Oligosaccharide Analogues of Polysaccharides

Part 15

Oligomers of Cellobiose-Derived Dialkynes and First Crystal Structure of an Anomeric Pair of Trichloroacetimidates[1])

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Dedicated to the Memory of *Steffen Vorwerk*

The cellobiose-derived dimer **18**, tetramer **48**, and octamer **49** have been prepared. Acetolytic debenzylation transformed the dimer **15**, obtained from the partially benzylated, dialkynylated cellobiose **2** (*Scheme 1*), into **16** that was deacetylated to **18** (*Scheme 2*), but the analogous debenzylation of the tetramer **14** proved unsatisfactory. We, therefore, avoided benzyl groups and prepared the cellobiose-derived monomer **32** by glycosidation of **27** with the crystalline trichloroacetimidates **30** or **31** (*Scheme 3*). The acceptor **27** was synthesised from 1,6-anhydroglucose in 7 steps (48% overall yield), and the trichloroacetimidates **30** and **31** were obtained in good overall yields from the alkynylated glucopyranoses **29** (*Scheme 3*). The structure of the anomeric trichloroacetimidates **30** and **31** was determined by single crystal X-ray analysis. The alkyne **34**, orthogonally *C*-protected by $SiMe_3$ and $GeMe_3$ groups, was transformed by a binomial strategy into the dimer **37**, the tetramer **41**, and the octamer **47** (*Scheme 4*). The unprotected mono- and oligomers **1**, **18**, **48**, and **49** are soluble in H_2O, MeOH, and DMSO. Their ^{1}H-NMR specta ((D_6)DMSO (**1**, **18**, **48**, **49**), CD_3OD (**1**, **18**, **48**), D_2O (**49**)) show no signs of association.

Introduction. – We plan to assess the influence of H-bonds on the structure and properties of cellulose by comparing cellooligosaccharides with a series of 'acetyleno-oligosaccharides' obtained from glucose- and cellobiose-glycans, and from higher β-D-1,4-glycans. In these, all or some glycosidic O-atoms are replaced by a butadiynediyl unit [1]. We have prepared a series of glucose-derived oligomers (up to the octamer), where no intramolecular H-bonds between the pyranose residues are possible [2][3]. We have also prepared the cellobiose-derived dialkyne **1** (*Fig. 1*) [4], which still possesses the strong intramolecular C(5)–OH···O–C(5′) H-bond typical for cellobiose [5][6].

Analogues of the glucose- and the cellobiose-derived series thus possess either none or one intramolecular H-bond in the monomeric unit, and this difference is expected to

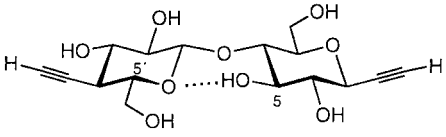

Fig. 1. *Structure of the deprotected monomer* **1** (adapted from [4]). The dotted line indicates the C(5′)–O··· HO–C(5) intramolecular H-bond.

[1]) Presented in part at the Royal Society of Chemistry Carbohydrate Group Spring Meeting, Birmingham, 1998, Abstract No. 9.

strongly affect the structure and properties of the analogues. Force-field calculations predict that the 'acetyleno-oligosaccharides' of the glucose-derived series possess a more or less linear, rigid-rod like shape [7]. Analogues of the cellobiose-derived series should possess several conformations of similar energy, depending on the relative orientation of the monomeric units [4] along the butadiynediyl moiety, and resulting in corrugated linear or helical shapes. ^{1}H-NMR studies of the deprotected oligomers of the glucose-derived series [2] showed no intermolecular association.

We now describe the binomial synthesis of higher oligomers derived from the partially benzylated cellobiose-derived dialkyne **2**, the problems encountered during acetolytic debenzylation of the tetramer **14**, and the synthesis of the mono-, di-, tetra-, and octamers using acetyl, 4-methoxybenzyl, and silyl instead of benzyl (Bn) protecting groups. For the preparation of the monomer, we glycosylated an ethynylated *β-C*-glucopyranoside by crystalline monoethynylated trichloroacetimidates, and report the crystal structure analysis of these trichloroacetimidates. We also report a comparison of physical properties of the deprotected oligomers with those of the glucose-derived analogues.

Results and Discussion. – The synthesis of the tetramer **14** started with the protodesilylation and bromodegermylation [3][4] of the orthogonally protected monomer **2** [4], yielding exclusively either the dialkyne **3** or the bromoalkyne **4**, respectively (*Scheme 1*). The bromoalkyne **4** was demethoxymethylated to **5** (HCl in THF, 92%) to ensure that the partners (**3** and **5**) for the *Cadiot-Chodkiewicz*-type cross coupling [8–11] differ sufficiently in polarity to facilitate the separation of the heterocoupled from the homocoupled products[2]). Cross coupling of **3** and **5** under the conditions developed in the glucose-derived series [3][11] gave 67% of the hetero-dimer **6**, easily separated by chromatography from the homocoupled **7** (2%) and **8** (2%). Continuing with the orthogonal deprotection/activation strategy, the dimer **6** was, on the one hand, fully desilylated to the mono-*C*-protected alkyne **9** (90%). On the other hand, **6** was acetylated and bromodegermylated to **10** (91%), again resulting in a sufficient difference in polarity of the coupling partners. Cross coupling of **9** and **10** as above yielded 60% of the tetramer **11** together with the homocoupled **12** (2%) and **13** (3%) (*Scheme 1*)[3]).

Acetolytic debenzylation is compatible with one glycosidic bond [15]; to check its compatibility with several glycosidic bonds, we examined the deprotection of the dimer **6** and of the tetramer **14** (*Scheme 2*). The dimer **6** was deprotected in three steps. Treatment with 1N aqueous HCl in MeOH at 40° removed both the methoxymethyl- (MOM) and the Me_3Ge groups to give 76% of the hexol **15**. Above 60°, one of the glycosidic bonds was selectively hydrolysed, as evidenced by the isolation of **17** after

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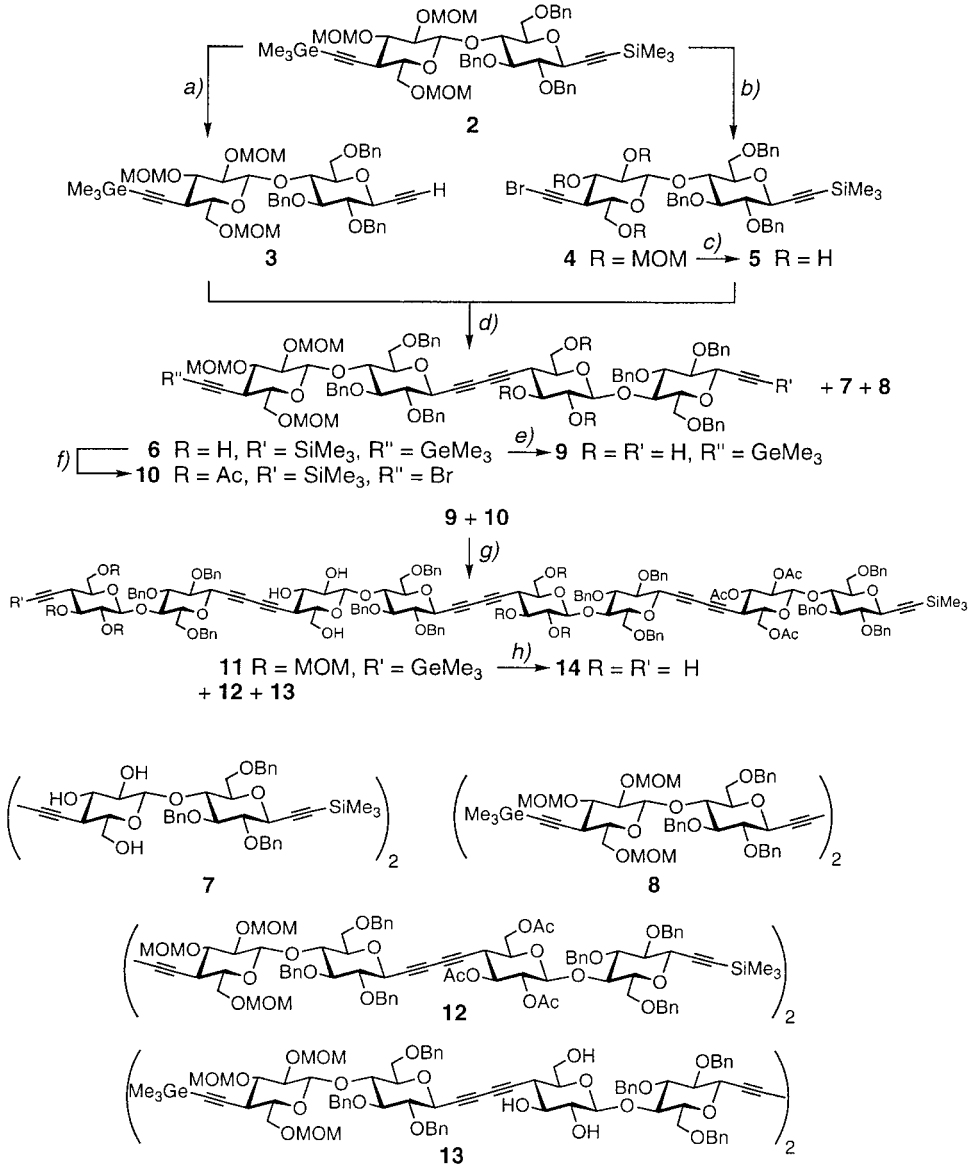
[2]) For a successful application of this strategy in the synthesis of cyclodextrin analogues, see [12–14].

[3]) Yields of the cross coupling are 20–25% below those for the benzylated glucose-derived oligomers, carrying *C*-DOPS and *C*-$GeMe_3$ groups [3]. TLC showed no evidence for the decomposition of **1** within 48 h under conditions of the cross coupling, but only 80–85% were recovered after chromatography. Besides the coupling products, polar fractions were obtained by silica-gel chromatography, consisting (^{1}H-NMR spectroscopy) of a mixture of unidentified, carbohydrate-derived compounds. The reasons for the different behaviour of glucose- and cellobiose-derived analogues have been analysed by *T. Bohner* (manuscript in preparation), and are related to the nature of the protecting groups.

Scheme 1

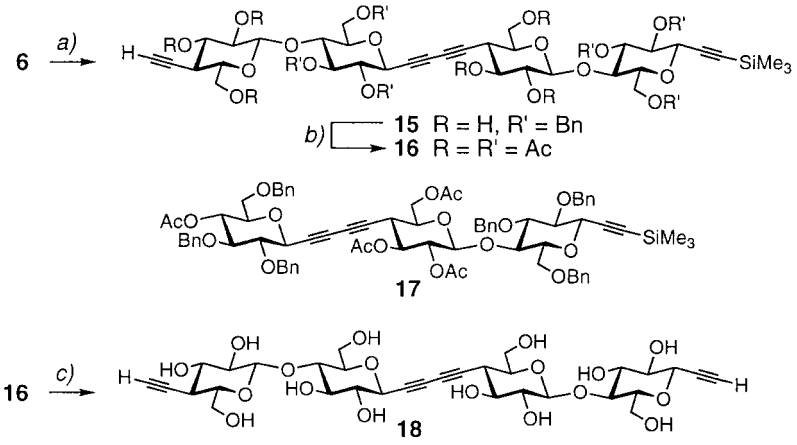


Ac = MeC(O), Bn = $PhCH_2$, MOM = $MeOCH_2$

a) K_2CO_3 in MeOH; 90% [4]. *b*) CuBr, NBS, acetone, 93% [4]. *c*) 1N HCl, THF; 92%. *d*) $[Pd_2(dba)_3]$/CuI (dba = dibenzylideneacetone), 1,2,2,6,6-pentamethylpiperidine, DMSO; **6** (67%), **7** (2%), **8** (2%). *e*) K_2CO_3 in MeOH/THF; 90%. *f*) 1. Ac_2O, pyridine; 2. NBS, CuBr, acetone; 91%. *g*) As *d*); **11** (60%), **12** (2%), **13** (3%). *h*) 1N HCl, THF; 74%.

acetylation of the crude. Acetolytic debenzylation of **15** proceeded best with Me_3SiOTf (10 mol-%) in Ac_2O yielding only 51% of the dodecaacetate **16**[4]). The fully deprotected dimer **18** was obtained in nearly quantitative yield by deacetylation of **16** (NaOMe in MeOH). This compound is readily soluble in H_2O, MeOH, and pyridine, but could not be crystallized.

Scheme 2



a) 1N HCl, THF; 76%. *b*) Ac_2O, Me_3SiOTf; 51%. *c*) NaOMe, MeOH, *Amberlite IR-120* (H^+); 95%.

All attempts to fully deprotect tetramer **11** failed. Acid-mediated protodegermylation and demethoxymethylation yielded 74% of **14** (*Scheme 1*), but the subsequent acetolysis using *Lewis* acids (such as Me_3SiOTf, $BF_3 \cdot OEt_2$, $FeCl_3$ [16], or ZnI_2) in Ac_2O at various temperatures and concentrations gave mixtures of partially debenzylated products together with unidentified polar material. Thus, we had to avoid Bn groups.

Cellobiose-derived dialkynes are most efficiently prepared by glycosidation of monoethynylated glycosyl acceptors with monoethynylated donors [4]. We required a synthesis of a glycosyl acceptor, and donor, devoid of BnO groups.

The glycosyl acceptor **27** was prepared from 1,6-anhydroglucose (**19**) (*Scheme 3*). Triethylsilylation [17] led to the 2,4-di-*O*-silyl ether **20** in 90% yield, besides 7% of the trisilyl ether **21**. Retentive ethynylating opening of the 1,3-dioxolane ring of **20** with lithium (trimethylsilyl)acetylide and freshly sublimed $AlCl_3$ in the presence of 1 equiv. of 2,4,6-trimethylpyridine gave the *C*-glucopyranoside **22**, which was purified by distillation and isolated in 68%. This modification of *Alzeer*'s method [1] constitutes the shortest and highest yielding way to ethynylated β-*C*-glucopyranosides[5]). The tetrol **23** was obtained in a nearly quantitative yield by acid-catalyzed desilylation.

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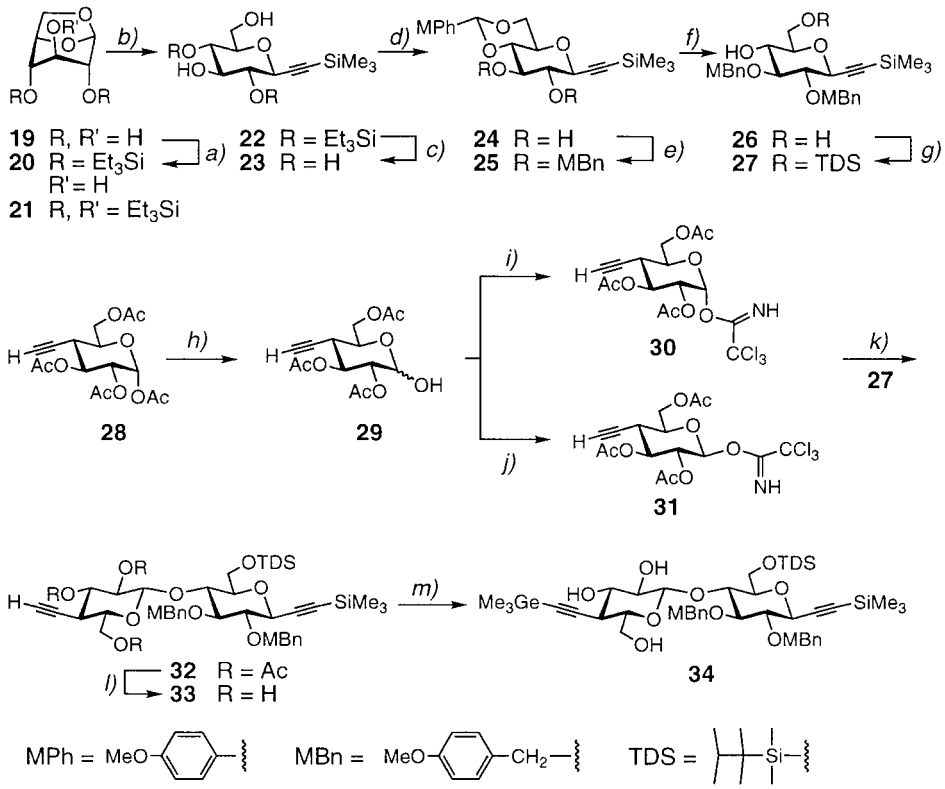
[4]) Only *ca.* 80% of the calculated mass balance of **16** was obtained after chromatography, including elution with MeOH. ^{1}H-NMR Data for the polar fractions evidence acetylated carbohydrate and aromatic residues.

[5]) Exploratory experiments indicate that aryl β-*C*-glucopyranosides are also available by this procedure.

Scheme 3



a) Et_3SiCl, 1*H*-imidazole, DMF; **20** (90%), **21** (7%). *b*) BuLi, HC≡CSiMe$_3$, $AlCl_3$, 2,4,6-trimethylpyridine, toluene; 68%. *c*) 0.1N HCl, THF/MeOH; 95%. *d*) 4-Methoxybenzaldehyde dimethyl acetal, TsOH · H_2O, DMF; 93%. *e*) 4-Methoxybenzyl trichloroacetimidate, TfOH, Et_2O; 82%. *f*) 80% AcOH; 99%. *g*) TDSCl, 1*H*-imidazole, DMF; 95%. *h*) H_2NNH_2 · HOAc, DMF; 93%. *i*) K_2CO_3, Cl_3CCN, CH_2Cl_2; 48 h; 85%. *j*) K_2CO_3, Cl_3CCN, CH_2Cl_2, 1.5 h; 70%. *k*) Me_3SiOTf, 4-Å mol. sieves, CH_2Cl_2; 90%. *l*) DIBAH, THF; 99%. *m*) 1. $(Me_3Si)_2NH$, Me_3SiCl, CH_2Cl_2; 2. LDA, Me_3GeCl, AcOH/THF/H_2O 1 : 1 : 1; 90%.

Transacetalization of **23** with anisaldehyde dimethyl acetal [18] yielded 93% of the crystalline **24** that was 4-methoxybenzylated (4-methoxybenzyl trichloroacetimidate, cat. TfOH [19]) to **25**. Hydrolysis of **25** (80% aq. AcOH [20]) gave **26** that was selectively *O*-silylated with (thexyl)(dimethyl)silyl chloride (= chlorodimethyl(1,1,2-trimethylpropyl)silane; TDSCl) [21]. This sequence yielded 84% of the glycosyl acceptor **27** from **24**.

The structure of **23** was established by X-ray analysis[6]) (*Fig. 2*). The intensities for **23** were recorded at 293 K ($R = 0.0442$). The pyranose ring adopts a $^4C_1$-conformation, as shown by the endocyclic torsion angles (*Table 1*). The *gg*-conformation of the CH_2OH group is characterized by the endocyclic torsion angles χ^1(O(7)–C(7)–

[6]) Coordinates and thermal parameters were deposited with the *Cambridge Crystallographic Data Center*, 12, Union Road, Cambridge CB2 1EZ, UK.

C(8)–O(8)) = –67.3(3)° and χ^2(C(6)–C(7)–C(8)–O(8)) = 53.0(4)°. The ethynyl substituent is nearly linear (C(1)–C(2)–C(3) bond angle = 177.0(4)°). All bond lengths are within standard values. Intermolecular H-bonds are found between O(6)···O(5′) (2.725(4) Å; $2-x, -0.5+y, 1-z$; O(6)–H···O(5′) = 1.84 Å), O(5′)···O(8″) (2.784(4) Å; $1+x,y,z$; O(5′)–H···O(8″) = 2.11 Å), and O(8″)···O(6′) (2.747(4) Å; $-1+x,y,z$; O(8″)–H···O(6′) = 1.79 Å) forming a two-dimensional network in the *a*,*b* plane and an infinite chain running along the *b* axis (*Fig. 2*). Thus, the cystal structure of **23** belongs to *Class I* according to the classification of H-bonding patterns in monosaccharides by *Jeffrey* and *Saenger* [22].

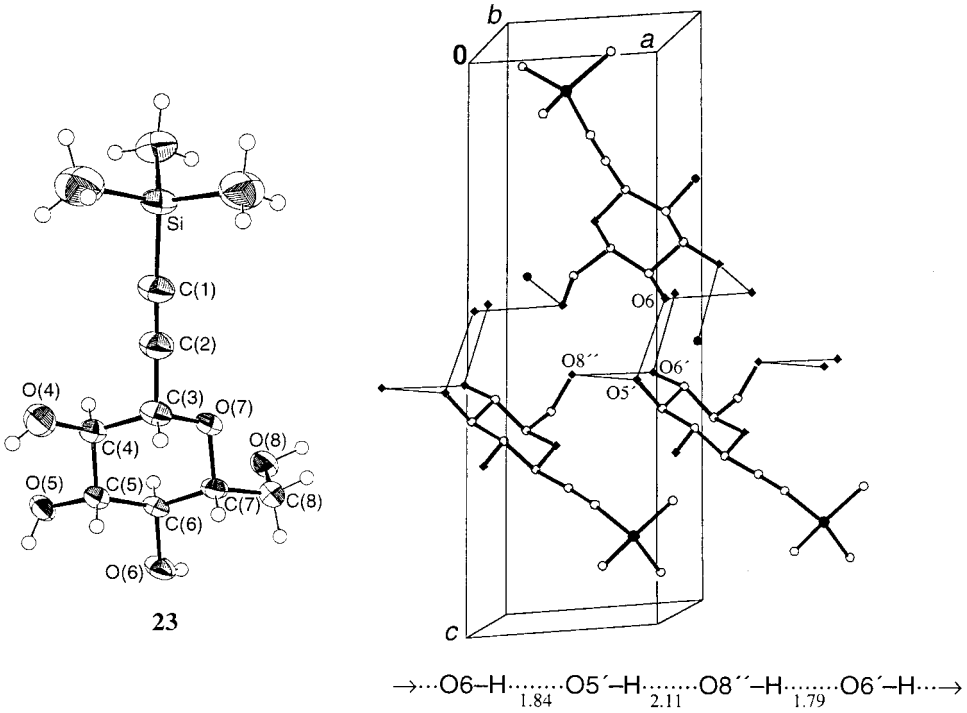


Fig. 2. *X-Ray crystal-structure analysis of the tetrol* **23**: *ORTEP* [36] *presentation* (ellipsoids enclose 50% of the electron density), *unit cell* (PLUTO [37]), *and H-bonding pattern*

Table 1. *Selected Torsion Angles* [°] *and Bond Lengths* [Å] *in* **23**. Standard deviations in parentheses.

Torsion Angle [°]		Bond Length [Å]	
χ^1(O(7)–C(7)–C(8)–O(8))	–67.3(3)	C(1)–C(2)	1.198(6)
χ^2(C(6)–C(7)–C(8)–O(8))	53.0(4)	C(2)–C(3)	1.466(5)
C(3)–C(4)–C(5)–C(6)	–53.4(4)	C(3)–C(4)	1.538(5)
C(4)–C(5)–C(6)–C(7)	55.0(4)	C(4)–C(5)	1.514(5)
C(5)–C(6)–C(7)–O(7)	–58.8(3)	C(5)–C(6)	1.520(4)
C(6)–C(7)–O(7)–C(3)	64.5(3)	C(6)–C(7)	1.531(4)
C(7)–O(7)–C(3)–C(4)	–63.7(4)	C(7)–C(8)	1.502(5)
O(7)–C(3)–C(4)–C(5)	57.1(4)	C(7)–O(7)	1.449(4)

Several Ac-protected ethynylated glucopyranosyl donors were examined for the glycosidation of **27**[7]). The best results were obtained with the glucopyranosyl trichloroacetimidates **30** and **31**. They were prepared from the known ethynylated acetate **28** [4] by selective deacetylation with hydrazinium acetate to **29** (93%, α-D/β-D 63:37) followed by base-catalyzed addition of Cl_3CCN under either thermodynamic or kinetic control, following *Schmidt*'s procedures [23]. Thus, treatment with Cl_3CCN in the presence of K_2CO_3 in CH_2Cl_2 for 48 h gave 85% of **30**/**31** (88:12), while the ratio **30**/**31** was 17:83 after a similar treatment for 1 h. The pure anomers **30** and **31** were obtained by recrystallization. Glycosidation of the acceptor **27** with either **30** or **31** in the presence of Me_3SiOTf in CH_2Cl_2 at $-10°$ led to the dialkyne **32** in 85–90% yield on a multigram scale. Deacetylation of **32** with diisobutylaluminium hydride (DIBAH) in THF [4] yielded 99% of **33**, and subsequent trimethylgermylation provided 90% of the orthogonally protected dialkyne **34** (*Scheme 3*).

Glycosyl trichloroacetimidates are presumably the most widely used class of glycosyl donors [24], but so far no solid-state structure of these compounds has been published. The structure of the pair of anomeric imidates **30** and **31** was determined by X-ray analysis[6]) (*Fig. 3*). The intensities for **30** were recorded at 293 K and for **31** at 203 K. Both structures show heavy disorder, which could not be resolved adequately, especially for **30** (see *Exper. Part*); the final R values are 0.092 (**30**) and 0.0573 (**31**), respectively. The discussion of bond lengths and angles can, therefore, only point to trends. Both imidates adopt the $^4C_1$ conformation, as shown by the endocyclic torsion angles (*Table 2*). The trichloroacetimidoyl group of the α-D-anomer **30** is nearly anticlinal to the C(1)–O(5) bond (Ψ(O)(5)–C(1)–O(1)–C(9)) = 119.1(9)°, whereas, in the β-D-anomer **31**, the torsion angle Ψ is $-83.4(4)°$. In both anomers, the imino group is *syn*-periplanar to the C(1)–O(1) bond (Θ(C(1)–O(1)–C(9)=N(9)) = $-1(2)°$ for **30** and $\Theta = 4.0(7)°$ for **31**). *Schmidt et al.* [25] have calculated the conformation of the imino group of an α-D-pyranosyl trichloroacetimidate in the gas phase, and found $\Psi = 70 \pm 1°$ (MM2) or $\Psi = 81.3°$ (MNDO) and $\Theta = 9 \pm 1°$ (MM2) or $\Theta = 19.8°$ (MNDO), *i.e.*, significantly differing from the solid-state values of **30** and **31**. The *gg*-conformation of the $AcOCH_2$ group in **30** is characterized by the endocyclic torsion angles χ^1(O(5)–C(5)–C(6)–O(6)) = $-68.2(11)°$ and χ^2(C(4)–C(5)–C(6)–O(6)) = 54.5(13)°, while the endocyclic torsion angles $\chi^1 = 64.7(4)°$ and $\chi^2 = -176.1(3)°$ characterize the *gt*-conformation of the $AcOCH_2$ group in **31**. The ethynyl substituent is nearly linear in both anomers; the bond angles C(4)–C(7)–C(8) being 178.5(13)° (**30**) and 178.4(5)° (**31**), respectively.

An anomeric effect in the α-D-anomer **30** is indicated by the shortening of the C(1)–O(5) (1.368(13) Å[8])) and lengthening of the C(1)–O(1) (1.448(13) Å) bond (*Table 2*). Although the conformation of the imidate moiety in the β-D-anomer is close to the one required for an *exo*-anomeric effect [26], the length of both C(1)–O bonds (1.423(5) and 1.413(5) Å) is in the normal range (*Table 2*). This is rationalized by the strong n(O(1)) $\rightarrow \pi^*$(C(9)=N) interaction, as supported by the short O(1)–C(9) bond (1.330(5) Å).

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[7]) Thiophenyl glycoside, phenyltetrazolyl glycoside, glycosyl fluoride, and glycosyl bromide [21].

[8]) The shortening is largely an effect of the disorder of the crystal structure.

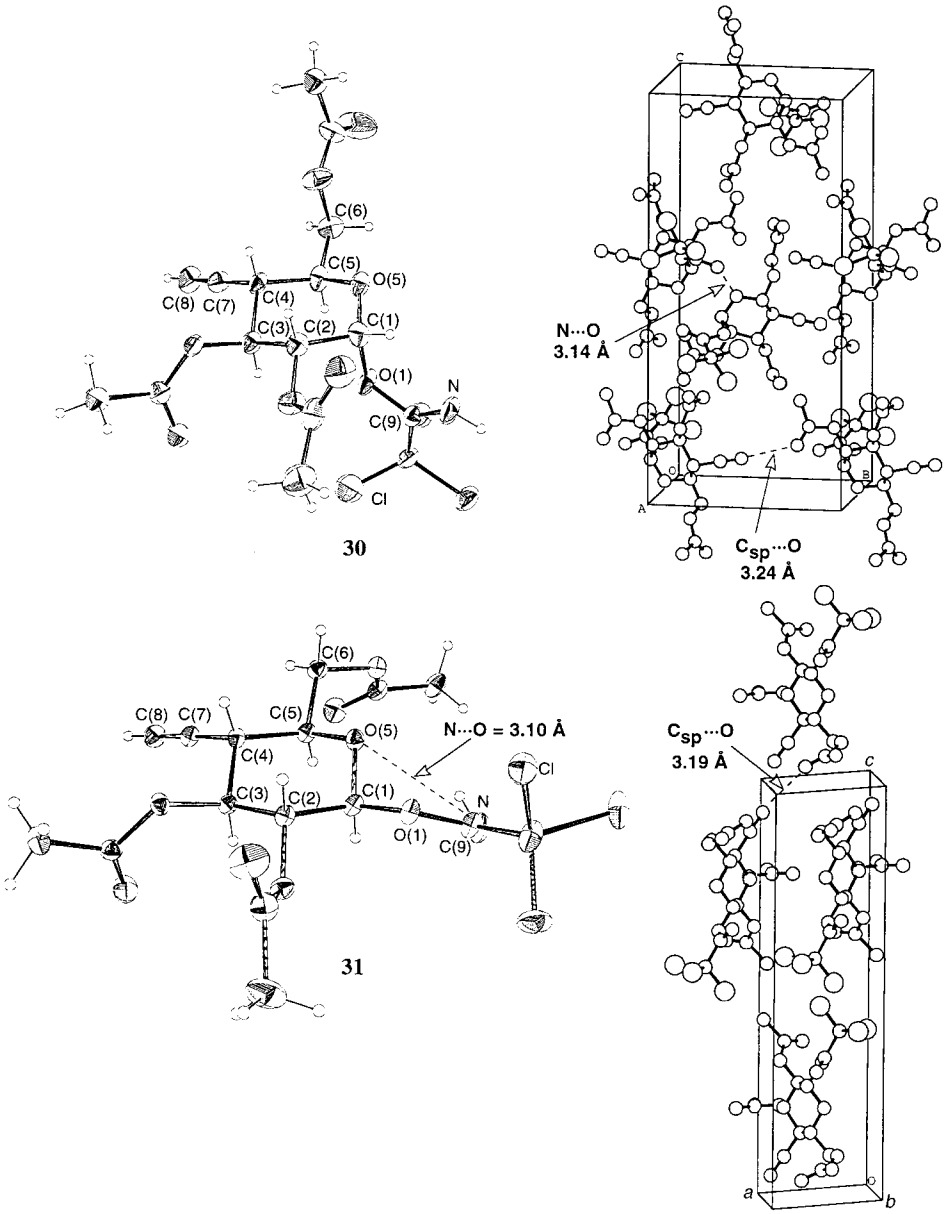
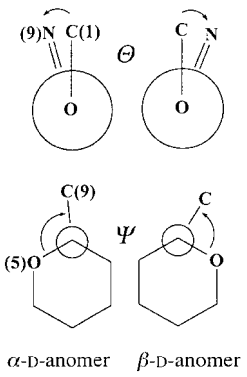


Fig. 3. *X-Ray crystal-structure analysis of* **30** *and* **31**: *ORTEP* [36] *presentation* (ellipsoids enclose 25% for **30** and 50% for **31** of the electron density) *and unit cell* (PLUTO [37]). Only one position of the disordered atoms is shown, arrows indicating the close contacts discussed in the text.

Only approximate intermolecular distances could be obtained for **30** because of the disordered Cl-atoms and C(3)–O/C(6)–O acyl groups. The N-atom of **30** is located 3.14(1) Å away from the neighbouring O(5) (*cf. Fig. 3*), a value close to the *van der*

Table 2. *Selected Torsion Angles* [°] *and Bond Lengths* [Å] *in* **30** *and* **31**. Standard deviations in parentheses. Numbering according to *Fig. 3*.

