156. Oligosaccharide Analogues of Polysaccharides

Part 14[1])

Carbocyclic Cyclodextrin Analogues. Synthesis of All Trimeric and Tetrameric Isomers by Homo- and Heterocoupling of 1,4-*cis*-Diethynylated 1,5-Anhydroglucitols

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Hetero- or homocoupling of protected 1,4-*cis*-diethynylated 1,5-anhydroglucitols leads to two isomeric cyclotrimers and to four isomeric cyclotetramers. The C_3-symmetric cyclotrimer **31**, the C_4-symmetric cyclotetramer **35**, and the D_2-symmetric cyclotetramer **6** have been prepared before. We have now synthesized the C_1-symmetric cyclotrimer **13**, and the C_1- and the C_2-symmetric cyclotetramers **22** and **27**, respectively. The cyclotrimer **13** was prepared by intramolecular, oxidative homocoupling and, alternatively, by a one-pot trimerization/cyclization of the monomer **36** (*Schemes 1* and *5*, resp.). Oxidative homocoupling was used for the cyclization of the tetramers **19** and **25**, leading to **22** and **27**. The tetramer **19** was made by sequential *Cadiot-Chodkiewicz* coupling (*Scheme 2*) and the tetramer **25** by a combination of a *Cadiot-Chodkiewicz* reaction and an intermolecular, oxidative homocoupling (*Scheme 3*). The acetates **34** and **38**, corresponding to **35** and **27**, respectively, were also made by a one-pot dimerization/cyclization of the dimer **37** (*Scheme 5*). Intramolecular oxidative heterocoupling is also feasible and results in an alternative, more convenient synthesis of the acetylated cyclotrimer **30** and the acetylated cyclotetramer **34** (corresponding to **31** and **35**, resp.; *Scheme 4*). The solid-state conformation of the C_4-symmetric cyclotetramer **34** corresponds well to the one predicted by force-field calculations. We compared the water-solubilities of the cyclotrimers **13** and **31** and the tetramers **6**, **22**, **27**, and **35**, their calculated conformations (MM3*), and the D-adenosine binding properties of the cyclotetramers **6**, **27**, and **35**.

Introduction. – Analogues of cyclodextrins (CDs) with a modified cavity are of interest as potentially specific host molecules [2–5][2]). Carbocyclic CD analogues are available by coupling *cis*-dialkynylated saccharides. Hetero- or homocoupling[3]) of an unsymmetric dialkyne, such as a 1,5-*cis*-diethynylated 1,5-anhydroglucitol [6], may lead to two isomeric cyclotrimers and to four isomeric cyclotetramers. We have described the coupling of 1,4-*cis*-diethynylated 1,5-anhydroglucitols resulting in a synthesis of the C_3-symmetric cyclotrimer **31** and of the C_4-symmetric cyclotetramer **35** [7]. We have also reported the synthesis of the D_2-symmetric cyclotetramer **5**, the D_3-symmetric cyclohexamer **7**, and the D_4-symmetric cyclooctamer **9** [1] from the homodimer **4**, as well as

[1]) Part 13: [1].

[2]) For leading references, see [4].

[3]) In the following, 'hetero-' and 'homocoupling' refer to the partial structure of the reacting alkynes; while heterocoupling means coupling between a propargylic and a homopropargylic alkynyl unit (propargyl alcohol = prop-2-yn-1-ol), homocoupling involves either one of these groups. Hence, we will apply the term homocoupling also to the coupling of two different propargylic or homopropargylic alkynes, and to the analogous cylization of a nonsymmetric precursor.

their deprotection to **6**, **8**, and **10**, respectively (*cf. Scheme 1*). We wondered to which extent the shape of the cavity and the properties of these tri- and tetrameric CD analogues depend on their symmetry, *i.e.*, on the hetero- and/or homocoupling of the monomers. Thus, we have prepared the remaining C_1-symmetric cyclotrimer **13**, and the C_1- and the C_2-symmetric cyclotetramers **22** and **27**, respectively. Heterocoupling according to a modification of the *Cadiot-Chodkiewicz* [8] reaction proceeds well, but requires the preparation of a starting material possessing both an alkynyl and a haloalkynyl group. We, therefore, wondered if an intramolecular oxidative heterocoupling is feasible[4]). We also wondered if a similar treatment of the dialkynes **36** and **37**, too small to cyclize, will first lead to an oligomer and then to a macrocycle. Finally, we describe the experimental details for the preparation of the homodimer **4** *via* **2**, and for the characterization and deprotection of the hexamer **7** (→ **8**) and the octamer **9** (→ **10**) (*Scheme 1*).

Results and Discussion. – *The C_1-Symmetric Cyclotrimer.* For the preparation of this cyclotrimer **13**, we desilylated the trimer **3** and subjected the resulting dialkyne **11** to the conditions of the *Eglinton* coupling (slow addition to $Cu(OAc)_2$ in pyridine [10]). This yielded 82% of the methoxymethylated (MOM) cyclotrimer **12** that was deprotected in high yields to **13** (94%). The trimer **3** had been obtained as a by-product in the *Glaser* coupling of the 1,4-*cis*-dialkynylated anhydroglucitol **1** (→ **2** and **3** [1]; *Scheme 1*).

The C_1-Symmetric Cyclotetramer. As the oxidative homocoupling of **11** and the multiple homocoupling of **4** [1] proceeded well, we intended to prepare the C_1-symmetric cyclotetramer **22** (*Scheme 2*) by oxidative homocoupling of the tetramer **19**. Similarly to **4** and **11**, **19** possesses two propargylic alkynyl groups. It was prepared from the *C*-trimethylgermylated dimer **15** [7] and the *C*-trimethylsilylated monomer **1**. The Me_3Si/Me_3Ge groups have proven useful as orthogonal protecting groups for dialkynes in the synthesis of 'acetyleno-oligosaccharides' [7] [11] [12].

Thus, heterocoupling of **15** with the iodoalkyne **14** (prepared [13] in 95% from **1**) followed by acetylation yielded 70% of the trimer **16**. Iododegermylation (*cf.* [7] [11] [12]) of **16** gave **17** in good yields. Coupling this trimeric iodoalkyne with the monomer **1** provided 78% of the bis-*C*-trimethylsilylated tetramer **18** that was desilylated to **19** (CsF, 96%). *Eglinton* coupling of **19** yielded 66% of the cyclotetramer **20** and a mixture of partially deacetylated cyclotetramers, from which 8% of the monodeacetylated **21** was isolated by HPLC[5]). Deprotection of **20** first with NaOMe and then by HCl in MeOH provided 90% of the desired **22**.

The C_2-Symmetric Cyclotetramer. We intended to prepare the cyclotetramer **27** (*Scheme 3*) by oxidative cyclization of the C_2-symmetric tetramer **25**, again possessing two propargylic alkynyl groups. For the synthesis of **25**, we first removed the Me_3Ge group of the known, orthogonally protected dimer **23** [7] with CuBr in THF/MeOH [11]

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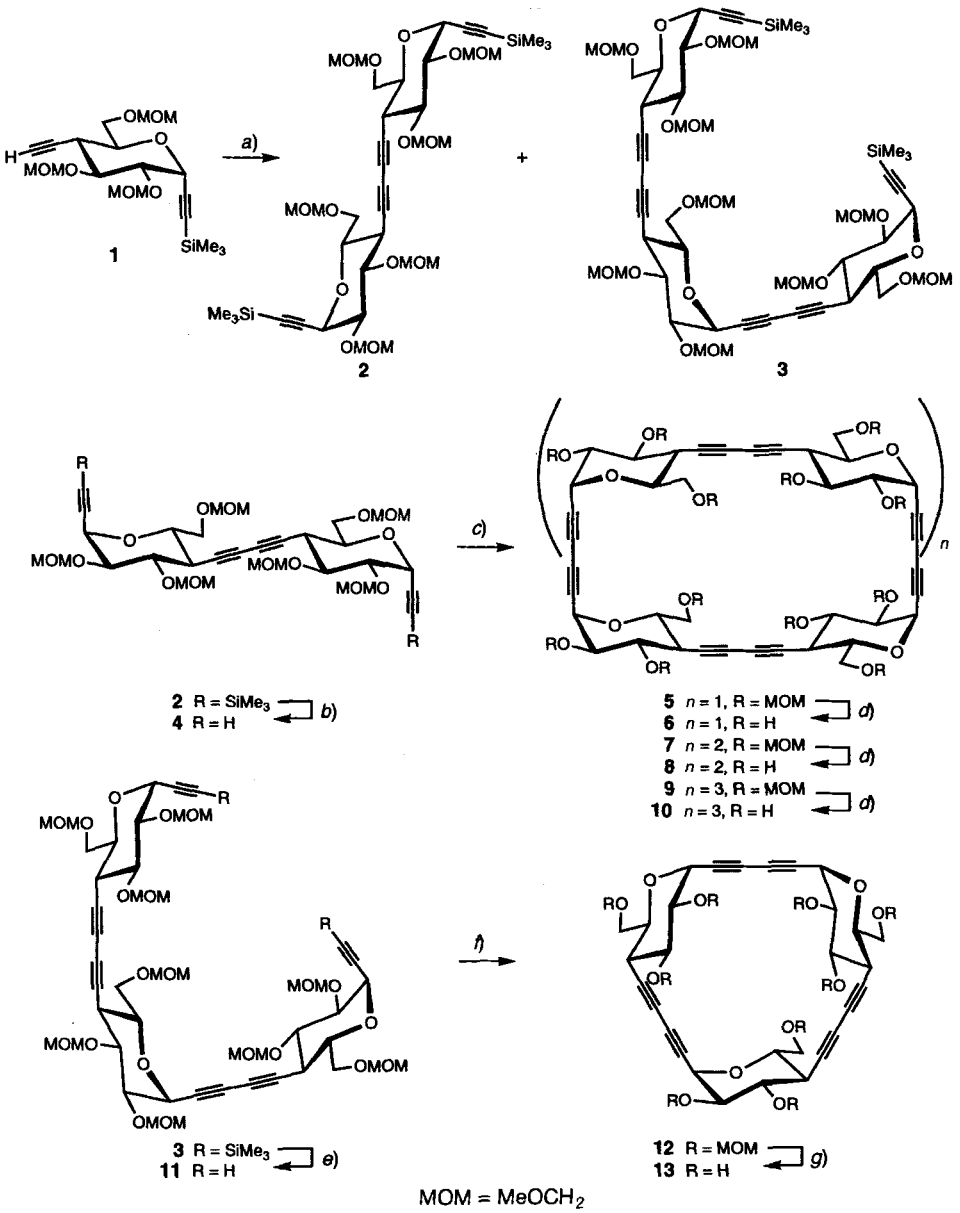
[4]) Intermolecular oxidative heterocoupling of two alkynes differing in their reactivity is known to produce only moderate yields of the heterocoupled product. Thus, treatment of a mixture of two 'acetyleno-saccharide'-derived alkynes, one bearing a propargylic and the other a homopropargylic alkynyl group, with CuCl in pyridine under O_2 has led in good yields to the symmetric homodimers only; no heterocoupled product was isolated [9].

[5]) The acetylated cyclotetramer **20** was partially deacetylated in the presence of $Cu(OAc)_2$ in pyridine at 50° for 18 h.

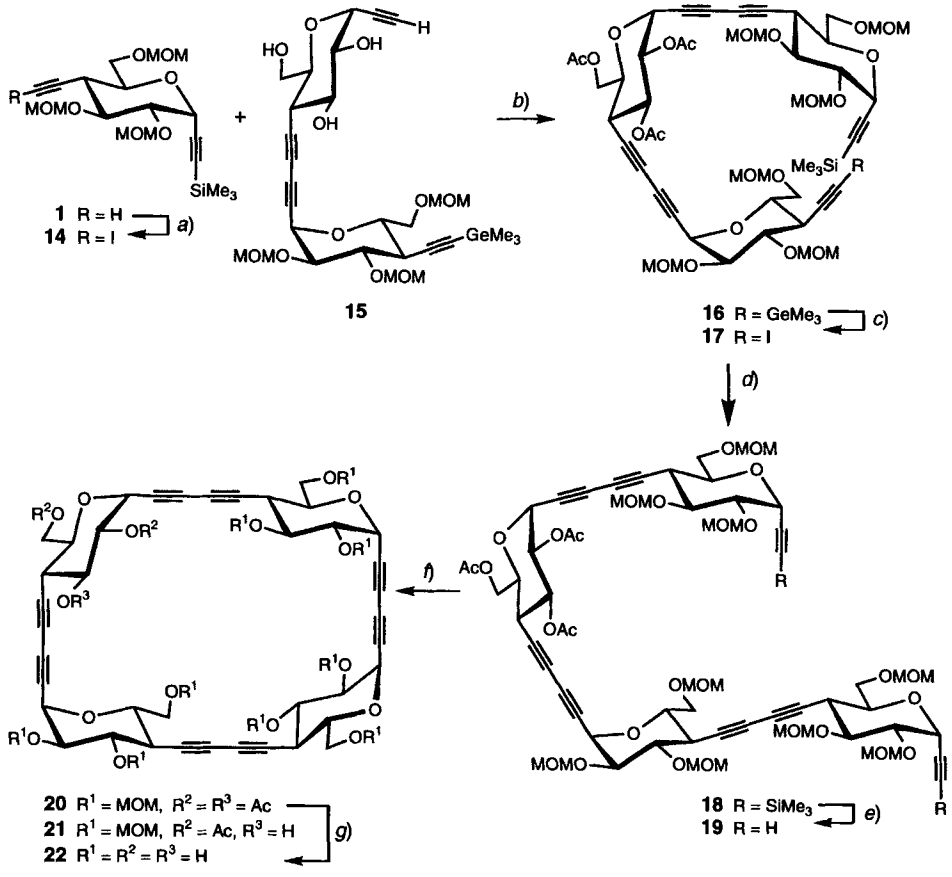
Scheme 1



a) CuCl, py, O_2; 83% of **2**, 9% of **3**. *b*) NaOMe, MeOH, THF; 98%. *c*) $Cu(OAc)_2$, py; 68% of **5**, 7% of **7**, 1.8% of **9**. *d*) HCl, MeOH; 91% of **6**, 94% of **8**, 81% of **10**. *e*) As *b*; 95%. *f*) As *c*; 82%. *g*) As *d*; 94%.

[12]. This led to both the degermylated dimer and the known homotetramer **24** [7], while starting material was still present. Repeating this deprotection in the presence of O_2 led to 55–64% of the bis-*C*-trimethylsilylated tetramer **24**. Base-promoted desilylation and

Scheme 2

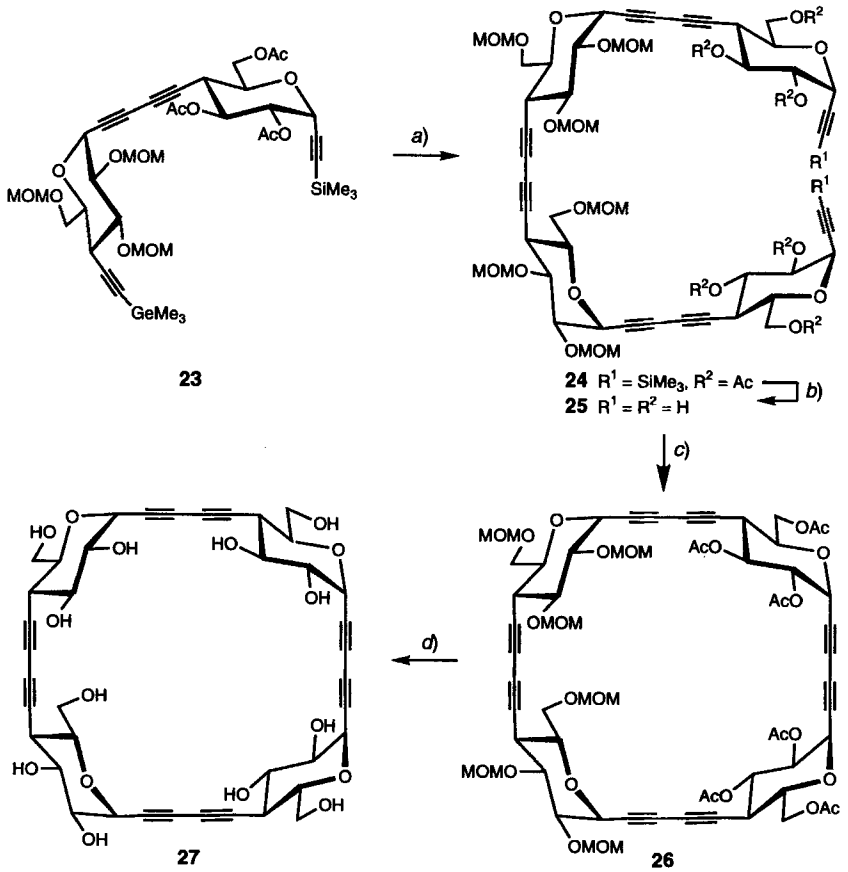


a) I_2, morpholine, toluene; 95%. *b*) $[Pd_2(dba)_3]$, $P(furyl)_3$, CuI, Et_3N, DMSO; Ac_2O, py; 70%. *c*) NIS, CuBr, acetone; 96%. *d*) **1**, $[Pd_2(dba)_3]$, $P(furyl)_3$, CuI, Et_3N, DMSO; 78%. *e*) CsF, DMF, MeOH; 96%. *f*) $Cu(OAc)_2$, py; 66% of **20** and 8% of **21**. *g*) NaOMe, MeOH; HCl, MeOH; 90%.

deacetylation of **24** provided the tetrameric dialkyne **25** that was slowly added to a solution of $Cu(OAc)_2$ in pyridine. After acetylation of the crude product, we obtained 69% of the macrocycle **26** that was deprotected by treatment with NaOMe and then with HCl in MeOH to yield 91% of the desired C_2-symmetric cyclotetramer **27**.

Intramolecular Oxidative Heterocoupling. To probe the intramolecular oxidative heterocoupling, we subjected the trimer **29** and the tetramer **33**, obtained by deprotection of **28** and **32** [7], respectively, to the conditions of the *Eglinton* reaction (*Scheme 4*). The cyclization of **29**, followed by acetylation, resulted in 51% of the known C_3-symmetric **30** that has been deacetylated to **31** [7]. While the known transformation of **28** to **31** involving an intramolecular *Cadiot-Chodkiewicz* reaction required 6 steps (60% overall),

Scheme 3

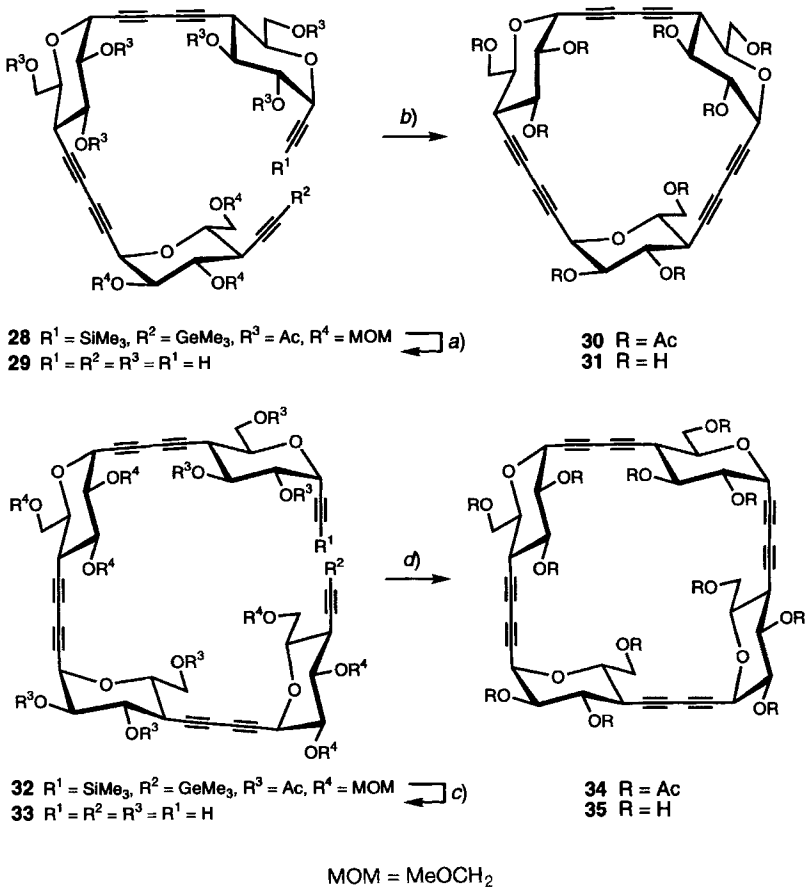


a) CuBr, THF, MeOH; 55%–64%. *b*) NaOMe, MeOH, THF; 98%. *c*) $Cu(OAc)_2$, py; Ac_2O; 69%. *d*) NaOMe, MeOH, THF; HCl, MeOH; 91%.

the oxidative procedure required one step less (48% overall) and proved more convenient, as the cyclization and acetylation are performed in one pot. Similar oxidative treatment of the tetramer **33** gave 45% of the crystalline C_4-symmetric **34**.

