Oligosaccharide Analogues of Polysaccharides

Part 17

Synthesis and Characterization of a Hexadecamer: Evidence for the Essential Structural Role of the Intramolecular, Interresidue C(3)–OH···O–C(5) Hydrogen Bond in Celluloses[1])

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The hexadecamer **63** dissolves readily in DMSO and shows no sign of association, in agreement with the essential structural role of the intramolecular, interresidue C(3)–OH···O–C(5) H-bond of celluloses. MM3 Calculations predict a rod-like shape for the cello-oligosaccharides. In agreement with this, nanocrystalline domains of parallel chains are observed by high-resolution electron microscopy (HREM) for **54** and **63** on carbon-coated copper grids. For the synthesis of the hexadecamer **54**, we studied the influence of protecting groups on the cross-coupling of acetyleno-oligosaccharides and on their solubility (*Scheme 2*). The octamer **12** derived from the minimally *O*-protected monomer **2** is insoluble, while the methoxymethyl- and triisopropylsilyl-protected hexadecamer **54**, prepared in twelve steps from the dimer **41** (*Scheme 4*), is readily soluble in a variety of solvents. *O*- and *C*-deprotection of **54** led in four steps and in 76% yield to the hexadecamer **63** (*Schemes 5* and *6*). There is only a small difference of spectroscopic properties between the protected octamer **50** and hexadecamer **54**, and, similarly, between the unprotected octamer **64** and hexadecamer **63** (*Fig. 3*).

Introduction. – The supramolecular structure of cellulose is determined by intra- and intermolecular H-bonds [1–3]. In both cellulose I and II, HO–C(3) is involved in intra- and intermolecular H-bonds [4–6]. The intramolecular, interresidue C(5′)O···HO–C(3) H-bond restricts the conformational mobility of the cellulose chains and is thought to be essential for their aggregation *via* intermolecular H-bonds and for the macroscopic properties of celluloses.

We decided to interrupt the intramolecular C(5′)O···HO–C(3) H-bonds by substituting the glycosidic O-atoms by butadiynediyl groups, and to evaluate the role of these H-bonds in celluloses by comparing the association of the acetylenosaccharides with the one of cello-oligosaccharides [7].

A binomial synthesis of such acetylenosaccharides up to the octamer has been described [8][9]. The synthesis of higher, *O*-benzyl-protected oligomers, however, is severely hampered by solubility problems. Thus, the yield of the fully benzylated dimeric product resulting from a (modified [10–12]) *Cadiot-Chodkiewicz* cross-coupling dropped from 83% for the octamer to 6% for the hexadecamer [13]. The low yield of the hexadecamer was rationalized by its poor solubility, leading to a slow

[1]) Presented in part at the 'Royal Society of Chemistry Carbohydrate Group Spring Meeting', Birmingham, 30.3.–1.4.1998.

precipitation after dissolution and severe losses during chromatography. Since the yields of the acetolytic *O*-debenzylation [14] also dropped for oligomeric acetylenosaccharides [15], we have investigated the influence of the number and kind of hydroxy-protecting groups on both cross-coupling and solubility of the oligomers with the goal of preparing oligosaccharides long enough to qualify as polymers. We describe the problems encountered during the synthesis of long oligomers and the preparation of a soluble *O*-protected hexadecamer, its deprotection, and characterization.

Results and Discussion. – We began by investigating the synthesis of minimally *O*-protected oligomers (*Scheme 1*) [16]. For this, we prepared the dimer **1** from the monomer **2** [16]. This synthesis constitutes a binomial cycle requiring four steps and proceeding in an overall yield of 69% (*Table 1*). The second binomial cycle, leading to the tetramer **6**, started by a selective desilylation of **1** to either **3** (MeONa, MeOH) or **5** (0.01N HCl, EtOH). Bromination of **3** to **4** proceeded rapidly and in high yields with *N*-bromosuccinimide (NBS) and $AgOCOCF_3$. The tetramer **6** was obtained in 64% by coupling **4** with **5**, besides 1–3% of the homocoupled tetramers **7** and **8** (*Scheme 1*). The third binomial cycle proceeded similarly *via* **9**–**11** and provided the octamer **12** besides the homocoupled products **13** and **14** (< 2% as judged by MALDI-TOF). The octamers were insoluble in H_2O and in most organic solvents[2]) except DMSO and, to some extent, sulfolane. The octamer **12** could not be purified by chromatography. Attempted crystallization of the octamer mixture resulted in co-precipitation of the three components. Thus, additional protection appeared desirable.

We first tested the influence of protecting groups on the cross-coupling. For this, we prepared the bromoalkynes **16**, **17**, and **18** from the bromoalkyne **15** [16], and the alkynes **20**, **21** [14], and **22** from **19** [16] using standard methods (*Scheme 2*)[3]).

Dimerization of monomers with HO–C(5) and HO–C(8) groups led to 79% of **1** (H,H dimer[4])), 2% of the homodimer **23** (derived from the bromoalkyne **15**), and < 1% of the homodimer **24** (from **19**) [16]. Acetylation of the monomers led to lower yields of the dimers. Coupling of **16** and **19** gave 66% of the Ac,H dimer[4]) **25** besides 1% of **26**, resulting from the bromoalkyne **16**. Coupling of the acetylated monomers **16** and **20** led in 34% yield to the Ac,Ac dimer **27**. The detrimental influence of *O*-Ac groups in the cross-coupling has been noted before [15][17]. No such influence was observed for triisopropylsilyl (TIPS), methoxymethyl (MOM), and benzyloxymethyl (BOM) groups. Cross-coupling of the triisopropylsilylated **17** with **19** yielded 76% of the dimer **28**. Similarly, the methoxymethylated **18** reacted with **19** to yield 78% of the MOM,H dimer **29**, besides 2% of the fully methoxymethylated homodimer **30**.

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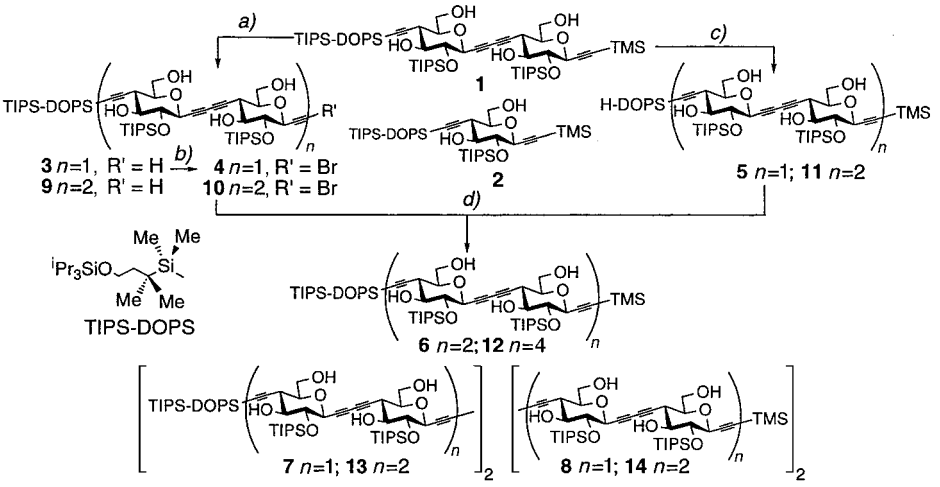
[2]) The following solvents were tested at 22° and 40°: hexane, pentane, cyclohexane, Et_2O, *t*-BuOMe, THF, CH_2Cl_2, $CHCl_3$, dichloroethane, trichloroethane, toluene, benzene, AcOEt, MeCN, acetone, CF_3COOH, pyridine, MeOH, EtOH, 2-methoxyethanol, DMF, hexamethylphosphoric triamide (HMPT), 1-methylpyrrolidin-2-one (NMP), 1,3-dimethylimidazolidin-2-one, and their mixtures.

[3]) Cross-coupling was carried out on a scale of 100–200 mg. Homocoupled by-products formed in yields below 1% were not characterized.

[4]) The structure of the dimers is indicated by a short-hand notation that takes into account that O–C(5) and O–C(8) of each monomer are protected in the same way. The *O*-substituents are abbreviated as indicated in the text, the left one referring to the monomer initially possessing the bromoalkyne substituent, and the right one to its partner.

Scheme 1



TMS = Me_3Si, TIPS = $(^iPr)_3Si$, DOPS = $OCH_2CH_2C(Me)_2Si(Me)_2$

a) 0.25M MeONa, MeOH. *b*) NBS, $AgOCOCF_3$, acetone. *c*) 0.01N HCl, EtOH, 45°. *d*) [$Pd_2(dba)_3$], CuI, $P(fur)_3$, Et_3N, DMSO.

Table 1. *Yields of the Binomial Cycles According to* Scheme 1

Conditions	$n=1$	$n=2$	$n=4$
a) NaOMe, MeOH	94%	94%	93%
b) NBS, $AgOCOCF_3$, acetone	97%	94%	94%
c) 0.01N HCl, EtOH	97%	91%	91%
d) $Pd_2(dba)_3$, CuI, $P(fur)_3$, Et_3N, DMSO	78%	79%	(78%)[a])
Overall yield	69%	64%	(62%)

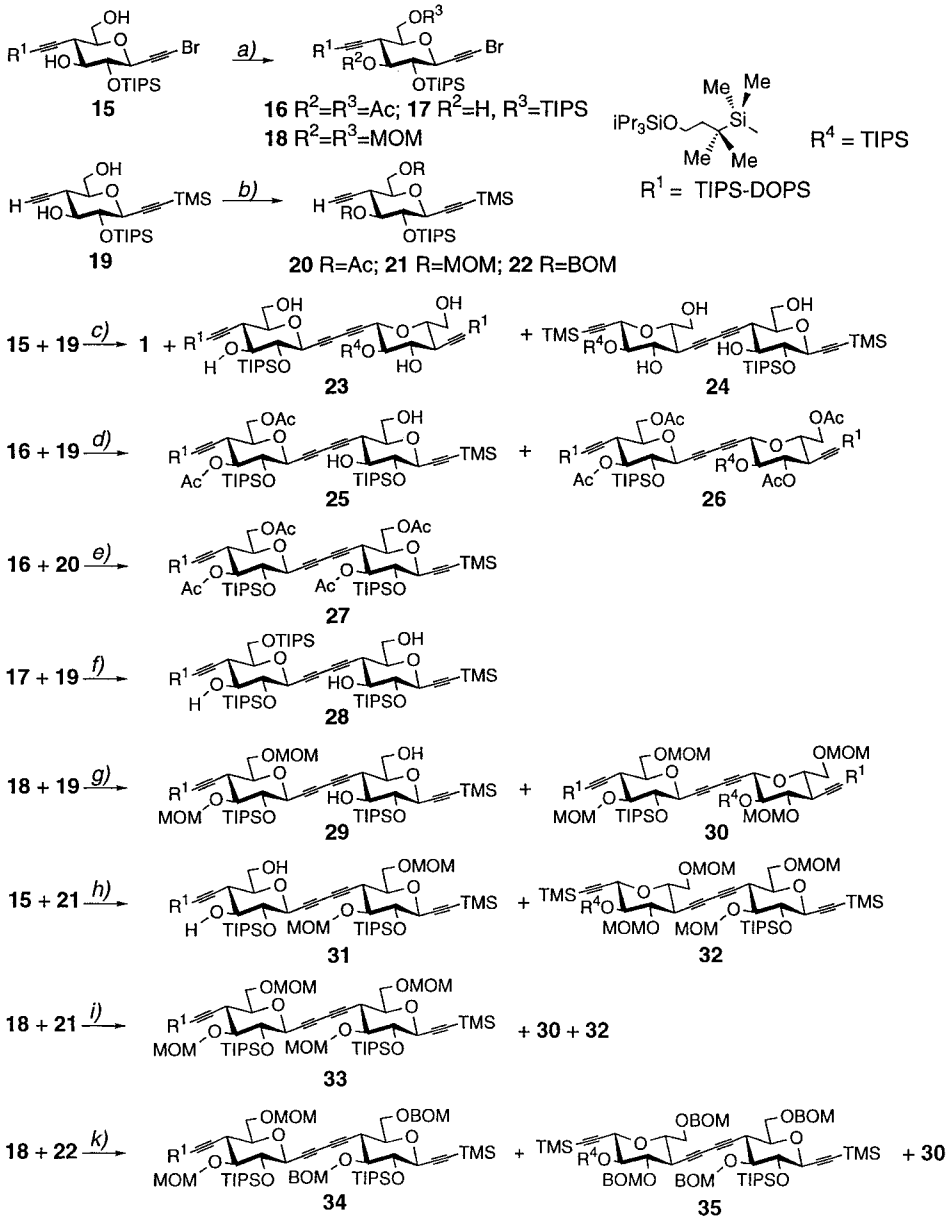
[a]) Yield of crude.

Coupling the diol **15** with the methoxymethylated alkyne **21** led in 78% yield to the H,MOM dimer **31** and in 3% to **32**, derived from **21**[5]). Cross-coupling of the methoxymethylated alkynes **18** and **21** gave 75% of the MOM,MOM dimer **33**, 6% of the homodimer **30** (from **18**), and 3% of the homodimer **32** (from **21**), indicating an enhanced tendency of the protected alkynes and bromoalkynes to homocoupling. Similarly, coupling of **18** with the benzyloxymethylated alkyne **22** led to 73% of the MOM,BOM dimer **34**, 8% of the homodimer **30** (from **18**) and 4% of the homodimer **35** (from **22**).

Among these dimers, we favoured those derived from differently protected monomers as they are readily separated from the homocoupled by-products [15][17]. In addition, such monomers lead to oligomers with alternating differently protected monomeric units; this should reduce the tendency of the (protected) oligomers to associate and enhance their solubility.

5) Homocoupling of the bromoalkyne **15** was not observed.

Scheme 2



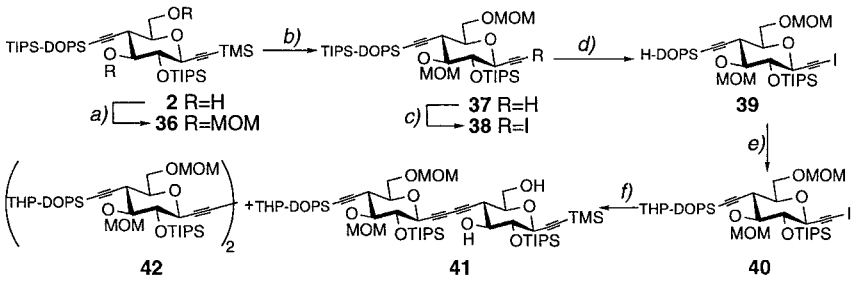
TMS = Me_3Si, TIPS = $(^iPr)_3Si$, DOPS = $OCH_2CH_2C(Me)_2Si(Me)_2$, MOM = $MeOCH_2$, BOM = $PhCH_2OCH_2$

a) Ac_2O, pyridine, 4-(dimethylamino)pyridine: **16** (89%); or TIPSOTf, pyridine: **17** (93%); or MOMCl, $(^iPr)_2NEt$, Bu_4NI, $(CH_2Cl)_2$: **18** (89%). *b*) Ac_2O, pyridine: **20** (90%); or methylal, P_2O_5, CH_2Cl_2: **21** (95%): or BOMCl, $(^iPr)_2NEt$, CH_2Cl_2: **22** (86%). *c*) $[Pd_2(dba)_3]$, CuI, $P(fur)_3$, Et_3N, DMSO: **1** (78%), **23** (2%), **24** (< 1%). *d*) as *c*); **25** (66%), **26** (1%). *e*) as *c*); **27** (34%). *f*) as *c*); **28** (76%). *g*) as *c*); **29** (79%), **30** (2%). *h*) as *c*); **31** (78%), **32** (3%). *i*) as *c*); **33** (75%), **30** (6%), **32** (3%). *k*) as *c*); **34** (73%), **30** (8%), **35** (4%).

These results and those described in the preceeding publication [16] suggested to use two monomers of which one carries an unprotected and a TMS-protected ethynyl and an *O*-TIPS group, while the other is protected by two *O*-MOM and one *O*-TIPS group and carries an iodoalkynyl substituent. What remained unclear was the optimal protecting group of the second alkynyl substituent, as the selective (acid-catalyzed) transformation of a TIPS-DOPS group into a H-DOPS group in the presence of the acid-labile methoxymethyl acetal was considered problematic. Indeed, *O*-desilylation of **29** to **45** (*cf. Scheme 4*) under previously established conditions (0.01M HCl, EtOH) could not be completed without partially removing the MOM groups. Therefore, the monomer **2** was methoxymethylated to **36**, transformed into the alkyne **37**, and iodinated with *N*-iodosuccinimide (NIS) to **38** (*Scheme 3*). The TIPS-DOPS moiety of **38** was replaced by the tetrahydro-2*H*-pyran-2-yl-substituted DOPS group (THP-DOPS), *via O*-desilylation to **39** followed by introduction of the THP group to give **40**. Cross-coupling of **40** and **19** gave 81% of the dimer **41**, besides 3% of the homodimer **42**. The dimer **41** was used for the synthesis of the tetramer **46**, the octamer **50**, and the hexadecamer **54** (*Scheme 4*).

The synthesis of the hexadecamer **54** proceeded uneventfully. The results are summarized in *Table 2*. Previously established conditions were used for the removal of

Scheme 3



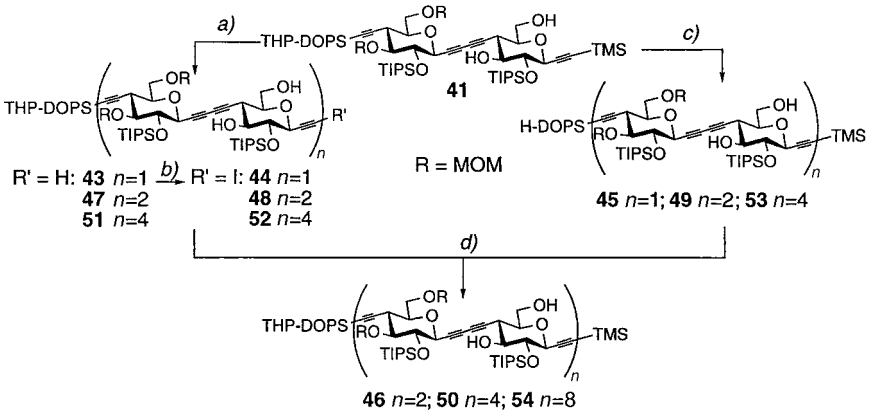
TMS = Me_3Si, TIPS = $(^iPr)_3Si$, DOPS = $OCH_2CH_2C(Me)_2Si(Me)_2$, MOM = $MeOCH_2$, THP = tetrahydro-2*H*-pyran-2-yl

a) MOM-Cl, $(^iPr)_2NEt$, $ClCH_2CH_2Cl$; 89%. *b*) 1M MeONa, MeOH; 94%. *c*) NIS, $AgOCOCF_3$; 99%. *d*) 0.01N HCl, EtOH, 0°; 96%. *e*) 3,4-Dihydro-2*H*-pyran, Py·TsOH, CH_2Cl_2; quant. *f*) **19**, $[Pd_2(dba)_3]$, CuI, $P(fur)_3$, Et_3N, DMSO; **41** (81%), **42** (3%).

the TMS group of **41**, **46**, and **50** yielding **43**, **47**, and **51**, and, for the subsequent iodination, yielding **44**, **48**, and **52**, respectively. THP Groups were removed by treating the products with *Amberlyst 15* in MeOH[6]) [9][18], the dimer **41** yielding 91% of **45** within 14 h. Longer reaction times were required for the deprotection of higher homologues. Raising the temperature to 40° and/or prolonging the reaction caused partial cleavage of the C(8)–OMOM group. The reaction was, therefore, terminated before completion, and starting material was recovered. Based on consumed starting material, the THP group was removed in 89% yield from the tetramer **46** and the octamer **50** to yield **49** and **53**, respectively. The yield of the cross-coupling steadily

[6]) 5% CH_2Cl_2 in MeOH was used for the octamer **50**.

Scheme 4



TMS = Me_3Si, TIPS = $(^iPr)_3Si$, DOPS = $OCH_2CH_2C(Me)_2Si(Me)_2$, MOM = $MeOCH_2$, THP = tetrahydro-2*H*-pyran-2-yl

a) CsF, DMF/MeOH 5:1. *b*) NIS, $AgOCOCF_3$, acetone. *c*) *Amberlyst 15*, MeOH or CH_2Cl_2/MeOH. *d*) [$Pd_2(dba)_3$], CuI, $P(fur)_3$, Et_3N, DMSO.

decreased from 81% for the dimer **41** to 67% for the hexadecamer **54** (*Table 2*). After flash chromatography, **54** still contained minor amounts of the two homohexadecamers (1–2%) that were removed after transforming **54** to **57** (*Scheme 5*), highlighting a known advantage of the DOPS group [13].

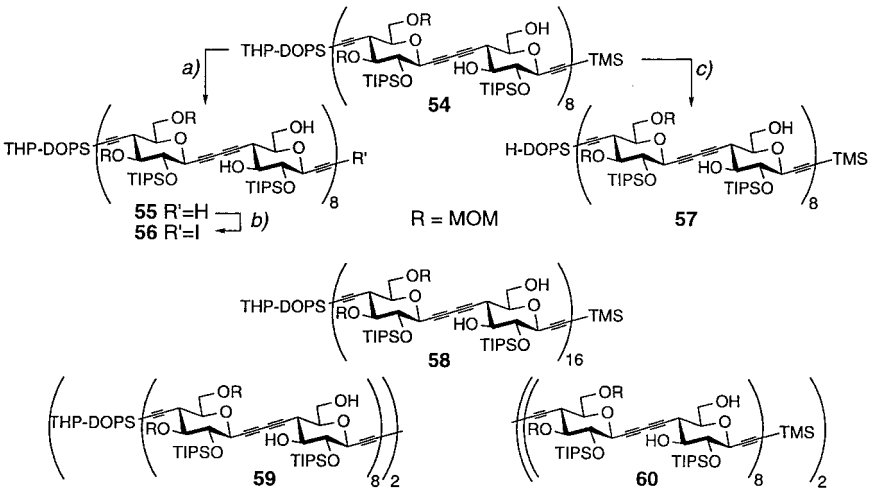
Table 2. *Yields of the Binomial Cycles According to* Scheme 4 *with R = MOM*

Conditons	$n=1$	$n=2$	$n=4$
a) CsF, DMF/MeOH 5:1	89%	88%	86%
b) NIS, $AgOCOCF_3$, acetone	96%	96%	95%
c) *Amberlyst 15*, MeOH	91%	89%	89%
d) [$Pd_2(dba)_3$], CuI, $P(fur)_3$, Et_3N, DMSO	81%	78%	67%
Overall yield	63%	59%	49%

To prepare the 32-mer, the hexadecamer **54** was *C*-desilylated in 85% to **55** (*Scheme 5*). Iodination with NIS and $AgOCOCF_3$ was no longer selective, partially removing the THP group of **55**, but I_2 in the presence of morpholine [14][19] transformed **55** in 86% to the iodoalkyne **56**. Similarly, the removal of the THP group with *Amberlyst 15* was no longer appropriate, yielding only 5–7% of the H-DOPS alkyne **57**. A variety of acidic ion-exchange resins (*Dowex 50WX8* [20], *Amberlite IR-120*, *Amberlite IRC-50* [21], and *Amberlite IRC-84*) were tested at either 22° or 40°, but none of them cleaved the THP group selectively in yields exceeding 10%. Dilute HCl, catalytic pyridinium tosylate (PPTS) in EtOH [22] or AcOH/THF/H_2O under reflux [23] gave similar results. However, catalytic amounts of $BF_3 \cdot OEt_2$ in 5% EtSH/CH_2Cl_2 at 0° [24] removed the THP group selectively[7]) and yielded 81% of **57**.

[7]) Cleavage of MOM groups at 22° proceeded only in the presence of several equiv. of $BF_3 \cdot OEt_2$ in EtSH [8][14][25].

Scheme 5



TMS = Me_3Si, TIPS = $(^iPr)_3Si$, DOPS = $OCH_2CH_2C(Me)_2Si(Me)_2$, MOM = $MeOCH_2$, THP = tetrahydro-2*H*-pyran-2-yl

a) CsF, DMF/MeOH; 84%. *b*) I_2, morpholine, toluene; 86%. *c*) $BF_3 \cdot Et_2O$, EtSH, CH_2Cl_2; 81%.

Cross-coupling of the hexadecamers **56** and **57** to the 32-mer **58** failed in DMSO, toluene, and CH_2Cl_2[8]). Neither raising the temperature, nor prolonging the reaction, nor using a 10–100-fold amount of catalysts or base, or recurring to ultrasound led to any of the desired 32-mer. In a single experiment in CH_2Cl_2, 35% of the homocoupled 32-mer **60** was isolated after 2 d by gel-permeation chromatography (GPC) on *TSK* gel (no **58** and **59** detected). However, this yield proved difficult to reproduce.

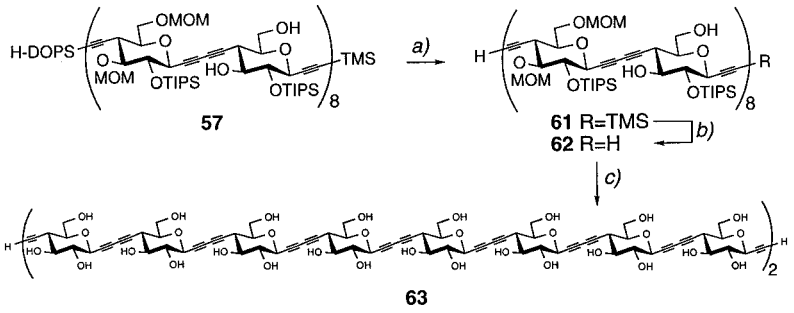
Oxidative coupling of **55** to **59** or of **57** to **60** under *Hay* [26] or *Eglington* [27] conditions gave conversions below 5%.

The unprotected monomer, dimer, tetramer, and octamer have been described [8]. To fully deprotect the hexadecamer, we treated **57** with Et_3N in MeOH to remove the H-DOPS group. *C*-Desilylation (MeONa, MeOH) of the resulting alkyne **61** gave **62** that was directly treated with 0.3N HCl in MeOH to cleave both the MOM and TIPS groups. This sequence led in 76% to the hexadecamer **63** (*Scheme 6*).