	30	**31**
Ψ(O(5)–C(1)–O(1)–C(9))	119.1(9)	– 83.4(4)
Θ(C(1)–O(1)–C(9)=N(9))	– 1(2)	4.0(7)
χ^1(O(5)–C(5)–C(6)–O(6))	– 68.2(11)	64.7(4)
χ^2(C(4)–C(5)–C(6)–O(6))	54.5(13)	– 176.1(3)
C(1)–C(2)–C(3)–C(4)	– 57.4(11)	– 53.2(4)
C(2)–C(3)–C(4)–C(5)	57.6(11)	50.8(4)
C(3)–C(4)–C(5)–O(5)	– 56.7(11)	– 54.9(4)
C(4)–C(5)–O(5)–C(1)	58.0(11)	65.0(4)
C(5)–O(5)–C(1)–C(2)	– 56.1(10)	– 67.7(4)
O(5)–C(1)–C(2)–C(3)	55.9(11)	60.6(4)
C(1)–O(5)	1.368(13)	1.413(5)
C(1)–O(1)	1.448(13)	1.423(5)
C(1)–C(2)	1.51(2)	1.523(5)
C(2)–C(3)	1.517(14)	1.514(5)
O(1)–C(9)	1.341(12)	1.330(5)
C(7)–C(8)	1.16(2)	1.187(7)



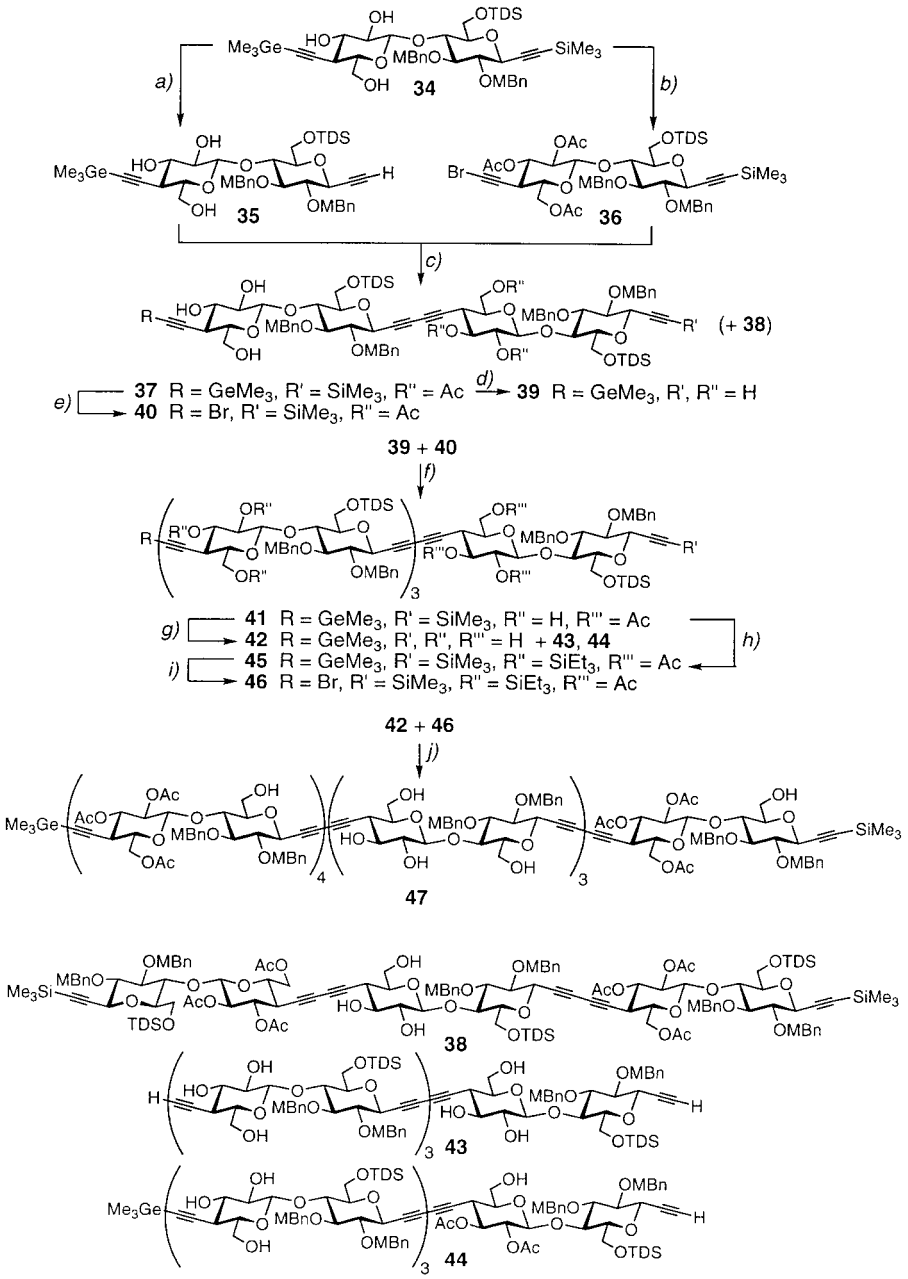
Waals distance indicating a weak intermolecular H-bond (N–H···O(5) = 2.38 Å); in the β-D-anomer **31** the distance of 3.10(1) Å between the N-atom and the ring O-atom indicates a intramolecular interaction (N–H···O(5) = 2.58 Å, ∢(N–H···O) = 116(3)°). Both anomers show an intermolecular C_{sp}–H···O H-bond [27][28], characterized by the distance between C(8) of the α-D-anomer **30** and the C(2)–OAc carbonyl O-atom of 3.24(2) Å. The shortest intermolecular contact in the β-D-anomer **31** (3.19(1) Å) is between C(8) and the C(6)–OAc carbonyl O-atom (*Fig. 3*). Similar short C_{sp}–H···O contacts have been observed, *e.g.*, in the crystal structures of *N*-methylpropiolamide (CSD MPROLA [29]) and (*o*-chlorobenzoyl)acetylene (CSD BYACCO [30]). Further evidence for an intermolecular C_{sp}–H···O H-bond derives from the solid-state (3% KBr) IR spectra of **30** and **31**. The wavenumbers for the $\tilde{\nu}$(≡C–H) stretching are significantly lower for **30** (3242 cm^{-1}) and **31** (3245 cm^{-1}) than for the tetraacetate **28** (3272 cm^{-1}). In solution (2% in CCl_4), **30**, **31**, and **28** show an IR $\tilde{\nu}$(≡C–H) absorption at 3111 cm^{-1}.

The new cellobiose-derived dialkyne **34** was transformed along similar lines as described for **2**. Protodesilylation of **34** (K_2CO_3/MeOH) yielded 91% of the dialkyne **35**, and acetylation followed by CuBr catalyzed bromodegermylation yielded 90% of the bromoalkyne **36** (*Scheme 4*).

Cross coupling of **35** and **36** in DMSO under the conditions of *Schreiber* and co-workers [31] and *Cai* and *Vasella* [11] led to the dimer **37** (66%). *Ca*. 2% of the trimer **38** was also isolated if the reaction was conducted for 27 h. A control experiment where the bromoalkyne **36** and the dimer **37** were cross-coupled under the same conditions showed a very slow transformation into the trimer **38** (marginal amounts were detectable on TLC after 48 h), possibly due to a CuI-catalyzed degermylation.

Treatment of the dimer **37** with K_2CO_3 in MeOH removed the Me_3Si and the Ac groups, and yielded 78% of the alkyne **39**, while treatment with *N*-bromosuccinimide (NBS) and CuBr transformed **37** into the bromoalkyne **40** without affecting the other

Scheme 4



a) K_2CO_3, MeOH/THF; 91%. *b*) 1. Ac_2O, pyridine; 2. NBS, CuBr, acetone; 90%. *c*) $[Pd_2(dba)_3]$/CuI, $P(furyl)_3$, Et_3N, DMSO; 65%. *d*) As *a*); 78%. *e*) NBS, CuBr, acetone; 81%. *f*) $Pd_2(dba)_3$/CuI, $P(furyl)_3$, Et_3N, DMSO; 54%. *g*) K_2CO_3, MeOH/THF; 55%. *h*) Et_3SiCl, 1*H*-imidazole, DMF; 92%. *i*) As *e*); 86%. *j*) 1. As *f*); 2. Ac_2O, pyridine; 3. HF·pyridine, THF, pyridine; 37%.

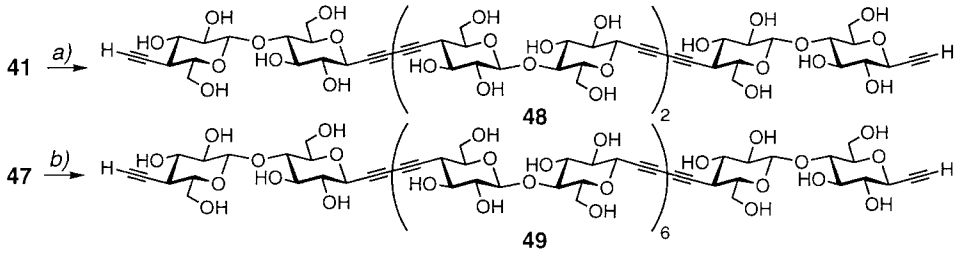
protecting groups. Cross coupling of **39** and **40**, similarly as before, gave the tetramer **41** in 54% yield.

Treatment of the tetramer **41** with K_2CO_3 in MeOH/THF gave only 55% of the completely deacetylated and *C*-desilylated alkyne **42** together with 2% of the degermylated alkyne **43** and 7% of the partially deacetylated alkyne **44**. Obviously, the concomitant deacetylation and *C*-desilylation of the tetramer was no longer selective, marking the limits of the scope of these conditions for the regioselective deprotection of the prop-2-ynyl ether moiety. To increase the polarity difference between the coupling partners, the tetramer **41** was first triethylsilylated to **45** (92%) and then bromodegermylated to **46** (86%). Cross coupling of **42** and **46** required twice as much of catalyst and phosphine ligand as for the preceding couplings and gave a mixture containing the desired product which could not be separated by column chromatography. The crude mixture was, therefore, acetylated, *O*-desilylated with HF in pyridine, and separated by chromatography, providing 39% of the octamer **47**.

Similarly as observed for the sequential binomial cycles starting with **2**, yields decreased in each cycle and were significantly lower than those realized for the glucose-derived dialkynes [3].

Deprotection of the tetramer **41** (*Scheme 5*) required the oxidative cleavage of the (4-methoxybenzyl)oxy groups with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (= 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile; DDQ) [32], *O*-desilylation with HF in pyridine, and deacetylation to give the deprotected tetramer **48** in 42% overall yield. The deprotected octamer **49** was obtained (34%) from **47** by treatment with DDQ and deacetylation.

Scheme 5



a) 1. DDQ, CH_2Cl_2/H_2O 9:1; 2. HF · pyridine, THF, pyridine; NaOMe, MeOH, *Amberlite IR-120* (H^+); 42%. *b*) 1. DDQ, CH_2Cl_2/H_2O 9:1; 2. NaOMe, MeOH, *Amberlite IR-120* (H^+); 34%.

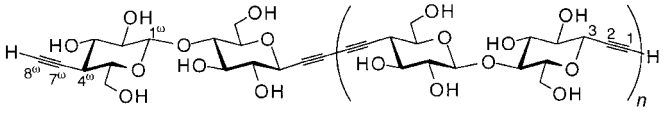
The deprotected dimer **18**, tetramer **48**, and octamer **49** are soluble in H_2O, MeOH, and DMSO, whereas, in the glucose-derived series, only the dimer was soluble in H_2O and MeOH, the tetramer and the octamer dissolving only in DMSO. The strong intramolecular C(5′)–C···HO–C(5) H-bonds within each cellobiose unit were evidenced for the dimer **18** by the temperature dependence of the chemical shift of the OH resonances (D_6)DMSO, C(5′)–O···HO–C(5) ($\Delta\delta/\Delta T = -1.65$ ppb · K^{-1}) and C(5‴)–O···HO–C(7″) ($\Delta\delta/\Delta T = -1.73$ ppb · K^{-1}), but the relative orientation of the monomeric units around the butydiynediyl bridge could not be deduced. The ^{1}H-NMR spectra of the oligomers are almost superimposable; the signals of the cellobiose units attached to a butadiynediyl unit appearing at slightly lower field ($\Delta\delta \approx 0.05 - 0.1$ ppm)

than those of the ethynylated residues. Qualitatively, the same behaviour has also been observed for the glucose-derived series. A comparison of selected ^{1}H-NMR data in CD_3OD, (D_6)DMSO, and D_2O of the deprotected cellobiose-derived oligomers (*Table 3*) shows no evidence for association of these compounds, in agreement with the observations in the glucose-derived series [2].

Table 3. *Selected ^{1}H-NMR Data* (23°) *of the Deprotected Oligomers.* Concentration in parentheses.

	1 [4] ($n=0$; $2.0\cdot10^{-2}$ M)		**18** ($n=1$; 10^{-2} M)		**48** ($n=3$; $2.0\cdot10^{-3}$ M)		**49** ($n=7$; $5.5\cdot10^{-4}$ M)	
Solvent	CD_3OD	(D_6)DMSO	CD_3OD	(D_6)DMSO	CD_3OD	(D_6)DMSO	D_2O	(D_6)DMSO
H–C(1)	2.89	3.33	2.88	3.34	2.88	[a])	2.90	[a])
H–C(3)	3.94	3.85	3.93	3.86	3.92	3.83	4.11	3.82
H–C(1$^\omega$)	4.40	4.27	4.40	4.27	4.41	4.26	4.47	4.27
H–C(4$^\omega$)	2.48	2.29	2.47	2.29	2.44	2.25	2.56	2.28
H–C(8$^\omega$)	2.56	2.96	2.56	2.97	2.55	2.95	2.59	2.96

[a]) Signal hidden by HDO resonance.



The δ(^{13}C) values of the propargylic and homopropargylic ethynyl groups of **1**–**6**, **9**–**11**, **15**–**18**, **32**–**42**, **44**–**46**, **48**, and **49** are given in *Table 4*. The assignments of the *s*'s of $C\equiv CSiMe_3$ and $C\equiv CGeMe_3$ are in agreement to the values of the analogous glucose-derived oligomers [2][3]. The *s*'s of the brominated ethynyl groups appear at significantly higher fields, *i.e.*, at 42.20–44.27 ppm for $BrC\equiv C$ and at 75.92–77.97 ppm for $BrC\equiv C$. The unprotected ethynyl groups show a *d* at 80.04–82.32 and a *s* at 73.65–77.97 ppm. The *d*'s for C(3) and C(4$^\omega$) resonate at 69.12–72.26 and 35.72–40.08 ppm, respectively.

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support, and Dr. *B. Bernet* for checking the experimental part.

Experimental Part

General. Solvents were distilled before use: THF and toluene from Na-benzophenone ketyl, CH_2Cl_2, MeCN, and MeOH from CaH_2 and acetone from $CaSO_4$. Cl_3CCN was distilled under Ar prior to use. K_2CO_3 was heated until glowing. HCl in aq. MeOH was prepared by mixing 83 ml of HCl (37%) with 917 ml of MeOH. Reactions were run under Ar or N_2. BuLi was titrated [33] before use. $AlCl_3$ was freshly sublimed and weighted in a glove-box under N_2. Workup: The mixture was diluted with the indicated solvent and H_2O, the layers were separated, and the aq. layer was extracted several times with the indicated solvent. The combined org. layers were washed once with brine, dried ($MgSO_4$), filtered, and the solvent was removed at 40° under reduced pressure. Qual. TLC: precoated silica-gel plates (*Merck* silica gel *60 F_{254}*), detection by spraying with 5% H_2SO_4 in EtOH followed by heating to *ca.* 200°. Flash chromatography (FC): silica gel *Merck 60* (0.04–0.063 mm). M.p's: uncorrected. Optical rotations: 1-dm cell at 20 or 25° and 589 nm. FT-IR: 1–2% soln. in the indicated solvent. ^{1}H- and ^{13}C-NMR: at 200, 300, 400 or 500 MHz; 50, 75, 100, or 125 MHz, resp. MS: Chemical ionization (CI) with NH_3, fast atom bombardment (FAB), or MALDI-TOF. NOBA: 3-Nitrobenzyl alcohol.

4-C-*(Bromoethynyl)-4-deoxy-β*-D-*glucopyranosyl-(1→6)-3,7-anhydro-4,5,8-tri*-O-*benzyl-1,2-dideoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**5**). A soln. of **4** [4] (1.5 g, 1.64 mmol) in THF (16 ml) was treated at r.t. with 1M aq. HCl in MeOH (10 ml), heated for 36 h at 40°, neutralized with *Amberlite IRA-900* (OH^-

Table 4. *Selected* ^{13}*C-NMR Data* (23°, 75, 100, or 125 MHz, *ca.* 10^{-2} M) *of the Alkynes* **1**–**6**, **9**–**11**, **15**–**18**, **32**–**42**, **44**–**46**, **48**, *and* **49**

		Solvent	OCH–C≡C–X	OCH–*C*≡C–X	OCH–C≡*C*–X	Y–*C*≡C–CH	Y–C≡*C*–CH	Y–C≡C–*C*H
1 X=H	Y=H	(D_6)DMSO	69.85	75.94	82.01	82.32	73.78	37.20
2 X=Me_3Si	Y=Me_3Ge	$CDCl_3$	70.49	102.61	91.08	88.75	103.03	38.07
3 X=H	Y=Me_3Ge	$CDCl_3$	69.87	74.20	81.08	88.78	102.03	38.06
4 X=Me_3Si	Y=Br	$CDCl_3$	70.38	102.50	91.06	42.20	77.20	37.84
5 X=Me_3Si	Y=Br	$CDCl_3$	70.41	102.28	91.50	43.34	76.13	37.95
6 X=Me_3Si	X=Me_3Ge	$CDCl_3$	70.29	101.92	91.47	88.71	102.26	37.94
9 X=H	Y=Me_3Ge	$CDCl_3$	69.67	74.49	80.79	88.60	102.12	37.85
10 X=Me_3Si	Y=Br	$CDCl_3$	70.14	102.17	91.08	42.37	77.14	37.72
11 X=Me_3Si	Y=Me_3Ge	$CDCl_3$	70.30	101.93	91.23	88.72	102.32	37.97
15 X=Me_3Si	Y=H	$CDCl_3$	70.11	102.21	91.45	80.04	72.73	37.41
16 X=Me_3Si	Y=H	C_6D_6	69.12	100.57	92.32	78.29	73.35	35.66
17 X=Me_3Si	Y=C≡C	C_6D_6	70.44	103.99	90.64	68.99	75.89	36.92
18 X=H	Y=H	(D_6)DMSO	69.75	75.87	81.92	82.22	73.70	37.11
32 X=Me_3Si	Y=H	$CDCl_3$	69.74	102.94	90.43	77.97	73.13	35.72
33 X=Me_3Si	Y=H	$CDCl_3$	69.72	102.85	90.61	80.21	72.78	36.94
34 X=Me_3Si	X=Me_3Ge	$CDCl_3$	69.57	102.90	90.33	89.34	100.46	38.35
35 X=H	Y=Me_3Ge	$CDCl_3$	69.44	73.65	81.07	90.05	100.02	38.61
36 X=Me_3Si	Y=Br	$CDCl_3$	69.67	102.95	90.38	44.27	77.97	36.88
37 X=Me_3Si	Y=Me_3Ge	$CDCl_3$	69.74	102.92	90.43	90.07	100.01	38.63
38 X=Me_3Si	Y=Me_3Si	$CDCl_3$	69.74	102.94	90.44	90.44	102.92	37.53
39 X=H	Y=Me_3Ge	$CDCl_3$	69.47	74.74	81.01	90.06	100.03	38.62
40 X=Me_3Si	Y=Br	$CDCl_3$	69.74	102.92	90.43	43.63	75.92	38.01
41 X=Me_3Si	Y=Me_3Ge	$CDCl_3$	69.74	102.93	90.44	90.06	100.02	38.62
42 X=H	Y=Me_3Ge	$CDCl_3$	69.43	74.80	81.04	89.93	100.21	38.60
44 X=H	Y=Me_3Ge	$CDCl_3$	69.60	75.75	81.02	90.09	99.96	38.61
45 X=Me_3Si	Y=Me_3Ge	$CDCl_3$	69.74	102.94	90.42	88.56	104.23	39.94
46 X=Me_3Si	Y=Br	$CDCl_3$	69.74	102.93	90.42	42.92	76.38	40.08
48 X=H	Y=H	CD_3OD	72.26	75.91	81.70	81.81	73.48	38.61
49 X=H	Y=H	(D_6)DMSO[a])	70.13	[b])	[b])	[b])	[b])	37.84

[a]) Conc. was $5.5 \cdot 10^{-4}$ M. [b]) Not observed or hidden.

form), filtered, and evaporated. FC (hexane/AcOEt 3:1 → 2:1 → 1:1) gave **5** (1.18 g, 92%) as a colourless oil. R_f (toluene/AcOEt 1:1) 0.51. $[\alpha]_D^{25} = +12.9$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3599*s*, 3420*m* (br.), 3090*w*, 3067*m*, 3033*m*, 2961*s*, 2900*s*, 2872*s*, 2182*w*, 1949*w*, 1876*w*, 1758*s*, 1678*w*, 1597*w*, 1550*w*, 1513*w*, 1498*m*, 1454*s*, 1363*s*, 1292*s*, 1251*s*, 1165*s*, 1073*s*, 1028*s*, 909*s*, 846*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40–7.22 (*m*, 15 arom. H); 4.98 (*d*, $J = 10.4$, PhC*H*); 4.87 (*d*, $J = 11.2$, PhC*H*); 4.82 (*d*, $J = 11.2$, PhC*H*); 4.78 (*d*, $J = 10.4$, PhC*H*); 4.69 (*d*, $J = 12.0$, PhC*H*); 4.51 (*d*, $J = 12.0$, PhC*H*); 4.39 (*d*, $J = 7.8$, H–C(1′)); 4.03 (*d*, $J = 9.3$, H–C(3)); 3.93 (*t*, $J \approx 9.4$, H–C(6)); 3.87 (*dd*, $J = 11.8, 3.5$, H_a–C(8)); 3.77 (*dd*, $J = 11.8, 2.3$, H_b–C(8)); 3.68–3.60 (*m*, addn. of $D_2O \rightarrow$ 3.64, *dd*, $J = 12.0, 2.5$, H_a–C(6′), → 3.63, *dd*, $J = 12.0, 4.6$, H_b–C(6′)); 3.59 (*t*, $J \approx 9.4$, H–C(5)); 3.53 (*t*, $J \approx 9.9$, H–C(4)); 3.45–3.33 (*m*, addn. of $D_2O \rightarrow$ 3.39, br. *ddd*, $J = 12.0, 5.0, 2.7$, H–C(5′), → 3.37, *t*, $J \approx 10.0$, H–C(3′), exchanged with D_2O, HO–C(2′)); 3.18–3.09 (*m*, addn. of $D_2O \rightarrow$ 3.13, *t*, $J \approx 8.8$, H–C(2′), → 3.13, br. *ddd*, $J \approx 11.3, 4.0, 2.5$, H–C(7)); 2.89 (br. *d*, exchanged with D_2O, $J \approx 2.2$, HO–C(3′)); 2.41 (*t*, $J \approx 10.4$, H–C(4′)); 2.03 (br. *s*, exchanged with D_2O, HO–C(6′)); 0.18 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.66 (*s*); 137.89 (*s*); 137.51 (*s*); 128.53 (2*d*); 128.39 (2*d*); 128.36 (2*d*); 128.33 (2*d*); 128.18 (2*d*); 127.98 (*d*); 127.87 (*d*); 127.65 (*d*); 127.08 (2*d*); 102.28 (*s*, *C*≡CSi); 102.04 (*d*, C(1′)); 91.50 (*s*, C≡*C*Si); 84.14 (*d*); 81.94 (*d*); 78.81 (*d*); 76.46 (*d*); 76.13 (*s*, *C*≡CBr); 75.51 (*t*, Ph*C*H$_2$); 75.31 (*t*, Ph*C*H$_2$); 75.24 (*d*); 74.75 (*d*); 74.48 (*d*); 73.66 (*t*, Ph*C*H$_2$); 70.41 (*d*); 68.33 (*t*); 62.92 (*t*); 43.34 (*s*, C≡*C*Br); 37.95 (*d*, C(4′)); −0.30 (*q*, Me_3Si). FAB-MS (NOBA): 779 (14, $[M(^{81}Br)]^+$), 777 (10, $[M(^{79}Br)]^+$), 531 (6), 307 (16), 181 (15), 154 (64), 91 (100). Anal. calc. for $C_{40}H_{47}BrO_9Si$ (779.80): C 61.61, H 6.07; found: C 61.27, H 6.16.

4-Deoxy-2,3,6-tris-O-*(methoxymethyl)-4*-C-*[2-(trimethylgermyl)ethynyl]-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri*-O-*benzyl-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-deoxy-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri-O-benzyl-1,2-dideoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**6**), *4-C,4′*-C-*(Buta-1,3-diyne-1,4-diyl)-bis[4-deoxy-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri*-O-*benzyl-1,2-dideoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol]* (**7**), *and 4-Deoxy-2,3,6-tris*-O-*(methoxymethyl)-4*-C-*[2-(trimethylgermyl)ethynyl]-β*-D-*glucopyranosyl-(1 → 3)-[4-deoxy-2,3,6-tris*-O-*(methoxymethyl)-4*-C-*[2-(trimethylgermyl)ethynyl-β*-D-*glucopyranosyl-(1 → 14)]-1,4,5,12,13,16-hexa*-O-*benzyl-7,8,9,10-tetradeoxy*-D-erythro-L-galacto-L-gulo-*hexadeca-7,9-diynitol* (**8**). To a degassed soln. of **3** (368 mg, 0.42 mmol), **5** (330 mg, 0.42 mmol), $[Pd_2(dba)_3]$ (11.6 mg, 3 mol-%), and CuI (2.0 mg, 3 mol-%) in DMSO (5 ml) was added 1,2,2,6,6-pentamethylpiperidine (PMP; 0.23 ml, 1.35 mmol). The mixture was stirred for 2.5 h at r.t., poured into ice-cold sat. NH_4Cl soln. (5 ml), and worked up (AcOEt). FC (hexane/AcOEt 3:1 → 2:1 → 1:1) gave **6** (443 mg, 67%), **7** (11.5 mg, 2%) and **8** (16 mg, 2%) as colourless oils.

Data of **6**: R_f (toluene/AcOEt 1:1) 0.65. $[\alpha]_D^{25} = +1.5$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3596*m*, 3429*m* (br.), 3090*w*, 3066*m*, 3032*m*, 2899*s*, 2824*m*, 2259*w*, 2173*w*, 1947*w*, 1873*w*, 1807*w*, 1605*w*, 1548*w*, 1497*m*, 1454*s*, 1361*s*, 1292*m*, 1251*s*, 1242*m*, 1213*s*, 1153*s*, 1061*s*, 922*m*, 908*s*, 845*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.38–7.22 (*m*, 30 arom. H); 5.04 (*d*, $J = 11.2$, PhC*H*); 4.99 (*d*, $J = 10.4$, PhC*H*); 4.93 (*d*, $J = 6.4$, MeOC*H*); 4.89 (*d*, $J = 6.4$, MeOC*H*); 4.86 (*s*, PhC*H*$_2$); 4.81 (*d*, $J = 10.6$, PhC*H*); 4.78 (*d*, $J = 10.4$, PhC*H*); 4.76 (*d*, $J = 10.6$, PhC*H*); 4.74 (*d*, $J = 6.2$, MeOC*H*); 4.70 (*d*, $J = 12.0$, PhC*H*); 4.69 (*d*, $J = 12.0$, PhC*H*); 4.65 (*d*, $J = 6.2$, MeOC*H*); 4.64 (*d*, $J = 10.7$, PhC*H*); 4.51 (*d*, $J = 12.0$, PhC*H*); 4.52 (*d*, $J = 6.5$, MeOC*H*); 4.48 (*d*, $J = 6.6$, MeOC*H*); 4.46 (*d*, $J = 12.1$, PhC*H*); 4.41 (*d*, $J = 7.8$, H–C(1‴)); 4.28 (*d*, $J = 7.9$, H–C(1′)); 4.04 (*d*, $J = 9.5$, H–C(5″)); 4.03 (*d*, $J = 9.6$, H–C(3)); 3.99 (*t*, $J \approx 10.0$, H–C(8″)); 3.93 (*t*, $J \approx 10.0$, H–C(6)); 3.89 (*dd*, $J = 11.4$, 3.0, H_a–C(6′)); 3.83 (*dd*, $J = 11.2$, 3.2, H_a–C(8)); 3.79–3.67 (*m*, addn. of $D_2O \rightarrow$ 3.77, *dd*, $J = 11.2$, 2.3, H_b–C(8), → 3.75, *dd*, $J \approx 11.0$, 2.0, H_a–C(6‴), → 3.74, *dd*, $J = 10.6$, 2.0, H_a–C(10″), → 3.70, *dd*, $J = 10.8$, 4.6, H_b–C(10″), → 3.68, *dd*, $J = 11.0$, 5.0, H_b–C(6′)); 3.61–3.59 (*m*, addn. of $D_2O \rightarrow$ 3.59, *dd*, $J = 12.0$, 2.5, H_b–C(6‴)); 3.58 (*t*, $J \approx 9.3$, H–C(6″)); 3.55 (*t*, $J \approx 9.1$, H–C(4)); 3.52 (*t*, $J \approx 9.0$, H–C(5)); 3.49 (*s*, MeO); 3.45 (*t*, $J \approx 9.5$, H–C(7″)); 3.44 (*dd*, $J = 10.4, 9.1$, H–C(3‴)); 3.40–3.36 (*m*, addn, of $D_2O \rightarrow$ 3.38, *dd*, $J = 10.4, 9.2$, H–C(3′) → 3.39, br. *ddd*, $J \approx 9.7, 5.0, 2.8$, H–C(5′)); 3.36 (*s*, MeO); 3.30 (*ddd*, $J \approx 10.0, 3.2, 2.1$, H–C(7)); 3.29 (*s*, MeO); 3.25 (br. *s*, exchanged with D_2O, HO–C(2′)); 3.25–3.20 (*m*, addn. of $D_2O \rightarrow$ 3.23, *dd*, $J = 9.1$, 8.0, H–C(2′), → 3.22, *ddd*, $J \approx 10.0, 4.5, 2.0$, H–C(9″)); 3.14 (*dd*, $J = 8.9, 7.8$, H–C(2‴)); 3.10 (*ddd*, $J = 10.3, 5.5, 2.4$, H–C(5‴)); 2.64 (br. *d*, $J \approx 3.0$, exchanged with D_2O, HO–C(3′)); 2.63 (*t*, $J \approx 10.5$, H–C(4‴)); 2.52 (*t*, $J \approx 10.4$, H–C(4′)); 1.88 (br. *t*, $J \approx 6.9$, exchanged with D_2O, HO–C(6′)); 0.34 (*s*, Me_3Ge); 0.19 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 139.01 (*s*); 138.66 (*s*); 137.86 (2*s*); 137.83 (*s*); 137.44 (*s*); 128.52–126.97 (several *d*); 102.26 (*s*, *C*≡CGe); 102.07 (*d*, C(1′)); 101.92 (*s*, *C*≡CSi); 101.62 (*d*, C(1‴)); 97.67 (*t*, MeO*C*H$_2$); 97.62 (*t*, MeO*C*H$_2$); 97.58 (*t*, MeO*C*H$_2$); 91.47 (*s*, C≡*C*Si); 88.71 (*s*, C≡*C*Ge); 84.19 (*d*); 84.03 (*d*); 81.94 (*d*); 81.01 (*d*); 79.41 (*d*); 78.92 (*d*); 78.75 (2*d*); 76.47 (*d*); 75.56 (*t*, Ph*C*H$_2$); 75.50 (*t*, Ph*C*H$_2$); 75.47 (*d*); 75.32 (*t*, Ph*C*H$_2$); 75.26 (*t*, Ph*C*H$_2$); 75.12 (*d*); 74.89 (*d*); 74.71 (*d*); 74.61 (*s*); 74.36 (*d*); 73.69 (*t*, Ph*C*H$_2$); 73.55 (*t*, Ph*C*H$_2$); 70.40 (*d*, C(5″)); 70.29 (*d*, C(3)); 70.18 (*s*); 68.41 (*s*); 68.31 (*t*); 67.98 (*t*); 67.26 (*t*); 62.82 (*t*); 56.60 (*q*, MeO); 56.33 (*q*, MeO); 55.19 (*q*, MeO); 37.94

(*d*, C(4‴)); 37.54 (*d*, C(4′)); −0.31 (*q*, Me_3Si, Me_3Ge); 1*s* for C≡C not observed or hidden. MALDI-TOF-MS: 1615 ($[M+K]^+$), 1599 ($[M+Na]^+$). Anal. calc. for $C_{86}H_{106}GeO_{21}Si$ (1576.47): C 65.52, H 6.78; found: C 65.33, H 6.56.

Data of **7**: R_f (toluene/AcOEt 1:1) 0.41. IR (CCl_4): 3595*m*, 3418*m*, 3090*w*, 3068*m*, 3032*m*, 2955*m*, 2875*m*, 1950*w*, 1808*w*, 1740*w*, 1606*w*, 1495*w*, 1455*w*, 1361*m*, 1250*s*, 1212*w*, 1164*m*, 1065*s*, 1030*s*. MALDI-TOF-MS: $C_{80}H_{94}O_{18}Si_2$ (1399.80): 1439 ($[M+K]^+$), 1423 ($[M+Na]^+$).

