ha-C(1)), 3.59 (*dd*, $^2J = 11.8$, $^3J(\text{Hb-C}(1),\text{H-C}(2)) = 3.4$, Hb-C(1)), 1.63 (*s*, *t*-BuO), 1.14 and 1.11 (2*s*, 2 *t*-BuSi), 0.37, 0.32, 0.28 and 0.26 (4*s*, 2 Me₂Si). ¹³C-NMR (100.6 MHz, toluene-d₈, 373 K): δ_{C} 157.1 (*s*), 80.2 (*s*), 78.6 (*d*, $^1J(\text{C,H}) = 152$), 76.2 (*d*, $^1J(\text{C,H}) = 151$), 70.7 (*d*, $^1J(\text{C,H}) = 145$), 64.1 (*t*, $^1J(\text{C,H}) = 143$), 62.8 (*d*, $^1J(\text{C,H}) = 141$), 53.3 (*t*, $^1J(\text{C,H}) = 144$), 28.2 (*q*, $^1J(\text{C,H}) = 130$), 25.7 (*q*, $^1J(\text{C,H}) = 125$), 25.6 (*q*, $^1J(\text{C,H}) = 125$), 19.7 and 19.6 (2*s*), 5.0 and 4.9 (2*q*, $^1J(\text{C,H}) = 118$). CI-MS (NH₃) *m/z*: 492 (1.8, *M*⁺), 392 (40), 334 (100).

(-)-*N*-Benzyloxycarbonyl-3,4-di-*O*-[*tert*-butyldimethylsilyl]-2,5-dideoxy-2,5-imino-L-xylose ((-)-**28**). A mixture of (-)-**26** (100 mg, 0.19 mmol), CH₂Cl₂ (2 mL), NaHCO₃ (32 mg) and Pb(OAc)₄ (126 mg, 0.28 mmol) was stirred at 20°C for 30 min. A saturated aqueous solution of NaHCO₃ (3 mL) was added. The mixture was extracted with CHCl₃ (5 mL, 3 times). After drying (MgSO₄) the solvent was evaporated giving pure (-)-**28** (90 mg, 96%) as a colorless oil. $[\alpha]_{\text{D}}^{25} = -60$, $[\alpha]_{\text{D}}^{25} = -62$, $[\alpha]_{\text{D}}^{25} = -69$, $[\alpha]_{\text{D}}^{25} = -120$, $[\alpha]_{\text{D}}^{25} = -150$ (*c* = 0.5, CHCl₃). UV (MeCN): $\lambda_{\text{max}} = 196$ nm ($\epsilon = 8700$). IR (film) ν : 2955, 2885, 2860, 1735, 1715, 1470, 1415, 1355, 1260, 1130, 1010, 835 cm⁻¹. ¹H-NMR (400 MHz, toluene-d₈, 298 K) mixture of two rotamers: δ_{H} 9.55, 9.46 (2*s*, HCO), 7.32 (*m*, 5 H arom.), 5.14, 4.30, 4.18 (3*m*, 3H), 3.99 (*br s*, 1H), 3.80 (*m*, 1H), 3.63 and 3.53 (2*d*, $^2J = 11.0$, 1H), 0.85 and 0.84 (2*s*, 2 *t*-Bu), 0.08, 0.07, 0.05 and 0.03 (4*s*, 2 Me₂Si). ¹³C-NMR (100.6 MHz, toluene-d₈, 373 K): δ_{C} 198.7 (*d*, 155.6 (*s*), 128.2 (C arom.), 76.1 and 68.0 (2*d*), 67.2 (*t*), 54.1 (*d*), 53.1 (*t*), 25.5 and 25.2 (2*q*), 17.7 (*s*), -4.9 and -5.1 (2*q*). Anal. Calcd for C₂₅H₄₃NO₅Si₂: C 60.81, H 8.77, N 2.83, Si 11.37. Found: C 60.73, H 8.70, N 2.75, Si 11.27.