Sequential Oligomerization and Cyclization. Oxidative treatment of a monomer or a dimer possessing two ethynyl substituents should lead to an open-chain oligomer; this may cyclize. Indeed, transformation under oxidative conditions of the homodimer **4** into the cyclotetramer **5**, the cyclohexamer **7**, and the cyclooctamer **9** shows that oligomerization and cyclization may follow each other in a one-pot reaction. We have now also subjected the heterodimer **37** (obtained from **15**) to the conditions of the *Eglinton* coupling (*Scheme 5*). After acetylation, this provided a mixture of the C_4- and C_2-symmetric cyclotetramers **34** (14%) and **38** (8%) showing the strong dependence of this

Scheme 4



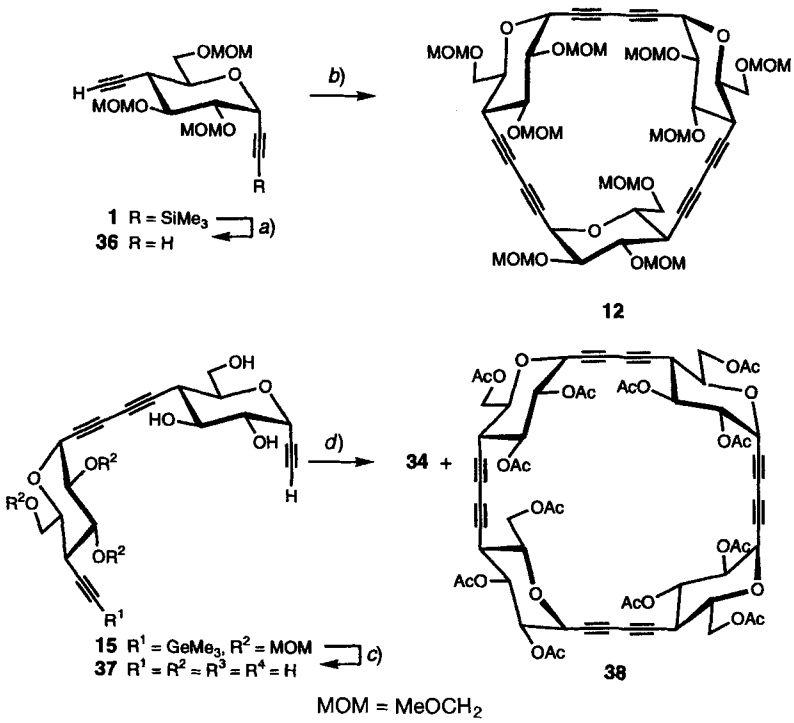
a) NaOMe, MeOH, THF; HCl, MeOH; 95%. *b*) $Cu(OAc)_2$, py; Ac_2O; 51%. *c*) As *a*; 81%. *d*) As *b*; 45%.

dimerization/cyclization on the structure of the starting material and product. Similar treatment of the monomer **36**, available in 98% from **1** yielded 19% of the C_1-symmetric cyclotrimer **12**, besides small amounts of a mixture containing cyclotetramers. Clearly, this potentially useful oligomerization/cyclization requires further optimization.

Characterization. The symmetry of the cyclooligomers was deduced from the ^{1}H- and ^{13}C-NMR spectroscopic data; while the C_1-symmetric cyclotrimer and -tetramer show one set of signals for *each* repetitive unit, the number of signals decreases, as expected, for the C_3-symmetric cyclotrimer, and the C_2-, the C_4-, and the D_2-symmetric cyclotetramers.

The conformation of the tetrameric macrocycles, *viz.* their deviation from planarity, was compared in the following way: the atoms of two buta-1,3-diyne-1,4-diyl groups that are attached to the same tetrahydropyranyl moiety define a least-squares fitted plane (*Fig. 1*, planes defined by the lines *a*, *b*, and *c*, *d*, resp.). Two such planes opposite to each

Scheme 5



a) NaOMe, MeOH; 98%. *b*) $Cu(OAc)_2$, py; 19%. *c*) HCl, MeOH; 94%. *d*) As *b*; 14% of **34**, 8% of **38**.

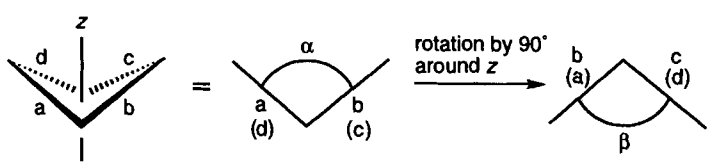


Fig. 1. *Schematic representation of the two angles α and β, describing the deviation of the cyclotetramers from planarity. a, b, c,* and *d* represent the buta-1,3-diyne-1,4-diyl moieties.

other, enclose an angle. As there are two pairs of planes in a cyclotetramer, its deviation from planarity is expressed by the two angles α and β[6]).

The structure of the acetylated C_4-symmetric cyclotetramer **34** was established by X-ray analysis[7]). The conformation of **34** in the solid state was compared to the one predicted by force-field calculations[8]). As expected from these calculations, the four

[6]) The least-squares fitted planes that are defined by the atoms of two buta-1,3-diyne-1,4-diyl units attached to one tetrahydropyran unit, and the angles α and β, were calculated with the programme MacMoMo (Version 2.0) by Prof. Dr. *M. Dobler*, Laboratorium für Organische Chemie, ETH-Zürich.

[7]) Coordinates and thermal parameters were deposited with the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EW, England.

[8]) Modelling was performed using the macromodel (MM3*, Version 4.5) programme.

buta-1,3-diyne-1,4-diyl units of **34** are not in one plane; they define planes that enclose angles, α and β, of 104° and 108° (calculated: 106° and 111°). In the solid state, **34** is only C_2-symmetric, mainly due to the conformation of the $AcOCH_2$ groups (*Fig. 2*, top); these groups adopt either a *gg* or a *gt* conformation (*g* = *gauche*, *t* = *trans*). The tetrahydropyran and the alkynyl groups of **34** enclose a cavity that is characterized by average distances of 9.7 and 9.9 Å between two opposite buta-1,3-diyne groups, in good agreement with the calculated values of 9.7 and 9.8 Å for these distances. The tetrahydropyran rings adopt the $^4C_1$ conformation[9]) (see *Fig. 2*). The buta-1,3-diyne groups are nearly linear; the C≡C and the C–C bond lengths are within normal values. As indicated in *Fig. 2* (bottom), two AcO groups adopt more than one conformation. The molecules of **34** stack to form parallel tubes. The structure includes one disordered molecule of AcOEt which is located between the tubes. It further contains a highly disordered solvent molecule (H_2O?) that is spread over at least four positions within the cavity of **34**.

As the calculated conformations of the acetylated C_4-symmetric cyclotetramer **34** and the deprotected D_2-symmetric cyclotetramer **6**[10]) [1] correspond well to the experimentally determined solid-state structure, we compared the calculated conformations[8]) of the isomeric cyclotrimers and -tetramers to each other. According to these calculations, the shape and size of the cavity of these constitutional isomers differ significantly from each other, as shown in *Fig. 3*. While the buta-1,3-diyne-1,4-diyl groups of the cyclotrimers lie in one plane, the cyclotetramers are tilted; this deviation from planarity is expressed by the two angles α and β, as described above. The calculated values of α and β (90–94°) for the deprotected cyclotetramers differ only slightly from each other. These values may be too low, since the experimentally determined α and β values of **6** are significantly larger (98°, 100°).

We have gravimetrically determined the solubility of the newly prepared cyclic 'acetyleno-saccharides' in H_2O and compared them with those of the known cyclooligomers (*Table 1*). Similarly as for cyclodextrins, the solubility in H_2O depends strongly on the size of the macrocycles [1]. It also depends, albeit to a minor extent, on their symmetry.

We have reported the free binding energies of the 1:1 complex of the D_2-symmetric cyclotetramer **6** with D- and L-adenosine [1]. Based on the high-field shift (^{1}H-NMR) of the signal of H–C(2)[11]) upon addition of adenosine, and the similar binding constants for D- and L-adenosine to **6**, we have assumed that the aromatic part of adenosine is bound in the cavity of **6**, while the ribosyl moiety is solvated. We have now also determined the free binding energies of D-adenosine to the C_2-symmetric cyclotetramer **27** and the known C_4-symmetric cyclotetramer **35** [7] in aqueous solutions[12]) (*Table 2*). Again, we followed the shift to higher field (^{1}H-NMR) of the H–C(2) signal, pointing

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[9]) The puckering parameters (Q = 0.595(10), 0.577(0) and θ = 5.7(10), 7.0(10)) confirm the $^4C_1$ conformation of the tetrahydropyran rings [14].

[10]) The average distances of the buta-1,3-diyne-1,4-diyl groups are 7.4 and 11.4 Å; the calculated ones are 7.8 and 11.2 Å.

[11]) The four H–C(2) of the cyclotetramer point into the cavity.

[12]) The H–C(2) and H–C(2′) signals of the C_2-symmetric cyclotetramer **27** are separated from each other. In contrast, the signals of the four H–C(2) of the C_1-symmetric cyclotetramer **22** show a *multiplet* from 4.05 to 4.00 ppm (in D_2O); hence, the determination of the complex constant of **22** and adenosine by a similar titration failed.

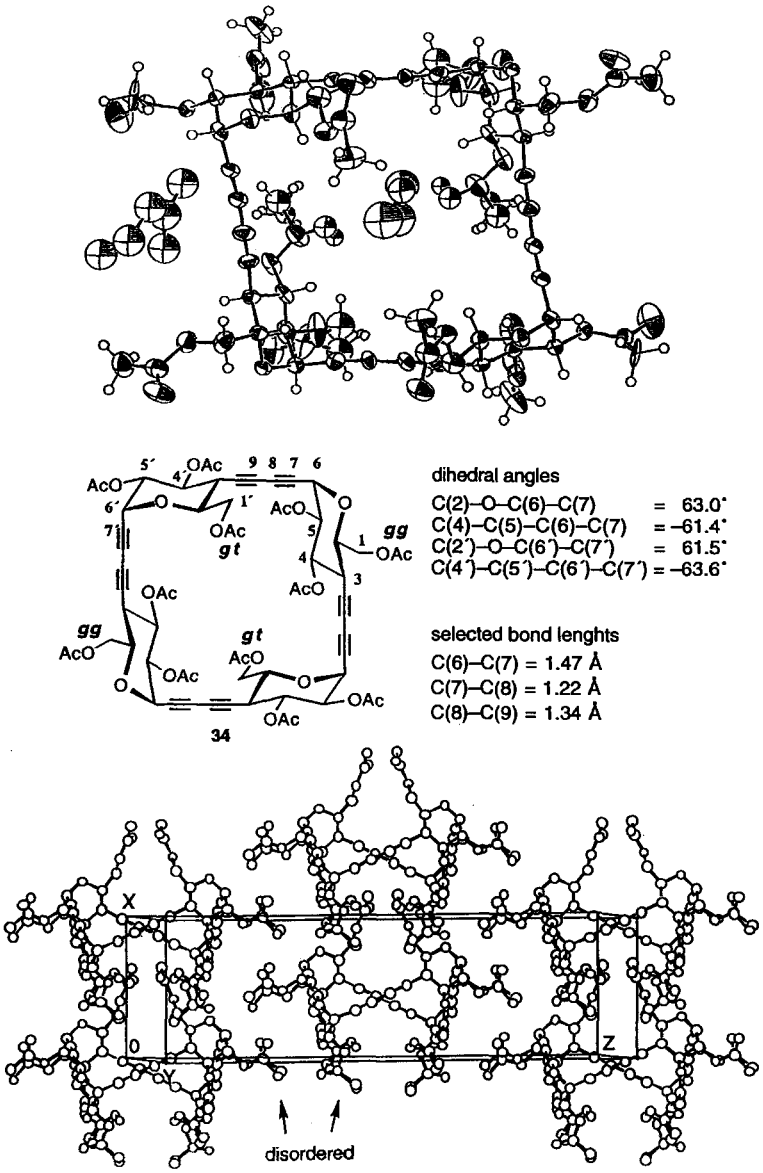

Fig. 2. *Solid-state structure of the acetylated* C_4*-symmetric cyclotetramer* **34** (containing AcOEt outside the cavity, and a further, disordered solvent molecule inside the cavity). Top: ORTEP presentation of **34**. Bottom: MacMoMo presentation of the crystal packing (side view); the solvent molecules are omitted for clarity.

into the cavity. As D-adenosine binds much more weakly to the cyclotetramers **27** and **35** than to the D_2-symmetric cyclotetramer **6**, additional amounts of D-adenosine had to be added during the titration; the limited water-solubility of adenosine allowed to titrate only up to 47% of saturation.

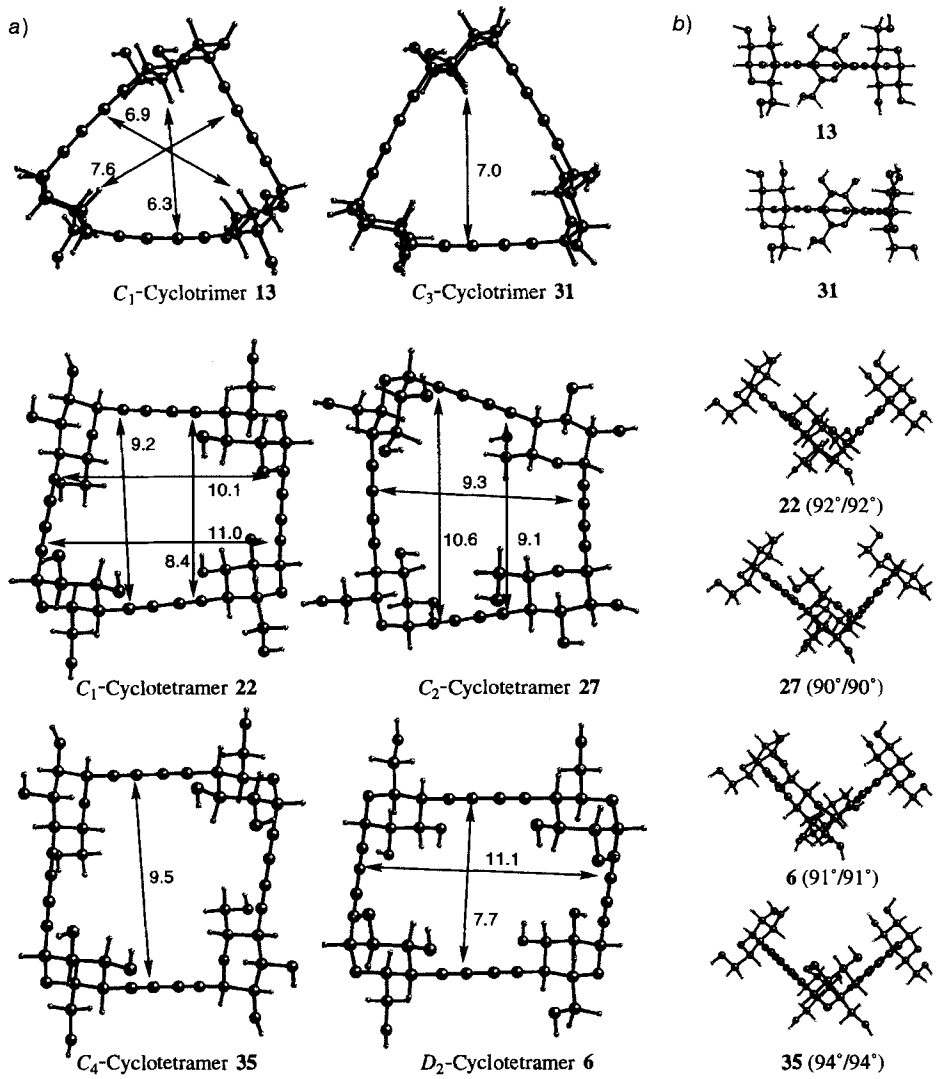

Fig. 3. *The isomeric cyclotrimers and the cyclotetramers, as calculated* (MM3*). *a*) Top view: significant distances between the centers of the indicated atoms in [Å]. *b*) Side view; the angles α and β between the planes, as defined in *Fig. 1*, in parenthesis.

The free energy for the complexation of D-adenosine with the C_2 and the C_4 symmetric cyclotetramers **27** and **35** is weaker than the one for the complexation with the D_2-symmetric cyclotetramer **6**, possibly as a direct consequence of the different dimensions of the cavity of **6**, **27**, and **35**. In adenosine, the calculated distance of the centers of the H-atoms at C(2) and C(8) is 6.6 Å; hence, the aromatic part of adenosine should fit into the cavity of all the isomeric cyclotetramers. However, the D_2-symmetric cyclotetramer **6** shows a significantly shorter distance between two opposite buta-1,3-diyne-1,4-

Table 1. *Solubility of the Cyclic 'Acetyleno-saccharides', in Water*

CD Analogue		Solubility in H_2O [mM][a])	CD Analogue		Solubility in H_2O [mM][a])
C_1-Cyclotrimer	**13**	350	C_4-Cyclotetramer	**35**	12.8[b])
C_3-Cyclotrimer	**31**	130[b])	D_2-Cyclotetramer	**6**	3.1[c])
C_1-Cyclotetramer	**22**	15.4	D_3-Cyclohexamer	**8**	117[c])
C_2-Cyclotetramer	**27**	2.4	D_4-Cyclooctamer	**10**	2.8[c])

[a]) Determined at 23–24°. Accuracy of the values *ca.* ± 10%. [b]) Reported in [7]. [c]) Reported in [1].

Table 2. *Association Constants* K_a *and Binding Free Energies* $\Delta G°$ *from* ^1H*-NMR Binding Titrations for 1:1 Complexes of the Cyclotetramers* **6**, **27**, *and* **35** *with* D-*Adenosine at* T *296 K in* D_2O[a])

Host	K_a [l mol^{-1}]	$-\Delta G°$ [kcal mol^{-1}]	Degree of saturation [%]
D_2-Cyclotetramer **6**	40	2.1	70
C_2-Cyclotetramer **27**	5	1.0	47
C_4-Cyclotetramer **35**	9	1.3	47

[a]) Titrations in buffered D_2O solutions (pD 6.8, $[K_2DPO_4] = [KD_2PO_4] = 1.35$ mM) at constant ion strength ([NaCl] = 1.35 mM); [Host] = 1 mM, [Guest] varied. The association constants were obtained by nonlinear least-squares curve fitting of the titration data [15]. Accuracy of the K_a values *ca.* ± 15%.

diyl groups than its isomers. This may enhance the interaction between the aromatic moiety and the buta-1,3-diyne-1,4-diyl groups in the adenosine/**6** complex as compared to the other complexes. It may also increase the desolvation of the aromatic group of the guest.

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. See [7]. Air was dried over $CaCl_2$.