Data of **8**: R_f (hexane/AcOEt 1:1) 0.61. IR (CCl_4): 3090*w*, 3030*w*, 2955*s*, 2928*s*, 2825*m*, 1740*w*, 1640*w*, 1555*w*, 1498*w*, 1455*m*, 1360*m*, 1217*m*, 1155*s*, 1095*s*, 1045*s*. MALDI-TOF-MS: $C_{92}H_{118}Ge_2O_{24}$ (1753.13): 1782 ($[M+K]^+$), 1766 ($[M+Na]^+$).

4-Deoxy-2,3,6-tris-O-*(methoxymethyl)-4*-C-*[(trimethylgermyl)ethynyl]-β*-D-*glucopyranosyl-(1→8)-5,9-anhydro-6,7,10-tri*-O-*benzyl-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→4*-C*)-4-deoxy-β*-D-*glucopyranosyl-(1→6)-3,7-anhydro-4,5,8-tri*-O-*benzyl-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol* (**9**). A soln. of **6** (158 mg, 0.1 mmol) in THF (2 ml) was treated dropwise at r.t. with cold sat. K_2CO_3 soln. in MeOH (0.1 ml), stirred for 1 h, neutralized with *Amberlite IR-120* (H^+ form) filtered, and evaporated. FC (hexane/AcOEt 1:1) gave **9** (136 mg, 90%) as a colourless oil. R_f (toluene/AcOEt 1:1) 0.56. $[\alpha]_D^{25} = +2.7$ ($c = 1.2$, $CHCl_3$). IR (CCl_4): 3587*m*, 3429*m* (br.), 3311*m*, 3090*w*, 3066*m*, 3032*m*, 2909*s*, 2824*m*, 2230*w*, 2171*w*, 1947*w*, 1868*w*, 1809*w*, 1603*w*, 1558*w*, 1540*w*, 1497*m*, 1454*s*, 1361*s*, 1293*m*, 1241*m*, 1212*m*, 1154*s*, 1062*s*, 922*m*, 832*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.40–7.28 (*m*, 30 arom. H); 5.07 (*d*, $J = 11.2$, PhC*H*); 5.02–4.88, 4.87–4.62, 4.54–4.46 (*m*, 11 PhC*H*, 6 MeOC*H*); 4.40 (*d*, $J = 7.8$, H–C(1‴)); 4.30 (*d*, $J = 7.9$, H–C(1′)); 4.06 (br. *d*, $J \approx 9.3$, H–C(5″), H–C(3)); 4.04 (*t*, $J \approx 8.8$, H–C(8″)); 3.97 (*t*, $J \approx 8.6$, H–C(6)); 3.87 (*dd*, $J = 12.0$, 2.8, H_a–C(6‴)); 3.80–3.71 (*m*, 6 H); 3.68–3.10 (*m*, 13 H); 3.51 (*s*, MeO); 3.39 (*s*, MeO); 3.31 (*s*, MeO); 3.00 (br. *s*, HO–C(3′)); 2.75 (*t*, $J \approx 10.4$, H–C(4‴)); 2.63 (*d*, $J = 2.2$, H–C(1)); 2.52 (*t*, $J \approx 10.5$, H–C(4′)); 2.15 (br. *s*, HO–C(6′)); 0.36 (*s*, Me_3Ge). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.09 (*s*); 138.39 (*s*); 137.73 (3*s*); 137.43 (*s*); 128.92–126.56 (several *d*); 102.12 (*s*, *C*≡CGe); 101.87 (*d*, C(1′)); 101.54 (*d*, C(1‴)); 97.56 (*t*, 2 MeO*C*H_2); 96.47 (*t*, MeO*C*H_2); 88.60 (*s*, C≡*C*Ge); 84.14 (*d*); 83.94 (*d*); 81.52 (*d*); 80.91 (*d*); 80.79 (*d*, C≡*C*H); 79.26 (*d*); 78.78 (2*d*); 78.65 (*d*); 78.52 (*d*); 76.20 (*d*); 75.65 (*d*); 75.49 (*t*, 2 Ph*C*H_2); 75.38 (*d*); 75.25 (*t*, 2 Ph*C*H_2); 75.09 (*d*); 74.79 (*d*); 74.62 (*d*); 74.49 (*s*, *C*≡CH); 74.35 (*s*); 74.24 (*d*); 73.46 (*t*, 2 Ph*C*H_2); 70.20 (*d*, C(5″)); 69.67 (*d*, C(3)); 68.25 (*s*); 68.00 (*t*); 67.87 (*t*); 67.15 (*t*); 62.91 (*t*); 56.52 (*q*, MeO); 56.24 (*q*, MeO); 55.10 (*q*, MeO); 37.85 (*d*, C(4‴)); 37.56 (*d*, C(4′)); −0.39 (*q*, Me_3Si, Me_3Ge); 2*s* for C≡C not observed or hidden. MALDI-TOF-MS: 1527 ($[M+Na]^+$). FAB-MS (NOBA): 1505 (16, M^+), 181 (100), 91 (100). Anal. calc. for $C_{83}H_{98}GeO_{21}$ (1504.28): C 66.27, H 6.57; found: C 66.04, H 6.50.

4-C-*(Bromoethynyl)-4-deoxy-2,3,6-tris*-O-*(methoxymethyl)-β*-D-*glucopyranosyl-(1→8)-5,9-anhydro-6,7,10-tri*-O-*benzyl-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→4*-C*)-2,3,6-tri*-O-*acetyl-4-deoxy-β*-D-*glucopyranosyl-(1→6)-3,7-anhydro-4,5,8-tri*-O-*benzyl-1,2-dideoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**10**). A soln. of **6** (103.3 mg, 65.54 μmol) in CH_2Cl_2 (2 ml), pyridine (0.2 ml), and Ac_2O (0.2 ml) was stirred for 12 h at r.t. and evaporated. The residue was codistilled (toluene) and dried under h.v. for 12 h. A soln. of the residue (R_f (hexane/AcOEt 5:4) 0.33) and NBS (12.25 mg, 68.8 μmol) in acetone (1 ml) was treated with CuBr (0.94 mg, 10 mol-%), stirred for 4 h at r.t., poured into ice-cold sat. $Na_2S_2O_3$ soln. (3 ml), and worked up (AcOEt). FC (hexane/AcOEt 3:1 → 2:1) gave **10** (98.2 mg, 90%) as a colourless oil. R_f (hexane/AcOEt 1:1) 0.71. $[\alpha]_D^{25} = -5.5$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3090*w*, 3066*m*, 3032*m*, 2954*m*, 2899*m*, 2172*w*, 1946*w*, 1868*w*, 1758*s*, 1700*w*, 1684*w*, 1653*w*, 1635*w*, 1558*w*, 1540*w*, 1497*m*, 1454*m*, 1365*s*, 1292*m*, 1230*s*, 1154*s*, 1117*s*, 1090*s*, 1053*s*, 922*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.40–7.20 (*m*, 30 arom. H); 5.07–4.59, 4.54–4.36 (*m*, H–C(2′), H–C(3′), 12 PhC*H*, 6 MeOC*H*); 4.43 (*d*, $J = 7.8$, H–C(1‴)); 4.24 (*d*, $J = 7.9$, H–C(1′)); 4.22–3.84 (*m*, 6 H); 3.84–3.62 (*m*, 5 H); 3.62–3.12 (*m*, 12 H); 3.49 (*s*, MeO); 3.36 (*s*, MeO); 3.29 (*s*, MeO); 2.79 (*t*, $J \approx 10.4$, H–C(4‴)); 2.65 (*t*, $J \approx 10.4$, H–C(4′)); 2.00 (*s*, Ac); 1.95 (*s*, Ac); 1.91 (*s*, Ac); 0.17 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.28 (*s*, C=O); 169.46 (*s*, C=O); 169.30 (*s*, C=O); 139.01 (*s*); 138.82 (*s*); 137.86 (*s*); 137.61 (2*s*); 137.52 (*s*); 128.61–127.02 (several *d*); 102.17 (*s*, *C*≡CSi); 101.46 (*d*, C(1′)); 99.56 (*d*, C(1‴)); 97.51 (*t*, MeO*C*H_2); 97.40 (*t*, MeO*C*H_2); 96.40 (*t*, MeO*C*H_2); 91.08 (*s*, C≡*C*Si); 83.81 (*d*); 83.68 (*d*); 81.45 (*d*); 80.71 (*d*); 79.19 (*d*); 78.63 (2*d*); 78.49 (*d*); 77.14 (*d*, C≡*C*H); 76.26 (*d*); 75.44 (*t*, Ph*C*H_2); 75.36 (*d*); 75.29 (*t*, Ph*C*H_2); 75.21 (*t*, Ph*C*H_2); 74.87 (*t*, Ph*C*H_2); 74.23 (*d*); 73.92 (*s*); 73.55 (*t*, Ph*C*H_2); 73.43 (*t*, Ph*C*H_2); 72.23 (2*d*); 72.01 (*d*); 70.19 (*d*, (C(5″)); 70.14 (*d*, C(3)); 69.70 (*s*); 68.51 (*s*); 67.76 (*t*); 67.49 (*t*); 66.97 (*t*); 63.65 (*t*); 56.21 (*q*, MeO); 55.01 (*q*, MeO); 53.68 (*q*, MeO); 42.37 (*s*, C≡*C*Br); 37.72 (*d*, C(4‴)); 36.15 (*d*, C(4′)); −0.41 (*q*, Me_3Si); 1*s* for C≡C not observed or hidden. FAB-MS (NOBA): 1688 (17, $[M+Na]^+$), 1664 (50, M^+), 181 (48), 91 (100). Anal. calc. for $C_{89}H_{103}BrO_{24}Si$ (1664.77): C 64.21, H 6.24, Br 4.80; found: C 64.34, H 6.19, Br 4.54.

4-Deoxy-2,3,6-tris-O-*(methoxymethyl)-4*-C-*[(trimethylgermyl)ethynyl]-β*-D-*glucopyranosyl-(1→8)-5,9-anhydro-6,7,10-tri*-O-*benzyl-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→4*-C*)-4-deoxy-β*-D-*glucopyranosyl-(1→8)-5,9-anhydro-6,7,10-tri*-O-*benzyl-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-*

*(1 → 4-*C*)-4-deoxy-2,3,6-tris-*O*-(methoxymethyl)-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**11**), *4-*C*,4′-*C*-(Buta-1,3-diyne-1,4-diyl)-bis[4-deoxy-2,3,6-tris-*O*-(methoxymethyl)-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol]* (**12**), *and 4-Deoxy-2,3,6-tris-*O*-(methoxymethyl)-4-*C*-[(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetra-deoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 3)-[4-deoxy-2,3,6-tris-*O*-(methoxymethyl)-4-*C*-[2-(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 14)]-1,4,5,12,13,16-hexa-*O*-benzyl-7,8,9,10-tetradeoxy-*D*-erythro-*L*-galacto-*L*-gulo-hexadeca-7,9-diynitol* (**13**). A degassed soln. of **9** (85.4 mg, 56.7 μmol), **10** (94.5 mg, 56.73 μmol), $[Pd_2(dba)_3]$ (1.56 mg, 3 mol-%), and CuI (0.32 mg, 3 mol-%) in DMSO (2 ml) was treated at r.t. with 1,2,2,6,6-pentamethylpiperidine (0.05 ml), stirred for 2.5 h, poured into ice-cold sat. NH_4Cl soln. (5 ml) and worked up (CH_2Cl_2). FC (hexane/AcOEt 2 : 1) gave **11** (105.2 mg, 60%), **12** (4.1 mg, 2%), and **13** (2.1 mg, 3%) as colourless oils.

Data of **11**: R_f (hexane/AcOEt 1:2) 0.26. $[\alpha]_D^{25} = -13.5$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3706*m*, 3596*m*, 3427*w* (br.), 3064*m*, 3032*m*, 2892*s* (br.), 2257*w*, 2170*w*, 1947*w*, 1873*w*, 1758*s*, 1691*w*, 1658*w*, 1640*w*, 1586*m*, 1552*m*, 1513*w*, 1497*m*, 1454*m*, 1365*s*, 1292*s*, 1230*s*, 1154*s*, 1055*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.40–7.20 (*m*, 60 arom. H); 5.04 (*d*, *J* = 11.2, PhC*H*); 5.01 (*d*, *J* = 11.3, PhC*H*); 4.96 (*d*, *J* = 11.5, PhC*H*); 4.95 (*d*, *J* = 11.8, PhC*H*); 4.93 (*d*, *J* = 11.2, PhC*H*); 4.93 (*d*, *J* = 6.5, MeOC*H*); 4.90 (*d*, *J* = 6.5, MeOC*H*); 4.86 (*d*, *J* = 6.4, MeOC*H*); 4.83–4.62 (*m*, 19 H); 4.61 (*d*, *J* = 6.2, MeOC*H*); 4.52 (*d*, *J* = 6.5, MeOC*H*); 4.51 (*d*, *J* = 12.0, PhC*H*); 4.49 (*d*, *J* = 6.2, MeOC*H*); 4.47 (*d*, *J* = 12.0, PhC*H*); 4.46 (*d*, *J* = 6.5, MeOC*H*); 4.44 (*d*, *J* = 7.7, H–C(1^{IV})); 4.42 (*d*, *J* = 12.0, PhC*H*); 4.41 (*d*, *J* = 7.8, H–C(1^{VIII})); 4.28 (*d*, *J* = 7.9, H–C(1^{VI})); 4.23 (*d*, *J* = 7.9, H–C(1^{II})); 4.17 (*dd*, *J* = 12.0, 2.5, 1 H); 4.01 (br. *d*, *J* ≈ 9.5, H–C(5^{VII}), H–C(5^{V})); 3.99 (*d*, *J* = 9.6, H–C(3^{I}), H–C(5^{III})); 4.10–3.91 (*m*, addn. of D_2O → signal changed, 6 H); 3.76–3.66 (*m*, addn. of D_2O → signal changed, 8 H); 3.61–3.52 (*m*, addn. of D_2O → 3.59, *dd*, *J* ≈ 11.5, 2.0, H–C(6^{VI}), → 3.78, br. *t*, *J* ≈ 9.0, 1 H, → 3.55, *t*, *J* ≈ 8.8, 1 H, → 3.54, br. *t*, *J* ≈ 9.0, 2 H, → 3.53, *t*, *J* ≈ 8.9, 1 H); 3.49 (*s*, MeO); 3.44 (*s*, MeO); 3.37 (*s*, MeO); 3.35 (*s*, MeO); 3.29 (*s*, MeO); 3.25 (*s*, MeO); 3.48 (*dd*, *J* = 10.4, 9.1, H–C(3^{VII})); 3.23 (*dd*, *J* = 9.1, 7.9, H–C(3^{VI})); 3.18 (*ddd*, *J* = 10.1, 4.3, 2.2, H–C(7^{I})); 3.16 (*dd*, *J* = 9.1, 7.9, H–C(2^{VIII})); 3.11 (*ddd*, *J* = 10.5, 5.5, 2.5, H–C(5^{VIII})); 3.44–3.20 (*m*, addn. of D_2O → signal changed, 12 H); 2.81 (*t*, *J* ≈ 10.6, H–C(4^{VIII})); 2.74 (*t*, *J* ≈ 10.4, H–C(4^{IV})); 2.63 (*t*, *J* ≈ 10.5, H–C(4^{II})); 2.60 (br. *s*, exchanged with D_2O, HO–C(3^{VI})); 2.52 (*t*, *J* ≈ 10.4, H–C(4^{VI})); 2.00 (*s*, Ac); 1.95 (*s*, Ac); 1.90 (*s*, Ac); 1.62 (br. *s*, exchanged with D_2O, HO–C(6^{VI})); 0.34 (*s*, Me_3Ge); 0.17 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.41 (*s*, C=O); 169.59 (*s*, C=O); 169.44 (*s*, C=O); 139.16–137.40 (several *s*); 128.72–126.86 (several *d*); 102.32 (*s*, *C*≡CGe); 102.10 (*d*, C(1^{VI})); 101.93 (*s*, *C*≡CSi); 101.64 (*d*, C(1^{VIII})); 101.52 (*d*, C(1^{IV})); 99.71 (*d*, C(1^{II})); 97.68 (*t*, 2 MeO*C*H$_2$); 97.63 (*t*, MeO*C*H$_2$); 97.56 (*t*, MeO*C*H$_2$); 96.59 (*t*, 2 MeO*C*H$_2$); 91.23 (*s*, C≡*C*Si); 88.72 (*s*, C≡*C*Ge); 84.20 (*d*); 84.05 (*d*); 83.92 (*d*); 83.83 (*d*); 81.81 (*d*); 81.62 (*d*); 81.03 (*d*); 80.88 (*d*); 79.43 (*d*); 79.34 (*d*); 78.93 (2*d*); 78.86 (*d*); 78.76 (*d*); 78.62 (*d*); 78.47 (*d*); 77.89 (*s*); 76.41 (*d*); 76.35 (*d*); 76.28 (*s*); 75.61 (*t*, Ph*C*H$_2$); 75.57 (*t*, 2 Ph*C*H$_2$); 75.49 (*d*); 75.38 (*d*); 75.33 (*t*, Ph*C*H$_2$); 75.26 (*t*, Ph*C*H$_2$); 75.07 (*d*); 74.98 (*d*); 74.67 (*d*); 74.40 (*d*); 74.25 (*t*, Ph*C*H$_2$); 74.06 (*s*); 73.96 (*s*); 73.81 (*t*, Ph*C*H$_2$); 73.69 (*t*, 2 Ph*C*H$_2$); 73.60 (*t*, Ph*C*H$_2$); 73.55 (*t*, 2 Ph*C*H$_2$); 72.39 (2*d*); 72.16 (*d*); 70.61 (*s*); 70.42 (*d*); 70.34 (*d*); 70.30 (2*d*); 70.12 (*s*); 69.86 (*s*); 68.65 (*s*); 68.52 (*s*); 68.22 (*t*); 67.99 (*t*); 67.90 (*t*); 67.67 (*t*); 67.27 (*t*); 67.13 (*t*); 63.78 (*t*); 62.80 (*t*); 56.61 (*q*, MeO); 56.43 (*q*, MeO); 56.34 (*q*, 2 MeO); 55.20 (*q*, 2 MeO); 37.97 (*d*, C(4^{VIII})); 37.58 (*d*, C(4^{VI})); 37.52 (*d*, C(4^{IV})); 36.32 (*d*, C(4^{II})); 20.73 (*q*, Me); 20.59 (*q*, Me); 20.57 (*q*, Me); −0.30 (*q*, Me_3Si, Me_3Ge); 2*s* for C≡C not observed or hidden. MALDI-TOF-MS: 3112 ($[M + Na]^+$). Anal. calc. for $C_{172}H_{200}GeO_{45}Si$ (3088.15): C 66.88, H 6.56; found: C 66.67, H 6.76.

Data of **12**: R_f (hexane/AcOEt 1:2) 0.68. IR (CCl_4): 3089*m*, 3066*m*, 3032*m*, 2895*s* (br.), 2183*w*, 1947*w*, 1759*s*, 1605*w*, 1497*m*, 1454*s*, 1366*s*, 1292*m*, 1230*s*, 1153*s*, 1116*s*, 1053*s*. MALDI-TOF-MS: $C_{178}H_{208}O_{48}Si_2$ (3171.78): 3195 ($[M + Na]^+$).

Data of **13**: R_f (toluene/AcOEt 1:2) 0.42. IR (CCl_4): 3590*m*, 3432*m*, 3090*w*, 3065*m*, 3030*m*, 2905*s*, 2825*m*, 2232*w*, 1945*w*, 1865*w*, 1605*w*, 1555*w*, 1542*w*, 1495*m*, 1454*s*, 1360*s*, 1295*m*, 1240*m*, 1155*s*, 1065*s*. MALDI-TOF-MS: $C_{166}H_{194}Ge_2O_{42}$ (3006.55): 3029 ($[M + Na]^+$).

*4-Deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**11**), *4-*C*,4′-*C*-(Buta-1,3-diyne-1,4-diyl)-bis[4-deoxy-2,3,6-tris-*O*-(methoxymethyl)-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol]* (**12**), *and 4-Deoxy-2,3,6-tris-*O*-(methoxymethyl)-4-*C*-[(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetra-deoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 3)-[4-deoxy-2,3,6-tris-*O*-(methoxymethyl)-4-*C*-[2-(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 14)]-1,4,5,12,13,16-hexa-*O*-benzyl-7,8,9,10-tetradeoxy-*D*-erythro-*L*-galacto-*L*-gulo-hexadeca-7,9-diynitol* (**13**). A degassed soln. of **9** (85.4 mg, 56.7 μmol), **10** (94.5 mg, 56.73 μmol), $[Pd_2(dba)_3]$ (1.56 mg, 3 mol-%), and CuI (0.32 mg, 3 mol-%) in DMSO (2 ml) was treated at r.t. with 1,2,2,6,6-pentamethylpiperidine (0.05 ml), stirred for 2.5 h, poured into ice-cold sat. NH_4Cl soln. (5 ml) and worked up (CH_2Cl_2). FC (hexane/AcOEt 2 : 1) gave **11** (105.2 mg, 60%), **12** (4.1 mg, 2%), and **13** (2.1 mg, 3%) as colourless oils.

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Data of **12**: R_f (hexane/AcOEt 1:2) 0.68. IR (CCl_4): 3089*m*, 3066*m*, 3032*m*, 2895*s* (br.), 2183*w*, 1947*w*, 1759*s*, 1605*w*, 1497*m*, 1454*s*, 1366*s*, 1292*m*, 1230*s*, 1153*s*, 1116*s*, 1053*s*. MALDI-TOF-MS: $C_{178}H_{208}O_{48}Si_2$ (3171.78): 3195 ($[M + Na]^+$).

Data of **13**: R_f (toluene/AcOEt 1:2) 0.42. IR (CCl_4): 3590*m*, 3432*m*, 3090*w*, 3065*m*, 3030*m*, 2905*s*, 2825*m*, 2232*w*, 1945*w*, 1865*w*, 1605*w*, 1555*w*, 1542*w*, 1495*m*, 1454*s*, 1360*s*, 1295*m*, 1240*m*, 1155*s*, 1065*s*. MALDI-TOF-MS: $C_{166}H_{194}Ge_2O_{42}$ (3006.55): 3029 ($[M + Na]^+$).

*4-Deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**11**), *4-*C*,4′-*C*-(Buta-1,3-diyne-1,4-diyl)-bis[4-deoxy-2,3,6-tris-*O*-(methoxymethyl)-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri-*O*-benzyl-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol]* (**12**), *and 4-Deoxy-2,3,6-tris-*O*-(methoxymethyl)-4-*C*-[(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetra-deoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 3)-[4-deoxy-2,3,6-tris-*O*-(methoxymethyl)-4-*C*-[2-(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri-*O*-benzyl-1,2,3,4-tetradeoxy-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 14)]-1,4,5,12,13,16-hexa-*O*-benzyl-7,8,9,10-tetradeoxy-*D*-erythro-*L*-galacto-*L*-gulo-hexadeca-7,9-diynitol* (**13**). A degassed soln. of **9** (85.4 mg, 56.7 μmol), **10** (94.5 mg, 56.73 μmol), $[Pd_2(dba)_3]$ (1.56 mg, 3 mol-%), and CuI (0.32 mg, 3 mol-%) in DMSO (2 ml) was treated at r.t. with 1,2,2,6,6-pentamethylpiperidine (0.05 ml), stirred for 2.5 h, poured into ice-cold sat. NH_4Cl soln. (5 ml) and worked up (CH_2Cl_2). FC (hexane/AcOEt 2 : 1) gave **11** (105.2 mg, 60%), **12** (4.1 mg, 2%), and **13** (2.1 mg, 3%) as colourless oils.

Data of **11**: R_f (hexane/AcOEt 1:2) 0.26. $[\alpha]_D^{25} = -13.5$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3706*m*, 3596*m*, 3427*w* (br.), 3064*m*, 3032*m*, 2892*s* (br.), 2257*w*, 2170*w*, 1947*w*, 1873*w*, 1758*s*, 1691*w*, 1658*w*, 1640*w*, 1586*m*, 1552*m*, 1513*w*, 1497*m*, 1454*m*, 1365*s*, 1292*s*, 1230*s*, 1154*s*, 1055*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.40–7.20 (*m*, 60 arom. H); 5.04 (*d*, *J* = 11.2, PhC*H*); 5.01 (*d*, *J* = 11.3, PhC*H*); 4.96 (*d*, *J* = 11.5, PhC*H*); 4.95 (*d*, *J* = 11.8, PhC*H*); 4.93 (*d*, *J* = 11.2, PhC*H*); 4.93 (*d*, *J* = 6.5, MeOC*H*); 4.90 (*d*, *J* = 6.5, MeOC*H*); 4.86 (*d*, *J* = 6.4, MeOC*H*); 4.83–4.62 (*m*, 19 H); 4.61 (*d*, *J* = 6.2, MeOC*H*); 4.52 (*d*, *J* = 6.5, MeOC*H*); 4.51 (*d*, *J* = 12.0, PhC*H*); 4.49 (*d*, *J* = 6.2, MeOC*H*); 4.47 (*d*, *J* = 12.0, PhC*H*); 4.46 (*d*, *J* = 6.5, MeOC*H*); 4.44 (*d*, *J* = 7.7, H–C(1^{IV})); 4.42 (*d*, *J* = 12.0, PhC*H*); 4.41 (*d*, *J* = 7.8, H–C(1^{VIII})); 4.28 (*d*, *J* = 7.9, H–C(1^{VI})); 4.23 (*d*, *J* = 7.9, H–C(1^{II})); 4.17 (*dd*, *J* = 12.0, 2.5, 1 H); 4.01 (br. *d*, *J* ≈ 9.5, H–C(5^{VII}), H–C(5^{V})); 3.99 (*d*, *J* = 9.6, H–C(3^{I}), H–C(5^{III})); 4.10–3.91 (*m*, addn. of D_2O → signal changed, 6 H); 3.76–3.66 (*m*, addn. of D_2O → signal changed, 8 H); 3.61–3.52 (*m*, addn. of D_2O → 3.59, *dd*, *J* ≈ 11.5, 2.0, H–C(6^{VI}), → 3.78, br. *t*, *J* ≈ 9.0, 1 H, → 3.55, *t*, *J* ≈ 8.8, 1 H, → 3.54, br. *t*, *J* ≈ 9.0, 2 H, → 3.53, *t*, *J* ≈ 8.9, 1 H); 3.49 (*s*, MeO); 3.44 (*s*, MeO); 3.37 (*s*, MeO); 3.35 (*s*, MeO); 3.29 (*s*, MeO); 3.25 (*s*, MeO); 3.48 (*dd*, *J* = 10.4, 9.1, H–C(3^{VII})); 3.23 (*dd*, *J* = 9.1, 7.9, H–C(3^{VI})); 3.18 (*ddd*, *J* = 10.1, 4.3, 2.2, H–C(7^{I})); 3.16 (*dd*, *J* = 9.1, 7.9, H–C(2^{VIII})); 3.11 (*ddd*, *J* = 10.5, 5.5, 2.5, H–C(5^{VIII})); 3.44–3.20 (*m*, addn. of D_2O → signal changed, 12 H); 2.81 (*t*, *J* ≈ 10.6, H–C(4^{VIII})); 2.74 (*t*, *J* ≈ 10.4, H–C(4^{IV})); 2.63 (*t*, *J* ≈ 10.5, H–C(4^{II})); 2.60 (br. *s*, exchanged with D_2O, HO–C(3^{VI})); 2.52 (*t*, *J* ≈ 10.4, H–C(4^{VI})); 2.00 (*s*, Ac); 1.95 (*s*, Ac); 1.90 (*s*, Ac); 1.62 (br. *s*, exchanged with D_2O, HO–C(6^{VI})); 0.34 (*s*, Me_3Ge); 0.17 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.41 (*s*, C=O); 169.59 (*s*, C=O); 169.44 (*s*, C=O); 139.16–137.40 (several *s*); 128.72–126.86 (several *d*); 102.32 (*s*, *C*≡CGe); 102.10 (*d*, C(1^{VI})); 101.93 (*s*, *C*≡CSi); 101.64 (*d*, C(1^{VIII})); 101.52 (*d*, C(1^{IV})); 99.71 (*d*, C(1^{II})); 97.68 (*t*, 2 MeO*C*H$_2$); 97.63 (*t*, MeO*C*H$_2$); 97.56 (*t*, MeO*C*H$_2$); 96.59 (*t*, 2 MeO*C*H$_2$); 91.23 (*s*, C≡*C*Si); 88.72 (*s*, C≡*C*Ge); 84.20 (*d*); 84.05 (*d*); 83.92 (*d*); 83.83 (*d*); 81.81 (*d*); 81.62 (*d*); 81.03 (*d*); 80.88 (*d*); 79.43 (*d*); 79.34 (*d*); 78.93 (2*d*); 78.86 (*d*); 78.76 (*d*); 78.62 (*d*); 78.47 (*d*); 77.89 (*s*); 76.41 (*d*); 76.35 (*d*); 76.28 (*s*); 75.61 (*t*, Ph*C*H$_2$); 75.57 (*t*, 2 Ph*C*H$_2$); 75.49 (*d*); 75.38 (*d*); 75.33 (*t*, Ph*C*H$_2$); 75.26 (*t*, Ph*C*H$_2$); 75.07 (*d*); 74.98 (*d*); 74.67 (*d*); 74.40 (*d*); 74.25 (*t*, Ph*C*H$_2$); 74.06 (*s*); 73.96 (*s*); 73.81 (*t*, Ph*C*H$_2$); 73.69 (*t*, 2 Ph*C*H$_2$); 73.60 (*t*, Ph*C*H$_2$); 73.55 (*t*, 2 Ph*C*H$_2$); 72.39 (2*d*); 72.16 (*d*); 70.61 (*s*); 70.42 (*d*); 70.34 (*d*); 70.30 (2*d*); 70.12 (*s*); 69.86 (*s*); 68.65 (*s*); 68.52 (*s*); 68.22 (*t*); 67.99 (*t*); 67.90 (*t*); 67.67 (*t*); 67.27 (*t*); 67.13 (*t*); 63.78 (*t*); 62.80 (*t*); 56.61 (*q*, MeO); 56.43 (*q*, MeO); 56.34 (*q*, 2 MeO); 55.20 (*q*, 2 MeO); 37.97 (*d*, C(4^{VIII})); 37.58 (*d*, C(4^{VI})); 37.52 (*d*, C(4^{IV})); 36.32 (*d*, C(4^{II})); 20.73 (*q*, Me); 20.59 (*q*, Me); 20.57 (*q*, Me); −0.30 (*q*, Me_3Si, Me_3Ge); 2*s* for C≡C not observed or hidden. MALDI-TOF-MS: 3112 ($[M + Na]^+$). Anal. calc. for $C_{172}H_{200}GeO_{45}Si$ (3088.15): C 66.88, H 6.56; found: C 66.67, H 6.76.

Data of **12**: R_f (hexane/AcOEt 1:2) 0.68. IR (CCl_4): 3089*m*, 3066*m*, 3032*m*, 2895*s* (br.), 2183*w*, 1947*w*, 1759*s*, 1605*w*, 1497*m*, 1454*s*, 1366*s*, 1292*m*, 1230*s*, 1153*s*, 1116*s*, 1053*s*. MALDI-TOF-MS: $C_{178}H_{208}O_{48}Si_2$ (3171.78): 3195 ($[M + Na]^+$).

Data of **13**: R_f (toluene/AcOEt 1:2) 0.42. IR (CCl_4): 3590*m*, 3432*m*, 3090*w*, 3065*m*, 3030*m*, 2905*s*, 2825*m*, 2232*w*, 1945*w*, 1865*w*, 1605*w*, 1555*w*, 1542*w*, 1495*m*, 1454*s*, 1360*s*, 1295*m*, 1240*m*, 1155*s*, 1065*s*. MALDI-TOF-MS: $C_{166}H_{194}Ge_2O_{42}$ (3006.55): 3029 ($[M + Na]^+$).

O-*acetyl-4-deoxy-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri*-O-*benzyl-1,2-dideoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**14**). A soln. of **11** (68 mg, 19.4 μmol) in THF (1 ml) and 1M aq. HCl in MeOH (0.5 ml) was stirred for 40 h at 40°, neutralized with *Amberlite IRA-900* (HO^- form), filtered, and evaporated. FC (toluene/AcOEt 1:4 → 1:7) gave **14** (39 mg, 74%) as a colourless oil. R_f (AcOEt) 0.72. IR ($CHCl_3$): 3570*s* (br.), 3311*m*, 3062*m*, 3032*m*, 2942*s*, 2890*m*, 1755*s*, 1615*m*, 1521*w*, 1446*m*, 1366*m*, 1301*m*, 1260*s*, 1175*w*, 1072*s*, 912*w*. ^{1}H-NMR (200 MHz, CD_3OD): 7.40–7.21 (*m*, 60 arom. H); 5.05–4.38 (*m*, 30 H); 4.05 (*d*, $J \approx 9.5$, 2 H); 4.00–3.68 (*m*, 19 H); 3.62–3.20 (*m*, 25 H); 2.81 (*t*, $J \approx 10.4$, H–C(4^{II}), H–C(4^{IV}), H–C(4^{VI})); 2.64 (*td*, $J \approx 10.4, 2.0$, H–C(4^{VIII})); 2.15 (*d*, $J = 2.1$, *H*C≡C); 2.02 (*s*, Ac); 2.01 (*s*, Ac); 1.99 (*s*, Ac); 0.18 (*s*, Me_3Si). MALDI-TOF-MS for $C_{157}H_{168}O_{39}Si$ (2707.15): 2730 ($[M+Na]^+$).