(-)-*N*-*tert*-Butyloxycarbonyl-3,4-di-*O*-[*tert*-butyldimethylsilyl]-2,5-dideoxy-2,5-imino-L-xylose ((-)-**29**). Same procedure as for the preparation of (-)-**28**, starting from (-)-**27**. Yield: 97%, pure (-)-**29**, colorless oil. $[\alpha]_{\text{D}}^{25} = -59$, $[\alpha]_{\text{D}}^{25} = -60$, $[\alpha]_{\text{D}}^{25} = -70$, $[\alpha]_{\text{D}}^{25} = -122$, $[\alpha]_{\text{D}}^{25} = -145$ (*c* = 0.5, CHCl₃). UV (MeCN): $\lambda_{\text{max}} = 196$ nm ($\epsilon = 9000$). ¹H-NMR (400 MHz, toluene-d₈, 298 K) 2:1 mixture of two rotamers: δ_{H} 9.49 (*d*, 0.36H, $^3J = 2.8$, H-C(1)), 9.43 (*d*, 0.64H, $^3J = 3.8$, H-C(1)), 4.26 (*m*, 1H), 4.18 (*dd*, 0.36H, $^3J(\text{H-C}(1),\text{H-C}(2)) = 2.9$, $^3J(\text{H-C}(2),\text{H-C}(3)) = 4.7$, H-C(2)), 4.03 (*dd*, 0.64H, $^3J = 4.0$, 3.8, H-C(2)), 3.96 (*m*, 1H), 3.70 (*dd*, 1H, $^2J = 11.3$, $^3J = 3.5$, Hb-C(5)), 3.54 (*br d*, 0.64H, $^2J = 11.3$, Ha-C(5)), 3.42 (*br d*, 0.36H, $^2J = 11.3$, Ha-C(5)), 1.40 (*s*, *t*-BuO), 0.84 and 0.83 (2*s*, 2 *t*-BuSi), 0.061, 0.058, 0.057 and 0.050 (4*s*, 2 Me₂Si). ¹³C-NMR (100.6 MHz, toluene-d₈, 373 K): δ_{C} 199.1 (*d*, $^1J(\text{C,H}) = 180$, C(1)), 154 (*s*, NCOO), 79.8 (*d*, $^1J(\text{C,H}) = 157$), 76.3 (*d*, $^1J(\text{C,H}) = 148$), 68.1 (*dd*, $^1J(\text{C,H}) = 148$, $^2J(\text{C,H}) = 22$, C(2)), 53.0 (*t*, $^1J(\text{C,H}) = 143$, C(5)), 28.1 (*q*, $^1J(\text{C,H}) = 127$, *t*-BuO), 25.5 (*q*, $^1J(\text{C,H}) = 127$, *t*-BuSi), 19.8 (*q*, $^1J(\text{C,H}) = 125$), 17.8 (2*s*), 5.0 and 0.9 (2*q*, $^1J(\text{C,H}) = 118$).