*3-C,3'-C-(Buta-1,3-diyne-1,4-diyl)bis[2,6-anhydro-3,7,8-trideoxy-1,4,5-tris-*O*-(methoxymethyl)-8-*C*-(trimethylsilyl)-*D*-glycero-*L*-gulo-oct-7-ynitol]* (**2**) *and 2,6-Anhydro-3-C-{2,6-anhydro-3-C-{4-[2,6-anhydro-3,7,8-trideoxy-1,4,5-tris-*O*-(methoxymethyl)-8-*C*-(trimethylsilyl)-*D*-glycero-*L*-gulo-oct-7-ynitol-3-C-yl]buta-1,3-diyn-1-yl}-3,7,8,9,10-pentadeoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-C-yl}-3,7,8-trideoxy-1,4,5-tris-*O*-(methoxymethyl)-8-*C*-(trimethylsilyl)-*D*-glycero-*L*-gulo-oct-7-ynitol* (= *3-C,3'-C-{[2,6-Anhydro-3-deoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-hexitol-3-C,6-C-diyl]bis(buta-1,3-diyne-4,1-diyl)}bis[2,6-anhydro-3,7,8-trideoxy-1,4,5-tris-*O*-(methoxymethyl)-8-*C*-(trimethylsilyl)-*D*-glycero-*L*-gulo-oct-7-ynitol]*; **3**) (*cf.* [16]). A soln. of **1** (4.00 g, 9.99 mmol) and CuCl (593 mg, 5.99 mmol) in pyridine (50 ml) was stirred for 9 h at 35°, while dry air was bubbled through it, and evaporated. The residue was diluted with sat. aq. NH_4Cl soln. and AcOEt. The solids were filtered off (*Celite*) and washed (AcOEt). Workup (AcOEt) of the filtrate and FC (toluene/AcOEt 9:1 → 3:2) gave **2** (3.31 g, 83%) as white crystals and **3** (355 mg, 9%) as a colourless oil.

Data of **2**: R_f (toluene/AcOEt 7:3) 0.39. M.p. 92.0–93.0°. $[\alpha]_D^{25} = +55.7$ ($c = 0.58$, $CHCl_3$). IR: 2956*m*, 2894*m*, 2827*w*, 2170*w*, 1602*w*, 1465*w*, 1405*w*, 1380*w*, 1355*w*, 1152*s*, 1114*s*, 1037*s* (br.), 960*w*, 915*m*, 846*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.93 (*d*, $J = 5.6$, H–C(6)); 4.90 (*d*, $J = 6.8$), 4.77 (*d*, $J = 6.6$), 4.71 (*d*, $J = 6.8$), 4.66 (*d*, $J = 6.8$, 2 MeOCH_2); 4.64 (*s*, MeOCH_2); 4.04 (br. *ddd*, $J \approx 2.2$, 3.8, 10.5, H–C(2)); 3.90 (br. *t*, $J \approx 10.0$, H–C(4)); 3.84 (br. *dd*, $J \approx 3.8$, 11.2, H–C(1)); 3.73 (br. *dd*, $J \approx 2.2$, 11.2, H'–C(1)); 3.46 (*dd*, $J \approx 5.6$, 9.4, H–C(5)); 3.46, 3.38, 3.36 (3*s*, 3 MeO); 2.81 (br. *t*, $J \approx 10.6$, H–C(3)); 0.18 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 99.96 (*s*, C(7)); 97.79 (2 C), 96.80 (2*t*, 3 MeOCH_2); 95.35 (*s*, C(8)); 79.01, 76.78 (2*d*, C(4), C(5)); 75.30

(*s*, *C*≡C); 72.99 (*d*, C(2)); 68.58 (*d*, C(6)); 68.28 (*s*, *C*≡C); 67.38 (*t*, C(1)); 56.26, 56.15, 55.36 (3*q*, 3 MeO); 37.38 (*d*, C(3)); −0.14 (*q*, Me_3Si). FAB-MS: 821 (14, $[M + Na]^+$), 799 (11, $[M + H]^+$), 798 (14, M^+), 767 (41), 691 (100), 615 (38). Anal. calc. for $C_{38}H_{62}O_{14}Si_2$ (799.07): C 57.12, H 7.82; found: C 57.36, H 7.62.

Data of **3**: R_f (toluene/AcOEt 7:3) 0.25. $[\alpha]_D^{25} = +78.8$ (*c* = 0.73, $CHCl_3$). IR: 2954*m*, 2894*m*, 2827*w*, 2255*w*, 2170*w*, 1603*w*, 1442*w*, 1355*w*, 1337*w*, 1152*s*, 1113*s*, 1036*s* (br.), 916*m*, 846*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.02 (br. *d*, *J* = 5.7), 4.97 (*d*, *J* = 5.7), 4.95 (*d*, *J* = 5.7, H–C(6), H–C(6′), H–C(6″)); 4.94 (*d*, *J* = 6.7), 4.91 (*d*, *J* = 6.6), 4.90 (*d*, *J* = 6.6), 4.80 (br. *d*, *J* ≈ 6.6, 2 H), 4.79 (*d*, *J* = 6.6), 4.74 (*d*, *J* = 6.9), 4.73 (*d*, *J* = 6.9), 4.72 (*d*, *J* = 6.9, 9 MeOC*H*); 4.69 (*s*, MeOCH_2); 4.69 (*d*, *J* = 6.9), 4.68 (*d*, *J* = 6.9), 4.675 (*d*, *J* = 6.9), 4.67 (br. *d*, *J* ≈ 6.6, 2 H), 4.65 (br. *d*, *J* ≈ 6.6, 2 H, 7 MeOC*H*); 4.10 (*ddd*, *J* = 2.0, 3.7, 10.5), 4.05 (*ddd*, *J* = 2.1, 3.7, 10.5), 4.01 (*ddd*, *J* = 2.0, 3.8, 10.5, H–C(2), H–C(2′), H–C(2″)); 3.95 (*dd*, *J* = 9.5, 10.3), 3.92 (br. *t*, *J* = 9.7), 3.89 (br. *t*, *J* = 9.9, H–C(4), H–C(4′), H–C(4″)); 3.90 (*dd*, *J* = 3.7, 11.3), 3.84 (br. *dd*, *J* = 2.1, 11.3, 2 H), 3.79 (*dd*, *J* = 2.1, 11.3), 3.75 (*dd*, *J* = 1.9, 11.2, 2 H, 2 H–C(1), 2 H–C(1′) 2 H–C(1″)); 3.52 (*dd*, *J* = 5.7, 9.4), 3.45–3.50 (*m*, 2 H, H–C(5), H–C(5′), H–C(5″)); 3.49, 3.477, 3.474, 3.409, 3.403, 3.397, 3.393, 3.38, 3.37 (9*s*, 9 MeO); 2.86 (br. *t*, *J* = 10.5), 2.83 (br. *t*, *J* = 10.4, 2 H, H–C(3), H–C(3′), H–C(3″)); 0.217, 0.210 (2*s*, 2 Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 99.75, 99.73 (2*s*, C(7), C(7″)); 97.69, 97.64 (2 C), 97.58 (2 C), 96.62 (3 C; 4*t*, 9 MeO*C*H_2); 95.12, 95.09 (2*s*, C(8), C(8″)); 78.88, 78.73, 78.51, 75.98, 75.88 (2 C; 5*d*, C(4), C(5), C(4′), C(5′), C(4″), C(5″)); 77.83, 75.39, 74.62, 73.55, (4*s*, 4 *C*≡C); 73.47, 72.82, 72.67, (3*d*, C(2), C(2′), C(2″)); 72.04 (*s*, *C*≡C); 68.57, 68.38 (2 C; 2*d*, C(6), C(6′), C(6″)); 68.49, 67.99, 67.61 (3*s*, 3 *C*≡C); 67.26, 67.19 (2 C; 2*t*, C(1), C(1′), C(1″)); 56.15 (2 C), 56.12 (2 C), 56.00 (3 C), 55.21 (2 C; 4*q*, 9 MeO); 37.40, 37.32, 37.28 (3*d*, C(3), C(3′), C(3″)); −0.14, −0.18 (2*q*, 2 Me_3Si). MALDI-MS: 1163 ($[M + K]^+$), 1147 ($[M + Na]^+$). Anal. calc. for $C_{54}H_{84}O_{21}Si_2$ (1125.42): C 57.63, H 7.52; found: C 57.83, H 7.60.

3,3′-(Buta-1,3-diyne-1,4-diyl)bis[2,6-anhydro-3,7,8-trideoxy-1,4,5-tris-O-*(methoxymethyl)*-D-glycero-L-gulo-*oct-7-ynitol]* (**4**). A soln. of **2** (3.29 g, 4.11 mmol) in THF (20 ml) and MeOH (20 ml) was treated at 0° under N_2 with 2% NaOMe soln. in MeOH (1.3 ml), stirred for 1 h, warmed to r.t., stirred for 1 h, neutralized with *Dowex* (H^+ form), and filtered. Evaporation left **4** (2.65 g, 98%). White crystals. A sample was recrystallized (MeOH). R_f (toluene/AcOEt 3:2) 0.30. M.p. 113.0–113.5°. $[\alpha]_D^{25} = +9.0$ (*c* = 0.59, $CHCl_3$). IR: 3304*m*, 3007*w*, 2952*m*, 2894*m*, 2118*w*, 1152*s*, 1112*s*, 1034*s* (br.), 917*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.92 (*dd*, *J* = 2.5, 5.6, H–C(6)); 4.89 (*d*, *J* = 6.8), 4.78 (*d*, *J* = 6.8), 4.74 (*d*, *J* = 6.8), 4.67 (*d*, *J* = 6.8, 2 MeOCH_2); 4.64 (*s*, MeOCH_2); 4.07 (br. *ddd*, *J* ≈ 2.0, 4.0, 10.4, H–C(2)); 3.94 (br. *t*, *J* ≈ 10.0, H–C(4)); 3.82 (*dd*, *J* = 4.0, 11.2, H–C(1)); 3.74 (*dd*, *J* = 2.2, 11.2, H′–C(1)); 3.51 (*dd*, *J* = 5.6, 9.3, H–C(5)); 3.44, 3.38, 3.35 (3*s*, 3 MeO); 2.79 (br. *t*, *J* ≈ 10.5, H–C(3)); 2.60 (*d*, *J* = 2.5, H–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$): 97.92, 97.79, 96.82 (3*t*, 3 MeO*C*H_2); 78.46, 76.05 (2*d*, C(4), C(5)); 78.31 (*d*, C(8)); 78.01, 75.26 (2*s*, C(7), *C*≡C); 73.20 (*d*, C(2)); 68.38 (*s*, *C*≡C); 67.99 (*d*, C(6)); 67.33 (*t*, C(1)); 56.31, 56.15, 55.39 (3*q*, 3 MeO); 37.40 (*d*, C3)). FAB-MS: 677 (23, $[M + Na]^+$), 655 (26, $[M + H]^+$), 654 (17, M^+), 547 (100). Anal. calc. for $C_{32}H_{46}O_{14}$ (654.71): C 58.71, H 7.08; found: C 58.72, H 6.79.

Treatment of **4** *with Cu(OAc)*$_2$ *in Pyridine*: **5**, **7**, *and* **9** (see [1]). *Data of 3,14″:14,3′:14′,3″-Tris(buta-1,3-diyne-1,4-diyl)tris[2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-1,4,5,12,13,16-hexakis*-O-*(methoxymethyl)*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol] (= 2,6:11,15-Dianhydro-3*-C,*14*-C-{(buta-1,3-diyne-1,4-diyl)bis{[2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-1,4,5,12,13,16-hexakis*-O-*(methoxymethyl)*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol-14*-C,*3*-C-*diyl](buta-1,3-diyne-4,1-diyl)}}-3,7,8,9,10,14-hexadeoxy-1,4,5,12,13,16-hexakis*-O-*(methoxymethyl)*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol*; **7**): R_f (toluene/AcOEt 3:7) 0.17. M.p. 105.0–107.0°. $[\alpha]_D^{25} = +148.5$ (*c* = 0.45, $CHCl_3$). IR: 2952*m*, 2894*m*, 2843*w*, 2158*w*, 1602*w*, 1465*m*, 1442*m*, 1333*m*, 1152*s*, 1113*s*, 1042*s* (br.), 918*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.06 (*d*, *J* = 5.6, H–C(6)); 4.92 (*d*, *J* = 6.8), 4.82 (*d*, *J* = 6.8), 4.75 (*d*, *J* = 6.9), 4.69 (*d*, *J* ≈ 6.9, 2 MeOCH_2); 4.66 (*s*, MeOCH_2); 4.06 (br. *ddd*, *J* ≈ 2.0, 3.8, 10.4, H–C(2)); 3.93 (br. *t*, *J* ≈ 10.0, H–C(4)); 3.91 (br. *dd*, *J* ≈ 3.8, 11.3, H–C(1)); 3.78 (br. *dd*, *J* ≈ 2.0, 11.3, H′–C(1)); 3.54 (*dd*, *J* = 5.6, 9.3, H–C(5)); 3.48, 3.39, 3.38 (3*s*, 3 MeO); 2.89 (br. *t*, *J* ≈ 10.5, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 97.97, 97.84 96.87 (3*t*, 3 MeO*C*H_2); 78.62, 76.61 (2*d*, C(4), C(5)); 75.04, 74.83 (2*s*, 2 *C*≡C); 73.85 (*d*, C(2)); 72.99 (*s*, *C*≡C); 68.80 (*d*, C(6)); 68.72 (*s*, *C*≡C); 67.17 (*t*, C(1)); 56.38, 56.25, 55.40 (3*q*, 3 MeO); 37.40 (*d*, C(3)). MALDI-MS: 1979 ($[M + Na]^+$). Anal. calc. for $C_{96}H_{132}O_{42}$ (1958.07): C 58.89, H 6.79; found: C 58.97, H 6.70.

Data of 3,14‴:14,3′:14′,3″:14″,3‴-Tetrakis(buta-1,3-diyne-1,4-diyl)tetrakis[2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-1,4,5,12,13,16-hexakis-O-*(methoxymethyl)*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol] (= 2,6:11,15-Dianhydro-3,7,8,9,10,14-hexadeoxy-3*-C:*14*-C-{*[2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-1,4,5,12,13,16-hexakis*-O-*(methoxymethyl)*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol-3*-C,*14*-C-*diyl]bis{(buta-1,3-diyne-4,1-diyl)[2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-1,4,5,12,13,16-hexakis*-O-*(methoxymethyl)*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol-14*-C,*3*-C-*diyl](buta-1,3-diyne-4,1-diyl)}}-1,4,5,12,13,16-hexakis*-O-*(methoxymethyl)*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol*; **9**): R_f (toluene/AcOEt 1:4) 0.17. M.p. 111.0–113.0°.

$[\alpha]_D^{25} = +152.6$ ($c = 0.41$, $CHCl_3$). IR: 3007*m*, 2956*m*, 2894*m*, 2848*w*, 2158*w*, 1442*w*, 1333*w*, 1261*m*, 1152*s*, 1111*s*, 1041*s* (br.), 918*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.04 (*d*, $J = 5.9$, H–C(6)); 4.89 (*d*, $J = 6.5$), 4.80 (*d*, $J = 6.5$), 4.74 (*d*, $J = 6.8$), 4.68 (*d*, $J = 6.8$, 2 MeOCH_2); 4.65 (*s*, MeOCH_2); 4.02 (br. *ddd*, $J \approx 1.2, 3.2, 10.4$, H–C(2)); 3.90 (br. *t*, $J \approx 10.0$, H–C(4)); 3.85 (*dd*, $J = 3.4, 10.9$, H–C(1)); 3.75 (br. *dd*, $J \approx 1.3, 11.0$, H′–C(1)); 3.53 (*d*, $J = 5.9, 9.3$, H–C(5)); 3.45, 3.39, 3.37 (3*s*, 3 MeO); 2.85 (br. *t*, $J \approx 10.5$, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 97.91, 97.81, 96.87 (3*t*, 3 MeOCH_2); 78.45, 76.15 (*d*, C(4), C(5)); 75.08, 74.90 (2*s*, 2 C≡C); 73.75 (*d*, C(2)); 72.99 (*s*, C≡C); 68.76 (*d*, C(6)); 68.63 (*s*, C≡C); 67.23 (*t*, C(1)); 56.33, 56.25, 55.38 (3*q*, 3 MeO); 37.42 (*d*, C(3)). MALDI-MS: 2631 ([*M* + Na]$^+$). FAB-MS: 2609 (37, [*M* + H]$^+$), 2502 (41), 2426 (62), 2350 (94), 2274 (100), 2230 (72), 2198 (57), 2111 (36).

3,14″:14,3′:14′,3″-Tris(buta-1,3-diyne-1,4-diyl)tris[2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol]* (= *2,6:11,15-Dianhydro-3*-C,*14*-C-*{(buta-1,3-diyne-1,4-diyl)bis{[2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol-14*-C,*3*-C-*diyl](buta-1,3-diyne-4,1-diyl)}}-3,7,8,9,10,14-hexadeoxy*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol*; **8**). A soln. of **7** (179 mg, 0.09 mmol) in 0.3M HCl in MeOH (6 ml) was refluxed for 31 h and evaporated. The residue was dissolved in boiling MeOH (*ca.* 3 ml), cooled to r.t., ultrasonicated for 2 min, and filtered. The solids were suspended in boiling EtOH and cooled to r.t. Filtration gave **8** (100 mg, 94%). White solid. R_f (AcOEt/MeOH/H_2O 13:6:1) *ca.* 0.26. M.p. > 243.0° (dec.). $[\alpha]_D^{25} = +192.9$ ($c = 0.37$, H_2O). UV (H_2O): 256 (1062), 242 (1061), 230 (1674). IR (KBr): 3655–3055*s* (br., max. at 3396), 2924*w*, 2155*w*, 1635*m* (br.), 1419*w*, 1333*m*, 1186*w*, 1123*m*, 1077*s* (br.), 869*w*, 753*w*, 701*w*, 655*w*, 612*w*, 555*w*, 475*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 5.62 (*d*, $J = 4.8$, partial exchange with D_2O, HO–C(5)); 5.56 (*d*, $J = 6.1$, partial exchange with D_2O, HO–C(4)); 4.82 (*t*, $J \approx 5.1$, partial exchange with D_2O, HO–C(1)); 4.81 (*d*, $J \approx 5.6$, H–C(6)); 3.69 (*ddd*, $J = 1.7$, 4.4, 10.4, H–C(2)); 3.67–3.63 (*m*, addn. of D_2O → change of signal, H–C(1)); 3.57–3.48 (*m*, addn. of D_2O → br. *dd* at 3.53, $J \approx 5.0, 12.1$, H′–C(1), → br. *t* at 3.51, $J \approx 9.9$, H–C(4)); 3.27 (br. *td*, $J \approx 5.4, 9.5$, addn. of D_2O → *dd*, $J = 5.7, 9.3$, H–C(5)); 2.51 (br. *t*, $J \approx 10.5$, H–C(3)). ^{13}C-NMR (100 MHz, (D_6)DMSO): 76.48, 75.98 (2*s*, 2 C≡C); 75.44 (*d*, C(2)); 71.65 (*s*, C≡C); 71.40 (*d*, C(4)); 70.93 (*d*, C(5)); 68.90 (*d*, C(6)); 67.38 (*s*, C≡C); 61.83 (*t*, C(1)); 37.65 (*d*, C(3)). MALDI-MS: 1187 ([*M* + Na]$^+$). Anal. calc. for $C_{60}H_{60}O_{24} \cdot 3\,H_2O$ (1165.11): C 59.11, H 5.46; found: C 59.24, H 5.48.

