Oligosaccharide Analogues of Polysaccharides

Part 25[1])

Synthesis of Mono- and Diethynylated Analogues of 2-Acetamido-2-deoxy-D-glucopyranose

by **Jürgen Stichler-Bonaparte**, **Bruno Bernet**, and **Andrea Vasella***

Laboratorium für Organische Chemie, ETH-Hönggerberg, CH-8093 Zürich

Für *Oskar Jeger* mit herzlichen Glückwünschen zum 85. Geburtstag

The ethynylated *gluco*-azide **11** was prepared from the dianhydrogalactose **7** by ethynylation, transformation into the dianhydromannose **10**, and opening of the oxirane ring by azide (*Scheme 1*). The retentive alkynylating ring opening of **11** and of the corresponding amine **12** failed. (2-Acetamidoglucopyranosyl)acetylenes were, therefore, prepared from the corresponding mannopyranosylacetylenes. Retentive alkynylating ring opening of the partially protected β-D-mannopyranose **15**, possessing a C(3)–OH group, gave a 85:15 mixture of **16** and the (*E*)-enyne **17**. The alkyne **16** was deprotected to the tetrol **18** that was selectively protected and transformed into the C(2)–O triflate **20**. Treatment with NaN_3 in DMF afforded a 85:15 mixture of the β-D-*gluco* configured azide **21** and the elimination product **22**. Similarly, the α-D-mannopyranosylacetylene **23** was transformed into the azide **26**. Retentive alkynylating ring opening of the ethynylated anhydromannose **28** gave the expected β-D-mannopyranosyl 1,4-dialkyne **29** as the main product besides the diol **28**, the triol **31**, and the (*E*)-enyne **30** (*Scheme 2*). This enyne was also obtained from **31** by a stereoselective carboalumination promoted by the *cis* (axial) HO–C(2) group. Deprotection of the dialkynylated mannoside **31** led to **32**, whereas selective silylation, triflation, and azidation gave a 3:7 mixture of the 1-ethynylglucal **35** and the β-D-*gluco* azide **36,** which was transformed into the diethynylated β-D-GlcNAc analogue **38**. Similarly, the diethynylated α-D-mannopyranoside **39** was transformed into the disilylated α-D-GlcNAc analogue **41**, and further into the diol **42** and the monosilyl ether **43** (*Scheme 5*). *Eglinton* coupling of **41** gave the symmetric buta-1,3-diyne **44**, which did not undergo any further *Eglinton* coupling, even under forcing conditions. However, *Eglinton* coupling of the monosilyl ether **43** and subsequent desilylation gave the C_1-symmetric cyclotrimer **45** in moderate yields.

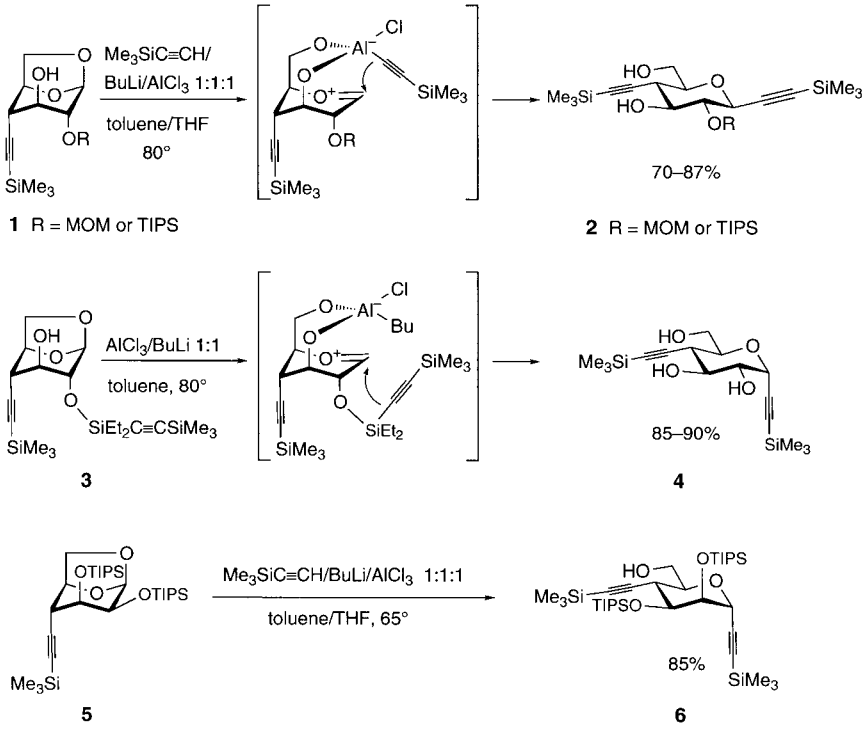
Introduction. – In the context of the synthesis of dialkynylated saccharides, we have prepared *C*(4)-ethynylated α-D- and β-D-glucopyranosylacetylenes [2–5] and *C*(4)-ethynylated α-D-mannopyranosylacetylenes [6]. These monomers were transformed into oligomeric buta-1,3-diynylated cellulose analogues (up to a hexadecamer [7][8]) and into *gluco*- and *manno*-configured analogues of cyclodextrins that are devoid of intramolecular, inter-residue H-bonds [6][9–11].

The *gluco*-configured monomers **2** and **4** are best prepared by alkynylating ring opening of 1,6-anhydro-β-D-glucopyranoses (*Scheme 1*). The stereochemical course of the transformation of **1** (R = MOM or TIPS) into **2** has been traced back to the axial HO–C(3) that forms a covalent bond with the alkynylaluminum halide. Coordination of the ensuing alkoxyaluminum halide with C(6)–O, ring opening to an oxycarbenium cation, and intramolecular alkynyl shift leads exclusively to the β-D-glucopyranosylacetylenes **2** [3][5]. Similarly, attachment of the alkynyl group, *via* a silicon tether, to the

[1]) Part 24, see [1].

axial O–C(2) group of **3** leads to an intramolecular, inverting alkynyl shift resulting in the exclusive formation of the α-D-glucopyranosylacetylene **4** [4]. Protection, in the 1,6-anhydro-β-D-mannopyranose **5**, of both HO–C(2) and HO–C(3) by the TIPS group prevents an intramolecular alkynyl shift. Opening of the anhydro ring, ring flip, and intermolecular, inverting alkynyl transfer from the less hindered, axial direction has led in good yields to the α-D-mannopyranosylacetylene **6** [6].

Scheme 1. *Reductive Alkynylating Ring Opening of 1,6-Anhydrohexoses Leading to the β-D-Glucopyranosylacetylenes* **2**, *the α-D-Glucopyranosylacetylene* **4**, *and the α-D-Mannopyranosylacetylene* **6**



The monomers **2**, **4**, and **6** are the first representatives of a complete set of monosaccharide-derived diynes. The (cross-)coupling of such monomers and, similarly, of the corresponding monoalkynes to buta-1,3-diynes, and the transformation of the monomers or oligomers, *e.g.*, by *C*-alkylation of acetylide anions, by reduction, or by any of the numerous transformations of the versatile alkynyl group into a plethora of products characterises these alkynes as ideal building blocks for a combinatorial synthesis of carbohydrate mimics.

Considering the essential biological functions of *N*-acetylglucosamine and its glycosides, most notably of chitin, we decided to prepare *C*(4)-ethynylated (2-acetamido-2-deoxy-D-glucopyranosyl)acetylenes. Both anomers should be available either by alkynylating ring opening of *C*(4)-ethynylated 1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranoses possessing a free or a TIPS-protected HO–C(3), or by substitution of HO–C(2) of *C*(4)-ethynylated α-D- and β-D-mannopyranosylacetylenes.

Results and Discussion. – A few *C*-alkynyl glycosides derived from GlcNAc and GalNAc have been prepared by *Verrières* and co-workers by the transformation of D-glucal and D-galactal into 2-azido-2-deoxy-D-hexopyranosylfluorides and -bromides and their *Lewis* acid-promoted alkynylation [12]. This resulted in acceptable yields of mostly the α-D-anomers. *Dondoni et al*. applied the methods of *Kishi* and co-workers, and *Sinaÿ* and co-workers [13a][13b] to the preparation of an unsubstituted 2-azido-β-D-galactopyranosylacetylene from a 2-azido-D-galactono-1,5-lactone by addition of acetylide anion, followed by deoxygenation, azide reduction, and *N*-acetylation [13c]. The corresponding α-D-anomer was prepared by a TMSOTf-promoted alkynylation of 2-azido-D-galactopyranosylacetates. GlcNAc Derivatives possessing a *C*(4)-alkynyl group are not known[2]).

These methods for the introduction of an anomeric alkynyl group suffer from the disadvantage of rather lengthy reaction sequences, required to introduce a second alkynyl group at C(4) (see, *e.g.*, [3] for a route starting with a *galacto*-configured tosylate). Levoglucosan, however, readily allows a combination of the functionalisation at C(4) and the substitution of HO–C(2) by an azido group [15]. We decided to use the anhydrogalactose **7** as starting material.

The original three-step procedure (silylation, addition, desilylation [3]) for the transformation of the *galacto*-epoxy alcohol **7** into the *gluco*-dihydroxyalkyne **8** was shortened; treatment of **7** with $LiC{\equiv}CSiMe_3/AlMe_3$ and subsequent methanolysis gave the alkyne **8** in 71% yield after *Soxhlet* extraction and crystallisation (*Scheme 2*). The conversion of **8** under *Mitsunobu* conditions [16] yielded 89% of the *manno*-epoxide **10**, and is an advantageous alternative to the previously used tosylation and epoxide formation.

Epoxide-ring opening with NaN_3 and NH_4Cl in boiling $EtOH/H_2O$ [15][17] gave the *gluco*-azide **11** (73%). This was reduced to the amine **12** (71–77%) with $LiAlH_4$ in THF or Mg/I_2 in MeOH. Acetolysis of **11** according to [15] led to a 94:6 mixture of the α-D- and β-D-acetates **13** (94%). However, all attempts to transform **11** into the corresponding β-D-glucopyranosylacetylene failed. Standard conditions (3 equiv. of $Me_3SiC{\equiv}CH$, BuLi, and $AlCl_3$, toluene/THF $\geq$ 9:1, 6 h at 80° [3]) hardly affected **11**. Less surprisingly, the amine **12** also remained unaffected by these conditions. Modified conditions ($Al(OTf)_3$, $Sc(OTf)_3$, $Yb(OTf)_3$, or TMSOTf instead of $AlCl_3$; generating $(Me_3SiC{\equiv}C)_3Al$ *in situ*, and performing the reactions in dioxane or THF) transformed **11** into several products. The main components did not possess an alkynyl group at C(1). Treatment of **11** with $(HC{\equiv}C)_3Al$ in boiling THF yielded 44% of 1,6-anhydro-2,4-dideoxy-4-ethynyl-2-(1,2,3-triazol-1-yl)-β-D-glucopyranose. Not surprisingly, a 1,3-dipolar cycloaddition was an undesired side reaction. These results prompted us to abandon this approach and to investigate the transformation of mannopyranosylacetylenes into GlcNAc acetylenes.

α-D-Mannopyranosylacetylenes have been prepared selectively by intermolecular alkynylating ring opening of 1,6-anhydromannoses [6] and by treatment of a mannopyranosylacetate with 1-(tributylstannyl) 2-(trimethylsilyl)acetylene and trimethylsilyl triflate [18]. Cross-coupling of a mannopyranosyl bromide with an alkyne under conditions of the *Sonogashira* reaction led, in modest yields, to anomeric

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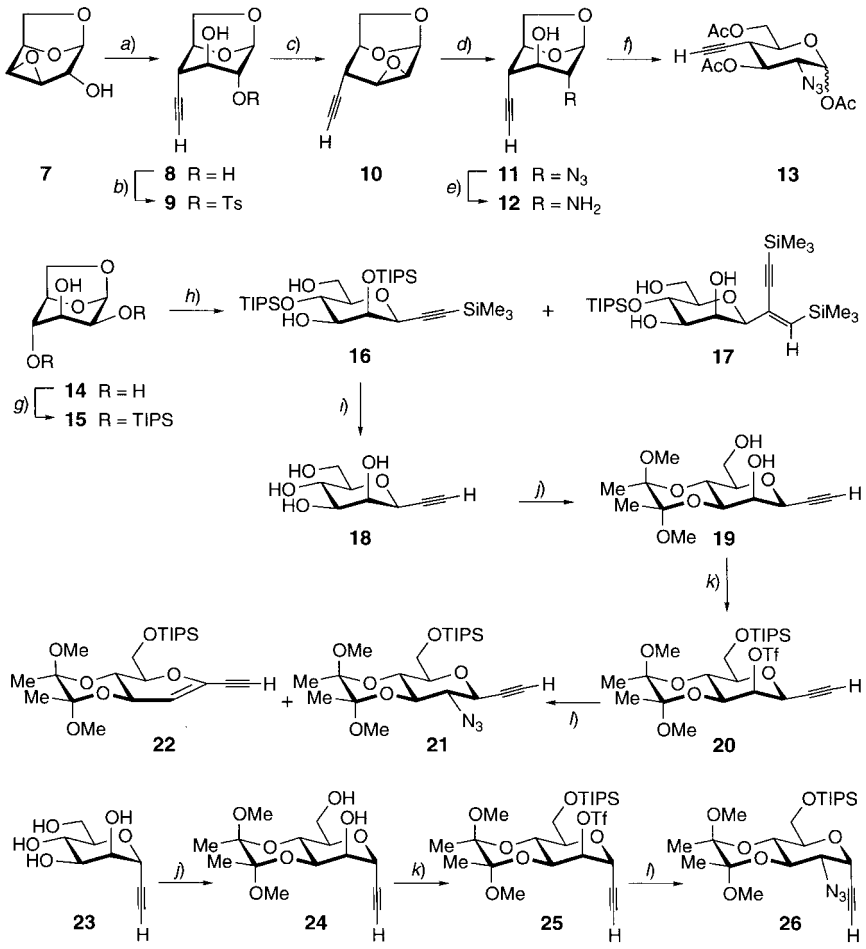
[2]) For *C*(1)- and *C*(4)-dialkylated GlcNAc derivatives, see [14].

Scheme 2



a) $Me_3SiC{\equiv}CLi$, $AlCl_3$, toluene/THF; NH_4Cl, MeOH; 71%. *b*) TsCl, CH_2Cl_2/pyridine 3:1; 96%. *c*) **8**, Ph_3P, diethyl azodicorboxylate (DEAD), THF; 89% or **9**, NaOMe, MeOH, 77%. *d*) NaN_3, NH_4Cl, EtOH/H_2O 5:1; 73%. *e*) Mg, I_2, MeOH; 77% or $LiAlH_4$, THF; 71%. *f*) Me_3SiOTf, Ac_2O; 94% (α-D/β-D 94:6). *g*) triisopropylsilyl trifluoromethanesulfonate (TIPSOTf), CH_2Cl_2/pyridine 1:1; 80%. *h*) $Me_3SiC{\equiv}CLi$, $AlCl_3$, toluene/THF; 71% of **16** and 12% of **17**. *i*) CF_3CO_2H/H_2O/THF 1:1:2; MeONa, MeOH; 94%. *j*) Butane-2,3-dione, $(MeO)_3CH$, $BF_3 \cdot OEt_2$, MeOH; 96% of **19**; 94% of **24**. *k*) TIPSOTf, then Tf_2O, CH_2Cl_2/pyridine; 90% of **20**; 76% of **25**. *l*) NaN_3, DMF; 83% of **21**/**22** 85:15; 70% of **26**.

mixtures of mostly the α-D-mannopyranosylacetylenes [19]. No completely selective procedure for the synthesis of β-D-mannopyranosylacetylenes is known. Even the reduction of the hemiketal prepared by addition of an acetylide to 2,3,4,6-tetra-*O*-benzyl-D-mannonolactone led to a mixture of anomers, and provided no more than 55% of the desired β-D-anomer [20]. Considering that the intramolecular, alkynylating ring opening of 1,6-anhydro-β-D-mannopyranoses might well be the method of choice to prepare either anomer, we selectively protected commercial 1,6-anhydro-β-D-

mannopyranose (**14**) by silylating it with 2.3 equiv. of TIPSOTf in CH_2Cl_2/pyridine. This yielded 80% of the 2,4-di-*O*-silylated **15** (*Scheme 2*). Treatment of **15** with a tenfold excess of $Me_3SiC{\equiv}CH/BuLi/AlCl_3$ gave a 85:15 mixture of the desired β-D-mannopyranosylacetylene **16** and the unexpected enyne **17**, a derivative of the triol formed from **16** by C(2)–O desilylation (see below). Flash chromatography afforded the pure crystalline β-D-anomer **16** (71%) and the (*E*)-configured enyne **17** (12%). This result confirms the directing influence of HO–C(3) on the diastereoselectivity of the alkynylating ring opening of 1,6-anhydro-D-hexoses (see *Scheme 1*). Subsequent *O*- and *C*-desilylation of **16** gave the unprotected acetylene **18** in 94% yield. The three-step synthesis of **18** from commercial **14** (53% overall yield) constitutes a fast and selective route to β-D-mannopyranosylacetylenes.

The conversion of **18** into a (2-azido-β-D-glucopyranosyl)acetylene requires selective protection of HO–C(3), HO–C(4), and HO–C(6), and activation of HO–C(2) (*Scheme 2*). This was achieved by acetalisation of **18** with butane-2,3-dione in the presence of $HC(OMe)_3$ and $BF_3 \cdot OEt_2$ [21], yielding the diol **19**. Selective silylation of the primary OH group and triflation afforded **20** in a yield of 86% from **18**. Treatment of **20** with NaN_3 in DMF at 0° yielded 83% of a 85:15 mixture of the g*luco* azide **21** and the 1-*C*-ethynylglucal **22**, resulting from a base-catalysed *trans*-elimination[3]). Crystallization from MeOH afforded pure **21**, whereas **22** was obtained pure only by flash chromatography after treatment of the mother liquor with propane-1,3-dithiol and Et_3N in MeOH (to reduce **21** to the corresponding amine).

