# 77. Oligosaccharide Analogues of Polysaccharides

Part 12[1])

## Synthesis of 'Acetyleno-saccharide'-Derived Cyclodextrin Analogues

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Dedicated to Prof. Dr. *Dieter Seebach* on the occasion of his 60th birthday

(11.III.97)

'Acetyleno-oligosaccharides' in which two terminal ethynyl substituents enclose an angle (significantly) below 180° are building blocks for the preparation of cyclodextrin analogues. This is illustrated by the preparation of a cyclotrimer and a cyclotetramer; the $C_3$-symmetrical cyclotrimer **18** (*Scheme 1*) was synthesized in 13 steps (7.7%) and the $C_4$-symmetrical cyclotetramer **51** (*Scheme 3*) in 14 steps (4.3%) from the known dialkyne **21**. The solubilities of **18** and **51** in $H_2O$ were determined by gravimetry; a saturated solution is 130 mM in the trimer **18** and 12.8 mM in the tetramer **51**. The dependence of the optical rotation of **18** and **51** in $H_2O$ on the concentration, and the concentration dependence of the $^1$H-NMR chemical shift of the signals of the CH groups of **51** ($D_2O$) suggest that there is no significant self-association of **18** and **51**.

**Introduction.** – Cyclodextrins (CDs) and their derivatives have been used as hosts to study noncovalent interactions with a large variety of guest molecules [2] [3][2]). CDs form a series of enantiomerically pure, $H_2O$-soluble homologues with increasing size of the cavity, and are conveniently derivatized at some or all OH groups[3]). Most of such derivatizations hardly influence the shape of the cavity, as it is required for a specific recognition of guest molecules. The shape and size of the cavity are modified to a much larger extent, *e.g.*, by changing the conformation and/or the configuration of the glycopyranosyl residues, as shown among others by the per(3,6-anhydro)cyclomaltooligosaccharides[4]) [14–16] or β-cycloaltrin [17]. Formal replacement of one or several glycoside residues by non-saccharide moieties also leads to an incisive change of the cavity, as illustrated by the 'glycophanes' [18–20].

We have reported the synthesis of analogues of cellooligosaccharides from 1,4-*trans*-diethynylated 1,5-anhydroglucose monomers [21–24]. The two alkynyl groups of these monomers enclose an angle of *ca.* 180°. Diethynylated monomers where the two alkynyl groups enclose an angle (significantly) below 180° should allow the construction of cyclic oligosaccharide analogues, independently of the location of the two ethynyl substituents.

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[1]) Part 11: [1].

[2]) They have also served as enzyme models [4–11].

[3]) For review articles, see [2] [3] [12].

[4]) A detailed overview of modifications that lead to a profound change of shape is given by *Ashton et al.* [13].

The cyclization products are CD analogues where one or more glycosidic O-atoms are formally substituted each by a buta-1,3-diyne-1,4-diyl moiety[5]). Variation of the number of monomeric units, their nature (size, position of the alkynyl groups, configuration), the mode of their connection (homo- or heterocoupled), and subsequent modifications should lead to a large variety of CD analogues.

We report the preparation of the trimer **18** and the tetramer **51**, derived from 1,4-*cis*-diethynylated 1,5-anhydroglucose [26]. These cyclo-oligomers represent a first type of CD analogues, derived from dialkynylated monosaccharides by exclusive heterocoupling.

The preparation of the linear and exclusively heterocoupled precursors of the CD analogues requires a regioselective deprotection, activation, and cross-coupling, similarly to the synthesis of analogues of cellooligosaccharides.

**Results and Discussion.** – For the cross-coupling, we applied the modification of the *Cadiot-Chodkiewicz* reaction that was devised for the cross-coupling of diequatorial glucose-derived dialkynes [23]. Depending upon the exact reaction conditions, either iodo- or bromoalkynes have led to higher yields of diynes [24] [27] [28]. We first coupled the iodoalkyne **4** with the known dialkyne **1** [26] to obtain the linear dimer **5** (*Scheme 1*). The iodoalkyne **4** was conveniently obtained from the known dialkyne **2** [26] in a yield of 88% by base-promoted selective desilylation [27] [29] and deacetylation, followed by iodination of the product **3** with $I_2$/morpholine [22] [30]. Cross-coupling of **1** and **4** led to a mixture of the heterodimer **5** (66%) and the homodimers **6** (17%) and **7** (14%)[6]). As expected, the choice of monomers with strongly differing polarities led to a facile chromatographic separation of the products. Similarly to the monomer **2**, the heterodimer **5** was converted to the mono-*C*-desilylated diol **8** and further to the iodoalkyne **9**. Coupling of the monomer **1** and the dimer **9** led to the trimer **10** (65%), and to the homocoupled dimer **7** (13%) and tetramer **11** (12%). De-*C*-trimethylsilylation and deacetylation of the trimer **10** (→ **12**) followed by iodination provided **13**. Remarkably, treatment of this iodoalkyne with CsF led exclusively to a mixture (*ca.* 1:1) of the expected iodoalkyne **14** and its regioisomer **15**, suggesting that **15** is formed by intramolecular transiodination. Hence, these iodoalkynes easily adopt conformations where the terminal alkynyl and iodoalkynyl groups are close to each other, auguring well for the cyclization. Indeed, slow addition of the mixture **14**/**15** to a dilute solution of $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone = 1,5-diphenylpenta-1,4-dien-3-one), $P(furyl)_3$, CuI, and $Et_3N$ in benzene or DMSO gave the cyclotrimer **16** in a yield of 65%.

Deallylation of the cyclotrimer **16** proved difficult. Acetolytic deallylation of the monomer **1** as model compound proved slow and incomplete[7]), whereas treatment of **1** with $FeCl_3$ in $CH_2Cl_2$ yielded 65% of the diol **20**. Similarly, $FeCl_3$ in $CH_2Cl_2$ trans-

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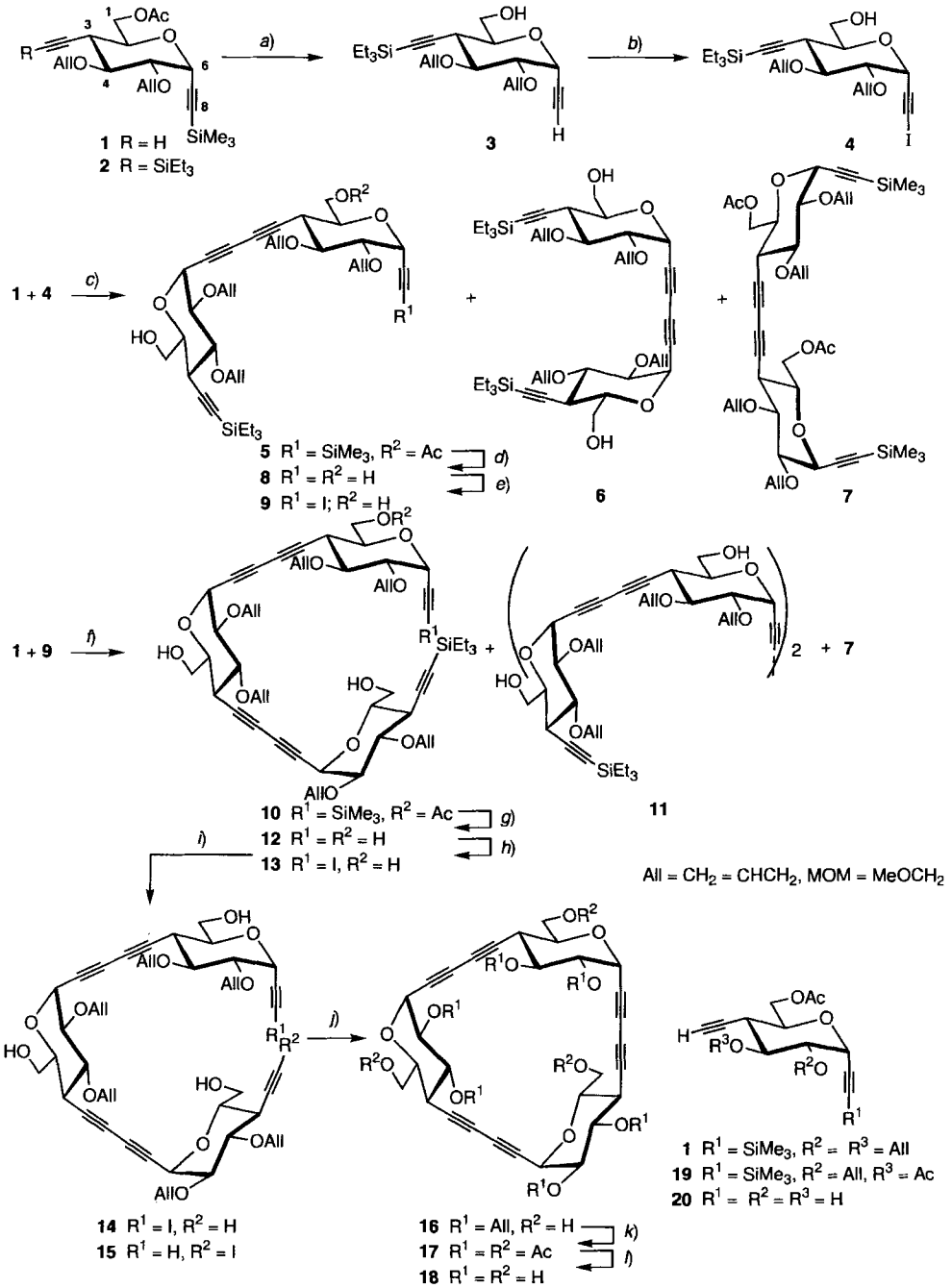
[5]) The buta-1,3-diyne-1,4-diyl moiety (with a length of *ca.* 6.7 Å, see below) may also be considered as a formal substitute of a 4-oxy-glucopyranosylidene unit; in α-CD, the distance between C(1″) and C(4) is *ca.* 7.0 Å [25].

[6]) In contrast to the original procedure, the reaction time was prolonged until both starting materials were consumed. This led to the formation of two homodimers instead of only one, as described in [24]. The separation of these products from each other proved easier than the separation of the products from starting material.

[7]) On a small scale (10 mg), $Ac_2O/FeCl_3$ selectively cleaved the 4-allyloxy group of **1**, yielding *ca.* 65% of the diacetate **19**.

*Scheme 1*




*a*) MeOH/$H_2O$/$Et_3N$ 10:4:1; 96%. *b*) $I_2$, morpholine, PhH, 45°; 92%. *c*) [$Pd_2(dba)_3$], P(furyl)$_3$), CuI, 1,2,2,6,6-pentamethylpiperidine, DMSO; 66% of **5**, 17% of **6**, 14% of **7**. *d*) As *a*); 88%. *e*) As *b*); 91%. *f*) As *c*); 13% of 7, 65% of **10**, 12% of **11**. *g*) NaOH, MeOH; 98%. *h*) As *b*); 74%. *i*) CsF, DMF/MeOH 5:1. *j*) [$Pd_2(dba)_3$], P(furyl)$_3$, CuI, $Et_3N$, PhH, 65% (from **13**). *k*) $FeCl_3$, $CH_2Cl_2$; $Ac_2O$, py; 39%. *l*) NaOMe, MeOH; 99%.

formed **16** into the hexol **18**, but the purification of **18** was cumbersome; it was finally obtained in a yield of 30 to 39% *via* the acetate **17**.

The cumbersome purification of **18** and the low yields of **17** obtained by deallylation of larger amounts (> 20 mg) of **16** prompted us to substitute the *O*-allyl by *O*-acetyl and *O*-methoxymethyl groups; both have been removed from 'acetyleno-oligosaccharides' in good yields [22]. We also chose the bromo instead of a iodoalkyne, and the orthogonal *C*-$SiMe_3$ and *C*-$GeMe_3$ protecting groups [24] [31]. They allow a binomial synthesis of the linear oligomers, a strategy that is advantageous for the preparation of larger CD analogues.

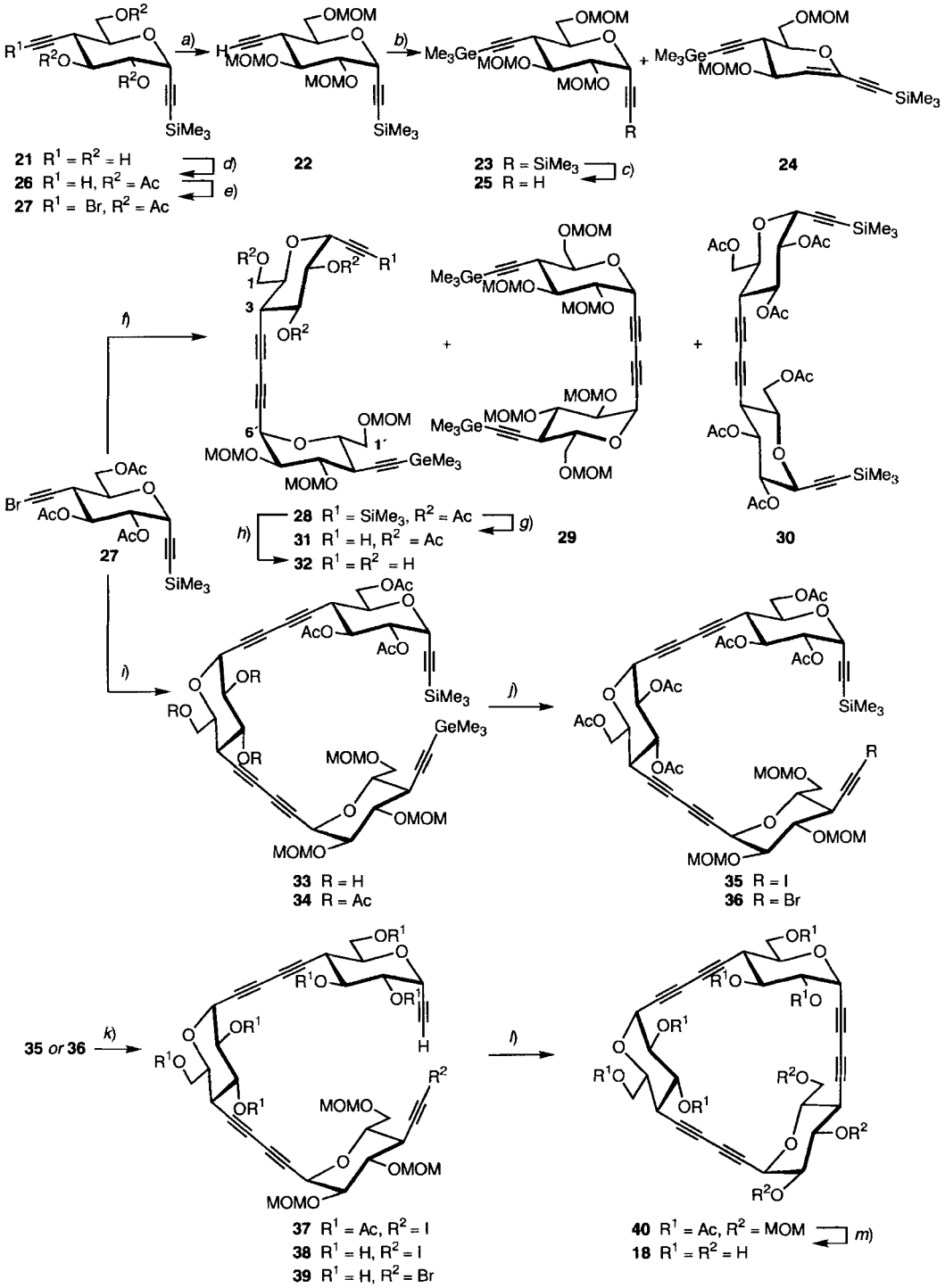
The desired monomers **25** and **27** (*Scheme 2*), again differing in their polarity, were prepared from the triol **21**, which is available in 8 steps and a yield of 36% from levoglucosan [26]. Methoxymethylation of **21** gave **22** (75–79%, *cf.* [27]). Treatment of **22** with BuLi and then with $Me_3GeCl$ yielded 75% of **23**, besides 17% of the enyne **24** as the major by-product. Substituting BuLi by freshly prepared EtMgBr in THF increased the yield of the (trimethylgermyl)alkyne **23** to 90%. In addition to **23**, we isolated 6% of starting material and 1% of **24**. Desilylation of **23** provided the (trimethylgermyl)-protected monomer **25**. The other monomer, the bromoalkyne **27**, was obtained in 92% by acetylation of the triol **21** and bromination of the resulting triacetate **26** with $CBr_4/PPh_3$ according to *Wagner et al.* [32]. Coupling of **25** with **27** gave the crystalline heterodimer **28** (72%) and the homodimers **29** (13%) and **30** (11%). Desilylation of **28** with CsF/DMF/MeOH yielded 95% of (trimethylgermyl)alkyne **31**. Coupling of **31** with the monomeric bromoalkyne **27** proceeded only above 40–45° and gave 55% of the trimer **34**, whereas coupling of **27** with the deacetylated dimer **32** (also obtained from **28**) gave 68% of the trimer **33** at room temperature[8]). Then, **33** was acetylated to give **34** (98%).

Starting from the trimer **34**, we prepared both, the iodoalkynes **37** and **38**, and the bromoalkyne **39**, and compared their cyclization. The iodoalkyne **35** was prepared from the (trimethylgermyl)alkyne **34** by iododegermylation with CuBr/NIS (*N*-iodosuccinimide) (96%; *cf.* [31] [33]). Treatment of **35** with CsF afforded exclusively the desilylated iodoalkyne **37**; no transiodination was observed. Slow addition of **37** to a dilute solution of $[Pd_2(dba)_3]$, $P(furyl)_3$, CuI, and $Et_3N$ in DMSO provided only 8% of the cyclotrimer **40**. As the protecting groups in the trimer appear to strongly influence the

[8]) This confirms observations that the yields of the cross-coupling of diequatorially substituted dialkynes depend on the nature of the protecting groups [28]; this is possibly due to an neighbouring group interaction with the metal(s) of an intermediary $\eta^2$-complex [23].

Legend for *Scheme 2*. *a*) $(MeO)_2CH_2$, $CH_2Cl_2$, $P_2O_5$; 79%. *b*) EtMgBr, THF, 35°, $Me_3GeCl$; 6% of **22**, 90% of **23**, 1% of **24**. *c*) CsF, DMF MeOH 5:1; 96%. *d*) $Ac_2O$, py; 95%. *e*) $CBr_4$, $PPh_3$, $CH_2Cl_2$; 97%. *f*) **25**, $[Pd_2(dba)_3]$, CuI, 1,2,2,6,6-pentamethylpiperidine, DMSO; 72% of **28**, 13% of **29**, 11% of **30**. *g*) As *c*); 95%. *h*) NaOMe, MeOH, THF; 88%. *i*) **31** or **32**, $[Pd_2(dba)_3]$, $P(furyl)_3$, CuI, 1,2,2,6,6-pentamethylpiperidine, DMSO; 55% of **34** (from **31**); 68% of **33** (from **32**). *j*) NIS or NBS, CuBr, acetone; 96% of **35** (with NIS); 98% of **36** (with NBS). *k*) **35**, CsF, DMF MeOH 5:1; 98% of **37**. **35** or **36**, NaOMe, MeOH, THF; 98% of **38** (from **35**); 98% of **39** (from **36**). *l*) **37**, $[Pd_2(dba)_3]$, $P(furyl)_3$, CuI, $Et_3N$, DMSO; 8% (from **37**). **38** or **39**, $[Pd_2(dba)_3]$, $P(furyl)_3$, CuI, $Et_3N$, DMSO, followed by $Ac_2O$ py; 35% (from **38**); 67% (from **39**). *m*) NaOMe, MeOH, THF, 0°; HCl, MeOH, reflux, 94%.

*Scheme 2*


21 R1 = R2 = H
26 R1 = H, R2 = Ac
27 R1 = Br, R2 = Ac
22
23 R = SiMe3
25 R = H
24
28 R1 = SiMe3, R2 = Ac
31 R1 = H, R2 = Ac
32 R1 = R2 = H
29
30
33 R = H
34 R = Ac
35 R = I
36 R = Br
37 R1 = Ac, R2 = I
38 R1 = H, R2 = I
39 R1 = H, R2 = Br
40 R1 = Ac, R2 = MOM
18 R1 = R2 = H
35 or 36

cyclization, we also examined the cyclization of the trimeric hexol **38**, obtained by treating the trimeric iodoalkyne **35** with NaOMe/MeOH. Again, no transiodination was observed. Cyclization of **38** proceeded in higher yields, but the isolation of the product was difficult[9]). Filtration of the crude product through silica gel and acetylation provided 35% of the cyclotrimer **40**[10]). Better yields were obtained by cyclizing the bromoalkyne **39**, which was prepared by bromodegermylation [31] [33] of the trimer **34** and deacetylation and desilylation of the resulting bromoalkyne **36**; slow addition of **39** to a dilute solution of $[Pd_2(dba)_3]$, $P(furyl)_3$, CuI, and $Et_3N$ in DMSO, followed by acetylation of the crude product yielded 67% of the acetylated cyclotrimer **40**. Deprotection of **40** with NaOMe/MeOH and then with HCl/MeOH gave the cyclotrimer **18** (94%), identical to the product resulting from the deprotection of **17**.

The solid state structure of the dimer **28** was established by X-ray analysis[11]) (*Fig.*), demonstrating that both pyranose rings adopt a flattened $^4C_1$ conformation, as shown by the values of 68.1, −62.7, 65.8, and −68.8° for the dihedral angles C(2)–O–C(6)–C(7), C(4)–C(5)–C(6)–C(7), C(2′)–O–C(6′)–C(7′), and C(4′)–C(5′)–C(6′)–C(7′). The bonds of the two terminal ethynyl groups define vectors that enclose an angle of 167°. The C–C and the C≡C bond lengths are within the normal values for single and triple bonds, and the butadiyne moiety is nearly linear; the distance between C(3) and C(6′) is 6.68 Å. While the $AcOCH_2$ group adopts a *gg* conformation, the $MeOCH_2OCH_2$ group adopts a *gt* conformation.

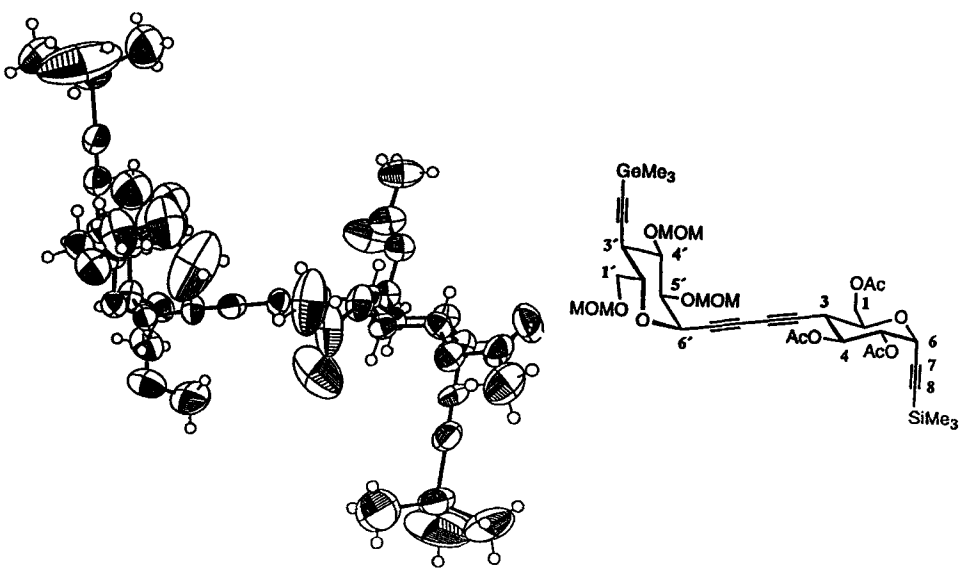



Figure. *X-Ray structure of the dimer* **28**. MOM = $MeOCH_2$.

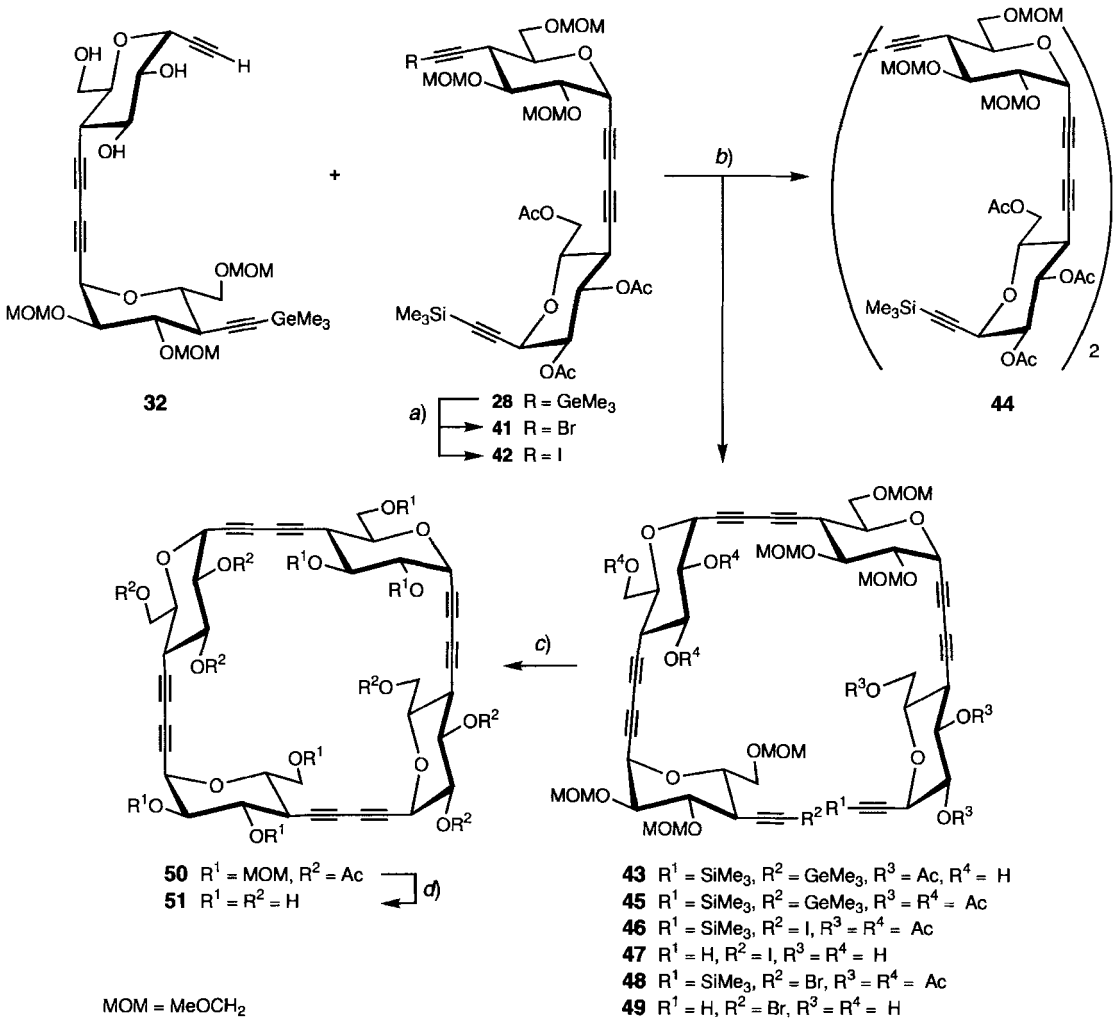
[9]) No starting material remained, but several considerably more polar products were formed.