4-Deoxy-4-C-*ethynyl-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-6,7,10-tri*-O-*benzyl-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-4-deoxy-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri*-O-*benzyl-1,2-dideoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**15**) *and 8*-O-*Acetyl-5,9-anhydro-6,7,10-tri*-O-*benzyl-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-2,3,6-tri*-O-*acetyl-4-deoxy-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-4,5,8-tri*-O-*benzyl-1,2-dideoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**17**). A soln. of **6** (22.1 mg, 14.0 μmol) in THF (1 ml) and 1M aq. HCl in MeOH (0.5 ml) was stirred for 36 h at 40°, neutralized with *Amberlite IRA-900* (HO^- form), filtered, and evaporated. FC (toluene/AcOEt 1:2) gave **15** (14.1 mg, 76%) as a colourless oil. In an analogous reaction, **6** (18 mg, 11.4 μmol) was stirred for 4 h at 40° and 1 h at 60–70°. Workup and chromatography gave **15** (9.5 mg, 63%) and a mixture of the combined other fractions which was acetylated in pyridine (0.5 ml) and Ac_2O (0.5 ml) for 12 h. Evaporation, co-distillation with toluene, and FC (hexane/AcOEt 3:1 → 2:1) gave **17** (1.8 mg, 12%) as a colourless oil.

Data of **15**: R_f (toluene/AcOEt 1:2) 0.23. IR ($CHCl_3$): 3595*m*, 3410*m* (br.), 3307*m*, 3008*m*, 2960*s*, 2910*m*, 2879*m*, 2840*w*, 2181*w*, 1613*m*, 1514*m*, 1442*m*, 1366*m*, 1301*m*, 1251*s*, 1173*m*, 1075*s*, 1035*s*, 912*w*, 845*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.20 (*m*, 30 arom. H); 5.02 (*d*, $J = 10.6$, PhC*H*); 4.94–4.79 (*m*, 6 PhC*H*); 4.71 (*d*, $J = 11.9$, PhC*H*); 4.68 (*d*, $J = 12.1$, PhC*H*); 4.60–4.53 (*m*, 3 PhC*H*); 4.41 (*d*, $J = 7.6$, H–C(1′)); 4.40 (*d*, $J = 7.8$, H–C(1‴)); 4.11 (br. *d*, $J \approx 9.0$, H–C(5″)); 4.06 (br. *d*, $J \approx 9.0$, H–C(3)); 3.99–3.89 (*m*, 3 H); 3.80–3.70 (*m*, 3 H); 3.70–3.51 (*m*, 7 H); 3.50–3.22 (*m*, 7 H); 3.21–3.11 (*m*, 3 H); 2.53 (*t*, $J \approx 10.5$, H–C(4′)); 2.41 (*td*, $J \approx 10.5$, 2.2, H–C(4‴)); 2.37–2.30 (*m*, OH); 2.22 (*d*, $J = 2.2$, H–C≡C); 2.20 (br. *d*, OH); 1.86–1.80 (*m*, OH); 1.68–1.62 (*m*, OH); 0.21 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.56 (*s*); 138.48 (*s*); 137.86 (*s*); 137.57 (*s*); 137.54 (*s*); 137.49 (*s*); 128.01–127.13 (several *d*); 102.21 (*s*, *C*≡CSi); 101.95 (2*d*, H–C(1′), H–C(1‴)); 91.45 (*s*, C≡CSi); 80.01 (2*d*); 81.77 (*d*); 81.30 (*d*); 80.04 (*d*, C≡CH); 78.86 (*d*); 78.68 (*d*); 76.26 (*d*); 76.14 (*s*); 75.50 (*d*); 75.37 (*t*, 2 PhCH); 75.25 (*t*, 2 Ph*C*H$_2$); 75.04 (*d*); 74.62 (*d*); 74.51 (*d*); 74.36 (*d*); 74.12 (*d*); 73.61 (*s*); 73.54 (*t*, Ph*C*H$_2$); 73.47 (*t*, Ph*C*H$_2$); 72.73 (*s*, *C*≡CH); 70.40 (*d*); 70.22 (*d*); 70.11 (*d*); 68.09 (*t*); 68.05 (*t*); 62.73 (*t*); 61.62 (*t*); 37.41 (*d*, C(4′)); 36.77 (*d*, C(4‴)); −0.57 (*q*, Me_3Si); 2*s* for C≡C not observed or hidden. FAB-MS (NOBA): $C_{77}H_{86}O_{18}Si$ (1327.6): 1350.5 (3, $[M+Na]^+$), 1327.5 (2, M^+), 181 (51), 91 (100).

Data of **17**: R_f (hexane/AcOEt 2:1) 0.10. IR ($CHCl_3$): 3307*m*, 3008*m*, 2959*m*, 2910*m*, 2876*m*, 2839*w*, 2182*w*, 1739*s*, 1613*m*, 1581*m*, 1514*m*, 1465*m*, 1367*m*, 1301*m*, 1251*s*, 1173*m*, 1087*s*, 1055*s*, 1035*s*, 907*w*, 845*s*. ^{1}H-NMR (500 MHz, C_6D_6, assignment based on H,H-COSY): 7.42–7.05 (*m*, 30 arom. H); 5.29 (*dd*, $J = 9.5$, 8.3, H–C(8″)); 5.27 (*t*, $J \approx 9.5$, H–C(3′)); 5.10 (*d*, $J = 10.5$, PhC*H*); 5.00 (*dd*, $J = 9.1$, 7.8, H–C(2′)); 4.97 (*d*, $J = 11.0$, PhC*H*); 4.87 (*d*, $J = 11.0$, PhC*H*); 4.76 (*d*, $J = 10.5$, PhC*H*); 4.73 (*d*, $J = 12.0$, PhC*H*); 4.70 (*d*, $J = 12.0$, PhC*H*); 4.66 (*d*, $J = 7.9$, H–C(1′)); 4.63 (*d*, $J = 11.0$, PhC*H*); 4.59 (*d*, $J = 12.0$, PhC*H*); 4.54 (*d*, $J = 12.1$, PhC*H*); 4.33 (*d*, $J = 12.1$, PhC*H*); 4.30 (*d*, $J = 12.1$, PhC*H*); 4.23 (*d*, $J = 12.0$, PhC*H*); 4.20 (*dd*, $J = 12.0$, 2.7, H_a–C(6′)); 4.14 (*dd*, $J = 12.0$, 4.7, H_b–C(6′)); 4.12 (*t*, $J \approx 9.5$, H–C(6)); 3.99 (*d*, $J = 9.4$, H–C(3)); 3.87 (*dd*, $J = 9.3$, 0.5, H–C(5″)); 3.74 (*dd*, $J = 11.0$, 3.0, H_a–C(8)); 3.59 (*t*, $J \approx 9.5$, H–C(4)); 3.58 (*dd*, $J = 10.9$, 1.2, H_b–C(8)); 3.54 (*dd*, $J = 11.5$, 3.5, H_a–C(10″)); 3.46 (*dd*, $J = 10.9$, 5.0, H_b–C(10″)); 3.44 (*t*, $J \approx 9.3$, H–C(6″)); 3.40 (*t*, $J \approx 9.2$, H–C(5)); 3.33 (*t*, $J \approx 9.0$, H–C(7″)); 3.23 (*ddd*, $J = 9.7$, 5.0, 3.5, H–C(9″)); 3.08 (*ddd*, $J = 10.5$, 4.6, 2.6, H–C(5′)); 2.97 (*ddd*, $J = 10.0$, 3.0, 1.2, H–C(7)); 2.72 (*t*, $J \approx 10.5$, H–C(4′)); 1.74 (*s*, Ac); 1.73 (*s*, Ac); 1.57 (*s*, Ac); 1.54 (*s*, Ac); 0.11 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, C_6D_6): 169.81 (*s*, C=O); 169.48 (*s*, C=O); 169.02 (*s*, C=O); 168.93 (*s*, C=O); 140.05 (*s*); 139.10 (2*s*); 138.63 (*s*); 138.58 (*s*); 138.42 (*s*); 128.98–127.46 (several *d*); 103.99 (*s*, *C*≡CSi); 100.43 (*d*, C(1′)); 90.64 (*s*, C≡*C*Si); 84.03 (*d*); 83.53 (*d*); 82.36 (*d*); 81.78 (*d*); 79.27 (*d*); 77.94 (*d*); 77.13 (*d*); 75.89 (*s*); 75.60 (*t*, Ph*C*H$_2$); 75.56 (*t*, Ph*C*H$_2$); 75.27 (*s*); 75.12 (*t*, Ph*C*H$_2$); 74.98 (*t*, Ph*C*H$_2$); 73.91 (*t*, Ph*C*H$_2$); 73.78 (*t*, Ph*C*H$_2$); 72.87 (2*d*); 72.58 (*d*); 70.87 (*d*); 70.75 (*d*); 70.44 (*d*); 70.37 (*s*); 70.09 (*t*); 68.99 (*s*); 68.29 (*t*); 63.86 (*t*); 36.92 (*d*); 20.49 (*q*, Me); 20.45 (*q*, Me); 20.21 (*q*, Me); 20.19 (*q*, Me); −0.30 (*q*, Me_3Si). FAB-MS (NOBA): $C_{77}H_{84}O_{18}Si$ (1324.5): 1347 (14, $[M+Na]^+$), 1324 (9, M^+), 181 (12), 91 (100).

2,3,6-Tri-O-*acetyl-4-deoxy-4*-C-*ethynyl-β*-D-*glucopyranosyl-(1 → 8)-6,7,10-tri*-O-*acetyl-5,9-anhydro-1,2,3,4-tetradeoxy*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-2,3,6-tri*-O-*acetyl-4-deoxy-β*-D-*glucopyranosyl-*

*(1 → 6)-4,5,8-tri-*O*-acetyl-3,7-anhydro-1,2-dideoxy-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**16**). A soln. of **15** (16.2 mg, 12.2 μmol) in Ac_2O (1 ml) was treated at 0° dropwise with Me_3SiOTf (0.1 ml), stirred for 12 h at +4°, poured into ice-cold sat. $NaHCO_3$ soln. (5 ml), stirred for 1 h, and worked up (AcOEt). FC (hexane/AcOEt 2:1 → 1:1 → 1:2) gave **16** (8.1 mg, 51%) as a white solid. R_f (hexane/AcOEt 1:1) 0.18. M.p. 260–262°. $[\alpha]_D^{25} = -9.4$ ($c = 0.8$, $CHCl_3$). IR (CCl_4): 3307*m*, 2956*m*, 2860*m*, 2122*w*, 1755*s*, 1601*w*, 1430*m*, 1386*s*, 1302*m*, 1248*s*, 1167*m*, 1050*s*, 975*w*, 951*w*, 901*w*, 848*m*. ^{1}H-NMR (500 MHz, C_6D_6, assignment based on H,H-COSY): 5.36 (*t*, $J \approx 9.7$, H–C(4)); 5.33 (*dd*, $J = 10.9, 9.3$, H–C(3′)); 5.26 (*t*, $J \approx 9.7$, H–C(6″)); 5.234 (*dd*, $J = 10.9, 9.3$, H–C(3‴)); 5.23 (*t*, $J \approx 9.3$, H–C(5)); 5.19 (*t*, $J \approx 9.3$, H–C(7″)); 4.95 (*dd*, $J = 9.3, 7.9$, H–C(2′)); 4.90 (*dd*, $J = 9.3, 7.9$, H–C(2‴)); 4.44 (*dd*, $J = 11.8, 1.8$, H_a–C(8)); 4.42 (*dd*, $J = 11.8, 1.7$, H_a–C(10″)); 4.29 (*dd*, $J = 12.2, 2.3$, H_a–C(6‴)); 4.23 (*dd*, $J = 12.1, 5.2$, H_b–C(6‴)); 4.17 (*d*, $J = 7.9$, H–C(1′)); 4.13 (*d*, $J = 8.0$, H–C(1‴)); 4.12 (*d*, $J = 4.6$, 2 H–C(6′)); 4.02 (*dd*, $J = 11.7, 6.5$, H_b–C(8)); 4.00 (*dd*, $J = 11.6, 6.5$, H_b–C(10″)); 3.92 (*d*, $J = 9.9$, H–C(3)); 3.85 (*dd*, $J = 9.8, 0.6$, H–C(5″)); 3.43 (*t*, $J \approx 9.5$, H–C(6)); 3.40 (*t*, $J \approx 9.4$, H–C(8″)); 3.26 (*ddd*, $J = 10.5, 5.1, 2.2$, H–C(5‴)); 3.08 (*dt*, $J \approx 10.3, 3.9$, H–C(5′)); 3.06 (*ddd*, $J = 10.1, 6.5, 2.0$, H–C(7)); 3.04 (*ddd*, $J = 10.2, 6.6, 1.9$, H–C(9″)); 2.57 (*td*, $J \approx 10.5, 2.4$, H–C(4‴)); 2.56 (*t*, $J \approx 10.5$, H–C(4′)); 1.95 (*s*, Ac); 1.92 (*s*, Ac); 1.88 (*s*, Ac); 1.87 (*s*, Ac); 1.86 (*s*, Ac); 1.83 (*s*, Ac); 1.78 (*s*, Ac); 1.77 (*s*, Ac); 1.68 (*d*, $J = 2.4$, H–C≡C); 1.67 (*s*, Ac); 1.66 (*s*, Ac); 1.62 (*s*, Ac); 1.60 (*s*, Ac); 0.06 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, C_6D_6): 170.06 (*s*, C=O); 170.03 (*s*, C=O); 169.87 (*s*, C=O); 169.76 (*s*, C=O); 169.51 (*s*, C=O); 169.49 (*s*, C=O); 169.34 (*s*, C=O); 169.33 (*s*, C=O); 169.22 (*s*, C=O); 169.19 (*s*, C=O); 169.12 (*s*, C=O); 169.03 (*s*, C=O); 101.41 (*d*, C(1′)); 101.32 (*d*, C(1‴)); 100.57 (*s*, *C*≡CSi); 92.32 (*s*, C≡*C*Si); 78.29 (*d*, C≡*C*H); 77.29 (*d*); 77.05 (*d*); 77.01 (*d*); 76.90 (*d*); 75.79 (*s*); 73.61 (2*d*); 73.45 (*s*); 73.35 (*s*, *C*≡CH); 73.00 (2*d*); 72.67 (*d*); 72.52 (*d*); 72.43 (*d*); 72.37 (*d*); 72.31 (*d*); 71.77 (*d*); 70.87 (*s*); 69.12 (*d*); 68.85 (*d*); 68.76 (*s*); 63.90 (*t*); 63.81 (*t*); 62.97 (*t*); 62.83 (*t*); 36.57 (*d*, C(4′)); 35.66 (*d*, C(4‴)); 20.60 (*q*, Me); 20.49 (*q*, Me); 20.43 (*q*, Me); 20.38 (*q*, Me); 20.35 (*q*, Me); 20.25 (*q*, Me); 20.22 (*q*, 3 Me); 20.18 (*q*, Me); 20.17 (*q*, Me); 20.10 (*q*, Me); −0.53 (*q*, Me_3Si). FAB-MS (NOBA): 1291 (21, $[M+1]^+$), 977 (12), 905 (100, $[M-\text{aglycone}]^+$), 845 (17), 369 (29), 297 (48), 237 (14), 195 (78), 154 (92). Anal. calc. for $C_{59}H_{73}O_{30}Si$ (1290.29): C 54.92, H 5.70; found: 54.74, H 5.66.

*4-Deoxy-4-*C*-ethynyl-β-D-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-D-glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-*D-glycero-D-gulo-*oct-1-ynitol* (**18**). A soln. of **16** (12.3 mg, 9.5 μmol) in MeOH (2 ml) was treated with 0.1M NaOMe in MeOH (0.2 ml) stirred for 3 h at r.t., neutralized with *Amberlite IR-120* (H^+ form), filtered, and evaporated. Drying for 24 h under h.v. gave **18** (6.8 mg, quant.) as a colourless oil. R_f (AcOEt/MeOH/H_2O 10:3:2) 0.39. IR (KBr): 3415*s* (br.), 2915*w*, 2126*w*, 1638*m*, 1425*m*, 1371*m*, 1305*m*, 1160*m*, 1090*s*, 1040*s*. ^{1}H-NMR (300 MHz, CD_3OD): 4.41 (*d*, $J = 7.8$, H–C(1′)); 4.40 (*d*, $J = 7.8$, H–C(1‴)); 4.03 (*d*, $J = 9.5$, H–C(5‴)); 3.93 (*dd*, $J = 9.5$, 2.0, H–C(3)); 3.92 (*dd*, $J \approx 11.5$, 3.0, H_a–C(6′)); 3.90–3.84 (*m*, H_a–C(8), H_a–C(6‴), H_a–C(10″)); 3.82 (*dd*, $J \approx 12.0, 3.8$, H_b–C(8)); 3.72 (*dd*, $J = 11.5, 6.0$, H_b–C(6′)); 3.70 (*dd*, $J = 11.2, 5.2$, H_b–C(6‴)); 3.61 (*dd*, $J \approx 11.0, 2.0$, H_b–C(10″)); 3.56 (br. *t*, $J \approx 9.5$, H–C(5)); 3.54 (br. *t*, $J \approx 9.4$, H–C(7″)); 3.53 (br. *t*, $J \approx 9.3$, H–C(3′), H–C(3‴)); 3.45 (*t*, $J \approx 10.6$, H–C(6), H–C(8″)); 3.39–3.37 (*m*, H–C(7), H–C(5′), H–C(5‴), H–C(9″)); 3.36 (br. *t*, $J \approx 9.5$, H–C(4), H–C(6″)); 3.14 (*t*, $J \approx 10.5$, H–C(2′), H–C(2‴)); 2.88 (*d*, $J = 2.0$, HC≡C–C(3)); 2.63 (*t*, $J \approx 10.5$, H–C(4′)); 2.56 (*d*, $J = 2.1$, HC≡C–C(4‴)); 2.47 (*td*, $J \approx 10.4$, 2.1, H–C(4‴)). ^{1}H-NMR (500 MHz, (D_6)DMSO, assignment based on H,H-COSY): 5.64 (*d*, $J = 6.0$, exchanged with D_2O, HO–C(6″)); 5.52 (*d*, $J = 6.1$, exchanged with D_2O, HO–C(3′)); 5.47 (*d*, $J = 6.0$, exchanged with D_2O, HO–C(4)); 5.42 (*d*, $J = 4.9$, exchanged with D_2O, HO–C(2′)); 5.34 (*d*, $J = 4.9$, exchanged with D_2O, HO–C(2‴)); 5.32 (*d*, $J = 6.1$, exchanged with D_2O, HO–C(3‴)); 4.87 (*t*, $J \approx 5.5$, exchanged with D_2O, HO–C(10″)); 4.78 (*dd*, $J = 6.0, 5.5$, exchanged with D_2O, HO–C(8)); 4.67 (*d*, $J = 1.6$, exchanged with D_2O, HO–C(7″)); 4.62 (*t*, $J = 5.6$, exchanged with D_2O, HO–C(6‴)); 4.59 (*t*, $J = 5.4$, exchanged with D_2O, HO–C(6′)); 4.58 (*d*, $J = 1.7$, exchanged with D_2O, HO–C(5)); 4.30 (*d*, $J = 7.9$, H–C(1′)); 4.27 (*d*, $J = 8.0$, H–C(1‴)); 4.01 (*d*, $J = 9.5$, H–C(5‴)); 3.86 (*dd*, $J = 9.7, 2.0$, H–C(3)); 3.73–3.62 (*m*, addn. of D_2O → br. *d*, $J \approx 11.2$, H_a–C(6‴), H_a–C(6′), H_a–C(8), → 3.66 br. *d*, $J \approx 10.0$, H_a–C(10″)); 3.59–3.52 (*m*, addn. of D_2O → 3.57, br. *dd*, $J \approx 12.0, 5.0$, H_b–C(6′), H_b–C(6‴)); 3.51–3.45 (*m*, addn. of D_2O → signal changed, H_b–C(8), H_b–C(10″), H–C(5′)); 3.42–3.24 (*m*, addn. of D_2O → 3.42, *ddd*, $J \approx 10.2, 6.0, 2.0$, H–C(5‴), → 3.38, *t*, $J \approx 9.2$, H–C(6), → 3.37, *t*, $J \approx 9.2$, H–C(8″), → 3.31, *dd*, $J = 10.3, 9.0$, H–C(3′), additionally H–C(7), H–C(9″), H–C(3‴), H–C(7″), H–C(5)); 3.34 (*d*, $J = 2.0$, H–C≡C–C(3)); 3.16 (br. *td*, $J \approx 9.0, 6.0$, addn. of D_2O → *t*, $J \approx 8.6$, H–C(6″)); 3.14 (br. *td*, $J \approx 9.0, 6.2$, addn. of D_2O → *t*, $J \approx 8.7$, H–C(4)); 2.97 (*d*, $J = 2.2$, H–C≡C–C(4‴)); 2.93 (br. *td*, $J \approx 9.0, 4.0$, addn. of D_2O → *t*, $J \approx 8.4$, H–C(2′)); 2.92 (br. *td*, $J \approx 9.0, 4.0$, addn. of D_2O → *t*, $J \approx 8.5$, H–C(2‴)); 2.52 (*t*, $J \approx 10.3$, H–C(4′)); 2.29 (*td*, $J \approx 10.5, 2.2$, H–C(4‴)). ^{13}C-NMR (125 MHz, (D_6)DMSO): 102.82 (*d*, C(1′)); 102.77 (*d*, C(1‴)); 82.22 (*d*, H*C*≡C–C(4‴)); 81.92 (*d*, H*C*≡C–C(3)); 79.77 (*d*); 79.67 (*d*); 78.92 (*s*); 78.79 (*d*); 78.67 (*d*); 75.87 (*s*, HC≡*C*–C(3)); 75.71 (*d*); 75.62 (*d*); 75.59 (*s*); 75.28 (*d*); 74.82 (*d*); 74.12 (*d*); 73.84 (*d*); 73.81 (*d*); 73.75 (*d*); 73.70 (*s*, HC≡*C*–C(4‴)); 73.27 (*d*); 73.16 (*d*); 70.07 (*d*); 69.75 (*d*); 69.22 (*s*); 66.57 (*s*); 61.65 (*t*); 61.59 (*t*); 60.09

(2*t*); 37.78 (*d*, C(4‴)); 37.11 (*d*, C(4′)). ESI-MS: 737.2 (100, $[M+Na]^+$), 732.4 (56, $[M+Na]^+$). MS-MS of *m*/*z* 732 ($[M+Na]^+$): 715 (56, $[M+1]^+$), 545 (42, $[M+NH_4-C_8H_{11}O_5]^+$), 527 (50, $[M-C_8H_{11}O_5]^+$), 357 (100, M^{++}).

1,6-Anhydro-2,4-bis-O-*(triethylsilyl)-β*-D-*glucopyranose* (**20**) *and 1,6-Anhydro-2,3,4-tris*-O-*(triethylsilyl)-β*-D-*glucopyranose* (**21**). A soln. of 1,6-anhydroglucose (**19**; 2.35 g, 14.5 mmol) in pyridine (5 ml) and CH_2Cl_2 (10 ml) was treated at 0° dropwise with Et_3SiCl (4.99 ml, 29.7 mmol) (→ white suspension), stirred for 25 min, diluted with hexane (50 ml), washed twice with 1M HCl, dried ($MgSO_4$), filtered, and evaporated. FC (hexane → hexane/AcOEt 20 : 1 → 10 : 1) gave **21** (511 mg, 7%) and **20** (5.1 g, 90%) as colourless oils.

Data of **20**: R_f (hexane/AcOEt 3 : 1) 0.53. $[\alpha]_D^{25} = -24.7$ ($c = 1.1$, $CHCl_3$). IR (CCl_4): 3621*w*, 3567*w*, 2955*s*, 2899*m*, 2877*s*, 1458*m*, 1414*m*, 1380*w*, 1327*w*, 1239*m*, 1106*s*, 1077*s*, 1017*s*, 973*m*, 895*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.30 (br. *s*, H–C(1)); 4.40 (br. *d*, $J \approx 4.6$, H–C(5)); 3.88 (*dd*, $J = 7.5, 0.8$, H_{endo}–C(6)); 3.68 (*dd*, $J = 7.5$, 5.4, H_{exo}–C(6)); 3.55–3.44 (*m*, H–C(2), H–C(3), H–C(4)); 2.11 (*d*, $J = 5.4$, HO–C(3)); 0.98 (*t*, $J = 7.9$, 2 ($MeCH_2$)$_3$Si); 0.65 (*q*, $J = 7.9$, 2 ($MeCH_2$)$_3$Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 103.50 (*d*, *C*(1)); 78.05 (*d*); 75.67 (*d*); 73.99 (*d*); 73.67 (*d*); 66.30 (*t*); 6.57 (6*q*); 4.57 (3*t*); 4.50 (3*t*). CI-MS: 408.3 (16, $[M+NH_4]^+$), 391 (100, $[M+1]^+$), 373(6), 343(6), 315(50), 301(46), 288(8), 276(5), 259(17), 241(6), 229(18), 211(6), 199(7), 183(12), 171(21), 157(16), 145(10), 132(19), 115(13), 103(12), 75(3), 49(9). Anal. calc. for $C_{18}H_{38}O_5Si_2$ (390.67): C 55.34, H 9.80; found: C 55.25, H 9.71.

Data of **21**: R_f (hexane/AcOEt 3 : 1) 0.90. $[\alpha]_D^{25} = -24.7$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.28 (br. *s*, H–C(1)); 4.37 (br. *d*, $J \approx 4.3$, H–C(5)); 4.09 (*dd*, $J = 6.4$, 0.9, H_{endo}–C(6)); 3.70–3.58 (*m*, H_{exo}–C(6), H–C(2)); 3.49 (br. *s*, H–C(3)); 3.43 (br. *d*, $J \approx 1.2$, H–C(4)); 0.98 (*t*, $J \approx 7.9$, 3 ($MeCH_2$)$_3$Si); 0.70–0.56 (*m*, 3 ($MeCH_2$)$_3$Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 102.20 (*d*, C(1)); 77.56 (*d*); 75.19 (*d*); 72.84 (*d*); 71.86 (*d*); 64.56 (*t*); 6.60 (6*q*); 6.53 (3*q*); 4.66 (3*t*); 4.59 (6*t*). CI-MS: 522 (4, $[M+NH_4]^+$), 505 (28, $[M+1]^+$), 475(11), 459(20), 429(12), 373(95), 343(16), 327(14), 315(10), 301(100), 288(75), 275(11), 259(11), 241(14), 199(17), 183(5), 157(6), 145(5), 132(44), 115(16).

3,7-Anhydro-1,2-dideoxy-4,6-bis-O-*(triethylsilyl)-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**22**). A soln. of (trimethylsilyl)acetylene (16.8 ml, 0.12 mol) in toluene (100 ml) was treated at −15° dropwise with 1.52M BuLi in hexane (79 ml, 0.12 mol) (→ white suspension), stirred for 30 min at r.t., diluted with THF (5 ml) (→ clear soln.), and added dropwise at −10° to a suspension of freshly sublimed $AlCl_3$ (16 g, 0.12 mol) in toluene (75 ml). The suspension was stirred at r.t. for 1 h (→ viscous slightly yellow suspension), heated to 60°, treated with a soln. of **20** (11.65 g, 0.03 mol) and 2,4,6-trimethylpyridine (4.3 ml, 0.033 mol) in toluene (20 ml) dropwise over 1 min, and heated for 70 min at 130° (→ black soln.). The mixture was cooled to 0°, poured carefully into ice-cold H_2O/1M aq. HCl 2 : 1 (200 ml) and worked up (AcOEt). Bulb-to-bulb distillation (160°/0.1 Torr) of the resulting black oil gave **22** (11.3 g, 77%). Slightly yellow oil. R_f (hexane/AcOEt 3 : 1) 0.61. IR (CCl_4): 3606*m*, 2957*s*, 2912*s*, 2892*m*, 2877*s*, 2180*w*, 1742*w*, 1458*m*, 1414*m*, 1379*m*, 1285*m*, 1251*s*, 1214*w*, 1147*s*, 1107*s*, 1090*s*, 1057*s*, 1034*m*, 1015*m*, 1004*s*, 917*w*, 846*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.94 (*d*, $J = 9.1$, H–C(3)); 3.86 (*ddd*, $J = 11.5$, 7.1, 2.8, H_a–C(8)); 3.67 (*ddd*, $J = 11.5$, 6.5, 5.7, H_b–C(8)); 3.50 (*t*, $J \approx 8.6$, H–C(4)); 3.49 (*t*, $J \approx 8.7$, H–C(6)); 3.34 (*td*, $J \approx 8.4$, 2.9, H–C(5)); 3.26 (br. *ddd*, $J \approx 9.0$, 5.7, 2.8, H–C(7)); 2.15 (*d*, $J = 2.9$, HO–C(5)); 2.01 (br. *d*, $J \approx 6.6$, HO–C(8)); 0.95–1.10 (*m*, 2 ($MeCH_2$)$_3$Si); 0.62–0.80 (*m*, 2 ($MeCH_2$)$_3$Si); 0.21 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 102.52 (*s*, *C*≡CSi); 91.03 (*s*, C≡*C*Si); 80.37 (*d*, C(5)); 79.41 (*d*, C(6)); 75.29 (*d*, C(4)); 71.54 (*d*, C(7)); 71.00 (*d*, C(3)); 62.18 (*t*, C(8)); 6.87 (3*q*); 6.78 (3*q*); 5.35 (3*t*); 5.10 (3*t*); −0.36 (*q*, Me_3Si). CI-MS: 506 (11, $[M+NH_4]^+$), 489 (100, $[M+1]^+$), 459(5), 399(5), 357(11), 327(13), 309(6), 281(8), 268(17), 255(22), 241(13), 201(10), 145(4), 120(16).

3,7-Anhydro-1,2-dideoxy-1-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**23**). A soln. of **22** (15.7 g, 32.15 mmol) in MeOH/H_2O/AcOH 1 : 1 : 1 was stirred for 1 h at 40°, evaporated, and co-distilled (toluene). The resulting yellow oil was crystallized from acetone/heptane to give **23** (5.1 g, 61%) as colourless needles. FC of the mother liquor ($CHCl_3$/MeOH 10 : 1) gave another 2.5 g (30%) of **23** as a white solid (total 7.6 g, 91%). R_f ($CHCl_3$/MeOH 9 : 1) 0.20. M.p. 148–149°. $[\alpha]_D^{25} = +6.7$ ($c = 1$, MeOH). IR (KBr): 3567*s*, 3406*s* (br.), 2958*s*, 2929*s*, 2178*m*, 1751*w*, 1630*w*, 1458*m*, 1383*m*, 1363*w*, 1304*w*, 1250*s*, 1190*w*, 1078*s*, 1015*s*, 978*m*, 843*s*. ^{1}H-NMR (200 MHz, CD_3OD): 3.90 (*d*, $J = 9.6$, H–C(3)); 3.88 (*dd*, $J = 11.8$, 1.6, H_a–C(8)); 3.84 (br. *d*, $J \approx 11.6$, H_b–C(8)); 3.35–3.24 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)); 0.14 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, CD_3OD): 103.98 (*s*, *C*≡CSi); 82.08 (*d*); 79.29 (*d*); 75.26 (*d*); 72.46 (*d*); 71.38 (*d*, C(3)); 62.84 (*t*, C(8)); −0.21 (*q*, Me_3Si); 1*d* for C(1) not observed or hidden. CI-MS: 278 (55, $[M+NH_4]^+$), 261 (9, $[M+1]^+$), 238(3), 227(5), 209(10), 195(13), 180(14), 163(18), 90(100), 74(19). Anal. calc. for $C_{11}H_{20}O_5Si$ (260.36): C 50.75, H 7.74; found: C 50.72, H 7.92.

X-Ray Analysis of **23**. Crystals were obtained by isothermic distillation of heptane into a *ca*. 10% soln. of **23** in acetone. $C_{11}H_{20}O_5Si$ (260.36), monoclinic, $P2_1$, $a = 6.126(1)$ Å, $b = 6.152(2)$ Å, $c = 18.478(5)$ Å, $\beta = 96.11(2)°$,

$V = 692.4$ Å^3, $Z = 2$, $D_{calc.} = 1.249$ Mg/m^3. The intensities were recorded on an *Enraf-Nonius-CAD-4* diffractometer (graphite monochromator, CuK_α, $\lambda = 1.54184$ Å) at 293(2) K. Of the 1400 total collected reflections, 1287 were independent. The structure was solved with direct methods (SHELXS86 [34]). The non-H-atoms were refined anisotropically with SHELXL92 [35]. The H-atoms were obtained from a difference *Fourier* map and refined isotropically. The final R value using 1221 reflections with $I > 3\sigma(I)$ was 0.0442.