The protected oligomers **41**, **46**, **50**, **54**, and **60** are readily soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, acetone, or AcOEt. The unprotected oligomers **63** and **64** (*Fig. 3*) dissolved only in DMSO. The protected and unprotected oligomers were identified by MALDI-TOF-MS [28] and NMR. The alkynyl-oligomers were characterized by their $[M + Na]^+$ and, in some cases, by their $[M + K]^+$ peaks.

[8]) Due to the high molecular weight of the hexadecamers **56** (M_r 6.7 kDa) and **57** (M_r 6.5 kDa), the coupling had to be carried out under high dilution to allow stirring. Thus, to get a 0.005M solution, 1 ml of solvent was added to 40 mg of each hexadecamer, resulting in an apparently homogeneous but highly viscous mixture.

Scheme 6



TMS = Me_3Si, TIPS = $(^iPr)_3Si$, DOPS = $OCH_2CH_2C(Me)_2Si(Me)_2$, MOM = $MeOCH_2$

a) Et_3N, MeOH, and *b*) MeONa, MeOH; 95%. *c*) 0.3N HCl, MeOH; 99%.

^{1}H- and ^{13}C-NMR chemical-shift values for the dimers **1** and **23**–**35** depend on the OH protecting groups (*Tables 3* and *4*; see *Exper. Part*). Assignment of the ^{13}C-NMR *s*'s of the butadiynediyl groups is based on heteronuclear multiple-bond correlation gradient-accelerated spectroscopic experiments (HMBC.GRASP [29]) and on a comparison with their homologues[9]). In the ^{1}H-NMR spectra of the oligomers **41**–**54**, the MeOCH_2 signals for the terminal pyranose rings possessing the THP-DOPS-ethynyl group appear at lower field than the corresponding MeOCH_2 signals of the internal pyranoses. The ratio of integrals of the MeOCH_2 signals of terminal and internal rings confirm the degree of polymerization. In the ^{13}C-NMR spectra, terminal and internal rings also give rise to different chemical shifts. Furthermore, the C(8) signals of methoxymethylated pyranose rings are shifted downfield as compared to those possessing a C(8)–OH group (*Table 4* in the *Exper. Part*).

The butadiynediyl IR band appears at 2260 cm^{-1}, with a relative intensity that is proportional to the number of monomeric units.

The octamer **50** and the hexadecamer **54** have no melting points. They decompose above 200–250° to brown oils that did not migrate on TLC plates in any solvent system tested.

We compared spectroscopic and chiroptic data of the octamer **50** and the hexadecamer **54**. Their IR spectra are nearly identical, and the ^{13}C signals of the octamer **50** and the hexadecamer **54** coincide. The dependence of the specific rotation $[\alpha]_D$ ($CHCl_3$) on the molecular weight of the oligomers is expressed in *Fig. 1,a*. The $[\alpha]_D$ values tend towards an extrapolated value of − 89, and the difference of the specific rotation of the octamer **50** (− 75) and the hexadecamer **54** (− 83) is small.

For the unprotected oligomers, the NMR spectra show three sets of signals, two for the terminal pyranosyl units and one for the central ones. The IR spectra of the octamer **64** and the hexadecamer **63** are nearly identical. The dependence of the specific rotation $[\alpha]_D$ (DMSO) of unprotected oligomers on their molecular weight is expressed in *Fig. 1,b*. The $[\alpha]_D$ values tend towards − 54; again there is only a small difference between the specific rotation of the octamer **64** (− 48) and the hexadecamer **63** (− 52).

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[9]) Locants are shown in *Fig. 4* in the *Exper. Part*.

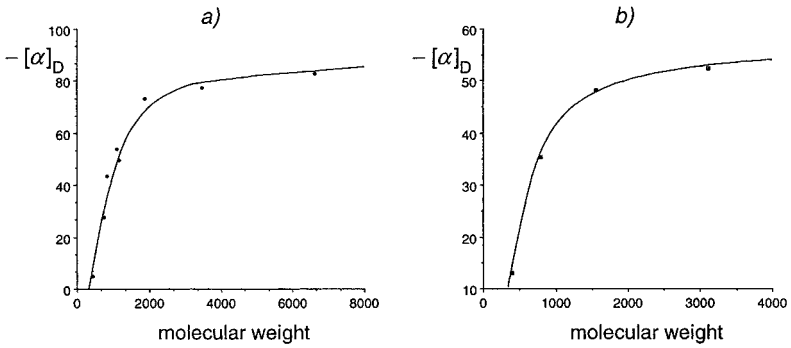

Fig. 1. *Dependence of optical rotation* $[\alpha]_D$ *on molecular weight:* a) *protected oligomers and* b) *unprotected oligomers*

In agreement with the *IUPAC* definition of polymers [30][10]), the hexadecamers **54** and **63** can be considered to possess polymer properties. Preparation of longer chains is, therefore, not required to characterize this class of acetyleno-saccharides.

According to force field calculations (Macromodel 4.5) of acetyleno-oligosaccharides [31], the hexadecamer **63** is a more or less rigid rod with a length of 150 Å. This linearity is almost completely maintained, with a difference in length of 5 Å, when every second glucose unit is rotated by 90°. In keeping with these results, high-resolution (transmission) electron microscopy (HREM) of the protected hexadecamer **54** showed a parallel arrangement of molecules in nanocrystalline domains (*Fig. 2,a*). The distance between two parallel chains is between 0.4 and 0.5 nm. It is not clear if the chains are arranged in a parallel or antiparallel orientation, and to which extent they are in phase. The two-dimensional diffraction pattern indicates the crystallinity of **54**. The identity distances are 0.53 nm in one direction and 0.78 nm in the other, with an angle of 87° between them. An indexing of the pattern is so far impossible, because no other lattice zones have been observed.

HREM of the deprotected hexadecamer **63** also shows domains of molecules in a parallel arrangement (*Fig. 2,b*). Due to the lack of atoms of higher molecular weight like silicon, the image of **63** is less well resolved.

The acetyleno-oligomers are well soluble in DMSO. The solubility in 1 ml of DMSO exceeds 150 mg for the tetramer, 120 mg for the octamer **64**, and 90 mg for the hexadecamer **63**, while it is less than 10 mg for cellotetraose, and less than 2 mg for cellooctaose[11]).

A comparison of the ^{1}H-NMR spectrum of **63** in (D_6)DMSO with those of the corresponding mono-, di-, tetra-, and octamers [8] showed no evidence for any

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[10]) 'A polymer is a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few of the constitutional units'.

[11]) Containing 3–5% of celloheptaose. We thank Dr. *J. A. Hyatt*, *Eastman Research Laboratory*, Kingsport, USA, for a generous sample of cellooligomers.

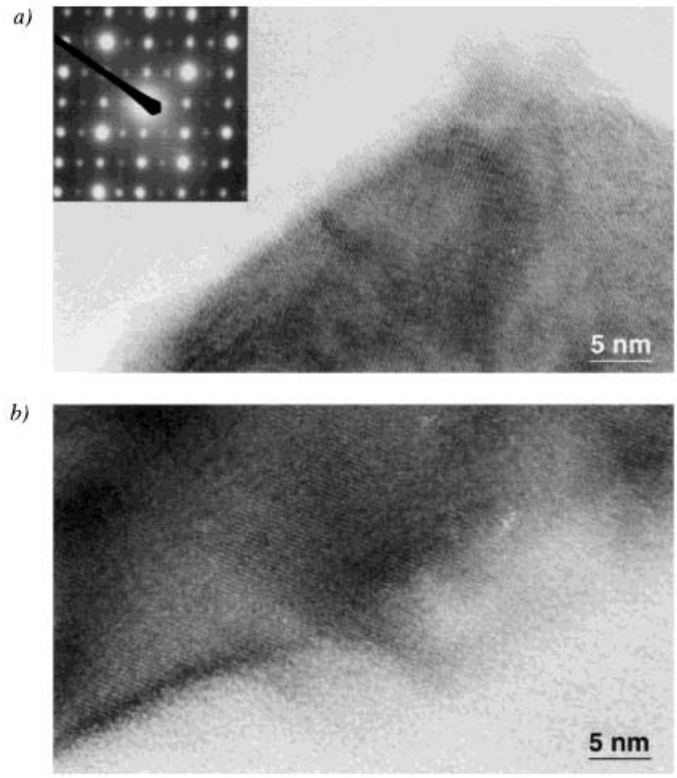

Fig. 2. *HREM Image of* a) *protected hexadecamer* **54**, b) *unprotected hexadecamer* **63**

association of these compounds (*Fig. 3*). H_2O does not dissolve **63**[12]), presumably being too weak a H-bond acceptor while DMSO breaks the relatively weak interchain H-bonds. The absence of association of the hexadecamer **63** and its excellent solubility in DMSO provide strong experimental evidence for the essential role of the C(3)–OH···O–C(5) H-bond in determining the association of cellulose molecules.

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Experimental Part

General. See [17]. HPLC: prepacked column *LiChrosorb* (*Merck*; 7 μm, 250 × 25 mm). Gel permeation chromatography (GPC): prepacked column *(TSK gel G3000 H8*, *Tosohass Co.*; 30 × 7.8 cm). High-Resolution Electron Microscopy (HREM) measurements were performed on a *JEOL 2010* at 200 kV; the samples were suspended in pentane (**54**) or CH_2Cl_2 (**63**) and mounted on a C-coated Cu-grid, and the solvent was evaporated. For the NMR assignment of oligomers, see numbering of C-atoms in *Fig. 4*.

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[12]) Similarly, the acetyleno-tetramer does not dissolve in H_2O while cellotetraose possesses a solubility of *ca.* 140 mg/ml in H_2O [32].

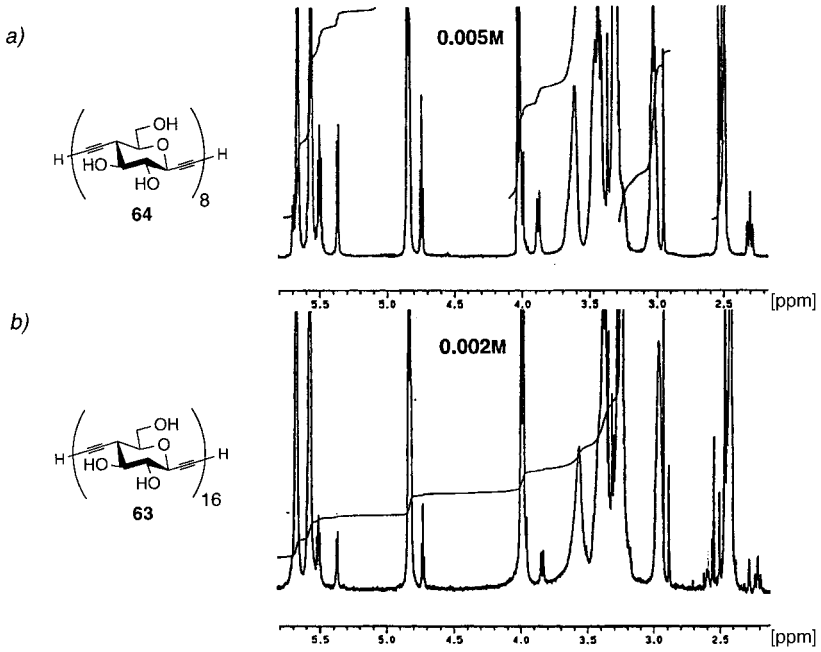

Fig. 3. *^{1}H-NMR Spectra* ((D_6)DMSO) *of* a) *unprotected octamer* **64** *and* b) *unprotected hexadecamer* **63**

C-*De-trimethylsilylation of Alkynes with Sodium Methoxide: General Procedure 1* (*GP1*). At 22°, a soln. of the silylated acetylene in dry, freshly distilled MeOH was treated with freshly prepared 0.25M MeONa in MeOH and stirred for the indicated time. After addition of *Amberlite IR-120*, the mixture was filtered and the filtrate evaporated.

C-*De-trimethylsilylation of Alkynes with Cesium Fluoride: General Procedure 2* (*GP2*). At 0°, a soln. of the silylated acetylene and CsF (1.05 equiv.) in MeOH was treated dropwise with cold DMF (MeOH/DMF 1:5) and stirred at 0° for the indicated time.

O-*De-triisopropylsilylation of Primary Alcohols: General Procedure 3* (*GP3*). A soln. of the silylated primary alcohol in EtOH (0.03–0.1M) was treated with 0.1N HCl (< 0.5 equiv.) and stirred at 50° for the indicated time. After completion, the solvent was evaporated.

Bromination or Iodination of Alkynes: General Procedure 4 (*GP4*). A soln. of the alkyne and NBS or NIS (1.1 equiv.) in dry acetone (0.03–0.1M) was treated with $AgOCOCF_3$ (0.05 equiv.) and stirred in the dark (Al foil) at 21° for the indicated time. After completion, the mixture was worked up normally (Et_2O, H_2O).

Cross-Coupling of Unprotected or DOPS-Protected Alkynes and Haloalkynes: General Procedure 5 (*GP5*). A soln. of the two coupling partners (1 equiv. each), $[Pd_2(dba)_3]$ (0.03 equiv.), CuI (0.03 equiv.), and $P(fur)_3$ (0.05 equiv.) in DMSO (0.03–0.1M) in a flame-dried *Schlenk* flask was degassed for 15 min, treated with dry Et_3N (3 equiv.), and stirred in the dark for the indicated time. After completion, the mixture was poured onto ice/H_2O, neutralized with 1N HCl, and subjected to normal workup (Et_2O, H_2O).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-{{[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]dimethylsilyl}ethynyl}-6-*O*-(triisopropylsilyl)*-D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→6-C)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**3**). According to *GP1*, with **1** (2.45 g, 2.28 mmol), 0.25M NaOMe (6.3 ml), and MeOH (330 ml; 5 h). FC (AcOEt/hexane 1:9) gave **3** (2.15 g, 94%). White foam. R_f (AcOEt/hexane 1:4) 0.10. M.p. 75–77°. $[\alpha]_D^{25} = -50.4$ ($c = 0.6$, $CHCl_3$). IR ($CHCl_3$): 3597*w*, 3306*w*, 3008*w*, 2962*s*, 2867*s*, 2362*w*, 2254*w*, 2170*w*, 1602*w*, 1464*m*, 1392*w*, 1329*w*, 1261*s* (br.), 1097*s*, 1015*s*, 883*m*, 818*s* (br.), 602*w*, 577*w*, 509*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.00 (*dd*, $J = 9.3, 0.6$, H–C(5′)); 3.97 (*d*, $J = 9.2, 2.1$, H–C(3)); 3.92 (*ddd*, $J \approx 12.1, 7.1, 2.6$, H–C(8)); 3.90 (*ddd*, $J \approx 12.1, 6.8, 2.4$, H–C(10′)); 3.77 (*t*, $J = 7.7$, CH_2CH_2OSi); 3.73–3.69 (*m*, H′–C(8), H′–C(10′)); 3.65 (*dd*, $J = 9.3, 8.3$, H–C(6′)); 3.64 (*dd*, $J = 9.2, 8.4$, H–C(4)); 3.57–3.50 (*m*, H–C(5), H–C(7′)); 3.49–3.42 (*m*, H–C(9′), H–C(7)); 2.68 (*td*, $J = 10.3, 0.6$, H–C(6)); 2.54 (*t*, $J = 10.3$,

H–C(8′)); 2.49 (*d*, *J* = 2.1, H–C(1)); 2.37 (*d*, *J* = 3.1, HO–C(5), HO–C(7′)); 2.00 (*dd*, *J* = 7.3, 6.3, HO–C(10′)); 1.96 (*t*, *J* = 6.8, HO–C(8)); 1.59 (*t*, *J* = 7.7, CH_2CH_2OSi); 1.26–1.05 (*m*, *3* $(Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.11 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 102.27 (*s*); 88.59 (*s*); 80.76 (*d*); 79.11 (*d*); 78.79 (*d*); 77.23 (*s*); 76.73 (*d*); 76.71 (*d*); 76.43 (*s*); 75.13 (*d*); 75.04 (*d*); 74.75 (*s*); 71.86 (*d*); 71.42 (*d*); 70.48 (*s*); 68.57 (*s*); 63.64 (*t*); 63.36 (*t*); 60.15 (*t*); 41.64 (*t*); 39.11 (*d*); 38.33 (*d*); 23.37 (*q*); 23.34 (*q*); 18.53 (*s*); 18.34–18.26 (12*q*); 18.08 (6*q*); 12.98 (3*d*); 12.96 (3*d*); 12.03 (3*d*); –4.12 (*q*); –4.14 (*q*). MALDI-TOF-MS: 1025 ($[M+Na]^+$). Anal. calc. for $C_{54}H_{98}O_9Si_4$ (1003.70): C 64.62, H 9.84; found: C 64.45, H 9.76.

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl}-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-1-*C*-bromo-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**4**). According to *GP4*, with **3** (0.99 g, 0.990 mmol), NBS (193.3 mg, 1.089 mmol), $AgOCOCF_3$ (10.9 mg, 0.0495 mmol), and acetone (30 ml; 5 h). FC (AcOEt/hexane 3 : 17 → 1 : 4) gave **4** (1.00 g, 94%). White foam. R_f (AcOEt/hexane 1 : 3) 0.43. M.p. 84.5–87°. $[\alpha]_D^{25} = -54.3$ (*c* = 0.51, $CHCl_3$). IR ($CHCl_3$): 3596*m*, 2945*s*, 2892*s*, 2867*s*, 2218*w*, 2171*w*, 1722*w* (br.), 1464*m*, 1384*m*, 1367*m*, 1329*w*, 1292*m*, 1269*m*, 1143*s*, 1078*s*, 1014*m*, 883*s*, 839*m*, 824*m*, 654*m*, 600*w*, 573*w*, 532*w*, 516*w*, 508*w*, 502*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.99 (*dd*, *J* = 9.3, 0.2, H–C(5′)); 3.98 (*d*, *J* = 9.3, H–C(3)); 3.91 (*ddd*, *J* ≈ 11.9, 7.4, 2.6, H–C(8)); 3.90 (*ddd*, *J* ≈ 11.8, 6.9, 2.4, H–C(10′)); 3.77 (*t*, *J* = 7.7, CH_2CH_2OSi); 3.73–3.67 (*m*, H′–C(8), H′–C(10′)); 3.64 (*dd*, *J* = 9.3, 8.3, H–C(6′), H–C(4)); 3.56–3.48 (*m*, H–C(5), H–C(7′)); 3.46–3.42 (*m*, H–C(9′), H–C(7)); 2.67 (*t*, *J* = 10.5, H–C(6)); 2.54 (*t*, *J* = 10.3, H–C(8′)); 2.37 (*d*, *J* = 3.3, HO–C(5)); 2.36 (*d*, *J* = 2.7, HO–C(7′)); 1.99 (*dd*, *J* = 7.3, 6.2, HO–C(10′)); 1.93 (*t*, *J* = 6.7, HO–C(8)); 1.59 (*t*, *J* = 7.7, CH_2CH_2OSi); 1.30–1.05 (*m*, 3 $(Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.11 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 102.25 (*s*); 88.59 (*s*); 79.09 (*d*); 78.73 (*d*); 77.19 (*s*); 76.73 (*d*); 76.64 (*d*); 76.35 (*s*); 75.18 (*d*); 75.14 (*s*); 75.11 (*d*); 72.29 (*d*); 71.85 (*d*); 70.47 (*s*); 68.56 (*s*); 63.64 (*t*); 63.31 (*t*); 60.14 (*t*); 47.50 (*s*); 41.64 (*t*); 39.11 (*d*); 38.25 (*d*); 23.36 (*q*); 23.34 (*q*); 18.52 (*s*); 18.28–18.08 (several *q*); 12.95 (3*d*); 12.89 (3*d*); 12.02 (3*d*); –4.12 (*q*); –4.14 (*q*). MALDI-TOF-MS: 1105 ($[M+Na]^+$). Anal. calc. for $C_{54}H_{97}BrO_9Si_4$ (1082.59): C 59.91, H 9.03; found: C 60.05, H 9.18.

Coupling of **4** *with* **5**. According to *GP5*, with **4** (1.60 g, 1.48 mmol), **5** (1.36 g, 1.48 mmol). $[Pd_2(dba)_3]$ (41.1 mg, 0.044 mmol), CuI (8.2 mg, 0.044 mmol), $P(fur)_3$ (17.0 mg, 0.074 mmol), Et_3N (0.62 ml, 4.44 mmol), and DMSO (15 ml; 15 h). HPLC (AcOEt/hexane 1 : 10 → 3 : 17) gave **6** (2.07 g, 79%), **7** (79.9 mg, 3%), and **8** (21.0 mg, < 1%) as white foams.

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl}-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**6**): R_f (SiO_2, AcOEt/hexane 1 : 2) 0.29. R_f ('cyanopropyl'; AcOEt/hexane 1 : 3) 0.23. M.p. 186–187°. $[\alpha]_D^{25} = -56.0$ (*c* = 0.24, $CHCl_3$). IR ($CHCl_3$): 3599*m*, 3458*w* (br.), 3007*m*, 2946*s*, 2893*s*, 2867*s*, 2262*w*, 2173*w*, 1464*m*, 1390*m*, 1367*m*, 1328*w*, 1292*m*, 1261*s* (br.), 1143*s*, 1083*s*, 883*s*, 845*s* (br.), 822*s*, 642*m*, 600*w*, 580*w*, 573*w*, 508*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.99 (*d*, *J* = 9.2, H–C(5′), H–C(5″)); 3.98 (*dd*, *J* = 9.2, 0.5, H–C(5‴)); 3.95 (*d*, *J* = 9.3, H–C(3)); 3.90–3.84 (*m*, H–C(8), H–C(10′), H–C(10″), H–C(10‴)); 3.77 (*t*, *J* = 7.6, CH_2CH_2OSi); 3.71–3.65 (*m*, H′–C(8), H′–C(10′), H–C(10″), H–C(10‴)); 3.65–3.61 (*m*, H–C(6′), H–C(6″), H–C(6‴)); 3.62 (*t*, *J* ≈ 9.4, H–C(4)); 3.54–3.48 (*m*, H–C(5), H–C(7′), H–C(7″), H–C(7‴)); 3.46–3.41 (*m*, H–C(7), H–C(9′), H–C(9″), H–C(9‴)); 2.73 (*t*, *J* = 10.3, H–C(8′), H–C(8″)); 2.68 (*td*, *J* = 10.2, 0.2, H–C(6)); 2.57 (*t*, *J* = 10.3, H–C(8‴)); 2.45 (*d*, *J* = 3.9, HO–C(7′), HO–C(7″)); 2.42 (*d*, *J* = 3.4, HO–C(5)); 2.39 (*d*, *J* = 2.7, HO–C(7‴)); 2.17–2.08 (*m*, HO–C(8), HO–C(10′), HO–C(10″), HO–C(10‴)); 1.59 (*t*, *J* = 7.7, CH_2CH_2OSi); 1.21–1.05 (*m*, 5 $(Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.17 (*s*, Me_3Si); 0.11 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 102.32 (*s*); 101.99 (*s*); 91.47 (*s*); 88.50 (*s*); 79.29 (*d*); 78.98 (*d*); 78.92 (*d*); 78.71 (*d*); 76.83 (2*d*); 76.56 (2*d*); 76.33 (*s*); 75.27 (*d*); 75.22 (*d*); 75.18 (*d*); 75.12 (*d*); 74.97 (*s*); 74.78 (*s*); 72.02 (3*d*); 71.86 (*d*); 70.81 (*s*); 70.72 (*s*); 70.54 (*s*); 68.61 (*s*); 68.49 (*s*); 68.33 (*s*); 63.55 (*t*); 63.36 (*t*); 63.19 (2*t*); 60.14 (*t*); 41.62 (*t*); 39.05 (2*d*); 38.27 (*d*); 38.17 (*d*); 23.36 (*q*); 23.34 (*q*); 18.52 (*s*); 18.35–18.08 (several *q*); 13.03 (3*d*); 12.95 (3*d*); 12.90 (3*d*); 12.66 (3*d*); 12.03 (3*d*); –0.39 (3*q*); –4.13 (2*q*). MALDI-TOF-MS: 1799 ($[M+Na]^+$). Anal. calc. for $C_{95}H_{166}O_{17}Si_7 \cdot H_2O$ (1794.92): C 63.61, H 9.38; found: C 63.56, H 9.35.

*Data of 5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl}-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 3-*C*)-2,6 : 11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-5,12-bis-*O*-(triisopropylsilyl)-*D*-erythro-*L*-galacto-*L*-gulo-hexadeca-7,9-diynitol-14-yl-(14 → 1-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl}-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol* (**7**): R_f ('cyanopropyl'; AcOEt/hexane 1 : 3) 0.15. ^{1}H-NMR

(500 MHz, $CDCl_3$): 4.02 (*d*, *J* = 9.2, H–C(6)); 3.98 (*d*, *J* = 9.2, H–C(5′)); 3.92–3.85 (*m*, H–C(1), H–C(10′)); 3.77 (*t*, *J* = 7.7, CH_2CH_2OSi); 3.73–3.69 (*m*, H′–C(1), H′–C(10′)); 3.64 (*dd*, *J* ≈ 9.1, 8.4), 3.63 (*dd*, *J* = 9.2, 8.4, H–C(5), H–C(6′)); 3.54–3.48 (*m*, H–C(4), H–C(7′)); 3.45–3.43 (*m*, H–C(2), H–C(9′)); 2.78 (*t*, *J* = 10.3, H–C(3)); 2.58 (*t*, *J* = 10.3, H–C(8′)); 1.60 (*t*, *J* = 7.7, CH_2CH_2OSi); 1.26–1.08 (*m*, 3 $(Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.11 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 102.27 (*s*); 88.47 (*s*); 79.42 (*d*); 78.97 (*d*); 76.97 (*s*); 76.76 (*d*); 76.62 (*d*); 76.32 (*s*); 75.30 (*s*); 75.11 (2*d*); 71.96 (*d*); 71.88 (*d*); 70.60 (*s*); 70.27 (*s*); 68.64 (*s*); 63.50 (*t*); 63.11 (*t*); 60.15 (*t*); 41.59 (*t*); 39.00 (*d*); 38.13 (*d*); 23.36 (*q*); 23.33 (*q*); 18.52 (*s*); 18.29–18.08 (several *q*); 12.95 (3*d*); 12.57 (3*d*); 12.03 (3*d*); –4.13 (2*q*, Me_2Si). MALDI-TOF-MS: 2028 ($[M + Na]^+$).