[10]) At a concentration < 1.6 mM. The yield was not increased by performing the reaction at a concentration of < 0.6 mM.

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

As it is found in the majority of cases [34], the H–C(1) signal of **28** at lower field (4.47 ppm; H′–C(1) at 4.29 ppm) shows the smaller vicinal coupling ($J(1,2) = 2.4$ *vs.* 4.5 Hz). The opposite relation is observed for the H–C(1′) signals (H–C(1′) at 3.91 ppm, $J(1,2) = 4.0$ Hz; H′–C(1′) at 3.77 ppm, $J(1,2) = 2.0$ Hz). This correlation was observed for all $MeOCH_2OCH_2$ residues.

*Scheme 3*




*a*) NBS or NIS, CuBr, acetone; 90% of **41** (with NBS); 93% of **42** (with NIS). *b*) **32**, $[Pd_2(dba)_3]$, $P(furyl)_3$, CuI, $Et_3N$, DMSO; 56% of **43** (from **41**); 77% of **43** and 4% of **44** (from **42**). *c*) $[Pd_2(dba)_3]$, $P(furyl)_3$, CuI, $Et_3N$, DMSO, followed by $Ac_2O$, py; 29% (from **47**); 57% (from **49**). *d*) NaOMe, MeOH, THF, 0°; HCl, MeOH, reflux; 89%.

For the preparation of the cyclotetramer **51** (*Scheme 3*), we again compared the cyclization of iodo- and bromoalkynes. The synthesis of their tetrameric precursor **43** requires, on the one hand, the protodesilylation of the dimer **28** (see above) and, on the

other hand, its halodegermylation, followed by the coupling of the resulting alkyne and haloalkyne. Bromodegermylation [33] of **28** yielded 90% of the bromoalkyne **41**. Coupling of **41** with the alkyne **32** (see *Scheme 2*) proceeded very slowly and did not go to completion. Substituting the bromo- by the iodoalkyne **42** (from **28** with CuBr/NIS) led to a significantly faster coupling; the heterotetramer **43** was obtained in a yield of 77%, besides the homotetramer **44** (4%). Acetylation of **43** (→ **45**), followed by iododegermylation yielded 92% of the iodoalkyne **46**. Treatment of **46** with NaOMe/MeOH provided the de-*C*-silylated hexol **47**. Slow addition of **47** to a dilute solution of $[Pd_2(dba)_3]$, $P(furyl)_3$, CuI, and $Et_3N$ in DMSO[10]), followed by acetylation of the crude product, yielded 29% of the acetylated cyclotetramer **50**. As in the preparation of the cyclotrimer, the tetrameric bromoalkyne **49** (prepared from **45** *via* **48**) proved superior to the iodoalkyne **47**; cyclization and acetylation, as above, yielded 57% of the acetylated cyclotetramer **50**. Treatment of **50** with NaOMe/MeOH and then with HCl/MeOH led to 89% of the cyclotetramer **51**.

The solubilities of **18** and **51** in $H_2O$ (at 23°) were determined by gravimetry; a saturated solution is 130 mM in the trimer **18** and 12.8 mM in the tetramer **51**. Both compounds are also soluble in DMSO, MeOH, and pyridine. The trimer **18** is stable up to 150° for 5 min, and the tetramer **51** up to 200°. The optical rotation of the trimer **18** was determined at 25°, 45°, and 60° and of the tetramer **51** at 25° at several concentrations. Both compounds show a linear dependence of the optical rotation ($\alpha_D$) on the concentration up to almost saturated solutions, suggesting that there is no significant self-association of the CD analogues **18** and **51** in $H_2O$. This is confirmed by the observation that the $^1$H-NMR spectra of **51** in $D_2O$ at concentrations between 3.6 and 11 mM show no significant change in the chemical shift for the CH groups.

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support, and Dr. *B. Schweizer* for the X-ray analysis.

## Experimental Part

*General.* Solvents were distilled before use: THF and toluene from Na and benzophenone, $CH_2Cl_2$ from $CaH_2$, MeOH from Mg, and DMSO from 4 Å molecular sieves. Acetone was stored over 4 Å molecular sieves. *N*-Iodo- and *N*-bromosuccinimide (NIS and NBS, resp.) were sublimed prior to use. Reactions were performed under Ar or $N_2$. Workup: The mixture was diluted with the indicated solvent and sat. aq. $NH_4Cl$ soln., the aq. layer extracted (3–5 times) with the indicated solvent, and the combined org. phase washed once with brine, dried ($MgSO_4$), and evaporated. For the determination of the solubility, $H_2O$ was purified by a *Millipore* apparatus. Qual. TLC: precoated silica-gel plates (*Merck* silica gel *60* $F_{254}$), detection by spraying with 5% $H_2SO_4$ in EtOH followed by heating to *ca.* 200°. Flash chromatography (FC): silica gel *Merck 60* (0.04–0.063 mm). M.p.s: uncorrected. Optical rotations: 1-dm cell at 25° (or at the indicated temp.), 589 nm. UV Spectra ($\lambda_{max}$ in nm ($\varepsilon$)): 1-cm quartz cell. FT-IR Spectra (in $cm^{-1}$): *ca.* 2% in $CHCl_3$ or KBr. $^1$H- and $^{13}$C-NMR Spectra: 300, 400, or 500 MHz ($^1$H); 75, 100, or 125 MHz ($^{13}$C), the $^1$H- and $^{13}$C-assignments for the pseudooligosaccharides are based on the comparison with the data obtained from the monomers. Mass spectra: chemical ionisation (CI) with $NH_3$; fast atom bombardment (FAB), or matrix-assisted laser-desorption ionization mass spectrometry (MALDI-MS; *cf.* [24]).

*4,5-Di-*O*-allyl-2,6-anhydro-3,7,8-trideoxy-3-*C*-[2-(triethylsilyl)ethynyl]*-D-glycero-L-gulo-*oct-7-ynitol* (**3**). A soln. of **2** (0.296 g, 0.63 mmol) in MeOH/$H_2$/$Et_3N$ 10:4:1 (7.5 ml) was stirred for 7 h at r.t. and neutralized with a sat. aq. $NH_4Cl$ soln. Workup ($Et_2O$) and FC (toluene/AcOEt 9:1) gave **3** (0.236 g, 96%). Colourless oil. $R_f$ (toluene/AcOEt 10:1) 0.22. $[\alpha]_D^{20} = 32.1$ ($c = 0.62$, $CHCl_3$). IR: 3596*w*, 3305*m*, 3083*w*, 3007*m*, 2957*s*, 2935*m*, 2913*m*, 2875*s*, 2173*w*, 1646*w*, 1603*w*, 1495*w*, 1458*m*, 1414*m*, 1345*m*, 1076*s* (br.), 1018*s* (br.), 932*m* (br.), 827*w*, 645*m*

(br.). $^1$H-NMR (400 MHz, $CDCl_3$): 6.04–5.88 (*m*, 2 C*H*=CH$_2$); 5.33–526 (*m*, CH=C*H*$_2$); 5.21–5.13 (*m*, CH=C*H*$_2$); 4.81 (*dd*, *J* = 2.3, 5.7, H–C(6)); 4.43–4.34 (*m*, 2 allyl. H); 4.25–4.13 (*m*, 2 allyl. H); 3.97 (*ddd*, *J* = 2.7, 5.5, 10.4, H–C(2)); 3.92 (*ddd*, *J* = 2.7, 6.7, 11.7, addn. of $D_2O$ → *dd*, *J* ≈ 2.7, 11.7, H–C(1)); 3.75 (*td*, *J* ≈ 5.9, 11.7, addn. of $D_2O$ → *dd*, *J* ≈ 5.9, 11.7, H′–C(1)); 3.70 (*dd*, *J* = 9.3, 10.3, H–C(4)); 3.34 (*dd*, *J* = 5.7, 9.3, H–C(5)); 2.60 (*d*, *J* = 2.3, H–C(8)); 2.56 (*t*, *J* = 10.4, H–C(3)); 1.86 (*t*, *J* ≈ 6.5, exchange with $D_2O$, OH–C(1)); 0.98 (*t*, *J* = 7.8, 3 Me); 0.58 (*q*, *J* = 7.8, 3 MeC*H*$_2$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 135.10, 134.55 (2*d*, 2 *C*H=CH$_2$); 117.76, 116.83 (2*t*, 2 CH=*C*H$_2$); 104.00 (*s*, *C*≡CSi); 86.10 (*s*, C≡*C*Si); 79.94, 78.17 (2*d*, C(4), C(5)); 78.37 (*d*, C(8)); 77.48 (*s*, C(7)); 74.55 (*t*, 1 allyl. C); 74.52 (*d*, C(2)); 72.48 (*t*, 1 allyl. C); 67.05 (*d*, C(6)); 63.61 (*t*, C(1)); 38.11 (*d*, C(3)); 7.46 (*q*, 3 Me); 4.36 (*t*, 3 MeC*H*$_2$). CI-MS ($NH_3$): 408 (100, $[M + NH_4]^+$). Anal. calc. for $C_{22}H_{34}O_4Si$ (390.60): C 67.65, H 8.77; found: C 67.64, H 9.08.

*4,5-Di-*O*-allyl-2,6-anhydro-3,7,8-trideoxy-8-C-iodo-3-*C*-[2-(triethylsilyl)ethynyl]-*D*-glycero-*L*-gulo-oct-7-ynitol* (**4**). A soln. of $I_2$ (64.9 mg, 0.51 mmol) in benzene (1.5 ml) was treated with morpholine (0.11 ml, 1.28 mmol) at r.t. under Ar and heated to 45° for 10 min. After the dropwise addn. of a soln. of **3** (50 mg, 0.13 μmol) in benzene (2 ml), stirring was continued overnight. The mixture was cooled to r.t., diluted with toluene, washed with 10% aq. $Na_2S_2O_3$ soln., sat. aq. $NaHCO_3$ soln., and brine, dried ($MgSO_4$), and evaporated. FC (hexane/$Et_2O$ 4:1) gave **4** (61 mg, 92%) as a colourless oil, which crystallized from hexane. $R_f$ (toluene/AcOEt 4:1) 0.50. M.p. 60–61°. $[\alpha]_D^{25}$ = 90.9 (*c* = 0.90, $CHCl_3$). IR: 3599*w*, 3083*w*, 3007*m*, 2956*s*, 2935*m*, 2912*m*, 2875*m*, 2175*m*, 1646*w*, 1602*w*, 1457*m*, 1414*w*, 1343*m*, 1139*m*, 1075*s*, 1018*s*, 932*m*, 909*w*, 858*w*, 835*w*, 649*w*, 630*w*. $^1$H-NMR (500 MHz, $CDCl_3$): 6.02–5.86 (*m*, 2 C*H*=CH$_2$); 5.32–5.26 (*m*, CH=C*H*$_2$); 5.20–5.14 (*m*, CH=C*H*$_2$); 4.94 (*d*, *J* = 5.7, H–C(6)); 4.43–4.33 (*m*, 2 allyl. H); 4.22–4.11 (*m*, 2 allyl. H); 3.94–3.90 (*m*, H–C(1), H–C(2)); 3.75–3.73 (*m*, H′–C(1)); 3.65 (*dd*, *J* = 9.4, 10.2, H–C(4)); 3.30 (*dd*, *J* = 5.7, 9.2, H–C(5)); 2.55 (*t*, *J* = 10.3, H–C(3)); 1.84–1.83 (*m*, OH–C(1)); 0.99 (*t*, *J* = 8.0, 3 Me); 0.59 (*q*, *J* = 8.0, 3 MeC*H*$_2$). $^{13}$C-NMR (125 MHz, $CDCl_3$): 135.06, 134.59 (2*d*, 2 *C*H=CH$_2$); 117.62, 116.81 (2*t*, 2 CH=*C*H$_2$); 104.01 (*s*, *C*≡CSi); 89.47 (*s*, C(7)); 86.19 (*s*, C≡*C*Si); 79.99, 78.45 (2*d*, C(4), C(5)); 74.76 (*d*, C(2)); 74.56 (*t*, 1 allyl. C); 72.35 (*t*, 1 allyl. C); 68.95 (*d*, C(6)); 63.62 (*t*, C(1)); 38.01 (*d*, C(3)); 7.48 (*q*, 3 Me); 5.83 (*s*, C(8)); 4.36 (*t*, 3 MeC*H*$_2$). CI-MS ($NH_3$): 534 (100, $[M + NH_4]^+$). Anal. calc. for $C_{22}H_{33}IO_4Si$ (516.49): C 51.16, H 6.44; found: C 51.35, H 6.28.

*Coupling Reaction of* **1** *with* **4**. A degassed soln. of **1** (302 mg, 0.77 mmol), [$Pd_2$(dba)$_3$] (10.6 mg, 23.2 μmol), P(furyl)$_3$ (10.9 mg, 46.4 μmol), and CuI (3.7 mg, 19.3 μmol) in DMSO (7 ml) was treated with 1,2,2,6,6-pentamethylpiperidine (420 μl, 2.32 mmol) at r.t. under Ar. Then a soln. of **4** (400 mg, 0.77 mmol) in DMSO (4 ml) was added dropwise within 4 h. After 8 h stirring, workup ($Et_2O$) and FC (toluene/AcOEt 15:1) gave **7** (86.3 mg, 14%) and **5** (395.5 mg, 66%) as oils, and **6** (102.4 mg, 17%) as a white solid.

*1-*O*-Acetyl-4,5-di-*O*-allyl-2,6-anhydro-3,7,8-trideoxy-3-*C*-{4,5-di-*O*-allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3-*C*-[2-(triethylsilyl)ethynyl]-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-yl}-8-C-(trimethylsilyl)-*D*-glycero-*L*-gulo-oct-7-ynitol* (**5**): $R_f$ (toluene/AcOEt 12:1) 0.17. $[\alpha]_D^{25}$ = 126.6 (*c* = 0.10, $CHCl_3$). IR: 3594*w*, 3083*w*, 3007*w*, 2958*m*, 2912*m*, 2875*m*, 2255*w*, 2172*w*, 1740*s* (br.), 1646*w*, 1602*w*, 1457*m*, 1421*m*, 1367*m*, 1332*m*, 1261*s*, 1096*s* (br.), 1017*s* (br.), 932*m*, 846*s*, 633*w*. $^1$H-NMR (500 MHz, $CDCl_3$): 6.03–5.86 (*m*, 4 C*H*=CH$_2$); 5.46–5.26 (*m*, 2 CH=C*H*$_2$); 5.22–5.14 (*m*, 2 CH=C*H*$_2$); 4.88 (br. *d*, *J* = 5.8, H–C(6′)); 4.80 (*d*, *J* = 5.6, H–C(6)); 4.44–4.32 (*m*, 4 allyl. H, H–C(2)); 4.26 (*dd*, *J* = 4.8, 12.1, H–C(1)); 4.15 (*dd*, *J* = 1.5, 12.1, H′–C(1)); 4.23–4.10 (*m*, 4 allyl. H); 3.95–3.90 (*m*, H–C(1′), H–C(2′)); 3.76 (br. *td*, *J* ≈ 5.6, 11.6, H′–C(1′)); 3.73 (*dd*, *J* = 9.3, 10.2, H–C(4)); 3.65 (*dd*, *J* = 9.4, 10.2, H–C(4′)); 3.35 (*dd*, *J* = 5.6, 9.2, H–C(5)); 3.34 (*dd*, *J* = 5.8, 9.3, H–C(5′)); 2.68 (*dt*, *J* ≈ 0.4, 10.3, H–C(3)); 2.57 (*t*, *J* = 10.4, H–C(3′)); 2.09 (*s*, Ac); 1.84 (br. *t*, *J* = 6.0, OH–C(1′)); 0.98 (*t*, *J* = 8.0, 3 Me); 0.59 (*q*, *J* = 8.0, 3 MeC*H*$_2$); 0.23 (*s*, $Me_3Si$). $^{13}$C-NMR (125 MHz, $CDCl_3$): 170.72 (*s*, C=O); 135.01, 134.93, 134.59, 134.49 (4*d*, 4 *C*H=CH$_2$); 117.77, 117.46, 117.16, 116.86 (4*t*, 4 CH=*C*H$_2$); 103.76 (*s*, *C*≡CSiEt$_3$); 99.34 (*s*, C(7)); 95.67 (*s*, C(8)); 86.34 (*s*, C≡*C*SiEt$_3$); 80.05, 78.77, 78.34, 78.31 (4*d*, C(4), C(5), C(4′), C(5′)); 77.19 (*s*, *C*≡C); 74.95 (*d*, C(2′)); 74.59 (*t*, 1 allyl. C); 74.44 (*t*, 1 allyl. C); 73.28 (*s*, *C*≡C); 72.48 (*t*, 1 allyl. C); 72.42 (*s*, *C*≡C); 71.76 (*t*, 1 allyl. C); 71.53 (*d*, C(2)); 67.96 (*s*, *C*≡C); 67.79, 67.48 (2*d*, C(6), C(6′)); 64.40, 63.58 (2*t*, C(1), C(1′)); 38.10, 37.73 (2*d*, C(3), C(3′)); 20.86 (*q*, Me); 7.46 (*q*, 3 Me); 4.33 (*t*, 3 MeC*H*$_2$); −0.12 (*q*, $Me_3Si$). FAB-MS: 801 (35, $[M + Na]^+$), 779 (100, $[M + H]^+$), 749 (78), 679 (64). Anal. calc. for $C_{43}H_{62}O_9Si_2$ (779.13): C 66.29, H 8.02; found: C 66.45, H 7.81.

*1,1′-(Buta-1,3-diyne-1,4-diyl)bis{(1*R*)-2,3-di-*O*-allyl-1,5-anhydro-4-deoxy-4-*C*-[2-(triethylsilyl)ethynyl]-*D*-glucitol}* (**6**): $R_f$ (toluene/AcOEt 12:1) 0.10. $[\alpha]_D^{25}$ = 154.6 (*c* = 0.14, $CHCl_3$). M.p. 97.0–97.5°. IR: 3597*m*, 3084*w*, 3007*m*, 2958*s*, 2928*s*, 2874*s*, 2172*m*, 1646*w*, 1602*w*, 1458*m*, 1414*m*, 1378*m*, 1330*m*, 1138*m*, 1076*s* (br.), 1017*s*, 934*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 6.04–5.85 (*m*, C*H*=CH$_2$); 5.35–5.14 (*m*, 2 CH=C*H*$_2$); 4.92 (*d*, *J* = 5.7, H–C(1)); 4.44–4.38 (*m*, 2 allyl. H); 4.23–4.15 (*m*, 2 allyl. H); 3.98–3.91 (*m*, H–C(5), H–C(6)); 3.84–3.71 (*m*, H′–C(6)); 3.69 (br. *t*, *J* ≈ 10.2, H–C(3)); 3.36 (*dd*, *J* = 5.8, 9.2, H–C(2)); 2.59 (*t*, *J* = 10.3, H–C(4)); 1.85 (*t*, *J* = 6.5, OH–C(6)); 0.99 (*t*, *J* = 8.0, 3 Me); 0.62 (*q*, *J* = 8.1, 3 MeC*H*$_2$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 134.98, 134.41 (2*d*,

2 CH=$CH_2$); 117.99, 116.87 (2*t*, 2 CH=$CH_2$); 103.68 (*s*, C≡CSi); 86.48 (*s*, C≡CSi); 80.07, 78.25 (2*d*, C(2), C(3)); 75.00 (*d*, C(5)); 74.75 (*s*, C≡C); 74.63 (*t*, 1 allyl. C); 72.86 (*s*, C≡C); 72.65 (*t*, 1 allyl. C); 67.86 (*d*, C(1)); 63.54 (*t*, C(6)); 38.11 (*d*, C(4)); 7.49 (*q*, 3 Me); 4.33 (*t*, 3 MeCH$_2$). FAB-MS: 801 (100, $[M + Na]^+$), 779 (83, $[M + H]^+$). Anal. calc. for $C_{44}H_{66}O_8Si_2$ (779.17): C 67.83, H 8.54; found: C 67.86, H 8.43.

*3,3′-(Buta-1,3-diyne-1,4-diyl)bis[1-*O*-acetyl-4,5-di-*O*-allyl-2,6-anhydro-3,7,8-trideoxy-8-*C*-(trimethylsilyl)-*D*-glycero-*L*-gulo-oct-7-ynitol]* (**7**): $R_f$ (toluene/AcOEt 12:1) 0.34. $[\alpha]_D^{25}$ = 109.6 (*c* = 0.14, $CHCl_3$). IR: 3083*w*, 3007*m*, 2960*m*, 2902*m*, 2179*w*, 1740*s* (br.), 1646*w*, 1606*w*, 1456*w*, 1422*w*, 1387*m*, 1369*m*, 1332*m*, 1142*s*, 1099*s* (br.), 996*m*, 932*m*, 902*m*, 846*s* (br.), 633*w*, 604*w*. $^1$H-NMR (300 MHz, $CDCl_3$): 6.02–5.85 (*m*, 2 CH=$CH_2$); 5.36–5.26 (*m*, CH=$CH_2$); 5.22–5.15 (*m*, CH=$CH_2$); 4.80 (*d*, *J* = 5.6, H–C(6)); 4.40–4.34 (*m*, H–C(1), 2 allyl. H); 4.26 (*dd*, *J* = 4.7, 12.1, H′–C(1)); 4.15–4.13 (*m*, 2 allyl. H); 4.12 (*ddd*, *J* ≈ 2.2, 4.5, 10.4, H–C(2)); 3.71 (br. *t*, *J* ≈ 9.8, H–C(4)); 3.34 (*dd*, *J* = 5.6, 9.3, H–C(5)); 2.64 (*t*, *J* ≈ 10.4, H–C(3)); 2.09 (*s*, Ac); 0.22 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 170.72 (*s*, C=O); 134.92, 134.58 (2*d*, 2 CH=$CH_2$); 117.33, 117.14 (2*t*, 2 CH=$CH_2$); 99.39 (*s*, C(7)); 95.66 (*s*, C(8)); 78.93, 78.26 (2*d*, C(4), C(5)); 74.81 (*s*, C≡C); 74.43, 71.76 (2*t*, 2 allyl. C); 71.63 (*d*, C(2)); 68.25 (*s*, C≡C); 67.47 (*d*, C(6)); 64.41 (*t*, C(1)); 37.61 (*d*, C(3)); 20.84 (*q*, Me); –0.14 (*q*, $Me_3Si$). FAB-MS: 801 (< 1, $[M + Na]^+$), 779 (< 1, $[M + H]^+$), 72 (100). Anal. calc. for $C_{42}H_{58}O_{10}Si_2$ (779.09): C 64.75, H 7.50; found: C 64.76, H 7.30.

*4,5-Di-*O*-allyl-2,6-anhydro-3,7,8-trideoxy-3-*C*-{4,5-di-*O*-allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3-*C*-[2-(triethylsilyl)ethynyl]-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-yl}-*D*-glycero-*L*-gulo-oct-7-ynitol* (**8**). A soln. of **5** (205 mg, 0.27 mmol) in MeOH (30 ml), $H_2O$ (12 ml), and $Et_3N$ (3 ml) was stirred for 3.5 h at r.t. and evaporated. Workup (AcOEt) and FC (hexane/AcOEt 4:1) gave **8** (153.6 mg, 88%). Colourless oil. $R_f$ (toluene/AcOEt 7:3) 0.33. $[\alpha]_D^{25}$ = 147.7 (*c* = 0.10, $CHCl_3$). IR: 3600*w*, 3304*w*, 3007*w*, 2961*m*, 2912*w*, 2875*w*, 2248*w*, 2172*w*, 1646*w*, 1457*w*, 1413*w*, 1343*w*, 1261*s*, 1097*s* (br.), 1015*s* (br.), 932*m*, 865*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 6.04–5.86 (*m*, 4 CH=$CH_2$); 5.34–5.26 (*m*, 2 CH=$CH_2$); 5.23–5.14 (*m*, 2 CH=$CH_2$); 4.88 (*d*, *J* = 5.7, H–C(6′)); 4.82 (*dd*, *J* = 2.3, 5.7, H–C(6)); 4.43–4.34 (*m*, 4 allyl. H); 4.24–4.11 (*m*, 4 allyl. H); 4.02 (*ddd*, *J* = 2.4, 4.8, 10.6, H–C(2)); 3.94–3.89 (*m*, H–C(1), H–C(1′), H–C(2′)); 3.80–3.73 (*m*, H′–C(1), H′–C(1′)); 3.76 (br. *t*, *J* ≈ 10.1, H–C(4)); 3.65 (br. *t*, *J* ≈ 9.5, H–C(4′)); 3.36 (*dd*, *J* = 5.7, 9.2, H–C(5)); 3.33 (*dd*, *J* = 5.8, 9.3, H–C(5′)); 2.70 (br. *t*, *J* ≈ 10.4, H–C(3)); 2.61 (*d*, *J* = 2.3, H–C(8)); 2.57 (*t*, *J* = 10.4, H–C(3′)); 1.85 (br. *t*, *J* ≈ 6.2), 1.81 (br. *t*, *J* = 6.2, OH–C(1), OH–C(1′)); 0.98 (*t*, *J* = 8.0, 3 Me); 0.59 (*q*, *J* = 7.9, 3 MeCH$_2$). $^{13}$C-NMR (125 MHz, $CDCl_3$): 135.02, 134.90, 134.52, 134.43 (4*d*, 4 CH=$CH_2$); 117.93, 117.70, 117.25, 116.84 (4*t*, 4 CH=$CH_2$); 103.78 (*s*, C≡CSi); 86.33 (*s*, C≡CSi); 80.59, 79.10, 78.34, 78.30 (4*d*, C(4), C(5), C(4′), C(5′)); 78.07 (*d*, C(8)); 77.81, 77.48 (2*s*, C(7), C≡C); 74.93, 74.04 (2*d*, C(2), C(2′)); 74.60, 74.48 (2*t*, 2 allyl. C); 73.28 (*s*, C≡C); 72.46, 72.44 (2*t*, 2 allyl. C); 72.31, 67.89 (2*s*, 2 C≡C); 67.76, 66.98 (2*d*, C(6), C(6′)); 63.57, 63.26 (2*t*, C(1), C(1′)); 38.08, 37.30 (2*d*, C(3), C(3′)); 7.47 (*q*, 3 Me); 4.34 (*t*, 3 MeCH$_2$). FAB-MS: 665 (14, $[M + H]^+$), 136 (40), 115 (88), (100). Anal. calc. for $C_{38}H_{52}O_8Si$ (664.91): C 68.64, H 7.88; found: C 68.90, H 7.85.