We have already described the three-step synthesis (silylation, alkynylating ring opening, deprotection) of the unprotected α-D-mannopyranosylacetylene **23** in an overall yield of 58% from **14** [6]. This tetrol **23** was transformed into the triflate **25** similarly as described above for the β-D-analogue **20**. Treatment of **25** with NaN_3 in DMF at 55–60° gave selectively the *gluco*-azide **26** (70%), the steric hindrance by the axial ethynyl group of **25** requiring a higher reaction temperature. Nevertheless, no glucal **22** was obtained; its formation is prevented, as it requires a *cis*-elimination[3]).

The *manno*-configuration of **16**–**20** and of **23**–**25** is evidenced by small $J(2,3)$ values (2.8–3.3 Hz), and the α-D-configuration of **23**–**25** by a slightly larger $J(1,2)$ value (1.8–2.1 Hz *vs.* 1.1–1.3 Hz for **16**–**20**) and by the downfield shift of H–C(3) and H–C(5) ($\Delta\delta = 0.37$–0.43 ppm for H–C(3) and 0.46–0.50 ppm for H–C(5) of the anomeric pairs **23**/**18**, **24**/**19**, and **25**/**20**, resp.). The N_3 group of **11**, **21**, and **26** shows the characteristic strong IR absorption at 2105–2113 cm^{-1}, whereas the ethynyl group gives rise to a weak band at 2222–2238 cm^{-1}. The *gluco*-configuration of **13**, **21**, and **26** is evidenced by $J(2,3) = 9.9$–10.6, and $J(1,2) = 3.6$ and 5.7 Hz for the α-D-anomers α-D-**13** and **26**, and $J(1,2) = 8.5$ and 9.7 Hz for β-D-anomers β-D-**13** and **21**, respectively.

The successful transformation of the β-D- and α-D-*manno*-configured triflates **20** and **25**, respectively, into g*luco*-configured azides suggests that 1,4-diethynylated GlcNAc analogues should similarly be accessible from mannopyranosyl-1,4-diacetylenes. The standard conditions for the retentive alkynylating ring opening (3 equiv. of $Me_3SiC{\equiv}CH$, BuLi, and $AlCl_3$ in toluene/THF $\geq 9:1$) gave rise to only a partial conversion of the silyl ether **27** [6] into **28**–**31**, with **29** as the main product (*Scheme 3*). The reaction stopped after *ca.* 6 h at 80°. A tenfold excess of reagents led to 90% and a

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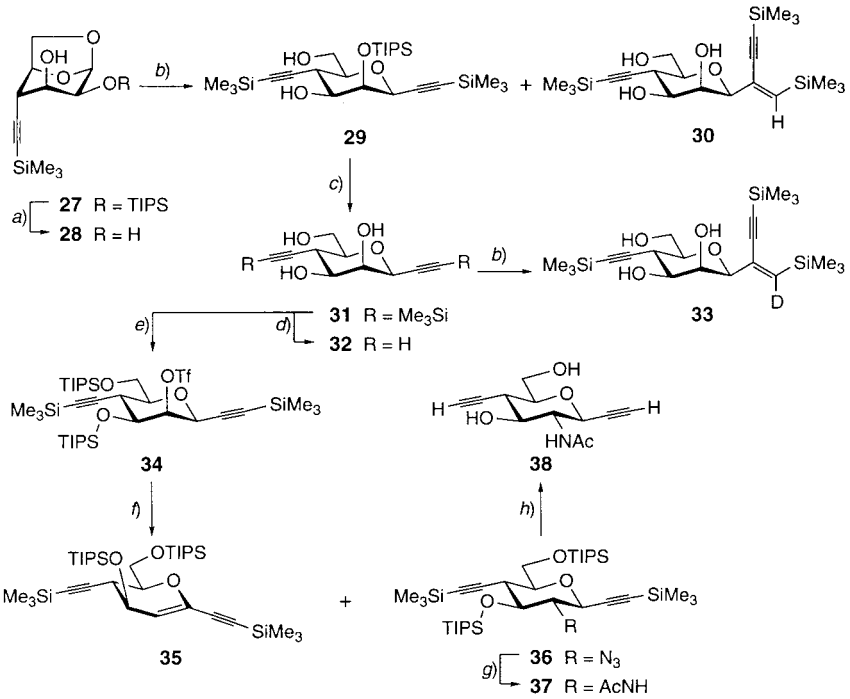
[3]) In the presence of a strong base (BuLi), both anomers of the perbenzylated mannopyranosylacetylene were transformed into the corresponding 1-alkynylglucal in 56 and 40% yield, respectively [22].

Scheme 3



a) CF_3CO_2H/H_2O/THF 1:1:2; 98%. *b*) $Me_3SiC{\equiv}CLi$, $AlCl_3$, toluene/THF; 65% of **29**, 17% of **30**, 5% of **28**, and 3% of **31**; 61% of **33/30** 92:8. *c*) CF_3CO_2H/H_2O/THF/MeOH 2:2:4:1; 93%. *d*) MeONa, MeOH; 99%. *e*) TIPSOTf, then Tf_2O, CH_2Cl_2/pyridine 5:1; *ca.* 96%. *f*) NaN_3, DMF; 29% of **35** and 70% of **36**. *g*) Zn, $CuSO_4 \cdot 5\ H_2O$, THF/Ac_2O/AcOH 3:2:1; 60%. *h*) Bu_4NF (TBAF) on silica gel, THF; 79%.

20-fold excess to complete conversion after 2.5 h at 65–70°. Flash chromatography of the crude product afforded the desired diacetylene **29** (65%), the (*E*)-enyne **30** (17%), the diol **28** (5%), and the triol **31** (3%). The latter two products were also obtained by *O*-desilylation of **27** and **29**. *C*-Desilylation of **31** gave the deprotected *manno*-diacetylene **32**. Selective di-*O*-silylation of **31** followed by triflation yielded the triflate **34**, which was transformed, similarly as **20**, with NaN_3 in DMF at 0° into a mixture of the glucal **35** and the desired *gluco*-azide **36**, which were separated by two sequential flash chromatographies to afford 29% of **35** and 70% of **36**. Reduction of **36** with Zn powder in THF/Ac_2O/AcOH 3:2:1 gave 60% of the acetamide **37**, which was deprotected in 79% yield to the 1,4-diethynylated β-D-configured GlcNAc analogue **38**.

The β-D-mannopyranosyl structure of the triol **31** was established by X-ray analysis[4]) (*Fig.*). There are two symmetrically independent molecules in the unit cell. The pyranose rings adopt a $^4C_1$ conformation and the CH_2OH groups prefer a *gt*

[4]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-184178. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax. +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

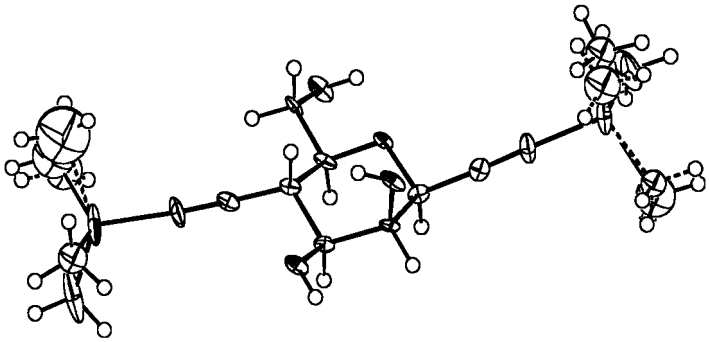


Figure. *X-Ray structure of the diequatorial mannopyranosyldiacetylene* **31**

arrangement. The propargylic C≡C bonds are slightly longer (1.199/1.189 Å) than the homoprargylic C≡C bonds (1.187/1.171 Å). The values accord well with the values from other ethynylated saccharides [9][23–25].

The regio- and diastereoselective formation of the enynes **17** and **30** prompted us to investigate the carboalumination leading to these novel glycosylbutenynes[5]). Under the same conditions as those used for the retentive alkynylating ring opening of **27**, the triol **31** gave 56% of the enyne **30** besides 26% of unchanged **31**, while the silyl ether **29** gave only 24% of **30** besides 64% of starting material. Similarly, the diol **28** gave only 19% of the enyne **30** besides 10% of the desilylated dialkyne **31**. These results suggest that the triol **31** (and not the corresponding silyl ether **29**) is the direct precursor of **30**. Only the alkynyl group at C(1) of **31** is carboaluminated. No corresponding addition has been observed in the retentive ring opening of 1,6-anhydro-β-D-glucopyranoses or in the invertive ring opening of 1,6-anhydro-β-D-gluco- and -mannopyranoses. This observation, and the high regio- and diastereoselectivity of the addition suggests neighbouring group participation of the *cis* (axial) C(2)–OH, while the equatorial C(3)–OH, *trans* to the C(4)–ethynyl group, does not facilitate its carboalumination. Covalent attachment of the *Lewis* acid ($Me_3SiC{\equiv}CAlCl_2$) to the *cis* OH group favours addition of acetylide species to the C≡C bond, forming a cyclic vinylaluminate[6]) (*Scheme 4*).

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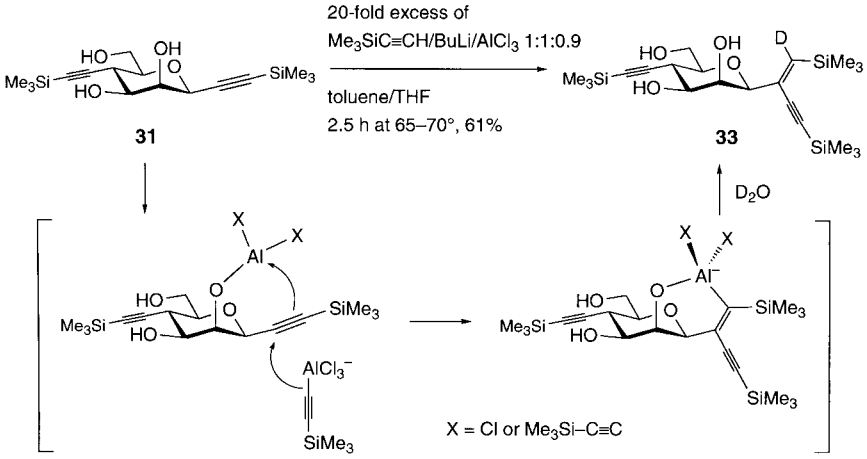
[5]) To the best of our knowlegde, glycopyranosyl- and glycofuranosyl-(1-ethynylethenes) are not known, while other derivatives of (*E*)- and (*Z*)-2-ethynylallyl alcohols are well-documented [26–30]. These enynes have been prepared by Pd-catalysed cross-coupling of bromoalkenes with terminal alkynes. 1,2-Dialkyl-1-ethynylethenes have also been obtained by transition metal (mostly Pd, but also Ti, Rh, Ni, Ru, and Cr) catalysed *cis*-addition of terminal alkynes to disubstituted alkynes [31–35].

[6]) The uncatalysed carboalumination of non-functionalised alkynes is slow even at elevated temperature [36], while the transition metal (usually Cp_2ZrCl_2)-catalysed carboalumination occurs already at low temperature and leads to products of a *cis*-addition [37] [38]. However, *trans*-adducts have been obtained in the dihexylmagnesium-promoted carboalumination of 1-(trimethylsilyl)alk-1-ynes [39] and in the Cp_2ZrCl_2-catalysed carboalumination of 1,4-bis(trimethylsilyl)buta-1,3-diyne [40]. For the Cp_2ZrCl_2-catalysed carboalumination of homopropargyl alcohols, *Negishi et al.* observed selective formation of *cis*-carboaluminated products at room temperature and their transformation into cyclic *trans*-carboaluminates at 50–60° [41]. The isomerisation of the *cis*- to *trans*-carboaluminated products is accelerated for silylated and germylated alkynes. The structure of a germylated chelated (*trans*) carboaluminate has been established by ^{1}H- and ^{13}C-NMR spectroscopy [41]. In the absence of a transition-metal catalyst, the chelated carboalumination intermediate leading to **30** and **33** must be directly obtained from **31** (see *Scheme 4*).

Scheme 4. *Neighbouring Group Participation in the Al-Promoted Formation of the* (E)*-Enyne* **33**



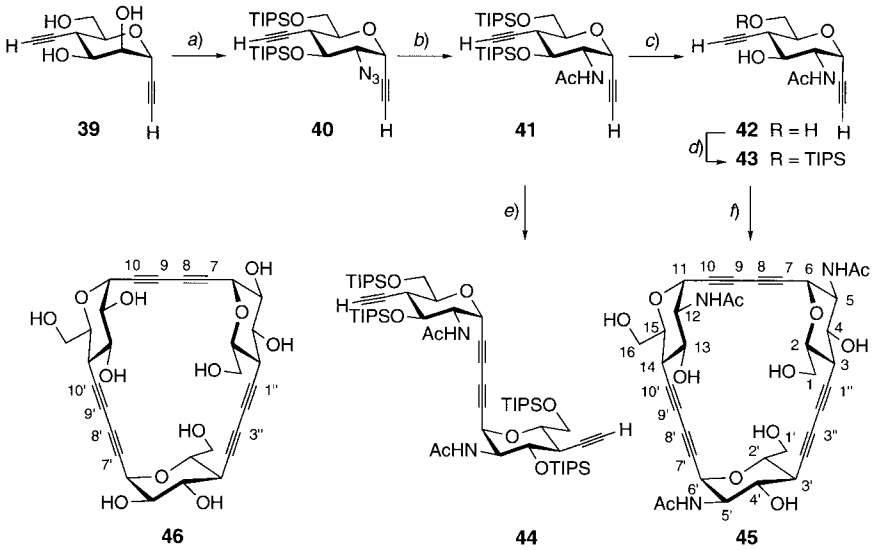
Vinylaluminum compounds hydrolyse with retention of configuration [37][38], and their hydrolysis with D_2O leads to a product selectively deuteriated at the C=C bond. Treatment of **31** under the conditions of retentive alkynylating ring opening followed by treating the products with D_2O, gave 61% of **33/30** 92:8. The high degree of deuteriation supports the intermediate formation of a vinylaluminum alkoxide, as proposed in *Scheme 4*. An analogous intermediate magnesium alkoxide has been postulated [42] for the *trans*-carbomagnesiation of propargylic and homopropargylic alcohols [42–44].

The *O*-desilylated by-products **28** and **31** were formed during the alkynylation of **27**, while no analogous desilylation products have been observed during the alkynylation of a 2,3-O-silylated analogue [6] or of the *gluco*-configured epimer **1** [3][5]. This specific desilylation suggests that the *Lewis* acid bound to O–C(3) of **27** coordinates with C(1)–O and with C(2)–OTIPS, activating C(2)–OTIPS for desilylation.

The β-D-*manno*-configuration of **29**–**34** is evidenced by the solid-state structure of **31** (see above), $J(1,2) = 0.7–1.2$ Hz, and the upfield shift of H–C(5) (3.36–3.43 ppm) and H–C(3) (**29**–**33**: 3.55–3.63 ppm, **34**: 4.04 ppm). The β-D-*gluco*-configuration of **36**–**38** is revealed by $J(1,2) = 10.0–10.3$ Hz. The enyne structure of **35** is evidenced by IR bands at 1637 and 2168 cm^{-1}, the downfield shift of the *d* for H–C(2) (5.14 ppm), the *s* for C(1) (136.98 ppm), and the *d* for C(2) (111.68 ppm). The alkenyl H of **30** resonates as a *d* at 6.39 ppm. The small coupling of 1.6 Hz is only compatible with an allylic, but not with an vicinal coupling (compare with $J(1,1') = 6.6–8.0$ Hz for β-D-glucopyranosylethylenes [45]), establishing that the glucopyranosyl and the (trimethylsilyl)ethynyl residue are attached at the same olefinic C-atom. The value of 1.6 Hz agrees better with the (*E*)- than with the (*Z*)-configuration (compare with $^3J(1,Me) = 1.1$ Hz for (*E*)-1.4-bis(trimethylsilyl)-2-methylbut-1-en-3-yne and an expected slightly larger coupling for the corresponding (*Z*)-isomer [40]). The (*E*)-configuration of **30** was unambiguously assigned by a NOE of 2% upon irradiation of the signal for H–C(1). In the $CDCl_3$ ^{13}C-NMR spectra of **17** and **30**, two *s* at 99.8–102.8 ppm are assigned to the ethynyl group, and one *s* at 133.6–133.8 ppm and one *d* at 139.0–139.4 ppm to the ethenyl group. Remarkably, the change of the solvent to CD_3OD leads to a strong downfield shift for the signal of the nonsilylated enyne C-atoms of **30** (from 102.8 to 106.2 and from 133.8 to 136.1 ppm), whereas the silylated C-atoms appear nearly at same position ($\Delta\delta \leq 0.25$ ppm). The CD_3OD ^{13}C-NMR spectra of **30** and **33** are very similar ($\Delta\delta$ for corresponding signals smaller than 0.14 ppm) with the exception of the expected absence of the *d* at 139.2 ppm in the spectrum of the deuteriated **33**.

The synthesis of the 4-*C*-ethynyl-α-D-mannopyranosylacetylene **39** has been described in [6]. Disilylation and triflation of **39** was performed similarly to the transformation of the β-D-anomer **31** (*Scheme 5*). The triflate was not isolated; the crude triflation product was treated with NaN_3 in DMF at 80–90° to yield 57% of the *gluco*-azide **40**. Only a poor conversion was observed, when **40** was reduced with Zn powder and $CuSO_4 \cdot 5\ H_2O$ or with propane-1,3-dithiol and Et_3N [46][47]. However, successive treatment of **40** with PPh_3 and Ac_2O/pyridine [48] yielded 83% of the α-D-configured GlcNAc derivative **41**, which was desilylated to **42** in 90% yield. The diol **42** was selectively silylated at the primary OH group to **43** (67%).