(3*R*)-1,6-Anhydro-2-*O*-benzyl-3-{3',6'-[*tert*-butoxycarbonyl]imino-1',2',3',6'-tetra-deoxy-4',5'-*O*-isopropylidene-*L*-arabino-hexitol-1'-C-yl}-3-deoxy- β -D-*erythro*-hexopyran-4-ulose (**36**). A solution of enone ((+)-**31**) (28.6 mg, 0.057 mmol)⁴⁰ in anhydrous THF (2 mL) previously degassed with argon was heated under reflux for 5 h in the presence of Mo(CO)₆ (3.5 mg, 0.013 mmol) and PhSiH₃ (14 μ L, 0.114 mmol). Then water (2 mL) was added and the mixture was extracted with CH₂Cl₂ (6 mL, 3 times). The combined extracts were dried (MgSO₄) and concentrated. FC (EtOAc/light petroleum ether 1:2.5) gave 18.3 mg (64%) of **36** as a colorless oil. ¹H-NMR (400 MHz, CDCl₃, 333 K): δ_{H} 7.38-7.28 (*m*, 5H arom.), 5.64 (*s*, H-C(1)), 4.71 (*d*, ²*J* = 11.6, CH₂(Bn)), 4.72-4.65 (*m*, 2H, H-C(4'), H-C(5')), 4.65 (*d*, ²*J* = 11.6, CH₂(Bn)), 4.55 (*d*, ³*J* = 5.1, H-C(5)), 3.89-3.82 (*m*, 2H, H-C(3'), Ha-C(6')), 3.85 (*d*, ³*J* = 7.6, H_{endo}-C(6)), 3.74 (*dd*, ³*J* = 7.6, 5.1, H_{exo}-C(6)), 3.36 (*d*, ³*J* = 6.0, H-C(2)), 3.27 (*dd*, ²*J* = 12.1, ³*J* = 4.1, Hb-C(6')), 2.76 (*q*, ³*J* = 6.0, H-C(3)), 1.95-1.76 (*m*, 3H), 1.73-1.62 (*m*, 1H), 1.50 (*s*, 3H, Me₂C), 1.47 (*s*, 9H, Boc), 1.33 (*s*, 3H, Me₂C).

1,6-Anhydro-2-*O*-benzyl-3-{3',6'-[*tert*-butoxycarbonyl]imino-1',2',3',6'-tetra-deoxy-4',5'-*O*-isopropylidene-*L*-arabino-hexitol-1'-C-yl}-3-deoxy- β -D-galactopyranose (**37**). 1 M LiAlH₄ in THF (72 μ L) was added dropwise to a solution of **36** (18.3 mg, 0.036 mmol) in dry THF (0.5 mL) cooled to -78°C under argon atmosphere. After stirring at -78°C for 2 h, Et₂O (0.3 mL) and then water (0.5 mL) were added dropwise. The mixture was acidified with 0.5 M aqueous HCl, then extracted with CH₂Cl₂ (5 mL, 3 times). The combined organic extracts were washed with saturated aqueous solution of NaHCO₃, dried (MgSO₄), concentrated under reduced pressure and purified by FC (light petroleum ether/EtOAc 1:1.5) to give 11.6 mg (63%) of **37** as a colorless oil. ¹H-NMR (400 MHz, CDCl₃, 333K): δ_{H} 7.37-7.28 (*m*, 5H arom.), 5.39 (*s*, H-C(1)), 4.76-4.69 (*m*, H-C(4'), H-C(5')), 4.59 (*s*, 2H, CH₂(Bn)), 4.51 (*t*, ³*J* = 5.3, H-C(5)), 4.38 (*t*, ³*J* = 5.9, H-C(4)), 4.12 (*br d*, ²*J* = 7.3, H_{endo}-C(6)), 3.98-3.95 (*m*, H-C(3')), 3.84 (*dd*, ²*J* = 12.5, ³*J* = 6.9, Ha-C(6')), 3.51 (*dd*, ²*J* = 7.3, ²*J* = 5.2, H_{exo}-C(6)), 3.29 (*dd*, ²*J* = 12.5, ³*J* = 4.1, Hb-C(6')), 3.23 (*d*, ³*J* = 3.9, H-C(2)), 2.01-1.98 (*m*, H-C(3)), 1.85-1.79 (*m*, Ha-C(2')), 1.70-1.63 (*m*, 3H, Hb-C(2')), Ha-C(1'), Hb-C(1')), 1.52 (*s*, 3H, Me₂C), 1.47 (*s*, 9H, Boc), 1.37 (*s*, 3H, Me₂C). ¹³C-NMR (100.6 MHz, CDCl₃, 333K): δ_{C} 155.2 (*s*), 138.0 (*s*), 128.4 (*d*, 2C), 128.0 (*d*, 2C), 127.8 (*d*), 113.3 (*s*), 101.6 (*d*, C(1)), 80.6 (*d*), 79.6 (*d*, C(2)), 78.1 (*d*), 74.3 (*d*, C(5)), 71.4 (*t*, CH₂(Bn)), 64.6 (*d*, C(4)), 62.6 (*t*, C(6)), 57.2 (*d*, C(3')), 49.8 (*t*, C(6')), 38.5 (*d*, C(3)), 28.4 (*q*, 3C, Boc), 26.8 (*t*, C(2')), 26.2, 25.2 (2*q*), 20.8 (*t*, C(1')).