*Data of 8,8″-(Buta-1,3-diyne-1,4-diyl)bis[5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol]* (**8**): R_f ('cyanopropyl'; AcOEt/hexane 1:3) 0.09. IR ($CHCl_3$): 3597*w*, 3008*w*, 2963*s*, 2904*m*, 2868*m*, 2263*w*, 2181*w*, 1944*w*, 1602*w*, 1463*w*, 1412*m*, 1261*s*, 1098*s*, 864*s*, 818*s*, 603*w*, 576*w*, 526*w*, 518*w*, 510*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.99 (*dd*, *J* = 9.2, 0.6, H–C(5′)); 3.95 (*d*, *J* = 9.3, H–C(3)); 3.91–3.89 (*m*, H–C(8), H–C(10′)); 3.72–3.65 (*m*, H′–C(8), H′–C(10′)); 3.62 (*dd*, *J* = 9.2, 8.4, H–C(6′)); 3.61 (*dd*, *J* = 9.3, 8.4, H–C(4)); 3.56–3.50 (*m*, H–C(5), H–C(7′)); 3.45 (*ddd*, *J* = 9.8, 5.3, 2.3, H–C(9′)); 3.43 (*ddd*, *J* = 10.1, 5.7, 2.5, H–C(7)); 2.68 (*t*, *J* = 10.2, H–C(8′)); 2.66 (*td*, *J* = 10.1, 0.2, H–C(6)); 2.55 (*m*, HO–C(5), HO–C(7)); 2.44 (*m*, HO–C(8), HO–C(10′)); 1.26–1.09 (*m*, 2 $(Me_2CH)_3Si$); 0.17 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 101.98 (*s*); 91.44 (*s*); 78.93 (*d*); 78.69 (*d*); 76.87 (*s*); 76.80 (*d*); 76.50 (*d*); 75.25 (*d*); 75.13 (*d*); 74.71 (*s*); 74.43 (*s*); 72.00 (*d*); 71.82 (*d*); 70.80 (*s*); 68.82 (*s*); 68.35 (*s*); 63.35 (*t*); 63.31 (*t*); 38.28 (*d*); 38.05 (*d*); 18.34–18.24 (several *q*); 13.03 (3*d*); 12.92 (3*d*); –0.40 (3*q*). MALDI-TOF-MS: 1571 ($[M + Na]^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl}-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**9**). According to *GP1*, with **6** (113.1 mg, 0.066 mmol), 0.25M NaOMe (0.3 ml), and MeOH (5 ml; 6 h). FC (AcOEt/hexane 1:2) gave **9** (100.9 mg, 93%). Yellow powder. R_f ('cyanopropyl'; AcOEt/hexane 1:3) 0.26. IR ($CHCl_3$): 3598*m*, 3306*w*, 2946*s*, 2867*s*, 2266*w*, 2166*w*, 1602*w*, 1464*m*, 1367*m*, 1293*m*, 1261*s*, 1143*s*, 1086*s*, 1016*s*, 883*s*, 818*s* (br.). ^{1}H-NMR (500 MHz, $CDCl_3$): 4.00 (*dd*, *J* ≈ 9.2, 0.2), 3.99 (*dd*, *J* ≈ 9.1, 0.2), 3.98 (*dd*, *J* ≈ 8.8, 0.2, H–C(5′), H–C(5″), H–C(5‴)); 3.97 (*dd*, *J* = 9.2, 2.1, H–C(3)); 3.91–3.85 (*m*, H–C(8), H–C(10′), H–C(10″), H–C(10‴)); 3.77 (*t*, *J* = 7.6, CH_2CH_2OSi); 3.72–3.68 (*m*, H′–C(8), H′–C(10′), H′–C(10″), H′–C(10‴)); 3.644 (*dd*, *J* = 9.2, 8.4), 3.638 (*dd*, *J* ≈ 9.5, 8.1), 3.634 (*dd*, *J* ≈ 9.2, 8.2, H–C(6′), H–C(6″), H–C(6‴)); 3.633 (*dd*, *J* = 9.3, 8.3, H–C(4)); 3.57–3.49 (*m*, H–C(5), H–C(7′), H–C(7″), H–C(7‴)); 3.48–3.43 (*m*, H–C(7), H–C(9′), H–C(9″), H–C(9‴)); 2.76 (*t*, *J* ≈ 10.3, H–C(8′), H–C(8″)); 2.70 (*t*, *J* ≈ 10.3, H–C(6)); 2.58 (*t*, *J* ≈ 10.3, H–C(8‴)); 2.49 (*d*, *J* = 2.1, H–C(1)); 2.47 (*d*, *J* = 4.2, HO–C(7′), HO–C(7″)); 2.43 (*d*, *J* = 3.9, HO–C(5)); 2.39 (*d*, *J* = 3.2, HO–C(7‴)); 2.22 (*t*, *J* ≈ 6.9), 2.19 (*t*, *J* ≈ 7.2, HO–C(10′), HO–C(10″)); 2.16 (*t*, *J* = 6.8, HO–C(8)); 2.07 (*t*, *J* = 7.0, HO–C(10‴)); 1.59 (*t*, *J* = 7.6, CH_2CH_2O-Si); 1.27–1.08 (*m*, 4 $(Me_2CH)_3Si$); 1.21–1.05 (*m*, $(Me_2CH)_3Si$); 0.95 (*s*, Me_2C); 0.11 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 102.34 (*s*); 88.47 (*s*); 80.80 (*d*); 79.34 (*d*); 79.03 (*d*); 78.98 (*d*); 78.80 (*d*); 77.23 (*d*); 76.78 (*d*); 76.64 (*s*); 76.54 (*d*); 76.36 (*s*); 75.31 (*d*); 75.25 (*d*); 75.19 (*d*); 75.12 (*d*); 75.03 (3*s*); 74.83 (2*s*); 71.86 (3*d*); 71.41 (*d*); 70.77 (*s*); 70.57 (3*s*); 68.60 (*s*); 68.49 (*s*); 68.41 (*s*); 63.52 (*t*); 63.38 (*t*); 63.16 (2*t*); 60.14 (*t*); 41.61 (*t*); 39.01 (*d*); 38.31 (2*d*); 38.13 (*d*); 23.37 (*q*); 23.34 (*q*); 18.52 (*s*); 18.34–18.24 (several *q*); 18.08 (several *q*); 12.98 (3*d*); 12.95 (3*d*); 12.90 (6*d*); 12.03 (3*d*); –4.14 (2*q*). MALDI-TOF-MS: 1725 ($[M + Na]^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl}-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-1-*C*-bromo-4-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**10**). According to *GP4*, with **9** (430.1 mg, 0.252 mmol), NBS (47.2 mg, 0.265 mmol), $AgOCOCF_3$ (3.0 mg, 0.013 mmol), and acetone (1 ml; 12 h). FC (AcOEt/hexane 1:2) gave **10** (423.2 g, 94%). White foam. R_f ('cyanopropyl'; AcOEt/hexane 1:3) 0.34. IR ($CHCl_3$): 3602*m* (br.), 3008*m*, 2946*s*, 2892*m*, 2867*s*, 2262*w*, 2168*w*, 1602*w*, 1464*m*, 1384*m*, 1367*m*, 1292*m*, 1144*s*, 1082*s*, 998*m*, 970*m*, 883*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.98 (*d*, *J* = 9.2, H–C(5‴)); 3.97 (*d*, *J* = 9.2, H–C(3)); 3.967 (*dd*, *J* ≈ 9.2, 0.2, H–C(5′), H–C(5″)); 3.90–3.82 (*m*, H–C(8), H–C(10′), H–C(10″), H–C(10‴)); 3.77 (*t*, *J* = 7.6, CH_2CH_2O-Si); 3.78–3.67 (*m*, H′–C(8), H′–C(10′), H′–C(10″), H′–C(10‴)); 3.64 (*dd*, *J* = 9.3, 8.2, H–C(6′), H–C(6″)); 3.632 (*dd*, *J* = 9.2, 8.4, H–C(4)); 3.629 (*dd*, *J* ≈ 9.2, 8.3, H–C(6‴)); 3.56–3.47 (*m*, H–C(5), H–C(7′), H–C(7″), H–C(7‴)); 3.46–3.43 (*m*, H–C(7), H–C(9′), H–C(9″), H–C(9‴)); 2.74 (*t*, *J* ≈ 10.3), 2.63 (*t*, *J* = 10.3), 2.58 (*t*, *J* ≈ 10.3, H–C(6), H–C(8′), H–C(8″), H–C(8‴)); 2.47–2.40 (*m*, HO–C(5), HO–C(7′),

HO–C(7″), HO–C(7‴), HO–C(8), HO–C(10′), HO–C(10″), HO–C(10‴)); 1.59 (*t*, *J* = 7.7, C*H*$_2$CH$_2$OSi); 1.23–1.05 (*m*, 5 (Me$_2$CH)$_3$Si); 0.96 (*s*, Me$_2$C); 0.11 (*s*, Me$_2$Si). ^{13}C-NMR (125 MHz, CDCl$_3$): 102.53 (*s*); 88.21 (*s*); 79.77 (*d*); 79.37 (*d*); 79.26 (*d*); 78.88 (*d*); 77.23 (*s*); 76.85 (*d*); 76.63 (*s*); 76.54 (*d*); 76.40 (*d*); 75.61 (*d*); 75.50 (*d*); 75.41 (*s*); 75.27 (2*s*); 75.12 (*d*); 74.93 (2*s*); 71.88 (3*d*); 71.86 (*d*); 71.84 (*d*); 71.39 (*d*); 70.93 (*s*); 70.90 (*s*); 70.83 (*s*); 68.52 (*s*); 68.39 (*s*); 68.33 (*s*); 63.42 (*t*); 63.31 (*t*); 62.93 (2*t*); 60.13 (*t*); 47.96 (*s*); 41.56 (*t*); 38.86 (*d*); 38.38 (*d*); 37.93 (2*d*); 23.35 (*q*); 23.34 (*q*); 18.51 (*s*); 18.33–18.08 (several *q*); 12.98 (3*d*); 12.94 (3*d*); 12.89 (3*d*); 12.88 (3*d*); 12.02 (3*d*); −4.15 (2*q*). MALDI-TOF-MS: 1823 ([*M* + K]$^+$), 1807 ([*M* + Na]$^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{[(hydroxy-1,1-dimethylpropyl)dimethylsilyl]ethynyl}-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1→6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**11**). According to *GP3*, at 45° with **6** (103.9 mg, 0.059 mmol), 0.1N HCl (0.33 ml), and EtOH (1.7 ml; 8 h). FC (AcOEt/hexane 4:6) gave **11** (86.5 mg, 91%). White foam. R_f ('cyanopropyl'; AcOEt/hexane 1:3) 0.17. IR (CHCl$_3$): 3599*m*, 3485*m*, 3007*m*, 2945*s*, 2867*s*, 2256*w*, 2174*w*, 1733*w*, 1464*m*, 1385*m*, 1328*w*, 1292*m*, 1252*s* (br.), 1147*s*, 1120*s*, 1071*s*, 1016*m*, 883*s*, 846*s*, 682*m*. ^{1}H-NMR (500 MHz, CDCl$_3$): 3.996 (*d*, *J* = 9.2), 3.992 (*d*, *J* = 9.2, H–C(5′), H–C(5″)); 3.98 (*dd*, *J* = 9.2, 0.5, H–C(5‴)); 3.95 (*d*, *J* = 9.3, H–C(3)); 3.92–3.85 (*m*, H–C(8), H–C(10′), H–C(10″), H–C(10‴)); 3.77 (*t*, *J* = 7.6, CH$_2$C*H*$_2$OSi); 3.78–3.61 (*m*, H′–C(8), H′–C(10′), H–C(10″), H–C(10‴), H–C(4), H–C(6′), H–C(6″), H–C(6‴)); 3.53–3.44 (*m*, H–C(5), H–C(7′), H–C(7″), H–C(7‴), H–C(7), H–C(9′), H–C(9″), H–C(9‴)); 2.82 (*t*, *J* = 10.3), 2.79 (*t*, *J* = 10.3, H–C(8′), H–C(8″)); 2.69 (*t*, *J* = 10.2, H–C(6)); 2.62 (*t*, *J* = 10.3, H–C(8‴)); 1.61 (*t*, *J* = 7.5, C*H*$_2$CH$_2$OSi); 1.23–1.05 (*m*, 5 (Me$_2$CH)$_3$Si); 0.95 (*s*, Me$_2$C); 0.17 (*s*, Me$_3$Si); 0.12 (*s*, Me$_2$Si). ^{13}C-NMR (125 MHz, CDCl$_3$): 103.14 (*s*); 102.02 (*s*); 91.48 (*s*); 88.13 (*s*); 79.59 (*d*); 79.13 (*d*); 79.02 (*d*); 78.75 (*d*); 77.23 (*s*); 76.77 (*d* and *s*); 76.48 (2*d*); 76.43 (*s*); 75.40 (*d*); 75.36 (*d*); 75.23 (*d*); 75.13 (*d*); 74.94 (*s*); 72.03 (2*d*); 71.87 (2*d*); 70.86 (several *s*); 68.44 (*s*); 68.29 (2*s*); 63.34 (2*t*); 63.03 (*t*); 59.92 (*t*); 42.83 (*t*); 38.96 (*d*); 38.29 (2*d*); 38.11 (*d*); 23.97 (2*q*); 18.52 (*s*); 18.35–18.15 (several *q*); 13.03 (3*d*); 12.95 (3*d*); 12.90 (6*d*); 12.66 (3*d*); 12.03 (3*d*); −0.38 (3*q*); −4.00 (2*q*). MALDI-TOF-MS: 1658 ([*M* + K]$^+$), 1642 ([*M* + Na]$^+$).

*5,8-Di-*O*-acetyl-3,7-anhydro-1-*C*-bromo-1,2,6-trideoxy-6-*C*-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl}-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**16**). A soln. of **15** (108.6 mg, 0.148 mmol) and 4-(dimethylamino)pyridine (15 mg) in Ac$_2$O (3 ml) and pyridine (1.5 ml) was stirred for 35 h. Evaporation and FC (AcOEt/hexane 1:49) gave **16** (106.7 mg, 89%). White foam. R_f (AcOEt/hexane 3:17) 0.47. $[\alpha]_D^{25} = -10.1$ (*c* = 0.4, CHCl$_3$). IR (CHCl$_3$): 2946*s*, 2892*m*, 2867*s*, 2180*w*, 1746*s*, 1602*w*, 1463*m*, 1367*m*, 1260*s*, 1155*m*, 1092*s*, 1069*s*, 1015*s*, 883*m*, 818*m*, 543*w*, 518*w*. ^{1}H-NMR (300 MHz, CDCl$_3$): 5.12 (*dd*, *J* = 10.8, 8.9, H–C(5)); 4.38 (*dd*, *J* = 12.1, 2.0, H–C(8)); 4.24 (*dd*, *J* = 12.1, 5.7, H′–C(8)); 4.04 (*d*, *J* = 9.3, H–C(3)); 3.81 (*t*, *J* ≈ 9.0, H–C(4)); 3.75 (*t*, *J* ≈ 7.8, CH$_2$C*H*$_2$OSi); 3.65 (*ddd*, *J* = 10.4, 5.7, 2.0, H–C(7)); 2.68 (*t*, *J* = 10.6, H–C(6)); 2.11 (*s*, Ac); 2.10 (*s*, Ac); 1.56 (*t*, *J* ≈ 7.8, C*H*$_2$CH$_2$OSi); 1.23–1.07 (*m*, 2 (Me$_2$CH)$_3$Si); 0.93 (*s*, Me$_2$C); 0.07 (*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, CDCl$_3$): 170.59 (*s*); 169.24 (*s*); 100.53 (*s*); 88.67 (*s*); 76.93 (*s*); 76.73 (*d*); 75.75 (*d*); 73.14 (*d*); 72.84 (*d*); 64.51 (*t*); 60.09 (*t*); 48.06 (*s*); 41.30 (*t*); 37.50 (*d*); 23.21 (*q*); 23.10 (*q*); 21.11 (*q*); 20.88 (*q*); 18.37 (*s*); 18.08–18.04 (several *q*); 13.50 (3*d*); 12.00 (3*d*); −4.38 (2*q*). CI-MS: 819 (1), 818 (1), 817 (3, [*M* + 1]$^+$); 816 (1, *M*$^+$), 771 (3), 693 (3), 303 (1), 302 (3), 301 (12, TIPS-DOPS$^+$), 247 (9), 175 (5), 174 (14), 173 (100), 157 (3, TIPS$^+$), 145 (2, DOPS$^+$), 43 (1, Ac). Anal. calc. for $C_{39}H_{71}BrO_7Si_3$ (816.11): C 57.40, H 8.77; found: C 57.54, H 8.74.

*3,7-Anhydro-1-*C*-bromo-1,2,6-trideoxy-6-*C*-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl}-4,8-bis-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**17**). At 22°, a soln. of **15** (264.1 mg, 0.36 mmol) in pyridine (10 ml) was treated dropwise with ^{i}Pr$_3$SiOTf (0.291 ml, 1.08 mmol), stirred for 1 h, and quenched with ice/H$_2$O (10 ml). Usual workup (Et$_2$O, H$_2$O) and FC (AcOEt/hexane 1:19) gave **17** (297.4 mg, 93%). Transparent syrup. R_f (AcOEt/hexane 1:9) 0.66. $[\alpha]_D^{25} = -7.9$ (*c* = 0.23, CHCl$_3$). IR (CCl$_4$): 3593*w*, 2944*s*, 2892*s*, 2867*s*, 2725*w*, 2221*w*, 2170*w*, 1464*s*, 1384*m*, 1366*w*, 1292*w*, 1252*m*, 1145*s*, 1094*s*, 1069*s*, 1014*m*, 998*m*, 947*w*, 918*m*, 883*s*, 839*m*, 682*s*. ^{1}H-NMR (300 MHz, CDCl$_3$): 4.04 (*dd*, *J* = 11.2, 1.6, H–C(8)); 3.92 (*d*, *J* = 9.2, H–C(3)); 3.87 (*dd*, *J* = 11.2, 5.1, H′–C(8)); 3.78 (*t*, *J* = 7.7, CH$_2$C*H*$_2$OSi); 3.61 (*t*, *J* ≈ 8.8, H–C(4)); 3.49 (*td*, *J* = 10.6, 2.5, H–C(5)); 3.38 (*ddd*, *J* = 10.3, 5.0, 1.6, H–C(7)); 2.62 (*t*, *J* = 10.3, H–C(6)); 2.35 (*d*, *J* = 2.6, HO–C(5)); 1.60 (*t*, *J* ≈ 7.7, C*H*$_2$CH$_2$OSi); 1.26–1.04 (*m*, 3 (Me$_2$CH)$_3$Si); 0.96 (*s*, Me$_2$C); 0.07 (*s*, Me$_2$Si). ^{13}C-NMR (75 MHz, CDCl$_3$): 103.43 (*s*); 87.54 (*s*); 79.87 (*d*); 77.76 (*s*); 77.00 (*d*); 75.14 (*d*); 72.08 (*d*); 64.33 (*t*); 60.14 (*t*); 46.23 (*s*); 41.56 (*t*); 38.75 (*d*); 23.34 (2*q*); 18.52 (*s*); 18.20 (6*q*); 18.07 (6*q*); 17.97 (6*q*); 12.94 (3*d*); 12.05 (3*d*); 12.02 (3*d*); −4.16 (2*q*). CI-MS: 889 (3, [*M* + 1]$^+$), 888 (1, *M*$^+$), 887 (2), 845 (6), 541 (5), 539 (3), 303 (20), 302 (52), 301 (100, TIPS-DOPS$^+$), 248 (14), 231 (7), 174 (11), 172 (11), 157 (14, TIPS$^+$), 119 (42), 118 (9). Anal. calc. for $C_{44}H_{87}BrO_5Si_4$ (888.41): C 59.49, H 9.87; found: C 59.50, H 9.76.

*3,7-Anhydro-1-*C*-bromo-1,2,6-trideoxy-6-*C*-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}-ethynyl}-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**18**). At 0°, a soln. of **15** (918.9 mg, 1.255 mmol) and *Hünig*'s base (4.3 ml, 25.10 mmol) in $ClCH_2CH_2Cl$ (10 ml) was treated dropwise with methoxymethyl chloride (0.95 ml, 12.55 mmol) and stirred for 24 h at 22°. Removal of the solvents (cooling trap!) and FC (AcOEt/hexane 1:19) gave **18** (915.4 mg, 89%). Transparent syrup. R_f (AcOEt/hexane 3:17) 0.64. $[\alpha]_D^{25} = -43.4$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3008*m*, 2945*s*, 2891*s*, 2867*s*, 2224*w*, 2173*w*, 1653*w*, 1464*m*, 1384*w*, 1366*w*, 1292*w*, 1254*m*, 1152*s*, 1096*s*, 1038*s*, 920*m*, 884*s*, 839*m*, 823*s*, 656*m*, 621*w*, 611*w*, 528*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.98 (*d*, $J = 5.6$, MeOC*H*); 4.79 (*d*, $J = 5.6$, MeOC*H*); 4.66 (*s*, CH_2OMe); 3.95 (*d*, $J = 9.3$, H–C(3)); 3.88 (*dd*, $J \approx 11.1$, 2.0, H–C(8)); 3.82–3.71 (*m*, H′–C(8), H–C(4), CH_2CH_2OSi); 3.51 (*ddd*, $J \approx 10.3$, 5.0, 2.0, H–C(7)); 3.48 (*dd*, $J \approx 10.0$, 7.8, H–C(5)); 3.45 (*s*, MeO); 3.37 (*s*, MeO); 2.73 (*t*, $J = 10.3$, H–C(6)); 1.59 (*t*, $J = 7.8$, CH_2CH$_2$OSi); 1.25–1.08 (*m*, 2 $(Me_2CH)_3Si$); 0.97 (*s*, Me_2C); 0.10 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.49 (*s*); 98.17 (*t*); 96.74 (*t*); 87.46 (*s*); 82.31 (*d*); 78.73 (*d*); 77.54 (*s*); 74.95 (*d*); 72.62 (*d*); 67.59 (*t*); 60.00 (*t*); 56.72 (*q*); 55.31 (*q*); 47.59 (*s*); 41.25 (*t*); 37.85 (*d*); 23.10 (2*q*); 18.39 (*s*); 18.07–17.95 (6*q*); 13.59 (3*d*); 11.86 (3*d*); −4.42 (2*q*). ES-MS: 843 ($[M + Na]^+$), 838 ($[M + NH_4]^+$).

*5,8-Di-*O*-acetyl-3,7-anhydro-1,2,6-trideoxy-6-*C*-ethynyl-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**20**). A soln. of **19** (236.0 mg, 0.464 mmol) and 4-(dimethylamino)pyridine (10 mg) in Ac_2O (3 ml) and pyridine (1.5 ml) was stirred for 48 h at 22°. Evaporation and FC (AcOEt/hexane 1:9) gave **20** (212.4 mg, 90%). White foam. R_f (AcOEt/hexane 3:17) 0.27. M.p. 90.5–91.5°. $[\alpha]_D^{25} = -9.8$ ($c = 1.78$, $CHCl_3$). IR ($CHCl_3$): 3308*m*, 3008*m*, 2947*s*, 2894*m*, 2868*s*, 2181*w*, 1743*s*, 1602*w*, 1464*m*, 1371*m*, 1293*m*, 1251*s*, 1154*s*, 1131*s*, 1068*s*, 1039*m*, 1018*m*, 974*w*, 946*w*, 884*m*, 846*s*, 655*s*, 604*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.09 (*dd*, $J = 10.9$, 8.7, H–C(5)); 4.38 (*dd*, $J = 12.1$, 1.9, H–C(8)); 4.23 (*dd*, $J = 12.1$, 5.6, H′–C(8)); 4.01 (*d*, $J = 9.0$, H–C(3)); 3.78 (*dd*, $J = 9.0$, 8.7, H–C(4)); 3.65 (*ddd*, $J = 10.3$, 5.6, 2.2, H–C(7)); 2.64 (*td*, $J = 10.6$, 2.5, H–C(6)); 2.10 (*d*, $J = 2.5$, H–C(2′)); 2.09 (*s*, 2 Ac); 1.11–1.05 (*m*, $(Me_2CH)_3Si$); 0.15 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.88 (*s*); 169.69 (*s*); 101.58 (*s*); 91.81 (*s*); 78.17 (*d*); 76.44 (*d*); 75.97 (*d*); 73.22 (*s*); 72.86 (*d*); 72.54 (*d*); 64.47 (*t*); 36.22 (*d*); 20.93 (*q*); 20.77 (*q*); 18.05–17.97 (6*q*); 13.49 (3*d*); −0.63 (3*q*). CI-MS: 526 (3, $[M + NH_4]^+$), 509 (3, M^+), 363 (1), 275 (2), 174 (15), 173 (100), 157 (1, $TIPS^+$), 131 (2), 103 (1), 73 (1, Me_3Si^+), 49 (3). Anal. calc. for $C_{26}H_{44}O_6Si_2$ (508.77): C 61.38, H 8.72; found: C 61.57, H 8.49.

*3,7-Anhydro-5,8-bis-*O*-[(benzyloxy)methyl]-1,2,6-trideoxy-6-*C*-ethynyl-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**22**). At 0°, a soln. of **19** (348.1 mg, 0.820 mmol) and *Hünig*'s base (0.49 ml, 2.869 mmol) in CH_2Cl_2 (0.5 ml) was treated dropwise with freshly distilled (benzyloxy)methyl chloride (0.34 ml, 2.459 mmol) and stirred for 24 h at 22°. Removal of the solvents (cooling trap!) and FC (AcOEt/hexane 1:19) gave **22** (445.9 mg, 86%). Transparent syrup. R_f (AcOEt/hexane 3:17) 0.44. $[\alpha]_D^{25} = -66.7$ ($c = 0.63$, $CHCl_3$). IR ($CHCl_3$): 3306*m*, 3008*s*, 2947*s*, 2893*m*, 2868*s*, 2174*w*, 1602*w*, 1497*w*, 1455*m*, 1383*w*, 1289*w*, 1252*s*, 1140*s*, 1026*s*, 931*m*, 884*m*, 846*s*, 652*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42–7.26 (*m*, 10 arom. H); 5.12 (*d*, $J = 6.3$, BnOC*H*); 4.97 (*d*, $J = 6.2$, BnOC*H*); 4.86 (*s*, BnOC*H*); 4.85 (*s*, BnOC*H*); 4.72 (*d*, $J = 11.5$, PhC*H*); 4.69 (*s*, PhCH_2); 4.65 (*d*, $J = 11.5$, PhC*H*); 4.00 (*d*, $J = 9.3$, H–C(3)); 4.00–3.96 (*m*, 2 H–C(8)); 3.82 (*dd*, $J = 9.3$, 8.1, H–C(4)); 3.62 (*dd*, $J = 10.3$, 8.1, H–C(5)); 3.60 (*ddd*, $J = 10.5$, 6.5, 3.1, H–C(7)); 2.83 (*td*, $J = 10.3$, 2.2, H–C(6)); 2.04 (*d*, $J = 2.2$, H–C(2′)); 1.30–1.10 (*m*, $(Me_2CH)_3Si$); 0.18 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.25 (*s*); 137.93 (*s*); 128.49–127.49 (several *d*); 102.37 (*s*); 96.30 (*t*); 94.73 (*t*); 91.41 (*s*); 83.13 (*d*); 81.51 (*d*); 78.51 (*d*); 74.95 (*d*); 72.45 (*d* and *s*); 70.29 (*t*); 69.25 (*t*); 67.58 (*t*); 36.65 (*d*); 18.11–18.08 (*q*, 3 *Me*$_2$C); 13.68 (*d*, 3 Me$_2$*C*H); −0.62 (*q*, Me_3Si). CI-MS (NH_3): 684 (100), 683 (53), 682 (95, $[M + NH_4)^+$), 439 (18), 395 (15), 393 (13), 297 (15), 246 (13), 237 (10), 216 (14), 148 (33), 120 (11), 107 (60), 92 (18), 91 (62), 90 (63). Anal. calc. for $C_{38}H_{56}O_6Si_2$ (665.00): C 68.63, H 8.49; found: C 68.76, H 8.64.