Scheme 5



a) TIPSOTf, then Tf_2O, pyridine; NaN_3, DMF; 57%. *b*) PPh_3, then MeOH, THF; Ac_2O, pyridine; 83%. *c*) TBAF on silica gel, THF; 90%. *d*) TIPSOTf, pyridine; 87%. *e*) $Cu(OAc)_2$, pyridine; 83%. *f*) $Cu(OAc)_2$, pyridine; TBAF $\cdot$ 3 H_2O, THF; 33%

Exploratory experiments indicated that a diluted solution (1 mM) of the diol **42** did not yield any cyclisation product under the conditions of the *Eglinton* coupling. In the presence of 5 equiv. of $Cu(OAc)_2$, **42** was transformed almost completely into a complex mixture, both at 23° and 60°. The silyl ether **41** gave selectively the linear dimer **44** in 83% yield. All attempts to transform **44** at higher temperature (>100°) into a cyclodimer or cyclotetramer failed; only complex mixtures were obtained. This failure contrasts with the successful cyclodimerisation of the 2,3-bis-*O*-TIPS-protected alcohol derived from **39** that afforded a linear dimer at 23° and a strained cyclic dimer at 100° [6]. Possibly, the four TIPS groups of **44** obstruct the second *Eglinton* coupling. We considered that the less-hindered homopropargylic ethynyl group of the monosilyl ether **43** may be reactive enough to undergo an *Eglinton* coupling. Indeed, **43** reacted with $Cu(OAc)_2$ and pyridine at 80° to afford a C_1-symmetric cyclotrimer, which could not be completely purified. The impure brown foam obtained by filtration through

silica gel was, therefore, desilylated, and the product was purified by flash chromatography, providing a slightly impure sample of **45** (*ca.* 48%). Crystallization from MeOH gave pure colourless **45** (33%), decomposing above 250°.

Crystalline **45** is more soluble in H_2O and DMSO than in MeOH[7]) and can be stored at room temperature for several weeks without degradation. The absence of any C_3-symmetric cyclotrimer indicates that the propargylic ethynyl group of **43** is more reactive than the homopropargylic one, in agreement with a similar observation in the glucose series where 2,3,6-tris-*O*-MOM-protected 4-deoxy-4-ethynyl-α-D-glucopyranosylacetylene was cyclotrimerised under *Eglinton* conditions to yield 19% of the C_1-symmetric cyclotrimer **46** [11]. The structural similarity between **45** and **46** was verified by comparing the coupling constants for the tetrahydropyran protons and by force-field calculations (MM3*, gas phase [49]). The calculations show that the buta-1,3-diynyl groups are linear, and that the tetrahydropyran rings adopt the usual $^4C_1$ conformation, as evidenced by the values of the ^{1}H-NMR coupling constants.

The appearance of a strong IR absorption at 2107 cm^{-1} evidences the presence of the N_3 group in **40**; this absorption is replaced in **41**–**43** by a C=O band (1674–1679 cm^{-1} for **40** and **43** in $CHCl_3$ and 1631 cm^{-1} for **42** in KBr) and a N–H band at 3415–3438 cm^{-1}. $J(1,2) = 5.0–5.6$ and $J(2,3) = 9.5–10.5$ Hz establish the α-D-*gluco* configuration of **40**–**43**. The peak at *m/z* 706.2619 for $[M+H]^+$ in the high-resolution (HR) FAB-MS of **45** and the absence of a HC≡C signal the ^{1}H-NMR spectrum confirm the cylcotrimeric structure. The C_1-symmetry of **45** is indicated by three sets of signals in the ^{1}H- and ^{13}C-NMR spectrum. An unambiguous assignment of the NMR signals is based on ^{1}H,^{1}H- and ^{1}H,^{13}C-2D-NMR spectra. Small long-range couplings ($^7J(H,H) = 1.2–1.3$ Hz) between H–C(6) and H–C(11) at 5.06 and 5.16 ppm, H–C(14) and H–C(6′) at 2.74 and 4.87 ppm, and H–C(3) and H–C(3′) at 2.57 and 2.59 ppm, resp., were revealed by selective irradiation experiments (see *Exper. Part*). These long-range couplings allow a correlation of the NMR signals to the monomeric units of **45** as detailed in the *Exper. Part.*

The ^{13}C-NMR chemical shifts for ethynyl groups reflect mainly the location at the pyranosyl ring; the configuration, the other substituents of the pyranosyl ring, and the solvent have only a weak influence upon the chemical shift (*Table 1*). The silylated C-atom of the $Me_3SiC{\equiv}C$ group resonates always at higher field than the nonsilylated C-atom (*cf.* [50]). The HC≡C signals are readily assigned, since the tertiary C-atom gives rise to a stronger signal in the H-decoupled spectrum than the quaternary C-atom[8]). The tertiary C-atom resonates upfield to the quaternary C-atom, with the exception of α-D-glycopyranosylacetylenes, where the quaternary C-atom usually resonates slightly upfield. The $\Delta\delta$(C(1′)/C(2′)) increases for both $Me_3SiC{\equiv}C$ and HC≡C substituents from α-D-glycopyranosylacetylenes to β-D-glycopyranosylacetylenes and to *C*(4)-ethynylated pyranosyl derivatives.

A similar dependence of the chemical shifts upon the site of attachment at the pyranosyl ring is expected also for the buta-1,3-diyndiyl group. Here, the assignment is facilitated by the fact that – at least for 1,4-diglycosylated buta-1,3-diynes – the central C(2)- and C(3)-atoms show stronger signals in the H-decoupled spectra than the peripheral C(1) and C(4).

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7) At 23°, 5 mg of **45** dissolved completely in 0.20 ml of H_2O or DMSO, but incompletely in 0.20 ml of MeOH.

8) Standard DEPT spectra are not useful for this assignment. Due to characteristic *J*(C,H) couplings, the quartenary C-atom appears in the standard DEPT spectrum as a weak positive signal, whereas the tertiary C-atom gives no (or at the best a very weak positive) signal (cf. also [51]).

Table 1. *Typical ^{13}C-NMR Chemical Shifts* [ppm] *for the $Me_3SiC{\equiv}C$ and $HC{\equiv}C$ Groups Attached at C(4) and C(1) of Gluco- and Mannopyranosyl Residues*

	C(2′)	C(1′)
eq. $Me_3SiC{\equiv}C$ at C(4)	88.8 – 90.1	103.0 – 105.8
eq. $Me_3SiC{\equiv}C$ at C(1)	90.5 – 92.3	97.7 – 103.0
ax. $Me_3SiC{\equiv}C$ at C(1)	95.4 – 95.6[a])	99.5 – 100.0 [4] [9]
eq. $HC{\equiv}C$ at C(4)	72.4 – 73.6	80.7 – 82.9
eq. $HC{\equiv}C$ at C(1)	74.5 – 76.2	76.4 – 81.1
ax. $HC{\equiv}C$ at C(1)	77.2 – 79.4	77.6 – 79.7

[a]) Data from [11]. Assignment based on a HMBC.GRASP spectrum.

The ^{13}C-NMR spectrum of **45** in D_2O shows six *s*′s of stronger intensity at 69.74, 70.29, 70.58, 75.28, 75.73, and 77.33 ppm and six *s*'s of weaker intensity at 73.88, 76.56, 76.79, 79.03, 79.54, and 80.44 ppm (*Table 2*). The assignment is based on a comparison with the data of **46** in (D_6)DMSO, where an unambigous assignment is made possible by a ^{1}H,^{13}C long-range-coupling correlation spectrum [11]. As compared to **46**, the signals for the peripheral C-atoms of **45** resonate downfield by 0.7 – 1.1 ppm and those of the central C-atoms downfield by 3.7 – 4.0 ppm. Characteristic pairs of signals ($\Delta\delta \leq 0.51$ ppm) were assigned to C(7)/C(10), C(8)/C(9), C(1″)/C(4″), and C(2″)/C(3″) of the symmetrically substituted buta-1,3-diynyl groups. The chemical shift of the remaining (unpaired) four *s*′s are in keeping with values expected for unsymmetrically substituted buta-1,3-diynyl groups, 80.44 to C(10′), 73.88 to C(7′), 77.33 to C(8′), and 69.74 ppm to C(9′). We have already observed a downfield shift of 2.3 – 3.4 ppm for the central C-atoms of the enynyl unit of **30** by exchanging an aprotic by a protic solvent ($CDCl_3 \rightarrow CD_3OD$; see above). This suggests a similar downfield shift for the central C-atoms of buta-1,3-diynes in D_2O relative to the aprotic (D_6)DMSO. The *s*'s for the buta-1,3-diynyl groups of **46** in D_2O appear at a similar position as those of **45** in D_2O ($\Delta\delta \leq 0.41$ ppm), evidencing a neglible influence of the acetamido group on these chemical shifts. Indeed, a strong downfield shift ($\Delta\delta = 3.7 – 4.1$ ppm) is observed for the central C-atoms of the buta-1,3-diynyl groups of **46** upon changing the solvent from (D_6)DMSO to D_2O, whereas the downfield shift for the peripheral C-atoms is only 0.8 – 1.3 ppm. In agreement with this finding, the *s*′s for the buta-1,3-diynyl group of **44** in $CDCl_3$ appear at a similar position (75.25 and 72.66 ppm) as C(7)/C10) and C(8)/C(9) of **46** in (D_6)DMSO.

Table 2. *^{13}C-NMR Chemical Shifts* [ppm] *for the Buta-1,3-diynyl Groups of* **45** *and* **46**

	C(7), C(10)	C(8), C(9)	C(1″), C(4″)	C(2″), C(3″)	C(7′)	C(8′)	C(9′)	C(10′)
45 in D_2O	76.56, 76.79	75.28, 75.73	79.03, 79.54	70.29, 70.58	73.88	77.33	69.74	80.44
46 in D_2O	76.79, 77.10	75.34, 75.81	79.00, 79.56	70.12, 70.37	74.31	77.20	69.67	80.18
46 in (D_6)DMSO[a])	75.58, 75.83	71.21, 71.74	77.92, 78.77	66.22, 66.59	73.06	73.07	66.01	79.04

[a]) Data from [11]. Assignment based on a HMBC.GRASP spectrum.

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Experimental Part

General. See [3].

*1,6-Anhydro-4-deoxy-4-ethynyl-β-*D*-glucopyranose* (**8**) [3]. A soln. of (trimethylsilyl)acetylene (83.1 ml, 0.60 mol, stored over molecular sieves 4 Å) in toluene (1.00 l) was cooled to $-10°$, treated with 1.6M BuLi in hexane (376 ml, 0.60 mol; → white suspension) and THF (50 ml; → clear soln.), warmed to 23°, stirred for 30 min, cooled to $-10°$, treated with a 2M soln. of $AlMe_3$ in heptane (200 ml, 0.40 mol; → white suspension),

warmed to 70°, treated dropwise over 40 min with a soln. of **7** (28.8 g, 0.20 mol) in THF (200 ml), and stirred for 10 min. The mixture was cooled to 0°, treated cautiously over 40 min (gas evolution!) with MeOH (500 ml), stirred at 23° for 4 h, treated with sat. aq. NH_4Cl soln., stirred for 1 h, and filtered. The filtrate (2 phases) was evaporated, and the resulting cake was dried and submitted to a *Soxhlet* extraction with $CHCl_3$ during 5 days, affording crude **8**. Crystallization from AcOEt and FC (150 g, hexane/AcOEt 7:3) of the mother liquors gave pure **8** (24.2 g, 71%). White solid. R_f (hexane/AcOEt 1:1) 0.46. The spectroscopic data of **8** are in accordance with those given in [3].

*1,6-Anhydro-4-deoxy-4-ethynyl-2-*O*-tosyl-β-*D*-glucopyranose* (**9**). A soln. of **8** (1.70 g, 10 mmol) in CH_2Cl_2/pyridine 3:1 (40 ml) was treated with TsCl (2.28 g, 12 mmol), stirred for 48 h, treated with H_2O (100 ml), stirred for 30 min, and extracted with CH_2Cl_2. Drying of the combined org. layers ($MgSO_4$) and evaporation at 20 mbar and 23° gave crude **9**. Crystallization from CH_2Cl_2/hexane gave **9** (3.10 g, 96%). White solid. R_f (toluene/AcOEt 1:1) 0.49. M.p. 70–71°. IR (KBr): 3525*s*, 3370*m* (br.), 3289*s*, 2978*w*, 2913*w*, 2150*w*, 1596*w*, 1350*m*, 1347*m*, 1334*m*, 1309*w*, 1266*w*, 1223*w*, 1188*s*, 1172*s*, 1138*s*, 1096*m*, 1069*m*, 1041*m*, 1016*s*, 988*m*, 960*s*, 934*w*, 910*m*, 875*m*, 825*m*, 811*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.23 (*d*, $J = 2.5$, HC≡C); 2.20–2.60 (br. *s*, exchange with D_2O, HO–C(3)); 2.45 (*s*, Me); 2.64 (*dt*, $J \approx 1.6, 0.8$, H–C(4)); 3.70 (*dd*, $J = 7.5, 5.0$, H_{exo}–C(6)); 4.02–4.06 (*m*, addn. of $D_2O \rightarrow$ change, H–C(3)); 4.04 (*d*, $J \approx 7.1$, H_{endo}–C(6); 4.24 (br. *s*, H–C(2)); 4.64 (br. *d*, $J \approx 4.6$, H–C(5)); 5.37 (br. *s*, H–C(1)); 7.35 (*d*, $J = 8.3$, 2 arom. H); 7.84 (*d*, $J = 8.3$, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3;* additionally, 21.54 (*q*, Me); 128.04 (*d*, 2 arom. C); 130.06 (*d*, 2 arom. C); 133.15, 145.48 (2*s*, 2 arom. C). CI-MS: 344 (11), 343 (18), 342 (100, $[M + NH_4]^+$). Anal. calc. for $C_{15}H_{16}O_6S$ (324.35): C 55.55, H 4.97, S 9.89; found: C 55.61, H 5.05, S 9.96.

*1,6:2,3-Dianhydro-4-deoxy-4-ethynyl-β-*D*-mannopyranose* (**10**). a) *From* **8**: A soln. of **8** (85 mg, 0.50 mmol), Ph_3P (262 mg, 2.0 mmol) and DEAD (122 µl, 2.0 mmol) in THF (10 ml) was stirred at 0° for 20 min and under reflux for 1.5 h. Addn. of H_2O, extraction with AcOEt, drying ($MgSO_4$), evaporation at 23°/14 mbar, and FC (5 g, hexane/AcOEt 7:3) gave **10** (68 mg, 89%).

b) *From* **9**: A soln of **9** (2.76 g, 8.5 mmol) and phenolphthalein (2 mg) in MeOH (100 ml) was treated with 1M MeONa in MeOH (20 ml), stirred for 8 h, and treated with NH_4Cl until the pink colour vanished. After evaporation at 23°/12 mbar, a soln. of the residue in AcOEt was washed with H_2O, dried ($MgSO_4$), and evaporated at 23°/15 mbar. Crystallization from EtOH (7 ml) gave **10** (1.11 g, 77%). White solid. R_f (toluene/AcOEt 3:1) 0.59. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.25 (*d*, $J = 2.5$, HC≡C); 2.97 (*dd*, $J \approx 2.2, 0.6$, H–C(4)); 3.28 (*ddd*, $J = 4.4, 1.2, 0.6$, irrad. at 4.52 → *dd*, $J = 4.4, 0.6$, H–C(3)); 3.44 (*dd,* $J = 3.9, 3.2$, irrad. at 5.75 → *d*, $J = 3.7$, H–C(2)); 3.71 (*dd*, $J = 7.2, 2.5$, irrad. at 4.52 → *d*, $J = 7.4$, H_{endo}–C(6)); 3.73 (*dd*, $J = 7.2, 5.6$, irrad. at 4.52 → *d*, $J = 7.2$, H_{exo}–C(6)); 4.52 (*ddd*, $J = 5.6, 2.5, 1.2$, H–C(5)); 5.75 (*d*, $J = 3.1$, H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*. EI-MS: 152 (3, M^+), 123 (49), 107 (25), 106 (37), 105 (57), 95 (63), 94 (33), 93 (41), 81 (95), 79 (35), 78 (100), 77 (30), 65 (54). Anal. calc. for $C_8H_8O_3$ (152.15): C 63.15, H 5.30; found: C 62.76, H 5.38.

*1,6-Anhydro-2-azido-2,4-deoxy-4-ethynyl-β-*D*-glucopyranose* (**11**). A soln. of **10** (860 mg, 6.0 mmol) and NH_4Cl (2.46 g) in EtOH/H_2O 5:1 (36 ml) was treated with NaN_3 (2.46 g, 6.6 mmol), stirred under reflux for 70 h, and diluted with H_2O. Extraction with AcOEt, drying of the combined org. layers ($MgSO_4$), evaporation of at 40°/13 mbar, FC (4 × 12 cm, hexane/AcOEt 7:3), and crystallization from hexane/CH_2Cl_2 1:2 gave **11** (860 mg, 73%). White solid. R_f (hexane/AcOEt 1:1) 0.41. R_f (AcOEt) 0.56. M.p. 119–120°. IR (KBr): 3388*s*, 3246*s*, 2985*w*, 2903*m*, 2238*w*, 2105*s*, 1466*w*, 1420*w*, 1348*w*, 1303*m*, 1277*m*, 1258*m*, 1217*w*, 1194*w*, 1138*m*, 1099*w*, 1065*m*, 1045*m*, 1003*m*, 990*m*, 942*w*, 911*m*, 890*m*, 823*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.34 (*d*, $J = 2.5$, HC≡C); 2.55–2.9 (br. *s*, exchange with D_2O, HO–C(3)); 2.73 (br. *q*, $J \approx 2.1$, H–C(4)); 3.41 (br. *s*, H–C(2)); 3.75 (*dd*, $J = 7.5, 5.0$, H_{exo}–C(6)); 4.00 (br. *s*, H–C(3)); 4.11 (*d*, $J = 7.5$, H_{endo}–C(6); 4.68 (br. *d*, $J \approx 5.0$, H–C(5)); 5.51 (br. *s*, H–C(1)). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 3*. CI-MS: 213 (12, $[M + NH_4]^+$), 172 (15), 171 (11), 170 (100, $[M - N_3H + NH_4]^+$), 168 (52), 110 (11), 94 (13), 81 (12), 66 (13). Anal. calc. for $C_8H_9N_3O_3$ (195.18): C 49.23, H 4.65, N 21.53; found: C 49.29, H 4.55, N 21.64.