*4,5-Di-*O*-allyl-2,6-anhydro-3,7,8-trideoxy-3-*C*-{4,5-di-*O*-allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3-*C*-[2-(triethylsilyl)ethynyl]-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-yl}-8-*C*-iodo-*D*-glycero-*L*-gulo-oct-7-ynitol* (**9**). A soln. of $I_2$ (390 mg, 3.07 mmol) in benzene (15 ml) was treated with morpholine (588 µl, 6.75 mmol) at r.t. under Ar, stirred at 45° for 10 min, treated dropwise with a soln. of **8** (204 mg, 0.30 mmol) in benzene (10 ml), and stirred overnight. The mixture was cooled to r.t., diluted with toluene and filtered through cotton. The filtrate was washed with 10% aq. $Na_2S_2O_3$ soln. and $H_2O$, dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 4:1) gave **9** (220 mg, 91%). Colourless oil. $R_f$ (toluene/AcOEt 7:3) 0.37. $[\alpha]_D^{25}$ = 117.5 (*c* = 0.76, $CHCl_3$). IR: 3598*m*, 3083*w*, 3007*m*, 2957*s*, 2913*m*, 2875*s*, 2255*w*, 2174*m*, 1646*w*, 1602*w*, 1457*m*, 1421*m*, 1343*m* (br.), 1261*m*, 1075*s* (br.), 1017*s* (br.), 933*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 6.05–5.85 (*m*, 4 CH=$CH_2$); 5.37–5.26 (*m*, 2 CH=$CH_2$); 5.26–5.14 (*m*, 2 CH=$CH_2$); 4.96 (*d*, *J* = 5.6, H–C(6)); 4.89 (br. *d*, *J* = 5.6, H–C(6′)); 4.42–4.36 (*m*, 4 allyl. H); 4.23–4.10 (*m*, 4 allyl. H); 3.89 (*ddd*, *J* = 2.3, 4.7, 10.5, H–C(2)); 3.96–3.89 (*m*, H–C(1), H–C(1′), H–C(2′)); 3.80–3.75 (*m*, H′–C(1), H′–C(1′)); 3.72 (br. *t*, *J* ≈ 9.8, H–C(4)); 3.66 (br. *t*, *J* ≈ 9.8, H–C(4′)); 3.34 (*dd*, *J* = 5.8, 9.3, H–C(5′)); 3.32 (*dd*, *J* = 5.7, 9.2, H–C(5)); 2.70 (br. *t*, *J* ≈ 10.4, H–C(3)); 2.58 (*t*, *J* = 10.4, H–C(3′)); 1.92–1.72 (*m*, OH–C(1), OH–C(1′)); 0.99 (*t*, *J* = 8.0, 3 Me); 0.58 (*q*, *J* = 7.9, 3 MeCH$_2$). $^{13}$C-NMR (125 MHz, $CDCl_3$): 135.02, 134.97, 134.51, 134.46 (4*d*, 4 CH=$CH_2$); 117.80, 117.74, 117.21, 116.85 (4*t*, 4 CH=$CH_2$); 103.78 (*s*, C≡CSi); 89.11 (*s*, C(7)); 86.32 (*s*, C≡CSi); 80.06, 79.11, 78.58, 78.32 (4*d*, C(4), C(5), C(4′), C(5′)); 77.42 (*s*, C≡C); 74.94, 74.26 (2*d*, C(2), C(2′)); 74.61, 74.52 (2*t*, 2 allyl. C); 73.28 (*s*, C≡C); 72.45 (*t*, 1 allyl. C); 72.35 (*s*, C≡C); 72.33 (*t*, 1 allyl. C); 68.52, 67.77 (2*d*, C(6), C(6′)); 67.93 (*s*, C≡C); 63.55, 63.25 (2*t*, C(1), C(1′)); 38.07, 37.30 (2*d*, C(3), C(3′)); 7.49 (*q*, 3 Me); 6.39 (*s*, C(8)); 4.34 (*t*, 3 MeCH$_2$). FAB-MS: 791 (4, $[M + H]^+$), 115 (85), 87 (100). Anal. calc. for $C_{38}H_{51}IO_8Si$ (790.81): C 57.72, H 6.50; found: C 57.88, H 6.63.

*Coupling Reaction of* **1** *with* **9**. A degassed soln. of **1** (130.2 mg, 0.33 mmol), [$Pd_2$(dba)$_2$] (3.8 mg, 8.3 µmol), P(furyl)$_3$ (3.9 mg, 16.6 µmol), and CuI (1.0 mg, 5.2 µmol) in DMSO (5.2 ml) was treated with 1,2,2,6,6-pentame-

thylpiperidine (300 µl, 1.65 mmol) at r.t. under Ar. Then a soln. of **9** (220 mg, 0.28 mmol) in DMSO (3.5 ml) was added dropwise within 3 h. After 8 h stirring, workup ($Et_2O$) and FC (toluene/AcOEt 9:1 → 7:3) gave **7** (17 mg, 13%), **10** (189 mg, 65%), and **11** (23 mg, 12%) as oils.

*1-O-Acetyl-4,5-di-O-allyl-2,6-anhydro-3,7,8-trideoxy-3-C-{4,5-di-O-allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3-C-{4,5-di-O-allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3-C-[2-(triethylsilyl)ethynyl]*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}-8-C-(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**10**). $R_f$ (toluene/AcOEt 15:1) 0.35. $[\alpha]_D^{25} = 155.6$ ($c = 0.55$, $CHCl_3$). IR: 3598*w*, 3083*w*, 3007*m*, 2957*m*, 2913*m*, 2875*m*, 2255*w*, 2171*w*, 1704*m* (br.), 1646*w*, 1602*w*, 1457*m*, 1421*m*, 1367*w*, 1343*m*, 1074*s* (br.), 1017*m*, 932*m*, 846*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 6.05–5.85 (*m*, 6 C*H*=CH$_2$); 5.59–5.26 (*m*, 3 CH=C*H*$_2$); 5.23–5.13 (*m*, 3 CH=C*H*$_2$); 4.90 (*d*, $J = 5.8$), 4.88 (*d*, $J = 5.8$, H–C(6′), H–C(6″)); 4.80 (*d*, $J = 5.6$, H–C(6)); 4.43–4.34 (*m*, H–C(2), 6 allyl. H); 4.27 (*dd*, $J = 4.7$, 12.1, H–C(1)); 4.23–4.10 (*m*, H′–C(1), 6 allyl. H); 3.98–3.88 (*m*, H–C(1′), H–C(2′), H–C(1″), H–C(2″)); 3.80–3.75 (*m*, H′–C(1′), H′–C(1″)); 3.74 (br. *t*, $J \approx 9.5$), 3.70 (br. *t*, $J \approx 9.8$, H–C(4), H–C(4′)); 3.64 (br. *t*, $J \approx 10.2$, H–C(4″)); 3.35 (*dd*, $J = 5.8$, 9.3), 3.34 (*dd*, $J = 5.8$, 9.2), 3.33 (*dd*, $J = 5.8$, 9.3, H–C(5), H–C(5′), H–C(5″)); 2.72, 2.69 (2 br. *t*, $J \approx 10.5$, H–C(3), H–C(3′)); 2.57 (*t*, $J = 10.4$, H–C(3″)); 2.10 (*s*, Ac); 1.84–1.80 (*m*, OH–C(1′), OH–C(1″)); 0.98 (*t*, $J = 7.7$, 3 Me); 0.59 (*q*, $J = 7.9$, 3 MeC*H*$_2$); 0.23 (*s*, $Me_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170 (*s*, C=O); 135.12, 135.05, 134.92, 134.68, 134.63, 134.45 (6*d*, 6 *C*H=CH$_2$); 118.06, 117.78, 117.46, 117.34, 117.25, 116.93 (6*t*, 6 CH=*C*H$_2$); 103.83 (*s*, *C*≡CSiEt$_3$); 99.43 (*s*, C(7)); 95.74 (*s*, C(8)); 86.39 (*s*, C≡*C*SiEt$_3$); 80.15, 79.37, 78.92, 78.54, 78.40 (2 C; 5*d*, C(4), C(5), C(4′), C(5′), C(4″), C(5″)); 77.57, 77.32, 77.26 (3*s*, *C*≡C); 75.04, 74.70 (2*d*, C(2′), C(2″)); 74.65, 74.56 (2 C; 2*t*, 3 allyl. C); 73.66, 73.27 (2*s*, *C*≡C); 72.58, 72.51, 71.86 (3*t*, 3 allyl. C); 71.60 (*d*, C(2)); 72.13, 68.18, 67.865 (3*s*, 3 *C*≡C); 67.86 (br. *d*, C(6′), C(6″)); 67.56 (*d*, C(6)); 64.51, 63.61, 63.33 (3*t*, C(1), C(1′), C(1″)); 38.14, 37.81, 37.42 (3*d*, C(3), C(3′), C(3″)); 20.92 (*q*, Me); 7.57 (*q*, 3 Me); 4.43 (*t*, 3 MeCH$_2$); −0.01 (*q*, $Me_3Si$). FAB-MS: 1075 (14, $[M + Na]^+$), 1054 (83), 1053 (75, $[M + H]^+$), 1051 (50), 996 (58), 995 (58), 953 (44), 937 (45), 936 (57), 935 (100), 71 (56). Anal. calc. for $C_{59}H_{80}O_{13}Si_2$ (1053.45): C 67.27, H 7.65; found: C 67.23, H 7.71.

*1,1′-(Buta-1,3-diyne-1,4-diyl)bis{(1R)-2,3-di-O-allyl-1,5-anhydro-4-deoxy-4-C-{4,5-di-O-allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3-C-[2-(triethylsilyl)ethynyl]*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}*-D-*glucitol*} (**11**): $R_f$ (toluene/AcOEt 15:1) 0.07. $[\alpha]_D^{25} = 201.4$ ($c = 0.93$, $CHCl_3$). IR: 3595*w*, 3084*w*, 3007*w*, 2956*m*, 2914*m*, 2875*m*, 2255*w*, 2172*w*, 1646*w*, 1457*m*, 1421*w* (br.), 1332*m* (br.), 1075*s* (br.), 1017*m* (br.), 933*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 6.05–5.84 (*m*, 4 C*H*=CH$_2$); 5.39–5.13 (*m*, 4 CH=C*H*$_2$); 4.93 (*d*, $J = 5.6$, H–C(1)); 4.89 (*d*, $J = 5.6$, H–C(6′)); 4.45–4.34 (*m*, 4 allyl. H); 4.24–4.10 (*m*, 4 allyl. H); 4.02–3.89 (*m*, H–C(1′), H–C(2′), H–C(5), H–C(6)); 3.84–3.70 (*m*, H′–C(1′), H′–C(6)); 3.71 (br. *t*, $J \approx 10.0$, H–C(3)); 3.65 (*dd*, $J = 9.4$, 10.2, H–C(4′)); 3.37 (*dd*, $J = 5.8$, 10.3, H–C(5′)); 3.33 (*dd*, $J = 5.8$, 9.4, H–C(2)); 2.73 (br. *t*, $J \approx 10.4$, H–C(4)); 2.57 (*t*, $J = 10.3$, H–C(3′)); 1.91 (br. *t*, $J \approx 6.5$, OH); 1.81 (br. *t*, $J = 6.3$, OH); 0.99 (*t*, $J = 7.0$, 3 Me); 0.59 (*q*, $J \approx 7.7$, 3 MeC*H*$_2$). $^{13}$C-NMR (125 MHz, $CDCl_3$): 135.02, 134.82, 134.53, 134.36 (4*d*, 4 *C*H=CH$_2$); 118.11, 117.69, 117.23, 116.85 (4*t*, 4 CH=*C*H$_2$); 103.74 (*s*, *C*≡CSi); 86.31 (*s*, C≡*C*Si); 80.05, 79.35, 78.42, 78.30 (4*d*, C(2), C(3), C(4′), C(5′)); 77.20 (*s*, *C*≡C); 74.98, 74.57 (2*d*, C(2′), C(5)); 74.60 (*t*, 2 allyl. C); 73.21, 73.00 (2*s*, *C*≡C); 72.55 (*t*, 1 allyl. C); 72.49 (*s*, *C*≡C); 72.41 (*t*, 1 allyl. C); 68.11 (*s*, *C*≡C); 67.76 (*d*, C(1), C(6′)); 63.52, 63.22 (2*t*, C(1′), C(6)); 38.07, 37.41 (2*d*, C(3′), C(4)); 7.48 (*q*, 3 Me); 4.34 (*t*, 3 MeCH$_2$); 1*s* for *C*≡C is missing. FAB-MS: 1350 (29), 1327 (58, $[M + H]^+$), 1325 (12, $[M - H]^+$), 1269 (38), 1267 (81), 1266 (100), 1174 (53), 1138 (38), 1045 (28). Anal. calc. for $C_{76}H_{102}O_{16}Si_2$ (1327.81): C 68.75, H 7.74; found: C 68.75, H 7.97.

*4,5-Di-O-allyl-2,6-anhydro-3,7,8-trideoxy-3-C-{4,5-di-O-allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3-C-{4,5-di-O-allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3-C-[2-(triethylsilyl)ethynyl]*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}*-D-glycero-L-gulo-*oct-7-ynitol* (**12**). A soln. of **10** (570 mg, 0.54 mmol) in MeOH (30 ml) was treated with 0.1M NaOH in MeOH (6.3 ml) at 0° under $N_2$, warmed to r.t., stirred for 2 h, cooled to 0°, treated with *Dowex* ($H^+$ form), and stirred for 1 h. The solids were filtered off and washed with MeOH. Evaporation of the filtrate gave **12** (501 mg, 98%), as a colourless oil, which was used directly for the next step. A sample was purified by FC (toluene/AcOEt 4:1). $R_f$ (toluene/AcOEt 6:4) 0.29. $[\alpha]_D^{25} = 131.9$ ($c = 1.48$, $CHCl_3$). IR: 3596*m*, 3304*m*, 3007*w*, 2956*m*, 2914*m*, 2875*m*, 2255*w*, 2172*w*, 1646*w*, 1458*m*, 1421*m* (br.), 1343*m* (br.), 1075*s* (br.), 1016*s* (br.), 933*m*. $^1$H-NMR (500 MHz, $CDCl_3$): 6.04–5.86 (*m*, 6 C*H*=CH$_2$); 5.38–5.26 (*m*, 3 CH=C*H*$_2$); 5.22–5.14 (*m*, 3 CH=C*H*$_2$); 4.88 (br. *d*, $J \approx 5.8$, H–C(6′), H–C(6″)); 4.83 (*dd*, $J = 2.3$, 5.7, H–C(6)); 4.43–4.34 (*m*, 6 allyl. H); 4.24–4.12 (*m*, 6 allyl. H); 4.03 (*ddd*, $J = 2.4$, 4.9, 10.6, H–C(2″)); 3.89 (*ddd*, $J = 2.3$, 4.6, 10.5, H–C(2′)); 3.95–3.89 (*m*, H–C(1), H–C(2), H–C(1′), H–C(1″)); 3.81–3.75 (*m*, H′–C(1), H′–C(1′), H′–C(1″)); 3.77 (*dd*, $J \approx 9.4$, 10.3), 3.71 (*dd*, $J \approx 9.4$, 10.3), 3.64 (*dd*, $J \approx 9.4$, 10.3, H–C(4), H–C((4′), H–C(4″)); 3.36 ($J \approx 5.7$, 9.2), 3.35 ($J \approx 5.7$, 9.2), 3.34 (*dd*, $J \approx 5.7$, 9.2, H–C(5), H–C(5′), H–C(5″)); 2.71 (br. *t*, $J \approx 10.4$), 2.70 (br. *t*, $J \approx 10.4$, H–C(3), H–C(3′)); 2.61 (*d*, $J = 2.3$, H–C(8)); 2.57 (*t*, $J = 10.4$, H–C(3″)); 1.86 (br. *t*, $J \approx 6.1$), 1.84 (br. *t*, $J \approx 6.6$), 1.80 (br. *t*, $J \approx 6.6$, OH–C(1), OH–C(1′), OH–C(1″)); 0.98 (*t*, $J = 8.0$,

3 Me); 0.59 (*q*, $J \approx 7.9$, 3 MeC$H_2$). $^{13}$C-NMR (125 MHz, $CDCl_3$): 135.02, 134.93, 134.84, 134.52, 134.43, 134.39 (6*d*, 6 *C*H=CH$_2$); 117.91, 117.89, 117.73, 117.24, 117.19, 116.85 (6*t*, 6 CH=*C*H$_2$); 103.73 (*s*, *C*≡CSi); 86.33 (*s*, C≡*C*Si); 80.06, 79.27, 79.14, 78.48, 78.31, 78.27 (6*d*, C(4), C(5), C(4′), C(5′), C(4″), C(5″)); 78.07 (*d*, C(8)); 77.82 (3 C), 77.23 (2*s*, 3 *C*≡C, C(7)); 74.95, 74.45, 74.03 (3*d*, C(2), C(2′), C(2″)); 74.61, 74.55, 74.50 (3*t*, 3 allyl. C); 73.61, 73.20, (2*s*, 2 *C*≡C); 72.45, 72.44, 72.42 (3*t*, 3 allyl. C); 71.89, 68.02 (2*s*, 2 *C*≡C); 67.78, 67.70, 66.98 (3*d*, *C*(6), C(6′), C(6″)); 67.70 (*s*, *C*≡C); 63.54, 63.27, 63.23 (3*t*, C(1), C(1′), C(1″)); 38.07, 37.31, 37.29 (3*d*, C(3), C(3′), C(3″)); 7.48 (*q*, 3 Me); 4.34 (*t*, 3 MeC$H_2$). FAB-MS: 939 (100, $[M + H]^+$), 881 (31), 821 (29), 767 (27), 657 (25). Anal. calc. for $C_{54}H_{70}O_{12}Si$ (939.23): C 69.06, H 7.51; found: C 69.20, H 7.79.

*4,5-Di*-O-*allyl-2,6-anhydro-3,7,8-trideoxy-3*-C-{*4,5-di*-O-*allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3*-C-{*4,5-di*-O-*allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3*-C-*[2-(triethylsilyl)ethynyl]*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-*8*-C-*iodo*-D-glycero-L-gulo-*oct-7-ynitol* (**13**). A soln. of $I_2$ (194.5 mg, 1.53 mmol) in benzene (5.2 ml) was treated with morpholine (267 µl, 3.07 mmol) at r.t. under Ar, stirred at 45° for 15 min, treated dropwise with a soln. of **12** (80 mg, 0.30 mmol) in benzene (3.5 ml), and stirred for 10 h. The mixture was cooled to r.t., diluted with toluene, and filtered through cotton. The filtrate was washed with 10% aq. $Na_2S_2O_3$ soln. and $H_2O$, dried ($MgSO_4$), and evaporated. FC (toluene/AcOEt 7:3) gave **13** (67.3 mg, 74%). Slightly yellow oil. $R_f$ (toluene/AcOEt 3:2) 0.30. IR: 3597*m*, 3495*w* (br.), 3082*w*, 3007*w*, 2958*m*, 2913*m*, 2875*m*, 2255*w*, 2174*w*, 2114*m*, 1646*m*, 1602*w*, 1457*m*, 1421*w*, 1367*m*, 1343*m* (br.), 1077*s* (br.), 1015*s*, 933*m*. $^1$H-NMR (500 MHz, $CDCl_3$): 6.04–5.86 (*m*, 6 *CH*=CH$_2$); 5.35–5.26 (*m*, 3 CH=*CH*$_2$); 5.23–5.14 (*m*, 3 CH=*CH*$_2$); 4.95 (*d*, $J = 5.6$, H–C(6)); 4.89 (br. *d*, $J = 5.7$), 4.88 (br. *d*, $J = 5.7$, H–C(6′), H–C(6″)); 4.43–4.34 (*m*, 6 allyl. H); 4.22–4.11 (*m*, 6 allyl. H); 4.00–3.89 (*m*, H–C(1), H–C(2), H–C(1′), H–C(2′), H–C(1″), H–C(2″)); 3.80–3.74 (*m*, H′–C(1), H′–C(1′), H′–C(1″)); 3.71 (br. *t*, $J \approx 10.1$, H–C(4), H–C(4′)); 3.64 (*dd*, $J \approx 9.3$, 10.3, H–C(4″)); 3.35 ($J \approx 5.8$, 9.4), 3.33 (*dd*, $J \approx 5.8$, 9.4, H–C(5′), H–C(5″)); 3.31 (*dd*, $J = 5.6$, 9.2, H–C(5)); 2.71 (br. *t*, $J \approx 10.4$), 2.70 (br. *t*, $J \approx 10.4$, H–C(3), H–C(3′)); 2.57 (*t*, $J = 10.4$, H–C(3″)); 1.87–1.77 (*m*, OH–C(1), OH–C(1′), OH–C(1″)); 0.98 (*t*, $J = 8.0$, 3 Me); 0.59 (*q*, $J \approx 7.7$, 3 MeC$H_2$). $^{13}$C-NMR (125 MHz, $CDCl_3$): 135.04, 134.91, 134.85, 134.54, 134.47, 134.39 (6*d*, 6 *C*H=CH$_2$); 117.92, 117.78, 117.73, 117.24, 117.14, 116.86 (6*t*, 6 CH=*C*H$_2$); 103.73 (*s*, *C*≡CSi); 89.10 (*s*, C(7)); 86.34 (*s*, C≡*C*Si); 80.06, 79.28, 79.21, 78.55, 78.48, 78.31 (6*d*, C(4), C(5), C(4′), C(5′), C(4″), C(5″)); 77.77 (*s*, *C*≡C); 74.94, 74.45, 74.26 (3*d*, C(2), C(2′), C(2″)); 74.61, 74.56, 74.54 (3*t*, 3 allyl. C); 73.62, 73.23 (2*s*, 2 *C*≡C); 72.43 (*t*, 2 allyl. C); 72.33 (*t*, 1 allyl. C); 71.93, 68.03 (2*s*, 2 *C*≡C); 68.51, 67.78, 67.71 (3*d*, C(6), C(6′), C(6″)); 67.78, 67.75 (2*s*, 2 *C*≡C); 63.55, 63.26, 63.23 (3*t*, C(1), C(1′), C(1″)); 38.07, 37.30, 37.30 (3*d*, C(3), C(3′), C(3″)); 7.49 (*q*, 3 Me); 6.45 (*s*, C(8)); 4.35 (*t*, 3 MeC$H_2$); 1*s* for *C*≡C is missing. FAB-MS: 1065 (100, $M^+$).

*4,5-Di*-O-*allyl-2,6-anhydro-3,7,8-trideoxy-3*-C-*[4,5-di*-O-*allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3*-C-*(4,5-di*-O-*allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3*-C-*ethynyl*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]-8*-C-*iodo*-D-glycero-L-gulo-*oct-7-ynitol* (**14**) *and 4,5-Di*-O-*allyl-2,6-anhydro-3,7,8-trideoxy-3*-C-*[4,5-di*-O-*allyl-2,6-anhydro-3,7,8,9-10-pentadeoxy-3*-C-*(4,5-di*-O-*allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-3*-C-*(2-iodoethynyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]*-D-glycero-L-gulo-*oct-7-ynitol* (**15**). A soln. of **13** (200 mg, 0.187 mmol) and CsF (228 mg, 1.5 mmol) in DMF (12.5 ml) and MeOH (2.5 ml) was stirred at r.t. for 2 h. Workup ($CHCl_3$) and evaporation gave **14/15** (*ca.* 190 mg) as an oil, which was used for the next step. $R_f$ (toluene/AcOEt 9:11) 0.41. IR: 3598*m*, 3459*m* (br.), 3306*m*, 3083*w*, 3007*w*, 2922*m*, 2880*m*, 2255*w*, 2180*w*, 1646*w*, 1457*m*, 1422*m*, 1343*m* (br.), 1074*s* (br.), 1014*s*, 998*m*, 933*m*. $^1$H-NMR (500 MHz, $CDCl_3$, **14/15** *ca.* 1:1): 6.04–5.86 (*m*, 6 *CH*=CH$_2$); 5.47–5.28 (*m*, 3 CH=*CH*$_2$); 5.22–5.15 (*m*, 3 CH=*CH*$_2$); 4.96 (*d*, $J = 5.6$, 0.5 H, H–C(6) of **14**); 4.89 (*d*, $J \approx 5.6$, 0.5 H), 4.88 (*d*, $J \approx 5.6$, 0.5 H), 4.86 (br. *d*, $J \approx 5.6$, 1 H, H–C(6′), H–C(6″)); 4.83 (*dd*, $J = 2.3$, 5.7, 0.5 H, H–C(6) of **15**); 4.43–4.34 (*m*, 6 allyl. H); 4.24–4.11 (*m*, 6 allyl. H); 4.03 (*ddd*, $J = 2.4$, 4.9, 10.6, 0.5 H–C(2″)); 4.00–3.88 (*m*, H–C(1), H–C(2), H–C(1′), H–C(2′), H–C(1″), 0.5 H–C(2″)); 3.81–3.70 (*m*, H′–C(1), H–C(4), H′–C(1′), H–C(4′), H′–C(1″), H–C(4″)); 3.37 (*dd*, $J \approx 5.6$, 9.3, 0.5 H), 3.36 (br. *dd*, $J \approx 5.6$, 9.3, 1 H), 3.35 (*dd*, $J \approx 5.6$, 9.3, 0.5 H), 3.32 (*dd*, $J \approx 5.6$, 9.3, 0.5 H), 3.31 (*dd*, $J \approx 5.6$, 9.3, 0.5 H, H–C(5), H–C(5′), H–C(5″)); 2.71 (br. *t*, $J \approx 10.5$, H–C(3), H–C(3′)); 2.70 (*t*, $J = 10.4$, 0.5 H, H–C(3″) of **15**); 2.61 (*d*, $J = 2.3$, 0.5 H, H–C(8) of **15**); 2.56 (*dt*, $J = 2.3$, 10.5, 0.5 H, H–C(3″) of **14**); 2.20 (*d*, $J = 2.3$, 0.5 H, C≡CH of **14**); 1.88–1.84 (*m*, OH–C(1), OH–C(1′), OH–C(1″)). $^{13}$C-NMR (125 MHz, $CDCl_3$, **14/15** *ca.* 1:1): 135.05–134.40 (several *d*, *C*H=CH$_2$); 117.90–116.87 (several *t*, CH=*C*H$_2$); 90.95 (*s*, *C*≡CI of **15**); 89.12 (*s*, C(7) of **14**); 80.85 (*s*, *C*≡C); 79.80, 79.72, 79.30 (2 C), 79.18, 79.14, 78.57 (6*d*); 78.47–78.43 (several *d*); 78.29, 78.10 (2*d*); 77.82 (*d*, C(8) of **15**, H*C*≡C–C(3″) of **14**); 77.85, 77.78, 77.48, 77.44 (4*s*, 4 *C*≡C); 74.79 (*d*); 74.56–74.50 (several *t*, several allyl. C); 74.47, 74.04 (2*d*); 73.63, 73.62, 73.41, 73.40 (4*s*, 4 *C*≡C); 72.44–72.31 (several *t*, several allyl. C); 72.26, 72.24, 72.20 (2 C); 71.94, 71.91 (5*s*, 6 *C*≡C); 68.52, 67.92 (2*d*); 67.78, 67.73 (2*s*, 2 *C*≡C); 67.71–67.69 (several *d*); 66.97 (*d*); 63.27–63.25 (several *t*, C(1), C(1′), C(1″)); 38.66, 37.31 (2 C), 37.28 (2 C), 36.58 (4*d*, C(3), C(3′), C(3″)); 6.50 (*s*, C(8) of **14**); −1.06 (*s*, I*C*≡C of **15**). FAB-MS: 1902 (100, $[2M + 2H]^+$), 1901 (83, $[2M + H]^+$), 951 (67, $[M + H]^+$), 950 (23, $M^+$).