*3,7-Anhydro-1,2-dideoxy-6,8-*O*-(4-methoxybenzylidene)-1-*C*-(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**24**). A soln. of **23** (7.6 g, 29.23 mmol) and anisaldehyde dimethyl acetal (6.6 ml, 35 mmol) in MeCN (170 ml) was treated with TsOH · H_2O (277 mg, 5 mol-%), stirred at r.t. for 1 h (→ dark-violet soln.), treated with Et_3N (0.3 ml) (→ yellow soln.), and evaporated. FC (100 g of *Si-60*, CH_2Cl_2/toluene/Et_3N 1:1:0.01 → CH_2Cl_2/toluene/MeOH/Et_3N 20:1:1:0.01) gave **24** (11.06 g, 92%) as a colourless oil. An anal. sample was crystallized from AcOEt/heptane. R_f (hexane/AcOEt 1:1) 0.25. M.p. 154°. $[\alpha]_D^{25} = +15.7$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3608*m*, 3457*w* (br.), 2960*m*, 2901*m*, 2178*w*, 1741*w*, 1616*m*, 1589*m*, 1518*m*, 1465*w*, 1383*m*, 1303*m*, 1251*s*, 1172*m*, 1113*s*, 1095*m*, 1054*m*, 1039*m*, 1012*m*, 973*m*, 926*w*, 846*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.47–7.40 (*m*, 2 arom. H); 6.95–6.90 (*m*, 2 arom. H); 5.51 (*s*, ArC*H*); 4.36 (*dd*, $J = 10.4$, 4.6, H_{eq}–C(8)); 4.13 (*d*, $J = 9.1$, H–C(3)); 3.83 (*s*, MeO); 3.80 (*td*, $J \approx 10.8$, 2.5, H–C(5)); 3.72 (*td*, $J \approx 9.1$, 2.9, H–C(4)); 3.61–3.41 (*m*, H–C(6), H–C(7), H_{ax}–C(8)); 2.73 (*d*, $J = 2.1$, HO–C(5)); 2.51 (*d*, $J = 2.9$, HO–C(4)); 0.14 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 160.29 (*s*); 129.41 (*s*); 127.66 (2*d*); 113.73 (2*d*); 101.73 (*d*); 100.62 (*s*, *C*≡CSi); 92.36 (*s*, C≡*C*Si); 82.27 (*d*); 74.24–73.89 (*m*); 71.48 (*d*); 70.49 (*d*); 68.43 (*t*, C(8)); 55.19 (*q*, MeO); –0.39 (*q*, Me_3Si). CI-MS: 379 (22, $[M+1]^+$), 137 (100), 121 (44), 90 (18), 74 (5), 35 (33). Anal. calc. for $C_{19}H_{26}O_6Si$ (378.50): C 60.29, H 6.92; found: C 60.22, H 6.97.

*3,7-Anhydro-1,2-dideoxy-4,5-bis-*O*-(4-methoxybenzyl)-6,8-*O*-(4-methoxybenzylidene)-1-*C*-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol* (**25**). A soln. of **24** (108 mg, 0.285 mmol) and 4-methoxybenzyl trichloroacetimidate [19] (166 mg, 0.588 mmol) in THF/Et_2O 1:1 (5 ml) was treated at 0° dropwise with a 0.05M soln. of TfOH in Et_2O (0.17 ml, 3 mol-%), stirred for 1 h, neutralized with *Amberlite IRA-900* (OH^- form), filtered, and evaporated. FC (hexane/AcOEt/Et_3N 6:1:0.05) gave **25** (144.6 mg, 82%) as a colourless oil. R_f (hexane/AcOEt) 0.74. $[\alpha]_D^{25} = +21.2$ ($c = 1.0$, $CHCl_3$). IR (CCl_4): 3001*w*, 2956*m*, 2935*m*, 2907*m*, 2872*m*, 2836*m*, 2183*w*, 1614*m*, 1587*w*, 1515*s*, 1464*m*, 1441*w*, 1382*m*, 1367*m*, 1250*s*, 1172*m*, 1101*s*, 1042*s*, 1003*m*, 928*w*, 846*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41–7.21 (*m*, 6 arom. H); 6.91–6.82 (*m*, 6 arom. H); 5.51 (*s*, ArC*H*); 4.88 (*d*, $J = 10.4$, ArC*H*); 4.84 (*d*, $J = 11.1$, ArC*H*); 4.76 (*d*, $J = 10.3$, ArC*H*); 4.71 (*d*, $J = 10.9$, ArC*H*); 4.34 (*dd*, $J = 10.6$, 5.0, H_{eq}–C(8)); 4.15 (*d*, $J = 8.7$, H–C(3)); 3.81 (*s*, MeO); 3.80 (*s*, MeO); 3.79 (*s*, MeO); 3.80–3.61 (*m*, H–C(4), H–C(5), H–C(6), H_{eq}–C(8)); 3.43–3.32 (*m*, H–C(7)); 0.21 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 160.10 (*s*); 159.46 (*s*); 159.31 (*s*); 130.71 (*s*); 130.26 (*s*); 129.85 (2*d*); 129.69 (2*d*); 127.31 (2*d*); 113.79 (4*d*); 113.57 (2*d*); 102.04 (*s*, *C*≡CSi); 101.06 (*d*, ArCH); 91.38 (*s*, C≡*C*Si); 81.64 (*d*); 81.44 (*d*); 75.54 (*d*); 74.75 (*d*); 70.78 (*t*, 2 Ph*C*H_2); 70.62 (*d*, C(3)); 68.56 (*t*, C(8)); –0.42 (*q*, Me_3Si); 1*s* for C≡C not observed or hidden. FAB-MS (NOBA): 619 (56, $[M+1]^+$), 497 (100), 121 (76). Anal. calc. for $C_{35}H_{42}O_8Si$ (618.8): C 67.94, H 6.84; found: C 67.75, H 6.89.

*3,7-Anhydro-1,2-dideoxy-4,5-bis-*O*-(4-methoxybenzyl)-1-*C*-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol* (**26**). A soln. of **25** (128 mg, 0.21 mmol) in 80% aq. AcOH was stirred at r.t. for 90 min, evaporated, and co-distilled (toluene). The resulting clear oil was dried under h.v. for 14 h to give **26** (103 mg, 99%). R_f (hexane/AcOEt 4:3) 0.15. $[\alpha]_D^{25} = -43.0$ ($c = 2$, $CHCl_3$). IR (CCl_4): 3605*m*, 3455*w* (br.), 3001*w*, 2957*m*, 2935*m*, 2909*m*, 2836*m*, 2180*w*, 1741*m*, 1613*m*, 1586*m*, 1514*s*, 1464*m*, 1355*m*, 1302*m*, 1250*s*, 1180*m*, 1089*s*, 1040*s*, 846*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.38–7.24 (*m*, 4 arom. H); 6.94–6.88 (*m*, 4 arom. H); 5.01 (*d*, $J = 10.4$, ArC*H*); 4.91 (*d*, $J = 11.2$, ArC*H*); 4.76 (*d*, $J = 10.2$, ArC*H*); 4.64 (*d*, $J = 11.2$, ArC*H*); 4.10 (*d*, $J = 9.6$, H–C(3)); 3.83 (*s*, MeO); 3.82 (*s*, MeO); 3.95–3.70 (*m*, addn. of D_2O → 3.87, *dd*, $J = 12.0$, 3.3, H_a–C(8), → 3.73, *dd*, $J = 12.0$, 5.0, H_b–C(8)); 3.57 (*t*, $J \approx 9.3$, H–C(5)); 3.52 (*td*, $J \approx 8.9$, 2.2, addn. of D_2O → *t*, $J \approx 9.0$, H–C(6)); 3.38 (*t*, $J \approx 9.2$, H–C(4)); 3.29 (*ddd*, $J = 9.5$, 5.0, 3.3, H–C(7)); 2.44 (*d*, $J = 1.7$, exchanged with D_2O, HO–C(6)); 2.21 (br. *t*, $J \approx 6.2$, exchanged with D_2O, HO–C(8)); 0.23 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 159.51 (*s*); 159.48 (*s*); 130.60 (*s*); 130.16 (*s*); 129.87 (2*d*); 129.59 (2*d*); 114.05 (2*d*); 113.85 (2*d*); 102.46 (*s*, *C*≡CSi); 91.46 (*s*, C≡*C*Si); 84.71 (*d*); 81.73 (*d*); 79.27 (*d*); 74.82 (*d*); 74.82 (*t*, Ar*C*H_2); 70.09 (*d*, *C*(3)); 70.09 (*t*, Ar*C*H_2); 62.34 (*t*, C(8)); 55.17 (*q*, MeO); 55.14 (*q*, MeO); –0.49 (*q*, Me_3Si). FAB-MS (NOBA): 499 (46, $[M-1]^+$), 379 (95, $[M - C_8H_9O]^+$), 361 (8), 241 (7), 137 (11), 121 (100), 73 (7). Anal. calc. for $C_{27}H_{36}O_7Si$ (500.66): C 64.77, H 7.25; found: C 64.49, H 7.39.

*3,7-Anhydro-1,2-dideoxy-4,5-bis-*O*-(4-methoxybenzyl)-8-*O*-(thexyldimethylsilyl)-1-*C*-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol* (**27**). A soln. of **26** (400 mg, 0.8 mmol) and 1*H*-imidazole (136.2 mg, 2 mmol) in DMF (2.5 ml) was treated at r.t. dropwise with thexyldimethylsilyl chloride (TDSCl; 0.19 ml, 0.96 mmol), stirred for 12 h, poured into ice-cold hexane/1M aq. HCl (1:1, 10 ml), and worked up (hexane). FC (hexane → hexane/

AcOEt 20 : 1 → 10 : 1) gave **27** (494 mg, 95%). Colourles oil. R_f (hexane/AcOEt 4 : 3) 0.77. $[\alpha]_D^{25} = -22.9$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3575*m* (br.), 3507*m*, 3001*m*, 2958*s*, 2909*s*, 2876*s*, 2836*m*, 2182*w*, 1878*w*, 1613*s*, 1586*m*, 1514*s*, 1464*s*, 1441*m*, 1394*w*, 1378*w*, 1354*m*, 1319*m*, 1301*m*, 1248*s*, 1216*m*, 1178*m*, 1173*s*, 1140*s*, 1089*s*, 1040*s*, 1012*m*, 908*m*, 845*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.31–7.26 (*m*, 4 arom. H); 6.89–6.85 (*m*, 4 arom. H); 4.92 (*d*, $J = 10.1$, ArC*H*); 4.82 (*d*, $J = 11.0$, ArC*H*); 4.79 (*d*, $J = 11.0$, ArC*H*); 4.73 (*d*, $J = 10.1$, ArC*H*); 4.02 (*d*, $J = 9.5$, H–C(3)); 3.90 (*dd*, $J = 10.5$, 4.7, H_a–C(8)); 3.80 (*s*, MeO); 3.79 (*s*, MeO); 3.79 (*dd*, $J = 10.5$, 5.9, H_b–C(8)); 3.63 (*td*, $J \approx 9.1$, 2.2, addn. of $D_2O \rightarrow t$, $J \approx 9.1$, H–C(6)); 3.50 (*t*, $J \approx 9.3$, H–C(5)); 3.41 (*t*, $J \approx 8.9$, H–C(4)); 3.27 (*ddd*, $J = 10.5$, 5.9, 4.7, H–C(7)); 3.05 (*d*, $J = 1.4$, exchanged with D_2O, HO–C(6)); 1.61 (*sept.*, $J = 6.9$, Me_2CH); 0.88 (br. *d*, $J = 6.9$, Me_2CH); 0.85 (*s*, Me_2SiC); 0.19 (*s*, Me_3Si); 0.13 (*s*, MeSi); 0.12 (*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.36 (*s*); 159.26 (*s*); 130.96 (*s*); 130.35 (*s*); 129.84 (2*d*); 129.56 (2*d*); 113.88 (2*d*); 113.60 (2*d*); 102.62 (*s*, *C*≡CSi); 91.03 (*s*, C≡*C*Si); 84.92 (*d*, C(6)); 81.36 (*d*, C(5)); 78.02 (*d*, C(7)); 75.00 (*t*, 2 Ar*C*H_2); 73.41 (*d*, C(4)); 69.98 (*d*, C(3)); 64.68 (*t*, C(8)); 55.29 (*q*, MeO); 55.27 (*q*, MeO); 34.10 (*d*, Me_2*C*H); 25.22 (*s*, Me_2*C*Si); 20.33 (*q*, Me); 20.26 (*q*, Me); 18.50 (*q*, Me); 18.48 (*q*, Me); −0.27 (*q*, Me_3Si); −3.46 (*q*, MeSi); −3.47 (*q*, MeSi). FAB-MS (NOBA): 641 (22, $[M-1]^+$), 521 (31, $[M-C_8H_9O]^+$), 281(6), 241(11), 207(10), 121(100), 73(12). Anal. calc. for $C_{35}H_{54}O_7Si_2$ (642.98): C 65.38, H 8.46; found: C 65.32, H 8.42.

2,3,6-Tri-O-*acetyl-4-deoxy-4*-C-*ethynyl-α*-D-*glucopyranose* (**29**). A soln. of **28** (300 mg, 0.84 mmol), in DMF (2 ml), was treated in one batch with hydrazinium acetate (232 mg, 1.52 mmol), stirred for 5 h at 35°, poured into ice-cold 0.5M aq. HCl (10 ml) and worked up (Et_2O). Drying for 12 h at h.v. gave **29** (245.6 mg, 93%) as a colourless oil.

Data of α-D/*β*-D-**29** (63 : 37): R_f (hexane/AcOEt 1 : 1) 0.30. $[\alpha]_D^{20} = +57.2$ ($c = 1.05$, $CHCl_3$). IR ($CHCl_3$): 3595*m*, 3305*s*, 3040*m*, 2960*w*, 1745*s*, 1430*w*, 1370*s*, 1140*m*, 1045*s*, 935*w*, 905*m*, 655*m*, 605*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.61 (*t*, $J \approx 10.6$, 0.63 H, H–C(3)); 5.45 (*t*, $J \approx 3.3$, 0.63 H, H–C(1)); 5.36–5.24 (*m*, 0.37 H, H–C(2)); 4.79 (*dd*, $J = 10.1$, 3.5, 0.63 H, H–C(2)); 4.72 (*t*, $J \approx 10.4$, 0.37 H, H–C(3)); 4.72 (*dd*, $J = 9.0$, 6.0, 0.37 H, H–C(1)); 4.52–4.40 (*m*, H_a–C(6)); 4.34–4.25 (*m*, 1.63 H, H–C(5), H_b–C(6)); 3.76 (*ddd*, $J = 10.5$, 5.3, 2.3, 0.37 H, H–C(5)); 3.50 (br. *d*, $J = 5.9$, 0.37 H, HO–C(1)); 3.05 (br. *d*, $J = 2.9$, 0.63 H, HO–C(1)); 2.87–2.72 (*m*, H–C(4)); 2.17 (*d*, $J = 2.8$, 0.37 H, H–C≡C); 2.16 (*d*, $J = 2.6$, 0.63 H, H–C≡C); 2.12 (*s*, 2 Ac); 2.09 (*s*, Ac); 2.08 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): *α*-D-anomer: 171.26 (*s*, C=O); 170.79 (*s*, C=O); 170.28 (*s*, C=O); 90.97 (*d*, C(1)); 78.43 (*d*, C≡*C*H); 73.31 (*s*, *C*≡CH); 71.90 (*d*); 69.25 (*d*); 68.67 (*d*); 64.19 (*t*); 36.11 (*d*); 20.97 (2*q*); 20.90 (*q*); *β*-D-anomer: 171.44 (*s*, C=O); 95.87 (*d*, C(1)); 73.78 (*s*); 72.14 (2*d*); 64.67 (*t*); 36.20 (*d*); 21.23 (*q*); 20.81 (*q*). CI-MS: 332 (85, $[M+NH_4]^+$), 297 (65, $[M-OH]^+$), 272(48), 255(51), 195(100), 153(64), 135(50). Anal. calc. for $C_{14}H_{16}O_8$ (314.29): C 53.50, H 5.77; found: C 53.49, H 5.77.

2,3,6-Tri-O-*acetyl-4-deoxy-4*-C-*ethynyl-α*-D-*glucopyranosyl Trichloroacetimidate* (**30**). A soln. of **29** (21.2 g, 67.9 mmol) and Cl_3CCN (40.8 ml, 0.407 mol) in CH_2Cl_2 (600 ml) was treated in one batch with K_2CO_3 (5.4 g), stirred at r.t. for 48 h, filtered through *Celite*, concentrated to *ca.* 20 ml, and directly chromatographed (∅ 5 cm, 200 g of *Si-60*, hexane/AcOEt/Et_3N 2 : 1 : 0.1). The product-containing fractions were concentrated to *ca.* 100 ml and stored for 13 h at −20°. Filtration gave **30**/**31** *ca.* 88 : 12 (22.6 g, 73%) as colourless needles. Evaporation of the mother liquor gave additional **30**/**31** *ca.* 10 : 1 (3.2 g, 10%) as a white solid (total 25.8 g, 83%). Pure **30** was obtained after recrystallization from hexane/AcOEt. R_f (hexane/AcOEt 1 : 1) 0.61. M.p. 135–136°. $[\alpha]_D^{25} = +89.8$ ($c = 0.5$, $CHCl_3$). IR (CCl_4): 3350*w*, 3311*m*, 2957*w*, 2110*w*, 1758*s*, 1676*s*, 1551*w*, 1430*w*, 1369*s*, 1293*m*, 1228*s*, 1148*m*, 1072*s*, 1024*s*, 971*m*, 948*w*, 914*m*, 900*m*, 834*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.65 (br. *s*, NH); 6.54 (*d*, $J = 3.6$, H–C(1)); 5.65 (*t*, $J \approx 10.5$, H–C(3)); 5.01 (*dd*, $J = 10.0$, 3.6, H–C(2)); 4.43 (*dd*, $J = 12.1$, 2.3, H_a–C(6)); 4.30 (*dd*, $J = 12.0$, 4.3, H_b–C(6)); 4.23 (*ddd*, $J = 10.8$, 4.3, 2.3, H–C(5)); 2.95 (*td*, $J \approx 10.8$, 2.4, H–C(4)); 2.19 (*d*, $J = 2.3$, H–C≡C); 2.11 (*s*, Ac); 2.10 (*s*, Ac); 2.01 (*s*, Ac). ^{13}C-NMR (100 MHz, C_6D_6): 169.73 (*s*, C=O); 169.53 (*s*, C=O); 168.95 (*s*, C=O); 161.11 (*s*, C=N); 94.10 (*d*, C(1)); 91.10 (*s*, CCl_3); 78.04 (*d*, C≡*C*H); 73.57 (*s*, *C*≡CH); 71.86 (*d*); 70.85 (*d*); 69.32 (*d*); 63.70 (*t*, C(6)); 36.04 (*d*, C(4)); 20.28 (*q*, Me); 20.15 (*q*, Me); 19.90 (*q*, Me). CI-MS: 297 (100, $[M-$ aglycone$]^+$), 254(28), 237(71), 195(66), 177(20), 166(11), 152(17), 134(23), 124(18), 60(12), 43(15). Anal. calc. for $C_{16}H_{18}Cl_3NO_8$ (458.68): C 41.90, H 3.96, N 3.05; found: C 41.70, H 4.14, N 2.97.

X-Ray Analysis of **30**. Crystals were obtained by isothermic distillation of heptane into a *ca.* 10% soln. of **30** in AcOEt. $C_{16}H_{18}Cl_3NO_8$ (458.68). Orthorhombic, $P2_12_12_1$, $a = 9.433(3)$ Å, $b = 10.516(3)$ Å, $c = 22.293(13)$ Å, $V = 2211(2)$ Å^3, $Z = 4$, $D_{calc.} = 1.378$ Mg/m^3. The intensities were recorded on a *Enraf-Nonius-CAD-4* diffractometer (graphite monochromator, MoK_α, $\lambda = 0.71073$ Å) at 293(2) K. Of the 2289 total collected reflections, 2234 were independent. The structure was solved with direct methods (SHELXS96 [38]). The non-H-atoms were refined anisotropically with SHELXL92 [35]. The H-atoms were calculated at idealised positions and included in the structure factor calculation with fixed isotropic displacement parameters. Two of the three

Cl-atoms and the 3-*O*- and 6-*O*-acyl groups were refined over two positions. The structure converged at an *R* value of 0.0916 using 1578 reflections with $I > 3\sigma(I)$.

2,3,6-Tri-O-*acetyl-4-deoxy-4*-C-*ethynyl-β*-D-*glucopyranosyl Trichloroacetimidate* (**31**). A soln. of **29** (586.2 mg, 1.87 mmol) and Cl_3CCN (1.87 ml, 18.65 mmol) in CH_2Cl_2 (20 ml), was treated in one batch with K_2CO_3 (327 mg), stirred at r.t. for 90 min, filtered through *Celite*, concentrated to *ca.* 8 ml and directly chromatographed (∅ 1 cm, 8 g of *Si-60*, hexane/AcOEt/Et_3N 2 : 1 : 0.1). The product-containing fractions were concentrated to *ca.* 7 ml and stored for 4 h at −20°. Filtration gave **31**/**30** *ca.* 83 : 17 (470 mg, 55%) as colourless needles. Evaporation of the mother liquor gave additional **31**/**30** *ca.* 2 : 1 (128 mg 15%) as a white solid (total 598 mg, 70%). Pure **31** was obtained after recrystallization from heptane/ether. R_f (hexane/AcOEt 1 : 1) 0.61. M.p. 174–175°. $[\alpha]_D^{25} = -6.9$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3584*w* (br.), 3349*w*, 3311*m*, 2957*w*, 2111*w*, 1761*s*, 1677*s*, 1430*w*, 1367*s*, 1301*m*, 1227*s*, 1154*m*, 1125*w*, 1084*s*, 1060*s*, 948*w*, 898*m*, 837*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.73 (br. *s*, NH); 5.87 (*d*, $J = 7.9$, H−C(1)); 5.36 (*dd*, $J = 10.8$, 9.6, H−C(3)); 5.16 (*t*, $J = 9.6$, 8.3, H−C(2)); 4.50 (*dd*, $J = 12.1$, 2.5, H_a−C(6)); 4.38 (*dd*, $J = 12.0$, 4.6, H_b−C(6)); 3.93 (*ddd*, $J = 10.6$, 4.5, 2.5, H−C(5)); 2.95 (*td*, $J \approx 10.6$, 2.4, H−C(4)); 2.21 (*d*, $J = 2.3$, H−C≡C); 2.13 (*s*, Ac); 2.12 (*s*, Ac); 2.04 (*s*, Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.72 (*s*, C=O); 169.99 (*s*, C=O); 169.41 (*s*, C=O); 161.04 (*s*, C=N); 95.80 (*d*, C(1)); 90.41 (*s*, CCl_3); 77.53 (*d*, C≡*C*H); 73.73 (*d*); 73.51 (*s*, *C*≡CH); 72.67 (*d*); 70.67 (*d*); 63.39 (*t*, C(6)); 35.23 (*d*, C(4)); 20.65 (*q*, Me); 20.47 (*q*, Me); 20.44 (*q*, Me). CI-MS: 458 (2, M^+), 297 (34, [*M* − aglycone]$^+$), 254 (10), 237 (38), 195 (100), 177 (35), 166 (21), 153 (16), 135 (55), 124 (28), 84 (26), 43 (45). Anal. calc. for $C_{16}H_{18}Cl_3NO_8$ (458.68): C 41.90, H 3.96, N 3.05; found: C 41.87, H 3.81, N 3.08.

X-Ray Analysis of **31**. Crystals were obtained by isothermic distillation of pentane into a *ca.* 10% soln. of **31** in *t*-BuOMe. $C_{16}H_{18}Cl_3NO_8$ (458.68). Monoclinic, $P2_1$, $a = 5.581(2)$ Å, $b = 8.891(3)$ Å, $c = 20.951(4)$ Å, $\beta = 94.39(3)°$, $V = 1036.5(6)$ Å^3, $Z = 2$, $D_{calc.} = 1.470$ Mg/m^3. The crystals were measured on an *Enraf-Nonius-CAD-4* diffractometer (graphite monochromator, CuK_α, $\lambda = 1.54184$ Å) at 203(2) K. Of the 2178 total collected reflections, 1983 were independent. An empirical absorption correction was done by PSI scans of selected reflections. Part of the structure was solved with direct methods, the remaining non-H-atoms were found from a difference *Fourier* map with SHELXS96 [38]. The non-H-atoms were refined anisotropically with SHELXL97 [39]. The H-atoms were refined isotropically except the H-atoms of the Me and alkyne groups, which were calculated at idealized positions and included in the structure-factor calculation with fixed isotropic displacement parameters. The disordered Cl-atoms were refined over two positions. The structure converged at an *R* value of 0.0573 using 1867 reflections with $I > 3\sigma(I)$.

2,3,6-Tri-O-*acetyl-4-deoxy-4*-C-*ethynyl-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**32**). A soln. of **27** (6.69 g, 10.39 mmol) and **30** (5.23 g, 11.42 mmol) in CH_2Cl_2 (100 ml) was treated with powdered 4-Å molecular sieves (4 g) and stirred at r.t. for 30 min. The mixture was cooled to −10°, treated dropwise with 1.41M Me_3SiOTf in CH_2Cl_2 (0.18 ml, 2.5 mol-%), stirred for 5 min, poured into ice-cold sat. $NaHCO_3$ soln. (10 ml), filtered through *Celite*, and worked up (CH_2Cl_2). FC (hexane/AcOEt 5 : 1 → 7 : 2) gave **32** (8.8 g, 90%). Colourless oil. R_f (hexane/AcOEt 2 : 1) 0.53. $[\alpha]_D^{25} = -11.15$ ($c = 2$, $CHCl_3$). IR (CCl_4): 3311*m*, 2985*s*, 2902*m*, 2836*m*, 2183*w*, 1759*s*, 1613*m*, 1587*w*, 1514*s*, 1464*m*, 1441*w*, 1366*m*, 1294*m*, 1251*s*, 1231*s*, 1178*m*, 1089*s*, 1040*s*, 908*m*, 845*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.28 (*dt*, *AA′BB′*, $J_{AB} = 8.9$, $J_{AB'} \approx J_{AA'} \approx 2.0$, 2 arom. H); 7.20 (*dt*, *AA′BB′*, $J_{AB} = 8.9$, $J_{AB'} \approx J_{AA'} \approx 2.0$, 2 arom. H); 6.83 (*dt*, *AA′BB′*, $J_{AB} = 8.9$, $J_{AB'} \approx J_{AA'} \approx 2.0$, 2 arom. H); 6.81 (*dt*, *AA′BB′*, $J_{AB} = 8.9$, $J_{AB'} \approx J_{AA'} \approx 2.0$, 2 arom. H); 5.19–5.14 (*m*, *M* of *ABMX*, virtual coupling, $J_{MX} \approx 10.6$, $J_{AM} \approx 9.2$, H−C(3′)); 4.92 (*d*, $J = 10.9$, ArC*H*); 4.82–4.77 (*m*, H−C(1′), H−C(2′), ArC*H*); 4.65 (*d*, $J = 11.0$, ArC*H*); 4.61 (*d*, $J = 11.0$, ArC*H*); 4.33 (*dd*, $J = 12.1$, 2.5, H_a−C(6′)); 4.28 (*dd*, $J = 12.1$, 4.6, H_b−C(6′)); 3.91 (*d*, $J = 9.3$, H−C(3)); 3.89–3.80 (*m*, 2 H−C(8), H−C(6)); 3.81 (*s*, MeO); 3.79 (*s*, MeO); 3.58 (*ddd*, $J = 10.4$, 4.6, 2.5, H−C(5′)); 3.44 (*t*, $J \approx 8.6$, H−C(5)); 3.40 (*t*, $J \approx 8.7$, H−C(4)); 3.08 (br. *ddd*, $J \approx 9.0$, 2.4, 1.5, H−C(7)); 2.81 (*td*, $J \approx 10.5$, 2.4, H−C(4′)); 2.13 (*d*, $J = 2.4$, H−C(8′)); 2.06 (*s*, Ac); 2.03 (*s*, Ac); 2.00 (*s*, Ac); 1.66 (*sept.*, $J = 6.9$, Me_2CH); 0.93 (*d*, $J = 6.9$, *Me*CH); 0.92 (*d*, $J = 6.9$, *Me*CH); 0.879 (*s*, *Me*CSi); 0.876 (*s*, *Me*CSi); 0.17 (*s*, Me_3Si); 0.16 (*s*, MeSi); 0.15 (*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 170.66 (*s*, C=O); 169.96 (*s*, C=O); 169.55 (*s*, C=O); 159.26 (*s*); 158.97 (*s*); 131.46 (*s*); 130.45 (*s*); 129.80 (2*d*); 129.13 (2*d*); 113.68 (2*d*); 113.55 (2*d*); 102.94 (*s*, *C*≡CSi); 99.98 (*d*, C(1′)); 90.43 (*s*, C≡*C*Si); 83.30 (*d*); 81.67 (*d*); 79.45 (*d*); 77.97 (*d*, H*C*≡C); 76.36 (*d*); 75.16 (*t*, Ar*C*H$_2$); 74.71 (*t*, Ar*C*H$_2$); 73.13 (*s*, HC≡*C*); 72.96 (*d*); 72.82 (*d*); 72.51 (*d*); 69.74 (*d*, C(3)); 63.95 (*t*, C(6′)); 61.14 (*t*, C(8)); 55.27 (*q*, 2 MeO); 35.72 (*d*, C(4′)); 34.27 (*d*, Me_2*C*H); 25.23 (*s*, Me_2*C*Si); 20.77 (*q*, Me); 20.73 (*q*, Me); 20.65 (*q*, Me); 20.53 (*q*, *Me*CH); 20.32 (*q*, *Me*CH); 18.76 (*q*, *Me*CSi); 18.60 (*q*, *Me*CSi); −0.30 (*q*, Me_3Si); −2.90 (*q*, MeSi); −3.21 (*q*, MeSi). FAB-MS (NOBA): 938 (60, [*M* − 1]$^+$), 817 (86, [*M* − $C_8H_{10}O$]$^+$), 297 (8, [*M* − aglycone]$^+$), 241 (6), 195 (8), 121 (100), 73 (20, Me_3Si^+). Anal. calc. for $C_{49}H_{70}O_{14}Si_2$ (939.25): C 62.66, H 7.51; found: C 62.86, H 7.62.

4-Deoxy-4-C-*ethynyl-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**33**). A soln. of **32** (12.3 g, 13.09 mmol) in THF (160 ml) was treated dropwise at 0° with 1.5M DIBAH in toluene (78.54 ml, 117.81 mmol), stirred for 15 min, poured into ice/$CHCl_3$ (1 : 1, 400 ml) and filtered through *Celite*. Workup ($CHCl_3$) and drying for 12 h under h.v. gave **33** (10.5 g, 99%) as a colourless oil, which was used for the next step. An anal. sample was purified by FC (hexane/AcOEt 1 : 2 → 1 : 4). R_f (hexane/AcOEt 1 : 4) 0.36. $[\alpha]_D^{25} = +25.5$ ($c = 2$, $CHCl_3$). IR (CCl_4): 3597*m*, 3442*m* (br.), 3310*m*, 2958*s*, 2905*m*, 2836*m*, 2182*w*, 1613*s*, 1586*w*, 1514*s*, 1464*m*, 1441*w*, 1353*w*, 1294*m*, 1282*m*, 1260*s*, 1180*w*, 1151*m*, 1080*s*, 1062*s*, 1039*s*, 913*w*, 845*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.29–7.21 (*m*, 4 arom. H); 6.89–6.82 (*m*, 4 arom. H); 4.91 (*d*, $J = 10.0$, ArC*H*); 4.82 (*d*, $J = 10.9$, ArC*H*); 4.77 (*d*, $J = 10.9$, ArC*H*); 4.72 (*d*, $J = 10.0$, ArC*H*); 4.65 (*d*, $J = 7.8$, H–C(1′)); 3.97 (*d*, $J = 9.3$, H–C(3)); 3.91 (*t*, $J \approx 9.5$, H–C(6)); 3.91–3.84 (*m*, 2 H–C(8)); 3.81 (*s*, MeO); 3.79 (*s*, MeO); 3.83–3.78 (*m*, addn. of $D_2O \rightarrow$ 3.80, *dd*, $J \approx 11.0$, 2.5, H_a–C(6′)); 3.64–3.50 (*m*, addn. of $D_2O \rightarrow$ 3.62, *dd*, $J = 10.5$, 5.6, H_b–C(6′)); 3.56 (*t*, $J \approx 10.0$, H–C(3′)); 3.51 (*t*, $J \approx 9.0$, H–C(5)); 3.46 (*t*, $J \approx 8.9$, H–C(4)); 3.34 (*ddd*, $J = 10.3$, 5.6, 2.5, H–C(5′)); 3.25–3.20 (*m*, HO–C(2′), H–C(7), addn. of $D_2O \rightarrow$ 3.23, *t*, $J \approx 9.0$, H–C(2′)); 2.77 (br. *s*, exchanged with D_2O, HO–C(3′)); 2.50 (*td*, $J \approx 10.4$, 2.4, H–C(4′)); 2.20 (*d*, $J = 2.4$, H–C≡C); 1.99 (br. *t*, $J \approx 0.8$, exchanged with D_2O, HO–C(6′)); 1.64 (*sept.*, $J = 7.0$, Me_2CH); 0.89 (*d*, $J \approx 7.0$, *Me*CH); 0.87 (*d*, $J \approx 6.9$, *Me*CH); 0.86 (*s*, 2 *Me*CSi); 0.19 (*s*, Me_3Si); 0.16 (*s*, MeSi); 0.14 (*s*, MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 159.41 (*s*); 159.28 (*s*); 130.74 (*s*); 130.29 (*s*); 129.82 (2*d*); 129.24 (2*d*); 113.76 (4*d*); 102.85 (*s*, *C*≡CSi); 101.75 (*d*, C(1′)); 90.61 (*s*, C≡*C*Si); 83.67 (*d*); 81.76 (*d*); 80.21 (*d*, H*C*≡C); 79.20 (*d*); 75.56 (*d*); 75.30 (*d*); 75.16 (*d*); 75.01 (*d*); 74.72 (*t*, 2Ar*C*H_2); 72.78 (*s*, HC≡*C*); 69.72 (*d*, C(3)); 62.81 (*t*, C(6′)); 61.41 (*t*, C(8)); 55.13 (2*q*, MeO); 36.94 (*d*, C(4′)); 33.97 (*d*, Me_2*C*H); 25.09 (*s*, Me_2*C*Si); 20.24 (*q*, *Me*CH); 20.10 (*q*, *Me*CH); 18.51 (*q*, *Me*CSi); 18.36 (*q*, *Me*CSi); −0.56 (*q*, Me_3Si); −3.11 (*q*, MeSi); −3.47 (*q*, MeSi). FAB-MS (NOBA): 811 (51, $[M-2]^+$), 691 (37, $[M - C_8H_{10}O]^+$), 241 (6), 121 (100), 73 (21, Me_3Si^+). Anal. calc. for $C_{43}H_{64}O_{11}Si_2$ (813.14): C 63.52, H 7.93; found: 63.06, H 8.16.