1,6-Anhydro-3-{3',6'-[*tert*-butoxycarbonyl]imino-1',2',3',6'-tetra-deoxy-4',5'-*O*-isopropylidene-*L*-arabino-hexitol-1'-C-yl}-3-deoxy- β -D-galactopyranose ((+)-**38**). A degassed mixture of (+)-**33**³⁹ (202 mg, 0.489 mmol), PtO₂ (100 mg) and EtOAc (30 mL) was stirred under H₂ atmosphere at 20°C for 16 h. The catalyst was filtered off, the solvent evaporated *in vacuo* and then FC (light petroleum ether/EtOAc 1:5) gave 193 mg (95%) of (+)-**38** as a waxy solid. [α]₅₈₉²⁵ = 49, [α]₅₇₇²⁵ = 54, [α]₅₄₆²⁵ = 61, [α]₄₃₅²⁵ = 103,

$[\alpha]_{405}^{25} = 125$ ($c = 0.6$, CHCl_3). UV (MeCN): $\lambda_{\text{max}} = 197$ nm ($\epsilon = 3400$). IR (KBr) ν : 3455, 2980, 1670, 1410, 1165, 1085 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 333 K): δ_{H} 5.33 (br s, H-C(1)), 4.78-4.69 (*m*, H-C(4'), H-C(5')), 4.44 (*t*, $^3J = 5.0$, H-C(5)), 4.33 (*dd*, $^3J = 7.1$, 5.2, H-C(4)), 4.09 (*d*, $^2J = 7.6$, H_{endo} -C(6)), 4.07-4.02 (*m*, H-C(3')), 3.88 (*dd*, $^2J = 12.5$, $^3J = 6.9$, Ha-C(6')), 3.57 (*dd*, $^2J = 7.6$, $^3J = 5.0$, H_{exo} -C(6)), 3.56 (br s, H-C(2)), 3.27 (*dd*, $^2J = 12.5$, $^3J = 4.3$, Hb-C(6')), 2.04-2.01 (*m*, H-C(3)), 1.84-1.77 (*m*, Ha-C(1'), Ha-C(2')), 1.72-1.65 (*m*, Hb-C(2')), 1.65-1.55 (*m*, Hb-C(1')), 1.52 (*s*, 3H), 1.47 (*s*, 9H, Boc), 1.36 (*s*, 3H). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3 , 333 K): δ_{C} 155.2 (*s*), 113.3 (*s*), 102.9 (*d*, C(1)), 80.5 (*s*, Boc), 79.9 (*d*, C(4')), 78.2 (*d*, C(5')), 75.1 (*d*, C(5)), 72.5 (*d*, C(2)), 64.9 (*d*, C(4)), 63.0 (*t*, C(6)), 57.8 (*d*, C(3')), 50.1 (*t*, C(6')), 42.8 (*d*, C(3)), 28.5 (*q*, Boc), 27.6 (*t*, C(2')), 26.3, 25.2 (2*q*, Me_2C), 21.5 (*t*, C(1')). $^1\text{H-NMR}$ (400 MHz, CD_3OD , 333 K): δ_{H} 5.24 (br s, H-C(1)), 4.83-4.73 (*m*, H-C(4'), H-C(5')), 4.53 (*t*, $^3J = 4.8$, H-C(5)), 4.27 (*dd*, $^3J = 7.4$, 4.7, H-C(4)), 4.10 (*d*, $^2J = 7.5$, H_{endo} -C(6)), 3.90-3.85 (*m*, H-C(3')), 3.81 (*dd*, $^2J = 12.2$, $^3J = 6.9$, Ha-C(6')), 3.56 (*t*, $^3J = 1.9$, H-C(2)), 3.51 (*dd*, $^2J = 7.5$, $^3J = 4.9$, H_{exo} -C(6)), 3.25 (*dd*, $^2J = 12.2$, $^3J = 4.3$, Hb-C(6')), 2.08-1.91 (*m*, Ha-C(1'), Ha-C(2')), 1.87-1.84 (*m*, H-C(3)), 1.79-1.71 (*m*, Hb-C(2')), 1.52 (*s*, 3H), 1.49 (*s*, Boc), 1.49-1.40 (*m*, Hb-C(1')), 1.36 (*s*, 3H). $^{13}\text{C-NMR}$ (100.6 MHz, CD_3OD , 333 K): δ_{C} 157.3 (*s*), 114.0 (*s*), 105.2 (*d*), 82.4 (*d*), 82.2 (*s*), 79.8 (*d*), 77.7 (*d*), 73.7 (*d*), 66.6 (*d*), 64.7 (*t*), 62.1 (*d*), 52.6 (*t*), 46.5 (*d*), 30.9 (*t*), 29.7 (*q*), 27.9, 26.3 (2*q*), 24.8 (*t*). CI-MS (NH_3) m/z : 416 (29, $[\text{M}+\text{H}]^+$), 415 (2, $\text{M}^{+\bullet}$), 397 (1), 360 (13), 316 (100), 142 (52). Anal. Calcd for $\text{C}_{20}\text{H}_{33}\text{NO}_8$: C 57.82, H 8.01, N, 3.37. Found: C 57.78, H 8.13, N 3.39.