*Tris(4,5-di-*O*-allyl-2,6-anhydro-7,8,9,10-tetradeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol) 3,10′:3′,10″:3″,10-Trianhydride* (= *Cyclotris-(3-*C *→ 10-*C*)-(4,5-di-*O*-allyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-yl)*; **16**). To a degassed soln. of $[Pd_2(dba)_3]$ (8.57 mg, 18.7 μmol), $P(furyl)_3$ (8.81 mg, 37.4 μmol), CuI (3.56 mg, 18.7 μmol), and $Et_3N$ (261 μl, 1.87 mmol) in benzene (3.25 ml) was added dropwise a soln. of **14/15** *ca.* 1:1 (*ca.* 190 mg, 0.187 mmol) in benzene (10 ml) within 5.5 h at 42° under Ar, and the mixture stirred overnight at 37°. Evaporation (40°/*ca.* 100 mbar), workup ($CHCl_3$), and FC (toluene/AcOEt 6:4) gave **16** (99.9 mg, 65% from **13**). Colourless oil. $R_f$ (toluene/AcOEt 4:6) 0.22. $[\alpha]_D^{25} = 116.3$ ($c = 0.77$, $CHCl_3$). IR: 3599*m*, 3472*m* (br.), 3083*w*, 3007*m*, 2924*m*, 2879*m*, 2254*m*, 1646*w*, 1602*w*, 1457*m*, 1422*m*, 1342*m* (br.), 1130*s* (br.), 1093*s* (br.), 1013*s*, 932*s*. $^1$H-NMR (400 MHz, $CDCl_3$): 6.05–5.85 (*m*, 2 C*H*=$CH_2$); 5.45–5.28 (*m*), 5.23–5.18 (*m*, 2 CH=C$H_2$); 4.81 (br. *d*, $J = 5.5$, H–C(6)); 4.43–4.34 (*m*, 2 allyl. H); 4.20–4.11 (*m*, 2 allyl. H, H–C(2)); 3.94 (*ddd*, $J \approx 2.3$, 6.2, 11.9, H–C(1)); 3.84 (br. *t*, $J \approx 9.6$, H–C(4)); 3.77 (*ddd*, $J \approx 4.8$, 6.3, 12.0, H′–C(1)); 3.37 (*dd*, $J = 5.5$, 9.3, H–C(5)); 2.65 (br. *t*, $J \approx 10.4$, H–C(3)); 1.80 (br. *t*, $J \approx 6.2$, OH–C(1)). $^{13}$C-NMR (100 MHz, $CDCl_3$): 134.97, 134.39 (2*d*, 2 *C*H=$CH_2$); 117.48, 117.30 (*t*, 2 CH=*C*$H_2$); 79.33, 78.44 (2*d*, C(4), C(5)); 78.53 (*s*, *C*≡C); 74.42 (*d*, C(2)); 74.25 (*t*, allyl. C); 74.18 (*s*, *C*≡C); 72.04 (*t*, allyl. C); 71.82 (*s*, *C*≡C); 67.50 (*d*, C(6)); 67.44 (*s*, *C*≡C); 63.30 (*t*, C(1)); 36.98 (*d*, C(3)). FAB-MS: 823 (1, $[M + H]^+$), 577 (4), 549 (5), 154 (29), 68 (98), 54 (100). Anal. calc. for $C_{48}H_{54}O_{12}$ (822.95): C 70.06, H 6.61; found: C 70.11, H 6.68.

*Tris(1,4,5-tri-*O*-acetyl-2,6-anhydro-7,8,9,10-tetradeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol) 3,10′:3′,10″:3″,10-Trianhydride* (= *Cyclotris-(3-*C *→ 10-*C*)-(1,4,5-tri-*O*-acetyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-yl)*; **17**). A suspension of **16** (21 mg, 25.5 μmol) and $FeCl_3$ (49.6 mg, 0.31 mmol) in $CH_2Cl_2$ (9 ml) was stirred at r.t. under $N_2$ for 9 h, treated with $FeCl_3$ (49.6 mg, 0.31 mmol), stirred for 20 h, and evaporated. The residue was treated with pyridine (2 ml) and $Ac_2O$ (1.5 ml), stirred for 12 h, evaporated, and co-evaporated with toluene (3×). Two FC (toluene/AcOEt 7:3 → 6:4) gave **17** (9.5 mg, 39%). Colourless oil. $R_f$ (toluene/AcOEt 1:1) 0.23. $[\alpha]_D^{25} = 175.7$ ($c = 0.49$, $CHCl_3$). IR: 2957*w*, 2256*w*, 1749*s* (br.), 1435*w*, 1370*m*, 1065*m* (br.). $^1$H-NMR (400 MHz, $CDCl_3$): 5.57 (*m*, $J = 0.3$, 10.3, with virtual coupling, H–C(4)); 4.92 (*AB* system, H–C(5), H–C(6)); 4.45 (*dd*, $J = 2.1$, 11.8, H–C(1)); 4.39 (*ddd*, $J = 2.0$, 4.7, 10.4, H–C(2)); 4.33 (*dd*, $J = 4.7$, 11.9, H′–C(1)); 2.93 (br. *t*, $J \approx 10.4$, H–C(3)); 2.13, 2.09, 2.06 (3*s*, 3 Ac). $^{13}$C-NMR (125 MHz, $CDCl_3$): 170.58, 170.08, 168.86 (3*s*, C=O); 76.58 (*s*, C(10)); 74.66, 70.94 (2*s*, C(8), C(9)); 71.96, 71.05, 69.85 (3*d*, C(2), C(4), C(5)); 70.94 (*s*, C(7)); 66.38 (*d*, C(6)); 63.84 (*t*, C(1)); 36.03 (*d*, C(3)); 20.84, 20.73, 20.70 (3*q*, 3 Me). FAB-MS: 983 (< 1, $[M + Na]^+$), 961 (< 1, $[M + H]^+$), 647 (1), 169 (45), 149 (23), 99 (42), 68 (100). Anal. calc. for $C_{48}H_{48}O_{21}$ (960.90): C 60.00, H 5.03; found: C 59.97, H 5.20.

*Tris(2,6-anhydro-7,8,9,10-tetradeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol) 3,10′:3′,10″:3″,10-Trianhydride* (= *Cyclotris-(3-*C *→ 10-*C*)-(2,6-anhydro-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-yl)*; **18**). A soln. of **17** (27 mg, 28.1 μmol) in MeOH (6 ml) was treated with a soln. of 1% NaOMe in MeOH (20 μl) at 0° under $N_2$, stirred for 8 h, treated with *Dowex* ($H^+$ form), and stirred for 10 min. The solids were filtered off and washed with MeOH. Evaporation of the filtrate gave **18** (16.2 mg, 99%). White solid. $R_f$ (AcOEt/MeOH 7:3) 0.24. M.p. > 200° (dec.). $[\alpha]_D^{25} = 62.0$ ($c = 0.52$, $H_2O$). UV ($H_2O$): 232 (783). IR (KBr): 3644–3022*s* (br., maximum at 3408), 2292*w*, 2254*w*, 1630*m* (br.), 1408*w*, 1337*m*, 1234*w*, 1119*s*, 1062*s* (br.), 902*w*, 845*w*, 789*w*, 656*m*, 610*w*, 556*w*, 526*w*. $^1$H-NMR (500 MHz, $(D_6)$DMSO)[12]: 5.65 (*d*, $J = 6.4$, OH–C(4)); 5.61 (*d*, $J = 4.4$, OH–C(5)); 4.85 (*t*, $J = 6.0$, OH–C(1)); 4.69 (*dd*, $J = 1.1$, 5.5, H–C(6)); 3.84 (*ddd*, $J = 1.8$, 4.9, 10.7, H–C(2)); 3.63–3.60 (*m*, H–C(1)); 3.60 (br. *dt*, $J = 6.5$, 9.9, H–C(4)); 3.52 (br. *td*, $J \approx 5.9$, 11.0, H′–C(1)); 3.26 (br. *ddd*, $J \approx 4.5$, 5.5, 9.5, H–C(5)); 2.47 (*dt*, $J \approx 1.1$, 10.6, H–C(3)). $^{13}$C-NMR (125 MHz, $(D_6)$DMSO): 79.85 (*s*, C(10)); 75.12 (*d*, C(2)); 73.20 (*s*, C(7)); 72.61 (*s*, C(8)); 71.93 (*d*, C(4)); 70.78 (*d*, C(5)); 68.73 (*d*, C(6)); 65.69 (*s*, C(9)); 61.85 (*t*, C(1)); 37.53 (*d*, C(3)). MALDI-MS: 605 ($[M + Na]^+$). Anal. calc. for $C_{30}H_{30}O_{12} \cdot 2\,H_2O$ (618.59): C 58.25, H 5.54; found: C 58.49, H 5.58.

*1,4-Di-*O*-acetyl-5-*O*-allyl-2,6-anhydro-3,7,8-trideoxy-3-*C*-ethynyl-8-*C*-(trimethylsilyl)-*D*-glycero-*L*-gulo-oct-7-ynitol* (**19**). A soln. of **1** (9.7 mg, 25 μmol) in $CH_2Cl_2$ (0.5 ml) was treated at 0° under $N_2$ with $FeCl_3$ (20 mg, 124 μmol) and $Ac_2O$ (12 μl, 124 μmol), stirred for 90 min, and treated with $CHCl_3$ and sat. aq. $NaHCO_3$ soln. Workup ($CHCl_3$) and FC (hexane/$Et_2O$ 7:3) gave **19** (*ca.* 6 mg, *ca.* 65%). Colourless oil. $R_f$ (hexane/$Et_2O$ 3:2) 0.24. $[\alpha]_D^{25} = 160.3$ ($c = 0.2$, $CHCl_3$). IR: 3307*m*, 2962*m*, 2901*w*, 2172*w*, 1744*s* (br.), 1455*w*, 1422*w*, 1371*m*, 1146*m*, 1124*m*, 1072*s* (br.), 1038*s*, 898*m*, 846*s*, 654*m*. $^1$H-NMR (500 MHz, $CDCl_3$): 5.84 (*tdd*, $J = 5.7$, 10.4, 17.2, C*H*=$CH_2$); 5.48 (*dd*, $J = 9.8$, 10.6, H–C(4)); 5.27 (*qd*, $J \approx 1.6$, 17.2), 5.17 (*qd*, $J \approx 1.3$, 10.4, CH=C$H_2$); 4.86 (*d*, $J = 5.6$, H–C(6)); 4.40 (*dd*, $J = 2.2$, 12.1, H–C(1)); 4.33 (*dd*, $J = 4.7$, 12.1, H′–C(1)); 4.20 (*ddd*, $J = 2.2$, 4.7,

[12]) The assignment of the signals in the $^1$H- and $^{13}$C-NMR spectra is based on H,H- and H,C-long-range correlation.

10.6, H–C(2)); 4.10 (*tdd*, $J$ = 1.4, 5.6, 13.2), 4.03 (*tdd*, $J$ = 1.4, 5.5, 13.2, 2 allyl. H); 3.42 (*dd*, $J$ = 5.6, 9.7, H–C(5)); 2.66 (*dt*, $J$ = 2.4, 10.6, H–C(3)); 2.13 (*d*, $J$ = 2.4, C≡CH); 2.12, 2.11 (2*s*, 2 Ac); 0.22 (*s*, $Me_3Si$). $^{13}$C-NMR (125 MHz, $CDCl_3$): 170.69, 169.69 (2*s*, 2 C=O); 134.31 (*d*, *C*H=$CH_2$); 117.45 (*t*, CH=*C*$H_2$); 98.76 (*s*, C(7)); 96.52 (*s*, C(8)); 78.58 (*d*, C≡*C*H); 76.16 (*d*, C(5)); 72.66 (*s*, *C*≡CH); 71.84, 71.74, (2*d*, C(2), C(4)); 71.47 (*t*, allyl. C); 67.54 (*d*, C(6)); 64.22 (*t*, C(1)); 35.88 (*d*, C(3)); 20.89, 20.84 (2*q*, 2 Me); –0.20 (*q*, $Me_3Si$). CI-MS ($NH_3$): 410 (8, $[M + NH_4]^+$), 393 (7, $[M + H]^+$), 225 (16), 180 (24), 100 (43), 73 (57), 49 (100). Anal. calc. for $C_{20}H_{28}O_6Si$ (392.52): C 61.20, H 7.19; found: C 61.17, H 7.35.

*1-O-Acetyl-2,6-anhydro-3,7,8-trideoxy-3-C-ethynyl-*D-glycero-L-gulo-*oct-7-ynitol* (**20**). A soln. of **1** (61 mg, 0.16 mmol) and $FeCl_3$ (152 mg, 0.94 mmol) in $CH_2Cl_2$ (8 ml) was stirred vigorously at r.t. under Ar for 48 h, treated with $Na_2CO_3$ (1 g), and stirred for 15 min. The solids were filtered off (*Celite*) and washed with acetone. Evaporation of the filtrate and FC (hexane/AcOEt 5:7) gave **20** (24 mg, 65%). Slightly yellow oil. $R_f$ (AcOEt) 0.51. $[\alpha]_D^{25}$ = 74.7 ($c$ = 0.10, $CHCl_3$). IR: 3588*m*, 3422*m* (br.), 3300*s*, 3022*m*, 2911*m*, 2111*w*, 1738*s* (br.), 1600*w*, 1450*w*, 1366*m*, 1072*s*, 1044*s*, 877*w* (br.), 644*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.87 (*dd*, $J$ = 2.3, 5.8, H–C(6)); 4.42 (*dd*, $J$ = 2.2, 12.1, H–C(1)); 4.31 (*dd*, $J$ = 5.1, 12.1, H′–C(1)); 4.16 (*ddd*, $J$ = 2.2, 5.1, 10.5, H–C(2)); 3.90 (br. *t*, $J \approx$ 9.7, H–C(4)); 3.63 (*dd*, $J$ = 5.8, 9.3, H–C(5)); 2.70–2.88 (*m*, exchange with $D_2O$, 2 OH); 2.67 (*d*, $J$ = 2.4, H–C(8)); 2.55 (*dt*, $J$ = 2.3, 10.3, H–C(3)); 2.27 (*d*, $J$ = 2.3, C≡CH); 2.11 (*s*, Ac). $^{13}$C-NMR (75 MHz, $CDCl_3$): 170.87 (*s*, C=O); 79.46 (*s*, *C*≡CH); 78.74 (*d*, C≡*C*H); 77.48 (*s*, *C*≡CH); 73.30 (*d*, C(8)); 73.16, 72.04 (2*d*, C(4), C(5)); 70.95 (*d*, C(2)); 68.18 (*d*, C(6)); 64.29 (*t*, C(1)); 37.54 (*d*, C(3)); 20.88 (*q*, Me). CI-MS: 256 (81, $[M + NH_4]^+$), 239 (100, $[M + H]^+$), 140 (66), 103 (32), 43 (23). Anal. calc. for $C_{12}H_{14}O_5$ (238.24): C 60.50, H 5.92; found: C 60.40, H 5.99.

*2,6-Anhydro-3,7,8-trideoxy-3-C-ethynyl-1,4,5-tris-O-(methoxymethyl)-8-C-(trimethylsilyl)-*D-glycero-L-gulo-*oct-7-ynitol* (**22**). A soln. of **21** (7.7 g, 28.7 mmol) in $CH_2Cl_2$ (85 ml) and formaldehyd dimethyl acetal (50 ml) was treated with $P_2O_5$ (*ca.* 30 g) at r.t. under $N_2$, until the suspension turned dark black. The mixture was poured into a mixture of sat. aq. $NaHCO_3$ soln. (100 ml) and ice (100 g). Separation of the layers, workup ($CH_2Cl_2$), and FC (hexane/$Et_2O$ 9:1) gave **22** (9.15 g, 79%). Colourless oil. $R_f$ (toluene/AcOEt 7:3) 0.45. $[\alpha]_D^{25}$ = 70.6 ($c$ = 0.75, $CHCl_3$). IR: 3307*m*, 3007*s*, 2956*m*, 2893*m*, 2170*w*, 1602*w*, 1522*w*, 1473*w*, 1442*w*, 1356*w*, 1152*s*, 1116*s*, 1037*s* (br.), 914*m*, 846*s*, 649*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.93 (*d*, $J$ = 5.6, H–C(6)); 4.89 (*d*, $J$ = 6.6), 4.82 (*d*, $J$ = 6.6), 4.72 (*d*, $J$ = 6.9), 4.65 (*d*, $J$ = 6.9, 2 MeOC*H*$_2$); 4.89 (*s*, MeOC*H*$_2$); 4.04 (*ddd*, $J$ = 2.0, 3.8, 10.5, H–C(2)); 3.91 (*t*, $J \approx$ 9.7, H–C(4)); 3.87 (*dd*, $J$ = 3.9, 11.1, H–C(1)); 3.75 (*dd*, $J$ = 2.1, 11.2, H′–C(1)); 3.46 (*dd*, $J$ = 5.6, 9.3, H–C(5)); 3.44, 3.37, 3.35 (3*s*, 3 MeO); 2.71 (*dt*, $J$ = 2.4, 10.5, H–C(3)); 2.17 (*d*, $J$ = 2.3, C≡CH); 0.17 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 100.01 (*s*, C(7)); 97.67, 97.60, 96.60 (3*t*, 3 MeO*C*$H_2$); 94.95 (*s*, C(8)); 81.27 (*d*, C≡*C*H); 78.82, 76.41 (2*d*, C(4), C(5)); 73.08 (*d*, C(2)); 71.95 (*s*, *C*≡CH); 68.40 (*d*, C(6)); 67.18 (*t*, C(1)); 56.29, 56.00, 55.29 (3*q*, 3 MeO); 36.56 (*d*, C(3)); –0.14 (*q*, $Me_3Si$). CI-MS ($NH_3$): 418 (100, $[M + NH_4]^+$), 153 (53), 45 (63). Anal. calc. for $C_{19}H_{32}O_7Si$ (400.54): C 56.97, H 8.05; found: C 56.94, H 7.98.

*Treatment of* **22** *with* $Me_3GeCl$. A soln. of **22** (8.97 g, 22.39 mmol) in THF (350 ml) was treated with EtMgBr (16.2 ml, 26.87 mmol; 1.66M in THF) at 0° under $N_2$, heated to 35°, stirred for 2 h, cooled to 0°, treated with $Me_3GeCl$ (3.31 ml, 26.87 mmol), and stirred for 1 h. Workup ($Et_2O$) and FC (hexane/$Et_2O$ 9:1 → 4:1) gave **24** (125 mg, 1%) as a slightly yellow oil, and **23** (10.45 g, 90%) and **22** (590 mg, 6%) as colourless oils.

*2,6-Anhydro-3,7,8-trideoxy-1,4,5-tris-O-(methoxymethyl)-3-C-[2-(trimethylgermyl)ethynyl]-8-C-(trimethylsilyl)-*D-glycero-L-gulo-*oct-7-ynitol* (**23**): $R_f$ (toluene/AcOEt 4:1) 0.50. $[\alpha]_D^{25}$ = 57.6 ($c$ = 0.67, $CHCl_3$). IR: 3007*m*, 2959*m*, 2894*m*, 2827*w*, 2170*w*, 1601*w*, 1432*w*, 1409*w*, 1355*w*, 1336*w*, 1152*m*, 1115*m*, 1074*m*, 1036*s* (br.), 961*w*, 914*m*, 845*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 4.93 (*d*, $J$ = 5.8, H–C(6)); 4.89 (*s*, MeOC*H*$_2$); 4.74 (*d*, $J$ = 6.9), 4.68 (*d*, $J$ = 6.9, MeOC*H*$_2$); 4.66 (*s*, MeOC*H*$_2$); 4.02 (*ddd*, $J$ = 2.0, 3.9, 10.5, H–C(2)); 3.91 (br. *t*, $J \approx$ 9.8, H–C(4)); 3.90 (*dd*, $J$ = 3.9, 11.0, H–C(1)); 3.75 (*dd*, $J$ = 2.1, 11.0, H′–C(1)); 3.47 (*dd*, $J$ = 5.7, 9.7, H–C(5)); 3.47, 3.39, 3.37 (3*s*, 3 MeO); 2.74 (*t*, $J$ = 10.5, H–C(3)); 0.26 (*s*, $Me_3Ge$); 0.20 (*s*, $Me_3Si$). $^{13}$C-NMR (78 MHz, $CDCl_3$): 101.96 (*s*, C≡CGe); 100.33 (*s*, C(7)); 97.63 (2 C), 96.61 (2*t*, 3 MeO*C*$H_2$); 94.89 (*s*, C(8)); 88.42 (*s*, C≡*C*Ge); 78.88, 76.51 (*d*, C(4), C(5)); 73.43 (*d*, C(2)); 68.47 (*d*, C(6)); 67.33 (*t*, C(1)); 56.29, 56.03, 55.23 (3*q*, 3 MeO); 37.77 (*d*, C(3)); –0.14, –0.27 (2*q*, $Me_3Ge$, $Me_3Si$). CI-MS ($NH_3$): 537 (39), 536 (100, $[M + NH_4]^+$), 535 (49), 534 (71), 533 (15), 532 (49), 337 (71), 136 (86), 119 (69). Anal. calc. for $C_{22}H_{40}GeO_7Si$ (517.25): C 51.09, H 7.79; found: C 50.90, H 7.78.

*3,7-Anhydro-1,2,4,6-tetradeoxy-5,8-bis-O-(methoxymethyl)-6-C-[2-(trimethylgermyl)ethynyl]-1-C-(trimethylsilyl)-*D-arabino-*oct-3-en-1-ynitol* (**24**): $R_f$ (toluene/AcOEt 4:1) 0.81. $[\alpha]_D^{25}$ = 26.4 ($c$ = 0.86, $CHCl_3$). UV ($CH_2Cl_2$): 268 (826). IR: 2959*m*, 2891*m*, 2825*w*, 2165*w*, 1637*m*, 1465*w*, 1409*w*, 1336*m*, 1181*s*, 1151*s*, 1097*s*, 1034*s* (br.), 912*m*, 852*s* (br.). $^1$H-NMR (400 MHz, $CDCl_3$): 5.44 (*d*, $J$ = 2.5, H–C(4)); 4.81 (*d*, $J$ = 6.9), 4.70 (*d*, $J$ = 6.9, MeOC*H*$_2$); 4.66 (*s*, MeOC*H*$_2$); 4.37 (*dd*, $J$ = 2.4, 9.2, H–C(5)); 3.99 (*ddd*, $J$ = 2.3, 4.3, 10.5, H–C(7)); 3.92 (*dd*, $J$ = 4.3, 11.1, H–C(8)); 3.86 (*dd*, $J$ = 2.2, 11.1, H′–C(8)); 3.41, 3.37 (2*s*, 2 MeO); 2.91 (*dd*, $J$ = 9.3, 10.5,

H–C(6)); 0.29 (*s*, $Me_3Ge$); 0.15 (*s*, $Me_3Si$). $^{13}C$-NMR (100 MHz, $CDCl_3$): 138.12 (*s*, C(3)); 109.32 (*d*, C(4)); 102.16 (*s*, *C*≡CGe); 98.44 (*s*, C(2)); 96.70, 95.26 (2*t*, 2 MeO*C*$H_2$); 94.64 (*s*, C(1)); 89.18 (*s*, C≡*C*Ge); 77.78 (*d*, C(5)); 72.81 (*d*, C(7)); 67.08 (*t*, C(8)); 55.58, 55.37 (2*q*, 2 MeO); 34.51 (*d*, C(6)); −0.31, −0.42 (2*q*, $Me_3Ge$, $Me_3Si$). CI-MS ($NH_3$): 457 (4), 455 (3, $[M + H]^+$), 397 (28), 396 (25), 395 (100), 394 (40), 393 (78), 392 (14), 391 (53), 118 (58). Anal. calc. for $C_{20}H_{34}GeO_5Si$ (455.18): C 52.77, H 7.53; found: C 52.84, H 7.62.

*2,6-Anhydro-3,7,8-trideoxy-1,4,5-tris-O-(methoxymethyl)-3-C-[2-(trimethylgermyl)ethynyl]*-D-glycero-L-gulo-*oct-7-ynitol* (**25**). A soln. of **23** (10.5 g, 20.3 mmol) and CsF (3.08 g, 20.3 mmol) in DMF (90 ml) and MeOH (18 ml) was stirred for 20 min at 0° under $N_2$. Workup ($Et_2O$) and FC (hexane/AcOEt 4:1) gave **25** (8.67 g, 96%). Colourless oil. $R_f$ (toluene/AcOEt 4:1) 0.38. $[\alpha]_D^{25} = 32.7$ ($c = 0.66$, $CHCl_3$). IR: 3305*m*, 3007*m*, 2894*m*, 2827*w*, 2170*w*, 1442*w*, 1406*w*, 1356*w*, 1337*w*, 1152*s*, 1114*s*, 1033*s* (br.), 959*m*, 916*m*. $^1H$-NMR (300 MHz, $CDCl_3$): 4.95 (*dd*, $J = 2.2$, 5.8, H–C(6)); 4.91 (*d*, $J \approx 6.5$), 4.89 (*d*, $J = 6.5$), 4.78 (*d*, $J = 6.8$), 4.7 (*d*, $J = 6.9$, 2 MeOC$H_2$); 4. 67 (*s*, MeOC$H_2$); 4.06 (*ddd*, $J = 1.9$, 4.1, 10.5, H–C(2)); 3.95 (br. *t*, $J \approx 9.7$, H–C(4)); 3.90 (*dd*, $J = 4.3$, 10.9, H–C(1)); 3.76 (*dd*, $J = 1.9$, 10.9, H′–C(1)); 3.52 (*dd*, $J = 5.8$, 9.5, H–C(5)); 3.47, 3.40, 3.38 (3*s*, 3 MeO); 2.75 (*t*, $J = 10.5$, H–C(3)); 2.60 (*d*, $J = 2.2$, H–C(8)); 0.32 (*s*, $Me_3Ge$). $^{13}C$-NMR (75 MHz, $CDCl_3$): 101.92 (*s*, *C*≡CGe); 97.79, 97.63, 96.85 (3*t*, 3 MeO*C*$H_2$); 88.82 (*s*, C≡*C*Ge); 78.58 (*d*, C(8)); 78.42, 76.23 (2*d*, C(4), C(5)); 73.59 (*d*, C(2)); 67.96 (*d*, C(6)); 67.33 (*t*, C(1)); 56.31, 56.06, 55.31 (3*q*, 3 MeO); 37.88 (*d*, C(3)); −0.27 (*q*, $Me_3Ge$); 1*s* for C(7) is missing. CI-MS ($NH_3$): 464 (16, $[M + NH_4]^+$), 463 (6), 462 (12), 297 (13), 266 (16), 265 (100), 221 (42). Anal. calc. for $C_{19}H_{32}GeO_7$ (445.07): C 51.28, H 7.25; found: C 51.02, H 7.20.

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3,7,8-trideoxy-3-C-ethynyl-8-C-(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**26**). A soln. of **21** (12.0 g, 44.6 mmol) in pyridine (100 ml) and $Ac_2O$ (80 ml) was stirred for 18 h at r.t. and evaporated. FC (hexane/AcOEt 15:1 → 9:1) gave **26** (16.73 g, 95%). White crystals. $R_f$ (toluene/AcOEt 4:1) 0.22. M.p. 70–71°. $[\alpha]_D^{25} = 112.3$ ($c = 0.94$, $CDCl_3$). IR: 3307*m*, 2962*w*, 2177*w*, 1747*s* (br.), 1371*m*, 1151*w*, 1126*w*, 1073*m*, 1040*m*, 908*m*, 847*m*. $^1H$-NMR (300 MHz, $CDCl_3$): 5.55 (br. *t*, $J \approx 10.4$, H–C(4)); 4.96 (*d*, $J = 5.7$, H–C(6)); 4.74 (*dd*, $J = 5.7$, 10.0, H–C(5)); 4.42 (*dd*, $J = 2.0$, 12.0, H–C(1)); 4.29 (*dd*, $J = 4.7$, 12.1, H′–C(1)); 4.17 (*ddd*, $J = 2.1$, 4.7, 10.5, H–C(2)); 2.74 (*dt*, $J = 2.5$, 10.8, H–C(3)); 2.16 (*d*, $J = 2.5$, C≡CH); 2.09, 2.08, 2.04 (3*s*, 3 Ac); 0.21 (*s*, $Me_3Si$). $^{13}C$-NMR (75 MHz, $CDCl_3$): 170.65, 170.10, 169.68 (3*s*, 3 C=O); 97.83 (*s*, C(7)); 96.78 (*s*, C(8)); 78.11 (*d*, C≡*C*H); 73.03, 70.14, 70.07 (3*d*, C(2), C(4), C(5)); 71.69 (*s*, *C*≡CH); 66.22 (*d*, C(6)); 63.91 (*t*, C(1)); 35.76 (*d*, C(3)); 20.81 (*q*, Me); 20.74 (*q*, 2 Me); −0.29 (*q*, $Me_3Si$). CI-MS ($NH_3$): 412 (100, $[M + NH_4]^+$), 395 (25, $[M + H]^+$). Anal. calc. for $C_{19}H_{26}O_7Si$ (394.50): C 57.85, H 6.64; found: C 57.71, H 6.74.