Coupling of **16** *with* **19**. According to *GP5*, with **16** (62.2 mg, 76.2 μmol), **19** (32.4 mg, 76.2 μmol), $[Pd_2(dba)_3]$ (2.1 mg, 2.3 μmol), CuI (0.4 mg, 2.3 μmol), $P(fur)_3$ (0.9 mg, 3.8 μmol), Et_3N (32 μl, 0.23 mmol), and DMSO (0.8 ml; 18 h). FC (AcOEt/hexane 3:17) gave **26** (0.8 mg, 1%) and **25** (58.3 mg, 66%) as white foams.

*Data of 7,10-Di-*O*-acetyl-5,9-anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]-propyl}dimethylsilyl}ethynyl}-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1→6-C)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**25**). R_f (AcOEt/hexane 1:4) 0.33. M.p. 66.5–69.5°. $[\alpha]_D^{25} = -21.6$ ($c = 0.38$, $CHCl_3$). IR ($CHCl_3$): 3597*w*, 3008*m*, 2946*s*, 2892*m*, 2867*s*, 2262*w*, 2180*w*, 1826*m*, 1745*s*, 1668*w*, 1603*w*, 1464*m*, 1368*m*, 1320*w*, 1293*m*, 1273*m*, 1248*s*, 1146*s*, 1127*s*, 1100*m*, 1068*m*, 1015*w*, 995*m*, 968*w*, 918*m*, 884*s*, 845*s*, 655*m*, 602*w*, 528*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.12 (*dd*, $J = 10.8$, 8.8, H–C(7′)); 4.37 (*dd*, $J = 12.0$, 2.1, H–C(10′)); 4.23 (*dd*, $J = 12.2$, 5.9, H′–C(10′)); 4.05 (*dd*, $J = 9.2$, 0.7, H–C(5′)); 3.95 (*d*, $J = 9.3$, H–C(3)); 3.89 (*ddd*, $J = 12.1$, 7.2, 2.5, H–C(8)); 3.80 (*t*, $J = 9.0$, H–C(6′)); 3.75 (*t*, $J = 7.6$, CH_2CH_2OSi); 3.68 (*dt*, $J = 12.1$, 6.0, H′–C(8)); 3.64 (*ddd*, $J = 10.5$, 5.9, 2.0, H–C(9′)); 3.62 (*dd*, $J = 9.3$, 8.3, H–C(4)); 3.51 (*ddd*, $J = 10.4$, 8.3, 3.3, H–C(5)); 3.42 (*ddd*, $J = 10.3$, ≈5.7, 2.5, H–C(7)); 2.67

(t, J = 10.5, H–C(8′)); 2.65 (td, J = 10.4, 0.7, H–C(6)); 2.34 (d, J = 3.3, HO–C(5)); 2.10 (*s*, Ac); 2.09 (*s*, Ac), 1.99 (dd, J = 7.0, 6.5, HO–C(8)); 1.57–1.55 (*m*, CH_2CH_2OSi); 1.23–1.05 (*m*, 3 (Me_2CH)$_3$Si); 0.93 (*s*, Me_2C); 0.17 (*s*, Me_3Si); 0.07 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.56 (*s*); 169.21 (*s*); 101.94 (*s*); 100.45 (*s*); 91.42 (*s*); 88.72 (*s*); 78.67 (*d*); 76.94 (*s*); 76.82 (2*d*); 75.70 (*d*); 75.06 (*d*); 74.36 (*s*); 73.13 (*d*); 72.36 (*d*); 71.97 (*d*); 71.07 (*s*); 68.39 (*s*); 64.44 (*t*); 63.31 (*t*); 60.08 (*t*); 41.30 (*t*); 38.23 (*d*); 37.50 (*d*); 23.20 (*q*); 23.09 (*q*); 21.09 (*q*); 20.85 (*q*); 18.55 (*s*); 18.33 (6*q*); 18.14 (6*q*); 18.07 (6*q*); 17.88 (*s*); 13.47 (3*d*); 13.01 (3*d*); 12.00 (3*d*); –0.40 (3*q*); –4.40 (2*q*). FAB-MS: 1160 (1, $[M+1]^+$). Anal. calc. for $C_{61}H_{110}O_{11}Si_5$ (1159.96): C 63.16, H 9.56; found: C 63.15, H 9.29.

*Data of 1,4,13,16-Tetra-*O*-acetyl-2,6 : 11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-3,14-bis[{[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]dimethylsilyl}ethynyl]-5,12-bis-*O*-(triisopropylsilyl)-*D*-erythro-*L*-galacto-*L*-gulo-hexadeca-7,9-diynitol* (**26**): R_f (AcOEt/hexane 1 : 4) 0.35. IR ($CHCl_3$): 2946*s*, 2892*m*, 2867*s*, 2180*w*, 1744*s*, 1602*w*, 1464*m*, 1368*m*, 1291*m*, 1252*s* (br.), 1153*m*, 1094*s*, 1069*s*, 1044*m*, 1015*m*, 919*w*, 883*s*, 842*m*, 823*m*, 514*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.11 (dd, J = 10.8, 8.8, H–C(4)); 4.37 (dd, J = 1.2, 2.0, H–C(1)); 4.23 (dd, J = 12.2, 5.7, H′–C(1)); 4.06 (d, J = 9.1, H–C(6)); 3.80 (dd, J = 9.0, 8.8, H–C(5)); 3.75 (t, J = 7.6, CH_2CH_2OSi); 3.64 (ddd, J = 10.5, 5.9, 2.0, H–C(2)); 2.67 (t, $J \approx$ 10.7, H–C(3)); 2.10 (*s*, Ac); 2.09 (*s*, Ac); 1.55 (t, $J \approx$ 7.6, CH_2CH_2OSi); 1.21–1.05 (*m*, 2 (Me_2CH)$_3$Si); 0.93 (*s*, Me_2C); 0.07 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.91 (*s*); 169.59 (*s*); 100.84 (*s*); 89.01 (*s*); 77.47 (*s*); 77.02 (*d*); 76.09 (*d*); 73.18 (*d*); 72.75 (*d*); 64.66 (*t*); 60.34 (*t*); 41.52 (*t*); 37.72 (*d*); 23.39 (*q*); 23.29 (*q*); 21.27 (*q*); 20.98 (*q*); 18.55 (*s*); 18.25 (several *q*); 13.64 (3*d*), 12.19 (3*d*); –4.25 (2*q*); 1*s* missing. MALDI-TOF-MS: 1512 ($[M+K]^+$), 1496 ($[M+Na]^+$).

*7,10-Di-*O*-acetyl-5,9-anhydro-1,2,3,4,8-pentadeoxy-8-*C*-[{[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl]-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-5,8-di-*O*-acetyl-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**27**). According to *GP5*, with **16** (50.1 mg, 61.4 μmol), **20** (31.2 mg, 61.4 μmol), [Pd_2(dba)$_3$] (1.7 mg, 1.8 μmol), CuI (0.4 mg, 1.8 μmol), P(fur)$_3$ (0.7 mg, 3.1 μmol), Et_3N (26 μl, 0.18 mmol), and DMSO (0.6 ml; 18 h). FC (AcOEt/hexane 3 : 17) gave **27** (25.9 mg, 34%). White foam. R_f (AcOEt/hexane 3 : 97) 0.35. M.p. 111–112°. $[\alpha]_D^{25} = -30.8$ (c = 0.40, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2946*s*, 2892*m*, 2868*s*, 2220*w*, 2175*w*, 1747*s*, 1464*m*, 1368*m*, 1295*w*, 1260*s* (br.), 1154*m*, 1091*s*, 1069*s*, 1048*s*, 1061*s*, 884*m*, 818*m* (br.), 654*m*, 606*w*, 560*w*, 534*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.10 (dd, $J \approx$ 10.8, 8.8, H–C(7′)); 5.09 (dd, J = 10.7, 8.8, H–C(5)); 4.36 (dd, J = 12.2, 1.9, H–C(10′)); 4.35 (dd, J = 12.2, 2.0, H–C(8)); 4.22 (dd, J = 12.2, 5.8, H′–C(10′)); 4.18 (dd, J = 12.2, 5.5, H′–C(8)); 4.05 (d, J = 9.2, H–C(3)); 4.03 (dd, J = 8.9, 0.1, H–C(5′)); 3.81 (t, $J \approx$ 9.1, 8.9, H–C(4)); 3.79 (dd, $J \approx$ 9.1, 9.0, H–C(6′)); 3.75 (t, J = 7.7, CH_2CH_2OSi); 3.65 (ddd, $J \approx$ 10.1, 5.4, 2.0, H–C(7)); 3.63 (ddd, $J \approx$ 10.3, 5.8, 1.9, H–C(9′)); 2.79 (td, J = 10.7, 0.1, H–C(6)); 2.66 (t, J = 10.6, H–C(8′)); 2.103 (*s*, Ac), 2.100 (*s*, 2 Ac); 2.09 (*s*, Ac); 1.55 (*m*, CH_2CH_2OSi); 1.19–1.05 (*m*, 3 (Me_2CH)$_3$Si); 0.93 (*s*, Me_2C); 0.17 (*s*, Me_3Si); 0.07 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.57 (*s*); 170.45 (*s*); 169.20 (*s*); 169.02 (*s*); 101.94 (*s*); 100.47 (*s*); 91.42 (*s*); 88.73 (*s*); 77.23 (*s*); 76.83 (*d*); 76.38 (*d*); 75.76 (*d*); 75.11 (*d*); 74.47 (*s*); 73.06 (*d*); 72.93 (*d*); 72.83 (*d*); 72.41 (*d*); 70.89 (*s*); 68.80 (*s*); 64.44 (*t*); 64.34 (*t*); 60.09 (*t*); 41.31 (*t*); 38.06 (*d*); 37.47 (*d*); 23.10 (*q*); 23.06 (*q*); 21.10 (*q*); 20.99 (*q*); 20.86 (*q*); 20.82 (*q*); 18.37 (*s*); 18.07 (several *q*); 13.50 (3*d*); 13.40 (3*d*); 12.00 (3*d*); –0.40 (3*q*); –4.40 (2*q*). MALDI-TOF-MS: 1282 ($[M+K]^+$), 1267 ($[M+Na]^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-[{[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl]-6,10-di-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**28**). According to *GP5*, with **17** (94.4 mg, 0.101 mmol), **19** (42.9 mg, 0.101 mmol), [Pd_2(dba)$_3$] (2.8 mg, 3.03 μmol), CuI (0.6 mg, 3.03 μmol), P(fur)$_3$ (1.2 mg, 5.05 μmol), Et_3N (42 μl, 0.303 mmol), and DMSO (1.0 ml; 9 h). FC (AcOEt/hexane 0 : 1 → 1 : 19) gave **28** (94.4 mg, 76%). White foam. R_f (AcOEt/hexane 3 : 17) 0.45. IR ($CHCl_3$): 3594*w*, 3474*w*, 2946*s*, 2892*s*, 2260*w*, 2174*w*, 1654*w*, 1602*w*, 1464*m*, 1391*w*, 1367*w*, 1325*w*, 1292*m*, 1260*m*, 1150*s*, 1100*s*, 1067*s*, 1040*s*, 1019*s*, 939*w*, 910*m*, 884*s*, 856*m*, 655*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.01 (dd, J = 11.2, 1.5, H–C(10′)); 3.95 (d, J = 9.0, H–C(3)); 3.94–3.87 (*m*, H–C(8)); 3.93 (d, J = 9.3, H–C(5′)); 3.86 (dd, J = 11.2, 5.2, H′–C(10′)); 3.77 (t, J = 7.7, CH_2CH_2OSi); 3.71 (dt, J = 12.1, 6.2, H′–C(8)); 3.63 (dd, J = 9.0, 8.1, H–C(4)); 3.60 (dd, $J \approx$ 9.0, 8.4, H–C(6′)); 3.55–3.33 (*m*, H–C(5), H–C(7′), H–C(7), H–C(9′)); 2.63 (t, J = 10.3, H–C(6)); 2.62 (t, J = 10.3, H–C(8′)); 2.36 (d, J = 3.4), 2.35 (d, J = 2.8, HO–C(5), HO–C(7′)); 2.04 (t, $J \approx$ 6.7, HO–C(8)); 1.59 (t, J = 7.8, CH_2CH_2OSi); 1.22–1.05 (*m*, 4 (Me_2CH)$_3$Si); 0.96 (*s*, Me_2C); 0.17 (*s*, Me_3Si); 0.10 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 103.44 (*s*); 102.12 (*s*); 91.29 (*s*); 87.65 (*s*); 80.04 (*d*); 78.70 (*d*); 77.00 (*d*); 76.84 (*d*); 75.79 (*s*); 75.63 (*s*); 75.09 (*d*); 75.03 (*d*); 71.99 (*d*); 71.71 (*d*); 69.87 (*s*); 68.86 (*s*); 64.22 (*t*); 63.33 (*t*); 60.11 (*t*); 41.51 (*t*); 38.69 (*d*); 38.29 (*d*); 23.53 (*q*); 23.23 (*q*); 18.39 (*s*); 18.19–17.85 (several *q*); 12.87 (6*d*); 12.84 (3*d*); 11.90 (3*d*); –0.57 (3*q*); –4.33 (2*q*). MALDI-TOF-MS: 1270 ($[M+K]^+$), 1254 ($[M+Na]^+$). Anal. calc. for $C_{66}H_{126}O_9Si_6$ (1232.20): C 64.33, H 10.31; found: C 64.44, H 10.16.

Coupling of **18** *with* **19**. According to *GP5*, with **18** (72.6 mg, 0.0885 mmol), **19** (37.6 mg, 0.0885 mmol), $[Pd_2(dba)_3]$ (2.4 mg, 2.66 μmol), CuI (0.5 mg, 2.66 μmol), $P(fur)_3$ (1.0 mg, 4.43 μmol), Et_3N (37 μl, 0.266 mmol), and DMSO (0.8 ml; 13 h). FC (AcOEt/hexane 1:19 → 3:17) gave **30** (2.4 mg, 2%) and **29** (81.4 mg, 78%) as white foams.

*Data of 5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**29**): R_f (AcOEt/hexane 3:17) 0.20. M.p. 60–61.5°. $[\alpha]_D^{25} = -49.6$ ($c = 1.1$, $CHCl_3$). IR ($CHCl_3$): 3603*w*, 3008*m*, 2946*s*, 2892*m*, 2867*s*, 2261*w*, 2175*w*, 1602*w*, 1464*m*, 1384*w*, 1366*w*, 1292*w*, 1252*m*, 1150*s*, 1098*s*, 1068*s*, 1044*s*, 1017*m*, 957*m*, 919*m*, 883*s*, 845*s*, 824*m*, 655*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*, $J = 5.6$, MeOC*H*); 4.79 (*d*, $J = 5.6$, MeOC*H*); 4.65 (*s*, MeOCH_2); 3.97 (*d*, $J \approx 9.0$, H–C(5′)); 3.95 (*d*, $J \approx 9.1$, H–C(3)); 3.95–3.80 (*m*, H–C(8), H–C(10′)); 3.77 (*t*, $J = 7.7$, CH_2CH_2OSi); 3.79–3.58 (*m*, H–C(4), H–C(6′), H′–C(8), H′–C(10′)); 3.54–3.48 (*m*, H–C(5), H–C(9′)); 3.45 (*s*, MeO); 3.46–3.33 (*m*, H–C(7), H–C(7′)); 3.36 (*s*, MeO); 2.72 (*dd*, $J = 10.3$, H–C(8′)); 2.63 (*td*, $J = 10.3, 0.3$, H–C(6)); 2.36 (*d*, $J = 3.1$, HO–C(5)); 2.08–2.05 (*m*, HO–C(8)); 1.60 (*t*, $J = 7.6$, CH_2CH_2OSi); 1.23–1.03 (*m*, 3 (Me_2CH)$_3$Si); 0.97 (*s*, Me_2C); 0.16 (*s*, Me_3Si); 0.10 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.39 (*s*); 102.03 (*s*); 98.12 (*t*); 96.74 (*t*); 91.39 (*s*); 87.49 (*s*); 82.21 (*d*); 78.88 (*d*); 78.65 (*d*); 77.44 (*s*); 76.83 (*d*); 75.00 (*d*); 74.99 (*s*); 74.87 (*d*); 72.12 (*d*); 71.94 (*d*); 70.82 (*s*); 68.61 (*s*); 67.62 (*t*); 63.29 (*t*); 60.00 (*t*); 56.72 (*q*); 55.29 (*q*); 41.22 (*t*); 38.19 (*d*); 37.82 (*d*); 23.08 (2*q*); 18.39 (*s*); 18.20 (6*q*); 18.08 (6*q*); 17.95 (6*q*); 13.54 (3*d*); 12.86 (3*d*); 11.86 (3*d*); −0.57 (3*q*); −4.42 (2*q*). MALDI-TOF-MS: 1202 ($[M + K]^+$), 1186 ($[M + Na]^+$). Anal. calc. for $C_{61}H_{114}O_{11}Si_5$ (1163.93): C 62.94, H 9.87; found: C 63.11, H 9.67.

*Data of 2.6:11,15-Dianhydro-3,7,8,9,10,14-hexadeoxy-3,14-bis{{[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]dimethylsilyl}ethynyl}-1,4,13,16-tetrakis-*O*-(methoxymethyl)-5,12-bis-*O*-(triisopropylsilyl)-*D*-erythro-*L*-galacto-*L*-gulo-hexadeca-7,9-diynitol* (**30**): R_f (AcOEt/hexane 3:17) 0.49. IR ($CHCl_3$): 3008*m*, 2945*s*, 2892*s*, 2867*s*, 2437*m*, 2173*m*, 1652*m*, 1622*s*, 1602*s*, 1577*m*, 1521*w*, 1496*w*, 1464*m*, 1450*m*, 1390*w*, 1340*m*, 1288*m*, 1252*m*, 1151*s*, 1098*s*, 1045*s*, 931*m*, 883*m*, 824*m*, 652*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*, $J = 5.6$, MeOC*H*); 4.78 (*d*, $J = 5.6$, MeOC*H*); 4.66 (*s*, MeOCH_2); 4.01 (*d*, $J = 9.0$, H–C(6)); 3.88–3.84 (*m*, H–C(1)); 3.77 (*t*, $J = 7.8$, CH_2CH_2OSi); 3.80–3.70 (*m*, H′–C(1), H–C(5)); 3.56–3.48 (*m*, H–C(2)); 3.49 (*dd*, $J = 9.6, 7.8$, H–C(4)); 3.45 (*s*, MeO); 3.37 (*s*, MeO); 2.72 (*dd*, $J = 10.3$, H–C(3)); 1.59 (*t*, $J = 7.7$, CH_2CH_2OSi); 1.22–1.05 (*m*, 2 (Me_2CH)$_3$Si); 0.97 (*s*, Me_2C); 0.10 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 104.58 (*s*); 97.95 (*t*); 96.71 (*t*); 87.38 (*s*); 82.24 (*d*); 78.71 (*d*); 77.63 (*s*); 74.49 (*d*); 72.27 (*d*); 70.35 (*s*); 67.73 (*t*); 60.02 (*t*); 56.62 (*q*); 55.23 (*q*); 41.23 (*t*); 37.70 (*d*); 23.10 (2*q*); 18.41 (*s*); 18.09–17.96 (several *q*); 13.45 (3*d*); 11.90 (3*d*); −4.39 (2*q*). MALDI-TOF-MS: 1502 ($[M + Na]^+$).

Coupling of **15** *with* **21**. According to *GP5*, with **15** (74.1 mg, 0.101 mmol), **21** (51.9 mg, 0.101 mmol) [8], $[Pd_2(dba)_3]$ (2.8 mg, 3.04 μmol), CuI (0.6 mg, 3.04 μmol), $P(fur)_3$ (1.2 mg, 5.06 μmol), Et_3N (42 μl, 0.304 mmol), and DMSO (1 ml; 13 h). FC (AcOEt/hexane 1:19 → 1:9) gave **32** (3.0 mg, 3%) and **31** (92.4 mg, 78%) as white foams.

*Data of 5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{[1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl]dimethylsilyl}ethynyl}-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**31**): R_f (AcOEt/hexane 3:17) 0.15. M.p. 60.0–61.0°. $[\alpha]_D^{25} = -51.4$ ($c = 1.7$, $CHCl_3$). IR ($CHCl_3$): 3603*w*, 3008*m*, 2945*s*, 2867*s*, 2259*w*, 2173*w*, 1602*m*, 1464*m*, 1367*m*, 1291*m*, 1252*s*, 1150*s*, 1094*s*, 1043*s*, 931*m*, 883*s*, 844*s*, 653*m*, 515*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.91 (*d*, $J = 6.2$, MeOC*H*); 4.72 (*d*, $J = 6.2$, MeOC*H*); 4.67 (*s*, MeOCH_2); 3.99 (*d*, $J = 9.3$, H–C(3)); 3.93 (*d*, $J = 9.0$, H–C(5′)); 3.95–3.86 (*m*, H–C(8), H–C(10′)); 3.85–3.77 (*m*, H′–C(8), H′–C(10′)); 3.77 (*t*, $J = 7.8$, CH_2CH_2OSi); 3.72 (*dd*, $J = 9.3$, 8.1, H–C(4)); 3.62 (*dd*, $J = 9.0$, 8.4, H–C(6′)); 3.53–3.38 (*m*, H–C(5), H–C(7), H–C(7′), H–C(9′)); 3.44 (*s*, MeO); 3.38 (*s*, MeO); 2.82 (*t*, $J = 10.3$, H–C(6)); 2.53 (*t*, $J = 10.3$, H–C(8′)); 2.38 (*d*, $J = 2.5$, HO–C(7′)); 2.10–2.08 (*m*, HO–C(10′)); 1.59 (*t*, $J = 7.8$, CH_2CH_2OSi); 1.16–1.04 (*m*, 3 (Me_2CH)$_3$Si); 0.95 (*s*, Me_2C); 0.13 (*s*, Me_3Si); 0.10 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 102.36 (*s*); 102.14 (*s*); 98.04 (*t*); 96.71 (*t*); 91.55 (*s*); 88.51 (*s*); 82.73 (*d*); 79.03 (*d*); 78.35 (*d*); 77.85 (*s*); 76.73 (*d*); 74.97 (*d*); 74.72 (*d*); 74.43 (*s*); 72.44 (*d*); 71.89 (*d*); 70.76 (*s*); 67.94 (*s*); 67.36 (*t*); 63.58 (*t*); 60.10 (*t*); 56.36 (*q*); 55.25 (*q*); 41.54 (*t*); 39.00 (*d*); 37.38 (*d*); 23.21 (*q*); 23.25 (*q*); 18.38 (*s*); 18.12–17.95 (several *q*); 13.65 (3*d*); 12.79 (3*d*); 11.86 (3*d*); −0.62 (3*q*), −4.31 (2*q*). MALDI-TOF-MS: 1202 ($[M + K]^+$), 1186 ($[M + Na]^+$). Anal. calc. for $C_{61}H_{114}O_{11}Si_5$ (1163.93): C 62.94, H 9.87; found: C 63.01, H 9.79.

*Data of 6,6′-(Buta-1,3-diyne-1,4-diyl)bis[3,7-anhydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol]* (**32**). R_f (AcOEt/hexane 3:17) 0.23. IR ($CHCl_3$): 3008*s*, 2946*s*, 2867*s*, 2269*w*, 2169*w*, 1726*w*, 1602*m*, 1522*w*, 1464*m*, 1369*m*, 1290*m*, 1252*s*, 1151*s*, 1043*s*,

931*m*, 883*m*, 845*m*, 651*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.94 (*d*, *J* = 6.2, MeOC*H*); 4.73 (*d*, *J* = 6.2, MeOC*H*); 4.69 (*s*, MeOCH_2); 3.95 (*d*, *J* = 9.1, H–C(3)); 3.97–3.70 (*m*, 2 H–C(8)); 3.74 (*dd*, *J* = 9.1, 8.3, H–C(4)); 3.53 (*ddd*, *J* = 10.3, 4.7, 2.5, H–C(7)); 3.51 (*dd*, *J* = 10.4, 8.3, H–C(5)); 3.47 (*s*, MeO); 3.40 (*s*, MeO); 2.81 (*t*, *J* = 10.4, H–C(6)); 1.22–1.09 (*m*, $(Me_2CH)_3Si$); 0.16 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 102.17 (*s*); 98.17 (*t*); 96.65 (*t*); 91.57 (*s*); 82.78 (*d*); 78.30 (*d*); 75.25 (*s*); 74.94 (*d*); 72.43 (*d*); 68.46 (*s*); 67.51 (*t*); 56.27 (*q*); 55.23 (*q*); 37.39 (*d*); 18.12 (6*q*); 13.71 (3*d*); –0.61 (3*q*). MALDI-TOF-MS: 1062 ($[M+K]^+$), 1046 ($[M+Na]^+$).