4-Deoxy-4-C-*[(trimethylgermyl)ethynyl]-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**34**). A soln. of **33** (1.26 mg, 1.55 mmol) and $(Me_3Si)_2NH$ (1.07 ml, 5.12 mmol) in CH_2Cl_2 (3 ml) was treated at r.t. with Me_3SiCl (0.1 ml, 0.78 mmol), stirred for 30 min, poured into ice-water (10 ml) and worked up (hexane). The resulting clear oil (1.6 g, R_f (hexane/AcOEt 4 : 1) 0.72) was dried for 8 h under h.v., dissolved in THF (15 ml), and Me_3GeCl (0.3 ml, 2.3 mmol), cooled to −78°, and treated dropwise with 1M LDA (freshly prepared from a soln. of (i-Pr)$_2$NH (0.43 ml, 3 mmol) in THF (0.47 ml) and 1.43M BuLi in hexane (2.1 ml, 3 mmol) at 0°) in THF/hexane (1.9 ml), stirred for 5 min, poured into ice/sat. NH_4Cl soln. (1 : 1, 20 ml) and worked up (hexane). The resulting clear oil (1.75 g, R_f (hexane/AcOEt 4 : 1) 0.74) was dissolved in H_2O/THF/AcOH 1 : 1 : 1 (30 ml), stirred for 30 min at r.t., neutralized with sat. $NaHCO_3$ soln., and worked up ($CHCl_3$). FC (hexane/AcOEt/CH_2Cl_2 6 : 1 : 1 → 4 : 1 : 1) gave **34** (1.3 g, 90%). Colourless oil. R_f (hexane/AcOEt 9 : 11) 0.34. $[\alpha]_D^{25} = +30.6$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3599*m*, 3431*m* (br.), 2958*s*, 2910*m*, 2876*m*, 2836*m*, 2122*w*, 1614*m*, 1586*w*, 1514*s*, 1464*m*, 1441*w*, 1365*w*, 1301*m*, 1251*s*, 1214*w*, 1172*w*, 1149*m*, 1089*s*, 1040*s*, 940*w*, 913*w*, 845*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.29–7.22 (*m*, 4 arom. H); 6.87 (*dt*, *AA′BB′*, $J_{AB} = 8.7$, $J_{AB'} \approx J_{AA'} \approx 2.0$, 2 arom. H); 6.83 (*dt*, *AA′BB′*, $J_{AB} = 8.7$, $J_{AB'} \approx J_{AA'} \approx 2.0$, 2 arom. H); 4.90 (*d*, $J = 10.0$, ArC*H*); 4.82 (*d*, $J = 10.6$, ArC*H*); 4.74 (*d*, $J = 10.6$, ArC*H*); 4.71 (*d*, $J = 10.0$, ArC*H*); 4.63 (*d*, $J = 7.8$, H–C(1′)); 3.97 (*d*, $J = 9.3$, H–C(3)); 3.98–3.95 (*m*, H_a–C(8)); 3.89 (*t*, $J \approx 9.4$, H–C(6)); 3.91–3.88 (*m*, H_b–C(8)); 3.81 (*s*, MeO); 3.79 (*s*, MeO); 3.83–3.78 (*m*, addn. of $D_2O \rightarrow$ *dd*, $J \approx 11.0$, 2.7, H_a–C(6′)); 3.62–3.50 (*m*, addn. of $D_2O \rightarrow$ 3.58, *dd*, $J = 10.5$, 6.3, H_b–C(6′), → 3.56 (*t*, $J \approx 10.4$, H–C(3′)); 3.50 (*t*, $J \approx 8.9$, H–C(5)); 3.46 (*t*, $J \approx 9.1$, H–C(4)); 3.33 (*ddd*, $J = 9.0$, 6.3, 2.7, H–C(5′)); 3.25 (*m*, H–C(2′), H–C(6), addn. of $D_2O \rightarrow$ 3.26, *dd*, $J = 9.0$, 7.8, H–C(2′)); 3.23 (br. *dt*, $J \approx 9.1$, 2.2, H–C(7)); 3.11 (*d*, $J = 2.1$, exchanged with D_2O, HO–C(2′)); 2.61 (*d*, $J = 2.3$, exchanged with D_2O, HO–C(3′)); 2.46 (*t*, $J \approx 10.4$, H–C(4′)); 2.07 (br. *s*, exchanged with D_2O, HO–C(6′)); 1.65 (*sept.*, $J = 6.9$, Me_2CH); 0.90 (*d*, $J = 6.8$, *Me*CH); 0.89 (*d*, $J = 6.9$, *Me*CH); 0.865 (*s*, *Me*CSi); 0.862 (*s*, *Me*CSi); 0.33 (*s*, Me_3Ge); 0.19 (*s*, Me_3Si); 0.16 (*s*, MeSi); 0.14 (*s*, MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 159.25 (*s*); 159.12 (*s*); 130.81 (*s*); 130.27 (*s*); 129.66 (2*d*); 129.04 (2*d*); 113.61 (4*d*); 102.90 (*s*, *C*≡CSi); 101.74 (*d*, C(1′)); 100.46 (*s*, GeC≡*C*); 90.33 (*s*, C≡*C*Si); 89.34 (*s*, Ge*C*≡C); 83.46 (*d*); 81.81 (*d*); 79.10 (*d*); 75.63 (*d*); 75.51 (*d*); 74.96 (*d*); 74.90 (2*t*, Ar*C*H_2); 74.62 (*d*); 69.57 (*d*, C(3)); 63.08 (*t*, C(6′)); 61.29 (*t*, C(8)); 54.93 (2*q*, MeO); 38.35 (*d*, C(4′)); 33.87 (*d*, Me_2*C*H); 24.96 (*s*, CSi); 20.15 (*q*, *Me*CH); 20.00 (*q*, *Me*CH); 18.40 (*q*, *Me*CSi); 18.27 (*q*, *Me*CSi); −0.35 (*q*, Me_3Ge); −0.44 (*q*, Me_3Si); −3.18 (*q*, MeSi); −3.57 (*q*, MeSi). FAB-MS (NOBA): 929 (10, M^+), 241 (31), 121 (100), 119 (30, Me_3Ge^+), 118 (12), 117 (32, Me_3Ge^+), 115 (19), 73 (21, Me_3Si^+). Anal. calc. for $C_{46}H_{72}GeO_{11}Si_2$ (929.85): C 59.42, H 7.80; found: C 59.55, H 7.56.

4-Deoxy-4-C-*[(trimethylgermyl)ethynyl]-β*-D-*glucopyranosyl-(1→6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**35**). A soln. of **34** (1.2 g, 1.29 mmol) in THF (13 ml) was treated at r.t. with cold sat. K_2CO_3 soln. in MeOH (1 ml), stirred for 1 h, neutralized with *Amberlite IR-120* (H^+ form), filtered, and evaporated. FC (hexane/AcOEt/CH_2Cl_2 5:1:1→4:1:1) gave **35** (1.01 g, 92%). Colourless oil. R_f (hexane/AcOEt 6:7) 0.42. $[\alpha]_D^{25} = +54.3$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3599*m*, 3466*m* (br.), 3311*m*, 2944*m*, 2900*m*, 2876*m*, 2836*m*, 2167*w*, 1741*w*, 1614*m*, 1586*w*, 1514*s*, 1465*m*, 1441*w*, 1355*w*, 1301*m*, 1249*s*, 1172*w*, 1150*m*, 1091*s*, 1040*s*, 938*w*, 832*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.29 (*dt*, *AA′BB′*, $J_{AB} \approx 8.8$, $J_{AB'} \approx J_{AA'} \approx 2.0$, 2 arom. H); 7.26 (*dt*, *AA′BB′*, $J_{AB} \approx 8.6$, $J_{AB'} \approx J_{AA'} \approx 2.1$, 2 arom. H); 6.87 (*dt*, *AA′BB′*, $J_{AB} = 8.9$, $J_{AB'} \approx J_{AA'} \approx 2.0$, 2 arom. H); 6.84 (*dt*, *AA′BB′*, $J_{AB} = 8.9$, $J_{AB'} \approx J_{AA'} \approx 2.0$, 2 arom. H); 4.88 (*d*, $J = 10.0$, ArC*H*); 4.83 (*d*, $J = 10.6$, ArC*H*); 4.75 (*d*, $J = 10.6$, ArC*H*); 4.74 (*d*, $J = 10.0$, ArC*H*); 4.64 (*d*, $J = 7.8$, H−C(1′)); 4.02–3.97 (*m*, addn. of $D_2O \rightarrow$ 3.99, *dd*, $J = 12, 2.7$, H_a−C(6′), → 3.98, *dd*, $J = 9.3, 2.1$, H−C(3)); 3.92–3.88 (*m*, H_a−C(8)); 3.90 (*t*, $J \approx 9.2$, H−C(6)); 3.80–3.76 (*m*, addn. of $D_2O \rightarrow$ signal changed, H_b−C(6′)); 3.80 (*s*, MeO); 3.79 (*s*, MeO); 3.82–2.79 (*m*, addn. of $D_2O \rightarrow$ signal changed, H_a−C(6′)); 3.58–3.52 (*m*, addn. of $D_2O \rightarrow$ 3.55, *dd*, $J = 10.4$, 9.0, H−C(3′), → 3.53, *dd*, $J \approx 11.0$, 2.2, H_b−C(8)); 3.52 (*t*, $J \approx 8.9$, H−C(5)); 3.47 (*t*, $J \approx 9.2$, H−C(4)); 3.33 (*ddd*, $J = 10.0, 6.0, 2.8$, H−C(5′)); 3.30–3.25 (*m*, addn. of $D_2O \rightarrow$ 3.27, *dd*, $J \approx 9.0, 7.8$, H−C(2′), → 3.25, br. *dt*, $J \approx 9.1, 2.0$, H−C(7)); 3.06 (*d*, $J = 2.0$, exchanged with D_2O, HO−C(2′)); 2.61 (*d*, $J = 2.3$, exchanged with D_2O, HO−C(3′)); 2.49 (*d*, $J = 2.1$, H−C(1)); 2.48 (*td*, $J \approx 10.3, 2.4$, H−C(4′)); 1.98 (br. *t*, $J \approx 7.5$, exchanged with D_2O, HO−C(6′)); 1.65 (*sept.*, $J = 6.9$, Me_2CH); 0.90 (*d*, $J = 6.8$, *Me*CH); 0.89 (*d*, $J = 6.9$, MeCH); 0.86 (*s*, Me_2CSi); 0.33 (*s*, Me_3Ge); 0.15 (*s*, MeSi); 0.14 (*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.39 (*s*); 159.17 (*s*); 130.91 (*s*); 130.22 (*s*); 129.85 (2*d*); 128.96 (2*d*); 113.38 (2*d*); 113.79 (2*d*); 101.96 (*d*, C(1′)); 100.02 (*s*, GeC≡*C*); 90.05 (*s*, Ge*C*≡C); 83.92 (*d*); 81.82 (*d*); 81.07 (*d*, C(1)); 79.53 (*d*); 75.72 (2*d*); 75.28 (*t*, Ar*C*H_2); 75.16 (*t*, Ar*C*H_2); 75.06 (*d*); 74.95 (*d*); 73.65 (*s*, C(2)); 69.44 (*d*, C(3)); 63.38 (*t*, C(6′)); 61.60 (*t*, C(8)); 55.31 (*q*, MeO); 55.30 (*q*, MeO); 38.61 (*d*, C(4′)); 34.12 (*d*, Me_2CH); 25.28 (*s*, Me_2CSi); 20.45 (*q*, *Me*CH); 20.25 (*q*, *Me*CH); 18.71 (*q*, *Me*CSi); 18.54 (*q*, *Me*CSi); −0.11 (*q*, Me_3Ge); 2.82 (*q*, MeSi); −3.27 (*q*, MeSi). FAB-MS (NOBA): 857 (52, M^+), 855 (35), 737 (31), 569 (6), 121 (100), 119 (13, Me_3Ge^+), 117 (10), 73 (16, Me_3Si^+). Anal. calc. for $C_{43}H_{64}GeO_{11}Si$ (857.67): C 60.22, H 7.52; found: C 60.05, H 7.27.

2,3,6-Tri-O-*acetyl-4*-C-*(bromoethynyl)-4-deoxy-β*-D-*glucopyranosyl-(1→6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**36**). A soln. of **34** (156 mg, 0.167 mmol) in CH_2Cl_2 (1 ml), pyridine (0.2 ml), and Ac_2O (0.15 ml) was stirrd for 12 h, evaporated, co-distilled (toluene), and dried under h.v. for 12 h. The resulting slightly yellow oil (R_f (hexane/AcOEt 2:1) 0.60) and NBS (44.6 mg, 0.25 mmol) were dissolved in acetone (1.6 ml), treated with CuBr (4.8 mg, 20 mol-%), stirred at r.t. for 2 h, poured into ice-cold 10% aq. $Na_2S_2O_3$ soln. (4 ml), and worked up (Et_2O). FC (hexane/AcOEt 6:1) gave **36** (152.8 mg, 90%). Colourless oil. R_f (hexane/AcOEt 6:7) 0.85. $[\alpha]_D^{25} = -2.5$ ($c = 1$, $CHCl_3$). IR (CCl_4): 2960*s*, 2902*m*, 2836*m*, 2183*w*, 1759*s*, 1613*m*, 1587*w*, 1514*s*, 1464*m*, 1441*w*, 1366*m*, 1301*m*, 1251*s*, 1230*s*, 1173*m*, 1089*s*, 1055*s*, 1040*s*, 901*m*, 845*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.28–7.19 (*m*, 4 arom. H); 6.83–6.79 (*m*, 4 arom. H); 5.20–5.10 (*m*, *M* of *ABMX*, virtual coupling, $J_{MX} \approx 10.2$, $J_{AM} \approx 9.1$, H−C(3′)); 4.89 (*d*, $J = 10.8$, ArC*H*); 4.84–4.72 (*m*, H−C(1′), H−C(2′), ArC*H*); 4.64 (*d*, $J = 11.0$, 2 ArC*H*); 4.61 (*d*, $J = 10.8$, ArC*H*); 4.32 (*dd*, $J = 11.5, 2.9$, H_a−C(6′)); 4.23 (*dd*, $J = 11.5, 4.5$, H_b−C(6′)); 3.92 (*d*, $J = 9.1$, H−C(3)); 3.86–3.76 (*m*, H_a−C(8), H_b−C(8), H−C(6)); 3.81 (*s*, MeO); 3.79 (*s*, MeO); 3.59 (*ddd*, $J = 10.0, 4.6, 2.9$, H−C(5′)); 3.44 (*t*, $J \approx 8.7$, H−C(5)); 3.39 (*t*, $J \approx 9.1$, H−C(4)); 3.08 (br. *d*, $J \approx 10.0$, H−C(7)); 2.82 (*t*, $J \approx 10.4$, H−C(4′)); 2.07 (*s*, Ac); 2.03 (*s*, Ac); 2.01 (*s*, Ac); 1.67 (*sept.*, $J = 7.0$, Me_2CH); 0.93 (*d*, $J = 7.0$, *Me*CH); 0.92 (*d*, $J = 7.0$, *Me*CH); 0.88 (*s*, Me_2CSi); 0.17 (*s*, Me_3Si); 0.16 (*s*, 2 MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.72 (*s*, C=O); 169.93 (*s*, C=O); 169.62 (*s*, C=O); 159.37 (*s*); 159.09 (*s*); 131.49 (*s*); 130.50 (*s*); 129.84 (2*d*); 129.16 (2*d*); 113.69 (2*d*); 113.58 (2*d*); 102.95 (*s*, *C*≡CSi); 99.94 (*d*, C(1′)); 90.38 (*s*, C≡*C*Si); 83.23 (*d*); 81.64 (*d*); 79.39 (*d*); 76.30 (*d*); 75.08 (*t*, Ar*C*H_2); 74.64 (*t*, Ar*C*H_2); 74.04 (*s*, BrC≡*C*); 72.75 (*d*); 72.49 (2*d*); 69.67 (*d*, C(3)); 63.98 (*t*, C(6′)); 61.05 (*t*, C(8)); 55.16 (*q*, 2 MeO); 44.27 (*s*, Br*C*≡C); 36.88 (*d*, C(4′)); 34.15 (*d*, Me_2CH); 25.10 (*s*, Me_2CSi); 20.59 (*q*, Me); 20.47 (*q*, Me); 20.39 (*q*, Me); 20.18 (*q*, Me_2CH); 18.60 (*q*, *Me*CSi); 18.44 (*q*, *Me*CSi); −0.51 (*q*, Me_3Si); −3.13 (*q*, MeSi); −3.39 (*q*, MeSi). FAB-MS (NOBA): 1017 (30, [*M*(^{81}Br)−1]$^+$), 1015 (24, [*M*(^{79}Br)−1]$^+$), 897 (46), 895 (40), 377 (8, [*M*(^{81}Br)−aglycone]$^+$), 375 (8, [*M*(^{79}Br)−aglycone]$^+$), 199 (13), 197 (13), 121 (100), 73 (19, Me_3Si^+). Anal. calc. for $C_{49}H_{69}BrO_{14}Si_2$ (1018.16): C 57.80, H 6.83; found: C 57.73, H 6.53.

4-Deoxy-4-C-*[(trimethylgermyl)ethynyl]-β*-D-*glucopyranosyl-(1→8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis*-O-*(4-methoxybenzyl)-10*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→4*-C*)-2,3,6-tri*-O-*acetyl-4-deoxy-β*-D-*glucopyranosyl-(1→6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**37**) *and 4-Deoxy-4*-C-*[4-[2,3,6-tri*-O-*acetyl-β*-D-*glucopyranose-1,4-diyl-(1→6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyl-*

dimethylsilyl)-1-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol-6-yl]buta-1,3-diyne-1-yl]-β*-D-*glucopyranosyl-(1→8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis*-O-*(4-methoxybenzyl)-10*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→4-C)-2,3,6-tri*-O-*acetyl-4-deoxy-β*-D-*glucopyranosyl-(1→6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**38**). A degassed soln. of **35** (432 mg, 0.504 mmol), **36** (513 mg, 0.504 mmol), $[Pd_2(dba)_3]$ (13.8 mg, 3 mol-%), CuI (2.9 mg, 3 mol-%), and P(furyl)$_3$ (7.0 mg, 6 mol-%) in DMSO (5 ml) was treated at r.t. with Et_3N (0.3 ml), stirred at r.t. for 6 h, poured into ice-cold sat. NH_4Cl soln. (5 ml), and worked up (CH_2Cl_2). FC (hexane/CH_2Cl_2/AcOEt 1:1:0→3:1:1→2:1:1→4:2:3) gave **36** (39.5 mg, 8%), **37** (586 mg, 65%), and **35** (18.6 mg, 4%) as colourless oils.

In an analogous experiment, the reaction time was extended to 17 h, and additionally **38** (2%) was isolated as a colourless oil.

Data of **37**: R_f (hexane/AcOEt 6:7) 0.40. $[\alpha]_D^{25} = -3.4$ ($c = 1.2$, $CHCl_3$). IR (CCl_4): 3599*m*, 3457*m* (br.), 2958*s*, 2908*m*, 2875*m*, 2836*m*, 2170*w*, 1759*s*, 1613*m*, 1587*m*, 1514*s*, 1464*m*, 1441*m*, 1366*m*, 1302*m*, 1250*s*, 1230*s*, 1172*m*, 1151*m*, 1089*s*, 1040*s*, 946*w*, 913*w*, 832*s*. ^{1}H-NMR (500 MHz, $CDCl_3$, assignment based on H,H-COSY): 7.28–7.19 (*m*, 8 arom. H); 6.88–6.80 (*m*, 8 arom. H); 5.18–5.12 (*m*, *M* of *ABMX*, virtual coupling, $J_{MX} \approx 10.6$, $J_{AM} \approx 9.3$, irrad. at 2.92 ppm → *ABM*, *m*, virtual coupling, $J_{AM} \approx 9.3$, irrad. at 4.99 → *d*, $J_{MX} = 10.6$, H–C(3′)); 4.89 (*d*, $J = 11.0$, ArC*H*); 4.83 (*d*, $J = 10.6$, ArC*H*); 4.82–4.78 (*m*, *AB* of H–C(1′)/H–C(2′), 2 ArC*H*); 4.74 (*d*, $J = 10.6$, ArC*H*); 4.72 (*d*, $J = 10.8$, ArC*H*); 4.64 (*d*, $J = 10.8$, ArC*H*); 4.62 (*d*, $J = 7.8$, H–C(1‴)); 4.60 (*d*, $J = 10.9$, ArC*H*); 4.31 (*dd*, $J = 11.8$, 2.7, H_a–C(6′)); 4.24 (*dd*, $J = 11.8$, 4.7, H_b–C(6′)); 4.00 (*d*, $J = 9.5$, H–C(3)); 3.96 (*dd*, $J = 9.0$, 2.8, H_a–C(8)); 3.90 (*d*, $J = 9.3$, H–C(5″)); 3.88 (*t*, $J \approx 10.0$, H–C(6)); 3.86–3.83 (*m*, H_a–C(10″), H_b–C(8)); 3.85 (*t*, $J \approx 9.2$, H–C(8″)); 3.81 (*s*, MeO); 3.80 (*s*, 2 MeO); 3.78 (*s*, MeO); 3.79–3.76 (*m*, addn. of D_2O, signal changed, H_a–C(6‴), H_b–C(10″)); 3.59 (*ddd*, $J = 10.3$, 4.6, 2.7, H–C(5′)); 3.57–3.50 (*m*, addn. of D_2O → 3.55, *dd*, $J = 10.2$, 9.1, H–C(3‴), → 3.52, *dd*, $J = 10.9$, 6.2, H_b–C(6‴), → 3.50, *t*, $J \approx 9.0$, H–C(5)); 3.43 (*t*, $J \approx 9.3$, H–C(4)); 3.42 (*t*, $J \approx 8.9$, H–C(7″)); 3.39 (*t*, $J \approx 9.0$, H–C(6′)); 3.35–3.33 (*m*, addn. of D_2O → 3.35, *ddd*, $J = 10.2$, 6.2, 2.6, H–C(5‴)); 3.26 (br. *t*, addn. of D_2O → *t*, $J \approx 8.4$, H–C(2‴)); 3.22 (br. *dt*, $J \approx 9.6$, 1.8, H–C(7)); 3.09–3.07 (*m*, addn. of D_2O → 3.09, br. *ddd*, $J \approx 9.7$, 2.8, 1.5, H–C(9″)); 3.04 (*d*, $J = 2.1$, exchanged with D_2O, HO–C(2‴)); 2.93 (*t*, $J \approx 10.3$, H–C(4′)); 2.66 (*d*, $J = 2.2$, exchanged with D_2O, HO–C(3‴)); 2.47 (*t*, $J \approx 10.4$, H–C(4‴)); 2.02 (*s*, Ac); 2.01 (*s*, Ac); 1.98 (*s*, Ac); 1.70–1.60 (*m*, HO–C(6‴), addn. of D_2O → 1.64, *sept.*, $J = 6.9$, Me_2CH, → 1.63, *sept.*, $J = 6.9$, Me_2CH); 0.92 (*d*, $J = 6.9$, *Me*CH); 0.91 (*d*, $J = 6.9$, *Me*CH); 0.90 (*d*, $J = 6.9$, *Me*CH); 0.89 (*d*, $J = 6.9$, *Me*CH); 0.869 (*s*, *Me*CSi); 0.866 (*s*, *Me*CSi); 0.857 (2*s*, *Me*CSi); 0.33 (*s*, Me_3Ge); 0.17 (*s*, Me_3Si); 0.152 (*s*, MeSi); 0.147 (*s*, MeSi); 0.143 (*s*, MeSi); 0.134 (*s*, MeSi). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.45 (*s*, C=O); 169.64 (*s*, C=O); 169.51 (*s*, C=O); 159.46 (*s*); 159.26 (*s*); 159.22 (*s*); 158.99 (*s*); 131.38 (*s*); 130.81 (*s*); 130.38 (*s*); 1 arom. *s* not observed or hidden; 129.92 (2*d*); 129.78 (2*d*); 129.12 (2*d*); 128.96 (2*d*); 113.92 (2*d*); 113.79 (2*d*); 113.68 (2*d*); 113.57 (2*d*); 102.92 (*s*, *C*≡CSi); 101.92 (*d*, C(1‴)); 100.01 (*s*, *C*≡CGe); 99.94 (*d*, C(1′)); 90.43 (*s*, C≡*C*Si); 90.07 (*s*, C≡*C*Ge); 83.85 (*d*); 83.22 (*d*); 81.68 (*d*); 81.45 (*d*); 79.75 (*d*); 79.43 (*d*); 76.39 (*d*); 75.73 (*d*); 75.66 (*d*); 75.32 (*t*, Ar*C*H$_2$); 75.26 (*s*, C(1″)); 75.17 (*t*, Ar*C*H$_2$); 75.14 (*t*, Ar*C*H$_2$); 75.09 (*d*); 74.91 (*d*); 74.71 (*t*, Ar*C*H$_2$); 73.87 (*s*, C(4″)); 72.57 (*d*); 72.46 (*d*); 72.41 (*d*); 70.01 (*d*, C(5″)); 69.74 (*d*, C(3)); 69.42 (*s*, C(3″)); 68.77 (*s*, C(2″)); 64.02 (*t*); 63.36 (*t*); 61.52 (*t*); 61.13 (*t*); 55.31 (*q*, MeO); 55.27 (*q*, 2 MeO); 55.25 (*q*, MeO); 38.63 (*d*, C(4‴)); 36.78 (*d*, C(4′)); 34.26 (*d*, Me_2CH); 34.21 (*d*, Me_2CH); 25.28 (*s*, Me_2CSi); 25.23 (*s*, Me_2CSi); 20.74 (*q*, Me); 20.67 (*q*, Me); 20.54 (*q*, Me); 20.46 (*q*, *Me*CH); 20.34 (*q*, *Me*CH); 20.32 (*q*, *Me*CH); 20.23 (*q*, *Me*CH); 18.75 (*q*, *Me*CSi); 18.70 (*q*, *Me*CSi); 18.59 (*q*, *Me*CSi); 18.52 (*q*, *Me*CSi); −0.12 (*q*, Me_3Ge); −0.31 (*q*, Me_3Si); −2.85 (*q*, MeSi); −2.90 (*q*, MeSi); −3.18 (*q*, MeSi); −3.24 (*q*, MeSi). MALDI-TOF-MS: 1834 ($[M+K]^+$), 1818 ($[M+Na]^+$). Anal. calc. for $C_{92}H_{132}GeO_{25}Si_3$ (1794.91): C 61.56, H 7.41; found: C 61.76, H 7.40.