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3*-C-*(bromoethynyl)-3,7,8-trideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**27**). A soln. of **26** (14.94 g, 37.8 mmol) and $CBr_4$ (37.68 g, 113.6 mmol) in $CH_2Cl_2$ (160 ml) was treated with $PPh_3$ (59.6 g, 227.2 mmol) at 0° under $N_2$, warmed to r.t., stirred for 2 h, and diluted with $Et_2O$. The solids were filtered off and washed extensively with $Et_2O$. The combined filtrates were washed with a sat. aq. $Na_2S_2O_3$ soln. and $H_2O$, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 9:1 → 4:1) gave **27** (17.42 g, 97%). White crystals. $R_f$ (hexane/AcOEt 4:1) 0.24. M.p. 74.5–75°. $[\alpha]_D^{25} = 124.7$ ($c = 0.63$, $CDCl_3$). IR: 2961*m*, 2219*w*, 2173*w*, 1744*s* (br.), 1454*w*, 1371*s*, 1151*m*, 1127*m*, 1070*s*, 907*m*, 846*s*. $^1H$-NMR (300 MHz, $CDCl_3$): 5.51 (br. *t*, $J \approx 10.3$, H–C(4)); 4.97 (*d*, $J = 5.9$, H–C(6)); 4.74 (*dd*, $J = 5.8$, 10.0, H–C(5)); 4.41 (*dd*, $J = 2.3$, 12.1, H–C(1)); 4.27 (*dd*, $J = 4.6$, 12.1, H′–C(1)); 4.17 (*ddd*, $J = 2.5$, 4.7, 10.3, H–C(2)); 2.77 (*t*, $J = 10.5$, H–C(3)); 2.11, 2.09, 2.05 (3*s*, 3 Ac); 0.22 (*s*, $Me_3Si$). $^{13}C$-NMR (75 MHz, $CDCl_3$): 170.67, 170.12, 169.53 (3*s*, 3 C=O); 97.74 (*s*, C(7)); 96.81 (*s*, C(8)); 74.23 (*s*, *C*≡CBr); 71.48, 70.05 (2 C; 2*d*, C(2), C(4), C(5)); 66.22 (*d*, C(6)); 64.01 (*t*, C(1)); 44.26 (*s*, C≡*C*Br); 37.01 (*d*, C(3)); 20.77 (*q*, 3 Me); −0.25 (*q*, $Me_3Si$). CI-MS ($NH_3$): 492 (36), 490 (33, $[M + NH_4]^+$), 475 (17), 473 (14, $[M + H]^+$), 412 (100, $[M - Br + H + NH_4]^+$), 395 (57, $[M - Br + 2\ H]^+$). Anal. calc. for $C_{19}H_{25}BrO_7Si$ (473.39): C 48.21, H 5.32; found: C 48.45, H 5.06.

*Coupling of* **25** *and* **27**. A degassed soln. of **27** (1.60 g, 3.37 mmol), $[Pd_2(dba)_3]$ (43.3 mg, 90.9 μmol), CuI (12.8 mg, 67.4 μmol), and 1,2,2,6,6-pentamethylpiperidine (1.64 ml, 9.09 mmol) in DMSO (18 ml) was treated at r.t. under $N_2$ with a soln. of **25** (1.50 g, 3.37 mmol) in DMSO (12 ml) and stirred for 7 h. Workup ($Et_2O$) and crystallization from $^t$BuOMe gave **28** (1.5 g), which was recrystallized in $^t$BuOMe (→ 0.94 g of **28**). FC (toluene/AcOEt 15:1 → 9:1) of the combined mother liquors gave **30** (150 mg, 11%) as a white foam, **28** (1.08 g, → total 72%) as white crystals, and **29** (0.20 g, 13%) as a white solid.

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3*-C-*{2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris-O-(methoxymethyl)-3*-C-*[2-(trimethylgermyl)ethynyl]*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}-3,7,8-trideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**28**): $R_f$ (toluene/AcOEt 4:1) 0.30. M.p. 99–99.5°. $[\alpha]_D^{25} = 133.5$ ($c = 0.66$, $CDCl_3$). IR: 2956*w*, 2827*w*, 2171*w*, 1749*s* (br.), 1602*w*, 1371*m*, 1152*m*, 1116*m*, 1038*s* (br.), 957*w*, 917*w*, 846*m*. $^1H$-NMR (500 MHz, $CDCl_3$): 5.54 (*dd*, $J = 10.1$, 10.5, H–C(4)); 5.02 (br. *d*, $J = 5.8$, H–C(6′)); 4.97 (*d*, $J = 5.7$, H–C(6)); 4.92 (*d*, $J = 6.5$), 4.90 (*d*, $J = 6.6$, MeOC$H_2$); 4.76 (*dd*, $J = 5.7$, 9.9, H–C(5)); 4.75 (*d*, $J = 7.0$), 4.69 (*d*, $J = 6.9$, MeOC$H_2$); 4.67 (br. *s*, MeOC$H_2$); 4.47 (*dd*, $J = 2.4$, 12.1, H–C(1)); 4.29 (*dd*, $J = 4.5$, 12.1, H′–C(1)); 4.23

(*ddd*, $J$ = 2.3, 4.4, 10.4, H–C(2)); 3.97 (*ddd*, $J$ = 1.9, 4.0, 10.5, H–C(2')); 3.91 (*dd*, $J$ = 4.0, 11.0, H–C(1')); 3.86 (*dd*, $J \approx 9.5$, 10.2, H–C(4')); 3.77 (*dd*, $J$ = 2.0, 11.0, H'–C(1')); 3.52 (*dd*, $J$ = 5.8, 9.4, H–C(5')); 3.47, 3.40, 3.38 (3*s*, 3 MeO); 2.90 (br. *t*, $J \approx 10.5$, H–C(3)); 2.76 (*t*, $J$ = 10.5, H–C(3')); 2.13, 2.11, 2.06 (3*s*, 3 Ac); 0.33 (*s*, $Me_3Ge$); 0.24 (*s*, $Me_3Si$). $^{13}$C-NMR (125 MHz, $CDCl_3$): 170.59, 170.08, 169.43 (3*s*, 3 C=O); 101.42 (*s*, *C*≡CGe); 97.79, 97.66 (2*t*, 2 MeO*C*H$_2$); 97.63 (*s*, C(7)); 96.73 (*t*, MeO*C*H$_2$); 96.94 (*s*, C(8)); 89.05 (*s*, C≡*C*Ge); 78.45, 76.43 (2*d*, C(4'), C(5')); 74.20 (*s*, *C*≡C); 74.10 (*d*, C(2')); 73.62, 72.74 (2*s*, 2 *C*≡C); 71.38, 70.12, 69.86 (3*d*, C(2), C(4), C(5)); 68.89 (*s*, *C*≡C); 68.69 (*d*, C(6')); 67.34 (*t*, C(1')); 66.24 (*d*, C(6)); 63.99 (*t*, C(1)); 56.36, 56.13, 55.32 (3*q*, 3 MeO); 37.89, 36.73 (2*d*, C(3), C(3')); 20.85, 20.77, 20.74 (3*q*, 3 Me); –0.24, –0.27 (2*q*, $Me_3Ge$, $Me_3Si$). FAB-MS: 839 (16, $[M + H]^+$), 838 (14), 837 (20), 807 (28), 747 (31), 657 (49), 119 (100). Anal. calc. for $C_{38}H_{56}GeO_{14}Si$ (837.55): C 54.49 H 6.74; found: C 54.40, H 6.71.

*1,1'-(Buta-1,3-diyne-1,4-diyl)bis{(1*R*)-1,5-anhydro-4-deoxy-2,3,6-tris*-O-*(methoxymethyl)-4*-C-*[2-(trimethylgermyl)ethynyl]*-D-glucitol} (**29**): $R_f$ (toluene/AcOEt 4:1) 0.19. M.p. 98.0–99.5°. IR: 3007*w*, 2952*m*, 2893*m*, 282*w*, 2169*w*, 1442*w*, 1333*w*, 1152*s*, 1114*m*, 1043*s* (br.), 958*w*, 917*w*, 834*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 5.05 (*d*, $J$ = 5.8, H–C(1)); 4.94 (*d*, $J$ = 6.5), 4.91 (*d*, $J$ = 6.5), 4.78 (*d*, $J$ = 6.8), 4.71 (*d*, $J$ = 6.8, 2 MeO*C*H$_2$); 4.68 (*s*, MeO*C*H$_2$); 4.05 (*ddd*, $J$ = 2.0, 3.9, 10.5, H–C(5)); 3.94 (*dd*, $J$ = 4.0, 11.0, H–C(6)); 3.91 (*dd*, $J$ = 9.6, 10.2, H–C(3)); 3.79 (*dd*, $J$ = 2.0, 11.0, H'–C(6)); 3.55 (*dd*, $J$ = 5.8, 9.3, H–C(2)); 3.48, 3.41, 3.40 (3*s*, 3 MeO); 2.78 (*t*, $J$ = 10.3, H–C(4)); 0.34 (*s*, $Me_3Ge$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 101.37 (*s*, *C*≡CGe); 97.72, 97.66, 96.69 (3*t*, 3 MeO*C*H$_2$); 89.02 (*s*, C≡*C*Ge); 78.33, 76.44 (2*d*, C(2), C(3)); 74.88 (*s*, *C*≡C); 74.07 (*d*, C(5)); 72.82 (*s*, *C*≡C); 68.69 (*d*, C(1)); 67.31 (*t*, C(6)); 56.32, 56.08, 55.28 (3*q*, 3 MeO); 37.86 (*d*, C(4)); –0.31 (*q*, $Me_3Ge$). FAB-MS: 889 (20, $[M + H]^+$), 888 (14, $M^+$), 813 (24), 761 (25), 707 (40), 655 (50), 119 (100).

*3,3'-(Buta-1,3-diyne-1,4-diyl)bis{1,4,5-tri*-O-*acetyl-2,6-anhydro-3,7,8-trideoxy-8*-C-*[2-(trimethylsilyl)ethynyl)*-D-glycero-L-gulo-*oct-7-ynitol*} (**30**): $R_f$ (toluene/AcOEt 4:1) 0.44. $[\alpha]_D^{25}$ = 145.1 ($c$ = 1.57, $CDCl_3$). IR: 3008*w*, 2961*m*, 2177*w*, 1749*s* (br.), 1371*s*, 1148*w*, 1122*w*, 1069*s* (br.), 1040*s*, 904*m*, 847*s*. $^1$H-NMR (400 MHz, $CDCl_3$): 5.51 (br. *t*, $J \approx 10.3$, H–C(4)); 4.97 (*d*, $J$ = 5.8, H–C(6)); 4.75 (*dd*, $J$ = 5.8, 9.9, H–C(5)); 4.41 (*dd*, $J$ = 2.3, 12.1, H–C(1)); 4.25 (*dd*, $J$ = 4.5, 12.1, H'–C(1)); 4.18 (*ddd*, $J$ = 2.1, 4.4, 10.3, H–C(2)); 2.84 (br. *t*, $J$ = 10.4, H–C(3)); 2.12, 2.11, 2.06 (3*s*, 3 Ac); 0.23 (*s*, $Me_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.51, 169.99, 169.46 (3*s*, 3 C=O); 97.55 (*s*, C(7)); 96.86 (*s*, C(8)); 72.70 (*s*, *C*≡C); 71.27, 69.94, 69.75 (3*d*, C(2), C(4), C(5)); 68.68 (*s*, *C*≡C); 66.18 (*d*, C(6)); 63.87 (*t*, C(1)); 36.60 (*d*, C(3)); –0.32 (*q*, $Me_3Si$). FAB-MS: 787 (100, $[M + H]^+$). Anal. calc. for $C_{38}H_{50}O_{14}Si_2$ (786.98): C 58.00, H 6.40; found: C 57.99, H 6.53.

*X-Ray Analysis of* **28**: Crystals were obtained from $^t$BuOMe at 4°. $C_{38}H_{56}GeO_{14}Si$ (837.5). Trigonal *Pbcn*; $a$ = 35.221(10), $b$ = 35.221(9), $c$ = 11.273(3) Å; $V$ = 12111(6) Å$^3$, $D_{calc}$ = 1.034 Mg/m$^3$; $Z$ = 9. The crystals were measured in the $\omega/2\theta$ mode on an *Enraf-Nonius-CAD-4* diffractometer (graphite monochromator, Mo$K_\alpha$, $\lambda$ = 1.54184 Å) at 293(2) K. Of the 4658 total collected reflections, 4652 were independent, $R$ = 0.0631, $R_w$ = 0.1647. Part of the structure was solved by direct methods, the remaining non-H-atoms were found from a difference *Fourier* map with SHELX86 [35]. The non-H-atoms were refined anisotropically with SHELXL-92.

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3*-C-*{2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)-3*-C-*[2-(trimethylgermyl)ethynyl]*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}-3,7,8-trideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**31**). A soln. of **28** (188 mg, 0.224 mmol) and CsF (34 mg, 0.224 mmol) in DMF (1 ml) and MeOH (0.2 ml) was stirred at 0° for 20 min. Workup (AcOEt) and FC (toluene/AcOEt 9:1) gave **31** (164 mg, 95%). White solid. $R_f$ (toluene/AcOEt 4:1) 0.20. M.p. 50–52°. $[\alpha]_D^{25}$ = 114.3 ($c$ = 0.56, $CDCl_3$). IR: 3304*m*, 2931*w*, 2827*w*, 2166*w*, 1748*s* (br.), 1601*m*, 1371*m*, 1152*m*, 1042*m*, 916*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 5.51 (br. *t*, $J \approx 10.3$, H–C(4)); 4.97 (br. *d*, $J$ = 5.8, H–C(6')); 4.93 (*dd*, $J$ = 2.3, 5.8, H–C(6)); 4.88 (*d*, $J$ = 6.6), 4.86 (*d*, $J$ = 6.6, MeO*C*H$_2$); 4.77 (*dd*, $J$ = 5.7, 9.9, H–C(5)); 4.61 (*d*, $J$ = 6.9), 4.64 (*d*, $J$ = 6.9, MeO*C*H$_2$); 4.63 (*s*, MeO*C*H$_2$); 4.44–4.40 (*m*, with virt. coupling, H–C(1)); 4.39–4.22 (*m*, *AB*, H'–C(1), H–C(2)); 3.92 (*ddd*, $J$ = 1.9, 3.9, 10.5, H–C(2')); 3.87 (*dd*, $J$ = 4.0, 10.9, H–C(1')); 3.82 (br. *t*, $J \approx 10.1$, H–C(4')); 3.72 (*dd*, $J$ = 1.8, 10.9, H'–C(1')); 3.48 (*dd*, $J$ = 5.8, 9.4, H–C(5')); 3.43, 3.35, 3.34 (3*s*, 3 MeO); 2.86 (br. *t*, $J \approx 10.6$, H–C(3)); 2.72 (*t*, $J$ = 10.5, H–C(3')); 2.64 (*d*, $J$ = 2.3, H–C(8)); 2.07, 2.06, 2.03 (3*s*, 3 Ac); 0.29 (*s*, $Me_3Ge$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.54, 170.00, 169.39 (3*s*, 3 C=O); 101.35 (*s*, *C*≡CGe); 97.72, 97.57, 96.64 (3*t*, 3 MeO*C*H$_2$); 88.97 (*s*, C≡*C*Ge); 78.99 (*s*, C(7)); 78.43, 76.31 (2*d*, C(4'), C(5')); 76.23 (*d*, C(8)); 74.02 (*d*, C(2')); 71.45, 69.86, 69.72 (3*d*, C(2), C(4), C(5)); 73.98, 73.61, 72.57, 68.88 (4*s*, 4*C*≡C); 68.60 (*d*, C(6')); 67.25 (*t*, C(1')); 65.63 (*d*, C(6)); 63.85 (*t*, C(1)); 56.25, 56.08, 55.29 (3*q*, 3 MeO); 37.79, 36.62 (2*d*, C(3), C(3')); 20.77, 20.68, 20.66 (3*q*, 3 Me); –0.34 (*q*, $Me_3Ge$). FAB-MS: 791 (16), 790 (20), 789 (57, $[M + Na]^+$), 788 (24), 787 (40), 585 (43), 154 (64), 119 (100). Anal. calc. for $C_{35}H_{48}GeO_{14}$ (765.37): C 54.93, H 6.32; found: C 55.09, H 6.29.

*2,6-Anhydro-3*-C-*{2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)-3*-C-*[2-(trimethylgermyl)-ethynyl]*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}-3,7,8-trideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**32**). A soln. of **28** (1.30 g, 1.55 mmol) in THF (10 ml) and MeOH (3 ml) was treated with 2% NaOMe soln. in MeOH (0.60 ml)

at 0° under $N_2$ and stirred for 7 h. Workup (AcOEt) and FC (hexane/AcOEt 3:7) gave **32** (0.87 g, 88%). White foam. $R_f$ (toluene/AcOEt 2:3) 0.11. $[\alpha]_D^{25} = 115.4$ ($c = 0.64$, $CHCl_3$). IR: 3599*m*, 3433*w* (br.), 3303*m*, 3007*m*, 2894*m* (br.), 2255*w*, 2170*w*, 1601*w*, 1336*w*, 1152*s*, 1116*s*, 1045*s* (br.), 916*w*, 833*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 4.98 (br. *d*, $J = 5.8$, H–C(6′)); 4.89 (*d*, $J = 6.6$), 4.86 (*d*, $J = 6.6$, MeOC$H_2$); 4.84 (*dd*, $J = 2.3$, 5.8, H–C(6)); 4.73 (*d*, $J = 6.8$), 4.66 (*d*, $J = 6.8$, MeOC$H_2$); 4.64 (*s*, MeOC$H_2$); 4.01 (*ddd*, $J = 2.3$, 4.4, 10.5, H–C(2′)); 3.96 (*ddd*, $J = 1.9$, 4.0, 10.5, H–C(2)); 3.90 (br. *dt*, $J \approx 3.5$, 10.2, H–C(4)); 3.87 (*dd*, $J = 4.4$, 11.0, H–C(1′)); 3.85 (br. *t*, $J \approx 10.2$, H–C(4′)); 3.83–3.77 (*m*, 2 H–C(1)); 3.73 (*dd*, $J = 1.9$, 11.0, H′–C(1′)); 3.57 (*td*, $J = 5.7$, 9.2, H–C(5)); 3.48 (*dd*, $J = 5.8$, 9.4, H–C(5′)); 3.44, 3.37, 3.35 (3*s*, 3 MeO); 3.26 (*d*, $J = 3.5$, OH–C(4)); 3.00 (*d*, $J = 5.7$, OH–C(5)); 2.72 (*t*, $J = 10.5$, H–C(3′)); 2.70 (br. *t*, $J \approx 10.3$, H–C(3)); 2.66 (*d*, $J = 2.3$, H–C(8)); 2.24 (*t*, $J = 6.5$, OH–C(1)); 0.30 (*s*, $Me_3Ge$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 101.31 (*s*, *C*≡CGe); 97.73, 97.52, 96.64 (3*t*, 3 MeO*C*$H_2$); 89.10 (*s*, C≡*C*Ge); 78.61, 77.68 (2*d*, C(4′), C(5′)); 78.39 (*d*, C(8)); 76.43, 76.33 (2*s*, C(7), *C*≡C); 74.14 (*d*, C(2′)); 73.99, 72.69, 71.14 (3*d*, C(2), C(4), C(5)); 72.95, 72.92, 68.48 (3*s*, 3 *C*≡C); 68.57, 68.14 (2*d*, C(6), C(6′)); 67.29 (*t*, C(1′)); 63.09 (*t*, C(1)); 37.82, 37.74 (2*d*, C(3), C(3′)); −0.31 (*q*, $Me_3Ge$). FAB-MS: 641 (25, $[M + H]^+$), 640 (14), 639 (24), 638 (10), 637 (18), 459 (27), 307 (47), 137 (90), 136 (84), 118 (100). Anal. calc. for $C_{29}H_{42}GeO_{11}$ (639.25): C 54.49, H 6.62; found: C 54.46, H 6.59.

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3*-C-{*2,6-anhydro-3*-C-{*2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)-3*-C-*[2-(trimethylgermyl)ethynyl]*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-*3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}*3,7,8-trideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**33**). A degassed soln. of **27** (309.5 mg, 0.65 mmol), **32** (418 mg, 0.65 mmol), $[Pd_2(dba)_3]$ (9.33 mg, 19.6 μmol), P(furyl)$_3$ (9.1 mg, 39.2 μmol), and CuI (3.1 mg, 16.3 μmol) in DMSO (7 ml) was treated with 1,2,2,6,6-pentamethylpiperidine (0.355 ml, 1.96 mmol) at r.t. under $N_2$, stirred for 20 h, and evaporated. FC (toluene/AcOEt 1:1) gave **33** (463 mg, 68%). Slightly yellow foam. $R_f$ (toluene/AcOEt 1:9) 0.50. $^1$H-NMR (400 MHz, $CDCl_3$): 5.53 (br. *t*, $J \approx 10.3$, H–C(4)); 5.01 (br. *d*, $J = 5.8$, H–C(6″)); 4.97 (*d*, $J = 5.8$, H–C(6)); 4.93 (br. *d*, $J \approx 6.1$, H–C(6′), MeOC*H*); 4.90 (*d*, $J = 6.6$), 4.76 (*d*, $J = 6.9$, 2 MeOC*H*); 4.76 (*dd*, $J = 5.8$, 9.8, H–C(5)); 4.69 (*d*, $J = 6.9$, MeOC*H*); 4.67 (*s*, MeOC$H_2$); 4.45 (*dd*, $J = 2.1$, 12.2, H–C(1)); 4.29 (*dd*, $J = 4.5$, 12.2, H′–C(1)); 4.22 (*ddd*, $J = 2.1$, 4.5, 10.5, H–C(2)); 4.00 (*ddd*, $J = 1.9$, 4.0, 10.5, H–C(2″)); 3.98–3.86 (*m*, H–C(1′), H–C(2′), H–C(4′), H–C(1″), H–C(4″)); 3.84 (br. *dd*, $J \approx 4.1$, 12.0, H′–C(1′)); 3.75 (*dd*, $J = 1.8$, 11.0, H′–C(1″)); 3.65–3.58 (*m*, H–C(5′)); 3.52 (*dd*, $J = 5.8$, 9.4, H–C(5″)); 3.48, 3.40, 3.39 (3*s*, 3 MeO); 3.01–2.86 (*m*, OH); 2.89 (br. *t*, $J \approx 10.5$, H–C(3)); 2.82–2.70 (*m*, OH); 2.76 (*t*, $J \approx 10.5$, H–C(3″)); 2.74 (br. *t*, $J \approx 10.5$, H–C(3′)); 2.02–1.96 (*m*, OH); 2.13, 2.12, 2.06 (3*s*, 3 Ac); 0.34 (*s*, $Me_3Ge$); 0.24 (*s*, $Me_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.63, 170.06, 169.52 (3*s*, 3 C=O); 101.35 (*s*, *C*≡CGe); 97.77, 97.60, 96.66 (3*t*, 3 MeO*C*$H_2$); 97.49 (*s*, C(7)); 97.00 (*s*, C(8)); 89.07 (*s*, C≡*C*Ge); 78.45, 76.33 (2*d*, C(4″), C(5″)); 75.84, 74.94 (2*s*, 2 *C*≡C); 74.58, 74.03, 72.88, 71.38, 71.18, 70.01, 69.73 (7*d*, C(2), C(4), C(5), C(2′), C(4′), C(5′), C(2″)); 73.74, 73.23, 72.83, 72.36, 68.93 (5*s*, 5 *C*≡C); 68.79, 68.64, 66.21 (3*d*, C(6), C(6′), C(6″)); 68.33 (*s*, *C*≡C); 67.25 (*t*, C(1″)); 63.91, 63.15 (2*t*, C(1), C(1′)); 56.32, 56.10, 55.30 (3*t*, 3 MeO); 37.83 (*d*, 2 C); 36.59 (*d*, C(3), C(3′), C(3″)); 20.81, 20.78, 20.70 (3*q*, 3 Me); −0.27, −0.29 (2*q*, $Me_3Ge$, $Me_3Si$).

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3,7,8-trideoxy*-C-{*1,4,5-tri*-O-*acetyl-2,6-anhydro-3*-C-{*2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)-3*-C-*[2-(trimethylgermyl)ethynyl]*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-*3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-*8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**34**). *a*) From **27** and **31**: A degassed soln. of **27** (57.2 mg, 0.12 mmol), **31** (92.5 mg, 0.12 mmol), $[Pd_2(dba)_3]$ (1.55 mg, 3.6 μmol), P(furyl)$_3$ (1.51 mg, 6.5 μmol), and CuI (0.46 mg, 2.4 μmol) in DMSO (1.1 ml) was treated with 1,2,2,6,6-pentamethylpiperidine (60 μl, 0.33 mmol) at r.t. under $N_2$, stirred for 4 h, heated to 45°, stirred for 7 h, and evaporated. FC (toluene/AcOEt 1:1) gave **34** (77 mg, 55%) as a slightly yellow foam.

*b*) From **33**: A soln. of **33** (430 mg) in pyridine (4 ml) and $Ac_2O$ (2 ml) was stirred at r.t. under $N_2$ for 12 h, and evaporated. FC (toluene/AcOEt 9:1 → 4:1) gave **34** (478 mg, 98%) as a white foam.