Coupling of **18** *with* **21**. According to *GP5*, with **18** (97.2 mg, 0.119 mmol), **21** (60.8 mg, 0.119 mmol), $[Pd_2(dba)_3]$ (3.3 mg, 3.56 μmol), CuI (0.7 mg, 3.56 μmol), $P(fur)_3$ (1.4 mg, 5.93 μmol), Et_3N (50 μl, 0.356 mmol), and DMSO (1.2 ml; 13 h). FC (AcOEt/hexane 1:49 → 1:19) gave **30** (6.9 mg, 6%), **33** (108.4 mg, 75%), and **32** (3.2 mg, 3%) as white foams.

*Data of 5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**33**): R_f (AcOEt/hexane 3:17) 0.37. $[\alpha]_D^{25} = -58.5$ (*c* = 2.0, $CHCl_3$). IR ($CHCl_3$): 3008*m*, 2946*s*, 2892*m*, 2867*s*, 2260*w*, 2174*m*, 1602*w*, 1465*m*, 1385*w*, 1367*m*, 1291*m*, 1252*m*, 1152*s*, 1096*s*, 1068*s*, 1041*s*, 1022*s*, 919*m*, 883*s*, 845*s*, 825*m*, 656*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.96 (*d*, *J* = 5.6, MeOC*H*); 4.89 (*d*, *J* = 5.9, MeOC*H*); 4.78 (*d*, *J* = 5.6, MeOC*H*); 4.70 (*d*, *J* = 5.9, MeOC*H*); 4.653 (*s*, MeOCH_2); 4.649 (*s*, MeOCH_2); 3.97 (*d*, *J* = 9.3), 3.93 (*d*, *J* = 9.0, H–C(3), H–C(5′)); 3.87–3.78 (*m*, H–C(8), H–C(10′)); 3.78–3.68 (*m*, H′–C(8), H′–C(10′), H–C(4), H–C(6′)); 3.76 (*t*, *J* ≈ 7.7, CH_2CH_2OSi); 3.52–3.34 (*m*, H–C(5), H–C(7), H–C(7′), H–C(9′)); 3.43 (*s*, MeO); 3.42 (*s*, MeO); 3.37 (*s*, MeO); 3.35 (*s*, MeO); 2.80 (*t*, *J* = 10.3, H–C(6)); 2.71 (*t*, *J* = 10.3, H–C(8′)); 1.58 (*t*, *J* = 7.7, CH_2CH_2OSi); 1.23–1.02 (*m*, 3 $(Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.13 (*s*, Me_3Si); 0.09 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.44 (*s*); 102.16 (*s*); 98.07 (*t*); 97.95 (*t*); 96.69 (2*t*); 91.47 (*s*); 87.46 (*s*); 82.60 (*d*); 82.29 (*d*); 78.83 (*d*); 78.35 (*d*); 77.80 (*s*); 77.44 (*s*); 74.72 (*d*); 74.67 (*d*); 74.55 (*s*); 72.41 (*d*); 72.23 (*d*); 71.12 (*s*); 68.14 (*s*); 67.57 (*t*); 67.31 (*t*); 59.99 (*t*); 56.65 (*q*); 56.33 (*q*); 55.25 (*q*); 55.21 (*q*); 41.23 (*t*); 37.79 (*d*); 37.35 (*d*); 23.07 (2*q*); 18.36 (*s*); 18.10–17.92 (several *q*); 13.60 (3*d*); 13.49 (3*d*); 11.84 (3*d*); –0.65 (3*q*); –4.45 (2*q*); 1*s* missing. MALDI-TOF-MS: 1275 ($[M+Na]^+$). Anal. calc. for $C_{65}H_{122}O_{13}Si_5$ (1252.05): C 62.35, H 9.82; found: C 62.62, H 9.73.

Coupling of **18** *with* **22**. According to *GP5*, with **18** (209.1 mg, 0.255 mmol), **22** (170.9 mg, 0.255 mmol), $[Pd_2(dba)_3]$ (7.1 mg, 7.71 μmol), CuI (1.5 mg, 7.71 μmol), $P(fur)_3$ (3.0 mg, 12.84 μmol), Et_3N (108 μl, 0.771 mmol), and DMSO (2.6 ml; 11 h). FC (AcOEt/hexane 1:19) gave **35** (15.2 mg, 4%), **34** (187.0 mg, 73%), and **30** (30.4 mg, 8%) as white foams.

*Data of 5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-5,8-bis-*O*-[(benzyloxy)methyl]-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**34**): R_f (AcOEt/hexane 1:4) 0.33. IR ($CHCl_3$): 3067*w*, 3008*m*, 2947*s*, 2892*m*, 2866*s*, 2251*w*, 2176*w*, 1602*w*, 1522*m*, 1499*w*, 1465*m*, 1367*m*, 1290*w*, 1252*m*, 1139*s*, 1098*s*, 1067*s*, 1026*s*, 933*m*, 884*s*, 844*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41–7.15 (*m*, 10 arom. H); 5.03 (*d*, *J* = 5.9, BnOC*H*); 4.97 (*d*, *J* = 5.6, MeOC*H*); 4.90 (*d*, *J* = 6.2, BnOC*H*); 4.80 (*s*, BnOCH_2); 4.79 (*d*, *J* = 5.6, MeOC*H*); 4.76 (*d*, *J* = 12.4, PhC*H*); 4.69 (*d*, *J* = 12.3, PhC*H*); 4.65 (*s*, PhCH_2); 4.64 (*s*, MeOCH_2); 3.96 (*d*, *J* = 9.3), 3.95 (*d*, *J* = 9.0, H–C(3), H–C(5′)); 3.89–3.66 (*m*, 2 H–C(8), 2 H–C(10′), H–C(4), H–C(6′)); 3.76 (*t*, *J* ≈ 7.7, CH_2CH_2OSi); 3.57–3.43 (*m*, H–C(5), H–C(7), H–C(7′), H–C(9′)); 3.45 (*s*, MeO); 3.34 (*s*, MeO); 2.87 (*t*, *J* = 10.3, H–C(6)); 2.74 (*t*, *J* = 10.3, H–C(8′)); 1.56 (*t*, *J* = 7.7, CH_2CH_2OSi); 1.23–1.09 (*m*, 3 $(Me_2CH)_3Si$); 0.97 (*s*, Me_2C); 0.16 (*s*, Me_3Si); 0.09 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.12 (*s*); 137.86 (*s*); 129.09–127.49 (several *d*); 125.36 (*s*); 104.61 (*s*); 102.27 (*s*); 98.05 (*t*); 96.74 (*t*); 95.77 (*t*); 94.72 (*t*); 91.43 (*s*); 87.41 (*s*); 82.58 (*d*); 82.27 (*d*); 78.82 (*d*); 78.39 (*d*); 77.91 (*s*); 74.94 (*s*); 74.74 (*d*); 74.53 (*d*); 72.45 (*d*); 72.16 (*d*); 71.06 (*s*); 70.39 (*t*); 69.23 (*t*); 68.46 (*s*); 67.63 (*t*); 63.64 (*t*); 56.65 (*q*); 55.24 (*q*); 37.88 (*t*); 37.83 (*d*); 37.38 (*d*); 23.10 (2*q*); 18.31 (*s*); 18.06 (several *q*); 13.52 (3*d*); 13.48 (3*d*); –0.64 (3*q*); –4.43 (2*q*). MALDI-TOF-MS: 1459 ($[M+K]^+$), 1443 ($[M+Na]^+$).

*Data of 6,6′-(Buta-1,3-diyne-1,4-diyl)bis{3,7-anhydro-1,2,6-trideoxy-5,8-bis-*O*-[(benzyloxy)methyl]-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol}* (**35**): R_f (AcOEt/hexane 1:4) 0.51. IR ($CHCl_3$): 3068*w*, 3008*m*, 2946*s*, 2892*m*, 2868*s*, 2179*w*, 1602*w*, 1521*m*, 1497*w*, 1456*m*, 1368*m*, 1290*w*, 1252*s*, 1140*s*, 1122*s*, 1027*s*, 931*m*, 883*s*, 846*s*, 654*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.35–7.27 (*m*, 10 arom. H); 4.95 (*d*, *J* = 6.2, BnOC*H*); 4.84 (*s*, BnOCH_2); 4.81 (*d*, *J* = 5.8, BnOC*H*); 4.72 (*s*, PhC*H*); 4.71 (*s*, PhC*H*); 4.61 (*d*, *J* = 11.8, PhC*H*); 4.51 (*d*, *J* = 12.0, PhC*H*); 3.86 (*d*, *J* = 9.3, H–C(3)); 3.73–3.67 (*m*, 2 H–C(8), H–C(4)); 3.44–3.29 (*m*, H–C(5), H–C(7)); 2.76 (*t*, *J* = 10.3, H–C(6)); 1.26–1.05 (*m*, $(Me_2CH)_3Si$); 0.13 (*s*, Me_3Si). MALDI-TOF-MS: 1367 ($[M+K]^+$), 1351 ($[M+Na]^+$).

3,7-Anhydro-1,2,6-trideoxy-6-C-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]dimethylpropyl}silyl}ethynyl}-5,8-bis-O-(methoxymethyl)-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-*oct-1-ynitol* (**36**). At 0°, a soln. of **2** (7.57 g, 10.4 mmol) and Bu_4NI (385.5 mg, 0.104 mmol) in $ClCH_2CH_2Cl$ (20 ml) and *Hünig*'s base (35.7 ml, 208.7 mmol) was treated dropwise with $MeOCH_2Cl$ (7.9 ml, 104.4 mmol) and stirred for 96 h at 22°. Removal of the solvents (cooling trap!) and FC (AcOEt/hexane 0:1 → 3:97) gave **36** (7.53 g, 89%). Transparent syrup. R_f (AcOEt/hexane 1:7) 0.58. $[\alpha]_D^{25} = -35.9$ ($c = 1.45$, $CHCl_3$). IR ($CHCl_3$): 2945*s*, 2892*m*, 2867*s*, 2174*w*, 1602*w*, 1464*m*, 1384*w*, 1366*w*, 1291*w*, 1251*m*, 1152*s*, 1096*s*, 1041*s*, 919*m*, 883*m*, 844*s*, 551*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.98 (*d*, $J = 5.6$, C*H*OMe); 4.79 (*d*, $J = 5.6$, C*H*OMe); 4.67 (*s*, CH_2OMe); 3.93 (*d*, $J = 9.3$, H–C(3)); 3.90 (*dd*, $J = 11.2, 1.9$, H–C(8)); 3.80 (*dd*, $J = 10.9, 5.0$, H′–C(8)); 3.77 (*t*, $J \approx 7.5$, CH_2CH_2OSi); 3.72 (*dd*, $J = 9.3, 8.4$, H–C(4)); 3.50 (*ddd*, $J = 10.3, 5.0, 1.9$, H–C(7)); 3.47 (*dd*, $J = 10.3, 8.4$, H–C(5)); 3.45 (*s*, MeO); 3.38 (*s*, MeO); 2.73 (*t*, $J = 10.3$, H–C(6)); 1.60 (*t*, $J \approx 7.5$, CH_2CH_2OSi); 1.26–1.05 (*m*, 2 $(Me_2CH)_3Si$); 0.97 (*s*, Me_2C); 0.15 (*s*, Me_3Si); 0.10 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.71 (*s*); 102.48 (*s*); 98.15 (*t*); 96.71 (*t*); 91.27 (*s*); 87.27 (*s*); 82.63 (*d*); 78.73 (*d*); 74.74 (*d*); 72.39 (*d*); 67.68 (*t*); 60.00 (*t*); 56.68 (*q*); 55.26 (*q*); 41.23 (*t*); 37.90 (*d*); 23.11 (2*q*); 18.37 (*s*); 18.15–17.93 (several *q*); 13.65 (3*d*); 11.85 (3*d*); −0.61 (3*q*); −4.42 (2*q*). CI-MS: 832(22), 831 (37, $[M + NH_4]^+$), 303(11), 302(29), 301 (100, TIPS-DOPS$^+$), 289(12), 248(10), 237(13), 231(40), 219(35), 157 (19, $TIPS^+$), 73 (11, Me_3Si^+). Anal. calc. for $C_{42}H_{84}O_7Si_4$ (831.43): C 62.01, H 10.41; found: C 61.77, H 10.47.

3,7-Anhydro-1,2,6-trideoxy-5,8-bis-O-(methoxymethyl)-6-C-{{{1,1-dimethyl-3-[(triisopropylsilyl)oxy]propyl}-dimethylsilyl}ethynyl}-4-O-(triisopropylsilyl)-D-glycero-D-gulo-*oct-1-ynitol* (**37**). According to *GP1*, with **36** (8.31 g, 10.21 mmol), 1M NaOMe (20 ml), and MeOH (20 ml; 1.5 h). FC (AcOEt/hexane 1:19) gave **37** (7.12 g, 94%). Transparent syrup. R_f (AcOEt/hexane 1:7) 0.44. $[\alpha]_D^{25} = -36.7$ ($c = 0.41$, $CHCl_3$). IR ($CHCl_3$): 3307*w*, 3006*w*, 2945*s*, 2892*m*, 2867*s*, 2173*w*, 1602*w*, 1464*m*, 1384*w*, 1367*w*, 1292*w*, 1252*m*, 1152*m*, 1096*s*, 1042*s*, 933*w*, 919*w*, 883*m*, 838*m*, 656*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.98 (*d*, $J = 5.6$, MeOC*H*); 4.79 (*d*, $J = 5.6$, MeOC*H*); 4.66 (*s*, $MeOCH_2$); 3.94 (*dd*, $J = 9.3, 2.2$, H–C(3)); 3.88 (*dd*, $J = 10.9, 1.9$, H–C(8)); 3.78 (*dd*, $J = 10.9, 5.0$, H′–C(8)); 3.76 (*t*, $J \approx 7.7$, CH_2CH_2OSi); 3.74 (*dd*, $J = 9.3, 8.4$, H–C(4)); 3.53 (*ddd*, $J = 10.3, 5.0, 1.9$, H–C(7)); 3.49 (*dd*, $J = 10.3, 8.3$, H–C(5)); 3.45 (*s*, MeO); 3.36 (*s*, MeO); 2.74 (*t*, $J = 10.3$, H–C(6)); 2.45 (*d*, $J = 2.2$, H–C(1)); 1.59 (*t*, $J \approx 7.7$, CH_2CH_2OSi); 1.17–1.03 (*m*, 2 $(Me_2CH)_3Si$); 0.97 (*s*, Me_2C); 0.10 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.60 (*s*); 98.06 (*t*); 96.71 (*t*); 87.35 (*s*); 82.36 (*d*); 81.06 (*d*); 78.76 (*d*); 74.95 (*s*); 74.70 (*d*); 71.69 (*d*); 67.70 (*t*); 59.98 (*t*); 56.65 (*q*); 55.24 (*q*); 41.23 (*t*); 37.83 (*d*); 23.18 (*q*); 23.10 (*q*); 18.37 (*s*); 18.15–17.96 (several *q*); 13.58 (3*d*); 11.87 (3*d*); −4.29 (*q*); −4.44 (*q*). CI-MS: 760(19), 759 (30, $[M + NH_4]^+$), 303(9), 302(27), 301 (100, TIPS-DOPS$^+$), 289(11), 248(12), 231(32), 219(41), 205(10), 157 (23, $TIPS^+$), 148(11), 145 (17, DOPS$^+$), 131(19), 115(12), 75 (12, Me_3Si^+), 48(14). Anal. calc. for $C_{39}H_{76}O_7Si_3$ (741.24): C 63.19, H 10.33; found: C 63.45, H 10.13.

3,7-Anhydro-1,2,6-trideoxy-1-C-iodo-5,8-bis-O-(methoxymethyl)-6-C-{{{1,1-dimethyl-3-[(triisopropylsilyl)-oxy]propyl}dimethylsilyl}ethynyl}-4-O-(triisopropylsilyl)-D-glycero-D-gulo-*oct-1-ynitol* (**38**). According to *GP4*, with **37** (8.44 g, 11.39 mmol), NIS (2.82 g, 12.53 mmol), $AgOCOCF_3$ (125.7 mg, 0.57 mmol), and acetone (115 ml, 4 h). FC (AcOEt/hexane 3:97) gave **38** (9.78 g, 99%). Transparent syrup. R_f (AcOEt/hexane 1:7) 0.44. $[\alpha]_D^{25} = -30.7$ ($c = 1.67$, $CHCl_3$). IR ($CHCl_3$): 3008*m*, 2945*s*, 2892*s*, 2867*s*, 2175*w*, 1602*w*, 1465*m*, 1384*w*, 1366*w*, 1291*w*, 1254*m*, 1152*s*, 1096*s*, 1068*s*, 1041*s*, 919*w*, 884*m*, 839*m*, 824*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.98 (*d*, $J = 5.6$, C*H*OMe); 4.79 (*d*, $J = 5.6$, C*H*OMe); 4.69 (*s*, C*H*OMe); 4.68 (*s*, C*H*OMe); 4.09 (*d*, $J = 9.3$, H–C(3)); 3.92 (*dd*, $J = 11.2, 1.9$, H–C(8)); 3.82 (*dd*, $J = 11.2, 5.0$, H′–C(8)); 3.77–3.70 (*m*, CH_2OH); 3.74 (*dd*, $J = 9.3, 8.1$, H–C(4)); 3.53 (*ddd*, $J = 10.6, 5.0, 1.8$, H–C(7)); 3.50 (*dd*, $J = 10.3, 8.1$, H–C(5)); 3.46 (*s*, MeO); 3.39 (*s*, MeO); 2.73 (*t*, $J = 10.3$, H–C(6)); 2.03 (*m*, CH_2CH_2OH); 1.63 (*t*, $J = 7.8$, CH_2CH_2OH); 1.25–1.05 (*m*, $(Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.11 (*s*, 2 Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.49 (*s*); 98.18 (*t*); 96.72 (*t*); 91.35 (*s*); 87.40 (*s*); 82.34 (*d*); 78.76 (*d*); 75.09 (*d*); 73.17 (*d*); 67.57 (*t*); 59.98 (*t*); 56.71 (*q*); 55.31 (*q*); 41.23 (*t*); 37.83 (*d*); 23.08 (*q*); 23.11 (*q*); 18.37 (*s*); 18.08 (6*q*); 17.58 (6*q*); 13.68 (3*d*); 11.85 (3*d*); 5.58 (*s*); −4.42 (2*q*). CI-MS: 885 (6, $[M + NH_4]^+$), 758(14), 303(10), 302(30), 301 (100, TIPS-DOPS$^+$), 248(15), 232(11), 231(17), 219(38), 205(10), 204(17), 203(11), 157 (30, $TIPS^+$), 148(27), 145 (16, DOPS$^+$), 131(51), 130(26), 103(24), 75(28), 48(31), 45(19). Anal. calc. for $C_{39}H_{75}IO_7Si_3$ (867.14): C 54.02, H 8.72; found: C 53.91, H 8.53.

3,7-Anhydro-1,2,6-trideoxy-6-C-{3-hydroxy-[(1,1-dimethylpropyl)dimethylsilyl]ethynyl}-1-C-iodo-5,8-bis-O-(methoxymethyl)-4-O-(triisopropylsilyl)-D-glycero-D-gulo-*oct-1-ynitol* (**39**). At 0°, a soln. of **38** (5.65 g, 6.52 mmol) in EtOH (430 ml) was treated dropwise with 0.1N HCl (43 ml) and stirred for 14 h at 22°. Normal workup (Et_2O, H_2O) and FC (AcOEt/hexane 1:3 → 1:2) gave **39** (4.46 g, 96%). Transparent syrup. R_f (AcOEt/hexane 17:3) 0.08. $[\alpha]_D^{25} = -57.1$ ($c = 0.58$, $CHCl_3$). IR ($CHCl_3$): 3492*w*, 3008*m*, 2946*s*, 2892*s*, 2867*s*, 2172*w*, 1602*w*, 1465*m*, 1412*w*, 1366*w*, 1348*w*, 1291*w*, 1260*m*, 1151*s*, 1096*s*, 1027*s*, 919*m*, 884*m*, 839*w*, 818*w*, 654*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.98 (*d*, $J = 5.6$, MeOC*H*); 4.79 (*d*, $J = 5.6$, MeOC*H*); 4.69 (*s*, $MeOCH_2$); 4.68 (*s*, MeOC*H*);

4.09 (*d*, *J* = 9.3, H–C(3)); 3.92 (*dd*, *J* = 1.2, 1.9, H–C(8)); 3.82 (*dd*, *J* = 1.2, 5.0, H–C(8′)); 3.77–3.70 (*m*, CH_2CH_2OH); 3.74 (*dd*, *J* = 9.3, 8.1, H–C(4)); 3.53 (*ddd*, *J* = 10.6, 5.0, 1.8, H–C(7)); 3.50 (*dd*, *J* = 10.3, 8.4, H–C(5)); 3.46 (*s*, MeO); 3.39 (*s*, MeO); 2.73 (*t*, *J* = 10.3, H–C(6)); 2.03 (*m*, $HOCH_2CH_2$); 1.63 (*t*, *J* = 7.8, CH_2CH_2OH); 1.25–1.05 (*m*, $(Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.11 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.54 (*s*); 98.16 (*t*); 96.64 (*t*); 91.28 (*s*); 87.48 (*s*); 82.50 (*d*); 78.70 (*d*); 75.12 (*d*); 73.13 (*d*); 67.69 (*t*); 59.46 (*t*); 56.70 (*q*); 55.39 (*q*); 42.27 (*t*); 37.88 (*d*); 23.34 (*q*); 23.26 (*q*); 18.57 (*s*); 13.70 (3*d*); 5.64 (*s*); −4.31 (2*q*). CI-MS: 728 (1, $[M+NH_4]^+$), 548 (9), 459 (15), 458 (51), 322 (12), 321 (48), 267 (11), 261 (12), 237 (24), 173 (11), 157 (18, $TIPS^+$), 149 (11), 148 (10), 146 (19), 145 (87, $DOPS^+$), 144 (19), 131 (36), 129 (85), 103 (22), 75 (100), 48 (55), 45 (35). Anal. calc. for $C_{30}H_{55}IO_7Si_2$ (710.80): C 50.69, H 7.80, I 17.85; found: C 50.60, H 7.68, I 17.81.

*3,7-Anhydro-1,2,6-trideoxy-6-C-{{{1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl}dimethylsilyl}ethynyl}-1-*C*-iodo-5,8-bis-*O*-(methoxymethyl)-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**40**). At 22°, a soln. of **39** (1.04 g, 1.46 mmol), 3,4-dihydro-2*H*-pyran, (0.6 ml, 7.3 mmol) and pyridinium tosylate (11.1 mg, 0.044 mmol) in CH_2Cl_2 (40 ml) was stirred for 15 h. Normal workup (H_2O, CH_2Cl_2) and FC (AcOEt/hexane 1:19) gave **40** (1.22 g, 100%). Transparent syrup. R_f (AcOEt/hexane 3:17) 0.31. $[\alpha]_D^{25} = -39.8$ ($c = 0.79$, $CHCl_3$). IR ($CHCl_3$): 3008*m*, 2946*s*, 2891*s*, 2867*s*, 2173*w*, 1722*w*, 1465*m*, 1385*w*, 1367*m*, 1354*m*, 1291*m*, 1252*m*, 1138*s*, 1117*s*, 1096*s*, 1077*s*, 1026*s*, 919*m*, 884*m*, 868*w*, 839*m*, 822*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.6, MeOC*H*); 4.78 (*d*, *J* = 5.6, MeOC*H*); 4.65 (*s*, MeOCH_2); 4.54 (*m*, OCHO); 4.07 (*d*, *J* = 9.3, H–C(3)); 3.89–3.72 (*m*, CHO, H–C(8), H′–C(8)); 3.72 (*dd*, *J* = 9.3, 8.4, H–C(4)); 3.54–3.35 (*m*, CHO, CH_2CH_2OTHP, H–C(7)); 3.48 (*dd*, *J* = 10.3, 8.0, H–C(5)); 3.44 (*s*, MeO); 3.36 (*s*, MeO); 2.72 (*t*, *J* = 10.3, H–C(6)); 1.82–1.51 (*m*, 4 CH_2); 1.16–1.03 (*m*, $(Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.09 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.55 (*s*); 99.03, 98.89 (2*d*); 98.13 (*t*); 96.69 (*t*); 91.27 (*s*); 87.31 (*s*); 82.29 (*d*); 78.63 (*d*); 75.08 (*d*); 73.09 (*d*); 67.54 (*t*); 64.14 (*t*); 62.38, 62.23 (2*t*); 56.66 (*q*); 55.26 (*q*); 37.80 (*t*); 37.78 (*d*); 30.67, 30.57 (2*t*); 29.00 (*t*); 25.31, 25.17 (2*t*); 23.06 (*q*); 22.93 (*q*); 19.59, 19.47 (2*t*); 18.86 (*t*); 18.27 (*s*); 18.03 (6*q*); 13.63 (3*d*); 5.67 (*s*); −4.50 (2*q*). CI-MS: 813 (6, $[M+NH_4]^+$), 460 (11), 459 (32), 458 (100), 321 (14), 146 (9), 145 (44, $DOPS^+$), 89 (13, THP^+).

Coupling of **40** *with* **19**. According to *GP5*, with **40** (1.28 g, 1.46 mmol), **19** (619 mg, 1.46 mmol), $[Pd_2(dba)_3]$ (40.0 mg, 0.0437 mmol), CuI (8.3 mg, 0.0437 mmol), $P(fur)_3$ (16.9 mg, 0.0729 mmol), Et_3N (0.61 ml, 4.37 mmol), and DMSO (15 ml; 10 h). FC (AcOEt/hexane 1:19 → 3:17) gave **42** (136.4 mg, 75%) and **41** (1.29 g, 81%) as white foams.