3,14‴:14,3′:14′,3″:14″,3‴-Tetrakis(buta-1,3-diyne-1,4-diyl)tetrakis[2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol]* (= *2,6:11,15-Dianhydro-3,7,8,9,10,14-hexadeoxy-3*-C:*14*-C-*{(2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol-3*-C,*14*-C-*diyl)-bis[(buta-1,3-diyne-4,1-diyl)(2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol-14*-C,*3*-C-*diyl)(buta-1,3-diyne,4,1-diyl)]}*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol*; **10**). A soln. of **9** (44 mg, 0.017 mmol) in 0.3M HCl/MeOH (5 ml) and THF (4 ml) was stirred for 23 h at 70° and evaporated. The residue was dissolved in MeOH (at *ca.* 50°, ultrasonication), cooled to r.t., and decanted. Repetition of this procedure (3 ×) and removal of the solvent gave **10** (21.1 mg, 81%). Slightly yellow solid. R_f (AcOEt/MeOH/H_2O 13:6:1) *ca.* 0.20. M.p. > 226° (dec.). UV (H_2O): 256 (2626), 242 (3487). IR: 3673–3019*s* (br., max. at 3396), 2925*m*, 2156*w*, 1636*m*, 1457*w*, 1332*m*, 1256*w*, 1189*w*, 1122*s*, 1074*s* (br.), 1027*s*, 856*w*, 700*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 5.10–4.10 (*m*, exchange with D_2O, 3 OH); 4.82 (*d*, $J = 5.7$, H–C(6)); 3.71 (br. *ddd*, $J \approx 1.0$, 4.1, 10.4, H–C(2)); 3.65 (br. *d*, $J \approx 11.9$, addn. of D_2O → change of signal, H–C(1)); 3.54 (br. *dd*, $J \approx 4.2, 12.0$, H′–C(1)); 3.51 (br. *t*, $J \approx 10.0$, H–C(4)); 3.28 (br. *dd*, $J \approx 5.7, 9.4$, H–C(5)); 2.51 (br. *t*, $J \approx 10.4$, H–C(3)). ^{13}C-NMR (100 MHz, (D_6)DMSO): 76.58, 76.11 (2*s*, 2 C≡C);); 75.45 (*d*, C(2)); 71.71 (*d*, C(4)); 71.46 (*s*, C≡C); 70.91 (*d*, C(5)); 68.89 (*d*, C(6)); 67.35 (*s*, C≡C); 61.83 (*t*, C(1)); 37.61 (*d*, C(3)). ESI-MS: 1570 ([*M* + NH_4]$^+$).

2,6-Anhydro-3-C-*{2,6-anhydro-3*-C-*{4-[2,6-anhydro-3,7,8-trideoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*oct-7-ynitol-3*-C-*yl](buta-1,3-diyn-1-yl)}-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10*-C-*yl}-3,7,8-trideoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*oct-7-ynitol* (= *3*-C,*3′*-C-*{[2,6-Anhydro-3-deoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*hexitol-3*-C,*6*-C-*diyl]bis(buta-1,3-diyne-4,1-diyl)}bis[2,6-anhydro-3,7,8-trideoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*oct-7-ynitol]*; **11**). A soln. of **3** (345 mg, 0.306 mmol) in THF (2 ml) and MeOH (5 ml) was treated with 2% NaOMe soln. in MeOH at 0° under Ar, stirred for 20 min, warmed to r.t., stirred for 1 h, neutralized with *Dowex* (H^+ form), filtered, and evaporated. FC (hexane/AcOEt 1:1) gave **11** (288 mg, 95%). White foam. R_f (toluene/AcOEt 1:1) 0.32. $[\alpha]_D^{25} = +44.0$ ($c = 0.72$, $CHCl_3$). IR: 3304*m*, 2952*m*, 2984*m*, 2848*w*, 2256*w*, 2217*w*, 1465*w*, 1442*w*, 1356*w*, 1152*s*, 1112*s*, 1034*s* (br.), 917*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.00 (br. *d*, $J = 5.7$, H–C(6′)); 4.95 (*dd*, $J \approx 2.3, 5.7$), 4.94 (*dd*, $J \approx 2.3, 5.7$, H–C(6), H–C(6″)); 4.95 (*d*, $J = 6.9$), 4.91 (*d*, $J = 6.6$), 4.90 (*d*, $J = 6.6$), 4.81 (*d*, $J \approx 6.4$), 4.80 (*d*, $J = 6.7$), 4.79 (*d*, $J \approx 6.4$), 4.71 (*d*, $J = 6.9$), 4.70 (*d*, $J \approx 6.9$, 8 MeOC*H*); 4.64–4.69 (*m*, 10 MeOC*H*); 4.15 (*ddd*, $J = 2.0, 3.9, 10.6$), 4.10 (*ddd*, $J = 2.2, 4.0, 10.6$), 3.91–3.81 (*m*, 4 H), 3.80 (*dd*, $J \approx 3.9, 11.2$), 3.76 (*dd*, $J = 3.9, 11.2$), 3.75 (*dd*, $J = 3.8, 11.2$, 2 H–C(1), H–C(2), 2 H–C(1′), H–C(2′), 2 H–C(1″), H–C(2″)); 4.02 (br. *t*, $J \approx 9.8$, 2 H), 3.97 (br. *t*, $J \approx 10.0$, H–C(4), H–C(4′), H–C(4″)); 3.55 (*dd*, $J = 5.7, 9.5$),

3.53 (*dd*, $J \approx 5.7, 9.5$), 3.52 (*dd*, $J \approx 5.7, 9.6$, H–C(5), H–C(5'), H–C(5'')); 3.49, 3.47, 3.46, 3.416, 3.412, 3.40, 3.39, 3.38 (2 C; 8*s*, 9 MeO); 2.87 (br. *t*, $J \approx 10.5$), 2.82 (br. *t*, $J \approx 10.5$, 2 H, H–C(3), H–C(3'), H–C(3'')); 2.63 (*d*, $J = 2.3$), 2.62 (*d*, $J = 2.3$, H–C(8), H–C(8'')). ^{13}C-NMR (100 MHz, $CDCl_3$): 97.72 (3 C), 97.64, 97.60 (2 C), 96.65 (3 C; 4*t*, 9 MeOCH_2); 78.53, 78.44, 78.28, 75.93, 75.90, 75.69 (6*d*, C(4), C(5), C(4'), C(5'), C(4''), C(5'')); 77.88, 77.81 (2*d*, C(8), C(8'')); 78.14 (2 C), 77.68, 75.25, 74.86, 73.53, 72.10, 68.38, 68.17, 67.74 (9*s*, 8 *C*≡C, C(7), C(7'')); 73.49, 73.04, 72.92 (3*d*, C(2), C(2'), C(2'')); 68.56, 67.84 (2 C; 2*d*, C(6), C(6'), C(6'')); 67.23, 67.18, 67.14 (3*t*, C(1), C(1'), C(1'')); 56.26, 56.18 (3 C), 56.04 (3 C), 55.29, 55.26 (5*q*, 9 MeO); 37.39, 37.32, 37.28 (3*d*, C(3), C(3'), C(3'')). FAB-MS: 1003 (94, $[M + Na]^+$), 949 (77), 873 (100). Anal. calc. for $C_{48}H_{68}O_{21}$ (981.05): C 58.77, H 6.99; found: C 58.78, H 6.87.

*3,3'-(Buta-1,3-diyne-1,4-diyl)-{2,6:11,15-dianhydro-14-*C*-[2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl]-3,7,8,9,10,14-hexadeoxy-1,4,5,12,13,16-hexakis-*O*-(methoxymethyl)-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol}* (= *2,6:11,15-Dianhydro-3-*C*,14-*C*-{[2,6-anhydro-3-deoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-hexitol-3-*C*,6-*C*-diyl]bis(buta-1,3-diyne-4,1-diyl)}-3,7,8,9,10,14-hexadeoxy-1,4,5,12,13,16-hexakis-*O*-(methoxymethyl)-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol}*; **12**). A soln. of $Cu(OAc)_2$ (2.61 g, 14.37 mmol) in pyridine (200 ml) was treated at 50° under N_2 with a soln. of **11** (0.282 g, 0.287 mmol) in pyridine (1 ml) within 9 h, stirred for 20 h, and evaporated. Workup (AcOEt) and FC (toluene/AcOEt 9:1 → 4:1) gave **12** (0.232 g, 82%). White foam. R_f (toluene/AcOEt 3:2) 0.14. M.p.: softening at 163.5–164.5°. $[\alpha]_D^{25} = +90.4$ ($c = 0.52$, $CHCl_3$). IR: 3007*m*, 2952*m*, 2894*m*, 2847*w*, 2254*w*, 2157*w*, 1464*w*, 1442*w*, 1354*w*, 1336*w*, 1152*s*, 1112*s*, 1040*s* (br.), 916*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.09 (*dd*, $J = 0.9, 5.8$), 5.02 (*d*, $J \approx 1.0, 5.9$), 4.92 (*dd*, $J = 1.1, 5.5$, H–C(6), H–C(11), H–C(6')); 5.05 (*d*, $J = 7.2$), 5.04 (*d*, $J = 6.8$), 4.89 (*d*, $J = 6.5$), 4.84 (*d*, $J = 6.5$), 4.83 (*d*, $J = 6.4$), 4.76 (*d*, $J = 7.2$), 4.73 (*d*, $J = 6.9$, 4.72 (*d*, $J = 7.1$), 4.71 (*d*, $J = 6.4$), 4.69 (*d*, $J \approx 7.0$), 4.68 (*d*, $J = 7.1$), 4.66 (*d*, $J = 6.5$, 12 MeOC*H*); 4.70 (*s*, MeOCH_2); 4.67 (br. *d*, $J \approx 6.5$, 2 H), 4.63 (br. *d*, $J \approx 6.5$, 2 H, 2 MeOCH_2); 4.50 (br. *ddd*, $J \approx 2.0, 3.0, 10.4$), 4.37 (br. *ddd*, $J \approx 2.0, 3.1, 10.5$), 4.28 (*ddd*, 2.1, 3.4, 10.6, H–C(2) H–C(15), H–C(2')); 4.10 (br. *t*, $J \approx 9.5$), 4.07 (br. *t*, $J \approx 9.5$), 4.02 (br. *t*, $J \approx 9.9$, H–C(4), H–C(13), H–C(4')); 4.01 (*dd*, $J \approx 3.3, 11.3$), 3.99 (*dd*, $J = 3.2, 11.3$), 3.85 (*dd*, $J \approx 3.6, 11.2$, H–C(1), H–C(16), H–C(1')); 3.87 (*dd*, $J = 1.9, 11.1$), 3.82 (*dd*, $J = 1.9, 11.3$), 3.72 (*dd*, $J = 2.0, 11.2$, H'–C(1), H'–C(16), H'–C(1')); 3.58 (*dd*, $J = 5.9, 9.4$), 3.56 (*dd*, $J = 5.7, 9.4$), 3.51 (*dd*, $J = 5.5, 9.4$, H–C(5), H–C(12), H–C(5')); 3.53 (*s*, 2 MeO); 3.48, 3.41, 3.40, 3.39, 3.38, 3.36, 3.35 (7*s*, 7 MeO); 2.94 (*dt*, $J \approx 1.1, 10.5$), 2.78 (*dt*, $J \approx 1.0, 10.4$), 2.75 (*dt*, $J \approx 1.1, 10.4$, H–C(3), H–C(14), H–C(3')). ^{13}C-NMR (100 MHz, $CDCl_3$): 97.83, 97.77, 97.69, 97.55, 97.47, 97.40, 96.75, 96.68, 96.58 (9*t*, 9 MeOCH_2); 78.98, 78.78, 78.75, 76.99, 76.68, 75.83 (6*d*, C(4), C(5), C(12), C(13), C(4'), C(5')); 78.20, 76.77, 76.76, 74.55, 74.50, 73.98, 73.54, 73.21, 71.66, 68.01, 67.93, 67.75 (12*s*, 12 *C*≡C); 73.71, 73.42, 73.28 (3*d*, C(2), C(15), C(2')); 68.67, 68.45 (2 C; 2*d*, C(6), C(11), C(6')); 67.20, 67.12, 66.90 (3*t*, C(1), C(16), C(1')); 56.21, 56.09 (2 C), 56.05 (2 C), 55.91, 55.36, 55.28, 55.25 (7*q*, 9 MeO); 37.09; 36.76, 36.72 (3*d*, C(3), C(14), C(3')). MALDI-MS: 1001 ($[M + Na]^+$). Anal. calc. for $C_{48}H_{66}O_{21}$ (979.04): C 58.89, H 6.79; found: C 58.68, H 6.75.

*3,3'-(Buta-1,3-diyne-1,4-diyl){2,6:11,15-dianhydro-14-*C*-(2,6-anhydro-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl)-3,7,8,9,10,14-hexadeoxy-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol}* (= *2,6:11,15-Dianhydro-3-*C*,14-*C*-[(2,6-anhydro-3-deoxy-*D*-glycero-*L*-gulo-hexitol-3-*C*,6-*C*-diyl)bis(buta-1,3-diyne-4,1-diyl)]-3,7,8,9,10,14-hexadeoxy-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol*; **13**). A soln. of **12** (230 mg, 0.234 mmol) in 0.3M HCl in MeOH (7 ml) was refluxed for 21 h and evaporated. The residue was dissolved in boiling MeOH and cooled to r.t. Addition of CH_2Cl_2 led to precipitation of a white solid, which was filtered off: **13** (128.4 mg, 94%). R_f (toluene/acetone 1:4) 0.42. M.p. > 191.0° (dec.). $[\alpha]_D^{25} = +61.8$ ($c = 0.50$, H_2O). UV (H_2O): 240 (859), 229 (869). IR (KBr): 3677–3011*s* (br., max. at 3404), 2922*w*, 2252*w*, 2154*w*, 1635*m* (br.), 1409*m* (br.), 1335*m*, 1252*w*, 1124*s*, 1076*s* (br.), 871*m*, 742*w*, 700*w*, 656*w*, 610*w*, 556*w*, 524*w*. ^{1}H-NMR (500 MHz, (D_6)DMSO)[13]: 5.65–5.52 (*m*, HO–C(4), HO–C(5), HO–C(12), HO–C(13), HO–C(4'), HO–C(5')); 4.95–4.84 (*m*, HO–C(1), HO–C(16), HO–C(1')); 4.84 (*dd*, $J = 1.0, 5.8$, H–C(11)); 4.79 (*dd*, $J = 1.0, 5.6$, H–C(6)); 4.65 (*dd*, $J \approx 1.0, 5.3$, H–C(6')); 3.86 (*ddd*, $J = 1.7, 4.9, 10.6$, H–C(2')); 3.79 (*ddd*, $J = 1.6, 5.1, 10.6$, H–C(2)); 3.76 (*ddd*, $J = 1.8, 5.1, 10.6$, H–C(15)); 3.61–3.58 (*m*, H–C(4')); 3.55–3.49 (*m*, H–C(4)); 3.52–3.48 (*m*, H–C(13)); 3.69–3.64 (*m*, H–C(1), H–C(16)); 3.63–3.57 (*m*, H–C(1')); 3.57–3.53 (*m*, H'–C(16)); 3.55–3.50 (*m*, H'–C(1)); 3.52–3.47 (*m*, H'–C(1')); 3.31–3.28 (*m*, H–C(12)); 3.30–3.26 (*m*, H–C(5)); 3.28–3.24 (*m*, H–C(5')); 2.51 (br. *dt*, $J \approx 1.0, 10.5$, H–C(14)); 2.37 (br. *dt*, $J \approx 0.9, 10.4$, H–C(3)); 2.35 (br. *dt*, $J \approx 0.9, 10.5$, H–C(3')). ^{13}C-NMR (125 MHz, (D_6)DMSO): 79.04 (*s*, C(10')); 78.77 (*s*, C(4'')); 77.92 (*s*, C(1'')); 75.83 (*s*, C(10)); 75.78 (*d*, C(2)); 75.66 (*d*, C(2'));

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

75.58 (*s*, C(7′)); 75.38 (*d*, C(15)); 73.07 (*s*, C(8′)); 73.06 (*s*, C(7)); 72.44 (*d*, C(4′)); 72.19 (*d*, C(4)); 71.74 (*s*, C(9)); 71.63 (*d*, C(13)); 71.21 (*s*, C(8)); 70.64 (*d*, C(5)); 70.73 (*d*, C(12), C(5′)); 68.88 (*d*, C(11)); 68.83 (*d*, C(6)); 68.71 (*d*, C(6′)); 66.59 (*s*, C(2″)); 66.22 (*s*, C(3″)); 66.01 (*s*, C(9′)); 61.90 (*t*, C(1), C(1′)); 61.82 (*t*, C(16)); 37.68 (*d*, C(14)); 37.51 (*d*, C(3)); 37.34 (*d*, C(3′)). MALDI-MS: 605 ([*M* + Na]$^+$). Anal. calc. for $C_{30}H_{30}O_{12} \cdot 0.5\,H_2O \cdot CH_3OH$ (582.56): C 59.71, H 5.66; found: C 59.98, H 5.74.

Solubility of **13** *in* H_2O. A suspension of **13** in H_2O (*ca.* 3.5 ml) was ultrasonicated for 5 min at 24°, and filtered. Lyophilization and drying (12 h, r.t./0.05 mbar) of 410 µl of the clear filtrate left 90 mg of **13**.

*2,6-Anhydro-3,7,8-trideoxy-3-*C*-(2-iodoethynyl)-1,4,5-tris-*O*-(methoxymethyl)-8-*C*-(trimethylsilyl)-*D-glycero-L-gulo-*oct-7-ynitol* (**14**). A soln. of I_2 (6.79 g, 53.5 mmol) in toluene (25 ml) was treated at 0° with a soln. of morpholine (9.33 ml, 107 mmol) in toluene (15 ml), heated to 45°, stirred for 45 min, treated with a soln. of **1** (1.43 g, 3.58 mmol) in toluene (15 ml), and stirred for 7 h. The suspension was cooled to 0° and filtered through cotton. The filtrate was diluted with AcOEt and sat. aq. $Na_2S_2O_3$ soln. Workup (AcOEt) and FC (hexane/Et_2O 7:3) gave **14** (1.78 g, 95%). Slightly yellow oil. R_f (hexane/Et_2O 3:2) 0.21. IR: 2956*m*, 2894*m*, 2829*w*, 2170*w*, 1142*w*, 1336*w*, 1152*s*, 1116*s*, 1075*s*, 1037*s* (br.), 960*m*, 915*s*, 845*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.94 (*d*, $J \approx 5.6$, H–C(6)); 4.92 (*d*, $J \approx 6.8$), 4.78 (*d*, $J = 6.8$), 4.72 (*d*, $J = 6.9$), 4.67 (*d*, $J \approx 6.9$, 2 MeOCH_2); 4.66 (*s*, MeOCH_2); 4.05 (br. *ddd*, $J \approx 2.0$, 3.7, 10.5, H–C(2)); 3.91 (br. *t*, $J \approx 9.9$, H–C(4)); 3.88 (*dd*, $J = 3.7$, 10.9, H–C(1)); 3.73 (*dd*, $J = 1.9$, 10.9, H′–C(1)); 3.48 (*dd*, $J \approx 5.6$, 9.3, H–C(5)); 3.48, 3.39, 3.38 (3*s*, 3 MeO); 2.90 (br. *t*, $J \approx 10.5$, H–C(3)); 0.20 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 100.13 (*s*, C(7)); 97.86, 97.79, 96.79 (3*t*, 3 MeOCH_2); 95.22 (*s*, C(8)); 91.49 (*s*, *C*≡CI); 79.14, 76.46 (2*d*, C(4), C(5)); 73.25 (*d*, C(2)); 68.56 (*d*, C(6)); 67.36 (*t*, C(1)); 56.48, 56.15, 55.36 (3*q*, 3 MeO); 38.73 (*d*, C(3)); −0.109 (*q*, Me_3Si); −1.45 (*s*, C≡*C*I). CI-MS: 544 (100, [*M* + NH_4]$^+$), 418 (32), 153 (33).