*Data of* **34**: $R_f$ (toluene/AcOEt 7:3) 0.27. $[\alpha]_D^{25} = 160.6$ ($c = 0.62$, $CDCl_3$). IR: 2958*w*, 2250*w*, 2172*w*, 1749*s* (br.), 1601*w*, 1441*w*, 1371*m*, 1152*w*, 1116*w*, 1039*s* (br.), 915*w*, 856*m*. $^1$H-NMR (500 MHz, $CDCl_3$): 5.55 (*dd*, $J = 10.2$, 10.4), 5.46 (br. *t*, $J \approx 10.3$, H–C(4), H–C(4″)); 5.05 (br. *d*, $J = 5.8$), 5.02 (br. *d*, $J = 5.8$, H–C(6′), H–C(6″)); 4.98 (*d*, $J = 5.7$, H–C(6)); 4.92 (*d*, $J = 6.5$), 4.90 (*d*, $J = 6.5$, MeOC$H_2$); 4.80 (*dd*, $J = 5.8$, 9.9), 4.77 (*dd*, $J = 5.8$, 9.9, H–C(5), H–C(5′)); 4.75 (*d*, $J = 6.8$), 4.68 (*d*, $J = 6.8$, MeOC$H_2$); 4.67 (*s*, MeOC$H_2$); 4.49 (*dd*, $J = 2.4$, 12.1), 4.47 (*dd*, $J = 2.4$, 12.1, H–C(1), H–C(1′)); 4.30 (*dd*, $J = 4.5$, 12.1), 4.29 (*dd*, $J = 4.5$, 12.1, H′–C(1), H′–C(1′)); 4.24 (*ddd*, $J = 2.2$, 4.3, 10.4), 4.19 (*ddd*, $J = 2.5$, 4.3, 10.5, H–C(2), H–C(2′)); 3.95 (*ddd*, $J = 1.9$, 3.9, 10.5, H–C(2″)); 3.91 (*dd*, $J = 4.0$, 10.9, H–C(1″)); 3.85 (*dd*, $J \approx 9.5$, 10.2, H–C(4″)); 3.76 (*dd*, $J = 1.8$, 10.9, H′–C(1″)); 3.51 (*dd*, $J = 5.8$, 9.4, H–C(5″)); 3.47, 3.39, 3.38 (3*s*, 3 MeO); 2.93 (br. *t*, $J \approx 10.5$), 2.92 (br. *t*, $J \approx 10.5$, H–C(3), H–C(3′)); 2.76 (*t*, $J = 10.5$, H–C(3″)); 2.15, 2.14, 2.13, 2.12, 2.10, 2.06 (6*s*, 6 Ac); 0.33 (*s*, $Me_3Ge$); 0.24 (*s*, $Me_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.57 (2 C), 170.09 (2 C), 169.56, 169.44 (4*s*, 6 C=O);

101.44 (*s*, *C*≡CGe); 97.79, 97.68, 96.73 (3*t*, 3 MeO*C*H$_2$); 97.59 (*s*, C(7)); 97.04 (*s*, C(8)); 89.05 (*s*, C≡*C*Ge); 78.46, 76.40 (2*d*, C(4″), C(5″)); 75.46 (*s*, *C*≡C); 74.14 (*d*, C(2″)); 74.06, 73.89, 73.76, 72.60 (4*s*, 4 C≡*C*); 72.03, 71.34, 70.09, 69.91, 69.88, 69.77 (6*d*, C(2), C(4), C(5), C(2′), C(4′), C(5′)); 70.93, 69.20 (2*s*, 2 *C*≡C); 68.70 (*d*, C(6″)); 68.33 (*s*, *C*≡C); 67.32 (*t*, C(1″)); 66.44, 66.26 (2*d*, C(6), C(6′)); 63.92, 63.84 (2*t*, C(1), C(1′)); 37.87, 36.78, 36.75 (3*d*, C(3), C(3′), C(3″)); 20.87 (2 C), 20.82 (2 C), 20.78, 20.76 (4*q*, 6 Ac); −0.22, −0.24 (2*q*, Me$_3$Ge, Me$_3$Si). FAB-MS: 1181 (12, [*M* + Na]$^+$), 1127 (33), 1051 (31), 885 (22), 119 (100). Anal. calc. for $C_{54}H_{72}GeO_{21}Si$ (1157.85): C 56.02, H 6.27; found: C 56.29, H 6.24.

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3,7,8-trideoxy-3*-C-{*1,4,5-tri*-O-*acetyl-2,6-anhydro-3*-C-*[2,6-anhydro-3,7,8,9,10-pentadeoxy-3*-C-*(2-iodoethynyl)-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-*8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**35**). A soln. of **34** (1.18 g, 1.01 mmol), NIS (286.6 mg, 1.27 mmol), and CuBr (36.5 mg, 0.25 mmol) in acetone (12 ml) was stirred at r.t. under Ar for 7 h in the absence of light and then diluted with a 10% aq. $Na_2S_2O_3$ soln. and AcOEt. Workup (AcOEt) and FC (hexane/AcOEt 1:1) gave **35** (1.13 g, 96%). White foam. $R_f$ (toluene/AcOEt 7:3) 0.27. M.p.: softening at 60.0–61.5°. $[\alpha]_D^{25}$ = 151.5 (*c* = 0.56, $CDCl_3$). IR: 2956*m*, 2230*w*, 1750*s* (br.), 1371*m*, 1153*m*, 1039*s* (br.), 915*w*, 847*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 5.55 (br. *t*, *J* ≈ 10.2), 5.46 (br. *t*, *J* ≈ 10.3, H–C(4), H–C(4′)); 5.05 (br. *d*, *J* = 5.8), 4.99 (br. *d*, *J* = 5.8, H–C(6′), H–C(6″)); 4.98 (*d*, *J* = 5.7, H–C(6)); 4.92 (*d*, *J* = 6.7, MeOC*H*); 4.80 (*dd*, *J* = 5.8, 9.9), 4.77 (*dd*, *J* = 5.8, 9.9, H–C(5), H–C(5′)); 4.80 (*d*, *J* = 6.7), 4.74 (*d*, *J* = 7.1), 4.68 (*d*, *J* = 7.1), 4.67 (*d*, *J* = 6.5), 4.65 (*d*, *J* = 6.5, 5 MeOC*H*); 4.49 (*dd*, *J* = 2.2, 12.0), 4.47 (*dd*, *J* = 2.2, 12.1, H–C(1), H–C(1′)); 4.31 (*dd*, *J* = 4.2, 12.1), 4.29 (*dd*, *J* = 4.3, 12.0, H′–C(1), H′–C(1′)); 4.24 (*ddd*, *J* = 2.1, 4.3, 10.5), 4.18 (*ddd*, *J* = 2.2, 4.3, 10.5, H–C(2), H–C(2′)); 4.00 (*ddd*, *J* = 1.9, 3.8, 10.5, H–C(2″)); 3.88 (*dd*, *J* ≈ 9.6, 10.1, H–C(4″)); 3.87 (*dd*, *J* = 3.9, 11.2, H–C(1″)); 3.74 (*dd*, *J* = 2.0, 11.2, H′–C(1″)); 3.51 (*dd*, *J* = 5.8, 9.5, H–C(5″)); 3.48, 3.40, 3.39 (3*s*, 3 MeO); 2.93 (br. *t*, *J* ≈ 10.5), 2.92 (br. *t*, *J* ≈ 10.5, H–C(3), H–C(3′)); 2.77 (*t*, *J* = 10.5, H–C(3″)); 2.14, 2.139, 2.136, 2.12, 2.10, 2.06 (6*s*, 6 Ac); 0.24 (*s*, Me$_3$Si). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.53 (2 C), 170.04 (2 C), 169.51, 169.39 (4*s*, 6 C=O); 97.62 (2 C), 96.60 (2*t*, 3 MeO*C*H$_2$); 97.50 (*s*, C(7)); 96.96 (*s*, C(8)); 90.89 (*s*, *C*≡CI); 78.47, 76.21 (2*d*, C(4″), C(5″)); 73.78 (*d*, C(2″)); 71.93, 71.25, 70.00, 69.82, 69.78, 69.68 (6*d*, C(2), C(4), C(5), C(2′), C(4′), C(5′)); 75.37, 73.98, 73.92, 73.41, 72.79, 70.84, 68.94, 68.25 (8*s*, 8 *C*≡C); 68.53 (*d*, C(6″)); 66.35, 66.17 (2*d*, C(6), C(6′)); 67.09 (*t*, C(1″)); 63.85, 63.76 (2*t*, C(1), C(1′)); 56.37, 56.11, 55.22 (3*q*, 3 MeO); 38.57, 36.65 (2C; 2*d*, C(3), C(3′), C(3″)); 20.80 (2 C), 20.76, 20.70 (3 C; 3*q*, 6 Me); −0.30 (*q*, Me$_3$Si); −0.88 (*s*, C≡*C*I). FAB-MS: 1189 (12, [*M* + Na]$^+$), 1059 (49), 963 (30), 136 (51), 73 (100).

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3,7,8-trideoxy-3*-C-{*1,4,5-tri*-O-*acetyl-2,6-anhydro-3*-C-*[2,6-anhydro-3*-C-*(2-bromoethynyl)-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-*1*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**36**). A soln. of **34** (174 mg, 0.15 mmol), NBS (33.4 mg, 0.19 mmol), and CuBr (5.4 mg, 37.5 µmol) in acetone (2 ml) was stirred at 23° under Ar for 8 h in the absence of light and then diluted with 10% aq. $Na_2S_2O_3$ soln. and AcOEt. Workup (AcOEt) and FC (hexane/AcOEt 4:1 → 1:1) gave **36** (166 mg, 98%). White foam. $R_f$ (toluene/AcOEt 7:3) 0.28. IR: 2955*m*, 2895*m*, 2827*w*, 2255*w*, 1750*s* (br.), 1371*m*, 1152*m*, 1117*m*, 1038*s* (br.), 909*s*, 847*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 5.48 (br. *t*, *J* ≈ 10.3), 5.46 (br. *t*, *J* ≈ 10.3, H–C(4), H–C(4′)); 5.04 (br. *d*, *J* = 5.9), 4.99 (br. *d*, *J* ≈ 5.6, H–C(6′), H–C(6″)); 4.97 (*d*, *J* ≈ 5.6, H–C(6)); 4.92 (*d*, *J* = 6.5, MeOC*H*); 4.82–4.72 (*m*, H–C(5), H–C(5′), 2 MeOC*H*); 4.67 (*d*, *J* ≈ 6.7, MeOC*H*); 4.66 (*s*, MeOC$H_2$); 4.48 (br. *dd*, *J* ≈ 2.0, 12.1), 4.47 (br. *dd*, *J* ≈ 2.1, 12.1, H–C(1), H–C(1′)); 4.28 (br. *dd*, *J* ≈ 4.1, 12.1, H′–C(1), H′–C(1′)); 4.23–4.14 (*m*, H–C(2), H–C(2′)); 3.98 (br. *ddd*, *J* ≈ 1.8, 4.0, 10.5, H–C(2″)); 3.87 (br. *t*, *J* ≈ 9.7, H–C(4″)); 3.86 (*dd*, *J* = 4.0, 11.2, H–C(1″)); 3.74 (br. *dd*, *J* ≈ 1.8, 11.1, H′–C(1″)); 3.51 (*dd*, *J* = 5.6, 9.3, H–C(5″)); 3.46, 3.38, 3.37 (3*s*, 3 MeO); 2.92 (br. *t*, *J* ≈ 10.4), 2.91 (br. *t*, *J* ≈ 10.5, H–C(3), H–C(3′)); 2.76 (*t*, *J* = 10.5, H–C(3″)); 2.13, 2.12, 2.11, 2.09, 2.05, 2.03 (6*s*, 6 Ac); 0.21 (*s*, Me$_3$Si). $^{13}$C-NMR (75 MHz, $CDCl_3$): 170.90 (2 C), 170.38, 169.87 (2 C), 169.75 (4*s*, 6 C=O); 97.81 (2 C), 97.70 (2*t*, 3 MeO*C*H$_2$); 97.15 (*s*, C(7)); 96.78 (*s*, C(8)); 78.62, 76.21 (2*d*, C(4″), C(5″)); 73.72 (*d*, C(2″)); 72.07, 71.39, 70.13, 69.95, 69.90, 69.81 (6*d*, C(2), C(4), C(5), C(2′), C(4′), C(5′)); 77.04, 75.52, 74.09, 73.53, 72.96, 70.97, 69.05, 68.40 (8*s*, 8 *C*≡C); 68.66 (*d*, C(6″)); 67.22 (*t*, C(1″)); 66.47, 66.30 (2*d*, C(6), C(6′)); 63.98, 63.90 (2*t*, C(1), C(1′)); 56.28, 56.25, 55.32 (3*q*, 3 MeO); 42.90 (*s*, C≡*C*Br); 37.69, 36.71 (2 C; 2*d*, C(3), C(3′), C(3″)); 21.06, 20.87, 20.82, 20.76 (3 C; 4*q*, 6 Me); −0.27 (*q*, Me$_3$Si); 1*s* for *C*≡C is missing. MALDI-MS: 1159 ([*M* + K]$^+$), 1143 ([*M* + Na]$^+$).

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3,7,8-trideoxy-3*-C-{*1,4,5-tri*-O-*acetyl-2,6-anhydro-3*-C-*[2,6-anhydro-3,7,8,9,10-pentadeoxy-3*-C-*(2-iodoethynyl)-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-D-glycero-L-gulo-*oct-7-ynitol* (**37**). A soln. of **35** (305 mg, 0.26 mmol), and CsF (39.6 mg, 0.26 mmol) in DMF (4 ml) and MeOH (0.8 ml) was stirred at 0° under Ar for 30 min. Workup (AcOEt) and FC (toluene/AcOEt 4:1) gave **37** (280 mg, 98%). White foam. $R_f$ (toluene/AcOEt 13:7) 0.27. IR: 3411*m* (br.), 3304*m*, 2955*m*, 2245*w*, 1751*s* (br.), 1602*w*, 1371*m*, 1155*m*, 1117*w*, 1043*s* (br.).

$^1$H-NMR (400 MHz, $CDCl_3$): 5.57 (br. *t*, $J \approx 10.2$), 5.46 (br. *t*, $J \approx 10.3$, H–C(4), H–C(4′)); 5.05 (br. *d*, $J = 5.8$), 5.00 (br. *d*, $J \approx 5.6$, H–C(6′), H–C(6″)); 4.98 (*dd*, $J = 2.3, 5.7$, H–C(6)); 4.92 (*d*, $J = 6.7$, MeOC*H*); 4.83–4.78 (*m*, H–C(5), H–C(5′), MeOC*H*); 4.74 (*d*, $J = 6.9$, MeOC*H*); 4.70–4.66 (*m*, 3 MeOC*H*); 4.49–4.45 (*m*, H–C(1), H–C(1′)); 4.33–4.27 (*m*, 3 H); 4.18 (*ddd*, $J = 2.2, 4.2, 10.5$, H′–C(1), H–C(2), H′–C(1′), H–C(2′)); 4.00 (*ddd*, $J = 1.9, 3.8, 10.5$, H–C(2″)); 3.89 (br. *t*, $J \approx 10.1$, H–C(4″)); 3.88 (*dd*, $J = 3.9, 11.2$, H–C(1″)); 3.75 (*dd*, $J = 1.8, 11.1$, H′–C(1″)); 3.51 (*dd*, $J = 5.8, 9.4$, H–C(5″)); 3.48, 3.40, 3.39 (3*s*, 3 MeO); 2.93 (br. *t*, $J \approx 10.5$), 2.92 (br. *t*, $J \approx 10.5$, H–C(3), H–C(3′)); 2.91 (*t*, $J = 10.5$, H–C(3″)); 2.69 (*d*, $J = 2.3$, H–C(8)); 2.143, 2.140 (2 Ac), 2.12, 2.10, 2.08 (5*s*, 6 Ac). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.56 (2 C), 170.07, 170.05, 169.50, 169.42 (5*s*, 6 C=O); 97.64 (2 C), 96.62 (2*t*, 3 MeO$CH_2$); 90.91 (*s*, *C*≡CI); 79.10 (*d*, C(8)); 78.48, 76.24 (2*d*, C(4″), C(5″)); 76.20, 75.29, 73.94, 73.91 (4*s*, C(7), 3 *C*≡C); 73.81 (*d*, C(2″)); 73.43, 72.81 (2*s*, *C*≡C); 71.95, 71.42, 69.84 (2 C), 69.79, 69.65 (5*d*, C(2), C(4), C(5), C(2′), C(4′), C(5′)); 70.90, 68.95 (2*s*, *C*≡C); 68.55 (*d*, C(6″)); 68.33 (*s*, *C*≡C); 67.11 (*t*, C(1″)); 66.34, 65.66 (2*d*, C(6), C(6′)); 63.80 (br. *t*, C(1), C(1′)); 56.39, 56.13, 5.29 (3*q*, 3 MeO); 38.59, 36.65 (2 C; *d*, C(3), C(3′), C(3″)); 20.82, 20.37 (2*q*, 6 Me); −0.89 (*s*, C≡*C*I). FAB-MS: 1117 (12, $[M + Na]^+$), 1063 (38), 987 (100).

*2,6-Anhydro-3*-C-{*2,6-anhydro-3*-C-*[2,6-anhydro-3,7,8,9,10-pentadeoxy-3*-C-*(2-iodoethynyl)-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}-3,7,8-trideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**38**). A soln. of **35** (1.30 g, 1.11 mmol) in THF (6.7 ml) and MeOH (26 ml) was treated at 0° under $N_2$ with 2% NaOMe soln. in MeOH (1.3 ml), stirred for 4 h, neutralized with *Dowex* ($H^+$ form), and filtered. Evaporation left **38** (0.925 g, 98%). White foam. $R_f$ (AcOEt/MeOH 19:1) 0.27. M.p.: softening at 80.0–83.5°. $[\alpha]_D^{25} = 102.1$ ($c = 0.31$, $CH_3OH$). IR: 3419*s* (br.), 3300 (sh), 2926*m* (br.), 2254*w*, 2111*w*, 1338*w*, 1031*s* (br.), 915*m*. $^1$H-NMR (300 MHz, $CD_3OD$): 4.98 (br. *d*, $J = 5.6$, H–C(6″)); 4.92–4.69 (*m*, H–C(6), H–C(6′), 2 MeO$CH_2$); 4.65 (*d*, $J = 6.5$), 4.62 (*d*, $J = 6.5$, MeO$CH_2$); 4.02–3.60 (*m*, 2 H–C(1), H–C(2), H–C(4), 2 H–C(1′), H–C(2′), H–C(4′), 2 H–C(1″), H–C(2″), H–C(4″)); 3.52–3.27 (*m*, H–C(5), H–C(5′), H–C(5″)); 3.47, 3.40, 3.37 (3*s*, 3 MeO); 3.01 (*d*, $J = 2.4$, H–C(8)); 2.76 (br. *t*, $J \approx 10.5$), 2.64 (br. *t*, $J \approx 10.5$), 2.62 (br. *t*, $J \approx 10.5$, H–C(3), H–C(3′), H–C(3″)). $^{13}$C-NMR (75 MHz, $CD_3OD$): 98.99, 98.78, 97.97 (3*t*, 3 MeO$CH_2$); 91.51 (*s*, *C*≡CI); 79.61 (*d*, C(8)); 80.12, 77.78 (2*d*, C(4″), C(5″)); 76.61, 76.11, 75.66, 73.75, 73.56, 72.80, 72.62, (7*d*, C(2), C(4), C(5), C(2′), C(4′), C(5′), C(2″)); 79.44, 79.32, 74.67, 74.60, 73.70 (2 C), 73.46, 68.40, 68.31 (8*s*, C(7), 8 *C*≡C); 70.82, 70.17, 69.77 (3*d*, C(6), C(6′), C(6″)); 68.95 (*t*, C(1″)); 64.50, 63.82 (2*t*, C(1), C(1′)); 57.04, 56.73, 55.82 (3*q*, 3 MeO); 39.89, 39.55 (2 C; 2*d*, C(3), C(3′), C(3″)); 4.64 (*s*, C≡*C*I). MALDI-MS: 865 ($[M + Na]^+$).

*2,6-Anhydro-3*-C-{*2,6-anhydro-3*-C-*[2,6-anhydro-3*-C-*(2-bromoethynyl)-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}-3,7,8-trideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**39**). A soln. of **36** (160 mg, 0.14 mmol) in THF (0.8 ml) and MeOH (3 ml) was treated at 0° under $N_2$ with 2% NaOMe soln. in MeOH (0.16 ml), stirred for 3 h, neutralized with *Dowex* ($H^+$ form), and filtered. Evaporation left **39** (111 mg, 98%). White foam. $R_f$ (AcOEt/MeOH 19:1) 0.29. IR (KBr): 3423*s* (br.), 3288 (sh), 2926*m* (br.), 2254*w*, 2114*w*, 1449*w*, 1337*m*, 1219*w*, 1153*m*, 1118*s*, 1030*s* (br.), 916*m*. $^1$H-NMR (300 MHz, $CD_3OD$): 4.99 (br. *d*, $J = 5.6$), 4.81 (br. *d*, $J = 5.9$, H–C(1′), H–C(1″)); 4.92 (*d*, $J = 6.9$, MeOC*H*); 4.78–4.70 (*m*, H–C(1), 3 MeOC*H*); 4.64 (*d*, $J \approx 6.4$), 4.63 (*d*, $J \approx 6.4$, MeO$CH_2$); 4.00 (*ddd*, $J = 2.2, 4.1, 10.3$), 3.96 (*ddd*, $J = 2.2, 4.1, 10.3$, H–C(2), H–C(2′)); 3.93 (br. *ddd*, $J \approx 1.9, 3.9, 10.3$, H–C(2″)); 3.85 (br. *t*, $J \approx 10.0$, H–C(4″)); 3.82–3.70 (*m*, 2 H–C(1), H–C(4), H–C(5), 2 H–C(1′), H–C(4′), H–C(5′), 2 H–C(1″)); 3.50 (*dd*, $J = 5.9, 9.3$, H–C(5″)); 3.46, 3.40, 3.37 (3*s*, 3 MeO); 3.03 (*d*, $J = 2.2$, H–C(8)); 2.68 (*t*, $J \approx 10.5$, H–C(3″)); 2.64 (br. *t*, $J \approx 10.3$), 2.61 (br. *t*, $J \approx 10.3$, H–C(3), H–C(3′)). $^{13}$C-NMR (75 MHz, $CD_3OD$): 98.98, 98.80, 97.97 (3*t*, 3 MeO$CH_2$); 80.10, 77.57 (2*d*, C(4″), C(5″)); 76.62 (*d*, C(2″)); 79.50 (2 C), 79.32, 78.40, 74.71, 74.60, 73.69, 73.41, 68.90 (8*s*, 9 *C*≡C); 76.10, 75.36, 73.75, 73.56, 72.78, 72.62 (6*d*, C(2), C(4), C(5), C(2′), C(4′), C(5′)); 70.83, 70.18, 69.77 (3*d*, C(6), C(6′), C(6″)); 68.38 (*t*, C(1″)); 63.80 (*t*, C(1), C(1′)); 56.79, 56.73, 55.78 (3*q*, 3 MeO); 44.55 (*s*, C≡*C*Br); 39.54, 39.49, 38.99 (3*d*, C(3), C(3′), C(3″)); 1*d* for C(8) and 1*s* for *C*≡C are missing. MALDI-MS: 834 ($[M + K]^+$), 818 ($[M + Na]^+$).

*Bis(1,4,5-tri*-O-*acetyl-2,6-anhydro-7,8,9,10-tetradeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol)-(2,6-anhydro-7,8,9,10-tetradeoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol) 3,10′:3′,10″:3″,10-Trianhydride* (= *1$^I$,1$^{II}$,4$^I$,4$^{II}$,5$^I$,5$^{II}$-Hexa*-O-*acetyl-1$^{III}$,4$^{III}$,5$^{III}$-tris*-O-*(methoxymethyl)-cyclotris-(3*-C → *10*-C)-*(2,6-anhydro-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-3-yl)*; **40**). *a*) From **37**: A degassed soln. of $[Pd_2(dba)_3]$ (5.54 mg, 11.6 μmol), P(furyl)$_3$ (5.4 mg, 23.2 μmol), CuI (2.21 mg, 11.6 μmol), and $Et_3N$ (0.16 ml, 1.16 mmol) in DMSO (140 ml) was treated at 45° under $N_2$ with a soln. of **37** (0.255 g, 0.23 mol) in DMSO (1 ml) for 12 h, stirred for 12 h, and evaporated. FC (hexane/AcOEt 1:1 → 2:3) gave **40** (17 mg, 8%) as a white solid.

*b*) From **38**: A degassed soln. of $[Pd_2(dba)_3]$ (25.9 mg, 54.5 μmol), P(furyl)$_3$ (25.3 mg, 0.11 mmol), CuI (10.4 mg, 54.5 μmol), and $Et_3N$ (1.52 ml, 10.9 mmol) in DMSO (700 ml) was treated at 45° under $N_2$ with a soln. of **38** (0.92 g, 1.09 mmol) in DMSO (10 ml) for 8 h, stirred for 21 h, and evaporated. FC (AcOEt/MeOH 19:1)

gave a brown oil, which was dried (45°/0.1 mbar, 48 h), dissolved in $Ac_2O$ (5 ml), pyridine (10 ml), and $^i$PrOH (0.3 ml), stirred for 12 h at r.t., and evaporated. FC (toluene/AcOEt 4:1 → 3:2) of the residue gave **40** (363 mg, 35%) as a white solid.

*c*) From **39**: A degassed soln. of $[Pd_2(dba)_3]$ (3.4 mg, 7.16 μmol), $P(furyl)_3$ (3.3 mg, 14.3 μmol), CuI (1.36 mg, 7.16 μmol), and $Et_3N$ (0.1 ml, 0.72 mmol) in DMSO (120 ml) was treated at 45° under $N_2$ with a soln. of **39** (57 mg, 71.6 μmol) in DMSO (1 ml) for 9 h, stirred for 19 h, and evaporated. FC (AcOEt/MeOH 9:1) gave a brown oil, which was dried (0.1 mbar, 48 h), dissolved in pyridine (5 ml) and $Ac_2O$ (2.5 ml), stirred for 12 h at r.t., and evaporated. FC (toluene/AcOEt 9:1 → 7:3) of the residue gave **40** (46.4 mg, 67%) as a white solid.

*d*): As *c*), but with **38** (161 mg, 0.19 mmol), $[Pd_2(dba)_3]$ (9.1 mg, 19.1 μmol), $P(furyl)_3$ (8.9 mg, 38.2 μmol), CuI (3.6 mg, 19.1 μmol), and $Et_3N$ (0.27 ml, 1.91 mmol) in DMSO (320 ml): **40** (61 mg, 33%).

*Data of* **40**: $R_f$ (toluene/AcOEt 2:3) 0.31. M.p. 119.5–122.0°. $[\alpha]_D^{25} = 148.9$ ($c = 0.47$, $CDCl_3$). IR: 2955*m*, 2894*m*, 2256*w*, 1749*s* (br.), 1442*w*, 1370*s*, 1152*m*, 1111*w*, 1044*s* (br.), 909*s*. $^1$H-NMR (400 MHz, $CDCl_3$): 5.63 (br. *t*, $J \approx 9.9$), 5.57–5.55 (*m*, $J = 9.2$, 10.3, with virt. coupling, H–C(4), H–C(4′)); 5.11 (*d*, $J = 6.4$, MeOC*H*); 4.94 (*d*, $J = 5.7$), 4.85 (*dd*, $J = 5.6$, 9.6), 4.92–4.88 (*m*, 3 H, H–C(5), H–C(6), H–C(5′), H–C(6′), H–C(6″)); 4.81 (*d*, $J = 6.4$), 4.73 (*d*, $J = 6.9$, 2 MeOC*H*); 4.69 (*s*, MeOC$H_2$); 4.68 (*d*, $J \approx 6.9$, MeOC*H*); 4.46 (*dd*, $J = 2.1$, 12.0), 4.45–4.34 (*m*, 4 H); 4.33 (*dd*, $J = 4.3$, 12.0, 2 H–C(1), H–C(2), 2 H–C(1′), H–C(2′)); 4.24 (*ddd*, $J = 2.0$, 3.9, 10.4, H–C(2″)); 4.21 (br. *t*, $J \approx 9.9$, H–C(4″)); 3.89 (*dd*, $J = 4.1$, 11.3, H–C(1″)); 3.78 (*dd*, $J = 2.0$, 11.3, H′–C(1″)); 3.60 (*s*, MeO); 3.55 (*dd*, $J = 5.5$, 9.4, H–C(5″)); 3.39, 3.37 (2*s*, 2 MeO); 2.97 (br. *dt*, $J \approx 0.8$, 10.4), 2.90 (br. *t*, $J \approx 10.4$), 2.80 (br. *dt*, $J \approx 0.8$, 10.4, H–C(3), H–C(3′), H–C(3″)); 2.14, 2.13, 2.11, 2.08, 2.06, 2.02 (6*s*, 6 Ac). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.50 (2 C), 170.02, 169.83, 169.14, 168.99 (5*s*, 6 C=O); 98.03, 97.51, 96.70 (3*t*, 3 MeO$CH_2$); 78.91, 76.00 (2*d*, C(4″), C(5″)); 73.23 (*d*, C(2″)); 71.95 (2 C), 71.29, 70.51, 70.26, 69.87 (5*d*, C(2), C(4), C(5), C(2′), C(4′), C(5′)); 79.56, 76.13, 75.46, 75.37, 74.54, 73.75, 72.73, 70.92, 69.55, 68.70, 68.39, 66.99 (12*s*, 12 *C*≡C); 68.32 (*d*, C(6″)); 67.33 (*t*, C(1″)); 66.32, 66.29 (2*d*, C(6), C(6′)); 63.75 (*t*, C(1), C(1′)); 56.13, 55.88, 55.35 (3*q*, 3 MeO); 37.19, 36.03, 35.74 (3*d*, C(3), C(3′), C(3″)); 20.77 (3 C), 20.64 (2 C), 20.52 (3*q*, 6 Me). FAB-MS: 989 (5, $[M + Na]^+$), 967 (3, $[M + H]^+$), 935 (16), 891 (27), 860 (47), 859 (100). Anal. calc. for $C_{48}H_{54}O_{21}$ (966.94): C 59.62, H 5.63; found: C 59.84, H 5.85.