*Data of 5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-{{{1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl}dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1 → 6)-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**41**): R_f (AcOEt/hexane 1:4) 0.29. $[\alpha]_D^{25} = -54.0$ ($c = 0.76$, $CHCl_3$). IR ($CHCl_3$): 3592*m*, 3008*m*, 2946*s*, 2892*s*, 2867*s*, 2261*w*, 2174*w*, 1734*w*, 1604*w*, 1467*m*, 1385*w*, 1366*w*, 1353*m*, 1324*w*, 1291*m*, 1252*s*, 1140*s*, 1099*s*, 1068*s*, 1024*s*, 995*m*, 919*m*, 884*s*, 846*s*, 598*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.96 (*d*, *J* = 5.6, MeOC*H*); 4.78 (*d*, *J* = 5.6, MeOC*H*); 4.65 (*s*, MeOCH_2); 4.55 (*m*, OCHO); 3.98 (*d*, *J* = 9.3, H–C(5′)); 3.94 (*d*, *J* = 9.3, H–C(3)); 3.89–3.37 (*m*, 2 H–C(8), 2 H–C(10′), H–C(4), H–C(6′), CH_2O, CH_2CH_2OTHP, H–C(5), H–C(7), H–C(7′), H–C(9′)); 3.44 (*s*, MeO); 3.35 (*s*, MeO); 2.71 (*t*, *J* = 10.2, H–C(8′)); 2.62 (*t*, *J* = 10.2, H–C(6)); 2.39 (*d*, *J* = 3.4,

Table 3. *Selected ^{1}H-NMR* ($CDCl_3$) *Chemical-Shift Values* [ppm] *of Dimers*

	25	**27**	**28**	**29**	**31**	**33**	**34**
H–C(3)	3.95	4.05	3.95	3.95	3.99	3.97	3.96
H–C(4)	3.63	3.81	3.63	~3.7	3.72	~3.7	~3.7
H–C(5)	3.51	5.09	~3.5	~3.5	~3.5	~3.5	~3.5
H–C(6)	2.65	2.79	2.63	2.63	2.82	2.80	2.87
H–C(7)	3.42	3.65	~3.4	~3.4	~3.4	~3.4	~3.4
H–C(8)	3.89	4.35	~3.9	~3.9	~3.9	~3.9	~3.9
H′–C(8)	3.68	4.18	3.71	~3.7	~3.8	~3.7	~3.7
H–C(5′)	4.05	4.03	3.93	3.97	3.93	3.93	3.95
H–C(6′)	3.80	3.79	3.60	~3.7	3.62	~3.7	~3.7
H–C(7′)	5.12	5.10	~3.5	~3.4	~3.5	~3.5	~3.5
H–C(8′)	2.67	2.66	2.62	2.72	2.53	2.71	2.74
H–C(9′)	3.64	3.63	~3.4	~3.5	~3.4	~3.4	~3.4
H–C(10′)	4.37	4.36	4.01	~3.9	~3.9	~3.9	~3.9
H′–C(10′)	4.23	4.22	3.86	~3.7	~3.8	~3.7	~3.7

Table 4. *Selected ^{13}C-NMR* ($CDCl_3$) *Chemical-Shift Values* [ppm] *of Dimers*

	25	**27**	**28**	**29**	**31**	**33**	**34**	**41**	**43**	**44**	**45**
C(1)	91.42	91.42	91.29	91.39	91.55	91.47	91.43	91.27	80.72	5.07	91.20
C(2)	101.94	101.94	102.17	102.03	102.14	102.16	102.27	102.01	74.67	91.61	102.06
C(3)	71.97	72.84	71.99	71.94	72.44	72.41	72.45	71.89	71.31	72.71	71.89
C(4)	75.06	75.76	75.03	74.87	74.72	74.72	74.53	74.83	74.83	74.85	74.84
C(5)	76.82	73.06	76.84	76.83	78.35	78.35	78.39	76.76	76.61	76.76	76.83
C(6)	38.23	37.06	38.29	38.19	37.38	37.35	37.83	38.14	38.17	38.08	38.17
C(7)	78.67	76.38	78.70	78.65	82.73	82.60	82.58	78.63	78.75	78.67	78.68
C(8)	63.31	64.34	63.33	63.29	67.94	67.57	69.25	63.22	63.20	63.20	63.17
C(1′)	76.94	77.23	75.79	[a])	77.85	77.47	77.91	76.48	76.32	75.87	76.63
C(2′)	68.39	68.80	68.86	68.61	67.94	68.14	68.46	68.54	68.62	68.65	68.47
C(3′)	71.07	70.89	69.87	70.82	70.76	71.12	71.06	70.77	70.72	70.74	70.87
C(4′)	74.36	74.47	74.73	74.99	74.43	74.55	74.96	75.06	75.14	[a])	74.93
C(5′)	72.36	72.83	71.71	72.12	71.89	72.23	72.16	72.03	72.02	72.05	72.03
C(6′)	75.70	75.11	75.63	75.00	74.97	74.67	74.74	74.95	74.90	74.85	74.94
C(7′)	73.13	72.93	77.00	78.88	76.73	78.83	78.82	78.75	78.75	78.80	78.73
C(8′)	37.50	37.47	38.65	37.82	39.00	37.79	37.38	37.38	37.80	37.80	37.80
C(9′)	76.82	76.83	80.04	82.21	79.03	82.29	82.27	82.18	82.16	82.19	82.31
C(10′)	64.44	64.44	64.22	67.62	63.58	67.31	67.63	67.60	67.58	67.60	67.65
C(1″)	100.45	100.47	103.44	104.39	102.36	104.44	104.61	104.47	104.45	104.47	104.44
C(2″)	88.72	88.73	87.65	87.49	88.51	87.46	87.41	87.37	87.39	87.40	87.42

[a]) Hidden by other signals.

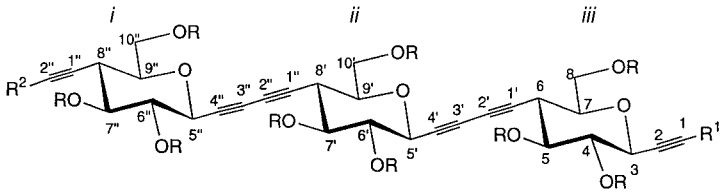

Fig. 4. *Numbering of oligomers*

HO–C(5)); 2.11 (*t*, $J \approx 6.7$, HO–C(8)); 1.73–1.52 (*m*, 4 CH_2); 1.22–1.08 (*m*, 2 (Me_2CH)$_3$Si); 0.96 (*s*, Me_2C); 0.15 (*s*, Me_3Si); 0.09 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.47 (*s*); 102.01 (*s*); 99.02 (*d*); 98.06 (*t*); 96.69 (*t*); 91.27 (*s*); 87.37 (*s*); 82.18 (*d*); 78.75 (*d*); 78.63 (*d*); 76.76 (*d*); 76.48 (*s*); 75.06 (*s*); 74.95 (*d*); 74.83 (*d*); 72.03 (*d*); 71.89 (*d*); 70.77 (*s*); 68.54 (*s*); 67.60 (*t*); 64.14 (*t*); 63.22 (*t*); 62.34 (*t*); 56.63 (*q*); 55.24 (*q*); 38.14 (*d*); 37.80 (*t*); 37.77 (*d*); 30.67 (*t*); 25.31 (*t*); 23.06 (*q*); 22.93 (*q*); 19.55 (*t*); 18.27 (*s*); 18.16 (6*q*); 18.03 (6*q*); 13.49 (3*d*); 12.81 (3*d*); −0.62 (3*q*); −4.50 (2*q*). MALDI-TOF-MS: 1114 ($[M+Na]^+$). Anal. calc. for $C_{57}H_{102}O_{12}Si_4$ (1091.71): C 62.71, H 9.42; found: C 62.87, H 9.22.

*Data of 2,6:11,15-Dianhydro-3,7,8,9,10,14-hexadeoxy-3,14-bis{{[1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl]dimethylsilyl}ethynyl}-1,4,13,16-tetrakis-*O*-(methoxymethyl)-5,12-bis-*O*-(triisopropylsilyl)-*D*-erythro-*L*-galacto-*L*-gulo-hexadeca-7,9-diynitol* (**42**): R_f (AcOEt/hexane 1:2) 0.83. $[\alpha]_D^{25} = -47.7$ ($c = 0.62$, $CHCl_3$). IR ($CHCl_3$): 3007*m*, 2946*s*, 2892*s*, 2868*s*, 2172*w*, 1728*w*, 1602*w*, 1465*m*, 1384*w*, 1367*w*, 1353*m*, 1288*w*, 1252*m*, 1151*s*, 1137*s*, 1113*s*, 1076*s*, 1024*s*, 918*w*, 884*w*, 841*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.96 (*d*, $J = 5.6$, MeOC*H*); 4.78 (*d*, $J = 5.6$, MeOC*H*); 4.65 (*s*, MeOCH_2); 4.56–4.54 (*m*, OCHO); 4.02 (*d*, $J = 9.3$, H–C(6)); 3.89–3.77 (*m*, CHO, 2 H–C(1)); 3.72 (*dd*, $J = 9.0$, 8.1, H–C(5)); 3.57–3.40 (*m*, CH_2CH_2OTHP, CHO, H–C(4), H–C(2)); 3.44 (*s*, MeO); 3.36 (*s*, MeO); 2.71 (*t*, $J = 10.6$, H–C(3)); 1.82–1.52 (*m*, 4 CH_2); 1.22–1.07 (*m*, (Me_2CH)$_3$Si); 0.96 (*s*, Me_2C); 0.10 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.70 (*s*); 99.06 (*d*); 97.92 (*t*); 96.71 (*t*); 87.35 (*s*); 82.27 (*d*); 78.65 (*d*); 77.13 (*s*); 74.49 (*d*); 71.89 (*d*); 70.68 (*s*); 67.73 (*t*); 64.18 (*t*); 62.37 (*t*); 56.59 (*q*); 55.23 (*q*); 37.89 (*t*); 37.70 (*d*); 30.72 (*t*); 25.39 (*t*); 23.13 (*q*); 23.01 (*q*); 19.61 (*t*); 18.34 (*s*); 18.09 (6*q*); 13.42 (3*d*); −4.45 (2*q*). MALDI-TOF-MS: 1375 ($[M+K]^+$), 1359 ($[M+Na]^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{[1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl]dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1→6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**43**). According to *GP2*, with **41** (3.78 g, 3.46 mmol) and CsF (552.1 mg, 3.63 mmol) in MeOH/DMF 1:5 (112 ml; 7 h). Normal workup (Et_2O/hexane 2:1, H_2O) and FC (AcOEt/hexane 1:9) gave **43** (2.76 g, 84%). White foam. R_f (AcOEt/hexane 1:3) 0.28. $[\alpha]_D^{25} = -59.8$ ($c = 0.41$, $CHCl_3$). IR ($CHCl_3$): 3601*w*, 3306*w*, 3008*m*, 2946*s*, 2892*s*, 2867*s*, 2173*w*, 1601*w*, 1465*m*, 1385*w*, 1367*m*, 1292*m*, 1253*m*, 1140*s*, 1097*s*, 1068*s*, 1025*s*, 919*w*, 884*m*, 823*m*, 653*w*, 503*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.96 (*d*, *J* = 5.6, C*H*OMe); 4.78 (*d*, *J* = 5.6, C*H*OMe); 4.65 (*s*, CH_2OMe); 4.55 (*m*, OCHO); 3.97 (*d*, *J* ≈ 9.0, H–C(5′)); 3.95 (*dd*, *J* = 9.3, 2.2, H–C(3)); 3.97–3.60 (*m*, 2 H–C(8), 2 H–C(10′), CHO, H–C(4), H–C(6′)); 3.54–3.30 (*m*, CH_2CH_2OTHP, H–C(5), H–C(7), H–C(7′), H–C(9′), CHO); 3.44 (*s*, MeO); 3.35 (*s*, MeO); 2.71 (*t*, *J* = 10.3, H–C(8′)); 2.65 (*t*, *J* = 10.3, H–C(6)); 1.78–1.51 (*m*, 4 CH_2); 1.24–1.07 (*m*, 2 $(Me_2CH)_3Si$); 0.96 (2*s*, Me_2C); 0.09 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.45 (*s*); 99.02 (2*d*); 98.06 (*t*); 96.67 (*t*); 87.39 (*s*); 82.16 (*d*); 80.72 (*d*); 78.75 (2*d*); 76.61 (*d*); 76.32 (*s*); 75.14 (*s*); 74.90 (*d*); 74.83 (*d*); 74.67 (*s*); 72.02 (*d*); 71.31 (*d*); 70.72 (*s*); 68.62 (*s*); 67.58 (*t*); 64.14 (*t*); 63.20 (*t*); 62.33 (*t*); 56.65 (*q*); 55.24 (*q*); 38.17 (*d*); 37.80 (*d* and *t*); 30.67 (*t*); 25.31 (*t*); 23.06 (*q*); 22.93 (*q*); 19.55 (*t*); 18.27 (*s*); 18.16 (6*q*); 18.03 (6*q*); 13.49 (3*d*); 12.76 (3*d*); −4.50 (2*q*). MALDI-TOF-MS: 1057 ($[M+K]^+$), 1041 ($[M+Na]^+$). Anal. calc. for $C_{54}H_{94}O_{12}Si_3$ (1019.52): C 62.71, H 9.42; found: C 62.87, H 9.22.

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{[1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl]dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1→6-*C*)-3,7-anhydro-1,2,6-trideoxy-1-*C*-iodo-4-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**44**). According to *GP4*, with **43** (0.917 g, 0.899 mmol), NIS (212.5 mg, 0.945 mmol), $AgOCOCF_3$ (9.9 mg, 0.0450 mmol), and acetone (9 ml; 6 h). FC (AcOEt/hexane 1:4→1:3) gave **44** (1.012 g, 98%). White foam. R_f (AcOEt/hexane 1:3) 0.27. $[\alpha]_D^{25} = -53.75$ ($c = 0.42$, $CHCl_3$). IR ($CHCl_3$): 3597*w*, 3008*m*, 2946*s*, 2867*s*, 2261*w*, 2174*w*, 1496*w*, 1465*m*, 1367*m*, 1353*m*, 1324*s*, 1291*m*, 1024*s*, 995*s*, 919*m*, 884*s*, 845*s*, 655*m*, 596*w*, 559*w*, 518*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.6, C*H*OMe); 4.79 (*d*, *J* = 5.6, MeOC*H*); 4.65 (*s*, $MeOCH_2$); 4.56 (*m*, OCHO); 4.08 (*d*, *J* = 9.3, H–C(5′)); 3.99 (br. *d*, *J* = 9.3, H–C(3)); 3.89–3.59 (*m*, 2 H–C(8), 2 H–C(10′), CHO, H–C(4), H–C(6′)); 3.53–3.38 (*m*, CH_2OTHP, CHO, H–C(5), H–C(7), H–C(7′), H–C(9′)); 3.44 (*s*, MeO); 3.36 (*s*, MeO); 2.72 (*d*, *J* = 10.2, H–C(8′)); 2.64 (*t*, *J* = 10.3, H–C(6)); 2.35 (*d*, *J* = 3.1, HO–C(5)); 1.80–1.52 (*m*, 4 CH_2, HO–C(8)); 1.25–1.08 (*m*, 2 $(Me_2CH)_3Si$); 0.97 (2*s*, Me_2C); 0.10 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.47 (*s*); 99.07 (*d*); 98.10 (*t*); 96.72 (*t*); 91.61 (*s*); 87.40 (*s*); 82.19 (*d*); 78.80 (*d*); 78.67 (*d*); 76.76 (*d*); 75.27 (*s*); 74.85 (2*d*); 72.71 (*d*); 72.05 (*d*); 70.74 (*s*); 68.65 (*s*); 67.60 (*t*); 64.16 (*t*); 63.20 (*t*); 62.41 (*t*); 56.68 (*q*); 55.27 (*q*); 38.08 (*d*); 37.80 (*d* and *t*); 30.70 (*t*); 25.34 (*t*); 23.10 (*q*); 22.95 (*q*); 19.59 (*t*); 18.31 (*s*); 18.11–18.06 (several *q*); 13.50 (3*d*); 12.77 (3*d*), 5.07 (*s*); −4.49 (2*q*); 1*s* missing. MALDI-TOF-MS: 1167 ($[M+Na]^+$). Anal. calc. for $C_{54}H_{93}IO_{12}Si_3$ (1145.42): C 56.62, H 8.18, I 11.08; found: C 56.90, H 8.12, I 10.79.

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{[(3-hydroxy-1,1-dimethylpropyl)dimethylsilyl]ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1→6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-oct-1-ynitol* (**45**). At 22°, a soln. of **41** (1.42 g, 1.302 mmol) in MeOH (90 ml) was treated with *Amberlyst 15* (750 mg) and stirred for 12 h. Filtration, evaporation, and FC (AcOEt/hexane 1:4→2:3) gave **45** (1.19 g, 91%). White foam. R_f (AcOEt/hexane 1:2) 0.48. M.p. 82.5–84°. $[\alpha]_D^{25} = -60.6$ ($c = 0.61$, $CHCl_3$). IR ($CHCl_3$): 3593*w*, 3472*w* (br.), 3008*m*, 2946*s*, 2893*s*, 2867*s*, 2262*w*, 2174*w*, 1724*w*, 1602*w*, 1465*s*, 1386*m*, 1366*m*, 1351*m*, 1292*m*, 1252*s*, 1150*s*, 1099*s*, 1067*s*, 1041*s*, 920*m*, 884*m*, 846*s*, 822*m*, 594*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.95 (*d*, *J* = 5.6, MeOC*H*); 4.77 (*d*, *J* ≈ 5.6, MeOC*H*); 4.65 (*s*, $MeOCH_2$); 3.98 (*d*, *J* ≈ 9.0, H–C(5′)); 3.93 (*d*, *J* ≈ 9.1, H–C(3)); 3.87 (*ddd*, *J* ≈ 12.5, 5.0, 2.0, H–C(8)); 3.86–3.82 (*m*, H–C(10′)); 3.80–3.64 (*m*, H′–C(8), H′–C(10′), CH_2OH, H–C(6′)); 3.59 (*dd*, *J* = 9.0, 8.4, H–C(4)); 3.54–3.35 (*m*, H–C(5), H–C(7), H–C(9′)); 3.48 (*dd*, *J* = 10.3, 8.4, H–C(7′)); 3.43 (*s*, MeO); 3.36 (*s*, MeO); 2.70 (*t*, *J* = 10.3, H–C(8′)); 2.61 (br. *t*, *J* = 10.3, H–C(6)); 2.46 (*d*, *J* = 3.4, HO–C(5)); 2.18 (br. *s*, HO–C(8), CH_2CH_2OH); 1.59 (*t*, *J* = 7.6, CH_2CH_2OH); 1.26–1.15 (*m*, 2 $(Me_2CH)_3Si$); 0.94 (*s*, Me_2C); 0.14 (*s*, Me_3Si); 0.09 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.44 (*s*); 102.06 (*s*); 98.02 (*t*); 96.58 (*t*); 91.20 (*s*); 87.42 (*s*); 82.31 (*d*); 78.73 (*d*); 78.68 (*d*); 76.73 (*d*); 76.63 (*s*); 74.95 (*d*); 74.93 (*s*); 74.85 (*d*); 72.03 (*d*); 71.89 (*d*); 70.87 (*s*); 68.47 (*s*); 67.65 (*t*); 63.17 (*t*); 59.32 (*t*); 56.58 (*q*); 55.29 (*q*); 42.09 (*t*); 38.17 (*d*); 37.80 (*d*); 23.29 (*q*); 23.23 (*q*); 18.50 (*s*); 18.15 (6*q*); 18.02 (6*q*); 13.49 (3*d*); 12.81 (3*d*); −0.62 (3*q*); −4.38 (2*q*). MALDI-TOF-MS: 1047 ($[M+K]^+$), 1030 ($[M+Na]^+$). Anal. calc. for $C_{52}H_{94}O_{11}Si_4$ (1007.59): C 61.98, H 9.40; found: C 61.83, H 9.34.

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{[1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl]dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D*-glycero-*D*-gulo-deca-1,3-diynitol-1-yl-(1→8-*

C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1→6-C)-3,7-anhydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol (**46**). According to *GP5*, with **44** (2.02 g, 1.76 mmol), **45** (1.78 g, 1.76 mmol), $[Pd_2(dba)_3]$ (48.4 mg, 0.0529 mmol), CuI (10.1 mg, 0.0529 mmol), $P(fur)_3$ (20.5 mg, 0.0881 mmol), Et_3N (0.74 ml, 5.29 mmol), and DMSO (18 ml; 11 h). FC (AcOEt/hexane 3:97→1:3) gave **46** (2.69 g, 81%). Slightly yellow foam. R_f (AcOEt/hexane 1:2) 0.54. M.p. 141–149°. $[\alpha]_D^{25} = -73.3$ ($c = 1.04$, $CHCl_3$). IR ($CHCl_3$): 3592*w*, 3008*m*, 2946*s*, 2892*s*, 2868*s*, 2261*w*, 2175*w*, 1730*w*, 1602*w*, 1465*m*, 1384*m*, 1369*m*, 1352*m*, 1325*w*, 1292*m*, 1252*m*, 1150*s*, 1112*s*, 1068*s*, 1041*s*, 919*m*, 884*m*, 845*m*, 818*m*, 645*m*, 601*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.97 (*d*, $J = 5.6$, MeOC*H*); 4.90 (*d*, $J = 6.2$, MeOC*H*); 4.79 (*d*, $J = 5.5$, MeOC*H*); 4.72 (*d*, $J = 6.2$, MeOC*H*); 4.66 (*s*, MeOCH_2); 4.65 (*s*, MeOCH_2); 4.56–4.55 (*m*, OCHO); 4.00 (br. *d*, $J \approx 9.9$, H–C(5″)); 3.99 (br. *d*, $J \approx 9.1$, H–C(5‴)); 3.98 (br. *d*, $J \approx 9.7$, H–C(5′)); 3.95 (*d*, $J = 9.3$, H–C(3)); 3.89–3.83 (*m*, H–C(8), H–C(10′), H–C(10″), H–C(10‴), CHO); 3.80–3.66 (*m*, H′–C(8), H′–C(10), H′–C(10″), H′–C(10‴), CH_2CH_2OTHP, CHO); 3.74 (*dd*, $J = 9.1$, 8.2, H–C(6′)); 3.73 (*dd*, $J = 9.1$, 8.2, H–C(6‴)); 3.61 (*dd*, $J = 9.1$, 8.4, H–C(4), H–C(6″)); 3.56–3.40 (*m*, H–C(5), H–C(7′), H–C(7″), H–C(7‴), H–C(7), H–C(9′), H–C(9″), H–C(9‴), CHO); 3.47 (*s*, MeO); 3.44 (*s*, MeO); 3.372 (*s*, MeO); 3.367 (*s*, MeO); 2.82 (*t*, $J = 10.3$, H–C(8′)); 2.72 (*t*, $J = 10.3$, H–C(8‴)); 2.64 (*t*, $J = 10.3$, H–C(6), H–C(8″)); 2.34 (*d*, $J = 3.2$, HO–C(7″)); 2.33 (*d*, $J = 3.2$, HO–C(5)); 1.99–1.97 (*m*), 1.92–1.90 (*m*, HO–C(8), HO–C(10″)); 1.84–1.50 (*m*, 4 CH_2); 1.27–1.09 (*m*, 4 $(Me_2CH)_3Si$); 0.98 (*s*, MeC); 0.97 (*s*, MeC); 0.17 (*s*, Me_3Si); 0.11 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 104.50 (*s*); 102.00 (*s*); 99.05 (*d*); 98.09 (*t*); 97.99 (*t*); 96.75 (2*t*); 91.39 (*s*); 87.50 (*s*); 82.29 (*d*); 82.26 (*d*); 78.87 (*d*); 78.80 (*d*); 78.67 (*d*); 78.44 (*d*); 77.68 (*s*); 77.23 (*d*); 76.86 (*d*); 76.71 (*d*); 76.67 (*s*); 76.18 (*s*); 75.37 (*s*); 75.08 (*d*); 74.98 (*d*); 74.87 (*d*); 74.25 (*s*); 72.22 (*d*); 72.13 (*d*); 72.00 (*d*); 71.95 (*d*); 70.96 (*s*); 70.90 (*s*); 70.74 (*s*); 68.84 (*s*); 68.57 (*s*); 68.06 (*s*); 67.71 (*t*); 67.38 (*t*); 64.24 (*t*); 63.35 (*t*); 63.29 (*t*); 62.47 (*t*); 56.75 (*q*); 56.44 (*q*); 55.35 (2*q*); 38.31 (*d*); 38.28 (*d*); 37.99 (*t*); 37.95 (*d*); 37.41 (*d*); 30.85 (*t*); 25.50 (*t*); 23.26 (*q*); 23.12 (*q*); 19.76 (*t*); 18.48 (*s*); 18.34–18.18 (several *q*); 13.67 (6*d*); 13.02 (3*d*); 12.88 (3*d*); −0.40 (3*q*); −4.27 (2*q*); 1*s* missing. MALDI-TOF-MS: 1920 ($[M+K]^+$), 1905 ($[M+Na]^+$).

5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-[{[1,1-dimethyl-3-[(tetrahydro-2H-pyran-2-yl)oxy]propyl}dimethylsilyl]ethynyl]-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1→8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1→8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1→6-C)-3,7-anhydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (**47**). According to *GP2*, with **46** (1.64 g, 0.870 mmol), CsF (138.7 mg, 0.913 mmol), and MeOH/DMF 1:5 (30 ml; 7 h). Normal workup (Et_2O/hexane 2:1, H_2O) and FC (AcOEt/hexane 3:17→7:18) gave **47** (1.25 g, 79%). White foam. R_f (AcOEt/hexane 1:2) 0.36. IR ($CHCl_3$): 3603*m*, 3445*w* (br.), 3306*m*, 3008*m*, 2946*s*, 2892*s*, 2868*s*, 2261*w*, 2173*w*, 1602*w*, 1519*w*, 1465*m*, 1368*m*, 1292*w*, 1252*m*, 1150*s*, 1097*s*, 1067*s*, 1041*s*, 919*m*, 883*m*, 818*m*, 654*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.96 (*d*, $J = 5.6$, MeOC*H*); 4.89 (*d*, $J = 6.2$, MeOC*H*); 4.78 (*d*, $J = 5.5$, MeOC*H*); 4.71 (*d*, $J = 6.2$, MeOC*H*); 4.643 (*s*, MeOCH_2); 4.640 (*s*, MeOCH_2); 4.56–4.54 (*m*, OCHO); 3.99 (*d*, $J \approx 9.0$), 3.98 (*d*, $J \approx 8.8$), 3.97 (*d*, $J \approx 9.0$, H–C(5′), H–C(5″), H–C(5‴)); 3.94 (*dd*, $J = 9.3$, 1.9, H–C(3)); 3.89–3.60 (*m*, 2 H–C(8), 2 H–C(10′), 2 H–C(10″), 2 H–C(10‴), CHO, H–C(4), H–C(6′), H–C(6″), H–C(6‴)); 3.57–3.35 (*m*, H–C(5), H–C(7′), H–C(7″), H–C(7‴), H–C(7), H–C(9′), H–C(9″), H–C(9‴), CH_2CH_2OTHP, CHO); 3.434 (*s*, MeO); 3.426 (*s*, MeO); 3.36 (*s*, MeO); 3.35 (*s*, MeO); 2.81 (*t*, $J = 10.3$, H–C(8′)); 2.71 (*t*, $J = 10.3$, H–C(8‴)); 2.65 (*t*, $J = 10.3$), 2.63 (*t*, $J = 10.3$, H–C(6), H–C(8″)); 2.47 (*d*, $J = 1.9$, H–C(1)); 2.44 (*d*, $J = 3.4$), 2.43 (*d*, $J = 3.1$, HO–C(5), HO–C(7″)); 2.10 (*t*, $J = 6.8$), 2.03 (*t*, $J = 6.7$, HO–C(8), HO–C(10″)); 1.81–1.48 (*m*, 4 CH_2); 1.24–1.05 (*m*, 4 $(Me_2CH)_3Si$); 0.96 (2*s*, MeC); 0.09 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.49 (*s*); 99.00 (*d*); 98.06 (*t*); 97.97 (*t*); 96.71 (2*t*); 87.44 (*s*); 82.24 (2*d*); 80.75 (*d*); 78.78 (2*d*); 78.38 (*d*); 77.58 (2*s*); 77.23 (*d*); 76.61 (2*d*); 76.21 (2*s*); 75.27 (*s*); 74.96 (*d*); 74.82 (2*d*); 74.23 (*s*); 72.16 (*d*); 72.05 (*d*); 71.87 (*d*); 71.32 (*d*); 70.87 (*s*); 70.79 (*s*); 70.69 (*s*); 68.72 (*s*); 68.54 (2*s*); 67.97 (*t*); 67.60 (*t*); 64.14 (*t*); 63.20 (2*t*); 62.33 (*t*); 56.62 (*q*); 56.33 (*q*); 55.24 (2*q*); 38.19 (2*d*); 37.80 (*d* and *t*); 37.25 (*d*); 30.68 (*t*); 25.34 (*t*); 23.09 (*q*); 22.95 (*q*); 19.55 (*t*); 18.3 (*s*); 18.15–18.05 (several *q*); 13.49 (6*d*); 12.77 (3*d*); 12.69 (3*d*); −4.49 (2*q*); 1*s* missing. MALDI-TOF-MS: 1848 ($[M+K]^+$), 1832 ($[M+Na]^+$).