Data of **38**: R_f (hexane/AcOEt 6:9) 0.37. $[\alpha]_D^{25} = +6.7$ ($c = 1.2$, $CHCl_3$). IR (CCl_4): 3596*m*, 3460*m* (br.), 2959*s*, 2907*m*, 2876*m*, 2836*m*, 2172*w*, 1759*s*, 1613*m*, 1587*m*, 1515*s*, 1464*m*, 1441*m*, 1365*m*, 1302*m*, 1251*s*, 1229*s*, 1172*m*, 1151*m*, 1089*s*, 1041*s*, 946*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.28–7.15 (*m*, 12 arom. H); 6.88–6.77 (*m*, 12 arom. H); 5.18–5.13 (*m*, *M* of *ABMX*, virtual coupling, $J_{MX} \approx 10.5$, $J_{AM} \approx 9.4$, H–C(3′)); 5.12–5.08 (*m*, *M* of *ABMX*, virtual coupling, $J_{MX} \approx 10.6$, $J_{AM} \approx 9.3$, H–C(3^{IV})); 4.89 (*d*, $J = 11.3$, ArC*H*); 4.88 (*d*, $J = 11.2$, ArC*H*); 4.82–4.67 (*m*, H–C(1′), H–C(2′), H–C(1^{IV}), H–C(2^{IV}), 8 ArC*H*); 4.64 (*d*, $J = 10.5$, ArC*H*); 4.63 (*d*, $J = 7.8$, H–C(1‴)); 4.61 (*d*, $J = 11.2$, ArC*H*); 4.32 (br. *dd*, $J \approx 11.5$, 2.3, H_a–C(6′), H_a–C(6^{IV})); 4.24 (*dd*, $J = 12.0$, 4.9, H_b–C(6′)); 4.23 (*dd*, $J = 12.0$, 5.0, H_b–C(6^{IV})); 4.01 (br. *d*, $J \approx 9.5$, H–C(3), H–C(3^V)); 3.96 (br. *dd*, $J \approx 11.5$, 2.5, H_a–C(8)); 3.95 (*dd*, $J \approx 11.5$, 2.2, H_a–C(8^V)); 3.91 (*d*, $J = 9.3$, H–C(5″)); 3.89–3.72 (*m*, addn. of D_2O → signal changed, H_b–C(8), H_b–C(8^V), H_a–C(10″), H–C(6), H–C(8″), H–C(6^{IV})); 3.809 (*s*, MeO); 3.806 (*s*, MeO); 3.80 (*s*, MeO); 3.79 (*s*, MeO); 3.78 (*s*, 2 MeO); 3.76–3.64 (*m*, addn. of D_2O → signal changed, H_b–C(10″), H_a–C(6‴)); 3.62–3.53 (*m*, addn. of D_2O → 3.59, *ddd*, $J = 11.5$, 4.7, 2.5, H–C(5′), → 3.58,

dd, J = 10.5, 9.1, H–C(3‴), → 3.55, *ddd*, $J \approx$ 10.0, 4.9, 2.8, H–C(5^{IV})); 3.52–3.46 (*m*, addn. of D_2O → 3.49, *dd*, J = 11.0, 5.5, H_b–C(6‴), → 3.48 *t*, $J \approx$ 9.1, H–C(5), → 3.47, *t*, $J \approx$ 9.2, H–C(5^{V})); 3.43 (*t*, $J \approx$ 9.4, H–C(4)); 3.42 (*t*, $J \approx$ 9.0, H–C(7″)); 3.41 (*t*, $J \approx$ 8.9, H–C(4^{V})); 3.39 (*t*, $J \approx$ 8.7, H–C(6″)); 3.12 (br. *ddd*, addn. of D_2O → *ddd*, J = 10.2, 5.4, 2.1, H–C(5‴)); 3.25–3.19 (*m*, addn. of D_2O → 3.22, *dd*, J = 9.1, 7.8, H–C(2‴), additionally H–C(7), H–C(7^{V})); 3.16 (br. *d*, $J \approx$ 2.1, exchanged with D_2O, HO–C(2‴)); 3.08 (br. *dt*, $J \approx$ 8.8, 1.3, H–C(9″)); 2.93 (*t*, $J \approx$ 10.5, H–C(4′)); 2.89 (*t*, $J \approx$ 10.4, H–C(4^{IV})); 2.71 (*d*, J = 2.9, exchanged with D_2O, HO–C(3‴)); 2.58 (br. *td*, addn. of D_2O → *t*, $J \approx$ 10.5, H–C(4‴)); 2.07 (*s*, Ac); 2.019 (*s*, Ac); 2.018 (*s*, Ac); 2.01 (*s*, Ac); 1.99 (*s*, Ac); 1.98 (*s*, Ac); 1.81 (br. *s*, exchanged with D_2O, HO–C(6‴)); 1.65 (*sept.*, $J \approx$ 6.9, 2 Me_2CH); 1.64 (*sept.*, J = 6.9, Me_2CH); 0.94 (*d*, J = 6.9, *Me*CH); 0.93 (*d*, J = 6.9, *Me*CH); 0.92 (*d*, J = 6.9, *Me*CH); 0.91 (*d*, J = 6.9, *Me*CH); 0.89 (*d*, J = 6.9, *Me*CH); 0.88 (*d*, J = 6.9, *Me*CH); 0.88 (*s*, *Me*CSi); 0.879 (*s*, *Me*CSi); 0.868 (*s*, *Me*CSi); 0.865 (*s*, *Me*CSi); 0.855 (*s*, 2 *Me*CSi); 0.173 (*s*, Me_3Si); 0.172 (*s*, Me_3Si); 0.16 (*s*, MeSi); 0.15 (*s*, 2 MeSi); 0.146 (*s*, 2 MeSi); 0.14 (*s*, MeSi). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.59 (*s*, C=O); 170.45 (*s*, C=O); 169.80 (*s*, C=O); 169.64 (*s*, C=O); 169.52 (*s*, C=O); 169.50 (*s*, C=O); 159.49 (*s*); 159.27 (2*s*); 159.24 (*s*); 158.99 (*s*); 158.98 (*s*); 131.43 (*s*); 131.39 (*s*); 130.75 (*s*); 130.44 (2*s*); 129.94 (2*d*); 129.88 (*s*); 129.79 (4*d*); 129.11 (2*d*); 129.07 (2*d*); 128.75 (2*d*); 113.93 (2*d*); 113.84 (2*d*); 113.68 (4*d*); 113.57 (4*d*); 102.94 (*s*, *C*≡CSi); 102.92 (*s*, *C*≡CSi); 101.99 (*d*, C(1‴)); 99.95 (*d*, C(1′)); 99.90 (*d*, C(1^{IV})); 90.44 (*s*, C≡*C*Si); 90.42 (*s*, C≡*C*Si); 83.98 (*d*); 83.28 (*d*); 83.23 (*d*); 81.68 (2*d*); 81.47 (*d*); 79.60 (*d*); 79.43 (2*d*); 76.40 (*d*); 76.37 (*d*); 75.65 (*d*); 75.33 (*t*, 2 Ar*C*H_2); 75.15 (*t*, 2 Ar*C*H_2); 75.15 (*d*); 75.08 (*d*); 74.72 (*t*, 2 Ar*C*H_2); 74.36 (*d*); 73.95 (*s*); 72.58 (*d*); 72.56 (*d*); 72.53 (2*d*); 72.45 (*d*); 72.41 (*d*); 72.05 (*s*); 70.04 (*d*); 69.74 (2*d*); 69.49 (*s*); 69.06 (*s*); 68.74 (*s*); 68.55 (*s*); 67.93 (*s*); 64.05 (*t*); 64.02 (*t*); 63.01 (*t*); 61.57 (*t*); 61.14 (*t*); 61.11 (*t*); 55.33 (*q*, 3 MeO); 55.27 (*q*, 3 MeO); 37.53 (*d*); 36.78 (*d*); 36.50 (*d*); 34.28 (*d*, 2 Me*C*H); 34.08 (*d*, Me*C*H); 25.32 (*s*, Me*C*Si); 25.25 (*s*, Me*C*Si); 25.24 (*s*, Me*C*Si); 20.75 (*q*, 2 Me); 20.71 (*q*, Me); 20.67 (*q*, Me); 20.56 (*q*, Me); 20.54 (*q*, Me); 20.52 (*q*, Me); 20.47 (*q*, Me); 20.35 (*q*, 2 Me); 20.34 (*q*, Me); 20.25 (*q*, Me); 18.78 (*q*, Me); 18.75 (*q*, Me); 18.71 (*q*, Me); 18.61 (*q*, Me); 18.60 (*q*, Me); 18.52 (*q*, Me); −0.30 (*q*, Me_3Si); −2.88 (*q*, MeSi); −2.90 (*q*, MeSi); −2.92 to −3.18 (*q*, 2 MeSi); −3.20 (*q*, MeSi); 1*s* for C≡C not observed or hidden. MALDI-TOF-MS: 2639 ([M + Na]$^+$). Anal. calc. for $C_{138}H_{193}O_{39}Si_5 \cdot$ AcOEt (2692.58): C 62.69, H 7.45; found: 62.40, H 7.27.

4-Deoxy-4-C-*[(trimethylgermyl)ethynyl]-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis*-O-*(4-methoxybenzyl)-10*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-4-deoxy-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**39**). A soln. of **37** (721 mg, 0.4 mmol) in THF (10 ml) was treated dropwise at 0° with cold sat. K_2CO_3 soln. in MeOH (0.5 ml), stirred for 6 h, neutralized with *Amberlite IR-120* (H^+ form), filtered, and evaporated. FC ($CHCl_3$ → $CHCl_3$/MeOH 20 : 1) gave **39** (497 mg, 78%). Colourless oil. R_f ($CHCl_3$/MeOH 20 : 1) 0.31. $[\alpha]_D^{25} = +21.8$ (c = 1.1, $CHCl_3$). IR (CCl_4): 3593*m*, 3481*m* (br.), 3312*m*, 2957*m*, 2878*m*, 2836*m*, 2169*w*, 1613*m*, 1586*w*, 1558*w*, 1514*s*, 1464*m*, 1441*w*, 1356*w*, 1301*m*, 1273*w*, 1250*s*, 1172*m*, 1150*m*, 1090*s*, 1061*s*, 1040*s*, 910*w*, 874*w*, 832*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.30–7.21 (*m*, 8 arom. H); 6.88–6.80 (*m*, 8 arom. H); 4.88 (*d*, J = 10.0, ArC*H*); 4.84 (*d*, J = 10.6, ArC*H*); 4.81 (*d*, J = 10.6, ArC*H*); 4.80 (*d*, J = 10.5, ArC*H*); 4.76 (*d*, J = 11.9, 2 ArC*H*); 4.74 (*d*, J = 11.8, ArC*H*); 4.73 (*d*, J = 10.1, ArC*H*); 4.65 (*d*, J = 8.3, H–C(1‴)); 4.63 (*d*, J = 7.7, H–C(1′)); 4.04–3.93 (*m*, addn. of D_2O → 4.02, *d*, J = 9.5, H–C(5″), → 3.98, *dd*, J = 9.4, 2.1, H–C(3), → 3.97, *dd*, $J \approx$ 11.0, 2.4, H_a–C(6′), → 3.95, *dd*, $J \approx$ 11.0, 4.0, H_a–C(6‴)); 3.91 (*t*, $J \approx$ 9.6, H–C(6)); 3.88 (*t*, $J \approx$ 9.5, H–C(8″)); 3.88 (br. *dd*, $J \approx$ 12.0, 2.0, H_a–C(8)); 3.86 (br. *dd*, $J \approx$ 12.0, 1.5, H_a–C(10″)); 3.81 (*s*, MeO); 3.79 (*s*, MeO); 3.786 (*s*, MeO); 3.784 (*s*, MeO); 3.81–3.75 (*m*, addn. of D_2O → signal changed, H_b–C(6′), H_b–C(6‴)); 3.60–3.50 (*m*, H_b–C(8), H_b–C(10″), addn. of D_2O → 3.61, *dd*, J = 10.4, 9.0, H–C(3′), → 3.56, *dd*, J = 10.3, 9.0, H–C(3‴), → 3.52, *t*, $J \approx$ 9.0, H–C(7″), → 3.51, *t*, $J \approx$ 9.0, H–C(5)); 3.47 (*t*, $J \approx$ 9.3, H–C(4)); 3.43 (*t*, $J \approx$ 9.4, H–C(6″)); 3.38–3.31 (*m*, addn. of D_2O → signal changed, H–C(5′), H–C(5‴)); 3.26–3.23 (*m*, addn. of D_2O → signal changed, H–C(7′), H–C(9″), HO–C(3′), → 3.26, *dd*, J = 9.0, 7.8, H–C(2′), → 3.25, *t*, $J \approx$ 8.8, H–C(2‴)); 3.25 (br. *s*, exchanged with D_2O, HO–C(2′)); 3.08 (br. *s*, exchanged with D_2O, HO–C(2‴)); 2.66 (*t*, $J \approx$ 10.4, H–C(4′)); 2.63 (br. *s*, exchanged with D_2O, HO–C(3‴)); 2.50 (*d*, J = 2.1, H–C(1)); 2.48 (*t*, $J \approx$ 10.3, H–C(4‴)); 2.01 (br. *t*, $J \approx$ 6.0, addn. of D_2O, HO–C(6′)); 1.93 (br. *t*, $J \approx$ 6.5, addn. of D_2O, HO–C(6‴)); 1.65 (*sept.*, J = 6.9, Me_2CH); 1.64 (*sept.*, J = 6.9, Me_2CH); 0.90 (*d*, J = 6.9, *Me*CH); 0.89 (*d*, J = 6.9, *Me*CH); 0.883 (*d*, J = 6.9, *Me*CH); 0.875 (*d*, J = 6.9, *Me*CH); 0.86 (*s*, 2 *Me*CSi); 0.85 (*s*, 2 *Me*CSi); 0.33 (*s*, Me_3Ge); 0.150 (*s*, MeSi); 0.145 (*s*, MeSi); 0.14 (*s*, 2 MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.41 (2*s*); 159.23 (*s*); 159.22 (*s*); 130.18 (2*s*); 130.03 (2*s*); 129.99 (2*d*); 129.86 (2*d*); 128.99 (2*d*); 128.83 (2*d*); 113.93 (2*d*); 113.84 (2*d*); 113.83 (2*d*); 113.81 (2*d*); 101.99 (*d*, C(1‴)); 101.94 (*d*, C(1′)); 100.03 (*s*, *C*≡CGe); 90.06 (*s*, C≡*C*Ge); 84.02 (*d*); 83.98 (*d*); 81.82 (*d*); 81.51 (*d*); 81.01 (*d*, C≡*C*H); 79.69 (*d*); 79.40 (*d*); 76.20 (*s*); 75.72 (*d*); 75.68 (*d*); 75.65 (*d*); 75.34 (*t*, Ar*C*H_2); 75.34 (*d*); 75.27 (*t*, Ar*C*H_2); 75.18 (*t*, Ar*C*H_2); 75.13 (*t*, Ar*C*H_2); 75.13 (*d*); 75.09 (*d*); 74.91 (*d*); 74.75 (*s*, *C*≡CH); 74.47 (*d*); 73.75 (*s*); 70.04 (*d*, C(5″)); 69.76 (*s*);

69.47 (*d*, C(3)); 69.52 (*s*); 63.36 (*t*); 63.02 (*t*); 61.63 (*t*); 61.51 (*t*); 55.31 (*q*, 4 MeO); 38.62 (*d*, C(4‴)); 37.66 (*d*, C(4′)); 34.21 (*d*, Me*C*H); 34.10 (*d*, Me*C*H); 25.30 (*s*, Me*C*Si); 25.28 (*s*, Me*C*Si); 20.47 (*q*, 2 *Me*CH); 20.46 (*q*, *Me*CH); 20.24 (*q*, *Me*CH); 18.72 (*q*, *Me*CSi); 18.71 (*q*, *Me*CSi); 18.53 (*q*, 2 *Me*CSi); −0.11 (*q*, Me_3Ge); −2.79 (*q*, MeSi); −2.83 (*q*, MeSi); −3.24 (*q*, MeSi); −3.26 (*q*, MeSi). MALDI-TOF-MS: 1620 ($[M+Na]^+$). Anal. calc. for $C_{83}H_{118}GeO_{22}Si_2 \cdot CH_3OH$ (1628.65): C 61.96, H 7.55; found: C 61.79, H 7.35.

4-C-*(Bromoethynyl)-4-deoxy-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis*-O-*(4-methoxybenzyl)-10*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-2,3,6-tri*-O-*acetyl-4-deoxy-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**40**). A soln. of **37** (550 mg, 0.306 mmol) and NBS (65.4 mg, 0.37 mmol) in acetone (3 ml) was treated with CuBr (13.19 mg, 30 mol-%), stirred for 1 h, poured into ice-cold sat. $Na_2S_2O_3$ soln. (5 ml), and worked up (CH_2Cl_2). FC (hexane/CH_2Cl_2/AcOEt 1 : 1 : 1 → 4 : 2 : 3) gave **40** (441 mg, 81%). Amorphous solid. R_f (hexane/AcOEt 6 : 7) 0.40. $[\alpha]_D^{25} = -2.6$ ($c = 1.1$, $CHCl_3$). IR (CCl_4): 3589*m*, 3466*m* (br.), 2959*s*, 2875*m*, 2837*m*, 2178*w*, 1743*s*, 1613*m*, 1587*m*, 1514*s*, 1464*m*, 1441*m*, 1370*m*, 1301*m*, 1250*s*, 1172*m*, 1151*m*, 1089*s*, 1041*s*, 913*w*, 844*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.28–7.19 (*m*, 16 arom. H); 6.88–6.80 (*m*, 16 arom. H), 5.18–5.12 (*m*, *M* of *ABMX*, virtual coupling, $J_{MX} \approx 10.6$, $J_{AM} \approx 9.4$, H−C(3′)); 4.89 (*d*, $J = 11.0$, ArC*H*); 4.82–4.78 (*m*, *AB* of H−C(1′), H−C(2′), 3 ArC*H*); 4.75 (*d*, $J = 10.8$, ArC*H*); 4.71 (*d*, $J = 10.4$, ArC*H*); 4.63 (*d*, $J = 10.9$, ArC*H*); 4.62 (*d*, $J = 7.8$, H−C(1‴)); 4.60 (*d*, $J = 11.0$, ArC*H*); 4.32 (*dd*, $J = 12.0$, 2.8, H_a−C(6′)); 4.24 (*dd*, $J = 12.0$, 5.0, H_b−C(6′)); 4.01 (*d*, $J = 9.5$, H−C(3)); 3.96 (*dd*, $J = 12.0$, 2.5, H_a−C(8)); 3.91 (*d*, $J = 9.5$, H−C(5‴)); 3.89 (*t*, $J \approx 9.8$, H−C(6)); 3.88 (br. *d*, $J \approx 12.0$, H_b−C(8)); 3.85 (br. *d*, $J \approx 11.9$, H_a−C(10″)); 3.85 (*t*, $J \approx 9.2$, H−C(8″)); 3.81 (*s*, MeO); 3.80 (*s*, 2 MeO); 3.78 (*s*, MeO); 3.81–3.78 (*m*, H_b−C(10″)); 3.76–3.74 (*m*, addn. of $D_2O \rightarrow$ 3.76, *dd*, $J = 12.0$, 2.2, H_a−C(6‴)); 3.59 (*ddd*, $J = 10.4$, 5.0, 2.8, H−C(5′)); 3.57–3.49 (*m*, addn. of $D_2O \rightarrow$ 3.56, *t*, $J \approx 9.6$, H−C(3‴), → 3.51, *dd*, $J = 11.9$, 6.0, H_b−C(6‴)); 3.49 (*t*, $J \approx 9.0$, H−C(5)); 3.43 (*t*, $J \approx 9.4$, H−C(4)); 3.42 (*t*, $J \approx 9.0$, H−C(7″)); 3.40 (*t*, $J \approx 8.9$, H−C(6″)); 3.33–3.30 (*m*, addn. of $D_2O \rightarrow$ 3.32, *ddd*, $J = 10.2$, 5.8, 2.2, H−C(5‴)); 3.23 (br. *t*, addn. of $D_2O \rightarrow$ *t*, $J \approx 8.6$, H−C(2‴)); 3.21 (br. *dt*, $J \approx 10.0$, 1.5, H−C(7)); 3.17 (br. *s*, exchanged with D_2O, HO−C(2‴)); 3.09–3.07 (*m*, addn. of $D_2O \rightarrow$ 3.08, br. *ddd*, $J \approx 9.8$, 2.2, 1.3, H−C(9″)); 2.92 (*t*, $J \approx 10.3$, H−C(4′)); 2.60 (br. *s*, exchanged with D_2O, HO−C(3‴)); 2.52 (*t*, $J \approx 10.3$, H−C(4‴)); 2.02 (*s*, Ac); 2.01 (*s*, Ac); 1.98 (*s*, Ac); 1.88 (*m*, exchanged with D_2O, HO−C(6‴)); 1.65 (*sept.*, $J = 6.9$, Me_2CH); 1.64 (*sept.*, $J = 6.9$, Me_2CH); 0.92 (*d*, $J = 6.9$, *Me*CH); 0.91 (*d*, $J = 6.9$, *Me*CH); 0.90 (*d*, $J = 6.9$, *Me*CH); 0.89 (*d*, $J = 6.9$, *Me*CH); 0.869 (*s*, *Me*CSi); 0.866 (*s*, *Me*CSi); 0.857 (*s*, 2 *Me*CSi); 0.17 (*s*, Me_3Si); 0.153 (*s*, MeSi), 0.147 (*s*, 2 MeSi); 0.135 (*s*, MeSi). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.46 (*s*, C=O); 169.64 (*s*, C=O); 169.51 (*s*, C=O); 159.48 (*s*); 159.27 (*s*); 159.22 (*s*); 158.99 (*s*); 131.39 (*s*); 130.18 (*s*); 130.43 (*s*); 130.01 (*s*); 129.93 (2*d*); 129.79 (2*d*); 129.11 (2*d*); 128.78 (2*d*); 113.93 (2*d*); 113.82 (2*d*); 113.67 (2*d*); 113.57 (2*d*); 102.92 (*s*, *C*≡CSi); 101.98 (*d*, C(1‴)); 99.94 (*d*, C(1′)); 90.43 (*s*, C≡*C*Si); 83.99 (*d*); 83.22 (*d*); 81.68 (*d*); 81.47 (*d*); 79.60 (*d*); 79.43 (*d*); 76.39 (*d*); 75.92 (*s*, *C*≡CBr); 75.58 (*d*); 75.34 (*d*); 75.33 (*s*, C(1″)); 75.15 (*t*, 2 Ar*C*H$_2$); 75.12 (*d*); 75.12 (*t*, Ar*C*H$_2$); 74.71 (*t*, Ar*C*H$_2$); 74.56 (*d*); 73.93 (*s*, C(4″)); 72.56 (*d*); 72.45 (*d*); 72.41 (*d*); 70.03 (*d*, C(5″)); 69.74 (*d*, C(3)); 69.48 (*s*, C(3″)); 68.74 (*s*, C(2″)); 64.01 (*t*); 63.04 (*t*); 61.57 (*t*); 61.13 (*t*); 55.32 (*q*, MeO); 55.27 (*q*, 2 MeO); 55.25 (*q*, MeO); 43.63 (*s*, C≡*C*Br); 38.01 (*d*, C(4‴)); 36.77 (*d*, C(4′)); 34.27 (*d*, Me*C*H); 34.08 (*d*, Me*C*H); 25.31 (*s*, Me*C*Si); 25.23 (*s*, Me*C*Si); 20.74 (*q*, Me); 20.67 (*q*, Me); 20.54 (*q*, Me); 20.54 (*q*, *Me*CH); 20.46 (*q*, *Me*CH); 20.34 (*q*, *Me*CH); 20.23 (*q*, *Me*CH); 18.75 (*q*, *Me*CSi); 18.70 (*q*, *Me*CSi); 18.59 (*q*, *Me*CSi); 18.51 (*q*, *Me*CSi); −0.30 (*q*, Me_3Si); −2.86 (*q*, MeSi); −2.90 (*q*, MeSi); −3.18 (*q*, MeSi); −3.23 (*q*, MeSi). MALDI-TOF-MS: 1796 ($[M+K]^+$), 1780 ($[M+Na]^+$). Anal. calc. for $C_{89}H_{123}BrO_{25}Si_3$ (1757.10): C 60.84, H 7.06, Br 4.55; found: C 60.25, H 6.72, Br 4.28.

4-Deoxy-4-C-*[(trimethylgermyl)ethynyl]-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis*-O-*(4-methoxybenzyl)-10*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-4-deoxy-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis*-O-*(4-methoxybenzyl)-10*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-4-deoxy-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis*-O-*(4-methoxybenzyl)-10*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-2,3,6-tri*-O-*acetyl-4-deoxy-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**41**). A degassed soln. of **40** (383 mg, 0.217 mmol), **39** (340 mg, 0.213 mmol), [Pd_2(dba)$_3$] (5.9 mg, 3 mol-%), CuI (1.2 mg, 3 mol-%), and P(furyl)$_3$ (3.0 mg, 6 mol-%) in DMSO (5 ml) was treated at r.t. with Et_3N (0.1 ml), stirred for 2.5 h, poured into ice-cold sat. NH_4Cl soln. (5 ml), and worked up (CH_2Cl_2). FC ($CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH/toluene 60 : 1 : 2 → 120 : 4 : 3) gave **41** (376.4 mg, 54%). Colourless oil. R_f (CH_2Cl_2/toluene/MeOH 30 : 1 : 1) 0.21. $[\alpha]_D^{25} = -1.5$ ($c =$ 1.0, $CHCl_3$). IR (CCl_4): 3573*s* (br.), 3477*s* (br.), 2957*s*, 2880*m*, 2831*m*, 2805*m*, 2178*w*, 1755*s*, 1644*w*, 1611*s*, 1586*m*, 1514*s*, 1366*m*, 1298*m*, 1250*s*, 1173*m*, 1149*m*, 1089*s*, 1039*s*, 913*w*, 832*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–7.18 (*m*, 16 arom. H); 6.78–6.94 (*m*, 16 arom. H); 5.19–5.12 (*m*, *M* of *ABMX*, virtual coupling, $J_{MX} \approx 10.6$, $J_{AM} \approx 9,6$,

H−C(3^{II})); 4.92–4.52 (*m*, H−C(1^{II}), H−C(2^{II}), H−C(1^{IV}), H−C(1^{VI}), H−C(1^{VIII}), 16 ArC*H*); 4.31 (*dd*, *J* ≈ 11.5, 2.2, H_a−C(6^{II})); 4.24 (*dd*, *J* = 11.8, 4.4, H_b−C(6^{II})); 4.02 (*d*, *J* = 9.3, H−C(3^{I})); 4.00 (*d*, *J* = 9.0, H−C(5^{III})); 3.97–3.67 (*m*, 19 H); 3.81 (*s*, MeO); 3.80 (*s*, MeO); 3.79 (*s*, 3 MeO); 3.787 (*s*, 3 MeO); 3.66–3.18 (*m*, 26 H, addn. of D_2O → signal changed, 2 H exchanged); 3.12–3.04 (*m*, addn. of D_2O → 1 H exchanged, → 3.08 br. *d*, *J* ≈ 10, 1 H); 2.93 (*t*, *J* ≈ 10.6, H−C(4^{II})); 2.84 (br. *s*, exchanged with D_2O, OH); 2.65 (br. *s*, exchanged with D_2O, 2 OH); 2.65 (*t*, *J* ≈ 10.4, H−C(4^{IV}), H−C(4^{VI})); 2.48 (*t*, *J* ≈ 10.4, H−C(4^{VIII})); 2.02 (*s*, Ac); 2.01 (*s*, Ac); 1.98 (*s*, Ac); 1.78–1.55 (*m*, addn. of D_2O → 3 H exchanged, 4 Me_2CH); 0.95–0.78 (*m*, 16 Me); 0.33 (*s*, Me_3Ge); 0.17 (*s*, Me_3Si); 0.18–0.12 (*m*, 8 MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 170.46 (*s*, C=O); 169.64 (*s*, C=O); 169.51 (*s*, C=O); 159.49 (*s*); 159.41 (2*s*); 159.27 (2*s*); 159.23 (2*s*); 158.99 (*s*); 131.39 (2*s*); 130.85 (2*s*); 130.76 (2*s*); 130.44 (2*s*); 129.99–128.75 (several *d*); 113.93 (4*d*); 113.84 (4*d*); 113.81 (4*d*); 113.68 (2*d*); 113.57 (2*d*); 102.93 (*s*, *C*≡CSi); 101.99 (*d*, C(1^{IV}), C(1^{VIII})); 101.95 (*d*, C(1^{VI})); 100.02 (*s*, *C*≡CGe); 99.95 (*d*, C(1^{II})); 90.44 (*s*, C≡*C*Si); 90.06 (*s*, C≡*C*Ge); 84.06 (*d*); 83.97 (2*d*); 83.23 (*d*); 81.68 (2*d*); 81.51 (2*d*); 79.68 (*d*); 79.56 (*d*); 79.43 (2*d*); 76.40 (*d*); 76.26 (*d*); 76.20 (*s*); 75.72 (2*d*); 75.68 (*d*); 75.64 (2*d*); 75.33 (*t*, 3 ArCH_2); 75.33 (*d*); 75.15 (*t*, 3 ArCH_2); 75.15 (*d*); 75.08 (2*d*); 74.91 (2*d*); 74.77 (*s*); 74.71 (*t*, 2 ArCH_2); 74.46 (*d*); 73.96 (*s*); 72.56 (*d*); 72.45 (*d*); 72.41 (*d*); 70.04 (2*d*); 69.81 (*s*); 69.74 (2*d*); 69.50 (*s*); 68.74 (*s*); 68.52 (*s*); 68.49 (*s*); 64.02 (*t*); 63.36 (2*t*); 63.00 (2*t*); 61.51 (2*t*); 61.14 (*t*); 38.62 (*d*, C(4^{VIII})); 37.64 (*d*, C(4^{VI})); 37.50 (*d*, C(4^{IV})); 36.78 (*d*, C(4^{II})); 34.27 (*d*, Me*C*H); 34.09 (*d*, 3 Me*C*H); 25.35 (*s*, Me*C*Si); 25.30 (*s*, Me*C*Si); 25.28 (*s*, Me*C*Si); 25.24 (*s*, Me*C*Si); 20.75 (*q*, Me); 20.67 (*q*, Me); 20.54 (*q*, 2 Me); 20.47 (*q*, 3 Me); 20.33 (*q*, Me); 20.24 (*q*, 3 Me); 18.76 (*q*, Me); 18.72 (*q*, 3 Me); 18.60 (*q*, Me); 18.53 (*q*, 3 Me); −0.11 (*q*, Me_3Ge); −0.30 (*q*, Me_3Si); −2.79 (*q*, 2 MeSi); −2.85 (*q*, MeSi); −2.89 (*q*, 2 MeSi); −3.18 (*q*, MeSi); −3.23 (*q*, 2 MeSi); 3*s* for C≡C not observed or hidden. MALDI-TOF-MS: 3296 ([*M* + Na]$^+$). Anal. calc. for $C_{172}H_{240}GeO_{47}Si_5$ (3272.82): C 63.12, H 7.39; found: C 62.95, H 7.27.

*4-Deoxy-4-*C*-[(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis-*O*-(4-methoxybenzyl)-8-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**42**), *4-Deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-C)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis-*O*-(4-methoxybenzyl)-8-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**43**), *and 4-Deoxy-4-*C*-[(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3-di-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis-*O*-(4-methoxybenzyl)-8-*O*-(thexyldimethylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**44**). A soln. of **41** (325 mg, 99.3 μmol) in THF (6 ml) was treated dropwise at 0° with cold sat. K_2CO_3 soln. in MeOH (0.3 ml), stirred for 10 h at 0°, neutralized with *Amberlite IR-120* (H^+ form), filtered, and evaporated. FC ($CHCl_3$ → $CHCl_3$/MeOH/toluene 60 : 1 : 2 → 120 : 3 : 4) gave **44** (19.5 mg, 7%), **42** (168 mg, 55%) and **43** (7.2 mg, 2%) as colourless oils.

Data of **42**: R_f (CH_2Cl_2/toluene/MeOH 20 : 1 : 1) 0.24. $[\alpha]_D^{25}$ = +6.2 (*c* = 2, $CHCl_3$). IR (CCl_4): 3589*m*, 3411*m* (br.), 3311*m*, 3007*m*, 2955*s*, 2922*m*, 2872*m*, 2255*w*, 2167*w*, 1613*s*, 1514*s*, 1465*m*, 1364*m*, 1301*m*, 1251*s*, 1150*m*, 1089*s*, 1035*s*, 912*m*, 826*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.18 (*m*, 16 arom. H); 6.86–6.78 (*m*, 16 arom. H); 4.94–4.50 (*m*, H−C(1^{II}), H−C(1^{IV}), H−C(1^{VI}), H−C(1^{VIII}), 16 ArC*H*); 4.18–3.66 (*m*, addn. of D_2O → signal changed, 17 H); 3.81 (*s*, MeO); 3.78 (*s*, 2 MeO); 3.778 (*s*, 2 MeO); 3.775 (*s*, MeO); 3.76 (*s*, MeO); 3.74 (*s*, MeO); 3.64–3.10 (*m*, addn. of D_2O → signal changed, 3 H exchanged, 31 H); 2.80 (br. *s*, exchanged with D_2O, OH); 2.65 (*t*, *J* ≈ 10.4, H−C(4^{VI})); 2.62 (br. *t*, *J* ≈ 10.3, H−C(4^{II}), H−C(4^{IV})); 2.50 (*d*, *J* = 2.0, HC≡C−C(3^{I})); 2.47 (*t*, *J* ≈ 10.4, H−C(4^{VIII})); 2.14 (br. *s*, exchanged with D_2O, 4 OH); 2.02 (*d*, *J* = 3.0, exchanged with D_2O, OH); 1.92 (br. *s*, exchanged with D_2O, 3 OH); 1.70–1.54 (*m*, 4 Me_2CH); 0.92–0.80 (*m*, 16 Me); 0.33 (*s*, Me_3Ge); 0.18–0.10 (*m*, 8 MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.37 (2*s*); 159.32 (2*s*); 159.24 (2*s*); 159.20 (2*s*); 130.88 (2*s*); 130.76 (4*s*); 130.19 (2*s*); 130.09–128.99 (several *d*); 113.92–113.78

(several *d*); 101.98 (*d*, C(1^{IV}), C(1^{VIII})); 101.90 (*d*, C(1^{II}), C(1^{VI})); 100.21 (*s*, *C*≡CGe); 89.93 (*s*, C≡*C*Ge); 83.91 (2*d*); 83.84 (2*d*); 81.79 (2*d*); 81.68 (2*d*); 81.49 (*d*); 81.04 (*d*, C≡*C*H); 79.50 (4*d*); 75.76 (2*d*); 75.62 (2*d*); 75.27 (*t*, Ar*C*H$_2$); 75.27 (2*d*); 75.27 (*t*, 2 Ar*C*H$_2$); 75.21 (*t*, 2 Ar*C*H$_2$); 75.11 (4*d*); 74.95 (2*d*); 74.80 (*s*, *C*≡CH); 74.51 (2*d*); 74.38 (2*d*); 73.75 (*s*); 69.88 (2*d*); 69.66 (*s*); 69.43 (*d*); 68.35 (*s*); 63.29 (2*t*); 63.05 (2*t*); 61.58 (2*t*); 61.46 (2*t*); 55.29 (*q*, 5 MeO); 55.26 (2*q*, MeO); 55.24 (*q*, MeO); 38.60 (*d*, C(4^{VIII})); 37.88 (*d*, *C*(4^{IV}), C(4^{VI})); 37.72 (*d*, C(4^{II})); 34.11 (*d*, 2 *Me*CH); 34.09 (*d*, 2 *Me*CH); 25.27 (*s*, 8 CSi); 20.49 (*q*, 2 *Me*CH); 20.48 (*q*, 3 *Me*CH); 20.25 (*q*, 3 *Me*CH); 18.74 (*q*, 4 *Me*CSi); 18.54 (*q*, 4 *Me*CSi); 0.11 (*q*, Me$_3$Ge); −2.78 (*q*, MeSi); −2.82 (*q*, 2 MeSi); −2.85 (*q*, MeSi); −3.21 (*q*, 3 MeSi); −3.25 (*q*, MeSi); 9*s* for C≡C not observed or hidden. MALDI-TOF-MS: 3098 ([*M* + Na]$^+$). Anal. calc. for $C_{163}H_{226}GeO_{44}Si_4$ (3074.50): C 63.68, H 7.41; found: C 63.56, H 7.50.

Data of **43**: R_f (CH_2Cl_2/toluene/MeOH 20 : 1 : 1) 0.20. IR ($CHCl_3$): 3605*m*, 3400*m* (br.), 3308*m*, 3007*m*, 2960*s*, 2878*m*, 2177*w*, 1613*s*, 1442*m*, 1366*m*, 1301*m*, 1248*s*, 1173*m*, 1150*m*, 1089*s*, 1036*s*, 931*m*, 910*m*, 874*m*, 826*s*. MALDI-TOF-MS for $C_{160}H_{218}O_{44}Si_4$ (2957.84): 2981 ([*M* + Na]$^+$), 2997 ([*M* + K]$^+$).