*Deprotection of* **40** *to* **18**. A soln. of **40** (0.345 g, 0.36 mmol) in THF (2 ml) and MeOH (8 ml) was treated with 2% NaOMe soln. in MeOH (0.4 ml) at 0° under Ar, stirred for 6 h, neutralized with *Dowex* ($H^+$ form), filtered, and evaporated. The residue was dissolved in 0.3M HCl in MeOH (10 ml), refluxed for 23 h, and evaporated. The residue was dissolved in boiling MeOH, cooled to r.t., and treated with $Et_2O$. The precipitated solids were filtered off, and the filtrate was evaporated and the residue dissolved in MeOH/$Et_2O$ 1:1 (2 ml) and ultrasonicated. The precipitated solids were filtered. Drying of the combined precipitates gave **18** (197 mg, 94%), identical (spectroscopic data) with **18** from **17**.

*Thermal Stability of* **18**. Trimer **18** was kept at 150° for 5 min. It remained colourless, and the $R_f$ value was identical to **18** before heating. After 5 min at 200°, **18** turned slightly brown.

*Solubility of* **18** *in* $H_2O$. A suspension of **18** in $H_2O$ (1.5 ml) was ultrasonicated for 5 min at 23° and filtered. Evaporation and drying (12 h, 0.05 mbar, r.t.) of 0.800 ml of the clear filtrate left 65.3 mg of **18**.

Table 1. *Dependence of the Optical Rotation* ($\alpha_D$) *of* **18** *upon Concentration and Temperature*

| **18** [mM] | 25° | 45° | 60° |
|---|---|---|---|
| 5.57 | 0.228 | 0.213 | 0.186 |
| 11.1 | 0.445 | 0.429 | 0.410 |
| 16.7 | 0.674 | 0.64 | 0.609 |
| 40.1 | 1.565 | 1.494 | 1.444 |
| 62.9 | 2.527 | 2.427 | 2.343 |
| 86.7 | 3.451 | 3.296 | 3.183 |
| 115.6 | 4.532 | 4.353 | 4.201 |
| 131.9 | 5.762 | 5.421 | 5.262 |

*1,4,5-Tri-*O*-acetyl-2,6-anhydro-3-*C*-[2,6-anhydro-3-*C*-(2-bromoethynyl)-3,7,8,9,10-pentadeoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-yl]-3,7,8-trideoxy-8-*C*-(trimethylsilyl)-*D*-glycero-*L*-gulo-oct-7-ynitol* (**41**). A soln. of **28** (118.8 mg, 0.14 mmol), NBS (30.3 mg, 0.17 mmol), and CuBr (4.06 mg, 28.3 μmol)

in acetone (1.5 ml) was stirred at r.t. under $N_2$ for 75 min in the absence of light, and then diluted with 10% aq. $Na_2S_2O_3$ soln. and AcOEt. Workup (AcOEt) and FC (hexane/AcOEt 7:3) gave **41** (101 mg, 90%). White foam. $R_f$ (toluene/AcOEt 7:3) 0.47. $[\alpha]_D^{25} = 134.2$ ($c = 0.35$, $CDCl_3$). IR: 2960*m*, 2895*m*, 2827*w*, 1749*s* (br.), 1601*w*, 1371*m*, 1152*m*, 1036*s* (br.), 916*w*, 846*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 5.53 (br. *t*, $J \approx 10.3$, H–C(4)); 5.00 (br. *d*, $J \approx 5.8$, H–C(6′)); 4.98 (*d*, $J = 5.8$, H–C(6)); 4.93 (*d*, $J = 6.7$), 4.79 (*d*, $J = 6.7$, 2 MeOC*H*); 4.76 (*dd*, $J = 5.8$, 9.9, H–C(5)); 4.74 (*d*, $J \approx 7.0$), 4.69 (*d*, $J = 6.7$), 4.68 (*d*, $J = 6.6$), 4.66 (*d*, $J = 6.6$, 4 MeOC*H*); 4.47 (*dd*, $J = 2.3$, 12.1, H–C(1)); 4.29 (*dd*, $J = 4.5$, 12.1, H′–C(1)); 4.23 (*ddd*, $J = 2.1$, 4.4, 10.3, H–C(2)); 4.01 (*ddd*, $J = 2.0$, 3.9, 10.5, H–C(2′)); 3.89 (*dd*, $J = 9.6$, 10.4, H–C(4′)); 3.88 (*dd*, $J = 3.9$, 11.2, H–C(1′)); 3.76 (*dd*, $J = 2.0$, 11.2, H′–C(1′)); 3.53 (*dd*, $J = 5.8$, 9.9, H–C(5′)); 3.48, 3.40, 3.39 (3*s*, 3 MeO); 2.90 (br. *t*, $J \approx 10.6$, H–C(3)); 2.77 (*t*, $J = 10.5$, H–C(3′)); 2.13, 2.11, 2.06 (3*s*, 3 Ac); 0.24 (*s*, $Me_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.60, 170.06, 169.43 (3*s*, 3 C=O); 97.67, 97.64, 96.65 (3*t*, 3 MeO*C*H$_2$); 97.57 (*s*, C(7)); 96.93 (*s*, C(8)); 78.46, 76.12 (2*d*, C(4′), C(5′)); 74.39 (*s*, *C*≡C); 73.59 (*d*, C(2′)); 73.16, 72.98 (2*s*, 2 *C*≡C); 71.33, 70.07, 69.79 (3*d*, C(2), C(4), C(5)); 68.66 (*s*, *C*≡C); 68.56 (*d*, C(6′)); 67.17 (*t*, C(1′)); 66.20 (*d*, C(6)); 63.96 (*t*, C(1)); 56.20, 56.13, 55.24 (3*q*, 3 MeO); 42.83 (*s*, C≡*C*Br); 37.70, 36.65 (2*d*, C(3), C(3′)); 20.82, 20.74, 20.71 (3*q*, 3 Me); −0.27 (*q*, $Me_3Si$); 1*s* for C≡C is missing. FAB-MS: 799 (16, $[M + H]^+$), 797 (13, $[M + H]^+$), 693 (27), 137 (100). Anal. calc. for $C_{35}H_{47}BrO_{14}Si$ (799.74): C 52.57, H 5.92; found: C 52.38, H 5.85.

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3*-C-*[2,6-anhydro-3,7,8,9,10-pentadeoxy-3*-C-*(2-iodoethynyl)-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]-3,7,8-trideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**42**). A soln. of **28** (1.30 g, 1.55 mmol), NIS (0.419 mg, 1.86 mmol), and CuBr (22.3 mg, 0.155 mmol) in acetone (15 ml) was stirred for 5 h in the absence of light, and diluted with 10% aq. $Na_2S_2O_3$ soln. and AcOEt. Workup (AcOEt) and FC (hexane/AcOEt 1:1) gave **42** (1.22 g, 93%). White solid. $R_f$ (toluene/AcOEt 7:3) 0.47. M.p. 105–107°. $[\alpha]_D^{25} = 121.2$ ($c = 0.58$, $CDCl_3$). IR: 3007*m*, 2957*m*, 2895*m*, 2255*w*, 2166*w*, 1749*s* (br.), 1442*w*, 1371*w*, 1152*s*, 1039*s* (br.), 958*m*, 917*m*, 847*s*. $^1$H-NMR (400 MHz, $CDCl_3$): 5.53 (*dd*, $J = 10.1$, 10.4, H–C(4)); 5.00 (br. *d*, $J = 5.8$, H–C(6′)); 4.98 (*d*, $J = 5.8$, H–C(6)); 4.93 (*d*, $J = 6.7$), 4.80 (*d*, $J = 6.7$, 2 MeOC*H*); 4.76 (*dd*, $J = 5.8$, 9.9, H–C(5)); 4.74 (*d*, $J = 6.9$), 4.69 (*d*, $J = 6.9$, MeOC$H_2$); 4.68 (*d*, $J = 6.5$), 4.66 (*d*, $J = 6.5$, 2 MeOC*H*); 4.47 (*dd*, $J = 2.3$, 12.1, H–C(1)); 4.29 (*dd*, $J = 4.5$, 12.1, H′–C(1)); 4.22 (*ddd*, $J = 2.2$, 4.4, 10.3, H–C(2)); 4.01 (*ddd*, $J = 2.0$, 3.9, 10.5, H–C(2′)); 3.89 (br. *t*, $J \approx 10.2$, H–C(4′)); 3.88 (*dd*, $J = 3.9$, 11.2, H–C(1′)); 3.75 (*dd*, $J = 2.0$, 11.2, H′–C(1′)); 3.52 (*dd*, $J = 5.8$, 9.4, H–C(5′)); 3.48, 3.40, 3.39 (3*s*, 3 MeO); 2.91 (*t*, $J = 10.5$, H–C(3′)); 2.90 (br. *t*, $J \approx 10.4$, H–C(3)); 2.13, 2.12, 2.06 (3*s*, 3 Ac); 0.24 (*s*, $Me_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.60, 170.06, 169.44 (3*s*, 3 C=O); 97.68, 97.65, 96.65 (3*t*, 3 MeO*C*H$_2$); 97.57 (*s*, C(7)); 96.93 (*s*, C(8)); 90.92 (*s*, *C*≡CI); 78.50, 76.25 (2*d*, C(4′), C(5′)); 74.38 (*s*, *C*≡C); 73.80 (*d*, C(2′)); 73.18, 72.96 (2*s*, 2 *C*≡C); 71.33, 70.07, 69.80 (3*d*, C(2), C(4), C(5)); 68.68 (*s*, *C*≡C); 68.57 (*d*, C(6′)); 67.16 (*t*, C(1′)); 66.20 (*d*, C(6)); 63.96 (*t*, C(1)); 56.41, 56.13, 55.26 (3*q*, 3 MeO); 38.64, 36.65 (2*d*, C(3), C(3′)); 20.83, 20.76, 20.71 (3*q*, 3 Me); −0.27 (*q*, $Me_3Si$); −0.90 (*s*, C≡*C*I). FAB-MS: 869 (15, $[M + Na]^+$), 847 (14, $[M + H]^+$), 815 (65), 739 (79), 679 (47), 137 (100). Anal. calc. for $C_{35}H_{47}IO_{14}Si$ (846.74): C 49.65, H 5.59; found: C 49.58, H 5.45.

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3*-C-{*2,6-anhydro-3*-C-{*2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)3*-C-*[2-(trimethylgermyl)ethynyl]*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}*-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}*-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}*-3,7,8-trideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**43**). *a*) From **32** and **41**: A degassed soln. of **32** (50.4 mg, 79 μmol), **41** (62.3 mg, 79 μmol), $[Pd_2(dba)_3]$ (1.0 mg, 2.1 μmol), $P(furyl)_3$ (1.0 mg, 4.2 μmol), and CuI (0.3 mg, 1.6 μmol) in DMSO (0.8 ml) was treated with 1,2,2,6,6-pentamethylpiperidine (39 μl, 0.21 mmol) at r.t. under Ar and stirred. After 6 h, the mixture was treated with additional $[Pd_2(dba)_3]$ (1.0 mg, 2.1 μmol) and CuI (0.3 mg, 1.6 μmol), stirred for 16 h, heated to 45°, and stirred for 4 h. Workup (AcOEt) and FC (hexane/AcOEt 1:1 → 3:7) gave **43** (60 mg, 56%) as a white foam.

*b*) From **32** and **42**: A degassed soln. of **32** (0.869 g, 1.35 mmol), **42** (1.15 g, 1.35 mmol), $[Pd_2(dba)_3]$ (19.4 mg, 40.7 μmol), $P(furyl)_3$ (18.9 mg, 81.5 μmol), and CuI (6.47 mg, 33.9 μmol) in DMSO (13 ml) was treated with $Et_3N$ (568 μl, 4 mmol) at r.t. under Ar and stirred for 12 h. Workup (AcOEt) and FC (hexane/AcOEt 1:1) gave **44** (80 mg, 4%) as a white solid and **43** (1.429 g, 77%) as a white foam.

*Data of* **43**: $R_f$ (toluene/AcOEt 1:9) 0.46. $[\alpha]_D^{25} = 124.2$ ($c = 0.60$, $CDCl_3$). M.p.: softening at 85–87°. IR: 3428*s* (br.), 3003*w*, 2955*m*, 2895*m*, 2255*w*, 2171*w*, 1749*s* (br.), 1602*m*, 1371*m*, 1152*s*, 1040*s* (br.), 917*w*. $^1$H-NMR (400 MHz, $CDCl_3$): 5.52 (br. *t*, $J \approx 10.3$, H–C(4)); 4.99 (br. *d*, $J \approx 5.9$), 4.98 (br. *d*, $J \approx 5.8$, H–C(6′), H–C(6‴)); 4.96 (*d*, $J = 5.8$, H–C(6)); 4.92 (*d*, $J = 6.7$), 4.91 (*d*, $J = 6.5$, 2 MeOC*H*); 4.90 (br. *d*, $J \approx 5.7$, H–C(6″)); 4.88 (*d*, $J = 6.6$), 4.79 (*d*, $J = 6.8$), 4.75 (*d*, $J \approx 6.8$, 3 MeOC*H*); 4.75 (*dd*, $J \approx 5.8$, 9.5, H–C(5)); 4.73 (*d*, $J \approx 6.7$), 4.67 (*d*, $J \approx 6.9$, 2 MeOC*H*); 4.66 (*s*, MeOC$H_2$); 4.65 (*s*, MeOC$H_2$); 4.64 (*d*, $J \approx 6.9$, MeOC*H*); 4.45 (*dd*, $J = 2.3$, 12.1, H–C(1)); 4.27 (*dd*, $J = 4.6$, 12.1, H′–C(1)); 4.22 (*ddd*, $J = 2.1$, 4.3, 10.4, H–C(2)); 4.04 (*ddd*, $J = 1.9$, 3.7, 10.5), 3.97 (*ddd*, $J = 1.8$, 3.7, 10.5, H–C(2′), H–C(2‴)); 3.94–3.81 (*m*, H–C(1′), H–C(4′), 2 H–C(1″), H–C(2″),

H–C(4''), H–C(1'''), H–C(4'''); 3.77 (*dd*, *J* = 1.8, 11.2), 3.74 (*dd*, *J* = 1.8, 11.0, H'–C(1'), H'–C(1''')); 3.60–3.57 (br. *m*, H–C(5'')); 3.52 (*dd*, *J* ≈ 5.8, 9.4), 3.51 (*dd*, *J* ≈ 5.9, 9.1, H–C(5'), H–C(5''')); 3.47, 3.46, 3.393, 3.390, 3.38, 3.37 (6*s*, 6 MeO); 3.17 (br. *d*, *J* ≈ 3.0, OH); 2.89 (br. *t*, *J* ≈ 10.5), 2.83 (br. *t*, *J* ≈ 10.5), 2.73 (br. *t*, *J* ≈ 10.5, H–C(3), H–C(3'), H–C(3'')); 2.75 (*t*, *J* = 10.5, H–C(3''')); 2.74 (br. *s*, OH); 2.13, 2.10, 2.04 (3*s*, 3 Ac); 2.01 (br. *t*, *J* ≈ 5.7, OH–C(1'')); 0.32 (*s*, $Me_3Ge$); 0.23 (*s*, $Me_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.98, 170.04, 169.46 (3*s*, 3 C=O); 101.35 (*s*, *C*≡CGeMe$_3$); 97.73, 97.65, 97.61, 97.58, 96.69, 96.64 (6*t*, 6 MeO*C*H$_2$); 97.53 (*s*, C(7)); 96.96 (*s*, *C*(8)); 89.03 (*s*, *C*≡*C*GeMe$_3$); 78.42, 78.28, 76.31, 76.04 (4*d*, *C*(4'), *C*(5'), C(4'''), C(5''')); 74.58, 74.01 (2*d*, C(2'), C(2'')); 73.43, 72.84, 71.48, 71.21, 70.04, 69.78 (6*d*, C(2), C(4), C(5), C(2''), C(4''), C(5'')); 78.05, 75.98, 74.51, 74.14, 73.20, 73.16, 71.83, 71.66, 68.77, 68.56, 67.57 (11*s*, 11 *C*≡C); 68.81, 68.60, 68.49 (3*d*, C(6'), C(6''), C(6''')); 66.17 (*d*, C(6)); 67.23 (*t*, C(1'), C(1''')); 64.16, 63.12 (2*t*, C(1), C(1'')); 56.29 (2 C), 56.14, 56.06, 55.35, 55.27 (5*q*, 6 MeO); 37.82, 37.80, 37.31, 36.66 (4*d*, C(3), C(3'), C(3''), C(3''')); 20.86, 20.72, 20.68 (3*q*, 3 Me); −0.30, −0.31 (2*q*, $Me_3Ge$, $Me_3Si$); 1*s* for *C*≡C is missing. MALDI-MS: 1380 ([*M* + Na]$^+$). Anal. calc. for $C_{64}H_{88}GeO_{25}Si$ (1358.08): C 56.60, H 6.53; found: C 56.51, H 6.64.

*Data of 3,3'-(Buta-1,3-diyne-1,4-diyl)bis{2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)-10*-C-*[1,4,5-tri*-O-*acetyl-2,6-anhydro-3,7,8-trideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol-3-yl]*-D-glycero-L-gulo-*deca-7,9-diynitol}* (**44**): $R_f$ (toluene/AcOEt 7:3) 0.15. M.p. 61.0–62.5°. $[\alpha]_D^{25}$ = 134.5 (*c* = 0.46, $CDCl_3$). IR: 2957*m*, 2895*m*, 2827*w*, 2254*w*, 1749*s* (br.), 1442*w*, 1371*s*, 1152*s*, 1113*m*, 1030*s* (br.), 909*s*, 847*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 5.52 (br. *t*, *J* ≈ 10.3, H–C(4')); 5.01 (br. *d*, *J* ≈ 5.9, H–C(6)); 4.96 (*d*, *J* = 5.6, H–C(6')); 4.88 (*d*, *J* = 6.6), 4.80 (*d*, *J* = 6.6, MeO*C*H$_2$); 4.74 (*dd*, *J* = 5.6, 9.8, H–C(5')); 4.73 (*d*, *J* = 6.9), 4.67 (*d*, *J* = 6.9, MeO*C*H$_2$); 4.64 (br. *s*, MeO*C*H$_2$); 4.45 (*dd*, *J* = 1.9, 11.8, H–C(1')); 4.27 (*dd*, *J* = 4.7, 12.0, H'–C(1')); 4.20 (br. *ddd*, *J* ≈ 2.0, 4.8, 10.5, H–C(2')); 3.98 (br. *ddd*, *J* ≈ 1.8, 3.8, 10.5, H–C(2)); 3.86 (br. *t*, *J* ≈ 10.0, H–C(4)); 3.83 (*dd*, *J* ≈ 3.8, 11.2, H–C(1)); 3.74 (*dd*, *J* ≈ 1.8, 11.2, H'–C(1)); 3.51 (*dd*, *J* = 5.9, 9.7, H–C(5)); 3.45, 3.38, 3.36 (3*s*, 3 MeO); 2.89 (br. *t*, *J* ≈ 10.5), 2.81 (br. *t*, *J* ≈ 10.5, H–C(3), H–C(3')); 2.11, 2.10, 2.04 (3*s*, 3 Ac); 0.22 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 170.88, 170.40, 169.77 (3*s*, 3 C=O); 97.94, 97.79 (2 C, 2*t*, 3 MeO*C*H$_2$); 97.10 (*s*, C(7')); 96.89 (*s*, C(8')); 78.47, 76.16 (2*d*, C(4), C(5)); 75.06, 74.59 (2*s*, 2 *C*≡C); 73.67 (*d*, C(2)); 73.20, 73.15 (2*s*, 2 *C*≡C); 71.49, 70.21, 69.92 (3*d*, C(2'), C(4'), C(5')); 68.74 (*d*, C(6)); 68.61, 68.75 (2*s*, 2 C≡C); 66.32 (*d*, C(6')); 67.33 (*t*, C(1)); 64.06 (*t*, C(1')); 56.34, 56.28, 55.40 (3*q*, 3 MeO); 37.46, 36.72 (2*d*, C(3), C3')); 20.86, 20.81 (2 C; 2*q*, 3 Me); −0.25 (*q*, $Me_3Si$). MALDI-MS: 1461 ([*M* + Na]$^+$). Anal. calc. for $C_{70}H_{94}O_{28}Si_2$ (1439.67): C 58.40, H 6.58; found: C 58.61, H 6.38.

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3*-C-*{2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)-3*-C-*{1,4,5-tri*-O-*acetyl-2,6-anhydro-3*-C-*{2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)-3*-C-*[2-(trimethylgermyl)ethynyl]-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl}-3,7,8-trideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**45**). A soln. of **43** (1.428 g) in pyridine (6 ml) and $Ac_2O$ (3 ml) was stirred for 13 h at r.t. under $N_2$ and evaporated. FC (toluene/AcOEt 9:1 → 1:1) gave **45** (1.483 g, 95%). White foam. $R_f$ (toluene/AcOEt 1:1) 0.48. $[\alpha]_D^{25}$ = 169.8 (*c* = 0.51, $CDCl_3$). M.p.: softening at 79–82°. IR: 3007*w*, 2985*w*, 2827*w*, 2257*w*, 2166*w*, 1749*s* (br.), 1371*m*, 1152*m*, 1114*m*, 1038*s* (br.), 917*m* (br.), 846*m* (br.). $^1$H-NMR (400 MHz, $CDCl_3$): 5.53 (br. *t*, *J* ≈ 10.2), 5.46 (br. *t*, *J* ≈ 10.3, H–C(4), H–C(4'')); 5.05 (br. *d*, *J* = 5.9), 5.03 (br. *d*, *J* = 5.8), 5.02 (br. *d*, *J* = 5.8, H–C(6'), H–C(6''), H–C(6''')); 4.98 (*d*, *J* = 5.8, H–C(6)); 4.97 (*d*, *J* = 6.8), 4.92 (*d*, *J* = 6.6), 4.90 (*d*, *J* = 6.6, 3 MeO*CH*); 4.80 (*dd*, *J* = 5.8, 9.9), 4.76 (*dd*, *J* = 5.8, 9.9, H–C(5), H–C(5'')); 4.80 (*d*, *J* = 6.8), 4.75 (*d*, *J* = 6.8, 2 H), 4.70 (*d*, *J* = 6.8, 4 MeO*CH*); 4.69 (*s*, MeO*C*H$_2$); 4.68 (*d*, *J* = 6.8, MeO*CH*); 4.67 (*s*, MeO*C*H$_2$); 4.46 (*dd*, *J* = 2.3, 12.1), 4.45 (*dd*, *J* = 2.3, 12.1, H–C(1), H–C(1'')); 4.29 (*dd*, *J* = 4.6, 12.2), 4.28 (*dd*, *J* = 4.5, 12.1, H'–C(1), H'–C(1'')); 4.22 (*ddd*, *J* = 2.4, 4.5, 10.5), 4.16 (*ddd*, *J* = 2.5, 4.6, 10.5, H–C(2), H–C(2'')); 4.05 (*ddd*, *J* = 2.1, 3.8, 10.4), 3.95 (br. *ddd*, *J* ≈ 1.9, 4.2, 10.5, H–C(2'), H–C(2''')); 3.94 (br. *t*, *J* = 10.3, H–C(4')); 3.93–3.88 (*m*, H–C(1'), H–C(1''')); 3.85 (*dd*, *J* ≈ 9.9, 10.2, H–C(4''')); 3.80 (*dd*, *J* = 2.0, 11.4), 3.76 (br. *dd*, *J* ≈ 1.6, 10.7, H'–C(1'), H'–C(1''')); 3.55 (*dd*, *J* = 5.7, 9.3), 3.52 (*dd*, *J* ≈ 5.8, 9.4, H–C(5'), H–C(5''')); 3.51, 3.47, 3.42, 3.41, 3.40, 3.38 (6*s*, 6 MeO); 2.92 (br. *t*, *J* ≈ 10.6, 2 H); 2.90 (br. *t*, *J* ≈ 10.5, H–C(3), H–C(3'), H–C(3'')); 2.77 (*t*, *J* = 10.4, H–C(3''')); 2.131, 2.129, 2.12, 2.11, 2.08, 2.06 (6*s*, 6 Ac); 0.33 (*s*, $Me_3Ge$); 0.24 (*s*, $Me_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.59, 170.54, 170.08, 170.03, 169.46, 169.28 (6*s*, 6 *C*=O); 101.42 (*s*, *C*≡CGeMe$_3$); 97.61 (*s*, C(7)); 96.94 (*s*, C(8)); 89.01 (*s*, C≡*C*GeMe$_3$); 78.48 (2 C), 76.37, 75.92, (3*d*, C(4'), C(5'), C(4'''), C(5''')); 74.10, 73.41 (2*d*, C(2'), C(2''')); 71.96, 71.37, 70.10, 69.95, 69.80, 69.76 (6*d*, C(2), C(4), C(5), C(2''), C(4''), C(5'')); 78.41, 74.55, 74.48, 73.85, 73.70, 73.13, 72.99, 72.54, 69.14, 67.61 (10*s*, 10 *C*≡C); 68.67, 68.63 (2*d*, C(6'), C(6''')); 66.41, 66.22 (2*d*, C(6), C(6'')); 67.29, 67.20 (2*t*, C(1'), C(1''')); 63.96, 63.83 (2*t*, C(1), C(1'')); 37.83, 37.45, 36.75, 36.68 (4*d*, C(3), C(3'), C(3''), C(3''')); 20.83, 20.79, 20.72 (3*q*, 6 Me); −0.25, −0.27 (2*q*, $Me_3Ge$, $Me_3Si$); 2*s* for *C*≡C are missing. MALDI-MS: 1523 ([*M* + K]$^+$), 1507 ([*M* + Na]$^+$). Anal. calc. for $C_{70}H_{94}GeO_{28}Si$ (1484.19): C 56.65, H 6.38; found: C 56.55, H 6.18.