1,6-Anhydro-2-*O*-cyclohexylmethyl-3-{3',6'-[*tert*-butoxycarbonyl]imino-1',2',3',6'-tetra-deoxy-4',5'-*O*-isopropylidene-L-*arabino*-hexitol-1'-C-yl}-3-deoxy- β -D-galactopyranose (**39**) and 1,6-Anhydro-2-*O*-cyclohexylmethyl-3-{3',6'-[*tert*-butylcarbonyl]imino-1',2',3',6'-tetra-deoxy-4',5'-*O*-isopropylidene-L-*arabino*-hexitol-1'-C-yl}-3-deoxy- β -D-gulopyranose (**40**). A degassed mixture of (+)-**32** (39.3 mg, 0.078 mmol), PtO_2 (40 mg) and EtOAc (6 mL) was stirred under H_2 (1 atm) at 20°C for 16 h. The catalyst was filtered off (Celite), the solvent evaporated *in vacuo*. FC (light petroleum ether/EtOAc 1:1) afforded 13.2 mg (33%) of **39** and 10.4 mg (26%) of **40**.

Data of **39**: $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 333 K): δ_{H} 5.35 (*s*, H-C(1)), 4.77 (*dd*, $^3J = 6.6$, 6.5, H-C(4')), 4.71 (*ddd*, $^3J = 6.7$, 6.8, 4.5, H-C(5')), 4.51 (*dd*, $^3J = 5.5$, 5.4, H-C(5)), 4.34 (*dd*, $^3J = 6.5$, 6.4, H-C(4)), 4.14 (*d*, $^2J = 7.4$, H_{endo} -C(6)), 3.97-3.92 (*m*, H-C(3')), 3.83 (*dd*, $^2J = 12.4$, $^3J = 6.9$, Ha-C(6')), 3.49 (*dd*, $^2J = 7.4$, $^3J = 5.2$, H_{exo} -C(6)), 3.36 (*dd*, $^2J = 9.2$, $^3J = 6.2$, 1H), 3.30 (*dd*, $^2J = 12.4$, $^3J = 4.5$, Hb-C(6')), 3.23 (*dd*, $^2J = 9.2$, $^3J = 6.5$, 1H), 3.03 (*d*, $^3J = 4.5$, H-C(2)), 1.96-1.83 (*m*, 2H, Ha-C(2'), H-C(3)), 1.80-1.54 (*m*, 8H, Hb-C(2'), Ha-C(1'), Hb-C(1'), 5H cyclohexyl), 1.53 (*s*, 3H), 1.49 (*s*, 9H), 1.37 (*s*, 3H), 1.35-1.16 (*m*, 4H), 1.01-0.88 (*m*, 2H). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3 , 333 K): δ_{C} 155.0 (*s*), 113.1 (*s*), 101.9 (*d*, C(1)), 81.1 (*d*, C(2)), 80.3 (*s*, Boc), 80.2 (*d*, C(4')), 78.0 (*d*, C(5')), 75.8 (*t*, $\text{CH}_2\text{O-C}(2)$), 74.2 (*d*, C(5)),