*2-Amino-1,6-anhydro-2,4-dideoxy-4-ethynyl-β-*D*-glucopyranose* (**12**). *a*) A soln. of **11** (39 mg, 0.20 mmol) in MeOH (0.50 ml) was treated with Mg turnings (49 mg, 2.0 mmol) and I_2 (2 mg), stirred for 3 days, and filtered. Evaporation at 23°/14 mbar and FC (6 g, CH_2Cl_2/MeOH 10:1) gave **12** (26 mg, 77%).

b) A soln. of **11** (39 mg, 0.20 mmol) in THF (2.0 ml) was cooled to 0°, treated dropwise with 1M $LiAH_4$ in THF (200 µl), stirred for 20 min, treated with sat. aq. NH_4Cl soln. (5.0 ml), and diluted with H_2O. Extraction with AcOEt, drying ($MgSO_4$), and FC (6 g, CH_2Cl_2/MeOH 10:1) gave **12** (25 mg, 71%). White solid. R_f (CH_2Cl_2/MeOH 10:1) 0.21. ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.58 (br. *s*, exchange with D_2O, H_2N–C(2)); 2.52 (br. *s*, H–C(2)); 2.54 (br. *s*, H–C(4)); 3.07 (*d*, $J = 2.8$, HC≡C); 3.53 (*dd*, $J = 6.8, 5.8$, irrad. at 4.47 ≈ *d*, $J = 6.8$, H_{exo}–C(6)); 3.68 (br. *s*, addn. of $D_2O \rightarrow$ *t*, $J = 1.4$, irrad. at 4.47 → *d*, $J = 1.2$, H–C(3)); 4.07 (br. *d*, $J = 6.8$, irrad.

Table 3. *Selected ^{13}C-NMR Chemical Shifts* [ppm] *of* **8**–**13**, **15**–**26**, *and* **28**–**44**

	Solvent	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	*C*≡C–C(1)	C≡*C*–*C*(1)	C≡C–C(4)	C≡*C*–C(4)
8 [3]	$CDCl_3$	102.27	72.43	72.43	36.01	75.16	67.26	–	–	70.64	82.21
9	$CDCl_3$	99.86	70.09[a])	71.58[a])	36.14	74.69	67.78	–	–	77.38	81.71
10	$CDCl_3$	97.86	49.27[a])	53.42[a])	32.86	71.72	67.86	–	–	71.33	81.14
11	$CDCl_3$	100.87	62.56	71.89	36.78	75.13	67.99	–	–	71.03	81.41
12	(D_6)DMSO	103.33	55.32	73.05	35.92	73.94	66.19	–	–	72.93	84.65
α-D-**13**	CD_3OD	91.98	61.85	72.27[a])	36.60	71.31[a])	64.84	–	–	75.02	78.86
β-D-**13**	CD_3OD	94.01	64.36	73.61[a])	36.66	74.81[a])	64.84	–	–	75.05	78.80
15	$CDCl_3$	101.76	68.19	72.47[a])	72.77[a])	76.80	64.83	–	–	–	–
16	$CDCl_3$	70.04	73.25	75.95	69.76	80.99	62.07	91.28	101.91	–	–
17	$CDCl_3$	79.69	70.56	75.74	69.98	80.67	62.65 [b])			–	–
18[c])	CD_3OD	71.05	73.29	75.74	68.30	82.36	62.95	75.43	80.98	–	–
19	$CDCl_3$	70.13[a])	70.14[a])	70.83[a])	62.58	78.72	61.41	75.15	78.76	–	–
20	$CDCl_3$	68.07[a])	83.95	68.55[a])	61.52	79.13	61.37	76.14	76.40	–	–
21[c])	$CDCl_3$	69.30	63.02	72.72	65.06	78.61	61.40	74.53	79.43	–	–
22	$CDCl_3$	136.70	107.41	63.98	65.60	77.79	60.48	75.92	77.42	–	–
23[c]) [6]	CD_3OD	70.49	73.94	72.88	68.60	77.42	62.86	78.70	79.67	–	–
24	$CDCl_3$	68.46[a])	69.06[a])	71.01	62.96	73.41	61.15	77.28	78.31	–	–
25	$CDCl_3$	65.94[a])	84.66	67.44[a])	61.91	74.65	61.34	77.20	78.78	–	–
26[c])	$CDCl_3$	66.97	59.40	70.21	65.59	73.79	61.31	77.80	78.10	–	–
28	$CDCl_3$	102.14	66.99	70.95	39.70	74.70	67.21	–	–	87.79	103.63
29	$CDCl_3$	70.96[a])	71.02[a])	73.77	34.16	79.47	63.62	91.08	101.60	89.55	103.02
30	$CDCl_3$	79.14[a])	67.34	73.76	34.36	79.78[a])	63.51 [b])			89.52	102.98
30	CD_3OD	81.28[a])	69.38	75.02	34.95	81.40[a])	64.17 [b])		[b])	88.82	105.15
33	CD_3OD	81.25[a])	69.36	74.99	34.93	81.38[a])	64.15 [b])		[b])	88.79	105.11
31	CD_3OD	71.20	71.59	73.79	34.73	81.46	64.06	90.98	103.01	88.83	105.78
32[c])	CD_3OD	71.18	71.23	73.85	33.69	81.42	64.05	75.49	81.07	73.28	82.89
34	$CDCl_3$	67.95	85.83	72.22	34.40	80.93	63.78	92.93	97.73	90.12	103.47
35	$CDCl_3$	136.98	111.68	68.88	36.90	79.08	63.85	93.77	99.15	88.54	104.82
36	$CDCl_3$	68.17	70.03	74.87	39.47	81.51	64.25	92.09	100.96	88.79	103.90
37	$CDCl_3$	68.75	58.91	73.76	40.30	80.43	64.33	90.50	101.70	88.81	104.65
38[c])	CD_3OD	70.44	57.63	74.75	39.41	81.58	63.85	75.75	80.99	73.62	82.02
39[c]) [6]	CD_3OD	70.69	71.61	70.81	33.90	76.49	63.95	79.07	79.38	73.11	82.95
40	$CDCl_3$	66.91	65.38	72.21	38.18	75.54	63.86	77.86	77.64	72.65	81.98
41	$CDCl_3$	65.92	53.13	71.83	37.73	75.73	63.76	78.45	76.96	72.40	82.46
42[c])	CD_3OD	67.81	55.02	70.99	39.56	76.34	63.68	79.44	79.09	73.59	82.07
43	$CDCl_3$	66.56	52.67	72.06	38.01	75.08	63.82	77.90	78.26	72.54	80.74
44	$CDCl_3$	66.32	53.70	71.87	37.43	76.58	63.73	71.98	75.25	72.66	82.42

[a]) Assignments may be interchanged. [b]) SiC≡C of **30** in $CDCl_3$: 99.78 and 102.78 ppm; SiC≡C of **17**: 100.09 and 102.79 ppm; SiC≡C of **30** in CD_3OD: 99.53 and 106.17 ppm; SiC≡C of **33**: 99.48 and 106.31 ppm; SiHC≡C of **30** in $CDCl_3$: 139.02 and 133.84 ppm; SiHC≡C of **17**: 139.49 and 133.64 ppm; SiHC≡C of **30** in CD_3OD: 139.19 and 136.13 ppm; SiDC≡C of **33**: hidden by the noise and 136.07 ppm. [c]) Assignment based on a HSQC.GRASP spectrum.

at 4.47 → *d*, *J* = 6.9, H_{endo}–C(6)); 4.47 (br. *d*, *J* → 5.0, H–C(5)); 5.17 (br. *d*, *J* → 2.5, exchange with D_2O, HO–C(3)); 5.21 (br. *s*, H–C(1)). ^{13}C-NMR (75 MHz, (D_6)DMSO): see *Table 3*.

*1,3,6-Tri-*O*-acetyl-2-azido-2,4-dideoxy-4-ethynyl-*D*-glucopyranose* (**13**). A soln. of **11** (39 mg, 0.20 mmol) in Ac_2O (1.80 ml) was cooled to −20°, treated with Me_3SiOTf (25 µl), stirred for 15 min, treated with a sat. aq. soln. of $NaHCO_3$ (2.0 ml), warmed to 20°, and treated dropwise with sat. aq. $NaHCO_3$ soln., until gas evolution ceased. Extraction with AcOEt, drying ($MgSO_4$), and evaporation at 40°/13 mbar gave crude **13** (77 mg). FC (5 g, CH_2Cl_2/MeOH 10:1) gave α/β-D-**13** 94:6 (64 mg, 94%). White solid. R_f (hexane/AcOEt 7:3) 0.36. M.p. 88–89°. IR (KBr): 3302*m*, 2995*w*, 2940*w*, 2130*s*, 1754*s*, 1748*s*, 1458*m*, 1438*m*, 1377*s*, 1314*m*, 1245*m*, 1221*s*, 1141*s*,

1073*s*, 1024*s*, 939*s*, 900*s*, 884*m*, 864*m*. ^{1}H-NMR (400 MHz, CD_3OD, α-D-**13**/β-D-**13** 94:6): data of α-D-**13**: 2.057, 2.15, 2.18 (3*s*, 3 AcO); 2.68 (*d*, *J* = 2.4, HC≡C); 2.94 (*td*, *J* = 10.8, 2.4, H−C(4)); 3.68 (*dd*, *J* = 10.4, 3.6, H−C(2)); 4.15 (*ddd*, *J* = 10.8, 4.8, 2.4, H−C(5)); 4.29 (*dd*, *J* = 12.2, 4.8, H−C(6)); 4.36 (*dd*, *J* = 12.2, 2.4, H′−C(6)); 5.46 (*t*, *J* = 10.6, H−C(3)); 6.27 (*d*, *J* = 3.6, H−C(1)); data of β-D-**13**: 2.062, 2.139, 2.142 (3*s*, 3 AcO); 2.65 (*d*, *J* = 2.4, HC≡C); 2.85 (*td*, *J* = 10.6, 2.4, H−C(4)); 3.61 (*dd*, *J* = 10.0, 8.5, H−C(2)); 3.96 (*ddd*, *J* = 10.5, 5.2, 2.2, H−C(5)); 4.27 (*dd*, *J* = 12.2, 5.2, H−C(6)); 4.41 (*dd*, *J* = 12.2, 2.2, H′−C(6)); 5.24 (*dd*, *J* = 10.8, 10.0, H−C(3)); 5.63 (*d*, *J* = 8.5, H−C(1)). ^{13}C-NMR (100 MHz, CD_3OD): see *Table 3*, additionally for α-D-**13**: 20.63, 20.69, 20.83 (3*q*, 3 Me); 170.38, 171.34, 172.28 (3*s*, 3 C=O); additionally for β-D-**13**: 20.77 (*q*, Me); 170.20, 171.08, 172.18 3*s*, 3 C=O); signal for 2 Me hidden by signals of α-D-**13**. DCI-MS: 358 (19), 357 (100, $[M+NH_4]^+$), 312 (4), 296 (6, $[M-Ac]^+$), 254 (5), 252 (9), 237 (5), 224 (4), 220 (6), 210 (9), 191 (6), 162 (4), 149 (4).

1,6-Anhydro-2,4-bis-O-*(triisopropylsilyl)*-β-D-*mannopyranose* (**15**). A soln. of **14** (*Sigma*; 1.62 g, 10 mmol) in CH_2Cl_2/pyridine 1:1 (20 ml) was cooled to 0°, treated with TIPSOTf (5.64 ml, 21 mmol), stirred for 2 h, treated with an additional portion of TIPSOTf (0.534 ml, 2 mmol), and stirred for 3 h. After addition of H_2O and extraction with Et_2O, the combined org. layers were washed with 2N HCl and brine, dried ($MgSO_4$), and evaporated at 23°/12 mbar. FC (150 g, hexane/Et_2O 10:1) of the residue (5.5 g) gave **15** (3.78 g, 80%). Colourless syrup. R_f (hexane/AcOEt 10:1) 0.33. IR (neat): 3554*w*, 2944*s*, 2867*s*, 1464*m*, 1112*s* (br.), 1038*m*, 993*w*, 882*s*, 851*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.05–1.18 (*m*, 2 $(Me_2CH)_3Si$); 3.17 (*d*, *J* = 1.2, exchange with D_2O, HO−C(3)); 3.68 (*dd*, *J* = 7.7, 5.3, H_{exo}−C(6)); 3.91 (*dt*, *J* = 5.1, 1.5, addn. of $D_2O \rightarrow$ *dd*, *J* = 5.1, 1.8, H−C(3)); 3.93 (*dd*, *J* = 5.2, 1.8, H−C(2)); 4.01 (*t*, *J* ≈ 1.6, H−C(4)); 4.24 (*dd*, *J* = 7.7, 0.8, H_{endo}−C(6); 4.42 (br. *d*, *J* = 5.1, H−C(5)); 5.33 (*t*, *J* ≈ 1.3, H−C(1)). ^{13}C-NMR (100 MHz, $CDCl_3$): see *Table 3*; additionally, 12.19 (*d*, 2 $(Me_2CH)_3Si$); 18.00 (*q*, 2 $(Me_2CH)_3Si$). DCI-MS (CH_2Cl_2): 492 (21, $[M+NH_4]^+$), 476 (23), 475 (56, $[M+1]^+$), 457 (18), 431 (26), 319 (22), 318 (97), 302 (22), 301 (100), 257 (67), 229 (24), 185 (45), 174 (28), 173 (21). Anal. calc. for $C_{24}H_{50}O_5Si_2$ (474.83): C 60.71, H 10.61; found: C 60.57, H 10.57.

Alkynylating Acetal Opening of **15**. A soln. of (trimethylsilyl)acetylene (0.70 ml, 5.0 mmol) in toluene (2.0 ml) was cooled to −5°, treated dropwise with 2.5M BuLi in hexane (0.20 ml, 5.0 mmol) and THF (0.050 ml), stirred for 10 min, cooled to −10°, treated with $AlCl_3$ (0.60 g, 4.5 mmol), stirred at 23° for 1 h and at 90° for 10 min, treated dropwise over 30 s with a soln. of **15** (237 mg, 0.50 mmol) in toluene (1.0 ml), and stirred at 90° for 70 min. The brown suspension was cooled to 0°, treated with ice (20 g), stirred for 30 min, and diluted with Et_2O (10 ml). The solid was dissolved by portionwise addition of 2N HCl (20 ml). After saturation of the aq. phase with NaCl and extraction with Et_2O, the combined org. layers were dried ($MgSO_4$) and evaporated at 40°/10 mbar. FC (30 g, toluene → toluene/AcOEt 10:1 → 10:3, 120 ml each) gave **16** (204 mg, 71%) and **17** (30 mg, 12%).

3,7-Anhydro-1,2,6-trideoxy-4,6-bis-O-*(triisopropylsilyl)-1-(trimethylsilyl)*-D-glycero-D-galacto-*oct-1-ynitol* (**16**). White solid. M.p. 125–126°. R_f (toluene/AcOEt 20:1) 0.58. IR (KBr): 3444*s* (br.), 2944*s*, 2866*s*, 2187*w*, 2131*w*, 1464*m*, 1387*m*, 1250*m*, 1117*s*, 1048*m*, 1016*m*, 962*w*, 920*w*, 884*m*, 859*s*, 842*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.17 (*s*, Me_3Si); 1.06–1.33 (*m*, 2 $(Me_2CH)_3Si$); 2.07 (*dd*, *J* = 7.3, 6.1, exchange with D_2O, HO−C(8)); 2.12 (*d*, *J* = 9.0, exchange with D_2O, HO−C(5)); 3.27 (*ddd*, *J* = 8.4, 4.8, 2.9, H−C(7)); 3.45 (*td*, *J* ≈ 8.7, 3.1, addn. of $D_2O \rightarrow$ *dd*, *J* = 8.4, 3.1, H−C(5)); 3.80 (*ddd*, *J* = 11.8, 7.4, 4.9, addn. of $D_2O \rightarrow$ *dd*, *J* = 11.8, 5.0, H−C(8)); 3.87 (*ddd*, *J* = 11.8, 6.0, 2.9, addn. of $D_2O \rightarrow$ *dd*, *J* = 11.8, 3.1, H′−C(8)); 3.94 (*t*, *J* = 8.4, H−C(6)); 4.22 (*dd*, *J* = 3.1, 1.3, H−C(4)); 4.28 (*d*, *J* = 1.3, H−C(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): see *Table 3*; additionally, −0.45 (*q*, Me_3Si); 13.05, 13.49 (2*d*, 2 $(Me_2CH)_3Si$); 18.28, 18.35 (2*q*, 2 $(Me_2CH)_3Si$). DCI-MS (MeOH)): 573 (5, $[M+1]^+$), 529 (5), 297 (10), 283 (8), 253 (9), 211 (10), 199 (9), 187 (8), 173 (13), 157 (14), 148 (50), 132 (17), 131 (100),115 (11), 103 (62), 102 (20), 76 (12), 75 (81), 74 (35), 73 (40), 61 (27), 60 (19), 59 (11). Anal. calc. for $C_{29}H_{60}O_5Si_3$ (573.05): C 60.78, H 10.55; found: C 60.68, H 10.31.

4,8-Anhydro-1,2,3-trideoxy-1-(trimethylsilyl)-7-O-*(triisopropylsilyl)-3-[(*E*)-(trimethylsilyl)methylidene]*-D-glycero-D-galacto-*non-1-ynitol* (**17**). Slightly yellow solid. R_f (toluene/AcOEt 10:3) 0.41. M.p. 119–120°. IR (KBr): 3424*s* (br.), 2960*s*, 2894*m*, 2806*s*, 2144*w*, 1578*w*, 1466*m*, 1400*w*, 1285*w*, 1249*s*, 1135*s*, 1106*s*, 1072*s*, 985*m*, 884*s*, 855*s*, 839*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.19, 1.195 (2*s*, 2 Me_3Si); 1.05–1.34 (*m*, $(Me_2CH)_3Si$); 1.92 (*d*, *J* = 4.4, exchange with D_2O, HO−C(5)); 2.05 (br. *t*, *J* ≈ 6.2, exchange with D_2O, HO−C(9)); 2.44 (*d*, *J* = 9.3, exchange with D_2O, HO−C(6)); 3.31 (*ddd*, *J* = 9.3, 5.9, 2.8, H−C(8)); 3.58 (*td*, *J* ≈ 9.0, 3.4, addn. of $D_2O \rightarrow$ *dd*, *J* = 8.8, 3.5, H−C(6)); 3.80 (br. *dt*, *J* ≈ 11.8, 5.6, addn. of $D_2O \rightarrow$ *dd*, *J* = 11.8, 5.9, H−C(9)); 3.83 (*t*, *J* = 9.0, H−C(7)); 3.97 (br. *ddd*, *J* = 11.8, 5.9, 2.5, addn. of $D_2O \rightarrow$ *dd*, *J* = 11.8, 2.8, H′−C(9)); 4.00 (*dd*, *J* = 1.9, 1.2, H−C(4)); 4.26 (br. *td*, *J* ≈ 4.0, 1.2, addn. of $D_2O \rightarrow$ *dd*, *J* = 3.5, 1.2, H−C(5)); 6.36 (*d*, *J* = 1.9, H−C(1′)). ^{13}C-NMR (100 MHz, $CDCl_3$): see *Table 3*; additionally, −1.12, −0.41 (2*q*, 2 Me_3Si); 12.99 (*d*, $(Me_2CH)_3Si$); 18.31, 18.28 (2*q*, $(Me_2CH)_3Si$). DCI-MS (MeOH)): 516 (11), 515 (24, $[M+1]^+$), 321 (10), 251 (15), 239 (15),

233 (12), 215 (14), 203 (15), 185 (20), 173 (33), 157 (12), 148 (12), 147 (18), 133 (13), 131 (53), 103 (38), 75 (60), 74 (22), 73 (100, Me_3Si^+), 61 (18), 60 (14), 45 (13).