*2,6-Anhydro-3,7,8-trideoxy-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]-*D-glycero-L-gulo-*deca-7,9-diynitol-10-*C*-yl}-3,7,8,9,10-pentadeoxy-*D-glycero-L-gulo-*deca-7,9-diynitol-10-*C*-yl}-8-*C*-(trimethylsilyl)-*D-glycero-L-gulo-*oct-7-ynitol* (= *2,6-Anhydro-10-*C*-{1,4,5-tri-*O*-acetyl-2,6-anhydro-10-*C*-[2,6-anhydro-3,7,8-trideoxy-1,4,5-tris-*O*-(methoxymethyl)-8-*C*-(trimethylsilyl)-*D-glycero-L-gulo-*oct-7-ynitol-3-*C*-yl]-3,7,8,9,10-pentadeoxy-*D-glycero-L-gulo-*deca-7,9-diynitol-3-*C*-yl}-3,7,8,9,10-pentadeoxy-1,4,5-tris-*O*-(methoxymethyl)-3-*C*-[2-(trimethylgermylethynyl]-*D-glycero-L-gulo-*deca-7,9-diynitol;* **16**). A soln. of **14** (1.55 g, 2.94 mmol), **15** (1.88 g, 2.94 mmol), [Pd_2(dba)$_3$] (42 mg, 88.2 µmol; dba = dibenzylideneacetone = 1,5-diphenylpenta-1,4-dien-3-one), P(furyl)$_3$ (40.9 mg, 0.18 mmol), and CuI (14 mg, 73.5 µmol) in DMSO (28 ml) was stirred for 5 min at 25° under Ar, treated with Et_3N (1.23 ml, 8.82 mmol), and stirred for 14 h. Workup (Et_2O) and FC (toluene/AcOEt 1:1 → 3:2 → 7:3) gave a yellow foam (2.23 g, R_f (AcOEt) 0.36), which was dissolved in pyridine (10 ml), Ac_2O (5 ml), and ^{i}PrOH (0.5 ml), and stirred for 13 h. Evaporation and FC (hexane/AcOEt 3:2 → 1:1) gave **16** (2.39 g, 70%). White foam. R_f (toluene/AcOEt 7:3) 0.21. $[\alpha]_D^{25} = +149.3$ ($c = 0.66$, $CHCl_3$). IR: 2954*m*, 2245*w*, 2169*w*, 1749*s* (br.), 1371*w*, 1152*s*, 1114*s*, 1036*s* (br.), 915*m*, 845*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.47 (br. *t*, $J \approx 10.3$, H–C(4′)); 5.05 (br. *d*, $J \approx 5.8$), 5.01 (br. *d*, $J = 5.8$, H–C(6′), H–C(6″)); 4.97 (*d*, $J = 5.7$, H–C(6)); 4.96 (*d*, $J = 6.7$), 4.92 (*d*, $J = 6.6$), 4.89 (*d*, $J = 6.5$, 3 MeOC*H*); 4.80 (*dd*, $J = 5.8$, 10.0, H–C(5′)); 4.79 (*d*, $J = 6.8$), 4.75 (*d*, $J = 6.7$), 4.74 (*d*, $J = 6.7$), 4.69 (*d*, $J = 6.8$, 4 MeOC*H*); 4.69 (*s*, MeOCH_2); 4.68 (*d*, $J \approx 6.8$, MeOC*H*); 4.67 (*s*, MeOCH_2); 4.46 (*dd*, $J = 2.4$, 12.2, H–C(1′)); 4.29 (*dd*, $J = 4.6$, 12.2, H′–C(1′)); 4.19 (*ddd*, $J = 2.3$, 4.4, 10.5, H–C(2′)); 4.11 (*ddd*, $J = 2.0$, 3.7), 3.85 (br. *dd*, $J \approx 9.9$, 10.2), 3.99–3.89 (*m*, 4 H, H–C(1), H–C(2), H–C(4), H–C(1″), H–C(2″), H–C(4″)); 3.79 (*dd*, $J = 2.0$, 11.3), 3.76 (br. *dd*, $J \approx 2.0$, 11.0, H′–C(1), H′–C(1″)); 3.52 (*s*, MeO); 3.52 (*dd*, $J \approx 5.8$, 9.7), 3.50 (*dd*, $J = 5.8$, 9.8, H–C(5), H–C(5″)); 3.47, 3.41 (2 Me), 3.39, 3.38 (4*s*, 5 MeO); 2.90 (br. *t*, $J \approx 10.6$, H–C(3), H–C(3′)); 2.76 (*t*, $J = 10.4$, H–C(3″)); 2.13, 2.11, 2.07 (3*s*, 3 Ac); 0.33 (*s*, Me_3Ge); 0.21 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 170.47, 169.93, 169.24 (3*s*, 3 C=O); 101.37 (*s*, C(7)); 99.70 (*s*, *C*≡CGe); 97.73, 97.70, 97.62, 97.59, 96.66, 96.63 (6*t*, 6 MeO*C*H$_2$); 95.15 (*s*, C(8)); 88.95 (*s*, C≡*C*Ge); 78.84, (*s*, *C*≡C); 78.91, 78.43, 76.35, 75.90 (4*d*, C(4), C(5), C(4″), C(5″)); 74.56, 73.80, 73.69, 72.50 (4*s*, 4 *C*≡C); 74.06, 72.64, 71.91, 69.96, 69.75 (5*d*, C(2), C(2′), C(4′), C(5′), C(2″)); 69.80, 69.10 (2*s*, 2 *C*≡C); 68.63, 68.41 (2*d*, C(6), C(6″)); 67.25 (*t*, C(1), C(1″)); 67.24 (*s*, *C*≡C); 66.37 (*d*, C(6′)); 63.81 (*t*, C(1′)); 56.30, 56.26, 56.10, 56.02, 55.29, 55.25 (6*q*, 6 MeO); 37.79, 37.42, 36.71 (3*d*, C(3), C(3′), C(3″)); 20.77, 20.66, 20.63 (3*q*, 3 Me); −0.13, −0.32 (2*q*, Me_3Ge, Me_3Si). FAB-MS: 1163 (32, [*M* + H]$^+$), 1057 (31), 907 (53), 831 (47), 307 (46), 119 (100). Anal. calc. for $C_{54}H_{78}GeO_{21}Si$ (1163.89): C 55.73, H 6.75; found: C 55.50, H 6.69.

*2,6-Anhydro-3,7,8-trideoxy-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-*C*-yl}-3,7,8,9,10-pentadeoxy-*D-glycero-L-gulo-*deca-7,9-diynitol-10-*C*-yl}-8-*C*-(trimethylsilyl)-*D-glycero-L-gulo-*oct-7-ynitol* (= *2,6-Anhydro-10-*C*-{1,4,5-tri-*O*-acetyl-2,6-anhydro-10-*C*-[2,6-anhydro-3,7,8-trideoxy-1,4,5-tris-*O*-(methoxymethyl)-8-*C*-(trimethylsilyl)-*D-glycero-L-gulo-*oct-7-ynitol-3-*C*-yl]-3,7,8,9,10-pentadeoxy-*D-gly-

cero-L-gulo-*deca-7,9-diynitol-3*-C-*yl}-3,7,8,9,10-pentadeoxy-3*-C-*(2-iodoethynyl)-1,4-5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol;* **17**). In the absence of light, a soln. of **16** (2.05 g, 1.76 mmol), *N*-iodosuccinimide (NIS; 495 mg, 2.20 mmol), and CuBr (63.1 mg, 0.44 mmol) in acetone (21 ml) was stirred at r.t. under Ar for 9 h. The mixture was treated with aq. sat. $Na_2S_2O_3$ soln. and AcOEt. Workup (AcOEt) and FC (hexane/AcOEt 3:2) gave **17** (1.97 g, 96%). White foam. R_f (toluene/AcOEt 7:3) 0.21. M.p.: softening at 61–63°. IR: 2955*m*, 2894*m*, 2827*w*, 2256*w*, 1753*s* (br.), 1442*w*, 1371*m*, 1154*s*, 1114*m*, 1037*s* (br.), 959*w*, 916*m*, 846*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.44 (br. *t*, $J \approx 10.3$, H–C(4′)); 5.02 (br. *d*, $J = 5.6$), 4.97 (br. *d*, $J = 5.6$, H–C(6′), H–C(6″)); 4.94 (*d*, $J = 5.9$, H–C(6)); 4.93 (*d*, $J = 6.8$), 4.89 (*d*, $J = 6.8$), 4.77 (*d*, $J \approx 6.7$), 4.76 (*d*, $J \approx 6.6$, 2 MeOCH_2); 4.77 (*dd*, $J \approx 5.6$, 9.8, H–C(5′)); 4.71 (br. *d*, $J \approx 7.0$, 2 MeOC*H*); 4.67–4.62 (*m*, 6 MeOC*H*); 4.42 (*dd*, $J = 2.2$, 12.1, H–C(1′)); 4.27 (*dd*, $J = 4.7$, 12.2, H′–C(1′)); 4.16 (*ddd*, $J = 1.9$, 4.0, 10.3, H–C(2′)); 4.06 (br. *ddd*, $J \approx 1.9$, 3.9, 10.4), 3.97 (br. *ddd*, $J \approx 1.9$, 3.7, 10.3, H–C(2), H–C(2″)); 3.89–3.82 (*m*, H–C(1), H–C(4), H–C(1″), H–C(4‴)); 3.76 (*dd*, $J = 1.9$, 11.2), 3.72 (*dd*, $J = 1.9$, 11.2, H′–C(1), H′–C(1″)); 3.50–3.45 (*m*, H–C(5), H–C(5‴)); 3.49, 3.45, 3.38 (2 Me), 3.37, 3.36 (5*s*, 6 MeO); 2.88 (br. *t*, $J \approx 10.5$, H–C(3), H–C(3′), H–C(3‴)); 2.10 2.09, 2.04 (3*s*, 3 Ac); 0.18 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.95, 170.37, 169.69 (3*s*, 3 C=O); 99.88 (*s*, C(7)); 97.89, 97.86, 97.83, 97.79, 96.78 (2 C; 5*t*, 6 MeO*C*H$_2$); 95.35 (*s*, C(8)); 91.03 (*s*, *C*≡CI); 79.08, 78.69, 76.41, 76.04 (4*d*, C(4), C(5), C(4″), C(5‴)); 73.93, 72.75, 72.04, 70.08, 69.87 (5*d*, C(2), C(2′), C(4′), C(5′), C(2‴)); 78.96, 74.73, 74.08, 73.54, 72.93, 69.94 (6*s*, 6 *C*≡C); 68.67, 68.55 (2*d*, C(6), C(6‴)); 67.38, 67.22 (2*t*, C(1), C(1‴)); 66.49 (*d*, C(6′)); 63.97 (*t*, C(1′)); 56.51, 56.40, 56.27, 56.17, 55.42, 55.34 (6*q*, 6 MeO); 38.65, 37.47, 36.71 (3*d*, C(3), C(3′), C(3‴)); 20.87 (2 C), 20.77 (2*q*, 3 Me); −0.09 (*q*, Me_3Si); −0.69 (*s*, *C*≡CI); 2 signals for *C*≡C are missing. FAB-MS: 1197 (13), 1196 (32), 1195 (56, $[M + Na]^+$), 1171 (77), 1065 (56), 989 (100).

2,6-Anhydro-3,7,8-trideoxy-1,4,5-tris-O-*(methoxymethyl)-3*-C-*{1,4,5-tri*-O-*acetyl-2,6-anhydro-3*-C-*{2,6-anhydro-3*-C-*{4-[2,6-anhydro-3,7,8-trideoxy-1,4,5-tris*-O-*(methoxymethyl)-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol-3*-C-*yl]buta-1,3-diyn-1-yl}-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10*-C-*yl}3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10*-C-*yl}-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**18**). A soln. of **17** (1.97 g, 1.68 mmol), **1** (0.807 g, 2.01 mmol), $[Pd_2(dba)_3]$ (24.0 mg, 50.3 μmol), P(furyl)$_3$ (23.4 mg, 0.1 mmol), and CuI (8.0 mg, 41.9 μmol) in DMSO (16 ml) was stirred for 5 min at 23° under Ar, treated with Et_3N (700 μl, 5.04 mmol), and stirred for 17 h. Workup (Et_2O) and FC (toluene/AcOEt 4:1 → 3:2) gave **18** (1.89 g, 78%). White foam. R_f (toluene/AcOEt 1:1) 0.37. M.p.: softening at 59–63°. $[\alpha]_D^{25} = +120.6$ ($c = 0.60$, $CHCl_3$). IR: 2955*m*, 2894*m*, 2848*w*, 2257*w*, 2168*w*, 1749*m* (br.), 1412*w*, 1374*w*, 1152*s*, 1113*s*, 1037*s* (br.), 959*w*, 916*m*, 846*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.47 (br. *t*, $J \approx 10.3$, H–C(4′)); 5.05 (br. *d*, $J = 5.8$), 5.01 (br. *d*, $J = 5.8$, H–C(6′), H–C(6″)); 4.97 (*d*, $J \approx 5.6$), 4.95 (*d*, $J \approx 5.7$, H–C(6), H–C(6‴)); 4.96 (*d*, $J = 6.7$), 4.92 (*d*, $J = 6.7$), 4.90 (*d*, $J = 6.6$), 4.79 (*d*, $J = 6.6$, 2 H), 4.78 (*d*, $J = 6.7$), 4.75–4.72 (*m*, 3 H), 4.70–4.64 (*m*, 9 H, 9 MeOCH_2); 4.80 (*dd*, $J = 5.8$, 9.8, H–C(5′)); 4.46 (*dd*, $J = 2.3$, 12.3, H–C(1′)); 4.29 (*dd*, $J = 4.6$, 12.3, H′–C(1′)); 4.18 (*ddd*, $J = 2.2$, 4.4, 10.5, H–C(2′)); 4.11 (*ddd*, $J = 2.0$, 3.7, 10.5), 4.05 (*ddd*, $J = 2.0$, 3.8, 10.5), 3.99 (*ddd*, $J = 2.0$, 3.7, 10.5, H–C(2), H–C(2″), H–C(2‴)); 3.96 (*dd*, $J = 9.4$, 10.3), 3.91 (*dd*, $J \approx 9.5$, 10.3), 3.88 (*dd*, $J \approx 9.4$, 10.3, H–C(4), H–C(4″), H–C(4‴)); 3.91 (*dd*, $J = 3.9$, 11.3), 3.84 (*dd*, $J = 3.7$, 11.3), 3.83 (*dd*, $J = 3.7$, 11.2, H–C(1), H–C(1″), H–C(1‴)); 3.79 (*dd*, $J = 2.0$, 11.3), 3.75 (br. *dd*, $J \approx 2.0$, 11.2, 2 H, H′–C(1), H′–C(1″), H′–C(1‴)); 3.52 (*dd*, $J = 5.8$, 9.3), 3.50 (*dd*, $J = 5.7$, 9.3), 3.48 (*dd*, $J = 5.8$, 9.2, H–C(5), H–C(5″), H–C(5‴)); 3.52, 3.478, 3.473, 3.410, 3.409, 3.402, 3.400, 3.38, 3.37 (9*s*, 9 MeO); 2.90 (br. *t*, $J \approx 10.4$, 2 H), 2.84 (br. *t*, $J \approx 10.2$), 2.82 (br. *t*, $J \approx 10.2$, H–C(3), H–C(3′), H–C(3″), H–C(3‴)); 2.13, 2.11, 2.07 (3*s*, 3 Ac); 0.216, 0.210 (2*s*, 2 Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.48, 169.98, 169.31 (3*s*, 3 C=O); 99.82, 99.76 (2*s*, C(7), C(7‴)); 97.75, 97.73, 97.65 (2 C), 96.71, 96.68 (2 C), 96.67 (2 C; 6*t*, 9 MeO*C*H$_2$); 95.21, 95.19 (2*s*, C(8), C(8‴)); 78.97, 78.79, 78.44, 76.06 (2 C), 75.95 (5*d*, C(4), C(5), C(4″), C(5″), C(4‴), C(5‴)); 78.91, 75.48, 74.68, 74.62, 74.05, 73.34, 72.88, 69.85, 68.93, 68.57, 68.09, 67.31 (12*s*, 12 *C*≡C); 73.61, 72.88, 72.69, 71.97, 70.00, 69.78 (6*d*, C(2), C(2′), C(4′), C(5′), C(2″), C(2‴)); 68.62, 68.47 (2 C; 2*d*, C(6), C(6″), C(6‴)); 67.27 (2 C), 67.23 (2*t*, C(1), C(1″), C(1‴)); 66.42 (*d*, C(6′)); 63.79 (*t*, C(1′)); 56.31, 56.24, 56.22, 56.19, 56.08, 56.06, 55.35, 55.28 (2 C; 8*q*, 9 MeO); 37.48, 37.37 (2 C), 36.74 (3*d*, C(3), C(3′), C(3″), C(3‴)); 20.81, 20.70, 20.69 (3*q*, 3 Me); −0.07, −0.11 (2*q*, 2 Me_3Si). MALDI-MS: 1483 ($[M + K]^+$), 1467 ($[M + Na]^+$). Anal. calc. for $C_{70}H_{100}O_{28}Si_2$ (1445.71): C 58.16, H 6.97; found: C 57.95, H 6.86.

2,6-Anhydro-3,7,8-trideoxy-1,4,5-tris-O-*(methoxymethyl)-3*-C-*{1,4,5-tri*-O-*acetyl-2,6-anhydro-3*-C-*{2,6-anhydro-3*-C-*{4-[2,6-anhydro-3,7,8-trideoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*oct-7-ynitol-3*-C-*yl]-buta-1,3-diyn-1-yl}-3,7,8,9,10-pentadeoxy-1,4,5-tris*-O-*(methoxymethyl)*-D-glycero-L-gulo-*deca-7,9-diynitol-10*-C-*yl}-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10*-C-*yl}*-D-glycero-L-gulo-*oct-7-ynitol* (**19**). A soln. of **18** (1.89 g, 1.31 mmol) and CsF (485 mg, 3.19 mmol) in DMF (15 ml) and MeOH (3 ml) was stirred at 0° under Ar for 1 h and diluted with sat. aq. NH_4Cl soln. and Et_2O. Workup (Et_2O) and FC (hexane/AcOEt 1:1) gave **19** (1.632 g, 96%). White foam. R_f (toluene/AcOEt 2:3) 0.37. IR: 3304*m*, 2953*m*, 2893*m*, 2827*w*, 2257*w*, 1749*m* (br.),

1442*w*, 1371*m*, 1152*s*, 1112*s*, 1035*s* (br.), 917*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.41 (br. *t*, *J* = 10.2, H–C(4')); 4.97 (br. *d*, *J* ≈ 5.8), 4.95 (br. *d*, *J* ≈ 5.8, H–C(6'), H–C(6'')); 4.91–4.83 (*m*, H–C(6), H–C(6'''), 4 MeOC*H*); 4.76–4.57 (*m*, H–C(5'), 7 MeOCH_2); 4.39 (br. *dd*, *J* ≈ 1.9, 12.1, H–C(1')); 4.23 (br. *dd*, *J* ≈ 4.2, 12.0, H'–C(1')); 4.14–4.08 (*m*, 2 H), 3.70 (br. *d*, *J* ≈ 1.9, 11.1, 2 H), 4.06–3.73 (*m*, 9 H, 2 H–C(1), H–C(2), H–C(4), H–C(2'), 2 H–C(1''), H–C(2''), H–C(4''), 2 H–C(1'''), H–C(2'''), H–C(4''')); 3.51–3.41 (*m*, H–C(5), H–C(5''), H–C(5''')); 3.45, 3.41, 3.40, 3.34, (3 Me), 3.33, 3.30 (2 Me; 6*s*, 9 MeO); 2.84 (br. *t*, *J* ≈ 10.5), 2.83 (br. *t*, *J* ≈ 10.5), 2.76 (br. *t*, *J* ≈ 10.5), 2.75 (br. *t*, *J* ≈ 10.5, H–C(3), H–C(3'), H–C(3''), H–C(3''')); 2.60 (*d*, *J* = 2.5), 2.59 (*d*, *J* = 2.5, H–C(8), H–C(8''')); 2.06, 2.05, 2.00 (3*s*, 3 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.79, 170.22, 169.61 (3*s*, 3 C=O); 97.86 (2 C), 97.83 (2 C), 97.79, 97.73, 96.76 (2 C), 96.80 (6*t*, 9 MeOCH_2); 78.25 (*d*, C(8), C(8''')); 78.59, 78.51, 78.40, 76.12, 75.97, 75.73 (6*d*, C(4), C(5), C(4''), C(5''), C(4'''), C(5''')); 73.66, 73.14, 72.96, 72.01, 70.03, 69.82 (6*d*, C(2), C(2'), C(4'), C(5'), C(2''), C(2''')); 78.82, 78.17, 78.07, 75.37, 74.90, 74.63, 74.16, 73.37, 72.96, 69.94, 68.95, 68.50, 68.29, 67.41 (14*s*, 12 *C*≡C, C(7), C(7''')); 68.66, 67.93, (2 C; 2*d*, C(6), C(6''), C(6''')); 67.25 (br. *t*, C(1), C(1''), C(1''')); 66.43, (*d*, C(6')); 63.85 (*t*, C(1')); 56.40, 56.28, 56.25 (2 C), 56.09 (2 C), 55.38, 55.33 (2 C; 6*q*, 9 MeO); 37.40, 37.34, 36.66, 36.46 (4*d*, C(3), C(3'), C(3''), C(3''')); 20.80, 20.69, 20.66 (3*q*, 3 Me). MALDI-MS: 1339 ([*M* + K]$^+$), 1323 ([*M* + Na]$^+$).