5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-C-[{[1,1-dimethyl-3-[(tetrahydro-2H-pyran-2-yl)oxy]propyl}dimethylsilyl]ethynyl]-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1→8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1→8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-D-glycero-D-gulo-deca-1,3-diynitol-1-yl-(1→6-C)-3,7-anhydro-1,2,6-trideoxy-1-C-iodo-4-O-(triisopropylsilyl)-D-glycero-D-gulo-oct-1-ynitol (**48**). According to *GP4*, with **47** (495.0 mg, 0.274 mmol), NIS (64.7 mg, 0.287 mmol), $AgOCOCF_3$ (3.0 mg, 0.0137 mmol), and acetone (4.5 ml; 9 h). FC (AcOEt/hexane 1:4→1:2) gave **48** (508.0 g, 96%).

White foam. R_f (AcOEt/hexane 1:2) 0.31. M.p. 94–96°. IR ($CHCl_3$): 3600*w*, 3411*w*, 2946*s*, 2867*s*, 2172*w*, 1730*w*, 1602*w*, 1465*m*, 1368*m*, 1292*m*, 1260*m*, 1143*s*, 1098*s*, 1067*s*, 1039*s*, 1022*s*, 938*w*, 919*m*, 884*m*, 822*m*, 597*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.6, MeOC*H*); 4.90 (*d*, *J* = 6.2, MeOC*H*); 4.79 (*d*, *J* = 5.6, MeOC*H*); 4.72 (*d*, *J* = 6.2, MeOC*H*); 4.66 (*s*, MeOCH_2); 4.65 (*s*, MeOCH_2); 4.57–4.54 (*m*, OCHO); 4.09 (*d*, *J* = 9.0, H–C(3)); 4.00 (*d*, *J* ≈ 9.0), 3.99 (*d*, *J* ≈ 9.0), 3.98 (*d*, *J* ≈ 8.7, H–C(5′), H–C(5″), H–C(5‴)); 3.90–3.36 (*m*, 2 H–C(8), 2 H–C(10′), 2 H–C(10″), 2 H–C(10‴), CH_2O, H–C(4), H–C(6′), H–C(6″), H–C(6‴), H–C(5), H–C(7′), H–C(7″), H–C(7‴), H–C(7), H–C(9′), H–C(9″), H–C(9‴), CH_2CH_2OTHP); 3.45 (*s*, MeO); 3.44 (*s*, MeO); 3.370 (*s*, MeO); 3.365 (*s*, MeO); 2.82 (*t*, *J* = 10.3), 2.72 (*t*, *J* = 10.3), 2.65 (*t*, *J* = 10.3), 2.64 (*t*, *J* = 10.3, H–C(6), H–C(8′), H–C(8″), H–C(8‴)); 2.35 (*d*, *J* = 3.1), 2.33 (*d*, *J* = 3.4, HO–C(5), HO–C(7″)); 1.92 (*t*, *J* = 6.5), 1.91 (*t*, *J* = 6.5, HO–C(8), HO–C(10″)); 1.83–1.52 (*m*, 4 CH_2); 1.25–1.09 (*m*, 4 ($Me_2CH)_3Si$); 0.97 (*s*, Me_2C); 0.10 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.52 (*s*); 99.03 (*d*); 98.06 (*t*); 97.97 (*t*); 96.74 (2*t*); 91.12 (*s*); 87.48 (*s*); 82.24 (2*d*); 78.80 (*d*); 78.72 (2*d*); 78.41 (*d*); 76.64 (*d*); 76.58 (3*s*); 76.19 (*s*); 75.33 (*d*); 75.06 (2*s*); 74.95 (2*d*); 74.82 (2*d*); 72.75 (*d*); 72.17 (*d*); 72.08 (*d*); 71.90 (*d*); 70.82 (*s*); 70.87 (*s*); 70.69 (*s*); 68.77 (*s*); 68.56 (*s*); 68.01 (*s*); 67.65 (*t*); 67.33 (*t*); 64.16 (*t*); 63.20 (2*t*); 62.33 (*t*); 56.63 (*q*); 56.34 (*q*); 55.24 (2*q*); 38.22 (*d*); 38.12 (*d*); 37.88 (*t*); 37.83 (*d*); 37.28 (*d*); 30.70 (*t*); 25.36 (*t*); 23.11 (*q*); 22.98 (*q*); 19.57 (*t*); 18.32 (*s*); 18.16–18.06 (several *q*); 13.49 (6*d*); 12.79 (3*d*); 12.71 (3*d*); 5.06 (*s*); –4.49 (2*q*); 1*s* missing. MALDI-TOF-MS: 1975 ([*M* + K]$^+$), 1958 ([*M* + Na]$^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{[(3-hydroxy-1,1-dimethylpropyl)dimethylsilyl]ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo*-oct-1-ynitol* (**49**). At 22°, a soln. of **46** (1.63 g, 0.866 mmol) in MeOH (60 ml) was treated with *Amberlyst 15* (500 mg) and stirred for 14 h. Filtration, evaporation, and FC (AcOEt/hexane 1:4 → 2:3) gave **46** (921.0 mg, 57%) and **49** (640.6 mg, 41%) as white foams. **49**: R_f (AcOEt/hexane 1:2) 0.13. IR ($CHCl_3$): 3601*m*, 3470*m* (br.), 3008*m*, 2947*s*, 2868*s*, 2261*w*, 2174*w*, 1723*m*, 1602*w*, 1506*w*, 1464*m*, 1438*m*, 1409*w*, 1373*m*, 1277*s*, 1252*m*, 1150*s*, 1118*s*, 1106*s*, 1067*s*, 1039*s*, 1020*s*, 919*w*, 883*m*, 846*m*, 818*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.6, MeOC*H*); 4.90 (*d*, *J* = 6.2, MeOC*H*); 4.79 (*d*, *J* = 5.6, MeOC*H*); 4.72 (*d*, *J* = 6.2, MeOC*H*); 4.67 (*s*, MeOCH_2); 4.65 (*s*, MeOCH_2); 4.00 (*d*, *J* ≈ 9.0, H–C(5″), H–C(5‴)); 3.98 (*d*, *J* ≈ 9.0, H–C(5′)); 3.95 (*d*, *J* ≈ 9.0, H–C(3)); 3.91–3.64 (*m*, 2 H–C(8), 2 H–C(10′), 2 H–C(10″), 2 H–C(10‴), CH_2OH); 3.73 (*dd*, *J* = 9.0, 8.4, H–C(6′), H–C(6‴)); 3.61 (*dd*, *J* = 9.0, 8.4, H–C(4), H–C(6″)); 3.53–3.37 (*m*, H–C(5), H–C(7′), H–C(7″), H–C(7‴), H–C(7), H–C(9′), H–C(9″), H–C (9‴)); 3.45 (*s*, MeO); 3.44 (*s*, MeO); 3.38 (*s*, MeO); 3.37 (*s*, MeO); 2.82 (*t*, *J* = 10.3, H–C(8′)); 2.71 (*t*, *J* = 10.3, H–C(8‴)); 2.63 (*t*, *J* = 10.3, H–C(6), H–C(8″)); 2.36 (*d*, *J* = 3.1, HO–C(5), HO–C(7″)); 2.03 (*t*, *J* ≈ 6.5), 2.00 (*t*, *J* ≈ 6.5, HO–C(8), HO–C(10″)); 1.61 (*t*, *J* = 7.6, C$H_2$$CH_2$OH); 1.23–1.05 (*m*, 4 ($Me_2CH)_3Si$); 0.95 (*s*, Me_2C); 0.16 (*s*, Me_3Si); 0.10 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.52 (*s*); 102.06 (*s*); 98.06 (*t*); 97.98 (*t*); 96.75 (*t*); 96.66 (*t*); 91.37 (*s*); 87.56 (*s*); 82.39 (*d*); 82.29 (*d*); 78.83 (2*d*); 78.68 (*d*); 78.42 (*d*); 77.68 (*s*); 76.82 (*d*); 76.61 (*d*); 76.29 (2*s*); 75.23 (2*s*); 75.06 (*d*); 75.00 (*d*); 74.82 (2*d*); 72.18 (*d*); 72.09 (*d*); 71.96 (*d*); 71.92 (*d*); 70.91 (*s*); 70.85 (*s*); 70.80 (*s*); 68.75 (*s*); 68.52 (*s*); 68.02 (*s*); 67.77 (3*t*); 63.28 (3*t*); 56.62 (*q*); 56.36 (*q*); 55.24 (2*q*); 38.21 (2*d*); 37.88 (*d*); 37.32 (*d*); 23.32 (2*q*); 18.58 (*s*); 18.18–18.06 (several *q*); 13.52 (6*d*); 12.87 (3*d*); 12.73 (3*d*); –0.57 (3*q*); –4.31 (2*q*); 2*s* missing. MALDI-TOF-MS: 1836 ([*M* + K]$^+$), 1820 ([*M* + Na]$^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl}dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo*-oct-1-ynitol* (**50**). According to *GP5*, with **48** (602.0 mg, 0.311 mmol), **49** (559.1 mg, 0.311 mmol), [$Pd_2(dba)_3$] (8.5 mg, 0.00933 mmol), CuI (2.0 mg, 0.00933 mmol), $P(fur)_3$ (4.1 mg, 0.0156 mmol), Et_3N (0.13 ml, 0.933 mmol), and DMSO (5 ml; 10 h). FC (AcOEt/hexane 1:2) gave **50** (864.2 mg, 80%). White foam. R_f (AcOEt/hexane 4:6) 0.51. M.p. 143–159°. $[\alpha]^{25}_{D} = -75.4$ ($c = 0.36$, $CHCl_3$). IR ($CHCl_3$): 3591*w*, 3481*w* (br.), 3008*m*, 2946*s*, 2892*s*, 2868*s*, 2260*w*, 2174*w*, 1602*m*, 1521*w*, 1464*m*, 1390*w*, 1367*m*, 1292*m*, 1252*m*, 1150*s*, 1067*s*, 1040*s*, 920*m*, 883*s*, 845*m*, 818*m*. ^{1}H-NMR

(500 MHz, $CDCl_3$): 4.98 (*d*, *J* = 5.7, MeOC*H*); 4.90 (*d*, *J* = 6.2, 3 MeOC*H*); 4.79 (*d*, *J* = 5.6, MeOC*H*); 4.72 (*d*, *J* = 6.2, 3 MeOC*H*); 4.656 (*s*, MeOCH_2); 4.651 (*s*, 3 MeOCH_2); 4.56–4.55 (*m*, OCHO); 4.00 (*d*, *J* ≈ 9.8, 3 H); 3.99 (*d*, *J* ≈ 9.5, 1 H), 3.98 (*d*, *J* ≈ 9.9, 3 H, H–C(3), H–C($5^{i–vi}$)); 3.95 (*d*, *J* ≈ 9.3, H–C(5^{vii})); 3.89–3.36 (*m*, 2 H–C(8), 2 H–C($10^{i–vii}$), CH_2CH_2OTHP, CH_2O, H–C(4), H–C($6^{i–vii}$), H–C(5), H–C($7^{i–vii}$), H–C(7), H–C($9^{i–vii}$); 3.45 (*s*, MeO); 3.44 (*s*, 3 MeO); 3.372 (*s*, 3 MeO); 3.366 (*s*, MeO); 2.82 (*t*, *J* = 10.2, H–C(8^{i}), H–C(8^{iii}), H–C(8^{v})); 2.72 (*t*, *J* = 10.2, H–C(8^{vii})); 2.645 (*t*, *J* = 10.2, 2 H), 2.639 (*t*, *J* = 10.3, 2 H, H–C(6), H–C(8^{ii}), H–C(8^{iv}), H–C(8^{vi})); 2.33 (*d*, *J* = 3.2, 3 H), 2.32 (*d*, *J* = 3.2, 1 H, HO–C(5), HO–C(7^{ii}), HO–C(7^{iv}), HO–C(7^{vi})); 1.97 (*t*, *J* = 6.8, 1 H), 1.89 (*t*, *J* = 6.8, 3 H, HO–C(8), HO–C(10^{ii}), HO–C(10^{iv}), HO–C(10^{vi})); 1.82–1.51 (*m*, 4 CH_2); 1.23–1.08 (*m*, 8 $(Me_2CH)_3Si$); 0.98 (*s*, MeC); 0.97 (*s*, MeC); 0.17 (*s*, Me_3Si); 0.11 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 104.48 (*s*); 101.99 (*s*); 99.06 (*d*); 98.09 (*t*); 97.99 (3*t*); 96.75 (4*t*); 91.40 (*s*); 87.50 (*s*); 82.28 (4*d*); 78.79 (*d*); 78.66 (*d*); 78.44 (*d*); 77.22 (*d*); 76.86 (*d*); 76.69 (several *d*); 75.08 (*d*); 74.99 (several *d*); 74.86 (several *s*); 74.20 (*s*); 72.20 (several *d*); 72.13 (several *d*); 71.99 (several *s*); 71.94 (several *d*); 70.89 (*s*); 70.88 (*s*); 70.72 (*s*); 68.57 (*s*); 68.04 (several *s*); 67.70 (*s*); 67.37 (4*t*); 64.26 (*t*); 63.29 (4*t*); 62.33 (*t*); 56.74 (*q*); 56.44 (3*q*); 55.35 (4*q*); 38.27 (4*d*); 37.98 (*d*); 37.80 (*t*); 37.40 (3*d*); 30.85 (*t*); 25.50 (*t*); 23.24 (*q*); 23.11 (*q*); 19.75 (*t*); 18.48 (*s*); 18.34–18.19 (several *q*); 13.66 (9*d*); 13.02 (3*d*); 12.87 (12*d*); –0.40 (3*q*); –4.28 (2*q*). MALDI-TOF-MS: 3500 ([*M* + K]$^+$), 3482 ([*M* + Na]$^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl}dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**51**). According to *GP2*, with **50** (204.4 mg, 0.0591 mmol), CsF (9.4 mg, 0.0621 mmol), and MeOH/DMF 1 : 5 (2 ml; 7 h). Normal workup (Et_2O/hexane 2 : 1, H_2O) and FC (AcOEt/hexane 1 : 3 → 2 : 3) gave **51** (172.2 mg, 86%). White foam. R_f (AcOEt/hexane 4 : 6) 0.43. IR ($CHCl_3$): 3595*w*, 3307*w*, 3008*m*, 2946*s*, 2892*m*, 2868*s*, 2261*w*, 2172*w*, 1602*w*, 1521*w*, 1465*m*, 1368*m*, 1292*m*, 1261*m*, 1150*s*, 1067*s*, 1040*s*, 920*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.6, MeOC*H*); 4.90 (*d*, *J* = 6.2, 3 MeOC*H*); 4.79 (*d*, *J* = 5.6, MeOC*H*); 4.72 (*d*, *J* = 6.2, 3 MeOC*H*); 4.65 (*s*, 4 MeOCH_2); 4.56–4.55 (*m*, OCHO); 4.01–3.37 (*m*, H–C(3), H–C($5^{i–vii}$), 2 H–C(8), 2 H–C($10^{i–vii}$), CH_2CH_2OTHP, CH_2O, H–C(4), H–C($6^{i–vii}$), H–C(5), H–C($7^{i–vii}$), H–C(7), H–C($9^{i–vii}$)); 3.44 (*s*, 4 MeO); 3.37 (*s*, 4 MeO); 2.82 (*t*, *J* = 10.2, H–C(8^{i}), H–C(8^{iii}), H–C(8^{v})); 2.72 (*t*, *J* ≈ 10.2, H–C(8^{vii})); 2.67 (*t*, *J* ≈ 10.2, 2 H), 2.64 (*t*, *J* = 10.3, 2 H, H–C(6), H–C(8^{ii}), H–C(8^{iv}), H–C(8^{vi})); 2.48 (*d*, *J* = 2.2, H–C(1)); 2.35 (*d*, *J* = 3.1, 3 H), 2.34 (*d*, *J* = 2.8, 1 H, HO–C(5), HO–C(7^{ii}), HO–C(7^{iv}), HO–C(7^{vi})); 1.97–1.89 (*m*, HO–C(8), HO–C(10^{ii}), HO–C(10^{iv}), HO–C(10^{vi})); 1.86–1.53 (*m*, 4 CH_2); 1.26–1.05 (*m*, 8 $(Me_2CH)_3Si$); 0.97 (*s*, Me_2C); 0.10 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.52 (*s*); 99.06 (*d*); 97.98 (4*t*); 96.74 (4*t*); 87.51 (*s*); 82.27 (4*d*); 80.78 (*d*); 78.79 (several *d*); 78.43 (several *d*); 76.68 (several *d*); 75.35 (*s*); 74.97 (several *d*); 74.81 (several *s*); 74.21 (*s*); 72.18 (several *d*); 71.89 (several *d*); 71.38 (several *s*); 70.87 (several *s*); 68.68 (several *s*); 68.02 (several *s*); 67.60–67.35 (4*t*); 64.18 (*t*); 63.29–63.17 (4*t*); 62.37 (*t*); 56.65 (*q*); 56.37 (3*q*); 55.26 (4*q*); 38.21 (4*d*); 37.89 (*d* and *t*); 37.32 (3*d*); 30.72 (*t*); 25.39 (*t*); 23.13 (*q*); 23.01 (*q*); 19.61 (*t*); 18.27 (*s*); 18.09–17.85 (several *q*); 13.52 (9*d*); 12.85 (3*d*); 12.76 (9*d*); 12.18 (3*d*); –4.45 (2*q*). MALDI-TOF-MS: 3426 ([*M* + K]$^+$), 3410 ([*M* + Na]$^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl}dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-1-*C*-iodo-4-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**52**). According to *GP4*, with **51** (194.2 mg, 0.0573 mmol), NIS (14.2 mg, 0.0630 mmol), $AgOCOCF_3$ (0.6 mg, 2.86 μmol), and acetone (0.5 ml; 8 h). FC (AcOEt/hexane 3 : 17 → 1 : 4) gave **52** (190.1 mg, 95%). White foam. R_f (AcOEt/hexane 4 : 6) 0.43. IR ($CHCl_3$): 3592*w*, 3008*m*, 2946*s*, 2867*s*, 2260*w*, 2172*w*, 1731*m*, 1602*m*, 1496*w*, 1464*m*, 1374*m*, 1292*m*, 1265*m*, 1252*m*, 1150*s*, 1097*s*, 1067*s*,

1042*s*, 937*w*, 919*w*, 884*m*, 657*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.6, MeOC*H*); 4.90 (*d*, *J* = 6.2, 3 MeOC*H*); 4.79 (*d*, *J* = 5.6, MeOC*H*); 4.72 (*d*, *J* = 6.2, 3 MeOC*H*); 4.65 (*s*, 4 MeOCH_2); 4.57 – 4.54 (*m*, OCHO); 4.08 (*d*, *J* = 9.3, H−C(3)); 4.00 (*d*, *J* = 9.0, 3 H), 3.98 (*d*, *J* = 9.0, 4 H, H−C($5^{\text{i–vii}}$)); 3.89 – 3.58 (*m*, 2 H−C(8), 2 H−C($10^{\text{i–vii}}$), CH_2CH_2OTHP, CHO, H−C(4), H−C($6^{\text{i–vii}}$)); 3.53 – 3.36 (*m*, H−C(5), H−C($7^{\text{i–vii}}$), H−C(7), H−C($9^{\text{i–vii}}$), CHO); 3.50 (*s*, MeO); 3.44 (*s*, MeO); 3.43 (*s*, 2 MeO); 3.37 (*s*, 4 MeO); 2.82 (*t*, *J* = 10.3, H−C(8^{i}), H−C(8^{iii}), H−C(8^{v})), 2.72 (*t*, *J* ≈ 10.3, H−C(8^{vii})); 2.64 (br. *t*, *J* ≈ 10.2, H−C(6), H−C(8^{ii}), H−C(8^{iv}), H−C(8^{vi})); 2.38 – 2.35 (*m*, HO−C(5), HO−C(7^{ii}), HO−C(7^{iv}), HO−C(7^{vi})); 1.97 – 1.92 (*m*, HO−C(8), HO−C(10^{ii}), HO−C(10^{iv}), HO−C(10^{vi})); 1.84 – 1.51 (*m*, 4 CH_2); 1.25 – 1.05 (*m*, 8 $(Me_2CH)_3Si$); 0.97 (*s*, Me_2C); 0.10 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 104.47 (*s*); 99.06 (*d*); 98.01 (*t*); 97.98 (3*t*); 96.74 (4*t*); 91.09 (*s*); 87.46 (*s*); 82.27 (4*d*); 78.78 (several *d*); 78.43 (*d*); 77.10 (*s*); 76.65 (several *d*); 75.35 (*s*); 74.94 (several *d*); 74.81 (several *s*); 74.21 (*s*); 72.75 (*s*); 72.18 (several *d*); 71.89 (several *d*); 70.87 (several *s*); 68.73 – 68.65 (several *s*); 68.02 (several *s*); 67.71 – 67.35 (4*t*); 64.18 (*t*); 63.22 (several *t*); 62.40 (several *t*); 56.69 (*q*); 56.37 (3*q*); 55.29 (4*q*); 38.18 (4*d*); 37.86 (*d* and *t*); 37.32 (3*d*); 30.75, 30.67 (2*t*); 25.39, 25.15 (2*t*); 23.13 (*q*); 23.01 (*q*); 19.61 (*t*); 18.34 (*s*); 18.09 (several *q*); 13.52 (12*d*); 12.76 (12*d*); 5.07 (*s*); −4.45 (2*q*). MALDI-TOF-MS: 3553 ([M + K]$^+$), 3537 ([M + Na]$^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{[(3-hydroxy-1,1-dimethylpropyl)dimethylsilyl]ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo*-oct-1-ynitol* (**53**). At 22°, a soln. of **50** (3.669 g, 1.061 mmol) in MeOH (70 ml) was treated with *Amberlyst 15* (600 mg) and stirred for 14 h. Filtration, evaporation, and FC (AcOEt/hexane 1 : 3 → 2 : 3) gave **50** (2.274 g, 62%) and **53** (1.282 g, 34%) as white foams. **53**: R_f (AcOEt/hexane 4 : 6) 0.10. IR ($CHCl_3$): 3592*w*, 3008*m*, 2946*s*, 2892*s*, 2867*s*, 2260*w*, 2174*w*, 1728*w*, 1519*w*, 1464*m*, 1368*w*, 1292*m*, 1253*m*, 1150*s*, 1096*s*, 1067*s*, 1040*s*, 1019*s*, 930*m*, 884*m*, 844*w*, 818*m*, 654*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.9, MeOC*H*); 4.90 (*d*, *J* = 6.2, 3 MeOC*H*); 4.80 (*d*, *J* = 5.9, MeOC*H*); 4.72 (*d*, *J* = 6.2, 3 MeOC*H*); 4.65 (*s*, 4 MeOCH_2); 4.00 (*d*, *J* ≈ 9.3, 4 H), 3.98 (*d*, *J* ≈ 9.9, 4 H, H−C(3), H−C($5^{\text{i–vii}}$)); 3.92 – 3.84 (*m*, H−C(8), H−C($10^{\text{i–vii}}$)); 3.83 – 3.36 (*m*, H′−C(8), H′−C($10^{\text{i–vii}}$), CH_2OH, H−C(4), H−C($6^{\text{i–vii}}$), H−C(5), H−C($7^{\text{i–vii}}$), H−C(7), H−C($9^{\text{i–vii}}$)); 3.45 (*s*, MeO); 3.44 (*s*, 3 MeO); 3.38 (*s*, MeO); 3.37 (*s*, 3 MeO); 2.82 (*t*, *J* = 10.3, H−C(8^{i}), H−C(8^{iii}), H−C(8^{v})); 2.71 (*t*, *J* = 10.3, H−C(8^{vii})); 2.64 (*t*, *J* = 10.3, 2 H), 2.639 (*t*, *J* = 10.3, 2 H, H−C(6), H−C(8^{ii}), H−C(8^{iv}), H−C(8^{vi})); 2.35 (*d*, *J* = 3.1, HO−C(5), HO−C(7^{ii}), HO−C(7^{iv}), HO−C(7^{vi})); 2.01 – 2.00 (*m*, CH_2O*H*); 1.95 – 1.92 (*m*, HO−C(8), HO−C(10^{ii}), HO−C(10^{iv}), HO−C(10^{vi})); 1.62 – 1.58 (*m*, CH_2CH_2OH); 1.25 – 1.05 (*m*, 8 $(Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.16 (*s*, Me_3Si); 0.11 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 104.48 (*s*); 102.01 (*s*); 97.98 (*t*); 96.74 (several *t*); 91.41 (*s*); 87.55 (*s*); 82.27 (4*d*); 78.78 (2*d*); 78.65 (*d*); 78.43 (*d*); 76.81 (*d*); 76.65 (several *d*); 75.00 (*d*); 74.94 (several *d*); 74.81 (several *s*); 74.21 (several *s*); 72.18 (several *d*); 72.09 (several *d*); 71.96 (*d*); 71.89 (*d*); 70.84 (several *s*); 68.75 (*s*); 68.68 (2*s*); 68.48 (*s*); 67.99 (several *s*); 67.71 (2*t*); 67.35 (2*t*); 63.22 (4*t*); 56.65 (*q*); 56.37 (3*q*); 55.36 (*q*); 55.26 (3*q*); 38.18 (4*d*); 37.89 (*d*); 37.32 (3*d*); 23.39 (*q*); 23.33 (*q*); 18.41 (*s*); 18.21 – 17.58 (several *q*); 13.55 (9*d*); 12.88 (3*d*); 12.76 (12*d*); −0.55 (3*q*); −4.29 (2*q*). MALDI-TOF-MS: 3414 ([M + K]$^+$), 3398 ([M + Na]$^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl}dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl)-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo*-deca-1,3-diynitol-1-yl-*