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3*-C-{*2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)-3*-C-{*1,4,5-tri*-O-*acetyl-2,6-anhydro-3*-C-*[2,6-anhydro-3,7,8,9,10-pentadeoxy-3-C(2-iodoethynyl)-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-*3,7,8-trideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**46**). A soln. of **45** (1.49 g, 1.00 mmol), NIS (282 mg, 1.25 mmol), and CuBr (36 mg, 0.25 mmol) in acetone (10 ml) was stirred at r.t. under Ar for 7 h in the absence of light and then diluted with 10% aq. $Na_2S_2O_3$ soln. and AcOEt. Workup (AcOEt) and FC (hexane/AcOEt 1:1) gave **46** (1.45 g, 97%). White foam. $R_f$ (toluene/AcOEt 1:1) 0.49. M.p.: softening at 60–62.5°. $[\alpha]_D^{25} = 151.1$ ($c = 0.52$, $CDCl_3$). IR: 3007*w*, 2958*m*, 2894*w*, 2257*w*, 1751*s* (br.), 1371*m*, 1153*m*, 1036*s* (br.), 917*m*, 846*m*. $^1$H-NMR (500 MHz, $CDCl_3$): 5.53 (br. *t*, $J \approx 10.2$), 5.46 (br. *t*, $J \approx 10.3$, H–C(4), H–C(4″)); 5.04 (br. *d*, $J = 5.8$), 5.02 (br. *d*, $J = 5.8$), 5.00 (br. *d*, $J = 5.8$, H–C(6′), H–C(6″), H–C(6‴)); 4.97 (*d*, $J = 5.7$, H–C(6)); 4.97 (*d*, $J = 6.9$), 4.92 (*d*, $J = 6.7$, 2 MeOC*H*); 4.81 (*dd*, $J = 5.8$, 9.9), 4.75 (*dd*, $J = 5.8$, 9.9, H–C(5), H–C(5″)); 4.80 (br. *d*, $J \approx 6.8$, 2 H), 4.75 (*d*, $J = 6.9$), 4.74 (*d*, $J = 6.9$), 4.70 (*d*, $J \approx 5.0$, 5 MeOC*H*); 4.69 (*s*, MeOC$H_2$); 4.68 (*d*, $J = 4.9$), 4.67 (*d*, $J = 6.5$), 4.65 (*d*, $J = 6.5$, 3 MeOC*H*); 4.46 (*dd*, $J = 2.3$, 12.2), 4.44 (*dd*, $J = 2.3$, 12.2, H–C(1), H–C(1″)); 4.29 (*dd*, $J = 4.6$, 12.2), 4.28 (*dd*, $J = 4.5$, 12.2, H′–C(1), H′–C(1″)); 4.22 (*ddd*, $J = 2.2$, 4.4, 10.4), 4.17 (*ddd*, $J = 2.3$, 4.4, 10.5, H–C(2), H–C(2″)); 4.05 (*ddd*, $J = 1.9$, 3.7, 10.5), 3.99 (*ddd*, $J = 2.0$, 3.7, 10.5, H–C(2′), H–C(2‴)); 3.94 (*dd*, $J \approx 9.8$, 10.1, H–C(4′)); 3.90 (*dd*, $J \approx 3.8$, 11.5), 3.88 (*dd*, $J = 3.9$, 11.2, H–C(1′), H–C(1‴)); 3.82 (*dd*, $J \approx 9.7$, 10.3, H–C(4‴)); 3.80 (*dd*, $J = 2.0$, 11.4), 3.75 (*dd*, $J = 2.0$, 11.2, H′–C(1′), H′–C(1‴)); 3.55 (*dd*, $J = 5.8$, 9.3), 3.51 (*dd*, $J = 5.7$, 9.3, H–C(5′), H–C(5‴)); 3.52, 3.48, 3.41, 3.40, 3.397, 3.390 (6*s*, 6 MeO); 2.91 (*t*, $J = 10.5$, H–C(3‴)); 2.909 (br. *t*, $J \approx 10.6$, 2 H), 2.901 (br. *t*, $J \approx 10.6$, H–C(3), H–C(3′), H–C(3″)); 2.13, 2.129, 2.124, 2.11, 2.08, 2.06 (6*s*, 6 Ac); 0.24 (*s*, $Me_3Si$). $^{13}$C-NMR (125 MHz, $CDCl_3$): 170.57, 170.54, 170.06, 170.00, 169.46, 169.29 (6*s*, 6 C=O); 97.75, 97.71 (2 C), 97.68 (2 C; 3*t*, 5 MeO$CH_2$); 96.95 (*s*, C(7)); 96.72 (*s*, C(8)); 96.67 (*t*, MeO$CH_2$); 90.97 (*s*, *C*≡CI); 78.56, 78.49, 76.30, 75.92 (4*d*, C(4′), C(5′), C(4‴), C(5‴)); 73.87, 73.42 (2*d*, C(2′), C(2‴)); 71.96, 71.37, 70.10, 69.96, 69.82, 69.77 (6*d*, C(2), C(4), C(5), C(2″), C(4″), C(5″)); 78.42, 74.56, 74.50, 73.96, 73.48, 73.14, 73.01, 72.81, 68.98, 68.61, 67.60 (11*s*, 11 *C*≡C); 68.64, 68.59 (2*d*, C(6′), C(6‴)); 66.41, 66.23 (2*d*, C(6), C(6″)); 67.22, 67.17 (2*t*, C(1′), C(1‴)); 63.97, 63.83 (2*t*, C(1), C(1″)); 38.64, 37.46, 36.72, 36.69 (4*d*, C(3), C(3′), C(3″), C(3‴)); 20.83, 20.82, 20.79, 20.727, 20.719, 20.714 (6*q*, 6 Me); −0.24 (*q*, $Me_3Si$); −0.79 (*s*, C≡*C*I); 1*s* for *C*≡C is missing. MALDI-MS: 1396 ([*M* + K]$^+$).

*2,6-Anhydro-3*-C-{*2,6-anhydro-3*-C-{*2,6-anhydro-3*-C-*[2,6-anhydro-3,7,8,9,10-pentadeoxy-3*-C-*(2-iodoethynyl)-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-*3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-*3,7,8-trideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**47**). A soln. of **46** (1.44 g, 0.96 mmol) in THF (6.7 ml) and MeOH (26 ml) was treated with 2% NaOMe soln. in MeOH (11.3 ml) at 0° under $N_2$, then stirred for 4 h, neutralized with *Dowex* ($H^+$ form), and filtered. Evaporation left **47** (1.11 g, 98%). White foam. $R_f$ (AcOEt/MeOH 19:1) 0.29. M.p.: softening at 78.0–81.5°. $[\alpha]_D^{25} = 115.4$ ($c = 0.24$, MeOH). IR: 3411*s* (br.), 3290 (sh), 2910*m* (br.), 2245*w*, 2112*w*, 1359*m*, 1031*s* (br.), 915*m*. $^1$H-NMR (300 MHz, $CD_3OD$): 5.00 (br. *d*, $J \approx 5.6$, H–C(6′), H–C(6‴)); 4.97 (*d*, $J \approx 7.1$), 4.91 (*d*, $J = 6.6$, 2 MeOC*H*); 4.83–4.62 (*m*, H–C(6), H–C(6″), 10 MeOC*H*); 4.10–3.28 (*m*, 2 H–C(1), H–C(2), H–C(4), H–C(5), 2 H–C(1′), H–C(2′), H–C(4′), H–C(5′), 2 H–C(1″), H–C(2″), H–C(4″), H–C(5″), 2 H–C(1‴), H–C(2‴), H–C(4‴), H–C(5‴)); 3.52, 3.47, 3.412, 3.410, 3.39, 3.38 (6*s*, 6 MeO); 3.02 (*d*, $J = 2.2$, H–C(8)); 2.81 (br. *t*, $J \approx 10.5$), 2.64 (br. *t*, $J \approx 10.5$), 2.63 (br. *t*, $J \approx 10.5$, H–C(3), H–C(3′), H–C(3″)); 2.78 (*t*, $J = 10.5$, H–C(3‴)). $^{13}$C-HMR (125 MHz, $CD_3OD$): 98.97 (2 C), 98.79 (2 C), 97.97 (2 C; 3*t*, 6 MeO$CH_2$); 91.58 (*s*, *C*≡CI); 79.57 (*d*, C(8)); 80.11 (2 C), 77.78, 77.39 (3*d*, C(4′), C(5′), C(4‴), C(5‴)); 76.74, 76.06, 75.63, 75.24, 73.86, 73.54, 72.75, 72.65 (8*d*, C(2), C(4), C(5), C(2′), C(2‴), C(4‴), C(5‴), C(2‴)); 79.83, 79.54 (2 C), 78.88, 74.87, 74.62, 74.41 (3 C), 73.20, 68.86, 68.30, 68.14 (10*s*, 12 *C*≡C, C(7)); 70.82, 70.17, 69.77 (2 C; 3*d*, C(6), C(6′), C(6″), C(6‴)); 68.95, 68.86 (2*t*, C(1′), C(1‴)); 64.50, 63.85 (2*t*, C(1), C(1″)); 57.15, 57.04, 56.76 (2 C), 55.94, 55.84 (5*q*, 6 MeO); 39.91, 39.55 (2 C), 38.68 (3*d*, C(3), C(3′), C(3″), C(3‴)); 4.65 (*s*, C≡*C*I). MALDI-MS: 1191 ([*M* + Na]$^+$).

*1,4,5-Tri*-O-*acetyl-2,6-anhydro-3*-C-{*2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)-3*-C-{*1,4,5-tri*-O-*acetyl-2,6-anhydro-3*-C-*[2,6-anhydro-3*-C-*(2-bromoethynyl)-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl]-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*-D-glycero-L-gulo-*deca-7,9-diynitol-10-yl*}-*3,7,8-trideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**48**). A soln. of **45** (198 mg, 0.13 mmol), NBS (30 mg, 0.16 mmol), and CuBr (4.8 mg, 33 μmol) in acetone (2 ml) was stirred at r.t. under Ar for 8 h in the absence of light and then diluted with 10% aq. $Na_2S_2O_3$ soln. and AcOEt. Workup (AcOEt) and FC (toluene/AcOEt 7:3) gave **48** (184 mg, 95%). White foam. $R_f$ (toluene/AcOEt 1:1) 0.49. IR: 2958*m*, 2895*w*, 2256*w*, 1749*s* (br.), 1371*m*, 1152*s*, 1037*s* (br.), 915*m*, 846*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 5.51 (br. *t*, $J \approx 10.3$), 5.44 (br. *t*, $J \approx 10.3$, H–C(4), H–C(4″)); 5.02 (br. *d*, $J \approx 5.6$), 5.00 (br. *d*, $J \approx 5.9$), 4.98 (br. *d*, $J \approx 5.9$, H–C(6′), H–C(6″), H–C(6‴)); 4.95 (*d*, $J = 5.6$, H–C(6)); 4.94 (*d*, $J = 7.1$), 4.91 (*d*, $J = 6.9$), 4.79

(*d*, $J = 6.2$, 3 MeOC*H*); 4.77–4.70 (*m*, H–C(5), H–C(5″), 3 MeOC*H*); 4.67 (br. *s*, 2 MeOC$H_2$); 4.64 (*s*, MeOC$H_2$); 4.44 (br. *dd*, $J \approx 2.0, 11.9$), 4.42 (br. *dd*, $J \approx 2.1, 12.1$, H–C(1), H–C(1″)); 4.26 (br. *dd*, $J \approx 4.3, 11.9$, H′–C(1), H′–C(1″)); 4.19 (*ddd*, $J \approx 2.1, 4.0, 10.5$), 4.15 (*ddd*, $J = 2.1, 4.0, 10.5$, H–C(2), H–C(2″)); 4.04 (br. *ddd*, $J \approx 1.9, 3.6, 10.4$), 3.98 (*ddd*, $J \approx 2.0, 3.7, 10.4$, H–C(2′), H–C(2‴)); 3.96–3.79 (*m*, 5 H), 3.72 (*dd*, $J = 1.9, 11.2$, 2 H–C(1′), H–C(4′), 2 H–C(1‴), H–C(4‴)); 3.52 (*dd*, $J = 5.8, 9.3$), 3.50 (*dd*, $J \approx 5.8, 9.3$, H–C(5′), H–C(5‴)); 3.49, 3.45, 3.388, 3.378, 3.372, 3.36 (6*s*, 6 MeO); 2.88 (br. *t*, $J \approx 10.5$, 2 H), 2.87 (br. *t*, $J \approx 10.5$, H–C(3), H–C(3′), H–C(3″)); 2.75 (*t*, $J = 10.5$, H–C(3‴)); 2.105, 2.102, 2.098, 2.091, 2.05, 2.03 (6*s*, 6 Ac); 0.21 (*s*, $Me_3Si$). $^{13}$C-NMR (75 MHz, $CDCl_3$): 170.89, 170.85, 170.37, 170.30, 169.75, 169.59 (6*s*, 6 C=O); 97.86 (2 C), 97.83 (2 C), 97.78, 96.81 (4*t*, 6 MeO*C*$H_2$); 97.08 (*s*, C(7)); 96.86 (*s*, C(8)); 78.67, 78.62, 76.25, 76.99 (4*d*, C(4′), C(5′), C(4‴), C(5‴)); 78.53, 74.66, 74.61, 74.08, 73.54, 73.24, 73.09, 72.95, 69.05, 67.69 (10*s*, 10 *C*≡C); 73.74, 73.51 (2*d*, C(2′), C(2‴)); 72.06, 71.47, 71.18, 71.05, 69.89, 69.84 (6*d*, C(2), C(4), C(5), C(2″), C(4″), C(5″)); 68.72, 68.67 (2*d*, C(6′), C(6‴)); 67.25 (br. *t*, C(1′), C(1‴)); 66.49, 66.31 (2*d*, C(6), C(6″)); 64.06, 63.92 (2*t*, C(1), C(1″)); 56.49, 56.30 (2 C), 56.25, 55.46, 55.33 (5*q*, 6 MeO); 42.89 (*s*, C≡*C*Br); 37.71, 37.47, 36.71 (2 C; 3*d*, C(3), C(3′), C(3″), C(3‴)); 20.85 (*q*, 3 Me); 20.72 (*q*, 3 Me); −0.27 (*q*, $Me_3Si$); 3*s* for *C*≡C are missing. ESI-MS: 1469, 1467 ([*M* + Na]$^+$), 1465, 1245, 1217, 1189.

*2,6-Anhydro-3-*C*-{2,6-anhydro-3-*C*-{2,6-anhydro-3-*C*-[2,6-anhydro-3-*C*-(2-bromoethynyl)-3,7,8,9,10-pentadeoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-yl]-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-yl}-3,7,8,9,10-pentadeoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-yl}-3,7,8-trideoxy-*D*-glycero-*L*-gulo-oct-7-ynitol* (**49**). A soln. of **48** (172 mg, 0.12 mmol) in THF (1.3 ml) and MeOH (3.5 ml) was treated with 2% NaOMe soln. in MeOH (1 ml) at 0° under Ar and stirring for 3 h, neutralized with *Dowex* ($H^+$ form), and filtered. Evaporation left **49** (130 mg, 97%). White foam. $R_f$ (AcOEt/MeOH 19:1) 0.29. IR (KBr): 3677–3122*s* (br. maximum at 3439), 3300 (sh), 2925*m*, 2254*w*, 2112*w*, 1630*w*, 1457*m*, 1362*m*, 1339*m*, 1219*m*, 1154*s*, 1112*s*, 1032*s* (br.), 916*m*. $^1$H-NMR (300 MHz, $CD_3OD$): 5.01 (br. *d*, $J = 5.6$), 5.00 (br. *d*, $J \approx 5.6$), 4.80 (br. *d*, $J \approx 5.8$, H–C(6′), H–C(6″), H–C(6‴)); 4.96 (*d*, $J = 6.9$), 4.92 (*d*, $J = 6.9$), 4.78 (br. $J \approx 6.9$, 3 H, 5 MeOC*H*); 4.74–4.70 (*m*, H–C(6), 3 MeOC*H*); 4.68–4.62 (*m*, 4 MeOC*H*); 4.04 (br. *ddd*, $J \approx 1.9, 3.7, 10.4$), 4.01 (*ddd*, $J \approx 2.1, 4.0, 10.4$), 3.99 (*ddd*, $J \approx 2.1, 4.0, 10.4$, H–C(2), H–C(2′), H–C(2″)); 3.94–3.71 (*m*, 2 H–C(1), H–C(4), H–C(5), 2 H–C(1′), H–C(4′), 2 H–C(1″), H–C(4″), H–C(5″), 2 H–C(1‴), H–C(2‴), H–C(4‴)); 3.53 (*dd*, $J \approx 5.9, 9.3$), 3.47 (*dd*, $J \approx 5.9, 9.3$, H–C(5′), H–C(5‴)); 3.52, 3.46, 3.40 (2 C), 3.39, 3.37 (5*s*, 6 MeO); 3.03 (*d*, $J = 2.2$, H–C(8)); 2.81 (br. *t*, $J \approx 10.5$, H–C(3′)); 2.69 (*t*, $J = 10.3$, H–C(3″)); 2.64 (br. *t*, $J \approx 10.4$), 2.63 (br. *t*, $J \approx 10.3$, H–C(3), H–C(3″)). $^{13}$C-NMR (75 MHz, $CD_3OD$): 98.96 (3 C), 98.81 (2 C), 97.97 (3*t*, 6 MeO*C*$H_2$); 80.14, 80.08, 77.60, 77.36 (4*d*, C(4′), C(5′), C(4‴), C(5‴)); 79.59 (*d*, C(8)); 79.84, 79.60, 78.88, 78.44, 74.85, 74.66, 74.40, 73.51, 73.19, 68.27, 68.12 (11*s*, 11 *C*≡C); 76.73, 76.07 (2*d*, C(2′), C(2‴)); 75.32, 75.24, 73.85, 73.48, 72.75, 72.64 (6*d*, C(2), C(4), C(5), C(2″), C(4″), C(5″)); 70.83, 70.18, 68.76 (2 C; 3*d*, C(6), C(6′), C(6″), C(6‴)); 68.92, 68.85 (2*t*, C(1′), C(1‴)); 63.84 (br. *t*, C(1), C(1″)); 57.12, 56.78, 56.75 (2 C), 55.91, 55.81 (5*q*, 6 MeO); 44.50 (*s*, C≡*C*Br); 39.54, 39.46, 39.02, 38.66 (4*d*, C(3), C(3′), C(3″), C(3‴)); 2*s* for *C*≡C are missing.

*Bis{1,4,5-tri-*O*-acetyl-2,6-anhydro-3-*C*-[2,6-anhydro-7,8,9,10-tetradeoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-yl]-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol}3′,10‴:3,10‴-Dianhydride (= 1$^I$,1$^{III}$,4$^I$,4$^{III}$,5$^I$,5$^{III}$-Hexa-*O*-acetyl-1$^{II}$,1$^{IV}$,4$^{II}$,4$^{IV}$,5$^{II}$,5$^{IV}$-hexakis-*O*-(methoxymethyl)cyclotetrakis-(3-C → 10-C)-(2,6-anhydro-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-yl)*; **50**). *a*) From **47**: A degassed soln. of [$Pd_2$(dba)$_3$] (24.4 mg, 51.3 μmol), P(furyl)$_3$, (23.8 mg, 0.10 mmol), CuI (9.8 mg, 51.3 μmol), and $Et_3N$ (1.43 ml, 10.2 mmol) in DMSO (700 ml) was treated at 45° under $N_2$ with a soln. of **47** (1.20 g, 1.02 mmol) in DMSO (10 ml) for 8 h, stirred for 21 h, and evaporated. FC (toluene/AcOEt 1:1 → AcOEt/MeOH 19:1) gave a yellow oil, which was dissolved in $Ac_2O$ (5 ml), pyridine (10 ml), and $^i$PrOH (0.3 ml), stirred for 12 h at r.t., and evaporated. FC (toluene/AcOEt 4:1 → 1:1) of the residue gave **50** (378 mg, 29%) as a white solid.

*b*) From **49**: A degassed soln. of [$Pd_2$(dba)$_3$] (5.3 mg, 11.1 μmol), P(furyl)$_3$, (5.2 mg, 22.2 μmol), CuI (2.12 mg, 11.1 μmol), and $Et_3N$ (0.16 ml, 1.11 mmol) in DMSO (200 ml) was treated at 45° under $N_2$ with a soln. of **49** (125 mg, 0.11 mmol) in DMSO (10 ml) for 16 h, stirred for 24 h, and evaporated. FC (AcOEt/MeOH 19:1) gave a yellow oil, which was dissolved in pyridine (10 ml), $Ac_2O$ (5 ml), and $^i$PrOH (0.1 ml), stirred for 12 h at r.t., and evaporated. FC (toluene/AcOEt 4:1 → 2:3) of the residue gave **50** (82.7 mg, 57%) as a slightly yellow solid.

*c*): As *b*), but with **47** (194 mg, 0.17 mmol) [$Pd_2$(dba)$_3$] (7.9 mg, 16.5 μmol), P(furyl)$_3$ (7.7 mg, 33.1 μmol), CuI (3.16 mg, 16.5 μmol), and $Et_3N$ (0.23 ml, 1.65 mmol) in DMSO (280 ml); **50** (60.9 mg, 28%).

*Data of* **50**: $R_f$ (toluene/AcOEt 2:3) 0.32. M.p. 151.0–153.5°. $[\alpha]_D^{25} = 168.3$ ($c = 0.45$, $CDCl_3$). IR: 2954*m*, 2893*m*, 2258*w*, 1749*s* (br.), 1602*w*, 1422*w*, 1371*m*, 1152*m*, 1112*w*, 1038*s* (br.), 916*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 5.43 (br. *t*, $J \approx 10.3$, H–C(4)); 5.03 (br. *d*, $J = 5.8$), 5.02 (br. *d*, $J \approx 5.7$, H–C(6), H–C(6′)); 5.01 (*d*, $J = 6.8$, MeOC*H*); 4.79 (*dd*, $J = 5.7, 9.9$, H–C(5)); 4.78 (*d*, $J = 6.8$), 4.74 (*d*, $J = 7.0$), 4.70 (*d*, $J = 7.0$, 3 MeOC*H*); 4.67

(*s*, MeOC$H_2$); 4.45 (br. *dd*, $J \approx 2.0, 12.2$, H–C(1)); 4.33 (*dd*, $J \approx 4.2, 12.1$, H′–C(1)); 4.30 (*ddd*, $J = 2.1, 4.4, 10.5$, H–C(2)); 4.03 (*ddd*, $J = 2.0, 3.3, 10.5$, H–C(2′)); 3.96 (*dd*, $J \approx 9.3, 10.4$, H–C(4′)); 3.89 (*dd*, $J = 3.7, 11.4$, H–C(1′)); 3.79 (*dd*, $J = 1.9, 11.4$, H′–C(1′)); 3.62 (*s*, MeO); 3.52 (*dd*, $J = 5.8, 9.3$, H–C(5′)); 3.40, 3.39 (2*s*, 2 MeO); 2.91 (br. *t*, $J \approx 10.5$), 2.89 (br. *t*, $J \approx 10.4$, H–C(3), H–C(3′)); 2.14, 2.06, 2.05 (3*s*, 3 Ac). $^{13}$C-NMR (100 MHz, $CDCl_3$): 170.57, 169.92, 168.96 (3*s*, 3 C=O); 98.10, 97.79, 96.72 (3*t*, 3 MeO$CH_2$); 79.29, 75.69 (2*d*, C(4′), C(5′)); 73.38 (*d*, C(2′)); 71.85, 69.91, 69.79 (3*d*, C(2), C(4), C(5)); 78.14, 74.72, 74.09, 73.06, 72.87, 69.62, 68.68, 67.42 (8*s*, 8 *C*≡C); 68.61 (*d*, C(6′)); 67.17 (*t*, C(1′)); 66.34 (*d*, C(6)); 63.76 (*t*, C(1)); 37.24, 36.38 (2*d*, C(3), C(3′)); 20.79, 20.63, 20.52 (3*q*, 3 Me). FAB-MS: 1315 (26, $[M + Na]^+$), 1293 (10, $[M + H]^+$), 1292 (13, $M^+$), 1109 (100), 621 (50). Anal. calc. for $C_{64}H_{76}O_{28}$ (1293.29): C 59.44, H 5.92; found: C 59.47, H 5.91.

*Tetrakis(2,6-anhydro-7,8,9,10-tetradeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol) 3,10′:3′,10″:3″,10‴:3‴,10-Tetraanhydride* (= *Cyclotetrakis-(3-*C → *10-*C*)-(2,6-anhydro-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-yl)*; **51**). A soln. of **50** (0.348 g, 0.269 mmol) in THF (2 ml) and MeOH (8 ml) was treated with 2% NaOMe soln. in MeOH (0.4 ml) at 0° under $N_2$, stirred for 9 h, neutralized with *Dowex* ($H^+$ form), filtered, and evaporated. The residue was dissolved in 0.3M HCl/MeOH (7 ml), refluxed for 21 h, and evaporated. The residue was dissolved in boiling MeOH and treated with $Et_2O$. Filtration of the precipitate gave **51** (185 mg, 89%). White solid. $R_f$ (AcOEt/MeOH 3:2) 0.38. M.p. > 250° (dec.). $[\alpha]_D^{25} = 123.4$ ($c = 0.50$, $H_2O$). UV ($H_2O$): 258 (1019), 244 (1553), 232 (1503). IR (KBr): 3600–3055*s* (br. max. at 3423), 2878*m*, 2257*w*, 1635*w*, 1463*w*, 1340*m* (br.), 1281*w*, 1232*w*, 1125*s*, 1092*s*, 1036*s*, 907*w*, 866*w*, 658*m*, 614*w*, 547*w*. $^1$H-NMR (400 MHz, ($D_6$)DMSO: 5.57–5.55 (*m*, OH–C(4), OH–C(5)); 4.80 (*t*, $J \approx 5.4$, OH–C(1)); 4.79 (*d*, $J = 5.7$, H–C(6)); 3.75 (br. *ddd*, $J \approx 1.5, 4.7, 10.5$, H–C(1)); 3.63 (br. *ddd*, $J = 1.3, 5.3, 10.5$, H–C(2)); 3.57–3.49 (*m*, H′–C(1), H–C(4)); 3.26 (br. *td*, $J \approx 4.9, 9.8$, H–C(5)); 2.53 (*t*, $J = 10.4$, H–C(3)). $^{13}$C-NMR (100 MHz, ($D_6$)DMSO): 78.88 (*s*, C(10)); 75.07 (*d*, C(2)); 73.54 (*s*, C(7)); 72.25 (*s*, C(8)); 71.61 (*d*, C(4)); 70.86 (*d*, C(5)); 68.86 (*d*, C(6)); 66.52 (*s*, C(9)); 61.84 (*t*, C(1)); 37.81 (*d*, C(3)). MALDI-MS: 799 ($[M + Na]^+$). Anal. calc. for $C_{40}H_{40}O_{16} \cdot 2\,H_2O$ (812.77): C 59.11, H 5.46; found: C 59.16, H 5.54.

*Thermal Stability of* **51**. The tetramer **51** was kept at 200° for 5 min. It remained colourless, and the $R_f$ value was identical to **51** before heating.

*Solubility of* **51** *in* $H_2O$. A suspension of **51** in $H_2O$ (*ca.* 2 ml) was ultrasonicated for 5 min at 23° and filtered (2 times). Evaporation and drying (12 h, 0.05 mbar, r.t.) of 1.000 ml of the clear filtrate left 10.4 mg of **51**.

*Optical Rotation of* **51**. See *Table 2*.

Table 2. *Dependence of the Optical Rotation* ($\alpha_D$) *of* **51** *upon Concentration at 25°*

| **51** [mM] | 1.756 | 3.511 | 4.389 | 5.486 | 6.858 | 8.572 | 10.71 | 12.80 |
|---|---|---|---|---|---|---|---|---|
| $\alpha_D$ | 0.185 | 0.37 | 0.452 | 0.564 | 0.706 | 0.884 | 1.11 | 1.289 |

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