3,7-Anhydro-1,2,6-trideoxy-D-glycero-D-galacto-*oct-1-ynitol* (**18**). A soln. of **16** (180 mg, 0.314 mmol) in THF (20 ml) was treated with CF_3CO_2H/H_2O 1:1 (20 ml), stirred under reflux for 24 h, and evaporated at 30°/12 mbar. The residue was purified by FC (10 g, AcOEt/MeOH/H_2O 17:3:2) and treated with 0.01M NaOMe in MeOH (10 ml), stirred at 23° for 12 h, treated with phenolphthalein (2 mg) and solid NH_4Cl until disappearance of the pink colour. Evaporation at 23°/12 mbar and FC (AcOEt/MeOH/H_2O 17:3:2) gave **18** (56 mg, 94%). White solid. R_f (AcOEt/MeOH/H_2O 17:3:2) 0.27. M.p. 204–205° (dec.). IR (KBr): 3535*s*, 3395*s*, 3282*s*, 3184*s*, 3147*s*, 2929*m*, 2869*m*, 2116*w*, 1405*w*, 1363*m*, 1326*w*, 1296*w*, 1135*m*, 1105*m*, 1084*s*, 1069*s*, 1052*s*, 1008*w*, 922*m*, 888*w*, 848*m*. ^{1}H-NMR (500 MHz, CD_3OD): 2.87 (*d*, *J* = 2.3, H–C(1)); 3.22 (*ddd*, *J* = 9.6, 5.8, 2.3, irrad. at 4.33 → NOE of 7%, H–C(7)); 3.47 (*dd*, *J* = 9.5, 3.3, irrad. at 4.33 → NOE of 5%, irrad. at 3.22 → NOE of 4%, H–C(5)); 3.56 (*t*, *J* = 9.5, irrad. at 3.22 → NOE of 2%, H–C(6)); 3.68 (*dd*, *J* = 11.9, 5.8, irrad. at 3.22 → NOE of 2%, H–C(8)); 3.84 (*dd*, *J* = 11.9, 2.3, irrad. at 3.22 → NOE of 4%, H′–C(8)); 3.86 (*dd*, *J* = 3.3, 1.1, irrad. at 4.33 → NOE of 6%, H–C(4)); 4.33 (*dd*, *J* = 2.3, 1.2, irrad. at 3.22 → NOE of 11%, H–C(3)). ^{13}C-NMR (125 MHz, CD_3OD): see *Table 3*. HR-ESI-MS (MeOH, NH_4Cl): 189.0763 ($[M+H]^+$, $C_8H_{13}O_5$; calc. 189.0763), 206.1029 ($[M+NH_4]^+$, $C_8H_{16}NO_5$; calc. 206.1028), 211.0583 ($[M+Na]^+$, $C_8H_{12}NaO_5$; calc. 211.0582). Anal. calc. for $C_8H_{12}O_5$ (188.18): C 51.06, H 6.43; found: C 50.98, H 6.36.

3,7-Anhydro-1,2,6-trideoxy-5,6-O-*[(2*S*,3*S*)-2,3-dimethoxybutane-2,3-diyl]*-D-glycero-D-galacto-*oct-1-ynitol* (**19**). A soln. of **18** (35 mg, 0.19 mmol) in MeOH (1.0 ml) was heated to 50°, treated with freshly distilled butane-2,3-dione (36 µl, 0.41 mmol), $(MeO)_3CH$ (81 µl, 0,76 mmol) and freshly distilled $BF_3 \cdot OEt_2$ (50 µl, 0.37 mmol), stirred for 2 h, cooled to 23°, and treated with Et_3N (200 µl). Evaporation at 23°/10 mbar and FC (10 g, pentane/AcOEt 1:5) gave **19** (54 mg, 96%). White solid. R_f (AcOEt) 0.29. M.p. 159–160°. IR (KBr): 3425*s*, 3281*s*, 2957*m*, 2911*m*, 2858*m*, 2125*w*, 1458*w*, 1420*w*, 1396*m*, 1378*m*, 1310*w*, 1290w, 1235*m*, 1160*s*, 1142*s*, 1128*s*, 1118*s*, 1100*s*, 1077*s*, 1049*s*, 1031*s*, 1015*m*, 948*w*, 922*m*, 884*m*, 848*w*, 835*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.28, 1.35 (2*s*, 2 Me); 2.04 (br. *s*, exchange with D_2O, HO–C(8)); 2.61 (*d*, *J* = 2.2, H–C(1)); 3.10 (br. *s*, exchange with D_2O, HO–C(4)); 3.26, 3.28 (2*s*, 2 MeO); 3.49 (*ddd*, *J* = 9.8, 5.0, 2.7, H–C(7)); 3.76 (*dd*, *J* = 12.2, 5.0, H–C(8)); 3.78 (*dd*, *J* = 10.2, 3.0, H–C(5)); 3.89 (*dd*, *J* = 12.1, 2.7, H′–C(8)); 4.02 (*dd*, *J* = 3.0, 1.2, H–C(4)); 4.09 (*t*, *J* = 10.0, H–C(6)); 4.37 (*dd*, *J* = 2.2, 1.3, H–C(3)). ^{13}C-NMR ($CDCl_3$, 100 MHz): see *Table 3*, additionally, 17.68, 17.73 (2*q*, 2 Me); 47.97, 48.14 (2*q*, 2 MeO); 99.86, 100.48 (2*s*, 2 *C*Me(OMe)). ESI-MS (MeOH, NH_4OAc): 341 (17, $[M+K]^+$), 325 (28, $[M+Na]^+$), 320 (100, $[M+NH_4]^+$), 271 (6, $[M-MeO]^+$). Anal. calc. for $C_{14}H_{22}O_7$ (302.32): C 55.62, H 7.33; found: C 55.30, H 7.30.

3,7-Anhydro-1,2,6-trideoxy-5,6-O-*[(2*S*,3*S*)-2,3-dimethoxybutane-2,3-diyl]-4*-O-*[(trifluoromethyl)sulfonyl]-8*-O-*(triisopropylsilyl)*-D-glycero-D-galacto-*oct-1-ynitol* (**20**). A soln. of **19** (150 mg, 0.50 mmol) in CH_2Cl_2/pyridine 3:1 (4.0 ml) was cooled to −15°, treated dropwise with TIPSOTf (166 µl, 0.60 mmol), warmed to 23°, treated dropwise with Tf_2O (98 µl, 0.60 mmol), warmed to 23°, stirred for 30 min, and treated with sat. aq. $NaHCO_3$ soln. (1.0 ml), until gas evolution ceased. The mixture was diluted with CH_2Cl_2 (10 ml) and H_2O (10 ml). After separation of the org. layer, the aq. layer was extracted with CH_2Cl_2 (3 × 10 ml). The combined org. layers were dried ($MgSO_4$) and evaporated at 23°/10 mbar. FC (20 g, pentane/AcOEt 10:3) gave **20** (264 mg, 90%). Colourless syrup. R_f (heptane/AcOEt 10:3) 0.60. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.04–1.12 (*m*, $(Me_2CH)_3Si$); 1.27, 1.28 (2*s*, 2 Me); 2.59 (*d*, *J* = 2.2, irrad. at 4.45 → *s*, H–C(1)); 3.24, 3.26 (2*s*, MeO); 3.43 (*ddd*, *J* = 10.0, 3.2, 2.1, H–C(7)); 3.88 (*dd*, *J* = 10.3, 2.8, irrad. at 5.02 → *d*, *J* = 10.3, H–C(5)); 3.90 (*dd*, *J* = 11.5, 3.4, H–C(8)); 3.96 (*dd*, *J* = 11.5, 2.0, H′–C(8)); 4.14 (*t*, *J* = 10.1, H–C(6)); 4.45 (*t*, *J* ≈ 1.4, irrad. at 5.02 → *d*, *J* = 2.2, H–C(3)); 5.02 (br. *d*, *J* = 2.5, irrad. at 4.45 → *d*, *J* = 2.5, H–C(4)). ^{13}C-NMR ($CDCl_3$, 75 MHz): see *Table 3*; additionally, 12.03 (*d*, $(Me_2CH)_3Si$); 17.13, 17.61 (2*q*, 2 Me); 17.81, 17.89 (2*q*, $(Me_2CH)_3Si$); 48.07, 48.27 (2*q*, 2 MeO); 99.84, 100.60 (2*s*, 2 *C*Me(OMe)); *q* of CF_3 hidden by the noise. ^{19}F-NMR ($CDCl_3$, 280 MHz): −73.32. DCI-MS (MeOH): 608 (3, $[M+NH_4]^+$), 576 (6, $[M-MeO+NH_3]^+$), 560 (20), 559 (57, $[M-MeO]^+$), 527 (9), 353 (12), 311 (10), 309 (12), 285 (18), 239 (12), 225 (17), 217 (16), 211 (10), 185 (19), 174 (20), 173 (58), 148 (50), 145 (26), 139 (30), 131 (85), 130 (27), 116 (42), 115 (100), 107 (52), 103 (59), 102 (25), 101 (76), 95 (27), 81 (30), 75 (46), 74 (22), 60 (31), 59 (20), 43 (30). Anal. calc. for $C_{24}H_{41}F_3O_9SSi$ (590.73): C 48.80, H 7.00; found: C 48.89, H 7.17.

Treatment of **20** *with* NaN_3. A soln. of **20** (260 mg, 0.44 mmol) in DMF (3.0 ml) was cooled to 0°, treated with NaN_3 (143 mg, 2.2 mmol), stirred for 16 h, diluted with Et_2O (20 ml), washed with H_2O (2 ml) and brine (3 × 2 ml), dried ($MgSO_4$), and evaporated at 23°/10 mbar. FC (30 g, pentane/Et_2O 5:1 → 10:3) of the yellow solid (208 mg) gave **21**/**22** 85:15 (175 mg, 83%). Crystallization from MeOH (1.0 ml) gave pure **21** (119 mg, 56%).

Treatment of **21**/**22** 85:15 with propane-1,3-dithiol/Et_3N in MeOH at 23° for 26 h and FC (cyclohexane/AcOEt 5:1) gave pure **22**.

*3,7-Anhydro-4-azido-1,2,4-trideoxy-8-*O*-(triisopropylsilyl)-5,6-*O*-[(2*S*,3*S*)-2,3-dimethoxybutane-2,3-diyl]-*D*-glycero-*D*-gulo-oct-1-ynitol* (**21**). White solid. R_f (heptane/Et_2O 10:3) 0.56. IR (KBr): 3316*m*, 3263*m*, 2944*m*, 2895*m*, 2867*m*, 2222*w*, 2112*s*, 1465*m*, 1389*m*, 1371*w*, 1318*w*, 1283*m*, 1263*w*, 1224*w*, 1202*w*, 1145*s*, 1135*s*, 1112*s*, 1084*m*, 1042*s*, 1014*m*, 973*w*, 957*w*, 918*w*, 885*m*, 848*w*, 805*m*. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.03–1.12 (*m*, $(Me_2CH)_3Si$); 1.29, 1.36 (2*s*, 2 Me); 2.52 (*d*, *J* = 2.1, H–C(1)); 3.28, 3.33 (2*s*, 2 MeO); 3.36 (*ddd*, *J* = 9.7, 3.5, 2.0, H–C(7)); 3.57 (*t*, *J* = 9.9, H–C(4)); 3.65 (*t*, *J* = 9.9, H–C(5)); 3.81 (*t*, *J* = 9.7, H–C(6)); 3.855 (*dd*, *J* = 11.5, 3.5, H–C(8)); 3.895 (*dd*, *J* = 9.7, 2.2, irrad. at 2.51 → *d*, *J* = 9.7, H–C (3)); 3.92 (*dd*, *J* = 11.5, 2.0, H′–C(8)). ^{13}C-NMR ($CDCl_3$, 125 MHz): see *Table 3*; additionally, 12.04 (*d*, $(Me_2CH)_3Si$); 17.59, 17.66 (2*q*, 2 Me); 17.91, 18.00 (2*q*, $(Me_2CH)_3Si$); 48.08, 48.17 (2*q*, 2 MeO); 99.73, 100.15 (2*s*, 2 *C*Me(OMe)). DEI-MS (CH_2Cl_2): 452 (1, $[M - MeO]^+$), 440 (3, $[M - N_3H]^+$), 412 (4), 173 (9), 157 (6), 145 (9), 131 (10), 127 (5), 116 (11), 115 (17), 103 (12), 101 (21), 88 (11), 86 (67), 84 (100), 51 (23), 49 (76), 47 (12).

*3,7-Anhydro-1,2,4-trideoxy-8-*O*-(triisopropylsilyl)-5,6-*O*-[(2*S*,3*S*)-2,3-dimethoxybutane-2,3-diyl]-*D*-arabino-oct-3-en-1-ynitol* (**22**). Colourless oil. R_f (heptane/Et_2O 10:3) 0.56. R_f (cyclohexane/AcOEt 5:1) 0.50. IR (neat): 3305*w*, 2944*s*, 2903*m*, 2867*s*, 2113*w*, 1632*m*, 1463*m*, 1376*m*, 1338*w*, 1280*m*, 1192*m*, 1131*s*, 1114*s*, 1083*s*, 1054*s*, 1038*m*, 1013*m*, 998*m*, 966*m*, 925*m*, 883*s*, 848*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.02–1.15 (*m*, $(Me_2CH)_3Si$); 1.31, 1.32 (2*s*, 2 Me); 2.83 (*d*, *J* = 0.6, irrad. at 4.49 → *s*, H–C(1)); 3.25, 3.29 (2*s*, 2 MeO); 3.97–4.06 (*m*. H–C(7), 2 H–C(8)); 4.06 (*t*, *J* ≈ 10.0, irrad. at 4.49 → br. *d*, *J* = 10.6, H–C(6)); 4.49 (br. *ddt*, *J* ≈ 8.5, 22, 1.1, irrad. at 2.83 → *dt*, *J* ≈ 8.4, 2.0, irrad. at 5.17 → *dt*, *J* ≈ 8.1, 1.3, H–C(5)); 5.17 (*d*, *J* = 1.9, irrad. at 4.49 → *s*, H–C(4)). ^{13}C-NMR ($CDCl_3$, 75 MHz): see *Table 3*; additionally, 11.88 (*d*, $(Me_2CH)_3Si$); 17.64, 17.68 (2*q*, 2 Me); 17.74, 17.84 (2*q*, $(Me_2CH)_3Si$); 47.88, 48.03 (2*q*, 2 MeO); 100.26 (*s*, 2 *C*Me(OMe)). DEI-MS (MeOH): 441 (23), 440 (81, M^+), 292 (24), 252 (39), 210 (39), 185 (20), 173 (69), 157 (44), 145 (54), 139 (20), 131 (33), 116 (52), 115 (100), 103 (26), 101 (77), 89 (24), 75 (20), 73 (20).

*2,6-Anhydro-7,8-dideoxy-3,4-*O*-[(2*S*,3*S*)-2,3-dimethoxybutane-2,3-diyl]-*D*-glycero-*D*-manno-oct-7-ynitol* (**24**). A soln. of **23** [6] (800 mg, 4.25 mmol) in MeOH (24.0 ml) was heated to 60°, treated with freshly distilled butane-2,3-dione (817 µl, 9.35 mmol), $(MeO)_3CH$ (1.86 ml, 17.0 mmol) and freshly distilled $BF_3 \cdot OEt_2$ (1.05 ml, 8.50 mol), stirred for 4 h, cooled to 23°, treated with Et_3N (5.0 ml), and stirred for 30 min. Filtration over a pad of silica gel (3 × 2 cm, 250 ml of AcOEt/Et_3N 100:1) and FC (75 g, AcOEt) gave **24** (1.21 g, 94%). White solid. R_f (AcOEt) 0.41. IR ($CHCl_3$): 3586*m*, 3488*m* (br.), 3305*s*, 3006*m*, 2929*s*, 2851*m*, 2100*w*, 1451*m*, 1378*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.23, 1.32 (2*s*, 2 Me); 2.09 (*dd*, *J* = 7.8, 5.3, exchange with D_2O, HO–C(1)); 2.58 (*d*, *J* = 2.5, H–C(8)); 2.83 (*d*, *J* = 1.9, exchange with D_2O, HO–C(5)); 3.26, 3.29 (2*s*, 2 MeO); 3.77 (*ddd*, *J* = 11.8, 7.8, 4.4, addn. of D_2O → *dd*, *J* = 11.8, 4.4, H–C(1)); 3.86 (*ddd*, *J* = 11.8, 5.3, 2.5, addn. of D_2O → *dd*, *J* = 11.8, 2.5, H′–C(1)); 3.95 (*ddd*, *J* = 9.5, 4.5, 2.8, H–C(2)); 4.03 (br. *q*, *J* ≈ 2.5, addn. of D_2O → *dd*, *J* = 2.8, 1.9, H–C(5)); 4.08 (*t*, *J* = 10.0, H–C(3)); 4.15 (*dd*, *J* = 10.1, 2.8, H–C(4)); 4.78 (*t*, *J* ≈ 1.9, H–C(6)). ^{13}C-NMR ($CDCl_3$, 75 MHz): 17.66, 17.25 (2*q*, 2 Me); 47.93, 48.07 (2*q*, 2 MeO); 61.15 (*t*, C(1)); 62.96 (*d*, C(3)); 68.46, 69.06 (2*d*, C(5), C(6)); 71.01 (*d*, C(4)); 73.41 (*d*, C(2)); 77.28 (*s*, C(8)); 78.31 (*s*, C(7)); 99.91, 100.43 (2*s*, 2 *C*Me(OMe)). DEI-MS (MeOH): 271 (6, $[M - MeO]^+$), 213 (4), 153 (7), 149 (5), 135 (5), 123 (22), 106 (38), 101 (78), 100 (100), 82 (51), 80 (30), 73 (30), 72 (20), 69 (25).