*(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**54**). According to *GP5*, with **52** (352.6 mg, 0.1004 mmol), **53** (338.8 mg, 0.1004 mmol), $[Pd_2(dba)_3]$ (2.8 mg, 3.01 μmol), CuI (0.6 mg, 3.01 μmol), $P(fur)_3$ (1.2 mg, 5.02 μmol), Et_3N (42 μl, 0.3011 mmol), and DMSO (1 ml; 14 h). FC (AcOEt/hexane 1:3→2:3) gave **54** (444.9 mg, 67%). White foam. R_f (AcOEt/hexane 4:6) 0.32. M.p. > 220° (dec.). $[\alpha]_D^{25} = -83.1$ ($c = 0.89$, $CHCl_3$). IR ($CHCl_3$): 3597*w*, 3431*w* (br.), 3008*m*, 2947*s*, 2893*s*, 2868*s*, 2260*w*, 2178*w*, 1730*m*, 1465*m*, 1371*m*, 1292*m*, 1252*m*, 1150*s*, 1119*s*, 1098*s*, 1067*s*, 1042*s*, 1022*s*, 919*m*, 883*s*, 843*m*, 655*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.6, MeOC*H*); 4.90 (*d*, *J* = 6.2, 7 MeOC*H*); 4.79 (*d*, *J* = 5.5, MeOC*H*); 4.71 (*d*, *J* = 6.2, 7 MeOC*H*); 4.65 (*s*, 8 MeOCH_2); 4.56–4.55 (*m*, OCHO); 4.01–3.36 (*m*, H–C(3), H–C(5^{i-xv}), 2 H–C(8), 2 H–C(10^{ii-xv}), CH_2O, CH_2CH_2OTHP, H–C(4), H–C(6^{i-xv}), H–C(5), H–C(7^{i-xv}), H–C(7), H–C(9^{i-xv})); 3.44 (*s*, MeO); 3.43 (*s*, 7 MeO); 3.372 (*s*, MeO); 3.367 (*s*, 7 MeO); 2.82 (*t*, *J* = 10.3, H–C(8^{i}), H–C(8^{iii}), H–C(8^{v}), H–C(8^{vii}), H–C(8^{ix}), H–C(8^{xi}), H–C(8^{xiii})); 2.72 (*t*, *J* = 10.3, H–C(8^{xv})); 2.64 (*t*, *J* = 10.3, H–C(6), H–C(8^{ii}), H–C(8^{iv}), H–C(8^{vi}), H–C(8^{viii}), H–C(8^{x}), H–C(8^{xii}), H–C(8^{xiv})); 2.36 (*d*, *J* = 2.5, HO–C(5), HO–C(7^{ii}), HO–C(7^{iv}), HO–C(7^{vi}), HO–C(7^{viii}), HO–C(7^{x}), HO–C(7^{xii}), HO–C(7^{xiv})); 1.95 (*t*, *J* = 6.8, HO–C(8), HO–C(10^{ii}), HO–C(10^{iv}), HO–C(10^{vi}), HO–C(10^{viii}), HO–C(10^{x}), HO–C(10^{xii}), HO–C(10^{xiv})); 1.71–1.53 (*m*, 4 CH_2); 1.25–1.07 (*m*, several $(Me_2CH)_3Si$); 0.97 (*s*, Me_2C); 0.16 (*s*, Me_3Si); 0.10 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 104.26 (*s*); 102.03 (*s*); 98.95 (*d*); 97.93 (several *t*); 96.67 (several *t*); 91.29 (*s*); 87.50 (*s*); 82.24 (5*d*); 82.26 (3*d*); 78.78 (several *d*); 78.36 (2*d*); 78.67 (several *d*); 78.44 (several *d*); 77.68 (*s*); 77.23 (*d*); 76.86 (several *d*); 76.71 (2*d*); 76.57 (several *s*); 76.19 (several *s*); 75.37 (several *s*); 75.08 (several *d*); 74.90 (3*d*); 74.78 (several *d*); 74.25 (several *s*); 72.10 (several *d*); 72.13 (several *d*); 71.86 (several *d*); 70.79 (several *s*); 68.57 (several *s*); 67.94 (several *s*); 67.60 (several *s*); 67.28 (8*t*); 64.12 (*t*); 63.14 (several *t*); 62.35 (*t*); 56.58 (*q*); 56.29 (*q*); 55.19 (8*q*); 38.19 (8*d*); 37.85 (*d* and several *t*); 37.24 (7*d*); 30.65 (*t*); 25.31 (*t*); 23.03 (*q*); 22.93 (*q*); 19.49 (*t*); 18.52 (*s*); 18.00–17.85 (several *q*); 13.44 (several *d*); 12.66 (several *d*); −0.62 (3*q*); −4.52 (2*q*). MALDI-TOF-MS: 6654 ($[M + K]^+$), 6639 ($[M + Na]^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl}dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,5,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,5,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→6-*C*)-3,7-anhydro-1,2,6-trideoxy-4-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**55**). According to *GP2*, **54** (22.7 mg, 3.43 μmol) and CsF (0.57 mg, 3.77 μmol) in MeOH/DMF 1:5 (0.3 ml; 9 h). Normal workup (Et_2O/hexane 2:1, H_2O) and FC (AcOEt/hexane 3:7) gave **55** (19.1 mg, 85%). White foam. R_f (AcOEt/hexane 1:1) 0.31. M.p. > 220° (dec.). IR ($CHCl_3$): 3599*w* (br.), 3410*w* (br.), 2961*s*, 2929*s*, 2869*s*, 2260*w*, 2178*w*, 1731*m*, 1466*m*, 1375*m*, 1292*m*, 1262*s*, 1141*s*, 1098*s*, 1017*s*, 933*w*, 883*m*, 818*s* (br.), 655*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.6, MeOC*H*); 4.90 (*d*, *J* = 6.2, 7 MeOC*H*); 4.79 (*d*, *J* = 5.6, MeOC*H*); 4.72 (*d*, *J* = 6.2, 7 MeOC*H*); 4.65 (*s*, 8 MeOCH_2); 4.56 (br. *m*, OCHO); 4.01–3.36 (*m*, H–C(3), H–C(5^{i-xv}), 2 H–C(8), 2 H–C(10^{ii-xv}), CH_2O, CH_2OH, H–C(4), H–C(6^{i-xv}), H–C(5), H–C(7^{i-xv}), H–C(7), H–C(9^{i-xv})); 3.45 (*s*, MeO); 3.44 (*s*, 7 MeO); 3.38 (*s*, MeO); 3.37 (*s*, 7 MeO); 2.82 (*t*, *J* ≈ 10.6, H–C(8^{i}), H–C(8^{iii}), H–C(8^{v}), H–C(8^{vii}), H–C(8^{ix}), H–C(8^{xi}), H–C(8^{xiii})); 2.72 (*t*, *J* ≈ 10.6, H–C(8^{xv})); 2.64 (*t*, *J* ≈ 10.3, H–C(6), H–C(8^{ii}), H–C(8^{iv}), H–C(8^{vi}), H–C(8^{viii}), H–C(8^{x}),

H–C(8^{xii}), H–C(8^{xiv})); 2.48 (*d*, *J* = 1.9, H–C(1)); 2.35 (*d*, *J* = 2.5, HO–C(5), HO–C(7^{ii}), HO–C(7^{iv}), HO–C(7^{vi}), HO–C(7^{viii}), HO–C(7^{x}), HO–C(7^{xii}), HO–C(7^{xiv})); 1.95–1.91 (*m*, HO–C(8), HO–C(10^{ii}), HO–C(10^{iv}), HO–C(10^{vi}), HO–C(10^{viii}), HO–C(10^{x}), HO–C(10^{xii}), HO–C(10^{xiv})); 1.71–1.53 (*m*, 4 CH_2); 1.28–1.07 (*m*, several $(Me_2CH)_3Si$); 0.97 (*s*, Me_2C); 0.08 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 104.50 (*s*); 99.05 (*d*); 98.00 (several *t*); 96.72 (several *t*); 87.45 (*s*); 82.54 (8*d*); 80.74 (*d*); 79.48 (*d*); 78.78 (several *d*); 78.39 (several *d*); 76.65 (several *d*); 76.58 (several *s*); 76.19 (several *s*); 75.63 (several *s*); 74.93 (several *d*); 74.22 (several *s*); 72.15 (several *d*); 71.89 (several *d*); 71.22 (several *d*); 70.85 (several *s*); 68.64 (several *s*); 67.99 (several *s*); 67.33 (8*t*); 64.17 (*t*); 63.20 (several *t*); 62.36 (*t*); 56.65–56.34 (8*q*); 55.26 (8*q*); 38.19 (8*d*); 37.85 (*d*); 37.28 (7*d*); 30.72 (*t*); 25.36 (*t*); 23.10 (*q*); 22.97 (*q*); 19.59 (*t*); 18.33 (*s*); 18.09 (several *q*); 13.50 (several *d*); 13.10 (several *d*); 12.73 (several *d*); –4.47 (2*q*), 1*s* missing. MALDI-TOF-MS: 6581 ([*M* + K]$^+$), 6565 ([*M* + Na]$^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{{{1,1-dimethyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]propyl}dimethylsilyl}ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,-3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 6-*C*)-3,7-anhydro-1,2,6-trideoxy-1-*C*-iodo-4-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**56**). At 45°, a soln. of morpholine (8.5 µl, 0.098 mmol) in toluene (0.3 ml) was added dropwise to a soln. of I_2 (9.9 mg, 0.0392 mmol) in toluene (0.7 ml). The mixture was stirred for 0.5 h, treated with a soln. of **54** (64.1 mg, 9.8 µmol) in toluene (ml), stirred for further 10 h at 45°, cooled to 20°, and filtered through cotton. The filtrate was treated with sat. aq. Na_2SO_3 soln. (1 ml), stirred for 0.5 h, washed with brine, and dried ($MgSO_4$). Evaporation and FC (AcOEt/hexane 3 : 7) gave **56** (56.1 mg, 86%). White foam. R_f (AcOEt/hexane 1 : 1) 0.31. M.p. > 220° (dec.). IR ($CHCl_3$): 3601*w* (br.), 3410*w* (br.), 2962*s*, 2929*s*, 2871*s*, 2262*w*, 2179*w*, 1731*m*, 1468*m*, 1375*m*, 1293*m*, 1262*s*, 1141*m*, 1098*s*, 1017*s*, 935*w*, 883*m*, 818*s* (br.). ^{1}H-NMR (500 MHz, $CDCl_3$): 4.97 (*d*, *J* = 5.6, MeOC*H*); 4.90 (*d*, *J* = 6.2, 7 MeOC*H*); 4.79 (*d*, *J* = 5.6, MeOC*H*); 4.72 (*d*, *J* = 6.1, 7 MeOC*H*); 4.65 (*s*, 8 MeOCH_2); 4.56 (br. *m*, OCHO); 4.02 (*d*, *J* ≈ 9.2, H–C(3)); 3.99–3.35 (*m*, H–C(5$^{i–xv}$), 2 H–C(8), 2 H–C(10^{ii-xv}), CH_2O, CH_2OH, H–C(4), H–C(6$^{i–xv}$), H–C(5), H–C(7$^{i–xv}$), H–C(7), H–C(9$^{i–xv}$)); 3.45 (*s*, MeO); 3.44 (*s*, 7 MeO); 3.38 (*s*, MeO); 3.37 (*s*, 7 MeO); 2.82 (*t*, *J* ≈ 10.6, H–C(8^{i}), H–C(8^{iii}), H–C(8^{v}), H–C(8^{vii}), H–C(8^{ix}), H–C(8^{xi}), H–C(8^{xiii})); 2.72 (*t*, *J* ≈ 10.6, H–C(8^{xv})); 2.65 (*t*, *J* ≈ 10.3, H–C(6), H–C(8^{ii}), H–C(8^{iv}), H–C(8^{vi}), H–C(8^{viii}), H–C(8^{x}), H–C(8^{xii}), H–C(8^{xiv})); 2.35 (*d*, *J* = 2.5, HO–C(5), HO–C(7^{ii}), HO–C(7^{iv}), HO–C(7^{vi}), HO–C(7^{viii}), HO–C(7^{x}), HO–C(7^{xii}), HO–C(7^{xiv})); 1.95–1.91 (*m*, HO–C(8), HO–C(10^{ii}), HO–C(10^{iv}), HO–C(10^{vi}), HO–C(10^{viii}), HO–C(10^{x}), HO–C(10^{xii}), HO–C(10^{xiv})); 1.71–1.55 (*m*, 4 CH_2); 1.26–1.09 (*m*, several $(Me_2CH)_3Si$); 0.98 (*s*, Me_2C); 0.09 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 104.51 (*s*); 99.07 (*d*); 98.01 (several *t*); 96.72 (several *t*); 91.09 (*s*); 87.45 (*s*); 82.54 (8*d*); 79.48 (*d*); 78.78 (several *d*); 78.39 (several *d*); 76.64 (several *d*); 76.61 (several *s*); 76.19 (several *s*); 75.61 (several *s*); 74.95 (several *d*); 74.22 (several *s*); 72.15 (several *d*); 71.89 (several *d*); 71.22 (several *d*); 70.85 (several *s*); 68.64 (several *s*); 67.99 (several *s*); 67.33 (8*t*); 64.17 (*t*); 63.20 (several *t*); 62.36 (*t*); 56.68–56.38 (8*q*); 55.26 (8*q*); 38.19 (8*d*); 37.81 (*d*); 37.28 (7*d*); 30.72 (*t*); 25.36 (*t*); 23.10 (*q*); 22.97 (*q*); 19.59 (*t*); 18.33 (*s*); 18.09 (several *q*); 13.50 (several *d*); 13.16 (several *d*); 12.73 (several *d*); 5.09 (*s*); –4.47 (2*q*). MALDI-TOF-MS: 6707 ([*M* + K]$^+$), 6691 ([*M* + Na]$^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-{[(3-hydroxy-1,1-dimethylpropyl)dimethylsilyl]ethynyl}-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-*O*-(methoxymethyl)-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-*O*-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-*C*)-*

*5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,-3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 6-C)-3,7-anhydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol* (**57**). At −20°, a soln. of **54** (157.9 mg, 0.0239 mmol) and EtSH (24 µl, 5 vol-%) in dry CH_2Cl_2 (0.5 ml) was treated with $BF_3 \cdot Et_2O$ (0.3 µl, 2.387 µmol), and the soln. was allowed to warm to 0° during 1 h. Normal workup ($NaHCO_3$ soln./CH_2Cl_2) and FC (AcOEt/hexane 2 : 3 → 1 : 1) gave **50** (127.7 mg, 81%). White foam. R_f (AcOEt/hexane 1 : 1) 0.24. M.p. > 220° (dec.). IR ($CHCl_3$): 3599*w* (br.), 3431*w* (br.), 3010*m*, 2946*s*, 2891*s*, 2867*s*, 2262*w*, 2173*w*, 1733*m*, 1467*m*, 1371*m*, 1291*m*, 1251*m*, 1150*s*, 1119*s*, 1099*s*, 1067*s*, 1043*s*, 1021*s*, 920*m*, 883*s*, 655*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.97 (*d*, *J* ≈ 5.9, MeOC*H*); 4.90 (*d*, *J* = 6.2, 7 MeOC*H*); 4.79 (*d*, *J* = 5.6, MeOC*H*); 4.72 (*d*, *J* = 6.2, 7 MeOC*H*); 4.67 (*s*, MeOCH_2); 4.65 (*s*, 7 MeOCH_2); 4.02 – 3.37 (*m*, H–C(3), H–C(5^{i-xv}), 2 H–C(8), 2 H–C(10^{ii-xv}), CH_2O, CH_2OH, H–C(4), H–C(6^{i-xv}), H–C(5), H–C(7^{i-xv}), H–C(7), H–C(9^{i-xv})); 3.45 (*s*, MeO); 3.44 (*s*, 7 MeO); 3.39 (*s*, MeO); 3.37 (*s*, 7 MeO); 2.82 (*t*, *J* ≈ 10.6, H–C(8^{i}), H–C(8^{iii}), H–C(8^{v}), H–C(8^{vii}), H–C(8^{ix}), H–C(8^{xi}), H–C(8^{xiii})); 2.72 (*t*, *J* ≈ 10.6, H–C(8^{xv})); 2.64 (*t*, *J* ≈ 10.6, H–C(6), H–C(8^{ii}), H–C(8^{iv}), H–C(8^{vi}), H–C(8^{viii}), H–C(8^{x}), H–C(8^{xii}), H–C(8^{xiv})); 2.34 (*d*, *J* = 3.1, HO–C(5), HO–C(7^{ii}), HO–C(7^{iv}), HO–C(7^{vi}), HO–C(7^{viii}), HO–C(7^{x}), HO–C(7^{xii}), HO–C(7^{xiv})); 1.93 (*t*, *J* = 6.8, HO–C(8), HO–C(10^{ii}), HO–C(10^{iv}), HO–C(10^{vi}), HO–C(10^{viii}), HO–C(10^{x}), HO–C(10^{xii}), HO–C(10^{xiv})); 1.62 (*t*, *J* = 7.6, C$H_2$$CH_2OH$); 1.25 – 1.07 (*m*, several $(Me_2CH)_3Si$); 0.96 (*s*, Me_2C); 0.17 (*s*, Me_3Si); 0.11 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 104.38 (*s*); 102.01 (*s*); 98.01 (several *t*); 96.74 (several *t*); 87.62 (*s*); 82.27 (8*d*); 78.75 (several *d*); 78.40 (several *d*); 77.20 (*d*); 76.65 (several *d*); 76.57 (several *s*); 76.19 (several *s*); 75.39 (several *s*); 75.02 (several *d*); 74.94 (several *d*); 74.21 (several *s*); 72.18 (several *d*); 71.89 (several *d*); 70.84 (several *s*); 68.67 (several *s*); 68.01 (several *s*); 67.75 (several *s*); 67.37 (8*t*); 63.22 (several *t*); 56.37 (8*q*); 55.29 (8*q*); 38.18 (8*d*); 37.80 (*d*); 37.29 (7*d*); 18.31 (*s*); 18.09 (several *q*); 13.55 (several *d*); 12.76 (several *d*); −0.48 (3*q*); −4.29 (2*q*), 1*s* missing. MALDI-TOF-MS: 6571 ([*M* + K]$^+$), 6554 ([*M* + Na]$^+$).

*8,8″-(Buta-1,3-diyne-1,4-diyl)bis[5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropyl silyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-7,10-bis-O-(methoxymethyl)-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-1,2,3,4,8-pentadeoxy-6-O-(triisopropylsilyl)-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1 → 8-C)-5,9-anhydro-yl-(1 → 6-C)-3,7-anhydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-*D-glycero-D-gulo-*oct-1-ynitol]* (**60**). According to *GP5*, with **56** (10.9 mg, 1.63 µmol), **57** (10.7 mg, 1.63 µmol), [$Pd_2(dba)_3$] (0.4 mg, 0.49 µmol), CuI (0.1 mg, 0.49 µmol), $P(fur)_3$ (0.2 mg, 0.82 µmol), Et_3N (7 µl, 49.1 µmol), and CH_2Cl_2 (70 µl; 50 h). GPC (THF) gave **60** (7.3 mg, 35%). White to yellow foam. R_f (AcOEt/hexane 4 : 6) 0.34. IR ($CHCl_3$): 3597*w* (br.), 3431*w* (br.), 3008*m*, 2948*s*, 2893*s*, 2868*s*, 2262*w*, 2179*w*, 1730*m*, 1632*m*, 1465*m*, 1371*m*, 1292*m*, 1252*m*, 1150*s*, 1119*s*, 1098*s*, 1067*s*, 1042*s*, 1022*s*, 919*m*, 883*s*, 843*w*, 658*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.97

(*d*, $J \approx 5.9$, MeOC*H*); 4.90 (*d*, $J = 6.2$, 7 MeOC*H*); 4.79 (*d*, $J = 5.6$, MeOC*H*); 4.72 (*d*, $J = 6.2$, 7 MeOC*H*); 4.67 (*s*, MeOCH_2); 4.65 (*s*, 7 MeOCH_2); 4.02–3.37 (*m*, H–C(3), H–C(5^{i-xv}), 2 H–C(8), 2 H–C(10^{ii-xv}), CH_2O, CH_2OH, H–C(4), H–C(6^{i-xv}), H–C(5), H–C(7^{i-xv}), H–C(7), H–C(9^{i-xv})); 3.45 (*s*, 8 MeO); 3.39 (*s*, 8 MeO); 2.82 (*t*, $J \approx 10.6$, H–C(8^{i}), H–C(8^{iii}), H–C(8^{v}), H–C(8^{vii}), H–C(8^{ix}), H–C(8^{xi}), H–C(8^{xiii})); 2.72 (*t*, $J \approx 10.6$, H–C(8^{xv})); 2.64 (*t*, $J \approx 10.6$, H–C(6), H–C(8^{ii}), H–C(8^{iv}), H–C(8^{vi}), H–C(8^{viii}), H–C(8^{x}), H–C(8^{xii}), H–C(8^{xiv})); 2.34 (*m*, HO–C(5), HO–C(7^{ii}), HO–C(7^{iv}), HO–C(7^{vi}), HO–C(7^{viii}), HO–C(7^{x}), HO–C(7^{xii}), HO–C(7^{xiv})); 1.93 (*m*, HO–C(8), HO–C(10^{ii}), HO–C(10^{iv}), HO–C(10^{vi}), HO–C(10^{viii}), HO–C(10^{x}), HO–C(10^{xii}), HO–C(10^{xiv})); 1.25–1.07 (*m*, several ($Me_2CH)_3Si$); 0.17 (*s*, Me_3Si). MALDI-TOF-MS: 12805 ($[M + Na + 8]^+$).

*5,9-Anhydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→8-*C*)-5,9-anhydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*deca-1,3-diynitol-1-yl-(1→6-*C*)-3,7-anhydro-1,2,6-trideoxy-*D-glycero-D-gulo-*oct-1-ynitol* (**63**). A soln. of **57** (22.4 mg, 3.43 μmol) in Et_3N (0.1 ml) and MeOH (0.2 ml) was stirred for 10 h at 22°. Evaporation gave **61** which was dissolved in CH_2Cl_2/MeOH 1:1 (0.2 ml) and treated with 0.25M NaOMe (0.01 ml). After 8 h, *Amberlite IR-120* was added. Filtration and evaporation gave **62** (20.6 mg, 95%). A soln. of **62** (20.6 mg, 3.26 μmol) in 0.3N HCl was stirred at 55° for 62 h. The soln. was cooled to 0°, filtered, and washed with hexane, cold H_2O, and Et_2O. Drying under HV gave **63** (10.0 mg, 99%) as an amorphous powder. M.p. 212–225° (dec.). $[\alpha]_D^{25} = -52.4$ ($c = 0.9$, (D_6)DMSO). IR (KBr): 3538*s* (br.), 3284*s* (br.), 2952*s*, 2904*s*, 2261*m*, 2173*w*, 1720*w*, 1704*w*, 1617*w*, 1459*m*, 1408*m*, 1377*m*, 1302*m*, 1292*m*, 1222*w*. ^{1}H-NMR (500 MHz, (D_6)DMSO): 5.66 (*d*, $J = 5.6$, 14 OH); 5.58 (*d*, $J \approx 5.9$, OH); 5.57 (*d*, $J \approx 5.9$, 15 OH); 5.51 (*d*, $J = 6.4$, OH); 5.37 (*d*, $J = 6.1$, OH); 4.84 (*t*, $J = 5.6$, HO–C(8), HO–C(10^{i-xiv})); 4.74 (*t*, $J = 5.9$, HO–C(10^{xv})); 4.02 (br. *d*, $J = 9.2$, H–C(5^{i-xiv})); 4.00 (br. *d*, $J \approx 9.2$, H–C(5^{xv})); 3.88 (*dd*, $J \approx 9.3$, 1.8, H–C(3)); 3.68–3.29 (*m*, 2 H–C(8), 2 H–C(10^{i-xv}), H–C(5), H–C(7^{i-xiv}), H–C(7), H–C(9^{i-xiv}), H–C(1)); 3.05–3.00 (*m*, H–C(4), H–C(6^{i-xiv})); 2.95 (*d*, $J = 2.2$, H–C≡C–C(8^{xv})); 2.54–2.50 (*m*, H–C(6), H–C(8^{i-xiv})); 2.30 (*td*, $J \approx 10.3$, 2.3, H–C(8^{xv})). ^{13}C-NMR (75 MHz, (D_6)DMSO): 82.74 (*d*); 82.12 (*d*); 79.76 (several *d*); 79.76 (several *d*); 79.71–79.68 (several *s*); 79.50 (several *s*); 79.21 (several *d*); 75.91 (*s*); 75.81 (*s*); 75.69 (several *s*); 75.61 (several *s*); 75.21 (several *d*); 74.82 (several *d*); 74.78 (several *d*); 74.01 (several *s*); 73.93–73.90 (several *d*); 70.81 (several *d*); 70.78 (several *d*); 69.59 (several *s*); 68.99 (several *s*); 66.71 (several *s*); 62.02 (several *t*); 61.98 (several *t*); 37.59 (several *d*); 37.20 (2*d*). MALDI-TOF-MS: 3132 ($[M + Na]^+$).

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