Treatment of **19** *with Cu(OAc)$_2$ in Pyridine.* A soln. of $Cu(OAc)_2$ (11.37 g, 62.6 mmol) in pyridine (900 ml) was treated at 50° under N_2 dropwise with a soln. of **19** (1.63 g, 1.25 mmol) in pyridine (10 ml) within 8.5 h, stirred for 18 h, and evaporated. Workup (AcOEt) and 3 FC (toluene/AcOEt 7:3 → 1:2) gave **20** (1.07 g, 66%) as a white foam and a mixture of several products (*ca.* 200 mg). HPLC (hexane/AcOEt 4:1 → 1:1) of this mixture gave **21** (123 mg, 8%) as a white foam.

*Data of 3,3'''-(Buta-1,3-diyne-1,4-diyl){2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-1,4,5,12,13,16-hexakis-*O*-(methoxymethyl)-14-*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)-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl]-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl}-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol}* (**20**): R_f (toluene/AcOEt 3:7) 0.46. $[\alpha]_D^{25}$ = +137.5 (*c* = 0.75, $CHCl_3$). M.p.: softening at 118–120°. IR: 2952*m*, 2893*m*, 2827*w*, 2258*w*, 2166*w*, 1749*s* (br.), 1442*w*, 1371*w*, 1334*w*, 1152*s*, 1113*s*, 1041*s* (br.), 917*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.46 (br. *t*, *J* ≈ 10.3, H–C(4')); 5.10 (br. *d*, *J* = 5.8), 5.06 (br. *d*, *J* ≈ 5.8), 5.05 (br. *d*, *J* ≈ 5.8, H–C(6), H–C(11), H–C(6'')); 5.00 (*d*, *J* = 6.7, MeOC*H*); 4.98 (br. *d*, *J* ≈ 5.8, H–C(6')); 4.97 (*d*, *J* ≈ 6.7), 4.90 (*d*, *J* = 6.4), 4.84 (br. *d*, *J* ≈ 6.7, 2 H), 4.83 (*d*, *J* = 6.4, 5 MeOC*H*); 4.80 (*dd*, *J* = 5.8, 9.9, H–C(5')); 4.77 (*d*, *J* = 7.0), 4.76 (*d*, *J* = 6.7), 4.75 (*d*, *J* = 6.7, 3 MeOC*H*); 4.72–4.67 (*m*, 5 MeOC*H*); 4.66–4.64 (*m*, 4 MeOC*H*); 4.44 (*dd*, *J* = 2.2, 12.3, H–C(1')); 4.30 (*dd*, *J* = 4.5, 12.3, H'–C(1')); 4.22 (*ddd*, *J* = 2.1, 4.4, 10.5, H–C(2')); 4.13 (*ddd*, *J* = 2.0, 3.4, 10.5), 4.06 (*ddd*, *J* = 2.0, 3.4, 10.5), 4.01 (*ddd*, *J* = 2.0, 3.5, 10.5, H–C(2), H–C(15), H–C(2'')); 3.98 (*dd*, *J* = 9.6, 10.3), 3.95 (br. *t*, *J* ≈ 9.9), 3.88 (br. *t*, *J* ≈ 9.8, H–C(4), H–C(13), H–C(4'')); 3.96 (*dd*, *J* ≈ 3.5, 11.1), 3.88 (*dd*, *J* = 3.6, 11.2), 3.84 (*dd*, *J* ≈ 3.5, 11.2, H–C(1), H–C(16), H–C(1'')); 3.83 (*dd*, *J* ≈ 2.0, 11.2), 3.77 (*dd*, *J* = 1.9, 11.2), 3.76 (*dd*, *J* = 2.0, 11.2, H'–C(1), H'–C(16), H'–C(1'')); 3.58, 3.51, 3.48, 3.41, 3.402, 3.398, 3.390, 3.38, 3.37 (9*s*, 9 MeO); 3.55 (*dd*, *J* ≈ 5.8, 9.3), 3.54 (*dd*, *J* ≈ 5.8, 9.3), 3.50 (*dd*, *J* ≈ 5.8, 9.3, H–C(5), H–C(12), H–C(5'')); 2.96 (br. *t*, *J* ≈ 10.4), 2.92 (br. *t*, *J* ≈ 10.5), 2.85 (br. *t*, *J* ≈ 10.5), 2.82 (br. *t*, *J* ≈ 10.5, H–C(3), H–C(14), H–C(3'), H–C(3'')); 2.12, 2.10, 2.07 (3*s*, 3 Ac). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.55, 170.01, 169.19 (3*s*, 3 C=O); 98.00, 97.95, 97.87 (2 C), 97.78 (2 C), 96.82, 96.78, 96.71 (7*t*, 9 MeOCH_2); 78.73, 78.59, 78.53, 76.36, 76.18, 75.93 (6*d*, C(4), C(5), C(12), C(13), C(4''), C(5'')); 78.18, 75.10, 74.82, 74.64, 74.56, 74.53, 73.95 (7*s*, 7 *C*≡C); 73.74, 73.59, 73.48 (3*d*, C(2), C(15), C(2'')); 73.09, 73.08, 72.79, 72.72 (4*s*, 4 *C*≡C); 72.01, 70.06, 69.76 (3*d*, C(2'), C(4'), C(5')); 69.95, 68.82, 68.49, 68.35, 67.79 (5*s*, 5 *C*≡C); 68.77, 68.71, 68.59 (3*d*, C(6), C(11), C(6'')); 67.26 (2 C), 67.13 (2*t*, C(1), C(16), C(1'')); 66.43 (*d*, C(6')); 63.81 (*t*, C(1')); 56.56, 56.34, 56.30, 56.16 (2 C), 56.07, 55.39, 55.29 (2 C; 7 *q*, 9 MeO); 37.51, 37.33, 37.15, 36.56 (4*d*, C(3), C(14), C(3'), C(3'')); 20.76, 20.69, 20.58 (3*q*, 3 Me). MALDI-MS: 1337 ([*M* + K]$^+$), 1321 ([*M* + Na]$^+$). Anal. calc. for $C_{64}H_{82}O_{28}$ (1299.34): C 59.16, H 6.36; found: C 59.34, H 6.22.

*Data of 3,3''-(Buta-1,3-diyne-1,4-diyl){2,6:11,15-dianhydro-3,7,8,9,10,14-hexadeoxy-14-*C*-{1,5-di-*O*-acetyl-2,6-anhydro-3-*C*-[2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl]-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl}-1,4,5,12,13,16-hexakis-*O*-(methoxymethyl)-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol}* (**21**): R_f (toluene/AcOEt 3:7) 0.40. $[\alpha]_D^{25}$ = +156.7 (*c* = 0.50, $CHCl_3$). M.p.: softening > 123°. IR: 3400*w* (br.), 2953*m*, 2894*m*, 2827*w*, 2257*w*, 2159*w*, 1743*m* (br.), 1442*w*, 1371*w*, 1334*w*, 1152*s*, 1112*s*, 1042*s* (br.), 917*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.10 (br. *d*, *J* ≈ 6.0), 5.09 (br. *d*, *J* ≈ 6.0), 5.07 (br. *d*, *J* = 5.8), 4.99 (br. *d*, *J* ≈ 5.9, H–C(6), H–C(11), H–C(6'), H–C(6'')); 4.97 (*d*, *J* ≈ 6.7), 4.96 (*d*, *J* ≈ 6.7), 4.92 (*d*, *J* = 6.7), 4.86 (*d*, *J* = 6.7), 4.82 (*d*, *J* = 6.7, 2 H, 6 MeOC*H*); 4.77–4.73 (*m*, 3 MeOC*H*); 4.72–4.66 (*m*, H–C(5'), 7 MeOC*H*); 4.66 (*d*, *J* = 6.5), 4.64 (*d*, *J* = 6.5, 2 MeOC*H*); 4.43 (*dd*, *J* = 2.2, 12.2, H–C(1')); 4.28 (*dd*, *J* = 4.8, 12.3, H'–C(1')); 4.14 (*ddd*, *J* = 2.1, 4.6, 10.5, H–C(2')); 4.11–4.04

(*m*, addn. of D_2O → change of signal, 3 H), 4.03 (*ddd*, *J* = 2.1, 3.6, 10.5, H–C(2), H–C(15), H–C(4'), H–C(2'')); 3.96 (*dd*, *J* = 9.5, 10.4), 3.94 (br. *t*, *J* ≈ 10.1), 3.92 (br. *t*, *J* ≈ 9.9, H–C(4), H–C(13), H–C(4'')); 3.96 (*dd*, *J* = 3.7, 11.4), 3.91 (*dd*, *J* = 3.7, 11.2), 3.85 (*dd*, *J* ≈ 4.0, 11.3, H–C(1), H–C(16), H–C(1'')); 3.84 (*dd*, *J* ≈ 2.1, 11.3), 3.80 (*dd*, *J* = 2.1, 11.3), 3.75 (*dd*, *J* = 2.0, 11.3, H'–C(1), H'–C(16), H'–C(1'')); 3.56 (*dd*, *J* = 5.9, 9.3), 3.54 (*dd*, *J* = 5.8, 9.4), 3.52 (*dd*, *J* = 5.8, 9.4, H–C(5), H–C(12), H–C(5'')); 3.52, 3.51, 3.48, 3.41, 3.404, 3.401, 3.399, 3.394, 3.37 (9*s*, 9 MeO); 2.96 (br. *t*, *J* ≈ 10.4), 2.87 (br. *t*, *J* ≈ 10.4), 2.83 (br. *t*, *J* ≈ 10.4), 2.78 (br. *t*, *J* ≈ 10.4, H–C(3), H–C(14), H–C(3'), H–C(3'')); 2.77 (*d*, *J* = 4.0, exchange with D_2O, OH); 2.14, 2.11 (2*s*, 2 Ac). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.64, 170.34 (2*s*, 2 C=O); 97.90, 97.86, 97.83, 97.81, 97.70 (2 C), 96.81, 96.78, 96.74 (8*t*, 9 MeO*C*H_2); 78.60, 78.56, 78.46, 76.18, 76.07, 75.98 (6*d*, C(4), C(5), C(12), C(13), C(4''), C(5'')); 77.84, 75.31, 75.27, 74.86, 74.69, 74.65, 73.89, 73.29, 72.82, 72.76, 72.73, 70.79, 69.04, 68.42, 68.23, 67.86 (16*s*, 16 C≡*C*); 73.72, 73.60, 73.50, 72.03, 71.93, 70.17 (6*d*, C(2), C(15), C(2'), C(4'), C(5'), C(2'')); 68.75, 68.71, 68.52 (3*d*, C(6), C(11), C(6'')); 67.33, 67.24, 67.15 (3*t*, C(1), C(16), C(1'')); 66.21 (*d*, C(6')); 64.05 (*t*, C(1')); 56.37 (2 C), 56.26, 56.17 (3 C), 55.40 (2 C), 55.31 (5*q*, 9 MeO); 38.94, 37.52, 37.37, 37.15 (4*d*, C(3), C(14), C(3'), C(3'')); 20.87, 20.79 (2*q*, 2 Me). MALDI-MS: 1295 ($[M + K]^+$), 1279 ($[M + Na]^+$). Anal. calc. for $C_{62}H_{80}O_{27}$ (1257.29): C 59.23, H 6.41; found: C 58.92, H 6.33.

3,3''-(Buta-1,3-diyne-1,4-diyl){2,6:11,15-dianhydro-14-C-*[2,6-anhydro-3*-C-*(2,6-anhydro-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10*-C-*yl)-3,7,8,9,10-pentadeoxy*-D-glycero-L-gulo-*deca-7,9-diynitol-10*-C-*yl]-3,7,8,9,10,14-hexadeoxy*-D-erythro-L-ido-L-gulo-*hexadeca-7,9-diynitol}* (**22**). A soln. of **20** (0.89 g, 0.68 mmol) in THF (8 ml) and MeOH (15 ml) was treated at 0° under Ar with 2% NaOMe soln. in MeOH (1 ml), stirred for 4 h, neutralized with *Dowex* (H^+ form), filtered, and evaporated. The residue was dissolved in 0.3M HCl in MeOH (10 ml), stirred for 24 h at 60°, and evaporated. The residue was dissolved in MeOH (*ca.* 20 ml), treated with activated charcoal (*ca.* 1 g), heated to 50°, stirred for 30 min, and filtered. Evaporation of the filtrate left **22** (479 mg, 90%). White solid. R_f (acetone) 0.55. M.p. 175° (dec.). $[\alpha]_D^{25}$ = 109.8 (*c* = 0.46, H_2O). UV (H_2O): 256 (1048), 242 (1653), 230 (1582). IR (KBr): 3700–3022*s* (br. max. at 3404), 2923*m*, 2253*w*, 2154*w*, 1636*m* (br.), 1458*w*, 1335*m*, 1250*w*, 1189*w*, 1122*s*, 1077*s* (br.), 1022*m*, 848*w*, 654*w*. ^{1}H-NMR (500 MHz, (D_6)DMSO): 5.61 (br. *d*, *J* ≈ 4.5, partial exchange with D_2O), 5.60 (br. *d*, *J* ≈ 4.5, partial exchange with D_2O), 5.58 (br. *d*, *J* ≈ 4.5, partial exchange with D_2O), 5.57 (br. *d*, *J* ≈ 4.0, partial exchange with D_2O, OH–C(5), OH–C(12), OH–C(5'), OH–C(5'')); 5.59 (br. *d*, *J* ≈ 6.3, partial exchange with D_2O), 5.56 (br. *d*, *J* ≈ 6.0, partial exchange with D_2O), 5.52 (*d*, *J* = 6.2, partial exchange with D_2O), 5.48 (*d*, *J* = 6.2, partial exchange with D_2O, HO–C(4), HO–C(13), HO–C(4'), HO–C(4'')); 4.84–4.80 (*m*, 5 H, partial exchange with D_2O), 4.87 (br. *d*, *J* = 5.8), 4.80 (br. *d*, *J* ≈ 5.8), 4.76 (br. *d*, *J* = 5.6, HO–C(1), H–C(6), H–C(11), HO–C(16), HO–C(1'), H–C(6'), HO–C(1''), H–C(6'')); 3.77 (br. *ddd*, *J* ≈ 1.7, 4.4, 10.4), 3.76–3.71 (*m*, 2 H), 3.70 (br. *ddd*, *J* ≈ 2.1, 4.7, 10.5, H–C(2), H–C(15), H–C(2'), H–C(2'')); 3.68–3.60 (*m*, addn. of D_2O → change of signal, H–C(1), H–C(16), H–C(1'), H–C(1'')); 3.58–3.49 (*m*, addn. of D_2O → change of signal, H'–C(1), H–C(4), H–C(13), H'–C(16), H'–C(1'), H–C(4'), H'–C(1''), H–C(4'')); 3.32–3.24 (*m*, addn. of D_2O → br. *dd* at 3.29, *J* ≈ 5.7, 9.3 → br. *dd* at 3.27, *J* ≈ 5.7, 9.3, → br. *dd* at 3.25, *J* ≈ 5.7, 9.3, 2 H, H–C(5), H–C(12), H–C(5'), H–C(5'')); 2.57 (br. *t*, *J* ≈ 10.4), 2.54 (br. *t*, *J* ≈ 10.4), 2.50 (br. *t*, *J* ≈ 10.4), 2.46 (br. *t*, *J* ≈ 10.4, H–C(3), H–C(14), H–C(3'), H–C(3'')). ^{13}C-NMR (125 MHz, (D_6)DMSO): 78.87, 78.45, 76.74, 76.38, 75.99, 75.85 (6*s*, 6 C≡*C*); 75.36, 75.25, 75.14, 75.01 (4*d*, C(2), C(15), C(2'), C(2'')); 73.56, 73.37, 72.30, 72.28, 71.29, 71.11 (6*s*, 6 C≡*C*); 71.83, 71.68, 71.51, 71.40, (4*d*, C(4), C(13), C(4'), C(4'')); 70.91, 70.80, 70.79, 70.70 (4*d*, C(5), C(12), C(5'), C(5'')); 68.88, 68.82 (2 C), 68.74 (3*d*, C(6), C(11), C(6'), C(6'')); 67.22, 67.05, 66.87, 66.36 (4*s*, 4 *C*≡C); 61.77 (br. *t*, C(1), C(16), C(1'), C(1'')); 37.90, 37.69, 37.54, 37.49 (4*d*, C(3), C(14), C(3'), C(3'')). MALDI-MS: 799 ($[M + Na]^+$). Anal. calc. for $C_{40}H_{40}O_{16} \cdot 2\ H_2O$ (776.75): C 59.11, H 5.46; found: C 59.19, H 5.51.

Solubility of **22** *in* H_2O. A suspension of **22** in H_2O was ultrasonicated for 5 min at 24°, and filtered. Lyophilization and drying (12 h, r.t./0.05 mbar) of 900 µl of the clear filtrate left 11.3 mg of **22**.

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*-C-*yl]*-D-glycero-L-gulo-*deca-7,9-diynitol}* (**24**). A soln. of **23** (400 mg, 0.48 mmol) and CuBr (34.2 mg, 0.24 mmol) in THF (3 ml) and MeOH (3 ml) was stirred in the absence of light at r.t. under O_2 for 27 h. Workup (AcOEt) and FC (toluene/AcOEt 9:1 → 3:2) gave **24** (190 mg, 55%[14])) as a white solid. The spectroscopic data of **24** correspond to the data obtained from an authentic sample [7].

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-*[2,6-anhydro-3,7,8-trideoxy*-D-glycero-L-gulo-*oct-7-ynitol-3*-C-*yl]*-D-glycero-L-gulo-*deca-7,9-diynitol}* (**25**). A soln. of **24**

[14]) On a 100-mg scale, 64% of **24** were obtained.