*2,6-Anhydro-7,8-dideoxy-3,4-*O*-[(2*S*,3*S*)-2,3-dimethoxybutane-2,3-diyl]-5-*O*-(trifluoromethylsulfonyl)-1-*O*-(triisopropylsilyl)-*D*-glycero-*D*-manno-oct-7-ynitol* (**25**). A soln. of **24** (226 mg, 0.75 mmol) and pyridine (0.45 ml) in CH_2Cl_2 (4.5 ml) was cooled to −15°, treated dropwise with TIPSOTf (230 µl, 0.823 mmol), stirred for 15 min, treated with pyridine (3.0 ml) and Tf_2O (150 µl, 0.90 mmol), warmed to 23°, stirred for 3 h, treated with CH_2Cl_2 (50 ml) and sat. aq. $NaHCO_3$ soln. (50 ml), and stirred for 1 h. Extraction with CH_2Cl_2 (3 × 50 ml), filtration over cotton, evaporation at 27°/13 mbar, and FC (40 g, pentane/AcOEt 20:1) gave **25** (264 mg, 76%). Colourless oil. R_f (pentane/AcOEt 20:1) 0.28. IR ($CHCl_3$): 3303*m*, 2944*s*, 2890*m*, 2866*s*, 2113*w*, 1416*s*, 1142*s*, 1120*m*, 1100*w*, 1090*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.04–1.10 (*m*, $(Me_2CH)_3Si$); 1.28, 1.29 (2*s*, 2 Me); 2.67 (*d*, *J* = 2.4, H–C(8)); 3.25, 3.28 (2*s*, 2 MeO); 3.89 (*ddd*, *J* = 9.7, 3.2, 2.1, H–C(2)); 3.92 (*dd*, *J* = 11.5, 2.1, H–C(1)); 3.96 (*dd*, *J* = 11.6, 3.4, H′–C(1)); 4.14 (*t*, *J* ≈ 10.0, H–C(3)); 4.31 (*dd*, *J* = 10.3, 2.8, H–C(4)); 4.88 (*t*, *J* ≈ 2.0, H–C(6)); 5.01 (*t*, *J* = 2.3, H–C(5)). ^{13}C-NMR ($CDCl_3$, 100 MHz): see *Table 3*; additionally, 12.02 (*d*, $(Me_2CH)_3Si$); 17.27, 17.67 (2*q*, 2 Me); 17.80, 17.87 (2*q*, $(Me_2CH)_3Si$); 48.04, 48.13 (2*q*, 2 MeO); 99.86, 100.62 (2*s*, 2 *C*Me(OMe)); 118 (*q*, *J* ≈ 322, CF_3).

*2,6-Anhydro-5-azido-5,7,8-trideoxy-1-*O*-(triisopropylsilyl)-3,4-*O*-[(2*S*,3*S*)-2,3-dimethoxybutane-2,3-diyl]-*D*-glycero-*D*-manno-oct-7-ynitol* (**26**). A soln. of **25** (220 mg, 0.37 mmol) and NaN_3 (224 mg, 3.7 mmol) in DMF (2.6 ml) was stirred for 3.5 h at 55–60° and for 14 h at 23°. Addition of Et_2O (20 ml), washing with H_2O (2 ml) and brine (3 × 2 ml), drying ($MgSO_4$), evaporation at 23°/10 mbar, and 2 FC (30 g, pentane/Et_2O 10:1) gave **26** (125 mg, 70%). White solid. R_f (pentane/Et_2O 10:1) 0.55. M.p. 75–76°. IR ($CHCl_3$): 3304*w*, 2990*w*, 2945*m*, 2867*m*, 2230*w*, 2113*s*, 1463*w*, 1395*w*, 1200*m*, 1170*s*, 1150*s*, 1110*m*, 1045*m*, 1010*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz):

1.04–1.10 (*m*, $(Me_2CH)_3Si$); 1.31, 1.37 (2*s*, 2 Me); 2.58 (*d*, *J* = 2.3, H–C(8)); 3.29, 3.37 (2*s*, 2 MeO); 3.64 (*dd*, *J* = 10.6, 5.7, H–C(5)); 3.82 (*t*, *J* ≈ 9.5, H–C(3)); 3.86–3.95 (*m*, H–C(2), 2 H–C(1)); 4.19 (*dd*, *J* = 10.5, 9.5, H–C(4)); 4.76 (*dd*, *J* = 5.7, 2.3, H–C(6)). ^{13}C-NMR ($CDCl_3$): see *Table 3*; additionally, 12.02 (*d*, $(Me_2CH)_3Si$); 17.70, 17.76 (2*q*, 2 Me); 17.91, 18.00 (2*q*, $(Me_2CH)_3Si$); 48.22, 48.36 (2*q*, 2 MeO); 99.82, 100.02 (2*s*, 2 *C*Me(OMe)). DEI-MS (CH_2Cl_2): 452 (7, $[M - MeO]^+$), 441 (22), 440 (78, $[M - N_3H]^+$), 412 (12), 292 (23), 252 (45), 210 (40), 173 (82), 157 (61), 145 (74), 131 (53), 116 (59), 115 (99), 111 (22), 110 (23), 103 (43), 101 (100), 86 (20), 84 (30), 75 (35), 73 (36). Anal. calc. for $C_{23}H_{41}N_3O_6Si$ (483.68): C 57.11, H 8.54, N 8.69; found: C 57.23, H 8.47, N 8.69.

*1,6-Anhydro-4-deoxy-4-[2-(trimethylsilyl)ethynyl]-β-*D*-mannopyranose* (**28**). A soln. of **27** [6] (400 mg, 1.0 mmol) in $THF/CF_3CO_2H/H_2O$ 2:1:1 (40 ml) was heated for 4 h under reflux and evaporated at 40°/12 mbar. FC (50 g, CH_2Cl_2/AcOEt 3:4) of the yellow oil (574 mg) gave **28** (238 mg, 98%). White solid. R_f (CH_2Cl_2/AcOEt 1:1) 0.29. IR (KBr): 3394*s* (br.), 2958*m*, 2174*m*, 1452*w*, 1420*w*, 1351*m*, 1247*s*, 1192*m*, 1118*m*, 1085*s*, 1075*s*, 1060*w*, 1033*s*, 1011*m*, 977*m*, 892*m*, 845*s*, 811*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.15 (*s*, Me_3Si); 2.99 (br. *s*, H–C(4)); 3.07, 3.19 (2 br. *s*, exchange with D_2O, HO–C(2), HO–C(3)); 3.74 (*dd*, *J* = 7.2, 5.3, H_{exo}–C(6)); 3.82 (br. *d*, *J* = 3.7, addn. of $D_2O \rightarrow$ *dd*, *J* = 5.0, 1.9, H–C(2)); 4.14 (br. *d*, *J* = 3.7, addn. of $D_2O \rightarrow$ *dq*, *J* = 5.0, 1.4, H–C(3)); 4.21 (*d*, *J* = 7.2, H_{endo}–C(6)); 4.56 (br. *d*, *J* = 5.0, H–C(5)); 5.40 (br. *s*, H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, −0.04 (*q*, Me_3Si). DCI-MS (MeOH): 260 (1, $[M + NH_4]^+$), 243 (1, $[M + 1]^+$), 225 (1), 209 (2), 86 (12), 84 (21), 73 (100, Me_3Si^+).

Reductive Acetal Opening of **27**. At −5°, a soln. of trimethylsilylacetylene (13.9 ml, 100 mmol) in toluene (200 ml) was treated dropwise with 2.5M BuLi in hexane (40.0 ml, 0.10 mol) and with THF (4.0 ml), stirred for 10 min at −5°, cooled to −10°, and treated below 0° with $AlCl_3$ (12.0 g, 90 mmol). The white suspension was stirred at 23° for 1 h, warmed to 65° within 20 min, treated dropwise over 4 min with a soln. of **27** (1.99 g, 5.0 mmol) in toluene (10.0 ml), and stirred at 65–70° for 2.5 h. The brown suspension was cooled to 0° and treated with ice (150 g), stirred for 30 min, treated with Et_2O (100 ml) and portionwise with 2N HCl (400 ml) until complete dissolution of the solid. The aq. phase was saturated with NaCl and extracted with with three portions of Et_2O. The combined org. layers were dried ($MgSO_4$) and evaporated at 40°/10 mbar. FC (200 g, pentane/Et_2O 5:1 (1.2 l) → pentane/AcOEt 2:1 (0.6 l) → AcOEt (0.5 l)) of the brown oily residue (4.83 g) gave **29** (1.62 g, 65%), **30** (365 mg, 17%), **31** (85 mg, 3%), and **28** (61 mg, 5%).

*3,7-Anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-(trimethylsilyl)-6-[2-(trimethylsilyl)ethynyl]-*D*-glycero-*D*-galacto-oct-1-ynitol* (**29**). White solid. R_f (pentane/Et_2O 5:2) 0.31. R_f (CH_2Cl_2) 0.31. $[\alpha]_D^{27} = -30.8$ (*c* = 0.5, MeOH). M.p. 102–103°. IR (KBr): 3516*m* (br.), 3395*m* (br.), 2960*s*, 2866*s*, 2170*w*, 1465*w*, 1369*w*, 1336*w*, 1250*s*, 1167*s*, 1115*s*, 1054*s*, 1019*w*, 956*w*, 885*m*, 845*s*, 820*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.15, 0.17 (2*s*, 2 Me_3Si); 1.12, 1.13 (2*d*, *J* = 7.3, $(Me_2CH)_3Si$); 1.26 (*sept.*, *J* ≈ 7.2, $(Me_2CH)_3Si$); 2.11 (br. *t*, *J* ≈ 6.7, exchange with CD_3OD, HO–C(8)); 2.18 (*d*, *J* = 6.9, exchange with CD_3OD, HO–C(5)); 2.87 (*t*, *J* = 10.3, H–C(6)); 3.39 (*ddd*, *J* = 10.2, 5.3, 2.6, H–C(7)); 3.55 (*ddd*, *J* = 10.3, 6.9, 2.6, irrad. at 4.19 → *dd*, *J* = 10.5, 6.7, addn. of $CD_3OD \rightarrow$ *dd*, *J* = 10.3, 2.6, H–C(5)); 3.74 (br. *dt*, *J* ≈ 11.8, 6.0, addn. of $CD_3OD \rightarrow$ *dd*, *J* = 11.8, 5.3, H–C(8)); 3.93 (*ddd*, *J* = 11.7, 6.2, 2.6, addn. of $CD_3OD \rightarrow$ *dd*, *J* = 11.7, 2.6, H′–C(8)); 4.18 (br. *d*, *J* = 2.6, H–C(4)); 4.20 (*d*, *J* = 0.7, H–C(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): see *Table 3*; additionally, −0.46, −0.01 (2*q*, 2 Me_3Si); 13.39 (*d*, $(Me_2CH)_3Si$); 18.35 (*q*, $(Me_2CH)_3Si$). DCI-MS (MeOH): 498 (10), 497 (22, $[M + 1]^+$), 453 (16), 203 (11), 173 (33), 157 (10), 147 (13), 133 (19), 131 (40), 115 (13), 103 (30), 75 (40), 74 (19), 73 (100, Me_3Si^+). Anal. calc. for $C_{25}H_{48}O_4Si_3$ (496.91): C 60.43, H 9.74; found: C 60.55, H 9.77.

*4,8-Anhydro-1,2,3,7-tetradeoxy-1-(trimethylsilyl)-7-[2-(trimethylsilyl)ethynyl]-3-[(*E*)-(trimethylsilyl)-methylidene]-*D*-glycero-*D*-galacto-non-1-ynitol* (**30**). Slightly yellow solid. R_f (CH_2Cl_2/AcOEt 2:1) 0.68. R_f (pentane/Et_2O 1:1) 0.45. M.p. 94–95°. IR (KBr): 3451*s* (br.), 2959*s*, 2899*m*, 2175*w*, 2145*w*, 1579*w*, 1410*w* (br.), 1249*s*, 1148*w*, 1110*s*, 1084*s*, 1045*m*, 1035*m*, 980*w*, 842*s* (br.). ^{1}H-NMR (300 MHz, CD_3OD): 0.14, 0.18, 0.185 (3*s*, 3 Me_3Si); 2.70 (*t*, *J* = 10.6, irrad. at 3.65 → *d*, *J* = 10.0, irrad. at 3.43 → *d*, *J* = 10.0, H–C(7)); 3.43 (*ddd*, *J* = 10.3, 5.3, 2.2, irrad. at 2.70 → *dd*, *J* = 5.3, 2.2, irrad. at 3.89 → NOE of 8%, H–C(8)); 3.65 (*dd*, *J* = 10.6, 2.8, irrad. at 4.09 → *d*, *J* = 10.9, irrad. at 2.70 → *d*, *J* = 3.1, irrad. at 3.89 → NOE of 6%, H–C(6)); 3.78 (*dd*, *J* = 11.8, 5.3, irrad. at 3.43 → *d*, *J* = 11.5, H–C(9)); 3.89 (*t*, *J* ≈ 1.6, irrad. at 6.43 → *d*, *J* = 1.3, irrad. at 4.09 → *d*, *J* = 1.9, H–C(4)); 3.95 (*dd*, *J* = 11.8, 1.9, irrad. at 3.43 → *d*, *J* = 11.5, H′–C(9)); 4.09 (*br. d*, *J* ≈ 2.8, irrad. at 3.89 → *d*, *J* = 2.2, irrad. at 3.65 → *d*, *J* = 1.3, irrad. at 3.89 → NOE of 8%, H–C(5)); 6.43 (*d*, *J* = 1.8, irrad. at 3.89 → *s*, irrad. at 3.89 → NOE of 2%, irrad. at 0.183 → weak NOE, H–C(1′)). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.15, 0.18, 0.19 (3*s*, 3 Me_3Si); 2.10–2.80 (br. *s*, HO–C(5), HO–C(6), HO–C(9)); 2.78 (*t*, *J* = 10.4, H–C(7)); 3.43 (*ddd*, *J* = 10.6, 5.6, 3.1, H–C(8)); 3.72 (*dd*, *J* = 10.6, 2.8, H–C(6)); 3.83 (*dd*, *J* = 11.8, 5.0, H–C(9)); 3.92–3.97 (*m*, H′–C(9), H–C(4)); 4.22 (*br. d*, *J* = 2.5, H–C(5)); 6.39 (*d*, *J* = 1.6, H–C(1″)). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 3*; additionally, −0.71, 0.13, 0.21 (3*q*, 3 Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, −1.12,

– 0.39, 0.01 ((3*q*, 3 Me_3Si). DCI-MS (MeOH): 456 (8, $[M+NH_4]^+$), 439 (24, $[M+1]^+$), 239 (16), 238 (28), 237 (74, $[M-Me_3Si+NH_4]^+$), 149 (19), 147 (19), 75 (28), 74 (26), 73 (100, Me_3Si^+). Anal. calc. for $C_{21}H_{38}O_4Si_3$ (438.79): C 57.48, H 8.73; found: C 57.43, H 8.69.

3,7-Anhydro-1,2,6-trideoxy-1-(trimethylsilyl)-6-[2-(trimethylsilyl)ethynyl]-D-glycero-D-galacto-*oct-1-ynitol* (**31**). A soln. of **29** (100 mg, 0.20 mmol) in THF (20 ml) was treated with CF_3CO_2H/H_2O/MeOH 1:1 (20 ml; → emulsion), stirred at reflux for 2 h, treated with MeOH (5 ml; → clear soln.), and stirred at reflux for 40 h. Evaporation at 40°/12 mbar gave a brown oil (345 mg). FC (6 g, pentane/AcOEt 10:3) gave a slightly yellow solid (73 mg), which, upon an additional FC (8 g, pentane/AcOEt 10:3), afforded **31** (63 mg, 93%). White solid. R_f (pentane/AcOEt 5:2) 0.38. R_f (CH_2Cl_2/AcOEt 5:2) 0.39. M.p. 181–182°. IR (KBr): 3516*m* (br.), 3433*m* (br.), 3356*m* (br.), 2958*m*, 2899*w*, 2172*w*, 1314*w*, 1250*m*, 1108*m*, 1051*s* (br.), 844*s* (br.). ^{1}H-NMR (400 MHz, CD_3OD): 0.13, 0.15 (2*s*, 2 Me_3Si); 2.69 (br. *t*, *J* = 10.6, H–C(6)); 3.36 (*ddd*, *J* = 10.4, 5.6, 2.0, H–C(7)); 3.59 (*dd*, *J* = 10.7, 3.0, H–C(5)); 3.71 (*dd*, *J* = 12.0, 5.7, H–C(8)); 3.75 (*br. d*, *J* = 2.8, H–C(4)); 3.89 (*dd*, *J* = 12.0, 2.0, H′–C(8)); 4.31 (*d*, *J* = 1.2, H–C(3)). ^{13}C-NMR (100 MHz, CD_3OD): see *Table 3*; additionally, – 0.21, 0.04 (2*q*, 2 Me_3Si). DCI-MS (MeOH): 359 (13), 358 (45, $[M+NH_4]^+$), 341 (6, $[M+1]^+$), 155 (12), 154 (13), 153 (11), 151 (11), 147 (13), 142 (10), 141 (25), 140 (11), 139 (22), 125 (33), 117 (11), 90 (27), 75 (32), 74 (38), 73 (100, Me_3Si^+). Anal. calc. for $C_{16}H_{28}O_4Si_2$ (340.57): C 56.43, H 8.29; found: C 56.25, H 8.06.