64.7 (d, C(4)), 62.2 (t, C(6)), 58.7 (d, C(3')), 50.6 (t, C(6')), 39.4 (d, C(3)), 38.3 (d, cyclohexyl), 30.2 (t), 28.5 (q), 27.2 (t), 26.7 (q), 26.5 (t), 25.9 (t), 25.3 (q), 22.0 (t). CI-MS (NH₃) m/z: 529 (2, $M^{\bullet+}+18$), 512 (29, $[M+H]^+$), 511 (2, $M^{\bullet+}$), 462 (7), 412 (100), 339 (20), 338 (51), 191 (11), 142 (22).

Data of **40**: ¹H-NMR (400 MHz, CDCl₃, 333 K): δ_H 5.44 (d, ³J = 2.1, H-C(1)), 4.72-4.65 (m, 2H, H-C(4'), H-C(5')), 4.34 (dd, ³J = 4.4, 4.3, H-C(5)), 4.07 (d, ³J = 7.5, H_{endo}-C(6)), 3.89-3.76 (m, 3H, H-C(4), H-C(3'), Ha-C(6')), 3.65 (dd, ²J = 7.4, ³J = 4.9, H_{exo}-C(6)), 3.40 (dd, ²J = 8.9, ³J = 6.1, 1H), 3.30-3.26 (m, 2H, H-C(2), Hb-C(6')), 3.24 (dd, ²J = 8.9, ³J = 6.8, 1H), 1.89-1.54 (m, 10H, Ha-C(1'), Hb-C(1'), Ha-C(2'), Hb-C(2'), H-C(3), 5H cyclohexyl), 1.53 (s, 3H), 1.47 (s, 9H), 1.36 (s, 3H), 1.28-1.15 (m, 4H cyclohexyl), 1.00-0.92 (m, 2H cyclohexyl). ¹³C-NMR (100.6 MHz, CD₃OD, 333 K): δ_C 154.7 (s), 112.8 (s), 99.8 (d, C(1)), 80.3 (d), 79.9 (s), 77.9 (d), 77.6 (d, C(2)), 77.3 (t), 75.6 (d, C(5)), 69.3 (d, C(4)), 63.6 (t, C(6)), 60.2 (d, C(3')), 50.8 (t, C(6')), 40.7 (d, C(3)), 38.6 (d), 30.1 (t), 28.5 (q), 26.8 (q), 26.7 (t), 26.5 (t), 25.9 (t), 25.3 (q), 23.9 (t). CI-MS (NH₃) m/z: 512 (17, $[M+H]^+$), 511 (2, $M^{\bullet+}$), 462 (45), 412 (100), 338 (41), 191 (20), 142 (65).