(370 mg, 0.257 mmol) in THF (1.6 ml) and MeOH (6.6 ml) was treated at 0° under N_2 with a soln. of NaOMe in MeOH (330 µl, 2%), stirred for 3 h, and neutralized with *Dowex* (H^+ form). The solids were filtered off and washed with MeOH. Evaporation of the filtrate and FC (AcOEt) gave **25** (265 mg, 98%). Colourless oil. R_f (AcOEt/MeOH 19:1) 0.26. $[\alpha]_D^{25} = +81.4$ ($c = 0.46$, MeOH). IR: 3423*m* (br.), 3302*m*, 2932*m*, 2894*m*, 2166*w*, 1442*w*, 1337*m*, 1152*s*, 1113*s*, 1039*s* (br.). ^{1}H-NMR (300 MHz, CD_3OD): 5.00 (br. *d*, $J = 5.6$, H–C(6)); 4.74 (*dd*, $J \approx 2.2, 5.9$, H–C(6′)); 4.92 (*d*, $J = 6.9$), 4.79 (*d*, $J = 6.9$), 4.75 (*d*, $J = 6.9$), 4.71 (*d*, $J \approx 6.9$), 4.65 (*d*, $J = 6.8$), 4.63 (*d*, $J = 6.8$, 3 MeOCH_2); 4.01 (*ddd*, $J = 1.9, 3.7, 10.5$, H–C(2)); 3.98 (*ddd*, $J = 2.2, 4.6, 10.5$, H–C(2′)); 3.87 (br. *t*, $J \approx 10.0$), 3.81 (br. *t*, $J \approx 10.0$, H–C(4), H–C(4′)); 3.82–3.73 (*m*, 2 H–C(1), H–C(1′)); 3.73 (*dd*, $J = 4.6, 12.2$, H′–C(1′)); 3.52 (*dd*, $J = 5.6, 9.3$, H–C(5′)); 3.43 (*dd*, $J = 5.9, 9.3$, H–C(5)); 3.48, 3.41, 3.37 (3*s*, 3 MeO); 3.03 (*d*, $J = 2.2$, C(8′)); 2.78 (br. *t*, $J \approx 10.5$), 2.64 (br. *t*, $J \approx 10.5$, H–C(3), H–C(3′)). ^{13}C-NMR (75 MHz, CD_3OD): 99.01, 98.85, 98.02 (3*t*, 3 MeOCH_2); 80.03, 79.82, 76.86, 74.84, 73.20, 69.34, 68.11 (7*s*, 7 *C*≡C); 79.58 (*d*, C(8′)); 79.61, 77.49 (2*d*, C(4), C(5)); 76.07, 75.32, 73.53, 72.64 (4*d*, C(2), C(2′), C(4′), C(5′)); 70.18, 69.81 (2*d*, C(6), C(6′)); 68.97 (*t*, C(1)); 63.84 (*t*, C(1′)); 56.95, 56.73, 55.88 (3*q*, 3 MeO); 39.52, 38.62 (2*d*, C(3), C(3′)). MALDI-MS: 1065 ($[M + Na]^+$).

*3′,3″-(Buta-1,3-diyne-1,4-diyl){1,4,5,12,13,16-hexa-*O*-acetyl-2,6:11,15-dianhydro-3,14-bis-*C*-[2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl]-3,7,8,9,10,14-hexadeoxy-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol}* (= *1,4,5,12,13,16-Hexa-*O*-acetyl-2,6:11,15-dianhydro-3-*C*,14-*C*-{(buta-1,3-diyne-1,4-diyl)bis[2,6-anhydro-3,7,8,9,10-pentadeoxy-1,4,5-tris-*O*-(methoxymethyl)-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-*C*,10-*C*-diyl]}-3,7,8,9,10,14-hexadeoxy-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol*; **26**). A soln. of $Cu(OAc)_2$ (2.30 g, 12.67 mmol) in pyridine (180 ml) was treated with a soln. of **25** (264.5 mg, 0.253 mmol) in pyridine (1 ml) at 50° under N_2 within 8 h, stirred for 23 h, concentrated to *ca.* 10 ml, treated with Ac_2O (5 ml), stirred for 12 h, and evaporated. The residue was suspended in AcOEt and sat. aq. NH_4Cl soln. The solids were filtered off and washed (AcOEt). Workup (AcOEt) of the filtrate and FC (CH_2Cl_2/AcOEt 9:1 → 7:3), gave **26** (226.1 mg, 69%). White solid. R_f (toluene/AcOEt 2:3) 0.31. M.p. 153.0–156.0°. $[\alpha]_D^{25} = +146.5$ ($c = 0.44$, $CHCl_3$). IR: 2953*m*, 2888*m*, 2166*w*, 1750*s* (br.), 1602*w*, 1412*w*, 1371*m*, 1152*m*, 1113*m*, 1040*s* (br.), 915*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.47 (br. *t*, $J \approx 10.3$, H–C(4)); 5.14 (br. *d*, $J = 5.9$, H–C(6′)); 4.98 (br. *d*, $J = 5.5$, H–C(6)); 4.97 (*d*, $J = 6.8$, MeOC*H*); 4.82 (*dd*, $J = 5.9, 9.8$, H–C(5)); 4.80 (*d*, $J \approx 6.8$), 4.74 (*d*, $J = 7.0$), 4.69 (*d*, $J = 7.0$), 4.65 (*d*, $J = 6.6$), 4.63 (*d*, $J = 6.6$, 5 MeOC*H*); 4.50 (br. *dd*, $J \approx 1.0, 12.2$, H–C(1)); 4.36 (*dd*, $J = 4.3, 12.2$, H′–C(1)); 4.32 (*ddd*, $J = 2.1, 4.3, 10.5$, H–C(2)); 3.99 (br. *ddd*, $J \approx 1.5, 3.6, 10.5$, H–C(2′)); 3.91 (br. *t*, $J \approx 9.8$, H–C(4′)); 3.81 (*dd*, $J = 3.8, 11.3$, H–C(1′)); 3.74 (*dd*, $J = 1.9, 11.2$, H′–C(1′)); 3.51 (*dd*, $J = 5.7, 9.3$, H–C(5′)); 3.50, 3.39, 3.36 (3*s*, 3 MeO); 2.96 (br. *t*, $J \approx 10.5$), 2.79 (br. *t*, $J \approx 10.5$, H–C(3), H–C(3′)); 2.16, 2.10, 2.09 (3*s*, 3 Ac). ^{13}C-NMR (100 MHz, $CDCl_3$): 170.58, 170.06, 169.25 (3*s*, 3 C=O); 97.92, 97.64, 96.69 (3*t*, 3 MeOCH_2); 78.58, 76.30 (2*d*, C(4′), C(5′)); 73.71 (*d*, C(2′)); 72.19, 69.97, 69.90 (3*d*, C(2), C(4), C(5)); 68.52 (*d*, C(6′)); 66.39 (*d*, C(6)); 67.18 (*t*, C(1′)); 63.78 (*t*, C(1)); 75.14, 73.83, 73.34, 73.25, 73.13, 72.90, 68.85, 68.20 (8*s*, 8 *C*≡C); 56.40, 56.10, 55.29 (3*q*, 3 MeO); 37.09, 36.51 (2*d*, C(3), C(3′)); 20.85, 20.76, 20.66 (3*q*, 3 Me). MALDI-MS: 1315 ($[M + Na]^+$). Anal. calc. for $C_{64}H_{76}O_{28}$ (1293.29): C 59.44, H 5.92; found: C 59.37, H 6.17.

*3′,3″-(Buta-1,3-diyne-1,4-diyl){2,6:11,15-dianhydro-3,14-bis-*C*-[2,6-anhydro-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl]-3,7,8,9,10,14-hexadeoxy-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol}* (= *2,6:11,15-Dianhydro-3-*C*,14-*C*-{(buta-1,3-diyne-1,4-diyl)bis[2,6-anhydro-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-*C*,10-*C*-diyl]}-3,7,8,9,10,15-hexadeoxy-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol*; **27**). A soln. of **26** (226 mg, 0.175 mmol) in MeOH (8 ml) and THF (4 ml) was treated with 2% NaOMe soln. in MeOH (400 µl) at 0° under Ar, stirred for 6 h, neutralized with *Dowex* (H^+ form), and filtered. The filtrate was evaporated, dissolved in 0.3M HCl in MeOH, refluxed for 21 h, and evaporated. The residue was dissolved in MeOH (at *ca.* 40°) and precipitated with CH_2Cl_2 (3 times) affording **27** (124 mg, 91%). Slightly yellow solid. R_f (acetone) 0.55. M.p. > 230° (dec.). $[\alpha]_D^{25} = +94.6$ ($c = 0.36$, H_2O). UV (H_2O): 256 (1074), 243 (1625), 231 (1578). IR (KBr): 3633–3044*s* (br., max. at 3395), 2918*w*, 2253*w*, 2155*w*, 1627*w* (br.), 1333*m*, 1227*w*, 1122*m*, 1072*s*, 1028*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 5.59 (*d*, $J = 4.7$, exchange with D_2O), 5.55 (*d*, $J = 4.6$, exchange with D_2O, HO–C(4), HO–C(4′)); 5.53 (*d*, $J = 6.3$, exchange with D_2O), 5.48 (*d*, $J = 6.2$, exchange with D_2O, HO–C(5), HO–C(5′)); 4.84 (br. *d*, $J = 5.8$), 4.74 (br. *d*, $J = 5.6$, H–C(6), H–C(6′)); 4.83 (*t*, $J = 5.9$, exchange with D_2O), 4.80 (*t*, $J = 5.7$, exchange with D_2O, HO–C(1), HO–C(1′)); 3.74 (br. *ddd*, $J \approx 1.4, 4.5, 10.4$, H–C(2), H–C(2′)); 3.65–3.58 (*m*, addn. of D_2O → change of signal, H–C(1), H–C(1′)); 3.56–3.49 (*m*, addn. of D_2O → change of signal, H′–C(1), H′–C(1′), → br. *t* at 3.51, $J \approx 9.8$, H–C(4), H–C(4′)); 3.29–3.22 (*m*, addn. of D_2O → *dd* at 3.28, $J = 5.9, 9.3$, → *dd* at 3.26, $J = 5.7, 9.4$, H–C(5), H–C(5′)); 2.57 (br. *t*, $J = 10.3$), 2.45 (br. *t*, $J = 10.4$, H–C(3), H–C(3′)). ^{13}C-NMR (100 MHz, (D_6)DMSO): 78.68, 76.89, 76.06 (3*s*, 3 *C*≡C); 75.35, 75.19 (2*d*, C(2), C(2′)); 73.46, 72.46, 71.50 (3*s*, 3 *C*≡C); 71.87, 71.34, 70.93 (2 C; 3*d*, C(4), C(5), C(4′), C(5′)); 69.95, 68.84 (2*d*, C(6),

C(6')); 66.98, 66.70 (2*s*, 2*C*≡C); 61.86 (*t*, H–C(1), H–C(1')); 37.80, 37.53 (2*d*, C(3), C(3')). MALDI-MS: 794 ($[M + NH_4]^+$), 777 ($[M + H]^+$). ESI-MS: 794 ($[M + NH_4]^+$), 777 ($[M + H]^+$). Anal. calc. for $C_{40}H_{40}O_{16} \cdot 2.5\ H_2O$ (776.75): C 58.46, H 5.52; found: C 58.59, H 5.57.

Solubility of **27** *in* H_2O. A suspension of **27** in H_2O (*ca.* 3.5 ml) was ultrasonicated for 5 min at 24° and centrifuged. The supernatant liquor was filtered (2 times). Lyophilization and drying (12 h, r.t./0.05 mbar) of 2.700 ml of the clear filtrate left 5.4 mg of **27**.

*2,6-Anhydro-3-*C*-[2,6-anhydro-3-*C*-(2,6-anhydro-3,7,8,9,10-pentadeoxy-3-*C*-ethynyl-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-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* (= *2,6-Anhydro-10-*C*-[2,6-anhydro-10-*C*-(2,6-anhydro-3,7,8-trideoxy-*D*-glycero-*L*-gulo-oct-7-ynitol-3-*C*-yl)-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-*C*-yl]-3,7,8,9,10-pentadeoxy-3-*C*-ethynyl-*D*-glycero-*L*-gulo-deca-7,9-diynitol*; **29**). A soln. of **28** (400 mg, 0.35 mmol) in MeOH (10 ml) and THF (2 ml) was treated at 0° under Ar with a 2% NaOMe soln. in MeOH (1 ml), stirred for 4 h, neutralized with *Dowex* (H^+ form), and filtered. The filtrate was evaporated and the residue dissolved in 0.3M HCl in MeOH (15 ml), heated to 60°, stirred for 22 h, and evaporated. FC (CH_2Cl_2/MeOH 3:1) gave a dark yellow solid. This solid was dissolved in MeOH, treated with activated charcoal, stirred at 55° for 2 h, and filtered. Evaporation left **29** (192 mg, 95%). White foam. R_f (AcOEt/MeOH 7:3) 0.51. M.p. > 145° (dec.). $[\alpha]_D^{25} = +138.2$ (*c* = 0.40, H_2O). IR (KBr): 3395*s* (br.), 3268*s*, 2928*m*, 2882*m*, 2259*w*, 2109*w*, 1635*w* (br.), 1466*m*, 1444*m*, 1340*m*, 1290*m*, 1232*w*, 1218*w*, 1185*m*, 1120*m*, 1080*s* (br.), 1031*s*, 985*m*, 847*m*, 734*m*, 670*m*, 622*m*. UV (H_2O): 258 (413), 244 (697), 232 (675). ^{1}H-NMR (500 MHz, (D_6)DMSO)[13]: 5.60 (*d*, *J* = 4.5, exchange with D_2O, HO–C(5')); 5.56 (*d*, *J* = 6.1, exchange with D_2O, HO–C(4)); 5.54 (*d*, *J* = 4.5, exchange with D_2O, HO–C(5'')); 5.49 (*d*, *J* = 6.1, exchange with D_2O, HO–C(4')); 5.43 (*d*, *J* = 4.5, exchange with D_2O, HO–C(5)); 5.33 (*d*, *J* = 6.1, exchange with D_2O, HO–C(4'')); 4.84 (*t*, *J* = 6.1, exchange with D_2O), 4.81 (*t*, *J* = 6.1, exchange with D_2O), 4.75 (*t*, *J* = 6.1, exchange with D_2O; HO–C(1), HO–C(1'), HO–C(1'')); 4.78 (br. *d*, *J* ≈ 5.9, H–C(6')); 4.77 (br. *d*, *J* ≈ 6.0, H–C(6'')); 4.61 (*dd*, *J* = 2.3, 5.6, H–C(6)); 3.78 (*ddd*, *J* = 1.8, 4.6, 10.5, H–C(2)); 3.72 (*ddd*, *J* = 1.7, 4.6, 10.4, H–C(2')); 3.70–3.67 (*m*, addn. of D_2O → *ddd*, *J* ≈ 1.7, 4.8, 10.4, H–C(2'')); 3.68–3.60 (*m*, addn. of D_2O → change of signal, H–C(1), H–C(1'), H–C(1'')); 3.58–3.48 (*m*, addn. of D_2O → change of signal, H'–C(1), H'–C(1'), H'–C(1'')); 3.57–3.53 (*m*, addn. of D_2O → change of signal, H–C(4)); 3.54–3.49 (*m*, addn. of D_2O → change of signal, H–C(4')); 3.50–3.45 (*m*, addn. of D_2O → change of signal, H–C(4'')); 3.47 (*d*, *J* = 2.3, H–C(8)); 3.28–3.26 (*m*, addn. of D_2O → br. *dd*, *J* ≈ 5.6, 9.3, H–C(5')); 3.27–3.24 (*m*, addn. of D_2O → br. *dd*, *J* ≈ 5.6, 9.3, H–C(5'')); 3.25–3.22 (*m*, addn. of D_2O → br. *dd*, *J* ≈ 5.6, 9.2, H–C(5)); 2.98 (*d*, *J* = 2.3, CH≡C–C(3'')); 2.52 (br. *t*, *J* = 10.4, H–C(3')); 2.51 (br. *t*, *J* = 10.4, H–C(3)); 2.30 (*dt*, *J* = 2.3, 10.4, H–C(3'')). ^{13}C-NMR (125 MHz, (D_6)DMSO): 82.51 (*d*, *C*H≡C–C(3'')); 79.43 (*d*, C(8)); 79.37, 79.28, 78.95, 73.91, 73.77 (2 C), 72.30, 72.11 (7*s*, 8 C≡*C*); 75.55 (*d*, C(2'')); 75.10 (*d*, C(2')); 74.47, (*d*, C(2)); 71.90 (*d*, C(4'')); 71.59 (*d*, C(4')); 71.33 (*d*, C(4)); 71.01, 70.90, 70.81 (3*d*, C(5), C(5'), C(5'')); 68.80 (*d*, C(6')); 68.74 (*d*, C(6'')); 68.13 (*d*, C(6)); 66.46, 66.24 2*s*, C(9'), C(9'')); 37.74 (*d*, C(3')); 37.69 (*d*, C(3)); 36.92 (*d*, C(3'')). ESI-MS (in MeOH/H_2O 1:1 + 1% AcOH + LiCl): 1175 ($[2M + Li]^+$), 591 ($[M + Li]^+$). Anal. calc. for $C_{30}H_{22}O_{12} \cdot H_2O$ (584.57): C 59.80, H 5.69; found: C 59.82, H 5.60.

Treatment of **29** *with* $Cu(OAc)_2$ *in Pyridine*. A soln. of $Cu(OAc)_2$ (931 mg, 5.13 mmol) in pyridine (80 ml) was treated at 50° under N_2 with a soln. of **29** (60 mg, 0.10 mmol) in pyridine (1 ml) within 11 h, stirred for 20 h, concentrated to *ca.* 10 ml, treated with Ac_2O (5 ml), stirred for 14 h at r.t., and evaporated. FC (toluene/AcOEt 9:1 → 7:3) gave **30** (50 mg, 51%). White solid. The spectroscopic data of **30** correspond to the data obtained from an authentic sample [7].