X-Ray Analysis of **31**[4]). Crystallization of **31** from AcOEt by slow evaporation of the solvent at ambient temp. gave crystals suitable for X-ray analysis: $C_{16}H_{28}O_4Si_2$ (340.56); monoclinic $P2_1$; $a = 9.049$ (2), $b = 16.152$ (5), $c = 14.076$ (3). $\beta = 93.59$ (5)°; $V = 2053.3$ (9) Å^3; $D_{calc.} = 1.102$ Mg/m^3; $Z = 4$. From a crystal of size 0.5 × 0.4 × 0.25 mm 4825 reflexions were measured on an *Enraf-Nonius CAD-4* Diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71069$ Å) at 173 K. $R = 0.1388$, $R_w = 0.3152$. Part of the structure was solved by direct methods with SHELXS-97, the remaining non-H-atoms were found from a difference *Fourier* map. There are two symmetrically independent molecules in the cell. The non-H-atoms were refined anisotropically with SHELXL-97. Disordered Me groups were refined isotropically at two positions with occupancy 50%. H-Atoms were calculated at idealised positions and included in the structure factor calculation with fixed isotropic displacement parameters.

3,7-Anhydro-1,2,6-trideoxy-6-ethynyl-D-glycero-D-galacto-*oct-1-ynitol* (**32**). A soln. of **31** (60 mg, 0.176 mmol) in MeOH (6.0 ml) was treated with NaOMe (32 mg), stirred for 1 h, and treated with phenolphthalein (2 mg) and NH_4Cl until disappearance of the pink colour. After evaporation at 40°/12 mbar, the solid residue was suspended in boiling AcOEt (5.0 ml) and filtered (washing of the filter cake with 2.0 ml of hot AcOEt) The filtrate was warmed to 30° and diluted with pentane (7.0 ml). Crystallization at – 10° gave **32** (34 mg, 99%). White solid. R_f (AcOEt) 0.25. M.p. 160–161° (dec.). IR (KBr): 3522*s*, 3465*s*, 3361*s*, 3268*s*, 3249*s*, 3217*s*, 2948*w*, 2919*w*, 2856*w*, 2128*w*, 1484*w*, 1406*w*, 1359*m*, 1337*w*, 1316*w*, 1256*w*, 1181*w*, 1141*m*, 1102*m*, 1077*m*, 1050*m*, 1026*m*, 916*m*, 888*w*, 845*m*. ^{1}H-NMR (500 MHz, CD_3OD): 2.49 (*d*, *J* = 2.4, irrad. at 2.68 → *s*, HC≡C–C(6)); 2.68 (br. *td*, *J* = 10.6, 2.3, H–C(6)); 2.88 (*d*, *J* = 2.3, irrad. at 4.32 → *s*, H–C(1)); 3.40 (*ddd*, *J* = 10.4, 5.6, 2.0, irrad. at 2.68 → *dd*, *J* = 5.7, 1.8, H–C(7)); 3.63 (*dd*, *J* = 10.7, 3.0, irrad. at 2.68 → *d*, *J* = 3.0, H–C(5)); 3.72 (*dd*, *J* = 12.0, 5.6, H–C(8)); 3.78 (*ddd*, *J* = 3.0, 1.1, 0.5, irrad. at 2.68 → *dd*, *J* = 3.0, 1.1, H–C(4)); 3.90 (*dd*, *J* = 12.0, 2.0, H′–C(8)); 4.32 (*dd*, *J* = 2.3, 1.2, irrad. at 2.88 → *d*, *J* = 1.2, H–C(3)). ^{13}C-NMR (125 MHz, CD_3OD): see *Table 3*. DCI-MS (MeOH): 214 (9, $[M+NH_4]^+$), 197 (6, $[M+1]^+$), 147 (12), 124 (14), 119 (15), 111 (25), 110 (37), 108 (36), 95 (33), 92 (11), 91 (27), 82 (28), 81 (60), 77 (21), 69 (23), 68 (89), 65 (21), 55 (30), 54 (18), 53 (43), 52 (19), 44 (26), 43 (43), 41 (31), 40 (38), 39 (100). Anal. calc. for $C_{20}H_{12}O_4$ (196.20): C 61.22, H 6.16; found: C 61.28, H 6.23.

*4,8-Anhydro-1,2,3,7-tetradeoxy-1-(trimethylsilyl)-7-[2-(trimethylsilyl)ethynyl]-3-{(*E*)-(trimethylsilyl)[1-*^{2}*H]methylidene}*-D-glycero-D-galacto-*non-1-ynitol* (**33**). Conversion of **31** (68 mg, 0.20 mmol) under conditions (80–85° for 15 h) similar to those used for the alkynylating acetal opening of **27**, addn. of D_2O (3.0 ml) prior to the addn. of ice, workup, and FC (30 g, CH_2Cl_2/AcOEt 5:1 → 10:3) gave **33** (54 mg, 61%) and **31** (10 mg, 15%). Slightly yellow solid. R_f (CH_2Cl_2/AcOEt 2:1) 0.68. IR (CDCl3): 3585*w*, 3450*w* (br.), 3009*w*, 2962*m*, 2900*w*, 2173*w*, 2148*w*, 1569*w*, 1407*w*, 1141*w*, 1102*m*, 1048*m*, 928*w*, 870*s*, 848*s*. ^{1}H-NMR (300 MHz, CD_3OD): 0.14, 0.18 0.185, (3*s*, 3 Me_3Si); 2.70 (*t*, *J* = 10.6, H–C(7)); 3.43 (*ddd*, *J* = 10.3, 5.3, 1.9, H–C(8)); 3.65 (*dd*, *J* = 10.6, 3.1, H–C(6)); 3.78 (*dd*, *J* = 11.8, 5.3, H–C(9)); 3.90 (*d*, *J* = 1.3, H–C(4)); 3.94 (*dd*, *J* = 11.9, 1.9, H′–C(9)); 4.89 (br. *d*, *J* = 2.8, H–C(5)). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 3*; additionally, – 0.77, – 0.18, 0.15 (3*q*, 3 Me_3Si). DCI-MS (MeOH): 457 (1, $[M+NH_4]^+$), 440 (3.5, $[M+1]^+$), 238 (17), 147 (13), 75 (37), 74 (32), 73 (100, Me_3Si^+).

*3,7-Anhydro-1,2,6-trideoxy-4-*O*-(trifluoromethylsulfonyl)-5,8-bis-*O*-(triisopropylsilyl)-1-(trimethylsilyl)-6-[2-(trimethylsilyl)ethynyl]*-D-glycero-D-galacto-*oct-1-ynitol* (**34**). A soln. of **31** (341 mg, 1.0 mmol) in CH_2Cl_2/pyridine 5:1 (24.0 ml) was cooled to – 17°, treated dropwise with TIPSOTf (609 µl, 2.2 mmol), stirred for

40 min, warmed to 22°, stirred for 10 min, cooled to −17°, treated dropwise with Tf_2O (168 µl, 4.0 mmol), warmed to 22°, and stirred for 19 h. The soln. was diluted with Et_2O (100 ml), washed with H_2O (10 ml), 2N HCl (3 × 10 ml), and brine (3 × 10 ml), dried ($MgSO_4$), and evaporated at 22°/12 mbar. FC (50 g, hexane/AcOEt 40:1 → 30:1) of the yellow oil (1.05 g) gave slightly impure **34** (751 mg, *ca.* 96%). Colourless oil. R_f (hexane/AcOEt 20:1) 0.49. IR ($CHCl_3$): 2946*s*, 2868*s*, 2175*w*, 1446*m*, 1410*s*, 1141*s*, 1101*m*, 1088*m*, 939*s*, 884*s*, 862*s*, 845*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.12, 0.16 (2*s*, 2 Me_3Si); 1.03–1.37 (*m*, 2 $(Me_2CH)_3Si$); 3.06 (*t*, *J* = 10.3, H−C(6)); 3.40 (*ddd*, *J* = 10.3, 4.0, 1.9, H−C(7)); 3.995 (*dd*, *J* = 11.2, 4.0, H−C(8)); 4.04 (*dd*, *J* = 10.3, 2.2, H−C(5)); 4.05 (*dd*, *J* = 11.2, 1.9, H′−C(8)); 4.30 (br. *s*, H−C(3)); 5.00 (br. *d*, *J* = 2.5, H−C(4)). ^{13}C-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, −0.64, −0.38 (2*q*, 2 Me_3Si); 12.04, 13.19 (2*d*, 2 $(Me_2CH)_3Si$); 17.84, 17.87, 18.32 (3*q*, 2 $(Me_2CH)_3Si$); *q* of CF_3 hidden by noise. ^{19}F-NMR (70 MHz, $CDCl_3$): −73.63. ESI-MS (MeOH): 809 (26), 808 (56), 807 (100, $[M+Na]^+$).

Treatment of **34** *with* NaN_3. A soln. of **34** (40 mg, 51 µmol) in DMF (2.0 ml, freshly distilled from CaH_2) was was cooled to 0°, treated with NaN_3 (33 mg, 0.51 mmol), and stirred for 2 h. After the addition of Et_2O (10 ml), the org. layer was washed with H_2O (3 × 1 ml), dried ($MgSO_4$), and evaporated at 22°/12 mbar. FC (4 g, hexane/AcOEt 30:1) of the colourless oil (38 mg) followed by an additional FC (5 g, hexane/toluene 20:3), gave **35** (9 mg, 29%) and **36** (24 mg, 70%).

*3,7-Anhydro-1,2,4,6-tetradeoxy-6-[2-(trimethylsilyl)ethynyl]-5,8-bis-*O*-(triisopropylsilyl)-1-(trimethylsilyl)-*D-arabino-*oct-3-en-1-ynitol* (**35**). Colourless oil. R_f (hexane/toluene 10:3) 0.52. IR (neat): 2944*s*, 2900*m*, 2868*s*, 2168*w*, 1637*m*, 1464*m*, 1384*w*, 1365*w*, 1334*m*, 1250*s*, 1184*m*, 1152*m*, 1096*m*, 1065*m*, 1014*m*, 960*m*, 882*m*, 844*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.10, 0.19 (2*s*, 2 Me_3Si); 1.05–1.28 (*m*, 2 $(Me_2CH)_3Si$); 2.81 (*dd*, *J* = 10.0, 8.4, irrad. at 4.55 → *d*, *J* = 10.0, H−C(6)); 3.92 (*ddd*, *J* = 10.0, 4.1, 2.5, H−C(7)); 4.04 (*dd*, *J* = 10.9, 4.3, H−C(8)); 4.08 (*dd*, *J* = 11.2, 2.8, H′−C(8)); 4.55 (*dd*, *J* = 8.4, 2.5, irrad. at 5.14 → *d*, *J* = 8.4, H−C(5)); 5.14 (*d*, *J* = 2.5, irrad. at 4.55 → *s*, H−C(4)). ^{13}C-NMR ($CDCl_3$, 75 MHz): see *Table 3*; additionally, −0.36, −0.20 (2*q*, 2 Me_3Si); 12.08, 12.63 (2*d*, 2 $(Me_2CH)_3Si$); 17.98, 18.24 (2*q*, 2 $(Me_2CH)_3Si$). ESI-MS (MeOH): 673 (7, $[M+K]^+$), 659 (28), 658 (55), 657 (100, $[M+Na]^+$).

*3,7-Anhydro-4-azido-1,2,4,6-tetradeoxy-6-[2-(trimethylsilyl)ethynyl]-5,8-bis-*O*-(triisopropylsilyl)-1-(trimethylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**36**). Colourless oil. R_f (hexane/toluene 10:3) 0.47. IR (neat): 2943*s*, 2890*s*, 2867*s*, 2213*w*, 2179*m*, 2111*s*, 1464*s*, 1384*m*, 1366*m*, 1338*m*, 1293*m*, 1251*s*, 1225*w*, 1152*s*, 1130*s*, 1115*s*, 1089*s*, 1050*m*, 1035*m*, 1016*s*, 998*m*, 947*m*, 918*m*, 883*s*, 846*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.10, 0.18 (2*s*, 2 Me_3Si); 1.04–1.30 (*m*, 2 $(Me_2CH)_3Si$); 2.62 (*t*, *J* ≈ 10.3, H−C(6)); 3.23 (*dd*, *J* = 10.0, 9.0, H−C(4)); 3.33 (*ddd*, *J* = 10.6, 5.0, 1.6, H−C(7)); 3.53 (*dd*, *J* = 9.7, 9.0, H−C(5)); 3.88 (*d*, *J* = 10.0, H−C(3)); 3.89 (*dd*, *J* = 11.2, 5.0, H−C(8)); 4.05 (*dd*, *J* = 11.2, 1.6, H′−C(8)). ^{13}C-NMR ($CDCl_3$, 75 MHz): see *Table 3*; additionally, −0.46, −0.33 (2*q*, 2 Me_3Si); 12.06, 13.21 (2*d*, 2 $(Me_2CH)_3Si$); 17.97, 18.31, 18.37 (3*q*, 2 $(Me_2CH)_3Si$). ESI-MS (MeOH): 716 (6, $[M+K]^+$), 702 (31), 701 (56), 700 ($[M+Na]^+$). Anal. calc. for $C_{34}H_{67}N_3O_3Si_4$ (678.26): C 60.21, H 9.96, N 6.20; found: C 60.40, H 9.93, N 6.04.

*4-Acetamido-3,7-anhydro-1,2,4,6-tetradeoxy-6-[2-(trimethylsilyl)ethynyl]-5,8-bis-*O*-(triisopropylsilyl)-1-(trimethylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**37**). A soln. of **36** (90 mg, 0.133 mol) in THF/Ac_2O/AcOH 3:2:1 (10 ml) was treated with Zn powder (200 mg) and $CuSO_4 \cdot 5\,H_2O$ (4 mg), stirred at 22° for 2 h, and filtered over *Celite* (1 × 2 cm, washing with 5.0 ml of THF). The filtrate was evaporated at 50°/12 mbar. A suspension of the residue in pentane/AcOEt 1:1 (2 ml) was filtered and the filtrate evaporated. FC (11 g, pentane/AcOEt 10:1) gave **37** (42 mg, 60%). White solid. R_f (hexane/toluene 10:3) 0.52. M.p. 167–168°. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.10, 0.14 (2*s*, 2 Me_3Si); 1.03–1.28 (*m*, 2 $(Me_2CH)_3Si$); 1.95 (*s*, AcN); 2.63 (*t*, *J* ≈ 10.3, H−C(6)); 3.39 (br. *q*, *J* ≈ 9.6, addn. of D_2O → *t*, *J* ≈ 10.0, H−C(4)); 3.42 (*ddd*, *J* = 10.6, 4.7, 1.7, H−C(7)); 3.90 (*dd*, *J* = 10.9, 4.7, H−C(8)); 4.05 (*dd*, *J* = 10.9, 1.6, H′−C(8)); 4.15 (*t*, *J* = 9.3, H−C(5)); 4.42 (*d*, *J* = 10.3, H−C(3)); 5.44 (*d*, *J* = 8.4, exchange with D_2O, NH). ^{13}C-NMR ($CDCl_3$, 75 MHz): see *Table 3*; additionally, −0.33 (br. *q*, 2 Me_3Si); 12.05, 13.41 (2*d*, 2 $(Me_2CH)_3Si$); 17.95, 18.33, 18.43 (3*q*, 2 $(Me_2CH)_3Si$); 23.70 (*q*, Me); 169.73 (*s*, C=O). ESI-MS (MeOH): 732 (12, $[M+K]^+$), 719 (20), 718 (43), 717 (82), 716 (100, $[M+Na]^+$), 694 (12, $[M+1]^+$). Anal. calc. for $C_{36}H_{71}NO_4Si_4$ (694.30): C 62.28, H 10.31, N 2.02; found: C 62.36, H 10.20, N 2.14.

*4-Acetamido-3,7-anhydro-1,2,4,6-tetradeoxy-6-ethynyl-*D-glycero-D-gulo-*oct-1-ynitol* (**38**). A soln. of **37** (70 mg, 0.101 mmol) in THF (4.0 ml) was treated with TBAF on silica gel (91 mg, 1.1 mmol F^-/g), stirred at 22° for 20 h, treated with a further portion of TBAF on silica gel (91 mg, 1.1 mmol F^-/g), stirred at 22° for 2 h and at 50–60° for 2 h, and filtered over *Celite* (1 × 0.5 cm, washing with 2 ml of THF). Evaporation at 22°/12 mbar and FC (11 g, AcOEt/MeOH 10:1) gave **38** (19 mg, 79%). White solid. R_f (AcOEt/MeOH 10:1) 0.30. M.p. 174–176°. IR (KBr): 3478*s*, 3416*s*, 3270*s*, 3244*s*, 3099*m*, 2956*m*, 2860*m*, 2123*w*, 1649*s*, 1562*s*, 1462*m*, 1430*m*, 1377*m*, 1360*w*, 1317*m*, 1298*m*, 1261*m*, 1126*s*, 1115*w*, 1074*s*, 1050*s*, 1031*s*, 1001*s*, 966*w*, 948*w*, 905*w*. ^{1}H-NMR (CD_3OD, 500 MHz): 1.98 (*s*, AcN); 2.50 (*td*, *J* = 10.3, 2.3, H−C(6)); 2.56 (*d*, *J* = 2.3, HC≡C−C(6)); 2.82 (*d*, *J* = 2.2,

H–C(1)); 3.43 (*ddd*, *J* = 10.4, 5.5, 2.0, H–C(7)); 3.55 (*t*, *J* = 10.1, H–C(4)); 3.714 (*dd*, *J* = 12.1, 5.5, H–C(8)); 3.722 (*t*, *J* = 10.1, H–C(5)); 3.90 (*dd*, *J* = 12.1, 2.0, H′–C(8)); 4.14 (*dd*, *J* = 10.3, 2.2, H–C(3)). ^{13}C-NMR (CD_3OD, 125 MHz): see *Table 3*; additionally, 22.99 (*q*, Me); 173.76 (*s*, C=O).