1,6-Anhydro-3-deoxy-3-{1',2',3',6'-tetra-deoxy-3',6'-[trifluoromethylcarbonyl]imino-4',5'-O-isopropylidene-L-arabino-hexitol-1'-C-yl}-β-D-galactopyranose (**41**). Aminodiol (+)-**38** (190 mg, 0.458 mmol) was dissolved in trifluoroacetic acid (8 mL) and trifluoroacetic anhydride (4 mL) and the mixture was stirred at 20°C for 15 h. The solvent was evaporated *in vacuo*, the residue dissolved in MeOH (12 mL). 4 Drops of 12% aqueous NH₃ were added (TLC control showed the disappearance of the starting material after 10 min). The solvent was then evaporated *in vacuo*. FC (EtOAc) gave 146 mg (78%) of **41** as a colorless oil. ¹H-NMR (400 MHz, CDCl₃, 298 K): δ_H 5.34 (br s, H-C(1)), 4.84-4.78 (m, 2H, H-C(4'), H-C(5')), 4.46 (t, ³J = 4.9, H-C(5)), 4.39-4.34 (m, H-C(3')), 4.34-4.31 (m, H-C(4)), 4.07 (d, ²J = 7.7, H_{endo}-C(6)), 4.07-4.04 (m, Ha-C(6')), 3.59-3.50 (m, 3H, H_{exo}-C(6), H-C(2), Hb-C(6')), 1.96-1.89 (m, 2H, Ha-C(2'), H-C(3)), 1.83-1.70 (m, 2H, Hb-C(2'), Ha-C(1')), 1.68-1.59 (m, H-C(1')), 1.54 and 1.38 (2s, Me₂C). ¹⁹F-NMR (376.5 MHz, CDCl₃, 298 K) δ_F -75.6. ¹³C-NMR (100.6 MHz, CDCl₃, 298 K): δ_C 156.2 (q, ²J(C,F) = 36.7, C=O), 115.9 (q, ¹J(C,F) = 288, CF₃), 114.1 (s), 102.7 (d, C(1)), 78.2 and 77.2 (2d, C(4'), C(5')), 74.8 (d, C(5)), 72.2 (d, C(2)), 64.5 (d, C(4)), 62.9 (t, C(6)), 59.4 (d, C(3')), 50.3 (t, C(6')), 42.6 (d, C(3)), 26.5 (q), 26.4 (t, C(2')), 25.2 (q), 21.7 (t, C(1')). CI-MS (NH₃) m/z: 429 (100, $[M+NH_4]^+$), 412 (16, $[M+H]^+$), 411 (3, $M^{\bullet+}$), 396 (4).

2,4-Di-O-Acetyl-1,6-anhydro-3-deoxy-3-{1',2',3',6'-tetra-deoxy-3',6'-[trifluoromethylcarbonyl]imino-4',5'-O-isopropylidene-L-arabino-hexitol-1'-C-yl}-β-D-galactopyranose (**42**). Diol (**41**) (131 mg, 0.319 mmol) was dissolved in pyridine (4 mL) and acetic anhydride (2.6 mL). After stirring at 20°C for 15 h, the mixture was concentrated *in vacuo*. FC (light petroleum ether/EtOAc 3:2) afforded 148 mg (94%) of

C(3),H-C(4)) = 5.9, H-C(3)), 2.18-2.11 (*m*, Ha-C(1')), 1.94-1.91 (*m*, Ha-C(2')), 1.66-1.52 (*m*, 2H, Hb-C(1'), Hb-C(2')). ¹³C-NMR (100.6 MHz, D₂O, 298 K): δ_C 98.8 (*d*, C(1)), 90.5 (*d*, C(4)), 75.9 (*d*, C(2)), 74.8 (*d*, C(4')), 74.3 (*d*, C(5)), 69.6 (*d*, C(5')), 63.5 (*t*, C(6)), 60.5 (*d*, C(3')), 56.3 (*t*, C(6')), 46.5 (*d*, C(3)), 27.7 (*t*, C(1')), 25.6 (*t*, C(2')). HR-MS for C₁₂H₂₂NO₆⁺ (**44**-OH⁺). Calcd mass: 276.144713. Found: 276.144711.

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