*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*-ethynyl-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl)-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl]-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl}-3,7,8-trideoxy-*D*-glycero-*L*-gulo-oct-7-ynitol* (= *2,6-Anhydro-10-*C*-{2,6-anhydro-10-*C*-[2,6-anhydro-10-*C*-(2,6-anhydro-3,7,8-trideoxy-*D*-glycero-*L*-gulo-oct-7-ynitol-3-*C*-yl)-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-*C*-yl]-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-*C*-yl}-3,7,8,9,10-pentadeoxy-3-*C*-ethynyl-*D*-glycero-*L*-gulo-deca-7,9-diynitol*; **33**). A soln. of **32** (300 mg, 0.20 mmol) in MeOH (6 ml) and THF (1.6 ml) was treated at 0° under N_2 with a 2% NaOMe soln. in MeOH (1.5 ml), stirred for 3.5 h, neutralized with *Dowex* (H^+ form), filtered, and evaporated. The residue was dissolved in 0.3M HCl in MeOH, stirred at 55° for 21 h, and evaporated. The residue was dissolved in MeOH/H_2O 9:1, treated with activated charcoal, refluxed for 0.5 h, and filtered. Evaporation of the filtrate gave **33** (127 mg, 81%). White powder. R_f (AcOEt/MeOH 7:3) 0.28. M.p. > 155° (dec.). IR (KBr): 3611–3000*s* (br., max. at 3396), 3277 (sh), 2928*w*, 2883*w*, 2259*w*, 1636*w* (br.), 1466*m*, 1444*m*, 1373*w*, 1340*m*, 1290*w*, 1261*w*, 1217*w*, 1185*m*, 1132*m*, 1119*m*, 1081*s* (br.), 1063*s*, 1031*s*, 985*m*, 847*w*, 766*w*, 735*w*, 672*m*, 621*m*. ^{1}H-NMR (500 MHz, (D_6)DMSO): 5.59 (br. *d*, *J* ≈ 4.6, partial exchange with D_2O, 2 H), 5.51 (*d*, *J* = 4.6, partial exchange

with D_2O), 5.42 (*d*, $J = 4.6$, partial exchange with D_2O, HO–C(5), HO–C(5′), HO–C(5″), HO–C(5‴)); 5.56 (*d*, $J = 6.2$, partial exchange with D_2O), 5.55 (*d*, $J = 6.2$, partial exchange with D_2O), 5.48 (*d*, $J = 6.2$, partial exchange with D_2O), 5.32 (*d*, $J = 6.1$, partial exchange with D_2O, HO–C(4), HO–C(4′), HO–C(4″), HO–C(4‴)); 4.85 (br. *t*, $J \approx 6.1$, partial exchange with D_2O), 4.84 (br. *t*, $J \approx 6.0$, partial exchange with D_2O), 4.82 (br. *t*, $J \approx 6.0$, partial exchange with D_2O), 4.75 (br. *t*, $J \approx 6.1$, partial exchange with D_2O, HO–C(1), HO–C(1′), HO–C(1″), HO–C(1‴)); 4.79 (br. *d*, $J = 5.6$), 4.78 (br. *d*, $J = 5.8$), 4.76 (br. *d*, $J \approx 5.8$, H–C(6′), H–C(6″), H–C(6‴)); 4.61 (*dd*, $J = 2.2, 5.7$, H–C(6)); 3.57–3.48 (*m*, addn. of D_2O → change of signal, H–C(1), H–C(4), H–C(1′), H–C(4′), H–C(1″), H–C(4″), H–C(1‴), H–C(4‴)); 3.78 (*ddd*, $J = 1.8, 4.5, 10.5$, H–C(2‴)); 3.73–3.58 (*m*, addn. of D_2O → change of signal, H′–C(1), H–C(2), H′–C(1′), H–C(2′), H′–C(1″), H–C(2″), H′–C(1‴)); 3.47 (*d*, $J = 2.2$, H–C(8)); 3.29–3.22 (*m*, addn. of D_2O → br. *dd* at 3.28, $J \approx 5.7, 9.3$, 2 H, → br. *dd* at 3.27, $J \approx 5.7, 9.3$, → br. *dd* at 3.25, $J \approx 5.7, 9.3$, H–C(5), H–C(5′), H–C(5″), H–C(5‴)); 2.98 (*d*, $J = 2.3$, C≡CH); 2.53 (br. *t*, $J \approx 10.3$, H–C(3), H–C(3′), H–C(3″)); 2.30 (*dt*, $J = 2.3$, 10.4, H–C(3‴)). ^{13}C-NMR (125 MHz, (D_6)DMSO): 82.49 (*d*, *C*H≡C–C(3‴)); 79.41 (*d*, C(8)); 79.41, 79.36, 79.32, 79.09, 78.91 (5*s*, 5 *C*≡C); 75.56, 75.11 (2 C), 74.47 (3*d*, C(2), C(2′), C(2″), C(2‴)); 73.90, 73.65, 73.56, 73.51, 72.59, 72.28, 72.26 (7*s*, 7 *C*≡C); 72.11, 72.57 (2 C), 71.31 (3*d*, C(4), C(4′), C(4″), C(4‴)); 70.97, 70.85 (2 C), 70.78 (3*d*, C(5), C(5′), C(5″), C(5‴)); 68.81 (2 C), 68.74, 68.14 (3*d*, C(6), C(6′), C(6″), C(6‴)); 66.48, 66.23 (2*s*, 2 *C*≡C); 61.77 (3 C), 61.68 (2*t*, C(1), C(1′), C(1″), C(1‴)); 37.74 (3 C), 36.94 (2*d*, C(3), C(3′), C(3″), C(3‴)). ESI-MS: 796 ($[M + NH_4]^+$), 779 ($[M + H]^+$). Anal. calc. for $C_{40}H_{42}O_{16} \cdot 2\,H_2O$ (778.76): C 58.96, H 5.69; found: C 59.01, H 5.67.

*Cyclotetrakis-(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-*C*-yl)* (**34**). A soln. of $Cu(OAc)_2$ (828 mg, 4.55 mmol) in pyridine (90 ml) was treated at 50° under N_2 with a soln. of **33** (71 mg, 91 μmol) in pyridine (1 ml) within 9 h, stirred for 20 h, concentrated to *ca.* 10 ml, treated with Ac_2O (5 ml), stirred for 12 h at r.t., and evaporated. FC (toluene/AcOEt 4:1 → 3:2) gave **34** (52 mg, 45%). White solid. R_f (toluene/AcOEt 1:1) 0.38. M.p. 175–176°. $[\alpha]_D^{25} = +254.2$ ($c = 0.97$, $CHCl_3$). IR: 2957*w*, 2258*w*, 1749*s* (br.), 1371*m*, 1066*m* (br.), 909*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.45 (br. *t*, $J \approx 10.3$, H–C(4)); 5.03 (br. *d*, $J \approx 5.8$, H–C(6)); 4.80 (*dd*, $J = 5.6, 9.7$, H–C(5)); 4.43 (br. *dd*, $J \approx 1.9, 12.1$, H–C(1)); 4.35 (br. *dd* $J \approx 4.0, 12.1$, H′–C(1)); 4.24 (br. *ddd*, $J \approx 1.8, 4.0, 10.4$, H–C(2)); 2.94 (br. *t*, $J \approx 10.5$, H–C(3)); 2.12, 2.11, 2.08 (3*s*, 3 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.85, 170.42, 169.37 (3*s*, 3 C=O); 75.29, 74.14, 71.04, 68.63 (4*s*, 4 *C*≡C); 72.09, 70.07, 69.95 (3*d*, C(2), C(4), C(5)); 66.52 (*d*, C(6)); 63.79 (*t*, C(1)); 36.43 (*d*, C(3)); 20.85 (*q*, Me); 20.77 (*q*, 2 Me). FAB-MS: 1305 (5, $[M + Na]^+$), 1281 (100, $[M + H]^+$). Anal. calc. for $C_{64}H_{64}O_{28}$ (1281.19): C 60.00, H 5.03; found: C 59.95, H 5.22.

X-Ray Analysis of **34**: Crystals were obtained from a soln. of **34** in toluene/^{t}BuOMe/AcOEt/MeOH/H_2O at r.t. $C_{64}H_{64}O_{28} + H_2O + C_4H_8O_2$ (1404.28). Monoclinic C_2; $a = 30.973(12)$, $b = 9.225(4)$, $c = 13.179(9)$ Å; $\beta = 96.50(4)$ deg. $V = 3742(3)$ Å^3; $D_{calc} = 1.246$ Mg/m^3; $Z = 2$. The crystals were measured in the $\omega/2\theta$ mode on an *Enraf-Nonius-CAD-4* diffractometer (graphite-monochromator, MoK_α, $\lambda = 0.71073$ Å) at 143(2) K. Of the 3700 total collected reflections, 3511 were independent, $R = 0.0853$, $R_w = 0.2214$. Part of the structure was solved by direct methods, the remaining non-H-atoms were found from a difference *Fourier* map with SHELX86. The non-H-atoms were refined anisotropically with SHELXL-92 with the exception of the disordered atoms and the solvent atoms which were refined isotropically. H-Atoms were calculated at idealized positions and included in the structure factor calculation with fixed isotropic displacement parameters.

*2,6-Anhydro-3,7,8-trideoxy-3-*C*-ethynyl-tris-1,4,5-*O*-(methoxymethyl)-*D*-*glycero*-*L*-*gulo*-oct-7-ynitol* (**36**). A soln. of **1** (3.60 g, 8.99 mmol) in MeOH (40 ml) was treated at 0° under N_2 with 0.37M NaOMe in MeOH (1.0 ml), warmed to r.t., stirred for 2.5 h, neutralized with *Dowex* (H^+ form), filtered, and evaporated. FC (hexane/AcOEt 4:1) gave **36** (2.90 g, 98%). Colourless oil. R_f (toluene/AcOEt 7:3) 0.51. $[\alpha]_D^{25} = +28.4$ ($c = 0.41$, $CHCl_3$). IR: 3306*s*, 2952*m*, 2893*m*, 2827*w*, 2118*w*, 1442*w*, 1358*w*, 1152*s*, 1114*s*, 1035*s* (br.), 961*w*, 917*m*, 646*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.95 (*dd*, $J = 2.3, 5.6$, H–C(6)); 4.91 (*d*, $J = 6.5$), 4.87 (*d*, $J = 6.5$), 4.78 (*d*, $J = 6.8$), 4.70 (*d*, $J = 6.8$, 2 MeOC*H*$_2$); 4.67 (*s*, MeOC*H*$_2$); 4.10 (*ddd*, $J = 1.9, 4.0, 10.5$, H–C(2)); 3.99 (*dd*, $J = 4.0, 11.1$, H–C(1)); 3.97 (br. *t*, $J \approx 10.0$, H–C(4)); 3.79 (*dd*, $J = 1.9, 11.0$, H′–C(1)); 3.54 (*dd*, $J = 5.6, 9.3$, H–C(5)); 3.46, 3.40, 3.38 (3*s*, 3 MeO); 2.74 (*dt*, $J \approx 2.2, 10.5$, H–C(3)); 2.60 (*d*, $J = 2.2$, H–C(8)); 2.19 (*d*, $J = 2.2$, C≡CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 97.97, 97.88, 96.86 (3*t*, 3 MeO*C*H$_2$); 81.24, 77.80 (2*d*, C(8), C≡*C*H); 78.51, 76.36 (2*d*, C(4), C(5)); 73.43 (*d*, C(2)); 72.33 (*s*, C≡*C*); 68.03 (*d*, C(6)); 67.32 (*t*, C(1)); 56.49, 56.15, 55.46 (3*q*, 3 MeO); 36.69 (*d*, C(3)); 1*s* for *C*≡C is missing. CI-MS: 346 (100, $[M + NH_4]^+$), 235 (58). Anal. calc. for $C_{16}H_{24}O_7$ (328.36): C 58.53, H 7.37; found: C 58.52, H 7.62.

Treatment of **36** *with Cu(OAc)$_2$ in Pyridine.* A soln. of $Cu(OAc)_2$ (5.86 g, 32.2 mmol) in pyridine (500 ml) was treated at 50° under N_2 with a soln. of **36** (212 g, 0.645 mmol) in pyridine (9 ml) within 28 h, stirred for 48 h, and evaporated. The residue was suspended in AcOEt, and filtered. Workup (AcOEt) of the filtrate and FC (toluene/AcOEt 1:1 → MeOH) gave 3 fractions as dark red oils. These fractions were dissolved in MeOH/AcOEt

(*ca.* 1:1), treated with activated charcoal (*ca.* 300 mg), refluxed for 30 min, filtered (*Celite*), and evaporated. Thus, the 1st fraction yielded **12** (40 mg, 19%) as a slightly yellow solid, with spectroscopic data corresponding to those of **12** obtained from **11**. The 2nd fraction (5.5 mg, 2.5%) contained a mixture (according to ^{1}H-NMR) of cyclotetramers (according to MALDI-MS). The MALDI-MS spectrum of the 3rd fraction (42 mg, 20%), a dark red oil, did not show any signals that could be assigned to oligomers of **36**.

Data of the Second Fraction: ^{1}H-NMR (300 MHz, $CDCl_3$): 5.11–4.65 (*m*, 7 H); 4.14–3.73 (*m*, 4 H); 3.60–3.35 (*m*, 10 H); 2.97–2.70 (*m*, 1 H). MALDI-MS: 1327 ($[M + Na]^+$).

*2,6-Anhydro-3-*C*-(2,6-anhydro-3,7,8,9,10-pentadeoxy-3-*C*-ethynyl-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl)-3,7,8-trideoxy-*D*-glycero-*L*-gulo-oct-7-ynitol* (= *2,6-Anhydro-10-*C*-(2,6-anhydro-3,7,8-trideoxy-*D*-glycero-*L*-gulo-oct-7-ynitol-3-*C*-yl)-3,7,8,9,10-pentadeoxy-3-*C*-ethynyl-*D*-glycero-*L*-gulo-deca-7,9-diynitol*; **37**). A soln. of **15** (125 mg, 0.20 mmol) in 0.1M HCl in MeOH (3 ml) was stirred at 40° for 16 h and evaporated. FC (AcOEt/MeOH 19:1) gave **37** (72 mg, 94%). White solid. R_f (AcOEt/MeOH 7:3) 0.73. M.p. 88°. $[\alpha]_D^{25} = +97.1$ (*c* = 0.44, H_2O). IR: 3688–3044*s* (br., max. at 3406), 3288 (sh), 2925*m*, 2254*w*, 2113*w*, 1636*w* (br.), 1457*w*, 1375*w*, 1339*w*, 1251*m* (br.), 1188*w*, 1122*s*, 1077*s* (br.), 1033*s*, 875*w*, 658*m* (br.). ^{1}H-NMR (400 MHz, (D_6)DMSO): 5.50 (*d*, *J* = 4.6, partial exchange with D_2O), 5.40 (*d*, *J* = 4.6, partial exchange with D_2O, HO–C(5), HO–C(5′)); 5.46 (*d*, *J* = 6.2, partial exchange with D_2O), 5.30 (*d*, partial exchange with D_2O, HO–C(4), HO–C(4′)); 4.80 (*t*, partial exchange with D_2O), 4.73 (br. *t*, *J* ≈ 6.0, partial exchange with D_2O, HO–C(1), HO–C(1′)); 4.75 (br. *d*, *J* ≈ 5.8, H–C(6′)); 4.61 (*dd*, *J* = 2.3, 5.7, H–C(6)); 3.78 (*ddd*, *J* = 1.9, 4.7, 10.5), 3.68–3.59 (*m*, addn. of D_2O → change of signal, H–C(1), H–C(2), H–C(1′), H–C(2′)); 3.58–3.46 (*m*, addn. of D_2O → change of signal, H′–C(1), H′–C(1′), H–C(4), H–C(4′)); 3.47 (*d*, *J* = 2.3, H–C(8)); 3.27–3.21 (*m*, addn. of D_2O → br. *dd* at 3.26, *J* ≈ 5.7, 9.3, → br. *dd* at 3.25, *J* ≈ 5.7, 9.3 H–C(5), H–C(5′)); 2.98 (*d*, *J* = 2.3, C≡CH); 2.51 (br. *t*, *J* ≈ 10.5, H–C(3)); 2.30 (*dt*, *J* = 2.3, 10.4, H–C(3′)). ^{13}C-NMR (100 MHz, (D_6)DMSO): 82.50 79.41 (2*d*, 2 *C*≡CH); 79.30, 79.27 (2*s*, 2 *C*≡C); 75.57, 74.48 (2*d*, C(2), C(2′)); 73.76, 73.55, 72.14 (3*s*, 3 *C*≡C); 71.88, 71.32 (2*d*, C(4), C(4′)); 70.98, 70.81 (2*d*, C(5), C(5′)); 68.75, 68.14 (2*d*, C(6), C(6′)); 66.23 (*s*, *C*≡C); 61.77, 61.70 (2*t*, C(1), C(1′)); 37.73, 36.95 (2*d*, C(3), C(3′)). ESI-MS: 1193 ($[2M + Na]^+$), 803 ($[2M + Na]^+$), 798 ($[2M + NH_4]^+$), 781 ($[2M + H]^+$), 413 ($[M + Na]^+$), 408 ($[M + NH_4]^+$). Anal. calc. for $C_{20}H_{22}O_8 \cdot H_2O$ (390.39): C 58.82, H 5.92; found: C 59.05, H 6.11.

Treatment of **37** *with Cu(OAc)$_2$ in Pyridine*. A soln. of $Cu(OAc)_2$ (1.69 g, 9.28 mmol) in pyridine (183 ml) was treated at 50° under N_2 with a soln. of **37** (72 mg, 185 μmol) within 7 h, stirred for 18 h, and concentrated *ca.* 20 ml. The mixture was treated with Ac_2O (10 ml), stirred for 14 h, and evaporated. The residue was suspended in AcOEt, and filtered (*Celite*). Workup (AcOEt) of the filtrate and FC (toluene/AcOEt 9:1 → 7:3) gave **34**/**38**. Prep. HPLC (hexane/AcOEt 4:1) gave **38** (9.4 mg, 8%) and **34** (16.4 mg, 14%). White solids.

*Data of 3′,3″-(Buta-1,3-diyne-1,4-diyl){1,4,5,12,13,16-hexa-*O*-acetyl-3,14-bis-*C*-[1,4,5-tri-*O*-acetyl-2,6-anhy-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-10-*C*-yl]-2,6:11,15-dianhydro-3,7-8,9,10,14-hexadeoxy-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol}* (= *1,4,5,12,13,16-Hexa-*O*-acetyl-2,6:11,15-dianhydro-3-*C*,14-*C*-{(buta-1,3-diyne-1,4-diyl)bis[1,4,5-tri-*O*-acetyl-2,6-anhydro-3,7,8,9,10-pentadeoxy-*D*-glycero-*L*-gulo-deca-7,9-diynitol-3-*C*,10-*C*-diyl]}-3,7,8,9,10,14-hexadeoxy-*D*-erythro-*L*-ido-*L*-gulo-hexadeca-7,9-diynitol*; **38**). R_f (toluene/AcOEt 1:1) 0.45. IR: 2955*w*, 2255*w*, 1750*s* (br.), 1371*m*, 1069*m* (br.), 908*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.48 (br. *t*, *J* ≈ 10.2), 5.45 (br. *t*, *J* ≈ 10.3, H–C(4), H–C(4′)); 5.16 (br. *d*, *J* = 5.9), 5.00 (br. *d*, *J* = 5.7, H–C(6), H–C(6′)); 4.83 (*dd*, *J* = 5.9, 9.9), 4.78 (*dd*, *J* = 5.7, 10.0, H–C(5), H–C(5′)); 4.52 (br. *dd*, *J* ≈ 2.0, 12.1), 4.39 (br. *dd*, *J* ≈ 2.1, 12.2, H–C(1), H–C(1′)); 4.38 (br. *dd*, *J* ≈ 4.2, 12.1), 4.31 (*dd*, *J* = 3.9, 12.3, H′–C(1), H′–C(1′)); 4.37 (*ddd*, *J* = 2.2, 4.3, 10.5), 4.18 (*ddd*, *J* = 2.1, 4.1, 10.5, H–C(2), H–C(2′)); 2.97 (br. *t*, *J* ≈ 10.5), 2.83 (br. *t*, *J* ≈ 10.5, H–C(3), H–C(3′)); 2.18, 2.12, 2.11, 2.107, 2.102, 2.09 (6*s*, 6 Ac). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.79, 170.53, 170.18, 170.08, 169.22, 169.08 (6*s*, 6 C=O); 74.78, 74.07, 73.36, 73.34, 72.74, 70.74, 68.64, 68.50 (8*s*, 8 *C*≡C); 72.10 (2 C), 69.99, 69.92 (2 C), 69.83 (4*d*, C(2), C(4), C(5), C(2′), C(4′), C(5′)); 66.41, 66.37 (2*d*, C(1), C(1′)); 63.97, 63.71 (2*t*, C(1), C(1′)); 36.65, 36.21 (2*d*, C(3), C(3′)); 20.90–20.64 (several *q*, 6 Me). FAB-MS: 1282 (100), 1281 (97, $[M + H]^+$).

REFERENCES

[1] R. Bürli, A. Vasella, *Angew. Chem.* **1997**, *109*, 1945.
[2] T. Ogawa, *Chem. Soc. Rev.* **1994**, 397.
[3] G. Wenz, *Angew. Chem.* **1994**, *106*, 851.
[4] P. R. Ashton, C. L. Brown, S. Mezner, S. A. Nepogodiev, J. F. Stoddart, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 580.

[5] K. Fujita, Y. Okabe, K. Ohta, *Tetrahedron Lett.* **1996**, *37*, 1825.
[6] R. Bürli, A. Vasella, *Helv. Chim. Acta* **1996**, *79*, 1159.
[7] R. Bürli, A. Vasella, *Helv. Chim. Acta* **1997**, *80*, 1027.
[8] C. Cai, A. Vasella, *Helv. Chim. Acta* **1996**, *79*, 225.
[9] J. Alzeer, A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 177.
[10] G. Eglinton, A. R. Galbraith, *J. Chem. Soc.* **1959**, 889.
[11] A. Ernst, A. Vasella, *Helv. Chim. Acta* **1996**, *79*, 1279.
[12] A. Ernst, L. Gobbi, A. Vasella, *Tetrahedron Lett.* **1996**, *37*, 7959.
[13] D. Michelot, *Synthesis* **1983**, 130.
[14] D. Cremer, J. A. Pople, *J. Am. Chem. Soc.* **1975**, *97*, 1354.
[15] B. Peterson, Ph. D. Thesis, University of California, Los Angeles, CA, 1994.
[16] C. Glaser, *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422.