2,6-Anhydro-5-azido-3,5,7,8-tetradeoxy-3-ethynyl-1,4-bis-O-*(triisopropylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**40**). A soln. of **39** [6] (100 mg, 0.51 mmol) in pyridine (10.0 ml) was cooled to −16°, treated with TIPSOTf (297 µl, 1.07 mmol), stirred for 2 h, treated with Tf_2O (429 µl, 2.55 mmol), stirred at 23° for 3 h, and treated with Et_2O (20 ml) and 2N HCl (→ pH 0). After extraction with Et_2O, the combined org. layers were dried ($MgSO_4$) and evaporated at 20°/12 mbar. The yellow oil (424 mg) was filtered over silica gel (20 g; cyclohexane/Et_2O 10:1). A soln. of the colourless oil (293 mg) in DMF (10.0 ml) was treated with NaN_3 (143 mg, 2.20 mmol), stirred at 80–90° for 40 min, cooled to r.t., and treated with H_2O (20 ml). After extraction with Et_2O, the org. layer was dried ($MgSO_4$) and evaporated at 23°/12 mbar. FC (20 g, cyclohexane/Et_2O 20:1) gave **40** (155 mg, 57%). White solid. R_f (cyclohexane/Et_2O 30:1) 0.37. M.p. 62–63°. IR (neat): 3310*m*, 2944*s*, 2887*s*, 2200*w*, 2107*s*, 1464*m*, 1384*w*, 1268*m*, 1146*s*, 1084*m*, 1016*m*, 919*w*, 883*s*, 820*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.02–1.32 (*m*, 2 $(Me_2CH)_3Si$); 2.13 (*d*, *J* = 2.3, HC≡C–C(3)); 2.59 (*d*, *J* = 2.2, H–C(8)); 2.65 (*td*, *J* ≈ 10.0, 2.2, irrad. at 2.13 → *t*, *J* ≈ 10.1, H–C(3)); 3.34 (*dd*, *J* = 9.7, 5.3, H–C(5)); 3.95 (*dt*, *J* = 10.6, 3.0, H–C(2)); 3.99 (*d*, *J* = 3.1, 2 H–C(1)); 4.06 (*t*, *J* = 9.8, H–C(4)); 4.88 (*dd*, *J* = 5.6, 2.2, irrad. at 2.59 → *d*, *J* = 5.3, H–C(6)). ^{13}C-NMR ($CDCl_3$, 75 MHz): see *Table 3*, additionally, 11.93, 13.33 (2*d*, 2 $(Me_2CH)_3Si$); 17.84, 18.21 (2*q*, 2 $(Me_2CH)_3Si$). ESI-MS (MeOH): 556 (100, $[M+Na]^+$), 557 (44), 558 (16), 572 (10, $[M+K]^+$). Anal. calc. for $C_{28}H_{51}N_3O_3Si_2$ (533.90): C 62.99, H 9.63, N 7.87; found: C 63.03, H 9.53, N 7.67.

5-Acetamido-2,6-anhydro-3,5,7,8-tetradeoxy-3-ethynyl-1,4-bis-O-*(triisopropylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**41**). A soln. of **40** (1.60 g, 3.0 mmol) in THF (25 ml) was treated with PPh_3 (1.34 g, recryst. from hexane), stirred at 55° for 2.5 h, treated with MeOH (50 ml), stirred at 55° for 3 h, cooled to r. t., and evaporated at 23°/14 mbar. A soln. of the residue in toluene was filtered over silica gel (60 g, toluene/MeOH 30:1). The resulting solid (1.28 g) was dissolved in pyridine (100 ml), treated with Ac_2O, and stirred at 23° for 30 min. After evaporation at 35°/12 mbar, a soln. of the residue in Et_2O (250 ml) was washed with brine (3 × 20 ml), dried($MgSO_4$), and evaporated. Filtration over silica gel (20 g, toluene/MeOH 20:1) and crystallisation from cyclohexane gave **41** (1.37 g, 83%). White solid. R_f (toluene/MeOH 30:1) 0.31. M.p. 147–148°. IR ($CHCl_3$): 3438*w*, 3306*s*, 3010*s*, 2945*s*, 2867*s*, 2116*w*, 1679*s*, 1510*s*, 1464*m*, 1370*m*, 1270*m*, 1148*s*, 1110*m*, 1086*m*, 1062*m*, 1035*w*, 1013*m*, 998*m*, 962*w*, 909*s*, 884*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.03–1.31 (*m*, 2 $(Me_2CH)_3Si$); 2.00 (*s*, AcN); 2.13 (*d*, *J* = 2.2, HC≡C–C(3)); 2.53 (*d*, *J* = 2.2, H–C(8)); 2.70 (*td*, *J* ≈ 9.0, 2.2, H–C(3)); 3.94 (*dt*, *J* = 9.6, 3.3, H–C(2)); 3.995 (*d*, *J* = 3.4, 2 H–C(1)); 4.008 (*td*, *J* ≈ 9.0, 5.0, addn. of D_2O → *dd*, *J* ≈ 9.0, 5.0, H–C(5)); 4.09 (*t*, *J* = 8.9, H–C(4)); 4.86 (*dd*, *J* = 5.0, 2.2, H–C(6)); 5.48 (br. *d*, *J* = 8.7, exchange with D_2O, NH). ^{13}C-NMR ($CDCl_3$, 75 MHz): see *Table 3*; additionally, 11.89, 13.32 (2*d*, 2 $(Me_2CH)_3Si$); 17.83, 18.24 (2*q*, 2 $(Me_2CH)_3Si$); 23.35 (*q*, Me); 169.76 (*q*, C=O). FAB-MS: 551 (16), 550 (36, $[M+1]^+$), 508 (22), 507 (45), 506 (100, $[M-iPr]^+$). Anal. calc. for $C_{30}H_{55}NO_4Si_2$ (549.94): C 65.52, H 10.08, N 2.55; found: C 65.40, H 10.15, N 2.68.

5-Acetamido-2,6-anhydro-3,5,7,8-tetradeoxy-3-ethynyl-D-glycero-L-gulo-*oct-7-ynitol* (**42**). A soln. of **41** (80 mg, 0.145 mmol) in THF (5.0 ml) was treated with TBAF on silica gel (396 mg, 1.1 mmol F^-/g), stirred at 23° for 14 h, warmed to 50°, treated with an additional portion of TBAF on silica gel (396 mg, 1.1 mmol F^-/g), and stirred for 4 h. After filtration of the suspension and washing of the filter cake with MeOH (5.0 ml), the combined filtrate and washing were evaporated at 22°/15 mbar. FC (20 g, AcOEt/MeOH 10:1) of the brown oil (261 mg) gave **42** (31 mg, 90%). White solid. R_f (AcOEt/MeOH 10:1) 0.28. M.p. 154–155°. IR (KBr): 3539*s*, 3477*s*, 3415*s*, 2944*w*, 2113*w*, 1631*m*, 1621*m*, 1549*w*, 1472*m*, 1426*w*, 1385*w*, 1127*w*, 1076*w*, 1030*w*. ^{1}H-NMR (CD_3OD, 500 MHz): 1.99 (*s*, AcN); 2.51 (*ddd*, *J* ≈ 10.7, 9.5, 2.4, H–C(3)); 2.58 (*d*, *J* = 2.4, HC≡C–C(3)); 3.07 (*d*, *J* = 2.3, H–C(8)); 3.75 (*dd*, *J* = 12.1, 5.0, H–C(1)); 3.80 (*dd*, *J* = 10.5, 5.3, H–C(5)); 3.83 (*dd*, *J* = 10.7, 9.6, H–C(4)); 3.85 (*dd*, *J* = 12.1, 2.1, H′–C(1)); 3.93 (*ddd*, *J* = 10.6, 5.0, 2.1, H–C(2)); 4.88 (*dd*, *J* = 5.0, 2.3, irrad. at 3.07 → *d*, *J* = 5.0, H–C(6)). ^{13}C-NMR (CD_3OD): see *Table 3*; additionally, 22.54 (*q*, Me); 173.90 (*s*, C=O). HR-ESI-MS: 238.1085 ($C_{10}H_{13}NO_3$, $[M+1]^+$; calc. 238.1079).

5-Acetamido-2,6-anhydro-3,5,7,8-tetradeoxy-3-ethynyl-1-O-*(triisopropylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**43**). A soln. of **42** (1.80 g, 7.59 mmol) in pyridine (100 ml) was cooled to −15°, treated with TIPSOTf (2.31 ml, 8.36 mmol), stirred for 30 min, treated with MeOH (3.0 ml), warmed to 23°, and evaporated at 40°/12 mbar. A soln. of the residue in AcOEt/Et_2O 1:1 (1.0 l) was washed with H_2O (3 × 10 ml), dried ($MgSO_4$), and evaporated at 30°/12 mbar. Filtration over silica gel (AcOEt/MeOH) and crystallization from AcOEt gave **43** (2.60 g, 87%). Slightly yellow solid. R_f (AcOEt) 0.23. M.p. 225–226°. IR ($CHCl_3$): 3589*w*, 3422*w*, 3305*m*, 3032*s*, 2945*m*, 2867*m*, 1674*m*, 1512*s*, 1467*w*, 1422*w*, 1375*w*, 1150*m*, 1117*w*, 1090*m*, 1011*w*, 930*m*, 884*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.03–1.16 (*m*, $(Me_2CH)_3Si$); 2.07 (*s*, AcN); 2.23 (*d*, *J* = 2.4, HC≡C–C (3)); 2.60 (*d*, *J* = 2.3, H–C(8)); 2.73 (*td*, *J* = 10.3, 2.4, H–C(3)); 2.90 (br. *d*, *J* = 4.3, exchange with D_2O, HO–C(4)); 3.83 (br. *td*, *J* =

10.3, 4.1, addn. of $D_2O \rightarrow t$, $J = 10.3$, H–C(4)); 3.91 (*dt*, $J = 10.3, 2.9$, H–C(2)); 4.00 (*d*, $J = 3.0$, 2 H–C(1)); 4.03 (*ddd*, $J = 10.3, 8.1, 5.6$, H–C(5)); 4.91 (*dd*, $J = 5.6, 2.3$, H–C(6)); 5.69 (br. *d*, $J = 8.1$, slow exchange with D_2O, NH). ^{13}C-NMR ($CDCl_3$, 100 MHz): see *Table 3*; additionally, 12.00 (*d*, $(Me_2CH)_3Si$); 17.97 (*q*, $(Me_2CH)_3Si$); 23.42 (*q*, Me); 171.32 (*q*, C=O). ESI-MS (MeOH/0.1% HCOOH): 453 (24), 448 (60), 432 (32, $([M+K]^+)$), 417 (32), 416 (100, $([M+Na]^+)$), 411 (32, $([M+NH_4]^+)$), 395 (32), 394 (97, $([M+1]^+)$). Anal. calc. for $C_{21}H_{35}NO_4Si$ (393.60): C 64.08, H 8.96, N 3.56; found: C 64.10, H 8.95, N 3.59.

*1,1′-(Buta-1,3-diyne-1,4-diyl)bis[(1*R*)-2-acetamido-1,5-anhydro-2,4-dideoxy-4-ethynyl-3,6-bis*-O-*(triisopropylsilyl)*-D-*glucitol]* (**44**). A soln. of **41** (80 mg, 0.145 mmol) in pyridine (10 ml) was treated with $Cu(OAc)_2$ (100 mg, 0.501 mmol), stirred for 2 d, diluted with Et_2O (100 ml), washed with H_2O (4 × 20 ml), dried ($MgSO_4$), and evaporated. FC (5 g, AcOEt) gave **44** (66 mg, 83%). Slightly yellow solid. R_f (hexane/AcOEt cyclohexane : AcOEt 4 : 3) 0.54. IR ($CHCl_3$): 3441*w*, 3307*m*, 3005*w*, 2946*s*, 2905*m*, 2868*s*, 1680*s*, 1508*s*, 1464*m*, 1369*m*, 1290*w*, 1148*s*, 1118*s*, 1082*s*, 1062*s*, 1014*m*, 1000*m*, 920*w*, 883*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.03–1.25 (*m*, 2 $(Me_2CH)_3Si$); 2.02 (*s*, AcN); 2.17 (*d*, $J = 2.2$, HC≡C–C(4)); 2.73 (*td*, $J = 8.7, 2.2$, H–C(4)); 3.91 (*ddd*, $J = 9.0, 4.4, 3.0$, H–C(5)); 3.96–4.08 (*m*, H–C(2), 2 H–C(6)); 4.06 (*t*, $J \approx 9.0$, H–C(3)); 5.01 (*d*, $J = 4.4$, H–C(1)); 5.48 (br. *d*, $J = 7.8$, NH). ^{13}C-NMR ($CDCl_3$, 75 MHz): see *Table 3*, additionally, 11.90, 13.26 (2*d*, 2 $(Me_2CH)_3Si$); 17.82, 18.19, 18.23 (3*q*, 2 $(Me_2CH)_3Si$); 23.37 (*q*, Me); 170.14 (*s*, C=O). MALDI-TOF-MS: 1098 (22, $[M+1]^+$), 1120 (100, $[M+Na]^+$), 1136 (35, $[M+K]^+$).

*3,3′-(Buta-1,3-diyne-1,4-diyl){2,6:11,15-dianhydro-14-*C*-[5-acetamido-2,6-anhydro-3,5,7,8,9,10-hexadeoxy-*D-glycero-L-gulo*-deca-7,9-diynitol-10-yl]-3,5,7,8,9,10,12,14-octadeoxy-*D-erythro-L-ido-L-gulo*-hexadeca-7,9-diynitol* (**45**). A soln. of **43** (395 mg, 1.0 mmol) in pyridine (1.0 l) was heated to 80°, treated with $Cu(OAc)_2$ (1.00 g, 5 mmol), stirred for 2 h, cooled to 20°, diluted with AcOEt (1.5 l) and Et_2O (1.5 l), and washed with H_2O (1.0 l). The aq. phase was extracted with Et_2O (3 × 100 ml). The combined org. layers were washed with brine (3 × 50 ml), dried ($MgSO_4$), and evaporated at 40°/12 mbar. Filtration over silica gel (70 g, AcOEt/MeOH 20 : 1) gave a brown foam (220 mg), which was dissolved in THF (30 ml), treated with TBAF · 3 H_2O (390 mg, 1.2 mmol), stirred for 4 h, treated with MeOH (5.0 ml), and stirred for 1 h. Evaporation at 23°/12 mbar and FC (70 g, AcOEt/H_2O/MeOH 10 : 3 : 2) of the red oil (660 mg) gave slightly impure (^{1}H-NMR) **45** (112 mg, *ca.* 48%). Crystallization from MeOH (3.0 ml) gave pure **45** (78 mg, 33%). White solid. R_f (AcOEt/MeOH/H_2O 5 : 3 : 2) 0.45. M.p > 250° (decomp.). IR (KBr): 3445*m* (br.), 3247*m*, 2943*m*, 2866*m*, 2116*w*, 1636*s*, 1555*m*, 1463*w*, 1379*w*, 1329*w*, 1315*w*, 1146*m*, 1092*s*, 1067*s*, 1008*w*, 996*w*, 948*w*, 885*m*. ^{1}H-NMR (D_2O, 500 MHz, assignment based on a DQFCOSY.GRASP spectrum): 2.04 (*s*, 2 AcN); 2.05 (*s*, AcN); 2.57 (*td*, $J \approx 10.3, 1.2$), 2.59 (*td*, $J \approx 10.3, 1.2$) (H–C(3), H–C(3′)); 2.74 (*td*, $J = 10.3, 1.3$, irrad. at 4.87 → *t*, $J = 10.3$, H–C(14)); 3.807 (*dd*, $J \approx 12.4, 5.2$), 3.831 (*dd*, $J \approx 12.0, 5.2$), 3.836 (*dd*, $J = 12.6, 5.2$) (H–C(1), H–C(16), H–C(1′)); 3.890 (*dd*, $J = 10.5, 5.2$, H–C(5′)); 3.885–3.96 (*m*, H–C(5), H–C(12), H′–C(1), H′–C(16), H′–C(1′)); 4.054 (br. *t*, $J \approx 10.3$, H–C(4), H–C(4′); 4.067 (*t*, $J = 10.3$, H–C(13)); 4.13–4.18 (*m*, H–C(2), H–C(15), H–C(2′); 4.87 (*dd*, $J = 5.2, 1.2$, irrad. at 2.74 → *d*, $J = 5.2$, H–C(6′)); 5.01 (*dd*, $J = 5.4, 1.2$, H–C(6)); 5.06 (*dd*, $J = 5.5, 1.2$, H–C(11)); irrad. at 2.58 → no change of the signals for H–C(6), H–C(11), and H–C(6′); irrad. at 5.01 or 5.06 → no change of the signals for H–C(3), H–C(14), and H–C(3′). ^{13}C-NMR (D_2O, 125 MHz assignment based on a HSQC.GRASP spectrum): see *Table 2*; additionally, 24.57 (*q*, Me); 24.59 (*q*, 2 Me); 40.61, 40.82 (2*d*, C(3), C(3′)); 40.95 (*d*, C(14)); 55.51 (*d* C(5′)); 55.69 (*d*, C(5), C(12)); 64.61 (*t*, C(1), C(1′)); 64.64 (*t*, C(16)); 69.83 (*d*, C(6), C(11), C(6′)); 72.18, 72.63, 73.03 (3*d*, C(4), C(13), C(4′)); 77.48 (*d*, C(15)); 77.85 (*d*, C(2), C(2′)); 177.41 (*s*, 3 C=O). HR-FAB-MS: 706.2619 ($[M+1]^+$; calc. 706.2612). Anal. calc. for $C_{36}H_{39}N_3O_{12} \cdot 2\,H_2O$ (741.76): C 58.29, H 5.84, N 5.66; found: C 58.69, H 5.92, N 5.71.

*3,3′-(Buta-1,3-diyne-1,4-diyl){2,6 : 11,15-dianhydro-14-*C*-[2,6-anhydro-3,7,8,9,10-pentadeoxy-*D-glycero-L-gulo*-deca-7,9-diynitol-10-yl]-3,7,8,9,10,14-hexadeoxy-*D-erythro-L-ido-L-gulo*-hexadeca-7,9-diynitol* (**46**). See [11]. ^{13}C-NMR (D_2O, 125 MHz): see *Table 2*; additionally, 40.10, 40.17, 40.41 (3*d*, C(3), C(14), C(3′)); 64.56 (*t*, C(1), C(1′)); 64.64 (*t*, C(16)); 71.52 (*d*, C(6′)); 71.56 (*d*, C(6), C(11)); 72.92 (*d*, C(5′)); 73.03 (*d*, C(5), C(12)); 74.49, 75.15, 75.46 (3*d*, C(4), C(13) C(4′)); 77.33 (*d*, C(15)); 77.74 (*d*, C(2), C(2′)).

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