Data of **44**: R_f (CH_2Cl_2/toluene/MeOH 20 : 1 : 1) 0.29. IR ($CHCl_3$): 3603*m*, 3400*m* (br.), 3306*m*, 3007*m*, 2959*s*, 2878*m*, 2178*w*, 1754*m*, 1613*s*, 1514*s*, 1465*m*, 1377*w*, 1302*m*, 1248*s*, 1088*s*, 1035*s*, 827*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.30–7.20 (*m*, 16 arom. H); 6.90–6.80 (*m*, 16 arom. H); 5.15 (*dd*, *J* = 10.7, 8.8, H−C(3^{II})); 4.90–4.70, 4.66–4.63 (2*m*, 16 Ar*CH*, H−C(1^{II}), H−C(1^{IV}), H−C(1^{VI}), H−C(1^{VIII}), H−C(2^{II})); 4.02 (br. *d*, *J* ≈ 9.3, H−C(5^{III}), H−C(5^{V}), H−C(5^{VII})); 4.03–3.85 (*m*, addn. of D_2O → signal changed, 14 H); 3.81 (*s*, MeO); 3.80 (*s*, MeO); 3.792 (*s*, MeO); 3.790 (*s*, 2 MeO); 3.788 (*s*, MeO); 3.786 (*s*, MeO); 3.783 (*s*, MeO); 3.81–3.74 (*m*, addn. of D_2O → signal changed, 2 H); 3.63–3.39 (*m*, addn. of D_2O → signal changed, 17 H); 3.37–3.32 (*m*, addn. of D_2O → signal changed, 3 H); 3.28–3.20 (*m*, addn. of D_2O → signal changed, 6 H, 2 H exchanged); 3.12 (br. *dt*, *J* ≈ 10.0, 2.7, 1 H); 3.02 (br. *s*, exchanged with D_2O, 1 OH); 2.86 (*t*, *J* ≈ 10.5, H−C(4^{II})); 2.72 (br. *s*, exchanged with D_2O, 2 OH); 2.66 (br. *t*, *J* ≈ 10.6, H−C(4^{IV}), H−C(4^{VI})); 2.58 (br. *d*, *J* ≈ 2.1, exchanged with D_2O, OH); 2.48 (*t*, *J* ≈ 10.5, H−C(4^{VIII})); 2.47 (*d*, *J* = 2.1, HC≡C−C(3^{I})); 2.02 (*s*, Ac); 2.01 (*s*, Ac); 1.91 (br. *s*, exchanged with D_2O, OH); 1.79 (br. *s*, exchanged with D_2O, 2 OH); 1.67–1.58 (*m*, 4 Me_2CH, 1 H exchanged with D_2O); 0.92–0.84 (*m*, 16 Me); 0.33 (*s*, Me$_3$Ge); 0.20–0.07 (*m*, 8 MeSi). ^{13}C-NMR (125 MHz, $CDCl_3$): 169.67 (*s*, C=O); 169.56 (*s*, C=O); 159.49 (*s*); 159.41 (*s*); 159.32 (2*s*); 159.36 (*s*); 159.22 (3*s*); 131.02 (*s*); 130.86 (2*s*); 130.77 (3*s*); 130.28 (2*s*); 129.98–128.74 (several *d*); 113.93 (5*d*); 113.84 (6*d*); 113.80 (5*d*); 102.01 (*d*, C(1^{IV}), C(1^{VI})); 101.96 (*d*, C(1^{VIII})); 99.96 (*s*, *C*≡CGe); 99.87 (*d*, C(1^{II})); 90.09 (*s*, C≡*C*Ge); 84.10 (*d*); 83.99 (2*d*); 83.50 (*d*); 81.84 (*d*); 81.60 (2*d*); 81.52 (2*d*); 81.02 (*d*, C≡*C*H); 79.69 (*d*); 79.65 (*d*); 79.54 (2*d*); 79.37 (*s*); 78.10 (*s*); 76.45 (*s*); 76.15 (*d*); 75.68 (br., 3*d*); 75.34 (2*t*); 75.34 (*d*); 75.29 (2*d*); 75.11 (3*t*); 75.07 (2*t*); 74.93 (*t*); 74.82 (2*d*); 75.75 (*s*, *C*≡CH); 74.74 (*d*); 74.44 (2*d*); 74.30 (*s*); 73.75 (*s*); 73.56 (*s*); 72.71 (*d*); 72.57 (*d*); 70.05 (2*d*); 69.82 (*s*); 69.75 (*s*); 69.60 (*d*); 69.48 (*d*); 69.38 (*d*); 68.56 (*s*); 68.55 (*s*); 68.51 (*s*); 63.36 (2*t*); 62.99 (2*t*); 62.72 (*t*); 61.59 (2*t*); 60.97 (*t*); 55.31 (*q*, 5 MeO); 55.29 (*q*, 3 MeO); 38.61 (*d*, C(4^{VIII}), C(4^{IV})); 37.62 (*d*, C(4^{VI})); 36.27 (*d*, C(4^{II})); 34.20 (*d*, 2 Me*C*H); 34.09 (*d*, 2Me*C*H); 25.30 (*s*, Me*C*Si); 25.28 (*s*, Me*C*Si); 25.20 (*s*, 2 Me*C*Si); 20.75 (*q*, Me); 20.57 (*q*, Me); 20.51 (*q*, 2 Me); 20.47 (*q*, 3 Me); 20.23 (*q*, 3 Me); 18.72 (*q*, 3 Me); 18.53 (*q*, 5 Me); −0.11 (*q*, Me$_3$Ge); −2.80 (*q*, 3 MeSi); −2.94 (*q*, MeSi); −3.25 (*q*, 4 MeSi). MALDI-TOF-MS for $C_{167}H_{230}GeO_{46}Si_4$ (3158.13): 3181 ([*M* + Na]$^+$), 3197 ([*M* + K]$^+$).

4-Deoxy-2,3,6-tris-O-*(triethylsilyl)-4*-C-*[(trimethylgermyl)ethynyl]-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis*-O-*(4-methoxybenzyl)-10*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-4-deoxy-2,3,6-tris*-O-*(triethylsilyl)-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis*-O-*(4-methoxybenzyl)-10*-O-*(thexyldimethylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4*-C*)-4-deoxy-2,3,6-tris*-O-*(triethylsilyl)-β*-D-*glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis*-O-*(4-methoxybenzyl)-10*-O-*(thexyldimethylsilyl)*-D-*glycero*-D-*gulo-deca-1,3-diynitol-1-yl-(1 → 4*-C*)-2,3,6-tri*-O-*acetyl-4-deoxy-β*-D-*glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis*-O-*(4-methoxybenzyl)-8*-O-*(thexyldimethylsilyl)-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**45**). A soln. of **41** (200 mg, 0.061 mmol) and 1*H*-imidazole (166.4 mg, 2.44 mmol) in DMF (4 ml) was treated at 0° with Et_3SiCl (193.1 µl, 1.83 mmol), stirred at r.t. for 5 h, poured into ice-water (5 ml) and worked up (hexane). FC (hexane/Et_3N 1 : 0.01 → hexane/AcOEt/Et_3N 9 : 2 : 0.01) gave **45** (241 mg, 92%). Colourless oil. R_f (hexane/AcOEt 3 : 1) 0.71. $[\alpha]_D^{25} = -29.3$ (*c* = 2, $CHCl_3$). IR (CCl_4): 2956*s*, 2911*s*, 2876*s*, 2166*w*, 1759*m*, 1613*m*, 1514*s*, 1464*m*, 1366*m*, 1250*s*, 1173*m*, 1087*s*, 909*m*, 832*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–7.18 (*m*, 16 arom. H); 6.78–6.94 (*m*, 16 arom. H); 5.20–5.10 (*m*, *M* of *ABMX*, virtual coupling, $J_{MX} \approx 10.6$, $J_{AM} \approx 9.3$, H−C(3^{II})); 4.98 (*d*, *J* = 10.6, Ar*CH*); 4.95 (br. *d*, *J* ≈ 10.0, 2 Ar*CH*); 4.89 (*d*, *J* = 11.2, Ar*CH*); 4.80–4.58 (*m*, H−C(1^{II}), H−C(2^{II}), H−C(1^{IV}), H−C(1^{VI}), H−C(1^{VIII}), 12 Ar*CH*); 4.44–4.36 (*m*, 2 H); 4.31 (*dd*, *J* = 11.8, 2.8, H_a−C(6^{II})); 4.23 (*dd*, *J* = 11.8, 4.7, H_b−C(6^{II})); 4.10–3.73 (*m*, 20 H); 3.80 (*s*, MeO); 3.797 (*s*, 2 MeO); 3.793 (*s*, 2 MeO); 3.788 (*s*, 3 MeO); 3.66–3.54 (*m*, 5 H); 3.52–3.42 (*m*, 10 H); 3.32–3.12 (*m*, 6 H); 3.08 (br. *d*, *J* ≈ 10.0, 1 H); 2.92 (*t*, *J* ≈ 10.6, H−C(4^{II})); 2.64

(t, $J \approx 10.3$, H–C(4^{IV})); 2.63 (t, $J \approx 10.4$, H–C(4^{VI})); 2.44 (t, $J \approx 10.6$, H–C(4^{VIII})); 2.02 (s, Ac); 2.00 (s, Ac); 1.97 (s, Ac); 1.72–1.52 (m, 4 Me_2CH); 1.00–0.80 (m, 129 H); 0.78–0.52 (54 H); 0.33 (s, Me_3Ge); 0.17 (s, Me_3Si); 0.19–0.09 (m, 8 MeSi). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.46 (s, C=O); 169.65 (s, C=O); 169.52 (s, C=O); 159.35 (s); 159.32 (s); 159.27 (s); 159.02 (2s); 159.00 (2s); 158.97 (s); 131.64 (s); 131.47 (s); 131.44 (s); 131.39 (s); 130.45 (s); 130.38 (s); 130.30 (s); 130.25 (s); 130.12–129.13 (several d); 113.82 (s); 113.75 (s); 113.73 (s); 113.68 (s); 113.58 (s); 113.41 (2s); 113.39 (s); 104.23 (s, $C{\equiv}$CGe); 102.94 (s, $C{\equiv}$CSi); 101.34 (d, C(1^{IV}), C(1^{VIII})); 101.28 (d, C(1^{VI})); 99.94 (d, C(1^{II})); 90.42 (s, C$\equiv C$Si); 88.56 (s, C$\equiv C$Ge); 83.23 (2d); 83.13 (2d); 83.08 (d); 83.01 (d); 81.74 (d); 81.69 (2d); 81.31 (d); 79.92 (d); 79.84 (2d); 79.74 (d); 79.45 (d); 78.87 (s); 78.83 (s); 77.97 (2d); 77.29 (d); 76.50 (d); 76.44 (2d); 76.39 (d); 76.21 (d); 75.78 (s); 75.30 (d); 75.30 (t, ArCH_2); 75.15 (t, ArCH_2); 74.72 (t, 2 ArCH_2); 74.64 (t, 2 ArCH_2); 74.59 (t, ArCH_2); 74.52 (t, ArCH_2); 73.50 (s); 72.60 (2d); 72.49 (d); 72.40 (d); 70.03 (2d); 69.74 (2d); 69.54 (s); 69.50 (s); 68.94 (s); 68.70 (s); 68.68 (s); 64.06 (t); 63.77 (3t); 61.15 (2t); 61.02 (2t); 55.28 (q, MeO); 55.27 (q, MeO); 55.26 (q, 2 MeO); 55.25 (q, 2 MeO); 55.18 (q, 2 MeO); 39.94 (d, C(4^{VII})); 39.66 (d, C(4^{IV}), C(4^{VI})); 36.82 (d, C(4^{II})); 34.31 (d, MeCH); 34.29 (d, MeCH); 34.27 (d, MeCH); 34.24 (d, MeCH); 25.24 (s, MeCSi); 25.23 (s, 3 MeCSi); 20.76 (q, Me); 20.68 (q, Me); 20.55 (q, 3 Me); 20.54 (q, 2 Me); 20.34 (q, Me); 20.28 (q, Me); 20.26 (q, 2 Me); 18.79 (q, Me); 18.76 (q, 3 Me); 18.60 (q, Me); 18.56 (q, Me); 18.54 (q, 2 Me); 7.09 (q, 6 Me); 7.07 (q, 4 Me); 7.04 (q, 4 Me); 7.01 (q, 6 Me); 6.91 (q, 3 Me); 6.88 (q, 4 Me); 5.59 (4t); 5.50 (5t); 5.34 (6t); 4.50 (4t); 4.42 (4t); 4.41 (4t); −0.30 (q, Me_3Si); −0.44 (q, Me_3Ge); −2.84, −2.86, −2.88, −2.90, −3.17, −3.40, −3.49, −3.56 (8q, 8 MeSi); 3s for C≡C not observed or hidden. MALDI-TOF-MS for $C_{226}H_{366}GeO_{47}Si_{14}$ (4301.20): 4324 ([M + Na]$^+$).

*4-*C*-(Bromoethynyl)-4-deoxy-2,3-6-tris-*O*-(triethylsilyl)-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-2,3,6-tris-*O*-(triethylsilyl)-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-2,3,6-tris-*O*-(triethylsilyl)-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-10-*O*-(thexyldimethylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis-*O*-(4-methoxybenzyl)-8-*O*-(thexyldimethylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**46**). A soln. of **45** (57.8 mg, 13.4 μmol) and NBS (3.1 mg, 17.5 μmol) in acetone (0.5 ml), was treated with CuBr (0.6 mg, 30 mol-%), stirred at r.t. for 8 h, poured into ice-cold sat. $Na_2S_2O_3$ soln. (2 ml), and worked up (CH_2Cl_2). Drying for 4 h under h.v. gave **46** (49.3 mg, 86%) as a colourless oil which was directly used for the next step. R_f (hexane/AcOEt 3:1) 0.71. $[\alpha]_D^{25} = -27$ ($c = 1.1$, $CHCl_3$). IR (CCl_4): 2956s, 2911s, 2876s, 2280w, 2166w, 2077w, 1759m, 1613m, 1587m, 1514s, 1464m, 1414m, 1366m, 1301m, 1250s, 1173m, 1117s, 1087s, 1041s, 912m, 832s. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–7.18 (m, 16 arom. H); 6.78–6.94 (m, 16 arom. H); 5.20–5.10 (m, M of $ABMX$, virtual coupling, $J_{MX} \approx 10.6$, $J_{AM} \approx 9.3$, H–C(3^{II})); 5.00 (d, $J = 10.5$, ArCH); 4.96 (br. d, $J \approx 11.0$, 2 ArCH); 4.89 (d, $J = 11.2$, ArCH); 4.80–4.57 (m, H–C(1^{II}), H–C(2^{II}), H–C(1^{IV}), H–C(1^{VI}), H–C(1^{VIII}), 12 ArCH); 4.45–4.36 (m, 4 H); 4.32 (dd, $J =$ 11.8, 2.9, H_a–C(6^{II})); 4.24 (dd, $J = 11.8$, 4.7, H_b–C(6^{II})); 4.06–3.70 (m, 18 H); 3.81 (s, MeO); 3.80 (s, 4 MeO); 3.79 (s, 3 MeO); 3.66–3.54 (m, 5 H); 3.52–3.30 (m, 10 H); 3.32–3.10 (m, 6 H); 3.08 (br. d, $J \approx 11.0$, 1 H); 2.92 (t, $J \approx 10.5$, H–C(4^{II})); 2.65 (t, $J \approx 10.3$, H–C(4^{IV})); 2.64 (t, $J \approx 10.4$, H–C(4^{VI})); 2.54 (t, $J \approx 10.6$, H–C(4^{VIII})); 2.02 (s, Ac); 2.00 (s, Ac); 1.98 (s, Ac); 1.72–1.54 (m, 4 Me_2CH); 1.00–0.81 (m, 129 H); 0.78–0.54 (54 H); 0.18 (s, Me_3Si); 0.19–0.09 (m, 8 MeSi). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.46 (s, C=O); 169.65 (s, C=O); 169.53 (s, C=O); 159.35 (2s); 159.27 (2s); 159.01 (4s); 131.50 (s); 131.46 (s); 131.43 (s); 131.38 (s); 130.45 (s); 130.32 (s); 130.24 (s); 1 arom. s not observed or hidden; 130.10–129.13 (several d); 113.81–113.41 (several d); 102.93 (s, $C{\equiv}$CSi); 101.34 (d, C(1^{IV}), C(1^{VIII})); 101.28 (d, C(1^{VI})); 99.93 (d, C(1^{II})); 90.42 (s, C$\equiv C$Si); 83.23 (d); 83.07 (2d); 83.01 (d); 81.74 (2d); 81.68 (2d); 81.30 (d); 79.92 (d); 79.75 (d); 79.45 (2d); 79.16 (d); 78.88 (s); 77.96 (2d); 77.43 (2d); 76.44 (2d); 76.38 (s, $C{\equiv}$CBr); 76.35 (2d); 76.20 (d); 75.77 (s); 75.31 (d); 75.15 (t, ArCH_2); 74.72 (t, 2 ArCH_2); 74.64 (t, 2 ArCH_2); 74.59 (t, ArCH_2); 74.56 (t, ArCH_2); 74.52 (t, ArCH_2); 74.32 (s); 73.50 (s); 72.60 (2d); 72.49 (d); 72.39 (d); 70.03 (2d); 69.74 (2d); 69.54 (s); 68.94 (s); 68.67 (s); 64.05 (t); 63.87 (2t); 63.77 (2t); 61.14 (2t); 61.01 (t); 55.28 (q, MeO); 55.27 (q, 2 MeO); 55.25 (q, 2 MeO); 55.18 (q, 3 MeO); 42.92 (s, C$\equiv$CBr); 40.08 (d, C(4^{VIII})); 39.65 (d, C(4^{IV}), C(4^{VI})); 36.81 (d, C(4^{II})); 34.31 (d, MeCH); 34.29 (d, MeCH); 34.27 (d, MeCH); 34.23 (d, MeCH); 25.24 (s, MeCSi); 25.22 (s, 3 MeCSi); 20.76 (q, Me); 20.68 (q, Me); 20.53 (q, 3 Me); 20.34 (q, 2 Me); 20.26 (q, 4 Me); 18.76 (q, 2 Me); 18.59 (q, 4 Me); 18.56 (q, Me); 18.53 (q, 3 Me); 7.08 (q, 8 Me); 7.03 (q, 5 Me); 7.01 (q, 7 Me); 6.88 (q, 7 Me); 5.58 (t); 5.50 (7t); 5.47 (2t); 5.34 (8t); 4.50 (t); 4.45 (2t); 4.41 (3t); 4.40 (3t); −0.30 (q, Me_3Si); −2.86, −2.88, −2.90, −3.17, −3.20, −3.41, −3.49, −3.56 (8q, 8 MeSi); 5s for C≡C not observed or hidden. MALDI-TOF-MS for $C_{223}H_{357}BrO_{47}Si_{14}$ (4263.41): 4287 ([M + Na]$^+$).

*2,3,6-Tri-*O*-acetyl-4-deoxy-4-*C*-[(trimethylgermyl)ethynyl]-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3-6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl) – *D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-6,7-bis-*O*-(4-methoxybenzyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-2,3,6-tri-*O*-acetyl-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-4,5-bis-*O*-(4-methoxybenzyl)-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo*-oct-1-ynitol* (**47**). A degassed soln. of **42** (15.9 mg. 5.2 µmol), **46** (22 mg, 5.2 µmol), [Pd_2(dba)$_3$] (0.5 mg, 10 mol-%), CuI (0.1 mg, 10 mol-%), and P(furyl)$_3$ (0.24 mg, 20 mol-%) in DMSO/toluene (1 : 1, 1 ml), was treated at r.t. with Et_3N (0.05 ml), stirred for 5 h, poured into ice-cold sat. NH_4Cl soln. (2 ml), and worked up ($CHCl_3$). A soln. of the residue in pyridine (0.5 ml) and Ac_2O (0.1 ml) was stirred at r.t. for 3 h, evaporated, co-distilled (toluene), and dried under h.v. for 6 h. The resulting orange oil (main product R_f (AcOEt/hexane 3 : 2) 0.13) was dissolved in a PE vessel (*Eppendorf*, 2 ml volume) in THF (1 ml), and the soln. was treated with a soln. of 70% HF · pyridine/pyridine/THF 1 : 2 : 4 (0.2 ml), stirred at r.t. for 3 h, neutralized with *Amberlite IRA-93* (OH^- form), filtered, and evaporated. FC (*Pasteur* pipette, 350 mg of *Si-60*, CH_2Cl_2/toluene/MeOH 7 : 1 : 1) gave **47** (10.5 mg, 37%). Yellow oil. R_f (CH_2Cl_2/toluene/MeOH 7 : 1 : 1) 0.48. IR (CCl_4): 3600*m* (br.), 3458*m* (br.), 2958*s*, 2910*m*, 2875*m*, 2836*m*, 2170*w*, 1759*s*, 1614*m*, 1587*w*, 1515*s*, 1465*s*, 1442*m*, 1367*s*, 1302*m*, 1251*s*, 1231*m*, 1172*s*, 1151*s*, 1089*s*, 1040*s*. ^{1}H-NMR (300 MHz, $CDCl_3/D_2O$ *ca.* 99 : 1): 7.40 – 7.05 (*m*, 32 arom. H); 6.91 – 6.70 (*m*, 32 arom. H); 5.22 – 5.10 (*m*, 5 H); 4.96 – 4.52 (*m*, 45 H); 4.30 – 4.10 (*m*, 16 H); 4.00 (br. *d*, *J* ≈ 8.7, 8 H); 3.90 – 3.34 (*m*, 55 H); 3.81 (*s*, 3 MeO); 3.80 (*s*, 5 MeO); 3.784 (*s*, 3 MeO); 3.776 (*s*, 3 MeO); 3.73 (*s*, 2 MeO); 3.25 – 3.10 (*m*, 16 H); 2.93 (br. *t*, *J* ≈ 10.5, 5 H); 2.79 (*t*, *J* ≈ 10.5, 3 H); 2.04 (*s*, 2 Ac); 2.036 (*s*, 2 Ac); 2.002 (*s*, 2 Ac); 1.996 (*s*, 2 Ac); 1.981 (*s*, Ac); 1.971 (*s*, 2 Ac); 1.952 (*s*, 2 Ac); 1.945 (*s*, 2 Ac); 0.32 (*s*, Me_3Ge); 0.18 (*s*, Me_3Si). MALDI-TOF-MS for $C_{292}H_{328}GeO_{103}Si$ (5594.55): 5618 ($[M + Na]^+$).

*4-Deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-*D-glycero-D-gulo*-oct-1-ynitol* (**48**). A soln. of **41** (22.9 mg, 7 µmol) in CH_2Cl_2/H_2O (9 : 1, 1 ml) was treated at r.t. with DDQ (15.9 mg, 70 µmol), stirred for 3 h, poured into ice-cold sat. $NaHCO_3$ soln. (2 ml), and worked up ($CHCl_3$). The residue was dissolved in $CHCl_3$/MeOH 4 : 1 (0.5 ml), and the soln. filtered through silica gel (*Pasteur* pipette, *ca.* 60 mg of *Si-60*, eluted with $CHCl_3$/MeOH 4 : 1 (5 ml)), and concentrated. The residue was dissolved in a PE vessel (*Eppendorf*, 2 ml volume) in THF (1 ml), and the soln. was treated with 70% HF · pyridine/pyridine/THF 1 : 2 : 4 (0.2 ml), stirred at r.t. for 2.5 h, neutralized with *Amberlite IRA-93* (OH^- form), filtered, and concentrated. A soln. of the resulting oil in MeOH (1 ml) was treated with 0.01M NaOMe in MeOH (0.05 ml), stirred at r.t. for 4 h, neutralized with *Amberlite IR-120* (H^+ form), filtered, and concentrated to give **48** (4.2 mg, 42%). Yellow oil. R_f (AcOEt/MeOH/H_2O 10 : 3 : 3) 0.34. IR (KBr): 3410*s* (br.), 2915*m*, 2260*w*, 2128*w*, 1640*m* (br.), 1427*m*, 1371*m*, 1305*m*, 1260*m*, 1160*m*, 1089*s*, 1039*s*, 961*m*. ^{1}H-NMR (300 MHz, CD_3OD): 4.41 (*d*, *J* = 7.8, H–C(1^{VIII})); 4.40 (*d*, *J* = 7.8, H–C(1^{II}), H–C(1^{IV}), H–C(1^{VI})); 4.02 (*d*, *J* = 9.7, H–C(5^{III}), H–C(5^{V}), H–C(5^{VII})); 3.92 (*dd*, *J* = 9.4, 2.2, H–C(3^{I})); 3.93 – 3.76 (*m*, 10 H); 3.76 – 3.62 (*m*, 6 H); 3.60 – 3.40 (*m*, 10 H); 3.43 (*t*, *J* ≈ 8.9, 2 H); 3.44 (*t*, *J* ≈ 8.9, 2 H); 3.40 – 3.22 (*m*, 10 H); 3.14 (*t*, *J* ≈ 9.5, 4 H); 2.88 (*d*, *J* = 2.2, HC≡C–C(3^{I})); 2.61 (br. *t*, *J* ≈ 9.9, H–C(4^{II}), H–C(4^{IV}), H–C(4^{VI})); 2.55 (*d*, *J* = 2.4, HC≡C–C(4^{VIII})); 2.44 (*td*, *J* ≈ 10.4, 2.5, H–C(4^{VIII})). ^{1}H-NMR (300 MHz, (D_6)DMSO): 5.62 (br. *d*, *J* ≈ 6.2, HO–C(6^{III}), HO–C(6^{V}), HO–C(6^{VII})); 5.49 (br. *d*, *J* ≈ 6.4, HO–C(3^{II}), HO–C(3^{IV}), HO–C(3^{VI})); 5.45 (*d*, *J* = 6.2, HO–C(4^{I})); 5.39 (br. *d*, *J* ≈ 4.5, HO–C(2^{II}), HO–C(2^{IV}), HO–C(2^{VI})); 5.32 (*d*, *J* = 4.5, HO–C(2^{VIII})); 5.29 (*d*, *J* = 6.4, HO–C(3^{VIII})); 4.88 – 4.82 (*m*, HO–C(10^{III}), HO–C(10^{V}), HO–C(10^{VII})); 4.76 (br. *t*, *J* ≈ 5,6, HO–C(8^{I})); 4.64 – 4.56 (*m*, 8 OH); 4.30 – 4.22 (*m*, H–C(1^{II}), H–C(1^{IV}), H–C(1^{VI}), H–C(1^{VIII})); 3.98 (br. *d*, *J* ≈ 9.7, H–C(5^{III}), H–C(5^{V}), H–C(5^{VII})); 3.83 (*dd*, *J* = 9.7, 2.0, H–C(3^{I})); 3.74 – 3.60 (*m*, 8 H); 3.58 – 3.20 (*m*, 29 H); 3.19 – 3.08 (*m*, 4 H); 2.95 (*d*, *J* = 2.2, HC≡C–C(4^{VIII})); 2.93 – 2.82 (*m*, 4 H); 2.52 (br. *t*, *J* ≈ 10.2, H–C(4^{II}), H–C(4^{IV}), H–C(4^{VI})); 2.26 (*td*, *J* ≈ 10.0, 2.0, H–C(4^{VIII})). ^{13}C-NMR (125 MHz, CD_3OD): 104.52 (*d*); 104.49 (3*d*); 81.81 (*d*, C≡*C*H); 81.70 (*d*, C≡*C*H); 80.63 (2*d*); 80.55 (*d*); 80.21 (*d*); 80.12 (*d*); 80.04 (*d*); 79.52 (2*d*); 79.26 (2*d*); 78.99 (2*d*); 78.40 (3*s*); 77.39 (2*d*); 77.27 (3*s*); 76.90 (2*d*); 75.91 (*s*, *C*≡CH); 75.70 (2*d*); 75.38

(2*d*); 75.09 (2*d*); 74.92 (2*d*); 74.48 (4*d*); 73.48 (*s*, *C*≡CH); 72.26 (2*d*); 71.85 (2*d*); 70.77 (3*s*); 68.66 (3*s*); 63.34 (4*t*); 61.86 (2*t*); 61.80 (2*t*); 39.29 (*d*); 39.29 (*d*); 39.25 (*d*); 38.61 (*d*). MALDI-TOF-MS for $C_{64}H_{82}O_{36}$ (1427.35): 1450 ([*M* + Na]$^+$).

*4-Deoxy-4-*C*-ethynyl-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetra-deoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,-3,4-tetradeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 8)-5,9-anhydro-1,2,3,4-tetradeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 4-*C*)-4-deoxy-β-*D*-glucopyranosyl-(1 → 6)-3,7-anhydro-1,2-dideoxy-*D-glycero-D-gulo-*oct-1-ynitol* (**49**). A soln. of **47** (6.1 mg, 1.1 μmol) in CH_2Cl_2/H_2O 9 : 1 (0.5 ml) was treated at r.t. with DDQ (4.5 mg, 20.0 μmol), stirred for 2 h, poured into ice-cold sat. $NaHCO_3$ soln. (2 ml), and worked up ($CHCl_3$). A soln. of the residue in MeOH (2 ml) was treated dropwise with 0.01M NaOMe in MeOH (0.05 ml), stirred at r.t. for 12 h, neutralized with *Amberlite IR-120* (H^+ form), filtered, and evaporated. Drying under h.v. for 6 h gave **49** (1.1 mg, 34%). Oil. ^{1}H-NMR (300 MHz, D_2O): 4.47 (br. *d*, *J* ≈ 7.8, H−C(1^{II}), H−C(1^{IV}), H−C(1^{VI}), H−C(1^{VIII}), H−C(1^{X}), H−C(1^{XII}), H−C(1^{XIV}), H−C(1^{XVI})); 4.19 (br. *d*, *J* ≈ 9.7, H−C(5^{III}), H−C(5^{V}), H−C(5^{VII}), H−C(5^{IX}), H−C(5^{XI}), H−C(5^{XIII}), H−C(5^{XV})); 4.11 (br. *dd*, *J* ≈ 9.3, 2.1, H−C(3^{I})); 4.00 – 3.86 (*m*, 16 H); 3.86 – 3.42 (*m*, 64 H); 3.30 – 3.18 (*m*, 8 H); 2.90 (*d*, *J* ≈ 2.2, HC≡C−C(3^{I})); 2.70 (br. *t*, *J* ≈ 10.5, H−C(4^{II}), H−C(4^{IV}), H−C(4^{VI}), H−C(4^{VIII}), H−C(4^{X}), H−C(4^{XII}), H−C(4^{XIV})); 2.59 (br. *d*, *J* ≈ 2.1, HC≡C−C(4^{XVI})); 2.56 (br. *td*, *J* ≈ 10.6, 2.2, H−C(4^{XVI})). ^{1}H-NMR (300 MHz, (D_6)DMSO): 5.63 (br. *d*, *J* ≈ 5.9, 7 OH); 5.52 – 5.46 (*m*, 8 OH); 5.41 (br. *d*, *J* ≈ 6.0, 7 OH); 5.33 – 5.27 (*m*, HO−C(2^{XVI}), HO−C(3^{XVI})); 4.88 – 4.82 (*m*, 7 OH); 4.75 (br. *t*, *J* ≈ 5.8, HO−C(8^{I})); 4.65 – 4.55 (*m*, 16 OH); 4.27 (br. *d*, *J* ≈ 7.9, H−C(1^{II}), H−C(1^{IV}), H−C(1^{VI}), H−C(1^{VIII}), H−C(1^{X}), H−C(1^{XII}), H−C(1^{XIV}), H−C(1^{XVI})); 4.01 (br. *d*, *J* ≈ 9.8, H−C(5^{III}), H−C(5^{V}), H−C(5^{VII}), H−C(5^{IX}), H−C(5^{XI}), H−C(5^{XIII}), H−C(5^{XV})); 3.82 (*td*, *J* ≈ 9.6, 2.0, H−C(3^{I})); 3.77 – 3.58 (*m*, 16 H); 3.56 – 3.18 (*m*, 56 H); 3.17 – 3.05 (*m*, 8 H); 2.96 (*d*, *J* = 2.1, HC≡C−C(4^{XVI})); 2.92 – 2.85 (*m*, 8 H); 2.51 (br. *t*, *J* ≈ 10.4, H−C(4^{II}), H−C(4^{IV}), H−C(4^{VI}), H−C(4^{VIII}), H−C(4^{X}), H−C(4^{XII}), H−C(4^{XIV})); 2.25 (*td*, *J* ≈ 10.3, 2.2, H−C(4^{XVI})). ^{13}C-NMR (125 MHz, (D_6)DMSO/CD_3OD *ca.* 99 : 1; br. signals): 102.87 (8*d*); 79.72 (8*d*); 78.86 (8*d*); 75.59 (8*d*); 74.92 (8*d*); 73.78 (8*d*); 73.13 (8*d*); 70.13 (8*d*); 69.78 (8*d*); 69.34 (7*s*); 66.70 (7*s*), 61.65 (8*t*); 60.09 (8*t*), 37.84 (8*d*); (2*d* for C≡*C*H and 16*s* for C≡C not observed or hidden. MALDI-TOF-MS for $C_{128}H_{162}O_{72}$ (2852.68): 2876 ([*M* + Na]$^+$), 2992 ([*M* + K]$^+$).

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